

way, show that a *Hanes plot* of $v/[S]$ against $[S]$ is also linear. Identify how the parameters may be determined from such a plot. The appropriately named enzyme, catalase, catalyses the decomposition of hydrogen peroxide, H_2O_2 . (c) By constructing Lineweaver–Burk, Eadie–Hofstee, and Hanes plots, use the following values for the rate of reaction for various

initial concentrations of hydrogen peroxide to determine the values of the Michaelis constant and the maximum velocity of the reaction.

$[H_2O_2]/(\text{mol dm}^{-3})$	0.300	0.400	0.500	0.600	0.700
$v/(\text{mol dm}^{-3} \text{ s}^{-1})$	4.431	4.518	4.571	4.608	4.634

FOCUS 7

Quantum theory

The very currency of chemistry—the structures and properties of atoms and molecules—cannot be understood without a firm grasp of the principal concepts of ‘quantum mechanics’. To prepare for applying quantum mechanics to chemistry this focus establishes the basic principles of quantum mechanics and then applies them to three basic types of motion, namely translation (motion through space), rotation, and vibration.

and the corresponding wavefunctions. Hence, quantization of energy emerges as a natural consequence of solving the Schrödinger equation and the conditions imposed on it. This Topic also introduces a striking non-classical feature of small particles, such as electrons and protons: their ability to penetrate into and through regions where classical physics would forbid them to be found.

7C.1 Motion in one dimension; 7C.2 Tunnelling;
7C.3 Motion in two dimensions

7A The emergence of quantum theory

Towards the end of the nineteenth century experimental evidence summarized in this Topic showed that classical mechanics, which was very successful at explaining the motion of planets and everyday objects such as pendulums and projectiles, failed when it was applied to very small particles, such as individual atoms, nuclei, and electrons, and when the transfers of energy were very small.

7A.1 The evidence for discrete energies; 7A.2 The evidence for radiation as particles; 7A.3 The evidence for particles as waves

7D Rotation

This Topic switches attention from motion in a line to motion first on a circle and then on the surface of a sphere, and by imposing certain constraints on the wavefunction shows how the energy and angular momentum of a rotating particle are quantized. The conclusions are crucial to the description of electrons in atoms and of rotating molecules.

7D.1 Rotation in two dimensions; 7D.2 Rotation in three dimensions

7B The dynamics of microscopic systems

It took until 1926 to formulate the appropriate concepts and equations of quantum theory. The central concept is that particles spread through space like waves described mathematically by a ‘wavefunction’, which is obtained by solving the ‘Schrödinger equation’. This Topic shows how the wavefunction is interpreted. It also introduces the ‘uncertainty principle’, one of the most profound departures of quantum mechanics from classical mechanics.

7B.1 The Schrödinger equation; 7B.2 The Born interpretation; 7B.3 The uncertainty principle

7C Translation

According to quantum theory, a particle confined to a finite region of space can possess only certain discrete energies

7E Vibration

A molecule is not just a frozen, static array of atoms: all of them are in constant motion relative to one another. This Topic introduces the ‘harmonic oscillator’, a simple but very important model for the description of molecular vibrations and shows that the energies of vibration are restricted to certain values. The acceptable wavefunctions also show that the oscillator may be found at extensions and compressions that are forbidden by classical physics.

7E.1 The harmonic oscillator; 7E.2 The quantum mechanical treatment

TOPIC 7A

The emergence of quantum theory

► Why do you need to know this material?

Experimental results motivated the development of quantum theory, which describes the structure of atoms and molecules and is the basis of spectroscopy. Quantum theory is the foundation of many explanations in chemistry.

► What is the key idea?

Experimental evidence led to the conclusions that energy cannot in general be varied continuously and that the classical concepts of 'particle' and 'wave' blend together when applied to radiation, atoms, and molecules.

► What do you need to know already?

You need to be familiar with basic principles of classical physics (*The chemist's toolkit* 3 in Topic 1B, 7 in Topic 2A, and 18 in this Topic).

Classical mechanics, which has its origins in the laws of motion introduced by Isaac Newton in the

seventeenth century, predicts a precise trajectory for particles, with specified locations and momenta at each instant. It also allows the translational, rotational, and vibrational modes of motion to be excited to any energy simply by controlling the forces that are applied. These conclusions agree with everyday experience. Everyday experience, however, does not extend to individual electrons and atoms, and careful experiments have shown that classical mechanics fails when applied to the transfers of very small energies and to objects of very small mass.

Three experiments dating from the late nineteenth to the early twentieth century were crucially important. One showed—contrary to what had been supposed for two centuries—that energy was transferred only in discrete amounts. Another showed that electromagnetic radiation (which includes visible light), long considered to be a wave (*The chemist's toolkit* 18), in fact also behaves like a stream of particles. A third showed that electrons, which since their discovery in 1897 had been supposed to be particles, in fact also behave like waves. These observations suggested a new picture of radiation and matter, and led to the formulation of the entirely new and very successful quantum theory.

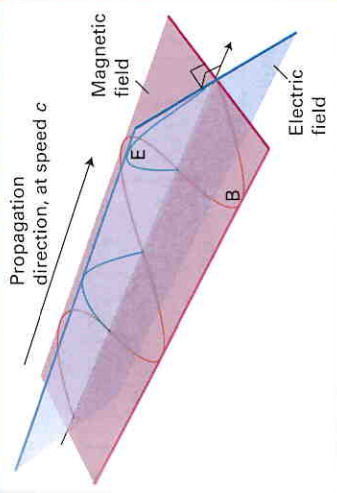
The chemist's toolkit 18 Electromagnetic waves

Electromagnetic radiation consists of oscillating electric and magnetic disturbances that propagate as waves. The two components of an electromagnetic wave are mutually perpendicular and perpendicular to the direction of propagation (Sketch 1). The electric field acts on both stationary and moving charged particles but the magnetic field acts only on moving charged particles. Electromagnetic waves travel through a vacuum at a constant speed called the **speed of light**, c , which has the defined value of exactly

$$c = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$$

Electromagnetic waves propagate more slowly in media such as air, water, and glass. The ratio of the speed in a vacuum to the speed in a medium is the **refractive index**, n , of the medium: $n = c/c_{\text{medium}}$.

A wave is characterized by its **wavelength**, λ (lambda), the distance between consecutive peaks of the wave (Sketch 2). The classification of electromagnetic radiation according to its wavelength is shown in Sketch 3. Light, which is electromagnetic radiation that is visible to the human eye, has a wavelength in the range 420 nm (violet light) to 700 nm



Sketch 1

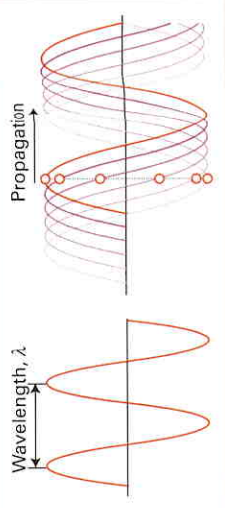
(red light). The properties of a wave may also be expressed in terms of its **frequency**, ν (nu), the number of oscillations in a time interval divided by the duration of the interval. Frequency is reported in hertz, Hz, with $1 \text{ Hz} = 1 \text{ s}^{-1}$. Light spans the frequency range from 710 THz (violet light) to 430 THz (red light). The **period** of an oscillation is the reciprocal of the frequency, $1/\nu$. During this period the wave propagates by one complete wavelength, λ . It follows that the speed of propagation is

$$c = \frac{\text{distance of propagation during one period of oscillation}}{\text{period of one oscillation}} = \frac{\lambda}{1/\nu}$$

or

$$c = \lambda\nu$$

The relation between wavelength and frequency in a vacuum



Sketch 2

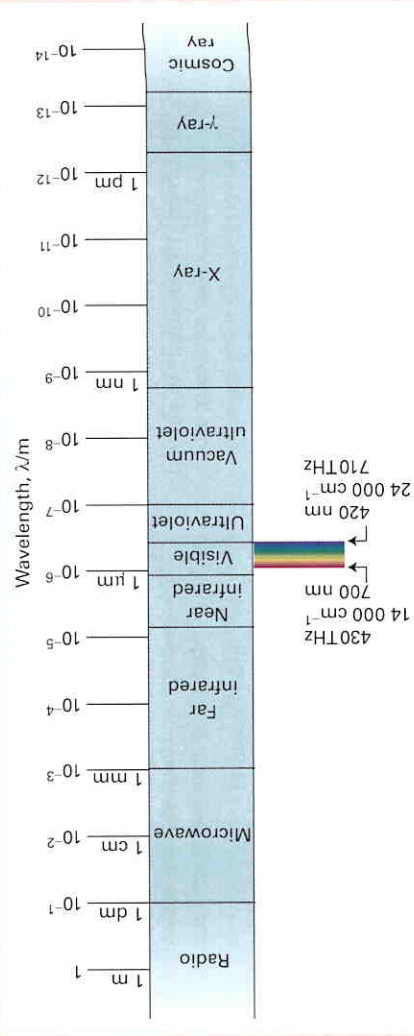
The properties of an electromagnetic wave are also expressed in terms of its **wavenumber**, $\tilde{\nu}$ (nu tilde), which is defined as

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

Wavenumber [definition]

Thus, wavenumber is the reciprocal of the wavelength and can be interpreted as the number of wavelengths in a given distance. In spectroscopy, for historic reasons, wavenumber is usually reported in units of reciprocal centimetres (cm^{-1}). Visible light therefore corresponds to electromagnetic radiation with a wavenumber of $14\,000 \text{ cm}^{-1}$ (red light) to $24\,000 \text{ cm}^{-1}$ (violet light).

Electromagnetic radiation that consists of a single frequency (and therefore single wavelength) is known as **monochromatic**, because it represents a single colour. *White light* consists of electromagnetic waves with a continuous, but not necessarily uniform, spread of frequencies throughout the visible region of the spectrum.



Sketch 3

7A.1 The evidence for discrete energies

A **spectrum** is a display of the frequencies, wavelengths, or wavenumbers of electromagnetic radiation that are absorbed or emitted by an atom or

molecule. Energetically excited atoms and molecules can be produced in a number of ways, such as by passing an electric discharge through a gas or vapour, exposing a sample to a hot flame or to electromagnetic radiation. Figure 1 shows a typical atomic emission spectrum obtained when excited atoms discard their excess energy as radiation. Atoms and

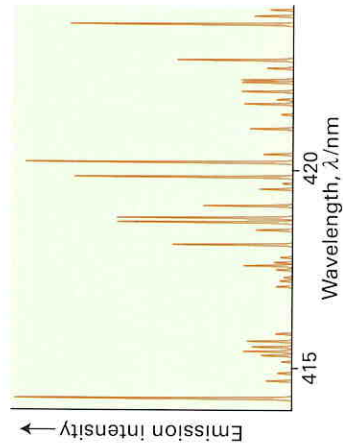


Fig. 1 A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).

molecules can also absorb energy from electromagnetic radiation. Figure 2 shows a typical molecular absorption spectrum.

The obvious feature of the spectra shown in Figs. 1 and 2 is that *radiation is absorbed or emitted at a series of discrete frequencies*. The absorption and emission of radiation at discrete frequencies can be understood if it is supposed that

- The energy of the 'internal modes' of motion of atoms or molecules (the distribution of their electrons and, for molecules, their rotations and vibrations) is confined to discrete values, for then energy can be discarded or absorbed only in packets as the atom or molecule jumps between its allowed states (Fig. 3).
- The frequency of the radiation is related to the energy difference between the initial and final states.

The simplest assumption is that the frequency ν (nu) of the radiation absorbed or emitted is directly

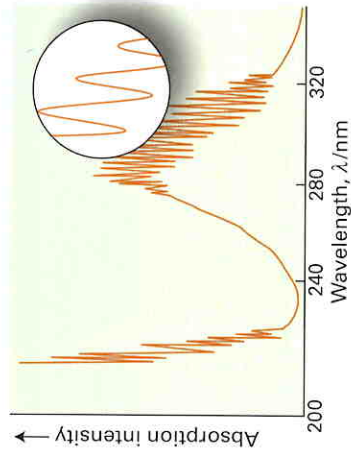


Fig. 2 When a molecule changes its state, it does so by absorbing radiation at definite frequencies. This spectrum is part of that due to sulfur dioxide (SO_2) molecules. This observation suggests that molecules can possess only discrete energies, not a continuously variable energy.

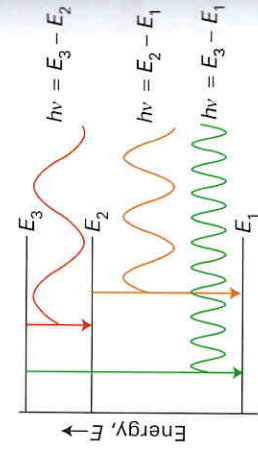


Fig. 3 Spectral lines can be accounted for, if we assume that a molecule emits or absorbs radiation as it changes between discrete energy levels. The figure illustrates the process of emission from high-energy states to lower-energy states. High frequency radiation is emitted when the two states involved in the transition are widely separated in energy; low frequency radiation is emitted when the two states are close in energy.

proportional to the difference in energy ΔE between the initial and final states of the atom or molecule. The result is the **Bohr frequency relation**,

$$\Delta E = h\nu \quad \text{Bohr frequency condition} \quad (1)$$

where h is the constant of proportionality. The additional evidence described below confirms this simple relation and gives the value $h = 6.626 \times 10^{-34} \text{ J s}$. This constant is now known as **Planck's constant**, for it had arisen in another related context, the spectra of radiation emitted by heated solids, that had been explained by the German physicist Max Planck.

Brief illustration 7A.1 The Bohr frequency condition

The yellow light emitted by sodium atoms in some street lamps has wavelength 589 nm. As seen in *The chemist's toolkit 18*, wavelength and frequency are related by $\nu = c/\lambda$, so the light is emitted when a sodium atom loses an energy $\Delta E = hc/\lambda$. It follows that

$$\begin{aligned} \Delta E &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{5.89 \times 10^{-7} \text{ m}} \\ &= 3.4 \times 10^{-19} \text{ J} = 0.34 \text{ aJ} \end{aligned}$$

Self-test 7A.1

Neon lamps emit red light of wavelength 736 nm. What is the energy separation of the levels (in joules) responsible for the emission?

Answer: 0.270 aJ

The conclusion at this stage is that any system of mechanics must accommodate an important feature of nature: that the internal modes of atoms and

molecules are quantized, that is, can possess only certain energies.

7A.2 The evidence for radiation as particles

By the middle of the nineteenth century, the generally acceptable view was that electromagnetic radiation is a wave, as described in *The chemist's toolkit 18*. But a conflicting view began to emerge when experimental evidence suggested that electromagnetic radiation can also be understood as a stream of particles. This interpretation arose from attempts to explain the **photoelectric effect**, the ejection of electrons from metals when they are exposed to ultraviolet radiation (Fig. 4). The characteristics of the photoelectric effect are as follows:

1. No electrons are ejected, regardless of the intensity of the radiation, unless the frequency exceeds a threshold value characteristic of the metal.
2. The kinetic energy of the ejected electrons varies linearly with the frequency of the incident radiation but is independent of its intensity.
3. Even at low light intensities, electrons are ejected immediately if the frequency is above the threshold value.

Data from experiments on several metals reveal a relation between the kinetic energy, E_k , of the ejected electron (which is equal to $\frac{1}{2}mv^2$, when the speed of the electron is v) and the frequency ν of the incident radiation:

$$E_k = h\nu - \phi \quad \text{The photoelectric effect} \quad (2)$$

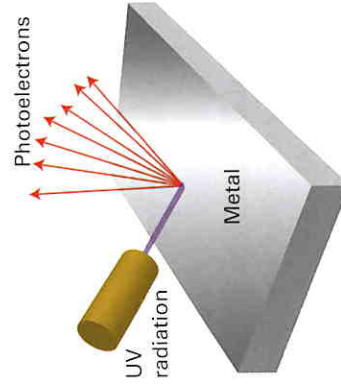


Fig. 4 The experimental arrangement to demonstrate the photoelectric effect. A beam of ultraviolet radiation is used to irradiate a patch of the surface of a metal, and electrons are ejected from the surface if the frequency of the radiation is above a threshold value that depends on the metal.

where h is Planck's constant and the quantity ϕ (uppercase phi) is called the **work function** of the metal, the minimum energy needed to remove an electron from the metal, and the analogue of the ionization energy of an atom.

A note on good practice The kinetic energy and work function are often expressed in electronvolts (eV): 1 eV is the kinetic energy gained by an electron when it is accelerated through a potential difference of 1 V. It turns out that 1 eV = $1.602 \times 10^{-19} \text{ J} = 0.1602 \text{ aJ}$.

These observations inspired Albert Einstein to suggest in 1905 that an electron is ejected in a collision with a particle-like projectile, now called the **photon**, when it carries enough energy to expel the electron from the metal. Einstein also proposed that a photon of radiation of frequency ν is

$$E_{\text{photon}} = h\nu \quad \text{Energy of a photon} \quad (3)$$

Because a photon has this energy, the conservation of energy requires that the kinetic energy, E_k , of the electron should be equal to this value less the energy ϕ required to remove the electron from the metal (Fig. 5). This interpretation is consistent with eqn 2. The model also explains the characteristics of the photoelectric effect:

- When $h\nu < \phi$, photoejection (the ejection of electrons by radiation) cannot occur because the photon supplies insufficient energy to expel the electron: this conclusion is consistent with observation 1.
- Equation 2 predicts that the kinetic energy of an ejected electron should increase linearly with the frequency, in agreement with observation 2.
- During a collision with an electron, the photon gives up all its energy, so electrons are expected to appear as soon as the collisions begin, provided the photons carry sufficient energy: this conclusion agrees with observation 3.

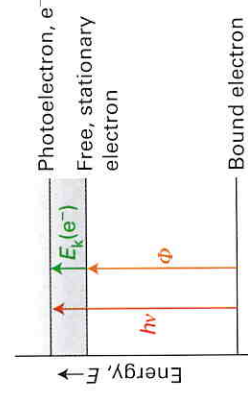


Fig. 5 In the photoelectric effect, an incoming photon brings a definite quantity of energy, $h\nu$. It collides with an electron close to the surface of the metal target, and transfers its energy to it. The difference between the work function, ϕ , and the energy $h\nu$ appears as the kinetic energy of the ejected electron.

Example 7A.1**Calculating a threshold for photoejection**

A photon of radiation with $\lambda = 305 \text{ nm}$ ejects an electron from a metal with $E_k = 1.77 \text{ eV}$. Calculate the threshold for photoejection, the frequency and wavelength of the radiation able to remove the electron from the metal but not give it any excess energy.

Collect your thoughts Begin by expressing the work function of the metal in terms of the data by using eqn 2 rearranged into $\phi = h\nu - E_k$ and combined with $v = c/\lambda$. At the threshold frequency, ν_{min} , the photoelectron escapes with $E_k = 0$, so $\phi = h\nu_{\text{min}}$. Therefore use the value of ϕ just calculated to find $\nu_{\text{min}} = \phi/h$. Then express ν_{min} as a maximum wavelength by using $\lambda_{\text{max}} = c/\nu_{\text{min}}$. To convert E_k from electronvolts to joules, use $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

The solution From $\phi = h\nu - E_k$ and $v = c/\lambda$, it follows that

$$\phi = \frac{hc}{\lambda} - E_k$$

Then, from $\nu_{\text{min}} = \phi/h$, the minimum frequency for photoejection is

$$\nu_{\text{min}} = \frac{\phi}{h} = \frac{hc/\lambda - E_k}{h} = \frac{c}{\lambda} - \frac{E_k}{h}$$

The wavelength of the incident photon is $\lambda = 305 \text{ nm} = 3.05 \times 10^{-7} \text{ m}$, and the kinetic energy of the electron it ejects is

$$E_k = 1.77 \text{ eV} \times (1.602 \times 10^{-19} \text{ J eV}^{-1}) = 2.8 \dots \times 10^{-19} \text{ J}$$

so it follows that

$$\nu_{\text{min}} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{3.05 \times 10^{-7} \text{ m}} - \frac{2.8 \dots \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 5.55 \dots \times 10^{14} \text{ s}^{-1}$$

or 555 THz . The maximum wavelength is therefore

$$\lambda_{\text{max}} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{5.55 \dots \times 10^{14} \text{ s}^{-1}} = 5.40 \times 10^{-7} \text{ m}$$

or 540 nm , corresponding to green light.

Self-test 7A.2

When ultraviolet radiation of wavelength 165 nm strikes a certain metal surface, electrons are ejected with a speed of 1.24 Mm s^{-1} ($1 \text{ Mm} = 10^6 \text{ m}$). Calculate the speed of electrons ejected by radiation of wavelength 265 nm .

Answer: 735 km s^{-1}

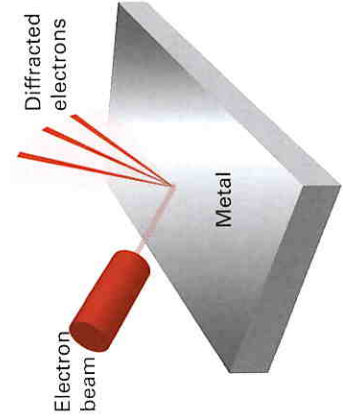


Fig. 7 In the Davisson-Germer experiment, a beam of electrons was directed on a single crystal of nickel, and the scattered electrons showed a variation in intensity with angle that corresponded to the pattern that would be expected if the electrons had a wave character and were diffracted by the layers of atoms in the solid.

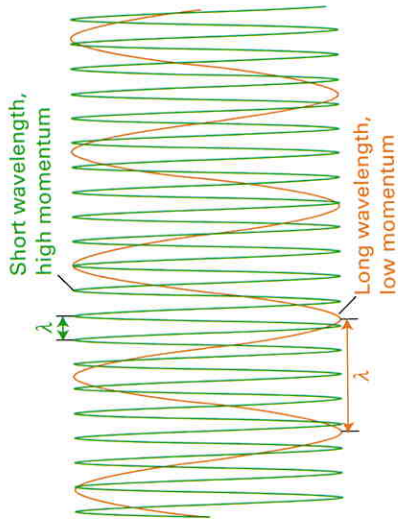
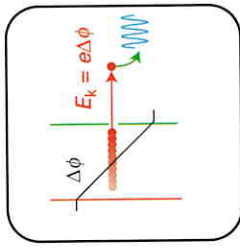


Fig. 8 According to the de Broglie relation, a particle with low momentum has a long wavelength whereas a particle with high momentum has a short wavelength. A high momentum can result either from a high mass or from a high velocity (because $p = mv$). Macroscopic objects have such large masses that, even if they are travelling very slowly, their wavelengths are undetectably short.

Example 7A.2**Estimating a de Broglie wavelength**

Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 1.00 kV .

Collect your thoughts You need to establish a string of relations, from potential difference to kinetic energy, then from kinetic energy to linear momentum, and finally from linear momentum to wavelength. For the first step you need to know that the kinetic energy acquired by an electron of charge $-e$ accelerated from rest by falling through a potential difference $\Delta\phi$ is $E_k = e\Delta\phi$. For the second step you need to express the electron's kinetic energy in terms of its linear momentum by combining $E_k = \frac{1}{2}m_e v^2$ with $p = m_e v$ (The chemist's toolkit 3 in Topic 1B). For the final step, use that linear momentum in the de Broglie relation, eqn 4, to calculate the wavelength. You will need the relations $1 \text{ CV} = 1 \text{ J}$ and $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$.



The solution From $E_k = \frac{1}{2}m_e v^2$ and $p = m_e v$ it follows that $E_k = p^2/2m_e$, and therefore $p = (2m_e E_k)^{1/2}$. Then, because for the accelerated electron $E_k = e\Delta\phi$,

Use this expression in eqn 4, which becomes

$$\lambda = \frac{h}{(2m_e e\Delta\phi)^{1/2}}$$

in the path of waves and occurs when the dimensions of the object are comparable to the wavelength of the radiation. Light waves, with wavelengths of the order of 500 nm , are diffracted by narrow slits and had been taken as compelling evidence that light is wavelike. However, the American physicists Clinton Davisson and Lester Germer carried out an experiment that demonstrated the diffraction of electrons (Fig. 7), and had to conclude that electrons, which in other respects behaved as particles, have the characteristics of waves.

There was an understandable confusion—which continues to this day—about how to combine both aspects of matter into a single description. Some progress was made by the French scientist Louis de Broglie when, in 1924, he suggested that any particle travelling with a linear momentum, $p = mv$, should have (in some sense) a wavelength λ given by what is now called the **de Broglie relation**:

$$\lambda = \frac{h}{p} \quad \text{de Broglie relation} \quad (4)$$

The de Broglie relation implies that the wavelength of what de Broglie called a 'matter wave' should decrease as the particle's speed increases (Fig. 8). Equation 4 was confirmed by the Davisson-Germer experiment, for the wavelength it predicts for the electrons they used in their experiment agrees with the details of the pattern of diffraction they observed.

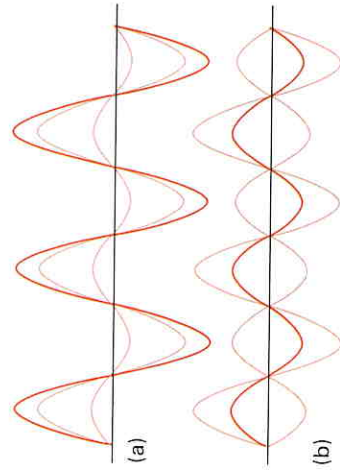


Fig. 6 When two waves (drawn as thin lines) are in the same region of space they interfere. Depending on their relative phase, they may interfere (a) constructively, to give an enhanced amplitude, or (b) destructively, to give a smaller amplitude.

7A.3 The evidence for particles as waves

In sum, a beam of electromagnetic radiation can be imagined to consist of a stream of photons, each having an energy $h\nu$. According to the particle picture of electromagnetic radiation, an intense beam of monochromatic (single-frequency) radiation consists of a dense stream of identical photons; a weak beam of radiation of the same frequency consists of a relatively small number of the same type of photons.

The photoelectric effect shows that electromagnetic radiation has certain properties of particles. Although contrary to the long-established wave theory of radiation, a similar view had been held before (by Newton, for instance), but discarded. No significant scientist, however, had taken the view that matter is wavelike. Nevertheless, experiments carried out in the early 1920s forced people to question even that possibility.

A characteristic property of waves is that they interfere with one another, which means that they result in a greater amplitude where their displacements add and a smaller amplitude where their displacements subtract (Fig. 6). The former is called 'constructive interference' and the latter 'destructive interference'. The regions of constructive and destructive interference show up as regions of enhanced and diminished intensity. The phenomenon of **diffraction** is the interference caused by an object

Now substitute the data:

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{\left\{ 2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-19} \text{ C}) \times (1.00 \times 10^3 \text{ V}) \right\}^{1/2}}$$

$$= \frac{6.626 \times 10^{-34}}{\left\{ 2 \times (9.109 \times 10^{-31}) \times (1.602 \times 10^{-19}) \times (1.00 \times 10^3) \right\}^{1/2}}$$

$$\times \frac{\text{kg m}^2 \text{ s}^{-1}}{(\text{kg C V})^{1/2}}$$

$$= 3.88 \times 10^{-11} \text{ m, or } 38.8 \text{ pm}$$

Comment The wavelength of 38.8 pm is comparable to typical bond lengths in molecules (about 100 pm). Electrons accelerated in this way are used in the technique of *electron diffraction*, in which the diffraction pattern generated by interference when a beam of electrons passes through a sample is interpreted in terms of the locations of the atoms.

Self-test 7A.3

Calculate the wavelength of an electron in a 10 MeV particle accelerator ($1 \text{ MeV} = 10^6 \text{ eV}$).

Answer: 0.39 pm

The Davisson–Germer experiment, which has since been repeated with other particles (including molecular hydrogen and C_{60}), shows clearly that ‘particles’ have wavelike properties. But other experiments (for instance, the photoelectric effect) show that ‘waves’ also have particle-like properties. It follows that, when examined on an atomic scale, the concepts of particle and wave melt together, particles taking on the characteristics of waves, and waves the characteristics of particles. This joint wave–particle character of matter and radiation is called **wave–particle duality**. It is the heart of modern physics, and will be central to all that follows.

Checklist of key concepts

- 1 Atomic and molecular spectra show that the energies of atoms and molecules are **quantized**.
- 2 The **photoelectric effect** is the ejection of electrons when radiation of greater than a threshold frequency is incident on a metal.
- 3 The wave-like character of electrons was demonstrated by the Davisson–Germer diffraction experiment.
- 4 The joint wave–particle character of matter and radiation is called **wave–particle duality**.

TOPIC 7B

The dynamics of microscopic systems

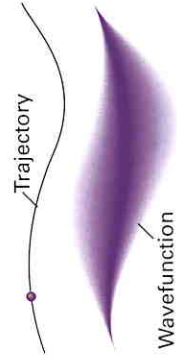


Fig. 1 According to classical mechanics, a particle may have a well-defined trajectory, with a precisely specified position and momentum at each instant (as represented by the precise path in the diagram). According to quantum mechanics, a particle cannot have a precise trajectory; instead, there is only a probability that it may be found at a specific location at any instant. The wavefunction that determines its probability distribution is a kind of blurred version of the trajectory. Here, the wavefunction is represented by areas of shading: the darker the area, the greater the probability of finding the particle there.

- **Why do you need to know this material?** Quantum theory provides the essential foundation for understanding of the properties of electrons in atoms and molecules and a number of key concepts for an understanding of chemistry.
- **What is the key idea?** All the dynamical properties of a system are contained in the wavefunction, which is obtained by solving the Schrödinger equation.
- **What do you need to know already?** You need to be aware of the shortcomings of classical physics that drove the development of quantum theory (Topic 7A), and specifically that electrons have wavelike character.

How can the facts that atoms and molecules can possess only certain energies, that waves exhibit the properties of particles, and that particles exhibit the properties of waves (as established in Topic 7A) be reconciled? The de Broglie relation is the starting point, along with abandoning the classical concept of particles moving along ‘trajectories’, precise paths at definite speeds. These aspects have been accommodated by the development of **quantum mechanics**, in which equations are set up that treat a particle as being spread through space like a wave.

To describe this wavelike character, quantum mechanics introduces the concept of a **wavefunction**, ψ (psi), and then sets up a scheme for calculating and interpreting it. To a very crude first approximation, a wavefunction can be visualized as a blurred version of a path (Fig. 1) but this picture must be

refined, as described in the following section. The formal definition is

A **wavefunction** is a mathematical function that contains all the dynamical information about the state of a system.

By ‘dynamical information’ is meant information about all aspects of the particle’s motion, such as its location, momentum, and energy.

7B.1 The Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed an equation for calculating the wavefunction of a particle. The **Schrödinger equation**, specifically the *time-independent* Schrödinger equation, for a single particle of mass m moving with energy E in one dimension is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad (1a)$$

The Schrödinger equation

The chemist's toolkit 19 Ordinary differential equations

An **ordinary differential equation** is a relation between derivatives of a function of one variable and the function itself, as in

$$(a) \ a \frac{dy}{dx} + by + c = 0 \quad (b) \ a \frac{d^2y}{dx^2} + b \frac{dy}{dx} + cy + d = 0$$

The coefficients a , b , etc., may be constants or functions of x . The **order** of the equation is the order of the highest derivative that occurs in it, so (a) is a first-order equation and (b) is a second-order equation. 'Solving' a differential equation is the process of determining the function, in this case $y(x)$, that satisfies it. Only very rarely are orders higher than 2 encountered in science.

In many cases it is found that various constants appear in the solution. These constants are determined by imposing various **boundary conditions** on the solutions, values that the solution must have at specified points, such as $y = 0$ at the locations $x = 0$ and $x = L$, which would be written $y(0) = 0$ and $y(L) = 0$. For example, the general solution of the equation $d^2y/dx^2 + y = 0$ (the solution with the constants unspecified)

where $V(x)$ is the potential energy and \hbar (which is read h -bar) is a convenient modification of Planck's constant:

$$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J s}$$

The Schrödinger equation is a 'differential equation', and in this case a second-order ordinary differential equation (see *The chemist's toolkit 19*) because it is expressed in terms of the second derivative of the function ψ . A feature to keep in mind for when we turn to the interpretation of wavefunctions is that because the energy of a particle is the sum of its potential and kinetic energies, the first term in eqn 1a can be identified with the kinetic energy of the particle:

$$\underbrace{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}}_{\text{Kinetic energy } \times \psi} + \underbrace{V(x)\psi}_{\text{Potential energy } \times \psi} = \underbrace{E\psi}_{\text{Total energy } \times \psi}$$

Equation 1a is often written in the very compact form

$$\hat{H}\psi = E\psi \quad (1b)$$

The Schrödinger equation (compact form)

where ' $\hat{H}\psi$ ' stands for everything on the left of eqn 1a. The quantity \hat{H} is called the **hamiltonian**

is $y(x) = A \sin ax + B \cos ax$. The solution taking into account the two boundary conditions would be obtained by requiring $y(0) = 0$ and $y(L) = A \sin aL = 0$. Because $\sin \theta = 0$ for $\theta = 0, \pi, 2\pi, \dots$, it follows that $aL = n\pi$, with $n = 0, 1, 2, \dots$ so $a = n\pi/L$. In this case, the acceptable solution would be simply $y(x) = A \sin(n\pi x/L)$ with $n = 0, 1, 2, \dots$. There may be other requirements on the solution that lead to a value for A . For instance, if the solution is a wavefunction, then the total probability of finding the particle somewhere must be 1 (this point is developed in the text).

A first-order differential equation requires one boundary condition; a second-order equation requires two. For time-dependent solutions, the 'boundary condition' is termed an **initial condition**, and is typically the value that the solution must have at $t = 0$.

Simple ordinary differential equations are solved by elementary methods; others, though, require sophisticated techniques. Many of these techniques are included in mathematical software; other solutions can simply be written down by reference to tables of solutions that have been compiled

of the system after the Irish mathematician William Hamilton, who had formulated a version of classical mechanics that used equations similar to eqn 1a. It is written with a '^' (a 'hat' or 'caret') to signify that it is an 'operator' (*The chemist's toolkit 20*), a mathematical action on ψ , such as taking the second derivative. A lot of quantum mechanics is formulated in terms of operators but they are used sparingly in this text.

The fact that the Schrödinger equation is a differential equation should not cause too much consternation, for in most cases the solutions will be quoted without going into the sometimes tricky details of how they are found. The rare cases in which the explicit forms of its solution are needed will involve very simple functions, as shown in the following *Justification*. For example, three simple but important cases, omitting various constants in order to emphasize the form of the functions and to show that they are familiar, are as follows:

- The wavefunction for a freely moving particle is $\sin x$, exactly as for de Broglie's matter wave.
- The wavefunction for a particle free to oscillate to-and-fro near a point is e^{-x^2} , where x is the displacement from the point.

¹See, for instance, our *Physical chemistry: thermodynamics, structure, and change* (2014).

The chemist's toolkit 20 Operators

A mathematical **operator**, which in general is often denoted $\hat{\Omega}$ ('omega hat'), is a collection of mathematical symbols that, when applied to an algebraic expression, generates another expression (or, in certain cases, leaves it unchanged). Thus, differentiation is represented by the operator $\hat{\Omega} = d/dx$, which when applied to a function $f(x)$ produces $df(x)/dx$. For instance, the effect of the operator d/dx on the function x^2 produces $2x$. Taking a logarithm can also be expressed as the outcome of the operator \log applied to an expression (including a number). For instance, applying it to x^2 produces $\log(x^2) = 2 \log x$. Even multiplication by x can be regarded as the outcome of the operator $\hat{\Omega} = x \times$ operating on a function. In this case, when applied to x^2 it produces $x \times x^2 = x^3$.

An operator is classified as **linear** if, when applied to a sum of functions, it operates on each function individually:

$$\text{Linear operator: } \hat{\Omega}(f + g) = \hat{\Omega}f + \hat{\Omega}g$$

Multiplication by x and differentiation with respect to x are both linear operators, but taking a logarithm is not (because $\log(f + g) \neq \log f + \log g$).

- The wavefunction for an electron in the lowest energy state of a hydrogen atom is proportional to e^{-r} , where r is the distance from the nucleus.

Justification 7B.1

The solution of the Schrödinger equation for a freely moving particle

The form of the Schrödinger equation can be justified to a certain extent by showing that it implies the de Broglie relation for a freely moving particle (eqn 4 of Topic 7A, $\lambda = h/p$).

Step 1: Simplify the Schrödinger equation

By free motion is meant motion in a region where the potential energy is constant and may be taken to be zero ($V = 0$ everywhere). Then, eqn 1a simplifies to

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (2)$$

The Schrödinger equation (freely moving particle)

Step 2: Verify that $\psi = \sin kx$ is a solution

A solution of eqn 2 is

$$\psi = \sin kx \quad k = \frac{(2mE)^{1/2}}{\hbar}$$

as can be verified by substitution of the solution into both sides of the equation:

$$\begin{aligned} \frac{d}{dx} \sin kx &= k \cos kx & \frac{d}{dx} \cos kx &= -k \sin kx \\ \frac{d^2}{dx^2} \sin kx &= -k^2 \sin kx & \frac{d^2}{dx^2} \cos kx &= -k^2 \cos kx \end{aligned}$$

$$\text{Lefthand side: } -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sin kx = -\frac{\hbar^2}{2m} (-k^2) \sin kx = \frac{\hbar^2 k^2}{2m} \sin kx$$

The order in which operators are applied is, in general, important. Thus, the outcome of differentiation of a function $f(x)$ followed by multiplication by x (denoted $x \times df/dx$) is in general different from multiplication followed by differentiation (denoted $d(x \times f)/dx$). Thus, with $f(x) = x^2$, the first outcome is $2x^2$ and the second outcome is $3x^2$.

Operators are of the greatest importance in quantum mechanics, where every observable (such as momentum and position) is represented by a linear operator. Thus the kinetic energy E_k of a particle of mass m moving along the x -axis, is represented by the operator $\hat{E}_k = -(\hbar^2/2m)d^2/dx^2$, and position on that axis, x , is represented by the operator $\hat{x} = x \times$. Both operators act on the wavefunction, and the outcome is interpreted in terms of the outcome of measuring the two observables. One very important operator, that for the total energy, is called the **hamiltonian operator**, and denoted \hat{H} .

Righthand side: $E \sin kx$

The function $\sin kx$ is a wave of wavelength $\lambda = 2\pi/k$, as can be seen by comparing $\sin kx$ with $\sin(2\pi x/\lambda)$, the standard form of a harmonic wave with wavelength λ (Fig. 2).

Step 3: Calculate the energy and momentum of the particle

The energy of the particle is entirely kinetic (because $V = 0$ everywhere), so the total energy of the particle is just its kinetic energy:

$$E = E_k = \frac{p^2}{2m}$$

Because E is related to k by $E = \hbar^2 k^2 / 2m$, it follows from a comparison of the two equations that $p = \hbar k$.

Step 4: Relate the momentum of the particle to the wavelength of its wavefunction

Because $\lambda = 2\pi/k$ and therefore $k = 2\pi/\lambda$, the linear momentum is related to the wavelength of the wavefunction by

$$p = \frac{\hbar}{\lambda} \times \frac{2\pi}{2\pi} = \frac{h}{\lambda}$$

which is the de Broglie relation. That is, in the case of a freely moving particle, the Schrödinger equation has led to an experimentally verified conclusion.

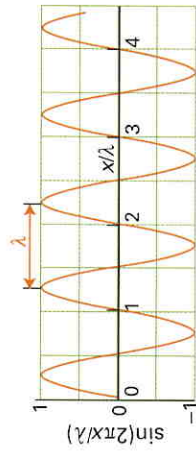


Fig. 2 The wavelength of a harmonic wave of the form $\sin(2\pi x/\lambda)$. The amplitude of the wave is the maximum height above the centre line.

7B.2 The Born interpretation

Before going any further, it will be helpful to begin to understand the physical significance of a wavefunction, and specifically what it reveals about the location of the particle it describes. The interpretation that is widely used is based on a suggestion made by the German physicist Max Born. He made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave is interpreted as its intensity and therefore (in quantum terms, Topic 7A) as the number of photons present. He argued that, by analogy, the square of a wavefunction gives an indication of the probability of finding a particle in a particular region of space. To be precise, the **Born interpretation** asserts that:

The probability of finding a particle in a small region of space of volume δV is proportional to $\psi^2 \delta V$, where ψ is the value of the wavefunction in the region.

In other words, ψ^2 is a **probability density**. As for other kinds of density, such as mass density (ordinary 'density'), the probability itself is obtained by multiplying the probability density ψ^2 by the volume δV of the region of interest.²

A note on good practice The symbol δ is used to indicate a small change in a parameter, as in x changing to $x + \delta x$. The symbol Δ is used to indicate a finite (measurable) difference between two quantities, as in $\Delta X = X_{\text{final}} - X_{\text{initial}}$. The sequence of symbols is Δ for measurable, δ for small, and d for infinitesimal.

For a small 'inspection volume' δV of given size, the Born interpretation implies that:

- Wherever ψ^2 is large, there is a high probability of finding the particle.

²The wavefunction ψ is supposed to be a real function (that is, one that does not depend on i , the square-root of -1). In general, ψ is complex (has both real and imaginary components), but complex functions are not considered in this book. For the role, properties, and interpretation of complex wavefunctions, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

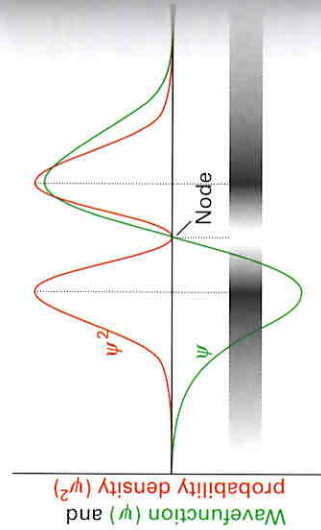


Fig. 3 A wavefunction (green) does not have a direct physical interpretation. However, its square (red), or its square modulus if it is complex, tells us the probability of finding a particle at each point. The probability density implied by the wavefunction shown here is depicted by the density of shading in the greyscale band below the x -axis.

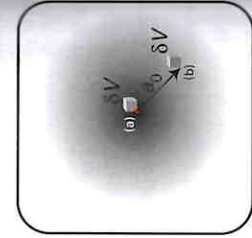
- Wherever ψ^2 is small, there is only a small chance of finding the particle.

The density of shading in Fig. 3 represents a **probabilistic interpretation**, which accepts that predictions can be made only about the probability of finding a particle somewhere. The probabilistic interpretation is in contrast to classical physics, which claims to be able to predict precisely that a particle will be at a given point on its path at a given instant.

Example 7B.1

Interpreting a wavefunction

The wavefunction of an electron in the lowest energy state of a hydrogen atom is proportional to e^{-r/a_0} , with $a_0 = 52.9$ pm and r the distance from the nucleus (Fig. 4). Calculate the relative probabilities of finding the electron inside a small cubic volume located at (a) the nucleus, (b) a distance a_0 from the nucleus.



Collect your thoughts According to the Born interpretation, the probability is proportional to $\psi^2 \delta V$ evaluated at the specified location. The volume of interest is so small (even on the scale of the atom) that you can ignore the variation of ψ within it. With ψ evaluated at the point in question, the probability is then

$$\text{Probability} \propto \psi^2 \delta V$$

The solution (a) At the nucleus, $r = 0$, so there $\psi^2 \propto 1.0$ (because $e^0 = 1$) and the probability is proportional to $1.0 \times \delta V$. (b) At a distance $r = a_0$ in an arbitrary direction, $\psi^2 \propto e^{-2} \times \delta V = 0.14 \times \delta V$. Therefore, the ratio of probabilities is $1.0/0.14 = 7.1$. It is more probable (by a factor of 7.1) that the electron will be

found at the nucleus than in the same tiny volume located at a distance a_0 from the nucleus.

Self-test 7B.1

The wavefunction for the lowest energy state in the ion He^+ is proportional to e^{-2r/a_0} . Repeat the calculation for this ion. Any comment?

Answer: 55; a more compact wavefunction on account of the higher nuclear charge

The Born interpretation also leads to the identification of conditions that a wavefunction must satisfy for it to be acceptable:

- It must be single-valued (that is, have only a single value at each point): there cannot be more than one probability density at each point.
- It cannot become infinite over a finite region of space: the total probability of finding a particle in a region cannot exceed 1.

Mathematically, these conditions are satisfied if the wavefunction takes on specific values at various points, such as at a nucleus, at the edge of a region, or at infinity. That is (in accord with the discussion of differential equations in *The chemist's toolkit 19*), the wavefunction must satisfy certain **boundary conditions**, values that the wavefunction must adopt at certain positions. Two further conditions stem from the Schrödinger equation itself, which could not be written unless:

- The wavefunction is continuous everywhere.
- It has a continuous slope everywhere.

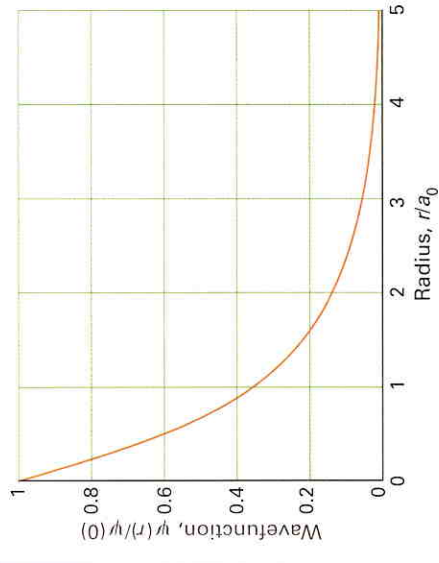


Fig. 4 The wavefunction for an electron in the ground state of a hydrogen atom is an exponentially decaying function of the form e^{-r/a_0} , where a_0 is the Bohr radius.

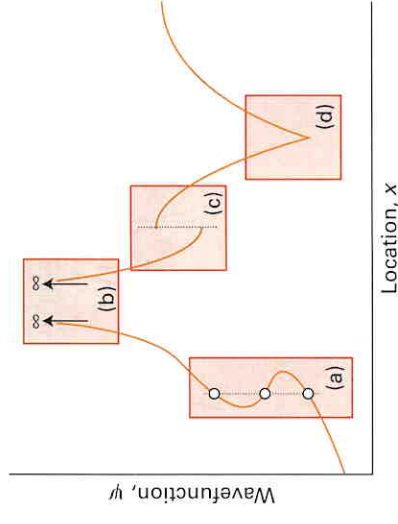


Fig. 5 This wavefunction is unacceptable because (a) it is not single-valued, (b) it is infinite over a finite range, (c) it is not continuous, (d) its slope is not continuous.

These last two conditions mean that the second derivative of ψ , the first term in eqn 1a, is well defined everywhere. All four conditions are summarized in Fig. 5.

These requirements have profound implications. One feature of the solution of any given Schrödinger equation, a feature common to all differential equations, is that an infinite number of possible solutions are allowed mathematically. For instance, if $\sin x$ is a solution of the equation, then so too is $a \sin bx$, where a and b are arbitrary constants, with each solution corresponding to a particular value of E . However, it turns out that only some of these solutions fulfil the requirements stated above. This feature lies at the heart of quantum mechanics: *the fact that only some solutions are acceptable, together with the fact that each solution corresponds to a characteristic value of E , implies that only certain values of the energy are acceptable*. That is,

When the Schrödinger equation is solved subject to the boundary conditions that the solutions must satisfy, it is found that the energy of the system is quantized (Fig. 6).

Boundary conditions can always be traced to a physical constraint on the system. For instance, a particle cannot be found where its potential energy is infinite, so a boundary condition would be that the wavefunction must vanish there. In some cases (an atom or molecule), an electron cannot be found at great distances from the nuclei (specifically at infinity), so a boundary condition would be that its wavefunction must approach zero at infinite distances. Wherever boundary conditions are imposed, they lead to the rejection of mathematically possible but physically

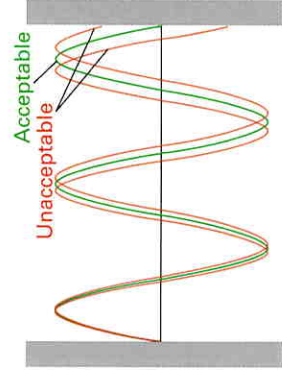


Fig. 6 Although an infinite number of solutions of the Schrödinger equation exist, not all of them are physically acceptable. Acceptable wavefunctions have to satisfy certain boundary conditions, which vary from system to system. In the example shown here, where the particle is confined between two impenetrable walls, the only acceptable wavefunctions are those that fit between the walls (like the vibrations of a stretched string). Because each wavefunction corresponds to a characteristic energy, and the boundary conditions rule out many solutions, only certain energies are permissible.

unacceptable wavefunctions and their corresponding energies. That is, boundary conditions result in the quantization of energy.

There is more information carried by ψ than the probability that a particle will be found somewhere: as remarked earlier, it contains *all* the dynamical information about a particle. A hint of that is found in the discussion of eqn 1 where the first term was taken as an indication of the relation between the kinetic energy of the particle and the second derivative of the wavefunction. Mathematically, the term $d^2\psi/dx^2$ in eqn 1a can be interpreted as a way of expressing the ‘curvature’ of the wavefunction at each point. Thus, if the wavefunction is sharply curved, then $d^2\psi/dx^2$ is large; if it is only slightly curved, then $d^2\psi/dx^2$ is small. But because the term proportional to $d^2\psi/dx^2$ is related to the kinetic energy, it follows that if the wavefunction is sharply curved, then the particle it describes has a high kinetic energy. Conversely, if the wavefunction has only a low curvature, then the particle has only a low kinetic energy (Fig. 7). This interpretation is consistent with the de Broglie relation, for a short wavelength corresponds to both a sharply curved wavefunction and a high linear momentum and therefore a high kinetic energy. For more complicated wavefunctions, the curvature changes from point to point, and the total contribution to the kinetic energy is an average over the entire extent of the wavefunction.

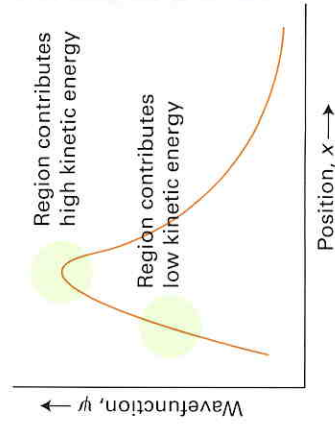


Fig. 7 The observed kinetic energy of a particle is the average of contributions from the entire space covered by the wavefunction. Sharply curved regions contribute a high kinetic energy to the average; slightly curved regions contribute only a small kinetic energy.

7B.3 The uncertainty principle

According to the de Broglie relation, the wavefunction $\sin(2\pi x/\lambda)$, a wave of constant wavelength, corresponds to a particle with a definite linear momentum $p = h/\lambda$. However, a wave does not have a definite location at a single point in space, so it is not possible to speak of the precise position of the particle if it has a definite momentum. Indeed, because a sine wave spreads throughout the whole of space, nothing can be said about the location of the particle: because the wave spreads everywhere, the particle may be found anywhere. This statement is one half of the **uncertainty principle** proposed by Werner Heisenberg in 1927:

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

More precisely, this is the *position–momentum uncertainty principle* (there are other versions of the principle).

Before discussing the principle further, the other half must be established: that if the exact position of a particle is known, then nothing can be said about its momentum. If the particle is at a definite location, then its wavefunction must be nonzero there and zero everywhere else (Fig. 8). Such a wavefunction can be simulated by forming a **superposition** of many wavefunctions; that is, by adding together the amplitudes of a large number of sine functions (Fig. 9). This procedure is successful because the amplitudes of the waves add together at one location to give a nonzero total amplitude but cancel everywhere else. In other words, a sharply localized wavefunction can be created by adding together wavefunctions corresponding to many different wavelengths

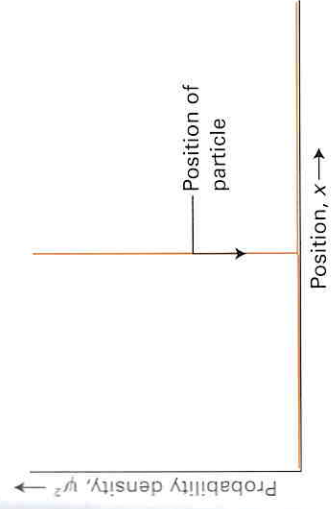


Fig. 8 The wavefunction for a particle with a well-defined position is a sharply spiked function that has zero amplitude everywhere except at the particle’s position.

and therefore, by the de Broglie relation, of many different linear momenta.

The superposition of a few sine functions gives a broad, ill-defined wavefunction (Fig. 9). As the number of functions increases, the wavefunction becomes sharper because of the more complete interference between the positive and negative regions of the components. When an infinite number of components are used, the wavefunction is a sharp, infinitely narrow spike like that in Fig. 8, which corresponds to perfect localization of the particle. Now the particle is perfectly localized, but at the expense of discarding all information about its momentum.

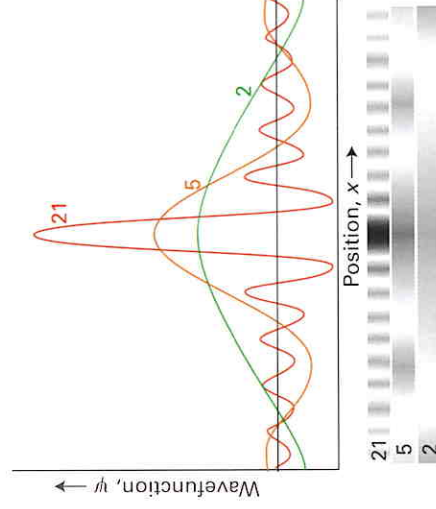


Fig. 9 The wavefunction for a particle with an ill-defined location can be regarded as the sum (superposition) of several wavefunctions of different wavelengths that interfere constructively in one place but destructively elsewhere. As more waves are used in the superposition, the location becomes more precise at the expense of uncertainty in the particle’s momentum. An infinite number of waves are needed to construct the wavefunction of a perfectly localized particle. The numbers against each curve are the number of sine waves used in the superpositions.

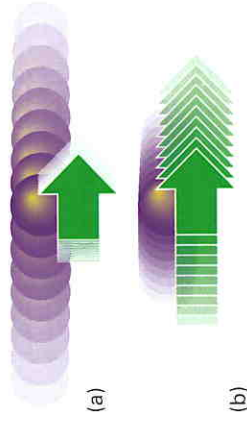


Fig. 10 A representation of the content of the uncertainty principle. The range of locations of a particle is shown by the spheres, and the range of momenta by the arrows. In (a), the position is quite uncertain, and the range of momenta is small. In (b), the location is much better defined, and now the momentum of the particle is quite uncertain.

The quantitative version of the position–momentum uncertainty relation is

$$\Delta p \Delta x \geq \frac{1}{2} h \quad \text{Position–momentum uncertainty relation} \quad (3)$$

The quantity Δp is the ‘uncertainty’ in the linear momentum and Δx is the uncertainty in position (which is proportional to the width of the peak in Fig. 9). Equation 3 expresses quantitatively the fact that the more closely the location of a particle is specified (the smaller the value of Δx), then the greater the uncertainty in its momentum (the larger the value of Δp) parallel to that coordinate, and vice versa (Fig. 10). When $\Delta x = 0$, which is the case when the location of the particle is known exactly, Δp must be infinite, implying complete ignorance about its linear momentum. Likewise, if $\Delta p = 0$ (certainty about the linear momentum), then $\Delta x = \infty$ (total ignorance about where the particle will be found).³

Brief illustration 7B.1 The uncertainty principle

Suppose that the speed of a certain projectile of mass 1.0 g is known to within $\Delta v = 1.0 \mu\text{m s}^{-1}$. From $\Delta p = m\Delta v$ and $\Delta p \Delta x \geq \frac{1}{2} h$, the uncertainty in its position along its line of flight is

$$\begin{aligned} \Delta x &\geq \frac{h}{2\Delta p} = \frac{h}{2m\Delta v} \\ &= \frac{6.626 \times 10^{-34} \text{ J s}}{2 \times (1.0 \times 10^{-3} \text{ kg}) \times (1.0 \times 10^{-6} \text{ m s}^{-1})} \\ &= 3.3 \times 10^{-26} \text{ m} \end{aligned}$$

$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$

³The position–momentum uncertainty principle applies to location and momentum *along the same axis*. It does not limit our ability to specify location on one axis and momentum along a perpendicular axis. For details, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

This degree of uncertainty is completely negligible for all practical purposes, which is why the need for quantum mechanics was not recognized for over 200 years after Newton had proposed his system of mechanics and why in daily life we are completely unaware of the restrictions it implies. However, when the mass is that of an electron, the same uncertainty in speed implies an uncertainty in position far larger than the diameter of an atom, so the concept of a trajectory—the simultaneous possession of a precise position and momentum—is untenable.

••• **Self-test 7B.2**

Estimate the minimum uncertainty in the speed of an electron in a hydrogen atom (taking its diameter as 100 pm).

Answer: 580 km s⁻¹

The uncertainty principle captures one of the principal differences between classical and quantum mechanics. Classical mechanics supposed, falsely as we now know, that the position and momentum of

a particle can be specified simultaneously with arbitrary precision. However, quantum mechanics shows that position and momentum along a given axis are **complementary**, that is, not simultaneously specifiable. Quantum mechanics requires a choice: position can be specified at the expense of momentum, or momentum at the expense of position. Certain other pairs of observables are also complementary, as explained in Topic 7D.

The uncertainty principle has profound implications for the description of electrons in atoms and molecules and therefore for chemistry as a whole. Early models of the atom supposed that the motion of an electron around the nucleus could be described by classical mechanics, and that the electron would move in some kind of orbit. But to specify an orbit, it is necessary to specify the position and momentum of the electron at each point of its path. The possibility of doing so is ruled out by the uncertainty principle. The properties of electrons in atoms, and therefore the foundations of chemistry, have had to be formulated in a completely different way.

Checklist of key concepts

- 1 A **wavefunction**, ψ , contains all the dynamical information about a system.
- 2 Wavefunctions are found by solving the appropriate **Schrödinger equation**.
- 3 **Boundary conditions** are the constraints on the solutions of the Schrödinger equation, and their imposition results in the quantization of energy.

□ 4 According to the **Born interpretation**, the probability of finding a particle in a small region of space of volume δV is proportional to $\psi^2 \delta V$, where ψ is the value of the wavefunction in the region.

□ 5 According to the **Heisenberg uncertainty principle**, it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle along a given axis.

TOPIC 7C Translation

► Why do you need to know this material?

The application of quantum theory to translation reveals the origin of quantization and other non-classical features of motion. These features are responsible for a variety of physical and chemical phenomena.

► What is the key idea?

The translational energy levels of a particle confined to a finite region of space are quantized, and under certain conditions particles can pass into and through classically forbidden regions.

► What do you need to know already?

You should be familiar with the classical description of translation (*The chemist's toolkit 3*) and with the de Broglie's relation (Topic 7B). You should know that the wavefunction is the solution of the Schrödinger equation, be familiar with the Born interpretation (Topic 7B), and be aware of the role of boundary conditions in the solutions of differential equations (*The chemist's toolkit 19* in Topic 7B).

Translation is motion through space. Gas-phase molecules, for instance, undergo translational motion, and their kinetic energy is a contribution to the total internal energy of the sample. Electrons migrate through metallic solids and give rise to electrical conductivity.

Classical mechanics allows the translational kinetic energy of a particle to be increased to any value by applying an appropriate force to the particle. As will become clear, quantum theory predicts a different outcome. When a particle is confined to a

finite region of space only certain energies are acceptable. That is, its translational energy is quantized. Quantum mechanics also reveals other non-classical features, including the ability of a particle to penetrate into and through regions where classical physics would forbid it to be found.

7C.1 Motion in one dimension

Consider the translational motion of a 'particle in a box', a particle of mass m that can travel in a straight line in one dimension (along the x -axis) but is confined between two walls separated by a distance L . The potential energy, V , of the particle can be taken to be zero inside the box but rises abruptly to infinity at the walls (Fig. 1). The classical model would be of a bead on a wire able to move freely between two stops.

The starting point for this discussion is the Schrödinger equation (eqn 1a of Topic 7B):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

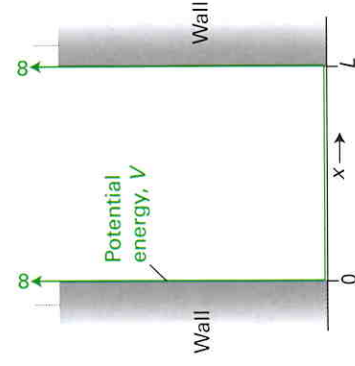


Fig. 1 A particle in a one-dimensional region with impenetrable walls at either end. Its potential energy is zero between $x = 0$ and $x = L$ and rises abruptly to infinity as soon as the particle touches either wall.

Because $V = 0$ inside the region where the particle can be found, for a particle in a box

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \text{Schrodinger equation (particle in a box)} \quad (1)$$

The general solution of this differential equation (*The chemist's toolkit 19* in Topic 7B) is

$$\psi = A \sin\left(\frac{2\pi x}{\lambda}\right) + B \cos\left(\frac{2\pi x}{\lambda}\right) \quad (2)$$

$$\text{with } \lambda = \frac{b}{(2mE)^{1/2}}$$

where A and B are constants. That is, the wavefunctions describe de Broglie's 'matter waves' (Topic 7B), with wavelengths λ that depend on the mass and total energy of the particle. Unlike the matter waves described in Topic 7B, the waves described by eqn 2 must obey two boundary conditions. These conditions recognize that because the particle cannot be found outside the box where its potential energy would be infinite. Therefore, because the wavefunction is continuous (no sudden steps) and is zero outside the box, it must be zero at the edges of the box, at $x = 0$ and at $x = L$.

First, the condition that $\psi(0) = 0$, when combined with $\sin 0 = 0$ and $\cos 0 = 1$ (and therefore $\psi(0) = B$), requires that $B = 0$. The second condition, that $\psi(L) = 0$, then requires that

$$\psi = A \sin\left(\frac{2\pi L}{\lambda}\right) = 0$$

The function $\sin \theta$ is zero when $\theta = n\pi$, with $n = 0, 1, 2, \dots$, so in this case the second boundary condition is satisfied if

$$\frac{2\pi L}{\lambda} = n\pi, \text{ and therefore} \\ \frac{2L}{\lambda} = n \quad \text{with } n = 0, 1, 2, \dots$$

It now follows that

$$\psi = A \sin\left(\frac{n\pi x}{L}\right) \quad \text{with } n = 1, 2, \dots$$

The value $n = 0$ has been discarded because it would give $\psi = 0$ everywhere (the particle would be found nowhere). It follows that the allowed wavefunctions must be such that an integral number of half-wavelengths (one half-wavelength, two half-wavelengths, ...) fit

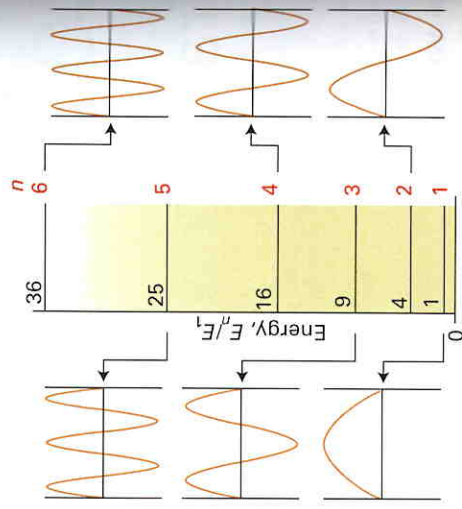


Fig. 2 The allowed energy levels and the corresponding (standing wave) wavefunctions for a particle in a box. Note that the energy levels increase as n^2 , and so their spacing increases as n increases. Each wavefunction is a standing wave, and successive functions possess one more half wave and a correspondingly shorter wavelength.

inside the box. Each wavefunction of the particle fits inside the box exactly, like the vibrations of a string pinned down at each end, as in a guitar (Fig. 2).

As shown in the following *Justification*, the constant of proportionality A , which in this context is denoted N , is $(2/L)^{1/2}$ and is called the **normalization constant**. Its value ensures that the total probability of finding the particle inside the box is 1. Therefore, the full form of the allowed wavefunctions is

$$\psi_n = N \sin\left(\frac{n\pi x}{L}\right) \quad \text{Wavefunctions of a particle in a one-dimensional box} \quad (3) \\ N = \left(\frac{2}{L}\right)^{1/2} \quad n = 1, 2, \dots$$

Each allowed wavefunction has been labelled with the number n , which is an example of a **quantum number**, an integer (in some cases, Topic 8B, a half-integer) that specifies the state of the system.

Justification 7C.1

The normalization constant

According to the Born interpretation, the probability of finding a particle in the infinitesimal region of length dx at the point x given that its normalized wavefunction has the value ψ at that point, is equal to $\psi^2 dx$. Therefore, the total probability of finding the particle between $x = 0$ and $x = L$ is the sum of all the probabilities of its being in each infinitesimal region. A sum of this type over infinitesimal increments is the integral of the

commonly specifies the value of certain physical properties of the system: in the present example, the energy of the particle by using its value in eqn 4.

The solutions of a particle in a box have the following important features:

- The permitted energies of the particle are shown in Fig. 2 together with the shapes of the wavefunctions for $n = 1-6$.

All the wavefunctions except the one of lowest energy ($n = 1$) possess points called **nodes** where the function passes through zero. Passing *through* zero is an essential part of the definition of a node: just becoming zero is not sufficient. The points at the edges of the box, where $\psi = 0$, are not nodes, because the wavefunction does not pass through zero there. The number of nodes in the wavefunctions shown in the illustration increases from 0 (for $n = 1$) to 5 (for $n = 6$), and in general is $n - 1$ for a particle in a one-dimensional box. It is a general feature of quantum mechanics that the wavefunction corresponding to the state of lowest energy has no nodes, and as the number of nodes in the wavefunctions increase, the energy increases too.

According to the Born interpretation (Topic 7B), the probability density at the location x when the quantum number of the particle is n is

$$\psi_n^2(x) = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) \quad \text{Probability density} \quad (5)$$

Provided the fine detail of the oscillations is ignored, Fig. 3 shows that the probability density $\psi_n^2(x)$ becomes more uniform as n increases. The probability density when n is large reflects the classical result that a particle bouncing between the walls spends equal times at all points. This behaviour is an illustration of the **correspondence principle**, which states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

- Because the quantum number n cannot be zero (for this system), the lowest energy that the particle may possess is not zero, as would be allowed by classical mechanics, but $b^2/8mL^2$ (the energy when $n = 1$).

This lowest, irremovable energy is called the **zero-point energy**. The existence of a zero-point energy is consistent with the uncertainty principle (Topic 7B). If a particle is confined to a finite region, its location is not completely indefinite; consequently its momentum cannot be specified precisely as zero, and therefore its kinetic energy cannot be zero either. The zero-point

function (*The chemist's toolkit 8* in Topic 2A). The calculation has the following steps.

Step 1: Write an expression for the total probability

Because the particle is certainly in the range somewhere, the total probability of finding the particle between the two walls of the box is 1:

$$\int_0^L \psi^2 dx = 1 \quad \text{Total probability of finding the particle between 0 and L}$$

Substitution of the form of the wavefunction, $\psi_n = N \sin(n\pi x/L)$, turns this expression into

$$N^2 \int_0^L \left(\sin\frac{n\pi x}{L}\right)^2 dx = 1$$

Step 2: Evaluate the integral

Use Integral T1 in the *Resource section* with $a = L$, so it follows that

$$\int_0^L \left(\sin\frac{n\pi x}{L}\right)^2 dx = \frac{1}{2}L$$

Step 3: Calculate N

From the results in steps 1 and 2 it follows that

$$N^2 \times \frac{1}{2}L = 1$$

and hence $N = (2/L)^{1/2}$. In this case, but not in general, the normalization constant is the same for all the wavefunctions regardless of the value of the quantum number.

It is now a straightforward matter to find the permitted energy levels because the only contribution to the energy is the kinetic energy of the particle: the potential energy is zero everywhere inside the box, and the particle is never outside the box. From $\lambda = h/(2mE)^{1/2}$ in eqn 2, $\lambda^2 = b^2/2mE$, and therefore

$$E = \frac{b^2}{2m\lambda^2} = \frac{b^2}{2m(2L/n)^2} = \frac{b^2}{2m(4L^2/n^2)}$$

which becomes

$$E_n = \frac{n^2 b^2}{8mL^2} \quad n = 1, 2, \dots \quad \text{Energies of a particle in a one-dimensional box} \quad (4)$$

with the energies labelled with the quantum number n . As well as acting as a label, a quantum number

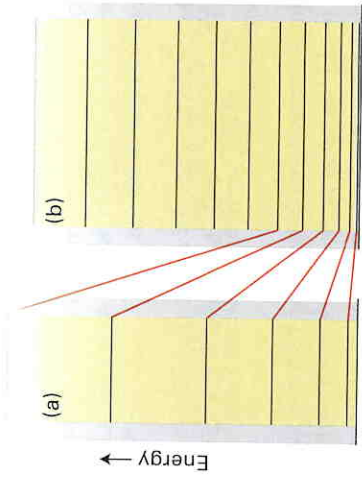


Fig. 3 (a) A narrow box has widely spaced energy levels; (b) a wide box has closely spaced energy levels. (In each case, the separations depend on the mass of the particle too.)

energy is not a special, mysterious kind of energy. It is simply the last remnant of energy that a particle cannot give up. For a particle in a box it can be interpreted classically as the energy arising from a ceaseless fluctuating motion of the particle between the two confining walls. The quantum origin of the zero-point energy is the fact that the wavefunction must be curved as it changes smoothly from 0 at $x = 0$ to 0 at $x = L$, and curvature is an indication of the possession of kinetic energy (Topic 7B).

- The energy difference between adjacent levels is

$$\begin{aligned} \Delta E = E_{n+1} - E_n &= \frac{h^2}{8mL^2} \frac{n^2 + 2n + 1}{(n+1)^2} - \frac{h^2}{8mL^2} n^2 \\ &= \frac{h^2}{8mL^2} \end{aligned} \quad (6)$$

This expression shows that the difference decreases as the length L of the box increases, and that it becomes zero when the walls are infinitely far apart (Fig. 4). Atoms and molecules free to move in laboratory-sized vessels may therefore be treated as though their translational energy is not quantized, because L is so large. The expression also shows that the separation decreases as the mass of the particle increases. Particles of macroscopic mass (like balls and planets, and even minute specks of dust) behave as though their translational motion is not quantized. Both the following conclusions are true in general:

- The greater the extent of the confining region, the less important the effects of quantization. Quantization of translation is very important for highly confining regions.

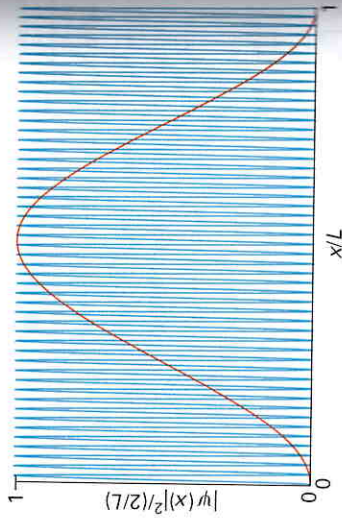


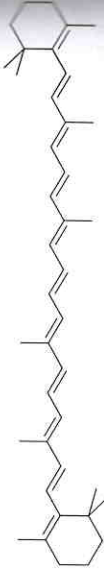
Fig. 4 The probability density $\psi^2(x)$ for large quantum number (here $n = 50$, blue, compared with $n = 1$, red). Notice that the high n the probability density is nearly uniform, provided the fine detail of the increasingly rapid oscillations are ignored

- The greater the mass of the particle, the less important the effects of quantization. Quantization of translation is very important for particles of very small mass.

Example 7C.1

Estimating an absorption wavelength

β -Carotene (1) is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If the length L of the molecular box in β -carotene is $L = 2.94$ nm. Estimate the wavelength of the light absorbed by this molecule when it undergoes a transition from its ground state to the next higher excited state.



1 β -Carotene

Collect your thoughts Treat the conjugated system of single and double bonds in β -carotene as a one-dimensional box containing the electrons that occupy π -orbitals. For reasons familiar from introductory chemistry (and discussed in more detail in Topic 9B), let each C atom contribute one π electron to the available states, with two electrons occupying each state. Then use eqn 6 to calculate the energy separation between the highest occupied and the lowest unoccupied levels. Convert that energy to a wavelength by using the Bohr frequency relation (eqn 1 of Topic 7A, $h\nu = \Delta E$) and the relation $\lambda = c/\nu$.

The solution There are 22 C atoms in the conjugated chain. Each contributes one π electron to the available states, so

each state up to $n = 11$ is occupied by two electrons. From eqn 6 the separation in energy between uppermost occupied level of the ground state of the molecule (with $n = 11$) and the empty state immediately above is

$$\begin{aligned} \Delta E = E_{12} - E_{11} &= (2 \times 11 + 1) \\ &\times \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8 \times (9.109 \times 10^{-31} \text{ kg}) \times (2.94 \times 10^{-9} \text{ m})^2} \\ &= 1.60 \dots \times 10^{-19} \text{ J} \end{aligned}$$

It follows from the Bohr frequency relation that the frequency of radiation required to cause this transition is

$$\nu = \frac{\Delta E}{h} = \frac{1.60 \dots \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 2.42 \dots \times 10^{14} \text{ s}^{-1}$$

or 242 THz (1 THz = 10^{12} Hz), corresponding to

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{2.42 \dots \times 10^{14} \text{ s}^{-1}} = 1.23 \dots \times 10^{-6} \text{ m}$$

or, after rounding up and limiting the answer to three significant figures, 1.24 μm .

Comment The experimental value is 603 THz ($\lambda = 497 \text{ nm} = 0.497 \mu\text{m}$), corresponding to radiation in the visible region of the electromagnetic spectrum. Considering the crudeness of the model, you should be encouraged by the thought that the computed and observed frequencies agree to within a factor of 2.5.

A note on good practice The ability to make such quick 'back-of-the-envelope' estimates of orders of magnitude of physical properties should be a part of every scientist's toolkit.

Self-test 7C.1

- Estimate a typical nuclear excitation energy in electronvolts (1 eV = $1.602 \times 10^{-19} \text{ J}$; 1 GeV = 10^9 eV) by calculating the first excitation energy of a proton confined to a one-dimensional box with a length equal to the diameter of a nucleus (approximately $1 \times 10^{-15} \text{ m}$, or 1 fm).

Answer: 0.6 GeV

7C.2 Tunneling

Now consider the possibility that the potential energy, V , of a particle does not rise to infinity at the walls of the container. Classically, the particle cannot escape from the container. In contrast, when the Schrödinger equation is set up and solved for a particle in a container of this kind, it is found that the wavefunction does not decay abruptly to zero at the walls. In fact,

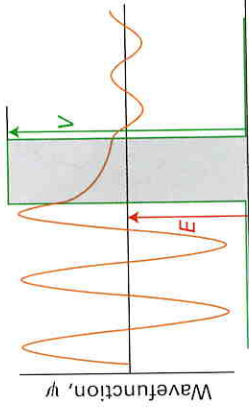


Fig. 5 A particle incident on a barrier from the left has an oscillating wavefunction, but inside the barrier there are no oscillations (for $E < V$). If the barrier is not too thick, the wavefunction is nonzero at its opposite face, and so oscillation begins again there.

the wavefunction oscillates inside the box like a trapped particle, decays exponentially inside the region representing the wall, and oscillates again on the other side of a wall of finite width (Fig. 5). If the walls are so thin and the mass of particle so small that the exponential decay of the wavefunction has not brought it to zero at the outside edge of the wall, the particle might be found outside the container even though according to classical mechanics it has insufficient energy to escape. Such leakage by penetration into or through classically forbidden zones is called **tunneling**.

The Schrödinger equation can be used to calculate the probability that a particle of mass m can tunnel through a barrier of width W and height V . The **transmission probability**, T , of a particle incident on a finite barrier, the probability that the particle of energy E will be found outside the wall, is

$$T = \left\{ 1 + \frac{(e^{\kappa W} - e^{-\kappa W})^2}{16\epsilon(1-\epsilon)} \right\}^{-1} \quad (7a)$$

Transmission probability [one-dimensional barrier]

$$\kappa = \frac{[2m(V-E)]^{1/2}}{\hbar}$$

where $\epsilon = E/V$. When the barrier is high (in the sense that $V/E \gg 1$) and wide (in the sense that the wavefunction loses much of its amplitude inside the barrier), eqn 7a becomes¹

$$T \approx 16\epsilon(1-\epsilon)e^{-2\kappa W} \quad (7b)$$

Transmission probability [high and wide one-dimensional barrier]

The transmission probability decreases exponentially with W and with $m^{1/2}$ (which appears in κ).

¹For details of the calculation, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

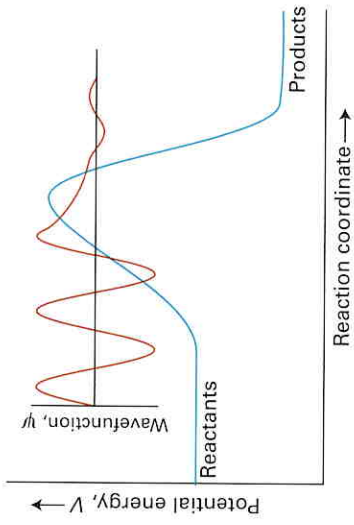


Fig. 6 A proton can tunnel through the activation energy barrier that separates reactants from products, so the effective height of the barrier is reduced and the rate of the proton transfer reaction is increased. The effect is represented here by drawing the wavefunction of the proton near the barrier. Proton tunnelling is important only at low temperatures, when most of the reactants are trapped on the left of the barrier.

It follows that particles of low mass are more able to tunnel through barriers than heavy ones. Hence, tunnelling is very important for electrons, moderately important for protons, and negligible for most other heavier particles.

The very rapid equilibration of proton transfer reactions (Topic 5D) is also a result of the ability of protons to tunnel through barriers and transfer quickly from an acid to a base. The process may be visualized as a proton passing *through* an activation barrier rather than having to acquire enough energy to travel over it (Fig. 6). Quantum mechanical tunnelling can be the dominant process in reactions involving hydrogen atom or proton transfer when the temperature is so low that very few reactant molecules can overcome the activation energy barrier. One indication that a proton transfer is taking place by tunnelling is that an Arrhenius plot (Topic 6D, a plot of $\ln k_r$ where k_r is a rate constant, against $1/T$) deviates from a straight line at low temperatures and the rate is higher than would be expected by extrapolation from room temperature.

Brief illustration 7C.1 Tunnelling in proton transfer reactions

Suppose that a proton of an acidic hydrogen atom is confined to an acid by a barrier of width 100 pm and, due to its binding to the neighbouring atom, lies 5.0 meV below the top of the barrier of height 2.000 eV (so $E = 1.995$ eV). The probability that it can escape from the acid by tunnelling is given by eqn 7a, with $\epsilon = E/V = (1.995 \text{ eV})/(2.000 \text{ eV}) = 0.9975$ and $V - E = 0.0050$ eV (corresponding to 8.0×10^{-22} J).

$$\kappa = \frac{\{2 \times (1.67 \times 10^{-27} \text{ kg}) \times (8.0 \times 10^{-22} \text{ J})\}^{1/2}}{1.055 \times 10^{-34} \text{ J s}} \\ = 1.55 \dots \times 10^{10} \text{ m}^{-1}$$

with $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$. It follows that

$$\kappa V = (1.55 \dots \times 10^{10} \text{ m}^{-1}) \times (100 \times 10^{-12} \text{ m}) = 1.55 \dots$$

Equation 7a then yields

$$T = \left\{ 1 + \frac{(e^{1.55 \dots} - e^{-1.55 \dots})^2}{16 \times 0.9975 \times (1 - 0.9975)} \right\}^{-1} = 1.96 \times 10^{-9}$$

To imagine the physical interpretation of this value, think of the proton as vibrating in its bond, and hitting the wall of the barrier on each of its outward swings. Then there is a probability of about 1 in 2000 that on that swing it will escape through the barrier.

Self-test 7C.2

Suppose that the junction between two semiconductors can be represented by a barrier of height 2.00 eV and width 100 pm. Calculate the probability that an electron of energy 1.95 eV can tunnel through the barrier.

Answer: $T = 0.100$

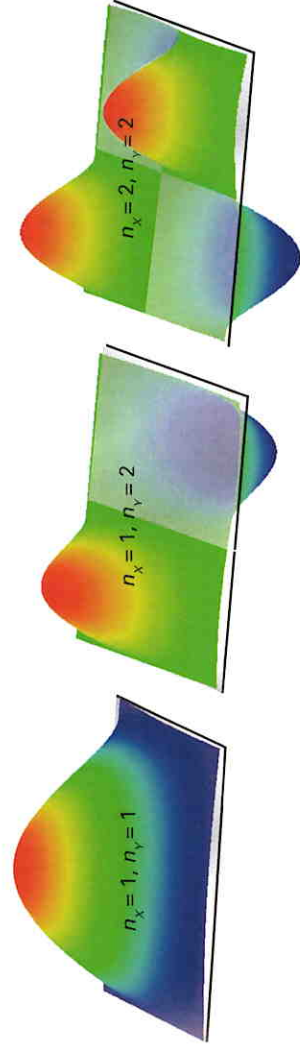


Fig. 8 Three wavefunctions of a particle confined to a rectangular surface.

varies across the floor of the box, so it is a function of both the x - and y -coordinates, written $\psi(x, y)$. As shown in the following *Justification*, the wavefunction can be expressed as a product of wavefunctions for each direction:

$$\psi(x, y) = X(x)Y(y) \quad (8)$$

with each wavefunction satisfying its 'own' one-dimensional Schrödinger equation like that in eqn 1. This conclusion is an example of the 'separation of variables' procedure described in the *Justification*. The solutions are

$$\psi_{n_x, n_y}(x, y) = X_{n_x}(x)Y_{n_y}(y) \quad (9a)$$

Wavefunctions of a particle in a two-dimensional box

$$X_{n_x}(x) = \left(\frac{2}{L_x} \right)^{1/2} \sin \left(\frac{n_x \pi x}{L_x} \right) \quad Y_{n_y}(y) = \left(\frac{2}{L_y} \right)^{1/2} \sin \left(\frac{n_y \pi y}{L_y} \right)$$

$$= \left(\frac{4}{L_x L_y} \right)^{1/2} \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \left(\frac{n_y \pi y}{L_y} \right)$$

with energies

$$E_{n_x, n_y} = E_{n_x} + E_{n_y} = \frac{n_x^2 b^2}{8mL_x^2} + \frac{n_y^2 b^2}{8mL_y^2} \quad (9b) \\ = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{b^2}{8m}$$

Energies of a particle in a two-dimensional box

There are two quantum numbers (n_x and n_y) in eqn 9, each allowed the values 1, 2, ... independently. In one dimension the wavefunctions of a particle in a box are like the vibrations of a guitar string clamped at each end; in two dimensions the wavefunctions are like the vibrations of a rectangular sheet clamped at its edges (Fig. 8).

Justification 7C.2

The separation of variables procedure

The wavefunction for a particle in a two-dimensional box depends on two variables, x and y . That is, the Schrödinger equation is a partial differential equation (The chemist's toolkit 21):

$$-\frac{\hbar^2 \nabla^2 \psi}{2m} = E\psi$$

For simplicity, write this equation as

$$\hat{H}_x \psi + \hat{H}_y \psi = E\psi$$

and solve it by the 'separation of variables' procedure as follows,

Step 1: Express the wavefunction as the product of two wavefunctions

Write $\psi = XY$ where X is a function of x and Y is a function of y , and substitute it on both sides of the last equation,

$$\hat{H}_x XY + \hat{H}_y XY = EXY$$

It follows from The chemist's toolkit 17 in Topic 6G that in this expression \hat{H}_x acts (by taking the second derivative with respect to x) on X , with Y treated as a constant, and \hat{H}_y similarly acts on only Y , with X treated as a constant. Therefore, $\hat{H}_x XY = Y\hat{H}_x X$ and $\hat{H}_y XY = X\hat{H}_y Y$, and the last equation becomes

$$Y\hat{H}_x X + X\hat{H}_y Y = EXY$$

Step 2: Extract the two ordinary differential equations

Divide both sides by XY and obtain

$$\frac{1}{X} \hat{H}_x X + \frac{1}{Y} \hat{H}_y Y = E$$

Here is the clever part of the argument. The first term on the left depends only on x and the second term depends

only on y . Therefore, if x changes, only the first term can change. But its sum with the unchanging second term is the constant E . Therefore, the first term cannot in fact change when x changes. That is, the first term is equal to a constant, written as E_x . The same argument applies to the second term when y is changed; so it too is equal to a constant, written as E_y , and the sum of these two constants is E . That is,

$$\frac{1}{X} \hat{H}_x X = E_x \quad \frac{1}{Y} \hat{H}_y Y = E_y$$

with $E_x + E_y = E$. On multiplication by X and Y , respectively, these two equations become

$$\hat{H}_x X = E_x X \quad \hat{H}_y Y = E_y Y$$

which have the form of eqn 1: they are Schrödinger equations for one-dimensional motion, one along the x -axis and the other along the y -axis.

Step 3. Solve the differential equations

Because the boundary conditions are essentially the same for each axis (the only difference being the actual values of the lengths L_x and L_y), the individual wavefunctions are essentially the same as those found for the one-dimensional case (eqn 3).

You should be aware that the separation of variables procedure does not always work: it requires, as here, the original differential equation to have a simple form.

The chemist's toolkit 21 Partial differential equations

Ordinary differential equations are described in *The chemist's toolkit 19* in Topic 7B. If the unknown function f depends on more than one variable, as in

$$a \left(\frac{\partial^2 f}{\partial x^2} \right)_y + b \left(\frac{\partial^2 f}{\partial y^2} \right)_x = cf$$

then the equation is called a **partial differential equation**. Here, f is a function of x and y , which could be written explicitly as $f(x,y)$, and the factors a , b , c may be constants or functions of either or both variables. Note the change in symbol from d to ∂ to signify a *partial derivative* (as described in *The chemist's toolkit 17* in Topic 6G).

In a number of important cases (but by no means all) the function f can be expressed as a product of functions of each variable, as in $f(x,y) = X(x)Y(y)$. In such cases the partial differential equation separates into a set of ordinary differential equations, the procedure being known as the **separation of variables**. The method is illustrated in *Justification 7C.2*.

Brief illustration 7C.2 The zero-point energy of a particle in a two-dimensional box

An electron trapped in a two-dimensional cavity of dimensions $L_x = 1.0$ nm and $L_y = 2.0$ nm can be regarded as a particle in a box. The zero-point energy of the electron is given by eqn 9b with $n_x = 1$ and $n_y = 1$:

$$E_{0,1} = \left\{ \frac{\hbar^2}{2} \left[\frac{\pi^2}{L_x^2} + \frac{\pi^2}{L_y^2} \right] \right\} \times \frac{6.626 \times 10^{-34} \text{ J s}}{2} \times 8 \times (9.109 \times 10^{-31} \text{ kg}) \times \frac{1}{2} = 7.5 \times 10^{-20} \text{ J}$$

This energy, which could be reported as 75 zJ ($1 \text{ zJ} = 10^{-21} \text{ J}$), corresponds to 0.47 eV .

Self-test 7C.3

Calculate the energy separation between the levels $n_x = n_y = 1$ and $n_x = n_y = 2$ of an electron trapped in a square cavity with sides of length 1.0 nm.

Answer: 0.36 eV , 2.2 eV

An especially interesting case arises when the rectangular region is square with $L_x = L_y = L$. The allowed energies are then

$$E_{n_x, n_y} = (n_x^2 + n_y^2) \frac{h^2}{8mL^2} \quad (10a)$$

This expression shows that different wavefunctions may correspond to the same energy. For example, the wavefunctions with $n_x = 1, n_y = 2$ and $n_x = 2, n_y = 1$ are different:

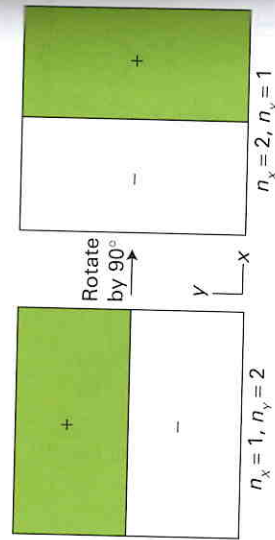


Fig. 9 Degeneracy is always associated with an aspect of symmetry. For a particle in a square box, rotation through 90° takes the $n_x = 1, n_y = 2$ wavefunction into the $n_x = 2, n_y = 1$ wavefunction. As a consequence the states described by the wavefunctions $\psi_{1,2}(x,y)$ and $\psi_{2,1}(x,y)$ have same energy; they are degenerate.

degenerate. Degeneracy is always associated with an aspect of symmetry. In this case, it should be easy to understand, because the confining region is square, and can be rotated through 90° , which takes the $n_x = 1, n_y = 2$ wavefunction into the $n_x = 2, n_y = 1$ wavefunction (Fig. 9). In other cases the symmetry might be harder to identify, but it is always there. Degeneracy is very important in atoms and underlies the structure of the periodic table.

$$\psi_{1,1}(x,y) = \frac{2}{L} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) \quad (10b)$$

$$\psi_{2,1}(x,y) = \frac{2}{L} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right)$$

but both have the energy $5h^2/8mL^2$. Different wavefunctions with the same energy are said to be

Checklist of key concepts

- 1 The energy levels of a particle of mass m in a box of length L are quantized and the wavefunctions are sine functions.
- 2 A **quantum number** specifies the state of a system and commonly can be used to calculate the value of a property.
- 3 A **normalization constant** ensures that the total probability of finding the particle in a system is 1.
- 4 A **node** is a point at which a wavefunction passes through zero.
- 5 The quantization of translation is most important for particles of low mass confined to small regions of space.
- 6 The **correspondence principle** states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.
- 7 The **zero-point energy** is the lowest permissible energy of a system.
- 8 Because wavefunctions do not, in general, decay abruptly to zero, particles may **tunnel** into or through classically forbidden regions.
- 9 Different wavefunctions with the same energy are said to be **degenerate**.

TOPIC 7D

Rotation

➤ Why do you need to know this material?

The investigation of rotational motion introduces the concept of angular momentum, which is central to the description of the electronic structure of atoms and molecules and the interpretation of atomic and molecular spectra.

➤ What is the main idea?

The energy and the angular momentum of a rotating object are quantized.

➤ What do you need to know already?

You should be familiar with the Schrödinger equation and the Born interpretation of the wavefunction (Topic 7B). The Topic uses the concept of boundary conditions (Topics 7B and 7C) and constraints on the wavefunction (Topic 7B).

The discussion of translational motion focuses on linear momentum, p . When rotational motion is considered, it is necessary to focus instead on the analogous *angular* momentum, J (*The chemist's toolkit 22*).

The chemist's toolkit 22 Angular momentum

Angular velocity. ω (omega), is the rate of change of *angular* position; it is reported in radians per second (rad s^{-1}). There are 2π radians in a circle, so 1 cycle per second is the same as 2π radians per second. For convenience, the 'rad' is often dropped, and the units of angular velocity are written as s^{-1} .

Expressions for other angular properties follow by analogy with the corresponding equations for linear motion

(*The chemist's toolkit 3* of Topic 1B). Thus, the **angular momentum**, J , is defined, by analogy with the linear momentum ($p = mv$):

$$J = I\omega$$

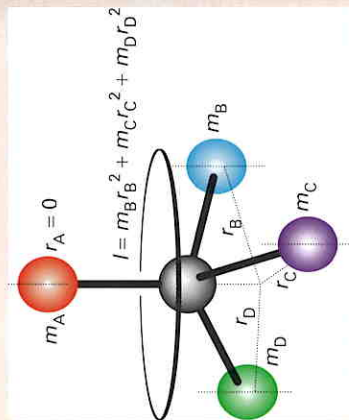
Angular momentum
(definition)

The quantity I is the **moment of inertia** of the body. It represents the resistance of the body to a change in the state of rotation in the same way that mass represents the resistance of the body to a change in the state of translation. The moment of inertia is defined as the sum of the product of the mass of each atom (if the rotating body is a molecule) multiplied by the square of the distance from the axis of rotation (Sketch 1). The SI units of moment of inertia are therefore kilogram metre² (kg m^2) and those of angular momentum are kilogram metre² per second ($\text{kg m}^2 \text{ s}^{-1}$).

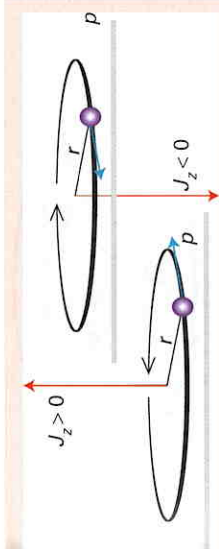
The angular momentum is a vector, a quantity with both a magnitude and direction (*The chemist's toolkit 23*). That is, for rotation in three dimensions, the angular momentum has three components: J_x , J_y , and J_z . For a particle travelling on a circular path of radius r about the z -axis, and therefore confined to the xy -plane, the angular momentum vector points in the z -direction only (Sketch 2), and its only component is

$$J_z = \pm pr$$

Angular momentum of a particle
moving on a circular path



Sketch 1



Sketch 2

where p is the magnitude of its linear momentum in the xy -plane at any instant. When $J_z > 0$, the particle travels in a clockwise direction, as viewed from below; when $J_z < 0$, the motion is anticlockwise. A particle that is travelling at high speed in a circle has a higher angular momentum than a particle of the same mass travelling more slowly. An object with a high angular momentum (like a flywheel) requires a strong braking force (more precisely, a strong 'torque') to bring it to a standstill.

By analogy with the expression for linear motion ($E_k = \frac{1}{2}mv^2 = p^2/2m$), the kinetic energy of a rotating body is

$$E_k = \frac{1}{2}I\omega^2 = \frac{J^2}{2I}$$

Kinetic energy
(angular motion)

For a given moment of inertia, high angular momentum corresponds to high kinetic energy. According to classical mechanics, all angular momenta and rotational kinetic energies are allowed. As may be verified, the units of rotational energy are joules (J).

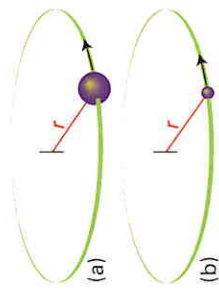


Fig. 1 A particle travelling on a circular path has a moment of inertia I that is given by mr^2 . (a) This heavy particle has a large moment of inertia about the central point; (b) this light particle is travelling on a path of the same radius, but it has a smaller moment of inertia. The moment of inertia plays a role in circular motion that is the analogue of mass for linear motion: a particle with a high moment of inertia is difficult to accelerate into a given state of rotation, and requires a strong braking force to stop its rotation.

where the quantity mr^2 is the **moment of inertia** of the particle about the z -axis, and denoted I (Fig. 1). It follows that the energy of the particle is

$$E = \frac{|J_z|^2}{2I} \quad (2)$$

Kinetic energy of a particle
on a ring in terms of I

From the de Broglie relation ($\lambda = h/p$), the angular momentum can be expressed in terms of the wavelength of the particle:

$$|J_z| = pr = \frac{h}{\lambda} r \quad (3)$$

Magnitude of the
angular momentum
of a particle on a ring

Suppose for the moment that λ can take an arbitrary value. In that case, the amplitude of the wavefunction varies with angle, as shown in Fig. 2. When the angle increases beyond 2π (that is, beyond 360°), the wavefunction continues to change on its next circuit.

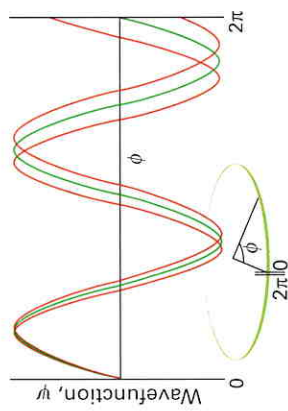


Fig. 2 Three solutions of the Schrödinger equation for a particle on a ring. The circumference has been opened out into a straight line; the points at $\phi = 0$ and 2π are identical. The solutions in red are unacceptable because they have different values after each circuit, and so each one interferes destructively with itself. The solution in green is acceptable because it reproduces itself on successive circuits.

7D.1 Rotation in two dimensions

To see what quantum mechanics reveals about rotational motion, consider a particle of mass m moving in a circular path of radius r in the xy -plane. According to classical mechanics (and as set out in *The chemist's toolkit 22*), the magnitude of the z -component of the angular momentum, $|J_z|$, around the z -axis (which lies perpendicular to the xy -plane and is the only component in this case) is $|J_z| = pr$. The energy of the particle is entirely kinetic because the potential energy is constant and can be set equal to zero everywhere. It follows that $E = p^2/2m$. But for this rotating particle $p = |J_z|/r$, so this energy can be expressed in terms of the angular momentum as

$$E = \frac{p^2}{2m} = \frac{|J_z|^2}{2mr^2} \quad (1)$$

Kinetic energy of a
particle on a ring

For an arbitrary wavelength it gives rise to a different amplitude at each point and the wavefunction will not be single-valued (a requirement for acceptable wavefunctions, Topic 7B). Thus, this arbitrary wave is not acceptable. An acceptable solution is obtained if the wavefunction reproduces itself on successive circuits in the sense that the wavefunction at $\phi = 2\pi$ (after a complete revolution) is the same as the wavefunction at $\phi = 0$: that is, the wavefunction must satisfy **cyclic boundary conditions**. Wavefunctions that match after each circuit have an integral number of wavelengths fitting round the circumference (of length $2\pi r$), and so $n\lambda = 2\pi r$ with $n = 0, 1, 2, \dots$. That is, the acceptable wavefunctions have wavelengths given by

$$\lambda = \frac{\text{Circumference of ring}}{n} = \frac{2\pi r}{n} \quad n = 0, 1, 2, \dots$$

The wavefunction with $n = 0$, with an infinite wavelength, corresponds to a uniform nonzero amplitude around the ring. It follows that the angular momentum is limited to the values

$$|J_z| = \frac{hr}{\lambda} = \frac{hr}{2\pi r/n} = \frac{nh}{2\pi} \quad n = 0, 1, 2, \dots$$

The sign of J_z also must be considered. When $J_z > 0$, the particle travels in a clockwise direction as viewed from below; when $J_z < 0$, the motion is anticlockwise (Fig. 3). The sign of J_z can be absorbed into the quantum number by replacing n by $m_l = 0, \pm 1, \pm 2, \dots$, where m_l (the conventional notation for this quantum number) is allowed to have positive and negative integer values. After replacing $h/2\pi$ by \hbar the z -component of the angular momentum is

$$J_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots \quad (4)$$

This simple expression captures both the magnitude (that is, $|J_z| = |m_l| \hbar$) and sign of J_z . It follows that

The angular momentum of the particle is quantized.

The quantized motion can be thought of in terms of the rotation of a bicycle wheel that can rotate with only a discrete series of angular momenta, so that as the wheel is accelerated, the angular momentum jerks from the values 0 (when the wheel is stationary) to \hbar , $2\hbar, \dots$ but can have no intermediate value. Of course, bicycle wheels do not seem to move in that way, but

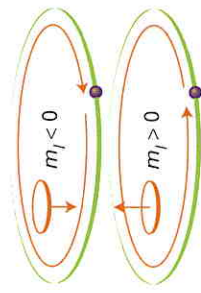


Fig. 3 The significance of the sign of m_l . When $m_l < 0$, the particle travels in an anticlockwise direction as viewed from below; when $m_l > 0$, the motion is clockwise.

this quantization is a central aspect of the rotational motion of electrons in atoms and of molecules.

The permitted energies of a particle on a ring, are

$$E_{m_l} = \frac{E = |J_z|^2/2I}{J_z = m_l \hbar} = \frac{m_l^2 \hbar^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \dots \quad (5)$$

Quantized energies of a particle on a ring

These energy levels are drawn in Fig. 4. Their features are as follows.

- The occurrence of m_l^2 means that two states of motion with opposite values of m_l , such as those with $m_l = +1$ and $m_l = -1$, correspond to the same energy (are 'degenerate').
- This degeneracy arises from the fact that the energy is independent of the direction of travel.
- The state with $m_l = 0$ is non-degenerate; the particle has an infinite wavelength and is 'stationary', so there is no direction of rotation.
- The particle does not have a zero-point energy: m_l may take the value 0, and $E_0 = 0$.

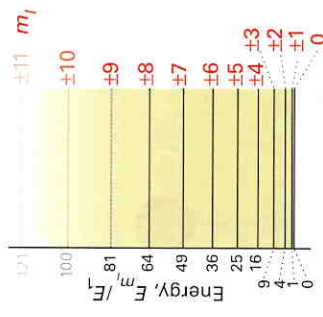


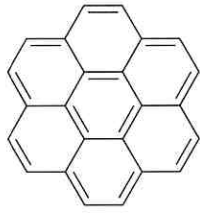
Fig. 4 The energy levels of a particle that can move on a circular path. Classical physics allowed the particle to travel with any energy (as represented by the continuous tinted band); quantum mechanics, however, allows only discrete energies. Each energy level, other than the one with $m_l = 0$, is doubly degenerate, because the particle may rotate either clockwise or anticlockwise with the same energy.

Comment The experimental value for a transition of this kind is 260 nm. That such a primitive model gives reasonably good agreement is encouraging. In addition, even though the model is primitive, it gives insight into the origin of the quantized π -electron energy levels in cyclic conjugated systems (Topic 9D).

Self-test 7D.1

Use the particle-on-a-ring model to calculate the minimum energy required for the excitation of a π electron in coronene, $C_{24}H_{18}$ (1). Assume that the radius of the ring is three times the carbon-carbon bond length in benzene and that the electrons are confined to the periphery of the molecule.

Answer: For a transition from $m_l = +3$ to $m_l = +4$; $\Delta E = 0.0147$ eV or 8.83 J mol $^{-1}$



1 Coronene

7D.2 Rotation in three dimensions

Rotational motion in three dimensions includes the motion of electrons around nuclei in atoms. Consequently, understanding rotational motion in three dimensions is crucial to understanding the electronic structures of atoms. Gas-phase molecules also rotate freely in three dimensions and by studying their allowed energies (using the spectroscopic techniques described in Topic 11B) it is possible to infer bond lengths and bond angles.

Just as a location on the surface of the Earth is specified by giving its latitude and longitude, the location of a particle free to move at a constant distance from a point is specified by two angles, the **colatitude** θ (theta) and the **azimuth** ϕ (phi) (Fig. 5). The wavefunction for the particle is therefore a function of both angles and is written $\psi(\theta, \phi)$. It turns out that this wavefunction factorizes by the separation of

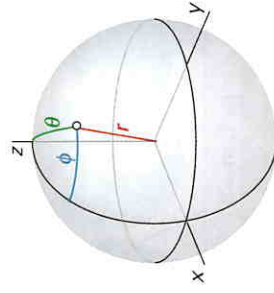
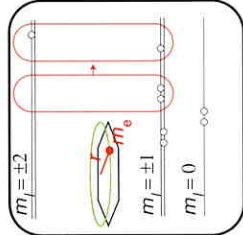


Fig. 5 The coordinates r (the radius), θ (the colatitude), and ϕ (the azimuth) used in the description of rotation in three dimensions.

Example 7D.1

Using the particle-on-a-ring model

The particle on a ring is a crude but illustrative model of cyclic, conjugated molecular systems. Treat the π electrons in benzene as particles freely moving over a circular ring of carbon atoms. Calculate the minimum energy required for the excitation of a π electron and express that difference as a frequency and wavelength. The carbon-carbon bond length in benzene is 140 pm.



Collect your thoughts The general features of the π -electron structure of benzene should be familiar from introductory chemistry. You need to consider features of the particle-on-a-ring model that can be used to approximate the electronic structure of benzene. First, because each carbon atom contributes one π electron, six electrons in the conjugated system move round the perimeter of the ring. Second, each state is occupied by two electrons, so only the $m_l = 0, +1$, and -1 states are occupied (with the last two being mutually degenerate). It follows that the minimum energy required for excitation corresponds to a transition of an electron from the $m_l = +1$ (or -1) state to the $m_l = +2$ (or -2) state, so you need to calculate $E_{+2} - E_{+1}$. The energies of the states can be calculated from eqn 4, with $l = m_l^2$, taking m as the mass of the electron, m_e , and $r = 140$ pm $= 1.40 \times 10^{-10}$ m (because benzene is hexagonal, the radius of the ring is the same as the carbon-carbon bond length). Finally, calculate the frequency and wavelength from the Bohr frequency condition ($\Delta E = h\nu$) and the relation $\lambda = c/\nu$.

The solution From eqn 5, the energy separation between the $m_l = +1$ and the $m_l = +2$ states is

$$\begin{aligned} \Delta E &= E_{+2} - E_{+1} = (2^2 - 1^2) \times \frac{\hbar^2}{2m_e r^2} \\ &= 3 \times \frac{\hbar^2}{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.40 \times 10^{-10} \text{ m})^2} \\ &= 9.35 \dots \times 10^{-19} \text{ J} \end{aligned}$$

Therefore the minimum energy required to excite an electron is 0.935 eV (after multiplication by N_A) 563 kJ mol $^{-1}$. The frequency of the transition is

$$\begin{aligned} \nu &= \frac{\Delta E}{h} = \frac{9.35 \dots \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.41 \dots \times 10^{15} \text{ s}^{-1} \\ \text{and the wavelength is} \end{aligned}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{1.41 \dots \times 10^{15} \text{ s}^{-1}} = 2.12 \dots \times 10^{-7} \text{ m}$$

That is, the absorption frequency is 1.41 PHz (1 PHz = 10^{15} Hz) and the wavelength is 212 nm.

A note on good practice Note that, when quoting the value of m_l , it is good practice always to give the sign, even if m_l is positive. Thus, write $m_l = +1$, not $m_l = 1$.

variables procedure (Topic 7C) into the product of a function of θ and a function of ϕ . The latter are exactly the same as those already found for a particle on a ring. In other words, motion of a particle over the surface of a sphere is like the motion of a particle over a stack of rings that can be regarded as forming the surface, with the additional freedom to migrate between rings.

Two cyclic boundary conditions limit the acceptability of solutions of the Schrödinger equation. One is that the wavefunctions must match as the particle travels round the equator (just like the particle on a ring); that boundary condition introduces the quantum number m_l . The other condition is that the wavefunction must match as the particle travels over the poles. This constraint introduces a second quantum number, which is called the **orbital angular momentum quantum number** and denoted l . Detailed calculation shows that the quantum numbers are allowed the following values:

$$l = 0, 1, 2, \dots \quad m_l = 0, \pm 1, \pm 2, \pm l$$

Note that m_l has values like those for a particle on a ring, but for reasons that will become clear is bounded by the value of l . There are $2l + 1$ values of m_l for a given value of l . The energy of the particle is given by the expression

$$E = l(l+1) \frac{\hbar^2}{2mr^2} \quad (6)$$

Quantized energies of a particle on a sphere

where r is the radius of the surface of the sphere on which the particle can be regarded as moving. For reasons that will also soon become clear, the energy depends on l and is independent of the value of m_l . The wavefunctions themselves appear in a number of applications, and are called **spherical harmonics**. They are commonly denoted $Y_{l,m_l}(\theta, \phi)$, and can be imagined as wavelike distortions of a spherical shell (Fig. 6).

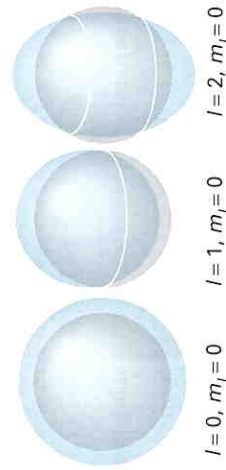


Fig. 6 The wavefunctions of a particle on a sphere can be imagined as having the shapes that the surface would have when the sphere is distorted. Three of these 'spherical harmonics' are shown here.

A very important additional conclusion can be drawn by comparing the expression for the energy in eqn 6 with the classical expression for the energy:

Classical Quantum mechanical

$$E = \frac{J^2}{2mr^2} \quad E_l = \frac{l(l+1)\hbar^2}{2mr^2}$$

where J is the magnitude of the angular momentum of the particle. It follows that the magnitude of the angular momentum is quantized and limited to the values

$$J = \{l(l+1)\}^{1/2} \hbar \quad (7)$$

Magnitude of the angular momentum of a particle on a sphere

Thus, the allowed values of the magnitude of the angular momentum are $0, 2^{1/2}\hbar, 6^{1/2}\hbar, \dots$

The angular momentum can be represented by a vector (*The chemist's toolkit 23*) with a length given by eqn 7 and pointing in a direction that depicts the orientation of the particle's motion. Its z -component, which expresses the contribution to the angular momentum that arises from motion around the z -axis (the polar axis of the sphere) is $m_l\hbar$ (Fig. 7). Several features now fall into place:

- The quantum number m_l is confined to a range of values that depend on l because the angular momentum around a single axis (as expressed by $m_l\hbar$) cannot exceed the magnitude of the angular momentum (as expressed by J).
- Providing the particle has a given angular momentum, its kinetic energy (its only source of energy) is independent of the orientation of its path; hence, the energy is independent of m_l , as asserted above.

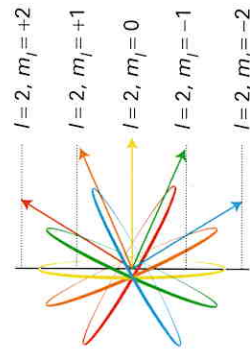


Fig. 7 The significance of the quantum numbers l and m_l shown for $l=2$: l determines the magnitude of the angular momentum (as represented by the length of the arrow), and m_l the component of that angular momentum about the z -axis.

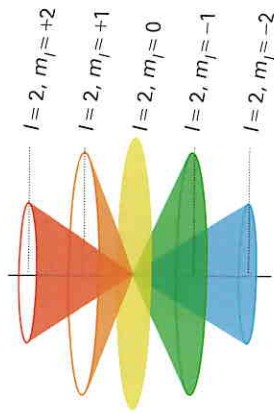


Fig. 8 The vector model of angular momentum acknowledges that nothing can be said about the x - and y -components of angular momentum if the z -component is known, by representing the states of angular momentum by cones.

one component is well defined, and the two other components are in general indeterminate.

Brief illustration 7D.1 The vector model of angular momentum

Suppose that a particle is in a state with $l=3$. You would then know that the magnitude of its angular momentum is $12^{1/2}\hbar$, so the angular momentum itself could be represented by a vector of length $12^{1/2} = 3.46 \dots$ units (Fig. 9a). The angular momentum could have any of seven orientations with z -components $m_l\hbar$, with $m_l = 0, \pm 1, \pm 2, \pm 3$, so it is represented by the vector lying in the orientations that give projections of length m_l units on the z -axis (Fig. 9b). Then invoke the uncertainty principle, which denies knowledge of the x - and y -components, and so replace the vectors by cones representing possible but unspecified orientations around the z -axis (Fig. 9c).

Self-test 7D.2

How should you express the vector model of angular momentum of a particle in a state with $l=4$?

Answer: Cones of side $20^{1/2} = 4.47 \dots$ units, components on z -axis are $0, \pm 1, \pm 2, \pm 3, \pm 4$ units.

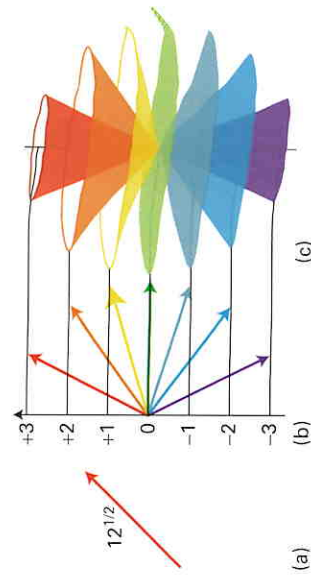


Fig. 9 (a) The angular momentum of a particle with $l=3$. (b) The seven orientations of the angular momentum vector. (c) The cones representing possible but unspecified orientations around the z -axis.

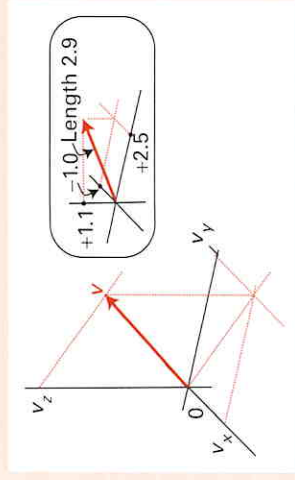
The chemist's toolkit 23 Vectors

A **vector** is a quantity with both magnitude and direction. The vector v shown in Sketch 1 has components on the x , y , and z axes with values v_x , v_y , and v_z , respectively, which may be positive or negative. For example, if $v_x = -1.0$, the x -component of the vector v has a magnitude of 1.0 and points in the $-x$ direction. The magnitude of a vector is denoted v or $|v|$ and is given by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

Thus, a vector with components $v_x = -1.0$, $v_y = +2.5$, and $v_z = +1.1$ has magnitude 2.9 and would be represented by an arrow of length 2.9 units and the appropriate orientation (as in the inset in the Sketch). Velocity and momentum are vectors; the magnitude of a velocity vector is called the speed. Force, too, is a vector. Electric and magnetic fields are two more examples of vectors.

The operations involving vectors (addition, multiplication, etc.) needed for this text are described in *The chemist's toolkit 24* in Topic 8D.



Sketch 1

What can be said about the component of angular momentum about the x - and y -axes? Almost nothing. These components cannot exceed the magnitude of the angular momentum, but there is no quantum number that gives their precise values. In fact, J_x , J_y , and J_z , the three components of angular momentum, are 'complementary observables' in the sense described in Topic 7B in connection with the uncertainty principle, and if one is known exactly (the value of J_x , for instance, as $m_l\hbar$), then the values of the other two cannot in general be specified. For this reason, the vector representing angular momentum is often represented as lying anywhere on a cone with a given z -component (indicating the value of m_l) and side (indicating the value of $\{l(l+1)\}^{1/2}$), but with indefinite projection on the x - and y -axes (Fig. 8). This **vector model** of angular momentum summarizes the quantum mechanical aspects of angular momentum, expressing the fact that the magnitude is well defined,

Checklist of key concepts

- 1 The **angular momentum** and the energy of a particle free to move on a circular ring are quantized; the quantum number is denoted m .
- 2 The wavefunctions of a particle on a ring and on a sphere must satisfy **cyclic boundary conditions** (the wavefunctions must repeat on successive cycles).
- 3 The angular momentum and the energy of a particle on a sphere are quantized with values determined by the quantum numbers l and m .
- 4 The wavefunctions for a particle on a sphere are the **spherical harmonics**.
- 5 The **vector model** of angular momentum represents the angular momentum by a vector of length $\sqrt{l(l+1)}\hbar$ units and z -component $m\hbar$ units lying at an indeterminate position on a cone around the z -axis.

TOPIC 7E

Vibration

► Why do you need to know this material?

The detection and interpretation of vibrational frequencies is the basis of infrared spectroscopy (Topic 11C), a widely used technique for identifying compounds. Molecular vibration also plays a role in the interpretation of thermodynamic properties (Topic 12B).

► What is the key idea?

The energy of a harmonic oscillator is quantized and the oscillator may be found at extensions not allowed classically.

► What do you need to know already?

You should know how to formulate the Schrödinger equation (Topic 7B), and be familiar with the Born interpretation of the wavefunction (Topic 7B), the role of boundary conditions (Topics 7B, 7C, and 7D), and the phenomenon of tunnelling (Topic 7C).

One very important type of motion of a molecule is its vibration, when bonds stretch, compress, and bend. One specific but important type of vibrational motion is considered here, that of 'harmonic motion' in one dimension. Topic 11C extends the discussion to polyatomic molecules with more than one mode of vibration, and explores the consequences of the vibration not being harmonic.

7E.1 The harmonic oscillator

A **harmonic oscillator** is one in which a particle vibrates backwards and forwards restrained by a spring that obeys Hooke's law of force. This law

states that the restoring force is proportional to the displacement, x :

$$\text{Restoring force} = -k_f x \quad (1)$$

Hooke's law

The constant of proportionality k_f is called the **force constant**: a stiff spring has a high force constant (the restoring force is strong even for a small displacement) and a weak spring has a low force constant. The SI units of k_f are newtons per metre (N m^{-1}), where the newton (N) is the SI unit of force ($1 \text{ N} = 1 \text{ kg m s}^{-2}$). The negative sign in eqn 1 is included because a displacement to the right (to positive x) corresponds to a force directed to the left (towards negative x).

To formulate the Schrödinger equation, it is necessary to know how the potential energy of an oscillator depends on its extension. In the following *Justification* it is shown that the potential energy of a particle subjected to a restoring force $-k_f x$ increases as the square of the displacement, and specifically

$$V(x) = \frac{1}{2} k_f x^2 \quad (2)$$

Potential energy of a harmonic oscillator

The variation of V with x is shown in Fig. 1: it has the shape of a parabola (a curve of the form $y = ax^2$), so a

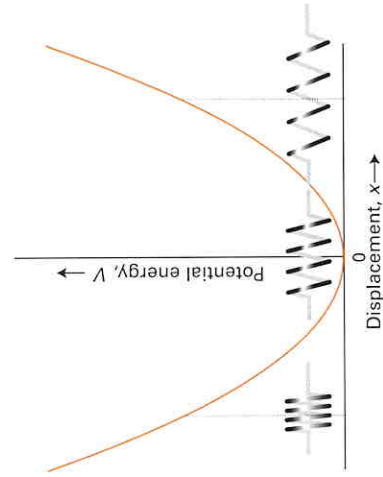


Fig. 1 The parabolic potential energy characteristic of a harmonic oscillator. Positive displacements correspond to extension of the spring; negative displacements correspond to compression of the spring.

particle undergoing harmonic motion is said to have a 'parabolic potential energy'.

Justification 7E.1

Potential energy of a harmonic oscillator

Force is the negative slope of the potential energy: $F = -dV/dx$ (The chemist's toolkit 7 in Topic 2A). Because the infinitesimal quantities may be treated as any other quantity in algebraic manipulations, rearrange the expression into $dV = -Fdx$ and then integrate both sides from $x = 0$, where the potential energy is $V(0)$, to x , where the potential energy is $V(x)$:

$$V(x) - V(0) = - \int_0^x F(x) dx$$

Now substitute $F(x) = -k_1x$:

$$V(x) - V(0) = - \int_0^x (-k_1x) dx = k_1 \int_0^x x dx = \frac{1}{2} k_1 x^2$$

Because the potential energy of the oscillator has its lowest value at $x = 0$, it is common to choose $V(0) = 0$, which then gives eqn 2.

7E.2 The quantum mechanical treatment

Unlike for translation (Topic 7C) and rotation (Topic 7D), the potential energy of a harmonic oscillator varies with position in the regions where the particle may be found, so a term $V(x)$ must be introduced in the Schrödinger equation, which for a particle of mass m becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} k_1 x^2 \psi = E\psi$$

The solutions of this equation must satisfy the appropriate boundary conditions. In this case, the wavefunctions must all go to zero for large displacements in either direction from $x = 0$ because the potential energy rises towards infinity, and the particle cannot be found where its potential energy is infinite. The implication of the boundary conditions, which can be expressed as $\psi(\pm\infty) = 0$, is that not all wavefunctions, and therefore not all energies, are allowed: vibrational motion is quantized.

Although advanced techniques are needed to find the solutions, they turn out to be very simple. For instance, the allowed energies are

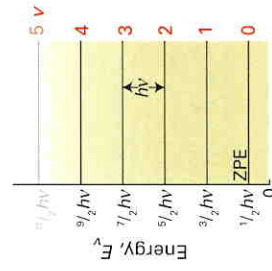


Fig. 2 The array of energy levels of a harmonic oscillator (the levels continue upwards to infinity). The separation depends on the mass and the force constant. Note the zero-point energy (ZPE).

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad v = 0, 1, 2, \dots$$

$$v = \frac{1}{2\pi} \left(\frac{k_1}{m}\right)^{1/2} t$$

Quantized energies of the harmonic oscillator

where ν is the **vibrational quantum number**.¹ These energies form a uniform ladder of values separated by $h\nu$ (Fig. 2). The quantity ν is a frequency (in cycles per second, or hertz, Hz), and is in fact the frequency that a classical oscillator of mass m and force constant k_1 would be calculated to have. The separation of adjacent energy levels is large for stiff springs (large k_1) and low masses (small m).

Brief illustration 7E.1 The vibrational frequency of a chemical bond

The force constant for an H—Cl bond is 516 N m^{-1} . Suppose that the chlorine atom is relatively very heavy, only the hydrogen atom moves; then m may be taken as the mass of the H atom ($1.67 \times 10^{-27} \text{ kg}$ for ^1H). It follows that

$$\nu = \frac{1}{2\pi} \left(\frac{k_1}{m}\right)^{1/2} = \frac{1}{2\pi} \left(\frac{516 \text{ N m}^{-1}}{1.67 \times 10^{-27} \text{ kg}}\right)^{1/2}$$

$$= 8.85 \times 10^{13} \text{ Hz}$$

1 Hz = 1 s⁻¹

or 88.5 THz. The energy separation between adjacent levels is h times this frequency, or $5.86 \times 10^{-20} \text{ J}$ (58.6 zJ), corresponding (after multiplication by N_A) to 35.3 kJ mol^{-1} .

Self-test 7E.1

The vibrational frequency of an H—I bond is 69.5 THz. Estimate the force constant for the bond on the basis that only the H atom moves.

Answer: 318 N m^{-1}

¹Be very careful to distinguish the quantum number ν (italic *ν*) from the frequency ν (Greek ν).

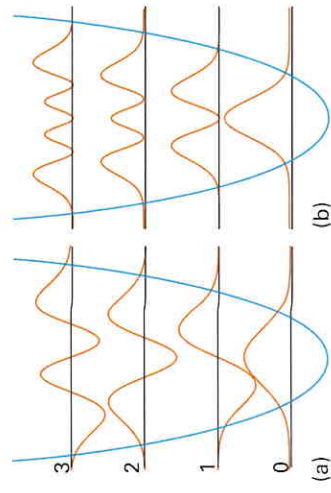


Fig. 3 (a) The wavefunctions and (b) the probability densities of the first three states of a harmonic oscillator. Note how the probability of finding the oscillator at large displacements increases as the state of excitation increases.

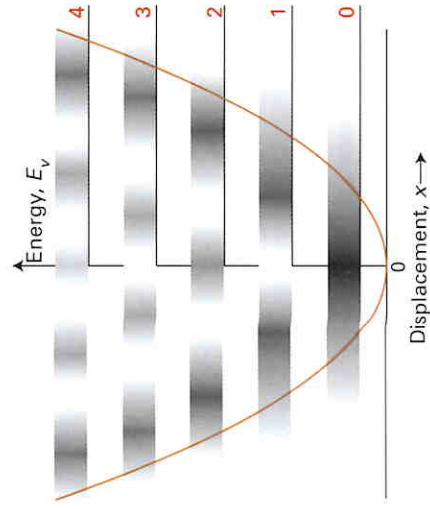


Fig. 4 A schematic illustration of the probability density for finding a harmonic oscillator at a given displacement. Classically, the oscillator cannot be found at displacements at which its total energy is less than its potential energy (because the kinetic energy cannot be negative). A quantum oscillator, though, may tunnel into regions that are classically forbidden.

Because $\nu = 0$ is allowed, an oscillator has a zero-point energy of $E_0 = \frac{1}{2} h\nu$, which cannot be removed. Classically, this energy would be the consequence of the oscillator ceaselessly fluctuating around zero displacement. Quantum mechanically it arises from the shape of the wavefunction, which must be curved (to satisfy the boundary conditions and not be zero everywhere), and therefore imparts kinetic energy to the oscillator.

Figure 5 shows the probability density for a wavefunction with a high value of the quantum number ν (in this case, $\nu = 25$). The probability density is highest at maximum displacement, just as expected for a classical oscillator (think of a pendulum, which is moving most slowly at the ends of its swing). This

Table 7E.1

Harmonic oscillator wavefunctions*

v	ψ_v
0	$\left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} e^{-y^2/2}$
1	$\left(\frac{2}{\alpha\pi^{1/2}}\right)^{1/2} ye^{-y^2/2}$
2	$\left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} (2y^2 - 1)e^{-y^2/2}$
3	$\left(\frac{1}{3\alpha\pi^{1/2}}\right)^{1/2} (2y^3 - 3y)e^{-y^2/2}$

*The wavefunctions are expressed in terms of the variable $y = x/\alpha$ and the parameter $\alpha = (\hbar^2/mk_1)^{1/4}$. Each one is normalized in the sense that $\int_{-\infty}^{\infty} \psi_v^2 dx = \alpha \int_{-\infty}^{\infty} \psi_v^2 dy = 1$.

Table 7E.1 lists the first four wavefunctions of a harmonic oscillator, and Fig. 3 shows their shapes. In each case, the probability density for finding a particle at a given displacement is proportional to the square of the value of the wavefunction at that displacement. The following features are important:

- The lowest energy wavefunction (corresponding to $\nu = 0$) is a bell-shaped curve, a curve of the form e^{-x^2} (a Gaussian function; see *The chemist's toolkit 4* in Topic 1B), with no nodes. The particle is most likely to be found at $x = 0$ (zero displacement), but may be found at greater displacements with decreasing probability.
- The first excited wavefunction ($\nu = 1$) has a node at $x = 0$ with positive and negative peaks on either side. In this state, the particle will be found most probably with the 'spring' stretched or compressed to the same amount. It has a higher energy because it is more curved (corresponding to higher kinetic energy) and samples regions of higher potential energy too.
- All the wavefunctions extend beyond the limits of motion of a classical oscillator (Fig. 4). That is, the particle tunnels into regions forbidden by classical mechanics.

Physical interpretation

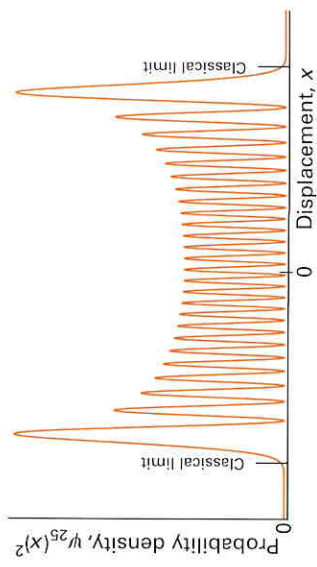


Fig. 5 At high values of the vibrational quantum number (here $v=25$) the probability density is beginning to resemble the distribution expected for a classical oscillator, which is most likely to be found at the ends of its swing where it is travelling most slowly.

property is another example of the correspondence principle (Topic 7C) that classical behaviour emerges at high quantum numbers.

Because the wavefunctions spread over a range of displacements, an oscillator has nonzero potential energy as well as a kinetic energy arising from its curvature. The average kinetic energy is equal to the average potential energy in any state of a harmonic oscillator: $\langle E_{k,v} \rangle = \langle V_{p,v} \rangle$ and therefore (because their sum must be the total energy E_v) that both average values are equal to $\frac{1}{2}E_v$ for all values of the quantum number v .²

²For a justification of this result, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

Checklist of key concepts

- 1 A particle undergoes harmonic motion if it is subjected to a Hooke's-law restoring force (a force proportional to the displacement) as characterized by the **force constant**, k_f .
- 2 The energy levels of a harmonic oscillator are equally spaced and specified by the **vibrational quantum number** $v=0, 1, 2, \dots$

- 3 The separation of neighbouring quantum levels increases with the force constant and decreases with the mass of the oscillating particle.

- 4 The oscillating particle can tunnel to classically forbidden displacements.

FOCUS 7 Quantum theory

Exercises

Topic 7A The emergence of quantum theory

7A.1 The wavelength of the bright red line in the spectrum of atomic hydrogen is 652 nm. What is the energy of the photon generated in the transition?

7A.2 What is the wavenumber of the radiation emitted when a hydrogen atom makes a transition corresponding to a change in energy of 10.20 eV?

7A.3 Calculate the size of the quantum involved in the excitation of (a) an electronic motion of frequency 1.0×10^{15} Hz, (b) a molecular vibration of period 20 fs, (c) a pendulum of period 0.50 s. Express the results in joules and in kilojoules per mole.

7A.4 The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (a) 750 nm, (b) 250 nm.

Topic 7B The dynamics of microscopic systems

7B.1 The speed of a certain proton is 350 km s^{-1} . If the uncertainty in its momentum is 0.0100 per cent, what uncertainty in its location must be tolerated?

7B.2 Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within $5.0 \mu\text{m}$ of a certain point on a bat.

Topic 7C Translation

7C.1 A particle is confined to a one-dimensional box of length L . Deduce the location of the positions within the box at which the particle is most likely to be found when the quantum number of the particle is (a) $n=1$, (b) $n=2$, and (c) $n=3$.

7C.2 A hydrogen atom, treated as a point mass, is confined to a one-dimensional square well of width 1.0 nm. How much

Topic 7D Rotation

7D.1 A particle is confined to a two-dimensional ring of radius 100 pm. What are the wavelengths of the wavefunctions of the three lowest rotational levels?

7D.2 A rotating HI molecule may be treated as a stationary I atom around which an H atom circulates in a plane at a distance of 161 pm. Calculate (a) the moment of inertia of

7A.5 Calculate the de Broglie wavelength of (a) a mass of 1.0 g travelling at 1.0 m s^{-1} , (b) the same, travelling at $1.00 \times 10^5 \text{ km s}^{-1}$, (c) a He atom travelling at 1000 m s^{-1} (a typical speed at room temperature).

7A.6 A diffraction experiment requires the use of electrons of wavelength 550 pm. Calculate the speed of the electrons.

7A.7 Calculate the de Broglie wavelength of yourself travelling at 8 km h^{-1} . What does your wavelength become when you stop?

7A.8 Calculate the linear momentum of photons of wavelength (a) 600 nm, (b) 70 pm, (c) 200 m.

7A.9 How fast would a particle of mass 1.0 g need to travel to have the same linear momentum as a photon of radiation of wavelength 300 nm?

7B.3 What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between $350.000001 \text{ m s}^{-1}$ and $350.000000 \text{ m s}^{-1}$?

7B.4 An electron is confined to a linear region with a length of the same order as the diameter of an atom (taken as 100 pm). Calculate the minimum uncertainties in its position and speed.

energy does it have to give up to fall from the first excited level with $n=2$ to the lowest energy level with $n=1$?

7C.3 An electron is confined to a one-dimensional box. The wavelength of the radiation required to excite the electron from the lowest level to the first excited level is 1.10 μm . What is the length of the box?

the molecule, (b) the wavelength of the radiation required to excite the molecule from the lowest to first excited level.

7D.3 Suppose that the magnitude of the angular momentum of a system rotating in three dimensions is $42^{1/2}\hbar$. Deduce the angular momentum quantum number of the system.

7D.4 For a system rotating in three dimensions, what is the degeneracy of the level with $l = 4$? What are the valid values of m ?

Topic 7E Vibration

7E.1 A bee of mass 1 g lands on the end of a horizontal twig, which starts to oscillate up and down with a period of 1 s. Treat the twig as a massless spring, and estimate its force constant.

7E.2 Treat a vibrating HI molecule as a hydrogen atom oscillating towards and away from a stationary iodine atom. Given

7D.5 A hydrogen atom rotates in three dimensions at a fixed distance of 100 pm from a fixed point. Calculate the energy of the level with rotational quantum number $J = 1$.

the force constant of the HI bond is 314 N m^{-1} , calculate the vibrational frequency of the molecule.

7E.3 The vibrational period of the C—H bond in tribromomethane, CHBr_3 , is 91.2 ps. Treating the molecule as an oscillating H atom and a stationary CBr_3 group, calculate the force constant for the C—H bond.

Discussion questions

71 Summarize the evidence that led to the introduction of quantum theory.

72 Discuss the physical origin of quantization energy for a particle confined to a one-dimensional box or on a ring.

73 Define, justify, and provide examples of zero-point energy.

Problems

71 Use the following data on the kinetic energy of photoelectrons ejected by radiation of different wavelengths from a metal to determine the value of Planck's constant and the work function of the metal.

λ/nm	300	350	400	450
E_k/eV	1.613	1.022	0.579	0.235

72 When an electron is accelerated through a potential difference $\Delta\phi$ it acquires a kinetic energy $e\Delta\phi$. Calculate the momentum, and hence the de Broglie wavelength, of an electron accelerated from rest through (a) 1.00 V, (b) 1.00 kV, (c) 100 kV.

73 Suppose that you designed a spacecraft to work by photon pressure. The sail was a completely absorbing fabric of area 1.0 km^2 and you directed a red laser beam of wavelength 650 nm on to it from a base on the Moon. What is (a) the force, (b) the pressure exerted by the radiation on the sail? (c) Suppose the mass of the spacecraft was 1.0 kg. Given that, after a period of acceleration from standstill, speed = (force/

mass) \times time, how long would it take for the craft to accelerate to a speed of 1.0 m s^{-1} ?

74 A certain wavefunction is zero everywhere except between $x = 0$ and $x = L$, where it has the constant value A . Normalize the wavefunction.

75 Suppose a particle has a wavefunction $\psi(x) = Ae^{-ax}$. Sketch the form of this wavefunction. Where is the particle most likely to be found? At what values of x is the probability of finding the particle reduced by 50 per cent from its maximum value?

76 Suppose a particle of mass m is in a region where its potential energy varies as ax^4 , where a is a constant. Write down the corresponding Schrödinger equation.

77 Calculate the probability that an electron will be found (a) between $x = 0.1$ and 0.2 nm , (b) between 4.9 and 5.2 nm in a box of length $L = 10 \text{ nm}$ when its wavefunction is $\psi = (2/L)^{1/2} \sin(2\pi x/L)$. Treat the wavefunction as a constant in the small region of interest and interpret δV as δx .

7.12 An electron is incident on a potential-energy barrier of width L and height $V = \hbar^2/2m_0L^2$. Estimate the probability that the electron will tunnel through the barrier if it has an energy (a) $V/10$ and (b) $V/100$.

7.13 The moment of inertia of an H_2O molecule about an axis bisecting the HOH angle is $1.91 \times 10^{-47} \text{ kg m}^2$. Its minimum angular momentum about that axis (other than zero) is \hbar . In classical terms, how many revolutions per second do the H atoms make about the axis when in that state? What is the minimum energy needed to excite the rotation of an H_2O molecule about the axis?

7.14 The moment of inertia of CH_4 can be calculated from the expression $I = \frac{8}{3}m_{\text{H}}R^2$, where $R = 109 \text{ pm}$ is the CH bond length. Calculate the minimum rotational energy (other than zero) of the molecule and the degeneracy of that rotational state.

7.15 A vibrating HI molecule may be treated as an oscillating H atom and a stationary I atom. By what factor will the vibrational frequency of the molecule change when H is replaced by deuterium?

of x for which $d\psi/dx = 0$. (b) Repeat part (a) for the first excited state of a harmonic oscillator, for which the wavefunction is proportional to $xe^{-ax^2/2}$.

7.3 The solutions of the Schrödinger equation for a harmonic oscillator also apply to diatomic molecules. The only complication is that both atoms joined by the bond move, so the mass of the oscillator has to be interpreted carefully. Detailed calculation shows that for two atoms of masses m_A and m_B joined by a bond of force constant k , the energy levels are given by eqn 3 of Topic 7E, but with m replaced by the effective mass $\mu = m_A m_B / (m_A + m_B)$. Consider the vibration of carbon monoxide. The bond in a $^{12}\text{C}^{16}\text{O}$ molecule has a force constant of 1860 N m^{-1} . (a) Calculate the vibrational frequency, ν , of the molecule. (b) In infrared spectroscopy it is common to convert the vibrational frequency of a molecule to its vibrational wavenumber, $\tilde{\nu}$, given by $\tilde{\nu} = \nu/c$. What is the vibrational wavenumber of a $^{12}\text{C}^{16}\text{O}$ molecule? (c) Assuming that isotopic substitution does not affect the force constant of the $\text{C}\equiv\text{O}$ bond, calculate the vibrational wavenumbers of the following molecules: $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{13}\text{C}^{18}\text{O}$.

Projects

The symbol \dagger indicates that calculus is required.

7.1† Calculus can be used to carry out more accurate calculations of probabilities. (a) Repeat Problem 7.7 but allow for the variation of the wavefunction in the region of interest by integrating $\psi^2 dx$ between the limits of interest. You will need to use the indefinite integral T1 as in *Justification 7C.1*. What are the relative errors in the approximate procedure used in Problem 7.7? What is the probability of finding a particle of mass m in (b) the left-hand one-third, (c) the central one-third, (d) the right-hand one-third of a box of length L when it is in the state with $n = 1$?

7.2† Here you are invited to explore the quantum-mechanical harmonic oscillator in more quantitative detail. (a) The ground-state wavefunction of a harmonic oscillator is proportional to $e^{-ax^2/2}$, where a depends on the mass and force constant. (i) Normalize this wavefunction; you will need the Integral G1 in the Resource section. (ii) At what displacement x is the oscillator most likely to be found in its ground state? Recall that the maximum or minimum of a function $f(x)$ occurs at the value

7.9 The pores in zeolite catalysts are so small that quantum mechanical effects on the distribution of atoms and molecules within them can be significant. Calculate the location in a box of length L at which the probability of a particle being found is 50 per cent of its maximum probability when $n = 1$.

7.10 The blue solution formed when an alkali metal dissolves in liquid ammonia consists of the metal cations and electrons trapped in a cavity formed by ammonia molecules. (a) Calculate the spacing between the levels with $n = 4$ and $n = 5$ of an electron in a one-dimensional box of length 5.0 nm . (b) What is the wavelength of the radiation emitted when the electron makes a transition between the two levels?

7.11 Suppose a particle has zero potential energy for $x < 0$, a constant value V , for $0 \leq x \leq L$, and then zero for $x > L$. Sketch the potential. Now suppose that wavefunction is a sine wave on the left of the barrier, declines exponentially inside the barrier, and then becomes a sine wave on the right, being continuous everywhere. Sketch the wavefunction on your sketch of the potential energy.

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FOCUS 8

Atomic structure

Atomic structure—the description of the arrangement of electrons in atoms—is an essential part of chemistry because it is the basis for understanding molecular and solid structures, and all the physical and chemical properties of elements and their compounds. This Focus explains how the principles of quantum mechanics introduced in Focus 7 are used to describe the internal structures of atoms and their spectroscopic transitions.

8A Hydrogenic atoms

A 'hydrogenic atom' is a one-electron atom or ion of general atomic number Z ; examples are H, He⁺, Li²⁺, O⁷⁺. Hydrogenic atoms are important because their Schrödinger equations can be solved exactly. They also provide a set of concepts that are used to describe the structures of many-electron atoms and of molecules too. This Topic begins with a discussion of experimental information from a study of the spectrum of atomic hydrogen and then describes the results of solving the Schrödinger equation. The wavefunctions so obtained are the hugely important 'atomic orbitals' of hydrogenic atoms.

- 8A.1 The permitted energies of hydrogenic atoms;
- 8A.2 Quantum numbers; 8A.3 The s orbitals;
- 8A.4 The p and d orbitals

8B Many-electron atoms

A 'many-electron atom' (or *polyelectronic atom*) is an atom or ion with more than one electron; examples include all neutral atoms other than H. So even He, with only two electrons, is a many-electron atom. In this Topic hydrogenic atomic orbitals are used in conjunction with the concept of 'spin' and the 'Pauli exclusion principle' to describe their structures.

- 8B.1 The orbital approximation; 8B.2 Electron spin; 8B.3 The Pauli principle; 8B.4 Penetration and shielding; 8B.5 The building-up principle;
- 8B.6 The occupation of d orbitals; 8B.7 The

- configurations of cations and anions;
- 8B.8 Self-consistent field orbitals

8C Periodic trends of atomic properties

This Topic extends the discussion in Topic 8B to account for the periodicity of atomic properties and the structure of the periodic table. Special attention is given to atomic and ionic radii, ionization energies, and electron affinities.

- 8C.1 Atomic and ionic radii; 8C.2 Ionization energy and electron affinity

8D Atomic spectroscopy

Atomic spectroscopy is an important way of determining the energies of electrons in atoms. This Topic begins with a review of the spectra of hydrogenic atoms, and then moves on to a discussion of many-electron atoms. The concept of 'selection rules' is used to predict which spectroscopic transitions can be observed. The spectra of many-electron atoms are more complicated than those of hydrogen because they are influenced by the Coulombic and magnetic interactions of electrons. They are described by using 'term symbols', which are based on the various contributions to the total angular momentum of the electrons.

- 8D.1 The spectra of hydrogenic atoms; 8D.2 The energies of many-electron atoms; 8D.3 Spin-orbit coupling; 8D.4 Selection rules for many-electron atoms

Web resource What is an application of this material?

Techniques of atomic spectroscopy are used to examine stars. By analysing their spectra it is possible to determine the composition of their outer layers and the surrounding gases, and to determine features of their physical state. See *Impact* 6 on the website of this book.

TOPIC 8A

Hydrogenic atoms

➤ Why do you need to know this material?

An understanding of the structure of the hydrogen atom is central to the understanding of all other atoms, the periodic table, and bonding in molecules.

➤ What is the key idea?

Atomic orbitals are labelled by three quantum numbers which specify the energy and angular momentum of an electron in a hydrogenic atom.

➤ What do you need to know already?

You need to be aware of the concept of wavefunction (Topic 7A) and its interpretation. You need to know how boundary conditions limit the solutions of the Schrödinger equation (Topics 7A–7D).

A **hydrogenic atom** is a one-electron atom or ion of atomic number Z . Hydrogenic atoms include H, He⁺, Li²⁺, C⁵⁺, and even U⁹¹⁺. Such very highly ionized atoms may be found in the outer regions of stars. A **many-electron atom** is an atom or ion that has more than one electron. Many-electron atoms include all neutral atoms other than H. For instance, helium, with its two electrons, is a many-electron atom in this sense. Hydrogenic atoms, and H in particular, are important because the Schrödinger equation can be solved for them exactly and the concepts they introduce are used to describe the structures of many-electron atoms (Topic 8B) and molecules (Topics 9A–9D).

8A.1 The permitted energies of hydrogenic atoms

Energetically excited atoms are produced when an electric discharge is passed through a gas or vapour, or when an element is exposed to a hot flame. These atoms emit electromagnetic radiation of discrete frequencies as they discard energy and return to the **ground state**, their state of lowest energy (Fig. 1). The record of frequencies (ν , typically in hertz, Hz), wavenumbers ($\tilde{\nu} = \nu/c$, typically in reciprocal centimetres, cm⁻¹), or wavelengths ($\lambda = c/\nu$, typically in nanometres, nm), of the radiation emitted is called the **emission spectrum** of the atom. The components of radiation present in a spectrum are widely referred to as spectroscopic 'lines'.¹

The first important contribution to understanding the spectrum of atomic hydrogen was made by the Swiss schoolteacher Johann Balmer. In 1885 he pointed out that (in modern terms) the wavenumbers

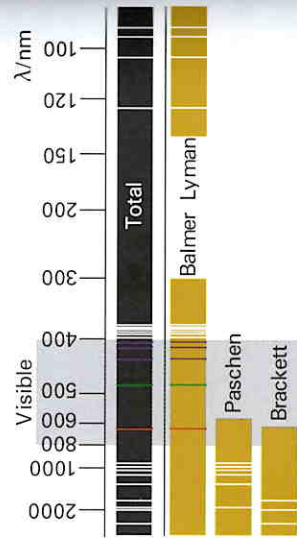


Fig. 1 The spectrum of atomic hydrogen. The spectrum is shown at the top, and is analysed into overlapping series below. The Balmer series lies largely in the visible region.

¹ In its earliest form, the radiation was detected photographically as a series of lines: the focused image of the slit through which the light was sampled.

of the light in the visible region of the electromagnetic spectrum fit the expression

$$\tilde{\nu} \propto \frac{1}{2} - \frac{1}{n^2}$$

with $n = 3, 4, \dots$. The lines described by this formula are now called the **Balmer series** of the spectrum. Later, another set of lines was discovered in the ultraviolet region of the spectrum, and is called the **Lyman series**. Yet another set was discovered in the infrared region when suitable detectors became available, and is called the **Paschen series**. With this additional information available, the Swedish spectroscopist Johannes Rydberg noted (in 1890) that all the lines are described by the expression

$$\tilde{\nu} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1)$$

with $n_1 = 1, 2, \dots, n_2 = n_1 + 1, n_1 + 2, \dots$, and $R_{\text{H}} = 109\,677 \text{ cm}^{-1}$. The constant R_{H} is now called the **Rydberg constant** for hydrogen. The first five series of lines then correspond to n_1 taking the values 1 (Lyman), 2 (Balmer), 3 (Paschen), 4 (Brackett), and 5 (Pfund).

As seen in Topic 7A, the existence of discrete spectroscopic lines strongly suggests that the energy of atoms is quantized, and that when an atom changes its energy by ΔE , this difference is carried away as a photon of frequency ν related to ΔE by the **Bohr frequency condition** (eqn 1 of Topic 7A, $\Delta E = h\nu$), which in terms of wavenumbers becomes

$$\Delta E = hc\tilde{\nu} \quad (2)$$

It follows that discrete lines can be observed if an electron in an atom can exist only in certain energy states, and electromagnetic radiation induces (for absorption) or results from (for emission) transitions between them.

Quantum theory explains these observations. The description is based on Rutherford's **nuclear model**, in which a hydrogenic atom is pictured as consisting of an electron outside a central nucleus of charge Ze , and then formulating and solving the corresponding Schrödinger equation. This equation includes the potential energy, V , of the Coulombic interaction between the nucleus of charge $+Ze$ and the electron of charge $-e$ (*The chemist's toolkit* 14 of Topic 5H, $V(r) = Q_1Q_2/4\pi\epsilon_0r$, with $Q_1 = Ze$ and $Q_2 = -e$):

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0r} \quad (3)$$

where $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ is the vacuum permittivity. The negative sign indicates that the potential energy falls (becomes more negative) as the distance between the nucleus and the electron decreases.

The wavefunctions, the solutions of the Schrödinger equation for an electron in the presence of the nucleus, must satisfy certain conditions in order to be acceptable. For a hydrogenic atom, these 'boundary conditions' are that the wavefunction must decay to zero as it extends to infinity, and that it must repeat itself (just like the particle on the surface of a sphere, Topic 7D) on circling the nucleus either over the poles or round the equator. With three conditions to satisfy, three quantum numbers are expected to emerge.

With a lot of work, the Schrödinger equation with a Coulombic potential energy and these conditions can be solved. As usual, the need to satisfy boundary conditions leads to the conclusion that the electron can have only certain energies, which is qualitatively in accord with the spectroscopic evidence. Schrödinger himself found that for a hydrogenic atom of atomic number Z with a nucleus of mass m_{N} , the allowed energy levels are given by the expression

$$E_n = -\frac{hcR_{\text{N}}Z^2}{n^2} \quad (4a)$$

where

$$R_{\text{N}} = \frac{\mu e^4}{8\epsilon_0^3 h^3 c} \quad \mu = \frac{m_e m_{\text{N}}}{m_e + m_{\text{N}}} \quad (4b)$$

and $n = 1, 2, \dots$. The quantity μ is called the **reduced mass** of the atom, which is a kind of effective mass that takes into account the fact that although most of the motion within an atom is that of the electron, the heavy nucleus is not completely stationary. Because $m_{\text{N}} \gg m_e$, even for hydrogen, in all but the most precise calculations, $\mu = m_e$. Schrödinger must have been thrilled to find that when he calculated R_{H} , the value he obtained was in almost exact agreement with the experimental value of $109\,677 \text{ cm}^{-1}$.

The most important features of eqn 4a are the role of n , the significance of the negative sign, and the appearance in the equation of Z^2 . We consider each in turn.

The quantum number n is called the **principal quantum number**. It is used to calculate the energy of the electron in the atom by substituting its value into eqn 4a. The resulting energy levels are depicted

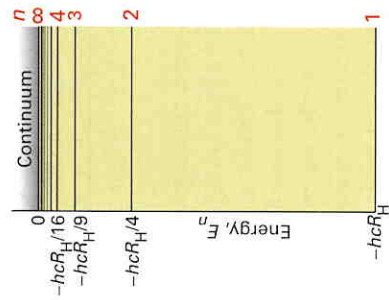


Fig. 2 The energy levels of the hydrogen atom. The energies are relative to a proton and an infinitely distant, stationary electron.

in Fig. 2. They are widely separated at low values of n , but then converge as n increases. At low values of n the electron is confined close to the nucleus by the attraction of opposite charges and the energy levels are widely spaced like those of a particle in a narrow box. At high values of n , when the electron has such a high energy that it can travel out to large distances, the energy levels are close together, like those of a particle in a large box.

Now consider the sign in eqn 4a. All the allowed energies are negative, which signifies that an electron in an atom has a lower energy than when it is free. The zero of energy (which occurs at $n = \infty$) corresponds to the infinitely widely separated (so that the Coulomb potential energy is zero) and stationary (so that the kinetic energy is zero) electron and nucleus. An electron can have any energy greater than zero if it has escaped from the atom and is moving, but its wavefunctions then obey different boundary conditions and its energies are no longer given by eqn. 4a. The state of lowest, most negative, energy, the ground state of the atom, is the one with $n = 1$ (the smallest permitted value of n and hence the most negative value of the energy). The energy of this state is $E_1 = -hcR_N Z^2$; the negative sign means that the ground state lies $hcR_N Z^2$ below the energy of the infinitely separated and stationary electron and nucleus. The first excited state of the atom, the state with $n = 2$, lies at $E_2 = -\frac{1}{4}hcR_N Z^2$. This energy level is $\frac{3}{4}hcR_N Z^2$ above the ground state.

These results explain the empirical expression for the spectroscopic lines observed in the emission spectrum of atomic hydrogen (for which R_N is R_H and $Z = 1$). In such a transition, an electron jumps from an energy level with one quantum number (n_2) to a

level with a lower energy (with quantum number n_1). As a result, the energy discarded is

$$\Delta E = \left(-\frac{hcR_H}{n_2^2} \right) - \left(-\frac{hcR_H}{n_1^2} \right) = hcR_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This energy is carried away by a photon of energy $hc\nu$. By equating this energy to ΔE , eqn 1 is obtained immediately.

Now consider the significance of Z^2 in eqn 4a. The fact that the energy levels are proportional to Z^2 stems from two effects. First, an electron at a given distance from a nucleus of charge Ze has a potential energy that is Z times more negative than an electron at the same distance from a proton (for which $Z = 1$). However, the electron is drawn in to the vicinity of the nucleus by the greater nuclear charge, so it is more likely to be found closer to the nucleus of charge Z than the proton. This effect is also proportional to Z , so overall the energy of an electron can be expected to be proportional to the square of Z , one factor representing the Z times greater strength of the nuclear field and the second factor representing the fact that the electron is Z times more likely to be found closer to the nucleus.

Brief illustration 8A.1 Transitions in hydrogenic atoms

The shortest wavelength transition in the Paschen series in hydrogen occurs at 821 nm. According to eqn 4a, the allowed energies of one-electron atoms and ions are proportional to Z^2 , so the wavenumbers of the transitions between the same two levels scale as Z^2 too. Because wavelength is inversely proportional to the wavenumber, it follows that the wavelength of the transition should scale as $1/Z^2$. Therefore, the same transition in Li^{2+} (for which $Z = 3$) can be expected to lie at $\frac{1}{9} \times 821 \text{ nm} = 91.2 \text{ nm}$. It does.

Self-test 8A.1

A transition in the Brackett series of Li^{2+} is observed at a wavelength of 450 nm. What is the quantum number of the upper energy level?

Answer: 6

The minimum energy needed to remove an electron completely from an atom is called the **ionization energy**, I . For a hydrogen atom, the ionization energy is the energy required to raise the electron from the ground state (with $n = 1$ and energy $E_1 = -hcR_H$) to the state corresponding to complete removal of the electron (the state with $n = \infty$ and zero energy). Therefore, the energy that must be supplied is $I = hcR_H = 2.179 \text{ aJ}$, which corresponds to 1312 kJ mol^{-1} or 13.59 eV .

Brief illustration 8A.2 Ionization energies of hydrogenic atoms

As in Brief illustration 8A.1, eqn 4a shows that the allowed energies are proportional to Z^2 . Therefore the ionization energies of one-electron species should also scale as Z^2 . Because the ionization energy of H is 13.59 eV, the ionization energy of He (for which $Z = 2$) should be $I_{\text{He}} = 4I_{\text{H}} = 54.36 \text{ eV}$. That is in fact its experimentally determined value.

Self-test 8A.2

What is the energy required to ionize a hydrogen atom initially in its first excited state?

Answer: $\frac{3}{4}hcR_H = 3.40 \text{ eV}$

8A.2 Quantum numbers

The wavefunction of the electron in a hydrogenic atom is called an **atomic orbital**. The name is intended to express something less definite than the 'orbit' of classical mechanics. An electron that is described by a particular wavefunction is said to 'occupy' that orbital. So, in the ground state of the atom, the electron occupies the orbital of lowest energy (that with $n = 1$).

As already mentioned, there are three mathematical conditions on the orbitals: every orbital must decay to zero as they extend to infinity, they must match as they encircle the equator, and they must match as they encircle the poles. Each condition gives rise to a quantum number, so each orbital is specified by three quantum numbers that act as a kind of 'address' of the electron that occupies it. The values allowed to the three quantum numbers are linked because, as in the discussion of a particle on a sphere (Topic 7D), to get the right shape on a polar journey the orbital depends on the shape as the particle travels round the equator. It turns out that the relations between the allowed values are very simple.

As remarked in Topic 7C, for some systems the Schrödinger equation separates into simpler equations for each coordinate. As may be expected for a spherically symmetrical, centrosymmetric system like a hydrogenic atom, its Schrödinger equation separates into one equation for the angular coordinates (corresponding to motion around the nucleus, the analogue of the particle on a sphere treated in Topic 7D) and an equation for the radial dependence. The wavefunction correspondingly factorizes, and is written

$$\psi_{n,l,m_l}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{Radial wavefunction}} \times \underbrace{Y_{l,m_l}(\theta,\phi)}_{\text{Angular wavefunction}} \quad \text{Hydrogenic orbital} \quad (5)$$

The factor $R_{n,l}(r)$ is called the **radial wavefunction**. The factor $Y_{l,m_l}(\theta,\phi)$ is called the **angular wavefunction** and is exactly the wavefunction found for a particle on a sphere and described in Topic 7D. As can be seen from this expression, the wavefunction is specified by three quantum numbers, all of which have already been met in different guises (Topics 7C and 7D):

Quantum number	Quantum Name	Allowed values	Determines
n	principal	1, 2, ...	Energy, through $E_n = -hcR_N Z^2/n^2$
l	orbital angular momentum	0, 1, ..., $n-1$	Orbital angular momentum, through $J = (l+1)^{1/2}h$
m_l	magnetic	0, $\pm 1, \dots, \pm l$	z-Component of orbital angular momentum, through $J_z = m_l h$

The radial wavefunction $R_{n,l}(r)$ depends only on n and l , so all wavefunctions of a given n and l have the same radial dependence regardless of the value of m_l . Similarly, the angular wavefunction $Y_{l,m_l}(\theta,\phi)$ depends only on l and m_l , so all wavefunctions of a given l and m_l have the same angular shape regardless of the value of n . The explicit expressions for some of the orbitals are shown in Table 8A.1; the notation used there is described immediately below.

Brief illustration 8A.3 Quantum numbers and orbitals

It follows from the restrictions on the values of the quantum numbers that there is only one orbital with $n = 1$, because when $n = 1$ the only value that l can have is 0, and that in turn implies that m_l can have only the value 0. Likewise, there are four orbitals with $n = 2$, because l can take the values 0 and 1, and in the latter case m_l can have the three values +1, 0, and -1. In general, there are n^2 orbitals with a given value of n .

A note on good practice Always give the sign of m_l , even when it is positive. So, write $m_l = +1$, not $m_l = 1$.

Self-test 8A.3

Specify the orbitals with $n = 3$.

Answer: 9 orbitals; one with $l = 0$, three with $l = 1$, and five with $l = 2$

Although all three quantum numbers are needed to specify a given orbital, eqn 4 shows that for hydrogenic atoms—and *only* for hydrogenic atoms—

Table 8A.1
Hydrogenic wavefunctions*

Orbital	Radial wavefunction	Angular wavefunction
1s	$\frac{1}{2} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	$\frac{1}{2\pi^{1/2}}$
2s	$\frac{1}{8^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	$\frac{1}{2\pi^{1/2}}$
2p _x	$\frac{1}{24^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \sin\theta \cos\phi$
2p _y		$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \sin\theta \sin\phi$
2p _z		$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \cos\theta$
3s	$\frac{2}{243^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right) e^{-Zr/3a_0}$	$\frac{1}{2\pi^{1/2}}$
3p _x	$\frac{2}{486^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{3a_0}\right) \left(\frac{Zr}{3a_0}\right) e^{-Zr/3a_0}$	$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \sin\theta \cos\phi$
3p _y		$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \sin\theta \sin\phi$
3p _z		$\frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \cos\theta$
3d _{xy}	$\frac{1}{2430^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{2Zr}{3a_0}\right)^2 e^{-Zr/3a_0}$	$\frac{1}{4} \left(\frac{15}{\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$
3d _{yz}		$\frac{1}{2} \left(\frac{15}{\pi}\right)^{1/2} \cos\theta \sin\theta \sin\phi$
3d _{zx}		$\frac{1}{2} \left(\frac{15}{\pi}\right)^{1/2} \cos\theta \sin\theta \cos\phi$
3d _{x²-y²}		$\frac{1}{4} \left(\frac{15}{\pi}\right)^{1/2} \sin^2\theta \cos 2\phi$
3d _{z²}		$\frac{1}{4} \left(\frac{5}{\pi}\right)^{1/2} (3 \cos^2\theta - 1)$

* $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$, the Bohr radius. All orbitals of a given subshell have the same radial wavefunction.

the energy depends only on the principal quantum number, n . Therefore, in hydrogenic atoms, and only in hydrogenic atoms, all orbitals of the same value of n but different values of l and m_l have the same energy. Wavefunctions are said to be 'degenerate' when they correspond to the same energy; so in hydrogenic atoms all orbitals with the same value of n are degenerate. This degeneracy arises because of the symmetry of the centrosymmetric Coulomb potential. It is partly removed for atoms with more than one electron because the high level of symmetry is broken.

As already seen, at low values of n the electron is likely to be found close to the nucleus, whereas at high values of n it is more likely to be found at large distances. Once the wavefunctions are available, these qualitative remarks can be expressed more precisely, and it can be calculated that the average distance of an electron from the nucleus in an orbital with quantum numbers n and l (and any allowed value of m_l) is

$$\langle r \rangle_{n,l,m_l} = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right\} \quad (6)$$

Mean radius

where a_0 is the 'Bohr radius' (see Table 8A.1 and the discussion below; $a_0 = 52.9177$ pm). Note the following:

- The average distance from the nucleus increases as n^2 , in accord with what is expected.
- For a given n , l the mean distance decreases with increasing Z : the electron is drawn closer to the nucleus as the latter's charge increases.
- Although the mean distance depends on l , with high- l orbitals closer to the nucleus, the dependence is weak on account of the n^2 in the denominator of the term inside the parentheses. So an electron in an orbital of a given n has about the same average distances from the nucleus.

For instance, the mean distance of an electron from the nucleus in orbitals with $n = 3$ is $27a_0/2Z$ (for $l = 0$), $2.5a_0/2Z$ (for $l = 1$), and $21a_0/2Z$ (for $l = 2$).

The degeneracy of all orbitals with the same value of n (there are n^2 of them) and their similar mean radii (the average distance from the nucleus) form the basis for saying that they all belong to the same shell of the atom. It is common to refer to successive shells by letters:

n 1 2 3 4 ...
 K L M N ...

Thus, all four orbitals of the shell with $n = 2$ form the L shell of the atom.

Orbitals with the same value of n but different values of l belong to different subshells of a given shell. These subshells are denoted by the letters s, p, ... using the following correspondence:²

l 0 1 2 3 4 ...
 s p d f g ...

Only the first four types of subshell (s, p, d, and f) are important in practice. For the shell with $n = 1$, there is only one subshell, the one with $l = 0$, namely the 1s subshell. For the shell with $n = 2$ (which allows $l = 0, 1$), there are two subshells, namely the 2s subshell (with $l = 0$) and the 2p subshell (with $l = 1$). The general pattern of the first three shells and their subshells is shown in Fig. 3. In a hydrogenic atom, all the subshells of a given shell correspond to the same energy (because the energy depends on n and not on l).

If the orbital angular momentum quantum number is l , then m_l can take the $2l + 1$ values $m_l = 0, \pm 1, \dots, \pm l$. Therefore, each subshell contains $2l + 1$ individual orbitals (corresponding to the $2l + 1$ values of m_l for each value of l). It follows that in any given subshell, the number of orbitals is

s p d f g ...
 1 3 5 7 9 ...

An orbital with $l = 0$ (and necessarily $m_l = 0$) is called an s orbital. A p subshell ($l = 1$) consists of three p orbitals (corresponding to $m_l = +1, 0, -1$). An electron that occupies an s orbital is called an s electron.

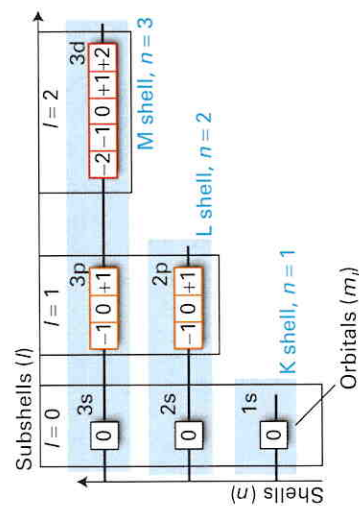


Fig. 3 The structures of atoms are described in terms of shells of electrons that are labelled by the principal quantum number n , and a series of n subshells of these shells, with each subshell of a shell being labelled by the quantum number l . Each subshell consists of $2l + 1$ orbitals.

² The letters have only a historical significance: they originally stood for *sharp*, *principal*, *diffuse*, and *fundamental*, referring to the characteristics of certain spectral lines.

Similarly, electrons are labelled as p, d, ... according to the orbitals they occupy.

Brief illustration 8A.4 The composition of a shell

As remarked in *Brief illustration 8A.3*, there are n^2 orbitals in a shell with principal quantum number n , so there are 25 orbitals in the shell with $n = 5$. The orbital angular quantum number l can take the values 0, 1, 2, 3, and 4, with $2l + 1$ orbitals in each subshell. It follows that the shell consists of one s, three p, five d, seven f, and nine g orbitals.

Self-test 8A.4

What subshells and orbitals are available in the N shell?

Answer: s (1), p (3), d (5), f (7)

8A.3 The s orbitals

The mathematical form of a 1s orbital (the wavefunction with $n = 1$, $l = 0$, and $m_l = 0$) for a hydrogen atom is

$$\psi_{1s} = 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \times \underbrace{\frac{Y_{0,0}}{2\pi^{1/2}}}_{\text{H 1s orbital}} = \frac{1}{\pi a_0^3} e^{-r/a_0} \quad (7a)$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad (7b)$$

Bohr radius [definition]

The features of this wavefunction are:

- It is normalized to 1 (Topic 7B), so the probability of finding the electron in a small volume of magnitude δV at a given point is *equal* to $\psi^2\delta V$, with ψ evaluated at a point in the region of interest, and provided that the volume δV is so small that the wavefunction does not vary inside it. The interpretation is precise when the volume is infinitesimal and δV is replaced by dV .
- The angular wavefunction, $Y_{0,0} = 1/2\pi^{1/2}$, is a constant, independent of the angles θ and ϕ . That is, the wavefunction is proportional to e^{-r} .
- The constant a_0 is called the **Bohr radius** (because it occurred in Bohr's calculation of the properties of the hydrogen atom) and has the value 52.9177 pm.

The general form of the wavefunction can be understood by considering the contributions of the potential and kinetic energies to the total energy of the atom.

The source of potential energy in a hydrogenic atom is Coulombic attraction, which becomes stronger the closer the electron is to the nucleus. This dependence suggests that the wavefunction should be sharply peaked, with large amplitude at the nucleus and close to zero everywhere else (Fig. 4a). However, this shape implies a very high kinetic energy, because the wavefunction is sharply curved. On the other hand, for the electron to have very low kinetic energy its wavefunction must have only a very low average curvature. However, such a wavefunction spreads to great distances from the nucleus and the average attraction of the electron to the nucleus is correspondingly weaker (Fig. 4b). The actual wavefunction is a compromise between these two extremes (Fig. 4c): the wavefunction spreads away from the nucleus (so the attraction is not as strong as in the first example, but nor is it very weak) and has a reasonably low average curvature (so the kinetic energy is not very low, but nor is it as high as in the first example.)

A 1s wavefunction depends only on the radius, r , of the point of interest and is independent of angle (the latitude and longitude of the point). Therefore, it has the same amplitude at all points at the same distance from the nucleus regardless of direction. Because the probability of finding an electron is proportional to the square of the wavefunction, the electron will be found with the same probability in any direction (for a given distance from the nucleus). That is, a 1s orbital is **spherically**

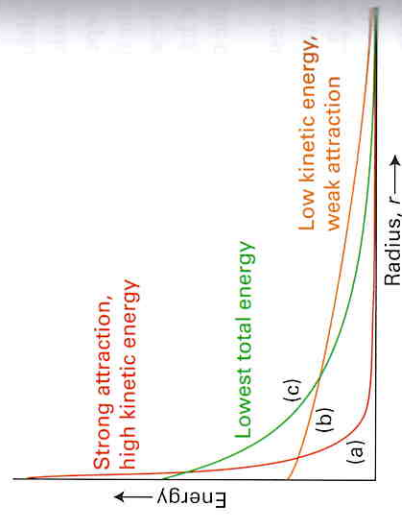


Fig. 4 The balance of kinetic and potential energies that counts for the structure of the ground state of hydrogen (and similar atoms). (a) An electron in the sharply curved but localized orbital has high kinetic energy and experiences a strong Coulombic attraction to the nucleus; (b) the kinetic energy is low, but the Coulombic attraction is weak; (c) the compromise of moderate kinetic energy and moderately favourable potential energy.

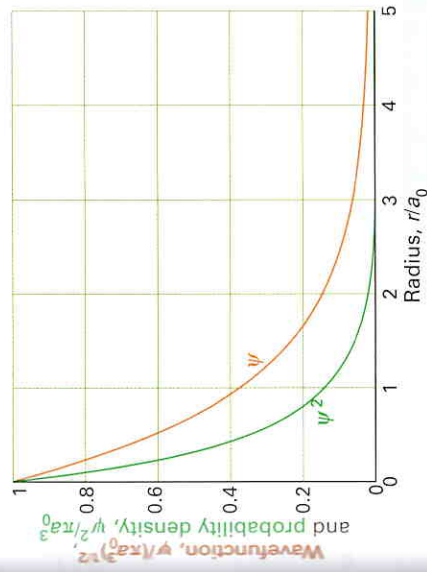


Fig. 5 The radial dependence of the wavefunction of a 1s orbital ($n = 1$, $l = 0$) and the corresponding probability density. The quantity a_0 is the Bohr radius (52.9 pm).

spherical. Because the same factor $Y_{0,0}$ occurs in all orbitals with $l = 0$, all s orbitals have the same spherical symmetry.

The wavefunction in eqn 4 decays exponentially towards zero from a maximum value at the nucleus (Fig. 5). It follows that *the probability density is highest at the nucleus itself*. A method of depicting the probability density throughout the atom is to represent ψ^2 by the density of shading in a diagram (Fig. 6). A simpler procedure is to show only the **boundary surface**, the shape that captures about 90 per cent probability of finding the electron in a region. For the 1s orbital, the boundary surface is a sphere centred on the nucleus (Fig. 7).

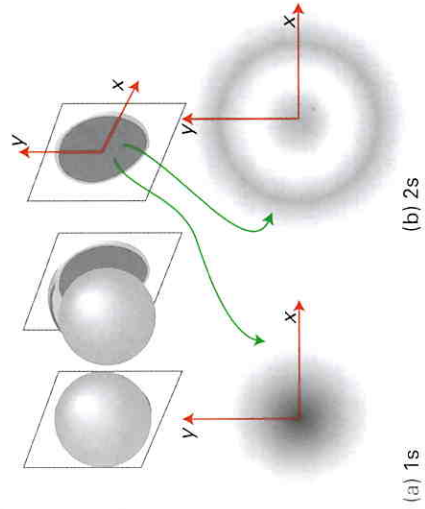


Fig. 6 Representations of the first two hydrogenic s orbitals. (a) 1s, (b) 2s, in terms of the electron densities in a slice through the centre of the atom (as represented by the density of shading) shown at the origin of the two green arrows. Note the presence of a radial node in the 2s orbital.

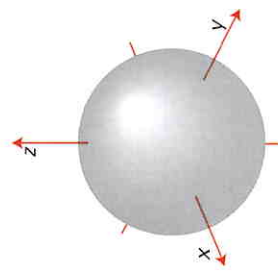


Fig. 7 The boundary surface of an s orbital within which there is a high probability of finding the electron.

Brief illustration 8A.5 A probability distribution

The probability of finding the electron in a volume of 1.0 pm^3 centred on the nucleus in a hydrogen atom is calculated by setting $r = 0$ in the expression for ψ , using $e^0 = 1$, and taking $\delta V = 1.0 \text{ pm}^3$. The value of ψ at the nucleus is $1/(\pi a_0^3)^{1/2}$. Therefore, $\psi^2 = 1/\pi a_0^3$ at the nucleus, the probability is

$$\begin{aligned} \text{Probability} &= \frac{1}{\pi a_0^3} \times \delta V = \frac{1}{\pi \times (52.9 \text{ pm})^3} \times (1.0 \text{ pm}^3) \\ &= \frac{1.0}{\pi \times 52.9^3} = 2.2 \times 10^{-6} \end{aligned}$$

This result means that the electron will be found in the volume on one observation in 455 000.

Self-test 8A.5

Repeat the calculation for finding the electron in the same volume located at the Bohr radius.

Answer: 3.0×10^{-7} , in 3.3 million observations

It is often necessary to know the probability that an electron will be found at a given distance from a nucleus regardless of its angular position (Fig. 8). The calculation is done by combining the wavefunction in eqn 5 with the Born interpretation. As shown in the following *Justification*, for an s orbital the answer can be expressed as

$$\begin{aligned} \text{Probability} &= P(r)\delta r \\ \text{with} \quad P(r) &= 4\pi r^2 \psi^2 \end{aligned} \quad (8a)$$

This expression is exactly true when the thickness of the shell is infinitesimal and δr is replaced by dr . The function P is called the **radial distribution function**. The more general form, which also applies to orbitals that depend on angle, is

$$P(r) = r^2 R(r)^2 \quad (8b)$$

General form of the radial distribution function

where $R(r)$ is the radial wavefunction.

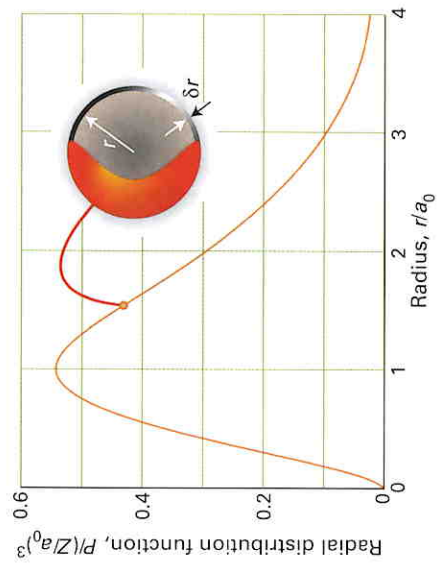


Fig. 8 The radial distribution function gives the probability that the electron will be found anywhere in a shell of radius r and thickness δr regardless of angle. The graph shows the output from an imaginary shell-like detector of variable radius and fixed thickness δr . The figure shows the radial distribution function for a 1s orbital in hydrogen, for which the maximum occurs at a_0 .

Example 8A.1

Using the radial distribution function

Consider an electron in a 1s orbital of a hydrogen atom of atomic number Z . Calculate the probability that the electron will be found anywhere in a shell formed by a region between a sphere of radius a_0 and a sphere of radius 1.0 pm greater. Apply the result to $Z = 1$.

Collect your thoughts Begin by establishing the form of the wavefunction by referring to Table 8A.1. Then substitute the wavefunction into the expression for P in eqn 8a, and evaluate it at $r = a_0$, with $\delta r = 1$ pm. This approach treats the thickness of the shell as so small that the wavefunction is uniform inside it.

The solution The hydrogenic 1s wavefunction is

$$\psi_{1s} = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \times \frac{1}{2\pi^{1/2}} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

So the radial distribution function for this orbital is

$$P(r) = 4\pi r^2 \left\{ \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \right\}^2 = 4 \left(\frac{Z}{a_0} \right)^3 r^2 e^{-2Zr/a_0}$$

Now substitute $r = a_0$ to find the radial distribution function at that distance:

$$P(a_0) = 4 \left(\frac{Z}{a_0} \right)^3 a_0^2 e^{-2Za_0/a_0} = \frac{4Z^3}{a_0} e^{-2Z}$$

For hydrogen, with $\delta r = 1.0$ pm and $Z = 1$, and

$$\text{Probability} = P(a_0)\delta r = \frac{4}{a_0} e^{-2} \times \delta r$$

$$= \frac{4}{52.92 \text{ pm}} \times e^{-2} \times (1.0 \text{ pm}) = 0.010$$

or about 1 inspection in 100.

Self-test 8A.6

Repeat the analysis for a 2s orbital.

Answer: 8.7×10^{-4} , 1 inspection in 1100

Justification 8A.1

The radial distribution function

Consider two spherical surfaces centred on the nucleus, one of radius r and the other of radius $r + \delta r$. The probability of finding the electron at a radius r regardless of its direction is equal to the probability of finding it between these two spherical surfaces, the 'shell' of thickness δr . To calculate the probability for an s orbital, follow these steps.

Step 1: Calculate the volume of the shell

The volume of the shell is equal to the surface area of its inner surface, $4\pi r^2$, multiplied by its thickness, δr , and is therefore $4\pi r^2 \delta r$.

Step 2: Use the Born interpretation to write an expression for the probability

According to the Born interpretation, the probability of finding an electron inside a small volume of magnitude δV is given, for a normalized wavefunction that can be treated as constant throughout the region, by the value of $\psi^2 \delta V$.

Step 3: Apply the result to an s orbital

An s orbital has the same value at all angles at a given distance from the nucleus, so it is constant throughout the shell (provided δr is very small). Therefore, interpreting δV as the volume of the shell,

$$\text{Probability} = \psi^2 \times (4\pi r^2 \delta r)$$

as in eqn 8a. The result applies only to s orbitals, which have no angular variation throughout the shell.

The radial distribution function gives the probability of finding an electron at a distance r from the nucleus regardless of its direction. It can be interpreted as follows:

- Because r^2 increases from 0 as r increases but ψ^2 decreases towards 0 exponentially, P starts at 0, goes through a maximum, and declines to 0 again.
- The location of the maximum marks the most probable *radius* (not point) at which the electron will be found. For a 1s orbital of hydrogen, the maximum occurs at a_0 , the Bohr radius.

Physical interpretation

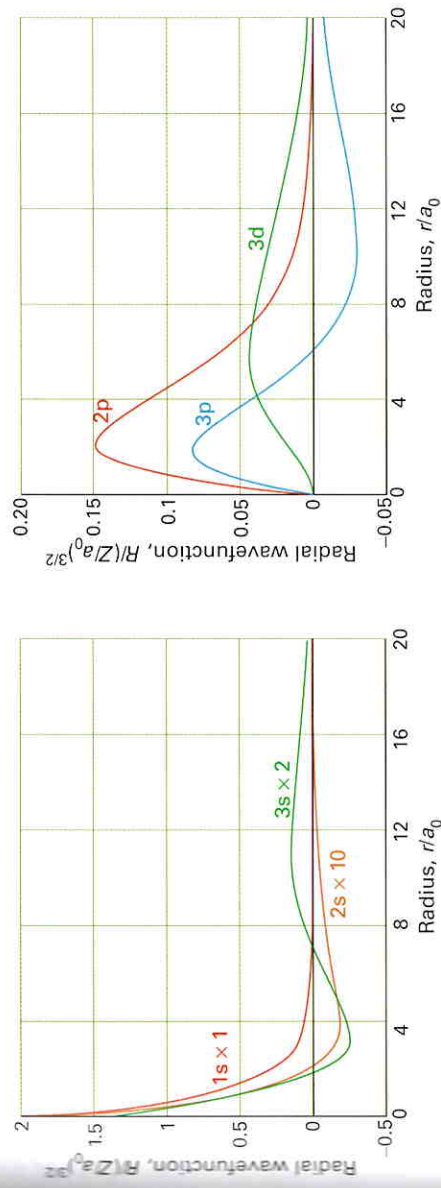


Fig. 9 The radial wavefunctions of some hydrogenic s, p, and d orbitals. Note that the s orbitals have a nonzero and finite value at the nucleus. The vertical scales are different in each case.

8A.4 The p and d orbitals

All p orbitals (orbitals with $l = 1$) have a double-lobed appearance like that shown in Fig. 10. The two lobes are separated by a **nodal plane** that cuts through the nucleus and arises from the angular wavefunction $Y_{l,m_l}(\theta, \phi)$. There is zero probability density for an electron on this plane.

Brief illustration 8A.6 The location of nodes

From Table 8A.1, the explicit form of the 2p_x orbital of a hydrogen atom ($Z = 1$) is

$$\psi = \frac{1}{2} \left(\frac{1}{6a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \times \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$$

$$= \left(\frac{1}{32\pi a_0^5} \right)^{1/2} r \cos \theta e^{-r/2a_0}$$

Because ψ has a factor r , it is zero at the nucleus, there is zero probability density of the electron at the nucleus. Because r does not extend to negative values, the wavefunction does not pass through zero at $r = 0$, so there is no radial node there. However, there is a nodal plane through the nucleus: the orbital is also zero everywhere on the plane with $\cos \theta = 0$, corresponding to $\theta = 90^\circ$ and the wavefunction changes sign on passing through this plane. The p_x and p_y orbitals are similar, but have nodal planes perpendicular to this one.

Self-test 8A.7

Where are the radial nodes of a 3p orbital of a hydrogenic atom?

Answer: at $r = 6a_0/2$

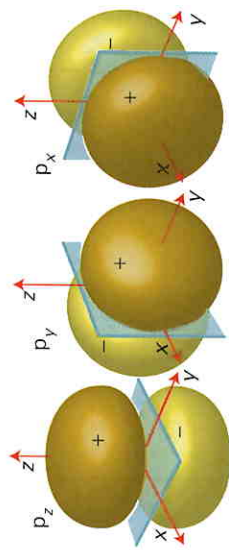


Fig. 10 The boundary surfaces of p orbitals. A nodal plane passes through the nucleus and separates the two lobes of each orbital.

The exclusion of the electron from the nucleus is a common feature of all atomic orbitals except s orbitals. To understand its origin, note that the value of the quantum number l gives the magnitude of the angular momentum of the electron around the nucleus (in classical terms, how rapidly it is circulating around the nucleus). For an s orbital, the orbital angular momentum is zero (because $l = 0$), and in classical terms the electron does not circulate around the nucleus. Because $l = 1$ for a p orbital, the magnitude of the angular momentum of a p electron is $2^{1/2}h$. As a result, a p electron—in classical terms—is flung away from the nucleus by the centrifugal force arising from its motion, but an s electron is not. The same centrifugal effect appears in all orbitals with angular momentum (those for which $l > 0$), such as d orbitals and f orbitals, and all such orbitals have nodal planes that cut through the nucleus.

Each p subshell consists of three orbitals ($m_l = 0, \pm 1$). The three orbitals are normally represented by their boundary surfaces, as depicted in Fig. 10. The p_x orbital has a symmetrical double-lobed shape directed along the x-axis, and similarly the p_y and p_z orbitals are directed along the y- and z-axes, respectively. As n increases, the p orbitals become bigger and have $n - 2$ radial nodes. However, their boundary surfaces retain the double-lobed shape shown in the illustration.

Each d subshell ($l = 2$) consists of five orbitals ($m_l = 0, \pm 1, \pm 2$). These five orbitals are normally represented by the boundary surfaces shown in Fig. 11 and labelled as shown there.

The quantum number m_l indicates, through the expression $m_l h$, the component of the electron's orbital angular momentum around an arbitrary axis passing through the nucleus. As explained in

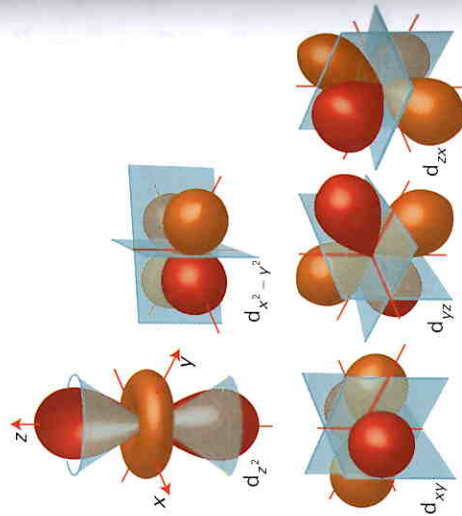


Fig. 11 The boundary surfaces of d orbitals. Two nodal planes in each orbital intersect at the nucleus and separate the four lobes of each orbital. (For a d_{z^2} orbital the planes are replaced by conical surfaces.) The light and dark tones denote regions of opposite sign of the wavefunction.

Topic 7D, positive values of m_l correspond to clockwise motion seen from below and negative values correspond to anticlockwise motion. An s electron has $m_l = 0$, and has no orbital angular momentum about any axis. A p electron can circulate clockwise about an axis as seen from below ($m_l = +1$). Of its total orbital angular momentum of $2^{1/2}h = 1.414h$, an amount h is due to motion around the selected axis (the rest is due to motion around the other two axes). A p electron can also circulate anticlockwise as seen from below ($m_l = -1$), or not at all ($m_l = 0$) about that selected axis. An electron in the d subshell can circulate with five different amounts of orbital angular momentum about an arbitrary axis ($0, \pm h, \pm 2h$).

Except for orbitals with $m_l = 0$, there is not a one-to-one correspondence between the value of m_l and the orbitals shown in the illustrations; it is not possible to say, for instance, that a p_x orbital has $m_l = +1$. For technical reasons, the orbitals are combinations of orbitals with opposite values of m_l (p_x , for instance, is the sum—a superposition—of the orbitals with $m_l = +1$ and -1).³

³ For more information on this point see our *Physical chemistry: thermodynamics, structure, and change* (2014).

Checklist of key concepts

- 1 Hydrogenic atoms are atoms with a single electron.
- 2 The wavefunctions of hydrogenic atoms are labelled with three quantum numbers, the **principal quantum number** $n = 1, 2, \dots$, the **orbital angular momentum quantum number** $l = 0, 1, \dots, n - 1$, and the **magnetic quantum number** $m_l = 0, \pm 1, \dots, \pm l$.
- 3 An **s orbital** is spherically symmetrical and has nonzero amplitude at the nucleus.
- 4 The **radial distribution function**, $P(r)$, is the probability density of finding an electron at a radius r regardless of direction; the probability of finding the electron between r and $r + \delta r$ is $P(r)\delta r$.
- 5 The magnitude of the orbital angular momentum of an electron is $\{(l + 1)^{1/2}h$ and the component of angular momentum about an axis is $m_l h$.

TOPIC 8B

Many-electron atoms

➤ Why do you need to know this material?

Many-electron atoms are the building blocks of all compounds. To understand their properties, including their ability to participate in chemical bonding, it is essential to understand their electronic structure.

➤ What is the key idea?

Electrons occupy the lowest energy available orbitals, subject to the requirements of the Pauli exclusion principle.

➤ What do you need to know already?

This Topic builds on the account of the structure of hydrogenic atoms (Topic 8A), especially their orbital and shell structure.

The Schrödinger equation for a many-electron atom is highly complicated because all the electrons interact with one another. Even for a He atom, with its two electrons, no mathematical expression for the orbitals and energies can be given, and approximations must be made. Modern computational techniques, though, refine the approximations introduced here, and permit highly accurate numerical calculations of energies and wavefunctions.

8B.1 The orbital approximation

A general rule in quantum mechanics, as explained in the following *Justification*, is that the wavefunction for several non-interacting particles is the product of the wavefunctions for each particle. This rule justifies the orbital approximation, in which it is supposed

described in Topic 8A, but with nuclear charges that are modified by the presence of all the other electrons in the atom. This resemblance is only approximate, but it is a useful model for discussing the properties of atoms. Indeed, it is the starting point for more sophisticated descriptions of atomic structure.

Brief illustration 8B.1 A two-electron wavefunction

If both electrons occupy the same 1s orbital for an atom with atomic number Z , the wavefunction for each electron in He ($Z=2$) is $\psi = (8/\pi a_0^3)^{1/2} e^{-2r/a_0}$. If electron 1 is at a radius r_1 and electron 2 is at a radius r_2 (and at any angle), then according to the orbital approximation the overall wavefunction for the two-electron atom is

$$\begin{aligned} \psi = \psi^{(1)}\psi^{(2)} &= \left(\frac{8}{\pi a_0^3} \right)^{1/2} e^{-2r_1/a_0} \times \left(\frac{8}{\pi a_0^3} \right)^{1/2} e^{-2r_2/a_0} \\ &= \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0} \end{aligned}$$

$e^{-r}e^{-r} = e^{-r-r}$

Self-test 8B.1

Construct the wavefunction for a state of the He atom with configuration $1s^2$. This is one of many possible excited states of the He atom. Use $Z=2$ for the 1s electron and $Z=1$ for the 2s electron. Why those values should be used will become clear shortly.

$$\text{Answer: } \psi = \left(\frac{1}{2} \pi a_0^3 \right)^{1/2} e^{-2r_1/a_0} e^{-r_2/a_0}$$

The orbital approximation allows the electronic structure of an atom to be expressed by reporting its **configuration**, a statement of the orbitals that are occupied (usually, but not necessarily, in its ground state). For example, because the ground state of a hydrogen atom consists of a single electron in a 1s orbital, its configuration is reported as $1s^1$ (read 'one s one'). A helium atom has two electrons. You can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a hydrogenic 1s orbital, but because $Z=2$ the orbital is more compact than in H itself. The second electron joins the first in the same 1s orbital, and so the electron configuration of the ground state of He is $1s^2$ (read 'one s two').

It is tempting to suppose that the electronic configurations of the atoms of successive elements with atomic numbers $Z=3, 4, \dots$, and therefore with Z electrons, are simply $1s^2, 1s^2 2s^1$. That, however, is not the case. The reason lies in two aspects of nature: that electrons possess 'spin' and their joint wavefunction must obey the very fundamental 'Pauli principle'.

8B.2 Electron spin

The spin of an electron is an *intrinsic* angular momentum that every electron possesses and which cannot be changed or eliminated (just like its mass or its charge). The name 'spin' is evocative of a ball spinning on its axis, and (so long as it is treated with caution) this classical interpretation can be used to help to visualize the motion. However, in fact spin is a purely quantum mechanical phenomenon and has no classical counterpart, so the analogy must be used with care.

Two properties of electron spin are important in a discussion of atomic structure (Fig. 1):

1. Electron spin is described by a **spin quantum number**, s (the analogue of l for orbital angular momentum), with s fixed at the single (positive) value of $\frac{1}{2}$ for all electrons at all times.
2. The spin can be clockwise or anticlockwise; these two states are distinguished by the **spin magnetic quantum number**, m_s , which can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

An electron with $m_s = +\frac{1}{2}$ is called an **α electron** and commonly denoted α or \uparrow ; an electron with $m_s = -\frac{1}{2}$ is called a **β electron** and denoted β or \downarrow .

The existence of electron spin was demonstrated by an experiment performed by Otto Stern and Walter Gerlach in 1922, who shot a beam of silver atoms through a strong, inhomogeneous magnetic field (Fig. 2). A silver atom has 47 electrons, and (as will be familiar from introductory chemistry) 23 of the spins are \uparrow and 23 spins are \downarrow ; the one remaining spin may be either \uparrow or \downarrow . Because the spin angular momenta of a \uparrow and a \downarrow electron cancel each other, the atom behaves as if it had the spin of a single electron. The idea behind the Stern–Gerlach experiment was that a rotating, charged body—in this case an electron—behaves like a magnet and interacts with the applied field. Because the magnetic field pushes or pulls the electron according to the orientation of the electron's spin, the initial beam of atoms should split into two beams, one

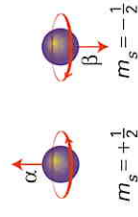


Fig. 1 A classical representation of the two allowed spin states of an electron. The magnitude of the spin angular momentum is $(3/2)\hbar$ in each case, but the directions of spin are opposite.

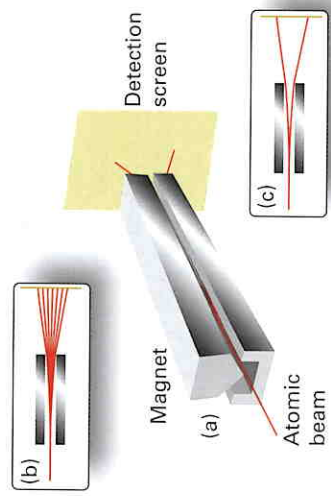


Fig. 2 (a) The experimental arrangement for the Stern-Gerlach experiment: the magnet is the source of an inhomogeneous field. (b) The classically expected result, when the orientations of the electron spins can take all angles. (c) The observed outcome using silver atoms, when the electron spins can adopt only two orientations (\uparrow and \downarrow).

corresponding to atoms with \uparrow spin and the other to atoms with \downarrow spin. This result was observed.

Other fundamental particles also have characteristic spins. For example, protons and neutrons are **spin- $\frac{1}{2}$ particles** (that is, for them $s = \frac{1}{2}$) so always spin with a single, irremovable angular momentum. Because the masses of a proton and a neutron are so much greater than the mass of an electron, yet they all have the same spin angular momentum, the classical picture of proton and neutron spin would be of particles spinning much more slowly than an electron. Some elementary particles are **spin-1 particles** (that is, for them $s = 1$) and therefore have a higher intrinsic angular momentum than an electron. The photon is a spin-1 particle. It is a very deep feature of nature that the fundamental particles from which matter is built have half-integral spin (such as electrons and quarks, all of which have $s = \frac{1}{2}$). The particles that transmit forces between these particles, so binding them together into entities like nuclei, atoms, and planets, all have integral spin (such as $s = 1$ for the photon, which transmits the electromagnetic interaction between charged particles). Fundamental particles with half-integral spin are called **fermions**; those with integral spin (including 0) are called **bosons**. Matter therefore consists of fermions bound together by the exchange of bosons.

Brief illustration 8B.2 Spin

The magnitude of the spin angular momentum, like any angular momentum, is $(s(s+1))^{1/2}\hbar$ (Topic 7D). For any spin- $\frac{1}{2}$ particle, not only electrons, this angular momentum is $(\frac{3}{4})^{1/2}\hbar = 0.866\hbar$, or 9.13×10^{-35} J s. The component on the z-axis is $m_s\hbar$, which for a spin- $\frac{1}{2}$ particle is $\pm\frac{1}{2}\hbar$, or $\pm 5.27 \times 10^{-35}$ J s.

Self-test 8B.2

Evaluate the spin angular momentum of a nitrogen-14 nucleus, a spin-1 particle.

Answer: $2^{1/2}\hbar = 1.49 \times 10^{-34}$ J s

8B.3 The Pauli principle

Lithium, with $Z = 3$, has three electrons. Two of its electrons occupy a 1s orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the 1s orbital because a 1s³ configuration is forbidden by a fundamental feature of nature summarized by the **Pauli exclusion principle**:

No more than two electrons may occupy any given orbital, and if two electrons do occupy one orbital, then their spins must be paired.

Electrons with **paired spins**, denoted $\uparrow\downarrow$, have zero net spin angular momentum because the spin angular momentum of one electron is cancelled by the spin of the other. The exclusion principle is the key to understanding the structures of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by the Austrian physicist Wolfgang Pauli in 1924 when he was trying to account for the absence of some lines in the spectrum of helium.

It follows from the discussion so far that lithium's third electron cannot enter the 1s orbital because that orbital is already full: the K shell ($n = 1$) is said to be **complete** and that the two electrons form a **closed shell**. Because a similar closed shell occurs in the He atom, it is denoted [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is one with $n = 2$ and hence belonging to the L shell. However, is the next available orbital the 2s orbital or one of the 2p orbitals, and is the lowest energy configuration of the atom [He]2s¹ or [He]2p¹?

8B.4 Penetration and shielding

Unlike in hydrogenic atoms, in many-electron atoms the 2s and 2p orbitals (and, in general, the subshells of a given shell) are not degenerate. For reasons we shall now explain, s electrons generally lie lower in energy than p electrons of a given shell, and p electrons lie lower than d electrons.

[†] See our *Physical chemistry: thermodynamics, structure, and change* (2014) for a justification of the Pauli exclusion principle.

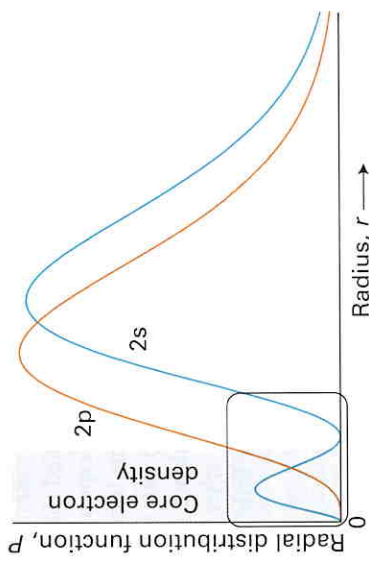


Fig. 4 An electron in an s orbital (here a 2s orbital) is more likely to be found close to the nucleus than an electron in a p orbital of the same shell. Hence it experiences less shielding and is more tightly bound.

and it therefore experiences greater shielding and an even smaller Z_{eff} .

The consequence of penetration and shielding is that, in general, the energies of orbitals in the same shell of a many-electron atom lie in the order $s < p < d < f$. The individual orbitals of a given subshell (such as the three p orbitals of the p subshell) remain degenerate because they all have the same radial distribution and so experience the same effective nuclear charge.

The average distance of the electron from the nucleus is not a good guide to the extent of shielding: it is important to examine the wavefunction close to the nucleus. For instance, as shown in Topic 8A to the average distance of an electron from the nucleus is greater when it occupies a 2p hydrogenic orbital than when it occupies a 2s hydrogenic orbital with the same nuclear charge. (Equation 6 of that Topic with $l = 0$ and $l = 1$ gives $3a_0/Z$ for a 2s electron and $5a_0/Z$ for a 2p electron.) However, the radial distribution function for a 2s orbital has an inner peak and so a 2s electron is more likely to be found close to the nucleus than a 2p electron is despite its average distance being greater. As a result a 2s electron in a many-electron atom has a lower energy than a 2p electron of the same atom. Similar remarks apply to the electrons in other shells.

The Li story can now be completed. Because the shell with $n = 2$ has two nondegenerate subshells, with the 2s orbital lower in energy than the three 2p orbitals, the third electron occupies the 2s orbital. This arrangement results in the ground-state configuration $1s^2 2s^1$, or [He]2s¹. It follows that the structure of the atom can be thought of as consisting of a central nucleus surrounded by a complete helium-like shell of two 1s electrons, and around that a more

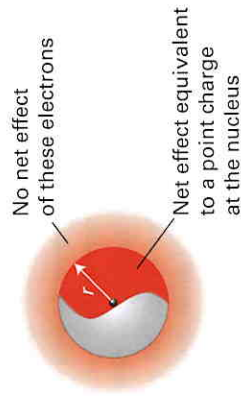


Fig. 3 An electron at a distance r from the nucleus experiences a Coulomb repulsion from all the electrons within a sphere of radius r and which is equivalent to a point negative charge located on the nucleus. The effect of the point charge is to reduce the apparent nuclear charge of the nucleus from Z to Z_{eff} .

An electron in a many-electron atom experiences a Coulomb repulsion from all the other electrons present. When the electron is at a distance r from the nucleus, the repulsion it experiences from the other electrons can be modelled by a point negative charge located on the nucleus and having a magnitude equal to the charge of the electrons within a sphere of radius r (Fig. 3). The effect of this point negative charge is to lower the full charge of the nucleus from Z to Z_{eff} , the **effective nuclear charge**. To express the fact that an electron experiences a nuclear charge that has been modified by the other electrons present, the electron is said to experience a **shielded nuclear charge**.

The electrons do not actually 'block' the full Coulomb attraction of the nucleus: the effective charge is simply a way of expressing the net outcome of the nuclear attraction and the electronic repulsions in terms of a single equivalent charge at the centre of the atom.

A note on good practice Commonly, Z_{eff} itself is referred to as the 'effective nuclear charge', although strictly that quantity is $Z_{\text{eff}}e$.

The effective nuclear charges experienced by s and p electrons are different because the electrons have different wavefunctions and therefore different distributions around the nucleus (Fig. 4). An s electron has a greater **penetration** through inner shells than a p electron of the same shell in the sense that an s electron is more likely to be found close to the nucleus than a p electron of the same shell. As a result of this greater penetration, an s electron experiences less shielding than a p electron of the same shell and therefore experiences a larger Z_{eff} . Consequently, by the combined effects of penetration and shielding, an s electron is more tightly bound than a p electron of the same shell. Similarly, a d electron penetrates less than a p electron of the same shell,

diffuse 2s electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** because they are largely responsible for the chemical bonds that the atom forms (and, as you will see, the extent to which an atom can form bonds is called its 'valence'). Thus, the valence electron in Li is a 2s electron, and lithium's other two electrons belong to its core, where they take little part in bond formation.

8B.5 The building-up principle

The extension of the procedure used for H, He, and Li to other atoms is called the **building-up principle**. The building-up principle, which is still widely called the *Aufbau principle* (from the German word for building up), specifies an order of occupation of atomic orbitals that reproduces the experimentally determined ground-state configurations of neutral atoms.

Starting with a bare nucleus of atomic number Z , the procedure feeds Z electrons into the available orbitals, one after the other. The first two rules of the building-up principle are:

- The order of occupation of orbitals is²
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 6p ...
- According to the Pauli exclusion principle, each orbital may accommodate up to two electrons.

The order of occupation is approximately the order of energies of the individual orbitals, because in general the lower the energy of the orbital, the lower the total energy of the atom as a whole when that orbital is occupied. An s subshell is complete as soon as two electrons are present in it. Each of the three p orbitals of a shell can accommodate two electrons, so a p subshell is complete as soon as six electrons are present in it. A d subshell, which consists of five orbitals, can accommodate up to ten electrons.

Brief illustration 8B.3 An electron configuration

Consider a carbon atom. Because $Z = 6$ for carbon, there are six electrons to accommodate. Two enter and fill the 1s orbital, two enter and fill the 2s orbital, leaving two electrons to occupy the orbitals of the 2p subshell. Hence its ground configuration is $1s^2 2s^2 2p^2$, or more succinctly $[\text{He}]2s^2 2p^2$, with $[\text{He}]$ the helium-like $1s^2$ core.

² Although this order will be seen to account for the layout of the periodic table, the best way to remember it is to refer to the table and the structure of blocks, groups, and periods to which it leads.

Self-test 8B.3

What is the ground-state configuration of a magnesium atom?

Answer: $[\text{Ne}]3s^2$

As demonstrated in the *Brief illustration*, the electron configuration of a carbon atom in its ground state is $[\text{He}]2s^2 2p^2$. However, it is possible to be more specific. On electrostatic grounds, the last two electrons are expected to occupy different 2p orbitals, for they will then be farther apart on average and repel each other less than if they were in the same orbital. Thus, one electron can be thought of as occupying the $2p_x$ orbital and the other the $2p_y$ orbital, and the lowest energy configuration of the atom is $[\text{He}]2s^2 2p_x^1 2p_y^1$. The same rule applies whenever degenerate orbitals of a subshell are available for occupation. Therefore, another rule of the building-up principle is:

- Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

It follows that a nitrogen atom ($Z = 7$) has the configuration $[\text{He}]2s^2 2p_x^1 2p_y^1 2p_z^1$. In oxygen ($Z = 8$) a 2p orbital is doubly occupied, giving the configuration $[\text{He}]2s^2 2p_x^2 2p_y^1$.

An additional point arises when electrons occupy some of the degenerate orbitals (such as the 2p orbitals) singly, as they do in C, N, and O, for there is then no requirement that their spins be paired. But is the lowest energy achieved when the electron spins are the same (both \uparrow , for instance, denoted $\uparrow\uparrow$, if there are two electrons in question, as in C and O) or when they are paired ($\uparrow\downarrow$)? This question is resolved by **Hund's rule**:

- In its ground state, an atom adopts a configuration with the greatest number of unpaired electrons.

The explanation of Hund's rule is complicated, but it reflects the quantum mechanical property of **spin correlation** that electrons in different orbitals with parallel spins have a quantum-mechanical tendency to stay well apart (a tendency that has nothing to do with their charge: even two 'uncharged electrons' would behave in the same way). Their mutual avoidance allows the atom to shrink slightly, so the electron-nucleus interaction is enhanced when the spins are parallel. So in the ground state of a C atom, the two 2p electrons have the same spin, all three 2p electrons in an N atom have the same spin, and the two electrons that singly occupy different 2p orbitals in an O atom have the same spin (the two in the 2p_x orbital are necessarily paired).

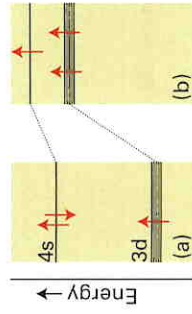


Fig. 5 Strong electron–electron repulsions in the 3d orbitals are minimized in the ground state of a scandium atom if (a) the atom has the configuration $[\text{Ar}]3d^1 4s^2$ instead of (b) $[\text{Ar}]3d^3 4s^1$. The total energy of the atom is lower when it has the configuration $[\text{Ar}]3d^1 4s^2$ despite the cost of populating the high-energy 4s orbital.

The effect just described is generally, but not always, true for scandium to zinc, so their electron configurations are of the form $[\text{Ar}]3d^N 4s^2$, where $N = 1$ for scandium and $N = 10$ for zinc. Exceptions include Cr and Zn, with observed electron configurations $[\text{Ar}]3d^5 4s^1$ and $[\text{Ar}]3d^{10} 4s^1$, respectively, even though their expected configurations are $[\text{Ar}]3d^4 4s^2$ and $[\text{Ar}]3d^{10} 4s^2$, respectively. In these cases, a half-filled or filled 3d subshell results in a configuration of lower energy.

At gallium, the energy of the 3d orbitals has fallen so far below those of the 4s and 4p orbitals that they (the full 3d orbitals) can be largely ignored, and the building-up principle can be used in the same way as in preceding periods. Now the 4s and 4p subshells constitute the valence shell, and the period terminates with krypton. Because 18 electrons have intervened since argon, this period is the first **long period** of the periodic table. The existence of the **d block** (which includes the 'transition metals' of Groups 3 to 10) reflects the stepwise occupation of the 3d orbitals, and the subtle shades of energy differences along this series gives rise to the rich complexity of inorganic (and bioinorganic) d-metal chemistry. A similar intrusion of the f orbitals in Periods 6 and 7 accounts for the existence of the **f block** of the periodic table (the lanthanoids and actinoids).

8B.7 The configurations of cations and anions

The configurations of cations of elements in the s, p, and d blocks of the periodic table are derived by removing electrons from the ground-state configuration of the neutral atom in a specific order. First, remove any valence p electrons, then the valence s electrons, and then as many d electrons as are necessary to achieve the stated charge. The configurations of anions are derived by continuing the building-up

Neon, with $Z = 10$, has the configuration $[\text{He}]2s^2 2p^6$, which completes the L ($n = 2$) shell. This closed-shell configuration is denoted $[\text{Ne}]$, and acts as a core for subsequent elements. The next electron must enter the 3s orbital and begin a new shell, and so a Na atom, with $Z = 11$, has the configuration $[\text{Ne}]3s^1$. Like lithium with the configuration $[\text{He}]2s^1$, sodium has a single s electron outside a complete core.

This analysis leads to the origin of chemical periodicity. The L shell is completed by eight electrons, and so the element with $Z = 3$ (Li) should have similar properties to the element with $Z = 11$ (Na). Likewise, Be ($Z = 4$) should be similar to Mg ($Z = 12$), and so on up to the noble gases He ($Z = 2$), Ne ($Z = 10$), and Ar ($Z = 18$).

8B.6 The occupation of d orbitals

Argon has complete 3s and 3p subshells, and as the 3d orbitals are high in energy, the atom effectively has a closed-shell configuration. Indeed, the 4s orbitals are so lowered in energy by their ability to penetrate close to the nucleus that the next electron (for potassium) occupies a 4s orbital rather than a 3d orbital and the K atom resembles a Na atom. The same is true of a Ca atom, which has the configuration $[\text{Ar}]4s^2$, resembling that of its partner in the same group, Mg, which is $[\text{Ne}]3s^2$.

Ten electrons can be accommodated in the five 3d orbitals, which accounts for the electron configurations of scandium to zinc. The building-up principle has less clear-cut predictions about the ground-state configurations of these elements, and a simple analysis no longer works. It is necessary to consider the total energy of the atom, including electron–electron repulsions in the valence shell.

Calculations show that for these atoms the energies of the 3d orbitals are always lower than the energy of the 4s orbital. However, spectroscopic results show that Sc has the configuration $[\text{Ar}]3d^1 4s^2$, instead of $[\text{Ar}]3d^3$ or $[\text{Ar}]3d^4 4s^1$. To understand this observation, consider the nature of electron–electron repulsions in 3d and 4s orbitals. The most probable distance of a 3d electron from the nucleus is less than that for a 4s electron, so two 3d electrons repel each other more strongly than two 4s electrons. As a result, Sc has the configuration $[\text{Ar}]3d^1 4s^2$ rather than the two alternatives, for then the strong electron–electron repulsions in the 3d orbitals are minimized. The total energy of the atom is least despite the cost of allowing electrons to populate the high energy 4s orbital (Fig. 5).

procedure and adding electrons to the neutral atom until the configuration of the next noble gas has been reached.

Brief illustration 8B.4 The electron configuration of an ion

Because the configuration of Fe is $[\text{Ar}]3d^64s^2$, an Fe^{3+} cation has the configuration $[\text{Ar}]3d^5$. The configuration of an O^{2-} ion is achieved by adding two electrons to $[\text{He}]2s^22p^4$, giving $[\text{He}]2s^22p^6$, the configuration of Ne.

Self-test 8B.4

Predict the ground-state electron configurations of (a) a Cu^{2+} ion and (b) an S^{2-} ion.

Answer: (a) $[\text{Ar}]3d^9$, (b) $[\text{Ne}]3s^23p^6$

8B.8 Self-consistent field orbitals

The treatment just given to the electronic configuration of many-electron species is only approximate because it is hopeless to expect to find exact solutions of a Schrödinger equation that takes into account the interaction of all the electrons with one another. However, computational techniques are available that give reliable approximate solutions for the wavefunctions and energies. The techniques were originally introduced by D.R. Hartree (before computers were available) and then modified by V. Fock to take into account the Pauli principle correctly. In broad outline, the **Hartree–Fock self-consistent field** (HF-SCF) procedure is as follows.

Checklist of key concepts

- 1 An electron possesses an intrinsic angular momentum, its **spin**, which is described by the quantum numbers $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$.
- 2 In the **orbital approximation**, each electron in a many-electron atom is supposed to occupy its own orbital.
- 3 The **Pauli exclusion principle** states that no more than two electrons may occupy any given orbital and if two electrons do occupy one orbital, then their spins must be paired.
- 4 In a many-electron atom, the orbitals of a given shell lie in the order $s < p < d < f$ as a result of the effects of penetration and shielding.

Start with an idea of the structure of the atom suggested by the building-up principle. In the Ne atom, for instance, the principle suggests the configuration $1s^22s^22p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now consider one of the $2p$ electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. Although the equation is for the $2p$ orbital, it depends on the wavefunctions of all the other occupied orbitals in the atom. To solve the equation, guess an approximate form of the wavefunctions of all the orbitals except $2p$ and then solve the Schrödinger equation for the $2p$ orbital. The procedure is then repeated for the $1s$ and $2s$ orbitals. This sequence of calculations gives the form of the $2p$, $2s$, and $1s$ orbitals, and in general they will differ from the set used to start the calculation. These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals and a better energy are obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the current cycle. The solutions are then self-consistent and accepted as solutions of the problem.

The outcomes of HF-SCF calculations are radial distribution functions that show the grouping of electron density into shells, as the building-up principle suggests. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity. They also extend that discussion considerably by providing detailed wavefunctions and precise energies.

□5 The **building-up principle** specifies an order of occupation of atomic orbitals that reproduces (in many cases) the experimentally determined ground state configurations of neutral atoms.

□6 The detailed specification of the configuration of an atom makes use of **Hund's rules** relating to the relative orientation of electron spins.

□7 The **Hartree–Fock self-consistent field** procedure leads to approximate solutions of the Schrödinger equation for many-electron atoms.

TOPIC 8C

Periodic trends of atomic properties

► Why do you need to know this material?

Knowledge of atomic structure is used to explain the structure of the periodic table and all the physical and chemical properties it summarizes.

► What is the key idea?

Trends in the variation of atomic and ionic radii and ionization energies can be correlated with the effective nuclear charges of atoms.

► What do you need to know already?

This Topic builds on the account of the structure of many-electron atoms (Topic 8B), especially the concepts of effective nuclear charge, penetration, and shielding.

The periodic recurrence of analogous ground-state electron configurations as the atomic number increases accounts for the periodic variation in the properties of atoms. Here two aspects of atomic periodicity are emphasized: atomic and ionic radius and ionization energy. Both can be correlated with the effective nuclear charge, and Fig. 1 shows how this quantity varies through the first three periods.

8C.1 Atomic and ionic radii

The **atomic radius** of an element is half the distance between the centres of neighbouring atoms in a solid (such as Cu) or, for non-metals, in a homonuclear molecule (such as H_2 or S_8). It is of great significance in chemistry, for the size of an atom is one of the most important controls on the number of chemical bonds the atom can form. Moreover, the size and shape of a

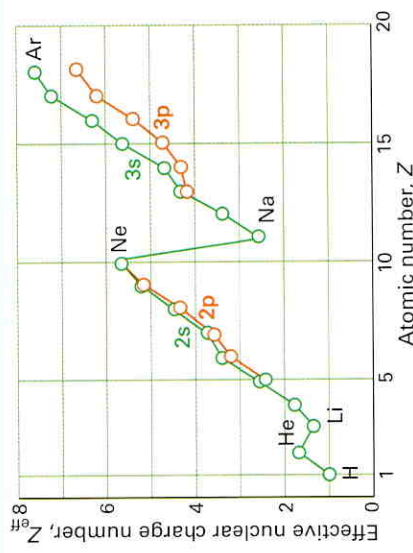


Fig. 1 The variation of the effective atomic number with actual atomic number for the elements of the first three periods. The value of Z_{eff} depends on the identity of the orbital occupied by the electron: we show the values only for the valence electrons.

molecule depend on the sizes of the atoms of which it is composed, and molecule size and shape are crucial aspects of a molecule's reactivity. Atomic radius also has an important technological aspect, because the similarity of the atomic radii of the d-block elements is the main reason why they can be blended together to form so many different alloys, particularly varieties of steel.

In general, atomic radii decrease from left to right across a period and increase down each group (Table 8C.1 and Fig. 2). The decrease across a period can be traced to the increase in nuclear charge, which draws the electrons in closer to the nucleus. The increase in nuclear charge is partly cancelled by the increase in the number of electrons, but because electrons are spread over a region of space, one electron does not fully shield one nuclear charge, so the increase in nuclear charge dominates. The increase in atomic radius down a group (despite the increase in nuclear charge) is explained by the fact that the valence shells of successive periods correspond to

Table 8C.1
Atomic radii of main-group elements, r/pm

Li	Be	B	C	N	O	F
157	112	88	77	74	66	64
Na	Mg	Al	Si	P	S	Cl
191	160	143	118	110	104	99
K	Ca	Ga	Ge	As	Se	Br
235	197	153	122	121	117	114
Rb	Sr	In	Sn	Sb	Te	I
250	215	167	158	141	137	133
Cs	Ba	Tl	Pb	Bi	Po	
272	224	171	175	182	167	

higher principal quantum numbers. That is, successive periods correspond to the start and then completion of successive (and more distant) shells of the atom that surround each other like the successive layers of an onion. The need to occupy a more distant shell leads to a larger atom despite the increased nuclear charge.

A modification of the increase down a group is encountered in Period 6, for the radii of the atoms late in the d block and in the following regions of the p block are not as large as would be expected by simple extrapolation down the group. The reason can be traced to the fact that in Period 6 the f orbitals are in the process of being occupied. An f electron is a very inefficient shielder of nuclear charge (for reasons connected with its radial extension), and as the atomic number increases from La to Yb, there is

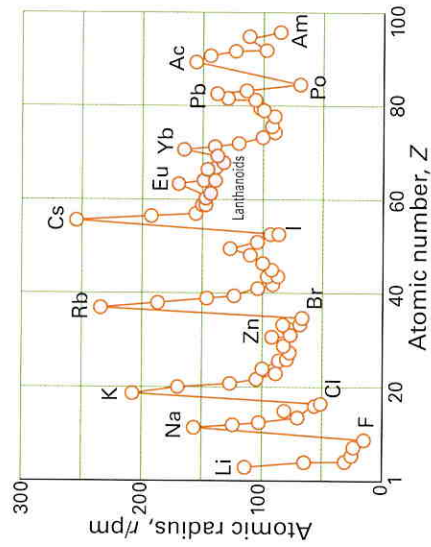


Fig. 2 The variation of atomic radius through the periodic table. Note the contraction of radius in Period 6 (following Yb, ytterbium).

a considerable contraction in radius. By the time the d block resumes (at hafnium, Hf), the poorly shielded but considerably increased nuclear charge has drawn in the surrounding electrons, and the atoms are compact. They are so compact, that the metals in this region of the periodic table (iridium to lead) are very dense. The reduction in radius below that expected by extrapolation from preceding periods is called the **lanthanide contraction**.

The ionic radius of an element is its share of the distance between neighbouring ions in an ionic solid. That is, the distance between the centres of a neighbouring cation and anion is the sum of the two ionic radii. The size of the 'share' leads to some ambiguity in the definition. One common definition sets the ionic radius of O^{2-} equal to 140 pm, but there are other scales, and care must be taken not to mix them. Ionic radii also vary with the number of counterions (ions of opposite charge) around a given ion; the values in this text have been corrected to correspond to an environment of six counterions.

When an atom loses one or more valence electrons to form a cation, the remaining atomic core is generally much smaller than the parent atom. Therefore, a cation is often smaller than its parent atom. For example, the atomic radius of Na, with the configuration $[Ne]3s^1$, is 191 pm, but the ionic radius of Na^+ , with the configuration $[Ne]$, is only 102 pm. Like atomic radii, cationic radii increase down each group because electrons are occupying shells with higher principal quantum numbers.

An anion is larger than its parent atom because the electrons added to the valence shell repel one another. Without a compensating increase in the nuclear charge, which would draw the electrons closer to the nucleus and each other, the ion expands. The variation in anionic radii shows the same trend as that for atoms and cations, with the smallest anions at the upper right of the periodic table, close to fluorine (Table 8C.2).

Brief illustration 8C.1 Ionic radii

The Ca^{2+} , K^+ , and Cl^- ions have the configuration $[Ar]$. However, their radii differ because they have different nuclear charges. The Ca^{2+} ion has the largest nuclear charge, so it has the strongest attraction for the electrons and the smallest radius. The Cl^- ion has the lowest nuclear charge of the three ions and, as a result, the largest radius.

Self-test 8C.1

Which ion is the smallest among Mg^{2+} , Na^+ , and F^- ?

Answer: Mg^{2+} .

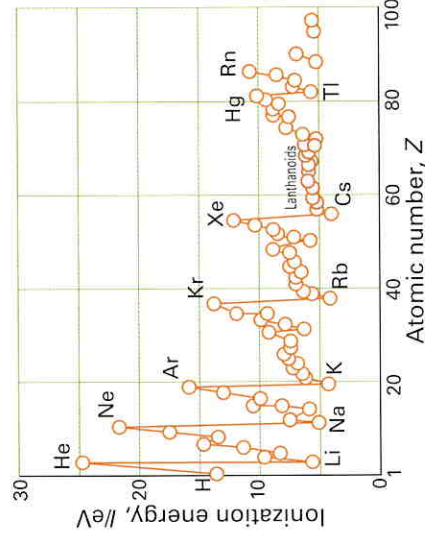


Fig. 3 The periodic variation of the first ionization energies of the elements.

ties at normal temperatures. The **standard enthalpy of ionization**, $\Delta_{\text{ion}}H^\ominus$, does differ because (in the notation used in Topic 2F, eqn 1 in the form $\Delta_{\text{ion}}H^\ominus = \Delta_{\text{ion}}U^\ominus + \Delta V_{\text{gas}}RT$ with $\Delta V_{\text{gas}} = +1$), $\Delta_{\text{ion}}H^\ominus = \Delta_{\text{ion}}U^\ominus + RT \approx I + RT$. But $RT = 2.5 \text{ kJ mol}^{-1}$ at 298 K is much smaller than most typical values of the ionization energy, that there is usually little reason, except in the most precise work, to distinguish between the ionization energy and the enthalpy of ionization.

The following trends are noteworthy:

- Lithium has a low first ionization energy: its outermost electron is well-shielded from the weakly charged nucleus by the core ($Z_{\text{eff}} = 1.3$ compared with $Z = 3$) and it is easily removed.

Table 8C.3

First ionization energies of main-group elements, /eV*

H	Li	Be	B	C	N	O	F	Ne
13.59	5.32	9.32	8.30	11.26	14.53	13.62	17.42	21.56
Na	Mg	Al	Si	P	S	Cl	Ar	
5.14	7.65	5.98	8.15	10.49	10.36	12.97	15.76	
K	Ca	Ga	Ge	As	Se	Br	Kr	
4.34	6.11	6.00	7.90	9.81	9.75	11.81	14.00	
Rb	Sr	In	Sn	Sb	Te	I	Xe	
4.18	5.70	5.79	7.34	8.64	9.01	10.45	12.13	
Cs	Ba	Tl	Pb	Bi	Po	At	Rn	
3.89	5.21	6.11	7.42	7.29	8.42	9.64	10.78	

* $1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$. See also Table 2E.2.

8C.2 Ionization energy and electron affinity

The minimum energy necessary to remove an electron from a many-electron atom is its **first ionization energy**, I_1 . The **second ionization energy**, I_2 , is the minimum energy needed to remove a second electron (from the singly charged cation):



$$I_1 = E(X^+) - E(X)$$



$$I_2 = E(X^{2+}) - E(X^+) \quad (1)$$

The variation of the first ionization energy through the periodic table is shown in Fig. 3 and some numerical values are given in Table 8C.3. The ionization energy of an element plays a central role in determining the ability of its atoms to participate in bond formation (for bond formation, Focus 9, is a consequence of the relocation of electrons from one atom to another). After atomic and ionic radius, it is the most important property for determining an element's chemical characteristics.

The **internal energy of ionization**, $\Delta_{\text{ion}}U$, takes into account the thermal population of states at the temperature of interest and strictly $\Delta_{\text{ion}}U$ can be identified with the ionization energy only at $T = 0$. However, in atoms, the excited states are so high in energy (compared with kT) that they are almost unpopulated and there is a negligible difference between the two quan-

* Numbers in parentheses are the coordination numbers of the ions, the numbers of species (e.g. counter ions, solvent molecules) around the ions. Values for ions without a coordination number stated are estimates.

Table 8C.2

Ionic radii, r/pm*

$Li^+(4)$	$Be^{2+}(4)$	$B^{3+}(4)$	$N^{3-}(6)$	$O^{2-}(6)$	$F^-(6)$
59	27	12	171	140	133
$Na^+(6)$	$Mg^{2+}(6)$	$Al^{3+}(6)$	$P^{3-}(6)$	$S^{2-}(6)$	$Cl^-(6)$
102	72	53	212	184	181
$K^+(6)$	$Ca^{2+}(6)$	$Ga^{3+}(6)$	$As^{3-}(6)$	$Se^{2-}(6)$	$Br^-(6)$
138	100	62	222	198	196
$Rb^+(6)$	$Sr^{2+}(6)$	$In^{3+}(6)$		$Te^{2-}(6)$	$I^-(6)$
149	116	79		221	220
$Cs^+(6)$	$Ba^{2+}(6)$	$Tl^{3+}(6)$			
167	136	88			

- Beryllium has a higher nuclear charge than lithium, and its outermost electron (one of the 2s electrons) is more difficult to remove: its ionization energy is larger.
- The ionization energy decreases between beryllium and boron because in the latter the outermost electron occupies a 2p orbital and is less strongly bound than if it had been a 2s electron.
- The ionization energy increases between boron and carbon because the latter's outermost electron is also 2p and the nuclear charge has increased.
- Nitrogen has a still higher ionization energy because of the further increase in nuclear charge.

There is now a kink in the curve because the ionization energy of oxygen is lower than would be expected by simple extrapolation.

- At oxygen a 2p orbital must become doubly occupied, and the electron–electron repulsions are increased above what would be expected by simple extrapolation along the row. (The kink is less pronounced in the next row, between phosphorus and sulfur, because their orbitals are more diffuse.)
- The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the nucleus for the outermost electrons.
- The outermost electron in sodium is 3s. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core.

As a result, the ionization energy of sodium is substantially lower than that of neon.

- The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

The **electron affinity**, E_{ea} , is the difference in energy between a neutral atom and its anion. It is the energy released in the process



The electron affinity is positive if the anion has a lower energy than the neutral atom. Care should be taken to distinguish the electron affinity from the standard electron-gain enthalpy (Topic 2E): they have very similar numerical values but differ in sign



An element with a positive electron affinity has a negative electron-gain enthalpy. By the same argument, as for ionization, but now with $\Delta V_{\text{abs}} = -1$, $\Delta_{\text{ea}}H^{\circ} \approx -E_{\text{ea}}$ and the difference between $\Delta_{\text{ea}}H^{\circ}$ and $-E_{\text{ea}}$ can normally be ignored. Moreover, in many thermodynamic calculations, ionization and electron gain both occur when electrons leave one substance and attach to another, and the 'correction' terms $+RT$ and $-RT$ cancel, so in such cases ignoring them introduces no error.

Electron affinities (Table 8C.4) vary much less systematically through the periodic table than

Table 8C.4

Electron affinities of main-group elements, $E_{\text{ea}}/\text{eV}^*$

H	He						
+0.75	<0 [†]						
Li	Be	B	C	N	O	F	Ne
+0.62	-0.19	+0.28	+1.26	-0.07	+1.46	+3.40	-0.30 [†]
Na	Mg	Al	Si	P	S	Cl	Ar
+0.55	-0.22	+0.46	+1.38	+0.46	+2.08	+3.62	-0.36 [†]
K	Ca	Ga	Ge	As	Se	Br	Kr
+0.50	-1.99	+0.3	+1.20	+0.81	+2.02	+3.37	-0.40 [†]
Rb	Sr	In	Sn	Sb	Te	I	Xe
+0.49	-1.51	+0.3	+1.20	+1.05	+1.97	+3.06	-0.42 [†]
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
+0.47	-0.48	+0.2	+0.36	+0.95	+1.90	+2.80	-0.42 [†]

* 1 eV = 96.485 kJ mol⁻¹. See also Table 2E.3.
† Calculated.

Collect your thoughts The reaction $\text{K}(\text{g}) + \text{Br}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{Br}^-(\text{g})$ can be thought of as the sum of the reactions $\text{K}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{e}^{-}(\text{g})$ and $\text{Br}(\text{g}) + \text{e}^{-}(\text{g}) \rightarrow \text{Br}^-(\text{g})$. Begin by using the first ionization energy of $\text{K}(\text{g})$ as the energy change ΔE_1 of the process $\text{K}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{e}^{-}(\text{g})$. That is, $\Delta E_1 = I(\text{K})$. Then, because the electron affinity of $\text{Br}(\text{g})$ is given by $E_{\text{ea}}(\text{Br}) = E(\text{Br}^-) - E(\text{Br})$, it follows that the energy change ΔE_2 of the process $\text{Br}(\text{g}) + \text{e}^{-}(\text{g}) \rightarrow \text{Br}^-(\text{g})$ is $\Delta E_2 = E(\text{Br}^-) - E(\text{Br})$. Finally, add the energies ΔE_1 and ΔE_2 to arrive at the energy change ΔE associated with the net process $\text{K}(\text{g}) + \text{Br}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{Br}^-(\text{g})$.

The solution Write



This value corresponds to +95 kJ mol⁻¹.

Self-test 8C.2

How is the first ionization energy of an anion related to the electron affinity of the parent atom?

Answer: $I(\text{X}^-) = E_{\text{ea}}(\text{X})$

ionization energies. However, the following general observations are important:

- Broadly speaking the highest electron affinities are found close to fluorine. In the halogens, the incoming electron enters the valence shell and experiences a strong attraction from the nucleus.
- The electron affinities of the noble gases are negative—which means that the anion has a higher energy than the neutral atom—because the incoming electron occupies an orbital outside the closed valence shell. It is then far from the nucleus and repelled by the electrons of the closed shells.
- The first electron affinity of oxygen is positive for the same reason as for the halogens. However, the second electron affinity (for the formation of O^{2-} from O^-) is strongly negative because although the incoming electron enters the valence shell, it experiences a strong repulsion from the net negative charge of the O^- ion.

Example 8C.1

Calculating the energy change of a reaction

The ionization energy of potassium is 4.34 eV and the electron affinity of Br is 3.36 eV. What is the change in energy in the reaction $\text{K}(\text{g}) + \text{Br}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{Br}^-(\text{g})$?

Checklist of key concepts

- 1 Atomic and ionic radii decrease from left to right across a period and increase down a group.
- 2 The first ionization energy is the minimum energy necessary to remove an electron from a many-electron atom.
- 3 Ionization energies increase from left to right across a period and decrease down a group.
- 4 The electron affinity is the difference in energy between a neutral atom and its anion.
- 5 Electron affinities are highest towards the top right of the periodic table (near fluorine).

TOPIC 8D

Atomic spectroscopy

► Why do you need to know this material?

A knowledge of the energies of electrons in atoms, which is obtained experimentally by spectroscopy, is essential for understanding many chemical concepts, such as chemical bonding, and underlies many techniques for the determination of the chemical composition of materials.

► What is the key idea?

Spectroscopic measurements confirm the theoretical prediction that the energy levels of atoms correlate with the contributions to the total angular momentum of their electrons.

► What do you need to know already?

This Topic draws on knowledge of the energy levels of hydrogenic atoms (Topic 8A) and the configurations of many-electron atoms (Topic 8B). In places, it uses the properties of angular momentum (Topic 7D) and the recognition that a photon is a spin-1 particle (Topic 8B).

The general idea behind atomic spectroscopy is straightforward: lines in the spectrum (in either emission or absorption) occur when the electron distribution in an atom undergoes a transition with a change of energy $|\Delta E|$, and emits or absorbs a photon of frequency $\nu = |\Delta E|/h$ and wavenumber $\tilde{\nu} = |\Delta E|/hc$. Hence, the spectrum gives information about the energies of electrons in atoms. The spectra of atoms can be very complicated, yet that complexity contains a great deal of detailed information about the distribution of electrons and their interactions and relates to simple ideas about atomic structure and electron configurations as set out in Topic 8B.

8D.1 The spectra of hydrogenic atoms

The energies of the hydrogenic atoms are given by eqn 4a of Topic 8A ($E_n = -hcR_\infty Z^2/n^2$). When the electron undergoes a transition, a change of state, from an orbital with quantum numbers n_1, l_1, m_{l1} to another orbital with quantum numbers n_2, l_2, m_{l2} , it undergoes a change of energy ΔE . If the second state is lower in energy than the first, the difference in energy is emitted as a photon. If the opposite is the case, then the transition may be driven by the absorption of a photon of that energy. The frequency ν of absorbed or emitted radiation is given by the Bohr frequency condition (Topic 7A) $\Delta E = h\nu$. Those frequencies (and the corresponding wavenumbers) are the basis of the description of the general features of the spectra of hydrogenic atoms in Topic 8A.

Not all possible transitions from one orbital to another contribute to the spectrum. Transitions are classified as either **allowed**, if they can contribute to the spectrum, or **forbidden**, if they cannot. The allowed or forbidden character of a transition can be traced to the fact that a photon is a spin-1 particle (Topic 8B). When a photon, is generated in a transition, the angular momentum of the electron must change by one unit to compensate for the angular momentum carried away by the photon. Thus, an electron in a d orbital of a hydrogenic atom (with $l = 2$) cannot make a transition into an s orbital (with $l = 0$) because the photon cannot carry away enough angular momentum. Similarly, an s electron cannot make a transition to another s orbital, because then there is no change in the electron's angular momentum to make up for the angular momentum carried away by the photon.

A **selection rule** is a statement about which spectroscopic transitions are allowed. They are

derived (for atoms) by identifying the transitions that leave the total angular momentum of the atom and the photon unchanged when a photon is emitted or absorbed. The selection rules for hydrogenic atoms are

$$\Delta l = \pm 1 \quad \Delta m_l = 0, \pm 1$$

The principal quantum number n can change by any amount consistent with the Δl for the transition because n does not relate directly to the angular momentum. Atoms can be excited to a variety of states by collisions, because the outcome of collisions is not governed by the same selection rules.

Brief illustration 8D.1 Selection rules for hydrogenic atoms

To identify the orbitals to which an electron in a 4d orbital of a hydrogenic atom may make spectroscopic transitions, you need to apply the selection rules, principally the rule concerning l . Because $l = 2$, the final orbital must have $l = 1$ or 3. Thus, an electron may make a transition from a 4d orbital to any *np* orbital (subject to $\Delta m_l = 0, \pm 1$) and to any *nf* orbital (subject to the same restriction). However, it cannot undergo a transition to any other orbital, so a transition to any *ns* orbital or another *nd* orbital is forbidden.

Self-test 8D.1

To what orbitals may a 4s electron make spectroscopic transitions?

Answer: *np* orbitals only

A **Grotrian diagram** (Fig. 1) summarizes the energies of the states and the allowed transitions between them. The thickness of a transition line in the diagram is sometimes used to indicate in a general way its relative intensity in the spectrum.

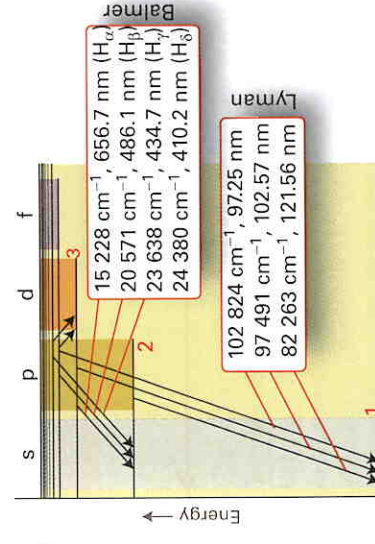


Fig. 1 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen.

8D.2 The energies of many-electron atoms

To interpret spectroscopic data on many-electron atoms, you need to know how the interactions between electrons affect the energy levels and which transitions are allowed. As will become clear, the outcome of these interactions can be correlated with which orbitals are occupied and (because each orbital corresponds to a certain angular momentum) with the total orbital angular momenta of the electrons, their total spin, and the relative alignment of these two sources of angular momentum.

A common scheme used to arrive at the total angular momentum of electrons in an atom is called **Russell–Saunders coupling**. It is based on the notion that the orbital momenta of the electrons couple together to give the total orbital angular momentum, then the spins are coupled together to give a total spin. Finally, the two total orbital and spin angular momenta are coupled together to give a grand total angular momentum.

The coupling scheme focuses on the valence electrons, for the electrons of the core are fully paired, and do not contribute to the overall angular momentum of an atom. Once these angular momenta have been identified, they are used to label the energy levels of the atom. For historical reasons, an energy level of an atom is called a **term**, and the notation used to specify the term is called a **term symbol**. A term symbol looks like 3D_2 , with each component (the 3, the D, and the 2) indicating something about the angular momentum.

The letter (D, for instance) denotes the total orbital angular momentum of the electrons in the atom. To find it, the **total orbital angular momentum quantum number**, L , must be calculated in the manner described below. Then the following code is used:

L	0	1	2	3	4	...
	S	P	D	F	G	...

The code is the same as for orbitals (Topic 8A), but uses uppercase Roman letters. The possible values of the quantum number L are calculated from the orbital angular momentum quantum numbers (l_1 and l_2 , for instance) of the electrons in the valence shell of the atom through the following series:

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

This and the analogous series for other types of angular momenta are called **Clebsch–Gordan series**.

The modulus sign (|...|) simply means that the series terminates at a positive value (because the quantum number L cannot be negative).

The highest total orbital angular momentum occurs when the two electrons are orbiting in the same direction (in classical terms, like two planets round the Sun). This image gives the first clue about how angular momentum correlates with energy. Because high L corresponds to electrons circulating in the same sense, they do not meet and their repulsive interaction is weak. A low value of L signifies that the electrons are circulating in opposite directions and so do meet with the result that their energy is increased. Note that the angular momentum itself is not responsible for the difference in energy, but merely signifies different contributions to the Coulombic interaction between the electrons.

Brief illustration 8D.2 Atomic term symbols

Consider the excited state configuration of carbon, $[\text{He}]2s^2 2p^3 3p^1$, in which a 2p electron has been promoted to a 3p orbital (in a collision). Only the angular momenta of the p electrons need to be taken into account because the s electrons have no orbital angular momentum. For each electron $l = 1$ (that is, $l_1 = 1$ and $l_2 = 1$ for the two p electrons). It follows that

$$L = 1 + 1, 1 + 1 - 1, \dots, |1 - 1| = 2, 1, 0$$

This result is shown pictorially in Fig. 2, which uses the rules for addition and subtraction of vectors (*The chemist's toolkit 24*). It follows that the configuration gives rise to D, P, and S terms, corresponding to the three allowed values of the total orbital angular momentum. Because as the value of L increases so does the average separation of the electrons as they circulate round the nucleus (because the higher the total orbital angular momentum, the more likely it is that the electrons are travelling in the same direction), it also follows that the likely order of energies is $D < P < S$.

Self-test 8D.2

Identify the terms that may arise from an excited calcium atom with an electronic configuration $[\text{Ar}]3d^1 4d^1$.

Answer: G, F, D, P, S

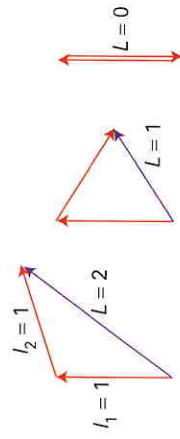
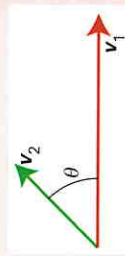


Fig. 2 A depiction of the rules for coupling two angular momenta into a resultant. In this case, $l_1 = l_2 = 1$ (each of length 2^{1/2}) to give resultants with $L = 2, 1$, and 0 (and lengths $6^{1/2}, 2^{1/2}$, and 0, respectively).

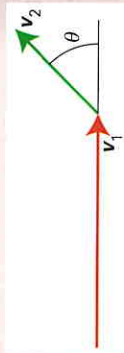
The chemist's toolkit 24 Addition and subtraction of vectors

Consider two vectors v_1 and v_2 making an angle θ , as shown in Sketch 1.



Sketch 1

The first step in the addition of v_2 to v_1 , consists of joining the tail of v_2 to the head of v_1 , as shown in Sketch 2.

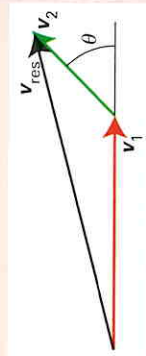


Sketch 2

In the second step, shown in Sketch 3, a vector v_{res} , the resultant vector, is drawn. It originates from the tail of v_1 to the head of v_2 . The magnitude, v_{res} , of the resultant vector is given by:

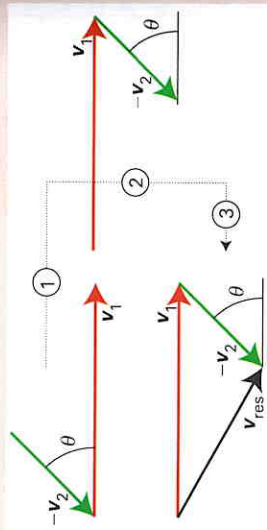
$$v_{\text{res}} = (v_1^2 + v_2^2 + 2v_1 v_2 \cos \theta)^{1/2}$$

where v_1 and v_2 are the magnitudes of the vectors v_1 and v_2 , respectively.



Sketch 3

The subtraction of vectors follows the same principles outlined above for addition by noting that subtraction of v_2 from v_1 is the same as addition of $-v_2$ to v_1 (Sketch 4).



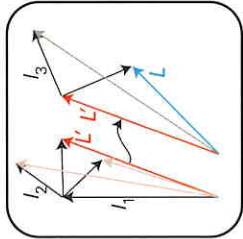
Sketch 4

Example 8D.1

Identifying the terms of a three-electron shell

Identify the terms that arise from the configuration p^3 .

Collect your thoughts When there are more than two electrons to couple together, use two Clebsch-Gordan series in succession. First, couple two electrons, then couple the third to each combination, and so on.



The solution The coupling of two electrons with orbital angular momentum quantum numbers $l_1 = l_2 = 1$ gives a minimum value of $|1 - 1| = 0$. Therefore, using L' to denote the total orbital angular momentum quantum number for these two electrons only, obtain

$$L' = 1 + 1, 1 + 1 - 1, \dots, 0 = 2, 1, 0$$

How go on to calculate the values of L , the total orbital angular momentum quantum number for the three-electron system.

Couple l_3 with $L' = 2$, to give $L = 3, 2, 1$

Couple l_3 with $L' = 1$, to give $L = 2, 1, 0$

Couple l_3 with $L' = 0$, to give $L = 1$

The overall result is

$$L = 3, 2, 2, 1, 1, 1, 0$$

giving one F, two D, three P, and one S term and reported as F, 2D, 3P, S

Self-test 8D.3

Identify the terms that can arise from the configuration $d^2 p^1$.

Answer: H, 2G, 3F, 3D, 3P, S

The total spin angular momentum quantum number, S , is obtained in the same way as L , by adding together the individual spin angular momentum quantum numbers:

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

For electrons, $s = 1/2$, so for two electrons

$$S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} - 1, \dots, |\frac{1}{2} - \frac{1}{2}| = 1, 0$$

Then the value of S is represented in the term symbol by writing the multiplicity of the term, the value of $2S + 1$, as a left superscript (the 3 in 3D_2 , for instance). The higher the multiplicity of a term, the more electrons there are in the atom with spin in the same direction. A term of the form 'X' (with X any letter) is called a singlet term, 1X a doublet term, 3X a triplet term, and so on.

An important point is that certain combinations of spin and orbital angular momentum are forbidden

by the Pauli principle. For instance, the total orbital angular momentum of a He atom in its ground state is $L = 0$, corresponding to an S term. Both electrons must be paired (they occupy the same 1s orbital), so although two electrons can give rise to $S = 0$ and 1, only the former is allowed and the ground state is unambiguously 'S'.

Brief illustration 8D.3 The multiplicities of terms

For the excited configuration of carbon, $[\text{He}]2s^2 2p^3 3p^1$, of *Brief illustration 8D.2*, the two p electrons each have $s = 1/2$, so $S = 1, 0$. The corresponding multiplicities are $2 \times 1 + 1 = 3$ (a triplet term) and $2 \times 0 + 1 = 1$ (a singlet term). The corresponding term symbols are

Triplet terms: $^3D, ^3P, ^3S$ Singlet terms: $^1D, ^1P, ^1S$

A note on good practice The name 'state' should not be used in place of 'term'. As explained below, in general a term consists of a number of different states.

Self-test 8D.4

Consider the configuration $\dots 2p^3$. What is the highest multiplicity of a term corresponding to this configuration?

Answer: $S = \frac{3}{2}$ and $2S + 1 = 4$, a quartet term

When a configuration can give rise to terms with several multiplicities (as in the *Brief illustration*) it is possible to identify the term of lowest energy by using a restatement of Hund's rule, which is introduced in Topic 8B. There the rule was stated as 'in its ground state, an atom adopts a configuration with the greatest number of unpaired electrons'; in terms of multiplicity this statement becomes more generally

For a given configuration, the term with the highest multiplicity lies lowest in energy.

As explained in Topic 8B, electrons with parallel spins tend (for quantum mechanical reasons) to avoid each other and so allow the atom to shrink slightly. As a result, their Coulombic interaction with the nucleus is enhanced and the energy of the atom is lowered.

8D.3 Spin-orbit coupling

The label displayed as a right subscript in a term symbol (the 2 in 3D_2 , for instance) is the total angular momentum quantum number, J , the total angular momentum being the vector sum of the orbital and the spin angular momenta. The possible values of J (a positive number) are found by forming the series

$$J = L + S, L + S - 1, \dots, |L - S|$$

If there are many electrons having spins in the same direction as their orbital motion, then J is large. If the spins are aligned against the orbital motion, then J is small. Each value of J corresponds to a particular level of a term.

Brief illustration 8D.4 The levels of a term

The levels that occur in the 3D term are found by setting $L = 2$ and $S = 1$; then

$$J = 2 + 1, 2 + 1 - 1, \dots, |2 - 1| = 3, 2, 1$$

That is, the levels of the 3D term are 3D_3 , 3D_2 , and 3D_1 (there are three levels for this triplet term). In the 3D_3 level, not only are the two p electrons orbiting in the same sense, the two spins are spinning in the same direction as each other, and the total spin is in the same direction as the orbital angular momentum. In 3D_1 , the total spin is aligned oppositely to the total orbital momentum and the overall total angular momentum is relatively low.

A note on good practice 'Levels' are still not 'states'. Each level with a quantum number J consists of $2J+1$ individual states distinguished by the quantum number M_J .

Self-test 8D.5

What terms and levels can arise from the configuration $4p^33d^1$?

Answer: 4F_3 , 4D_2 , 4P_1 , $^4F_{4,3,2}$, $^3D_{3,2,1}$, $^3P_{2,1,0}$

The different levels of a term have different energies that arise from magnetic effects (so far the interactions affecting terms have been Coulombic). An electron is a charged particle, so its orbital angular momentum gives rise to a magnetic field, just as an electric current in a loop gives rise to a magnetic field in an electromagnet. That is, an electron with orbital angular momentum acts like a tiny bar magnet. An electron also has a spin angular momentum, and this intrinsic 'spinning motion' means that it also acts as a tiny bar magnet. The magnet arising from the spin interacts with the magnet arising from the orbital motion and gives rise to the interaction called **spin-orbit coupling**.

The two magnets have a higher energy when they are parallel than when they are antiparallel (Fig. 3). Therefore, because the relative orientation of the magnets reflects the relative orientation of the orbital and spin angular momenta, the energy of the atom depends on the total angular momentum quantum number J (because its value also reflects the relative orientation of the two kinds of momentum). A low energy is obtained when the angular momenta, and therefore the bar magnets, are antiparallel to each other. That arrangement of angular momenta

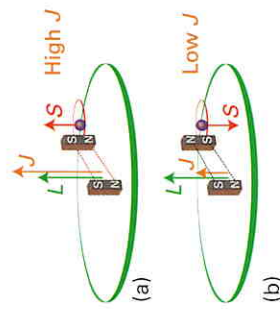


Fig. 3 The magnetic interaction responsible for spin-orbit coupling. (a) A high total angular momentum corresponds to a parallel arrangement of magnetic moments (represented by the bar magnets), and hence a high energy. (b) A low total angular momentum corresponds to an antiparallel arrangement of magnetic moments, and hence a low energy. Note that the difference in energy is not due *directly* to the differences in total angular momentum: the total simply specifies the relative orientations of the two magnetic moments.

corresponds to a low value of J . Therefore, the level with lowest value of J is predicted to lie lowest in energy. In the current example, the lowest level of the 3D term is predicted to be 3D_1 . A more general statement, which applies to many-electron systems, is as follows:

For atoms with shells that are less than half full, the level with lowest J lies lowest in energy; for atoms with shells that are more than half full, the level with highest J lies lowest.

Brief illustration 8D.5 Spin-orbit coupling

Consider a 4F term arising from a d^3 configuration (as in the Cr^{3+} ion). Because $L = 3$ (as implied by the symbol F) and $S = \frac{3}{2}$ (as implied by the multiplicity, $2S + 1 = 4$), $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$. The shell is less than half full, so the level with the lowest value of J has the lowest energy. It follows that the ground level is $^4F_{3/2}$.

Self-test 8D.6

Consider the 3F term arising from the configuration $4p^33d$. What is the symbol of the ground level?

Answer: 3F_4

The strength of the spin-orbit coupling increases sharply with atomic number. In Period 2 atoms it gives rise to splittings between levels of the order of 10^3 cm^{-1} , but in Period 3 the difference approaches 10^5 cm^{-1} . This increase can be understood by thinking about the source of the orbital magnetic field. To do so, imagine riding on the electron as it orbits the nucleus. From this viewpoint, the nucleus appears to orbit around the electron (rather as the pre-Copernicans thought the Sun revolved around the Earth). If the

nucleus has a high atomic number it will have a high charge, the electron will be at the centre of a strong electric current and so experience a strong magnetic field. If the nucleus has a low atomic number, the electron will experience a feeble magnetic field arising from the low current that encircles it.

Spin-orbit coupling has important consequences in photochemistry and in particular for the existence of the property of 'phosphorescence' (Topic 11E).

8D.4 Selection rules for many-electron atoms

As remarked in Section 8D.1, spectroscopic selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon is a spin-1 particle. They can therefore be expressed in terms of the term symbols, because the latter carry information about angular momentum. A detailed analysis leads to the following rules:

$$\Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta J = \pm 1$$

$$\Delta J = 0, \pm 1, \text{ but } J = 0 \leftrightarrow J = 0 \text{ is forbidden}$$

Brief illustration 8D.6 Transitions in many-electron atoms

A $^3D_2 \rightarrow ^3P_1$ transition is allowed because $\Delta S = 0$, $\Delta L = -1$ and $\Delta J = -1$. A $^3P_1 \rightarrow ^1S_0$ is forbidden in light atoms because $\Delta S = -1$, but is allowed in heavy atoms.

Self-test 8D.7

Is the transition $^3F_4 \rightarrow ^3D_3$ allowed?

Answer: Yes

Checklist of key concepts

- 1 A **term symbol** specifies the angular momentum states of an atom, and has the form $^{2S+1}L_J$.
- 2 Angular momenta are combined into a resultant by using the **Clebsch-Gordan series**.
- 3 Possible values of the **total orbital angular momentum** are expressed by values of the quantum number L .
- 4 The **multiplicity** of a term is the value of $2S+1$.
- 5 The total angular momentum in light atoms is obtained on the basis of **Russell-Saunders coupling**.
- 6 For a given configuration, the term with the highest multiplicity lies lowest in energy.
- 7 For atoms with shells that are less than half full, the level with lowest value of the total angular momentum quantum number J lies lowest in energy; for atoms with shells that are more than half full, the level with highest J lies lowest.
- 8 Different levels of a term have different energies on account of **spin-orbit coupling**, and the strength of spin-orbit coupling increases sharply with increasing atomic number.
- 9 Selection rules for light atoms include the statement that changes of total spin are forbidden.

The rule about ΔS (no change of overall spin) stems from the fact that the light does not affect the total spin directly. The rules about ΔL and ΔJ express the fact that the orbital angular momentum of an individual electron must change (so $\Delta l = \pm 1$), but whether or not this results in an overall change of orbital momentum depends on the coupling of angular momenta. These selection rules apply strictly for relatively light atoms, those near the top of the periodic table. As the atomic number increases, the rules progressively fail on account of significant spin-orbit coupling. So, for example, transitions between singlet and triplet states are allowed in heavy atoms and contribute to phosphorescence (Topic 11E).

FOCUS 8 Atomic structure

Exercises

Topic 8A Hydrogenic atoms

8A.1 Calculate the wavenumber and wavelength of the line with $n = 6$ in the Balmer series of the spectrum of atomic hydrogen.

8A.2 A line in the Balmer series of the spectrum of atomic hydrogen is observed at $23\,032\text{ cm}^{-1}$. What is the quantum number of the energy level?

8A.3 The frequency of one of the lines in the Paschen series of the spectrum of atomic hydrogen is $2.7415 \times 10^{15}\text{ Hz}$. Identify the principal quantum number of the energy level in the transition.

8A.4 The Li^{2+} ion is a hydrogenic atom. Calculate the value of the Rydberg constant for Li^{2+} . By what factor does it differ from the Rydberg constant for atomic hydrogen?

8A.5 The Rydberg constant depends on the mass of the nucleus. What is the difference in wavenumbers of the $3p \rightarrow 1s$ transition in hydrogen and deuterium?

8A.6 What transition in He^+ has the same frequency (disregarding mass differences) as the $2p \rightarrow 1s$ transition in H?

Topic 8B Many-electron atoms

8B.1 Classify the following as either a fermion or a boson: (a) an electron, (b) a proton, (c) a neutron, and (d) a photon.

8B.2 Predict the ground-state electronic configuration of (a) a C atom, (b) a Ti^{2+} ion, and (c) a Mn^{2+} ion.

Topic 8C Periodic trends of atomic properties

8C.1 Consider the atoms of the Period 2 elements of the periodic table. Predict which element has the lowest (a) first ionization energy and (b) second ionization energy.

Topic 8D Atomic spectroscopy

8D.1 Which of the following transitions are allowed in the electronic emission spectrum of an hydrogenic atom: (a) $2s \rightarrow 1s$, (b) $2p \rightarrow 1s$, (c) $3d \rightarrow 2p$, (d) $5d \rightarrow 2s$, (e) $5p \rightarrow 3s$, (f) $6f \rightarrow 4p$?

8D.2 To which orbitals may electrons in a $3p$ orbital make spectroscopic transitions in a hydrogenic atom?

8A.7 How many orbitals are present in the N shell of (a) H, (b) He, (c) Li^+ , (d) P^3+ ?

8A.8 What is the orbital angular momentum (as multiples of \hbar) of an electron in the orbitals (a) $1s$, (b) $3s$, (c) $3d$, (d) $2p$, (e) $3p$? Give the numbers of angular and radial nodes in each case.

8A.9 State the orbital degeneracy of the levels in the hydrogen atom that have energy (a) $-hcR_{\text{H}}$, (b) $-\frac{1}{9}hcR_{\text{H}}$, and (c) $-\frac{1}{25}hcR_{\text{H}}$.

8A.10 How many electrons can occupy subshells with the following values of l : (a) 0, (b) 3, (c) 5?

8A.11 The wavefunction of one of the d orbitals is proportional to $\sin\theta\cos\theta$. At what angles does it have nodal planes?

8A.12 For an atomic orbital with quantum numbers n and l , (a) how many radial, (b) angular, and (c) nodes are there?

8B.3 Why is the electronic configuration of the yttrium atom $[\text{Kr}]4d^15s^2$ and that of the silver atom $[\text{Kr}]4d^{10}5s^1$?

8C.2 What is the ionization energy of a Cl^- ion? Express your answer as a molar energy in units of kJ mol^{-1} .

8D.3 To what orbitals may a $5f$ electron in a hydrogenic atom make spectroscopic transitions?

8D.4 Use the Clebsch–Gordan series to deduce the possible values for the total orbital angular momentum of (a) two p electrons, (b) two d electrons.

8D.5 The Clebsch–Gordan series may be used successively to determine the possible values for the total angular momentum of several electrons. What are the total spin angular momenta that can arise from four electrons?

8D.6 What levels can the following terms possess: (a) ^1S , (b) ^3F , (c) ^3S , (d) ^5P ?

8D.7 What terms (expressed as S, D, etc.) can arise from the $[\text{He}]2s^22p^33d^1$ excited configuration of carbon?

8D.8 The ground configuration of a Ti^{2+} ion is $[\text{Ar}]3d^2$. (a) What is the term of lowest energy and which level of that term lies lowest? (b) How many states belong to that lowest level?

Discussion questions

8.1 List and describe the significance of the quantum numbers needed to specify the internal state of a hydrogenic atom.

8.2 Explain the significance of (a) a boundary surface and (b) the radial distribution function for hydrogenic orbitals.

8.3 Describe the orbital approximation for the wavefunction of a many-electron atom. What are the limitations of the approximation?

8.4 Discuss the relationship between the location of a many-electron atom in the periodic table and its electron configuration.

8D.9 What is the ground-state configuration of a Sc^{2+} ion? What levels arise from this configuration? Which of these levels lies lowest in energy?

8D.10 Use Hund's rules to deduce the term of the lowest level of a Ti atom.

8D.11 The lowest term of both the Al and Cl atoms is ^2P , which gives rise to $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ levels. Predict which level lies lower in energy for each atom.

8D.12 Which of the following transitions between terms are allowed in the normal electronic emission spectrum of a many-electron atom: (a) $^3\text{D}_2 \rightarrow ^3\text{P}_1$, (b) $^3\text{P}_2 \rightarrow ^1\text{S}_0$, (c) $^3\text{F}_4 \rightarrow ^3\text{D}_3$?

8.5 Describe the self-consistent field procedure for calculating the form of the orbitals and the energies of many-electron atoms.

8.6 Describe and account for the variation of first ionization energies along Period 2 of the periodic table. Would you expect the same variation in Period 3?

8.7 Explain the origin of spin–orbit coupling and how it affects the appearance of a spectrum.

8.8 Specify and account for the selection rules for spectroscopic transitions in (a) hydrogenic atoms and (b) many-electron atoms.

Problems

8.1 The distribution of isotopes of an element may yield clues about the nuclear reactions that occur in the interior of a star. Show that it is possible to use spectroscopy to confirm the presence of both $^4\text{He}^+$ and $^3\text{He}^+$ in a star by calculating the wavenumbers of the $n=3 \rightarrow n=2$ and of the $n=2 \rightarrow n=1$ transitions for each isotope.

8.2 Predict the ionization energy of Li^{2+} , given that the ionization energy of He^+ is 54.36 eV .

8.3 The Humphreys series is another group of lines in the spectrum of atomic hydrogen. It begins at $12\,368\text{ nm}$ and has been traced to 3281.4 nm . (a) What are the transitions involved? (b) What are the wavelengths of the intermediate transitions? (c) At what wavelength would you expect the longest wavelength transition of the Humphreys series to occur in He^+ ?

8.4 A series of lines in the spectrum of atomic hydrogen lies at 656.46 , 486.27 , 434.17 , and 410.29 nm . (a) What is the wavelength of the next line in the series? (b) What is the ionization energy of the atom when it is in the lower state of the transitions?

8.5 The Li^{2+} ion is hydrogenic and has a Lyman series of lines at $740\,747\text{ cm}^{-1}$, $877\,924\text{ cm}^{-1}$, $925\,933\text{ cm}^{-1}$, and beyond. (a) Show that the energy levels are of the form $-hcR_{\text{Li}}/n^2$ and find the value of R_{Li} for this ion. (b) Go on to predict the wavenumbers of the two longest wavelength transitions of the Balmer series of the ion and (c) find the ionization energy of the ion.

8.6 When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of $1.59 \times 10^6\text{ m s}^{-1}$. Calculate the ionization energy of krypton.

8.7 At what radius does the probability of finding an electron in a small volume located at a point in the ground state of an H atom fall to 30 per cent of its maximum value?

8.8 At what radius in the H atom does the radial distribution function of the ground state have (a) 30 per cent, (b) 5 per cent of its maximum value?

8.9 What is the probability of finding the electron in a volume of 6.5 pm^3 centred on the nucleus in (a) a hydrogen atom, (b) a He^+ ion?

8.10 Locate the radial nodes in (a) the 3s orbital, (b) the 4s orbital of an H atom.

8.11 One important function of atomic and ionic radius is in regulating the uptake of oxygen by haemoglobin, for the change in ionic radius that accompanies the conversion of Fe(II) to Fe(III) when O₂ attaches triggers a conformational

change in the protein. Which do you expect to be larger, Fe²⁺ or Fe³⁺? Why?

8.12 Two transitions in the [Ne]3p⁵ → [Ne]3s¹ emission spectrum of atomic sodium are observed at 589.0 nm and 589.6 nm. What is the difference in energy, expressed in electronvolts, between the ²P_{3/2} and ²P_{1/2} levels of the upper term?

Projects

The symbol \pm indicates that calculus is required.

8.1† Here you are invited to explore hydrogenic wavefunctions in more quantitative detail. (a) Find, by identifying the maximum in the radial distribution function of a hydrogenic 1s electron, the most probable distance of an electron from the nucleus in a hydrogen atom in its ground state? (b) The (normalized) wavefunction for a 2s orbital in hydrogen is

$$\psi = \left(\frac{1}{32\pi a_0^3} \right)^{1/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

Calculate the probability of finding an electron that is described by this wavefunction in a volume of 1.0 pm³ (i) centred on the nucleus, (ii) at the Bohr radius, (iii) at twice the Bohr radius. (c) Construct an expression for the radial distribution function of a hydrogenic 2s electron (see part (b) for the form of the orbital), and plot the function against r . What is the most probable radius at which the electron will be found? (d) For a more accurate determination of the radius at which an electron will most probably be found in an H2s orbital, differentiate the radial distribution function to identify where it is a maximum.

8.2 Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and

FOCUS 9

The chemical bond

The chemical bond, a link between atoms, is central to all aspects of chemistry. Reactions make them and break them, and the structures of solids and individual molecules depend on them. The physical properties of individual molecules and of bulk samples of matter also stem in large part from the shifts in electron density that take place when atoms form bonds.

There are two major approaches to the calculation of molecular structure, 'valence bond theory' (VB theory) and 'molecular orbital theory' (MO theory). Almost all modern computational work makes use of MO theory. However, VB theory has left its imprint on the language of chemistry, and it is important to know the significance of terms that chemists use every day.

9A Valence bond theory

This Topic begins with a procedure for writing wavefunction for a shared electron pair, which is then extended to account for the structures of a wide variety of molecules. The theory introduces the concepts of 'σ bonds', 'π bonds', 'promotion', and 'hybridization' that are used widely in chemistry.

9A.1 Diatomic molecules; 9A.2 Polyatomic molecules; 9A.3 Promotion and hybridization; 9A.4 Resonance; 9A.5 The language of valence bond theory

9B Molecular orbital theory: homonuclear diatomics

In MO theory the concept of atomic orbital is extended to that of 'molecular orbital', which is a wavefunction that spreads over all the atoms in a molecule. The Topic begins

with an account of the hydrogen molecule-ion, H₂⁺, which sets the scene for the application of MO theory to molecules in general. The principles established for the hydrogen molecule-ion are readily extended to other homonuclear diatomic species, the principal difference being that more types of atomic orbitals must be included to give a more varied collection of molecular orbitals.

9B.1 The construction of molecular orbitals; 9B.2 Bonding and antibonding orbitals; 9B.3 Inversion symmetry; 9B.4 The chemical bond in molecular orbital theory; 9B.5 Many-electron homonuclear diatomics; 9B.6 The configurations of Period 2 homonuclear diatomics; 9B.7 The criteria for building molecular orbitals

9C Molecular orbital theory: heteronuclear diatomics

The MO theory of heteronuclear diatomic molecules and ions introduces the possibility that the atomic orbitals on the two atoms contribute unequally to the molecular orbital. As a result, the molecule is polar. The polarity can be expressed in terms of the concept of 'electronegativity'.

9C.1 Polar bonds; 9C.2 The formulation of molecular orbitals; 9C.3 Molecular orbital diagrams

9D Molecular orbital theory: polyatomic molecules

Most molecules are polyatomic, so it is important to be able to account for their electronic structure. An early approach to the electronic structure of planar conjugated polyenes is the

'Hückel method'. It introduces severe approximations, but sets the scene for more sophisticated procedures, which are now used widely to predict molecular structure, physical properties, and chemical reactivity.

9D.1 **The molecular orbitals of H_2O** ; 9D.2 **The Hückel method**; 9D.3 **The molecular orbitals of benzene**; 9D.4 **Computational chemistry**

Web resource **What is an application of this material?**

Molecular orbital theory is used widely in the analysis of chemical and biochemical phenomena. For example, computer-aided molecular orbital calculations can contribute to the interpretation of molecular spectra and enhance understanding of electrochemical processes and the binding of drugs to receptor sites. See *Impact 7* on the website of this book.

TOPIC 9A

Valence bond theory

► Why do you need to know this material?

Valence bond theory was the first quantum mechanical theory of bonding to be developed. The language it introduced, which includes concepts such as spin pairings, σ and π bonds, and hybridization, is widely used throughout chemistry, especially in the description of the properties and reactions of organic compounds.

► What is the key idea?

A bond forms when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.

► What do you need to know already?

You need to know about atomic orbitals (Topic 8A) and the Pauli exclusion principle (Topic 8B).

The character of a **covalent bond** was identified by G.N. Lewis in 1916, before quantum mechanics was fully developed, as a shared pair of electrons (*The chemist's toolkit 25*). However, his theory was unable to account for the shapes adopted by molecules. The most elementary but qualitatively quite successful explanation of the shapes adopted by molecules is the **valence-shell electron pair repulsion model** (VSEPR model) in which it is supposed that the shape of a molecule is determined by the repulsions between electron pairs in the valence shell (*The chemist's toolkit 26*). The purpose of this Topic is to extend these general concepts with arguments grounded in quantum theory.

The chemist's toolkit 25 The Lewis theory of covalent bonding

In his original formulation of an early and simple theory of the covalent bond, which should be familiar from introductory chemistry courses, G.N. Lewis proposed that each bond consisted of one electron pair. Each atom in a molecule shared electrons until it had acquired an octet characteristic of a noble gas atom near it in the periodic table. (Hydrogen is an exception: it acquires a duplet of electrons.) Thus, to draw a Lewis structure:

1. Arrange the atoms as they are found in the molecule.
2. Add one electron pair (represented by dots, \cdot) between each bonded atom.
3. Use the remaining electron pairs to complete the octets (for H, the duplet) of all the atoms present either by forming lone pairs or by forming multiple bonds.
4. Replace bonding electron pairs by bond lines (—) but leave lone pairs as dots (\cdot).

A Lewis structure does not (except in very simple cases), portray the actual geometrical structure of the molecule; it portrays the 'connectivity' of the molecule, the linkages between neighbouring atoms.

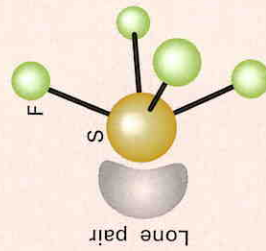
The chemist's toolkit 26 The VSEPR model

The basic assumption of the **valence-shell electron pair repulsion model** (VSEPR model) is that *the attached atoms and the lone pairs of the central atom adopt positions that maximize their separations*. Thus, if the atom has three attached atoms and one lone pair (as in $:NH_3$), then the atoms and the lone pair adopt a tetrahedral arrangement around the central atom. The arrangements adopted by these 'objects' (either atoms or lone pairs) are as follows:

Number of objects	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral
7	Pentagonal bipyramidal

Once the basic shape of the arrangement of the objects has been identified, the shape of the molecule is classified by noting the arrangement of the atoms around the central atom (not the lone pairs). Thus NH_3 is classified as trigonal pyramidal (not tetrahedral).

The next stage in the application of the VSEPR model is to accommodate the greater repelling effect of lone pairs compared with that of bonding pairs. That is, *bonding pairs tend to move away from lone pairs even though that might reduce their separation from other bonding pairs*. Thus, SF_4 adopts the shape shown in Sketch 1.



Sketch 1

All theories of molecular structure adopt the **Born–Oppenheimer approximation**. In this approximation, it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move around them. The nuclei can be thought of as being fixed at arbitrary locations, so the Schrödinger equation can be solved for the electrons alone. The approximation is quite good for molecules in their electronic ground-states, for calculations suggest that (in classical terms) the nuclei in H_2 move through only about 1 pm while the electron speeds through 1000 pm.

By invoking the Born–Oppenheimer approximation, the energies and wavefunctions of a diatomic molecule can be obtained by selecting an internuclear separation and then solving the Schrödinger equation for the electrons. Then the calculation can be repeated at a different internuclear separation, and

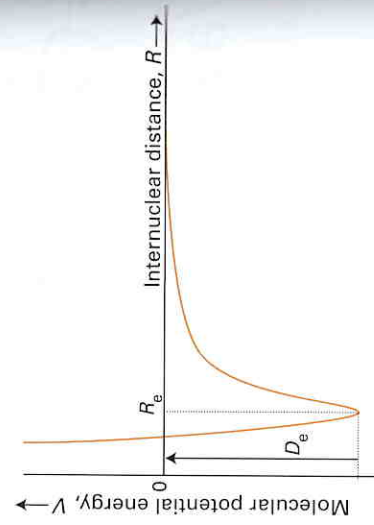


Fig. 1 A molecular potential energy curve. The equilibrium bond length R_e corresponds to the energy minimum D_e .

so on. In this way it is possible to explore how the energy of the molecule varies with bond length and obtain a **molecular potential energy curve**, a graph showing how the molecular energy depends on the internuclear separation (Fig. 1). The graph is called a **potential energy curve** because the nuclei are stationary and contribute no kinetic energy. Once the curve has been calculated, two important parameters can be identified: the **equilibrium bond length**, R_e , the internuclear separation at the minimum of the curve, and D_e , the depth of the minimum below the energy of the infinitely widely separated and stationary atoms. Similar considerations apply to polyatomic molecules, where bond angles may be varied as well as bond lengths.

9A.1 Diatomic molecules

In **valence bond theory** (VB theory), a bond is regarded as forming when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom (Fig. 2). To understand why this pairing leads to bonding, it is necessary to examine the wavefunction for the two electrons that form the bond.

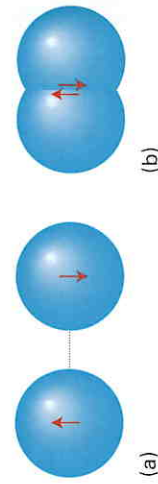


Fig. 2 In the valence bond theory, a σ bond is formed when two electrons in orbitals on neighbouring atoms, as in (a), pair and the orbitals merge to form a cylindrical electron cloud, as in (b).

Consider the simplest possible chemical bond, the one in molecular hydrogen, $\text{H}-\text{H}$. When the two ground-state H atoms are far apart, electron 1 is in ψ_A , the 1s orbital of atom A, denoted $\psi_A(1)$, and electron 2 is in ψ_B , the 1s orbital of atom B, denoted $\psi_B(2)$. A general rule in quantum mechanics is that the wavefunction for several non-interacting particles is the product of the wavefunctions for each particle (Topic 8B), so providing the interactions between the electrons can be ignored, the wavefunction for the two-electron system can be written as $\psi(1,2) = \psi_A(1)\psi_B(2)$. When the two atoms are close together, an equally likely arrangement is for electron 1 to escape from A and be found on B and for electron 2 to be on A. In this case the wavefunction is $\psi(1,2) = \psi_A(2)\psi_B(1)$. Whenever two outcomes are equally likely, the rules of quantum mechanics call for adding together the two corresponding wavefunctions, forming a **superposition**. Therefore, the (unnormalized) wavefunction for the two electrons in a hydrogen molecule is

$$\psi_{\text{H-H}}(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \quad (1)$$

This expression is the VB wavefunction for the electrons in molecular hydrogen and therefore describes the $\text{H}-\text{H}$ bond. It is built on the impossibility of keeping track of either electron and expresses the blending of their distributions. The wavefunction is only an approximation, because when the two atoms are close together it is not true that the electrons do not interact. However, this approximate wavefunction is a starting point for all discussions of the VB theory of bonding.

For technical reasons related to the Pauli exclusion principle, the wavefunction in eqn 1 can exist only if the two electrons it describes have opposite spins.¹ It follows that the merging of orbitals that gives rise to a bond is accompanied by the pairing of the two electrons that contribute to it. Bonds do not form *because* electrons tend to pair: bonds are *allowed* to form by the electrons pairing their spins.

Because $\psi_{\text{H-H}}$ is built from the merging of H1s orbitals, the overall distribution of the electrons in the molecule is expected to be sausage-shaped (as in Fig. 2). A VB wavefunction with cylindrical symmetry around the internuclear axis is called a **σ bond**. The bond is so called because, when viewed along the internuclear axis it resembles a pair of electrons in an s orbital (and σ , sigma, is the Greek equivalent of s). All VB wavefunctions are constructed in

¹For more information see our *Physical chemistry: thermodynamics, structure, and change* (2014).

a similar way, by using the atomic orbitals available on the participating atoms. In general, therefore, the (unnormalized) VB wavefunction for an A–B bond is

$$\psi_{\text{A-B}}(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \quad (2)$$

A valence bond wavefunction

To calculate the energy of a molecule for a series of internuclear separations R , the VB wavefunction is substituted into the Schrödinger equation for the molecule and the necessary mathematical manipulations are carried out to calculate the energy. When this energy is plotted against R , a curve like that shown in Fig. 1 is obtained. As R decreases from infinity, the energy falls below that of two separated H atoms as each electron becomes free to migrate to the other atom. This decrease in energy is the outcome of several effects:

- As the two atoms approach each other, there is an accumulation of electron density between the two nuclei (Fig. 3). The electrons attract the two nuclei, and the potential energy is lowered.
- This accumulation between the nuclei is at the expense of removing electron density from close to the nuclei, which contributes an increase in potential energy.
- The freedom of the electrons to migrate between the atoms is like the transfer of an electron from a small box to a bigger box, which (as seen in the discussion of a particle in a box, Topic 7C) results in a lowering of their kinetic energy.

In H_2 the last is the dominant effect, but the relative importance of changes in potential and kinetic energy is still unclear in more complex molecules and the lowering of energy is commonly attributed to the accumulation of electron density between the two nuclei.

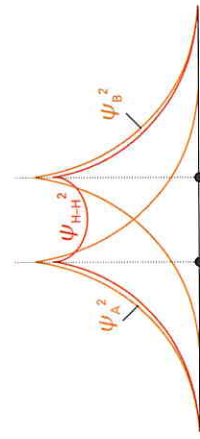


Fig. 3 The electron density in H_2 according to the valence-bond model of the chemical bond and the electron densities corresponding to the contributing atomic orbitals. The nuclei are denoted by large dots on the horizontal line. Note the accumulation of electron density in the internuclear region.

The overall decrease in energy due to the redistribution of electrons is counteracted by an increase in energy from the Coulombic repulsion between the two positively charged nuclei of charges $Z_A e$ and $Z_B e$, which has the form

$$V_{\text{nuc-nuc}}(R) = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} \quad (3)$$

Coulombic repulsion between two nuclei

(For H_2 , $Z_A = Z_B = 1$.) This positive contribution to the energy becomes large as R becomes small (and the decrease in electronic kinetic energy becomes less significant as the 'big box' is no longer much bigger than the initial two 'little boxes'). As a result, the total energy curve passes through a minimum and then climbs to a strongly positive value as the two nuclei are pressed together.

A similar description is used for molecules built from atoms that contribute more than one electron to the bonding. For example, the VB description of N_2 begins by noting the valence-electron configuration of each atom, which is $2s^2 2p_x^1 2p_y^1 2p_z^1$. The $2s$ orbitals of both atoms are filled completely, so according to VB theory they do not participate in bonding. It is conventional to take the z -axis to be the internuclear axis of a diatomic molecule, so each atom can be imagined as having a $2p_z$ orbital pointing towards a $2p_x$ orbital on the other atom, with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis (Fig. 4). According to the building-up principle, each of these p orbitals is occupied by one electron, so bonds are formed by the merging of matching orbitals on neighbouring atoms and the pairing of the electrons that occupy them. A cylindrically symmetric σ bond results from the merging of the two $2p_z$ orbitals and the pairing of the electrons they contain. However, the remaining p orbitals cannot

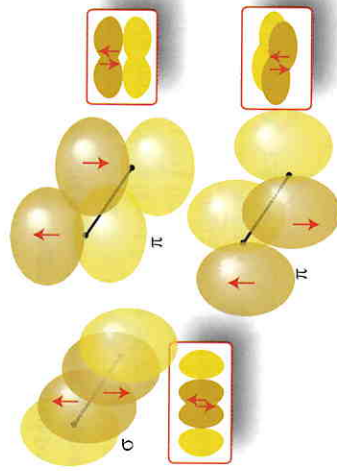


Fig. 4 The bonds in N_2 are built by allowing the electrons in the $N2p$ orbitals to pair. However, only one orbital on each atom can form a σ bond: the orbitals perpendicular to the axis form π -bonds.

merge to give σ bonds because they do not have cylindrical symmetry around the internuclear axis. Instead, the $2p_x$ orbitals merge and the two electrons pair to form a π bond. A π bond is so called because viewed along the internuclear axis, it resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p). Similarly, the $2p_y$ orbitals merge and their electrons pair to form another π bond. In general, a π bond arises from the merging of two p orbitals that approach side-by-side and the pairing of the electrons that they contain.

Brief illustration 9A.1 The bonding pattern in N_2 and O_2

It follows from the preceding discussion that the overall bonding pattern in N_2 is a σ bond plus two π bonds, which is consistent with the Lewis structure $:N \equiv N:$ in which the atoms are linked by a triple bond.

Self-test 9A.1

Predict the bonding pattern in O_2 .

Answer: One $\sigma(2p_x, 2p_x)$ bond and one $\pi(2p_y, 2p_y)$ bond. However, see Topic 9B for the continuing story about O_2 .

9A.2 Polyatomic molecules

Each σ bond in a polyatomic molecule is formed by the merging of orbitals with cylindrical symmetry about the relevant internuclear axis and the pairing of the spins of the electrons they contain. Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry (broadly speaking, of the appropriate shape).

Brief illustration 9A.2 A valence bond description of H_2O

The valence electron configuration of an O atom is $2s^2 2p_x^1 2p_y^1 2p_z^1$. The two unpaired electrons in the $O2p$ orbitals can each pair with an electron in a $H1s$ orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O—H internuclear distance). Because the $2p_x$ and $2p_y$ orbitals lie at 90° to each other, the two σ bonds they form also lie at 90° to each other (Fig. 5). It is predicted, therefore, that H_2O should be an angular molecule, which it is. However, the model predicts a bond angle of 90° , whereas the actual bond angle is 104° .

Self-test 9A.2

Give a VB description of NH_3 , and predict the bond angle of the molecule on the basis of this description.

Answer: three $\sigma(N2p, H1s)$ bonds; 90° ; the experimental bond angle is 107° .

orbitals provided by four other atoms (such as four $H1s$ orbitals if the molecule is CH_4), and as a result the atom can form four σ bonds.

Promotion is feasible if the energy it requires can be more than recovered in the greater strength or number of bonds that can be formed. The promotion energy of carbon is small because the promoted electron leaves a doubly occupied $2s$ orbital and enters a vacant $2p$ orbital, hence significantly relieving the electron–electron repulsion. Furthermore, the energy required for promotion is more than recovered by the atom's ability to form four bonds in place of the two bonds of the unpromoted atom. This is how VB theory explains the common occurrence of tetravalent carbon.

Promotion, however, appears to imply the presence of three σ bonds of one type (in CH_4 , from the merging of $H1s$ and $C2p$ orbitals) and a fourth σ bond of a distinctly different type (formed from the merging of $H1s$ and $C2s$). But it is well known that all four bonds in methane are equivalent in both their chemical and physical properties (their lengths, strengths, and stiffnesses). Moreover, the problem of molecular geometry remains unresolved.

The problems of equivalence and geometry are overcome in VB theory by drawing on another technical feature of quantum mechanics which allows the same electron distribution to be described in different ways. In this case, the electron distribution in the promoted atom can be described either as arising from four electrons in one s and three p orbitals, or as arising from four electrons in four different mixtures of these orbitals. Mixtures (more formally, 'linear combinations') of atomic orbitals on the same atom are called **hybrid orbitals**. The atomic orbitals interfere destructively or constructively in different regions and give rise to four new shapes. The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{aligned} b_1 &= s + p_x + p_y + p_z & b_2 &= s - p_x - p_y + p_z \\ b_3 &= s - p_x + p_y - p_z & b_4 &= s + p_x - p_y - p_z \end{aligned} \quad (4)$$

sp^3 hybrid orbitals

A note on good practice In general, a 'linear combination' of two functions f and g is $c_1 f + c_2 g$, where c_1 and c_2 are numerical coefficients, so a linear combination is a more general term than 'sum'. In a sum, $c_1 = c_2 = 1$.

As a result of the constructive and destructive interference between the positive and negative regions of the component orbitals, each hybrid orbital has a large lobe pointing towards one corner of a regular tetrahedron (Fig. 6). Because each hybrid

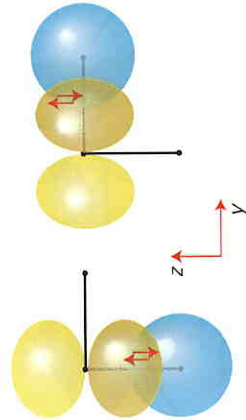


Fig. 5 The bonding in an H_2O molecule can be pictured in terms of the pairing of an electron in a $1s$ orbital (blue) of one H atom with an electron in an $O2p_x$ orbital (light and dark shades of yellow); the other bond is formed likewise, but using a perpendicular $O2p_y$ orbital. The predicted bond angle is 90° , which is in poor agreement with the experimental bond angle (104°).

While broadly correct in its predictions, *Brief illustration 9A.2* shows that VB theory seems to have two deficiencies. One is the poor estimate it provides for the bond angle in H_2O and other molecules, such as NH_3 . Indeed, the theory appears to make worse predictions than the qualitative VSEPR model, which predicts HOH and HNH bond angles of slightly less than 109° in H_2O and NH_3 , respectively. The second major deficiency is the apparent inability of VB theory to account for the number of bonds that atoms can form, and in particular the tetravalence of carbon. To appreciate the latter problem, note that the ground-state valence configuration of a carbon atom is $2s^2 2p_x^1 2p_y^1$, which suggests that it should be capable of forming only two bonds, not four.

9A.3 Promotion and hybridization

Two modifications solve both problems (the number of bonds that an atom can form and their geometrical arrangement). Starting from atoms that are in their lowest energy configurations, as predicted by the building-up principle, a valence electron is regarded as being **promoted** from a full atomic orbital to an empty atomic orbital as a bond is formed. Promotion should not be pictured as an actual excitation of the atom followed by the formation of bonds but simply as a way of interpreting one contribution to the overall change in energy that occurs when a molecule forms from its atoms. Promotion enables each electron to participate in the formation of a bond by pairing with an electron supplied by another atom. In carbon, for example, the promotion of a $2s$ electron to a $2p$ orbital leads to the configuration $2s^1 2p_x^1 2p_y^1 2p_z^1$, with four electrons in separate orbitals. These electrons may pair with four electrons in

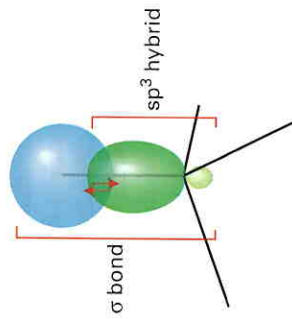


Fig. 6 The 2s and three 2p orbitals of a carbon atom hybridize, and the resulting hybrid orbitals point towards the corners of a regular tetrahedron. Each σ bond is formed by the pairing of an electron in an H 1s orbital with an electron in one of the hybrid orbitals, as shown here. The resulting molecule is regular tetrahedral.

is built from one s orbital and three p orbitals, it is called an **sp^3 hybrid orbital**.

It is now easy to see how the VB description of the methane molecule leads to a tetrahedral molecule containing four equivalent C—H bonds. Promotion in the carbon atom is energetically favourable (in the end, after bonding has been taken into account). The promoted configuration has a distribution of electrons that is equivalent to one electron occupying each of four tetrahedral hybrid orbitals. Each hybrid orbital of the promoted atom contains a single unpaired electron; a hydrogen 1s electron can pair with each one, giving rise to a σ bond pointing in a tetrahedral direction. Because each sp^3 hybrid orbital has the same composition, all four σ bonds are identical apart from their orientation in space.

Hybridization is also used in the VB description of alkenes. An ethene molecule is planar, with HCH and HCC bond angles close to 120° . To reproduce this σ -bonding structure, each C atom is promoted to a $2s^1 2p_x^1 2p_y^2$ configuration. However, instead of using all four orbitals to form hybrids, **sp^2 hybrid orbitals** are formed by allowing the s orbital and two of the p orbitals to interfere. As shown in Fig. 7, the three hybrid orbitals

$$\begin{aligned} b_1 &= s + 2^{1/2} p_x \\ b_2 &= s + \left(\frac{1}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \\ b_3 &= s - \left(\frac{1}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \end{aligned} \quad \text{sp}^2 \text{ hybrid orbitals} \quad (5)$$

lie in a plane and point towards the corners of an equilateral triangle. The third 2p orbital ($2p_z$) is not included in the hybridization, and its axis is perpendicular to the plane in which the hybrids lie. The coefficients $2^{1/2}$, etc. in the hybrids are chosen to give the correct directional properties of the hybrids. The *squares* of the coefficients give the proportion of each atomic orbital in the

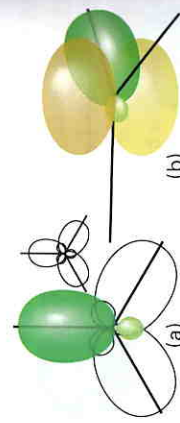


Fig. 7 (a) Trigonal planar hybridization is obtained when an s and two p orbitals are hybridized. The three lobes lie in a plane and make an angle of 120° to each other. (b) The remaining p orbital in the valence shell of an sp^2 -hybridized atom lies perpendicular to the plane of the three hybrids.

hybrid. All three hybrids have s and p orbitals in the ratio 1:2, as indicated by the designation sp^2 .

The sp^2 -hybridized C atoms each form three σ bonds with either the b_1 hybrid of the other C atom or with the H 1s orbitals. The σ framework therefore consists of bonds at 120° to each other. Moreover, the two electrons in the unhybridized $2p_z$ orbitals can pair and form a π bond (Fig. 8). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

Now consider a linear ethyne (acetylene) molecule, $H-C\equiv C-H$. The carbon atoms are **sp hybridized**, and the σ bonds are built from hybrid atomic orbitals of the form

$$b_1 = s + p_z \quad b_2 = s - p_z \quad \text{sp hybrid orbitals} \quad (6)$$

Note that the s and p orbitals contribute in equal proportions. The two hybrids lie along the z-axis. The electrons in them pair either with an electron in the corresponding hybrid orbital on the other C atom or with an electron in the H 1s orbitals. Electrons in the two remaining p orbitals on each atom, which are

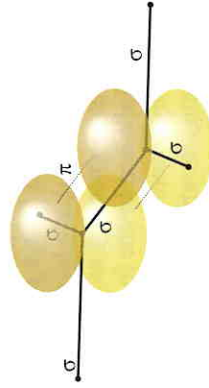


Fig. 8 The valence bond description of the structure of a carbon-carbon double bond, as in ethene. The electrons in the two sp^2 hybrids that point towards each other pair and form a σ bond. Electrons in the two p orbitals that are perpendicular to the plane of the hybrids pair, and form a π bond. The electrons in the remaining hybrid orbitals are used to form bonds to other atoms (in ethene itself, to H atoms).

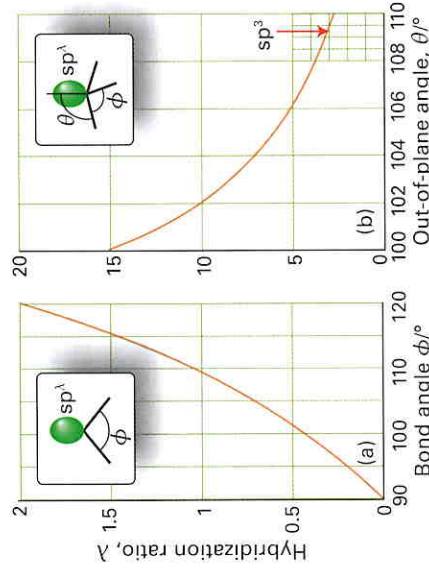


Fig. 10 The variation of hybridization with bond angle in (a) angular, (b) trigonal pyramidal molecules. The vertical axis gives the ratio of p to s character, so high values indicate mostly p character.

The 'pure' schemes in Table 9A.1 are not the only possibilities: it is possible to form hybrid orbitals with intermediate proportions of atomic orbitals. For example, as more p-orbital character is included in an sp -hybridization scheme, the hybridization changes towards sp^2 and the angle between the hybrids changes continuously from 180° for pure sp hybridization to 120° for pure sp^2 hybridization. If the proportion of p character continues to be increased (by reducing the proportion of s orbital), then the hybrids eventually become pure p orbitals at an angle of 90° to each other (Fig. 10). Figure 11 shows contour plots of hybrid orbitals as the ratio of 2p character to 2s character increases.

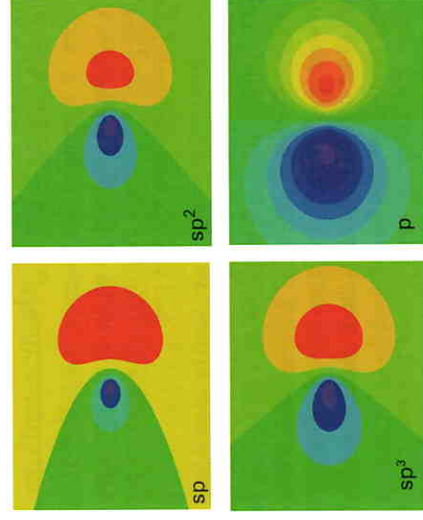


Fig. 11 Contour plots showing the amplitudes of sp^x hybrid orbitals. To construct these plots, hydrogenic 2s and 2p orbitals have been used with colours for positive and negative regions like those on geographical maps of mountains and sea depths.

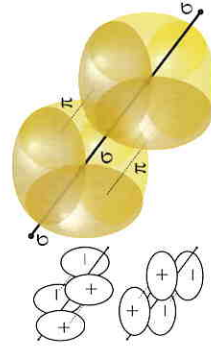


Fig. 9 The electronic structure of ethyne (acetylene). The electrons in the two sp hybrids on each atom pair to form σ bonds (shown as black lines) either with the other C atom or with an H atom. The remaining two unhybridized 2p orbitals on each atom (which are represented by the lobes coloured with two shades of yellow) are perpendicular to the axis: the electrons in corresponding orbitals on each atom pair to form two π bonds. The overall electron distribution is cylindrical.

perpendicular to the molecular axis, pair to form two perpendicular π bonds (as in Fig. 9).

Other hybridization schemes, particularly those involving d orbitals, are consistent with other molecular geometries (Table 9A.1).

An important point to note is that

The hybridization of N atomic orbitals always results in the formation of N hybrid orbitals.

Brief illustration 9A.3 Bonding in polyatomic molecules

In SF_6 , the six S—F bonds are σ bonds formed from six sp^3d^2 hybrid orbitals ($N = 1 + 3 + 2 = 6$) on the central S atom, pointing towards the corners of a regular octahedron (as noted in Table 9A.1). This octahedral hybridization scheme is sometimes invoked to account for the structure of octahedral molecules, such as SF_6 .

Self-test 9A.3

Describe the bonding in a PCl_5 molecule.

Answer: Five equivalent P—Cl bonds, with the P atom at the centre of the molecule. All bonds are σ bonds formed from sp^3d hybrid orbitals on the central P atom.

Table 9A.1
Hybrid orbitals

Number	Shape	Hybridization*
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

*Other combinations are possible.

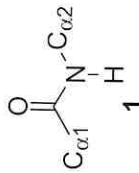
Now it is possible to solve the problems arising in *Brief illustration 9A.2* and account for the structure of H_2O , with its bond angle of 104° : Each $\text{O}-\text{H}$ σ bond is formed from an O atom hybrid orbital with a composition that lies between pure p (which would lead to a bond angle of 90°) and pure sp^2 (which would lead to a bond angle of 120°). The actual bond angle and hybridization adopted are found by calculating the energy of the molecule as the bond angle is varied, and identifying the angle at which the energy is a minimum.

In sum, promotion and hybridization are not observable physical processes; they are schemes invoked in VB theory to account for (or at least be consistent with) observed atomic valencies and molecular geometries.

Example 9A.1

Bonding in the amide group

Use VB theory to describe the CO , CN , and NH bonds of the amide group based on the structure shown in (1).



Collect your thoughts You need to account for hybrid and unhybridized orbitals, and then form single and double bonds as appropriate, given the known pattern of connections between atoms in the structure. To calculate the number of hybrid orbitals, note that each orbital can hold either one or two electrons. If it contains one electron, the hybrid orbital is ready to make a σ bond with an orbital on another atom; if it contains a pair of electrons, the hybrid orbital does not participate in bonding but acts as a lone pair.

The solution The O atom is sp^2 hybridized because it has two lone pairs and makes a σ bond with the C atom. The C atom is sp^2 hybridized because it makes three σ bonds: one with the O atom, one with the $\text{C}_{\alpha 1}$ atom, and one with the N atom. The N atom is sp^3 hybridized because it has one lone pair and makes three σ bonds: one with the H atom, one with the C atom, and one with the $\text{C}_{\alpha 2}$ atom.

In sum, the CO group has a σ bond between Csp^2 and Osp^2 hybrid orbitals and a π bond between unhybridized $\text{C}2p_z$ and $\text{O}2p_z$ orbitals (where again the z-axis is perpendicular to the plane containing the hybrid orbitals). The CN group has a σ bond between Csp^2 and Nsp^3 hybrid orbitals. Finally, the NH group has a σ bond between a Nsp^3 hybrid orbital and a $1s$ atomic orbital.

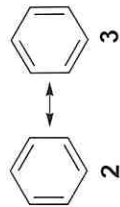
wavefunction in eqn 7 with λ a variable parameter. The variation theorem then states that:

The energy of a trial wavefunction is never less than the true energy.

The theorem implies that if λ is varied until the lowest energy is achieved, then the wavefunction with that value of λ is the best available of that particular kind. Equation 7 represents a specific type of resonance, namely ionic-covalent resonance, in which one structure is pure covalent and the other pure ionic. The interpretation of the wavefunction, which is called a resonance hybrid, is that if the molecule is inspected, then the probability that it would be found with an ionic structure is proportional to λ^2 . Resonance also occurs between purely covalent structures. In each case the nuclei are in the same locations but the bonding patterns of the electrons are different and might correspond to different energies.

Brief illustration 9A.4 Resonance hybrids

One of the most famous examples of resonance is in the VB description of benzene, where the wavefunction of the molecule is written as a resonance hybrid of the two covalent Kekulé structures (2) and (3):



$$\psi = \psi_{\text{covalent}} + \psi_{\text{ionic}}$$

The two contributing structures have identical energies, so one is not more favourable than the other. In the language of quantum theory, each structure contributes equally to the superposition.

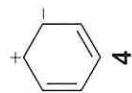
Self-test 9A.5

Consider a bond described by eqn 7, with $\lambda = 0.1$. What is the ratio of the probabilities of finding the molecule in its covalent and ionic forms?

Answer: Because $\lambda^2 = 0.1^2 = 0.01$, the ratio is 100:1

The effect of resonance (which is represented by a double-headed arrow, \leftrightarrow) in the case of benzene is to distribute double-bond character around the ring and so to make the lengths and strengths of all the carbon-carbon bonds identical (in the sense that, in the presence of resonance, the lowest energy is obtained when all the bonds have the same length

and the electron densities are the same in each C—C region). The wavefunction is improved by allowing resonance because it allows the distribution to adjust into a state of lower energy. This lowering is called the resonance stabilization of the molecule and, in the context of VB theory, is largely responsible for the enhanced stability of aromatic rings. Resonance always lowers the energy, and the lowering is greatest when the contributing structures have similar energies. The wavefunction of benzene is improved still further, and the calculated energy of the molecule is lowered further still, if ionic-covalent resonance is allowed too, by introducing a small admixture of structures such as that shown in (4).



In sum, resonance is not a flickering between the contributing states: it is a blending of their characteristics. It is only a mathematical device for achieving a closer approximation to the true wavefunction of the molecule than that represented by any single contributing structure alone.

9A.5 The language of valence bond theory

It will be helpful at this point to summarize the concepts that VB theory has introduced into chemistry and which still survive even though molecular orbital theory (Topics 9B–9D) is the dominant computational mode:

1. *The names of bond types:* σ and π bonds are formed by spin pairing of electrons on adjacent atoms and are distinguished by their symmetry around the internuclear axis.
2. *Promotion:* valence electrons may be promoted to empty orbitals if overall that results in a lowering of energy.
3. *Hybridization:* atomic orbitals may be hybridized to match the observed geometry of a molecule.
4. *Resonance:* the superposition of individual structures distributes multiple-bond character over the molecule and lowers the overall energy.

Checklist of key concepts

- 1 A **covalent bond** is formed when two atoms share a pair of electrons.
- 2 In the **Born–Oppenheimer approximation** nuclei are stationary while the electrons move around them.
- 3 In **valence bond theory** (VB theory), a bond is regarded as forming when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.
- 4 A VB wavefunction with cylindrical symmetry around the internuclear axis is a **σ bond**.
- 5 A **π bond** arises from the merging of two p orbitals that approach side by side and the pairing of electrons that they contain.
- 6 **Hybrid orbitals** are mixtures (linear combinations) of atomic orbitals on the same atom.
- 7 In VB theory, **hybridization** is invoked to be consistent with molecular geometries.
- 8 **Resonance** is the superposition of the wavefunctions representing different electron distributions in the same nuclear framework.

TOPIC 9B

Molecular orbital theory: homonuclear diatomics

► Why do you need to know this material?

Molecular orbital theory is the basis of almost all computational techniques for the prediction and analysis of the properties of molecules. Homonuclear diatomic molecules and ions are a good starting point not only because they are simple to describe, but because they include such important species as H_2 , N_2 , O_2 and its ions, such as the peroxide ion), and the dihalogens.

► What is the key idea?

Molecular orbitals are wavefunctions that spread over all the atoms in a molecule; each one can accommodate up to two electrons.

► What do you need to know already?

You need to be familiar with the shapes of atomic orbitals (Topic 8A), the Pauli exclusion principle, the building-up principle, and Hund's rule for many-electron atoms (Topic 8B). The entire discussion is within the framework of the Born–Oppenheimer approximation (Topic 9A).

ture, and then developed into a description of many-electron atoms. Here the simplest molecule of all, the one-electron hydrogen molecule-ion, H_2^+ , is used to introduce the essential features of bonding, and then used as a guide to the structures of more complex systems.

9B.1 The construction of molecular orbitals

A **molecular orbital** is a one-electron wavefunction that spreads throughout the molecule. The mathematical forms of such orbitals are highly complicated, even for such a simple species as H_2^+ , and they are unknown in general. All modern work builds approximations to the true molecular orbital by formulating models based on linear combinations of the atomic orbitals on the atoms in the molecule.

According to the general principles of quantum mechanics, if there are several possible outcomes, then the overall wavefunction is a superposition—a linear combination—of the wavefunctions that represent the individual outcomes. In H_2^+ , there are two possible outcomes: an electron may be found either in an atomic orbital ψ_A centred on A or in an atomic orbital ψ_B centred on B. Therefore, the overall wavefunction has the form

$$\psi = c_A \psi_A + c_B \psi_B \quad \text{An LCAO} \quad (1a)$$

where c_A and c_B are numerical coefficients. A wavefunction constructed in this way is called a **linear combination of atomic orbitals (LCAO)**, and the corresponding molecular orbital is called an LCAO-MO. The squares of the coefficients give the relative proportions of the atomic orbitals contributing to the molecular orbital. In a homonuclear diatomic molecule (such as H_2 , O_2 , or Cl_2) an electron can be

In **molecular orbital theory** (MO theory), electrons are treated as spreading throughout the entire molecule: every electron contributes to the strength of every bond. Applications of this theory have been more fully developed than valence bond theory and provide the language that is widely used in modern discussions of bonding in small inorganic molecules, d-metal complexes, and solids. To introduce it, the same strategy as in Topics 8A and 8B is followed. There the one-electron hydrogen atom is taken as the fundamental species for discussing atomic struc-

found with equal probability in orbital A or orbital B, so the *squares* of the coefficients must be equal, which implies that $c_B = \pm c_A$. The two possible (unnormalized) wavefunctions are therefore

$$\psi = \psi_A \pm \psi_B \quad \text{An LCAO for a homonuclear diatomic molecule} \quad (1b)$$

Consider the LCAO with the plus sign, $\psi = \psi_A + \psi_B$, as this molecular orbital will turn out to have the lower energy of the two. The form of this orbital is shown in Fig. 1. It is called a σ orbital because it resembles an s orbital when viewed along the axis. More precisely, it is so called because an electron that occupies a σ orbital has zero orbital angular momentum around the internuclear axis, just as an s electron has zero orbital angular momentum around an axis passing through the nucleus. Because it is the σ orbital of lowest energy, it is labelled 1σ . An electron that occupies a σ orbital is called a σ electron. In the ground-state of the H_2^+ ion, there is a single 1σ electron, so the ground-state configuration of H_2^+ is reported as $1\sigma^1$ (and read 'one-sigma-one').

The origin of the lowering of energy that is responsible for the formation of the bond can be explored by examining the form of the LCAO-MO. The two atomic orbitals are like waves centred on adjacent nuclei. In the internuclear region, the amplitudes interfere constructively and the wavefunction has an enhanced amplitude there (Fig. 2). The three contributions listed for bonding in valence bond theory (VB theory, Topic 9A) apply here too: there is an accumulation of electron density between the two nu-

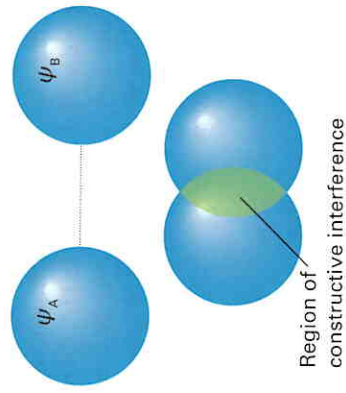


Fig. 1 The formation of a bonding molecular orbital (a σ orbital). (a) Two $1s$ orbitals come together. (b) The atomic orbitals overlap, interfere constructively, and give rise to an enhanced amplitude in the internuclear region. The resulting orbital has cylindrical symmetry about the internuclear axis. When it is occupied by two paired electrons, to give the configuration σ^2 , a σ bond is formed.

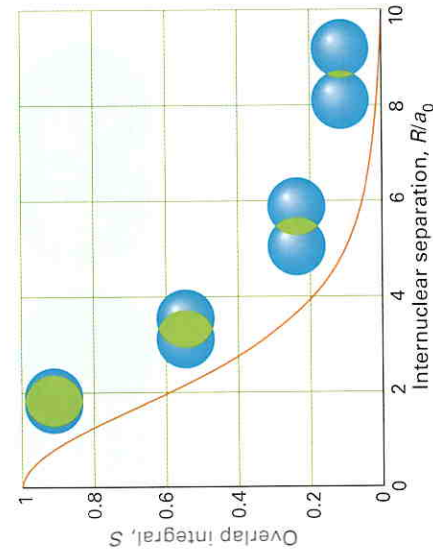


Fig. 4 The variation of the overlap integral with internuclear distance for two $1s$ orbitals.

Brief illustration 9B.1 An overlap integral

It is possible, but not easy, to evaluate the overlap integral for hydrogenic orbitals. For two $1s$ orbitals on hydrogen nuclei separated by a distance R , the result is

$$S_{111} = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) e^{-R/a_0} \quad (3)$$

where a_0 is the Bohr radius. This function is plotted in Fig. 4. The exponential factor guarantees that the overlap integral goes to zero at large separations. At $R = 0$, when the two orbitals coincide, $S_{111} = 1$.

Self-test 9B.1

By what factor does S_{111} decrease as the internuclear separation changes from a_0 to $2a_0$?

Answer: 0.68

9B.2 Bonding and antibonding orbitals

The Schrödinger equation, $H\psi = E\psi$, for the hydrogen molecule-ion has three types of contribution: the kinetic energy of the electron, its Coulomb attraction to the two nuclei, and the Coulomb repulsion between the two nuclei. To calculate the energy of an electron described by the wavefunction $\psi = \psi_A + \psi_B$, it is substituted into the equation with the nuclei at a fixed separation R , and the energy evaluated; then the calculation is repeated for another value of R . Figure 5 shows the molecular potential energy curve obtained by plotting the energy against R . The energy initially falls as R is decreased from large values because the electron is increasingly likely to be found in the internuclear region

as the two atomic orbitals interfere more effectively and electron density accumulates there. However, at small separations, there is too little space between the nuclei for significant accumulation of electron density there. Moreover, the nucleus–nucleus repulsion, which is proportional to $1/R$, becomes large. As a result, after the initial decrease, at small internuclear separations the energy passes through a minimum and then rises sharply to high values. Calculations on H_2^+ give the equilibrium bond length (the bond length corresponding to the minimum of the curve) as 130 pm and the bond dissociation energy (the depth of the well below zero) as 171 kJ mol^{-1} ; the experimental values are 106 pm and 250 kJ mol^{-1} , so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong. The crucial point is that an electron in the 1σ orbital bonds the nuclei together. It is an example of a **bonding orbital**, a molecular orbital which, if occupied, contributes to the strength of a bond between two atoms.

Now consider the alternative LCAO-MO in eqn. 1b, the one with a minus sign: $\psi = \psi_A - \psi_B$. Because this wavefunction is also cylindrically symmetrical around the internuclear axis it is also a σ orbital, and denoted $1\sigma^*$ (Fig. 6; the different signs of the contributing atomic orbitals are represented by different tints). When this ψ is substituted into the Schrödinger equation the calculated energy is higher than that of the bonding 1σ orbital and, indeed, higher than that of either of the two contributing atomic orbitals at all values of R . The origin of this high energy can be traced to the existence of a **nodal plane**, a plane on which the wavefunction passes through zero everywhere. This plane lies halfway between the nuclei and cuts through the internuclear axis. Everywhere on it ψ_A and ψ_B are equal, so in the combination $\psi = \psi_A - \psi_B$ they cancel

The $1\sigma^*$ orbital is an example of an **antibonding orbital**, an orbital that, if occupied, weakens a bond

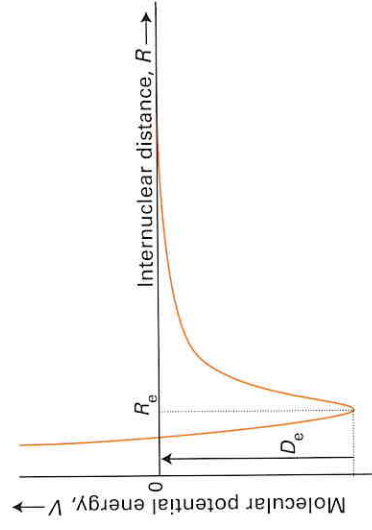


Fig. 5 A molecular potential energy curve. The equilibrium bond length R_e corresponds to the energy minimum D_e .

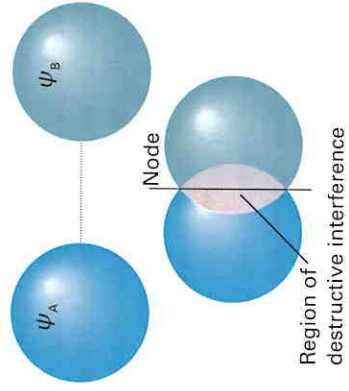


Fig. 6 The formation of an antibonding molecular orbital (a σ^* orbital). (a) Two $1s$ orbitals come together. (b) The atomic orbitals overlap with opposite signs (as depicted by different shades of blue), interfere destructively, and give rise to a decreased amplitude in the internuclear region. There is a nodal plane exactly half way between the nuclei, on which any electrons that occupy the orbital will not be found.

between two atoms. The antibonding character of the $1\sigma^*$ orbital is partly a result of the exclusion of the electron from the internuclear region and its relocation outside the bonding region where it helps to pull the nuclei apart rather than pulling them together (Fig. 7). An antibonding orbital is often slightly more strongly antibonding than the corresponding bonding orbital is bonding; although the 'gluing' effect of a bonding electron and the 'anti-gluing' effect of an antibonding electron are similar, the nuclei repel each other in both cases, and this repulsion pushes both levels up in energy.

9B.3 Inversion symmetry

A few points regarding notation are in order. For homonuclear diatomic molecules (such as O_2 or N_2), it is helpful to identify the **inversion symmetry** of a

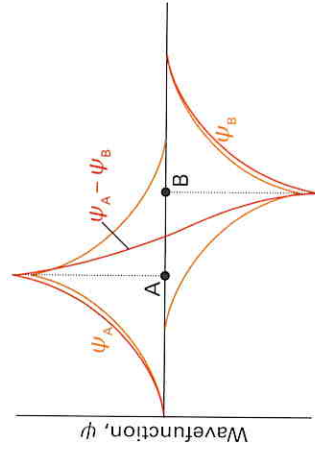


Fig. 7 The antibonding molecular orbital wavefunction along the internuclear axis. Note that there is a decrease in amplitude between the nuclei, so there is a decreased probability of finding the bonding electrons in that region.

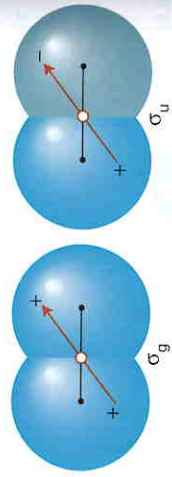


Fig. 8 The *gerade/ungerade* character of σ bonding and antibonding orbitals.

molecular orbital, especially when discussing electronic transitions (Topic 11D). By 'inversion symmetry' is meant the behaviour of a wavefunction when every point is projected through the centre of the molecule (the 'centre of inversion') and out an equal distance on the other side. If the sign of the wavefunction remains the same, as is the case for the 1σ orbital (Fig. 8), then the orbital is said to have **gerade symmetry** (from the German word for 'even') denoted by a subscript g , as in $1\sigma_g$. The same procedure applied to the antibonding σ^* orbital results in a change in sign of the wavefunction. This **ungerade symmetry** ('odd symmetry') is denoted by a subscript u , as in $1\sigma_u$. This inversion symmetry classification (or 'parity') is not applicable to heteronuclear diatomic molecules (like NO) as they do not have a centre of inversion.

9B.4 The chemical bond in molecular orbital theory

The development so far has shown that, unlike in VB theory where spin pairing is an essential feature (Topic 9A), according to MO theory a single electron can form a bond by occupying a bonding orbital alone. The spin pairing that is characteristic of Lewis's theory emerges in a different way, and to identify its origin it is necessary to consider the simplest many-electron molecule, H_2 , and draw on the Pauli exclusion principle as discussed in Topic 8B that no more than two electrons can occupy any given orbital (and must be paired).

The first step is to build the molecular orbitals. Because each H atom of H_2 contributes a $1s$ orbital (as in H_2^+), the 1σ (more precisely, $1\sigma_g$) and $1\sigma^*$ (that is, $1\sigma_u$) bonding and antibonding orbitals from them, in the way already described. At the equilibrium internuclear separation these orbitals have the energies represented by the horizontal lines in Fig. 9.

There are two electrons to accommodate (one from each atom). Both can enter the $1\sigma_g$ orbital, but according to the Pauli principle, they can do so only by pairing their spins (Fig. 10). It is important

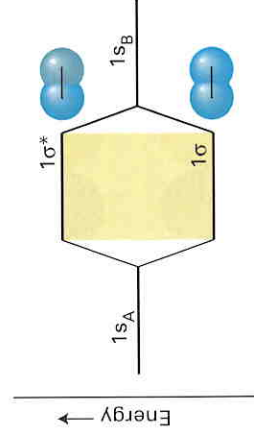


Fig. 9 A molecular orbital energy level diagram for orbitals constructed from ($1s$, $1s$)-overlap, the separation of the levels corresponding to the equilibrium bond length.

to appreciate that electrons do not 'want' to pair: it is only by pairing that they can enter the same orbital and thereby achieve the greatest lowering of energy of the molecule. It then follows that the ground-state configuration of H_2 is $1\sigma_g^2$, and that the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. These two electrons bind the two nuclei together more strongly and closely than the single electron in H_2^+ is able to do and the bond length is reduced from 106 pm to 74 pm. A pair of electrons in a σ orbital is called a **σ bond**, and is very similar to the σ bond of VB theory. The two differ in certain details of the electron distribution between the two atoms joined by the bond, but both have an accumulation of density between the nuclei.

An extension of this procedure shows why helium is a monatomic gas. Consider a hypothetical He_2 molecule. Like in H_2 , each He atom contributes a $1s$ orbital to the linear combination used to form the molecular orbitals $1\sigma_g$ and $1\sigma_u$. These orbitals differ in detail from those in H_2 because the He $1s$ orbitals are more compact, but the general shape is the same and for qualitative discussions the same molecular orbital energy level diagram as for H_2 can be used. Because each atom provides two electrons, there are four electrons to accommodate. Two can enter the $1\sigma_g$ orbital provided they pair (by the Pauli principle), but then it is full (by the Pauli exclusion principle). It follows that the next two electrons must pair and enter the an-

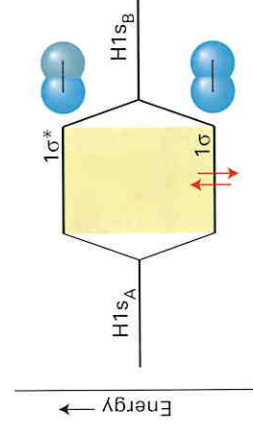


Fig. 10 The ground electronic configuration of He_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

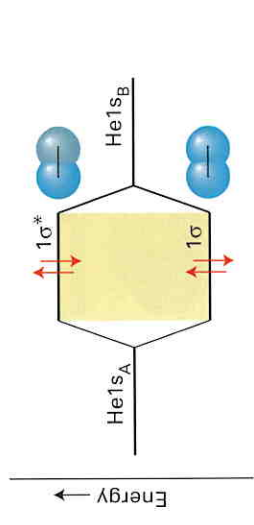


Fig. 11 The ground electronic configuration of the four-electron molecule He_2 has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so He_2 is unstable relative to two He atoms.

tribonding $1\sigma_u$ orbital (Fig. 11). The ground electronic configuration of He_2 is therefore $1\sigma_g^2 1\sigma_u^2$. Because an antibonding orbital is slightly more antibonding than a bonding orbital is bonding, the He_2 molecule has a higher energy than the separated atoms. Hence, two ground-state He atoms do not form bonds to each other, and helium is a monatomic gas.

The strength of a bond in a molecule in general is the net outcome of the bonding and antibonding effects of the electrons in its molecular orbitals. This net bonding effect can be assessed by calculating the **bond order**, b , which is defined as

$$b = \frac{1}{2}(N - N^*) \quad (4)$$

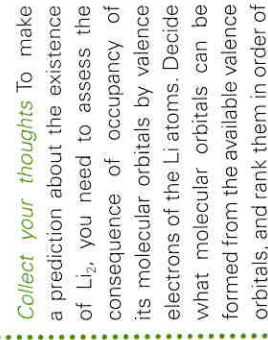
Bond order
(definition)

where N is the number of electrons in bonding orbitals and N^* is the number of electrons in antibonding orbitals. Each electron pair in a bonding orbital increases the bond order by 1 and each pair in an antibonding orbital decreases it by 1. For H_2 , $b = 1$, corresponding to a single bond between the two atoms: this bond order is consistent with the Lewis structure $H-H$ for the molecule. In He_2 , which has equal numbers of bonding and antibonding electrons (with $N = 2$ and $N^* = 2$), the bond order is $b = 0$, and there is no bond. The bond order in H_2^+ is $\frac{1}{2}$.

Example 9B.1

Judging the stability of diatomic molecules

Decide whether Li_2 is likely to exist on the assumption that only the valence s orbitals contribute to its molecular orbitals.



Collect your thoughts To make a prediction about the existence of Li_2 , you need to assess the consequence of occupancy of its molecular orbitals by valence electrons of the Li atoms. Decide what molecular orbitals can be formed from the available valence orbitals, and rank them in order of

energy. Then, feed in the electrons supplied by the valence orbitals of the atoms. Judge whether there is a net bonding or net antibonding effect between the atoms.

The solution The ground-state electron configuration of a Li atom is $1s^2 2s^1$, with the $2s$ orbital the relevant valence orbital. Each molecular orbital is built from two $2s$ atomic orbitals, which give one bonding and one antibonding combination ($1\sigma_g$ and $1\sigma_u$, respectively). Each atom supplies one valence electron; the two electrons fill the $1\sigma_g$ orbital, to give the configuration $1\sigma_g^2$, which is bonding.

Self-test 9B.2

Is LiH likely to exist if the Li atom uses only its $2s$ orbital for bonding?

Answer: Yes. A σ orbital forms between the Li $2s$ and H $1s$ atomic orbitals, and is occupied by two electrons.

9B.5 Many-electron homonuclear diatomics

The concepts introduced so far are easily extended to other homonuclear diatomic molecules, such as N_2 and Cl_2 , and diatomic ions such as O_2^{2-} . The general procedure is as follows:

1. Construct molecular orbitals by forming linear combinations of all suitable valence atomic orbitals supplied by the atoms (the meaning of 'suitable' is explained shortly); N atomic orbitals result in N molecular orbitals.
2. Accommodate the valence electrons supplied by the atoms so as to achieve the lowest overall energy subject to the constraint of the Pauli exclusion principle, that no more than two electrons may occupy a single orbital (and then must be paired).
3. If more than one molecular orbital of the same energy is available, add the electrons to each individual orbital before doubly occupying any one orbital (because that minimizes electron–electron repulsions).
4. Take note of Hund's rule for atoms (Topic 8B), which also applies to molecules, that if electrons occupy different degenerate orbitals, then they do so with parallel spins.

In Period 2, the valence orbitals are $2s$ and $2p$. The $2s$ orbitals on each atom overlap to form bonding and antibonding combinations, which are denoted $1\sigma_g$ and $1\sigma_u$, respectively. Likewise, the two $2p_z$ orbitals (by convention, the internuclear axis is the z -axis)

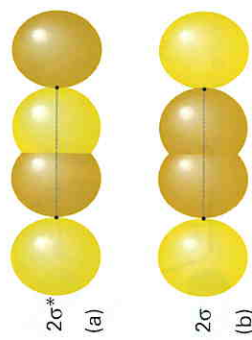


Fig. 12 (a) The interference leading to the formation of a σ bonding orbital and (b) the corresponding antibonding orbital when two p orbitals overlap along an internuclear axis.

have cylindrical symmetry around the internuclear axis. They may therefore participate in σ -orbital formation to give the bonding and antibonding combinations $2\sigma_g$ and $2\sigma_u$, respectively (Fig. 12). The resulting energy levels of the σ orbitals are shown in the MO energy level diagram in Fig. 13. Note that the σ_g orbitals are numbered in sequence ($1\sigma_g, 2\sigma_g, \dots$) and the σ_u orbitals likewise.

Strictly, the $2s$ and $2p_z$ orbitals on each atom should not be considered separately, because both of them have cylindrical symmetry about the internuclear axis and can therefore contribute to the formation of σ molecular orbitals. In a more advanced treatment, all four orbitals are considered together to form four σ molecular orbitals, each one of the form

$$\psi = c_1\psi_{A2s} + c_2\psi_{B2s} + c_3\psi_{A2p_z} + c_4\psi_{B2p_z}$$

The four coefficients, which represent the different contributions that each atomic orbital makes to the overall molecular orbital, are found by modifying

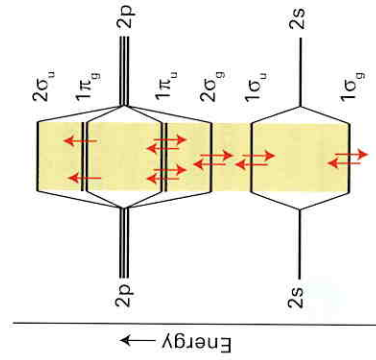


Fig. 13 A typical molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules. The valence atomic orbitals are drawn in the columns on the left and the right; the molecular orbitals are shown in the middle. Note that the π orbitals form doubly degenerate pairs. The sloping lines joining the molecular orbitals to the atomic orbitals show the principal composition of the molecular orbitals. This diagram is suitable for O_2 and F_2 ; the configuration of O_2 is shown.

their values until the energy of the lowest-energy LCAO is minimized. However, in practice, the two lowest energy combinations of this kind are very similar to the combination $1\sigma_g$ and $1\sigma_u$ of $2s$ orbitals already described, and the two highest energy combinations are very similar to the $2\sigma_g$ and $2\sigma_u$ combinations of $2p_z$ orbitals. In each case there are small differences: the $1\sigma_g$ orbital, for instance, has some $2p_z$ character and the $2\sigma_g$ orbital has some $2s$ character, and their energies will be slightly shifted from where they would be if they are considered only the 'pure' combinations. Nevertheless, the changes are not great, and the $1\sigma_g$ and $1\sigma_u$ orbitals can be thought of as being one bonding and antibonding pair, and of $2\sigma_g$ and $2\sigma_u$ as being another pair. The four orbitals are shown in the centre column of Fig. 14. There is no guarantee that $1\sigma_u$ and $2\sigma_g$ will be in the exact location shown in the illustration and the locations shown in Fig. 13 are found in some molecules (see below). The precise locations depend on the relative energies of the $2s$ and $2p$ orbitals and the extent of overlap between the neighbouring atoms.

Now consider the $2p$ orbitals of each atom, which are perpendicular to the internuclear axis and may overlap side-by-side. This overlap may be constructive or destructive and results in a bonding and an antibonding π orbital, which initially are labelled 1π and $1\pi^*$, respectively. The notation π is the analogue of p in atoms, for when viewed along the axis of the molecule, a π orbital looks like a p orbital (Fig. 15). More precisely, an electron in a π orbital has one unit of orbital angular momentum about the internuclear axis. The two $2p_x$ orbitals overlap to give a bonding and an antibonding π orbital, as do the two $2p_y$ orbitals too. The two bonding combinations have the same energy; likewise, the two antibonding combinations have the same energy. Hence,

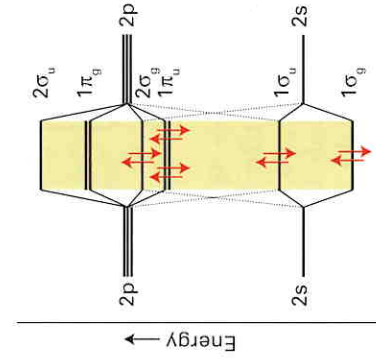


Fig. 14 A typical molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules up to and including N_2 .

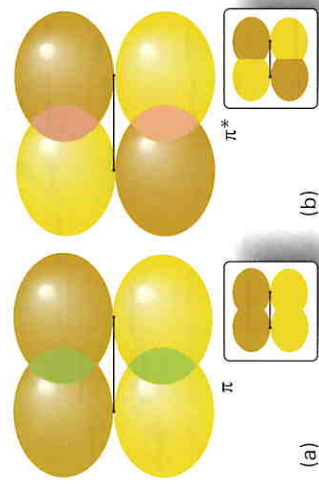


Fig. 15 (a) The interference leading to the formation of a π bonding orbital and (b) the corresponding antibonding orbital.

each π energy level is doubly degenerate and consists of two distinct orbitals. Typically (but not universally) the bonding effect of electrons in a π orbital is less than for a σ orbital in the same molecule because the π electron density does not lie between the nuclei so completely as in a σ orbital. Likewise, the antibonding effect of electrons in a π^* orbital is typically less than when they occupy a σ^* orbital in the same molecule. Two paired electrons in a π orbital constitute a π bond: such a bond resembles a π bond of VB theory, but the details of the electron distribution are slightly different.

The inversion-symmetry classification also applies to π orbitals. As seen in Fig. 16, a bonding π orbital changes sign on inversion through the centre of the molecule, and is therefore classified as u . On the other hand, the antibonding π^* orbital does not change sign on inversion, and is therefore g . The bonding and antibonding combinations will henceforth be denoted $1\pi_u$ and $1\pi_g$.

The relative order of the σ and π orbitals in a molecule cannot be predicted without detailed calculation and varies with the energy separation between the $2s$ and $2p$ orbitals of the atoms; in some molecules the order shown in Fig. 13 applies, whereas others have the order shown in Fig. 14. The change in order can be seen in Fig. 17, which shows the

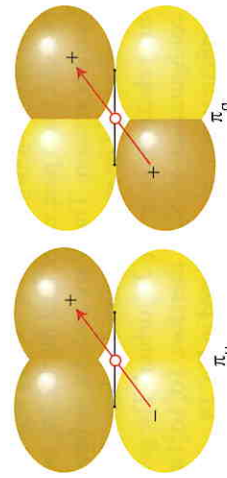


Fig. 16 The *gerade/ungerade* character of π bonding and antibonding orbitals.

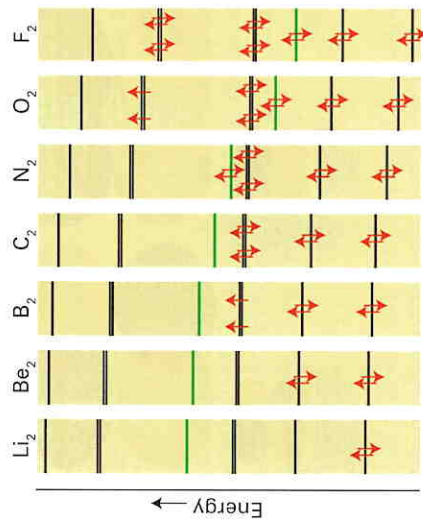


Fig. 17 The variation of the orbital energies of Period 2 homonuclear diatomic molecules. Only the valence-shell orbitals are shown.

calculated energy levels for the Period 2 homonuclear diatomic molecules. A useful rule is that, for neutral molecules, the order shown in Fig. 13 is valid for O_2 and F_2 , whereas the order shown in Fig. 14 is valid for the preceding elements of the period.

9B.6 The configurations of Period 2 homonuclear diatomics

With their molecular orbitals established, the electron configurations of the Period 2 homonuclear diatomics are derived as follows:

- Add the appropriate number of electrons to the orbitals by using the building-up procedure (as for atoms).
- Charged species (such as the peroxide ion, O_2^{2-} , and C_2^{+}) need either more or fewer electrons (for anions and cations, respectively) than the neutral molecules.

Consider N_2 , which has ten valence electrons, and has molecular orbitals arrayed as in Fig. 13. The first two electrons pair, enter, and fill the $1\sigma_g$ orbital. The next two electrons pair, enter, and fill the $1\sigma_u$ orbital. Six electrons remain. There are two $1\pi_u$ orbitals, so four electrons can be accommodated in them. The two remaining electrons enter the $2\sigma_g$ orbital. The ground-state configuration of N_2 is therefore $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$. This configuration is also depicted in Fig. 14.

The bond order (eqn 4) summarizes the bonding pattern. In N_2 , $1\sigma_g$, $2\sigma_g$, and $1\pi_u$ are bonding orbitals, and $N = 2 + 2 + 4 = 8$; however, $1\sigma_u$ (the antibond-

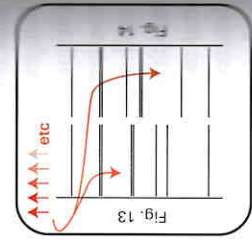
ing partner of $1\sigma_g$) is antibonding, so $N^* = 2$ and the bond order of N_2 is $b = \frac{1}{2}(8 - 2) = 3$. This value is consistent with the Lewis structure $:N \equiv N:$, in which there is a triple bond between the two atoms.

The bond order is a useful parameter for discussing the characteristics of bonds, because it correlates with bond length, and the greater the bond order between atoms of a given pair of atoms, the shorter the bond. The bond order also correlates with bond strength, and the greater the bond order, the greater the strength. The high bond order of N_2 is consistent with its high dissociation energy (942 kJ mol⁻¹).

Example 9B.2

Writing the electron configuration of a diatomic molecule

Write the ground-state electron configuration of O_2 and calculate the bond order.



Collect your thoughts To write ground-state electron configurations of homonuclear diatomic molecules and calculate bond orders, begin by deciding which MO energy level diagram to use (Fig. 13 or Fig. 14). Then count the valence electrons and accommodate them by using the building-up principle. Finally, use eqn 4 to calculate the bond order.

The solution Figure 13 is appropriate for oxygen. There are 12 valence electrons to accommodate. The first 10 electrons recreate the N_2 configuration (with a reversal of the order of the $2\sigma_g$ and $1\pi_u$ orbitals); the remaining two electrons must occupy the $1\pi_g$ orbitals. The configuration and bond order are therefore $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$. This configuration is also depicted in Fig. 13. Because $1\sigma_g$, $2\sigma_g$, and $1\pi_u$ are regarded as bonding and $1\sigma_u$ and $1\pi_g$ as antibonding, the bond order is $b = \frac{1}{2}(8 - 4) = 2$. This bond order accords with the classical view that oxygen has a double bond.

Self-test 9B.3

Write the electron configuration of F_2 and deduce its bond order.

Answer: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$, $b = 1$

As seen in Example 9B.2, the electron configuration of O_2 is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$. According to the building-up principle, the two $1\pi_g$ electrons in O_2 occupy different orbitals. One enters the $1\pi_g$ orbital formed by overlap of the $2p_x$ orbitals. The other enters its degenerate partner, the $1\pi_g$ orbital formed from overlap of the $2p_y$ orbitals. Because the two electrons occupy different orbitals, by Hund's rule they will have parallel spins ($\uparrow\uparrow$).

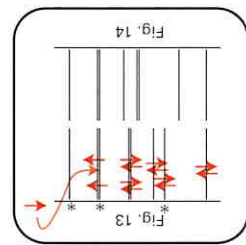
The electronic configuration of O_2 suggests that it will be magnetic because the magnetic fields generated by the two unpaired spins do not cancel. Specifically, O_2 is predicted to be a paramagnetic substance, a substance that is drawn into a magnetic field. Most substances (those with paired electron spins) are diamagnetic, and are pushed out of a magnetic field. That O_2 is in fact a paramagnetic gas is a striking confirmation of the superiority of the molecular orbital description of the molecule over the Lewis and VB descriptions (which require all the electrons to be paired). One application of the paramagnetism of oxygen is to monitor the oxygen content of incubators by measuring the magnetism of the gases they contain.

An F_2 molecule has two more electrons than an O_2 molecule, so its configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$ and its bond order is 1. It follows that F_2 is a singly-bonded molecule, in agreement with its Lewis structure. The low bond order is consistent with the low dissociation energy of F_2 (154 kJ mol⁻¹). A hypothetical Ne_2 molecule would have two further electrons; its configuration would be $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4 2\sigma_u^2$ and its bond order 0. The bond order of zero—which implies that two neon atoms do not bond together—is consistent with the monatomic character of neon.

Example 9B.3

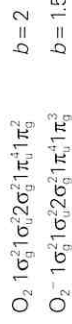
Judging the relative bond strengths of molecules and ions

The superoxide ion, O_2^- , plays an important role in the ageing processes that take place in organisms. Judge whether O_2^- is likely to have a higher or lower dissociation energy than O_2 .



Collect your thoughts Use the procedures outlined in Example 9B.2 to write the ground-state electron configuration of O_2^- by adding one electron to the ground-state electron configuration of O_2 . Because a species with the larger bond order is likely to have the larger dissociation energy, compare the electronic configurations of O_2^- and O_2 , and assess their bond orders.

The solution From Fig. 13 (the * in the thumbnail mark the antibonding orbitals) and Example 9B.2,



Because the anion has the smaller bond order, it can be expected to have the smaller dissociation energy. Indeed, whereas the dissociation energy of O_2 is 494 kJ mol⁻¹, that of O_2^- is 360 kJ mol⁻¹.

Self-test 9B.4

Which can be expected to have the higher dissociation energy, F_2 or F_2^+ ?

Answer: F_2^+

9B.7 The criteria for building molecular orbitals

It will be helpful at this point to summarize the steps taken to construct molecular orbitals of homonuclear diatomics. Initially, ignore the electrons that are available and focus only on the valence orbitals. Then:

- Use all available valence orbitals from both atoms.
- Consider only atomic orbitals of similar energies and of the same symmetry around the internuclear axis.
- Build σ and π orbitals from all atomic orbitals of a given symmetry.
- From N_σ atomic orbitals of σ symmetry, $N_\sigma \sigma$ orbitals can be built with progressively higher energy from strongly bonding to strongly antibonding.
- From N_π atomic orbitals of π symmetry, $N_\pi \pi$ orbitals can be built with progressively higher energy from strongly bonding to strongly antibonding. The π orbitals occur in doubly degenerate pairs.

Finally, feed in the available electrons into molecular orbitals of successively higher energy, paying regard to the Pauli exclusion principle and Hund's rule.

Checklist of key concepts

- 1 In **molecular orbital theory** (MO theory), electrons are treated as spreading throughout the entire molecule.
- 2 A **bonding orbital** is a molecular orbital that, if occupied, contributes to the strength of a bond between two atoms.
- 3 An **antibonding orbital** is a molecular orbital that, if occupied, decreases the strength of a bond between two atoms.
- 4 The **ground-state configuration** of a molecule is arrived at by adding electrons to the available orbitals, paying regard to the Pauli exclusion principle and Hund's rule.
- 5 The **bond order** is a measure of the number of bonds between neighbours and is related to the difference in numbers of electrons in bonding and antibonding orbitals.

TOPIC 9C

Molecular orbital theory: heteronuclear diatomics

► Why do you need to know this material?

Most molecules are heteronuclear, so you need to appreciate the differences in their electronic structure from homonuclear species, and how to treat those differences quantitatively.

► What is the key idea?

The bonding molecular orbital of a heteronuclear diatomic molecule or ion is composed mostly of the atomic orbital of the more electronegative atom; the opposite is true of the antibonding orbital.

► What do you need to know already?

You need to know about the molecular orbitals of homonuclear diatomics (Topic 9B) and the concept of normalization (Topic 7C).

A **heteronuclear diatomic molecule** is a diatomic molecule formed from atoms of two different elements; two examples are CO and HCl. Heteronuclear diatomic ions, such as CN^- , are also important in chemistry.

In a heteronuclear species the electron distribution in the covalent bond between the atoms is not symmetrical between the atoms because it is energetically favourable for a bonding electron pair to be found closer to one atom rather than the other. This imbalance results in a **polar bond**, which is a covalent bond in which the electron pair is shared unequally by the two atoms.

9C.1 Polar bonds

Molecular orbital theory takes polar bonds into its stride. A polar bond consists of two electrons in an orbital of the form

$$\psi = c_A \psi_A + c_B \psi_B \quad (1)$$

A general LCAO

with c_B^2 not equal to c_A^2 . If $c_B^2 > c_A^2$, the electrons have a greater probability of being found on B than on A and the molecule is polar in the sense $\delta^- \text{A}-\text{B}^{\delta+}$. A nonpolar bond, a covalent bond in which the electron pair is shared equally between the two atoms and there are zero partial charges on each atom, has $c_A^2 = c_B^2$. A pure ionic bond, in which one atom has obtained virtually sole possession of the electron pair (as in Cs^+F^- , to a first approximation), has one coefficient zero (so that A^+B^- would have $c_A^2 = 0$ and $c_B^2 = 1$).

It will be familiar from introductory chemistry that the unequal sharing of electrons is related to the **electronegativity**, χ (chi), of an element, its power to draw electrons to itself when it is part of a compound. A general feature of molecular orbitals between dissimilar atoms is that the atomic orbital with the higher electronegativity makes the larger contribution to the lower energy molecular orbital. The opposite is true of the orbital with higher energy (the antibonding orbital), for which the principal contribution comes from the atomic orbital with higher energy (the less electronegative atom):

$$\text{Bonding orbitals: for } \chi_A > \chi_B, c_A^2 > c_B^2$$

$$\text{Antibonding orbitals: for } \chi_A > \chi_B, c_A^2 < c_B^2$$

Figure 1 shows a schematic representation of this point.

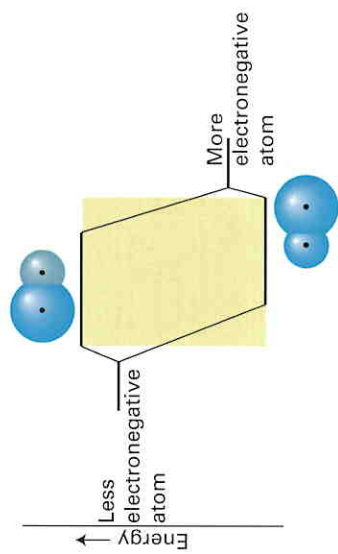


Fig. 1 A schematic representation of the relative contributions to bonding and antibonding molecular orbitals of atoms of different electronegativities. In the bonding orbital, the more electronegative atom makes the greater contribution (represented by the larger sphere), and the electrons of the bond are more likely to be found on that atom. The opposite is true of an antibonding orbital. A part of the reason why an antibonding orbital is of high energy is that the electrons that occupy it are likely to be found on the less electronegative atom.

Linus Pauling formulated a numerical scale of bond electronegativity based on considerations of bond dissociation energies, D_0 , and proposed that the difference in electronegativities could be expressed as

$$|\chi_A - \chi_B| = [D_0(AB) - \frac{1}{2}[D_0(AA) + D_0(BB)]]^{1/2} \quad (2)$$

Pauling electronegativity (definition)

where the $D_0(XY)$ are the numerical values of the bond dissociation energies (in electronvolts) of the $X-Y$ bonds. Table 9C.1 lists values of Pauling electronegativities for the main-group elements.

Table 9C.1
Electronegativities of the main-group elements*

H	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba	B	Al	Ga	In	Tl	C	Si	Ge	Sn	Pb	N	P	As	Sb	Bi	O	S	Se	Te	F	Cl	Br	I	Po
2.20	0.98	0.93	0.82	0.82	0.79	1.57	1.31	1.00	0.95	0.89	2.04	1.61	1.81	1.78	0.89	2.55	1.90	2.01	1.96	1.8	3.04	2.19	2.18	2.05	1.9	3.44	2.58	2.55	2.1	3.98	3.16	2.96	2.66	2.0

*Pauling values.

Robert Mulliken proposed an alternative definition in terms of the numerical values of the ionization energy, I , and the electron affinity, E_{ea} , of the element itself expressed in electronvolts:

$$\chi = \frac{1}{2}(I + E_{\text{ea}})/\text{eV} \quad (3)$$

Mulliken electronegativity scale (definition)

This relation is plausible, because an atom that has a high electronegativity is likely to be one that has a high ionization energy (so that it is unlikely to lose electrons to another atom in the molecule) and a high electron affinity (so that it is energetically favourable for an electron to move towards it). The relative values of the Mulliken electronegativities are broadly in line with (but numerically different from) the Pauling electronegativities.

Brief illustration 9C.1 Electronegativity

The bond dissociation energies of hydrogen, chlorine, and hydrogen chloride are 4.52 eV, 2.51 eV, and 4.47 eV, respectively. From eqn 2 it follows that

$$|\chi_{\text{Pauling}}(\text{H}) - \chi_{\text{Pauling}}(\text{Cl})| = [4.47 - \frac{1}{2}(4.52 + 2.51)]^{1/2} = 0.98 \approx 1.0$$

Self-test 9C.1

Repeat the analysis for HBr. The bond dissociation energies of bromine and hydrogen bromide are 190.2 kJ mol⁻¹ and 362.7 kJ mol⁻¹, respectively.

Answer: $|\chi_{\text{Pauling}}(\text{H}) - \chi_{\text{Pauling}}(\text{Br})| = 0.73$

Electronegativities show a periodicity, and the elements with the highest electronegativities are those close to fluorine in the periodic table (excluding, of course, the noble gases). As will now be shown, the Mulliken electronegativity is related directly to the values of the coefficients in the linear combination that describes the orbitals in a heteronuclear diatomic molecule.

9C.2 The formulation of molecular orbitals

The values of the coefficients in the linear combination of atomic orbitals (LCAO) of eqn 1 depend on the energies of the contributing atomic orbitals. These energies can be estimated from ionization energies and electron affinities of the two atoms. Thus, the extreme cases of an atom X (which stands for A or B in eqn 1) in a molecule are X⁺ if it has lost control

of the electron it supplied, X if it is sharing the electron pair equally with its bonded partner, and X⁻ if it has gained control of both electrons in the bond. If X⁺ is taken as defining the energy 0, then X lies at $-I(X)$ and X⁻ lies at $-[I(X) + E_{\text{ea}}(X)]$, where I is the ionization energy and E_{ea} the electron affinity (Fig. 2). The actual energy of the orbital lies at an intermediate value, and in the absence of further information, it is estimated as half-way down to the lowest of these values, namely $-\frac{1}{2}\{I(X) + E_{\text{ea}}(X)\}$, which, apart from sign and the units (for instance, electronvolts), will be recognized as the Mulliken electronegativity of X. It is conventional to denote this energy as α and, for reasons that will become clear, call it the **Coulomb integral**:

$$\alpha = -\frac{1}{2}(I + E_{\text{ea}}) \quad (4)$$

Coulomb integral

Solution of the Schrödinger equation for the LCAO of eqn 1 gives the following energies and coefficients when the overlap integral S_{AB} (Topic 9B) is very small:¹

$$E = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\{(\alpha_A - \alpha_B)^2 + 4\beta^2\}^{1/2} \quad (5a)$$

$$c_A = -\frac{\beta}{\{(\alpha_A - E)^2 + \beta^2\}^{1/2}} \quad (5b)$$

$$c_B = \frac{\alpha_A - E}{\{(\alpha_A - E)^2 + \beta^2\}^{1/2}} \quad (5c)$$

where β is called a **resonance integral** and is a measure of the strength of the interaction between the neighbouring atoms. It is negative and depends on the extent of overlap between the two orbitals. A typical value is -1.0 eV.

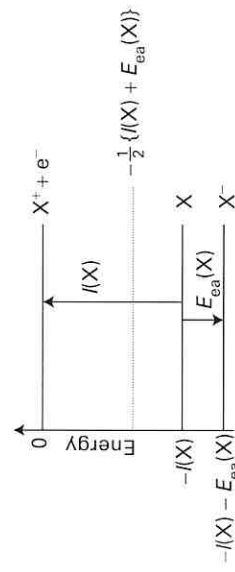


Fig. 2 The procedure for estimating the energy of an atomic orbital in a molecule.

¹For a derivation of these expressions, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

Example 9C.1

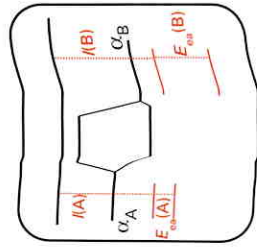
Assessing the molecular orbitals of HF

The features of polar bonds can be illustrated by considering HF. The general form of the molecular orbital is $\psi = c_1\psi_A + c_2\psi_B$, where ψ_A is an H1s orbital and ψ_B is an F2p_z orbital (with z along the internuclear axis, the convention for linear molecules). The relevant data are

	I/eV	E_{ea}/eV
H	13.6	0.75
F	174	3.40

Calculate the energies and coefficients of the bonding and antibonding orbitals made from this combination of atomic orbitals in HF.

Collect your thoughts From the data provided, estimate the energies α_X (X = H or F) of the atomic orbitals as $-\frac{1}{2}\{I(X) + E_{\text{ea}}(X)\}$. Use these energies and $\beta = -1.0$ eV (a typical value) to calculate the energies from eqn 5a. Then use the calculated energies E in the expressions for the coefficients, eqns 5b and 5c, noting that two sets of coefficients will be obtained, one corresponding to the bonding orbital (by using the lower value of E) and one to the antibonding orbital (by using the higher value of E).



The solution From the data provided and the table below

	$-\frac{1}{2}\{I + E_{\text{ea}}\}/\text{eV}$
H	7.2
F	10.4

it follows that the energies of the H1s and F2p orbitals can be taken as $\alpha_H = -7.2$ eV and $\alpha_F = -10.4$ eV, respectively. Substituting these values and $\beta = -1.0$ eV into eqn 5a gives

$$E/\text{eV} = \frac{1}{2}(-7.2 - 10.4) \pm \frac{1}{2}\{(-7.2 + 10.4)^2 + 4(-1.0)^2\}^{1/2} = -8.8 \pm 1.9$$

These values represent a bonding orbital at $E_{\text{bonding}} = -10.7$ eV and an antibonding orbital at $E_{\text{antibonding}} = -6.9$ eV, as shown in Fig. 3.

For the bonding orbital with energy $E_{\text{bonding}} = -10.7$ eV,

$$\{(\alpha_A - E)^2 + \beta^2\}^{1/2} = \{(-7.2 + 10.7)^2 + (-1.0)^2\}^{1/2} = 3.64 \dots \text{eV}$$

It follows that

$$c_H = \frac{-1.0 \text{ eV}}{3.64 \dots \text{eV}} = 0.27 \quad c_F = \frac{(-7.2 + 10.7) \text{ eV}}{3.64 \dots \text{eV}} = 0.96$$

For the antibonding orbital with energy $E_{\text{antibonding}} = -6.9 \text{ eV}$,

$$(\alpha_A - E^2 + \beta^2)^{1/2} = ((-7.2 + 6.9)^2 + (-1.0)^2)^{1/2} \text{ eV} \\ = 1.04 \dots \text{ eV}$$

It follows that

$$c_H = \frac{-1.0 \text{ eV}}{1.04 \dots \text{ eV}} = -0.96 \quad c_F = \frac{(-7.2 + 6.9) \text{ eV}}{1.04 \dots \text{ eV}} = -0.29$$

In summary, the results are:

$$E_{\text{bonding}} = -10.7 \text{ eV} \quad \psi_{\text{bonding}} = 0.27\psi_H + 0.96\psi_F \\ E_{\text{antibonding}} = -6.9 \text{ eV} \quad \psi_{\text{antibonding}} = 0.96\psi_H - 0.29\psi_F$$

Comment Notice how the lower energy orbital (the bonding orbital with energy -10.7 eV) has a composition that is more $F2p_z$ orbital than $H1s$, and that the opposite is true of the higher energy, antibonding orbital. Indeed, the probability of finding a σ electron in HF in an $F2p_z$ orbital is

$$c_F^2 \times 100 \text{ per cent} = (0.96)^2 \times 100 \text{ per cent} = 92 \text{ per cent}$$

Self-test 9C.2

Find the energies and forms of the σ orbitals and their coefficients in the HCl molecule using $\beta = -1.0 \text{ eV}$, in the limit of negligible overlap. Use data from Tables 8C.3 and 8C.4.

$$\text{Answer: } E_{\text{bonding}} = -8.9 \text{ eV}, E_{\text{antibonding}} = -6.6 \text{ eV}, \\ \psi_{\text{bonding}} = 0.51\psi_H + 0.86\psi_C, \psi_{\text{antibonding}} = 0.86\psi_H - 0.51\psi_C$$

9C.3 Molecular orbital diagrams

Molecular orbitals for Period 2 heteronuclear diatomics are constructed by using the same procedure as for homonuclear diatomics (Topic 9B):

1. Construct molecular orbitals by forming linear combinations of all suitable valence atomic orbitals supplied by the atoms; N atomic orbitals

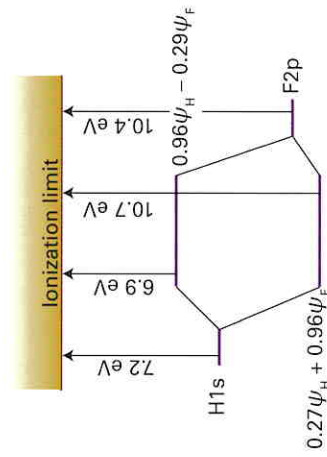


Fig. 3 The atomic orbital energy levels of H and F atoms and the molecular orbitals they form. The bonding orbital has predominantly F atom character and the antibonding orbital has predominantly H atom character.

result in N molecular orbitals. In Period 2, the valence orbitals are $2s$ and $2p$.

2. Accommodate the valence electrons supplied by the atoms so as to achieve the lowest overall energy subject to the constraint of the Pauli exclusion principle.
3. If more than one molecular orbital of the same energy is available, add the electrons to each individual orbital before doubly occupying any one orbital.
4. Apply Hund's rule, that if two electrons occupy orbitals, then the lowest energy is achieved if their spins are parallel.

The g, u designation used for homonuclear diatomics is inapplicable because the molecule is heteronuclear and do not possess a centre of inversion. Consequently, the σ orbitals are simply numbered in sequence, $1\sigma, 2\sigma, \dots$, and the π orbitals likewise.

Brief illustration 9C.2 Molecular orbital diagrams

Figure 4 shows the bonding scheme in CO and illustrates a number of points already made. Because the C atom has four valence electrons and the O atom has six valence electrons, ten electrons occupy the molecular orbitals subject to the Pauli exclusion principle. It follows that the ground-state configuration is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$. As expected, the lowest energy orbitals are predominantly of O character as that is the more electronegative element.

Self-test 9C.3

What is the ground-state configuration of NO? Is NO paramagnetic or diamagnetic?

Answer: $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^1$; paramagnetic

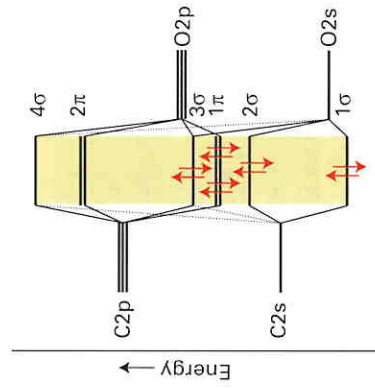


Fig. 4 The molecular orbital energy level diagram for CO. The orbitals of the O atom are lower in energy than the corresponding orbitals of the C atom because the effective nuclear charge of oxygen is greater than that of carbon.

π orbitals also largely on C is at the root of the importance of carbon monoxide in d-block chemistry, because it enables it to form an extensive series of carbonyl complexes by a combination of electron donation from the 3σ orbital and electron acceptance into the 2π orbitals. The HOMO and the LUMO jointly form the **frontier orbitals** of the molecule, and are of great importance for assessing its reactions.

Checklist of key concepts

- 1 The **electronegativity** of an element is the power of its atoms to draw electrons to itself when it is part of a compound.
- 2 In a bond between dissimilar atoms, the atomic orbital belonging to the more electronegative atom makes the larger contribution to the molecular orbital with the lowest energy. For the molecular orbital with the highest energy, the principal contribution comes from the atomic orbital belonging to the less electronegative atom.
- 3 The **frontier orbitals** of a molecule are its **highest occupied molecular orbital (HOMO)** and **lowest unoccupied molecular orbital (LUMO)**; they play important roles in chemical reactions.

TOPIC 9D

Molecular orbital theory: polyatomic molecules

► Why do you need to know this material?

Most molecules of interest in chemistry are polyatomic, so it is important to be able to discuss their electronic structure. Although computational procedures are now widely available, to understand and interpret them it is helpful to see how they emerged from the more primitive approach described here.

► What is the key idea?

Molecular orbitals can be expressed as linear combinations of all the atomic orbitals of the appropriate symmetry.

► What do you need to know already?

This Topic extends the approach used for heteronuclear diatomic molecules in Topic 9C. The principal mathematical technique used is that for solving systems of equations (*The chemist's toolkit 27* in this Topic).

The bonds in polyatomic molecules are built in the same way as in diatomic molecules, the only difference being that more atomic orbitals are used to construct the molecular orbitals, and these molecular orbitals spread over the entire molecule, not just the adjacent atoms of the bond, and contribute to binding all the atoms together. The general procedure is as follows:

1. Construct molecular orbitals by forming linear combinations of all suitable valence atomic orbitals supplied by the atoms; N atomic orbitals result in N molecular orbitals.
2. 'Suitable atomic orbitals' are those that have non-zero overlap with their neighbours.

3. Accommodate the valence electrons supplied by the atoms so as to achieve the lowest overall energy subject to the Pauli exclusion principle that no more than two electrons may occupy a single orbital (and then must be paired).
4. If more than one molecular orbital of the same energy is available, add the electrons to each individual orbital before doubly occupying any one orbital (because that minimizes electron-electron repulsions).
5. Take note of Hund's rule (Topics 8B and 9B), that if electrons occupy different degenerate orbitals, then they do so with parallel spins.

Although there are formal procedures for judging the symmetries of orbitals (this is the role of 'group theory'), for the present purposes intuition is an adequate guide. The lowest energy, most strongly bonding orbital has the least number of nodes between adjacent atoms. The highest energy, most strongly antibonding orbital has the greatest numbers of nodes between neighbouring atoms.

9D.1 The molecular orbitals of H₂O

A typical molecular orbital in H₂O constructed from H1s orbitals (denoted $\psi_{\text{H1s(A)}}$ and $\psi_{\text{H1s(B)}}$) and O2s, O2p_y, and O2p_z orbitals (denoted ψ_{O2s} , ψ_{O2p_y} , and ψ_{O2p_z}) has the composition

$$\psi = c_1\psi_{\text{H1s(A)}} + c_2\psi_{\text{H1s(B)}} + c_3\psi_{\text{O2s}} + c_4\psi_{\text{O2p}_y} + c_5\psi_{\text{O2p}_z} \quad (1)$$

The O2p_x orbital (which is perpendicular to the molecular plane) has zero overlap with the H1s orbitals (see Fig. 3 of Topic 9B) and is not involved in this linear combination (but is present in the molecule).

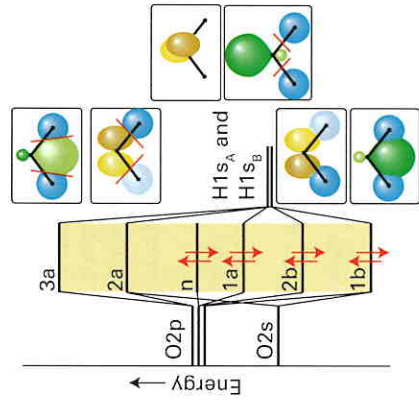


Fig. 1 Schematic form of the molecular orbitals of H₂O. The orbitals in blue are H1s atomic orbitals (the shades denote the signs: dark +, light -), a pure O2p orbital is shown in two shades of yellow, and the combinations of an O2p and O2s orbital are shown in two shades of green. Then, for example, the molecular orbital of lowest energy results from a bonding interaction between four orbitals: two H1s orbitals and one combination of the O2p and O2s orbitals. Red lines denote nodal planes. The 1a orbital is almost nonbonding.

Because five atomic orbitals are being used to form the linear combination of atomic orbitals (LCAO), there will be five possible molecular orbitals of this kind: the lowest energy (most bonding) orbital will have no internuclear nodes and the highest energy (most antibonding) orbital will have a node between each pair of neighbouring nuclei (Fig. 1). The unused O2p_x orbital lies at the same position as it has in the unbound oxygen atom: it is available to accommodate electrons but does not participate directly in the bonding.

The molecular orbital diagram for H₂O is shown in Fig. 1. The orbitals have been labelled b, n, and a for net bonding, nonbonding, and antibonding (these are not their group theoretical labels). You do not need to know how to deduce the shapes of the molecular orbitals, but it is important to gain some appreciation for why they have these shapes. In total, there are eight electrons (six from O, one from each H) to accommodate in the six molecular orbitals. Consequently, in the ground state of H₂O each of the four lowest-energy orbitals hold two electrons, as shown in Fig. 1, and its configuration is $1b^2 2b^2 1a^2 n^2$. Although you must always bear in mind that molecular orbital theory (MO theory) describes bonding in terms of electrons that are delocalized over the entire molecule, this configuration can be interpreted to show its connection to the Lewis description of H₂O:

- Most of the bonding is due to the four electrons in 1b and 2b (the 1a orbital is only very weakly anti-

bonding). In terms of bond order, therefore, there are two bonds shared between the HO and OH fragments, so each fragment can be interpreted as having an O—H single bond.

- The σ, π classification of molecular orbitals is not strictly applicable to nonlinear polyatomic molecules. However, that classification is relevant *locally*, in the sense that the two O—H bonds resemble σ bonds.
- Most of the electron density in 1a and all the electron density in n are confined to the O atom. The four electrons that occupy these two orbitals correspond to the two lone pairs of the Lewis description of the molecule.

9D.2 The Hückel method

An important example of the application of MO theory is to the orbitals that may be formed from the p orbitals perpendicular to a molecular plane of alkenes, aromatic hydrocarbons, and related compounds, such as that of a phenyl ring. A common procedure in elementary descriptions of the electronic structures of alkenes and arenes, and which is used here, is to treat the σ -bonding framework using the language of VB theory (Topic 9A), and to treat the π -electron system separately by MO theory. A computational scheme, the **Hückel theory** proposed by Erich Hückel, provides a simple way of establishing the molecular orbitals of the π -electron component of these systems and of estimating their relative energies.

Consider ethene, CH₂=CH₂. Each carbon atom is regarded as sp² hybridized and forming C—C and C—H σ bonds at 120° to each other by sp² hybridization and either (Csp², Csp²)- or (Csp², H1s)-orbital overlap (note the VB language). The unhybridized C2p_z orbitals perpendicular to the σ -framework, with ψ_A and ψ_B then used to construct molecular orbitals (Fig. 2):

$$\psi = c_A\psi_A + c_B\psi_B \quad (2)$$

As shown in the following *Justification*, to find the energies and coefficients of the two molecular orbitals that can be formed from these two atomic orbitals, the following simultaneous equations need to be solved:

$$\begin{aligned} (H_{AA} - E)c_A + (H_{AB} - ES)c_B &= 0 \\ (H_{BA} - ES)c_A + (H_{BB} - E)c_B &= 0 \end{aligned} \quad (3)$$

Secular equations for ethene

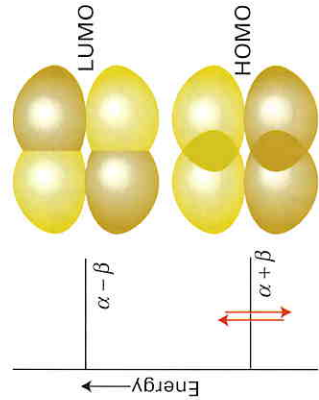


Fig. 2 The bonding and antibonding π molecular orbitals of ethene and their energies.

In the context of MO theory, these simultaneous equations are called **secular equations**. The H_{jk} are expressions that include various contributions to the energy, including the repulsion between electrons and their attractions to the nuclei; the S_{jk} are the overlap integrals between orbitals on atoms J and K .

Justification 9D.1

The secular equations of ethene

Substitution of eqn 2 into the Schrödinger equation written in the form $\hat{H}\psi = E\psi$ gives

$$\hat{H}(c_A\psi_A + c_B\psi_B) = E(c_A\psi_A + c_B\psi_B)$$

The followings steps are then taken to find the allowed values of E and the corresponding coefficients.

Step 1: Operate on the wavefunctions

Because the operators operate only on the ψ , not the numerical coefficients c , the preceding expression becomes

$$c_A\hat{H}\psi_A + c_B\hat{H}\psi_B = c_A E\psi_A + c_B E\psi_B$$

Step 2: Isolate expressions for E

Multiply both sides by ψ_A^* :

$$c_A\psi_A^*\hat{H}\psi_A + c_B\psi_A^*\hat{H}\psi_B = c_A E\psi_A^*\psi_A + c_B E\psi_A^*\psi_B$$

Then integrate each term in this expression over all space:

$$c_A \int \psi_A^* \hat{H} \psi_A \, d\tau + c_B \int \psi_A^* \hat{H} \psi_B \, d\tau = c_A E \int \psi_A^* \psi_A \, d\tau + c_B E \int \psi_A^* \psi_B \, d\tau$$

where E is a constant and has been taken outside the two integrals on the right. The relation $\int \psi_A^* \psi_A \, d\tau = 1$ follows from the fact that each atomic orbital is normalized; S_{AB} is the overlap integral between the orbitals on A and B (Topic 9B). It follows that

$$c_A H_{AA} + c_B H_{AB} = c_A E + c_B E S$$

Step 3: Rearrange the equation

Now bring the right hand side across to the left:

$$c_A H_{AA} + c_B H_{AB} - (c_A E + c_B E S) = 0$$

and collect terms involving c_A and c_B separately:

$$(c_A H_{AA} - c_A E) + (c_B H_{AB} - c_B E S) = 0$$

Finally, factor out the two coefficients:

$$c_A (H_{AA} - E) + c_B (H_{AB} - ES) = 0$$

This is the first of the two secular equations in eqn 3.

Step 4: Repeat steps 2 and 3

Return to step 2, but now multiply the equation from step 1 by ψ_B^* . Then the same procedure leads to the second secular equation of eqn 3.

To simplify the solution of the secular equations, Hückel introduced the following drastic approximations:

- All H_{jj} are set equal to a single quantity α called the **Coulomb integral**. It is negative and can be interpreted as the energy of the electron when it occupies an orbital on A or B.
- All H_{jk} are set equal to zero unless atoms J and K are adjacent, when it is set equal to a single quantity β (a negative quantity) called the **resonance integral**. It is a measure of the strength of the interaction between the neighbouring atoms.
- All S (but not the related β) are set equal to zero to simplify the resulting expressions.

With these 'Hückel approximations' the secular equations become

$$\begin{aligned} (\alpha - E)c_A + \beta c_B &= 0 \\ \beta c_A + (\alpha - E)c_B &= 0. \end{aligned} \quad (4)$$

Hückel approximation for ethene

As shown in the following *Justification*, the solutions are $E = \alpha \pm \beta$, and

$$\begin{aligned} \text{For } E = \alpha + \beta \quad c_A &= c_B, \text{ so } \psi = c_A(\psi_A + \psi_B) \\ \text{For } E = \alpha - \beta \quad c_A &= -c_B, \text{ so } \psi = c_A(\psi_A - \psi_B) \end{aligned}$$

(Remember that $\beta < 0$, so $E = \alpha + \beta$ is the lower energy of the two.)

Justification 9D.2

Solutions of the secular equations of ethene

Solving the secular equations entails finding expressions for E , c_A , and c_B . The following steps need to be taken:

Step 1: Find the energies

As set out in *The chemist's toolkit 27*, the simultaneous equations in eqn 4 have a solution only if the **secular determinant**, a determinant formed from the factors multiplying the coefficients, is zero:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0$$

Because $a^2 - b^2 = (a+b)(a-b)$, the expression can be written as

$$(\alpha - E + \beta)(\alpha - E - \beta) = 0$$

This condition is satisfied if either term in parentheses is equal to zero. It follows that

$$E = \alpha + \beta \quad \text{or} \quad E = \alpha - \beta$$

Step 2: Find the coefficients

Consider the value $E = \alpha + \beta$. Substitution into the secular equations (eqn 4) gives

$$-\beta c_A + \beta c_B = 0$$

from which it follows that $c_A = c_B$. For $E = \alpha - \beta$, the same procedure leads to the solution $c_A = -c_B$.

The energies and orbitals are represented in Fig. 2: they are the bonding and antibonding combinations of the $C2p_z$ atomic orbitals. The value of the one unknown, c_A , is found by ensuring that each molecular

orbital is normalized, but the explicit value is not needed for this discussion.

Because there are two electrons to be accommodated, both enter the lower energy orbital and contribute $2(\alpha + \beta)$ to the energy of the molecule. It follows from the fact that the separation of the bonding and antibonding orbitals is 2β , that the energy needed to excite a π electron to the antibonding combination is $2|\beta|$. A typical value of β in hydrocarbons is about -2.4 eV, or -230 kJ mol $^{-1}$.

Example 9D.1

Calculating the Hückel energies for butadiene

The Hückel equations for butadiene (1) are constructed like those for ethene and are

$$\begin{aligned} (\alpha - E)c_A + \beta c_B &= 0 \\ \beta c_A + (\alpha - E)c_B + \beta c_C &= 0 \\ \beta c_B + (\alpha - E)c_C + \beta c_D &= 0 \\ \beta c_C + (\alpha - E)c_D &= 0 \end{aligned}$$

Write down and solve the secular determinant for the energies of the π orbitals.



1 Butadiene

The chemist's toolkit 27 Simultaneous equations

Two simultaneous equations of the form

$$\begin{aligned} ax + by &= 0 \\ cx + dy &= 0 \end{aligned}$$

have solutions only if the 'determinant' of the coefficients is equal to zero. In this case

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0$$

where the term on the left is the determinant and has the following meaning:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Three simultaneous equations of the form

$$\begin{aligned} ax + by + cz &= 0 \\ dx + ey + fz &= 0 \\ gx + hy + iz &= 0 \end{aligned}$$

have a solution only if

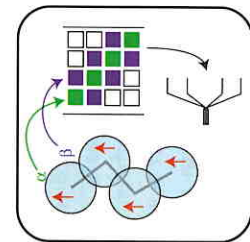
$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = 0$$

This 3×3 determinant expands as follows:

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

Note the alternation in signs for successive columns. The 2×2 determinants then expand like the one above. Determinants of higher dimension expand analogously, so a 4×4 determinant is expanded as an alternating sum of 3×3 determinants, each of which is expanded according to this rule, and so on.

Most mathematical software is capable of evaluating a determinant of any dimension with numerical values in each location and of solving secular equations in the form *determinant* = 0, where *determinant* has an unknown but required quantity E (such as the energy of a molecular orbital) in various locations.



Collect your thoughts Because there are four equations and four c_i , the secular determinant in this case has four rows and four columns. From left to right, the elements of the first row of the determinant are $\alpha - E$, β , 0 , and 0 ; that is, the terms multiplying c_A , c_B , c_C , and c_D , respectively, in the top equation. The remaining rows are constructed similarly by inspection of the remaining equations. Solve this determinant by one of two methods: manually by extension of the method described in *The chemist's toolkit 27*, or (more quickly) with mathematical software.

The solution The secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

1. *Solution using mathematical software*

The software looks for the four values of E that satisfy the expression 'determinant = 0'. In this case, the outcome is

$$E = \alpha \pm 1.62\beta, \alpha \pm 0.62\beta$$

Because α and β are both negative quantities, the order of increasing energy, from most bonding to most antibonding, is $\alpha + 1.62\beta$, $\alpha + 0.62\beta$, $\alpha - 0.62\beta$, $\alpha - 1.62\beta$.

2. *Solution by hand*

To solve the secular determinant by hand, first expand it by extension of the procedure in *The chemist's toolkit 27*, set it equal to 0, and find

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - (\alpha - E)\beta \begin{vmatrix} \beta & \beta \\ 0 & \alpha - E \end{vmatrix} - \beta^2 \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} + \beta^3 \begin{vmatrix} 0 & \beta \\ 0 & \alpha - E \end{vmatrix} = (\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4 = 0$$

With $x = (\alpha - E)^2$, this is a quadratic equation:

$$x^2 - 3\beta^2x + \beta^4 = 0$$

with the solutions (*The chemist's toolkit 13* in Topic 5b, using $a = 1$, $b = -3\beta^2$, $c = 1$)

$$x = \frac{1}{2}(3 \pm 5^{1/2})\beta^2 = 2.62\beta^2 \text{ and } 0.38\beta^2$$

or (noting that the square root of a positive number, here x , can be either positive or negative)

$$x^{1/2} = 1.62\beta, -1.62\beta, 0.62\beta, \text{ and } -0.62\beta$$

Then, from $x^{1/2} = (\alpha - E)$ and $-(\alpha - E)$, and therefore $E = \alpha + x^{1/2}$ and $\alpha - x^{1/2}$, it follows that

$$E = \alpha + 1.62\beta, \alpha - 1.62\beta, \alpha + 0.62\beta, \alpha - 0.62\beta$$

which are the four values of E calculated by using mathematical software.

Self-test 9D.1

The ' π -electron binding energy', E_{π} , is the total energy due to the electrons occupying π orbitals. What is the value of E_{π} for butadiene (in its ground-state)?

Answer: $4\alpha + 4.40\beta$

9D.3 The molecular orbitals of benzene

Exactly the same procedure used for ethene and butadiene can be used for benzene, C_6H_6 . Each C atom is regarded as sp^2 hybridized (note the VB language again for the σ framework) and forms a planar hexagonal framework of σ bonds (Fig. 3). There is an unhybridized $C2p_z$ orbital on each atom perpendicular to the ring which is used to form molecular orbitals;

$$\psi = c_A\psi_A + c_B\psi_B + c_C\psi_C + c_D\psi_D + c_E\psi_E + c_F\psi_F \quad (5)$$

The next steps are now familiar: six simultaneous equations for the coefficients are set up, the corresponding 6×6 secular determinant is written, and the

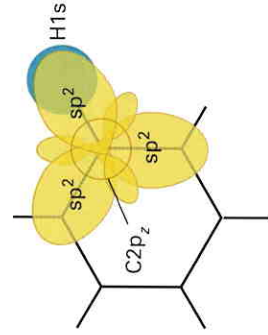


Fig. 3 The orbitals used to construct the molecular orbitals of benzene.

mediate orbitals (the pair labelled 2π and the pair labelled 3π) form two doubly degenerate pairs, one net bonding and the other net antibonding.

There are six electrons to be accommodated (one is supplied by each C atom), and they occupy the lowest three orbitals in Fig. 4 to give the configuration $1\pi^2 2\pi^4$. The resulting electron distribution is like a double doughnut. It is an important feature of the configuration that the only molecular orbitals occupied have a net bonding character, for this is one contribution to the stability (in the sense of low energy) of the benzene molecule.

A feature of the molecular orbital description of benzene is that each molecular orbital spreads either all around or partially around the C_6 ring. That is, π bonding is **delocalized**, and each electron pair helps to bind together several or all the C atoms. The delocalization of bonding influence is a primary feature of molecular orbital theory. The **delocalization energy**, E_{deloc} , is the additional lowering of energy of the molecule due to the spreading of the p electrons throughout the molecule instead of being localized in discrete bonding regions.

Brief illustration 9D.1 The delocalization energy of benzene

If the six π electrons in benzene occupied three localized ethene-like orbitals, then their energy would be $3 \times (2\alpha + 2\beta) = 6\alpha + 6\beta$. However, their energy in benzene is $2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$. The delocalization energy is the difference of these two energies:

$$E_{\text{deloc}} = (6\alpha + 8\beta) - (6\alpha + 6\beta) = 2\beta$$

or about -460 kJ mol^{-1} .

Self-test 9D.2

Calculate the delocalization energy of butadiene.

Answer: 0.48β

9D.4 Computational chemistry

Computational chemistry is now a standard part of chemical research. One major application is in pharmaceutical chemistry, where the likely pharmacological activity of a molecule can be assessed computationally from its shape and electron density distribution before expensive and ethically controversial *in vivo* trials are started. Commercial software is now widely available for calculating the electronic structures of molecules and displaying the results graphically. All such calculations work within the

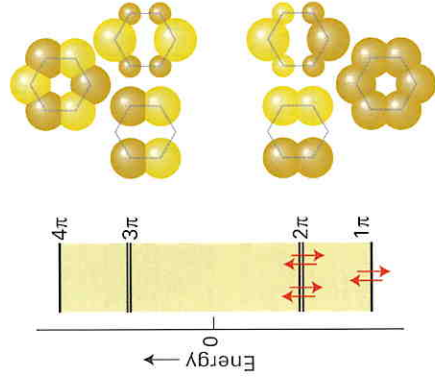


Fig. 4 The π orbitals of benzene and their energies. The lowest-energy orbital is fully bonding between neighbouring atoms, but the uppermost orbital is fully antibonding. The two pairs of doubly degenerate molecular orbitals have an intermediate number of internuclear nodes. As usual, different colours represent different signs of the wavefunction.

Hückel approximations are applied. The (unnormalized) molecular orbitals and their corresponding energies are then as follows (Fig. 4):

Energy	Molecular orbital
Highest (most antibonding)	
$\alpha - 2\beta$	$\psi = \psi_A - \psi_B + \psi_C - \psi_D + \psi_E - \psi_F$
$\alpha - \beta$	$\psi = 2^{1/2}\psi_A - \psi_B - \psi_C + 2^{1/2}\psi_D - \psi_E - \psi_F$
$\alpha - \beta$	$\psi = \psi_B - \psi_C + \psi_E - \psi_F$
$\alpha + \beta$	$\psi = 2^{1/2}\psi_A + \psi_B + \psi_C - 2^{1/2}\psi_D - \psi_E - \psi_F$
$\alpha + \beta$	$\psi = \psi_B + \psi_C - \psi_E - \psi_F$
$\alpha + 2\beta$	$\psi = \psi_A + \psi_B + \psi_C + \psi_D + \psi_E + \psi_F$
Lowest (most bonding)	

Note that the lowest energy, most bonding orbital (1π) has no internuclear nodes. It is strongly bonding because the constructive interference between neighbouring p orbitals results in a good accumulation of electron density between the nuclei (but slightly off the internuclear axis, as in the π bond of ethene). In the most antibonding orbital (4π) the alternation of signs in the linear combination results in destructive interference between neighbours, and the molecular orbital has a nodal plane between each pair of neighbours, as shown in the illustration. The four inter-

Born–Oppenheimer approximation and express the molecular orbitals as linear combinations of atomic orbitals.

There are two principal approaches to solving the Schrödinger equation numerically for many-electron polyatomic molecules. In the **semi-empirical methods**, certain expressions that occur in the Schrödinger equation are set equal to parameters that have been chosen to lead to the best fit to experimental quantities, such as enthalpies of formation. Semi-empirical methods are applicable to a wide range of molecules with a virtually limitless number of atoms, and are widely popular. In the more fundamental **ab initio methods**, an attempt is made to calculate structures from first principles, using only the atomic numbers of the atoms present. Such an approach is intrinsically more reliable than a semi-empirical procedure but is much more demanding computationally.

Both types of procedure typically adopt a **self-consistent field (SCF)** procedure, in which an initial guess about the composition of the LCAO is successively refined until the solution remains unchanged in a cycle of calculation. First, estimated values of the coefficients in the LCAO are used to build the molecular orbitals. Then, on the basis of this initial guess, the Schrödinger equation is solved for the coefficients of one occupied orbital given the initial guess for the other orbitals. In this way an improved approximation to the coefficients of that selected LCAO is obtained. The procedure is then repeated for all the other occupied molecular orbitals. At the end of that stage a new set of LCAO coefficients and an estimate of the energy of the molecule are obtained. The refined set of coefficients is used to repeat the calculation and calculate a new set of coefficients and a new energy. In general, these results will differ from the new starting point. However, there comes a stage when repetition of the calculation leaves the coefficients and energy unchanged to within a predetermined criterion. The orbitals are now said to be 'self-consistent', and are accepted as a description of the molecule.

The severe approximations of the Hückel method have been removed over the years in a succession of better approximations. Each has given rise to an acronym, such as AM1 ('Austin Model 1'). Software for all these procedures is now readily available, and reasonably sophisticated calculations can now be run even on tablets and laptops. A semi-empirical technique that has gained considerable ground in recent years to become one of the most widely used techniques for the calculation of molecular structure is **density functional theory (DFT)**. Its advantages in-

clude less demanding computational effort, less computer time, and—in some cases, particularly d-metal complexes—better agreement with experimental values than is obtained from other procedures.

The *ab initio* methods also simplify the calculations, but they do so by setting up the problem in a different manner, avoiding the need to estimate parameters by appeal to experimental data. In these methods, sophisticated techniques are used to solve the Schrödinger equation numerically. The difficulty with this procedure is the enormous time it takes to carry out the detailed calculation. That time can be reduced by replacing the hydrogenic atomic orbitals used to form the LCAO by a **gaussian-type orbital (GTO)** in which the exponential function e^{-r} characteristic of actual orbitals is replaced by a sum of gaussian functions of the form $e^{-\alpha r^2}$.

One of the most significant developments in computational chemistry has been the introduction of graphical representations of molecular orbitals and electron densities. The raw output of a molecular structure calculation is a list of the coefficients of the atomic orbitals in each molecular orbital and the energies of these orbitals. The graphical representation of a molecular orbital uses stylized shapes to represent the basis set, and then scales their size to indicate the value of the coefficient in the LCAO. Different signs of the wavefunctions are represented by different colours (Fig. 5).

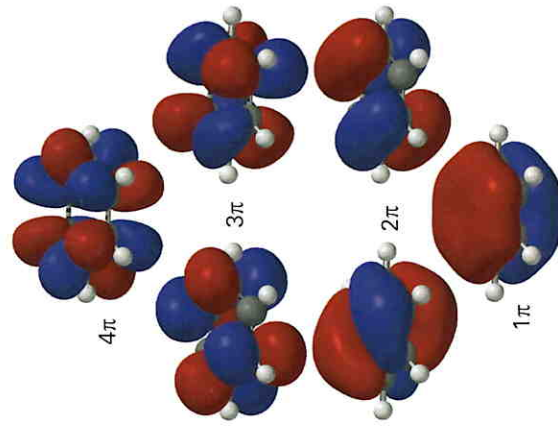


Fig. 5 The output of a computation of the π orbitals of benzene: opposite signs of the wavefunctions are represented by different colours. Compare these molecular orbitals with the more diagrammatic representation in Fig. 4.



Fig. 6 The isodensity surface of benzene obtained by using the same software as in Fig. 5.

Once the coefficients are known, a representation of the electron density in the molecule can be drawn by noting which orbitals are occupied and then forming the squares of those orbitals. The total electron density at any point is then the sum of the squares of the wavefunctions evaluated at that point. The outcome is commonly represented by an **isodensity surface**, a surface of constant total electron density (Fig. 6).

One of the most important aspects of a molecule other than its geometrical shape, which is commonly depicted as an **electrostatic potential surface** (an 'elpot surface'). The potential energy of an imaginary positive charge at a point is calculated by taking into ac-

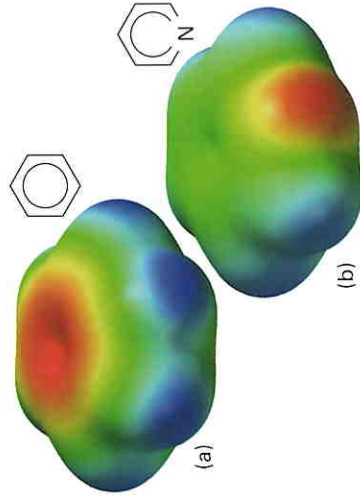


Fig. 7 The electrostatic potential surfaces of (a) benzene and (b) pyridine. Note the accumulation of electron density on the nitrogen atom of pyridine at the expense of the other atoms.

count its interaction with the nuclei and the electron density throughout the molecule. Then, because the potential energy is equal to the product of the charge and the electric potential (*The chemist's toolkit 14* in Topic 5H), the potential energy can be interpreted as a potential and depicted as an appropriate colour (Fig. 7). Electron-rich regions usually have negative potentials and electron-poor regions usually have positive potentials.

Checklist of key concepts

- 1 **Hückel theory** is a simple treatment of the molecular orbitals of π -electron systems. In hydrocarbons the technique consists of forming linear combinations of unhybridized C2p orbitals.
- 2 In the **self-consistent field procedure**, an initial guess about the composition of the molecular orbitals is successively refined until the solution remains unchanged in a cycle of calculations.

□ 3 In **semi-empirical methods** for the determination of electronic structure, the Schrödinger equation is written in terms of parameters chosen to agree with selected experimental quantities.

□ 4 In **ab initio methods** an attempt is made to calculate structures from first principles.

FOCUS 9 The chemical bond

Exercises

Topic 9A Valence bond theory

- 9A.1** Calculate the energy of Coulombic repulsion between two hydrogen nuclei at their equilibrium separation in H_2 (74.1 pm). Express your answer in kilojoules per mole. The result is the energy that must be overcome by the attraction from the electrons that form the bond.
- 9A.2** Write the valence bond wavefunction of the σ bond in a C—H group of a molecule.
- 9A.3** Write the valence bond wavefunction for the one σ and two π bonds in a nitrogen molecule, N_2 .

Topic 9B Molecular orbital theory: homonuclear diatomics

- 9B.1** Give the (g,u) parities of the first four levels of a particle-in-a-box wavefunction.
- 9B.2** Put the following species in order of increasing bond length: F_2 , F_2^+ , F_2^- . Identify the bond order of each of the species.
- 9B.3** Arrange the species O_2^+ , O_2 , O_2^- , O_2^{2-} in order of increasing bond length and identify the bond order of each.

Topic 9C Molecular orbital theory: heteronuclear diatomics

- 9C.1** Use Pauling electronegativities to predict the polarities of the bonds (a) P—H, (b) B—H.
- 9C.2** Some chemical reactions proceed by the initial loss or transfer of an electron to a diatomic species. Which of the molecules N_2 , NO, O_2 , C_2 , F_2 , and CN would you expect to be stabilized by (a) the addition of an electron to form AB^- , (b) the removal of an electron to form AB^+ ?

Topic 9D Molecular orbital theory: polyatomic molecules

- 9D.1** The ionization energy of a carbon atom is 11.26 eV and its electron affinity is 1.26 eV. Estimate the value of the Coulomb integral, α , expressing your answer both in electronvolts and as a molar energy in kilojoules per mole.
- 9D.2** Express the π electron binding energy of benzene in terms of the Hückel parameters α and β .
- 9D.3** The Hückel energies of the four π orbitals of cyclobutadiene are $\alpha + 2\beta$, α , α , and $\alpha - 2\beta$. What is the delocalization energy?

- 9A.4** Draw the three non-ionic contributions to the resonance structure of naphthalene, C_{10}H_8 .
- 9A.5** A normalized valence bond wavefunction turned out to have the form $\psi = 0.889\psi_{\text{cov}} + 0.458\psi_{\text{ion}}$. What is the chance that, in 1000 inspections of the molecule, both electrons of the bond will be found on one atom?

- 9B.4** Give the ground-state electron configurations of (a) H_2 , (b) Li_2 , (c) Be_2 , (d) C_2 , (e) N_2 , and (f) O_2 .
- 9B.5** From the ground-state electron configurations of B_2 and C_2 , predict which molecule should have the greater dissociation energy.
- 9B.6** How many molecular orbitals can be constructed from a diatomic molecule in which s, p, d, and f orbitals are all important for bonding?

- 9C.3** Two important diatomic molecules for the welfare of humanity are NO and N_2 ; the former is both a pollutant and a neurotransmitter, and the latter is the ultimate source of the nitrogen of proteins and other biomolecules. Use the electron configurations of NO and N_2 to predict which is likely to have the shorter bond length.

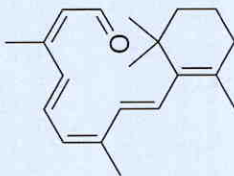
- 9D.4** The longest wavelength electronic transition in simple unsaturated hydrocarbons corresponds to a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Predict the energy of the HOMO to LUMO separation in (a) ethane, (b) butadiene, and (c) benzene.

Discussion questions

- 9.1** List and discuss the approximations built into valence bond theory and molecular orbital theory.
- 9.2** Discuss the steps involved in the construction of sp^3 , sp^2 , and sp hybrid orbitals.
- 9.3** Describe how molecular orbital theory accommodates all the conventional types of bonding.
- 9.4** Why is the electron pair such a central concept in theories of the chemical bond?
- 9.5** Describe and justify the Pauling and Mulliken electronegativity scales.
- 9.6** Why is orbital overlap a guide to assessing the strengths of chemical bonds? Why, in some cases, is it not?
- 9.7** Identify and justify the approximations used in the Hückel theory of conjugated hydrocarbons.
- 9.8** Explain the differences between semi-empirical and *ab initio* methods of electronic structure computation.

Problems

- 9.1** Write the valence bond wavefunction of a P_2 molecule. Why is P_4 a stable form of molecular phosphorus?
- 9.2** Predict, on the basis of valence bond theory, whether you would expect SO_2 to be linear or bent.
- 9.3** Write the valence bond wavefunction of CH_4 based on hybrid orbitals h on the carbon atom.
- 9.4** The structure of the visual pigment retinal is shown in (1). Label each atom with its state of hybridization and specify the composition of each of the different type of bond.



1 Retinal

- 9.5** Benzene is commonly regarded as a resonance hybrid of the two Kekulé structures, but other possible structures can also contribute. Draw three other structures in which there are only covalent π bonds (allowing for bonding between some non-adjacent C atoms) and two structures in which there is one ionic bond. Why may these structures be ignored in simple descriptions of the molecule?
- 9.6** Suppose that the π -electron molecular orbitals of naphthalene can be represented by the wavefunctions of a particle in a two-dimensional rectangular box. What are the parities of the occupied orbitals?

- 9.7** Draw diagrams to show the various orientations in which a p orbital and a d orbital on adjacent atoms may form bonding and antibonding molecular orbitals.
- 9.8** Three biologically important diatomic species, either because they promote or inhibit life, are (a) CO, (b) NO, and (c) CN. The first binds to haemoglobin, the second is a neurotransmitter, and the third interrupts the respiratory electron-transfer chain. Their biochemical action is a reflection of their orbital structure. Deduce their ground-state electron configurations. For heteronuclear diatomic molecules, a good first approximation is that the energy level diagram is much the same as for homonuclear diatomic molecules.

- 9.9** The existence of compounds of the noble gases was once a great surprise and stimulated a great deal of theoretical work. Sketch the molecular orbital energy level diagram for XeF and deduce its ground-state electron configurations. Is XeF likely to have a shorter or longer bond than XeF⁺?

- 9.10** Construct the molecular-orbital energy level diagrams of (a) ethene and (b) ethyne on the basis that the molecules are formed from the appropriately hybridized CH_2 or CH fragments.

- 9.11** Deduce the parities of the six π -orbitals of benzene.

- 9.12** Many of the colours of vegetation are due to electronic transitions in conjugated π -electron systems. In the *free-electron molecular orbital* (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length L . (a) Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict the minimum excitation energy of the molecule. (b) In many cases, an extra half bond-length is often added at each end of the box. The tetraene $\text{CH}_2=\text{CH}=\text{CH}=\text{CH}=\text{CH}_2$ can therefore be treated as a box of length $8R$, where

$R = 140$ pm. Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO.

9.13 The FEMO theory (Problem 9.12) of conjugated molecules is crude and marginally better results are obtained with simple Hückel theory. (a) For a linear conjugated polyene with each of N carbon atoms contributing an electron in a $2p$ orbital, the energies E_k of the resulting π molecular orbitals are given by:

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{N+1} \quad k = 1, 2, 3, \dots, N$$

Use this expression to estimate the resonance integral β for the series consisting of ethene, butadiene, hexatriene, and octatetraene given that ultraviolet absorptions from the HOMO, which is a bonding π orbital, to the LUMO, which is an antibonding π^* orbital, occur at 61 500, 46 080, 39 750, and 32 900 cm^{-1} , respectively. (b) Calculate the π -electron delocalization energy, $E_{\text{deloc}} = E_{\pi} - n(\alpha + \beta)$, of octatetraene, where E_{π} is the total π -electron binding energy and n is the total number of π -electrons.

9.14 For monocyclic conjugated polyenes (such as cyclobutadiene and benzene) with each of N carbon atoms contributing an electron in a $2p$ orbital, Hückel theory gives the following expression for the energies E_k of the resulting π molecular orbitals

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{N+1} \quad k = 0, \pm 1, \pm 2, \pm 3, \dots \left[\begin{array}{l} \pm \frac{1}{2}N \text{ (even } N) \\ \pm \frac{1}{2}(N-1) \text{ (odd } N) \end{array} \right], \dots$$

Calculate the energies of the π molecular orbitals of benzene and cyclooctatetraene. Comment on the presence or absence of degenerate energy levels. (b) Calculate and compare the delocalization energies of benzene and hexatriene using the expression from the preceding problem. What do you conclude from your results? (c) Calculate and compare the delocalization energies of cyclooctatetraene and (linear) octatetraene. Are your conclusions for this pair of molecules the same as for the pair of molecules investigated in part (b)?

9.15 By setting up and solving the secular determinant, use Hückel theory to find the energies of the three π orbitals of the propenyl radical, C_3H_3 . Suggest descriptions for each of the orbitals.

9.16 Predict the electronic configurations of (a) the benzene anion, (b) the benzene cation. Estimate the π -bond energy in each case.

Projects

The symbol † indicates that calculus is required.

9.1† Here you are invited to explore hybrid orbitals in more quantitative detail. Mathematical functions are said to be orthogonal if the integral of their product is zero. (a) Show that the orbitals $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x - p_y + p_z$ are orthogonal. Each atomic orbital individually normalized to 1. Also, note that: (i) s and p orbitals are orthogonal and, (ii) p orbitals with perpendicular orientations are orthogonal. (b) Show that the sp^2 hybrid orbital $(s + 2^{1/2}p)/3^{1/2}$ is normalized to 1 if the s and p orbitals are each normalized to 1. (c) Find another sp^2 hybrid orbital that is orthogonal to the hybrid orbital in part (b).

9.2† Show, if overlap is ignored, (a) that any molecular orbital expressed as a linear combination of two atomic orbitals may be written in the form $\psi = \psi_A \cos \theta + \psi_B \sin \theta$, where θ is a parameter that varies between 0 and $\pi/2$, and (b) that if ψ_A and ψ_B are orthogonal and normalized to 1, then ψ is also normalized to 1. (c) To what values of θ do the bonding and antibonding orbitals in a homonuclear diatomic molecule correspond?

9.3† Now you are invited to explore orbital overlap and overlap integrals in detail. (a) Without doing a calculation, sketch how the overlap between an $1s$ orbital and an $1s$ orbital

FOCUS 10

Molecular interactions

Atoms and molecules with complete valence shells are able to interact with one another even though all their valences are satisfied. They attract one another over a range of several atomic diameters and they repel one another when pressed together. These residual interactions are highly important. They account, for instance, for the condensation of gases to liquids and the structures of molecular solids. All organic liquids and solids, ranging from small molecules such as benzene to virtually infinite cellulose and the polymers from which fabrics are made, are bound together by the cohesive, nonbonding interactions explored here. These interactions are also responsible for the structural organization of biological macromolecules, for they pin molecular building blocks—such as polypeptides, polynucleotides, and lipids—together in the arrangement essential to their proper physiological function.

10A Electric properties of molecules

Molecular interactions can be traced to various aspects of the electron distributions in the interacting species and the shapes of molecules. This Topic is an account of the electric properties of individual molecules, including their 'electric dipole moments' and 'polarizabilities'. They reflect the degree to which the nuclei of atoms exert control over the electrons in a molecule, either by causing electrons to accumulate in particular regions or by permitting them to respond more or less strongly to applied electric fields.

10A.1 Electric dipole moments; 10A.2 Dipole moments of polyatomic molecules; 10A.3 Polarizabilities

10B Interactions between molecules

All liquids and solids are bound together by one or more of the cohesive interactions explored in this Topic, which concentrates on 'van der Waals interactions', 'hydrogen bonding', and the 'hydrophobic effect'. The strengths of the various van der Waals interactions are related to the dipole moments and polarizabilities introduced in Topic 10A.

10B.1 Interactions between partial charges; 10B.2 Charge-dipole interactions; 10B.3 Dipole-dipole interactions; 10B.4 Dipole-induced dipole interactions; 10B.5 Dispersion interactions; 10B.6 Hydrogen bonding; 10B.7 The hydrophobic effect; 10B.8 Modelling the total interaction

Web resource What is an application of this material?

Molecular interactions affect the efficiency of binding of a drug, a small molecule or protein, to a specific receptor site of a target molecule, such as a larger protein or nucleic acid. The chemical result of the formation of this assembly is the inhibition of the progress of disease. See *Impact 8* on the website of this book.

TOPIC 10A

Electric properties of molecules

► Why do you need to know this material?

The interactions responsible for the formation of condensed phases and large assemblies arise from the electric properties of molecules, so to understand bulk properties you need to know how these electrical properties are related to the electronic structures of molecules.

► What is the key idea?

The nuclei of atoms exert control over the electrons in a molecule, and can cause electrons to accumulate in particular regions, or permit them to respond more or less strongly to external fields.

► What do you need to know already?

You need to be familiar with vectors (*The chemist's toolkit* 23 and 24 in Topics 7D and 8D, respectively), molecular geometry (*The chemist's toolkit* 26 in Topic 9A), and the molecular orbital theory of polyatomic molecules (Topic 9D).

The electric properties of molecules, specifically the distribution of electric charge in them and the response of their electron distribution to electric fields, are responsible for many of the properties of bulk matter. One property, the 'electric dipole moment' turns out to be central to this discussion.

10A.1 Electric dipole moments

An electric dipole consists of two charges Q and $-Q$ separated by a distance l . A **point electric dipole** is an electric dipole in which l is very small compared with the distance to the observer. The electric dipole

moment is a vector μ (1) that points from the negative charge to the positive charge and has a magnitude given by

$$\mu = Ql$$

Magnitude of the electric dipole moment [definition] (1)

(See *The Chemist's toolkit* 23 in Topic 7D for more about vectors.) Although the SI units of dipole moment are coulomb metres (C m), it is still commonly reported in the non-SI unit debye, D, named after Peter Debye, a pioneer in the study of dipole moments of molecules:

$$1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m} \quad (2)$$

The magnitude of the dipole moment formed by a pair of charges $+e$ and $-e$ separated by 100 pm is 1.6×10^{-29} C m, corresponding to 4.8 D. The magnitudes of the dipole moments of small molecules are typically about 1 D.

A note on good practice The dipole is the electrical entity itself; the dipole moment is a measure of that dipole's electrical strength and is a vector. In casual conversation chemists typically refer to the 'dipole moment' when they actually mean its magnitude.

A **polar molecule** has a permanent electric dipole moment arising from the partial charges on its atoms (Topic 9C). A **nonpolar molecule** has no permanent electric dipole moment. All heteronuclear diatomic molecules are polar because the difference in electronegativities of their two atoms results in nonzero partial charges. Thus, the magnitudes of the dipole moments of HCl and HI are 1.08 D and 0.42 D, respectively (Table 10A.1). A very approximate relation between the magnitude of the dipole moment and the difference $\Delta\chi$ of Pauling electronegativities (Table 9C.1) χ_A and χ_B of two atoms A and B, is

$$\mu/D \approx \chi_A - \chi_B = \Delta\chi \quad (3)$$

Magnitude of the dipole moment and electronegativity difference

Table 10A.1

Dipole moments, polarizabilities, and polarizability volumes

	μ/D	$\alpha/(10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^3)$	$\alpha'/(10^{-30} \text{ m}^3)$
Ar	0	1.85	1.66
CCl ₄	0	11.7	10.3
C ₆ H ₆	0	11.6	10.4
H ₂	0	0.911	0.819
H ₂ O	1.85	1.65	1.48
NH ₃	1.47	2.47	2.22
HCl	1.08	2.93	2.63
HBr	0.80	4.01	3.61
HI	0.42	6.06	5.45

Brief illustration 10A.1 Dipole moment and electronegativity

The electronegativities of hydrogen and bromine are 2.1 and 2.8, respectively. The difference is 0.7, so the magnitude of the electric dipole moment of HBr is predicted to be about 0.7 D. The experimental value is 0.80 D.

Self-test 10A.1

What is the magnitude of the dipole moment of a C—H fragment in an organic molecule, which atom lies at the negative end of the dipole?

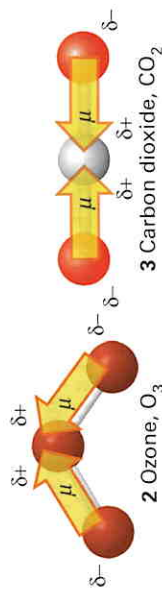
Answer: $\mu = 0.4 \text{ D}$; C

Because it attracts the electrons more strongly, the more electronegative atom is usually the negative end of the dipole. However, there are exceptions, particularly when antibonding orbitals are occupied. Because electrons in antibonding orbitals tend to be found closer to the less electronegative atom, they contribute a negative partial charge to that atom. If this contribution is larger than the opposite contribution from the electrons in bonding orbitals, then the net effect will be a small negative partial charge on the less electronegative atom. An example is CO (see Fig. 4 in Topic 9D), in which antibonding orbitals are occupied: its dipole moment is small (0.12 D) but the negative end of the dipole is on the C atom even though oxygen is more electronegative than carbon.

10A.2 Dipole moments of polyatomic molecules

Molecular symmetry is of the greatest importance in deciding whether a polyatomic molecule is polar or not. Indeed, molecular symmetry is more

important than the question of whether or not the atoms in the molecule belong to the same element. Homonuclear polyatomic molecules may be polar if they have low symmetry and the atoms are in inequivalent positions. For instance, the angular molecule ozone, O₃ (2), is homonuclear; however, it is polar because the central O atom is different from the outer two (it is bonded to two atoms, they are bonded only to one); moreover, the **bond dipoles**, the dipole moments associated with each bond, make an angle to each other and do not cancel. Heteronuclear polyatomic molecules may be nonpolar if they have high symmetry, because individual bond dipoles may then cancel. The heteronuclear linear triatomic molecule CO₂, for example, is nonpolar because, although there are partial charges on all three atoms, the dipole moment associated with the OC bond points in the opposite direction to the dipole moment associated with the CO bond, and the two cancel (3).

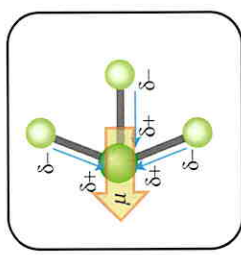


Example 10A.1

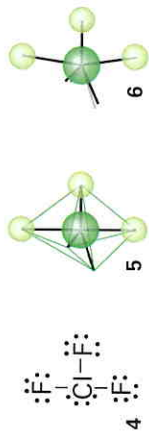
Assessing the polarity of a molecule

Is a ClF₃ molecule polar or nonpolar?

Collect your thoughts Judge whether the bonds are polar: if they are not, the molecule is nonpolar. Then predict the shape of the molecule by using the VSEPR theory (*The chemist's toolkit* 26 in Topic 9A). Finally, judge whether the bond dipoles, if any, cancel. If they do (as in CO₂ or a tetrahedral molecule), the molecule is nonpolar. If they do not cancel, then the molecule is polar.



The solution The electronegativities of Cl and F are 3.0 and 4.0, respectively; so each Cl—F fragment is polar with a dipole moment of magnitude of about 1 D. To apply VSEPR theory, note that the Lewis structure is shown in (4), with three atoms attached to the Cl atom and two lone pairs that are likely to be arranged as a trigonal bipyramid (5). The repulsion between the two lone pairs is least if they occupy the equatorial positions and move apart slightly. The three F atoms lie at the remaining positions, with the result that the molecule has a distorted T-shape (6). The three bond dipole moments do not cancel in this arrangement, so the molecule is polar.



Comment Electronegativity differences are a cautious but unreliable guide because atoms of the same element that lie in inequivalent locations might have different partial charges. A better estimate of molecular dipole moments can be calculated with software that uses the computational methods described in Topic 9D.

Self-test 10A.2

Is an SF_4 molecule polar?

Answer: Yes

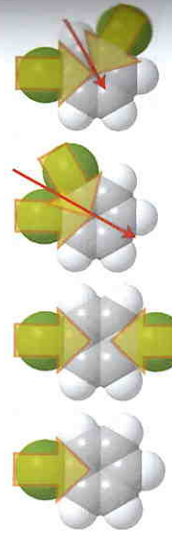
The dipole moment of a polyatomic molecule can be resolved, at least approximately, into contributions from various groups of atoms in the molecule and the directions in which these individual contributions lie (Fig. 1). Consider 1,4-dichlorobenzene and 1,2-dichlorobenzene and focus on the spatial arrangement of the strong C—Cl bond dipoles. 1,4-Dichlorobenzene is nonpolar by symmetry on account of the cancellation of two equal but opposing C—Cl moments, exactly as in carbon dioxide. (Note that the smaller C—H moments also cancel.) 1,2-Dichlorobenzene, however, has a dipole moment which is approximately the resultant of two chlorobenzene dipole moments arranged at 60° to each other. (The small C—H moments at positions 4 and 5 also contribute, though less importantly, to the net dipole moment of the molecule.) This technique of 'vector addition' (*The chemist's toolkit 24* in Topic 8D) can be applied with fair success to other series of related molecules, and the resultant μ_{res} of two dipole moments of magnitude μ_1 and μ_2 that make an angle θ to each other (7) is approximately

$$\mu_{\text{res}} \approx (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta)^{1/2} \quad (4)$$

This relation is not exact because the dipole moments of molecules are not strictly additive.

Brief illustration 10A.2 The resultant dipole

To estimate the ratio of the electric dipole moments of *ortho* (1,2-) and *meta* (1,3-) similarly disubstituted benzenes note that for the *ortho* isomer $\theta = 60^\circ$ and for the *meta* isomer



(a)	$\mu_{\text{obs}} = 1.57 \text{ D}$	(b)	$\mu_{\text{calc}} = 0$	(c)	$\mu_{\text{calc}} = 2.7 \text{ D}$	(d)	$\mu_{\text{calc}} = 1.6 \text{ D}$
			$\mu_{\text{obs}} = 0$		$\mu_{\text{obs}} = 2.25 \text{ D}$		$\mu_{\text{obs}} = 1.48 \text{ D}$

Fig. 1 The dipole moments of the dichlorobenzene isomers can be obtained approximately by vector addition of two chlorobenzene dipole moments (1.57 D). The result for the *para* isomer is exact (by symmetry).

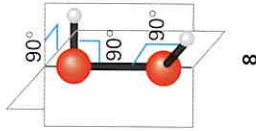
$\theta = 120^\circ$. The C—X group dipole moments are the same, so use eqn 4 with $\mu_1 = \mu_2$ in the form $\mu_{\text{res}} = 2^{1/2}\mu(1 + \cos\theta)^{1/2}$ in each case. Then the ratio is

$$\frac{\mu(\text{ortho})}{\mu(\text{meta})} = \frac{2^{1/2}\mu(1 + \cos 60^\circ)^{1/2}}{2^{1/2}\mu(1 + \cos 120^\circ)^{1/2}} = \frac{(3/2)^{1/2}}{(1/2)^{1/2}} = 3^{1/2} \approx 1.7$$

This calculation ignores the effects of the weaker C—H moments.

Self-test 10A.3

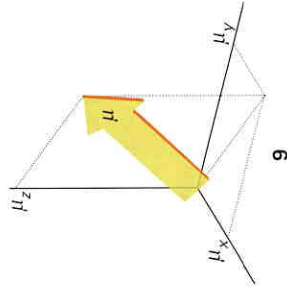
The O—H bond dipole moment is approximately 1.4 D. Estimate the dipole moment of a non-planar conformation of the H_2O_2 molecule with the conformation depicted in (8).



Answer: 2.0 D

Atoms in molecules in general have partial charges, and a better approach to the calculation of dipole moments is to take into account the locations and magnitudes of the partial charges on all the atoms. These partial charges are included in the output of many molecular structure software packages. The programs calculate the dipole moments of the molecules by noting that the electric dipole moment vector, μ , has three components, μ_x , μ_y , and μ_z (9). The direction of μ shows the orientation of the dipole in the molecule and the length of the vector is

its magnitude, μ . In common with all vectors, the magnitude is related to the three components by (*The chemist's toolkit 23* in Topic 7D)



$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (5a)$$

To calculate μ , the three components must be calculated and then substituted into this expression. To calculate the x -component, for instance, the partial charge on each atom and the atom's x -coordinate relative to a point in the molecule are used to form the sum

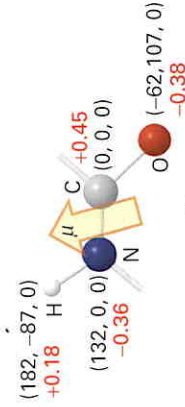
$$\mu_x = \sum_j Q_j x_j \quad (5b)$$

Here Q_j is the partial charge of atom j , x_j is the x -coordinate of atom j , and the sum is over all the atoms in the molecule. Analogous expressions are used for the y - and z -components. For an electrically neutral molecule, the origin of the coordinates is arbitrary, so it is best chosen to simplify the measurements.

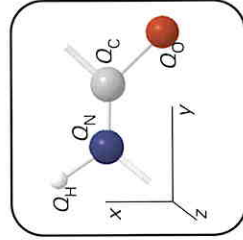
Example 10A.2

Calculating a molecular dipole moment

Estimate the magnitude and orientation of the electric dipole moment of the amide group shown in (10) by using the partial charges (as multiples of e) and the locations of the atoms shown, with distances in picometres.



Collect your thoughts Use eqn 5b to calculate each of the components of the dipole moment vector. Then use eqn 5a to assemble the three components into the magnitude of the dipole moment.



The solution The expression for μ_x is

$$\begin{aligned} \mu_x &= (-0.36e) \times (132 \text{ pm}) + (0.45e) \times (0 \text{ pm}) \\ &\quad + (0.18e) \times (182 \text{ pm}) + (-0.38e) \times (-62.0 \text{ pm}) \\ &= 8.8e \text{ pm} \\ &= 8.8 \times (1.602 \times 10^{-19} \text{ C}) \times (10^{-12} \text{ m}) = 1.4 \times 10^{-30} \text{ C m} \end{aligned}$$

corresponding to $\mu_x = +0.42 \text{ D}$. The expression for μ_y is:

$$\begin{aligned} \mu_y &= (-0.36e) \times (0 \text{ pm}) + (0.45e) \times (0 \text{ pm}) \\ &\quad + (0.18e) \times (-87 \text{ pm}) + (-0.38e) \times (107 \text{ pm}) \\ &= -56e \text{ pm} \\ &= -9.0 \times 10^{-30} \text{ C m} \end{aligned}$$

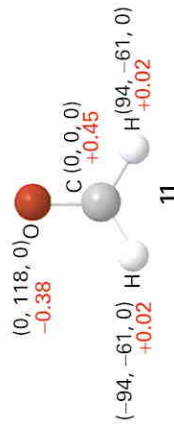
corresponding to $\mu_y = -2.7 \text{ D}$. The amide group is planar, so $\mu_z = 0$. Then, from eqn 5a,

$$\mu = [(0.42 \text{ D})^2 + (-2.7 \text{ D})^2]^{1/2} = 2.7 \text{ D}$$

The orientation of the dipole moment is represented by arranging an arrow of length 2.7 units of length to have x , y , and z components of 0.42, -2.7 , and 0 units; the orientation is superimposed on (10).

Self-test 10A.4

Calculate the magnitude of the electric dipole moment of methanal (formaldehyde) by using the information in (11).



Answer: 3.2 D

10A.3 Polarizabilities

A nonpolar molecule may acquire a temporary induced dipole moment, μ^* , as a result of the influence of an electric field generated by a nearby ion or polar molecule. The field distorts the electron distribution of the molecule, and gives rise to an electric dipole. The molecule is said to be *polarizable*. The magnitude of the induced dipole moment is proportional to the strength of the electric field, \mathcal{E} , so

$$\mu^* = \alpha \mathcal{E} \quad (6)$$

Polarizability (definition)

The proportionality constant α is the **polarizability** of the molecule. It has the following features:

- The greater the polarizability of the molecule, the greater is the distortion caused by a given strength of electric field.
- If the molecule has few electrons (such as N_2), they are tightly controlled by the nuclear charges and the polarizability of the molecule is low. If the molecule contains large atoms with electrons some distance from the nucleus (such as I_2), the nuclear control is less and the polarizability of the molecule may be high.
- The polarizability is low when the ionization energy of the molecule is high: the more tightly the electrons are bound, the more difficult it is to distort the electron distribution around the nuclei.
- The polarizability depends on the orientation of the molecule with respect to the field unless the molecule is tetrahedral (such as CCl_4), octahedral (such as SF_6), or icosahedral (such as C_{60}). Atoms and tetrahedral, octahedral, and icosahedral molecules have isotropic (orientation independent) polarizabilities; all other molecules have anisotropic (orientation dependent) polarizabilities.

The polarizabilities reported in Table 10A.1 are given as **polarizability volumes**, α' , which are often easier to use than the polarizabilities themselves:

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0} \quad \text{Polarizability volume (definition)} \quad (7)$$

Checklist of key concepts

- 1 An **electric dipole** consists of two electric charges $+Q$ and $-Q$ separated by a distance l .
- 2 The **electric dipole moment** μ is a vector that points from the negative charge to the positive charge of a dipole; its magnitude is μ .
- 3 Molecular dipole moments are approximately additive (as vectors).

The polarizability volume has the dimensions of volume (hence its name) and is comparable in magnitude to the volume of the molecule.

Brief illustration 10A.3 The induced dipole

To assess the strength of electric field required to induce an electric dipole moment of $1.0 \mu D$ in a molecule of polarizability volume $1.0 \times 10^{-29} \text{ m}^3$ (like CCl_4), write eqn 6 as $\mathcal{E} = \mu^*/\alpha$ and substitute the data. Use the fact that $1 D = 3.336 \times 10^{-30} \text{ C m}$ and convert the polarizability volume to polarizability by using eqn 7 in the form $\alpha = 4\pi\epsilon_0\alpha'$. Then

$$\begin{aligned} \mathcal{E} &= \frac{\mu^*}{\alpha} \\ &= \frac{3.336 \times 10^{-30} \times 1.0 \times 10^{-6} \text{ C m}}{4\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.0 \times 10^{-29} \text{ m}^3)} \\ &= \frac{3.3 \dots \times 10^{-36} \text{ C m}}{4\pi \times (8.854 \times 10^{-12}) \times (1.0 \times 10^{-29}) \text{ J}^{-1} \text{ C}^2 \text{ m}^2} \\ &= 3.0 \times 10^3 \text{ J C}^{-1} \text{ m}^{-1} = 3.0 \text{ kV m}^{-1} \end{aligned}$$

Self-test 10A.5

The polarizability volume of H_2O is $1.48 \times 10^{-30} \text{ m}^3$. What is the magnitude of the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength $1.0 \times 10^5 \text{ V m}^{-1}$?

Answer: $4.9 \mu D$

□ 4 A **polar molecule** is a molecule with a permanent electric dipole moment; the magnitude of a dipole moment is the product of the partial charge and the separation.

□ 5 The **polarizability** is a measure of the ability of an electric field to induce a dipole moment in a molecule.

TOPIC 10B

Interactions between molecules

► Why do you need to know this material?

A major feature of chemistry is its ability to relate bulk properties to the properties of individual molecules. To make this connection, you need to understand the many types of molecular interactions responsible for the formation of condensed phases and large molecular assemblies.

► What is the key idea?

Attractive interactions result in cohesion, but repulsive interactions prevent the complete collapse of matter to nuclear densities.

► What do you need to know already?

You need to be familiar with the Coulomb interaction (*The chemist's toolkit* 14 in Topic 5H) and the origin of the electric dipole moments and polarizabilities of molecules (Topic 10A). One section draws on the thermodynamic arguments introduced in Topic 3D.

The interactions between or within molecules (for example, within macromolecules) include the attractive and repulsive interactions involving partial electric charges and electron clouds of polar and non-polar molecules or functional groups, and the repulsive interactions that prevent the complete collapse of matter to densities as high as those characteristic of atomic nuclei. The repulsive interactions arise from the exclusion of electrons from regions of space where the orbitals of closed-shell species overlap. These attractive and repulsive interactions are called **van der Waals interactions**. The term excludes interactions that result from the formation of covalent or ionic bonds and is often restricted to interactions for which the potential energy is inversely proportional to the sixth power of the separation of the molecules. Table 10B.1 summarizes the strengths and distance dependence of the attractive interactions considered in the following sections.

10B.1 Interactions between partial charges

Atoms in molecules in general have partial charges (Topic 10A). When charges are separated by a vacuum, they attract or repel each other in accord with

Table 10B.1

Potential energy of molecular interactions

Interaction type	Distance dependence of potential energy	Typical energy $V/(kJ \text{ mol}^{-1})$	Comment
Ion-ion	$1/r$	250	Only between ions
Ion-dipole	$1/r^2$	15	Between stationary polar molecules
Dipole-dipole	$1/r^3$	2	Between rotating polar molecules
London (dispersion)	$1/r^6$	0.3	Between all types of molecules and ions
Hydrogen bonding	$1/r^6$	2	The interaction is for X—H—Y and occurs on contact for X, Y = N, O, or F.

Coulomb's law (with the potential energy E_p denoted V , as is conventional in this context):

$$V(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \quad (1a)$$

Interaction between charges

where Q_1 and Q_2 are the charges and r is their separation. However, it is possible that other parts of the molecule, or other molecules, lie between the charges, and decrease the strength of the interaction. The simplest procedure for taking into account these very complicated effects is to treat the medium surrounding the charges as a uniform substance, and to write

$$V(r) = \frac{Q_1 Q_2}{4\pi\epsilon r} \quad (1b)$$

where ϵ is the permittivity of the medium (see *The chemist's toolkit 14* in Topic 5H): a high permittivity means that the medium reduces the strength of the interaction between the two charges. As explained in the toolkit, the permittivity is usually expressed as a multiple of the vacuum permittivity by writing $\epsilon = \epsilon_r \epsilon_0$, where the dimensionless quantity ϵ_r is the 'relative permittivity'. The effect of the medium can be very large: for water at 25 °C, $\epsilon_r = 78$, so the potential energy of two charges separated by bulk water is reduced by nearly two orders of magnitude compared to the value it would have if the charges were separated by a vacuum (Fig. 1).

Brief illustration 10B.1 The interaction energy of two partial charges

The energy of interaction between a partial charge of -0.36 (that is, $Q_1 = -0.36e$) on the N atom of an amide group and the partial charge of $+0.45$ ($Q_2 = +0.45e$) on the carbonyl C atom

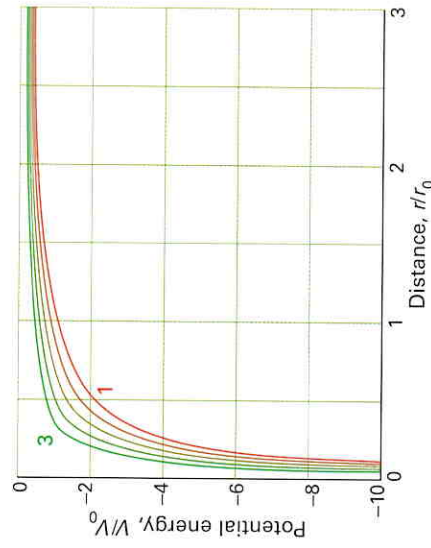


Fig. 1 The Coulomb potential for two charges and its dependence on their separation. The two curves correspond to different relative permittivities (1 for a vacuum, 3 for a fluid).

at a distance of 3.0 nm, on the assumption that the medium between them is a vacuum, is

$$\begin{aligned} V &= \frac{(-0.36e) \times (0.45e)}{4\pi\epsilon_0 \times (3.0 \text{ nm})} \\ &= -\frac{0.36 \times 0.45 \times (1.602 \times 10^{-19} \text{ C})^2}{4\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (3.0 \times 10^{-9} \text{ m})} \\ &= -1.2 \times 10^{-20} \text{ J, or } -12 \text{ zJ} \end{aligned}$$

where ϵ_0 is the vacuum permittivity. This energy (after multiplication by Avogadro's constant) corresponds to -7.5 kJ mol^{-1} . However, if the medium has a relative permittivity $\epsilon_r = \epsilon/\epsilon_0 = 3.5$, then the interaction energy is reduced by that factor, to -2.1 kJ mol^{-1} .

Self-test 10B.1

Repeat the calculation for bulk water as the medium.

Answer: $-0.096 \text{ kJ mol}^{-1}$

10B.2 Charge-dipole interactions

The potential energy when a dipole μ_1 is in the presence of a charge Q_2 is calculated by taking into account the interaction of the latter charge with the two charges of the dipole, one resulting in a repulsion and the other an attraction. As shown in the following *Justification*, the result for the arrangement shown in (1) is:

$$V(r) = -\frac{\mu_1 Q_2 \cos\theta}{4\pi\epsilon_0 r^2} \quad (2a)$$

Charge-dipole interaction

Justification 10B.1

The interaction energy of a charge and a dipole. Consider the arrangement in (1): the charge Q_2 is collinear with a dipole with charges Q_1 and $-Q_1$. The following steps are taken to arrive at eqn 2a:

Step 1: Account for all attractions and repulsions

The Coulomb potential energy of the charges is

$$\begin{aligned} V(r) &= \underbrace{\frac{Q_2 Q_1}{4\pi\epsilon_0 (r + \frac{1}{2}l)}}_{\text{Repulsion between } Q_2 \text{ and } +Q_1} - \underbrace{\frac{Q_2 Q_1}{4\pi\epsilon_0 (r - \frac{1}{2}l)}}_{\text{Attraction between } Q_2 \text{ and } -Q_1} \\ &= \frac{Q_2 Q_1}{4\pi\epsilon_0 (1 + l/2r)} - \frac{Q_2 Q_1}{4\pi\epsilon_0 (1 - l/2r)} \end{aligned}$$

Step 2: Simplify the expression for cases where r is large than the distance of the dipole. In the sense that $l/2r \ll 1$, then the terms $1/(1+l/2r)$ and $1/(1-l/2r)$ in the previous expression can be simplified by using the approximations (*The chemist's toolkit 6* in Topic 1C)

$$\begin{aligned} \frac{1}{1+x} &\approx 1-x \\ \frac{1}{1-x} &\approx 1+x \end{aligned}$$

It follows that

$$\frac{1}{\left(1 + \frac{l}{2r}\right)} \approx 1 - \frac{l}{2r} \quad \frac{1}{\left(1 - \frac{l}{2r}\right)} \approx 1 + \frac{l}{2r}$$

and that the potential energy of interaction can be written as in eqn 2a:

$$V(r) = \frac{Q_2 Q_1}{4\pi\epsilon_0 r^2} \left\{ \left(1 - \frac{l}{2r}\right) - \left(1 + \frac{l}{2r}\right) \right\} = -\frac{Q_2 Q_1 l}{4\pi\epsilon_0 r^2} = -\frac{\mu_1 Q_2}{4\pi\epsilon_0 r^2}$$

$\mu_1 = Q_1 l$

A similar calculation for the more general orientation shown in (2) gives

$$V(r) = -\frac{\mu_1 Q_2 \cos\theta}{4\pi\epsilon_0 r^2} \quad (2b)$$

Charge-dipole interaction

This expression is interpreted as follows:

- If Q_2 is positive, the energy is lowest when $\theta = 0$ (when $\cos\theta = 1$), because then the negative charge of the dipole lies closer than the positive charge to the point charge and the attraction outweighs the repulsion.
- The potential energy is zero when $\theta = 90^\circ$ because then Q_2 is equidistant from the two charges of the dipole and their effects cancel.
- The interaction energy decreases more rapidly with distance than that between two point charges (as $1/r^2$ rather than $1/r$) because, from the viewpoint of the single charge, the two charges of the dipole seem to merge and cancel as the distance r increases.

Physical interpretation

Brief illustration 10B.2 The energy of interaction of a point charge and a dipole

Consider a Li^+ ion and a water molecule ($\mu = 1.85 \text{ D}$) separated by 1.0 nm, with the point charge on the ion and the dipole of the molecule arranged as in (1). The energy of interaction is given by eqn 2b as

$$\begin{aligned} V &= -\frac{Q_1 \mu_{\text{H}_2\text{O}}}{4\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.0 \times 10^{-9} \text{ m})^2} \\ &= -8.9 \times 10^{-21} \text{ J, or } -8.9 \text{ zJ} \end{aligned}$$

This energy corresponds (after multiplication by Avogadro's constant) to -5.4 kJ mol^{-1} .

Self-test 10B.2

Consider the arrangement in (1), with a Li^+ ion and a water molecule separated by 300 pm. Calculate the molar energy required to reverse the orientation of the dipole moment of the water molecule.

Answer: 119 kJ mol^{-1}

10B.3 Dipole-dipole interactions

The interaction energy of two dipoles μ_1 and μ_2 in the orientation shown in (3) is calculated in a similar way, by taking into account all four charges of the two dipoles. The outcome is¹

$$V(r, \theta) = \frac{\mu_1 \mu_2 (1 - 3 \cos^2 \theta)}{4\pi\epsilon_0 r^3} \quad (3)$$

Dipole-dipole interaction (fixed orientations)

¹ For a derivation, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

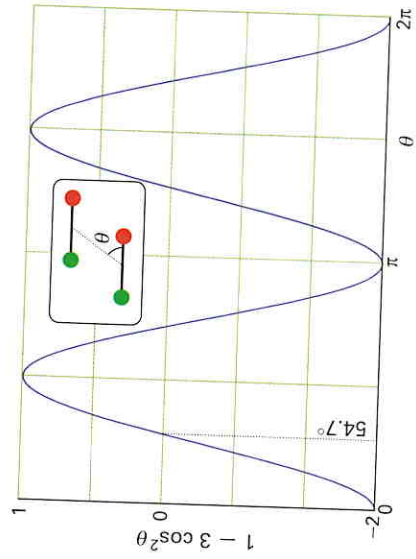
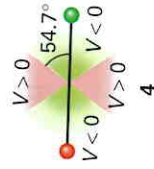


Fig. 2 The angular dependence of the potential energy of two parallel electric dipoles.

Figure 2 shows the angular dependence of the potential energy, and illustrates the following features of eqn 3:

- The potential energy decreases even more rapidly than in eqn 2 (as $1/r^3$ instead of $1/r^2$) because the charges of *both* dipoles seem to merge as the separation of the dipoles increases.
- The angular factor takes into account how the like or opposite charges come closer to one another as the relative orientation of the dipoles is changed.
- The energy is lowest when $\theta = 0$ or 180° (when $1 - 3 \cos^2 \theta = -2$), because opposite charges then lie closer together than like charges.
- The potential energy is negative (attractive) in some orientations when $\theta < 54.7^\circ$ (the angle at which $1 - 3 \cos^2 \theta = 0$, corresponding to $\cos \theta = 1/3^{1/2}$) because opposite charges are closer than like charges.
- The potential energy is positive (repulsive) when $\theta > 54.7^\circ$ because then like charges are closer than unlike charges.

- The potential energy is zero on the lines at 54.7° and $180 - 54.7 = 125.3^\circ$ because at those angles the two attractions and the two repulsions cancel (4).



Brief illustration 10B.3 The dipole-dipole interaction

To calculate the potential energy of the dipolar interaction between two amide groups separated in a vacuum by 3.0 nm

with $\theta = 180^\circ$, take $\mu_1 = \mu_2 = 2.7$ D, corresponding to 9.0×10^{-30} C m, and find

$$V(3.0 \text{ nm}, 180^\circ) = \frac{\mu_1 \mu_2 \cos^2 \theta}{4\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (3.0 \times 10^{-9} \text{ m})^3} \times (-2)$$

$$= \frac{(9.0 \times 10^{-30} \text{ C m})^2 \times (-2)}{4\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (3.0 \times 10^{-9} \text{ m})^3} \text{ C}^2 \text{ m}^2$$

$$= -5.4 \times 10^{-23} \text{ J, or } -0.054 \text{ zJ}$$

This value corresponds (after multiplication by Avogadro's constant) to -32 J mol^{-1} .

A note on good practice We reiterate the importance of including the units at every stage of the calculation, in part because the correct cancellation helps to monitor whether the calculation has been set up and carried out correctly.

Self-test 10B.3

Repeat the calculation for an amide group and a water molecule separated by 3.5 nm with $\theta = 90^\circ$, in a medium with relative permittivity 3.5.

Answer: -2.1 J mol^{-1}

The average potential energy of interaction between polar molecules that are freely rotating in a fluid (a gas or liquid) is zero because the attractions and repulsions cancel. However, because the interaction between nearby dipoles depends on their relative orientations, the molecules exert forces on each other and therefore do not in fact rotate completely freely, even in a gas. As a result, the lower energy orientations are marginally favoured, so there is a nonzero interaction between rotating polar molecules (Fig. 3). The detailed calculation of the interaction energy at a temperature T is quite complicated, but the final answer is reasonably simple:

$$V(r) = -\frac{2\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0)^2 kT r^6} \quad (4)$$

where k is Boltzmann's constant. The key features of this expression are:

- The interaction between dipoles is an example of a van der Waals interaction that varies as the inverse sixth power of the distance.
- The inverse temperature-dependence ($V \propto 1/T$) reflects the way that at higher temperatures the greater thermal motion overcomes the mutual orientating effects of the dipoles.

Physical interpretation

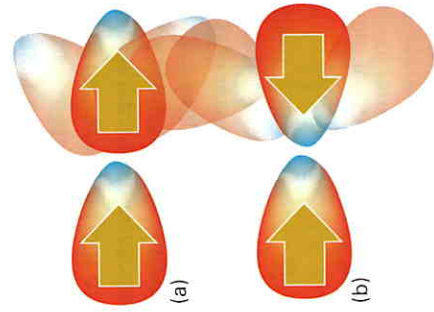


Fig. 3 A dipole-dipole interaction. When a pair of molecules can adopt all relative orientations with equal probability, the favourable orientations (a) and the unfavourable ones (b) cancel, and the average interaction is zero. In an actual fluid, the interactions in (a) slightly predominate.

Brief illustration 10B.4 The dipolar interaction of rotating molecules

At 25°C the average interaction energy for pairs of molecules with $\mu = 1.0$ D when the separation is 0.30 nm is

$$V(0.30 \text{ nm}) = \frac{\mu^2}{3(4\pi \times 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) \times (3.0 \times 10^{-10} \text{ m})^6}$$

$$= -\frac{3.3^2 \times 10^{-120} \text{ C}^4 \text{ m}^4}{3.4\pi \times 8.85^2 \times 1.381 \times 298 \times 3.0^6 \times 10^{-107} \text{ J}^{-1} \text{ C}^2 \text{ m}^2}$$

$$= -1.1 \times 10^{-21} \text{ J, or } -1.1 \text{ zJ}$$

This value corresponds to about -0.6 kJ mol^{-1} . Note that this energy is much less than the energies involved in the making and breaking of chemical bonds.

Self-test 10B.4

Suppose a water molecule ($\mu_1 = 1.85$ D) can rotate 1.0 nm from an amide group ($\mu_2 = 2.7$ D). Calculate the average energy, in units of joules per mole (J mol^{-1}), of their interaction at 25°C .

Answer: -24 J mol^{-1}

10B.4 Dipole-induced dipole interactions

A polar molecule with dipole moment μ_1 can induce a dipole moment in a nearby polarizable molecule (which may itself be either polar or nonpolar) because the partial charges of the polar molecule give rise to an electric field that distorts the second molecule. That induced dipole interacts with the permanent dipole of the first molecule, and the two are

attracted together. The energy of this dipole-induced dipole interaction is

$$V(r) = -\frac{\mu_1^2 \alpha'_2}{4\pi\epsilon_0 r^6} \quad (5)$$

where α'_2 is the polarizability volume of molecule 2 (polarizabilities and polarizability volumes are discussed in Topic 10A). The negative sign shows that the interaction is attractive; note the inverse sixth-order dependence of the energy on the separation. For a molecule with $\mu = 1$ D (such as HCl) near a molecule of polarizability volume $\alpha' = 1.0 \times 10^{-29} \text{ m}^3$ (such as benzene), the average interaction energy is about -0.8 kJ mol^{-1} when the separation is 0.3 nm.

10B.5 Dispersion interactions

What can be said about the interactions between species that have neither a net charge nor a permanent electric dipole moment (such as two Xe atoms in a gas)? Despite the absence of partial charges, uncharged, nonpolar species, such as benzene, hydrogen, and xenon, can form condensed phases. Therefore, they must interact.

The **dispersion interaction**, or **London interaction** (which is named for the German physicist Fritz London, who formulated a theory of the interaction), between nonpolar species arises from the transient dipoles that they possess as a result of fluctuations in the electron density distribution (Fig. 4). Suppose, for instance, that the electrons in one molecule flicker into an arrangement that results in partial positive and negative charges and thus gives it an instantaneous dipole moment μ_1 . While it exists, this dipole can polarize the other molecule and induce in it an instantaneous dipole moment μ_2 . The two dipoles attract each

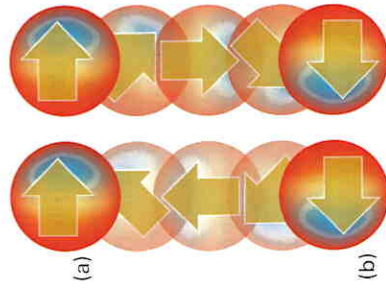


Fig. 4 In the dispersion interaction, an instantaneous dipole on one molecule induces a dipole on another molecule, and the two dipoles then interact to lower the energy. The directions of the two instantaneous dipoles are correlated, and, although they occur in different orientations at different instants, the interaction does not average to zero.

other and the potential energy of the pair is lowered. Although the first molecule will go on to change the size and direction of its dipole (perhaps within 10^{-16} s), the second will follow it; that is, the two dipoles are *correlated* in direction like two meshing gears, with a positive partial charge on one molecule appearing close to a negative partial charge on the other molecule and vice versa. Because of this correlation of the relative positions of the partial charges, and their resulting attraction, the interaction between the two instantaneous dipoles does not average to zero. Instead, it gives rise to a net attractive interaction.

The dispersion interaction is not confined to nonpolar molecules. Polar molecules also interact by a dispersion interaction as well as by dipole-dipole and dipole-induced dipole interactions, for their electron clouds also fluctuate and interact in the same way. Indeed, the dispersion interaction is often dominant. The calculation of the dispersion interaction is quite involved, but a reasonable approximation to the interaction energy is the **London formula**:

$$V(r) = -\frac{3}{2} \times \frac{\alpha'_1 \alpha'_2}{r^6} \times \frac{I_1 I_2}{I_1 + I_2} \quad (6)$$

London formula

where I_1 and I_2 are the ionization energies of the two molecules and α'_1 and α'_2 are their polarizability volumes (Topic 10A); polarizability volumes are related to polarizabilities α by $\alpha = 4\pi\epsilon_0\alpha'$. This expression is interpreted as follows:

- The strength of the dispersion interaction depends on the polarizability of the first molecule because the magnitude of the instantaneous dipole moment μ_1 depends on the looseness of the control that the nuclear charge has over the outer electrons. If that control is loose, the electron distribution can undergo relatively large fluctuations. Moreover, if the control is loose, then the electron distribution can also respond strongly to applied electric fields and hence have a high polarizability. It follows that a high polarizability is a sign of large fluctuations in local electron density.
- The strength also depends on the polarizability of the second molecule, for that polarizability determines how readily a dipole can be induced in molecule 2 by molecule 1. Therefore, it is reasonable to expect $V \propto \alpha'_1 \alpha'_2$, as in eqn 6.
- The interaction is an example of a van der Waals interaction that varies as the inverse sixth power of the distance.
- The potential energy of interaction increases with decreasing ionization energies.

Physical interpretation

The final comment may be puzzling at first sight, for the product of the ionization energies appears in the numerator of the right-hand side of eqn 6. However, broadly speaking, the polarizability is inversely proportional to the ionization energy, so $\alpha'_1 \alpha'_2 \propto (I_1 I_2)^{-1}$, and it then follows that $V \propto (I_1 + I_2)^{-1}$; the potential energy is inversely proportional to the sum of the two ionization energies.

Brief illustration 10B.5 The strength of a dispersion interaction

For two molecules with polarizability volume $1.0 \times 10^{-29} \text{ m}^3$ (as for benzene) with $I = 9.2 \text{ eV}$ (corresponding to $1.5 \times 10^{-18} \text{ J}$) separated by 0.30 nm , noting that $I_1/(I_1 + I_2) = \frac{1}{2}I$ when the ionization energies are the same,

$$\begin{aligned} V(0.30 \text{ nm}) &= -\frac{3}{2} \times \frac{(1.0 \times 10^{-29} \text{ m}^3)^2}{(3.0 \times 10^{-10} \text{ m})^6} \times \frac{1}{2} (1.5 \times 10^{-18} \text{ J}) \\ &= -\frac{1.0^2 \times 1.5 \times 10^{-76} \text{ J m}^6}{\frac{3}{2} \times 3.0^6 \times 10^{-60} \text{ m}^6} = -1.5 \times 10^{-19} \text{ J, or } -150 \text{ zJ} \end{aligned}$$

This value corresponds to about -93 kJ mol^{-1} .

Self-test 10B.5

Estimate the energy of the London interaction for two Ar atoms separated by 1.0 nm . Report the result in units of joules per mole (J mol^{-1}).

Answer: -3.1 J mol^{-1}

Differences in the strength of the dispersion interaction can explain trends in physical properties, such as the melting and boiling points of nonpolar substances. For example, the boiling and melting points of I_2 are higher than those of F_2 , implying that molecular interactions—more specifically, dispersion interactions—more strongly affect I_2 than F_2 . The effect can be traced through eqn 6 to differences in the polarizability of the two substances. As explained in Topic 10A, a molecule has a low polarizability if it has only a few electrons (such as F_2). It is likely to have a high polarizability if it has many electrons (such as I_2). Therefore, dispersion interactions are expected to be stronger between I_2 molecules than between F_2 molecules. As a result, iodine can be expected to have higher transition enthalpies and transition temperatures than fluorine, as is observed.

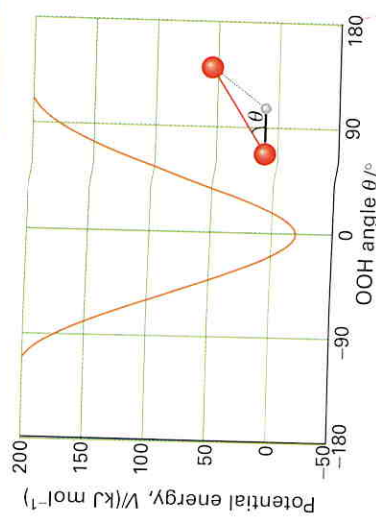


Fig. 5 The variation of the energy of interaction (on the electrostatic model) of a hydrogen bond as the angle between the O—H and :O groups is changed.

the overlap of an orbital on X, ψ_X , and a hydrogen 1s orbital, ψ_{1s} , and the lone pair on Y occupies an orbital on Y, ψ_Y , then when the two molecules are close together, three molecular orbitals can be built from the three atomic orbitals:

$$\psi = c_1\psi_X + c_2\psi_{1s} + c_3\psi_Y$$

One of the molecular orbitals is bonding, one almost nonbonding, and the third antibonding (Fig. 6). These three orbitals need to accommodate four electrons (two from the original X—H bond and two from the lone pair of Y), so two enter the bonding orbital and two enter the nonbonding orbital. The antibonding orbital remains empty, so the net effect—which depends on the precise location of the almost nonbonding orbital—may be a lowering of energy.

Experimental evidence and theoretical arguments have been presented in favour of both the electrostatic and molecular orbital models. Recent experiments suggest that the hydrogen bonds in ice have

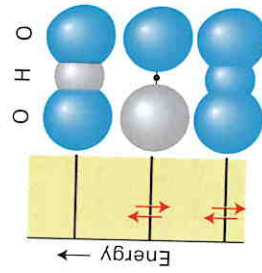


Fig. 6 A schematic portrayal of the molecular orbitals that can be formed from an X, H, and Y orbital and which give rise to an X—H...Y hydrogen bond. The lowest energy combination is fully bonding, the next nonbonding, and the uppermost is antibonding. The antibonding orbital is not occupied by the electrons provided by the X—H bond and the Y lone pair, so the configuration shown may result in a net lowering of energy in certain cases (namely when the X and Y atoms are N, O, or F).

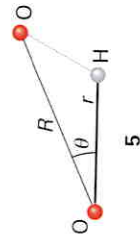
10B.6 Hydrogen bonding

The strongest intermolecular interaction arises from the formation of a **hydrogen bond**, in which a hydrogen atom lies between two strongly electronegative atoms and binds them together. The bond is normally denoted X—H...Y, with X and Y being nitrogen, oxygen, or fluorine. Unlike the other interactions already considered, hydrogen bonding is not universal but is restricted to molecules that contain these atoms. A common hydrogen bond is that formed between O—H groups and O atoms, as in liquid water and ice. The distance dependence of the hydrogen bond is quite different from the other interactions considered so far, and is best regarded as a ‘contact’ interaction, which turns on when the X—H group is in direct contact with the Y atom.

The most elementary description of the formation of a hydrogen bond is that it is the result of a Coulombic interaction between the partly exposed positive charge of a proton bound to an electronegative withdrawing X atom (in the fragment X—H) and the negative charge of a lone pair on the second atom Y, as in $\delta^+ \text{X—H}^{\delta+} \cdots \text{Y}^{\delta-}$.

Brief illustration 10B.6 The hydrogen bond

The electrostatic model of the hydrogen bond can be used to calculate the dependence of the molar potential energy of interaction on the OOH angle, denoted θ in Fig. 5, and the results are plotted in Fig. 5. At $\theta = 0$, when the OHO atoms lie in a straight line, the potential energy is -19 kJ mol^{-1} . Note how sharply the energy depends on angle.



Self-test 10B.6

Use Fig. 5 to explore the dependence of the interaction energy on angle: at what angle does the interaction energy become negative?

Answer: The energy is negative (and the interaction is attractive) only when the atoms are within $\pm 12^\circ$ of a linear arrangement.

Molecular orbital theory provides an alternative description that is more in line with the concept of delocalized bonding and the ability of an electron pair to bind more than one pair of atoms (Topic 9D). Thus, if the X—H bond is regarded as formed from

significant covalent character and are best described by a molecular orbital treatment. However, this interpretation of experimental results has been challenged by theoretical studies, which favour the electrostatic model. The matter has not yet been resolved.

When they can form, hydrogen bonds, with typical strengths of the order of 20 kJ mol^{-1} , dominate the van der Waals interactions. They account for the rigidity of molecular solids such as sucrose and ice, the low vapour pressure, and high surface tension of water, and the structure of DNA and hence the transmission of genetic information. Hydrogen bonding also contributes to the solubility in water of species such as ammonia and compounds containing hydroxyl groups, and to the hydration of anions. In this last case, even ions such as Cl^- and HS^- can participate in hydrogen bond formation with water, for their charge enables them to interact with the protons of H_2O .

10B.7 The hydrophobic effect

There is one further type of interaction to be discussed: it is an *apparent* force that influences the shape of a macromolecule and which is mediated by the solvent, water. First, consider why hydrocarbon molecules do not dissolve appreciably in water. Experiments indicate that the transfer of a hydrocarbon molecule from a non-polar solvent into water is often exothermic ($\Delta H < 0$). Therefore, the fact that dissolving is not spontaneous (in the sense that it does not proceed very far before equilibrium is attained) must mean that the entropy change is negative ($\Delta S < 0$).

The origin of the decrease in entropy that prevents hydrocarbons from dissolving in water is the formation of a solvent cage around the hydrophobic molecule (Fig. 7). The formation of this cage decreases the entropy of the system because the water molecules must adopt a less disordered arrangement than in the bulk liquid. However, when many solute molecules cluster together, fewer (but admittedly larger) cages are required and more solvent molecules are free to move. The net effect of formation of large clusters of hydrophobic molecules is then a decrease in the organization of the solvent and therefore a net increase in entropy of the system. This increase in entropy of the solvent is large enough to render spontaneous the association of hydrophobic molecules in a polar solvent.

The increase in entropy that results from the decrease in structural demands on the solvent is the

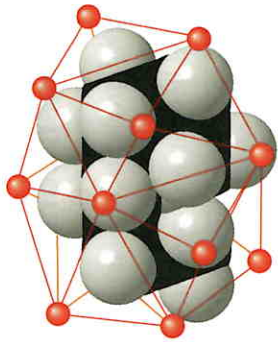


Fig. 7 When a hydrocarbon molecule (H atoms in grey and C atoms in black) is surrounded by water (only the O atoms are shown, as red spheres), the water molecules form a cage called a *clathrate*. As a result of this acquisition of structure, the entropy of the water decreases, so the dispersal of the hydrocarbon into water is entropy opposed; the coalescence of the hydrocarbon into a single large blob is entropy favoured.

origin of the **hydrophobic effect**, which tends to encourage the clustering together of hydrophobic groups in micelles and biopolymers. Thus, the presence of hydrophobic groups in polypeptides results in an increase in structure of the surrounding water, which would lead to a decrease in entropy. However, the entropy can increase if the hydrophobic groups are twisted into the interior of the molecule, which liberates the water molecules and results in an increase in their disorder. The hydrophobic interaction is an example of an ordering process, a kind of virtual force, that is mediated by a tendency toward greater disorder of the solvent.

10B.8 Modelling the total interaction

The total attractive interaction energy between rotating molecules that cannot participate in hydrogen bonding and are not subject to the hydrophobic effect is the sum of the contributions from the dipole-dipole, dipole-induced dipole, and dispersion interactions. (In more advanced treatments, there may be other 'multipolar' contributions.²) Only the dispersion interaction contributes if both molecules are nonpolar. All three interactions vary as the inverse sixth power of the separation, so the total attractive contribution to the van der Waals interaction energy can be written as

$$V(r) = -\frac{C}{r^6} \quad \text{van der Waals attraction} \quad (7)$$

² See our *Physical chemistry: thermodynamics, structure, and change* (2014) for more information.

where C is a coefficient that depends on the identity of the molecules and the type of interaction between them.

Repulsive terms become important and begin to dominate the attractive forces when molecules are in contact (Fig. 8), for instance, during the impact of a collision, under the force exerted by a weight pressing on a substance, or simply as a result of the attractive forces drawing the molecules together. These repulsive interactions arise in large measure from the Pauli exclusion principle, which forbids pairs of electrons being in the same region of space. The repulsions increase steeply with decreasing separation in a way that can be deduced only by very extensive, complicated molecular structure calculations. In many cases, however, progress can be made by using a greatly simplified representation of the potential energy, where the details are ignored and the general features expressed by a few adjustable parameters.

One such approximation is to express the short-range repulsive potential energy as inversely proportional to a high power of r :

$$V(r) = +\frac{C^*}{r^n} \quad \text{Repulsive contribution} \quad (8)$$

where C^* is another constant (the star signifies repulsion). Typically, n is set equal to 12, in which case the repulsion dominates the $1/r^6$ attractions strongly at short separations because then $C^*/r^{12} \gg C/r^6$. The sum of the repulsive interaction with $n = 12$ and the attractive interaction given by eqn 7 is called the

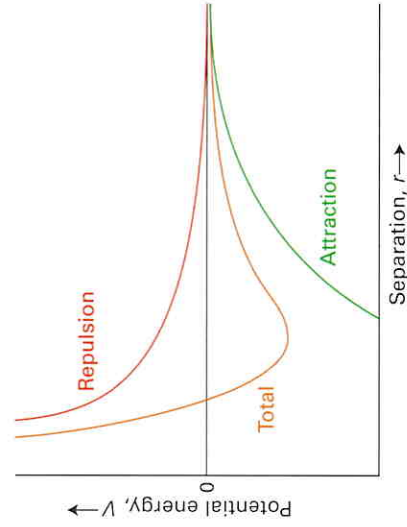


Fig. 8 The general form of an intermolecular potential energy curve (the graph of the potential energy of two closed shell species as the distance between them is changed). The attractive (negative) contribution has a long range, but the repulsive (positive) interaction increases more sharply once the molecules come into contact. The overall potential energy is shown by the orange line.

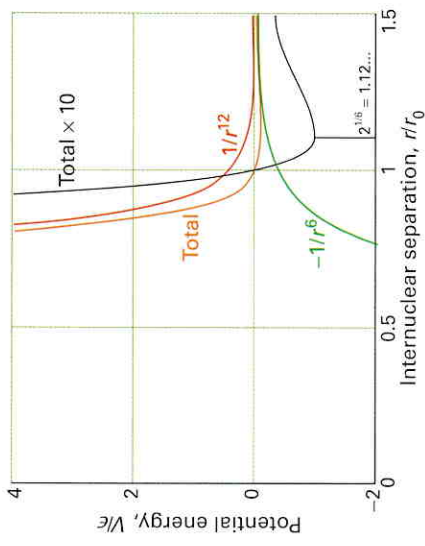


Fig. 9 The Lennard-Jones potential energy is another approximation to the true intermolecular potential energy curves. It models the attractive component by a contribution that is proportional to $1/r^6$, and the repulsive component by a contribution that is proportional to $1/r^{12}$. Specifically, these choices result in the Lennard-Jones (12,6)-potential energy. Although there are good theoretical reasons for the former, there is plenty of evidence to show that $1/r^{12}$ is only a very poor approximation to the repulsive part of the curve.

Lennard-Jones (12,6)-potential energy. It is normally written in the form

$$V(r) = 4\epsilon \left\{ \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right\} \quad \text{Lennard-Jones (12,6)-potential energy} \quad (9)$$

and is drawn in Fig. 9. The two parameters are now ϵ , the depth of the well in Fig. 9 (don't confuse this with the electric permittivity), and r_0 , the separation at which $V = 0$. Some typical values are listed in Table 10B.2. The well minimum occurs at $r = 2^{1/6} r_0$ where $V = -\epsilon$

The Lennard-Jones potential energies for pairs of atoms of the noble gases argon and xenon as a

Table 10B.2

Lennard-Jones parameters for the (12,6)-potential

	$\epsilon / (\text{kJ mol}^{-1})$	r_0 / pm
Ar	128	342
Br ₂	536	427
C ₆ H ₆	454	527
Cl ₂	368	412
H ₂	34	297
He	11	258
Xe	236	406

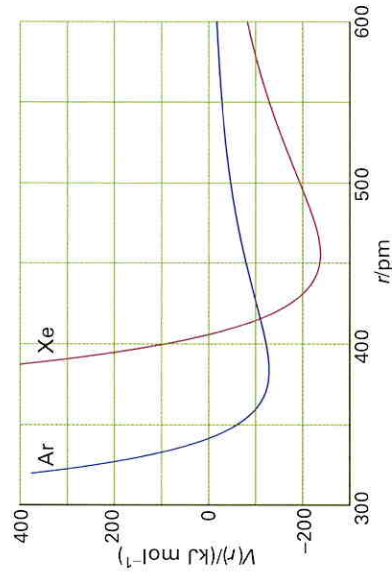


Fig. 10 The dependence of the Lennard-Jones potential energy of pairs of noble gas atoms on their separation.

function of separation are shown in Fig. 10. The location of the minimum moves to greater separations

on going down the group in the periodic table, as would be expected for these increasingly large atoms. The depth of the minimum increases too, because the polarizabilities of the atoms increase with number of electrons.

Although the (12,6)-potential energy has been used in many calculations, there is plenty of evidence to show that $1/r^{12}$ is a very poor representation of the repulsive potential energy, and that the exponential form $e^{-r/\sigma}$ is superior. An exponential function is more faithful to the exponential decay of atomic wavefunctions at large distances, and hence to the distance dependence of the overlap that is responsible for repulsion. However, a disadvantage of the exponential form is that it is slower to compute, which is important when considering the interactions between the large numbers of atoms in liquids and macromolecules.

Checklist of key concepts

- 1 van der Waals interactions are the nonbonding interactions between and within molecules.
- 2 The following attractive molecular interactions are important: charge-dipole, dipole-dipole, dipole-induced dipole, dispersion (London), hydrogen bonding, and the hydrophobic effect.
- 3 A hydrogen bond is an interaction of the form $X-H \cdots Y$, where X and Y are N, O, or F.
- 4 The hydrophobic effect is an ordering process mediated by a tendency toward greater disorder of the solvent: it causes hydrophobic groups to cluster together.
- 5 The Lennard-Jones (12,6)-potential is a model of the total intermolecular potential energy.

FOCUS 10 Molecular interactions

Exercises

Topic 10A Electric properties of molecules

10A.1 Calculate the molar potential energy of interaction between singly charged positive and negative ions that are separated by 50 nm in water.

10A.2 Estimate the dipole moment of (a) an HF molecule, (b) an HCl molecule, and (c) an HBr molecule from the electronegativities of the elements. Express your answers in debye and coulomb-metres.

10A.3 Use electronegativities to predict the direction and magnitude of the dipole moment in a carbon monoxide, CO.

Compare your answer with the magnitude and direction of the observed dipole moment as described in the text. Account for any difference.

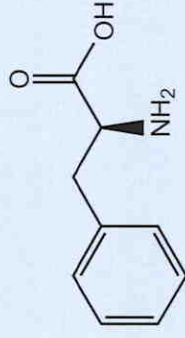
10A.4 Calculate the resultant of two dipoles moments of magnitude 1.20 D and 0.60 D that make an angle 107° to each other.

10A.5 (a) What are the units of polarizability α ? (b) Show that the units of polarizability volume are cubic metres, m^3 .

Topic 10B Interactions between molecules

10B.1 Estimate the energy of the dispersion interaction (use the London formula) for two Ar atoms separated by 1.0 nm.

10B.2 Phenylalanine (Phe, **1**) is a naturally occurring amino acid with a benzene ring. What is the energy of interaction between its benzene ring and the electric dipole moment of a neighbouring peptide group? Take the distance between the groups as 4.0 nm and treat the benzene ring as benzene itself. Take the dipole moment of the peptide group as 2.7 D.



1 Phenylalanine

10B.3 Using the parameters for the Lennard-Jones potential energy in Table 10B.2, calculate the separation at which the potential energy of interaction between two bromine molecules is lowest.

10B.4 The Lennard-Jones potential-energy function is sometimes expressed in the form

$$V(r) = A/r^{12} - B/r^6$$

For tetrachloromethane, CCl_4 , $A = 731 \times 10^{13} \text{ J pm}^{12}$ and $B = 1.24 \times 10^{-3} \text{ J pm}^6$. What is the depth of the well and the separation at which the potential energy is a minimum?

Discussion questions

10.1 Explain how the permanent dipole moment and the polarizability of a molecule arise and explain how they depend on the structure of the molecule.

10.2 Account for the theoretical conclusion that many attractive interactions between molecules vary with their separation as $1/r^6$.

10.3 Describe how van der Waals interactions depend on the structure of the molecules.

10.4 Explain why the values for the Lennard-Jones parameters ϵ and σ increase down Group 18 (the noble gases).

10.5 Describe the formation of a hydrogen bond in terms of (a) electrostatic interactions and (b) molecular orbitals. How would you identify the better model?

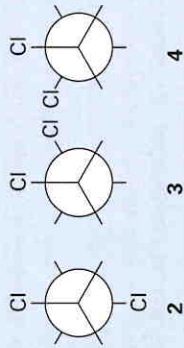
10.6 Account for the hydrophobic effect and discuss its manifestations.

Problems

10.1 Use VSEPR theory to judge whether PCl_5 is polar.

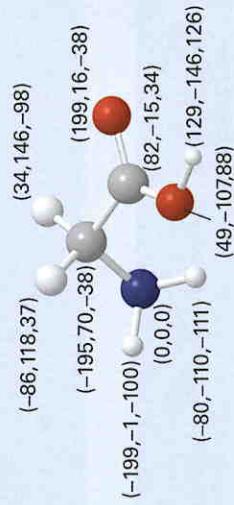
10.2 The electric dipole moment of methylbenzene (toluene) is 0.40 D. (a) Estimate the dipole moments of the three dimethylbenzenes (xylenes). (b) Also estimate the dipole moments of (i) 1,2,3-trimethylbenzene, (ii) 1,2,4-trimethylbenzene, and (iii) 1,3,5-trimethylbenzene. (c) Which of the values can you be sure about?

10.3 At low temperatures a substituted 1,2-dichloroethane molecule can adopt the three conformations (2), (3), and (4) with different probabilities. Suppose that the dipole moment of each C—Cl bond is 1.50 D. Calculate the mean dipole moment of the molecule when (a) all three conformations are equally likely, (b) only conformation (2) occurs, (c) the three conformations occur with probabilities in the ratio 2:1:1 and (d) 1:2:2.



10.4 Calculate the magnitude and direction of the dipole moment of the following arrangement of charges in the xy -plane: $3e$ at (0, 0), $-e$ at (0.32 nm, 0), and $-2e$ at an angle of 20° from the x -axis and a distance of 0.23 nm from the origin.

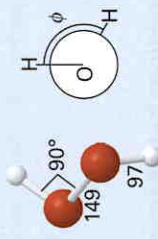
10.5 Calculate the electric dipole moment of a glycine molecule using the partial charges and the locations of the atoms shown in (5).



5 Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$

10.7 Outline the procedures used to calculate the motion of molecules in fluids and atoms in molecules.

10.6 (a) Plot the magnitude of the electric dipole moment of hydrogen peroxide as the H—OO—H (azimuthal) angle ϕ changes. Use the dimensions shown in (6). (b) Devise a way for depicting how the angle as well as the magnitude changes.



6 Hydrogen peroxide, H_2O_2

10.7 Calculate the molar energy required to reverse the direction of a water molecule located (a) 150 pm, (b) 350 pm from a Li^+ ion. Take the dipole moment of water as 1.85 D.

10.8 Show, by following the procedure in Justification 10B.1, that the potential energy of two electric dipole moments in structure (3) of Topic 10B is given by the expression for the dipole-dipole interaction energy.

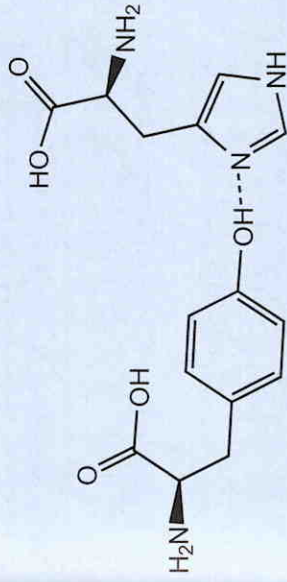
$$V(r, \theta) = \frac{\mu_1 \mu_2 (1 - 3 \cos^2 \theta)}{4\pi\epsilon_0 r^3}$$

10.9 What is the contribution to the total molar energy of (a) the kinetic energy, (b) the potential energy of interaction between hydrogen chloride molecules in a gas at 298 K when 0.50 mol of molecules are confined to 1.0 dm^3 ? Is the kinetic theory of gases justifiable in this case?

10.10 The magnitude of the electric field at a distance r from a point charge Q is equal to $Q/4\pi\epsilon_0 r^2$. How close to a water molecule (of polarizability volume $1.48 \times 10^{-30} \text{ m}^3$) must a proton approach before the dipole moment it induces is equal to the permanent dipole moment of the molecule (1.85 D)?

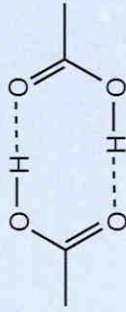
10.11 Now consider the London interaction between the benzene rings of two Phe residues (see Exercise 10B.2). Estimate the potential energy of attraction between two such rings (treated as benzene molecules) separated by 4.0 nm. For the ionization energy, use $I = 5.0 \text{ eV}$.

10.12 In a region of the oxygen-storage protein myoglobin, the OH group of a tyrosine residue is linked by a hydrogen bond to the N atom of a histidine residue in the geometry shown in (7). In calculations involving polypeptides, the following partial charges can be used: $\text{H}(-0.1)$, $+0.42e$; N , $-0.36e$.



7

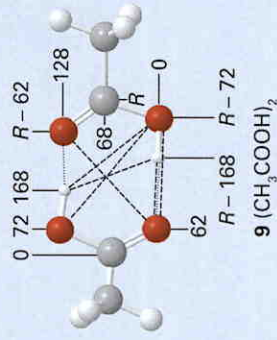
10.13 Ethanoic acid vapour contains a proportion of planar, hydrogen-bonded dimers (8). The apparent dipole moment of molecules in pure gaseous acetic acid increases with increasing temperature. Suggest an interpretation of the latter observation.



8

10.14 The coordinates of the atoms of an ethanoic acid dimer are set out in more detail in (9). Consider only the Coulombic interactions between the partial charges

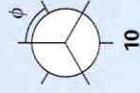
indicated by the dashed lines and their symmetry-related equivalents. At what distance R does the attraction become attractive?



9 (CH_3COOH)₂

10.15 Consider the arrangement shown in (5) of Topic 10B for a system consisting of an O—H group and an O atom, and then use the electrostatic model of the hydrogen bond to calculate the dependence of the molar potential energy of interaction on the angle θ . Set the partial charges on H and O to $0.45e$ and $-0.83e$, respectively, and take $R = 200 \text{ pm}$ and $r = 95.7 \text{ pm}$.

10.16 The potential energy of a CH_3 group in ethane as it is rotated around the C—C bond can be written $V = \frac{1}{2}V_0(1 + \cos 3\phi)$, where ϕ is the azimuthal angle (10) and $V_0 = 11.6 \text{ kJ mol}^{-1}$. (a) What is the change in potential energy between the trans and fully eclipsed conformations? (b) Show that for small variations in angle, the torsional (twisting) motion around the C—C bond can be expected to be that of a harmonic oscillator. (d) Estimate the vibrational frequency of this torsional oscillation.



10

Projects

The symbol † indicates that calculus is required.

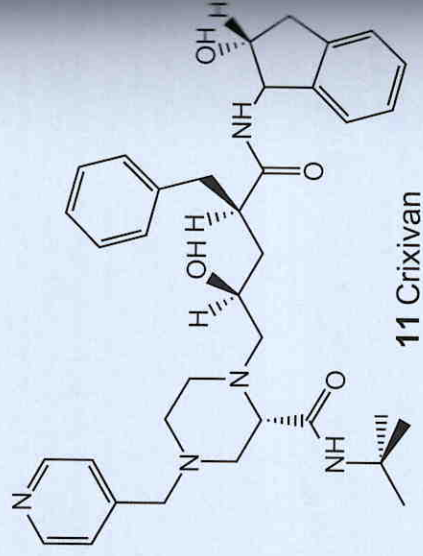
10.1† Here you are invited to explore London interactions in more detail. Given that force is the negative slope of the potential calculate the distance dependence of the force acting between two non-bonded groups of atoms in a polymeric chain that have a London dispersion interaction with each other. (a) What is the separation at which the force is zero? (b) First calculate the slope by considering the potential energy at R and $R + \delta R$, with $\delta R \ll R$, and evaluating $\{V(R + \delta R) - V(R)\}/\delta R$. You should use the expansions $(1+x)^{-1} \approx 1 - x + \dots$

$(1 \pm x + \dots)^0 = 1 \pm 6x + \dots$ and $(1 \pm x + \dots)^2 = 1 \pm 12x + \dots$. At the end of the calculation, let δR become vanishingly small. (c) Then repeat part (b) noting that $F(R) = -dV/dR$, and differentiating the expression for V .

10.2† Here you are invited to explore an alternative to the Lennard-Jones potential. (a) Suppose you distrust the Lennard-Jones (12,6)-potential for assessing a particular polymer conformation, and replaced the repulsive term by an exponential function of the form e^{r/r_0} . Sketch the form of the potential energy and locate the distance at which it

is a minimum. (b) Use calculus to identify the distance at which the exponential-6 potential described in part (a) is a minimum.

10.3 For mature HIV particles to form in cells of the host organism, several large proteins coded for by the viral genetic material must be cleaved by a protease enzyme. The drug Crixivan (**11**) is a competitive inhibitor of HIV protease and has several molecular features that optimize binding to the active site of the enzyme. Consult the literature and prepare a brief report summarizing molecular interactions between Crixivan and HIV protease that are thought to be responsible for the drug's efficacy.



FOCUS 11

Molecular Spectroscopy

The origin of spectral lines in molecular spectroscopy is the absorption, emission, or scattering of a photon when the energy of a molecule changes. The analysis of molecular spectra leads to values of important properties, such as bond strengths, lengths, and angles, and molecular orbital energies. The study of emission properties also gives insight into photochemical properties, and can be used in the measurement of distances between groups in large molecules.

11A General features of molecular spectroscopy

This Topic begins with a description of features of the instrumentation used to monitor the absorption, emission, and scattering of radiation spanning a wide range of frequencies. It also discusses the theory of absorption and emission of radiation, leading to the factors that determine the intensities and widths of spectral lines.

11A.1 Spectrometers; 11A.2 Absorption and emission; 11A.3 Raman scattering; 11A.4 Linewidths

11B Rotational spectroscopy

This Topic begins by deriving expressions for the rotational energy levels of diatomic and polyatomic molecules. Then it shows how to interpret rotational spectra, in which only the rotational state of a molecule changes.

11B.1 The rotational energy levels of molecules; 11B.2 Forbidden and allowed rotational states; 11B.3 Populations at thermal equilibrium; 11B.4 Microwave spectroscopy; 11B.5 Rotational Raman spectra

11C Vibrational spectroscopy

Expressions for the vibrational energy levels of diatomic molecules are first established by treating the molecules as harmonic oscillators (Topic 7E); they are then refined by taking into account deviations from harmonic motion. The Topic goes on to show how the vibrational spectra of gaseous samples show features that arise from the rotational transitions that accompany the excitation of vibrations. The vibrational spectra of polyatomic molecules are then discussed by imagining that they consist of a set of independent harmonic oscillators. In this way, the same approach as that employed for diatomic molecules may be used for the interpretation of vibrational spectra of large molecules.

11C.1 The vibrations of molecules; 11C.2 Vibrational transitions; 11C.3 Anharmonicity; 11C.4 Vibrational Raman spectra of diatomic molecules; 11C.5 The vibrations of polyatomic molecules; 11C.6 Vibrational rotation spectra; 11C.7 Vibrational Raman spectra of polyatomic molecules

11D Electronic spectroscopy

The core concept of this Topic is the 'Franck-Condon principle', which asserts that electronic transitions occur within a stationary nuclear framework. This principle is used to show how electronic transitions are accompanied by vibrational transitions, and in solution result in broad bands of absorption. The characteristic absorptions of some molecules can be ascribed to the presence of certain chromophores.

11D.1 Ultraviolet and visible spectra; 11D.2 Specific types of transitions; 11D.3 Analysis of mixtures by electronic spectroscopy; 11D.4 Photoelectron spectroscopy

11E The decay of excited states

Two modes of radiative decay are 'fluorescence' and 'phosphorescence', in which radiation is emitted spontaneously by molecules in excited states. The reduction in efficiency of emission through 'quenching' is interpreted in terms of the rates of physical and chemical processes that compete for the energy stored in excited states of molecules.

- 11E.1 Fluorescence and phosphorescence;**
11E.2 Mechanism of decay of excited states;
11E.3 Quenching; 11E.4 Resonance energy transfer

Web resource What is an application of this material?

Molecular spectroscopy is useful to environmental scientists, as the vibrational properties of its atmospheric constituents can affect the Earth's climate. See *Impact 9* on the website of this book.

TOPIC 11A

General features of molecular spectroscopy

> Why do you need to know this material?

Spectroscopy is one of the principal techniques for identifying and investigating matter. To interpret data from the wide range of varieties of molecular spectroscopy, you need to understand the experimental and theoretical features that all types of spectra have in common.

> What is the key idea?

Different arrangements of light sources, wavelength analysers, and detectors make possible the study of absorption, emission, and scattering of electromagnetic radiation by molecules in gaseous, liquid, and solid samples.

> What do you need to know already?

You need to be familiar with the nature of electromagnetic radiation (Topic 7A and *The chemist's toolkit 18* in that Topic), and the quantization of energy in atoms (Topics 8A–8D) and molecules (Topics 9A–9D). This Topic extends the discussion of spectroscopic transitions introduced in Topic 8D.

and vibrational states. Molecular spectra are more complicated than atomic spectra but they contain more information, including electronic energy levels, bond lengths, bond angles, and bond strengths. Molecular spectroscopy is also used to analyse materials and to monitor changing concentrations in kinetic studies (Topic 6A).

As in the discussion of atomic spectra, the frequency of a photon emitted or absorbed is given by the Bohr frequency condition (Topic 7A):

$$h\nu = |E_1 - E_2| \quad \text{Bohr frequency condition} \quad (1)$$

Here E_1 and E_2 are the energies of the two states between which the transition occurs and h is Planck's constant. This relation is often expressed in terms of the wavelength, λ (lambda), of the radiation by using the relation (as explained in *The chemist's toolkit 18* of Topic 7A)

$$\lambda = \frac{c}{\nu} \quad \text{Wavelength} \quad (2a)$$

where c is the speed of light, or in terms of the wavenumber, $\tilde{\nu}$ (nu tilde):

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad \text{Wavenumber} \quad (2b)$$

The units of wavenumber are almost always chosen to be reciprocal centimetres (cm^{-1}), so the wavenumber of radiation can be pictured as the number of complete wavelengths per centimetre. The chart in Fig. 1 summarizes the frequencies, wavelengths, and wavenumbers of the various regions of the electromagnetic spectrum.

A note on good practice People often speak of 'a frequency as so many wavenumbers'. This usage is doubly wrong. First, *frequency* and *wavenumber* are two distinct physical observables with different units, and should be distinguished. Second, 'wavenumber' is not a unit, it is an observable with the dimensions of 1/length and commonly reported in reciprocal centimetres (cm^{-1}).

Spectroscopy is the analysis of the electromagnetic radiation emitted, absorbed, or scattered by atoms and molecules. As seen in Topic 7D, photons act as messengers from inside atoms and atomic spectra can be used to obtain detailed information about electronic structure. Photons of radiation ranging from the radiofrequency region to the ultraviolet also bring information about molecules. The difference between molecular and atomic spectroscopy, however, is that the energy of a molecule can change not only as a result of electronic transitions but also because it can make transitions between its rotational

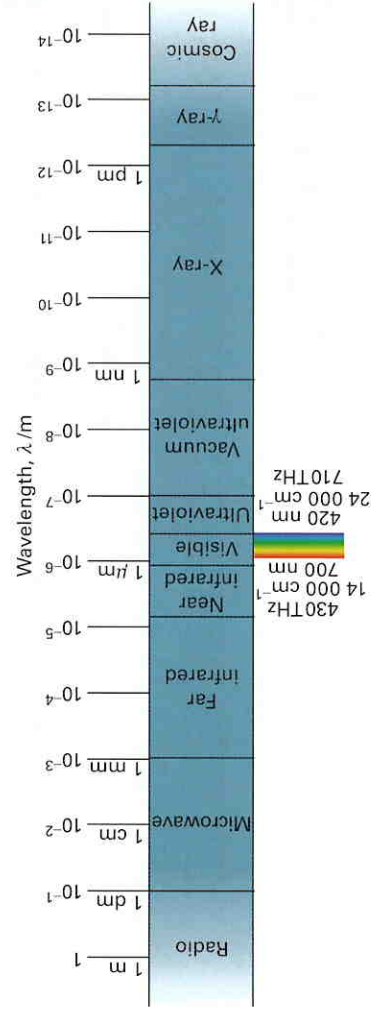


Fig. 1 The electromagnetic spectrum and its classification into regions (the boundaries are not precise).

11A.1 Spectrometers

Common to all spectroscopic techniques is a spectrometer, an instrument that detects the characteristics of radiation absorbed, emitted, or scattered by atoms and molecules. Figure 2 shows the general layout of an absorption spectrometer. Radiation from an appropriate source is directed toward a sample and the radiation transmitted strikes a device that separates it into different frequencies. The intensity of radiation absorbed at each frequency is then analysed by a suitable detector. In a conventional emission spectrometer for measuring the radiative process known as fluorescence, the source is tuned to a wavelength that causes electronic excitation of the molecule. Typically, the emitted radiation is detected perpendicular to the direction of the exciting beam of radiation (Fig. 3). In Raman spectroscopy, a laser beam is passed through the sample and the radiation scattered from the front face of sample is monitored (Fig. 4).

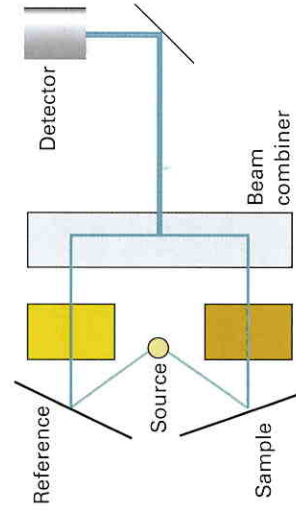


Fig. 2 The layout of a typical absorption spectrometer, in which the exciting beams of radiation pass alternately through a sample and a reference cell and the detector is synchronized with them so that the relative absorption can be determined.

Polychromatic sources that take advantage of radiation from hot materials can be used from the infrared to the ultraviolet regions of the electromagnetic spectrum. Examples include mercury arcs inside a quartz envelope ($35 \text{ cm}^{-1} < \tilde{\nu} < 200 \text{ cm}^{-1}$), *Nernst filaments* and *Globars* ($200 \text{ cm}^{-1} < \tilde{\nu} < 4000 \text{ cm}^{-1}$), and *quartz-tungsten-halogen lamps* ($320 \text{ nm} < \lambda < 2.500 \text{ nm}$).

A *gas discharge lamp* is a common source of ultraviolet and visible radiation. In a *xenon discharge lamp*, an electrical discharge excites xenon atoms to excited states, which then emit ultraviolet radiation. In a *deuterium lamp*, excited D_2 molecules dissociate into electronically excited D atoms, which emit intense radiation in the range 200–400 nm.

A common device for the separation of the wavelengths (or wavenumbers) in a beam of radiation is a *diffraction grating*, which consists of a glass or ceramic plate into which fine parallel grooves have been cut and covered with a reflective aluminium coating. For work in the visible region of the spectrum, the grooves are cut about 1000 nm apart (a spacing comparable to the wavelength of visible light). The grating causes interference between waves reflected from its surface, and constructive interference occurs at specific angles that depend on the wavelength of the radiation being used. Thus, each wavelength of light is directed into a specific direction (Fig. 5). In a *monochromator*, a narrow exit slit allows only a narrow range of wavelengths to reach the detector. Turning the grating around an axis perpendicular to the incident and diffracted beams allows different wavelengths to be analysed; in this way, the absorption spectrum is built up one narrow wavelength range at a time. In a *polychromator*, there is no slit and a broad range of wavelengths is analysed simultaneously by *array detectors*, such as those discussed below.

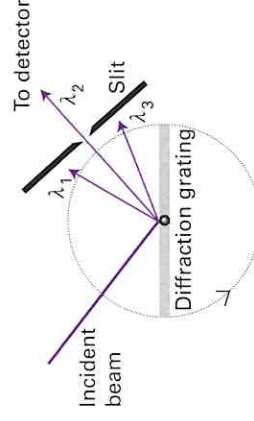


Fig. 5 A beam of light is dispersed by a diffraction grating into three component wavelengths λ_1 , λ_2 , and λ_3 . In the configuration shown, only radiation with λ_2 passes through a narrow slit and reaches the detector. Rotating the diffraction grating allows λ_1 and λ_3 to reach the detector.

Most spectrometers, particularly those operating in the infrared and near-infrared, use **Fourier transform techniques** of spectral detection and analysis. The heart of a Fourier transform spectrometer is a *Michelson interferometer*, a device for analysing the wavelengths present in a composite signal. The total signal from a sample is like a chord played on a piano, and the Fourier transform of the signal is equivalent to the separation of the chord into its individual notes, its spectrum. That transform is calculated on a computer that is an integral part of the spectrometer.

Detectors may consist of a single radiation sensing element or of several small elements arranged in one or two-dimensional arrays. A common detector is a *photodiode*, a solid-state device that conducts electricity when struck by photons because light-induced electron transfer reactions in the detector material create mobile charge carriers (negatively charged electrons and positively charged 'holes'). Silicon is sensitive in the visible region. A *charge-coupled device* (CCD) is a two-dimensional array of several million photodiode detectors. With a CCD, a wide range of wavelengths that emerge from a polychromator are detected simultaneously, so eliminating the need to measure light intensity one narrow wavelength range at a time. CCD detectors are used widely to monitor absorption, emission, and Raman scattering.

11A.2 Absorption and emission

In **absorption spectroscopy**, the observed signal is the *net* absorption, in the sense that when a sample is irradiated, both absorption and (if upper states are occupied) emission at a given frequency are stimulated, and the detector measures the difference. The intensity of an absorption line is related to the rate at which energy from electromagnetic radiation at a specified frequency is absorbed by a molecule. Albert Einstein identified three contributions to the rates of transitions between states. **Stimulated absorption** is the transition from a low energy state to one of higher energy that is driven by the electromagnetic field oscillating at the transition frequency. He reasoned that the more intense the electromagnetic field (the more intense the incident radiation), the greater the rate at which transitions are induced and hence the stronger the absorption by the sample. With these points in mind, he wrote the rate of stimulated absorption as

$$\text{Rate of stimulated absorption} = N B \rho(\nu) \quad (3a)$$

Stimulated absorption

In this expression N is the number of molecules in the lower state, the constant B is the **Einstein coefficient of stimulated absorption**. The quantity $\rho(\nu)$ is the energy density of radiation at the frequency of the transition, ν , in the sense that $\rho(\nu)\Delta\nu$ is the total energy in the frequency range ν to $\nu + \Delta\nu$ in a region of the electromagnetic field divided by the volume of the region. If B is large, then a given intensity of incident radiation will induce transitions strongly and the sample will be strongly absorbing.

Einstein considered that the radiation was also able to induce the molecule in the upper state to undergo a transition to the lower state, and hence to generate a photon of frequency ν . He wrote the rate of this **stimulated emission** as

$$\text{Rate of stimulated emission} = N'B'\rho(\nu) \quad (3b)$$

where N' is the number of molecules in the excited state and B' is the **Einstein coefficient of stimulated emission**. Note that only radiation of the same frequency as the transition can stimulate an excited state to fall to a lower state. However, he suggested that an excited state could also undergo **spontaneous emission** at a rate that is independent of the intensity of the radiation (of any frequency) that is already present. Einstein therefore wrote the total rate of transition from the upper to the lower state as

$$\text{Overall rate of emission} = N'(A + B'\rho(\nu)) \quad (3c)$$

The constant A is the **Einstein coefficient of spontaneous emission**. It can be shown that the coefficients of stimulated absorption and emission are equal (that is, $B' = B$ for a given transition), and that the coefficient of spontaneous emission is related to B by¹

$$A = \left(\frac{8\pi\nu^3}{c^3} \right) B \quad (4)$$

The equality of the coefficients of stimulated emission and absorption implies that if two states happen to have equal populations, then the rate of stimulated emission is equal to the rate of stimulated absorption, and there is then no net absorption. The decrease in the value of A with decreasing frequency implies that spontaneous emission can be largely ignored at the relatively low frequencies of rotational and vibrational transitions, and the intensities of these trans-

¹See our *Physical chemistry: thermodynamics, structure, and change* (2014) for the derivation.

sitions can be discussed solely in terms of stimulated emission and absorption. Then the net rate of absorption is given by

$$\text{Net rate of absorption} = NB\rho(\nu) - N'B'\rho(\nu) \\ = (N - N')B\rho(\nu)$$

and is proportional to the population difference of the two states involved in the transition. The ratio of populations of states of energies ϵ and ϵ' is given by the Boltzmann distribution (Topic 12A and the *Prologue*):

$$\frac{N'}{N} = e^{-(\epsilon' - \epsilon)/kT}, \text{ so } N - N' = N(1 - e^{-(\epsilon' - \epsilon)/kT})$$

Therefore

$$\text{Net rate of absorption} \\ = NB\rho(\nu)(1 - e^{-(\epsilon' - \epsilon)/kT}) \quad (5)$$

The exponential term is small when the temperature T is low or the energy separation $\Delta\epsilon = \epsilon' - \epsilon$ is large. It follows that:

- For a given energy difference the population difference and therefore the net intensity of absorption increases with decreasing temperature.
- For a specified temperature, the population difference, and therefore the intensity of absorption, increases with increasing energy separation between the states.

The ability of the electromagnetic field to drive a transition, and hence the value of B , depends on a quantity called the **transition dipole moment**. This quantity is a measure of the dipole moment associated with the shift of electric charge that accompanies a transition (Fig. 6).² The intensity of the transition is proportional to the square of the associated transition dipole moment. A large transition dipole moment indicates that the transition gives a strong 'thump' to the electromagnetic field, and conversely that the electromagnetic field interacts strongly with the molecule when driving the transition. A **selection rule** is a statement about when a transition dipole may be nonzero. There are two parts to a selection rule:

- A **gross selection rule** specifies the general features a molecule must have if it is to have a spectrum of a given kind.

²To be (nearly) precise, the transition dipole moment for the transition *initial state* \rightarrow *final state* is the value of the integral $\int \psi_{\text{final}} \mu_{\text{initial}} d\tau$; see our *Physical chemistry: thermodynamics, structure, and change* (2014) for more information.

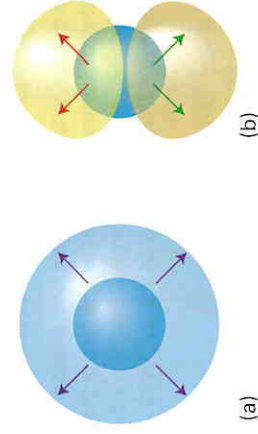


Fig. 6 The transition moment is a measure of the magnitude of the shift in charge during a transition. (a) A spherical redistribution of charge as in this transition has no associated dipole moment, and does not result in either absorption or emission of electromagnetic radiation. (b) This redistribution of charge has an associated dipole moment.

- A **specific selection rule** specifies what changes in quantum numbers may occur.

A transition that is permitted by a specific selection rule is classified as **allowed**. Transitions that are disallowed by a specific selection rule are called **forbidden**. Forbidden transitions sometimes occur weakly because the selection rule is based on an approximation that turns out to be slightly invalid. Gross and specific selection rules are different for different types of transitions, and are considered in the relevant Topic.

According to eqn 5, the intensity of absorption of radiation at a particular frequency is related to the number of absorbing species N and therefore to the molar concentration $[J]$ and the path length L through the sample. According to the Beer–Lambert law (Topic 6A):

$$I = I_0 10^{-\epsilon[J]L} \quad (6)$$

I_0 and I are the incident and transmitted intensities, respectively and ϵ (epsilon) is the **molar absorption coefficient** (formerly and still widely the 'extinction coefficient'), with dimensions of $l/(\text{concentration} \times \text{length})$. A typical value of ϵ for strong transitions is $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, indicating that in a solution of molar concentration 0.01 mol dm^{-3} the intensity of the incident radiation (of the relevant frequency) falls to 10 per cent of its initial value after passing through about 0.1 mm of solution (Fig. 7).

The **absorbance** $A = \epsilon[J]L$ of a sample is measured by using the incident and final intensities of a light beam:³

$$A = \log \frac{I_0}{I} \quad (7)$$

³Don't confuse this A with the Einstein coefficient of spontaneous emission.

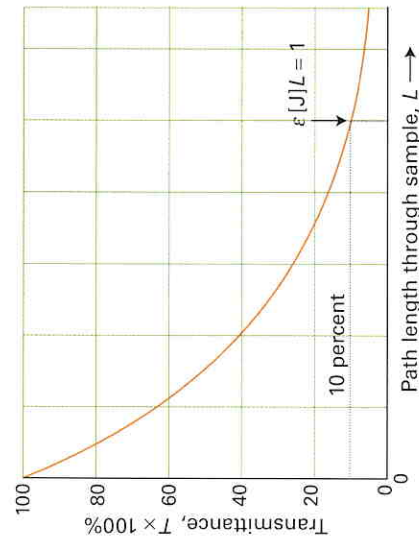


Fig. 7 The intensity of light transmitted by an absorbing sample decreases exponentially with the path length through the sample.

(The logarithm is a common logarithm, to the base 10.) It is common to report the absorption of radiation in terms of the **transmittance**, T , of a sample at a given frequency, where

$$T = \frac{I}{I_0} \quad (8)$$

Thus, $A = -\log T$. The Beer–Lambert law then takes either of the two following forms:

$$A = \epsilon[J]L, \quad T = 10^{-\epsilon[J]L} \quad (9)$$

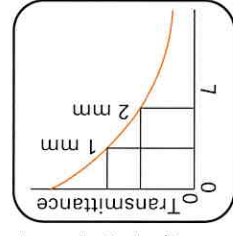
The Beer–Lambert law is an empirical result, but in the following *Justification* its form is justified by considering the passage of radiation through a uniform absorbing medium.

Example 11A.1

Determining a molar absorption coefficient

Radiation of wavelength 280 nm passed through 1.0 mm of a solution that contained an aqueous solution of the amino acid tryptophan at a concentration of $0.50 \text{ mmol dm}^{-3}$. The intensity of the radiation is reduced to 54 per cent of its initial value (so $T = 0.54$). Calculate the molar absorption coefficient and the absorbance of tryptophan at 280 nm. What would be the transmittance through a cell of thickness 2.0 mm?

Collect your thoughts From $A = -\log T = \epsilon[J]L$, write $\epsilon = -(\log T)/[J]L$ and calculate the molar absorption coefficient. Then calculate the transmittance through the thicker cell, from $T = 10^{-\epsilon L}$ and the value of ϵ calculated in the previous step.



The solution The molar absorption coefficient is

$$\epsilon = \frac{\log 0.54}{(5.0 \times 10^{-4} \text{ mol dm}^{-3}) \times (1.0 \text{ mm})} = 5.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ mm}^{-1}$$

These units are convenient for the rest of the calculation (but the outcome could be reported as $5.4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ if desired). With $T = 0.54$ the absorbance is

$$A = -\log 0.54 = 0.27$$

From the calculated value of ϵ , the absorbance of a sample of length 2.0 mm is

$$A = (5.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ mm}^{-1}) \times (5.0 \times 10^{-4} \text{ mol dm}^{-3}) \times (2.0 \text{ mm}) = 0.54$$

It follows that the transmittance is now

$$T = 10^{-A} = 10^{-0.54} = 0.29$$

That is, the radiation is reduced to 29 per cent of its incident intensity.

Self-test 11A.1

The transmittance of an aqueous solution that contained the amino acid tyrosine at a molar concentration of 0.10 mmol dm^{-3} was measured as 0.14 at 240 nm in a cell of length 5.0 mm. Calculate the molar absorption coefficient of tyrosine at that wavelength and the absorbance of the solution. What would be the transmittance through a cell of length 1.0 mm?

Answer: $1.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $A = 0.85$, $T = 0.68$

Justification 11A.1

The Beer–Lambert law

The Beer–Lambert law can be justified by following these three steps.

Step 1: Set up the model

Imagine the sample as consisting of a stack of infinitesimal slices, like sliced bread (Fig. 8). The thickness of each layer is dx . The change in intensity, dI , that occurs when electromagnetic radiation passes through one particular slice is proportional to the thickness of the slice, the concentration of the absorber J , and the intensity of the incident radiation at that slice of the sample, so $dI \propto JI dx$. Because dI is negative (the intensity is reduced by absorption), write

$$dI = -\kappa JI dx$$

where κ (kappa) is the proportionality coefficient. Division of both sides by I gives

$$\frac{dI}{I} = -\kappa J dx$$

This expression applies to each successive slice.

Step 2: Calculate the overall reduction in intensity

To obtain the intensity that emerges from a sample of thickness L when the intensity incident on one face of the sample is I_0 , sum all the successive changes. Because a sum over infinitesimally small increments is an integral, write

$$\int_0^L \frac{dI}{I} = -\kappa \int_0^L J dx$$

Then

$$\int_0^L \frac{dI}{I} = \ln \frac{I}{I_0} \quad \text{Integral A.2}$$

Provided the concentration of J is uniform, it can be taken outside the integral on the right:

$$-\kappa \int_0^L J dx = -\kappa J \int_0^L dx = -\kappa J L \quad \text{Integral A.1}$$

Therefore

$$\ln \frac{I}{I_0} = -\kappa J L$$

Step 3: Convert to common logarithms

The relation between natural and common logarithms is $\ln x = (10) \log x$. Therefore, write $\epsilon = \kappa/10$ and obtain

$$\log \frac{I}{I_0} = -\epsilon J L$$

On taking antilogarithms of both sides (10^x), the result is eqn 6

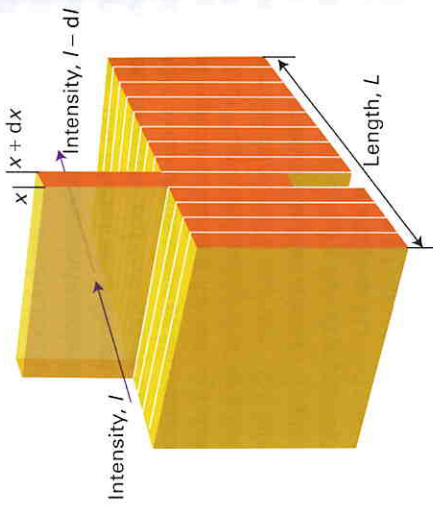


Fig. 8 To establish the Beer–Lambert law, the sample is supposed to be sliced into a large number of planes. The reduction in intensity caused by one plane is proportional to the intensity incident on it (after passing through the preceding planes), the thickness of the plane, and the concentration of absorbing species.

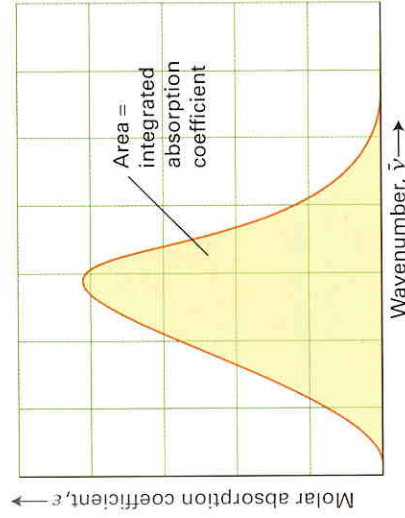


Fig. 9 The integrated absorption coefficient of a transition is the area under a plot of the molar absorption coefficient against the wavenumber of the incident radiation.

The molar absorption coefficient depends on the frequency (or, equivalently, the wavenumber and wavelength) of the incident radiation and is greatest when the absorption is most intense. The maximum value of the molar absorption coefficient, ϵ_{max} , is an indication of the intensity of a transition. However, because absorption bands generally spread over a range of wavenumbers, the absorption at a single wavenumber might not give a true indication of the intensity. The latter is best reported as the **integrated absorption coefficient**, A , the area under the plot of the molar absorption coefficient against wavenumber (Fig. 9).

11A.3 Raman scattering

Raman spectroscopy is based on a special mechanism in which photons are scattered by molecules. In Raman scattering, about 1 in 10^7 of the incident photons collide with the molecules, give up some of their energy, and emerge with a lower energy. These scattered photons constitute the longer-wavelength (lower-frequency) **Stokes radiation** from the sample (Fig. 10). Other incident photons may collect energy from the molecules (if they are already excited), and emerge as shorter-wavelength (higher-frequency) **anti-Stokes radiation**. The component of radiation scattered without change of frequency or wavelength is called **Rayleigh radiation**.

Raman spectroscopy can be used to study rotational and vibrational transitions in molecules because the result of a photon–molecule collision can be a change in the vibrational or rotational levels of molecules. Lasers are used as the source of the

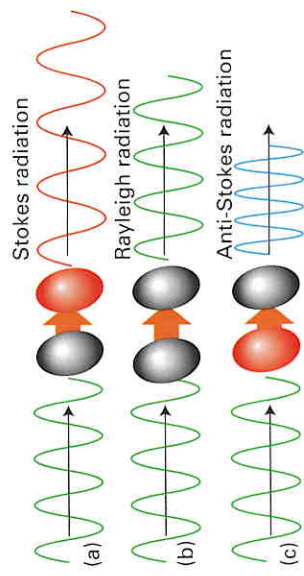


Fig. 10 In Raman scattering, an incident photon collides with and is scattered from a molecule. (a) Stokes radiation (energy deposited in the molecule). (b) Rayleigh radiation (no transfer of energy). (c) Anti-Stokes radiation (energy collected from the molecule).

incident radiation in Raman spectroscopy because an intense beam increases the intensity of scattered radiation. The monochromaticity of laser radiation makes possible the observation of frequencies of scattered light that differs only slightly from that of the incident radiation. Such high resolution is particularly useful for observing rotational transitions by Raman spectroscopy. The monochromaticity of laser radiation also allows observations to be made very close to absorption frequencies. Spectrometers using polychromators connected to CCD detectors are also very common.

11A.4 Linewidths

Spectral lines vary in breadth. An important broadening process in gaseous samples is the **Doppler effect**, in which radiation is shifted in frequency when the source is moving towards or away from the observer (Fig. 11). Molecules reach high speeds in all directions in a gas, and a stationary observer, the spectrometer, detects the corresponding Doppler-shifted range of frequencies. Some molecules approach the observer, some move away; some move quickly, others slowly. The detected spectroscopic ‘line’ is the absorption or emission profile arising from all the resulting Doppler shifts. The profile reflects the Maxwell distribution of molecular speeds (Topic 2) towards or away from the observer, and the outcome is a bell-shaped Gaussian curve (a curve of the form e^{-x^2} , Fig. 12). When the temperature is T and for a molecule of molar mass M , the width of the ‘line’ at half its maximum height (the ‘width at half-height’), $\delta\nu$, is

$$\delta\nu = \frac{2\nu}{c} \left(\frac{2RT \ln 2}{M} \right)^{1/2} \quad \text{Width at half-height} \quad (10)$$

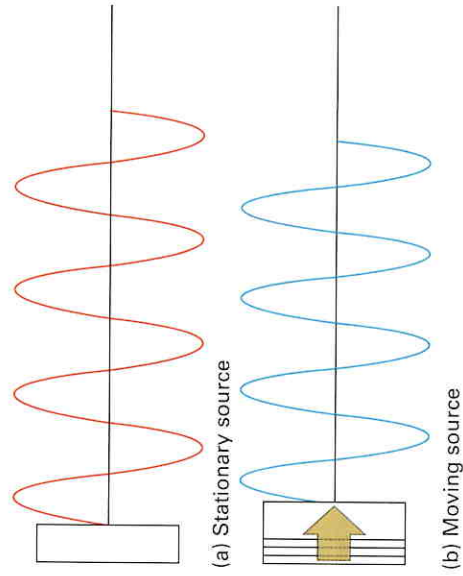


Fig. 11 The Doppler effect. (a) The radiation emitted by a stationary source. (b) When the same source moves towards the observer, the radiation appears to be shifted to higher frequencies. Similarly, a receding source shifts the radiation to lower frequencies.

which is best remembered as $\delta\nu \propto v(T/M)^{1/2}$. The Doppler width increases with frequency, so spectral lines in the ultraviolet–visible range are intrinsically broader than lines in the infrared range. The dependence on temperature arises because the molecules acquire a wider range of speeds at higher temperatures (Topic 1B). Therefore, to obtain gas-phase spectra of maximum sharpness, it is best to work with cold samples.

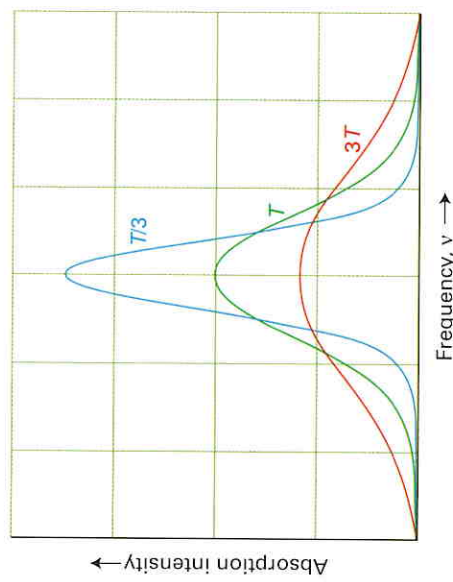


Fig. 12 The shape of a Doppler broadened spectral line reflects the Maxwell–Boltzmann distribution of speeds in the sample at the temperature of the experiment. Notice that the line broadens as the temperature is increased. The width at half height is given by eqn 10.

Brief illustration 11A.1 Doppler linewidth

A rotational transition of ^{35}Cl (of molar mass $35.973 \text{ g mol}^{-1}$), corresponding to $3.5973 \times 10^{-2} \text{ kg mol}^{-1}$ occurs at $6.356 \times 10^{11} \text{ s}^{-1}$. The Doppler width at 298 K is

$$\begin{aligned} \delta\nu &= \frac{2 \times (6.356 \times 10^{11} \text{ s}^{-1})}{2.998 \times 10^8 \text{ m s}^{-1}} \\ &\times \left(\frac{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln 2}{3.5973 \times 10^{-2} \text{ kg mol}^{-1}} \right)^{1/2} \\ &= \frac{2 \times 6.356 \times 10^{11}}{2.998 \times 10^8} \times \left(\frac{2 \times 8.3145 \times 298 \times \ln 2}{3.5973 \times 10^{-2}} \right)^{1/2} \\ &= 1.310 \times 10^6 \text{ s}^{-1} \end{aligned}$$

This value corresponds to a width of 1.310 MHz .

Self-test 11A.2

Determine the Doppler width of a transition of $^{12}\text{C}^{16}\text{O}$, which is observed at 461.0 MHz , at 400 K .

Answer: 1.248 kHz

Another source of line broadening is the finite lifetime of the states involved in the transition. When the Schrödinger equation is solved for a system that is changing with time, it is found that the states of the system do not have precisely defined energies. If the time-constant for the decay of a state is τ (tau), which is called the **lifetime** of the state (in the sense that the decay of the state is proportional to $e^{-t/\tau}$), then its energy levels are blurred by δE (corresponding to a frequency range of $\delta\nu = \delta E/h$), with

$$\delta E \approx \frac{h}{\tau} \quad \text{or} \quad \delta\nu \approx \frac{1}{2\pi\tau} \quad (11)$$

The energy spread inherent to the states of systems that have finite lifetimes is called **lifetime broadening**. Only if τ is infinite can the energy of a state be specified exactly (with $\delta E = 0$). However, no excited state has an infinite lifetime; therefore, all states are subject to some lifetime broadening, and the shorter the lifetimes of the states involved in a transition, the broader the spectral lines.

Brief illustration 11A.2 Lifetime broadening

For a transition from a state with lifetime 50 ps the broadening is

$$\delta\nu \approx \frac{1}{2\pi \times (5.0 \times 10^{-11} \text{ s})} = 3.2 \times 10^9 \text{ s}^{-1}$$

This width corresponds to 3.2 GHz .

Self-test 11A.3

The widths of lines in the spectrum of a short-lived excited state of NO_2 are due to lifetime broadening. Calculate the lifetime of the state that gives rise to a line with a lifetime-broadened width of 47 kHz .

Answer: $3.4 \mu\text{s}$

Checklist of key concepts

- **1 A spectrometer** is an instrument that detects the characteristics of radiation absorbed, emitted, or scattered by atoms and molecules.
- **2 In emission spectroscopy**, an atom or molecule undergoes a transition from a state of high energy to a state of lower energy, and emits the excess energy as a photon.
- **3 In absorption spectroscopy**, the net absorption of incident radiation is monitored as the frequency is varied.
- **4 In Raman spectroscopy**, the radiation scattered by molecules is monitored.
- **5 Stimulated absorption** is the process by which a molecule is driven to a state of higher energy by an oscillating electromagnetic field.
- **6 Stimulated emission** is the process by which a molecule is driven from a high energy state to one of lower energy by an oscillating electromagnetic field.
- **7 Spontaneous emission** is the process by which a transition takes place from high energy to low energy even in the absence of an oscillating electromagnetic field.
- **8** The importance of spontaneous emission increases as the cube of the transition frequency.
- **9** For a given energy difference between two states, the net intensity of absorption from the lower-energy state to the higher-energy state increases with decreasing temperature.
- **10 A gross selection rule** specifies the general features a molecule must have if it is to have a spectrum of a given kind.
- **11 A specific selection rule** is a statement about which changes in quantum number may occur in a transition.
- **12** The intensity of a transition is proportional to the square of the **transition dipole moment**.
- **13 A selection rule** is a statement about when the transition dipole moment may be nonzero.
- **14 Stokes radiation** is scattered radiation at lower frequency than the incident radiation.
- **15 Anti-Stokes radiation** is scattered radiation at higher frequency than the incident radiation.
- **16** The component of radiation scattered without change of frequency is called **Rayleigh radiation**.
- **17 Doppler broadening** of a spectral line is caused by the distribution of molecular and atomic speeds in a sample.
- **18 Lifetime broadening** arises from the finite lifetime of an excited state and a consequent blurring of energy levels.

TOPIC 11B

Rotational spectroscopy

► Why do you need to know this material?

Rotational spectroscopy provides very precise details of bond lengths and bond angles of molecules in the gas phase. Transitions between rotational levels also contribute to vibrational and electronic spectra and are used in the investigation of gas-phase reactions such as those taking place in the atmosphere.

► What is the key idea?

Analysis of rotational spectra yields the bond lengths and bond angles of molecules in the gas phase.

► What do you need to know already?

You should be familiar with the quantum mechanical treatment of molecular rotation (Topic 7D), the general principles of molecular spectroscopy (Topic 11A), and the Pauli principle (Topic 8B).

Very little energy is needed to change the state of rotation of a molecule, so the electromagnetic radiation emitted or absorbed lies in the microwave region, with wavelengths of the order of 0.1–1 cm and frequencies close to 10 GHz. The rotational spectroscopy of gas-phase samples is therefore also known as **microwave spectroscopy**. Gaseous samples are essential for rotational (microwave) spectroscopy, for in that phase molecules rotate freely.

11B.1 The rotational energy levels of molecules

The rotational states of molecules are based on a model system called a **rigid rotor**, a body that is not distorted by the stress of rotation. The simplest type

of rigid rotor is called a **linear rotor**, and corresponds to a linear molecule, such as HCl, CO₂, or HC≡CH, that is supposed not to be able to bend or stretch under the stress of rotation. As shown in the following *Justification*, the energies of a linear rotor are

$$E_J = hB(J+1) \quad \text{Rotational energy levels} \quad (1)$$

$J = 0, 1, 2, \dots$ (linear rotor)

where J is the **rotational quantum number**. The constant B (a frequency, with the units hertz, Hz, with 1 Hz denoting 1 cycle per second) is called the **rotational constant** of the molecule, and is defined as

$$B = \frac{h}{4\pi I} \quad \text{Rotational constant} \quad (2)$$

where I is the **moment of inertia** of the molecule (Topic 7D) and *The chemist's toolkit* 2.2 in that Topic). The moment of inertia of a molecule is the mass of each atom multiplied by the square of its perpendicular distance from the axis of rotation (Fig. 1):

$$I = \sum_i m_i r_i^2 \quad \text{Moment of inertia} \quad (3)$$

Table 11B.1 gives the expressions for the moments of inertia of various types of molecules in terms of

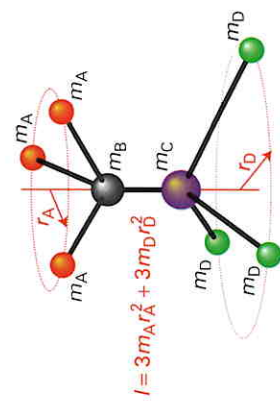
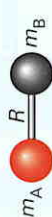


Fig. 1 The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the centre of mass lies on an axis passing through the B and C atoms, and the perpendicular distances are measured from this axis.

Table 11B.1

Moments of inertia*

1. Diatomic molecules



$$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$$

2. Triatomic linear rotors

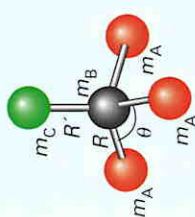


$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$



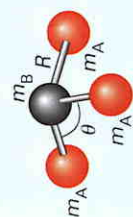
$$I = 2m_A R^2$$

3. Symmetric rotors



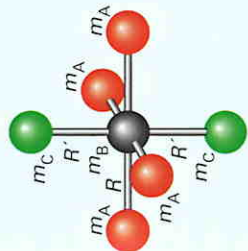
$$I_{\parallel} = 2m_A (1 - \cos \theta) R^2$$

$$I_{\perp} = m_A (1 - \cos \theta) R^2 + \frac{m_C}{m} (m_B + m_C) (1 + 2 \cos \theta) R^2 + \frac{m_C}{m} \left[(3m_A + m_B) R^2 + 6m_A R \left[\frac{1}{2} (1 + 2 \cos \theta) \right]^{1/2} \right] R'$$



$$I_{\parallel} = 2m_A (1 - \cos \theta) R^2$$

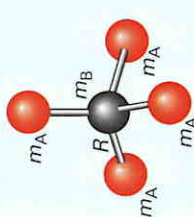
$$I_{\perp} = m_A (1 - \cos \theta) R^2 + \frac{m_A m_B}{m} (1 + 2 \cos \theta) R^2$$



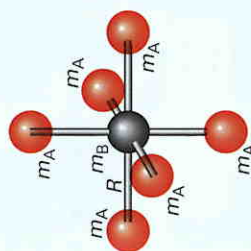
$$I_{\parallel} = 4m_A R^2$$

$$I_{\perp} = 2m_A R^2 + 2m_C R^2$$

4. Spherical rotors



$$I = \frac{5}{2} m_A R^2$$



$$I = 4m_A R^2$$

*Where it appears, m is the total mass of the molecule.

the masses of their atoms and their bond lengths and bond angles.

A note on good practice To calculate the moment of inertia precisely, the nuclide must be specified. Also, the mass to use is the actual atomic mass, not the element's molar mass. Nuclide masses are reported as multiples of the atomic mass constant, as in $16.00m_u$.

Justification 11B.1

Energy levels of a linear rotor

The starting point for this derivation draws on the concepts of energy and angular momentum introduced in *The chemist's toolkit 22* in Topic 7D. The strategy is to begin with a classical picture and then move to a quantum mechanical description.

Step 1: Write the classical expression for the energy

A linear rotor can rotate about two perpendicular axes fixed in the molecule with the x - and y -axes perpendicular to the molecular axis and the z -axis lying along it. The moment of inertia around the x - and y -axes is I (the same in each case) and is zero about the z -axis (because all the atoms lie on that axis); so the total rotational kinetic energy, and therefore the total energy when the body is rotating with an angular velocity ω_x around the axis $q = x, y$ is the sum of two contributions:

$$E = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2$$

In terms of the angular momentum $J_x = I\omega_x$ around each perpendicular axis:

$$E = \frac{J_x^2}{2I} + \frac{J_y^2}{2I} = \frac{J^2}{2I}$$

where J is the total angular momentum (there is no z -component for a linear rotor).

Step 2: Convert to the quantum mechanical expression

According to quantum mechanics, the square of the magnitude of angular momentum is $J(J+1)\hbar^2$, with the quantum number $J = 0, 1, 2, \dots$ (Topic 7D). It follows that the quantum mechanical expression for the energy of a linear rotor is

$$E = J(J+1)\frac{\hbar^2}{2I} = J(J+1)\frac{h}{2\pi} \times \frac{h}{2\pi} = h\frac{J(J+1)}{4\pi^2 I}$$

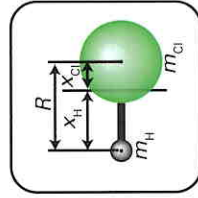
which, with $B = h/4\pi^2 I$, is eqn 1.

Example 11B.1

Evaluating a rotational constant

Evaluate the rotational constant of a $^1\text{H}^{35}\text{Cl}$ molecule.

Collect your thoughts Evaluate the moment of inertia of the molecule by using the appropriate expression from Table 11B.1. Then convert the moment of inertia to the rotational constant by using eqn 2.



The solution The masses of the two atoms are $1.008m_u$ and $34.969m_u$ for ^1H and ^{35}Cl , respectively; the equilibrium bond length is 127.4 pm . From Table 11B.1 the value of μ is

$$\begin{aligned} \mu &= \frac{m(^1\text{H})m(^{35}\text{Cl})}{m(^1\text{H}) + m(^{35}\text{Cl})} \\ &= \frac{1.008m_u \times 34.969m_u}{1.008m_u + 34.969m_u} \\ &= 1.008 \times 34.969 \times 10^{-27} \text{ kg} \times (1.274 \times 10^{-10} \text{ m})^2 \\ &= 2.6407 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

Therefore, the moment of inertia is

$$\begin{aligned} I &= \mu R^2 = 0.9798 \times (1.660 \times 10^{-27} \text{ kg}) \times (1.274 \times 10^{-10} \text{ m})^2 \\ &= 2.6407 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

It then follows from eqn 2 that the rotational constant of $^1\text{H}^{35}\text{Cl}$ is

$$\begin{aligned} B &= \frac{h}{4\pi^2 I} = \frac{1.054 \times 10^{-34} \text{ J s}}{4\pi^2 \times (2.6407 \times 10^{-47} \text{ kg m}^2)} \\ &= 3.1779 \times 10^{11} \frac{\text{kg m}^2 \text{ s}^{-2}}{\text{kg m}^2} = 3.1779 \times 10^{11} \text{ s}^{-1} \\ &= 3.1779 \times 10^{11} \frac{\text{kg m}^2 \text{ s}^{-2}}{\text{kg m}^2} = 3.1779 \times 10^{11} \text{ Hz} \text{ (or } 0.317 \text{ 79 THz)} \end{aligned}$$

This value corresponds to $3.1779 \times 10^{11} \text{ Hz}$ (or 0.317 79 THz). Expressed as a wavenumber, when it is denoted \tilde{B} (\tilde{B} with a tilde) with $\tilde{B} = B/c$, it is 10.600 cm^{-1} .

Self-test 11B.1

Evaluate the rotational constant of $^2\text{H}^{35}\text{Cl}$ ($m(^2\text{H}) = 2.0141m_u$).
 Answer: 0.163 50 THz

Figure 2 shows the energy levels predicted by eqn 1: note that the separation of neighbouring levels increases with J . Note also that, because J may be 0 (Topic 7D), the lowest possible energy is $E_0 = 0$: there is no zero-point rotational energy for molecules.

Molecules are not really *rigid* rotors: they distort under the stress of rotation. As their bond lengths increase, their energy levels become slightly closer together. This effect is taken into account by supposing that eqn 1 can be modified to

$$E_J = hB J(J+1) - bD J^2(J+1)^2 \quad \text{Centrifugal distortion (linear rotor)} \quad (4)$$

The parameter D is the **centrifugal distortion constant**. It is large when the bond is easily stretched, and so its magnitude is related to the force constants

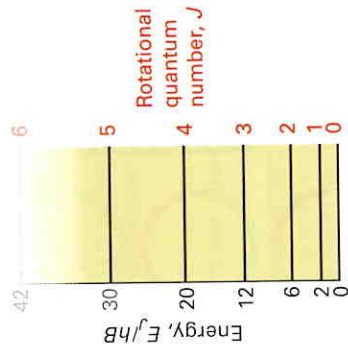


Fig. 2 The energy levels of a linear rigid rotor as multiples of hB .

of bonds, a measure of their rigidity (Topics 7D and 11C).

A number of nonlinear molecules, all of which can rotate around three axes, can be modelled as a **symmetric rotor**, a rigid rotor in which the moments of inertia about two axes are the same but different from a third (and all three are nonzero). The formal criterion of a molecule being a symmetric rotor is that it has an axis of threefold or higher symmetry. An example of a symmetric rotor is ammonia, NH_3 , and another is phosphorus pentachloride, PCl_5 (Fig. 3). As shown in the following *Justification*, the rotational energy levels of a symmetric rotor are

$$E_{J,K} = hB J(J+1) + b(A-B)K^2 \quad \text{Symmetric rotor} \quad (5)$$

$$J = 0, 1, 2, \dots; K = 0, \pm 1, \dots, \pm J$$

The rotational constants A and B are inversely proportional to the moments of inertia parallel and perpendicular to the axis of the molecule (Fig. 4):

$$A = \frac{h}{4\pi^2 I_{\parallel}} \quad B = \frac{h}{4\pi^2 I_{\perp}} \quad \text{Rotational constants} \quad (6)$$

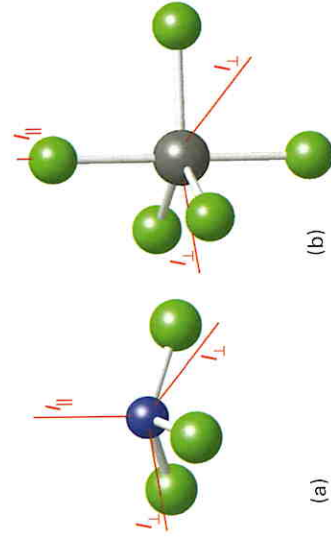


Fig. 3 The two different moments of inertia of (a) a trigonal pyramidal molecule and (b) a trigonal bipyramidal molecule.

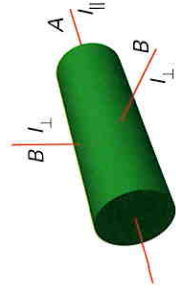


Fig. 4 The two rotational constants of a symmetric rotor, which are inversely proportional to the moments of inertia parallel and perpendicular to the axis of the molecule.

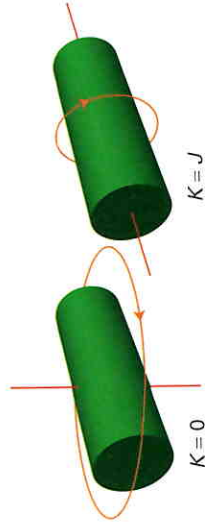


Fig. 5 When $K = 0$ for a symmetric rotor, the entire motion of the molecule is around an axis perpendicular to the symmetry axis of the rotor. When the value of $|K|$ is close to J , almost all the motion is around the symmetry axis.

The quantum number K gives, through $K\hbar$, the component of angular momentum around the molecular axis (Fig. 5). When $K = 0$, the molecule is rotating end-over-end and not at all around its own axis. When $K = \pm J$ (the greatest values in its range), the molecule is rotating mainly about its axis. Intermediate values of K correspond to a combination of the two modes of rotation.

Justification 11B.2

Energy levels of a symmetric rotor

As in the previous *Justification*, construct the classical expression first and then convert it to a quantum mechanical expression.

Step 1: Write the classical expression for the energy

The starting point is a generalization of the expression for the total energy of a linear rotor (in *Justification 11B.1*) to

$$E = \frac{J_x^2}{2I_{\perp}} + \frac{J_y^2}{2I_{\perp}} + \frac{J_z^2}{2I_{\parallel}} = \frac{1}{2I_{\perp}}(J_x^2 + J_y^2) + \frac{J_z^2}{2I_{\parallel}}$$

In terms of the magnitude of the angular momentum $J^2 = J_x^2 + J_y^2 + J_z^2$ (which is easy to convert to a quantum mechanical expression) this equation becomes,

$$\begin{aligned} E &= \frac{1}{2I_{\perp}}(J^2 - J_z^2) + \frac{J_z^2}{2I_{\parallel}} \\ &= \frac{J^2}{2I_{\perp}} + \left(\frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) J_z^2 \end{aligned}$$

Step 2: Convert to the quantum mechanical expression

According to quantum mechanics (Topic 7D), the square of the magnitude of angular momentum is $J(J+1)\hbar^2$, with $J=0, 1, 2, \dots$ and any component (such as J_z) is limited to the values $K\hbar$ with $K=0, \pm 1, \dots, \pm J$. By convention, the quantum number K plays the role of M_l for the component on an internally defined axis and M_l is reserved for the projection of the angular momentum on to an externally defined z -axis. It follows that the quantum mechanical expression for the energy of a symmetric rotor is

$$E = \frac{J(J+1)\hbar^2}{2I_A} + \left(\frac{1}{2I_B} - \frac{1}{2I_A} \right) K^2 \hbar^2 \quad \text{eqn 5}$$

With A and B defined as in eqn 6, this expression becomes eqn 5.

A special case of a symmetric rotor is a **spherical rotor**, a rigid body with three equal moments of inertia (like a sphere). Tetrahedral, octahedral, and icosahedral molecules (CH_4 , SF_6 , and C_{60} , for instance) are spherical rotors. Their energy levels are very simple: when $I_A = I_B = I_C$, the rotational constants A and B are equal and eqn 5 simplifies to eqn 1.

11B.2 Forbidden and allowed rotational states

Not all the rotational states with $J=0, 1, 2, \dots$ of symmetrical molecules, such as H_2 and CO_2 , are permitted. The elimination of certain states is rather like the exclusion of certain electron configurations by the Pauli exclusion principle (Topic 8B) and stems from a very deep feature of nature that is summarized by the more fundamental **Pauli principle**:

When the labels of any two identical fermions are exchanged, the total wavefunction changes sign. When the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

Fermions are particles with half-integral spins (like electrons and protons); bosons are particles with integral spins (including zero). The nuclear spin is denoted I (the analogue of s for electrons). The nuclear spins of common nuclei include $I=0$ for ^{16}O and ^{12}C , $I=1/2$ for ^1H , and $I=1$ for ^{14}N . Thus, if A and B are indistinguishable particles, and ψ is the total wavefunction (including spin), then

For fermions (half-integral spins): $\psi(B,A) = -\psi(A,B)$
For bosons (integral spins): $\psi(B,A) = \psi(A,B)$

A consequence of the Pauli principle for electrons is the Pauli exclusion principle. A consequence for the

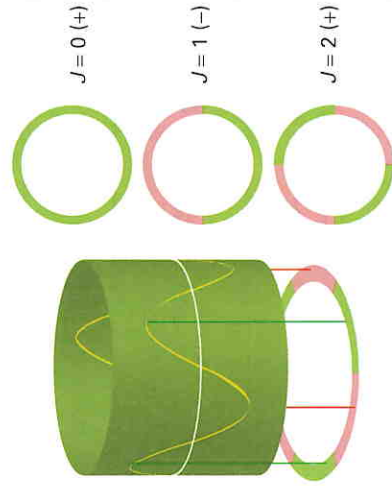


Fig. 6 The phases of the wavefunctions of a particle on a ring for the first few states: note that the parity of the wavefunction (its behaviour under inversion through the centre of the ring) is even, odd, even, ...

rotational motion of molecules is **nuclear statistics**, the relation between nuclear spin and the existence of certain rotational states of symmetrical molecules.

Consider a CO_2 molecule (more precisely, a $^{16}\text{O}_2^{12}\text{C}$), in which both O atoms are identical, as in $^{16}\text{O}^{16}\text{O}$), denoted as O_ACO_B . When the molecule rotates through 180° , it becomes O_BCO_A , with the two O atoms interchanged. Oxygen-16 is a boson, and therefore the wavefunction must remain unchanged by this interchange. However, when *any* molecule is rotated through 180° , its wavefunction changes by a factor of $(-1)^I$. To see why that is so, it is useful to draw the first few wavefunctions for a particle travelling on a ring as in Fig. 6, and see that a rotation of 180° leaves wavefunctions with $J=0, 2, \dots$ unchanged but changes the sign of those with $J=1, 3, \dots$. The only way for the two requirements (that the wavefunction does not change sign and the fact that it changes by a factor of $(-1)^I$) to be consistent is for J to be restricted to even values. That is, a CO_2 molecule can exist only in the rotational states with $J=0, 2, 4, \dots$

The analysis of the implications of nuclear statistics is more complex for molecules in which the nuclei have nonzero spin (which includes $^1\text{H}_2$, with its spin- $1/2$ nuclei) because the permitted rotational states depend on the relative orientation of the nuclear spins. However, the results can be expressed quite simply:

$$\begin{aligned} & \text{Number of ways of achieving odd } J \\ & \text{Number of ways of achieving even } J \\ & = \begin{cases} (I+1)/I & \text{for half-integral spin nuclei} \\ I/(I+1) & \text{for integral spin nuclei} \end{cases} \quad \text{Nuclear statistics (7)} \end{aligned}$$

where I is the nuclear spin quantum number.

Brief Illustration 11B.1 Nuclear statistics

For $^1\text{H}_2$, with its spin- $1/2$ nuclei,

$$\begin{aligned} \text{Number of ways of achieving odd } J &= \frac{I+1}{I} = \frac{1/2+1}{1/2} = 3 \\ \text{Number of ways of achieving even } J &= \frac{I}{I+1} = \frac{1/2}{1/2+1} = \frac{1}{3} \end{aligned}$$

There are therefore three times as many ways of achieving rotational levels with odd J than with even J . The levels with even J correspond to molecules with parallel nuclear spins, which are called *ortho*-hydrogen; levels with odd J correspond to paired nuclear spins and are called *para*-hydrogen. Different relative nuclear spin orientations change into one another only very slowly, so an H_2 molecule with parallel nuclear spins remains distinct from one with paired nuclear spins for long periods. The two forms of hydrogen can be separated by physical techniques, and stored.

Self-test 11B.2

Determine the ratio of the number of ways of achieving rotational levels with odd and even J for D_2 where D is deuterium, ^2H , for which $I=1$.

Answer: 1:2

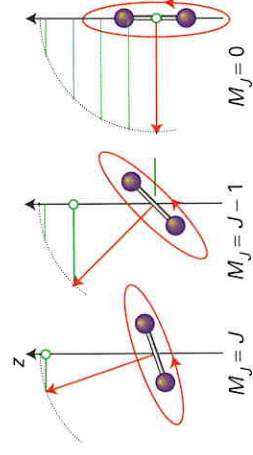


Fig. 7 The significance of the quantum number M_J (in this case, for $J=4$): it indicates the orientation of the molecular rotational angular momentum with respect to an external axis.

J rotational level. Each state has a population that is proportional to the Boltzmann factor, $e^{-E_J/kT}$, in this case with $E_J = hB(J+1)$. The total population, N_J , of a given energy level consisting of $2J+1$ individual states, relative to that of the lowest level with $J=0$ and its one state ($M_J=0$), is therefore $2J+1$ times the population of one of the states, and is

$$\frac{N_J}{N_0} = (2J+1)e^{-hB(J+1)/kT} \quad \text{Boltzmann population [linear rotor]} \quad (8)$$

Figure 8 shows how this population varies with J . As shown in the following *Justification*, it passes through a maximum at an integer value of J close to

$$J_{\text{max}} = \left(\frac{kT}{2hB} \right)^{1/2} - \frac{1}{2} \quad \text{Maximally populated level [linear rotor]} \quad (9)$$

Broadly speaking the absorption spectrum of the molecule should show a similar distribution of intensities.

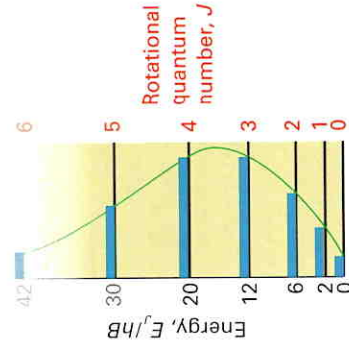


Fig. 8 The thermal equilibrium relative populations of the rotational energy levels of a linear rotor.

11B.3 Populations at thermal equilibrium

Because the rotational states of molecules are close together in energy, many states are occupied at ordinary temperatures. However, the degeneracy of the rotational levels needs to be taken into account when using the Boltzmann distribution (see the *Prologue* and Topic 12A) to assess their population, because although a given state may have a low population, there may be many states of the same energy, and the total population of an energy level may be quite large. A further complication is that nuclear statistics may forbid the existence of certain states and so affect the populations of the remaining ones.

To avoid the additional complication of nuclear spin statistics, consider a linear molecule that does not interchange identical nuclei as it rotates, such as HCl and OCS. The angular momentum of the molecule may have $2J+1$ different orientations with respect to an external axis, each designated by the value of the quantum number $M_J = 0, \pm 1, \dots, \pm J$ (Fig. 7, just as in atoms, where there are $2l+1$ orientations of the orbital angular momentum, one corresponding to each permitted value of m_l ; Topic 7D). The energy of the molecule is independent of its plane of rotation, so all $2J+1$ states have the same energy. There are therefore $(2J+1)$ states of the same energy for each

Brief illustration 11B.2 The most populated level

In Example 11B.1 it is established that $B = 3.1779 \times 10^{11}$ Hz for $^{1}\text{H}^{35}\text{Cl}$. Therefore, the most populated rotational energy level at 298 K is at an integer value of J close to

$$J_{\text{max}} = \left\{ \frac{k}{h} \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{2 \times (6.626 \times 10^{-34} \text{ J s}) \times (3.1779 \times 10^{11} \text{ Hz})} \right\}^{1/2} - \frac{1}{2} = 2.6$$

The closest integer is 3, so the level with $J = 3$ (with its 7 states) is the most populated at 298 K. The molecule has a low moment of inertia as virtually the whole of the rotational motion is that of the H atom around a nearly stationary Cl atom, so its energy levels are widely separated and only a few (about 3) are thermally accessible at low temperatures.

Self-test 11B.3

Repeat the calculation for the linear molecule OCS at 298 K, with $B = 0.2 \text{ cm}^{-1}$.

Answer: $J_{\text{max}} = 30$

Justification 11B.3

The most populated level

The task is to find the value of J for which P_J is a maximum. To proceed, note that to find the value of x corresponding to the extremum (maximum or minimum) of any function $f(x)$, differentiate the function, set the result equal to zero, and solve the resulting equation for x .

Step 1: Differentiate the function

If J is treated as a continuous variable, differentiation of eqn 8 gives, using the rules set out in *The chemist's toolkit 5* in Topic 1C:

$$\begin{aligned} \frac{d}{dJ} (2J+1) e^{-hB(J+1)/kT} &= \left\{ \frac{d}{dJ} (2J+1) \right\} e^{-hB(J+1)/kT} + (2J+1) \left\{ \frac{d}{dJ} e^{-hB(J+1)/kT} \right\} \\ &= \left\{ 2 - \frac{hB(2J+1)}{kT} \right\} e^{-hB(J+1)/kT} \end{aligned}$$

Step 2: Find the maximum value of J

The preceding expression is equal to zero when the term multiplying the (blue) exponential function is zero. Therefore, after setting $J = J_{\text{max}}$, solve

$$2 - \frac{hB(2J_{\text{max}} + 1)}{kT} = 0$$

which gives eqn 9. This derivation has treated J as a continuous variable, whereas in fact it is confined to integer values. Therefore, the actual value of J corresponding to the maximum population is interpreted as the integer lying closest to the calculated J_{max} .

11B.4 Microwave spectroscopy

The gross selection rule for rotational transitions in microwave spectroscopy is that a molecule must have a permanent electric dipole moment. That is

For a molecule to give a pure rotational spectrum it must be polar.

The classical basis of this rule is that a stationary observer watching a rotating polar molecule sees its partial charges moving backwards and forwards and their motion shakes the electromagnetic field into oscillation (Fig. 9). Because the molecule must be polar, it follows that tetrahedral (CH_4 , for instance), octahedral (SF_6), symmetric linear (CO_2), and homonuclear diatomic (H_2) molecules do not have rotational spectra. On the other hand, heteronuclear diatomic (HCl) and less symmetrical polar polyatomic molecules (NH_3) are polar and do have rotational spectra. Polar molecules are said to be **rotationally active**, whereas nonpolar molecules are **rotationally inactive**.

The specific selection rules for rotational transitions are

$$\Delta J = \pm 1 \quad \Delta K = 0 \quad \text{Rotational selection rules} \quad (10)$$

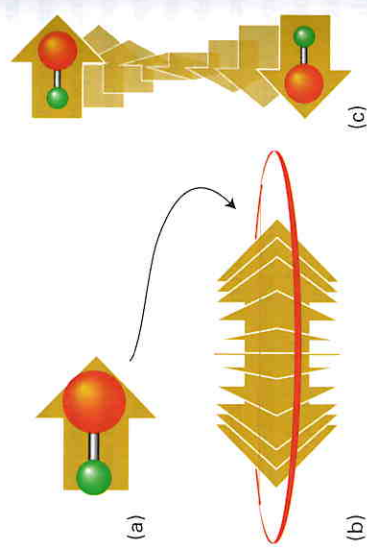


Fig. 9 To an external observer, (a) a rotating polar molecule has (b) an electric dipole (the arrow) that (c) appears to oscillate. This oscillating dipole can interact with the electromagnetic field.

The first of these selection rules can be traced, like the rule $\Delta l = \pm 1$ for atoms (Topic 8D), to the conservation of angular momentum when a photon is absorbed or created. A photon is a spin-1 particle, and when one is absorbed or created the angular momentum of the molecule must change by a compensating amount. Because J is a measure of the angular momentum of the molecule, J can change only by ± 1 (for pure rotational transitions, $\Delta J = +1$ corresponds to absorption, $\Delta J = -1$ to emission). The second selection rule ($\Delta K = 0$; that is, the quantum number K may not change) can be traced to the fact that the dipole moment of a polar molecule does not move when a molecule rotates around its symmetry axis (think of NH_3 rotating around its threefold axis). As a result, there can be no acceleration or deceleration of the rotation of the molecule about that axis by the absorption or emission of electromagnetic radiation.

When a rigid, unsymmetrical linear molecule changes its rotational quantum number from J to $J + 1$ in an absorption, the change in rotational energy of the molecule is

$$\begin{aligned} \Delta E &= E_{J+1} - E_J = bB(J+1)(J+2) - bB J(J+1) \\ &= bB(J^2 + 3J + 2) - (J^2 + J) \\ &= 2bB(J+1) \end{aligned}$$

The same expression applies to a symmetric rotor because K does not change in a transition. The frequency of the radiation absorbed in a transition starting from the level J is therefore

$$\nu_J = 2B(J+1) \quad \text{Rotational transition frequencies [rigid rotor]} \quad (11a)$$

and the absorption lines occur at $2B, 4B, 6B, \dots$. The intensity distribution will be like that in Fig. 10 with a maximum intensity at $\nu_{J_{\text{max}}}$, with J_{max} given by two effects: the population effect summarized by eqn 9, and the variation of the magnitude of the transition dipole moment, which also depends on J . A rotational spectrum of a polar linear molecule (HCl) and of a polar symmetric rotor (NH_3) therefore consists of a series of lines at frequencies separated by $2B$.

Brief illustration 11B.3 Rotational transition frequencies

In Example 11B.1 the rotational constant of $^{1}\text{H}^{35}\text{Cl}$ was calculated as 3.1779×10^{11} Hz (or 317.79 GHz). Therefore the rotational spectrum of this molecule consists of a series of lines spaced by 635.6 GHz, at the frequencies 635.6 GHz, 1271.2 GHz, 1906.8 GHz, The wavelength of the first of these lines is 0.472 mm.

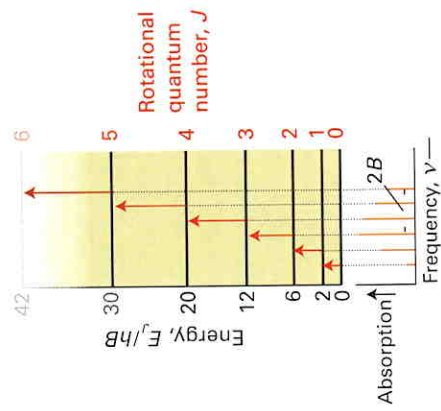


Fig. 10 The allowed rotational transitions (shown as absorptions) for a linear molecule. The separation between any two adjacent spectral lines is $2B$.

Self-test 11B.4

What is the frequency and wavelength of the $J = 1 \leftarrow 0$ transition in the $^{2}\text{H}^{35}\text{Cl}$ molecule? The mass of ^2H is $2.014m_u$. Before commencing the calculation, decide whether the frequency should be higher or lower than for $^{1}\text{H}^{35}\text{Cl}$.

Answer: 3270 GHz, 0.9167 mm

If centrifugal distortion is significant, eqn 4 is used in the same way, and

$$\nu_J = 2B(J+1) - 4D(J+1)^3 \quad \text{Rotational transition frequencies [non-rigid rotor]} \quad (11b)$$

Now, because the second term subtracts ever larger amounts from the first term as J increases, the lines converge as J increases. To find a way to determine B and D experimentally, divide both sides by $J+1$, to obtain

$$\frac{\nu_J}{J+1} = \frac{\text{intercept} + \text{slope} \times x}{J+1} = \frac{2B - 4D \times (J+1)^2}{J+1} \quad (12)$$

Therefore, by plotting the $\nu_J/(J+1)$ against $(J+1)^2$, a straight line should be obtained with intercept $2B$ and slope $-4D$ (see Problem 11.4).

Once the separation between adjacent lines in a rotational spectrum of a molecule has been measured and converted it to B , the value of B can be used to obtain the moment of inertia I_r . For a diatomic molecule, that value can be converted to a value of the bond length, R , by using eqn 2. Highly accurate bond lengths can be obtained in this way. In some cases, isotopic substitution can help. A classic case is the determination of the two bond lengths in the molecule

OCS. Analysis of the microwave spectrum of this linear molecule gives a single quantity, the rotational constant, and from this single quantity it is not possible to infer the two different bond lengths. However, by recording the absorption of the two isotopomers (molecules of different isotopic composition) $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ and $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ and assuming that isotopic substitution leaves the bond lengths unchanged, two pieces of information are obtained, the moment of inertia of each isotopomer, and it is now possible to infer the two bond lengths (see Problem 11.4).

11B.5 Rotational Raman spectra

The gross selection rule for rotational Raman spectra is that

To have a rotational Raman spectrum the molecule must have an anisotropic polarizability.

As seen in Topic 10A, the polarizability of a molecule is a measure of the extent to which an applied electric field can induce an electric dipole moment ($\mu = \alpha E$). The anisotropy of this polarizability is its variation with the orientation of the molecule (Fig. 11). Tetrahedral (CH_4), octahedral (SF_6), and icosahedral (C_{60}) molecules, like all spherical rotors, have the same polarizability regardless of their orientations, so these molecules are **rotationally Raman inactive**: they do not have rotational Raman spectra. All other molecules, including homonuclear diatomic molecules such as H_2 , are **rotationally Raman active**.

The specific selection rules for the rotational Raman transitions of linear molecules (the only ones considered here) are

$$\begin{aligned} \Delta J &= +2 \text{ (Stokes lines)} \\ \Delta J &= -2 \text{ (anti-Stokes lines)} \end{aligned} \quad (13)$$

Rotational Raman selection rules

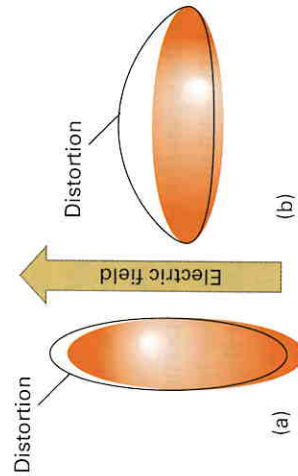


Fig. 11 The anisotropy of polarizability is depicted here by the different distortion induced by an electric field when the molecule is aligned (a) parallel to and (b) perpendicular to the field.

It follows that the change in energy when a rigid rotor makes the transition $J \rightarrow J+2$ is

$$\begin{aligned} \Delta E &= E_{J+2} - E_J = hB(J+2)(J+3) - hBJ(J+1) \\ &= hB\{J^2 + 5J + 6 - (J^2 + J)\} \\ &= 2hB(2J+3) \end{aligned}$$

Therefore, the shift in frequency for the transition $J \rightarrow J+2$ is

$$\Delta \nu_J = 2B(2J+3) \quad (14)$$

Raman shift (Stokes lines)

It follows that when a photon scatters from molecules in the rotational states $J=0, 1, 2, \dots$, and transfers some of its energy to the molecule, the frequency of the photon is decreased by $6B, 10B, 14B, \dots$ from the frequency of the incident radiation. If the photon acquires energy during the collision, then a similar argument shows that the anti-Stokes lines occur with frequencies $6B, 10B, 14B, \dots$ higher than the incident radiation (Fig. 12). It follows that from a measurement of the separation of the Raman lines, the value of B can be determined and, from it, the bond length can be calculated. Because homonuclear diatomic species are rotationally Raman active, this technique can be applied to them as well as to heteronuclear species.

There is an important qualification of these remarks for symmetrical molecules, such as H_2 and C^{16}O_2 . Nuclear statistics either rule out certain states or leads to an alternation of populations. For instance, C^{16}O_2 can exist only in states with even values of J . As a result, its rotational Raman spectrum consists of lines at $6B, 14B, 22B, \dots$ and separated by $8B$ because the lines starting from odd values of J are missing. For molecules with non-zero nuclear

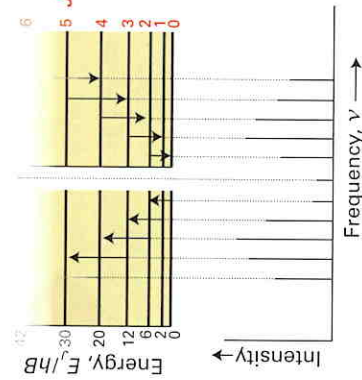


Fig. 12 The transitions responsible for the Stokes and anti-Stokes lines of a rotational Raman spectrum of an unsymmetrical linear molecule, such as NO or N_2O .

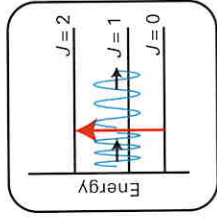
spin, all the Raman lines are present but they show an alternation of intensities: for H_2 , the odd- J lines are three times more intense than the even- J lines, whereas for D_2 and N_2 , even- J lines are twice as intense as the odd- J lines.

Example 11B.2

Predicting the form of a rotational Raman spectrum

Predict the wavenumber of the $0 \rightarrow 2$ line of the rotational Raman spectrum of $^{14}\text{N}_2$, for which $\tilde{B} = 1.99 \text{ cm}^{-1}$, when it is exposed to 336.732 nm laser radiation.

Collect your thoughts The molecule is rotationally Raman active because end-over-end rotation modulates its polarizability as viewed by a stationary observer. Because the rotational constant is given in wavenumbers, use eqn 14 in the equivalent form $\Delta \tilde{\nu} = 2\tilde{B}(2J+3)$ to



calculate the Raman shift in wavenumbers. Then convert the wavelength of the incident radiation to a wavenumber, $\tilde{\nu}$. Because this is a Stokes line, the wavenumber of the scattered radiation is lower than that of the incident radiation, so calculate the wavenumber of the line as $\tilde{\nu}_i - \Delta \tilde{\nu}$.

The solution Equation 14, written as $\Delta \tilde{\nu} = 2\tilde{B}(2J+3)$, gives $\Delta \tilde{\nu} = 11.9 \text{ cm}^{-1}$ for $J=0$. Because $\lambda_i = 336.732 \text{ nm}$ corresponds to $\tilde{\nu}_i = 1/\lambda_i = 29\,697.2 \text{ cm}^{-1}$, it follows that the $0 \rightarrow 2$ line appears at a wavenumber of $\tilde{\nu}_i - \Delta \tilde{\nu} = (29\,697.2 - 11.9) \text{ cm}^{-1} = 29\,685.3 \text{ cm}^{-1}$.

Self-test 11B.5

Repeat the calculation for the rotational Raman spectrum of NH_3 ($\tilde{B} = 9.977 \text{ cm}^{-1}$).

Answer: $29\,637.3 \text{ cm}^{-1}$

Checklist of key concepts

- 1 The **populations** of rotational energy levels are given by the Boltzmann distribution in connection with noting the degeneracy of each level.
- 2 The **gross selection rule for rotational transitions** is that the molecule must be polar.
- 3 The consequences of the Pauli principle for rotational states are called **nuclear statistics**.

□4 The microwave spectrum of a polar linear molecule and of a polar symmetric rotor consists of a series of lines at frequencies separated by $2B$.

□5 The **gross selection rule for rotational Raman spectra** is that the polarizability of the molecule must be anisotropic.

TOPIC 11C

Vibrational spectroscopy

► Why do you need to know this material?

The observation of transitions between the vibrational states of a molecule gives information about the identity of the molecule and provides quantitative information about the flexibility of its bonds. Infrared and Raman methods are valuable and widely used analytical tools.

► What is the key idea?

The vibrational spectrum of a molecule can be interpreted by using the harmonic oscillator model, with modifications that account for bond dissociation and the coupling of rotational and vibrational motion.

► What do you need to know already?

You need to be familiar with the harmonic oscillator (Topic 7E) and rigid rotor (Topics 7D and 11B) models of molecular motion, the general principles of spectroscopy (Topic 11A), and the interpretation of rotational spectra (Topic 11B).

All molecules are capable of vibrating, and complicated molecules may do so in a large number of different modes. Even a benzene molecule, with 12 atoms, can vibrate in 30 different modes, some of which involve the periodic swelling and shrinking of the ring and others its buckling into various distorted shapes. A molecule as big as a protein can vibrate in thousands of different ways, twisting, stretching, and bending in different regions and in different manners. Many of these vibrations can be excited by the absorption of electromagnetic radiation. The detection of the frequencies at which this absorption occurs gives very valuable information about the identity of

The potential energy in eqn 1 has the same form as that for the harmonic oscillator (Topic 7E), so the solutions of the Schrödinger equation given there can be used here. The only complication is that both atoms joined by the bond move, so the ‘mass’ of the oscillator has to be interpreted carefully. Detailed calculation shows that for two atoms of masses m_A and m_B joined by a bond of force constant k , the energy levels are

$$E_\nu = \left(\nu + \frac{1}{2}\right)h\nu \quad (2a)$$

$$\nu = 0, 1, 2, \dots$$

where

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \quad (2b)$$

and

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (2c)$$

The effective mass of the molecule, μ , is a measure of the quantity of matter moved during the vibration. The effective masses of polyatomic molecules are complicated combinations of the atomic masses with each atomic mass contributing in a manner reflecting how much that atom moves. Vibrational transitions are commonly expressed as a wavenumber (in reciprocal centimetres), so it is often convenient to write eqn 2a as

$$\tilde{\nu} = \left(\nu + \frac{1}{2}\right)hc\tilde{\nu} \quad \tilde{\nu} = \nu/c \quad (2d)$$

Figure 2 illustrates these energy levels: they form a uniform ladder with separation $hc\tilde{\nu}$ between neighbours.

A note on good practice The effective mass is widely called the *reduced mass*. However, that is only because the effective vibrational mass of a diatomic molecule happens to be given by the same expression as its reduced mass, a quantity that occurs in the separation of the internal motion of a molecule from its overall translation. For polyatomic molecules the effective mass is not the same as the reduced mass, and depends on the vibrational mode. It is better to distinguish the two from the outset.

At first sight it might be puzzling that the effective mass appears rather than the total mass of the two atoms. However, the presence of μ is physically plausible. If atom A were as heavy as a brick wall, it would not move at all during the vibration and the vibrational frequency would be determined by the lighter, mobile atom. Indeed, if A was a brick wall, m_B could be neglected compared with m_A in the denominator of μ and $\mu \approx m_B$, the mass of the lighter atom. This is approxi-

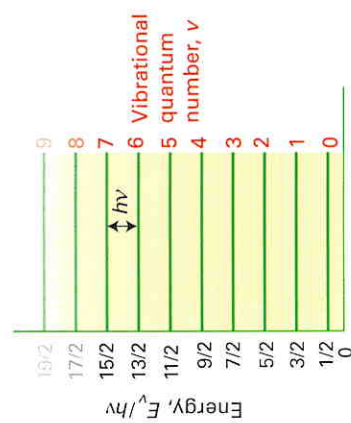


Fig. 2 The energy levels of a harmonic oscillator. The quantum number ν ranges from 0 to infinity, and the permitted energy levels form a uniform ladder with spacing $h\nu$.

mately the case in HI, for example, where the I atom barely moves as the molecule vibrates and $\mu \approx m_H$. In the case of a homonuclear diatomic molecule, for which $m_A = m_B = m$, the effective mass is half the mass of one atom: $\mu = \frac{1}{2}m$.

Brief illustration 11C.1 The vibrational frequency

An $^1\text{H}^{35}\text{Cl}$ molecule has a force constant of 516 N m^{-1} , a reasonably typical value. Its effective mass is

$$\begin{aligned} \mu &= \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{(1.008 m_{\text{u}}) \times (34.969 m_{\text{u}})}{1.008 m_{\text{u}} + 34.969 m_{\text{u}}} \\ &= \frac{1.008 \times 34.969}{1.008 + 34.969} m_{\text{u}} = 0.9797 \dots m_{\text{u}} \end{aligned}$$

Therefore, its vibrational frequency is

$$\begin{aligned} \nu &= \frac{1}{2\pi} \left(\frac{k}{0.9797 \dots \times (1.66054 \times 10^{-27} \text{ kg})} \right)^{1/2} \\ &= 8.96 \times 10^{13} \text{ s}^{-1} \end{aligned}$$

The frequency corresponds to 89.6 THz . The corresponding wavenumber is

$$\tilde{\nu} = \frac{\nu}{c} = \frac{8.96 \times 10^{13} \text{ s}^{-1}}{2.998 \times 10^8 \text{ m s}^{-1}} = 2.99 \times 10^5 \text{ m}^{-1}$$

This value corresponds to $2.99 \times 10^3 \text{ cm}^{-1}$.

Self-test 11C.1

The vibrational frequency ν of $^{35}\text{Cl}_2$ is 16.94 THz . What is the force constant of the bond?

Answer: 3278 N m^{-1}

the molecule and provides quantitative information about the flexibility of its bonds.

11C.1 The vibrations of molecules

Figure 1 shows a typical potential energy curve of a diatomic molecule as its bond is lengthened by pulling one atom away from the other or shortened by pressing it into the other. In regions close to the equilibrium bond length R_e (at the minimum of the curve) the potential energy can be approximated by a parabola (a curve of the form $y \propto x^2$), and

$$V(x) = \frac{1}{2} k_t x^2 \quad (1)$$

where $x = R - R_e$ is the displacement from equilibrium and k_t is the force constant of the bond (units: newtons per metre, N m^{-1}), as in the discussion of vibrational motion in Topic 7E. The steeper the walls of the potential (the stiffer the bond), the greater is the force constant.

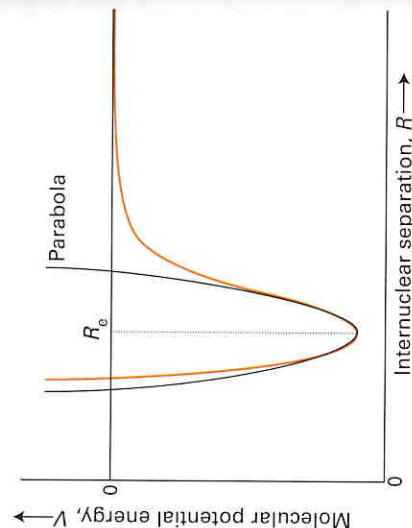


Fig. 1 A molecular potential energy curve can be approximated by a parabola near the bottom of the well. A parabolic potential results in harmonic oscillation. At high vibrational excitation energies the parabolic approximation is poor.

11C.2 Vibrational transitions

Because typical vibrational frequencies are of the order of 10^{13} – 10^{14} Hz, transitions can be induced with radiation of this frequency, which corresponds to infrared radiation. That is, vibrational transitions are observed by **infrared spectroscopy**. In infrared spectroscopy, transitions are normally expressed in terms of their wavenumbers and lie typically in the range 300–4000 cm^{-1} .

The gross selection rule for vibrational spectra is that

For a vibrational transition to occur as a result of absorption or emission of a photon, the electric dipole moment of the molecule must change during the vibration.

The basis of this rule is that the molecule can shake the electromagnetic field into oscillation only if it has an electric dipole moment that oscillates as the molecule vibrates (Fig. 3). The molecule need not have a permanent dipole: the rule requires only a *change* in dipole moment, possibly from zero. The stretching motion of a homonuclear diatomic molecule does not change its electric dipole moment from zero, so the vibrations of such molecules neither absorb nor generate radiation. Homonuclear diatomic molecules are said to be **infrared inactive**, because their dipole moments remain zero however long the bond. Heteronuclear diatomic molecules, which have a dipole moment that changes as the bond lengthens and contracts, are **infrared active**.

Example 11C.1

Using the gross selection rule

Identify which of the following molecules are infrared active: N_2 , CO_2 , OCS , H_2O , $\text{CH}_2=\text{CH}_2$, C_6H_6 .

Collect your thoughts Molecules that are infrared active (that is, have vibrational spectra) have dipole moments that change during the course of a vibration. Therefore, judge whether a distortion of the molecule can change its dipole moment (including changing it from zero).

The solution All the molecules except N_2 possess at least one vibrational mode that results in a change of dipole moment, so all except N_2 are infrared active. Note that not all the modes of complicated molecules are infrared active. For example, a vibration of CO_2 in which the O—C—O bonds stretch and contract symmetrically is inactive because it leaves the dipole

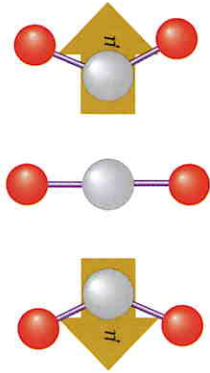


Fig. 3 The oscillation of a molecule, even if it is nonpolar, may result in an oscillating dipole that can interact with the electromagnetic field. Shown is a representation of a bending mode of CO_2 .

moment unchanged (at zero). A bending motion of the molecule, however, is active and can absorb radiation.

Self-test 11C.2

Repeat the question for H_2 , NO , and N_2O .

Answer: NO and N_2O .

The specific selection rule for vibrational transitions is

$$\Delta\nu = \pm 1 \quad \text{Vibrational selection rule} \quad (3)$$

The change in energy for the transition from a state with quantum number ν to one with quantum number $\nu + 1$ is

$$\Delta E = E_{\nu+1} - E_{\nu} = \left(\nu + \frac{1}{2}\right)hc\tilde{\nu} - \left(\nu - \frac{1}{2}\right)hc\tilde{\nu} = hc\tilde{\nu} \quad (4)$$

It follows that absorption occurs when the incident radiation provides photons with this energy, and therefore when the incident radiation has a wavenumber given by eqn 2d. Molecules with stiff bonds (large k_f) joining atoms with low masses (small μ) are usually less stiff than stretching modes, so bends typically occur at lower wavenumbers than stretches in a spectrum.

At room temperature, almost all the molecules are in their vibrational ground states initially (the state with $\nu = 0$). Therefore, the most intense spectral transition is from $\nu = 0$ to $\nu = 1$.

Brief illustration 11C.2

Vibrational transitions It follows from the calculation of $\tilde{\nu}$ for HCl (in Brief illustration 11C.1), that $\tilde{\nu} = 2992 \text{ cm}^{-1}$, so the infrared spectrum of the molecule will feature an absorption at that wavenumber. The corresponding frequency and wavelength are 89.7 THz and 3.34 μm , respectively.

Self-test 11C.3

The force constant of the bond in the CO group of a peptide link is approximately 1.2 kN m^{-1} . At what wavenumber would you expect it to absorb? *Hint:* For the effective mass, treat the group as a $^{12}\text{C}^{16}\text{O}$ molecule.

Answer: At approximately 1720 cm^{-1} .

11C.3 Anharmonicity

The vibrational transition energies in eqn 4 are only approximate because they are based on a parabolic approximation to the actual potential energy curve. A parabola cannot be correct at all extensions because it does not allow a molecule to dissociate. At high vibrational excitations the swing of the atoms (more precisely, the spread of the vibrational wavefunction) allows the molecule to explore regions of the potential energy curve where the parabolic approximation is poor. The motion then becomes **anharmonic**, in the sense that the restoring force is no longer proportional to the displacement. Because the actual curve is less confining than a parabola, the energy levels become less widely spaced at high excitation, just as the energy levels of a particle in a box get closer together as the length of the box is increased (Topic 7C).

The convergence of levels at high vibrational quantum numbers is expressed by replacing eqn 2d by

$$E_{\nu} = \left(\nu + \frac{1}{2}\right)hc\tilde{\nu} - \left(\nu + \frac{1}{2}\right)^2hc\tilde{\nu}x_e + \dots \quad \text{Anharmonicity correction} \quad (5)$$

where x_e is the (dimensionless) **anharmonicity constant**. Anharmonicity also accounts for the appearance of additional weak absorption lines called **overtones** corresponding to the transitions with $\Delta\nu = +2, +3, \dots$. These overtones appear because the usual selection rule is derived from the properties of harmonic oscillator wavefunctions, which are only approximately valid when anharmonicity is present. Overtones in a vibrational spectrum can appear in the near infrared region.

11C.4 Vibrational Raman spectra of diatomic molecules

In **vibrational Raman spectroscopy** the incident photon leaves some of its energy in the vibrational modes of the molecule it strikes, giving rise to the Stokes radiation, or collects additional energy from a vibration that has already been excited, giving rise to the anti-Stokes radiation. The Stokes lines are more intense than the anti-Stokes lines because

very few molecules are in an excited vibrational state initially.

The gross selection rule for vibrational Raman spectroscopy is that

For a Raman transition to occur, the molecular polarizability must change as the molecule vibrates.

The polarizability plays a role in vibrational Raman spectroscopy because the molecule must be squeezed and stretched by the incident radiation in order that a vibrational excitation may occur during the photon–molecule collision. Both homonuclear and heteronuclear diatomic molecules swell and contract during a vibration, and the control of the nuclei over the electrons, and hence the molecular polarizability, changes too. Both types of diatomic molecule are therefore vibrationally Raman active.

The specific selection rule for vibrational Raman transitions is the same as for infrared transitions:

$$\Delta\nu = \pm 1 \quad \text{Raman selection rule} \quad (6)$$

The Stokes lines are those for which $\Delta\nu = +1$; the anti-Stokes lines are those for which $\Delta\nu = -1$.

The information available from vibrational Raman spectra adds to that from infrared spectroscopy because homonuclear diatomic molecules can also be studied. The spectra can be interpreted in terms of the force constants, dissociation energies, and bond lengths, and some of the information obtained is included in Table 11C.1. It is used, for example, in the calculation of equilibrium constants (Topic 12C).

Table 11C.1
Properties of diatomic molecules

$\tilde{\nu}/\text{cm}^{-1}$	R_e/pm	$k_f/(\text{N m}^{-1})$	$D_0/(\text{kJ mol}^{-1})^*$
$^1\text{H}_2^+$	106	160	256
$^1\text{H}_2$	74	575	432
$^2\text{H}_2$	74	577	440
$^1\text{H}^{19}\text{F}$	92	955	564
$^1\text{H}^{35}\text{Cl}$	127	516	428
$^1\text{H}^{81}\text{Br}$	141	412	363
$^1\text{H}^{127}\text{I}$	161	314	295
$^{14}\text{N}_2$	110	2294	942
$^{16}\text{O}_2$	121	1177	494
$^{19}\text{F}_2$	142	445	154
$^{35}\text{Cl}_2$	199	323	239

* D_0 is the dissociation energy of the diatomic species, the energy required to break the bond when the species is in its ground vibrational state ($\nu = 0$).

11C.5 The vibrations of polyatomic molecules

How many modes of vibration are there for a polyatomic molecule? The answer to this question comes from consideration of how many ways each atom may change its location. As shown in the following *Justification*, for a molecule built from N atoms the number of vibrational modes, N_{vib} , is

$$\begin{aligned} \text{Nonlinear molecules: } N_{\text{vib}} &= 3N - 6 \\ \text{Linear molecules: } N_{\text{vib}} &= 3N - 5 \end{aligned}$$

Brief illustration 11C.3 The number of vibrational modes

A water molecule, H_2O , is triatomic ($N = 3$) and nonlinear, and has $N_{\text{vib}} = 3$ modes of vibration. Naphthalene, C_{10}H_8 , with $N = 18$ and nonlinear, has 48 distinct modes of vibration. Any diatomic molecule ($N = 2$) has one vibrational mode; carbon dioxide ($N = 3$) has four vibrational modes.

Self-test 11C.4

How many normal modes of vibration are there in (a) ethyne ($\text{HC}\equiv\text{CH}$) and (b) a protein molecule of 4000 atoms?

Answer: (a) 7, (b) 11 994

Justification 11C.4

The number of normal modes

Each atom can be displaced along any of three perpendicular axes. Therefore, the total number of such displacements in a molecule consisting of N atoms is $3N$. Three correspond to movement of the centre of mass of the molecule, so correspond to the translational motion of the molecule as a whole. The remaining $3N - 3$ displacements are 'internal' modes of the molecule that leave its centre of mass unchanged. Three angles are needed to specify the orientation of a nonlinear molecule in space (Fig. 4). Therefore three of the $3N - 3$ internal displacements leave all bond angles and bond lengths unchanged but change the orientation of the molecule as a whole. These three displacements are therefore rotations. That leaves $3N - 6$ displacements which change neither the centre of mass of the molecule nor the orientation of the molecule in space. These $3N - 6$ displacements are the vibrational modes. A similar calculation for a linear molecule, which requires only two angles to specify its orientation in space, gives $3N - 5$ as the number of vibrational modes.

The description of the vibrational motion of a polyatomic molecule is much simpler if various combinations of the stretching and bending motions of individual bonds are considered. For example, although two of the four vibrations of a CO_2 molecule

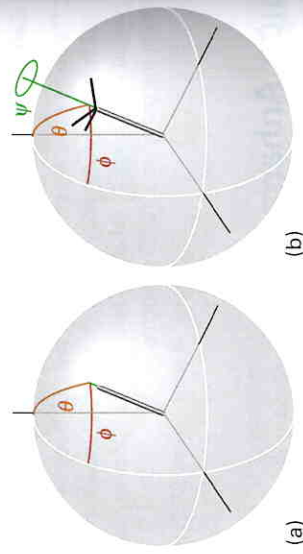


Fig. 4 (a) The orientation of a linear molecule requires the specification of two angles (the colatitude, θ , and longitude, ϕ , of its axis). (b) The orientation of a nonlinear molecule requires the specification of three angles (the latitude and longitude of its axis and the angle of twist (the azimuthal angle, ψ) around that axis).

could be described as individual carbon–oxygen bond stretches, ν_1 and ν_2 in Fig. 5, the description of the motion is much simpler if two combinations of these vibrations are used instead. One problem with dealing with individual bond stretches is that they are not independent: if one bond is stimulated to vibrate, the motion of the shared C atom quickly stimulates the other bond to vibrate. One combination is ν_1 in Fig. 6: this combination is the **symmetric stretch**. The other combination is ν_3 , the **antisymmetric stretch**, in which the two O atoms always move in the same directions and opposite to the C atom. The two modes are independent in the sense that if one is excited,

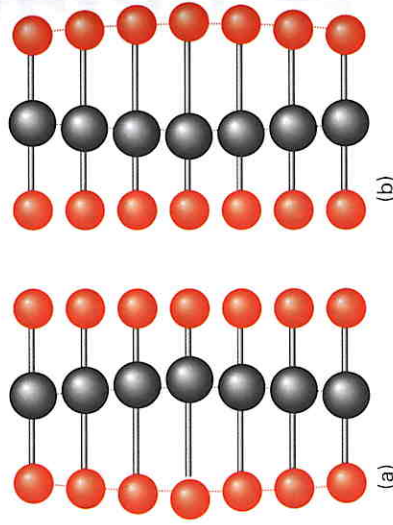


Fig. 5 The stretching vibrations of a CO_2 molecule can be represented in a number of ways. In this representation, (a) one $\text{O}=\text{C}$ bond vibrates and the remaining O atom is stationary, and (b) the $\text{C}=\text{O}$ bond vibrates while the other O atom is stationary. Because the stationary atom is linked to the C atom, it does not remain stationary for long. That is, if one vibration begins, it rapidly stimulates the other to occur.

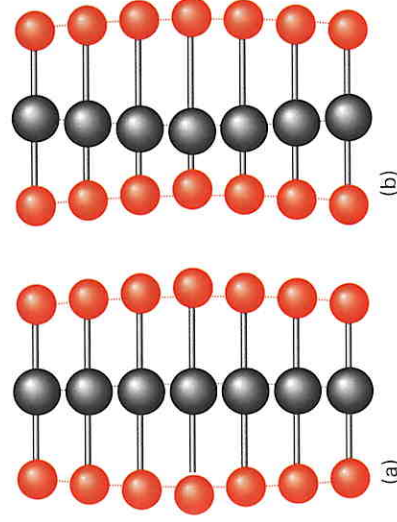


Fig. 6 Alternatively, linear combinations of the two modes can be taken to give these two normal modes of the molecule. The mode in (a) is the symmetric stretch and that in (b) is the antisymmetric stretch. The two modes are independent, and if either of them is stimulated, the other remains unexcited.

then its motion does not excite the other. They are two of the four 'normal modes' of the molecule, its independent, collective vibrational displacements. The two other (degenerate) normal modes are the **bending modes**, ν_2 . In general, a **normal mode** is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal mode.

The four normal modes of CO_2 , and the $3N - 6$ (or $3N - 5$) normal modes of polyatomic molecules in general (for instance, those of methane, Fig. 7), are the key to the description of molecular vibrations. Each normal mode behaves like an independent harmonic oscillator and the energies of the vibrational levels are given by the same expression as in eqn 4, but with an effective mass that depends on the extent to which each of the atoms contributes to the

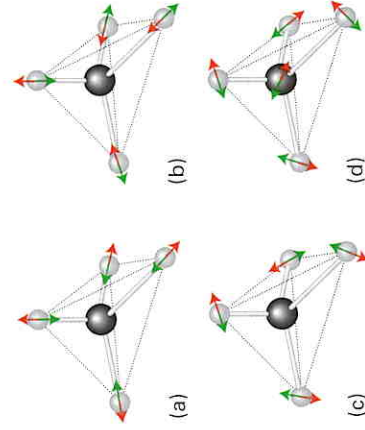


Fig. 7 Some of the normal modes of vibration of CH_4 . An arrow indicates the direction of motion of an atom during the vibration.

vibration. Atoms that do not move, such as the C atom in the symmetric stretch of CO_2 , do not contribute to the effective mass. The force constant also depends in a complicated way on the extent to which bonds bend and stretch during a vibration. Typically, a normal mode that is largely a bending motion has a lower force constant (and hence a lower frequency) than a normal mode that is largely a stretching motion.

The gross selection rule for the infrared activity of a normal mode is that

For a normal mode to be infrared active, the motion must give rise to a changing dipole moment.

Deciding whether the dipole moment changes can sometimes be done by inspection. For example, the symmetric stretch of CO_2 leaves the dipole moment unchanged (at zero), so this mode is infrared inactive and makes no contribution to the molecule's infrared spectrum. The antisymmetric stretch, however, changes the dipole moment because the molecule becomes unsymmetrical as it vibrates, so this mode is infrared active. The fact that the mode does absorb infrared radiation enables carbon dioxide to act as a 'greenhouse gas' by absorbing infrared radiation emitted from the surface of the Earth.

Brief illustration 11C.4 Infrared activity

The infrared spectrum of dinitrogen oxide (nitrous oxide, N_2O , with the structure $\text{N}=\text{N}=\text{O}$) differs from that of carbon dioxide in a variety of ways despite both being linear triatomic molecules. First, the corresponding vibrational modes have different frequencies on account of different atomic masses and force constants. In CO_2 , the symmetric stretch is not infrared active, so only three modes (the asymmetric stretch and the two degenerate bending modes) are active. In contrast, all four vibrational modes of N_2O are infrared active.

Self-test 11C.5

Identify a normal mode of C_6H_6 that is not infrared active.
Answer: A 'breathing' mode in which all the carbon–carbon bonds contract and stretch synchronously, while the C–H bonds either do not vibrate or stretch and contract synchronously (Fig. 8).

Some of the normal modes of organic molecules can be regarded as motions of individual functional groups. Others cannot be regarded as localized in this way and are better regarded as collective motions of the molecule as a whole. The latter are generally of relatively low frequency, and occur at wavenumbers below about 1500 cm^{-1} in the spectrum. The resulting

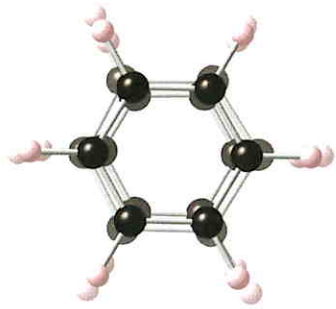


Fig. 8 The symmetrical breathing vibrational mode of C_6H_6 (benzene). This normal mode is not infrared active.

whole-molecule region of the absorption spectrum is called the **fingerprint region** of the spectrum, for it is characteristic of the molecule. The matching of the fingerprint region with a spectrum of a known compound in a library of infrared spectra is a powerful way of confirming the presence of a particular substance.

The characteristic vibrations of functional groups that occur outside the fingerprint region are very useful for the identification of an unknown compound. Most of these vibrations can be regarded as stretching modes, for the lower frequency bending modes usually occur in the fingerprint region and so are less readily identified.

11C.6 Vibration–rotation spectra

The vibrational spectra of gas-phase molecules are more complicated than the discussion so far implies, because the excitation of a vibration also results in the excitation of rotation. The effect is rather like what happens when ice skaters throw out or draw in their arms: they rotate more slowly or more rapidly. The effect on the spectrum is to break the single line resulting from a vibrational transition into a multitude of lines with separations between neighbours that depend on the rotational constant, B (or \tilde{B}), of the molecule.

To establish the so-called ‘band structure’ of a vibrational transition, it is necessary to write the expressions for the vibrational and rotational levels. For a rigid linear molecule (the only type considered here), combining eqns 1 in Topic 11B (in the form $E_J = hc\tilde{B}J(J+1)$, $J = 0, 1, 2, \dots$) for its rotational energies and eqn 4 for its vibrational energies gives

$$E_{v,J} = (v + \frac{1}{2})hc\tilde{\nu} + hc\tilde{B}J(J+1) \quad (7)$$

Vibration–rotation energies

The value of the rotational constant \tilde{B} depends on the vibrational state of the molecule, because the moment of inertia of the molecule changes as it vibrates. Therefore \tilde{B} depends on v , but that complication is ignored here. Provided the molecule is polar, or at least acquires a dipole moment in a vibrational transition (as when CO_2 bends or undergoes an asymmetric stretch), the rotational quantum number may change by ± 1 or (in some cases, see below) 0. With $\Delta v = 1$, the absorptions then fall into three groups called **branches** of the spectrum:

$$\Delta J = -1: \quad \tilde{\nu}_J = \tilde{\nu} - 2\tilde{B}J \quad (8a)$$

$$\Delta J = 0: \quad \tilde{\nu}_J = \tilde{\nu} \quad (8b)$$

$$\Delta J = +1: \quad \tilde{\nu}_J = \tilde{\nu} + 2\tilde{B}(J+1) \quad (8c)$$

The Q branch is not always allowed. For example, it is observed in the spectrum of NO, but not in the spectrum of HCl: the difference can be traced to the fact that NO, with an electron in a π orbital, has electronic angular momentum around its internuclear axis but HCl does not.¹

Figure 9 shows the resulting appearance of the branches of a typical spectrum. The separation between the lines in the P and R branches of a vibrational transition is $2\tilde{B}$. Therefore, the bond length can be deduced without needing to take a pure rotational microwave spectrum. However, the latter is more precise.

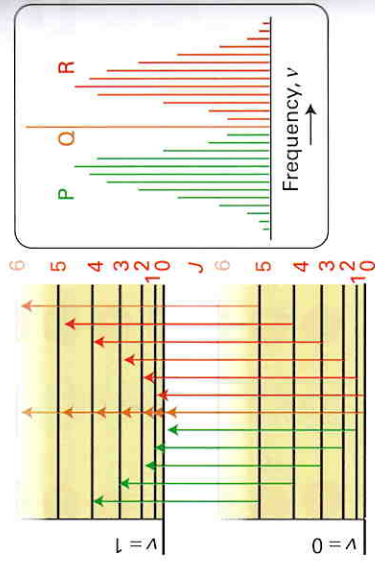


Fig. 9 The formation of P, Q, and R branches in a vibration–rotation spectrum. The intensities reflect the populations of the initial rotational levels.

¹For more information, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

Brief illustration 11C.5 The wavenumber of an R branch transition

Infrared absorption by ^{81}Br gives rise to an R branch from $v=0$. It follows from eqn 8c, $\tilde{\nu} = 2648.98 \text{ cm}^{-1}$, and $\tilde{B} = 8.465 \text{ cm}^{-1}$ that the wavenumber of the line originating from the rotational state with $J=2$ is

$$\tilde{\nu}_2 = \tilde{\nu} + 6\tilde{B} = (2648.98 \text{ cm}^{-1}) + 6 \times (8.465 \text{ cm}^{-1}) = 2699.77 \text{ cm}^{-1}$$

Self-test 11C.6

Infrared absorption by $^{1}H^{37}Cl$ gives rise to an R branch from $v=0$. What is the wavenumber of the line originating from the rotational state with $J=2$? Use $\tilde{\nu} = 2308.09 \text{ cm}^{-1}$, and $\tilde{B} = 6.511 \text{ cm}^{-1}$.

Answer: 2347.16 cm^{-1}

11C.7 Vibrational Raman spectra of polyatomic molecules

The gross selection rule for the vibrational Raman spectrum of a polyatomic molecule is that

For a normal mode to be Raman active, the vibration must be accompanied by a changing polarizability.

It is often quite difficult to judge by inspection when vibration affects polarizability. The symmetric stretch of CO_2 , for example, alternately swells and contracts the molecule: this motion changes its polarizability, so the mode is Raman active. The other modes of CO_2 are Raman inactive because the polarizability does not change as the atoms move collectively. A very simple explanation (which is not reliable in all cases) is that the polarizability of a molecule depends on its size, and whereas the symmetric stretch changes the size of the molecule neither the antisymmetric stretch nor the bending modes do—at least, to a first approximation.

In some cases it is possible to make use of a very general rule about the infrared and Raman activity of vibrational modes:

The exclusion rule states that if the molecule has a centre of inversion, then no modes are both infrared and Raman active.

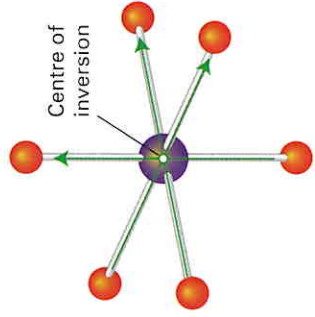


Fig. 10 In an inversion operation, we consider every point in a molecule, and project them all through the centre of the molecule out to an equal distance on the other side.

(A mode may be inactive in both.) A molecule has a ‘centre of inversion’ if it looks unchanged when each atom is projected through a single point and out an equal distance on the other side (Fig. 10). Because it is often possible to judge intuitively when a mode changes the molecular dipole moment, this rule can be used to identify modes that are not Raman active. The rule applies to CO_2 but to neither H_2O nor CH_4 because they have no centre of symmetry. Thus, both the antisymmetric stretch and the bending modes of CO_2 are infrared active, so we know at once that they are Raman inactive.

Brief illustration 11C.6 Raman activity

One vibrational mode of benzene is a ‘breathing mode’ in which the entire ring alternately expands and contracts symmetrically (Fig. 8). As it does so, the polarizability of the molecule changes because the electron distribution can be compressed or expanded. As a result, this mode is Raman active. As seen in *Self-test 11C.5*, it is not infrared active because the molecular dipole moment remains unchanged (at zero). As the molecule has a centre of inversion, this conclusion is consistent with the exclusion rule.

Self-test 11C.7

Predict whether the symmetric stretching mode of ethene, C_2H_4 , in which all of the C–H bonds stretch in phase, is infrared active, Raman active, or both.

Answer: Raman active only

Checklist of key concepts

- 1 The **gross selection rule for vibrational spectra** is that the electric dipole moment of the molecule must change during the vibration.
- 2 The **number of vibrational modes** of nonlinear molecules is $3N - 6$; for linear molecules the number is $3N - 5$.
- 3 Rotational transitions accompany vibrational transitions and split the spectrum into a **P branch** ($\Delta J = -1$), a **Q branch** ($\Delta J = 0$), and an **R branch** ($\Delta J = +1$).
- 4 A Q branch is observed only when the molecule possesses angular momentum around its axis.
- 5 The **gross selection rule for the vibrational Raman spectrum** of a polyatomic molecule is that the normal mode of vibration is accompanied by a changing polarizability.
- 6 The **exclusion rule** states that if the molecule has a centre of inversion, then no modes can be both infrared and Raman active.

TOPIC 11D

Electronic spectroscopy

► Why do you need to know this material?

To understand the colours of objects and how chemical reactions may be initiated by absorption of radiation, you need to explore the origins of electronic transitions in molecules. The spectroscopic techniques described here also provide experimental tests of molecular orbital theory.

► What is the key idea?

Electronic transitions occur within a stationary nuclear framework.

► What do you need to know already?

You need to be familiar with molecular orbital theory (Topics 9B–9D) and the general features of spectroscopy (Topic 11A). One part of the Topic draws on qualitative information about molecular vibrations (Topic 11C) and another the Beer–Lambert law (Topic 11A).

The energy needed to change the occupation of orbitals in a molecule is of the order of several electronvolts (an energy difference of 1 eV is equivalent to radiation of wavenumber 8066 cm^{-1}). Consequently, the photons emitted or absorbed when such changes occur lie in the visible and ultraviolet regions of the spectrum, which spread from about $14\,000 \text{ cm}^{-1}$ for red light to $21\,000 \text{ cm}^{-1}$ for blue light, and on to $50\,000 \text{ cm}^{-1}$ for ultraviolet radiation (Table 11D.1). Radiation of higher energy, in the deeper ultraviolet to X-ray range, can eject electrons from molecules.

11D.1 Ultraviolet and visible spectra

White light is a mixture of light of all different colours. The removal, by absorption, of any one of these colours from white light results in the complementary colour being observed. For instance, the absorption of red light from white light by an object results in that object appearing green, the complementary colour of red. Conversely, the absorption of

Table 11D.1
Colour, frequency, and energy of light

Colour	λ/nm	$\nu/(10^{14} \text{ Hz})$	$\tilde{\nu}/(10^4 \text{ cm}^{-1})$	E/eV	E/(kJ mol ⁻¹)
Infrared	>1000	<3.00	<1.00	<1.24	<120
Red	700	4.28	1.43	1.77	171
Orange	620	4.84	1.61	2.00	193
Yellow	580	5.17	1.72	2.14	206
Green	530	5.66	1.89	2.34	226
Blue	470	6.38	2.13	2.64	254
Violet	420	7.14	2.38	2.95	285
Ultraviolet	<400	>7.5	>2.5	>3.10	>300

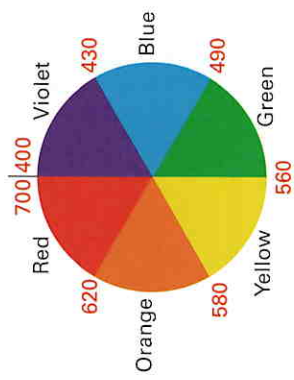


Fig. 1 An artist's colour wheel: complementary colours are opposite one another on a diameter. The numbers correspond to wavelengths of light in nanometres (nm).

green results in the object appearing red. The pairs of complementary colours are neatly summarized by the artist's colour wheel shown in Fig. 1, where complementary colours lie opposite one another along a diameter.

It should be stressed, however, that the perception of colour is a very subtle phenomenon. Although an object may appear green because it absorbs red light, it may also appear green because it absorbs all colours from the incident light *except* green. This is the origin of the colour of vegetation, because chlorophyll absorbs in two regions of the spectrum, leaving green to be reflected or transmitted (Fig. 2). Moreover, an absorption band may be very broad, and although it may be a maximum at one particular wavelength, it may have a long tail that spreads into other regions (Fig. 3). In such cases, it is very difficult to predict the perceived colour from the location of the absorption maximum.

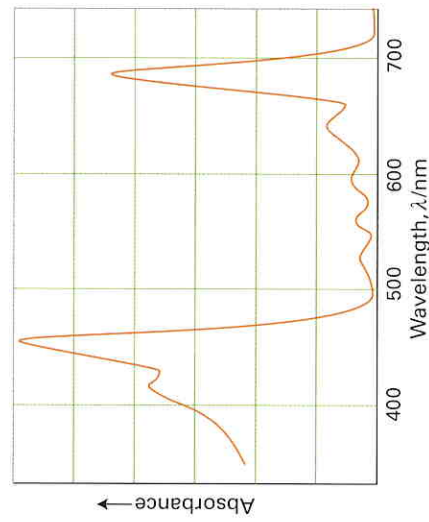


Fig. 2 The absorption spectrum of chlorophyll in the visible region. Note that it absorbs in the red and blue regions, and that green light is not absorbed.

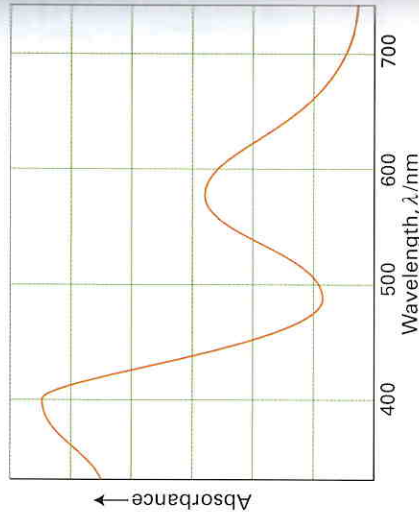


Fig. 3 An electronic absorption of a species in solution is typically very broad and consists of several broad bands.

Whenever an electronic transition takes place it is accompanied by the excitation of vibrations of the molecule. In the electronic ground state of a molecule, the nuclei take up locations in response to the Coulombic forces acting on them. These forces arise from the electrons and the other nuclei. Immediately after an electronic transition, when electron density has migrated to a different part of the molecule, the nuclei are subjected to different forces and the molecule may respond by bursting into vibration. As a result, some of the energy used to redistribute an electron is in fact used to stimulate the vibrations of the absorbing molecules. Therefore, instead of a single, sharp, and purely electronic absorption line being observed, the absorption spectrum consists of many lines. This vibrational structure of an electronic transition can be resolved if the sample is gaseous, but in a liquid or solid the lines usually merge together and result in a broad, almost featureless band (Fig. 4).

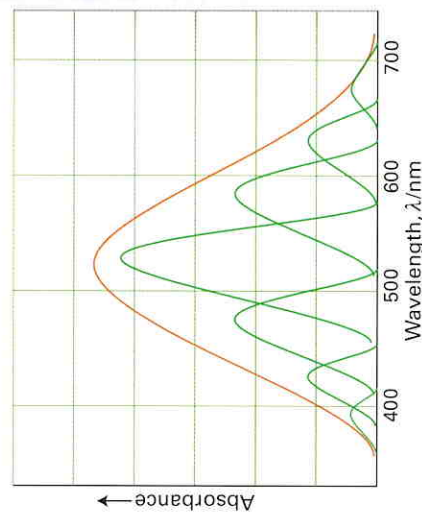


Fig. 4 An electronic absorption band consists of many superimposed bands which merge together to give a single broad band with unresolved vibrational structure.

The vibrational structure of a band is explained by the Franck–Condon principle:

Because nuclei are so much more massive than electrons, an electronic transition takes place faster than the nuclei can respond.

In an electronic transition, electron density is lost rapidly from some regions of the molecule and is built up rapidly in others. As a result, the initially stationary nuclei suddenly experience a new force field. They respond by beginning to vibrate, and (in classical terms) swing backwards and forwards from their original separation, which they maintained during the rapid electronic excitation. The initial, stationary, equilibrium separation of the nuclei in the initial electronic state therefore becomes the new, stationary turning point, one of the end points of a nuclear swing, in the final electronic state (Fig. 5).

To predict the most likely final vibrational state, a vertical line is drawn from the minimum of the lower curve (the starting point for the transition) up to the point at which the line intersects the curve representing the upper electronic state (the turning point of the newly stimulated vibration). This procedure gives rise to the name **vertical transition** for a transition in accord with the Franck–Condon principle. In practice, the electronically excited molecule may be formed in one of several excited vibrational states all with turning points nearly vertically above the minimum of the lower curve, so the absorption occurs at several different frequencies. As already remarked, in a condensed medium, the individual transitions merge together to give a broad, largely featureless band of absorption.

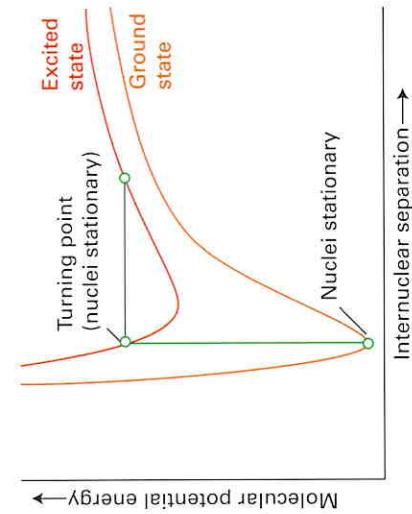


Fig. 5 According to the Franck–Condon principle, the most intense electronic transition is from the ground vibrational state to the vibrational state that lies vertically above it in the upper electronic state. Transitions to other vibrational levels also occur, but with lower intensity.

11D.2 Specific types of transitions

The absorption of a photon can often be traced to the excitation of an electron that is localized on a small group of atoms. For example, an absorption at about 290 nm is normally observed when a carbonyl group is present. Groups with characteristic optical absorptions are called **chromophores** (from the Greek for 'colour bringer'), and their presence often accounts for the colours of many substances.

The transition responsible for absorption in carbonyl compounds can be traced to the lone pairs of electrons on the O atom. One of these electrons may be excited into an empty π^* orbital of the carbonyl group (Fig. 6), which gives rise to an **n-to- π^* transition**, where n denotes a nonbonding orbital, an orbital that is neither bonding nor antibonding, such as that occupied by a lone pair. Typical absorption energies are about 4 eV.

A C=C or C=O double bond acts as a chromophore because the absorption of a photon excites a π electron into an antibonding π^* orbital (Fig. 7). The chromophore activity is therefore due to a **π -to- π^* transition**. Its energy is around 7 eV for an unconjugated double bond, which corresponds to an absorption at 180 nm (in the ultraviolet). When the double bond is part of a conjugated chain, the energies of the molecular orbitals lie closer together and the transition shifts into the visible region of the spectrum. In general, π -to- π^* transitions are stronger than n-to- π^* transitions, so assessment of relative absorption intensities can help in the assignment of a spectrum.

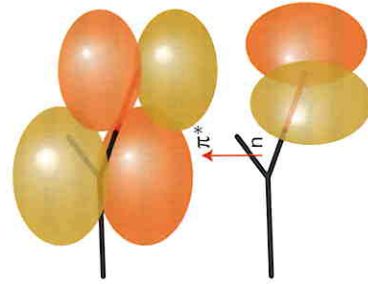


Fig. 6 A carbonyl group acts as a chromophore primarily on account of the excitation of a nonbonding O lone-pair electron to an antibonding $\text{CO } \pi^*$ orbital.

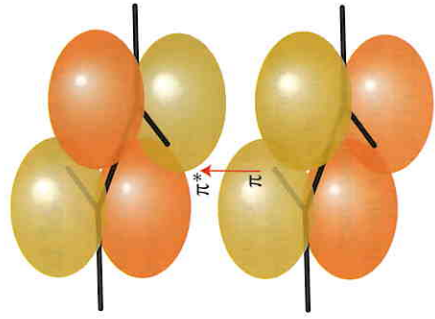


Fig. 7 A carbon-carbon double bond acts as a chromophore. One of its important transitions is the π -to- π^* transition illustrated here, in which an electron is promoted from a π orbital to the corresponding antibonding orbital.

Brief illustration 11D.1 π -to- π^* and n-to- π^* transitions

A $\text{CH}_3\text{CH}=\text{CHCHO}$ molecule has a strong absorption in the ultraviolet at $46\,950\text{ cm}^{-1}$ (213 nm) and a weak absorption at $30\,000\text{ cm}^{-1}$ (333 nm). The former is a π -to- π^* transition associated with the delocalized π -system $\text{C}=\text{C}-\text{C}=\text{O}$. Delocalization extends the range of the $\text{C}=\text{O}$ π -to- π^* transition to lower wavenumbers (longer wavelengths). The latter is an n-to- π^* transition associated with the carbonyl chromophore.

Self-test 11D.1

Propanone (acetone, $(\text{CH}_3)_2\text{CO}$), has a strong absorption at 189 nm and a weaker absorption at 280 nm. Assign these features to n-to- π^* or π -to- π^* transitions.

Answer: Both transitions are associated with the $\text{C}=\text{O}$ chromophore, with the weaker being an n-to- π^* transition and the stronger a π -to- π^* transition.

A d-metal complex may absorb light as a result of the transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa. In such **charge-transfer transitions** the electron moves through a considerable distance, which means that the redistribution of charge as measured by the transition dipole moment may be large and the absorption correspondingly intense. Indeed, the most intense electronic transitions responsible for the colours of many d-metal complexes are charge-transfer transitions. In the permanganate ion, MnO_4^- , the charge redistribution that accompanies the migration of an electron from the O atoms to the central Mn atom results in a charge-transfer transition in the range 420–700 nm and accounts for the intense purple colour of the ion.

11D.3 Analysis of mixtures by electronic spectroscopy

Electronic spectra are used to analyse mixtures of absorbing species and to determine their concentrations.

The concentration of an absorbing species can be determined by using the Beer-Lambert law (Topic 11A), in the form $[I] = A/\epsilon L$, where A is the absorbance of the sample, ϵ is the molar absorption coefficient of the chromophore, and L is the path length through the sample. If the sample is a mixture of two components A and B, then measurements at two wavelengths can be used to find the individual concentrations. For this analysis, the total absorbance at a given wavelength is written as

$$A = A_A + A_B = \epsilon_A[A]L + \epsilon_B[B]L = (\epsilon_A[A] + \epsilon_B[B])L$$

Then, for measurements of the total absorbance A_1 at wavelength λ_1 , at which the molar absorption coefficients are ϵ_{A1} and ϵ_{B1} , and then A_2 at λ_2 , at which they are ϵ_{A2} and ϵ_{B2} (Fig. 8),

$$(\epsilon_{A1}[A] + \epsilon_{B1}[B])L = A_1 \quad (\epsilon_{A2}[A] + \epsilon_{B2}[B])L = A_2$$

As shown in the following *Justification*, these two simultaneous equations can be solved for the two unknowns, the molar concentrations of A and B:

$$[A] = \frac{\epsilon_{B2}A_1 - \epsilon_{B1}A_2}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})L} \quad (1a)$$

$$[B] = \frac{\epsilon_{A1}A_2 - \epsilon_{A2}A_1}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})L} \quad (1b)$$

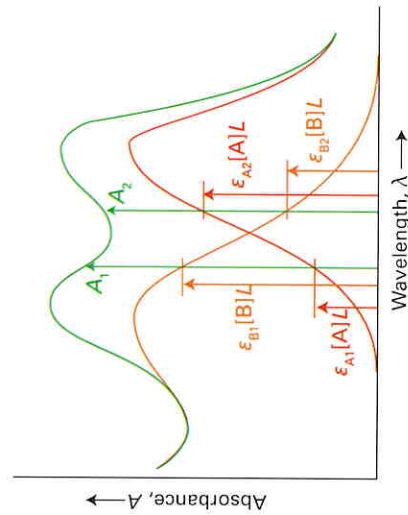


Fig. 8 The concentrations of two absorbing species in a mixture can be determined from their molar absorption coefficients and the measurement of their absorbances at two different wavelengths lying within their joint absorption region.

Brief illustration 11D.2 The analysis of a mixture

Suppose that the molar absorption coefficients of two substances A and B at two wavelengths λ_1 and λ_2 are $\epsilon_{A1} = 10.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, $\epsilon_{B1} = 15.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, $\epsilon_{A2} = 18.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, $\epsilon_{B2} = 12.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. The total absorbances of a solution at these two wavelengths in a cell of length $L = 0.20\text{ cm}$ were measured as $A_1 = 1.6$ and $A_2 = 2.4$. It follows from eqns 1a and 1b that

$$[A] = \frac{\epsilon_{B2}A_1 - \epsilon_{B1}A_2}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})L} = \frac{12.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 1.6 - 15.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 2.4}{(10.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 12.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} - 18.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 15.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}) \times (0.20\text{ cm})} = 0.56\text{ mol dm}^{-3}$$

$$[B] = \frac{\epsilon_{A1}A_2 - \epsilon_{A2}A_1}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})L} = \frac{10.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 2.4 - 18.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 1.6}{(10.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 12.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} - 18.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 15.0\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}) \times (0.20\text{ cm})} = 0.16\text{ mol dm}^{-3}$$

Self-test 11D.2

Repeat the calculation under these conditions: $L = 0.10\text{ cm}$, $A_1 = 0.53$, and $A_2 = 0.80$.

Answer: $[A] = 0.38\text{ mol dm}^{-3}$, $[B] = 0.11\text{ mol dm}^{-3}$

Justification 11D.1

Determining concentrations in a mixture

The two equations to solve for $[A]$ and $[B]$ are given in the text as $\epsilon_{A1}[A]L + \epsilon_{B1}[B]L = A_1$ and $\epsilon_{A2}[A]L + \epsilon_{B2}[B]L = A_2$. The aim is to extract expressions for the molar concentrations $[A]$ and $[B]$.

Step 1: Manipulate the equations to match terms

To match the two second terms of the preceding equations, multiply the first by ϵ_{B2} and the second by ϵ_{B1} , to obtain

$$\epsilon_{B2}\epsilon_{A1}[A]L + \epsilon_{B2}\epsilon_{B1}[B]L = \epsilon_{B2}A_1 \quad \epsilon_{B1}\epsilon_{A2}[A]L + \epsilon_{B1}\epsilon_{B2}[B]L = \epsilon_{B1}A_2$$

The matching terms are in blue.

Step 2: Solve for $[A]$

Subtract the second of these equations from the first, and obtain:

$$\epsilon_{B2}\epsilon_{A1}[A]L - \epsilon_{B1}\epsilon_{A2}[A]L = \epsilon_{B2}A_1 - \epsilon_{B1}A_2$$

which rearranges into eqn 1a.

Step 3: Solve for $[B]$

To obtain eqn 1b, repeat steps 1 and 2 by multiplying $\epsilon_{A1}[A]L + \epsilon_{B1}[B]L = A_1$ by ϵ_{A2} and $\epsilon_{A2}[A]L + \epsilon_{B2}[B]L = A_2$ by ϵ_{A1} , so that now the $[A]$ terms cancel when the two resulting equations are subtracted.

There may be a wavelength at which the molar absorption coefficients of the two species are equal; let that value be ϵ_{iso} (the notation ‘iso’ will become clear

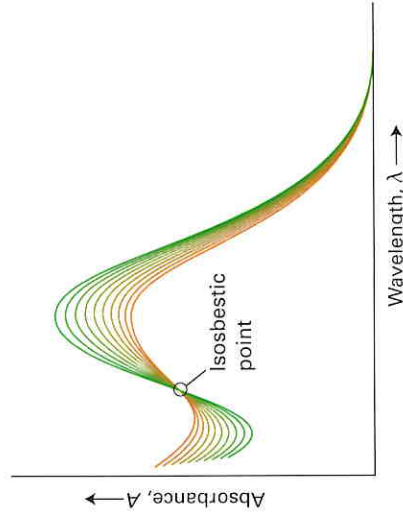


Fig. 9 One or more isobestic points are formed when there are two interrelated absorbing species in solution. Each curve corresponds to a different stage of the reaction $A \rightarrow B$.

in a moment) The total absorbance of the mixture at this wavelength is

$$A_{\text{iso}} = (\epsilon_{\text{iso}}[A] + \epsilon_{\text{iso}}[B])L = \epsilon_{\text{iso}}([A] + [B])L \quad (2)$$

Even if A and B are interconverted in a reaction of the form $A \rightarrow B$ or its reverse, then because their total concentration remains constant, so does A_{iso} . As a result, it is possible to observe one or more **isobestic points** (the name ‘isobestic’ comes from the Greek words for ‘the same’ and ‘extinguish’), which are invariant points in the absorption spectrum (Fig. 9). It is very unlikely that three or more species would have the same molar absorption coefficients at a single wavelength. Therefore, the observation of an isobestic point, or at least not more than one such point, is compelling evidence that a solution consists of only two solutes in equilibrium with each other with no intermediates.

11D.4 Photoelectron spectroscopy

The exposure of a molecule to high frequency radiation can result in the ejection of an electron. This **photoejection** is the basis of another type of electronic spectroscopy in which the energies of the ejected photoelectrons are monitored. If the incident radiation has frequency ν , the photon that causes photoejection has energy $h\nu$. If the ionization energy of the molecule is I , the difference in energy, $h\nu - I$, is carried away as the kinetic energy of the ejected electron. Because the kinetic energy of an electron travelling at a speed v is $\frac{1}{2}m_e v^2$, it follows that

$$h\nu = I + \frac{1}{2}m_e v^2 \quad (3)$$

Therefore, by monitoring the speed of the photoelectron, and knowing the frequency of the incident

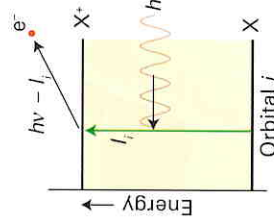


Fig. 10 The basic principle of photoelectron spectroscopy. An incoming photon of known energy collides with an electron in one of the orbitals and expels it with a kinetic energy that is equal to the difference between the energy supplied by the photon and the ionization energy from the occupied orbital. An electron from an orbital with a low ionization energy will emerge with a high kinetic energy (and high speed), whereas an electron from an orbital with a high ionization energy will be ejected with a low kinetic energy (and low speed).

radiation, the ionization energy of the molecule can be determined (Fig. 10). In this context the 'ionization energy' of the molecule has different values depending on the orbital that the photoelectron occupied, and the slower the ejected electron, the lower in energy the orbital from which it was ejected. The apparatus is a modification of a mass spectrometer (Fig. 11), in which the speed of the photoelectrons is measured by determining the strength of the electric field required to bend their paths on to the detector.

Figure 12 shows a typical photoelectron spectrum (of HBr). If the fine structure is disregarded, it is seen that the HBr lines fall into two main groups. The least tightly bound electrons (with the lowest ionization energies and hence highest kinetic energies when ejected) are those in the lone pairs of the Br atom. The next ionization energy lies at 15.2 eV, and corresponds to the removal of an electron from the H—Br σ bond.

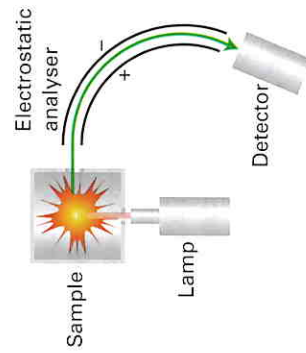


Fig. 11 A photoelectron spectrometer consists of a source of ionizing radiation, an electrostatic analyser, and an electron detector. The deflection of the electron paths caused by the analyser depends on their speed.

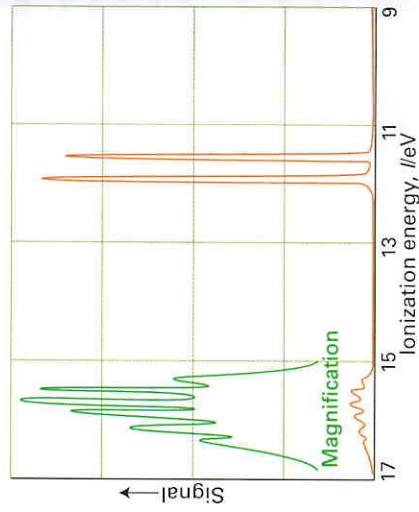


Fig. 12 The photoelectron spectrum of HBr. The lowest ionization energy band corresponds to the ionization of a Br lone pair electron. The higher ionization energy band corresponds to the ionization of a bonding electron. The structure on the latter is due to the vibrational excitation of HBr that results from the ionization.

The fine structure in the HBr spectrum shows that ejection of a σ electron is accompanied by a considerable amount of vibrational excitation. The Franck-Condon principle would account for this observation if ejection were accompanied by an appreciable change of equilibrium bond length between HBr and HBr⁺: if that is so, the ion is formed in a bond-compressed state, which is consistent with the important bonding effect of the σ electrons. The lack of much vibrational structure in the other band is consistent with the nonbonding role of the Br4p_x and Br4p_y lone-pair electrons, for the equilibrium bond length is little changed when one is removed.

Brief illustration 11D.3 The photoelectron spectrum of H₂O

The highest kinetic energy electrons in the spectrum of H₂O using 21.22 eV radiation are at about 9 eV and show a large vibrational spacing of 0.41 eV (1 eV = 8065.5 cm⁻¹). Because 0.41 eV corresponds to 3.3 × 10³ cm⁻¹, which is similar to the wavenumber of the symmetric stretching mode of the neutral H₂O molecule (3652 cm⁻¹), you should suspect that the electron is ejected from an orbital that has little influence on the bonding in the molecule. That is, photoejection is from a largely nonbonding orbital.

Self-test 11D.3

In the same spectrum of H₂O, the band near 7.0 eV shows a long vibrational series with spacing 0.125 eV. The bending mode of H₂O lies at 1596 cm⁻¹. What conclusions can you draw about the characteristics of the orbital occupied by the photoelectron?

Answer: The electron contributes to a molecular orbital with energy that changes significantly with the HOH bond angle.

Checklist of key concepts

- 1 The **Franck-Condon principle** states that because nuclei are so much more massive than electrons, an electronic transition takes place faster than the nuclei can respond.
- 2 A **chromophore** is a group with characteristic optical absorption.
- 3 In an **n-to- π^* transition** an electron in a nonbonding orbital is excited into an empty π^* orbital.
- 4 In a **π -to- π^* transition** absorption of a photon excites a π electron into an antibonding π^* orbital.
- 5 **Charge-transfer transitions** typically involve the migration of electrons between the ligands and the central metal atom.
- 6 An **isosbestic point** corresponds to a wavelength at which the total absorbance of a binary mixture is the same whatever the ratio of the concentrations of the two absorbing species.
- 7 **Photoelectron spectroscopy** is based on the photoejection of an electron by ultraviolet radiation or X-rays.

TOPIC 11E

The decay of excited states

► Why do you need to know this material?

Considerable information about the electronic structure of molecules in general, including synthetic and biological macromolecules, can be obtained by detecting the photons emitted when excited electronic states decay radiatively back to the ground state.

► What is the key idea?

Molecules in excited electronic states discard their excess energy by emission of electromagnetic radiation, transfer as heat to the surroundings, fragmentation, or reaction.

► What do you need to know already?

You need to be familiar with the general features of spectroscopy (Topic 11A), electronic transitions in molecules, particularly the Franck-Condon principle (Topic 11D), and the procedures for writing a rate law from a proposed mechanism (Topic 6F). You need to be aware of the difference between singlet and triplet states (Topic 8D).

In most cases, the excitation energy of a molecule that has absorbed a photon is degraded into the disordered thermal motion of its surroundings by the process called **non-radiative decay**. In other cases, its electrons may undergo a redistribution that results in it undergoing an **internal conversion** (IC), a radiationless conversion to another state of the same multiplicity (that is, spin state). However, an electronically excited molecule can discard its excess energy by **radiative decay**, in which an electron relaxes back into a lower energy orbital and in the process

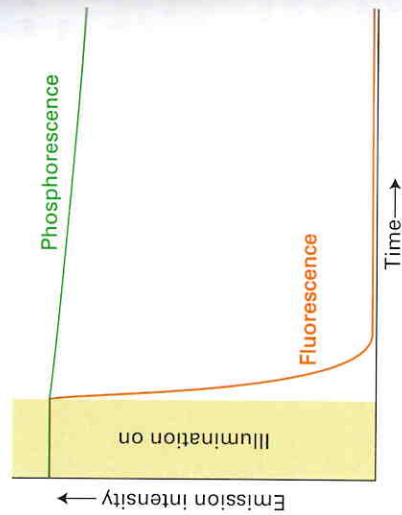


Fig. 1 The empirical (observation-based) distinction between fluorescence and phosphorescence is that the former is extinguished very quickly after the exciting source is removed, whereas the latter continues with relatively slowly diminishing intensity.

generates a photon. As a result, and if the emitted radiation is in the visible region of the spectrum, the sample glows.

There are two principal modes of radiative decay, fluorescence and phosphorescence (Fig. 1). In **fluorescence**, the spontaneously emitted radiation ceases very soon (within nanoseconds to milliseconds) after the exciting radiation is extinguished. In **phosphorescence**, the spontaneous emission may persist for long periods—even hours, but characteristically seconds or fractions of seconds. The difference suggests that fluorescence is an immediate conversion of absorbed light into re-emitted radiant energy whereas phosphorescence involves the storage of energy in a reservoir from which it slowly leaks.

Absorption might result in **dissociation**, or fragmentation (Fig. 2). The onset of dissociation can be detected in an absorption spectrum by seeing that the vibrational structure of a band terminates at a certain energy. Absorption occurs in a continuous band above this **dissociation limit**, the highest frequency before the onset of continuous absorption, because

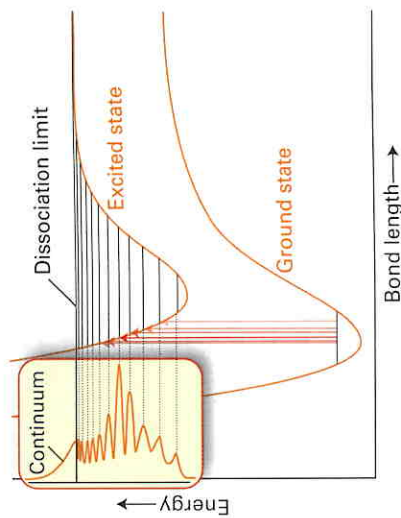


Fig. 2 When absorption occurs to unbound states of the upper electronic state, the molecule dissociates and the absorption is a continuum. Below the dissociation limit the electronic spectrum has a normal vibrational structure.

the final state is unquantized translational motion of the fragments. Locating the dissociation limit is a valuable way of determining the bond dissociation energy. Dissociation may also occur if the electronic transition takes place directly to a purely repulsive state, one that shows no minimum corresponding to bonding. Even if the excited state is a bound state, the molecule might flip across into an unbound state and dissociate at wavenumbers below those needed for dissociation of the bound state; this process is called **predissociation**.

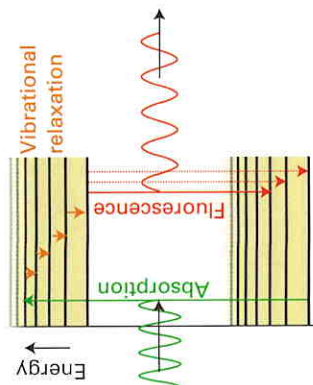


Fig. 3 A Jablonski diagram showing the sequence of steps leading to fluorescence. After the initial absorption the upper vibrational states undergo radiationless decay—the process of vibrational relaxation—by giving up energy to the surroundings. A radiative transition then occurs from the ground state of the upper electronic state. In practice, the separation of the ground states of the electronic states (the heavy horizontal lines) is 10 to 100 times greater than the separation of the vibrational levels.

Condon principle (Topic 11D), and the fluorescence spectrum has a vibrational structure characteristic of the lower electronic state (Fig. 4b).

Fluorescence occurs at a lower frequency than that of the incident radiation because the fluorescence radiation is emitted after some vibrational energy has been lost to the surroundings. The vivid oranges and greens of fluorescent dyes are an everyday manifestation of this effect: they absorb in the ultraviolet and fluoresce in the visible. The mechanism also suggests that the intensity of the fluorescence ought to depend on the ability of the surrounding molecules, such as those of a solvent, to accept the electronic and vibrational

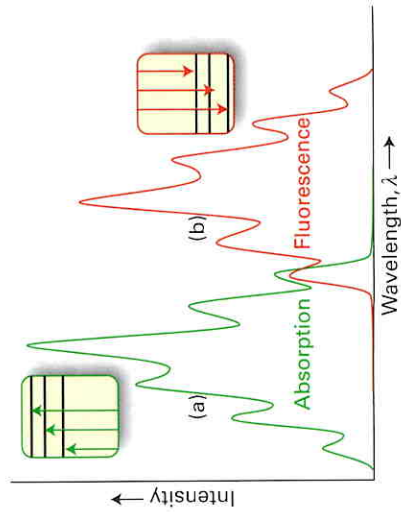


Fig. 4 The absorption spectrum (a) shows a vibrational structure characteristic of the upper state. The fluorescence spectrum (b) shows a structure characteristic of the lower state; it is also displaced to lower frequencies and resembles a mirror image of the absorption.

11E.1 Fluorescence and phosphorescence

Figure 3 shows a simple example of a Jablonski diagram, a schematic portrayal of molecular electronic and vibrational energy levels, which shows the sequence of steps involved in fluorescence. The initial absorption takes the molecule to an excited electronic state, and if the absorption spectrum were monitored it would look like the one shown in Fig. 4a. The excited molecule is subjected to collisions with the surrounding molecules, and as it gives up energy it steps down the ladder of vibrational levels. The surrounding molecules, however, might be unable to accept the larger energy needed to lower the molecule to the ground electronic state. The excited state might therefore survive long enough to generate a photon and emit the remaining excess energy as radiation. The downward electronic transition is vertical, which means in accord with the Franck-

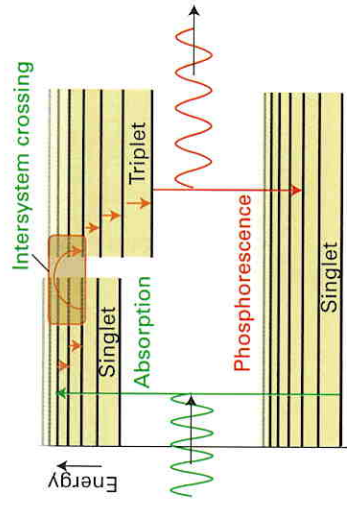


Fig. 5 The sequence of steps leading to phosphorescence. The important step is the intersystem crossing from an excited singlet to an excited triplet state. The triplet state acts as a slowly radiating reservoir because the return to the ground state is very slow.

quanta. It is indeed found that a solvent composed of molecules with widely spaced vibrational levels (such as water) may be able to accept the large quantum of electronic energy and so decrease the intensity of the solute's fluorescence.

Figure 5 is a Jablonski diagram showing the events leading to phosphorescence. The first steps are the same as in fluorescence, but the presence of a triplet state plays a decisive role. A **triplet state** is a state in which two electrons in different orbitals have parallel spins: the ground state of O_2 is an example (Topic 9B). The name 'triplet' reflects the (quantum mechanical) fact that the total spin of two parallel electron spins ($\uparrow\uparrow$) can adopt only three orientations with respect to an axis. An ordinary spin-paired state ($\uparrow\downarrow$) is called a **singlet state** because there is only one orientation in space for such a pair of spins. In the language of Topic 7D, a triplet state has $S = 1$ and M_S has one of the three values $+1$, 0 , and -1 ; a singlet state has $S = 0$ and M_S has the single value 0 .

The ground state of a typical phosphorescent molecule is a singlet because its electrons are all paired; the excited state to which the absorption excites the molecule is also a singlet. The peculiar feature of a phosphorescent molecule, however, is that it possesses an excited triplet state with an energy similar to that of the excited singlet state and into which the excited singlet state may convert. Hence, if there is a mechanism for unpairing two electron spins (and so converting $\uparrow\downarrow$ into $\uparrow\uparrow$), then the molecule may undergo **intersystem crossing (ISC)** and become a triplet state. The unpairing of electron spins is possible if the molecule contains a heavy atom, such as an atom of sulfur, with strong spin-orbit coupling (Topic 8D). Then the angular momentum needed to

convert a singlet state into a triplet state may be acquired from the orbital motion of the electrons.

After an excited singlet molecule crosses into a triplet state, it continues to discard energy into the surroundings and to step down the ladder of vibrational states. However, it is now stepping down the triplet's ladder and at the lowest vibrational energy level it is trapped. The surroundings cannot extract the final, large quantum of electronic excitation energy. Moreover, the molecule cannot radiate its energy: a triplet state cannot convert into a singlet state because the spin of one electron cannot reverse in direction relative to the other electron during a transition ($\Delta S = 0$ for electronic transitions). The radiative transition, however, is not totally forbidden because the spin-orbit coupling responsible for the intersystem crossing also breaks this rule. The molecules are therefore able to emit weakly and the emission may continue long after the original excited state was formed.

The mechanism of phosphorescence summarized in Fig. 5 accounts for the observation that the excitation energy seems to become trapped in a slowly leaking reservoir. It also suggests, as is confirmed experimentally, that phosphorescence should be most intense from solid samples: energy transfer is then less efficient and the intersystem crossing has time to occur as the singlet excited state loses vibrational energy. The mechanism also suggests that the phosphorescence efficiency should depend on the presence of a moderately heavy atom—with its ability to flip electron spins—which is in fact the case.

Brief illustration 11E.1 Fluorescence and phosphorescence of organic molecules

Fluorescence efficiency decreases, and the phosphorescence efficiency increases, in the series of compounds: naphthalene, 1-chloronaphthalene, 1-bromonaphthalene, 1-iodonaphthalene. The replacement of an H atom by successively heavier atoms enhances both intersystem crossing from the first excited singlet state to the first excited triplet state (thereby decreasing the efficiency of fluorescence) and the radiative transition from the first excited triplet state to the ground singlet state (thereby increasing the efficiency of phosphorescence).

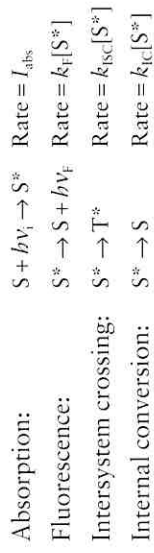
Self-test 11E.1

Consider an aqueous solution of a chromophore that fluoresces strongly. Is the addition of iodide ion to the solution likely to increase or decrease the efficiency of phosphorescence of the chromophore?

Answer: Increase

11E.2 Mechanism of decay of excited states

The following steps are involved in the formation and deactivation of an excited singlet state S^* in the absence of any chemical reaction involving S^* :



S is the initially absorbing species, T^* an excited triplet state, and $h\nu_F$ and $h\nu_I$ denote the incident and fluorescent photons, respectively. It follows that after the exciting radiation has been turned off and S^* is no longer being formed,

$$\text{Rate of decay of } S^* = k_F[S^*] + k_{\text{ISC}}[S^*] + k_{\text{IC}}[S^*] \quad (1)$$

$$= (k_F + k_{\text{ISC}} + k_{\text{IC}})[S^*]$$

That is, the excited state decays by a first-order process, so when the light is turned off, $[S^*]$ varies with time t as

$$[S^*]_t = [S^*]_0 e^{-(k_F + k_{\text{ISC}} + k_{\text{IC}})t} = [S^*]_0 e^{-t/\tau_0} \quad (2a)$$

where the **observed fluorescence lifetime**, τ_0 , is

$$\tau_0 = \frac{1}{k_F + k_{\text{ISC}} + k_{\text{IC}}} \quad (2b)$$

The observed fluorescence lifetime can be measured by using a pulsed laser technique. First, the sample is excited with a short light pulse from a laser using a wavelength at which S absorbs strongly. Then, the exponential decay of the fluorescence intensity after the pulse is monitored and its time-constant determined.

Not every excited molecule decays by fluorescence and it is useful to speak of the **quantum yield of fluorescence**, ϕ_F , which is the rate of fluorescence, ν_F , divided by the rate of photon absorption, I_{abs} :

$$\phi_F = \frac{\text{rate of fluorescence}}{\text{rate of photon absorption}} \quad (3)$$

$$= \frac{\nu_F}{I_{\text{abs}}}$$

The difference between the two rates in this definition is the rate at which excited states leak away non-

radiatively. The value of ϕ_F is measured by observing the ratio of the intensities of fluorescence and absorption, which are proportional to their respective rates. As shown in the following *Justification*, provided there is no chemical reaction, a condition indicated by attaching a subscript 0 to ϕ_F ,

$$\phi_{F,0} = \frac{k_F}{k_F + k_{\text{ISC}} + k_{\text{IC}}} \quad (4)$$

Quantum yield of fluorescence [no reactions]

Justification 11E.1

The quantum yield of fluorescence

The strategy consists of setting up an expression for the net rate of formation of the excited state in the presence of formation and decay processes.

Step 1: Set up an expression for the net rate of formation of S^* .

Most fluorescence measurements are conducted by illuminating a dilute sample with a continuous and intense beam of light. It follows that $[S^*]$ is then constant, and its net rate of formation is zero. That is,

$$\text{Rate of change of } [S^*] = \underbrace{I_{\text{abs}}}_{\text{rate of production of } S^* \text{ by absorption}} - \underbrace{k_F[S^*]}_{\text{rate of decay of } S^* \text{ by fluorescence}} - \underbrace{k_{\text{ISC}}[S^*]}_{\text{rate of decay of } S^* \text{ by intersystem crossing}} - \underbrace{k_{\text{IC}}[S^*]}_{\text{rate of decay of } S^* \text{ by internal conversion}}$$

$$= I_{\text{abs}} - (k_F + k_{\text{ISC}} + k_{\text{IC}})[S^*] = 0$$

Consequently,

$$I_{\text{abs}} = (k_F + k_{\text{ISC}} + k_{\text{IC}})[S^*]$$

This expression is ready to be substituted into the denominator of eqn 3.

Step 2: Write an expression for the fluorescence quantum yield

The rate of fluorescence itself is $k_F[S^*]$, which can be substituted into the numerator of eqn 3. It now follows that the quantum yield of fluorescence is given by

$$\phi_{F,0} = \frac{\nu_F}{I_{\text{abs}}} = \frac{k_F[S^*]}{(k_F + k_{\text{ISC}} + k_{\text{IC}})[S^*]}$$

which, after cancelling the $[S^*]$, becomes eqn 4.

With $\phi_{F,0}$ available from steady-state observations and τ_0 available from decay-rate observations, the

rate constant k_F can be determined. Thus, from eqns 2b and 4, it follows that

$$\tau_0 = \frac{1}{k_F + k_{ISC} + k_{IC}} = \left(\frac{k_F}{k_F + k_{ISC} + k_{IC}} \right) \times \frac{1}{k_F} \quad (5a)$$

$$= \frac{\phi_{F,0}}{k_F}$$

and therefore

$$k_F = \frac{\phi_{F,0}}{\tau_0} \quad (5b)$$

Brief illustration 11E.2 The fluorescence rate constant

The fluorescence quantum yield and observed fluorescence lifetime of tryptophan in water are $\phi_{F,0} = 0.20$ and $\tau_0 = 2.6$ ns, respectively. It follows from eqn 5 that the fluorescence rate constant k_F is

$$k_F = \frac{0.20}{2.6 \times 10^{-9} \text{ s}} = 7.7 \times 10^7 \text{ s}^{-1}$$

Self-test 11E.2

A substance has a fluorescence quantum yield of $\phi_{F,0} = 0.35$. In an experiment to measure the fluorescence lifetime of this substance, it was observed that the fluorescence emission decayed with a half-life of 5.6 ns. Determine the fluorescence rate constant of this substance.

Answer: $k_F = 4.3 \times 10^7 \text{ s}^{-1}$

11E.3 Quenching

A number of processes can decrease, or **quench**, the fluorescence or phosphorescence of a molecule. Examples of such processes include energy transfer, electron transfer, and reactions that are initiated by the absorption of light.

A molecule in an excited state must either decay to the ground state or form a photochemical product. As shown in the following *Justification*, the relation between the fluorescence quantum yields $\phi_{F,0}$ and ϕ_F in the absence and presence, respectively, of a quencher Q at a molar concentration [Q] is given by the **Stern–Volmer equation**:

$$\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q [Q] \quad (6)$$

Stern–Volmer equation

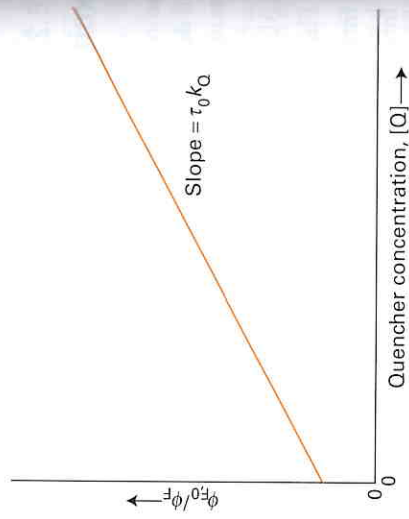


Fig. 6 The format of a Stern–Volmer plot and the interpretation of the slope in terms of the rate constant for quenching and the observed fluorescence lifetime in the absence of quenching.

It follows from this equation that a plot of $\phi_{F,0}/\phi_F$ against [Q] should be a straight line with slope $\tau_0 k_Q$. Such a plot is called a **Stern–Volmer plot** (Fig. 6). The method is quite general and may also be applied to the quenching of phosphorescence emission.

Justification 11E.2

The Stern–Volmer equation

The addition of a quencher, Q, opens an additional channel for deactivation of S^* :



As in *Justification* 11E.1, the approach involves writing the net rate of formation of $[S^*]$ under conditions of constant illumination by considering all the appropriate formation and decay processes.

Step 1: Set up the expression for the net rate of formation of S^*

Taking quenching into account, the net rate of change of $[S^*]$ is

$$\begin{aligned} \text{Rate of change of } [S^*] &= \text{rate of production of } S^* \text{ by fluorescence} - k_F[S^*] - k_{ISC}[S^*] - k_{IC}[S^*] \\ &= I_{\text{abs}} - (k_F + k_{ISC} + k_{IC} + k_Q[Q])[S^*] = 0 \end{aligned}$$

Step 2: Write expressions for the fluorescence quantum yields in the presence and absence of the quencher

By analogy with step 2 of *Justification* 11E.1, the fluorescence quantum yield in the presence of the quencher is

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC} + k_Q[Q]}$$

This expression becomes eqn 4 when $[Q] = 0$.

Step 3: Form the ratio of these fluorescence quantum yields

$$\begin{aligned} \frac{\phi_{F,0}}{\phi_F} &= \left(\frac{k_F}{k_F + k_{ISC} + k_{IC}} \right) \times \left(\frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F} \right) \\ &= \frac{k_F + k_{ISC} + k_{IC} + k_Q[Q]}{k_F + k_{ISC} + k_{IC}} = \frac{k_F + k_{ISC} + k_{IC}}{k_F + k_{ISC} + k_{IC}} + \frac{k_Q[Q]}{k_F + k_{ISC} + k_{IC}} \\ &= 1 + \frac{1}{\tau_0} \times k_Q[Q] = 1 + \tau_0 k_Q [Q] \end{aligned}$$

which is eqn 6.

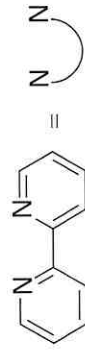
Because the fluorescence intensity and lifetime are both proportional to the fluorescence quantum yield (specifically, from eqn 5, $\tau = \phi_F/k_F$), plots of $I_{F,0}/I_F$ and τ_0/τ (where, as usual, the subscript 0 indicates a measurement in the absence of quencher) against [Q] should also be a straight line with the same slope and intercept as those shown for eqn 6.

Example 11E.1

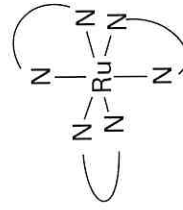
Determining the quenching rate constant

The molecule 2,2'-bipyridine (1, bpy) forms a complex with the Ru^{2+} ion. Ruthenium(II) tris-(2,2'-bipyridyl), $Ru(bpy)_3^{2+}$ (2), has a strong electronic absorption at 450 nm. The quenching of the $^*Ru(bpy)_3^{2+}$ excited state by $Fe(OH)_2^{2+}$ in acidic solution was monitored by measuring excited state lifetimes at 600 nm. Determine the quenching rate constant for this reaction from the following data:

$[Fe^{2+}]/(10^{-2} \text{ mol dm}^{-3})$	0	1.6	4.7	7	9.4
$\tau/(10^{-7} \text{ s})$	6	4.05	3.37	2.96	2.17



1 2,2'-Bipyridine (bpy)



2 $[Ru(bpy)_3]^{2+}$

Collect your thoughts Rewrite eqn 6 for use with lifetime data, then fit the data to a straight line. Finally, calculate the quenching rate constant from the slope of the plot.

The solution Note from eqn 5 that in the absence of a quencher $\phi_{F,0} = \tau_0 k_F$. But an analogous expression can be written when a quencher is present, so $\phi_F = \tau k_F$. Then eqn 6 becomes

$$\frac{\phi_{F,0}}{\phi_F} = \frac{\tau_0 k_F}{\tau k_F} = \frac{\tau_0}{\tau} = 1 + \tau_0 k_Q [Q]$$

Dividing through by τ_0 gives

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_Q [Q] \quad (7)$$

Because the axes of plots should be labelled with pure numbers, it is necessary to introduce and handle units before using eqn 7 for the analysis of the data. To bring the expression into a form suitable for plotting, write it as

$$\frac{1}{(10^{-7} \text{ s})\tau/(10^{-7} \text{ s})} = \frac{1}{\tau_0} + k_Q \frac{[Q] \times (10^{-2} \text{ mol dm}^{-3})}{(10^{-2} \text{ mol dm}^{-3})}$$

and therefore, after multiplying through by 10^7 s and collecting terms

$$\frac{1}{\tau/(10^{-7} \text{ s})} = \frac{10^{-7} \text{ s}}{\tau_0} + \underbrace{k_Q \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}}_{\text{slope}} \times \frac{[Q]}{(10^{-2} \text{ mol dm}^{-3})}$$

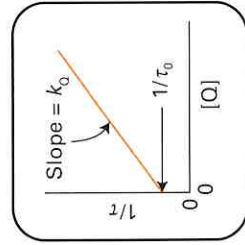
Figure 7 shows a plot of $1/(\tau/10^{-7} \text{ s})$ against $[Fe^{2+}]/(10^{-2} \text{ mol dm}^{-3})$ and the results of a fit to eqn 7. The slope of the line is $k_Q \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1} = 2.9$, so $k_Q = 2.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This example shows that measurements of excited state lifetimes are preferred over measurements of quantum yields because they give the value of k_Q directly. To determine the value of k_Q from intensity or quantum yield measurements, an independent measurement of τ_0 is also needed.

Self-test 11E.3

The quenching of tryptophan fluorescence by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process from the following data:

$[O_2]/(10^{-2} \text{ mol dm}^{-3})$	0	2.3	5.5	8	10.8
$\tau/(10^{-9} \text{ s})$	2.6	1.5	0.92	0.71	0.57

Answer: $1.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$



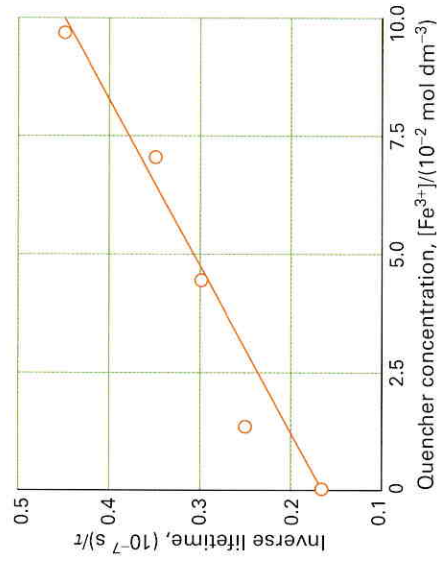


Fig. 7 The Stern-Volmer plot of the data for Example 11E.1.

It is useful to have some general idea of the magnitudes of the kinetic parameters discussed so far. Electronic transitions caused by absorption of ultraviolet and visible radiation occur within 10^{-16} – 10^{-15} s. The upper limit for the rate constant of a quenching process, such as a first-order photochemical reaction, is then expected to be about 10^{16} s $^{-1}$. Fluorescence is slower than absorption, with typical time constants of 10^{-12} – 10^{-6} s. Therefore, the excited singlet state can initiate very fast photochemical reactions in the femtosecond (10^{-15} s) to picosecond (10^{-12} s) timescale. Typical intersystem crossing and phosphorescence time constants for large organic molecules are 10^{-12} – 10^{-4} s and 10^{-6} – 10^{-1} s, respectively. As a consequence, excited triplet states are photochemically important. Indeed, because phosphorescence decay is several orders of magnitude slower than most typical reactions, species in excited triplet states can undergo a very large number of collisions with other reactants before deactivation.

Three common mechanisms for quenching of an excited singlet (or triplet) state are:



Collisional quenching is particularly efficient when Q is an electron-rich species, such as iodide ion, which receives energy from S^* and then decays non-radiatively to the ground state.

11E.4 Resonance energy transfer

In an absorption process the incident electromagnetic radiation induces a transition electric dipole (the dipole associated with the migration of charge

in the transition, Topic 11A) in the singlet S of the absorbing species. When the resulting excited state collapses back to the ground the resulting transition dipole can induce a corresponding transition dipole moment in a neighbouring molecule Q at a distance R. The transfer of energy by this process takes place with an efficiency, η_T , that can be expressed in terms of the fluorescence quantum yields in the absence and the presence of the quencher:

$$\eta_T = \frac{\phi_{F,0} - \phi_F}{\phi_{F,0}} \quad \text{Efficiency of energy transfer (definition)} \quad (8)$$

If $\phi_F = \phi_{F,0}$, then Q has no effect and $\eta_T = 0$. If $\phi_F = 0$, then Q has quenched all the fluorescence and $\eta_T = 1$ corresponding to perfect efficiency. According to the Förster theory of energy transfer, which was proposed by T. Förster in 1959, for donor-acceptor (S-Q) systems that are held rigidly either by covalent bonds or by a protein 'scaffold', η_T increases as R decreases:

$$\eta_T = \frac{R_0^6}{R_0^6 + R^6} \quad \text{Efficiency of energy transfer in terms of the donor-acceptor distance} \quad (9)$$

where R_0 is a parameter (with units of distance) that is characteristic of each donor-acceptor pair and has values typically close to about 4 nm. The efficiency approaches 1 when $R \ll R_0$ and approaches 0 when $R \gg R_0$. Equation 9 has been verified experimentally. According to the Förster theory, for a given separation, the efficiency is greatest when the emission spectrum of the donor molecule overlaps significantly with the absorption spectrum of the acceptor. In the overlap region, photons emitted by the donor can be absorbed resonantly by the acceptor for the energy gaps of the two molecules then match (Fig. 8), and the process is called resonance energy transfer.

The dependence of η_T on R forms the basis of fluorescence resonance energy transfer (FRET), a technique that can be used to measure distances in biological systems. In a typical FRET experiment, a site on a biopolymer or membrane is labelled covalently with an energy donor and another site is labelled covalently with an energy acceptor. The distance between the labels is then calculated from the known value of R_0 and a modified version of eqn 9. To modify it, first take the inverse of the equation, to give

$$\frac{1}{\eta_T} = \frac{R_0^6 + R^6}{R_0^6} = 1 + \frac{R^6}{R_0^6}, \text{ so } \frac{1}{\eta_T} - 1 = \frac{R^6}{R_0^6}$$

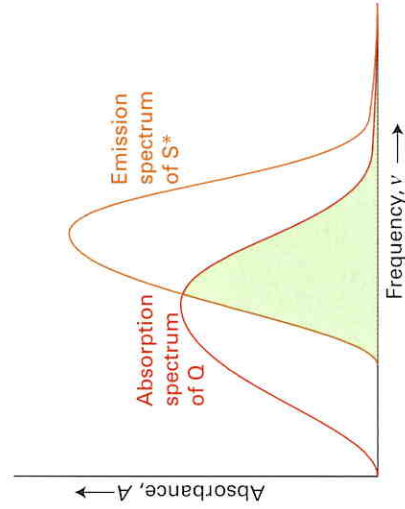


Fig. 8 According to the Förster theory, the rate of energy transfer from a molecule S* in an excited state to a quencher molecule Q is optimized at radiation frequencies in which the emission spectrum of S* overlaps with the absorption spectrum of Q, as shown in the shaded region.

Then, on taking the sixth root of both sides,

$$R = R_0 \left(\frac{1 - \eta_T}{\eta_T} \right)^{1/6} \quad \text{Donor-acceptor distance in terms of the efficiency of transfer} \quad (10)$$

Several tests have shown that the FRET technique is useful for measuring distances ranging from 1 to 9 nm.

Brief illustration 11E.3 The FRET technique

The pigment 11-cis-retinal, which absorbs light and initiates the biochemical events associated with vision, resides inside the protein rhodopsin. When an amino acid on the surface of rhodopsin was labelled covalently with a fluorescent molecule, the fluorescence quantum yield decreased from 0.75 to 0.68 due to quenching by 11-cis-retinal. It follows from eqn 8 that the efficiency of transfer is

$$\eta_T = \frac{0.75 - 0.68}{0.75} = 0.093$$

For this combination of S and Q, $R_0 = 5.4$ nm, so the distance R between the amino acid on the surface of the protein and 11-cis-retinal is obtained from eqn 10 as

$$R = (5.4 \text{ nm}) \times \left(\frac{1 - 0.093}{0.093} \right)^{1/6} = 7.9 \text{ nm}$$

Self-test 11E.4

An amino acid on the surface of a protein was labelled covalently with a molecule A and another was labelled covalently with B. The fluorescence quantum yield of A decreased by 10 per cent due to quenching by B. For this pair of dyes $R_0 = 4.9$ nm. What is the distance between the amino acids?

Answer: 7.1 nm

Checklist of key concepts

- 1 In fluorescence, the spontaneously emitted radiation ceases almost immediately (within nanoseconds) after the exciting radiation is extinguished.
- 2 In phosphorescence, the spontaneous emission may persist for long periods; the process involves intersystem crossing into a triplet state.
- 3 The fluorescence quantum yield is the rate of fluorescence divided by the rate of photon absorption.
- 4 A Stern-Volmer plot is used to analyse the kinetics of fluorescence quenching in solution.
- 5 Collisional deactivation, electron transfer, and resonance energy transfer are common fluorescence quenching processes.
- 6 The Förster theory predicts that the efficiency of resonance energy transfer decreases with increasing separation between energy donor and acceptor molecules.

FOCUS 11 Molecular spectroscopy

Exercises

Topic 11A General features of molecular spectroscopy

- 11A.1** Express a wavelength of 442 nm as (a) a frequency, (b) a wavenumber.
- 11A.2** What is (a) the wavenumber, (b) the wavelength of the radiation used by an FM radio transmitter broadcasting at 88.0 MHz?
- 11A.3** An aqueous solution of a triphosphate derivative of molar mass 502 g mol^{-1} was prepared by dissolving 172 mg in enough water to make 500 cm^3 of solution and a sample was transferred to a cell of length 1.00 cm. The absorbance was measured as 1.011. Calculate (a) the molar absorption coefficient; (b) the transmittance, expressed as a percentage, for a solution of twice the concentration.
- 11A.4** Radiation of wavelength 268 nm passed through 1.5 mm of a solution that contained benzene in a transparent solvent at a concentration of $0.080 \text{ mol dm}^{-3}$. The intensity of the radiation is reduced to 22 per cent of its initial value (so $T = 0.22$). (a) Calculate the absorbance and the molar absorption
- coefficient of the benzene. (b) What would be the transmittance through a cell of thickness 3.0 mm?
- 11A.5** What is the Doppler-shifted wavelength of a red (660 nm) traffic light approached at 65 m.p.h.? At what speed would it appear green (520 nm)?
- 11A.6** A spectral line of $^{48}\text{Tl}^{2+}$ in a distant star was found to be shifted from 654.2 nm to 706.5 nm and to be broadened to 61.8 pm. What are the speed of recession and the surface temperature of the star?
- 11A.7** Estimate the lifetime of a state that gives rise to a line of width (a) 0.10 cm^{-1} , (b) 1.0 cm^{-1} , (c) 1.0 GHz .
- 11A.8** A molecule in a liquid undergoes about 1.0×10^{13} collisions in each second. Suppose that every collision is effective in deactivating the molecule vibrationally and that one collision in 200 is effective. Calculate the width (in cm^{-1}) of vibrational transitions in the molecule.

Topic 11B Rotational spectroscopy

- 11B.1** The kinetic energy of a bicycle wheel rotating once per second is about 0.2 J. To what rotational quantum number does that correspond? For the moment of inertia, let the mass of the wheel (which is concentrated in its rim) be 0.75 kg and its radius be 70 cm.
- 11B.2** (a) Calculate the moment of inertia of (i) $^1\text{H}_2$, (ii) $^2\text{H}_2$, (iii) $^{12}\text{C}^{16}\text{O}_2$, (iv) $^{13}\text{CO}_2$. (b) Calculate the corresponding rotational constants, expressing your answers as a frequency in hertz (Hz) and as a wavenumber in reciprocal centimetres (cm^{-1}).
- 11B.3** (a) Express the moment of inertia of an octahedral AB_6 molecule in terms of its bond lengths and the masses of the B atoms. (b) Calculate the rotational constant of $^{32}\text{S}^{19}\text{F}_6$, for which the S-F bond length is 158 pm.
- 11B.4** Derive expressions for the two moments of inertia of a square-planar AB_4 molecule in terms of its bond lengths and the masses of the atoms.
- 11B.5** Suppose you were seeking the presence of (planar) SO_3 molecules in the microwave spectra of interstellar gas clouds. (a) You would need to know the rotational constants A and B. Calculate these parameters for $^{32}\text{S}^{16}\text{O}_3$, for which the S-O bond length is 143 pm. (b) Could you use microwave spectroscopy to distinguish the relative abundances of $^{32}\text{S}^{16}\text{O}_3$ and $^{34}\text{S}^{16}\text{O}_3$?
- 11B.6** A rotating methane molecule is described by the quantum numbers J, M_J , and K. (a) For methane, how many rotational states have an energy equal to $hB(J+1)$ with $J=8$? (b) Now consider chloromethane. How many rotational states have an energy equal to $hB(J+1)$ with $J=8$?
- 11B.7** The rotational constant of $^{127}\text{I}^{35}\text{Cl}$ is 3.423 GHz. Calculate the I-Cl bond length.
- 11B.8** The nuclear spin of deuterium, D, is $I=1$. Calculate the ratio of the number of ways of achieving rotational states with odd and even values of J.
- 11B.9** The rotational constant of $^{12}\text{C}^{16}\text{O}$ is 5765 GHz. Calculate the value of J for the most populated level at (a) 300 K and (b) 1000 K.

11B.10 Lines in the rotational spectrum of $^{63}\text{Cu}^1\text{H}$ are observed as part of the microwave spectrum of a flame. The most intense line in the spectrum, which corresponds to the transition from the most populated level, is observed to be $J=7 \leftarrow 6$. Estimate the temperature of the $^{63}\text{Cu}^1\text{H}$ molecules in the flame, given that the rotational constant is $B=234 \text{ GHz}$.

11B.11 Which of the following molecules can have (a) a pure rotational spectrum and (b) a rotational Raman spectrum: (i) HCl, (ii) N_2O , (iii) O_3 , (iv) SF_4 , (v) XeF_4 ?

11B.12 Suppose that hydrogen is replaced by deuterium in $^1\text{H}^{35}\text{Cl}$. Would you expect the $J=1 \leftarrow 0$ transition to move to higher or lower wavenumber?

Topic 11C Vibrational spectroscopy

11C.1 Suppose the C=O group in a peptide bond can be regarded as isolated from the rest of the molecule. Given the force constant of the bond in a carbonyl group is 908 N m^{-1} , calculate the vibrational wavenumber of (a) $^{12}\text{C}=\text{^{16}O}$, (b) $^{13}\text{C}=\text{^{16}O}$.

11C.2 How many normal modes of vibration are there for (a) NO_2 , (b) N_2O , (c) cyclohexane, (d) hexane?

11C.3 The wavenumber of the fundamental vibrational transition of Cl_2 is 565 cm^{-1} . Calculate the force constant of the bond.

11C.4 The hydrogen halides have the following fundamental vibrational wavenumbers:

	HF	HCl	HBr	HI
$\tilde{\nu}/\text{cm}^{-1}$	4138	2992	2649	2308

(a) Calculate the force constants of the hydrogen-halogen bonds. (b) Predict the fundamental vibrational wavenumbers of the deuterium halides.

Topic 11D Electronic spectroscopy

11D.1 The molar absorption coefficients of two substances A and B at two wavelengths (denoted 1 and 2) are as follows: $\epsilon_{A,1} = 75 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{B,1} = 10.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{A,2} = 12.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{B,2} = 8.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The total absorbances of a solution at these two wavelengths in a cell of length 5.0 mm were measured as 0.8 and 1.2, respectively. What are the molar concentrations of A and B in the solution?

11D.2 In an X-ray photoelectron experiment, a photon of wavelength 100 pm ejects an electron from the inner shell of an atom and it emerges with a speed of $2.34 \times 10^4 \text{ km s}^{-1}$. Calculate the binding energy of the electron.

11B.13 The rotational constant of $^1\text{H}^{35}\text{Cl}$ is 3178 GHz. What is the separation of the lines in its pure rotational spectrum (a) in gigahertz, (b) in reciprocal centimetres?

11B.14 For $^1\text{H}^{79}\text{Br}$, the rotational constant is 250 357 599 MHz and the centrifugal distortion constant is 10 320 MHz. Calculate the frequency of the $J=12 \leftarrow 11$ transition in the microwave spectrum of $^1\text{H}^{79}\text{Br}$.

11B.15 The rotational constant of $^{12}\text{C}^{16}\text{O}_2$ (from Raman spectroscopy) is 11.70 GHz. What is the CO bond length in the molecule?

11B.16 The wavenumber of the incident radiation in a Raman spectrometer is $20 623 \text{ cm}^{-1}$. What is the wavenumber of the scattered Stokes radiation for the $J=4 \leftarrow 2$ transition of $^{16}\text{O}_2$?

11C.5 Which of the following molecules may show infrared absorption spectra: (a) H_2 , (b) HCl, (c) CO_2 , (d) H_2O , (e) CH_3CH_3 , (f) CH_4 , (g) CH_3Cl , (h) N_2 ?

11C.6 Calculate the wavenumber of the first overtone transition with $v=2 \leftarrow 0$ in nitric oxide, NO, given that the value of the vibrational wavenumber is $\tilde{\nu} = 1904.03 \text{ cm}^{-1}$ and the anharmonicity constant is $x_e = 0.0073$.

11C.7 In the infrared spectrum of CO a strong vibrational transition is observed centred at 2143.29 cm^{-1} corresponding to the fundamental band with $v=1 \leftarrow 0$ with a weaker transition at 4259.66 cm^{-1} , corresponding to the overtone band with $v=2 \leftarrow 0$. What is the vibrational wavenumber, $\tilde{\nu}$, and anharmonicity constant, x_e , of CO?

11C.8 The rotational constant of $^1\text{H}^{81}\text{Br}$ is 8.360 cm^{-1} . Calculate the wavenumber of the R-branch line originating from the rotational state with $J=2$.

11C.9 Consider the vibrational mode of CH_4 that corresponds to the compression of one C-H bond while the other three C-H bonds stretch. Is it (a) Raman, (b) infrared active?

11D.3 The energy required for the ionization of a certain atom is 21.4 eV. The absorption of a photon of unknown wavelength ionizes the atom and ejects an electron with velocity $1.03 \times 10^6 \text{ m s}^{-1}$. Calculate the wavelength of the incident radiation.

11D.4 What is the kinetic energy of an electron that has been accelerated through a potential difference of 10.0 kV?

11D.5 What is (a) the energy, (b) the speed of an electron that has been ejected from an orbital of ionization energy 10.0 eV by a photon of radiation of wavelength 110 nm?

11D.6 In a particular photoelectron spectrum using 21.21 eV photons, electrons were ejected with kinetic energies of 11.01 eV, 8.23 eV, and 5.22 eV. Sketch the molecular orbital

Topic 11E The decay of excited states

11E.1 Consider a unimolecular photochemical reaction with rate constant $k_r = 1.7 \times 10^4 \text{ s}^{-1}$ that involves a reactant with an observed fluorescence lifetime of 1.0 ns and an observed phosphorescence lifetime of 1.0 ms. Is the excited singlet state or the excited triplet state the most likely precursor of the photochemical reaction?

11E.2 The observed fluorescence lifetime in the absence of a quencher is 1.4 ns. In the presence of a quencher the fluorescence lifetime is 0.8 ns. Calculate the quenching efficiency, which is the ratio of the fluorescence quantum yields in the presence and absence of the quencher, ϕ_f/ϕ_{f0} .

Discussion questions

11.1 Justify the form of the Beer–Lambert law. When might deviations from it be observed?

11.2 Describe the physical origins of linewidths in the absorption and emission spectra of gases, liquids, and solids. How may they be reduced?

11.3 Consider a diatomic molecule that is highly susceptible to centrifugal distortion in its ground vibrational state. Do you expect excitation to high rotational energy levels to change the equilibrium bond length of this molecule? Justify your answer.

11.4 Why does the vibrational state of a diatomic molecule affect its rotational constant? Is there an effect even if the potential is strictly parabolic?

11.5 Account physically for the fact that a linear polyatomic molecule composed of N atoms has one more vibrational mode than a non-linear molecule of N atoms.

11.6 Discuss the physical origins of the gross selection rules for microwave spectroscopy and rotational Raman spectroscopy.

Problems

11.1 A *Dubosq colorimeter* consists of a cell of fixed path length and a cell of variable path length. By adjusting the length of the latter until the transmission through the two cells is the same, the concentration of the second solution can be inferred from that of the former. Suppose that a plant dye of concentration $25 \mu\text{g dm}^{-3}$ is added to the fixed cell,

energy level diagram for the species, showing the ionization energies of the three identifiable orbitals.

11E.3 Fluorescence from the energy donor pyrene is quenched by the acceptor dye coumarin. In an experiment to investigate the binding of pyrene within a substrate, the fluorescence quantum yield of pyrene in the absence of any quencher was measured to be 0.65. With coumarin bound to the surface of the substrate, the quantum yield dropped to 0.49. Use Förster theory to calculate the separation between the donor and acceptor, given that the value of R_0 for the pyrene–coumarin pair is 3.9 nm.

11.7 Discuss the physical origins of the gross selection rules for infrared spectroscopy and vibrational Raman spectroscopy.

11.8 Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared absorption and Raman spectra of your sample?

11.9 Suggest a reason why the replacement of ^{12}C by ^{13}C in CO_2 affects some of its vibrational frequencies but not all.

11.10 Account for the appearance of P, Q, and R branches in the vibration–rotation spectrum of a diatomic molecule.

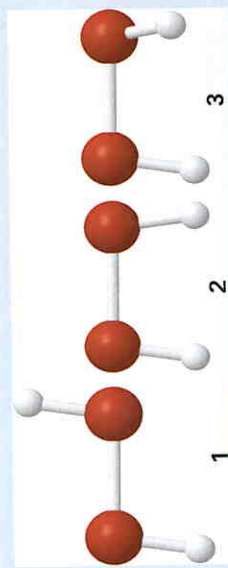
11.11 Explain the origin of the Franck–Condon principle and how it leads to the appearance of vibrational structure in an electronic transition.

11.12 Explain how colour can arise from molecules.

11.13 Describe the mechanisms of fluorescence and phosphorescence. How could you test the proposed mechanisms?

the length of which is 1.55 cm. Then a solution of the same dye, but of unknown concentration, is added to the second cell. It is found that the same transmittance is obtained when the length of the second cell is adjusted to 1.18 cm. What is the concentration of the second solution?

11.8 Suppose that three conformations are proposed for the nonlinear molecule H_2O_2 (**1**, **2**, and **3**). The infrared absorption spectrum of gaseous H_2O_2 has bands at 870, 1370, 2869, and 3417 cm^{-1} . The Raman spectrum of the same sample has bands at 877, 1408, 1435, and 3407 cm^{-1} . All bands correspond to fundamental vibrational wavenumbers and you may assume that (i) the 870 and 877 cm^{-1} bands arise from the same normal mode, and (ii) the 3417 and 3407 cm^{-1} bands arise from the same normal mode. (a) If H_2O_2 were linear, how many normal modes of vibration would it have? (b) Determine which of the proposed conformations is inconsistent with the spectroscopic data. Explain your reasoning.



11.9 Vibration–rotation transitions in the infrared spectrum of $^{1}\text{H}^{19}\text{F}$ were observed at 2886.50, 2908.51, 2930.43, 2974.55, 2996.57, 3018.58 cm^{-1} . (a) By considering the separations between pairs of lines, and by reference to Fig. 9 of Topic 11C, assign the transitions. (b) Determine the bond length of $^{1}\text{H}^{19}\text{F}$.

11.10 Lines are observed in the high-resolution infrared spectrum of HCl gas at 2841.42, 2843.55, 2862.26, 2864.43, 2903.96, 2906.19, 2924.80, and 2927.06 cm^{-1} . (a) Assign the observed lines to P and R-branch vibration–rotation transitions in either $^{1}\text{H}^{35}\text{Cl}$ or $^{1}\text{H}^{37}\text{Cl}$. (b) Hence calculate the rotational constant, \tilde{B} , for each isotopomer, assuming that the value does not depend upon the vibrational state and so is constant. (c) Also calculate the fundamental vibrational wavenumber, $\tilde{\nu}$, for each isotopomer. (d) Comment on any differences in the values.

11.11 When benzophenone is illuminated with ultraviolet radiation it is excited into a singlet state. This singlet changes rapidly into a triplet, which phosphoresces. Triethylamine acts as a quencher for the triplet. In an experiment in methanol as solvent, the phosphorescence intensity varied with amine concentration as shown below. A time-resolved laser spectroscopy experiment had also shown that the half-life of the fluorescence in the absence of quencher is 29 μs . What is the value of the quenching rate constant k_q ?

$[\text{Q}]/(\text{mol dm}^{-3})$	0.0010	0.0050	0.0100
$I_f/(\text{arbitrary units})$	0.41	0.25	0.16

11.2 The microwave spectrum of $^{1}\text{H}^{127}\text{I}$ consists of a series of lines separated by 384 GHz. (a) Compute its bond length. (b) What would be the separation of the lines in $^2\text{H}^{127}\text{I}$?

11.3 Rotational lines in the microwave spectrum of $^{127}\text{I}^{35}\text{Cl}$ are observed at 6.8291, 13.6582, 20.4872, and 20.3163 MHz . (a) Assign the transitions. (b) By plotting a graph, determine the value of the rotational constant. (c) Hence calculate the bond length in $^{127}\text{I}^{35}\text{Cl}$.

11.4 Transitions with the following wavenumbers are observed in the rotational spectrum of OCS: $1.217 1054 \text{ cm}^{-1}$, $1.622 8005 \text{ cm}^{-1}$, $2.028 4883 \text{ cm}^{-1}$, and $2.434 1708 \text{ cm}^{-1}$. Use the graphical procedure implied by eqn 11b of Topic 11B to determine the values of the rotational constant, B , and centrifugal distortion constant, D , for this molecule.

11.5 The axes about which a molecule rotates pass through the centre of mass of the molecule. The position of the centre of mass is such that

$$\sum m_i r_i = 0$$

with m_i the molecular mass of each atom and r_i the position of each atom relative to the centre of mass. (a) Show that for a linear molecule of the form ABC, the moment of inertia is

$$I = m_A R_{AB}^2 + m_C R_{BC}^2 - \frac{(m_A R_{AB} - m_C R_{BC})^2}{m_A + m_B + m_C}$$

where R_{AB} and R_{BC} are the bond lengths. (b) The microwave spectrum of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ gave absorption lines (in GHz) as follows:

J	1	2	3	4
^{32}S	24.325 92	36.488 82	48.651 64	60.814 08
^{34}S	23.732 33			47.462 40

Use the data to determine the rotational constants and the moments of inertia for $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ and $^{16}\text{O}^{12}\text{C}^{34}\text{S}$. (c) Assuming that the bond lengths are unchanged by isotopic substitution, calculate the C–O and C–S bond lengths in OCS.

11.6 The Morse potential-energy function

$$V(R) = D_e [1 - e^{-a(R-R_e)}]^2$$

may be used to describe how the potential energy, V , of a diatomic molecule varies with internuclear separation, R . (a) Sketch the function, taking $D_e = 50 \text{ kJ mol}^{-1}$, $R_e = 0.30 \text{ nm}$ and $a = 0.18 \text{ nm}^{-1}$ as typical values of the parameters. (b) Explain the significance of the parameters D_e , R_e , and a .

11.7 (a) Give the parities of the wavefunctions for the first four levels of a harmonic oscillator. (b) How may the parity be expressed in terms of the quantum number ν ?

11.12 The quenching of tryptophan fluorescence by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process from the following data:

$[O_2]/(10^{-2} \text{ mol dm}^{-3})$	0	2.3	5.5	8	10.8
τ/ns	2.6	1.5	0.92	0.71	0.57

11.13 The fluorescence of a solution of a plant pigment illuminated by 330 nm radiation was studied in the presence of a quenching agent, with the following results:

$[Q]/(\text{mmol dm}^{-3})$	1.0	2.0	3.0	4.0	5.0
I_0/I_{obs}	0.31	0.18	0.13	0.10	0.081

In a second series of experiments, the incident radiation was extinguished and the lifetime of the decay of the fluorescence was observed:

$[Q]/(\text{mmol dm}^{-3})$	1.0	2.0	3.0	4.0	5.0
τ/ns	76	45	32	25	20

Determine the quenching rate constant and the half-life of the fluorescence.

Projects

The symbol ‡ indicates that calculus is required.

11.1 Here you are invited to explore the process of human vision. (a) The flux of visible photons reaching Earth from the North Star is about $4 \times 10^3 \text{ mm}^{-2} \text{ s}^{-1}$. Of these photons, 30 per cent are absorbed or scattered by the atmosphere and 25 per cent of the surviving photons are scattered by the surface of the cornea of the eye. A further 9 per cent are absorbed inside the cornea. The area of the pupil at night is about 40 mm^2 and the response time of the eye is about 0.1 s. Of the photons passing through the pupil, about 43 per cent are absorbed in the ocular medium. How many photons from the North Star are focused on to the retina in 0.1 s? For a continuation of this story, see R. W. Rodieck, *The first steps in seeing*, Sinauer (1998). (b) In the free-electron molecular orbital theory of electronic structure, the π electrons in a conjugated molecule are treated as non-interacting particles in a box of length equal to the length of the conjugated system. On the basis of this model, at what wavelength would you expect all *trans*-retinal to absorb? Take the mean carbon-carbon bond length to be 140 pm.

11.2† The most populated rotational energy level of a linear rotor is given in eqn 9 of Topic 11B. By following the method used in *Justification 11B.3*, derive an expression for the most

11.14 Light-induced degradation of molecules, also called *photobleaching*, is a serious problem in *fluorescence microscopy*, in which a specimen (such as a biological cell) labelled with a fluorescent dye is observed under an optical microscope. A molecule of a dye commonly used to label biopolymers can withstand about 10^6 excitations by photons before light-induced reactions destroy its π system and the molecule no longer fluoresces. For how long will a single dye molecule fluoresce while being excited by 1.0 mW of 488 nm radiation from an argon ion laser? You may assume that the dye has an absorption spectrum that peaks at 488 nm and that every photon delivered by the laser is absorbed by the molecule.

11.15 The following data refer to a family of compounds with the general composition A–B_n–C in which the distance R between A and C was varied by increasing the number of B units in the linker:

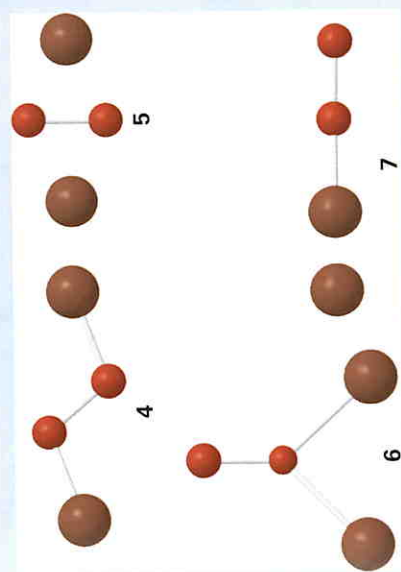
R/nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
η_I	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

Are the data described adequately by the Förster theory, as expressed through eqn 9 of Topic 11E? If so, what is the value of R_0 for the A–C pair?

populated rotational level of a spherical rotor, given that its degeneracy is $(2J + 1)^2$.

11.3 The protein haemerythrin (Her) is responsible for binding and carrying O_2 in some invertebrates. Each protein molecule has two Fe^{2+} ions that are in very close proximity and work together to bind one molecule of O_2 , forming an Fe_2O_2 group. (a) The Raman spectrum of oxygenated haemerythrin obtained with laser excitation at 500 nm has a band at 844 cm^{-1} which has been attributed to the O–O stretching mode of bound $^{16}O_2$. Why is Raman spectroscopy and not infrared spectroscopy the method of choice for the study of the binding of O_2 to haemerythrin? (b) Proof that the 844 cm^{-1} band in the Raman spectrum of oxygenated haemerythrin arises from a bound O_2 species may be obtained by conducting experiments on samples of haemerythrin that have been mixed with $^{18}O_2$, instead of $^{16}O_2$. Predict the fundamental vibrational wavenumber of the $^{18}O_2$ stretching mode in a sample of haemerythrin that has been treated with $^{18}O_2$. (c) The fundamental vibrational wavenumbers for the O–O stretching modes of O_2 , O_2^- (superoxide anion), and O_2^{2-} (peroxide anion) are 1555, 1107, and 878 cm^{-1} , respectively. (i) Explain this trend in terms of the electronic structures of O_2 , O_2^- , and O_2^{2-} . (ii) What are the bond orders of O_2 , O_2^- , and O_2^{2-} ? (d) Based on the data given in part (c), which of

the following species best describes the Fe_2O_2 group of haemerythrin: $Fe^{2+}O_2$, $Fe^{2+}Fe^{3+}O_2^-$, or $Fe^{3+}O_2^{2-}$? Explain your reasoning. (e) The Raman spectrum of haemerythrin mixed with ^{18}O has two bands that can be attributed to the O–O stretching mode of bound oxygen. Discuss how this observation may be used to exclude one or more of the four proposed schemes (4–7) for binding of O_2 to the Fe_2 site of haemerythrin.



11.4 Water, carbon dioxide, and methane are able to absorb some of the Earth's infrared emissions whereas nitrogen and oxygen cannot. The computational methods discussed in Topic 9D can also be used to simulate vibrational spectra and from the results of the calculation it is possible to determine the correspondence between a vibrational frequency and the atomic displacements that give rise to a normal mode. (a) Using molecular modelling software and the computational method of your instructor's choice, investigate and depict pictorially the vibrational normal modes of CH_4 , CO_2 , and H_2O in the gas phase. (b) Which vibrational modes of CH_4 , CO_2 , and H_2O are responsible for absorption of infrared radiation?

11.5 Consider the trapping of solar energy by photosynthetic organisms. In chlorophyll–protein complexes that capture solar energy, the fluorescence of a chlorophyll molecule is quenched by nearby chlorophyll molecules. Given that for a pair of chlorophyll *a* molecules $R_0 = 5.6 \text{ nm}$, by what distance should two chlorophyll *a* molecules be separated to shorten the fluorescence lifetime from 1 ns (a typical value for monomeric chlorophyll *a* in organic solvents) to 10 ps?

FOCUS 12

Statistical thermodynamics

Statistical thermodynamics provides the link between the microscopic properties of matter and its bulk properties. It provides a means of calculating thermodynamic properties from structural and spectroscopic data and gives insight into the molecular origins of chemical properties.

12A The Boltzmann distribution

The 'Boltzmann distribution', which is used to predict the populations of states in systems at thermal equilibrium, is among the most important equations in chemistry for it summarizes the populations of states; it also provides insight into the nature of 'temperature'.

12A.1 The population of states; 12A.2 The general form of the Boltzmann distribution; 12A.3 The origins of the Boltzmann distribution

12B The partition function

The Boltzmann distribution introduces the concept of a 'partition function', which is the central mathematical concept of the rest of the treatment of statistical thermodynamics. The Topic focuses on how to interpret the partition function and how to calculate it in a number of simple cases. The key conclusion is that a 'molecular partition function' is the

thermodynamic version of a wavefunction, and contains all the thermodynamic information about a system.

12B.1 The interpretation of the partition function; 12B.2 The molecular partition function; 12B.3 The translational partition function; 12B.4 The rotational partition function; 12B.5 The vibrational partition function; 12B.6 The electronic partition function; 12B.7 The significance of the molecular partition function

12C The origin of thermodynamic properties

This Topic shows how the molecular partition function is used to calculate (and give insight into) important thermodynamic functions: the internal energy, the heat capacity, the entropy, and the Gibbs energy. With the Gibbs energy available, a final step is taken into the calculations of chemically significant expressions by showing how equilibrium constants can be calculated from structural and spectroscopic data.

12C.1 The internal energy; 12C.2 The heat capacity; 12C.3 The entropy; 12C.4 The Gibbs energy; 12C.5 The equilibrium constant

TOPIC 12A

The Boltzmann distribution

► Why do you need to know this material?

The Boltzmann distribution is the key to understanding much of chemistry. All thermodynamic properties can be interpreted in its terms, as can the temperature dependence of equilibrium constants and the rates of chemical reactions. It also illuminates the meaning of 'temperature'. There is, perhaps, no more important unifying concept in chemistry.

► What is the key idea?

The most probable distribution of molecules over the available energy levels subject to certain restraints depends on a single parameter, the temperature.

► What do you need to know already?

You need to be aware that molecules can exist only in certain discrete energy levels (Topic 7A) and that in some cases more than one state has the same energy (Topics 7C and 7D).

The concept of the Boltzmann distribution was introduced in the opening pages of this text, and has been underlying all the descriptions of the relation between the individual properties of molecules and the properties of bulk matter. It expresses the **population** of a state, N_i , the number of molecules in that state, solely in terms of the energy of the state ϵ_i and the absolute temperature, regardless of the type of motion the state represents:

$$N_i \propto e^{-\epsilon_i/kT} \quad (1)$$

The Boltzmann distribution

where the constant k is Boltzmann's constant, $k = 1.380\,6488 \times 10^{-23} \text{ J K}^{-1}$. The approximation $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ is often used in calculations.

12A.1 The population of states

According to eqn 1, the relative populations, N_i and N_j , of two states depends upon the temperature T and the difference in their energies, ϵ_i and ϵ_j

$$\frac{N_j}{N_i} = e^{-(\epsilon_j - \epsilon_i)/kT} \quad (2a)$$

Relative populations

In chemical applications it is common to use not the individual energies but energies per mole of molecules, E_i , with $E_i = N_A \epsilon_i$, where N_A is Avogadro's constant. When both the numerator and denominator in the exponential are multiplied by N_A , eqn 2a becomes

$$\frac{N_j}{N_i} = e^{-(E_j - E_i)/RT} \quad (2b)$$

Relative populations in terms of molar energies

where $R = N_A k = 8.314\,4621 \text{ J K}^{-1} \text{ mol}^{-1}$. When such precision is not required, the approximate value $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ can be used. The constant R is called the (molar) **gas constant** because it originally arose in relation to the properties of gases (Topic 1A), but the fact that it is related to Boltzmann's constant and the Boltzmann distribution means that it has a much broader range of application than to gases alone.

This difference in the populations of the lower and higher energy states becomes more marked as the separation, $\Delta\epsilon$, between the states increases (Fig. 1). More specifically,

The relative population of the upper state decreases exponentially with its energy above the lower state.

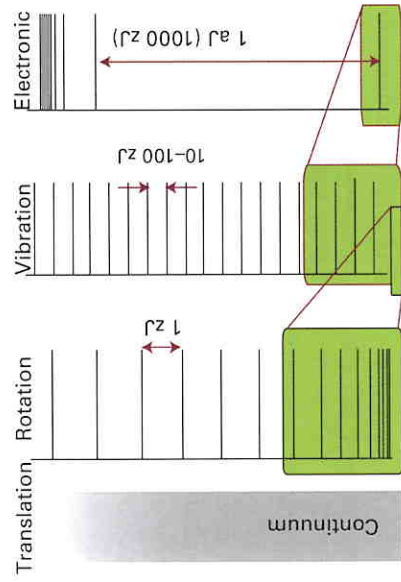


Fig. 1 The energy level separations typical of four types of motion. ($1 \text{ zJ} = 10^{-21} \text{ J}$; in molar terms, 1 zJ is equivalent to about 0.6 kJ mol^{-1} .)

For example, because the separation in energy between different electronic states is usually large, most atoms or molecules are found in the lowest electronic energy state and the population of excited electronic states is usually very low. In contrast, because the rotational energy states of molecules lie much closer in energy, the populations of excited rotational states can be significant (Topic 11B).

Through eqn 2 it is possible to see the significance of temperature: for a given set of quantum states,

The temperature is the single parameter that controls the relative population of the states.

The effect is shown in Fig. 2. When the temperature is low, there is only a small population of molecules in high energy states. When the temperature is high, many high energy states are populated. The same Boltzmann distribution of populations, at a given value of T , applies to any array of energy levels, be they translational, rotational, vibrational, or electronic, and regardless of the chemical identity of the

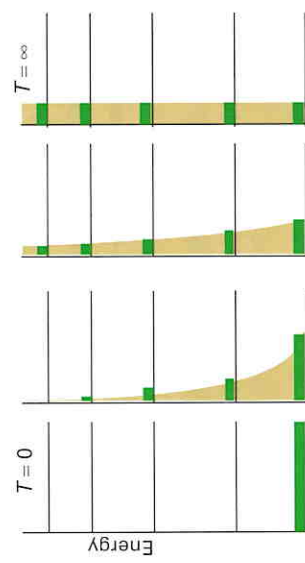


Fig. 2 The Boltzmann distribution of populations for a system of five states as the temperature is increased. At low temperature, the population of molecules in high energy states is small. At higher temperature, more high energy states are populated.

substance. That is why 'temperature' is a universally applicable property of matter and why the flow of energy as heat is from high to low temperature regardless of the natures of the substances in thermal contact.

In the same spirit, the Boltzmann distribution accounts for the stability of matter at low temperatures, when only low-energy states are occupied. It also accounts for the ability of matter to undergo change (by chemical reaction or physical transition) at high temperatures, when high-energy states are also abundantly occupied.

Brief illustration 12A.1 Relative populations

Methylcyclohexane molecules may exist in one of two conformations, with the methyl group in either an equatorial or axial position. The equatorial form is lower in energy with the axial form being 6.0 kJ mol^{-1} higher in energy. At 300 K , this difference in energy implies that the relative populations of molecules in the axial and equatorial states is

$$\frac{N_{\text{axial}}}{N_{\text{eq}}} = e^{-(\epsilon_{\text{axial}} - \epsilon_{\text{eq}})/RT} = e^{-(6.0 \times 10^3 \text{ J mol}^{-1}) / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K})} = 0.090$$

The number of molecules in an axial conformation is therefore just 9 per cent of those in the equatorial conformation.

Self-test 12A.1

- Determine the temperature at which the relative proportion of molecules in axial and equatorial conformations in a sample of methylcyclohexane is 0.30 or 30 per cent.

Answer: 600 K

12A.2 The general form of the Boltzmann distribution

Equation 1 is expressed as a proportionality. The complete form of the distribution is

$$N_i = \frac{N e^{-\epsilon_i/kT}}{q} \quad (3)$$

Boltzmann distribution

Here N is the total number of molecules. The term in the denominator, q , is the **partition function**:

$$q = \sum_i e^{-\epsilon_i/kT} = e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT} + \dots \quad (4)$$

Partition function (definition)

where the sum is over all the states of the system. The physical meaning of q is explored in Topic 12B. At this stage it is sufficient to think of the partition function as a kind of normalizing factor, for it ensures that the sum of all the populations is the total

number of molecules in the system: that is, with N_i given by eqn 3,

$$\sum_i N_i = \frac{N}{q} \sum_i e^{-\epsilon_i/kT} = N$$

One very important feature of the distribution is that it applies to the populations of *states*. In some cases (the hydrogen atom and rotating molecules are examples) several different states have the same energy. That is, some energy levels are *degenerate* (Topic 7C and 7D). The Boltzmann distribution can be used to calculate, for instance, the number of hydrogen atoms at a temperature T that have their electron in a $2p_x$ orbital. Because a $2p_y$ orbital has exactly the same energy, the number of atoms with an electron in a $2p_y$ orbital is the same as the number with an electron in a $2p_x$ orbital. The same is true of atoms with an electron in a $2p_z$ orbital, so $N(2p_x) = N(2p_y) = N(2p_z)$. Therefore, if the number of atoms with electrons in $2p$ orbitals, $N(2p)$, is $N(2p_x) + N(2p_y) + N(2p_z) = 3N(2p_x)$. In general, if the degeneracy of an energy level (that is, the number of states of that energy) is g_i , a factor of g_i must be used to get the population of the *level* (as distinct from an individual state). It is obviously very important to decide whether the quantity of interest is the population of an individual state or the population of an entire degenerate energy level. For levels denoted L_i ,

$$N_{L_i} = \frac{N g_i e^{-\epsilon_i/kT}}{q} \quad q = \sum_L g_L e^{-\epsilon_L/kT} \quad (5)$$

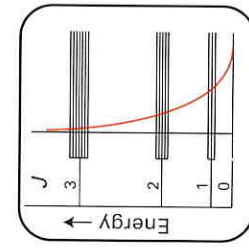
Boltzmann distribution (general form)

where N_{L_i} is the total number of molecules in the level L_i (the sum of populations of all the states of that level), g_{L_i} is its degeneracy, and ϵ_{L_i} is its energy.

Example 12A.1

Calculating the relative populations of rotational levels

Calculate the relative populations of the $J = 2$ and $J = 1$ rotational levels of HCl at 25 °C. For HCl the rotational constant is $B = 318.0$ GHz.



Collect your thoughts The rotational energy levels of diatomic molecules are discussed in Topic 11B. Because HCl is a linear rotor, calculate the energy of a level as $\epsilon_J = hBJ(J + 1)$, where B is the rotational constant. With $g_J = 2J + 1$ as the degeneracy of each level, calculate the relative populations of the $J = 2$ and $J = 1$ rotational levels by forming the ratio N_2/N_1 from eqn 5.

The solution The relevant quantities are

J	ϵ_J	g_J
1	$2hB$	3
2	$6hB$	5

From eqn 4, the ratio of populations of the levels is

$$\frac{N_2}{N_1} = \frac{N g_2 e^{-\epsilon_2/kT} / q}{N g_1 e^{-\epsilon_1/kT} / q} = \frac{g_2 e^{-\epsilon_2/kT}}{g_1 e^{-\epsilon_1/kT}}$$

Boltzmann distribution (cancel N and q)

$$= \frac{g_2 e^{-\epsilon_2/kT}}{g_1 e^{-\epsilon_1/kT}} = \frac{g_2}{g_1} e^{-(\epsilon_2 - \epsilon_1)/kT}$$

Boltzmann distribution

For HCl, $B = 318.0$ GHz, so at 25 °C (corresponding to 298 K), this ratio works out as

$$\frac{N_2}{N_1} = \frac{5}{3} e^{-\frac{6(2)(318.0 \times 10^9 \text{ Hz}) \times (298 \text{ K})}{k}} = 1.36$$

Comment There are more molecules in the level with $J = 2$ than in the level with $J = 1$, even though $J = 2$ corresponds to a higher energy. Each individual *state* with $J = 2$ has a lower population than each state with $J = 1$, but there are more states in the level with $J = 2$.

Self-test 12A.2

What is the ratio of the populations of the levels with $J = 1$ and $J = 0$ at the same temperature?

Answer: 2.71

One convenient and important convention we adopt in this text is that *all energies are measured relative to the ground state*. That is, the ground-state energy is set equal to zero, even if there is a zero-point energy. For instance, the energies of a harmonic oscillator (Topic 7E) are measured from zero for the ground state:

$$\text{Actual energies: } \epsilon = \frac{1}{2} h\nu, \frac{3}{2} h\nu, \frac{5}{2} h\nu, \dots$$

$$\text{Convention: } \epsilon = 0, h\nu, 2h\nu, \dots$$

Likewise, the energies of the hydrogen atom (Topic 8A) are measured from zero for the 1s orbital:

$$\text{Actual energies: } \epsilon = -hcR_{\text{H}}, -\frac{1}{4}hcR_{\text{H}}, -\frac{1}{9}hcR_{\text{H}}, \dots$$

$$\text{Convention: } \epsilon = 0, \frac{3}{4}hcR_{\text{H}}, \frac{5}{9}hcR_{\text{H}}, \dots$$

This convention greatly simplifies the interpretation of the significance of q in Topic 12B.

12A.3 The origins of the Boltzmann distribution

The conceptual basis of the derivation of the Boltzmann distribution is very simple. Imagine a stack of energy levels arranged like bookshelves, one above

the other. Then imagine being blindfolded and throwing balls (the molecules) at the shelves (the energy levels), and letting them land on the available shelves entirely at random, apart from one condition. That condition is that the total energy of the final arrangement must have the actual energy of the sample of matter being described. Provided the temperature is above absolute zero, not all the balls are allowed to land on the bottom shelf, for that would give a total energy of zero. Some of the balls might land on the bottom shelf, but there must then be others ending up on higher shelves to ensure that the total energy has the specified value. Throwing 100 balls at a set of shelves, results in one particular valid distribution. Repeating the experiment with the same number of balls results in a different but still valid distribution. If the experiment is repeated again and again, many different distributions will be found, but some of them will occur more often than others (Fig. 3).¹

When this game is analysed mathematically,² it turns out that the *most probable* distribution—the arrangement that turns up most often—is that given by eqn 5. In other words,

The Boltzmann distribution is the most probable outcome of blind chance occupation of energy levels, subject to the requirement that the total energy has a particular value.

When dealing with about 10^{23} molecules and repeat the experiment millions of times, the Boltzmann distribution turns out to be overwhelmingly the most probable outcome and can be used with confidence for all typical samples of matter.

Checklist of key concepts

- 1 The **Boltzmann distribution** gives the numbers of molecules in each state of a system at any temperature.
- 2 The temperature is the single parameter that controls the relative population of the states regardless of the type of motion they represent.
- 3 The relative populations of energy levels, as opposed to individual states, must take into account the degeneracies of the energy levels.
- 4 The Boltzmann distribution is the outcome of blind chance occupation of energy levels, subject to the requirement that the total energy has a particular value.

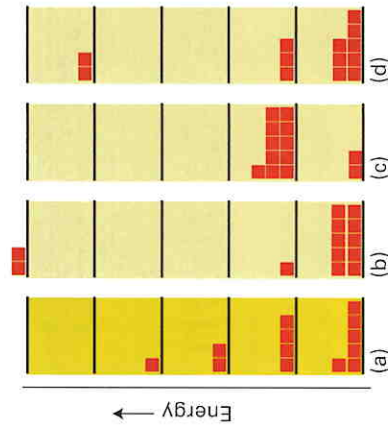


Fig. 3 The derivation of the Boltzmann distribution involves imagining that the molecules of a system (the squares) are distributed randomly over the available energy levels subject to the requirements that the number of molecules and the total energy is constant, and then looking for the most probable arrangement. Of the four (out of many possibilities) shown here, the numbers of ways of achieving each arrangement are (a) 181 180, (b) 858, (c) 78, (d) 12 870. The number of ways of achieving (a) is by far the greatest, so this distribution is the most probable; it corresponds to the Boltzmann distribution.

TOPIC 12B

The partition function

► Why do you need to know this material?

Statistical thermodynamics provides the link between molecular properties that have been calculated or derived from spectroscopy and thermodynamic properties, including equilibrium constants. The connection depends on the partition function. Therefore, this material is an essential foundation for understanding physical and chemical properties of bulk matter in terms of the properties of the constituent molecules.

► What is the key idea?

The partition function, an indication of the number of occupied states, is calculated by drawing on calculated or spectroscopically derived structural information about molecules.

► What do you need to know already?

You need to know that the Boltzmann distribution expresses the most probable distribution of molecules over the available energy levels (Topic 12A). You also need to be aware of the expressions for the rotational and vibrational levels of molecules (Topics 11B and 11C) and the translational energy levels of a particle in a box (Topic 7C).

The key concept of quantum mechanics is the existence of a wavefunction that contains in principle all the dynamical information about a system, such as its energy, the electron density, the dipole moment, and so on. Once the wavefunction of an atom or molecule is known, it is possible to extract all the dynamical information about the system. There is a similar concept in statistical thermodynamics. The partition

function, q , contains all the thermodynamic information about the system, such as its internal energy, entropy, heat capacity, and so on.

12B.1 The interpretation of the partition function

The population of a state is calculated from the Boltzmann distribution (Topic 12A) as

$$N_i = \frac{N e^{-\epsilon_i/kT}}{q} \quad (1)$$

Boltzmann distribution

with q defined as

$$q = \sum_i e^{-\epsilon_i/kT} = 1 + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT} + \dots \quad (2)$$

Partition function (definition)

The sum is over states, not (possibly degenerate) energy levels. The first term is 1 because, by convention, the energy of the ground state (ϵ_0) is set equal to 0, and $e^0 = 1$. In principle, calculating q amounts to substituting the values of the energies ϵ_i , evaluating each term $e^{-\epsilon_i/kT}$ for the temperature of interest, and adding all the terms together. However, that procedure does not give much insight.

To see the physical significance of q , suppose first that $T = 0$ so that $1/T = \infty$. Then, because $e^{-\infty} = 0$, all terms other than the first are equal to 0, and $q = 1$. At $T = 0$ only the ground state is occupied and (provided that state is non-degenerate) $q = 1$. Now consider the other extreme: a temperature so high that $\epsilon_i/kT = 0$ for all values of the energies. Then, because $e^0 = 1$, the partition function is $q = 1 + 1 + 1 + 1 + \dots = N_{\text{states}}$, where N_{states} is the total number of states of the molecule (and might be infinite). That is, at very high temperatures, all the states of the system are

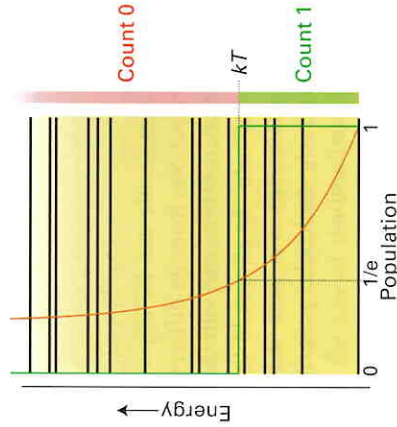


Fig. 1 The partition function is a measure of the number of thermally accessible states. Thus, for all states with $\epsilon < kT$ the exponential term is reasonably close to 1 whereas for all states with $\epsilon > kT$ the exponential term is close to 0. The states with $\epsilon < kT$ are significantly thermally accessible.

thermally accessible. It is beginning to become clear that the partition function is reporting on the number of states that are occupied at a given temperature.

Now consider an intermediate temperature, at which only some of the states are occupied significantly. Suppose that the temperature is such that kT is large compared to ϵ_1 and ϵ_2 but small compared to ϵ_3 and all subsequent terms (Fig. 1). Because ϵ_1/kT and ϵ_2/kT are both small compared to 1, and $e^x \approx 1 + x$ when x is very small (for instance, $e^{-0.01} = 0.990\dots$), the first three terms are all close to 1. However, because ϵ_3/kT is large compared to 1, and $e^{-x} \approx 0$ when x is large (for instance, $e^{-100} = 3.72 \times 10^{-44}$), all the remaining terms are close to 0. Therefore,

$$q = 1 + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT} + e^{-\epsilon_4/kT} + \dots$$

and $q \approx 1 + 1 + 1 + 0 + \dots = 3$. Once again, the partition function has a value corresponding to the number of significantly occupied states at the temperature of interest. That is the principal meaning of the partition function:

The partition function q gives the number of thermally accessible states at the temperature of interest.

Grasping the significance of q makes statistical thermodynamics much easier to understand. For example:

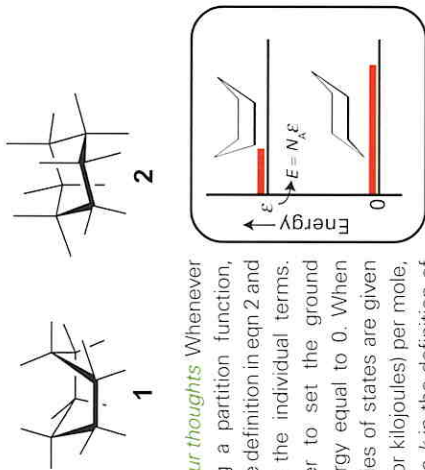
- Even before doing any calculations, it is expected that q increases with temperature, because more states become accessible as the temperature is raised.

- At low temperatures q is small, and falls to 1 as the temperature approaches absolute zero (when only one state, the ground state, is accessible and that state is non-degenerate).
- Molecules with numerous, closely spaced energy levels (like the rotational states of bulky molecules) can be expected to have very large partition functions.
- Molecules with widely spaced energy levels can be expected to have small partition functions, because only the few lowest states will be occupied at low temperatures.

Example 12B.1

Calculating a partition function

The boat conformation of cyclohexane (1) lies 22 kJ mol^{-1} higher in energy than the chair conformation (2). Calculate the partition function for the cyclohexane molecule, confining attention to these two conformations only. Show how the partition function varies with temperature.



Collect your thoughts Whenever calculating a partition function, start at the definition in eqn 2 and write out the individual terms. Remember to set the ground state energy equal to 0. When the energies of states are given in joules (or kilojoules) per mole, replace the k in the definition of q by $R = N_A k$.

The solution There are only two states, so the partition function has only two terms. The energy of the chair form is set at 0 and that of the boat form is $E = 22 \text{ kJ mol}^{-1}$. Then, with

$$\frac{E}{RT} = \frac{2.2 \times 10^4 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times T} = \frac{2.6 \dots \times 10^4}{T \text{ K}^{-1}}$$

cancel J mol⁻¹

it follows that

$$q = 1 + e^{-(2.6 \dots \times 10^4 \text{ K})/T}$$

This function is plotted in Fig. 2. Note that it rises from $q = 1$ (only the chair form is accessible at $T = 0$, when $(2.6 \times 10^4 \text{ K})/T = \infty$ and $e^{-\infty} = 0$) to $q = 2$ at $T = \infty$ (when $(2.6 \times 10^4 \text{ K})/T = 0$ and $e^0 = 1$); both states are thermally accessible at

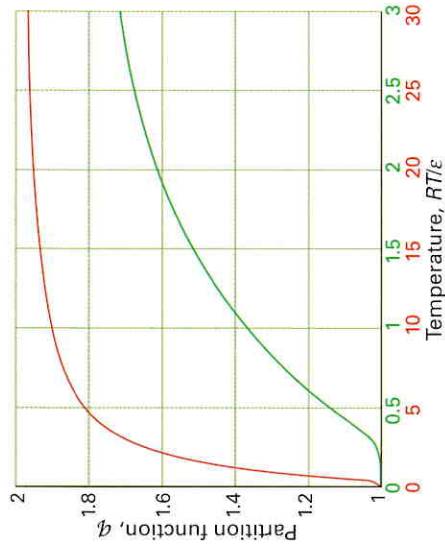


Fig. 2 The partition function for a two-level system with states at the energies 0 and ϵ . At 20 °C (293 K) and for $\epsilon = 22 \text{ kJ mol}^{-1}$, $kT/\epsilon = 0.11$, where $q = 1.0001$. Note how the partition function rises from 1 and approaches 2 at high temperatures.

high temperatures). At 20 °C, $q = 1.0001$, and there is a very small proportion of molecules in the boat form.

Self-test 12B.1

The ground configuration of a fluorine atom gives rise to a 4P term with two levels, the $J = \frac{3}{2}$ level (of degeneracy 4) and the $J = \frac{1}{2}$ level (of degeneracy 2) at an energy corresponding to 404.0 cm^{-1} above the ground state. Write down an expression for the partition function and plot it as a function of temperature. *Hint:* The notation used here is from Topic 8D. Take $\epsilon = hc\tilde{\nu}$ for the energy of the upper level. In this instance, the ground state is degenerate.

Answer: $q = 4 + 2e^{-hc\tilde{\nu}/kT}$, Fig. 3

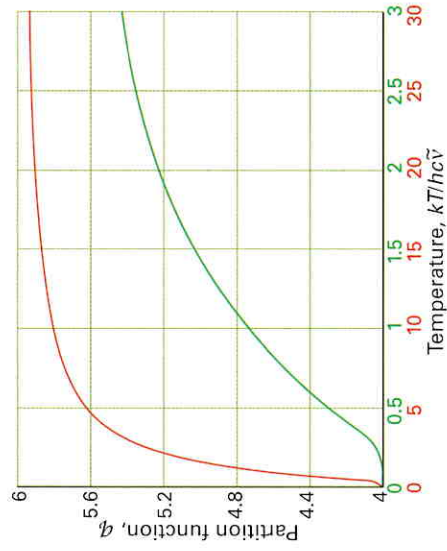


Fig. 3 The partition function for the six-level system treated in Self-test 12B.1. Note how q rises from 4 (when only the four states of the $^3P_{3/2}$ level are occupied) and approaches 6 (when the two states of the $^2P_{1/2}$ level are also accessible). At 20 °C, $kT/hc\nu = 0.504$, corresponding to $q = 4.28$.

12B.2 The molecular partition function

The energy of a molecule can be approximated as the sum of contributions from its different modes of motion (translation, rotation, and vibration), and the distribution of electrons. As shown in the following *Justification*, if the energy is a sum of independent contributions, then the **molecular partition function** is a product of contributions:

$$q = q^{\text{T}} q^{\text{R}} q^{\text{V}} q^{\text{E}} \quad \text{Molecular partition function} \quad (3)$$

where T denotes translation, R rotation, V vibration, and E the electronic contribution (including spin). The contribution from electronic spin is important in atoms or molecules containing unpaired electrons. The remainder of the Topic is devoted to development of expressions for these individual contributions to the molecular partition function.

Justification 12B.1

The factorization of the **molecular partition function** Suppose the energy can be expressed as the sum of contributions from two modes A and B (such as vibration and rotation), and that $\epsilon_{ij} = \epsilon_i^{\text{A}} + \epsilon_j^{\text{B}}$, where i denotes a state of mode A and j denotes a state of mode B, and the sums required are over both i and j independently. Then, the partition function is

$$\begin{aligned} q &= \sum_{ij} e^{-\epsilon_{ij}/kT} = \sum_{ij} e^{-(\epsilon_i^{\text{A}} + \epsilon_j^{\text{B}})/kT} \\ &= \sum_{ij} e^{-\epsilon_i^{\text{A}}/kT} e^{-\epsilon_j^{\text{B}}/kT} = \sum_i e^{-\epsilon_i^{\text{A}}/kT} \sum_j e^{-\epsilon_j^{\text{B}}/kT} = q^{\text{A}} q^{\text{B}} \end{aligned}$$

This argument is readily extended to three or more modes, as in eqn 3. It also applies to translation in three dimensions (in the sense that q^{T} is the product of partition functions for motion along each of three perpendicular axes), because motion along each axis is an independent mode.

12B.3 The translational partition function

Suppose a molecule of mass m is confined in a flask of volume V at a temperature T , then (as shown in the following *Justification*) to a good approximation for

typical containers and $T > 0$, the **translational partition function**, q^{T} , is

$$q^{\text{T}} = \frac{(2\pi mkT)^{3/2} V}{h^3} \quad \text{Translational partition function} \quad (4)$$

As expected, the partition function increases with temperature. However, q^{T} also increases with the volume of the flask. That should be expected too: the energy levels of a particle in a box become closer together as the size of the box increases (Topic 7C), so at a given temperature, more states are thermally accessible.

Brief illustration 12B.1 The translational partition function

Consider an O_2 molecule (of mass $32m_0$) in a flask of volume 100 cm^3 at 20 °C. Its translational partition function is

$$\begin{aligned} q^{\text{T}} &= \underbrace{(2\pi \times 32 \times (1.661 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}))^{3/2}}_m \times \underbrace{100 \times 10^{-6} \text{ m}^3}_V \\ &= 1.75 \times 10^{30} \end{aligned}$$

Note that a huge number of translational states are accessible at room temperature. This result is consistent with the derivation of eqn 3, which assumed that the translational energy levels form a near continuum in containers of macroscopic size.

A note on good practice All the units must cancel because all partition functions are dimensionless numbers. Here, because $J = 1 \text{ kg m}^2 \text{ s}^{-2}$, the units cancel as follows:

$$\begin{aligned} \frac{(\text{kg J K}^{-1} \text{ K})^{3/2} \text{ m}^3}{(\text{J s})^3} &= \frac{(\text{kg kg m}^2 \text{ s}^{-2})^{3/2} \text{ m}^3}{(\text{kg m}^2 \text{ s}^{-2} \text{ s})^3} \\ &= \frac{(\text{kg ms}^{-1})^3 \text{ m}^3}{(\text{kg m}^2 \text{ s}^{-1})^3} = \frac{\text{kg}^3 \text{ m}^6 \text{ s}^{-3}}{\text{kg}^3 \text{ m}^6 \text{ s}^{-3}} = 1 \end{aligned}$$

It might seem irksome to do this cancellation explicitly, but it is a very good way of making sure that you have set up the numerical calculation correctly.

Self-test 12B.2

Calculate the translational partition function for a H_2 molecule under the same conditions.

Answer: $q^{\text{T}} = 2.8 \times 10^{30}$

Justification 12B.2

The translational partition function

The starting point is the calculation of the partition function q_x for motion parallel to the x -axis.

Step 1: Write an expression for the energy levels in one dimension

The energy levels of a molecule of mass m in a container of length X are given by eqn 3 of Topic 7C ($E_n = n^2 h^2/8mL^2$) with $L = X$:

$$E_{n_x} = \frac{n_x^2 h^2}{8mX^2} \quad n_x = 1, 2, \dots$$

The lowest level ($n_x = 1$) has energy $h^2/8mX^2$, so the energies relative to that level are

$$E_{n_x} = (n_x^2 - 1)\epsilon_x \quad \epsilon_x = h^2/8mX^2$$

Step 2: Write an expression for the partition function for motion in one dimension

According to eqn 2, the partition function in the X dimension is the sum

$$q_x = \sum_{n_x=1}^{\infty} e^{-(n_x^2 - 1)\epsilon_x/kT}$$

The translational energy levels are very close together in a container the size of a typical laboratory vessel; therefore, they form a near continuum and the sum can be approximated by an integral:

$$q_x = \int_1^{\infty} e^{-(n_x^2 - 1)\epsilon_x/kT} dn_x \approx \int_0^{\infty} e^{-n_x^2 \epsilon_x/kT} dn_x$$

The extension of the lower limit to $n_x = 0$ and the replacement of $n_x^2 - 1$ by n_x^2 introduces negligible error but helps with evaluation of the integral.

Step 3: Evaluate the integral

The integral in step 2 can be evaluated by making the substitution $x^2 = n_x^2 \epsilon_x/kT$, implying that

$$\begin{aligned} n_x^2 &= \left(\frac{kT}{\epsilon_x}\right) x^2, \text{ so } n_x = \left(\frac{kT}{\epsilon_x}\right)^{1/2} x & \frac{dn_x}{dx} &= \left(\frac{kT}{\epsilon_x}\right)^{1/2} \\ \text{so } dn_x &= \left(\frac{kT}{\epsilon_x}\right)^{1/2} dx \end{aligned}$$

Therefore,

$$q_x = \left(\frac{kT}{\epsilon_x}\right)^{1/2} \int_0^{\infty} e^{-x^2} dx = \left(\frac{kT}{\epsilon_x}\right)^{1/2} \left(\frac{\pi^{1/2}}{2}\right) = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} X$$

where the integral is given in the Resource section (as Integral G1).

Step 4: Write partition functions for the X , Y , and Z dimensions

The same expression for the X dimension from step 3 applies to the other dimensions, so it follows that

$$q_X = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} X \quad q_Y = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} Y \quad q_Z = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} Z$$

Step 5: Write the expression for the partition function in three dimensions

Equation 4 follows after substitution of the expressions in step 4 into $q^\ddagger = q_X q_Y q_Z$:

$$q^\ddagger = q_X q_Y q_Z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} XYZ \\ = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V = \frac{(2\pi mkT)^{3/2} V}{h^3}$$

where $V = XYZ$ is the volume of the box.

12B.4 The rotational partition function

The rotational partition function, q^R , can also be approximated when the temperature is high enough for many rotational states to be occupied. As shown in the following *Justification*, for a linear rotor it turns out that for $T \gg hB/k$,

$$q^R = \frac{kT}{\sigma hB} \quad (5)$$

In this expression, B is the rotational constant (Topic 11B) and σ is the symmetry number: $\sigma = 1$ for an unsymmetrical linear rotor (such as HCl or HCN) and $\sigma = 2$ for a symmetrical linear rotor (such as H_2 or CO_2). The symmetry number reflects the fact that an unsymmetrical molecule is distinguishable after rotation by 180° about an axis perpendicular to the internuclear axis ($H-Cl \rightarrow Cl-H$) but a symmetrical molecule is not ($H-H \rightarrow H-H$). When evaluating q only distinguishable states are counted, and a symmetrical molecule has fewer distinguishable states than a less symmetrical molecule. A more formal explanation is that the Pauli principle (Topic 11B) excludes certain states of symmetrical molecules, so the number of thermally accessible states is smaller by the appropriate factor than for unsymmetrical molecules, where there is no such restriction.

Brief illustration 12B.2 The rotational partition function for $^1H^{35}Cl$, $\sigma = 1$ and $B = 318$ GHz. Then at 298 K

$$q^R = \frac{kT}{hB} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(6.626 \times 10^{-34} \text{ J s}) \times (3.18 \times 10^{11} \text{ s}^{-1})} = 19.5$$

That is, close to 20 rotational states are occupied at this temperature. Because $kT/hB \gg 1$ (that is, $T \gg hB/k$), the use of the approximate formula is justified.

Self-test 12B.3

Evaluate the rotational contribution to the partition function for $^1H^{35}Cl$ at $0^\circ C$.

Answer: 17/9

Justification 12B.3

The rotational partition function

The starting point for the calculation is

$$q^R = \sum_J (2J+1) e^{-\frac{hB}{kT}(J+1/2)^2} \quad (6)$$

To evaluate the sum, it is necessary to apply various approximations based on the temperature being so high that many states are occupied.

Step 1: Write an expression for the high-temperature limit. When kT is much larger than the separation between neighbouring states (specifically, $kT \gg hB$), many rotational states are occupied, the energy levels are so close that they form a continuum, and the sum can be approximated by an integral:

$$q^R \approx \int_0^\infty (2J+1) e^{-\frac{hB}{kT}(J+1/2)^2} dJ$$

Step 2: Evaluate the integral

Although the integral in step 1 looks complicated, it can be evaluated without much effort by noticing that because

$$\frac{d e^{a f(x)}}{d x} = a e^{a f(x)} \left(\frac{d f}{d x} \right) \\ \frac{d}{d J} e^{-\frac{hB}{kT}(J+1/2)^2} = -\frac{hB}{kT} (2J+1) e^{-\frac{hB}{kT}(J+1/2)^2}$$

and therefore

$$(2J+1) e^{-\frac{hB}{kT}(J+1/2)^2} = -\frac{kT}{hB} \left(\frac{d}{d J} e^{-\frac{hB}{kT}(J+1/2)^2} \right)$$

it can also be written as

$$q^R \approx -\frac{kT}{hB} \int_0^\infty \left(\frac{d}{d J} e^{-\frac{hB}{kT}(J+1/2)^2} \right) dJ$$

Then, because the integral of a derivative of a function (in blue) is the function itself,

$$q^R = -\frac{kT}{hB} e^{-\frac{hB}{kT}(J+1/2)^2} \Big|_0^\infty = \frac{kT}{hB}$$

Equation 5 is obtained by taking account of the reduction of the number of available states through division by the symmetry number σ .

A final point is to note that eqn 5 is valid provided that $T \gg hB/k$. The quantity hB/k has the dimensions of temperature and is known as the characteristic rotational temperature, T^R . For H_2 , $T^R = 88$ K; for Br_2 , $T^R = 10$ K. It is often the case that the temperature at which an approximation is valid can be expressed in terms of a characteristic temperature (in this case, $T \gg T^R$); the next section provides another example.

12B.5 The vibrational partition function

As shown in the following *Justification*, the vibrational partition function, q^V , is

$$q^V = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \quad (6)$$

This is the partition function for a harmonic oscillator or any vibrating diatomic molecule. Figure 4 shows how q^V varies with temperature. Note that:

- $q^V = 1$ at $T = 0$, when only the lowest state is occupied.
- As T becomes high, so q^V becomes infinite because all the states of the infinite ladder are thermally accessible.
- At room temperature, and for typical molecular vibrational frequencies, q^V is very close to 1 because only the vibrational ground state is occupied (see Exercise 12B.5).

The following *Justification* also shows that, when the temperature is so high that $T \gg T^V$, with the characteristic vibrational temperature, $T^V = h\nu/k$, eqn 5 simplifies to

$$q^V \approx \frac{kT}{h\nu} \quad (7)$$

It is only rarely possible to use this approximation because molecular vibrations have high frequencies. For H_2 , $T^V = 6332$ K; for Br_2 , $T^V = 465$ K.

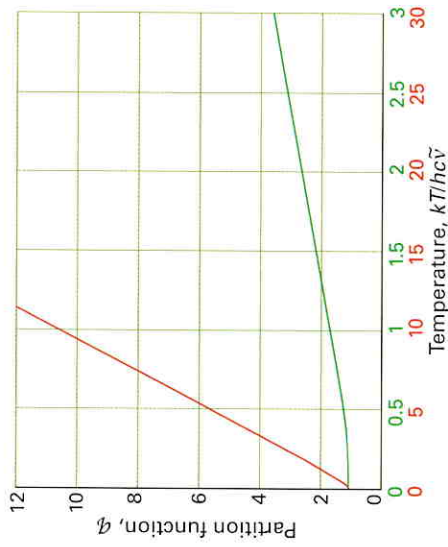


Fig. 4 The partition function for a harmonic oscillator. For an oscillator with $\tilde{\nu} = 1000 \text{ cm}^{-1}$, at $20^\circ C$, $kT/hc\tilde{\nu} = 0.204$, corresponding to $q = 1.01$.

Brief illustration 12B.3 The vibrational partition function

To calculate the partition function of I_2 molecules, note their vibrational frequency is $6.434 \times 10^{12} \text{ s}^{-1}$. Then at 298 K,

$$\frac{h\nu}{kT} = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (6.434 \times 10^{12} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} = 1.035 \dots$$

It follows from eqn 6 that

$$q^V = \frac{1}{1 - e^{-1.035 \dots}} = 1.55$$

from which can be inferred that only the ground and first excited states are significantly populated. Because $T^V = h\nu/k = 309$ K, and 298 K is not high compared to that value, it is inappropriate to use the high-temperature approximation for this molecule.

Self-test 12B.4

Evaluate the populations N_i of the first three vibrational states in a sample containing N molecules.

Answer: $N_0 = 0.645N$, $N_1 = 0.229N$, $N_2 = 0.081N$

Justification 12B.4

The vibrational partition function

The energy levels of a harmonic oscillator form a simple ladder-like array (Fig. 5). When the energy of the lowest state is set equal to zero, the energies of the states are

$$\epsilon_0 = 0, \quad \epsilon_1 = h\nu, \quad \epsilon_2 = 2h\nu, \quad \epsilon_3 = 3h\nu, \quad \text{etc.}$$

Now follow these steps to derive eqns 6 and 7.

Actual Conventional energy energy

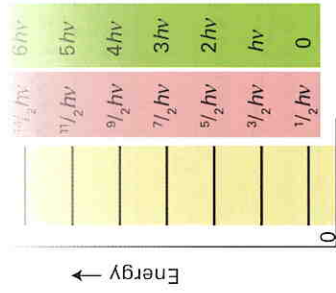


Fig. 5 The energy levels of a harmonic oscillator. When calculating a partition function, set the zero of energy at the lowest level, as shown on the right.

Step 1: Write a general expression for the partition function

From eqn 2, the vibrational partition function is

$$q^V = 1 + e^{-hv/kT} + e^{-2hv/kT} + e^{-3hv/kT} + \dots$$

$$e^x = (e^x)^n$$

$$= 1 + e^{-hv/kT} + (e^{-hv/kT})^2 + (e^{-hv/kT})^3 + \dots$$

According to *The chemist's toolkit 6* in Topic 1C, the sum of the infinite series $1 + x + x^2 + \dots$ is $1/(1 - x)$, so with $x = e^{-hv/kT}$,

$$q^V = \frac{1}{1 - e^{-hv/kT}}$$

which is eqn 6.

Step 2: Consider the high-temperature limit

When the temperature is so high that $hv/kT \ll 1$ (corresponding to $T \gg T^*$), eqn 6 can be simplified considerably by writing $e^{-x} \approx 1 - x$ (*The chemist's toolkit 6* in Topic 1C):

$$q^V \approx \frac{1}{1 - (1 - hv/kT)} = \frac{1}{hv/kT} = \frac{kT}{hv}$$

which is eqn 7.

12B.6 The electronic partition function

No closed form can be given for the electronic partition function, q^E , the partition function for the distribution of electrons over their available states (and

including any contribution from spin). Electronic energy separations from the ground state are usually very large, so for most cases $q^E = 1$ because only the ground state is occupied. An important exception arises in the case of atoms and molecules having electronically degenerate ground states, in which case $q^E = g^E$, where g^E is the degeneracy of the electronic ground state. In some cases, such as the one treated in the following *Brief illustration*, the degeneracy arises from the occurrence of unpaired electrons, and so the electronic partition function is in effect the electron-spin partition function.

Brief illustration 12B.4 The electronic partition function
The electronic configuration of the ground state of Na is $[\text{Ne}]3s^1$ (Topic 8B). Because there are two possible orientations of the electron spin in the $3s$ orbital, and both are equally likely, the ground electronic state of Na is doubly degenerate. It follows that the electronic partition function is $q^E = g^E = 2$. A more sophisticated approach is to recognize that the ground state is $^2S_{1/2}$ (Topic 8D), and that the $j = \frac{1}{2}$ level consists of the two degenerate states with $m_j = \pm \frac{1}{2}$.

Self-test 12B.5

A certain atom has a fourfold degenerate ground state and a sixfold degenerate excited state at 400 cm^{-1} above the ground state. Calculate its electronic partition function at 25°C .

Answer: 4.87

12B.7 The significance of the molecular partition function

In summary, the partition function is more than simply a symbol to denote the sum over states that occurs in the denominator of the Boltzmann distribution. First, it indicates the number of thermally accessible states at any temperature and for any mode of motion. Second, its value is based on dynamical information about the molecule. Because thermodynamic properties are averages that take into account the populations of the molecular states, the partition function also acts as a bridge between these properties and the underlying dynamical properties of the molecules. The stage is set, in fact, for the estimation of bulk thermodynamic properties (including equilibrium constants) from spectroscopic information. This task is undertaken in Topic 12C.

Checklist of key concepts

- 1 If the energy of a molecule is given by the sum of contributions, then the **molecular partition function** is a product of contributions from the different modes.
- 2 The **partition function** is an indication of the number of thermally accessible states at the temperature of interest.
- 3 The partition function increases with temperature.
- 4 Molecules with numerous, closely spaced energy levels can be expected to have very large partition functions. Molecules with widely spaced energy levels can be expected to have small partition functions.
- 5 The **symmetry number** takes into account the number of indistinguishable orientations of a symmetrical molecule.

TOPIC 12C

The origin of thermodynamic properties

► Why do you need to know this material?

This discussion provides a molecular interpretation of thermodynamic properties and acts as a bridge between spectroscopy and thermodynamics.

► What is the key idea?

The molecular partition function contains all the information needed to calculate the thermodynamic properties of a system of independent particles.

► What do you need to know already?

You need to be aware of the Boltzmann distribution (Topic 12A) and know how to calculate a molecular partition function from structural data (Topic 12B). You should also be familiar with the concepts of internal energy (Topic 2C) and entropy (Topics 3A and 3C). The final section makes use of the connection between the equilibrium constant and the standard Gibbs energy of reaction (Topic 5B).

The partition function, one of the central concepts of statistical thermodynamics, is introduced in Topic 12B:

$$q = \sum_i e^{-\epsilon_i/kT}$$

where the sum is over the states of the molecule and the ϵ_i are their energies. It is used to calculate and interpret thermodynamic properties of systems as small as atoms and as large as biopolymers. First-Law quantities (such as heat capacity and enthalpy)

can be calculated once the internal energy has been calculated from the partition function. Second-Law quantities (such as the Gibbs energy and equilibrium constants) can be calculated once the partition function has been used to calculate the entropy. Throughout this Topic only non-interacting particles (such as the atoms or molecules of a perfect gas) are considered. Interacting particles can be treated, but the techniques are much more complicated.

12C.1 The internal energy

The total energy, ϵ , of a system of independent molecules is calculated by noting the energy of each state (ϵ_i), multiplying that energy by the number of molecules in the state (N_i), and then adding together all these products:

$$\epsilon = N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \dots = \sum_i N_i\epsilon_i$$

In statistical thermodynamics, the populations are taken to be those of the overwhelmingly most probable distribution at the temperature of interest, which is given by the Boltzmann distribution (Topic 12A). It follows that the N_i in this expression are given by:

$$\epsilon = \sum_i \frac{\text{Population of state } i}{q} \times \text{Energy of state } i = \sum_i \frac{N e^{-\epsilon_i/kT}}{q} \times \epsilon_i = \frac{N}{q} \sum_i \epsilon_i e^{-\epsilon_i/kT} \quad (1)$$

where q is the partition function of the molecule. If the individual energies of the states are known (from spectroscopy, for instance), then the next step is to substitute their values into this expression. However, there is a much simpler method—or at least a much more succinct formula—available when an expression for the partition function, such as one of those given in Topic 12B, is used. As shown in the following

Justification, the energy depends upon how the partition function q varies with temperature as

$$\epsilon = \frac{NkT^2}{q} \frac{dq}{dT} \quad (2)$$

It follows that the energy can be calculated by evaluating the first derivative dq/dT of the expression for q as a function of T or, in other words, from the slope of a graph of q plotted against T .

Justification 12C.1

The internal energy from the partition function

The starting point is the realization that the sum on the right of eqn 1 resembles the definition of the partition function, but differs from it by having the ϵ_i factor multiplying each term. The strategy involves finding a way to remove the ϵ_i from inside the sum and to express the result in terms of the partition function itself.

Step 1: Differentiate the term $e^{-\epsilon_i/kT}$

Use the rules of differentiation set out in *The chemist's toolkit* 11 in Topic 4A to write

$$\frac{d}{dT} e^{-\epsilon_i/kT} = e^{-\epsilon_i/kT} \times \frac{d}{dT} \left(-\frac{\epsilon_i}{kT} \right) = \frac{\epsilon_i}{kT^2} e^{-\epsilon_i/kT}$$

Step 2: Substitute the result into the expression for the energy

It follows from step 1 that

$$\epsilon_i e^{-\epsilon_i/kT} = kT^2 \frac{d}{dT} e^{-\epsilon_i/kT}$$

Substitution of this expression into eqn 1 gives

$$\epsilon = \frac{N}{q} \sum_i kT^2 \frac{d}{dT} e^{-\epsilon_i/kT} = \frac{NkT^2}{q} \frac{d}{dT} \sum_i e^{-\epsilon_i/kT} = \frac{NkT^2}{q} \frac{dq}{dT}$$

because (in blue) kT^2 is a constant and the sum of derivatives is the derivative of the sum.

The remarkable feature of eqn 2 is that it is an expression for the total energy in terms of the partition function alone. The partition function is starting to fulfil its promise to deliver all thermodynamic information about the system.

There is one more detail to take into account before using eqn 2. As explained in Topic 12B, the zero of energy is set at the energy of the lowest state of the molecule. However, the internal energy of the system might be nonzero on account of zero-point energy,

and the ϵ in eqn 2 is the energy *above* the zero-point energy. That is, the internal energy at a temperature T is

$$U = U(0) + \epsilon \quad (3)$$

with ϵ given by eqn 2.

Example 12C.1

Calculating the internal energy

Calculate the molar internal energy of a monatomic gas.

Collect your thoughts The only mode of motion of a monatomic gas is translation (electronic excitation being ignored). Therefore, calculate the total translational energy of N molecules by substituting the translational partition function $q_t = (2\pi mkT)^{3/2} V/h^3$ into eqn 2. Then evaluate the internal energy from eqn 3. Finally, write $N = nN_A$, where N_A is Avogadro's constant, and divide through by n to obtain the molar internal energy.

The solution The partition function has the form $q = aT^{3/2}$, where $a = (2\pi mk)^{3/2} V/h^3$. The first derivative of q with respect to T is

$$\frac{dq}{dT} = \frac{d}{dT} (aT^{3/2}) = \frac{3}{2} aT^{1/2}$$

$$\frac{dx}{dx} = nx^{n-1}$$

Substitute this result into eqn 2 to obtain

$$\epsilon = \frac{NkT^2}{q} \times \frac{dq}{dT} = \frac{NkT^2}{aT^{3/2}} \times \frac{3}{2} aT^{1/2} = \frac{3}{2} NkT$$

The molar internal energy is obtained by using eqn 3 and writing $N = nN_A$, $N_A k = R$, and $U_m = U/n$,

$$U_m = U_m(0) + \frac{3}{2} N_A kT = U_m(0) + \frac{3}{2} RT$$

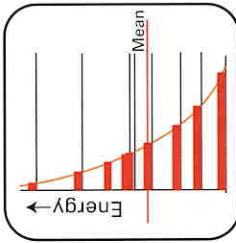
The term $U_m(0)$ contains all the contributions from the binding energy of the electrons and of the nucleons in the nucleus. The term $\frac{3}{2} RT$ is the contribution to the internal energy from the translational motion of the atoms in their container.

Comment The final expression is the same as that obtained from the equipartition theorem (Topic 2C).

Self-test 12C.1

Calculate the molar internal energy of a gas of diatomic molecules, taking into account contributions from translation and rotation (in the high-temperature limit).

Answer: $U_m = U_m(0) + \frac{5}{2} RT$, with $\frac{3}{2} RT$ the translational contribution and RT the rotational contribution.



12C.2 The heat capacity

Once the internal energy of a sample of molecules has been calculated as a function of temperature, it is a simple matter to calculate the heat capacity. The heat capacity at constant volume, C_V , is defined as the slope of the plot of internal energy against temperature (Topic 2C):

$$C_V = \frac{dU}{dT} \quad \text{at constant volume; } C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Therefore, the task is to evaluate the slope of the expression for U obtained from the partition function.

Brief illustration 12C.1 The heat capacity

The constant-volume molar heat capacity of a monatomic gas is obtained by substituting the molar internal energy, $U_m = U_m(0) + \frac{3}{2}RT$ into $C_V = dU/dT$:

$$C_V = \frac{d}{dT}(U_m(0) + \frac{3}{2}RT) = \frac{3}{2}R$$

To calculate $C_{p,m}$, use eqn 7 of Topic 2D ($C_{p,m} - C_{v,m} = R$) and obtain $C_{p,m} = \frac{5}{2}R$.

Self-test 12C.2

Calculate the contribution to the molar constant-volume heat capacity of a two-state system, like the chair-boat interconversion of cyclohexane (Example 12B.1, using the notation there) and show how the heat capacity varies with temperature.

Answer: $C_{v,m} = R(dRT)^2 e^{-dRT}/(1 + e^{-dRT})^2$, Fig. 1

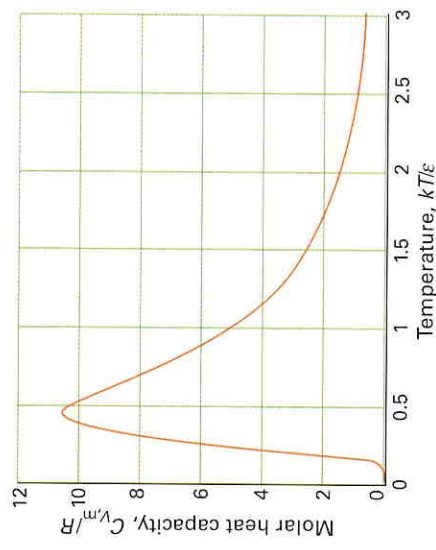


Fig. 1 The variation of the heat capacity of a two-level system with states at energies 0 and ϵ . Note how the heat capacity is zero at $T = 0$, passes through a maximum at $T = 0.417\epsilon/k$, and approaches 0 at high temperatures.

It is now possible to understand the molecular reason why different substances have different molar heat capacities. When the available energy levels are close together, a given quantity of energy can be accommodated with little adjustment of the populations and hence with little modification of the temperature that occurs in the Boltzmann distribution. The relative insensitivity of temperature to the arrival of energy corresponds to a high heat capacity (Fig. 2). When the energy levels are widely separated, the arriving energy must be accommodated by making use of the high energy levels with a consequent greater 'reach' of the Boltzmann distribution and hence a greater modification of the temperature. That is, widely spaced energy levels correlate with a low heat capacity.

The translational energy levels of molecules in a gas are very close together, and all monatomic gases have similar molar heat capacities. The separation of the vibrational energy levels of atoms bound together in solids depends on the stiffness of the bonds between them and on the masses of the atoms. As seen in Topic 11C, the stronger the bond and the lighter the atoms in a bond, the greater is the separation between vibrational energy levels. As a result, solids show a wide range of molar heat capacities. Very large molecules, like polymers, have large numbers of atoms and can vibrate in many different ways. Many of these ways correspond to collective motion of many atoms, so the vibrational energies are spaced closely. Hence, heat capacities of polymers may be large.

Water, as so often, is anomalous. It is a small, rigid molecule but its liquid phase has a high heat capacity. The anomaly can be traced to hydrogen bonds, which link many molecules together into clusters that vibrate in numerous ways. Consequently, the vibrational energies are close together, and the heat capacity of liquid water is larger than expected for a substance consisting of small molecules interacting weakly.

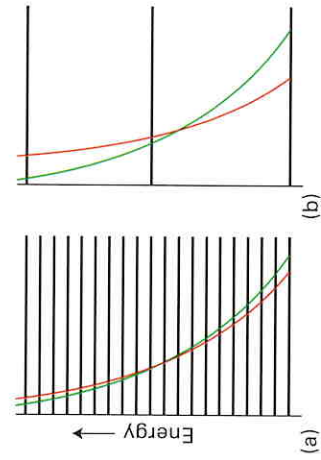


Fig. 2 The heat capacity depends on the availability of levels. (a) When the levels are close together, a high heat capacity. (b) When the levels are widely separated, the system has a low heat capacity. In each case the green line is the distribution at low temperature and the red line that at higher temperature.

12C.3 The entropy

Boltzmann showed that there is a close relation between the entropy and the partition function: both are measures of the number of arrangements available to the molecules. His starting point was to propose that the entropy is given by

$$S = k \ln W \quad (4a)$$

Boltzmann equation for the entropy

where W is the weight of the configuration, the quantity introduced in Topic 12A (the number of ways the molecules can be distributed over the available states for a given total energy). Boltzmann identified W with the weight of the most probable distribution (as given by the Boltzmann distribution) and went on to show that for *distinguishable* molecules (those locked in place in a solid)¹

$$S = \frac{U - U(0)}{T} + Nk \ln q \quad (4b)$$

The entropy in terms of the partition function (distinguishable particles)

The analogous term for *indistinguishable* molecules (identical molecules free to move, as in a gas) is

$$S = \frac{U - U(0)}{T} + Nk \ln q - Nk(\ln N - 1) \quad (4c)$$

The entropy in terms of the partition function (indistinguishable particles)

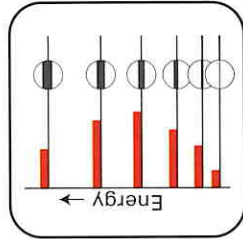
Because the first term on the right can be calculated from q , it is possible to calculate the entropy of any system of non-interacting molecules once its partition function is known.

Example 12C.2

Calculating the entropy

Calculate the contribution that rotational motion makes to the molar entropy of a gas of HCl molecules at 25 °C.

Collect your thoughts According to eqn 4c, you need both the (molar) internal energy and the partition function. For the molar entropy, take $N = nN_A$ and divide through by n ; then notice that $N_A k = R$. So begin by evaluating the rotational contribution to the molar internal energy. This quantity was calculated in Self-test 12C.1, so use that result. For this linear rotor, use the rotational partition function $q^r = kT/\sigma hB$, with



¹ For a derivation, see our *Physical chemistry: thermodynamics, structure, and change* (2014).

$\sigma = 1$ (eqn 5 of Topic 12B) and $B = 317.79$ GHz (Topic 11B). Finally, use these expressions in eqn 4b.

The solution The rotational contribution to the molar internal energy is $R\bar{T}$. So substitute $U_m - U_m(0) = R\bar{T}$ and $q = kT/hB$ into eqn 4a, and obtain (for $T > 0$)

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln \frac{kT}{hB} = R \left(1 + \ln \frac{kT}{hB} \right)$$

Substitution of the numerical values gives

$$S_m = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left\{ 1 + \ln \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(6.626 \times 10^{-34} \text{ J s}) \times (3.1779 \times 10^{11} \text{ s}^{-1})} \right\} = 33.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

This result could be expressed as $S_m = 3.98R$.

Comment Notice that the entropy increases with temperature (Fig. 3). At a given temperature, the entropy is larger the smaller the value of B . That is, bulky molecules (which have large moments of inertia and therefore small rotational constants) have a higher rotational entropy than small molecules.

Self-test 12C.3

The rotational partition function of an ethene molecule is 661 at 25 °C. What is the rotational contribution to its molar entropy?

Answer: 7.49R

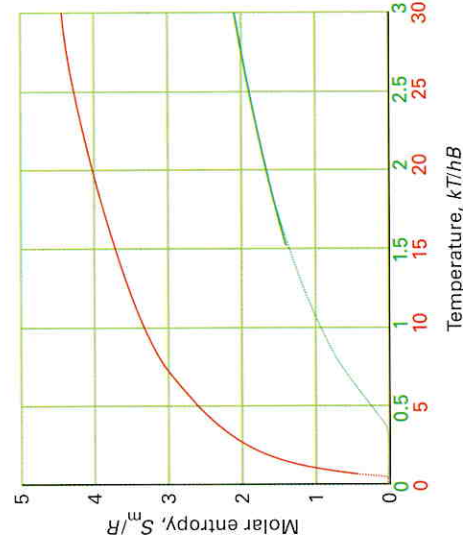


Fig. 3 The variation of the rotational contribution to the molar entropy with temperature. Note that eqn 4 is valid only for high temperatures, so the curves were terminated before they become invalid. The dotted lines show the correct behaviour.

12C.4 The Gibbs energy

The Gibbs energy, G , is central to the discussion of chemical thermodynamics, so it is important to see how to calculate G from the partition function and to interpret its value. As shown in the following *Justification*, for a gas of N independent molecules

$$G - G_m(0) = -NkT \ln \frac{q}{N} \quad (5)$$

The Gibbs energy in terms of the partition function [perfect gas]

Justification 12C.2

The Gibbs energy from the partition function

To set up the calculation, go back to first principles and express G in terms of the quantities you know how to calculate, namely U and S . The Gibbs energy is defined as $G = H - TS$, (Topic 3D) and the enthalpy, H , is defined as $H = U + pV$ (Topic 2D). Therefore

$$G = U - TS + pV$$

The stage is now set for introducing the partition function into the expression for G .

Step 1: Use the perfect gas law to express pV in terms of the temperature

For a perfect gas (Topic 1A) replace pV by $nRT = (N/N_A)N_A kT = NkT$ (because $N = nN_A$, and $R = N_A k$), and note that at $T = 0$, $G(0) = U(0)$ (because the terms TS and NkT vanish at $T = 0$). Therefore,

$$G - G(0) = U - U(0) - TS + NkT$$

Step 2: Substitute the expression for the entropy

Substitute eqn 4c for S , and obtain

$$G - G(0) = -NkT \ln \frac{q}{N} + kT(N \ln N - N) + NkT = -NkT(\ln \frac{q}{N} - \ln N)$$

Equation 5 now follows because $\ln \frac{q}{N} - \ln N = \ln(\frac{q}{N})$.

Equation 5 can be converted into an expression for the molar Gibbs energy by first writing $N = nN_A$, and then dividing both sides by n :

$$G_m - G_m(0) = -N_A kT \ln \frac{q}{nN_A} \quad (6)$$

The molar Gibbs energy [perfect gas]

At this stage it is convenient to introduce the molar partition function, $q_m = q/n$ (with units mol^{-1}), for then

$$G_m - G_m(0) = -RT \ln \frac{q_m}{N_A} \quad (7)$$

The molar Gibbs energy [perfect gas]

Brief illustration 12C.2 The molar Gibbs energy

The molar translational partition function of H_2 in a 100 cm^3 vessel at 25°C is $q_{\text{m,trans}} = 2.77 \times 10^{26} \text{ mol}^{-1}$. The contribution to the molar Gibbs energy due to translational motion is

$$G_m - G_m(0) = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{2.77 \times 10^{26} \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) = -15.2 \text{ kJ mol}^{-1}$$

Answer: $-15.5 \text{ kJ mol}^{-1}$

Self-test 12C.4

What is the total contribution to the molar Gibbs energy of the translational and rotational motion of the molecules? The rotational partition function of H_2 at 25°C is 1.14. Recall that a molecular partition function is equal to the product of partition functions associated with the contributing modes of motion.

As shown in the following *Justification*, for the special case of a perfect monatomic gas, it is possible to write eqn 6 in terms of the pressure as

$$G_m - G_m(0) = RT \ln \frac{a}{b} \quad (8)$$

The molar Gibbs energy [perfect monatomic gas]

Justification 12C.3

The Gibbs energy of a perfect monatomic gas

Use the translational partition function of the monatomic gas (the only mode of motion for gaseous atoms) in eqn 7, and then ensure that any variables (p , V) are expressed in terms of the temperature.

Step 1: Write the molecular partition function

The molar translational partition function for particles of mass m at a temperature T is

$$q_{\text{m,trans}} = \frac{q}{n} = \frac{(2\pi mkT)^{3/2} V/h^3}{n} = \frac{(2\pi mkT)^{3/2}}{h^3} \times \frac{V}{n}$$

Step 2: Convert V to p

According to the perfect gas law, $V/n = RT/p$, so

$$q_{\text{m,trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} \times \frac{RT}{p}$$

Then, from eqn 7,

$$G_m - G_m(0) = -RT \ln \frac{(2\pi mkT)^{3/2} RT}{ph^3 N_A}$$

12C.5 The equilibrium constant

It is now possible to write a statistical thermodynamic expression for the equilibrium constant. As shown in the following *Justification*, for the equilibrium $A(g) + B(g) \rightleftharpoons C(g)$,

$$K = \frac{q_{\text{m,C}}(C)N_A}{q_{\text{m,A}}(A)q_{\text{m,B}}(B)} e^{-\Delta E/RT} \quad (11)$$

The equilibrium constant in terms of the partition function

where ΔE is the difference in molar energy between the ground state of the product and that of the reactants. This expression has the same form as the equilibrium constant written in terms of the activities (Topic 5B), but with q_{m}°/N_A replacing each activity (and an additional exponential factor):

$$K = \frac{\overbrace{p_{\text{C}}/p^{\circ}}^{\text{Replace with } q_{\text{m,C}}^{\circ}(C)/N_A}} \overbrace{(p_{\text{A}}/p^{\circ})(p_{\text{B}}/p^{\circ})}^{\text{Replace with } q_{\text{m,A}}^{\circ}(A)q_{\text{m,B}}^{\circ}(B)/N_A}} e^{-\Delta E/RT}$$

Additional exponential factor

Equation 11 is obtained after cancelling the N_A .

Example 12C.3

Calculating an equilibrium constant

Calculate the equilibrium constant for the gas-phase ionization $\text{Cs}(g) \rightleftharpoons \text{Cs}^+(g) + e^-(g)$ at 500 K .

Collect your thoughts This is a

reaction of the form $A(g) \rightleftharpoons B(g) + C(g)$ rather than $A(g) + B(g) \rightleftharpoons C(g)$, so you need to modify eqn 11 slightly, but the form to use should be clear. Analyse each species individually, and write its partition function as the product

of partition functions for each mode of motion. Then evaluate these partition functions at the standard pressure (1 bar), and combine them as specified in eqn 11. For the difference in energy ΔE , use the ionization energy of $\text{Cs}(g)$.

The solution The equilibrium constant is

$$K = \frac{q_{\text{m}}^{\circ}(\text{Cs}^+, g)q_{\text{m}}^{\circ}(e^-, g)}{q_{\text{m}}^{\circ}(\text{Cs}, g)N_A} e^{-\Delta E/RT}$$

Step 3: Simplify the expression

Replace R by kN_A . The N_A then cancel and

$$G_m - G_m(0) = -RT \ln \frac{(2\pi m)^{3/2} (kT)^{3/2}}{ph^3} = -RT \ln \frac{1}{ap}$$

Recognize the a in eqn 8

$$-\ln x = \ln(1/x)$$

$$= RT \ln ap$$

as in eqn 8.

Equation 7 shows that G decreases (becomes more negative, logarithmically) with the number of states that are thermally accessible to a molecule. According to classical thermodynamics, the direction of spontaneous change (at constant temperature and pressure) is towards more negative Gibbs energy. That is, eqn 7 implies that this direction corresponds to a change towards a greater number of accessible states for each molecule. Spontaneous change is essentially a collapse into greater freedom for molecules to occupy the available states of the system.

The only further piece of information required for progress is the expression for the *standard* molar Gibbs energy, for that plays such an important role in the discussion of equilibrium properties. All that is needed is to calculate the partition function at p° . In general,

$$G_m^{\circ} - G_m^{\circ}(0) = -RT \ln \frac{q_{\text{m}}^{\circ}}{N_A} \quad (9)$$

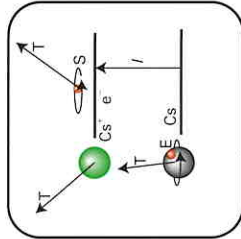
The standard molar Gibbs energy in terms of the standard molar partition function [perfect gas]

where the standard state sign on q_{m} signifies its value at p° . To calculate that value, use $V_m^{\circ} = RT/p^{\circ}$ wherever it appears in q_{m} . Thus, for a monatomic gas, eqn 8 becomes

$$G_m^{\circ} - G_m^{\circ}(0) = RT \ln \frac{ap^{\circ}}{b^3} \quad (10)$$

$$a = \frac{b^3}{(2\pi m)^{3/2} (kT)^{3/2}}$$

The standard molar Gibbs energy [monatomic perfect gas]



Note how, in this instance, Avogadro's constant appears in the denominator: its units, mol^{-1} , ensure that K is dimensionless. The electron has translational motion, so you need its translational partition function. The spin states contribute a factor of 2 to the electronic component of the molecular partition function. Therefore

$$q_{\text{m}}^{\ominus}(\text{e}^{-}) = 2 \times \frac{q_{\text{e}}^{\ominus}}{nh^3} \times \frac{2(2\pi m_{\text{e}} kT)^{3/2} RT}{p^{\ominus} h^3} \quad \left\{ \begin{array}{l} q_{\text{e}}^{\ominus} = nRT/p^{\ominus} \\ V^{\ominus} = nRT/p^{\ominus} \end{array} \right.$$

The Cs^+ ion, a closed shell species, has only translational freedom:

$$q_{\text{m}}^{\ominus}(\text{Cs}^+, \text{g}) = \frac{(2\pi m_{\text{Cs}} kT)^{3/2} RT}{p^{\ominus} h^3}$$

The partition function of the Cs atom has a translational and a spin contribution:

$$q_{\text{m}}^{\ominus}(\text{Cs}, \text{g}) = 2 \times \frac{q_{\text{e}}^{\ominus}}{(2\pi m_{\text{Cs}} kT)^{3/2} RT} \times \frac{q_{\text{Cs}}^{\ominus}}{p^{\ominus} h^3}$$

(No distinction is being made between the masses of the Cs atom and the Cs^+ ion.) Then, with $\Delta E = I$, the ionization energy of the atom,

$$K = \frac{q_{\text{Cs}}^{\ominus} q_{\text{e}}^{\ominus}}{q_{\text{Cs}}^{\ominus} q_{\text{Cs}}^{\ominus}} = \frac{\left\{ \frac{2(2\pi m_{\text{e}} kT)^{3/2} RT/p^{\ominus} h^3 \right\} \times \left\{ \frac{2(2\pi m_{\text{Cs}} kT)^{3/2} RT/p^{\ominus} h^3 \right\}}{\left\{ \frac{2(2\pi m_{\text{Cs}} kT)^{3/2} RT/p^{\ominus} h^3 \right\} \times N_{\text{A}}} \right\}}{p^{\ominus} h^3 N_{\text{A}}} \times e^{-I/RT}$$

(cancel blue term)

$$= \frac{(2\pi m_{\text{e}} kT)^{3/2} RT}{p^{\ominus} h^3 N_{\text{A}}} \times e^{-I/RT}$$

(R = $N_{\text{A}} k$)

$$= \frac{(2\pi m_{\text{e}} kT)^{3/2} kT}{p^{\ominus} h^3} \times e^{-I/RT}$$

That is,

$$K = \frac{(2\pi m_{\text{e}})^{3/2} (kT)^{5/2}}{p^{\ominus} h^3} \times e^{-I/RT}$$

Now substitute the data. Only the ionization energy is specific to the element, so it is convenient to separate the two factors (in case you wish to evaluate K for other elements):

$$\frac{(2\pi \times 9.109 \times 10^{-31} \text{ kg})^{3/2} \times (1.381 \times 10^{-23} \text{ J K}^{-1} \times 1000 \text{ K})^{5/2}}{(10^5 \text{ Pa}) \times (6.626 \times 10^{-34} \text{ J s})^3} = 10.54 \dots$$

$$e^{-I/RT} = e^{-13.76 \times 10^5 \text{ J mol}^{-1} / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times 1000 \text{ K}} = 2.29 \dots \times 10^{-20}$$

Therefore,

$$K = (10.54 \dots) \times (2.29 \dots \times 10^{-20}) = 2.42 \times 10^{-19}$$

A note on good practice Verify that the units do in fact all cancel (use $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ and $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$). The K calculated by the procedure described here is the thermodynamic equilibrium constant, which for gases is expressed in terms of the partial pressures of the reactants and products (relative to the standard pressure).

Self-test 12C.5

Calculate the equilibrium constant for the dissociation $\text{Na}_2(\text{g}) \rightleftharpoons 2 \text{Na}(\text{g})$ at 1000 K. You will need the following information about $\text{Na}_2(\text{g})$: $B = 46.38 \text{ MHz}$, $\tilde{\nu} = 159.2 \text{ cm}^{-1}$, the dissociation energy is 70.4 kJ mol^{-1} , and $q_{\text{e}}^{\ominus} = 2$.

Answer: 2.42

Justification 12C.4

The equilibrium constant for a reaction is related to the standard reaction Gibbs energy by eqn 6 in Topic 5A ($\Delta_r G^{\ominus} = -RT \ln K$). For the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$,

$$\Delta_r G^{\ominus} = G_{\text{m}}^{\ominus}(\text{C}) - \{G_{\text{m}}^{\ominus}(\text{A}) + G_{\text{m}}^{\ominus}(\text{B})\}$$

Therefore, to find an expression for K , it is necessary to establish and combine the three expressions for G_{m}^{\ominus} .

Step 1: Write an initial expression for the standard reaction Gibbs energy

From eqn 9

$$\Delta_r G^{\ominus} = \left\{ G_{\text{m}}^{\ominus}(\text{C}, 0) - RT \ln \frac{q_{\text{m}}^{\ominus}(\text{C})}{N_{\text{A}}} \right\} - \left\{ G_{\text{m}}^{\ominus}(\text{A}, 0) - RT \ln \frac{q_{\text{m}}^{\ominus}(\text{A})}{N_{\text{A}}} + G_{\text{m}}^{\ominus}(\text{B}, 0) - RT \ln \frac{q_{\text{m}}^{\ominus}(\text{B})}{N_{\text{A}}} \right\}$$

Step 2: Introduce the term ΔE

In the preceding expression, the first term in each of the braces (in blue) is just the difference in ground-state energies because $G = U$ at $T = 0$, so

$$G_{\text{m}}^{\ominus}(\text{C}, 0) - \{G_{\text{m}}^{\ominus}(\text{A}, 0) + G_{\text{m}}^{\ominus}(\text{B}, 0)\} = U_{\text{m}}^{\ominus}(\text{C}, 0) - \{U_{\text{m}}^{\ominus}(\text{A}, 0) + U_{\text{m}}^{\ominus}(\text{B}, 0)\} = \Delta E$$

Step 3: Combine the terms containing logarithms

The three logarithms are now combined to obtain

$$\ln \frac{q_{\text{m}}^{\ominus}(\text{C})}{N_{\text{A}}} - \left\{ \ln \frac{q_{\text{m}}^{\ominus}(\text{A})}{N_{\text{A}}} + \ln \frac{q_{\text{m}}^{\ominus}(\text{B})}{N_{\text{A}}} \right\} = \ln \frac{q_{\text{m}}^{\ominus}(\text{C}) N_{\text{A}}}{q_{\text{m}}^{\ominus}(\text{A}) q_{\text{m}}^{\ominus}(\text{B}) N_{\text{A}}^2}$$

(ln x - ln yz = ln(x/yz))

Step 4: Simplify the resulting expression

At this stage the standard reaction Gibbs energy is

$$\Delta_r G^{\ominus} = \Delta E - RT \ln \frac{q_{\text{m}}^{\ominus}(\text{C}) N_{\text{A}}}{q_{\text{m}}^{\ominus}(\text{A}) q_{\text{m}}^{\ominus}(\text{B})}$$

The ΔE can be brought inside the logarithm by writing

$$\Delta_r G^{\ominus} = -RT \ln e^{-\Delta E/RT} - RT \ln \frac{q_{\text{m}}^{\ominus}(\text{C}) N_{\text{A}}}{q_{\text{m}}^{\ominus}(\text{A}) q_{\text{m}}^{\ominus}(\text{B})}$$

(because $\ln e^x = x$). Therefore

$$\Delta_r G^{\ominus} = -RT \ln \left\{ \frac{q_{\text{m}}^{\ominus}(\text{C}) N_{\text{A}}}{q_{\text{m}}^{\ominus}(\text{A}) q_{\text{m}}^{\ominus}(\text{B})} e^{-\Delta E/RT} \right\}$$

(ln x + ln y = ln(xy))

Step 5: Compare with the thermodynamic expression for $\Delta_r G^{\ominus}$

Comparison of the expression in the previous step with the thermodynamic expression, $\Delta_r G^{\ominus} = -RT \ln K$, shows that the term $\left\{ \frac{q_{\text{m}}^{\ominus}(\text{C}) N_{\text{A}}}{q_{\text{m}}^{\ominus}(\text{A}) q_{\text{m}}^{\ominus}(\text{B})} e^{-\Delta E/RT} \right\}$ is the expression for K (eqn 11).

Equation 11 is quite extraordinary, for it provides a key link between partition functions, which can be derived from spectroscopy, and the equilibrium constant, which is central to the analysis of chemical reactions at equilibrium. It also gives insight into the significance of an equilibrium constant. If for the moment the ex-

ponential factor is ignored, then the ratio of partition functions is essentially the ratio of the number of thermally accessible states in the products and reactants. If there are more product states than reactant states available at the temperature of the reaction, then the ratio is large and K can be expected to be large: products are favoured. If the opposite is true, then reactants are favoured. At this stage, all the equilibrium constants is expressing is the relative number of accessible states available to the products and the reactants. The exponential factor modifies this interpretation, for it acknowledges that the product states lie at a higher energy than the reactant states (if $\Delta E > 0$; as for an endothermic reaction). The product states are therefore not as thermally accessible as the reactant states, and K is reduced by this Boltzmann-like factor.

Equation 11 also reveals why the Gibbs energy determines the equilibrium constant. The partition function, essentially the number of thermally accessible states, is related to the entropies of the reactants and products, and the exponential factor relates to the energy (and by implication the enthalpy). This alliance of entropy and enthalpy is essentially the Gibbs energy.

The statistical interpretation of the Gibbs energy implies that the direction of spontaneous change corresponds to a change towards a greater number of accessible states for each molecule in a system.

Checklist of key concepts

- 1 The partition function contains all the thermodynamic information about a system, and can be used to calculate thermodynamic properties, such as the internal energy, entropy, and the Gibbs energy.
- 2 The heat capacity is low when energy levels are spaced widely.
- 3 The statistical interpretation of the Gibbs energy implies that the direction of spontaneous change corresponds to a change towards a greater number of accessible states for each molecule in a system.
- 4 The equilibrium constant is related to the distribution of molecules over the available states of a system composed of reactants and products.

FOCUS 12 Statistical thermodynamics

Exercises

Topic 12A The Boltzmann distribution

12A.1 Suppose polyethylene molecules in solution can exist either as a single version of a random coil (that is, ignore the fact that a random coil can be achieved in many different ways) or fully stretched out, with the latter conformation 2.4 kJ mol^{-1} higher in energy. What is the ratio of the two conformations at 20°C ?

Topic 12B The partition function

12B.1 (a) Write down the expression for the partition function of a molecule that has three energy levels at 0 , 2ϵ , and 5ϵ with degeneracies 1 , 6 , and 3 , respectively. What are the values of q at (b) $T=0$, (c) $T=\infty$?

12B.2 Evaluate the translational partition function of (a) N_2 , (b) gaseous CS_2 in a flask of volume 10.0 cm^3 . Why is one so much larger than the other?

12B.3 Evaluate the translational partition function at 298 K of (a) a methane molecule trapped in the pore of a zeolite catalyst; take the pore to be spherical with a radius that allows the molecule to move through 1 nm in any direction (that is, the effective diameter is 1 nm), (b) a methane molecule in a flask of volume 100 cm^3 .

Topic 12C The origin of thermodynamic properties

12C.1 Derive an expression for the mean energy of a collection of molecules that have three energy levels at 0 , ϵ , and 3ϵ with degeneracies 1 , 5 , and 3 , respectively.

12C.2 What is the change in (a) the molar internal energy, and (b) the molar enthalpy of a sample of argon gas when it is heated from 273 to 373 K ?

Discussion questions

12.1 Outline the principles behind the derivation of the Boltzmann distribution.

12.2 What is temperature?

12.3 Describe the physical significance of the molecular partition function.

12.6 Justify the identification of the statistical entropy with the thermodynamic entropy.

12.7 Why (in both thermodynamic and molecular terms) should substances with high heat capacities have high entropies?

Problems

12.1 The rotational energy of a linear or spherical molecule with quantum number J is $E_J = hB/J(J+1)$. For a linear molecule, each rotational level has a degeneracy of $(2J+1)$. For a spherical molecule, the degeneracy is $(2J+1)^2$. (a) Calculate the ratio of populations of CO_2 molecules with $J=4$ and $J=2$ at 25°C , given that the rotational constant of CO_2 is $B = 11.70 \text{ GHz}$. (b) Also calculate the ratio of populations of CH_4 molecules with $J=4$ and $J=2$ at 25°C , given that the rotational constant of CH_4 is 157 GHz .

12.2 (a) Evaluate the rotational partition function of HBr ($\tilde{\nu} = 8.465 \text{ cm}^{-1}$) at 298 K by direct summation of the energy levels and by using the high-temperature approximation, eqn 5 in Topic 12B. (b) Use mathematical software to repeat the calculations and hence determine the temperature at which the approximate formula is 10 per cent in error.

12.3 N_2O and CO_2 have similar rotational constants (12.6 and 11.7 GHz , respectively) but strikingly different rotational partition functions. Why?

12.4 The vibrational wavenumber for O_2 is 1580 cm^{-1} . Use the exact and the approximate expressions, eqn 6 and 7, respectively, of Topic 12B to calculate the vibrational partition function at 298 K . Above what temperature is the high-temperature approximation in error by 10 per cent or less?

12.5 A CO_2 molecule has four vibrational modes with wavenumbers 1388 cm^{-1} , 2349 cm^{-1} , and 667 cm^{-1} (the last being a doubly degenerate bending motion). Calculate the total vibrational partition function at (a) 500 K , (b) 1000 K .

12.6 Calculate the molecular partition function for ethyne, C_2H_2 (with the isotopic composition ^{12}C and ^1H) at 298 K confined to a volume of 1.00 m^3 . The rotational constant of ethyne is $\tilde{B} = 1.177 \text{ cm}^{-1}$. Ethyne has seven normal modes of vibration; the modes with vibrational wavenumbers of 3374 , 1974 , and 3287 are singly degenerate and those with vibrational wavenumbers of 612 and 729 cm^{-1} are doubly degenerate.

12.7 The ground configuration of oxygen gives rise to the three levels $^3\text{P}_2$, $^3\text{P}_1$, and $^3\text{P}_0$ at 0 , 158.5 , and 226.5 cm^{-1} , respectively. (a) Before doing any calculation, state the value of the partition function at $T=0$. (b) Write an expression for the partition function at temperature T . Remember that a level with quantum number J has $2J+1$ states. Confirm that its value at $T=0$ is what you anticipated. (c) Calculate the value of the partition function at 298 K . (d) Derive an expression

12.8 Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

for the electronic contribution to the molar heat capacity of an oxygen atom and plot it as a function of temperature. (e) Evaluate the expression at 25°C .

12.8 The ground configuration of carbon gives rise to a triplet with the three levels $^3\text{P}_0$, $^3\text{P}_1$, and $^3\text{P}_2$ at wavenumbers 0 , 16.4 , and 43.5 cm^{-1} , respectively. (a) Evaluate the electronic partition function of carbon at (i) 10 K , (ii) 298 K . (b) Hence derive an expression for the electronic contribution to the molar internal energy and plot it as a function of temperature. (c) Evaluate the expression at 25°C .

12.9 Estimate the vibrational contribution to the molar entropy of the most common isotopomer of bromine, $^{79}\text{Br}_2$, at 1000 K . The vibrational wavenumber for $^{79}\text{Br}_2$ is 325 cm^{-1} . You may assume that at this temperature, the equipartition theorem and the high temperature approximation for the vibrational partition function are both valid.

12.10 Calculate the molar entropy of nitrogen gas at 298 K . Write the overall partition function as the product of the translational and rotational partition functions; the first excited vibrational state is sufficiently high in energy that the contribution from vibration of the molecule may be ignored at this temperature. The rotational constant of N_2 is 2.00 cm^{-1} .

12.11 Without carrying out an explicit calculation, explain the relative values of the standard molar entropies (at 298 K) of the following substances: (a) Ne(g) ($146 \text{ J K}^{-1} \text{ mol}^{-1}$) compared with Xe(g) ($170 \text{ J K}^{-1} \text{ mol}^{-1}$), (b) $\text{H}_2\text{O(g)}$ ($189 \text{ J K}^{-1} \text{ mol}^{-1}$) compared with $\text{D}_2\text{O(g)}$ ($198 \text{ J K}^{-1} \text{ mol}^{-1}$), (c) C(diamond) ($2.4 \text{ J K}^{-1} \text{ mol}^{-1}$) compared with C(graphite) ($5.7 \text{ J K}^{-1} \text{ mol}^{-1}$).

12.12 Calculate the standard molar Gibbs energy of carbon dioxide gas at 298 K relative to its value at $T=0$. The rotational constant of carbon dioxide is 0.3903 cm^{-1} . Carbon dioxide has four vibrational modes; the vibrational wavenumber of the doubly degenerate bending mode is 667 cm^{-1} and of the non-degenerate stretching modes is 1388 and 2349 cm^{-1} .

12.13 Calculate the equilibrium constant for the ionization equilibrium of sodium atoms at 1000 K . The ionization energy of sodium is $495.8 \text{ kJ mol}^{-1}$.

12.14 Calculate the equilibrium constant for the dissociation of $\text{I}_2(\text{g})$ at 500 K . The rotational constant of iodine is 0.0373 cm^{-1} and the vibrational wavenumber is 214 cm^{-1} . The lowest electronic level of the iodine atom is $^2\text{P}_{3/2}$. The bond enthalpy of the I-I bond is 151 kJ mol^{-1} .

Projects

The symbol † indicates that calculus is required.

12.1† Here you use statistical thermodynamics to calculate the internal energy and heat capacity of a system (such as the surface of an atomic solid) modelled as a collection of harmonic oscillators. (a) Derive an expression for the internal energy of a collection of harmonic oscillators. Start by substituting the expression for the vibrational partition function, eqn 6 of Topic 12B, into the statistical thermodynamic expression for internal energy, eqn 2 of Topic 12C. (b) Deduce from your expression the high-temperature approximation and identify the temperature above which it is reliable. (c) Now find an expression for the heat capacity of the oscillators and its high-temperature limit.

12.2† Use mathematical software or a spreadsheet to carry out the following procedures. (a) Consider a three-level system with levels 0, ϵ , and 2ϵ . Plot the partition function against kT/ϵ . (b) Plot the function dS/dT for a two-level system against kT/ϵ . Is there a temperature at which this coefficient passes through a maximum? If you find a maximum, explain its physical origins. (c) Plot the temperature dependence of the vibrational contribution to the molecular partition function for several values of the vibrational wavenumber. Estimate from your plots the temperature above which the harmonic oscillator is in the high-temperature limit.

FOCUS 13

Magnetic Resonance

One of the most widely used and helpful forms of spectroscopy, and a technique that has transformed the practice of chemistry and its dependent disciplines, makes use of the strong effective coupling that occurs when the frequencies of two oscillators are identical. This effect is called *resonance*, and is the basis of a number of everyday phenomena, including the response of radios to the weak oscillations of the electromagnetic field generated by a distant transmitter.

This Focus explores spectroscopic applications that when originally developed (and in some cases still) depend on matching a set of energy levels to a source of monochromatic radiation in the radiofrequency and microwave ranges, and observing the strong absorption by nuclei and electrons, respectively, that occurs at resonance. All spectroscopy is a form of resonant coupling between the electromagnetic field and the molecules; what distinguishes magnetic resonance is that the energy levels themselves are modified by the application of a magnetic field.

The interpretation of magnetic resonance spectra is a highly developed, specialist subject. This Focus aims to do no more than describe the underlying principles of the technique.

13A Nuclear magnetic resonance

The Topic begins with an account of the principles that govern spectroscopic transitions between spin states of nuclei in molecules. It also describes simple experimental arrangements for the detection of these transitions in 'nuclear magnetic resonance' (NMR) spectroscopy.

13A.1 Nuclei in magnetic fields; 13A.2 The resonance condition; 13A.3 The technique

13B The information in NMR spectra

The energy of a magnetic nucleus depends on its electronic environment and the presence of magnetic nuclei in its vicinity. These concepts are described in this Topic, leading to understanding of how molecular structure affects the appearance of NMR spectra.

13B.1 The chemical shift; 13B.2 The fine structure; 13B.3 The origin of spin-spin splitting; 13B.4 Spin relaxation; 13B.5 Conformational conversion and chemical exchange

13C Electron paramagnetic resonance

The experimental techniques for 'electron paramagnetic resonance' (EPR) spectroscopy resemble those used in the early days of NMR. The information obtained is used to investigate species with unpaired electrons. This Topic includes a brief survey of the applications of EPR to the study of organic radicals.

13C.1 Electrons in magnetic fields; 13C.2 The technique; 13C.3 The *g*-value; 13C.4 Hyperfine structure

Web resource What is an application of this material?

One of the most striking applications of nuclear magnetic resonance is in medicine. 'Magnetic resonance imaging' (MRI) is a portrayal of the concentrations of protons in a solid object. The technique is particularly useful for diagnosing disease. See *Impact 10* on the website of this book.