2. Interaction of the electromagnetic field with matter

2.1 Why the electromagnetic field must be quantised

Up to this point, when we considered time-dependent perturbations, the perturbation acting on the quantum system was specified as a given function of time. The quantum state of the particle changed under this perturbation, but the perturbing field itself was not treated as a quantum system.

For the interaction of matter with electromagnetic radiation, this description is incomplete. During emission and absorption, energy and momentum are exchanged between the atom and the electromagnetic field. The state of the field therefore changes together with the state of the atom. A consistent quantum description must consequently treat both parts of the system quantum mechanically.

The construction developed below follows the basic route introduced by Dirac in his seminal 1927 paper on the quantum theory of emission and absorption of radiation: the classical electromagnetic field is first decomposed into independent normal modes, each mode is identified with a harmonic oscillator, and these oscillators are then quantised.

Our first task is therefore to construct the quantum description of the free electromagnetic field, that is, the electromagnetic field in the absence of charges and currents. We begin with its classical description and identify the independent dynamical variables of the field. These variables will then be quantised in the same way as the coordinate and momentum of a mechanical system.

For the free field we choose the scalar potential to vanish and impose the transverse condition on the vector potential:

$$\varphi = 0, \qquad \nabla \cdot \mathbf{A} = 0. \tag{2.1}$$

The electromagnetic field is then completely determined by the vector potential $\mathbf{A}(\mathbf{r}, t)$. The electric and magnetic fields are

$$\mathbf{E}(\mathbf{r}, t) = -\frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}, \qquad \mathbf{H}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t). \tag{2.2}$$

Thus, once $\mathbf{A}(\mathbf{r}, t)$ is known, both physical fields are known.

In the absence of charges and currents, Maxwell's equations imply that the vector potential satisfies the wave equation

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla^2 \mathbf{A} = 0. \tag{2.3}$$

At this stage everything is still classical. The quantity $\mathbf{A}(\mathbf{r}, t)$ is an ordinary field, not an operator.

The next question is therefore:

How can a continuous electromagnetic field be brought into a form to which the usual rules of quantum mechanics can be applied?

The key step is to decompose the field into its independent normal modes. We shall show that each mode behaves mathematically as a harmonic oscillator. Once this has been established, quantisation requires no new principle: the coordinate and momentum associated with each field mode are promoted to operators exactly as for the quantum harmonic oscillator.

The logic of the construction is therefore

classical electromagnetic field → independent normal modes →

harmonic oscillators → quantised electromagnetic field.

Only after carrying out this construction will we identify the quantum excitations of the field with photons. This order is important: the photon concept will emerge from the quantised normal modes rather than being introduced as an additional assumption.

2.2 Normal modes of the classical free electromagnetic field

We now carry out the first step announced at the end of Section 2.1: we decompose the classical electromagnetic field into independent normal modes.

To make the mode decomposition explicit, consider the field in a large cubic volume

$$V = L^3,$$

and impose periodic boundary conditions. The volume V is introduced as a mathematical normalisation device. At the end, when necessary, we can take the limit $V \to \infty$.

With periodic boundary conditions, the vector potential can be expanded in Fourier modes as

$$\mathbf{A}(\mathbf{r},t) = \sqrt{\frac{4\pi c^2}{V}} \sum_{\mathbf{k}} \left[\mathbf{a}_{\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{a}_{\mathbf{k}}^*(t) e^{-i\mathbf{k}\cdot\mathbf{r}} \right]. \tag{2.4}$$

The second term is the complex conjugate of the first one, so that the vector potential is real:

$$\mathbf{A}^*(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t).$$

The periodic boundary conditions restrict the allowed wavevectors to

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \qquad n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \tag{2.5}$$

At this stage $\mathbf{k}$ is simply the wavevector that labels a Fourier mode of the classical field.

Transversality of each mode

The vector potential satisfies

$$\nabla \cdot \mathbf{A} = 0.$$

Substituting the Fourier expansion (2.4), each spatial derivative brings down a factor $i\mathbf{k}$. Since the Fourier modes are independent, the coefficient of each mode must vanish separately. Therefore

$$\mathbf{k} \cdot \mathbf{a}_{\mathbf{k}} = 0. \tag{2.6}$$

Thus the amplitude $\mathbf{a}_{\mathbf{k}}$ has no component parallel to $\mathbf{k}$.

This is the first important simplification. Although $\mathbf{A}$ is a three-component vector field, for a given wavevector $\mathbf{k}$ only the two components perpendicular to $\mathbf{k}$ are independent.

Time dependence of a Fourier mode

We now substitute the Fourier expansion into the free-field wave equation,

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla^2 \mathbf{A} = 0.$$

For a Fourier factor $e^{i\mathbf{k}\cdot\mathbf{r}}$,

$$\nabla^2 e^{i\mathbf{k}\cdot\mathbf{r}} = -k^2 e^{i\mathbf{k}\cdot\mathbf{r}}.$$

Therefore each Fourier amplitude satisfies its own equation,

$$\ddot{\mathbf{a}}_{\mathbf{k}} + c^2 k^2 \mathbf{a}_{\mathbf{k}} = 0. \tag{2.7}$$

Introducing

$$\omega_{\mathbf{k}} = ck, \tag{2.8}$$

we obtain

$$\ddot{\mathbf{a}}_{\mathbf{k}} + \omega_{\mathbf{k}}^2 \mathbf{a}_{\mathbf{k}} = 0.$$

This is precisely the equation of a harmonic oscillator.

Thus the wave equation for the electromagnetic field has been converted into a separate harmonic-oscillator equation for every allowed wavevector **k**.

The corresponding time dependence may be written as

$$\mathbf{a}_{\mathbf{k}}(t) \propto e^{-i\omega_{\mathbf{k}} t}, \qquad \mathbf{a}_{\mathbf{k}}^*(t) \propto e^{+i\omega_{\mathbf{k}} t}.$$

The appearance of harmonic oscillators here is therefore not an assumption. It follows directly from the Fourier decomposition of the free Maxwell field.

Two independent polarisations

Equation (2.6) tells us that, for a given **k**, the field amplitude lies in the plane perpendicular to **k**.

Choose two mutually orthogonal unit vectors in this plane,

$$\mathbf{e}_{\mathbf{k}1}, \qquad \mathbf{e}_{\mathbf{k}2},$$

such that

$$\mathbf{e}_{\mathbf{k}\alpha} \cdot \mathbf{e}_{\mathbf{k}\alpha'} = \delta_{\alpha\alpha'}, \qquad \mathbf{k} \cdot \mathbf{e}_{\mathbf{k}\alpha} = 0, \qquad \alpha = 1,2. \tag{2.9}$$

The index α therefore labels the two independent transverse polarisations of the mode.

For example, if **k** is directed along the z-axis, two possible linear polarisations are along the x- and y-axes.

We shall therefore eventually associate two independent dynamical degrees of freedom with every wavevector **k**.

Energy of the field

To identify the dynamical variables that are to be quantised, we now rewrite the classical electromagnetic-field energy in terms of the normal modes.

The total field energy is

$$E_{\text{field}} = \frac{1}{8\pi} \int_V (\mathbf{E}^2 + \mathbf{H}^2)\, d^3 r. \tag{2.10}$$

Using

$$\mathbf{E} = -\frac{1}{c}\dot{\mathbf{A}}, \qquad \mathbf{H} = \nabla \times \mathbf{A},$$

we can express both contributions in terms of the Fourier amplitudes.

When the Fourier expansions are substituted into (2.10), products of different modes appear. The spatial integration removes such cross terms because

$$\frac{1}{V}\int_V e^{\,i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\, d^3r = \delta_{\mathbf{k},\mathbf{k}'}. \tag{2.11}$$

Thus different wavevectors contribute independently to the total energy.

It is convenient to replace the complex amplitudes by real normal coordinates. For each mode define

$$\mathbf{Q}_\mathbf{k} = \mathbf{a}_\mathbf{k} + \mathbf{a}_\mathbf{k}^*, \qquad \dot{\mathbf{Q}}_\mathbf{k} = i\omega_\mathbf{k}(\mathbf{a}_\mathbf{k}^* - \mathbf{a}_\mathbf{k}). \tag{2.12}$$

Because $\mathbf{Q}_\mathbf{k}$ is also perpendicular to $\mathbf{k}$, it can be resolved along the two polarisation directions:

$$\mathbf{Q}_\mathbf{k} = \sum_{\alpha=1}^{2} \mathbf{e}_{\mathbf{k}\alpha}\, Q_{\mathbf{k}\alpha}. \tag{2.13}$$

Using the transversality condition, the orthogonality of the Fourier modes and $\omega_\mathbf{k} = ck$, the field energy takes the remarkably simple form

$$E_{\text{field}} = \frac{1}{2}\sum_\mathbf{k}\sum_{\alpha=1}^{2}\left[\dot{Q}_{\mathbf{k}\alpha}^2 + \omega_\mathbf{k}^2 Q_{\mathbf{k}\alpha}^2\right]. \tag{2.14}$$

Now compare this with the energy of a one-dimensional harmonic oscillator of unit mass,

$$E_{\text{osc}} = \frac{1}{2}\left(\dot{Q}^{\,2} + \omega^2 Q^2\right).$$

Equation (2.14) therefore shows that the classical free electromagnetic field is dynamically equivalent to a collection of independent harmonic oscillators. Each oscillator is specified by two labels:

$$(\mathbf{k}, \alpha),$$

where $\mathbf{k}$ specifies the wavevector and $\alpha = 1{,}2$ the transverse polarisation.

To put the result into canonical Hamiltonian form, introduce the momentum conjugate to each normal coordinate,

$$P_{\mathbf{k}\alpha} = \dot{Q}_{\mathbf{k}\alpha}. \tag{2.15}$$

The classical Hamiltonian of the free electromagnetic field is then

$$H_{\text{ph}} = \frac{1}{2}\sum_{\mathbf{k},\alpha}\left(P_{\mathbf{k}\alpha}^2 + \omega_\mathbf{k}^2 Q_{\mathbf{k}\alpha}^2\right). \tag{2.16}$$

This equation is the result we need for quantisation.

The continuous electromagnetic field has been rewritten as a set of independent canonical systems,

$$(Q_{\mathbf{k}\alpha}, P_{\mathbf{k}\alpha}),$$

and each of them has exactly the Hamiltonian of a harmonic oscillator.

At this point all quantities are still classical. In the next subsection we will promote

$$Q_{\mathbf{k}\alpha}, \quad P_{\mathbf{k}\alpha}$$

to operators and quantise each of these oscillators. The photon interpretation will then follow from the resulting quantum spectrum.

2.3 Quantisation of the field and the photon picture

In Section 2.2 we showed that the classical free electromagnetic field can be represented as a collection of independent harmonic oscillators. Each oscillator corresponds to a field mode specified by its wavevector $\mathbf{k}$ and polarisation index $\alpha = 1,2$.

The classical Hamiltonian is

$$H_{\mathrm{ph}} = \frac{1}{2}\sum_{\mathbf{k},\alpha}\left(P_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 Q_{\mathbf{k}\alpha}^2\right), \qquad \omega_{\mathbf{k}} = ck.$$

We now quantise these oscillators and determine the quantum states of the electromagnetic field.

Quantisation of the normal modes

Replace the classical canonical variables by operators,

$$Q_{\mathbf{k}\alpha} \to \hat{Q}_{\mathbf{k}\alpha}, \qquad P_{\mathbf{k}\alpha} \to \hat{P}_{\mathbf{k}\alpha},$$

satisfying the canonical commutation relations

$$\left[\hat{Q}_{\mathbf{k}\alpha}, \hat{P}_{\mathbf{k}'\alpha'}\right] = i\hbar\delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}. \tag{2.17}$$

The remaining commutators vanish:

$$\left[\hat{Q}_{\mathbf{k}\alpha}, \hat{Q}_{\mathbf{k}'\alpha'}\right] = 0, \qquad \left[\hat{P}_{\mathbf{k}\alpha}, \hat{P}_{\mathbf{k}'\alpha'}\right] = 0. \tag{2.18}$$

The Hamiltonian operator of the free electromagnetic field becomes

$$\hat{H}_{\mathrm{ph}} = \frac{1}{2}\sum_{\mathbf{k},\alpha}\left(\hat{P}_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 \hat{Q}_{\mathbf{k}\alpha}^2\right). \tag{2.19}$$

Each term is the Hamiltonian of a quantum harmonic oscillator of unit mass and frequency $\omega_{\mathbf{k}}$. Since the oscillators are independent, their stationary Schrödinger equations can be solved separately.

For the oscillator corresponding to mode $(\mathbf{k}, \alpha)$, the stationary Schrödinger equation in the normal-coordinate representation is

$$\left[-\frac{\hbar^2}{2}\frac{d^2}{dQ_{\mathbf{k}\alpha}^2} + \frac{\omega_{\mathbf{k}}^2 Q_{\mathbf{k}\alpha}^2}{2}\right]\phi_{N_{\mathbf{k}\alpha}} = \varepsilon_{N_{\mathbf{k}\alpha}}\phi_{N_{\mathbf{k}\alpha}}. \tag{2.20}$$

Here $\phi_{N_{\mathbf{k}\alpha}}$ is the oscillator eigenfunction, and $N_{\mathbf{k}\alpha}$ is its quantum number.

The familiar harmonic-oscillator spectrum gives

$$\varepsilon_{N_{\mathbf{k}\alpha}} = \hbar\omega_{\mathbf{k}}\left(N_{\mathbf{k}\alpha} + \frac{1}{2}\right), \qquad N_{\mathbf{k}\alpha} = 0,1,2,\ldots \tag{2.21}$$

At this stage, $N_{\mathbf{k}\alpha}$ is simply the quantum number specifying the energy level of the oscillator corresponding to the field mode $(\mathbf{k}, \alpha)$. We have not yet introduced photons.

Quantum states and energy of the electromagnetic field

Since the field consists of independent oscillators, an eigenstate of its Hamiltonian is specified by the quantum numbers of all the oscillators.

The corresponding wavefunction is the product of their individual eigenfunctions:

$$\Psi_{\{\ldots,N_{\mathbf{k}\alpha},\ldots\}} = \prod_{\mathbf{k},\alpha}\phi_{N_{\mathbf{k}\alpha}}(Q_{\mathbf{k}\alpha}).$$

In Dirac notation, we write the same field state as

$$|\dots, N_{\mathbf{k}\alpha}, \dots\rangle = \otimes_{\mathbf{k},\alpha} |N_{\mathbf{k}\alpha}\rangle. \tag{2.22}$$

The symbol $\otimes$ denotes the tensor product of the oscillator states. Thus the complete state is obtained by specifying the quantum state of every independent mode.

The energy of the field is the sum of the oscillator energies:

$$E_{\{\dots,N_{\mathbf{k}\alpha},\dots\}} = \sum_{\mathbf{k},\alpha} \hbar\,\omega_{\mathbf{k}} \left(N_{\mathbf{k}\alpha} + \frac{1}{2}\right). \tag{2.23}$$

These states therefore satisfy

$$\hat{H}_{\mathrm{ph}} |\dots, N_{\mathbf{k}\alpha}, \dots\rangle = E_{\{\dots,N_{\mathbf{k}\alpha},\dots\}} |\dots, N_{\mathbf{k}\alpha}, \dots\rangle. \tag{2.24}$$

We have obtained the quantum states and energy spectrum of the electromagnetic field without introducing any particle interpretation.

Momentum of the quantised field

To identify the physical meaning of the oscillator excitations, we must also determine the momentum carried by the field.

The classical electromagnetic-field momentum is

$$\mathbf{P}_{\mathrm{field}} = \frac{1}{4\pi c} \int_V \mathbf{E} \times \mathbf{H}\, d^3 r.$$

Expressing $\mathbf{E}$ and $\mathbf{H}$ through the normal modes introduced in Section 2.2 gives

$$\mathbf{P}_{\mathrm{field}} = \frac{1}{2} \sum_{\mathbf{k},\alpha} \frac{\mathbf{k}}{\omega_{\mathbf{k}}} \left(P_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 Q_{\mathbf{k}\alpha}^2\right). \tag{2.25}$$

Quantisation leads to the corresponding momentum operator,

$$\hat{\mathbf{P}}_{\mathrm{field}} = \frac{1}{2} \sum_{\mathbf{k},\alpha} \frac{\mathbf{k}}{\omega_{\mathbf{k}}} \left(\hat{P}_{\mathbf{k}\alpha}^2 + \omega_{\mathbf{k}}^2 \hat{Q}_{\mathbf{k}\alpha}^2\right). \tag{2.26}$$

Because the expression in parentheses is twice the Hamiltonian of the corresponding oscillator, the field states (2.22) are also eigenstates of $\hat{\mathbf{P}}_{\mathrm{field}}$.

Their momentum eigenvalues are

$$\mathbf{P}_{\{\dots,N_{\mathbf{k}\alpha},\dots\}} = \sum_{\mathbf{k},\alpha} \hbar\,\mathbf{k} \left(N_{\mathbf{k}\alpha} + \frac{1}{2}\right).$$

The allowed wavevectors occur in pairs $\mathbf{k}$ and $-\mathbf{k}$. The terms proportional to $1/2$ therefore cancel in the total momentum, leaving

$$\mathbf{P}_{\{\dots,N_{\mathbf{k}\alpha},\dots\}} = \sum_{\mathbf{k},\alpha} \hbar\,\mathbf{k} N_{\mathbf{k}\alpha}. \tag{2.27}$$

We can now determine the energy and momentum associated with exciting a single field oscillator.

Photon interpretation

Consider first the ground state of the electromagnetic field. In this state, every oscillator is in its lowest energy level:

$$N_{\mathbf{k}\alpha} = 0 \qquad \text{for all } \mathbf{k}, \alpha.$$

We denote this state by

$$|0\rangle = |\ \ldots, 0_{\mathbf{k}\alpha}, \ldots\rangle. \tag{2.28}$$

According to Eq. (2.23), its energy is

$$E_0 = \frac{1}{2}\sum_{\mathbf{k},\alpha} \hbar\,\omega_{\mathbf{k}}. \tag{2.29}$$

Its total momentum is zero:

$$\mathbf{P}_0 = 0. \tag{2.30}$$

Now consider a field state in which one particular oscillator, labelled by $(\mathbf{k}, \alpha)$, is in its first excited level, $N_{\mathbf{k}\alpha} = 1$, while every other oscillator remains in its ground state.

Relative to the field ground state, the energy increases by

$$\Delta E = \hbar\omega_{\mathbf{k}},$$

and the momentum by

$$\Delta\mathbf{P} = \hbar\mathbf{k}.$$

More generally, increasing the quantum number of one oscillator by unity,

$$N_{\mathbf{k}\alpha} \to N_{\mathbf{k}\alpha} + 1, \tag{2.31}$$

while leaving all other quantum numbers unchanged, produces the changes

$$\Delta E = \hbar\omega_{\mathbf{k}}, \qquad \Delta\mathbf{P} = \hbar\mathbf{k}. \tag{2.32}$$

These changes do not depend on the initial value of $N_{\mathbf{k}\alpha}$.

We therefore interpret the increase of the oscillator quantum number by one as the **creation of one quantum of the electromagnetic field**, called a *photon*.

A photon associated with mode $(\mathbf{k}, \alpha)$ has energy and momentum

$$\varepsilon_{\mathbf{k}} = \hbar\omega_{\mathbf{k}}, \qquad \mathbf{p}_{\mathbf{k}} = \hbar\mathbf{k}, \qquad \omega_{\mathbf{k}} = ck. \tag{2.33}$$

The state in which this single photon is present, with all other oscillators in their ground states, is denoted by

$$|\mathbf{k}, \alpha\rangle \equiv |\ \ldots, 0, 1_{\mathbf{k}\alpha}, 0, \ldots\rangle. \tag{2.34}$$

The state $|\mathbf{k}, \alpha\rangle$ is therefore a **one-photon state**, characterised by wavevector $\mathbf{k}$ and polarisation α.

The physical interpretation of the integers $N_{\mathbf{k}\alpha}$ now follows.

If the oscillator corresponding to mode $(\mathbf{k}, \alpha)$ has quantum number $N_{\mathbf{k}\alpha}$, the field contains $N_{\mathbf{k}\alpha}$ photons in the one-photon state $|\mathbf{k}, \alpha\rangle$.

Thus,

$$N_{\mathbf{k}\alpha} = \text{number of photons in the one-photon state } |\mathbf{k}, \alpha\rangle.$$

In the language of second quantisation, $N_{\mathbf{k}\alpha}$ is called the *occupation number* of this one-photon state.

The complete field state

$$|\ \ldots, N_{\mathbf{k}\alpha}, \ldots\rangle$$

therefore specifies the numbers of photons occupying all possible one-photon states.

This is the photon interpretation of the quantised electromagnetic field.

Photon creation and annihilation operators

Having identified a change of $N_{\mathbf{k}\alpha}$ by one with the creation or removal of a photon, we introduce operators that perform these changes.

For each mode $(\mathbf{k}, \alpha)$, define

$$\hat{B}_{\mathbf{k}\alpha} = \sqrt{\frac{\omega_{\mathbf{k}}}{2\hbar}}\left(\hat{Q}_{\mathbf{k}\alpha} + \frac{i}{\omega_{\mathbf{k}}}\hat{P}_{\mathbf{k}\alpha}\right),$$

$$\hat{B}^{\dagger}_{\mathbf{k}\alpha} = \sqrt{\frac{\omega_{\mathbf{k}}}{2\hbar}}\left(\hat{Q}_{\mathbf{k}\alpha} - \frac{i}{\omega_{\mathbf{k}}}\hat{P}_{\mathbf{k}\alpha}\right). \tag{2.35}$$

These are the familiar lowering and raising operators of the harmonic oscillator, now applied independently to every mode of the electromagnetic field.

The inverse relations are

$$\hat{Q}_{\mathbf{k}\alpha} = \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}}\left(\hat{B}_{\mathbf{k}\alpha} + \hat{B}^{\dagger}_{\mathbf{k}\alpha}\right),$$

$$\hat{P}_{\mathbf{k}\alpha} = i\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2}}\left(\hat{B}^{\dagger}_{\mathbf{k}\alpha} - \hat{B}_{\mathbf{k}\alpha}\right). \tag{2.36}$$

From the canonical commutation relations (2.17) and (2.18), we find

$$\left[\hat{B}_{\mathbf{k}\alpha}, \hat{B}^{\dagger}_{\mathbf{k}'\alpha'}\right] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}. \tag{2.37}$$

Furthermore,

$$\left[\hat{B}_{\mathbf{k}\alpha}, \hat{B}_{\mathbf{k}'\alpha'}\right] = 0, \qquad \left[\hat{B}^{\dagger}_{\mathbf{k}\alpha}, \hat{B}^{\dagger}_{\mathbf{k}'\alpha'}\right] = 0. \tag{2.38}$$

Their actions on the field states are

$$\hat{B}_{\mathbf{k}\alpha}|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle = \sqrt{N_{\mathbf{k}\alpha}}\,|\ldots, N_{\mathbf{k}\alpha} - 1, \ldots\rangle, \tag{2.39}$$

and

$$\hat{B}^{\dagger}_{\mathbf{k}\alpha}|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle = \sqrt{N_{\mathbf{k}\alpha} + 1}\,|\ldots, N_{\mathbf{k}\alpha} + 1, \ldots\rangle. \tag{2.40}$$

The operator $\hat{B}_{\mathbf{k}\alpha}$ removes one photon from the one-photon state $|\mathbf{k}, \alpha\rangle$, while $\hat{B}^{\dagger}_{\mathbf{k}\alpha}$ creates one photon in that state.

They are therefore called the **photon annihilation and creation operators**, respectively.

Operators of photon numbers

For each one-photon state $|\mathbf{k}, \alpha\rangle$, introduce the operator

$$\hat{N}_{\mathbf{k}\alpha} = \hat{B}^{\dagger}_{\mathbf{k}\alpha}\hat{B}_{\mathbf{k}\alpha}. \tag{2.41}$$

Its action on a field state follows from Eqs. (2.39) and (2.40):

$$\hat{N}_{\mathbf{k}\alpha}|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle = N_{\mathbf{k}\alpha}|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle. \tag{2.42}$$

Thus $\hat{N}_{\mathbf{k}\alpha}$ is the **operator of the number of photons in the one-photon state** $|\mathbf{k}, \alpha\rangle$. Its eigenvalues are the non-negative integers $N_{\mathbf{k}\alpha}$.

Substituting Eqs. (2.36) into the Hamiltonian (2.19), we obtain

$$\hat{H}_{\mathrm{ph}} = \sum_{\mathbf{k},\alpha} \hbar\,\omega_{\mathbf{k}} \left(\hat{B}^{\dagger}_{\mathbf{k}\alpha} \hat{B}_{\mathbf{k}\alpha} + \frac{1}{2} \right). \tag{2.43}$$

Similarly, the operator of the total field momentum becomes

$$\hat{\mathbf{P}}_{\mathrm{field}} = \sum_{\mathbf{k},\alpha} \hbar\,\mathbf{k} \hat{B}^{\dagger}_{\mathbf{k}\alpha} \hat{B}_{\mathbf{k}\alpha}. \tag{2.44}$$

The field ground state $|0\rangle$, introduced in Eq. (2.28), contains no photons. Hence,

$$\hat{B}_{\mathbf{k}\alpha}|0\rangle = 0 \qquad \text{for all } \mathbf{k}, \alpha. \tag{2.45}$$

It is called the *vacuum state* of the electromagnetic field. Although it contains no photons, its energy is the non-zero zero-point energy (2.29).

Fock space of the electromagnetic field

We have described the field in terms of states containing definite numbers of photons in the one-photon states $|\mathbf{k}, \alpha\rangle$.

The total number of photons is represented by

$$\hat{N} = \sum_{\mathbf{k},\alpha} \hat{N}_{\mathbf{k}\alpha}.$$

Unlike the number of electrons in an atom, the total number of photons need not remain constant. Emission and absorption of radiation change it.

Let $\mathcal{H}^{(N)}$ denote the space of states containing exactly N photons. In particular, $\mathcal{H}^{(0)}$ contains the vacuum state, $\mathcal{H}^{(1)}$ is the one-photon Hilbert space spanned by states $|\mathbf{k}, \alpha\rangle$, and $\mathcal{H}^{(2)}$ contains two-photon states. For photons, the multiphoton states are symmetric under exchange of identical particles.

The full state space must include all possible photon numbers. It is written as the direct sum

$$\mathcal{F} = \oplus_{N=0}^{\infty} \mathcal{H}^{(N)} = \mathcal{H}^{(0)} \oplus \mathcal{H}^{(1)} \oplus \mathcal{H}^{(2)} \oplus \cdots. \tag{2.46}$$

Here the symbol $\oplus$ denotes a direct sum: a general field state can contain mutually orthogonal components with different total photon numbers.

The space $\mathcal{F}$ is called the *Fock space* of the electromagnetic field.

The occupation-number states $|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle$ form a basis in this space. The creation and annihilation operators connect its sectors with different total photon numbers.

In the next subsection we express the vector potential, electric field and magnetic field through these operators and examine the properties of the vacuum state.

2.4 Field operators, the vacuum state and zero-point fluctuations

In Section 2.3 we quantised the normal coordinates and momenta of the electromagnetic field. The classical variables

$$Q_{\mathbf{k}\alpha}, \qquad P_{\mathbf{k}\alpha}$$

were replaced by operators, and the quantum state of the field was described in Fock space.

We now return to the electromagnetic quantities with which we started in Section 2.1,

$$\mathbf{A}, \qquad \mathbf{E}, \qquad \mathbf{H},$$

and construct the corresponding operators.

Vector-potential operator

In Section 2.2 the Fourier amplitudes $\mathbf{a}_{\mathbf{k}}$ were expressed through the real normal coordinates. Using

$$P_{\mathbf{k}\alpha} = \dot{Q}_{\mathbf{k}\alpha},$$

the inverse of Eq. (2.12) gives

$$\mathbf{a}_{\mathbf{k}} = \frac{1}{2}\sum_{\alpha} \mathbf{e}_{\mathbf{k}\alpha}\left(Q_{\mathbf{k}\alpha} + \frac{i}{\omega_{\mathbf{k}}} P_{\mathbf{k}\alpha}\right),$$

$$\mathbf{a}_{\mathbf{k}}^{*} = \frac{1}{2}\sum_{\alpha} \mathbf{e}_{\mathbf{k}\alpha}\left(Q_{\mathbf{k}\alpha} - \frac{i}{\omega_{\mathbf{k}}} P_{\mathbf{k}\alpha}\right). \tag{2.47}$$

Comparison with the definitions of the ladder operators, Eqs. (2.20) and (2.21), gives the replacements

$$\mathbf{a}_{\mathbf{k}} \to \sum_{\alpha} \mathbf{e}_{\mathbf{k}\alpha} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}}\, \hat{B}_{\mathbf{k}\alpha},$$

$$\mathbf{a}_{\mathbf{k}}^{*} \to \sum_{\alpha} \mathbf{e}_{\mathbf{k}\alpha} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}}\, \hat{B}_{\mathbf{k}\alpha}^{\dagger}. \tag{2.48}$$

We now substitute these expressions into the classical Fourier expansion (2.4). Restoring the harmonic time dependence of each free mode, the vector potential becomes the operator

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \sum_{\mathbf{k},\alpha} \sqrt{\frac{2\pi c^2 \hbar}{V \omega_{\mathbf{k}}}}\, \mathbf{e}_{\mathbf{k}\alpha}\left[e^{\,i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}} t)} \hat{B}_{\mathbf{k}\alpha} + e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}} t)} \hat{B}_{\mathbf{k}\alpha}^{\dagger}\right]. \tag{2.49}$$

The factors $e^{\mp i\omega_{\mathbf{k}} t}$ are the harmonic time dependence already obtained for the free modes in Section 2.2.

Equation (2.49) has an important structure. The vector-potential operator contains two types of terms: one proportional to $\hat{B}_{\mathbf{k}\alpha}$, which lowers the occupation number of a mode by one, and one proportional to $\hat{B}_{\mathbf{k}\alpha}^{\dagger}$, which raises it by one.

Electric- and magnetic-field operators

The classical relations introduced in Eq. (2.2),

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \qquad \mathbf{H} = \nabla \times \mathbf{A},$$

remain the definitions of the corresponding quantum-field operators.

Differentiating Eq. (2.49) with respect to time gives

$$\hat{\mathbf{E}}(\mathbf{r}, t) = i \sum_{\mathbf{k},\alpha} \sqrt{\frac{2\pi \hbar \omega_{\mathbf{k}}}{V}}\, \mathbf{e}_{\mathbf{k}\alpha}\left[e^{\,i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}} t)} \hat{B}_{\mathbf{k}\alpha} - e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}} t)} \hat{B}_{\mathbf{k}\alpha}^{\dagger}\right]. \tag{2.50}$$

Similarly, taking the curl with respect to $\mathbf{r}$,

$$\widehat{\mathbf{H}}(\mathbf{r},t) = i\sum_{\mathbf{k},\alpha}\sqrt{\frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}}}\,(\mathbf{k}\times\mathbf{e}_{\mathbf{k}\alpha})\big[e^{\,i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}\hat{B}_{\mathbf{k}\alpha} - e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}\hat{B}^{\dagger}_{\mathbf{k}\alpha}\big]. \tag{2.51}$$

Thus the electric and magnetic fields are now quantum observables. Their values in a given field state are determined, as for any other quantum observable, from the corresponding operators and the state of the system.

Photon number and field amplitudes

The field operators contain creation and annihilation operators. They therefore do not preserve the occupation number of a mode.

This follows directly from the commutation relations. For the number operator defined in Eq. (2.27),

$$\widehat{N}_{\mathbf{k}\alpha} = \hat{B}^{\dagger}_{\mathbf{k}\alpha}\hat{B}_{\mathbf{k}\alpha},$$

we obtain

$$\big[\widehat{N}_{\mathbf{k}\alpha}, \hat{B}_{\mathbf{k}'\alpha'}\big] = -\delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}\hat{B}_{\mathbf{k}'\alpha'},$$

$$\big[\widehat{N}_{\mathbf{k}\alpha}, \hat{B}^{\dagger}_{\mathbf{k}'\alpha'}\big] = +\delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}\hat{B}^{\dagger}_{\mathbf{k}'\alpha'}. \tag{2.52}$$

Since $\widehat{\mathbf{A}}$, $\widehat{\mathbf{E}}$, and $\widehat{\mathbf{H}}$ contain these operators linearly, a state with a definite photon number is not, in general, a state with a definite value of the electric or magnetic field.

This point is particularly important for the vacuum state.

Mean fields in the vacuum state

The vacuum state was defined in Eq. (2.44) by

$$\hat{B}_{\mathbf{k}\alpha}\,|\,0\rangle = 0 \tag{2.53}$$

for every mode.

For any field operator $\hat{X}$, we shall denote its expectation value in the vacuum state by

$$\langle\hat{X}\rangle_0 \equiv \langle 0|\hat{X}|0\rangle. \tag{2.54}$$

Taking the Hermitian conjugate of Eq. (2.53) also gives

$$\langle 0\,|\,\hat{B}^{\dagger}_{\mathbf{k}\alpha} = 0. \tag{2.55}$$

Equations (2.49)–(2.51) therefore immediately give

$$\langle\widehat{\mathbf{A}}\rangle_0 = \langle\widehat{\mathbf{E}}\rangle_0 = \langle\widehat{\mathbf{H}}\rangle_0 = 0. \tag{2.56}$$

Thus the vacuum contains no classical electromagnetic field in the sense of a non-zero mean electric or magnetic field.

This does not, however, imply that the field operators have definite value zero in the vacuum state.

Fluctuations of an observable

For an observable represented by an operator $\hat{X}$, define its fluctuation about its mean value by

$$\Delta\hat{X} = \hat{X} - \langle\hat{X}\rangle. \tag{2.57}$$

The mean-square fluctuation is

$$\Big\langle\big(\Delta\hat{X}\big)^2\Big\rangle = \langle\hat{X}^2\rangle - \langle\hat{X}\rangle^2. \tag{2.58}$$

For the vacuum electric field, Eq. (2.56) gives

$$\Delta\hat{\mathbf{E}} = \hat{\mathbf{E}}.$$

Hence its mean-square fluctuation is determined by

$$\langle(\Delta\hat{\mathbf{E}})^2\rangle_0 = \langle 0|\hat{\mathbf{E}}^2|0\rangle, \tag{2.59}$$

where

$$\hat{\mathbf{E}}^2 \equiv \hat{\mathbf{E}}\cdot\hat{\mathbf{E}}.$$

To evaluate this quantity, we first note that Eq. (2.24) gives

$$\hat{B}_{\mathbf{k}\alpha}\hat{B}^\dagger_{\mathbf{k}'\alpha'} = \hat{B}^\dagger_{\mathbf{k}'\alpha'}\hat{B}_{\mathbf{k}\alpha} + \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}.$$

Using the vacuum condition (2.53),

$$\langle 0|\hat{B}_{\mathbf{k}\alpha}\hat{B}^\dagger_{\mathbf{k}'\alpha'}|0\rangle = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}. \tag{2.60}$$

In contrast,

$$\langle 0|\hat{B}^\dagger_{\mathbf{k}\alpha}\hat{B}_{\mathbf{k}'\alpha'}|0\rangle = 0. \tag{2.61}$$

Substitution of Eq. (2.50) into Eq. (2.59) therefore gives

$$\langle(\Delta\hat{\mathbf{E}})^2\rangle_0 = \frac{2\pi\hbar}{V}\sum_{\mathbf{k},\alpha}\omega_{\mathbf{k}}. \tag{2.62}$$

The same calculation for the magnetic field gives

$$\langle(\Delta\hat{\mathbf{H}})^2\rangle_0 = \frac{2\pi\hbar}{V}\sum_{\mathbf{k},\alpha}\omega_{\mathbf{k}}. \tag{2.63}$$

The mean electric and magnetic fields therefore vanish in the vacuum, but their mean-square fluctuations do not.

These non-zero fluctuations of the electromagnetic field in its lowest-energy state are called zero-point fluctuations or vacuum fluctuations.

The distinction is important:

$$\langle\hat{\mathbf{E}}\rangle_0 = 0$$

does not mean

$$\hat{\mathbf{E}}\,|\,0\rangle = 0.$$

Indeed, Eq. (2.50) contains a creation operator. Acting on the vacuum,

$$\hat{\mathbf{E}}\,|\,0\rangle \neq 0. \tag{2.64}$$

The vacuum is therefore a state of definite photon number, $N = 0$, but it is not a state in which the electric and magnetic fields have sharply defined zero values.

Zero-point energy

The vacuum energy obtained in Section 2.3 was

$$E_0 = \langle 0|\hat{H}_{\rm ph}|0\rangle = \frac{1}{2}\sum_{\mathbf{k},\alpha}\hbar\,\omega_{\mathbf{k}}. \tag{2.65}$$

The connection between this energy and the field fluctuations can be seen directly from the electromagnetic-field energy,

$$\hat{H}_{\mathrm{ph}} = \frac{1}{8\pi}\int_V \left(\hat{\mathbf{E}}^{\,2} + \hat{\mathbf{H}}^{\,2}\right) d^3r. \tag{2.66}$$

Taking its vacuum expectation value and using Eqs. (2.62) and (2.63) reproduces Eq. (2.65).

Thus two related properties of the vacuum have emerged:

$$\text{no photons} \quad \not\Rightarrow \quad \text{zero field fluctuations},$$

and

$$N = 0 \quad \Rightarrow \quad E = E_0 \neq 0.$$

The absolute sum in Eq. (2.65) is divergent when arbitrarily high-frequency modes are included. We shall therefore not assign a finite value to the absolute vacuum energy here. What can have physical consequences is a change in the allowed vacuum modes produced by external conditions.

In the next subsection we shall examine precisely such a situation: the electromagnetic field between conducting boundaries. The resulting change in the zero-point energy leads to the Casimir force.

2.5 Casimir effect

In Section 2.4 we found that the vacuum energy of the quantised electromagnetic field is

$$E_0 = \frac{1}{2}\sum_{\mathbf{k},\alpha} \hbar\,\omega_{\mathbf{k}}.$$

This sum diverges because the electromagnetic field contains modes of arbitrarily high frequency.

The Casimir effect arises when conducting boundaries change the allowed electromagnetic modes and, consequently, their zero-point energies.

Consider two parallel, perfectly conducting plates separated by a distance a. We shall calculate the change in vacuum energy caused by the plates and determine the force acting between them.

One-dimensional case

We begin with a one-dimensional model, considering one transverse component of the vector potential between two conducting boundaries at $x = 0$ and $x = a$.

For a mode of frequency ω, write

$$\mathbf{A}(x,t) = \mathbf{e}\,u(x)e^{-i\omega t} + \text{c.c.},$$

where $\mathbf{e}$ is a unit vector perpendicular to the x-axis, $u(x)$ is the complex amplitude of the mode, and c.c. denotes the complex-conjugate term.

The wave equation for the vector potential gives

$$\frac{d^2u}{dx^2} + k^2u = 0, \qquad k = \frac{\omega}{c}.$$

At the surface of a perfect conductor, the tangential electric field vanishes. Since, in our gauge,

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t},$$

the boundary conditions for a mode of non-zero frequency are

$$u(0) = u(a) = 0.$$

The solution satisfying the first condition is

$$u(x) = C\sin(kx),$$

where C is a constant amplitude. The second condition requires $\sin(ka) = 0$. Therefore, the allowed wavevectors and frequencies are

$$k_n = \frac{\pi n}{a}, \qquad \omega_n = \frac{\pi c n}{a}, \qquad n = 1,2,\ldots \tag{2.67}$$

The value $n = 0$ gives a vanishing mode and is excluded.

Each allowed mode contributes a zero-point energy $\hbar\omega_n/2$. The vacuum energy of the field confined between the boundaries is consequently

$$E_0(a) = \sum_{n=1}^{\infty} \frac{\hbar\omega_n}{2} = \frac{\pi\hbar c}{2a} \sum_{n=1}^{\infty} n. \tag{2.68}$$

This sum diverges.

To isolate the effect of the boundaries, we compare it with the vacuum energy of the unbounded one-dimensional field.

For a large periodic interval of length L, the allowed wavevectors have spacing $2\pi/L$. Passing to the limit $L \to \infty$,

$$\begin{aligned} E_0^{\text{free}}(L) &= \frac{1}{2}\sum_k \hbar\, c|k| \\ &= \frac{\hbar c L}{4\pi}\int_{-\infty}^{\infty} |k|\; dk \\ &= \frac{\hbar c L}{2\pi}\int_0^{\infty} k\; dk. \end{aligned}$$

The reference vacuum energy per unit length is therefore

$$\frac{E_0^{\text{free}}(L)}{L} = \frac{\hbar c}{2\pi}\int_0^{\infty} k\; dk.$$

We define the change in vacuum energy per unit length by

$$\begin{aligned} \varepsilon(a) &= \frac{E_0(a)}{a} - \frac{E_0^{\text{free}}(L)}{L} \\ &= \frac{\pi\hbar c}{2a^2}\sum_{n=1}^{\infty} n - \frac{\hbar c}{2\pi}\int_0^{\infty} k\; dk. \end{aligned} \tag{2.69}$$

Both terms diverge. The physically relevant quantity is their difference, which we shall calculate by introducing the same regularisation in the sum and the integral.

Regularisation of the vacuum energy

Introduce the convergence factor $e^{-\nu k}$, where $\nu > 0$ has dimensions of length. The regularised energy difference is

$$\varepsilon_\nu(a) = \frac{\pi\hbar c}{2a^2}\sum_{n=1}^{\infty} n\, e^{-\pi\nu n/a} - \frac{\hbar c}{2\pi}\int_0^\infty k\, e^{-\nu k}\, dk. \tag{2.70}$$

For every $\nu > 0$, both terms are finite. We shall first perform the subtraction and only then take the limit $\nu \downarrow 0$.

Introduce the dimensionless variable $\lambda = \pi\nu/a$. Changing the integration variable to $x = ak/\pi$, Eq. (2.70) becomes

$$\varepsilon_\nu(a) = \frac{\pi\hbar c}{2a^2}\left[\sum_{n=1}^{\infty} n\, e^{-\lambda n} - \int_0^\infty x\, e^{-\lambda x}\, dx\right].$$

The integral is

$$\int_0^\infty x\, e^{-\lambda x}\, dx = \frac{1}{\lambda^2}.$$

To evaluate the sum, begin with the geometric series

$$\sum_{n=1}^{\infty} e^{-\lambda n} = \frac{1}{e^\lambda - 1}.$$

Differentiating with respect to λ,

$$-\sum_{n=1}^{\infty} n\, e^{-\lambda n} = -\frac{e^\lambda}{(e^\lambda - 1)^2}.$$

Hence,

$$\sum_{n=1}^{\infty} n\, e^{-\lambda n} = \frac{e^{-\lambda}}{(1 - e^{-\lambda})^2}.$$

Substituting these results,

$$\varepsilon_\nu(a) = \frac{\pi\hbar c}{2a^2}\left[\frac{e^{-\lambda}}{(1 - e^{-\lambda})^2} - \frac{1}{\lambda^2}\right].$$

For small λ,

$$\frac{e^{-\lambda}}{(1 - e^{-\lambda})^2} = \frac{1}{\lambda^2} - \frac{1}{12} + \frac{\lambda^2}{240} + O(\lambda^4).$$

The divergent terms cancel explicitly:

$$\varepsilon_\nu(a) = \frac{\pi\hbar c}{2a^2}\left[-\frac{1}{12} + \frac{\lambda^2}{240} + O(\lambda^4)\right].$$

Taking $\nu \downarrow 0$, equivalently $\lambda \downarrow 0$, gives

$$\varepsilon(a) = -\frac{\pi\hbar c}{24a^2}. \tag{2.71}$$

We have therefore obtained a finite difference between two divergent vacuum energies without assigning a finite value to either energy separately.

The total energy difference in the interval is

$$\Delta E(a) = a\varepsilon(a) = -\frac{\pi\hbar c}{24a}.$$

The force acting on the boundaries is

$$F(a) = -\frac{d\Delta E(a)}{da} = -\frac{\pi\hbar c}{24a^2}. \tag{2.72}$$

The negative sign means that the force acts towards decreasing a: the boundaries attract.

Three-dimensional electromagnetic field

We now consider the physical electromagnetic field between two large parallel conducting plates of area S, situated at $z = 0$ and $z = a$.

The wavevector components parallel to the plates, k_x and k_y, remain continuous in the limit of large plate area. The perpendicular component takes the discrete values

$$k_z = \frac{\pi n}{a}, \qquad n = 0,1,2, \ldots$$

Introduce the magnitude of the wavevector parallel to the plates,

$$q = \sqrt{k_x^2 + k_y^2}.$$

The corresponding mode frequencies are

$$\omega_{nq} = c\sqrt{q^2 + \left(\frac{\pi n}{a}\right)^2}. \tag{2.73}$$

The electromagnetic field has two independent transverse polarisations. However, the conducting boundary conditions require special treatment of $n = 0$.

For $n \geq 1$, both independent polarisations are allowed. For $n = 0$, only one independent electromagnetic mode remains: the transverse-electric mode with $n = 0$ is absent, while the transverse-magnetic mode is allowed.

Consequently, the vacuum energy per unit plate area is

$$\frac{E_0(a)}{S} = \frac{\hbar c}{2}\int \frac{d^2q}{(2\pi)^2}\, q + \hbar c \sum_{n=1}^{\infty} \int \frac{d^2q}{(2\pi)^2} \sqrt{q^2 + \left(\frac{\pi n}{a}\right)^2}. \tag{2.74}$$

The first term represents the single $n = 0$ polarisation. In the second term, the factor of two from the two polarisations has cancelled the factor $1/2$ in the zero-point energy of each oscillator.

For the unbounded electromagnetic field, the two polarisations are present for every non-zero wavevector. The vacuum energy of a volume Sa, divided by the plate area, is

$$\frac{E_0^{\text{free}}(a)}{S} = \hbar c a \int \frac{d^3k}{(2\pi)^3}\, k. \tag{2.75}$$

We calculate the difference between Eqs. (2.74) and (2.75) using the same exponential convergence factor $e^{-\nu k}$.

Reduction to a sum over perpendicular wavevectors

In the plane parallel to the plates, use polar coordinates,

$$d^2q = 2\pi q\, dq.$$

Introduce the function

$$G_\nu(s) = \int_0^\infty q\ dq\ \sqrt{q^2+s^2}\, e^{-\nu\sqrt{q^2+s^2}}, \qquad s \geq 0.$$

Here s represents the magnitude of the perpendicular component of the wavevector.

Making the substitution

$$k = \sqrt{q^2+s^2}, \qquad q\,dq = k\,dk,$$

we obtain

$$G_\nu(s) = \int_s^\infty k^2\, e^{-\nu k}\, dk. \tag{2.76}$$

The integral can be evaluated directly:

$$G_\nu(s) = e^{-\nu s}\left(\frac{s^2}{\nu} + \frac{2s}{\nu^2} + \frac{2}{\nu^3}\right).$$

Define $h = \pi/a$.

After performing the angular integration over the wavevectors parallel to the plates, the regularised vacuum energy between the plates becomes

$$\frac{E_{0,\nu}(a)}{S} = \frac{\hbar c}{2\pi}\left[\frac{1}{2}G_\nu(0) + \sum_{n=1}^{\infty} G_\nu\,(nh)\right].$$

For the unbounded field, the perpendicular wavevector is continuous. Using symmetry under $k_z \to -k_z$,

$$\frac{E_{0,\nu}^{\text{free}}(a)}{S} = \frac{\hbar c a}{2\pi^2}\int_0^\infty G_\nu\,(s)\, ds.$$

Since $a/\pi = 1/h$, the regularised change in vacuum energy per unit volume is

$$\varepsilon_\nu(a) = \frac{\hbar c}{2\pi a}\left[\frac{1}{2}G_\nu(0) + \sum_{n=1}^{\infty} G_\nu\,(nh) - \frac{1}{h}\int_0^\infty G_\nu\,(s)\, ds\right]. \tag{2.77}$$

This is the central mathematical expression of the three-dimensional calculation.

The first two terms represent the discrete electromagnetic modes between the conducting plates, including the correct polarisation counting. The last term represents the continuous modes of the unbounded field.

We must evaluate the difference between the discrete sum and its corresponding integral.

Evaluation using the Euler–Maclaurin formula

For a sufficiently smooth function $f(x)$ whose derivatives vanish at infinity, the Euler–Maclaurin formula gives

$$\sum_{n=1}^{\infty} f\,(n) = \int_0^\infty f\,(x)\, dx - \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f^{(3)}(0) - \cdots. \tag{2.78}$$

We apply it to $f(x) = G_\nu(hx)$.

First consider the integral term:

$$\int_0^\infty f\,(x)\,dx = \int_0^\infty G_\nu\,(hx)\,dx.$$

With $s = hx$,

$$\int_0^\infty f\,(x)\,dx = \frac{1}{h}\int_0^\infty G_\nu\,(s)\,ds.$$

This is exactly the third term in Eq. (2.77), with the opposite sign.

The second term in the Euler–Maclaurin formula is $-f(0)/2 = -G_\nu(0)/2$, which cancels the first term in Eq. (2.77).

Thus the integral contribution and the $n = 0$ contribution cancel, leaving the terms involving derivatives of $f(x)$.

We now evaluate those derivatives.

From Eq. (2.76),

$$G_\nu{}'(s) = -s^2 e^{-\nu s}.$$

Therefore, $G_\nu{}'(0) = 0$. Differentiating twice more,

$$G_\nu{}'''(s) = -e^{-\nu s}(2 - 4\nu s + \nu^2 s^2),$$

so $G_\nu{}'''(0) = -2$.

Since $f(x) = G_\nu(hx)$,

$$f'(0) = hG_\nu{}'(0) = 0,$$

and

$$f^{(3)}(0) = h^3 G_\nu{}'''(0) = -2h^3.$$

Substituting into the Euler–Maclaurin expression,

$$\frac{1}{2}G_\nu(0) + \sum_{n=1}^{\infty} G_\nu\,(nh) - \frac{1}{h}\int_0^\infty G_\nu\,(s)\,ds = -\frac{h^3}{360} + \text{higher-order terms.}$$

We must still verify that the omitted terms vanish as the regulator is removed.

To do this, expand $G_\nu(s)$ near $s = 0$. Integrating $G_\nu{}'(s) = -s^2 e^{-\nu s}$ gives

$$G_\nu(s) = \frac{2}{\nu^3} - \frac{s^3}{3} + \frac{\nu s^4}{4} - \frac{\nu^2 s^5}{10} + \cdots.$$

Hence the next odd derivative is $G_\nu^{(5)}(0) = -12\nu^2$. Its contribution to the Euler–Maclaurin expansion is proportional to ν^2 and therefore vanishes as $\nu \downarrow 0$.

The same conclusion holds for the remaining higher-order contributions. We can verify the limiting result directly, without relying only on the asymptotic expansion.

Direct verification of the finite result

From Eq. (2.76),

$$G_\nu(s) = \frac{d^2}{d\nu^2}\left(\frac{e^{-\nu s}}{\nu}\right).$$

Consequently, the expression in square brackets in Eq. (2.77) can be written as

$$D_\nu = \frac{d^2}{d\nu^2}\left\{\frac{1}{\nu}\left[\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\nu h n} - \frac{1}{h}\int_0^\infty e^{-\nu s}\, ds\right]\right\}.$$

The sum and integral are elementary:

$$\sum_{n=1}^{\infty} e^{-\nu h n} = \frac{1}{e^{\nu h} - 1},$$

$$\frac{1}{h}\int_0^\infty e^{-\nu s}\, ds = \frac{1}{h\nu}.$$

Using

$$\frac{1}{2} + \frac{1}{e^{\nu h} - 1} = \frac{1}{2}\coth\left(\frac{\nu h}{2}\right),$$

we obtain the exact expression

$$D_\nu = \frac{d^2}{d\nu^2}\left[\frac{1}{\nu}\left(\frac{1}{2}\coth\frac{\nu h}{2} - \frac{1}{\nu h}\right)\right].$$

For small ν,

$$\frac{1}{2}\coth\frac{\nu h}{2} = \frac{1}{\nu h} + \frac{\nu h}{12} - \frac{(\nu h)^3}{720} + O(\nu^5).$$

The divergent terms cancel before differentiation:

$$D_\nu = \frac{d^2}{d\nu^2}\left[\frac{h}{12} - \frac{\nu^2 h^3}{720} + O(\nu^4)\right]$$

$$D_\nu = -\frac{h^3}{360} + O(\nu^2).$$

This confirms the result obtained from Euler–Maclaurin and establishes the existence of the limit $\nu \downarrow 0$.

Substituting it into Eq. (2.77), with $h = \pi/a$, gives

$$\varepsilon(a) = \lim_{\nu\downarrow 0}\varepsilon_\nu(a)$$

$$\varepsilon(a) = \frac{\hbar c}{2\pi a}\left(-\frac{\pi^3}{360a^3}\right).$$

Therefore,

$$\varepsilon(a) = -\frac{\pi^2\hbar c}{720a^4}. \tag{2.79}$$

This is the Casimir interaction energy per unit volume between two perfectly conducting parallel plates.

Casimir force

The interaction energy per unit plate area is

$$\frac{\Delta E(a)}{S} = a\varepsilon(a) = -\frac{\pi^2\hbar c}{720a^3}.$$

The force per unit area, or pressure, is obtained by differentiating with respect to plate separation:

$$P(a) = -\frac{d}{da}\left[\frac{\Delta E(a)}{S}\right]$$

$$P(a) = -\frac{\pi^2 \hbar c}{240 a^4}. \tag{2.80}$$

The pressure is negative: the plates attract each other.

The result applies to perfectly conducting plates at zero temperature, with lateral dimensions much larger than their separation. Finite conductivity and temperature modify the result for real materials.

The Casimir force is therefore a measurable consequence of the dependence of the electromagnetic vacuum energy on the boundary conditions. The calculation does not require assigning a finite value to the absolute vacuum energy; it involves only the finite, separation-dependent difference between two mode spectra.

2.6 Hamiltonian of the coupled atom–field system

We now consider an atom interacting with the quantised electromagnetic field. The total Hamiltonian is

$$\hat{H} = \hat{H}_{\mathrm{a}} + \hat{H}_{\mathrm{ph}} + \hat{V}. \tag{2.81}$$

Here $\hat{H}_{\mathrm{a}}$ is the Hamiltonian of the atom in the absence of radiation, $\hat{H}_{\mathrm{ph}}$ is the Hamiltonian of the free electromagnetic field, and $\hat{V}$ describes their interaction.

We shall consider the interaction of the field with one atomic electron responsible for the emission and absorption of radiation. This electron is called the *optical electron*.

Its Hamiltonian, in the absence of the radiation field, is

$$\hat{H}_{\mathrm{a}} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r}), \tag{2.82}$$

where m is the electron mass, $\hat{\mathbf{p}} = -i\hbar\nabla$ is its momentum operator, and $U(\mathbf{r})$ is its potential energy due to the nucleus and the other atomic electrons.

The Hamiltonian of the free electromagnetic field was obtained in Section 2.3:

$$\hat{H}_{\mathrm{ph}} = \sum_{\mathbf{k},\alpha} \hbar\,\omega_{\mathbf{k}} \left(\hat{B}^{\dagger}_{\mathbf{k}\alpha}\hat{B}_{\mathbf{k}\alpha} + \frac{1}{2}\right).$$

It remains to determine the interaction operator $\hat{V}$.

Interaction Hamiltonian

In classical electrodynamics, the interaction of a charged particle with the electromagnetic field is introduced by replacing its canonical momentum according to

$$\mathbf{p} \to \mathbf{p} - \frac{e}{c}\mathbf{A}.$$

Here e denotes the **signed charge of the electron**, so $e < 0$.

For the quantised electromagnetic field, the corresponding substitution is

$$\hat{\mathbf{p}} \to \hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}(\mathbf{r}). \tag{2.83}$$

The operator $\widehat{\mathbf{A}}(\mathbf{r})$ is the vector-potential operator obtained in Eq. (2.49), evaluated at a fixed reference time. Its spatial argument is now the position operator of the optical electron.

The Hamiltonian of the electron interacting with the electromagnetic field becomes

$$\widehat{H}'_{\mathrm{a}} = \frac{1}{2m}\left(\widehat{\mathbf{p}} - \frac{e}{c}\widehat{\mathbf{A}}\right)^2 + U(\mathbf{r}).$$

Expanding the square, we obtain

$$\begin{aligned} \widehat{H}'_{\mathrm{a}} = \quad & \frac{\widehat{\mathbf{p}}^{\,2}}{2m} + U(\mathbf{r}) \\ & - \frac{e}{2mc}\left(\widehat{\mathbf{p}}\cdot\widehat{\mathbf{A}} + \widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}}\right) + \frac{e^2}{2mc^2}\widehat{\mathbf{A}}^2. \end{aligned} \tag{2.84}$$

The order of the operators in the term linear in $\widehat{\mathbf{A}}$ must be considered because the momentum operator differentiates the spatial dependence of the vector potential.

For an arbitrary electron wavefunction $\psi(\mathbf{r})$,

$$\begin{aligned} \left(\widehat{\mathbf{p}}\cdot\widehat{\mathbf{A}}\right)\psi \quad &= -i\hbar\nabla\cdot\left(\widehat{\mathbf{A}}\psi\right) \\ &= -i\hbar\left(\nabla\cdot\widehat{\mathbf{A}}\right)\psi + \widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}}\psi. \end{aligned}$$

The transverse condition introduced in Section 2.1 is

$$\nabla\cdot\widehat{\mathbf{A}} = 0.$$

Consequently,

$$\widehat{\mathbf{p}}\cdot\widehat{\mathbf{A}} = \widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}}. \tag{2.85}$$

Substituting this result into Eq. (2.84), we find

$$\widehat{H}'_{\mathrm{a}} = \widehat{H}_{\mathrm{a}} + \widehat{V},$$

where

$$\widehat{V} = -\frac{e}{mc}\widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}} + \frac{e^2}{2mc^2}\widehat{\mathbf{A}}^2. \tag{2.86}$$

The interaction Hamiltonian (2.86) contains a term linear and a term quadratic in the vector-potential operator. Since $\widehat{\mathbf{A}}$ contains photon creation and annihilation operators, the quadratic term contains products of two such operators and contributes, in particular, to two-photon processes. We shall leave these processes aside and consider only the emission and absorption of a single photon.

For these transitions, the interaction operator required in first-order perturbation theory is

$$\widehat{V}_1 = -\frac{e}{mc}\widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}}. \tag{2.87}$$

In the next subsection we calculate the corresponding transition probabilities between atomic energy levels.

2.7 One-photon emission and absorption

In Section 2.6 we obtained the interaction Hamiltonian for an atom coupled to the quantised electromagnetic field. For one-photon transitions, we retain the term

$$\widehat{V}_1 = -\frac{e}{mc}\widehat{\mathbf{A}}\cdot\widehat{\mathbf{p}}.$$

We shall now calculate the probabilities of photon emission and absorption using Fermi's golden rule, derived in Section 1.

Consider two stationary states of the atomic Hamiltonian $\hat{H}_\mathrm{a}$,

$$\hat{H}_\mathrm{a}|1\rangle = E_1|1\rangle, \hat{H}_\mathrm{a}|2\rangle = E_2|2\rangle, E_2 > E_1. \tag{2.88}$$

The state of the electromagnetic field is specified by the photon occupation numbers of all modes,

$$|\dots, N_{\mathbf{k}\alpha}, \dots\rangle.$$

The initial and final states of the combined atom–field system are products of atomic states and field states.

Emission of a photon

Suppose the atom is initially in the excited state $|2\rangle$. During the transition to $|1\rangle$, it emits one photon with wavevector $\mathbf{k}$, polarisation α, and frequency $\omega_\mathbf{k} = ck$.

The initial and final states of the combined system are

$$\begin{aligned} |i\rangle &= |2\rangle|\dots, N_{\mathbf{k}\alpha}, \dots\rangle, \\ |f\rangle &= |1\rangle|\dots, N_{\mathbf{k}\alpha} + 1, \dots\rangle. \end{aligned} \tag{2.89}$$

All other photon occupation numbers remain unchanged.

The final field energy exceeds the initial field energy by $\hbar\omega_\mathbf{k}$. Therefore, the difference between the final and initial energies of the uncoupled atom–field system is

$$E_f^{(0)} - E_i^{(0)} = E_1 - E_2 + \hbar\omega_\mathbf{k}. \tag{2.90}$$

From Fermi's golden rule, the transition probability per unit time is

$$w_\mathrm{em} = \frac{2\pi}{\hbar}|\langle f|\hat{V}_1|i\rangle|^2 \delta(E_1 - E_2 + \hbar\omega_\mathbf{k}). \tag{2.91}$$

We must therefore calculate the matrix element of the interaction operator.

The vector-potential operator at the electron position, obtained in Eq. (2.49), is

$$\hat{\mathbf{A}}(\mathbf{r}) = \sum_{\mathbf{k}',\alpha'} \sqrt{\frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}'}}}\, \mathbf{e}_{\mathbf{k}'\alpha'} \left[e^{i\mathbf{k}'\cdot\mathbf{r}}\hat{B}_{\mathbf{k}'\alpha'} + e^{-i\mathbf{k}'\cdot\mathbf{r}}\hat{B}^\dagger_{\mathbf{k}'\alpha'}\right].$$

Since the number of photons in the mode $(\mathbf{k}, \alpha)$ increases by one, the annihilation operator cannot contribute:

$$\langle \dots, N_{\mathbf{k}\alpha} + 1, \dots |\hat{B}_{\mathbf{k}'\alpha'}| \dots, N_{\mathbf{k}\alpha}, \dots\rangle = 0.$$

For the creation operator, Eq. (2.35) gives

$$\langle \dots, N_{\mathbf{k}\alpha} + 1, \dots |\hat{B}^\dagger_{\mathbf{k}'\alpha'}| \dots, N_{\mathbf{k}\alpha}, \dots\rangle = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}\sqrt{N_{\mathbf{k}\alpha} + 1}. \tag{2.92}$$

Thus only the creation operator for the emitted mode contributes to the matrix element.

Introduce the atomic matrix element

$$p_{12} = \langle 1|e^{-i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{p}})|2\rangle. \tag{2.93}$$

Here p_{12} depends on the wavevector and polarisation of the emitted photon. This dependence will become important when we consider the angular distribution of radiation.

Substituting the vector-potential operator into $\hat{V}_1$, and using Eq. (2.92), we obtain

$$\langle f|\hat{V}_1|i\rangle = -\frac{e}{mc}\sqrt{\frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}}}\, p_{12}\,\sqrt{N_{\mathbf{k}\alpha}+1} \tag{2.94}$$

The factor $\sqrt{N_{\mathbf{k}\alpha}+1}$ comes directly from the action of the photon creation operator.

Taking the squared modulus and substituting into the golden rule gives

$$w_{\text{em}} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}}\,|p_{12}|^2(N_{\mathbf{k}\alpha}+1)\delta(E_1 - E_2 + \hbar\omega_{\mathbf{k}}). \tag{2.95}$$

The delta function imposes energy conservation,

$$E_2 - E_1 = \hbar\omega_{\mathbf{k}}. \tag{2.96}$$

Thus the energy lost by the atom equals the energy of the emitted photon.

Absorption of a photon

We now consider the reverse process. The atom is initially in state $|1\rangle$ and absorbs a photon from mode $(\mathbf{k}, \alpha)$, making a transition to state $|2\rangle$.

The initial and final states are

$$\begin{aligned} |i\rangle &= |1\rangle|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle, \\ |f\rangle &= |2\rangle|\ldots, N_{\mathbf{k}\alpha} - 1, \ldots\rangle. \end{aligned} \tag{2.97}$$

The absorption process requires $N_{\mathbf{k}\alpha} \geq 1$.

The number of photons in the selected mode decreases by one. Consequently, only the annihilation operator contributes:

$$\langle \ldots, N_{\mathbf{k}\alpha} - 1, \ldots|\hat{B}_{\mathbf{k}',\alpha'}|\ldots, N_{\mathbf{k}\alpha}, \ldots\rangle = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}\sqrt{N_{\mathbf{k}\alpha}}. \tag{2.98}$$

The corresponding atomic matrix element is

$$\langle 2|e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{p}})|1\rangle.$$

Because the momentum operator is Hermitian and the field is transverse,

$$\mathbf{k}\cdot\mathbf{e}_{\mathbf{k}\alpha} = 0,$$

we have

$$\left[\mathbf{e}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{p}}, e^{i\mathbf{k}\cdot\mathbf{r}}\right] = 0.$$

Hence, for the real linear-polarisation vectors introduced in Section 2.2,

$$\langle 2|e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{p}})|1\rangle = p_{12}^{*}.$$

The matrix element of the interaction operator is therefore

$$\langle f|\hat{V}_1|i\rangle = -\frac{e}{mc}\sqrt{\frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}}}\, p_{12}^{*}\sqrt{N_{\mathbf{k}\alpha}}. \tag{2.99}$$

The corresponding transition probability per unit time is

$$w_{\text{abs}} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}}|p_{12}|^2 N_{\mathbf{k}\alpha}\delta(E_2 - E_1 - \hbar\omega_{\mathbf{k}}). \tag{2.100}$$

The energy-conservation condition is again

$$E_2 - E_1 = \hbar\omega_{\mathbf{k}}.$$

The energy gained by the atom equals the energy of the absorbed photon.

Spontaneous and stimulated emission

Compare the transition probabilities (2.95) and (2.100).

For the same pair of atomic states and the same photon mode, the atomic matrix element and the energy-conservation condition are identical. The difference is entirely in the photon occupation-number factors:

$$\begin{aligned} w_{\text{em}} &\propto N_{\mathbf{k}\alpha} + 1, \\ w_{\text{abs}} &\propto N_{\mathbf{k}\alpha}. \end{aligned} \tag{2.101}$$

For absorption, the factor $N_{\mathbf{k}\alpha}$ shows that a photon must already be present in the mode. If $N_{\mathbf{k}\alpha} = 0$, absorption from that mode is impossible.

For emission,

$$N_{\mathbf{k}\alpha} + 1 = N_{\mathbf{k}\alpha} + 1. \tag{2.102}$$

The two terms have different physical meanings.

The contribution proportional to $N_{\mathbf{k}\alpha}$ describes **stimulated emission**. The probability of emission into a mode increases with the number of photons already occupying that mode.

The additional contribution 1 remains even if the mode is initially empty:

$$N_{\mathbf{k}\alpha} = 0 \quad \Rightarrow \quad N_{\mathbf{k}\alpha} + 1 = 1.$$

Emission into an initially empty mode is called **spontaneous emission**.

Its existence follows directly from the creation-operator matrix element,

$$\hat{B}^{\dagger}_{\mathbf{k}\alpha}|0\rangle = |1_{\mathbf{k}\alpha}\rangle.$$

Thus an excited atom can emit a photon even when the electromagnetic field initially contains no photons. The emitted photon's energy comes from the atomic transition $E_2 - E_1$.

We have therefore obtained two distinct contributions to photon emission from the same interaction Hamiltonian: stimulated emission, proportional to the initial photon occupation number, and spontaneous emission, which is present even for the vacuum field.

The expressions above are the mode-resolved golden-rule contributions. To obtain a finite total emission or absorption rate for radiation in unbounded space, we must sum over the available photon modes, replacing the wavevector sum by the corresponding continuum integral as developed in Section 1.

Connection with laser operation

The distinction between spontaneous and stimulated emission is fundamental to the operation of a laser.

Spontaneous emission can provide the initial photons in an optical resonator. These photons can stimulate further emission from excited atoms into the same electromagnetic mode. Since the stimulated-emission probability is proportional to $N_{\mathbf{k}\alpha}$, the emission rate into that mode increases as its photon occupation number grows.

For this amplification to overcome absorption, the laser medium must maintain a **population inversion**, with more atoms in the upper energy level than in the lower one. This is achieved by supplying energy to the medium through pumping.

Thus, spontaneous emission can initiate laser oscillation, whereas **stimulated emission provides the amplification** responsible for laser operation.

In the next subsection we shall use the factors $N_{\mathbf{k}\alpha}$ and $N_{\mathbf{k}\alpha}+1$ to determine the photon occupation numbers at thermal equilibrium.

2.8 Detailed balance and the thermal photon distribution

In Section 2.7 we obtained the probabilities of one-photon emission and absorption. For a given electromagnetic mode $(\mathbf{k},\alpha)$, these probabilities contain different factors:

$$w_{\mathrm{em}} \propto N_{\mathbf{k}\alpha}+1, \qquad w_{\mathrm{abs}} \propto N_{\mathbf{k}\alpha}.$$

We now use these results to determine the mean number of photons in the electromagnetic field at thermal equilibrium.

Detailed balance

Consider atoms in thermal equilibrium with electromagnetic radiation at temperature T. Let ρ_1 and ρ_2 denote the probabilities that an atom occupies the stationary states $|1\rangle$ and $|2\rangle$, with energies $E_1 < E_2$.

The atomic populations obey the Boltzmann distribution,

$$\rho_1 = \frac{e^{-E_1/T}}{Z_{\mathrm{a}}}, \qquad \rho_2 = \frac{e^{-E_2/T}}{Z_{\mathrm{a}}},$$

where $Z_{\mathrm{a}} = \sum_n e^{-E_n/T}$ is the atomic partition function. Here and below, temperature is expressed in energy units, so that $k_{\mathrm{B}} = 1$.

Consequently,

$$\frac{\rho_2}{\rho_1} = e^{-(E_2-E_1)/T}. \tag{2.103}$$

At thermal equilibrium, the number of transitions from $|2\rangle$ to $|1\rangle$, accompanied by photon emission, must equal the number of reverse transitions accompanied by absorption.

This condition is called *detailed balance*:

$$\rho_2 \overline{w}_{\mathrm{em}} = \rho_1 \overline{w}_{\mathrm{abs}}. \tag{2.104}$$

Here $\overline{w}_{\mathrm{em}}$ and $\overline{w}_{\mathrm{abs}}$ are the transition rates averaged over the equilibrium photon-number distribution.

Let $\overline{N}_{\mathbf{k}\alpha}$ denote the mean number of photons in mode $(\mathbf{k},\alpha)$. In the weak-coupling equilibrium description, the photon distribution is independent of the state of an individual atom.

According to Eqs. (2.95) and (2.100), emission and absorption involve the same atomic transition matrix element and the same energy-conservation condition. Their respective photon-number factors are

$$\overline{N}_{\mathbf{k}\alpha}+1, \qquad \overline{N}_{\mathbf{k}\alpha}.$$

Therefore, Eq. (2.104) becomes

$$\rho_2\left(\overline{N}_{\mathbf{k}\alpha}+1\right)=\rho_1\overline{N}_{\mathbf{k}\alpha}. \tag{2.105}$$

Solving for the mean photon occupation number,

$$\overline{N}_{\mathbf{k}\alpha}=\frac{\rho_2}{\rho_1-\rho_2}=\frac{1}{\rho_1/\rho_2-1}.$$

Using Eq. (2.103),

$$\overline{N}_{\mathbf{k}\alpha}=\frac{1}{e^{(E_2-E_1)/T}-1}.$$

Energy conservation in the emission and absorption processes requires

$$E_2-E_1=\hbar\omega_{\mathbf{k}}.$$

Thus,

$$\overline{N}_{\mathbf{k}\alpha}=\frac{1}{e^{\hbar\omega_{\mathbf{k}}/T}-1}. \tag{2.106}$$

This is the **Planck distribution** for the mean photon occupation number of an electromagnetic mode at thermal equilibrium.

The result follows directly from the different occupation-number factors in emission and absorption. In particular, the additional 1 in the emission probability is essential: without spontaneous emission, the detailed-balance condition would not produce the Planck distribution.

Spectral energy density of thermal radiation

We now calculate the energy carried by the photons in the equilibrium electromagnetic field.

The Hamiltonian of the quantised electromagnetic field is

$$\widehat{H}_{\mathrm{ph}}=\sum_{\mathbf{k},\alpha}\hbar\,\omega_{\mathbf{k}}\left(\widehat{N}_{\mathbf{k}\alpha}+\frac{1}{2}\right).$$

Its mean energy at thermal equilibrium is therefore

$$\langle\widehat{H}_{\mathrm{ph}}\rangle=\sum_{\mathbf{k},\alpha}\hbar\,\omega_{\mathbf{k}}\left(\overline{N}_{\mathbf{k}\alpha}+\frac{1}{2}\right).$$

Subtracting the vacuum energy E_0, defined in Eq. (2.65), gives the energy associated with thermal photons:

$$\langle\widehat{H}_{\mathrm{ph}}\rangle-E_0=\sum_{\mathbf{k},\alpha}\hbar\,\omega_{\mathbf{k}}\overline{N}_{\mathbf{k}\alpha}. \tag{2.107}$$

For a large normalisation volume V, the sum over wavevectors becomes an integral,

$$\sum_{\mathbf{k}}\rightarrow\frac{V}{(2\pi)^3}\int d^3k.$$

Each wavevector has two independent transverse polarisations, as established in Section 2.2. Since their equilibrium occupation numbers are equal,

$$\sum_{\mathbf{k},\alpha}\rightarrow\frac{2V}{(2\pi)^3}\int d^3k. \tag{2.108}$$

Using $\omega_{\mathbf{k}} = ck$ and Eq. (2.106), the thermal energy per unit volume becomes

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \frac{2}{(2\pi)^3} \int d^3k \, \frac{\hbar ck}{e^{\hbar ck/T} - 1}.$$

The equilibrium radiation field is isotropic. In spherical coordinates in wavevector space,

$$d^3k = k^2 \, dk \, d\Omega, \qquad \int d\Omega = 4\pi.$$

Consequently,

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \frac{\hbar c}{\pi^2} \int_0^\infty \frac{k^3 \, dk}{e^{\hbar ck/T} - 1}.$$

Changing the integration variable from k to $\omega = ck$, we obtain

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 \, d\omega}{e^{\hbar\omega/T} - 1}. \tag{2.109}$$

Define the spectral energy density $u_\omega(T)$ by

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \int_0^\infty u_\omega \, (T) \, d\omega.$$

Comparison with Eq. (2.109) gives

$$u_\omega(T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/T} - 1}. \tag{2.110}$$

This is Planck's law for the spectral energy density of black-body radiation. The quantity $u_\omega(T) \, d\omega$ is the energy of thermal radiation per unit volume in the angular-frequency interval from ω to $\omega + d\omega$.

Total energy density

The total thermal radiation energy density follows by integrating Eq. (2.110) over all frequencies.

Introducing the dimensionless variable

$$x = \frac{\hbar\omega}{T},$$

we obtain

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \frac{T^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 \, dx}{e^x - 1}.$$

Using

$$\int_0^\infty \frac{x^3 \, dx}{e^x - 1} = \frac{\pi^4}{15},$$

we find

$$\frac{\langle \widehat{H}_{\mathrm{ph}} \rangle - E_0}{V} = \frac{\pi^2}{15\hbar^3 c^3} \, T^4. \tag{2.111}$$

Thus the total energy density of black-body radiation is proportional to the fourth power of temperature.

The derivation of the equilibrium photon distribution required no additional assumption about the photon occupation numbers. Their form followed from the emission and absorption probabilities obtained in Section 2.7 and the condition of detailed balance.

We have therefore established the connection between the quantum transitions of an atom and the thermal properties of electromagnetic radiation. In the next subsection we return to individual atomic transitions and introduce the electric-dipole approximation, which simplifies their matrix elements when the radiation wavelength is large compared with the atomic size.

2.9 Electric-dipole approximation

In Section 2.7 we obtained the probabilities of one-photon emission and absorption. Both probabilities depend on the atomic matrix element introduced in Eq. (2.93),

$$p_{12} = \langle 1 \left| e^{-i\mathbf{k}\cdot\mathbf{r}} (\mathbf{e}_{\mathbf{k}\alpha} \cdot \hat{\mathbf{p}}) \right| 2 \rangle,$$

where $\mathbf{k}$ and $\mathbf{e}_{\mathbf{k}\alpha}$ are the wavevector and polarisation vector of the photon, respectively.

We now simplify this matrix element for radiation whose wavelength is much larger than the atomic size.

Long-wavelength approximation

The atomic wavefunctions entering p_{12} are appreciably different from zero at distances of the order of the atomic size,

$$a \sim 1\,\text{Å}.$$

For visible radiation, with a typical wavelength $\lambda \sim 500$ nm, we have

$$ka = \frac{2\pi a}{\lambda} \sim 10^{-3} \ll 1. \tag{2.112}$$

Since the relevant electron coordinates satisfy $r \sim a$, the exponential factor in the matrix element can be expanded:

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = 1 - i\mathbf{k}\cdot\mathbf{r} + \cdots.$$

Consequently,

$$p_{12} = \langle 1 | \mathbf{e}_{\mathbf{k}\alpha} \cdot \hat{\mathbf{p}} | 2 \rangle - i \langle 1 | (\mathbf{k}\cdot\mathbf{r})(\mathbf{e}_{\mathbf{k}\alpha} \cdot \hat{\mathbf{p}}) | 2 \rangle + \cdots. \tag{2.113}$$

For $ka \ll 1$, we retain only the first term:

$$p_{12} \simeq \mathbf{e}_{\mathbf{k}\alpha} \cdot \langle 1 | \hat{\mathbf{p}} | 2 \rangle. \tag{2.114}$$

This is the **electric-dipole approximation**.

It amounts to neglecting the variation of the electromagnetic field across the atom. For radiation with wavelengths comparable to the atomic size, such as sufficiently short-wavelength X-rays, the expansion parameter is no longer small and the spatial dependence of the exponential must be retained.

Relation to the electric dipole moment

We now express the momentum matrix element in Eq. (2.114) through the electron coordinate.

Recall that the atomic Hamiltonian is

$$\hat{H}_{\text{a}} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r}).$$

Since $U(\mathbf{r})$ commutes with $\mathbf{r}$, and the canonical commutation relations give

$$\left[\hat{p}_i, r_j\right] = -i\hbar\delta_{ij},$$

we obtain

$$\left[\hat{\mathbf{p}}^{\,2}, r_j\right] = \sum_i \left(\hat{p}_i\left[\hat{p}_i, r_j\right] + \left[\hat{p}_i, r_j\right]\hat{p}_i\right) = -2i\hbar\hat{p}_j.$$

Therefore,

$$\left[\hat{H}_{\mathrm{a}}, \mathbf{r}\right] = -\frac{i\hbar}{m}\hat{\mathbf{p}}. \tag{2.115}$$

Taking the matrix element between the stationary atomic states $|1\rangle$ and $|2\rangle$,

$$\langle 1\big|\left[\hat{H}_{\mathrm{a}}, \mathbf{r}\right]\big|2\rangle = -\frac{i\hbar}{m}\langle 1|\hat{\mathbf{p}}|2\rangle.$$

Using

$$\hat{H}_{\mathrm{a}}|1\rangle = E_1|1\rangle, \qquad \hat{H}_{\mathrm{a}}|2\rangle = E_2|2\rangle,$$

the left-hand side becomes

$$\langle 1\big|\left[\hat{H}_{\mathrm{a}}, \mathbf{r}\right]\big|2\rangle = \langle 1\big|\hat{H}_{\mathrm{a}}\mathbf{r}\big|2\rangle - \langle 1\big|\mathbf{r}\hat{H}_{\mathrm{a}}\big|2\rangle.$$

$$\langle 1\big|\left[\hat{H}_{\mathrm{a}}, \mathbf{r}\right]\big|2\rangle = (E_1 - E_2)\langle 1|\mathbf{r}|2\rangle.$$

Hence,

$$\langle 1|\hat{\mathbf{p}}|2\rangle = \frac{m}{i\hbar}(E_2 - E_1)\langle 1|\mathbf{r}|2\rangle.$$

Introducing the atomic transition frequency

$$\omega = \frac{E_2 - E_1}{\hbar},$$

we obtain

$$\langle 1|\hat{\mathbf{p}}|2\rangle = -im\omega\langle 1|\mathbf{r}|2\rangle. \tag{2.116}$$

The electric dipole moment operator of the electron is

$$\hat{\mathbf{d}} = e\mathbf{r},$$

where e is the signed electron charge, as defined in Section 2.6.

Define the transition dipole moment by

$$\mathbf{d}_{12} = \langle 1\big|\hat{\mathbf{d}}\big|2\rangle = e\langle 1|\mathbf{r}|2\rangle. \tag{2.117}$$

Substituting Eq. (2.116) into Eq. (2.114), we finally obtain

$$p_{12} \simeq -\frac{im\omega}{e}(\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{d}_{12}). \tag{2.118}$$

Thus, in the electric-dipole approximation, the emission and absorption probabilities are determined by the transition dipole moment $\mathbf{d}_{12}$.

In particular, the squared modulus entering the transition rates becomes

$$|p_{12}|^2 \simeq \frac{m^2\omega^2}{e^2}|\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{d}_{12}|^2. \tag{2.119}$$

The dependence on the polarisation vector is explicit. The matrix element vanishes when the transition dipole moment has no component along the electric-field polarisation.

In the next subsection, we use Eq. (2.119) to calculate the dipole radiation intensity, its angular distribution, and the selection rules for atomic transitions.

2.10 Dipole transition rates and selection rules

In Section 2.9 we showed that, in the electric-dipole approximation, the matrix element determining one-photon emission and absorption is

$$p_{12} \simeq -\frac{im\omega}{e}(\mathbf{e}_{\mathbf{k}\alpha} \cdot \mathbf{d}_{12}),$$

where

$$\mathbf{d}_{12} = e\langle 1|\mathbf{r}|2\rangle, \qquad \omega = \frac{E_2 - E_1}{\hbar}.$$

We now calculate the intensity and angular distribution of spontaneous emission and determine which atomic transitions have non-zero electric-dipole matrix elements.

Intensity of spontaneous dipole radiation

Consider an atom initially in the excited state $|2\rangle$, with the electromagnetic field in its vacuum state. The atom makes a transition to the lower state $|1\rangle$ and emits a photon of frequency ω.

The transition probability per unit time into a specified photon mode $(\mathbf{k}, \alpha)$ was obtained in Eq. (2.95). For spontaneous emission, $N_{\mathbf{k}\alpha} = 0$.

To calculate the probability of emission into a given direction, we must sum over the available photon wavevectors. In the limit of a large normalisation volume V,

$$\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3}\int d^3k = \frac{V}{(2\pi)^3}\int_0^\infty k^2\, dk \int d\Omega.$$

Here $d\Omega$ is the element of solid angle specifying the direction of the emitted photon.

For a specified polarisation α, the spontaneous-emission probability per unit time and unit solid angle is

$$\frac{dw_{\mathrm{sp},\alpha}}{d\Omega} = \frac{V}{(2\pi)^3}\int_0^\infty k^2\, dk\, w_{\mathrm{em}}(\mathbf{k},\alpha)|_{N_{\mathbf{k}\alpha}=0}. \tag{2.120}$$

Substituting Eqs. (2.95) and (2.119), and using $\omega_{\mathbf{k}} = ck$, gives

$$\begin{aligned}\frac{dw_{\mathrm{sp},\alpha}}{d\Omega} = \quad & \frac{V}{(2\pi)^3}\int_0^\infty k^2\, dk\, \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi c^2\hbar}{V\omega_{\mathbf{k}}} \\ & \times \frac{m^2\omega^2}{e^2}|\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{d}_{12}|^2\delta(\hbar\omega_{\mathbf{k}} - \hbar\omega).\end{aligned}$$

The delta function fixes the magnitude of the photon wavevector:

$$\delta(\hbar ck - \hbar\omega) = \frac{1}{\hbar c}\delta\left(k - \frac{\omega}{c}\right).$$

Performing the integration over k, we obtain

$$\frac{dw_{\mathrm{sp},\alpha}}{d\Omega} = \frac{\omega^3}{2\pi\hbar c^3}|\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{d}_{12}|^2. \tag{2.121}$$

Each emitted photon carries energy $\hbar\omega$. The radiation intensity I_α, defined as the energy emitted per unit time and unit solid angle into polarisation α, is therefore

$$I_\alpha(\mathbf{k}) = \hbar\omega \frac{dw_{\mathrm{sp},\alpha}}{d\Omega} = \frac{\omega^4}{2\pi c^3} |\mathbf{e}_{\mathbf{k}\alpha} \cdot \mathbf{d}_{12}|^2. \tag{2.122}$$

This is the intensity of spontaneous electric-dipole radiation into a specified direction and polarisation.

Angular distribution of dipole radiation

For each wavevector $\mathbf{k}$, there are two independent transverse polarisations,

$$\mathbf{e}_{\mathbf{k}1}, \qquad \mathbf{e}_{\mathbf{k}2},$$

both perpendicular to $\mathbf{k}$.

The total intensity emitted in the direction $\mathbf{k}$ is obtained by summing over these polarisations:

$$I(\mathbf{k}) = \frac{\omega^4}{2\pi c^3} (|\mathbf{e}_{\mathbf{k}1} \cdot \mathbf{d}_{12}|^2 + |\mathbf{e}_{\mathbf{k}2} \cdot \mathbf{d}_{12}|^2).$$

The three vectors

$$\mathbf{e}_{\mathbf{k}1}, \quad \mathbf{e}_{\mathbf{k}2}, \quad \mathbf{n} = \frac{\mathbf{k}}{k}$$

form an orthonormal basis. Consequently,

$$|\mathbf{e}_{\mathbf{k}1} \cdot \mathbf{d}_{12}|^2 + |\mathbf{e}_{\mathbf{k}2} \cdot \mathbf{d}_{12}|^2 = |\mathbf{d}_{12}|^2 - |\mathbf{n} \cdot \mathbf{d}_{12}|^2.$$

Thus,

$$I(\mathbf{k}) = \frac{\omega^4}{2\pi c^3} (|\mathbf{d}_{12}|^2 - |\mathbf{n} \cdot \mathbf{d}_{12}|^2). \tag{2.123}$$

This expression is valid also when the transition dipole moment is complex.

When $\mathbf{d}_{12}$ is real up to an overall phase, let θ denote the angle between its direction and $\mathbf{k}$. Then

$$|\mathbf{n} \cdot \mathbf{d}_{12}|^2 = |\mathbf{d}_{12}|^2 \cos^2\theta,$$

and

$$I(\theta) = \frac{\omega^4}{2\pi c^3} |\mathbf{d}_{12}|^2 \sin^2\theta. \tag{2.124}$$

The radiation is maximal perpendicular to the transition dipole moment and vanishes along its direction.

To obtain the total emitted power, integrate over the solid angle. Since

$$\int d\Omega \sin^2\theta = 2\pi \int_0^\pi \sin^3\theta \, d\theta = \frac{8\pi}{3},$$

we find

$$I_{\mathrm{sp}} = \int d\Omega \, I(\mathbf{k}) = \frac{4\omega^4}{3c^3} |\mathbf{d}_{12}|^2. \tag{2.125}$$

The same result follows from Eq. (2.123) for a complex transition dipole moment.

Dividing the emitted power by the energy $\hbar\omega$ of one photon gives the total spontaneous transition rate from $|2\rangle$ to $|1\rangle$:

$$w_{2\to1}^{\mathrm{sp}} = \frac{4\omega^3}{3\hbar c^3}|\mathbf{d}_{12}|^2. \tag{2.126}$$

This expression will be used in Section 2.11 to calculate the lifetime of an excited atomic state.

Selection rules for electric-dipole transitions

The transition rate (2.126) is proportional to $|\mathbf{d}_{12}|^2$. An electric-dipole transition is therefore possible only if

$$\mathbf{d}_{12} = e\langle 1|\mathbf{r}|2\rangle \neq 0.$$

The conditions imposed on the initial and final atomic states by this matrix element are called the *electric-dipole selection rules*.

We derive them for an electron moving in a central potential $U(r)$.

The stationary wavefunctions can be written as

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\varphi), \tag{2.127}$$

where n labels the radial state, l is the orbital angular-momentum quantum number, and m is its projection quantum number.

For the transition under consideration, write

$$|1\rangle = |n,l,m\rangle, \qquad |2\rangle = |n',l',m'\rangle.$$

We must determine the conditions under which the matrix elements of the coordinate components x, y, and z are non-zero.

Linear polarisation

First consider radiation with its electric-field polarisation along the z-axis. The corresponding coordinate matrix element is

$$z_{12} = \langle n,l,m|z|n',l',m'\rangle.$$

Since $z = r\cos\theta$, we have

$$\begin{aligned} z_{12} = \quad & \int_0^\infty r^3\, dr\, R_{nl}^*(r)R_{n'l'}(r) \\ & \times \int d\Omega\, Y_{lm}^*(\theta,\varphi)\cos\theta\, Y_{l'm'}(\theta,\varphi). \end{aligned} \tag{2.128}$$

The radial and angular integrations are separated.

Using

$$Y_{lm}(\theta,\varphi) \propto e^{im\varphi},$$

the integration over φ contains

$$\int_0^{2\pi} e^{i(m'-m)\varphi}\, d\varphi = 2\pi\delta_{mm'}.$$

Thus the matrix element can be non-zero only if

$$m' = m.$$

To determine the allowed values of l', we use the spherical-harmonic identity

$$\cos\theta\, Y_{l'm'} = \sqrt{\frac{(l'+1)^2 - m'^2}{(2l'+1)(2l'+3)}}\, Y_{l'+1,m'} + \sqrt{\frac{l'^2 - m'^2}{(2l'-1)(2l'+1)}}\, Y_{l'-1,m'}. \tag{2.129}$$

The spherical harmonics are orthonormal:

$$\int d\Omega\, Y_{lm}^* Y_{l'm'} = \delta_{ll'}\delta_{mm'}.$$

Therefore the angular integral in Eq. (2.128) vanishes unless

$$l = l' + 1 \qquad \text{or} \qquad l = l' - 1.$$

For this linearly polarised electric-dipole transition, we have obtained

$$\Delta m = 0, \qquad \Delta l = \pm 1. \tag{2.130}$$

Here

$$\Delta m = m - m', \qquad \Delta l = l - l'$$

denote the changes in the atomic quantum numbers from the initial state $|2\rangle$ to the final state $|1\rangle$.

Circular polarisation

We now choose the direction of photon propagation along the z-axis,

$$\mathbf{k} = k\mathbf{e}_z.$$

The two linear-polarisation vectors can be chosen along the x- and y-axes. The corresponding circular-polarisation vectors are

$$\mathbf{e}_{\mathbf{k},\pm} = \frac{1}{\sqrt{2}}\left(\mathbf{e}_x \pm i\mathbf{e}_y\right). \tag{2.131}$$

For complex polarisation vectors, the coefficient of the photon creation operator in the vector-potential expansion contains $\mathbf{e}_{\mathbf{k},\pm}^*$. Thus the matrix element for photon emission contains

$$\mathbf{e}_{\mathbf{k},\pm}^* \cdot \mathbf{r} = \frac{x \mp iy}{\sqrt{2}}.$$

Using spherical coordinates,

$$x \pm iy = r\sin\theta\, e^{\pm i\varphi},$$

we obtain

$$\mathbf{e}_{\mathbf{k},\pm}^* \cdot \mathbf{r} = \frac{r}{\sqrt{2}}\sin\theta\, e^{\mp i\varphi}. \tag{2.132}$$

The angular part of the emission matrix element therefore contains

$$\int d\Omega\, Y_{lm}^*(\theta,\varphi)\sin\theta\, e^{\mp i\varphi} Y_{l'm'}(\theta,\varphi).$$

The integration over φ gives

$$\int_0^{2\pi} e^{-im\varphi}\, e^{\mp i\varphi} e^{im'\varphi}\, d\varphi = 2\pi\delta_{m,m'\mp 1}.$$

Consequently,

$$\Delta m = \mp 1 \tag{2.133}$$

for emission into the respective polarisation modes $\mathbf{e}_{\mathbf{k},\pm}$.

The restriction on l follows from the angular properties of the spherical harmonics. For example,

$$\sin\theta\, e^{i\varphi} Y_{l'm'} = -\sqrt{\frac{(l'+m'+1)(l'+m'+2)}{(2l'+1)(2l'+3)}}\, Y_{l'+1,m'+1} + \sqrt{\frac{(l'-m')(l'-m'-1)}{(2l'-1)(2l'+1)}}\, Y_{l'-1,m'+1}. \tag{2.134}$$

The corresponding identity for $\sin\theta\, e^{-i\varphi}$ contains only spherical harmonics with orbital quantum numbers $l'+1$ and $l'-1$, and magnetic quantum number $m'-1$.

By orthogonality, the circular-polarisation matrix elements therefore vanish unless

$$\Delta l = \pm 1.$$

Combining the results for linear and circular polarisations, the electric-dipole selection rules are

$$\Delta l = \pm 1, \qquad \Delta m = 0, \pm 1. \tag{2.135}$$

These conditions follow from the angular dependence of the coordinate operator $\mathbf{r}$.

Physical meaning of the selection rules

The change in magnetic quantum number is related to conservation of the angular-momentum projection of the combined atom–field system.

For circularly polarised photons propagating along the quantisation axis z, the photon carries angular-momentum projection $+\hbar$ or $-\hbar$. The corresponding change in the atomic angular-momentum projection has the opposite sign during emission, as expressed by Eq. (2.133).

The restriction $\Delta l = \pm 1$ is also consistent with parity. For a central potential, an atomic state with orbital angular momentum l has parity $(-1)^l$. The dipole operator $\mathbf{r}$ changes sign under spatial inversion. Its matrix element can therefore be non-zero only between states of opposite parity.

These selection rules are **necessary, but not sufficient**, conditions for a non-zero dipole transition amplitude. Even when they are satisfied, the radial integral in Eq. (2.128) may vanish for particular atomic states.

Transitions satisfying the selection rules are called *electric-dipole allowed*. If the dipole matrix element vanishes, the transition cannot proceed through the electric-dipole interaction considered here. Other, weaker transition mechanisms may still be possible, but they are outside the present approximation.

We have thus obtained the spontaneous-emission rate and the restrictions on the atomic states that can be connected by an electric-dipole transition. In the next subsection we use the spontaneous transition rates to describe the decay and finite lifetime of excited atomic states.

2.11 Spontaneous decay and lifetime of excited states

In Section 2.10 we calculated the probability per unit time for spontaneous emission from an excited atomic state. This result shows that an excited state of the atomic Hamiltonian $\widehat{H}_{\mathrm{a}}$ is not generally stationary when the atom interacts with the quantised electromagnetic field.

An excited atom can emit a photon and make a transition to a state of lower energy. We now determine how the probability of finding the atom in its initial excited state changes with time.

Spontaneous decay rate

Consider an atom initially in an excited state $|\, n\rangle$, with energy E_n, while the electromagnetic field is in its vacuum state.

The atom can undergo spontaneous transitions to lower-energy states $|\, f\rangle$, emitting a photon of frequency

$$\omega_{nf} = \frac{E_n - E_f}{\hbar}, \qquad E_f < E_n.$$

In the electric-dipole approximation, Eq. (2.126) gives the spontaneous transition rate

$$w^{\mathrm{sp}}_{n\to f} = \frac{4\omega^3_{nf}}{3\hbar c^3} |\, \mathbf{d}_{fn} \,|^2, \qquad \mathbf{d}_{fn} = e\langle f \,|\, \mathbf{r} \,|\, n\rangle. \tag{2.136}$$

If several lower-energy states are accessible, the atom can decay through any of these transitions. Since the final atomic states are orthogonal, the corresponding transition probabilities add.

The total spontaneous decay rate of state $|\, n\rangle$ is therefore

$$\gamma_n = \sum_{E_f<E_n} w^{\mathrm{sp}}_{n\to f}. \tag{2.137}$$

The sum includes all lower-energy states connected to $|\, n\rangle$ by an allowed electric-dipole transition.

Decay of the excited-state population

Let $P_n(t)$ denote the probability that an atom prepared in state $|\, n\rangle$ at $t = 0$ has not yet decayed by time t.

We consider spontaneous decay in vacuum, in the regime where the emitted photons escape and their subsequent interaction with the atom can be neglected. The decay rate γ_n can then be treated as time-independent.

During a short interval dt, the probability that an atom still in state $|\, n\rangle$ decays is $\gamma_n\, dt$. Consequently, the decrease of $P_n(t)$ satisfies

$$P_n(t + dt) - P_n(t) = -\gamma_n P_n(t)\, dt.$$

Taking the limit $dt \to 0$, we obtain

$$\frac{dP_n(t)}{dt} = -\gamma_n P_n(t). \tag{2.138}$$

With the initial condition $P_n(0) = 1$, integration gives

$$P_n(t) = e^{-\gamma_n t}. \tag{2.139}$$

Thus the probability of finding the atom in its initial excited state decreases exponentially.

The probability that the decay occurs between t and $t + dt$ is

$$-P_n{}'(t)\, dt = \gamma_n e^{-\gamma_n t}\, dt.$$

The mean time before decay is therefore

$$\tau_n = \int_0^\infty t\ \gamma_n e^{-\gamma_n t}\, dt = \frac{1}{\gamma_n}.$$

Hence,

$$\tau_n = \frac{1}{\gamma_n}. \tag{2.140}$$

The quantity τ_n is called the **lifetime of the excited state**. At $t = \tau_n$, the survival probability has decreased to $1/e$ of its initial value.

Quasistationary atomic states

Without the interaction with the electromagnetic field, an atomic energy eigenstate evolves according to

$$| n, t\rangle = e^{-iE_n t/\hbar} | n\rangle.$$

Its occupation probability remains constant.

When spontaneous emission is possible, we must instead consider the complete atom–field system. Its state can be written as

$$| \Psi(t)\rangle = a_n(t) | n\rangle | 0\rangle + \sum_{f,\mathbf{k},\alpha} a_{f,\mathbf{k}\alpha}(t) | f\rangle | 1_{\mathbf{k}\alpha}\rangle + \cdots. \tag{2.141}$$

Here $| 0\rangle$ is the photon vacuum, while $| 1_{\mathbf{k}\alpha}\rangle$ represents a field state containing one photon in mode $(\mathbf{k}, \alpha)$. The first term describes the atom remaining in its initial excited state with no emitted photons. The other terms describe states reached after photon emission; the ellipsis allows for subsequent radiative transitions.

The initial conditions are

$$a_n(0) = 1, \qquad a_{f,\mathbf{k}\alpha}(0) = 0.$$

Since the states appearing in Eq. (2.141) are mutually orthogonal, the probability that no decay has occurred is

$$P_n(t) = | a_n(t) |^2.$$

Combining this relation with Eq. (2.139), we find

$$| a_n(t) | = e^{-\gamma_n t/2}.$$

Retaining the phase evolution associated with the atomic energy E_n, the amplitude in the weak-coupling decay approximation takes the form

$$a_n(t) = e^{-iE_n t/\hbar} e^{-\gamma_n t/2}. \tag{2.142}$$

The factor $1/2$ in the exponent is necessary because the probability is the squared modulus of the amplitude.

An excited atomic state with a finite lifetime is called a *quasistationary state*. Its amplitude decreases in time, unlike that of a stationary state of the uncoupled atomic Hamiltonian.

The exponential in Eq. (2.142) can be written as

$$a_n(t) = \exp\left[-\frac{i}{\hbar}\left(E_n - \frac{i\hbar\gamma_n}{2}\right)t\right].$$

Thus the effect of spontaneous decay can formally be represented by replacing the real atomic energy with a complex quantity,

$$E_n \to E_n - \frac{i\hbar\gamma_n}{2}. \tag{2.143}$$

The imaginary part describes the decay of the amplitude. This complex energy is an effective description of the quasistationary state; it is not an eigenvalue of the full Hermitian Hamiltonian of the atom–field system.

The total probability remains conserved. As the probability $|\, a_n(t)\,|^2$ decreases, probability is transferred to the states containing emitted photons in Eq. (2.141).

Lifetime of a two-level atom

For an atom with only two relevant levels, $E_2 > E_1$, and one allowed radiative transition, Eq. (2.137) reduces to

$$\gamma_2 = w_{2\to 1}^{\mathrm{sp}}.$$

Using Eq. (2.126), its lifetime is

$$\tau_2 = \frac{3\hbar c^3}{4\omega^3\,|\,\mathbf{d}_{12}\,|^2}, \qquad \omega = \frac{E_2 - E_1}{\hbar}. \tag{2.144}$$

Allowed optical electric-dipole transitions commonly have lifetimes of the order of 10^{-8} s, although the actual value depends on the transition frequency and dipole matrix element.

If the electric-dipole matrix element vanishes, the corresponding decay rate in Eq. (2.136) is zero. The state may nevertheless decay through weaker processes not included in the electric-dipole approximation. Such states can have much longer lifetimes and are called *metastable states*.

For the atomic ground state, there is no lower-energy state available for spontaneous emission. Its spontaneous decay rate is therefore zero.

We have established that spontaneous emission gives excited atomic states finite lifetimes and replaces their stationary amplitudes by exponentially decaying amplitudes. In the next subsection, we shall show how this decay leads to the natural width of atomic spectral lines.

2.12 Natural linewidth

In Section 2.11 we showed that spontaneous emission gives an excited atomic state a finite lifetime. The probability amplitude of a quasistationary state |n⟩ has the time dependence

$$a_n(t) = e^{-iE_n t/\hbar} e^{-\gamma_n t/2},$$

where γ_n is the total decay rate of the state and $\tau_n = 1/\gamma_n$ is its lifetime.

We now determine how this exponential decay affects the spectral distribution of the emitted radiation.

From the energy-conservation delta function to a finite spectral width

Recall that Fermi's golden rule contains the factor

$$\delta\left(E_f^{(0)} - E_i^{(0)}\right),$$

which expresses energy conservation for transitions between stationary states of the unperturbed Hamiltonian.

Consider the emission of a photon of frequency ω in an atomic transition from an initial level i, with energy E_i, to a final level f, with energy $E_f < E_i$.

The energy difference between the final and initial states of the combined atom–field system is

$$\Delta E = E_f + \hbar\omega - E_i.$$

Define the atomic transition frequency

$$\omega_0 = \frac{E_i - E_f}{\hbar}.$$

Then

$$\Delta E = \hbar(\omega - \omega_0).$$

For strictly stationary atomic states, the golden-rule expression contains $\delta(\Delta E)$. Consequently, emission is possible only at $\omega = \omega_0$.

To account for the finite lifetimes of the atomic levels, recall the Fourier representation of the delta function:

$$\delta(\Delta E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{i\Delta E t/\hbar}\, dt. \tag{2.145}$$

Equivalently,

$$\delta(\Delta E) = \frac{1}{\pi\hbar}\int_{0}^{\infty} \cos(\Delta E t/\hbar)\, dt.$$

These expressions are understood in the sense of distributions.

Effect of finite lifetimes

If the initial and final atomic levels have decay rates γ_i and γ_f, their quasistationary amplitudes contain the factors

$$e^{-\gamma_i t/2}, \qquad e^{-\gamma_f t/2}.$$

In the weak-coupling exponential-decay approximation, the transition amplitude therefore acquires the damping factor

$$e^{-(\gamma_i+\gamma_f)t/2}.$$

Introduce

$$\gamma = \gamma_i + \gamma_f.$$

The delta function in the transition probability is then replaced by

$$\delta_\gamma(\Delta E) = \frac{1}{\pi\hbar}\int_{0}^{\infty} e^{-\gamma t/2}\cos(\Delta E t/\hbar)\, dt. \tag{2.146}$$

Unlike Eq. (2.145), this integral converges for $\gamma > 0$.

To evaluate it, write

$$\delta_\gamma(\Delta E) = \frac{1}{\pi\hbar}\mathrm{Re}\int_{0}^{\infty} e^{-(\gamma/2 - i\Delta E/\hbar)t}\, dt.$$

Using

$$\int_{0}^{\infty} e^{-zt}\, dt = \frac{1}{z}, \qquad \mathrm{Re}\, z > 0,$$

we obtain

$$\delta_\gamma(\Delta E) = \frac{1}{\pi\hbar}\,\mathrm{Re}\frac{1}{\gamma/2 - i\Delta E/\hbar}.$$

Multiplying the numerator and denominator by the complex conjugate of the denominator gives

$$\delta_\gamma(\Delta E) = \frac{1}{\pi\hbar}\frac{\gamma/2}{(\Delta E/\hbar)^2 + (\gamma/2)^2}. \tag{2.147}$$

Thus the infinitely narrow delta function is replaced by a function with a finite maximum and finite width.

Lorentzian spectral profile

Since $\Delta E = \hbar(\omega - \omega_0)$, Eq. (2.147) can be written as

$$\delta_\gamma(\Delta E) = \frac{1}{\hbar}L_\gamma(\omega),$$

where

$$L_\gamma(\omega) = \frac{1}{\pi}\frac{\gamma/2}{(\omega - \omega_0)^2 + (\gamma/2)^2}. \tag{2.148}$$

This function is called the *Lorentzian spectral profile*.

It has its maximum at the atomic transition frequency $\omega = \omega_0$:

$$L_\gamma(\omega_0) = \frac{2}{\pi\gamma}.$$

The profile is normalised over the real frequency axis,

$$\int_{-\infty}^{\infty} L_\gamma\,(\omega)\,d\omega = 1.$$

For a narrow atomic line, $\gamma \ll \omega_0$, extending the physical positive-frequency range to the entire real axis introduces a negligible correction.

To determine the linewidth, we find the frequencies at which the profile decreases to half its maximum:

$$L_\gamma(\omega) = \frac{1}{2}L_\gamma(\omega_0).$$

Substitution of Eq. (2.148) gives

$$(\omega - \omega_0)^2 = \frac{\gamma^2}{4}.$$

The two solutions are

$$\omega_\pm = \omega_0 \pm \frac{\gamma}{2}.$$

Their difference gives the **full width at half maximum** (FWHM):

$$\Delta\omega = (\omega_0 + \gamma/2) - (\omega_0 - \gamma/2) = \gamma.$$

Consequently,

$$\Delta\omega = \gamma_i + \gamma_f, \qquad \Delta E_{\text{line}} = \hbar\big(\gamma_i + \gamma_f\big). \tag{2.149}$$

The finite width arising from the finite lifetimes of the atomic states is called the *natural linewidth*.

Natural linewidth of a two-level atom

Consider an isolated two-level atom whose excited state $|2\rangle$ decays spontaneously to its ground state $|1\rangle$.

Since the ground state cannot decay by spontaneous emission,

$$\gamma_1 = 0.$$

The excited-state decay rate is

$$\gamma_2 = w_{2\to1}^{\mathrm{sp}}.$$

Using the dipole-transition rate obtained in Eq. (2.126),

$$\gamma_2 = \frac{4\omega_0^3}{3\hbar c^3}|\mathbf{d}_{12}|^2.$$

Therefore the natural linewidth is

$$\Delta\omega = \gamma_2 = \frac{1}{\tau_2}.$$

In energy units,

$$\Delta E_{\mathrm{line}} = \frac{\hbar}{\tau_2}.$$

The relationship between lifetime and linewidth can therefore be written as

$$\Delta\omega = \frac{1}{\tau_2}, \qquad \Delta E_{\mathrm{line}} = \frac{\hbar}{\tau_2}. \tag{2.150}$$

The shorter the lifetime of the excited state, the broader the corresponding spectral line.

The Lorentzian profile describes the natural linewidth of an isolated atom in the exponential-decay approximation. In a gas or condensed medium, collisions, atomic motion and other interactions can produce additional broadening.

The central result is that **spontaneous emission makes excited atomic states quasistationary, and their finite lifetimes produce a finite spectral width**. In particular, the Lorentzian profile follows directly from the Fourier integral of the exponentially decaying transition amplitude.

2.13 Quantum theory of dispersion

The refractive index of a medium generally depends on the frequency of the electromagnetic radiation propagating through it. This phenomenon is known as *dispersion of light*.

When an electromagnetic wave acts on an atom, its electric field induces an electric dipole moment. The dipole moments of the atoms produce the macroscopic polarisation of the medium, which determines its dielectric permittivity and, consequently, its refractive index.

The quantum theory of dispersion therefore requires us to calculate the electric dipole moment induced in an atom by a monochromatic electromagnetic field.

Polarisation of the medium and atomic polarizability

We consider a dilute medium consisting of N identical atoms in a volume V. The polarisation of the medium is the mean electric dipole moment per unit volume,

$$\mathbf{P} = \frac{N}{V}\langle \hat{\mathbf{d}} \rangle,$$

where $\langle \hat{\mathbf{d}} \rangle$ denotes the mean electric dipole moment of an atom. Throughout this section, we consider its field-induced contribution, oscillating at the frequency ω of the incident radiation.

In the linear-response approximation, the polarisation is proportional to the electric field. In general, this relation is tensorial:

$$P_\mu = \sum_\nu \alpha_{\mu\nu}(\omega) E_\nu,$$

where $\alpha_{\mu\nu}(\omega)$ is the electric susceptibility tensor of the medium and $\mu, \nu = x, y, z$ denote Cartesian components.

Similarly, the response of an individual atom is characterised by its *atomic polarizability tensor* $\beta_{\mu\nu}(\omega)$, defined by

$$\langle \hat{d}_\mu \rangle = \sum_\nu \beta_{\mu\nu}(\omega) E_\nu.$$

These relations describe the response at the frequency ω.

For a dilute medium, the interaction between neighbouring atoms can be neglected, and each atom experiences approximately the same electric field as the macroscopic field. The total polarisation is then obtained by adding their individual dipole moments. Consequently,

$$\alpha_{\mu\nu}(\omega) = \frac{N}{V}\beta_{\mu\nu}(\omega). \tag{2.151}$$

Here $\beta_{\mu\nu}$ is the polarizability of a representative atom. If the atoms have different orientations or occupy different atomic states, the tensor on the right-hand side must be understood as the corresponding average over the atoms in the medium. Equation (2.151) neglects corrections associated with the local electric field and interatomic interactions.

The connection with the refractive index follows from macroscopic electrodynamics. In Gaussian units, the electric displacement field satisfies

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}.$$

For an isotropic medium, this relation takes the scalar form

$$\mathbf{D} = \varepsilon(\omega)\mathbf{E}, \qquad \mathbf{P} = \alpha(\omega)\mathbf{E},$$

where $\varepsilon(\omega)$ is the dielectric permittivity and $\alpha(\omega)$ is the scalar susceptibility.

Therefore,

$$\varepsilon(\omega) = 1 + 4\pi\alpha(\omega).$$

For a non-magnetic medium, the refractive index $n_\mathrm{r}(\omega)$ satisfies

$$n_\mathrm{r}^2(\omega) = \varepsilon(\omega).$$

Thus, for the dilute isotropic medium considered here,

$$n_\mathrm{r}^2(\omega) = 1 + 4\pi\frac{N}{V}\beta(\omega). \tag{2.152}$$

The scalar polarizability $\beta(\omega)$ will be obtained below from the appropriate diagonal components of the atomic polarizability tensor.

Equation (2.152) shows that the problem of calculating the refractive index reduces to determining the response of an individual atom to the electromagnetic field.

Atomic dipole moment in a monochromatic electromagnetic field

For simplicity, we consider an atom with one optical electron of mass m and charge $e < 0$. The electric dipole moment operator is

$$\hat{\mathbf{d}} = e\mathbf{r},$$

where $\mathbf{r}$ is the position of the electron relative to the nucleus.

The Hamiltonian of the isolated atom is

$$\hat{H}_{\mathrm{a}} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r}).$$

When monochromatic electromagnetic radiation of angular frequency ω acts on the atom, the electron interacts with the electromagnetic field.

We consider a prescribed incident field. The electromagnetic wave is therefore described classically, while the atomic states are treated quantum mechanically. This approximation is appropriate for a phase-coherent radiation field with a macroscopic number of photons occupying the relevant mode.

As in Section 2.9, we use the electric-dipole approximation. The wavelength is assumed to be much larger than the atomic dimensions, so the spatial variation of the electromagnetic field across the atom can be neglected.

The vector potential then depends only on time and has the form

$$\mathbf{A}(t) = \frac{1}{2}\left(\mathbf{A}_0 e^{-i\omega t} + \mathbf{A}_0^{\star} e^{i\omega t}\right),$$

where $\mathbf{A}_0$ is its complex amplitude.

The corresponding electric field is

$$\mathbf{E}(t) = \frac{1}{2}\left(\mathbf{E}_0 e^{-i\omega t} + \mathbf{E}_0^{\star} e^{i\omega t}\right). \tag{2.153}$$

Since $\mathbf{E} = -\dot{\mathbf{A}}/c$, the amplitudes are related by

$$\mathbf{E}_0 = \frac{i\omega}{c}\mathbf{A}_0.$$

The Hamiltonian of the atom in the presence of the electromagnetic field becomes

$$\hat{H}(t) = \hat{H}_{\mathrm{a}} + \hat{V}(t),$$

where the interaction Hamiltonian, to first order in the field, is

$$\hat{V}(t) = -\frac{e}{mc}\mathbf{A}(t)\cdot\hat{\mathbf{p}}. \tag{2.154}$$

The term proportional to $\mathbf{A}^2$ is omitted because we are interested in the atomic response linear in the applied electromagnetic field.

The field modifies the atomic wavefunction and, consequently, the expectation value of the electric dipole moment. We calculate this change using first-order time-dependent perturbation theory.

Let $|n\rangle$ be a stationary state of the isolated atom with energy E_n,

$$\hat{H}_{\mathrm{a}}|n\rangle = E_n|n\rangle.$$

In the absence of radiation, its time dependence is

$$\left|\Psi_n^{(0)}(t)\right\rangle = e^{-iE_n t/\hbar}|n\rangle.$$

When the electromagnetic field is applied, the wavefunction acquires first-order contributions from other stationary states of the atom:

$$|\Psi(t)\rangle = e^{-iE_n t/\hbar}|n\rangle + \sum_{k\neq n} C_{kn}^{(1)}(t) e^{-iE_k t/\hbar}|k\rangle. \tag{2.155}$$

The coefficients $C_{kn}^{(1)}(t)$ are the first-order amplitudes of the states $|k\rangle$, produced by the interaction with the electromagnetic field.

According to time-dependent perturbation theory,

$$C_{kn}^{(1)}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} V_{kn}(t') e^{i\omega_{kn}t'} dt', \tag{2.156}$$

where

$$V_{kn}(t) = \langle k|\hat{V}(t)|n\rangle, \qquad \omega_{kn} = \frac{E_k - E_n}{\hbar}.$$

We assume that the electromagnetic field is switched on adiabatically from the distant past. The integral is understood with a convergence factor, removed after integration. This procedure selects the response to the applied monochromatic field.

The interaction Hamiltonian (2.154) contains the electron momentum operator. Its matrix elements can be expressed through those of the coordinate operator using the commutator derived in Section 2.9,

$$\left[\hat{H}_{\mathrm{a}}, \mathbf{r}\right] = -\frac{i\hbar}{m}\hat{\mathbf{p}}.$$

Taking its matrix element between the stationary states $|k\rangle$ and $|n\rangle$, we obtain

$$\mathbf{p}_{kn} = im\omega_{kn}\mathbf{r}_{kn}, \tag{2.157}$$

where

$$\mathbf{p}_{kn} = \langle k|\hat{\mathbf{p}}|n\rangle, \qquad \mathbf{r}_{kn} = \langle k|\mathbf{r}|n\rangle.$$

Using this relation and the expression for the vector potential, the interaction matrix element becomes

$$V_{kn}(t) = -\frac{e\omega_{kn}}{2\omega}\left[(\mathbf{E}_0 \cdot \mathbf{r}_{kn})e^{-i\omega t} - (\mathbf{E}_0^{\star} \cdot \mathbf{r}_{kn})e^{i\omega t}\right].$$

The two terms originate from the two harmonic components of the real electromagnetic field.

Substituting this result into Eq. (2.156) and integrating over time gives

$$C_{kn}^{(1)}(t) = \frac{e\omega_{kn}}{2\hbar\omega}\left(\frac{\mathbf{E}_0 \cdot \mathbf{r}_{kn}}{\omega_{kn} - \omega} e^{i(\omega_{kn}-\omega)t} - \frac{\mathbf{E}_0^{\star} \cdot \mathbf{r}_{kn}}{\omega_{kn} + \omega} e^{i(\omega_{kn}+\omega)t}\right). \tag{2.158}$$

The denominators $\omega_{kn} - \omega$ and $\omega_{kn} + \omega$ arise directly from the time integration. At this stage, we assume that the frequency of the electromagnetic wave is sufficiently far from the atomic resonance frequencies for first-order perturbation theory to be applicable.

We can now calculate the mean electric dipole moment of the atom using the perturbed wavefunction (2.155).

Its expectation value is

$$e\langle\Psi(t)|\mathbf{r}|\Psi(t)\rangle.$$

After substituting Eq. (2.155), this expression contains a contribution independent of the electromagnetic field, terms linear in the coefficients $C_{kn}^{(1)}$, and terms quadratic in these coefficients.

The field-independent contribution does not enter the polarizability, while the quadratic terms are of second order in the perturbation. Retaining only the field-induced contribution linear in the electromagnetic field, we obtain

$$\langle \hat{\mathbf{d}} \rangle(t) = e \sum_{k \neq n} \left[\mathbf{r}_{nk} C_{kn}^{(1)}(t) e^{-i\omega_{kn} t} + \text{c. c.} \right]. \tag{2.159}$$

Here c.c. denotes the complex conjugate of the preceding term.

After substituting the amplitudes (2.158), the factors involving the atomic transition frequencies cancel in the time dependence. The remaining terms oscillate with frequency ω, the frequency of the incident electromagnetic wave.

The dipole moment induced by the electromagnetic field therefore has the same frequency as the applied field. Its dependence on the field amplitude determines the atomic polarizability.

Quantum-mechanical atomic polarizability

As introduced at the beginning of this section, the atomic polarizability is generally a tensor. In terms of the complex amplitude $\mathbf{E}_0$, the mean dipole moment can be written as

$$\langle \hat{d}_\mu \rangle(t) = \text{Re} \left[e^{-i\omega t} \sum_\nu \beta_{\mu\nu}(\omega) E_{0,\nu} \right]. \tag{2.160}$$

Substituting Eq. (2.158) into Eq. (2.159), and comparing the result with Eq. (2.160), gives the atomic polarizability tensor:

$$\beta_{\mu\nu}(\omega) = \frac{e^2}{\hbar\omega} \sum_{k \neq n} \omega_{kn} \left(\frac{r_{nk}^\mu r_{kn}^\nu}{\omega_{kn} - \omega} - \frac{r_{kn}^\mu r_{nk}^\nu}{\omega_{kn} + \omega} \right).$$

Here $r_{kn}^\mu = \langle k | r_\mu | n \rangle$.

The components of the polarizability tensor are therefore expressed in terms of the atomic transition frequencies and coordinate matrix elements.

A particularly simple form is obtained in a reference frame whose coordinate axes coincide with the principal axes of the polarizability tensor, for the case in which the tensor is diagonal in this frame. Its off-diagonal components then vanish, and the response along each principal axis is characterised by the corresponding diagonal component.

For the x-axis, the expression becomes

$$\beta_{xx}(\omega) = \frac{e^2}{\hbar\omega} \sum_{k \neq n} \omega_{kn} |x_{kn}|^2 \left(\frac{1}{\omega_{kn} - \omega} - \frac{1}{\omega_{kn} + \omega} \right), \tag{2.161}$$

where

$$x_{kn} = \langle k | x | n \rangle.$$

The two fractions can be combined using

$$\frac{1}{\omega_{kn} - \omega} - \frac{1}{\omega_{kn} + \omega} = \frac{2\omega}{\omega_{kn}^2 - \omega^2}.$$

Consequently, the polarizability along the x-axis is

$$\beta_{xx}(\omega) = \frac{2e^2}{\hbar} \sum_{k \neq n} \frac{\omega_{kn} |x_{kn}|^2}{\omega_{kn}^2 - \omega^2}. \tag{2.162}$$

Analogous expressions are obtained for β_{yy} and β_{zz} by replacing the x-coordinate matrix elements by those of y and z, respectively.

We have thus expressed the atomic polarizability through the stationary energy levels and wavefunctions of the isolated atom.

Oscillator strength and refractive index

The structure of Eq. (2.162) can be understood by comparing it with the classical theory of dispersion.

In the classical model, a bound optical electron of mass m and charge e is represented by a harmonic oscillator with natural frequency Ω. Under the action of an external electric field, its equation of motion is

$$m\ddot{x} + m\Omega^2 x = eE(t).$$

For a monochromatic electric field,

$$E(t) = \mathrm{Re}\left[E_0 e^{-i\omega t}\right],$$

the stationary response has the same frequency,

$$x(t) = \mathrm{Re}\left[x_0 e^{-i\omega t}\right].$$

Substitution into the equation of motion gives

$$m(\Omega^2 - \omega^2)x_0 = eE_0,$$

and therefore

$$x_0 = \frac{eE_0}{m(\Omega^2 - \omega^2)}.$$

The amplitude of the induced electric dipole moment is $d_0 = ex_0$. Its ratio to the amplitude of the electric field gives the classical oscillator polarizability,

$$\beta_{\mathrm{osc}}(\omega) = \frac{e^2}{m(\Omega^2 - \omega^2)}.$$

In the classical theory of dispersion, an atom is represented by a system of optical electrons with different natural frequencies. Electrons having the same frequency contribute equally to the polarizability.

If N_j electrons have the natural frequency Ω_j, their contributions add, giving

$$\beta_{\mathrm{cl}}(\omega) = \frac{e^2}{m}\sum_j \frac{N_j}{\Omega_j^2 - \omega^2}.$$

The coefficient N_j is called the *classical oscillator strength* associated with the resonance at frequency Ω_j. In this model, it represents the number of optical electrons contributing to that resonance and is therefore a non-negative integer.

The quantum-mechanical expression (2.162) can be written in an analogous form:

$$\beta_{xx}(\omega) = \frac{e^2}{m}\sum_{k\neq n} \frac{(2m\omega_{kn}/\hbar)|x_{kn}|^2}{\omega_{kn}^2 - \omega^2}.$$

The classical oscillator frequencies are now replaced by the atomic transition frequencies,

$$\omega_{kn} = \frac{E_k - E_n}{\hbar},$$

while the coefficients of the individual terms are determined by the corresponding coordinate matrix elements.

By comparison with the classical expression, the quantum-mechanical oscillator strength is defined as

$$f_{kn} = \frac{2m\omega_{kn}}{\hbar}|x_{kn}|^2. \tag{2.163}$$

The oscillator strength is dimensionless. It characterises the contribution of a particular atomic transition to the optical polarizability.

Unlike the classical oscillator strength, f_{kn} need not be an integer. Its value is determined by the energy difference between the atomic states and the corresponding coordinate matrix element.

Furthermore, the sign of f_{kn} depends on the sign of ω_{kn}. When the atom initially occupies its ground state, all transition frequencies to higher-energy levels are positive, and therefore $f_{kn} \geq 0$. If the atom initially occupies an excited state, transitions to lower-energy levels have negative oscillator strengths.

The quantum-mechanical oscillator strength thus plays the same role as the number of resonant optical electrons in the classical dispersion formula, but its value follows from the quantum states of the atom rather than from counting classical oscillators.

Using the definition (2.163), the atomic polarizability becomes

$$\beta_{xx}(\omega) = \frac{e^2}{m} \sum_{k \neq n} \frac{f_{kn}}{\omega_{kn}^2 - \omega^2}. \tag{2.164}$$

For the dilute isotropic medium considered at the beginning of this section, the atomic polarizability entering Eq. (2.152) is the same for all spatial directions. Hence,

$$\beta(\omega) = \beta_{xx}(\omega) = \beta_{yy}(\omega) = \beta_{zz}(\omega).$$

Substituting Eq. (2.164) into Eq. (2.152), we finally obtain

$$n_{\mathrm{r}}^2(\omega) = 1 + \frac{4\pi e^2 N}{mV} \sum_{k \neq n} \frac{f_{kn}}{\omega_{kn}^2 - \omega^2}. \tag{2.165}$$

This is the quantum-mechanical expression for the dispersion of light in a dilute isotropic medium.

It has the same mathematical form as the classical dispersion formula. In quantum mechanics, however, the frequencies are determined by differences between atomic energy levels, while the oscillator strengths are calculated from the corresponding coordinate matrix elements.

The expression was obtained in first-order perturbation theory, assuming stationary atomic states. It is therefore applicable away from the atomic resonance frequencies, where the denominators in Eq. (2.165) do not vanish. Near resonance, the finite lifetimes of the atomic states must be taken into account.

2.14 Photoelectric effect

In the preceding sections, we considered the absorption and emission of photons during transitions between discrete atomic energy levels. When the energy of an absorbed photon is sufficiently large, the electron can leave the atom and enter a state of the continuous energy spectrum. This process is called the *photoelectric effect*, or *photoionisation*.

We consider an atom initially in a bound state $|\,1\rangle$, with energy $E_1 = -I$, where $I > 0$ is the ionisation energy. After absorbing a photon of energy $\hbar\omega$, the electron enters a continuum state with momentum $\mathbf{p}$ and kinetic energy $p^2/(2m)$.

The photoelectric effect is therefore a quantum transition from a bound atomic state to a continuum state. Its probability can be calculated using the one-photon absorption theory developed in Section 2.7.

Transition probability and photoionisation cross section

The incident electromagnetic field contains one photon with frequency ω, wavevector $\mathbf{k}$, and polarisation $\mathbf{e}_{\mathbf{k}\alpha}$, where

$$\omega = ck, \qquad \mathbf{e}_{\mathbf{k}\alpha} \cdot \mathbf{k} = 0.$$

In the photon-number representation, the initial field contains one photon in the mode specified above, while all other modes are empty. After absorption, the electron occupies a continuum state and the entire electromagnetic field is in its vacuum state. The initial and final states of the atom–field system are therefore

$$\begin{aligned} |i\rangle &= |1\rangle|0, \dots, 0, N_{\mathbf{k}\alpha} = 1, 0, \dots\rangle, \\ |f\rangle &= |\mathbf{p}\rangle|0, \dots, 0, 0, \dots\rangle. \end{aligned} \tag{2.166}$$

The state $|\,\mathbf{p}\rangle$ belongs to the continuous spectrum of the electron. Its wavefunction depends, in general, on the interaction between the electron and the residual ion. For sufficiently energetic photoelectrons, this interaction can be neglected in the first approximation, and the final wavefunction is represented by a plane wave,

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{2.167}$$

where V is the normalisation volume.

The initial and final energies of the combined system are

$$E_i^{(0)} = -I + E_0 + \hbar\omega, \qquad E_f^{(0)} = \frac{p^2}{2m} + E_0, \tag{2.168}$$

where E_0 is the vacuum energy of the electromagnetic field.

Energy conservation gives

$$\hbar\omega = I + \frac{p^2}{2m}. \tag{2.169}$$

This is Einstein's photoelectric equation: the energy of the absorbed photon is used to ionise the atom, while the remaining energy becomes the kinetic energy of the emitted electron. The threshold for photoionisation is therefore $\hbar\omega = I$.

The probability per unit time for a transition between the initial and final states follows from Fermi's golden rule,

$$w_{i\to f} = \frac{2\pi}{\hbar} \left|\langle f \mid \hat{V} \mid i\rangle\right|^2 \delta\left(E_f^{(0)} - E_i^{(0)}\right).$$

For one-photon absorption, the relevant interaction Hamiltonian is

$$\hat{V} = -\frac{e}{mc} \widehat{\mathbf{A}} \cdot \widehat{\mathbf{p}}.$$

The matrix element of this operator was calculated in Section 2.7. For the present transition, the resulting probability per unit time is

$$w_{i\to\mathbf{p}} = \frac{4\pi^2 e^2}{m^2 V \omega} \left|M_{\mathbf{p}}\right|^2 \delta\left(\frac{p^2}{2m} + I - \hbar\omega\right), \tag{2.170}$$

where

$$M_{\mathbf{p}} = \langle \mathbf{p} \mid e^{i\mathbf{k}\cdot\mathbf{r}} (\mathbf{e}_{\mathbf{k}\alpha} \cdot \widehat{\mathbf{p}}) \mid 1\rangle.$$

The delta function ensures energy conservation, while the matrix element $M_{\mathbf{p}}$ determines the probability of emission into a particular electron state.

The electron can be emitted with different momenta. Consequently, the total photoionisation rate is obtained by summing over all final electron states,

$$w = \sum_{\mathbf{p}} w_{i\to\mathbf{p}}.$$

The *photoionisation cross section* is defined as the total transition rate divided by the incident photon flux density j,

$$\sigma = \frac{w}{j}. \tag{2.171}$$

For one photon in the normalisation volume V, the photon number density is $1/V$, and hence $j = c/V$.

The sum over final electron momenta is replaced by an integral over the continuous spectrum,

$$\sum_{\mathbf{p}} \to \frac{V}{(2\pi\hbar)^3}\int d^3p.$$

In spherical momentum coordinates, $d^3p = p^2 dp\, d\Omega$. The differential photoionisation cross section therefore becomes

$$\frac{d\sigma}{d\Omega} = \frac{V}{c}\frac{V}{(2\pi\hbar)^3}\int_0^\infty p^2\, w_{i\to\mathbf{p}}\, dp. \tag{2.172}$$

This quantity describes the angular distribution of the emitted electrons. Its evaluation requires the atomic matrix element $M_{\mathbf{p}}$.

Photoionisation matrix element

To calculate the matrix element explicitly, we now take the initial bound state to be the hydrogenic $1s$ state,

$$\psi_1(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a},$$

where a is the Bohr radius for hydrogen.

The interaction matrix element is

$$M_{\mathbf{p}} = \langle \mathbf{p} \mid e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{p}}) \mid 1\rangle.$$

Using the Hermiticity of the momentum operator and the transversality condition $\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{k} = 0$, its complex conjugate can be written as

$$M_{\mathbf{p}}^\star = \langle 1 \mid e^{-i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k}\alpha}^\star\cdot\hat{\mathbf{p}}) \mid \mathbf{p}\rangle.$$

The final plane wave is an eigenfunction of the momentum operator,

$$\hat{\mathbf{p}} \mid \mathbf{p}\rangle = \mathbf{p} \mid \mathbf{p}\rangle.$$

Substitution of the two wavefunctions therefore gives

$$M_{\mathbf{p}}^\star = \frac{\mathbf{e}_{\mathbf{k}\alpha}^\star\cdot\mathbf{p}}{\sqrt{\pi a^3 V}}\int d^3r\, e^{-r/a} e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{2.173}$$

where

$$\mathbf{q} = \frac{\mathbf{p}}{\hbar} - \mathbf{k}.$$

The remaining integral is the Fourier transform of the radial function $e^{-r/a}$:

$$\int d^3r\, e^{-r/a} e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{8\pi a^3}{(1+a^2q^2)^2}.$$

Thus,

$$M_{\mathbf{p}}^{\star} = \frac{8\pi a^3}{\sqrt{\pi a^3 V}} \frac{\mathbf{e}_{\mathbf{k}\alpha}^{\star}\cdot\mathbf{p}}{(1+a^2q^2)^2}. \tag{2.174}$$

The matrix element depends on both the magnitude and direction of the emitted electron momentum. We can now determine the corresponding differential cross section.

Angular distribution of photoelectrons

Substitution of Eq. (2.174) into Eq. (2.170), followed by integration over the momentum magnitude in Eq. (2.172), gives

$$\frac{d\sigma}{d\Omega} = 32\frac{e^2a^3p}{mc\omega\hbar^3} \frac{|\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{p}|^2}{(1+a^2q^2)^4}, \tag{2.175}$$

where the magnitude of the electron momentum is fixed by energy conservation,

$$p = \sqrt{2m(\hbar\omega - I)}.$$

The angular dependence is contained in the scalar product with the photon polarisation and in the quantity q^2. From its definition,

$$q^2 = \frac{p^2}{\hbar^2} + k^2 - \frac{2pk}{\hbar}\cos\theta, \tag{2.176}$$

where θ is the angle between the photoelectron momentum $\mathbf{p}$ and the incident photon wavevector $\mathbf{k}$.

For the hydrogenic $1s$ state,

$$I = \frac{\hbar^2}{2ma^2}.$$

Using this relation, together with the photoelectric equation (2.169) and $k = \omega/c$, we obtain

$$1 + a^2q^2 = \frac{\hbar\omega}{I}\left(1 + \frac{\hbar\omega}{2mc^2} - \frac{v}{c}\cos\theta\right), \tag{2.177}$$

where $v = p/m$ is the electron speed.

In the nonrelativistic regime, $\hbar\omega \ll mc^2$, the term $\hbar\omega/(2mc^2)$ can be neglected in comparison with unity and the correction of order v/c.

For linearly polarised radiation, the coordinate axes are taken along the photon propagation direction and its electric-field polarisation: $\mathbf{k}$ along z, and $\mathbf{e}_{\mathbf{k}\alpha}$ along x. The scalar product in Eq. (2.175) then becomes

$$\mathbf{e}_{\mathbf{k}\alpha}\cdot\mathbf{p} = p\sin\theta\cos\varphi,$$

where φ is the azimuthal angle.

The differential cross section consequently takes the form

$$\frac{d\sigma}{d\Omega} = 64\frac{e^2a^2}{\hbar c}\left(\frac{ap}{\hbar}\right)^3\left(\frac{I}{\hbar\omega}\right)^5 \frac{\sin^2\theta\cos^2\varphi}{(1-v\cos\theta/c)^4}. \tag{2.178}$$

In the leading approximation $v/c \ll 1$, the angular distribution is proportional to

$$\sin^2\theta\cos^2\varphi.$$

Thus photoelectron emission is most probable along the polarisation direction of the incident wave. The differential cross section vanishes in the direction of photon propagation, $\theta = 0$.

The correction in the denominator of Eq. (2.178) increases the probability of emission into the forward hemisphere relative to the backward hemisphere.

Total photoionisation cross section

The total cross section follows from integration over the directions of the emitted electron,

$$\sigma = \int \frac{d\sigma}{d\Omega}\, d\Omega.$$

In the leading nonrelativistic approximation, $v/c \ll 1$, the denominator in Eq. (2.178) can be replaced by unity. The angular integral is then

$$\int_0^{2\pi} d\,\varphi \int_0^{\pi} \sin^3\theta\cos^2\varphi\, d\theta = \frac{4\pi}{3}.$$

Using

$$\left(\frac{ap}{\hbar}\right)^2 = \frac{\hbar\omega}{I} - 1,$$

the total photoionisation cross section becomes

$$\sigma(\omega) = \frac{256\pi}{3}\frac{e^2a^2}{\hbar c}\left(\frac{I}{\hbar\omega}\right)^5\left(\frac{\hbar\omega}{I} - 1\right)^{3/2}, \qquad \hbar\omega \geq I. \tag{2.179}$$

Below the ionisation threshold, $\hbar\omega < I$, the cross section vanishes.

At photon energies much larger than the ionisation energy, while remaining in the nonrelativistic regime,

$$\sigma(\omega) \propto \left(\frac{I}{\hbar\omega}\right)^{7/2}.$$

The photoionisation cross section therefore decreases rapidly with increasing photon energy.

The result (2.179) was obtained using the plane-wave approximation for the final electron state. It is consequently appropriate for sufficiently energetic photoelectrons, but not for a quantitative description close to the ionisation threshold.

Photoelectric absorption

Photoionisation removes photons from the incident electromagnetic beam and contributes to the attenuation of radiation propagating through matter.

For a dilute medium containing N atoms in a volume V, the photoelectric absorption coefficient, assuming one electron per atom contributes to the process, is

$$\kappa_{\mathrm{ph}}(\omega) = \frac{N}{V}\sigma(\omega). \tag{2.180}$$

The radiation intensity then decreases with the distance z according to

$$I_{\mathrm{rad}}(z) = I_{\mathrm{rad}}(0)e^{-\kappa_{\mathrm{ph}}z}.$$

The photoelectric effect is one mechanism of radiation absorption. Other interactions, including scattering processes, may also contribute to the attenuation of an electromagnetic beam.

Concluding remarks

The interaction of atoms with electromagnetic radiation is described by the same microscopic coupling between the electromagnetic field and the charged particles of the atom. Its consequences depend on the initial and final states involved in the interaction.

For transitions between discrete atomic energy levels, the absorption and emission of photons are governed by the corresponding transition matrix elements. These determine the transition probabilities, electric-dipole selection rules and spontaneous decay rates. The finite lifetimes of excited states give rise to the natural linewidth of spectral lines.

When an electromagnetic wave acts on an ensemble of atoms, the induced atomic dipole moments determine the polarisation of the medium. The quantum-mechanical calculation of the atomic polarizability establishes the connection between atomic transition frequencies, oscillator strengths and the refractive index of the medium.

When the photon energy exceeds the atomic ionisation energy, absorption can transfer an electron from a bound state to the continuous spectrum. The probability of this process is characterised by the photoionisation cross section, which also determines the photoelectric contribution to the attenuation of radiation.

Thus, the energy levels and transition matrix elements of atoms determine both their microscopic interaction with photons and the optical properties of matter.