§2.5 Interaction of an atom with E.M. field

Quantisation of free E.M. field.

We will start with classical picture where E.M. field is presented as a system of harmonic oscillator. Which next will be replased by quantum oscillators.

E.M. = system of quantum oscillators.

The goal is to find expressions for operators of Energy, $\vec{E}$, $\vec{H}$, $\vec{A}$ and calculating energy spectrum and wave functions.

No charges and currents, we may set $\varphi = 0$ → scalar potential.

while $\vec{A}(\vec{r}, t)$ is satisfies transversal condition:

$$\cancel{\text{div}}\ (\vec{\nabla} \cdot \vec{A}) = 0$$

El. and magnetic fields.

$$\begin{cases} \vec{E} = -\frac{1}{c}\dot{\vec{A}} \\ \vec{H} = \vec{\nabla} \times \vec{A} \end{cases} \Rightarrow$$

$$\begin{cases} \nabla \cdot E = \nabla \cdot H = 0 \\ -\frac{\partial H}{\partial t} = \nabla \times E \\ \mu \cdot \varepsilon_0 \frac{\partial E}{\partial t} = \nabla \times H \end{cases} \qquad c = \frac{1}{\sqrt{\mu \varepsilon_0}}$$

wave equation upon $\vec{A}$

and Maxwell's equations can be reduced to

$$\frac{1}{c^2}\ddot{\vec{A}} - \vec{\nabla}^2 \vec{A} = 0$$

Field confined in a box $V = L^3$

expand $\vec{A}$ in a Fourier series:

$$\vec{A} = \sqrt{\frac{4\pi c^2}{V}} \cdot \sum_{\vec{k}} \left(\vec{a}_{\vec{k}} e^{i\vec{k}\vec{r}} + \vec{a}^{*}_{\vec{k}} e^{-i\vec{k}\vec{r}} \right)$$

↙ just for math convenience

$\vec{A}^{*} = \vec{A}$

where the prefactor is introduced for convenience

$\vec{A}^* = \vec{A}$ (explicitly visible from the expansion)

$$\operatorname{div} \vec{A} = 0$$

$$\Downarrow$$

$$\sum_{\vec{k}} \left(i \underbrace{(\vec{k} \cdot \vec{a}_{\vec{k}})}_{\| \; 0} e^{i\vec{k}\vec{r}} + i \underbrace{(\vec{k}\, \vec{a}^*_{\vec{k}})}_{\| \; 0} e^{-i\vec{k}\vec{r}} \right) = 0$$

$$(\vec{k} \cdot \vec{a}_{\vec{k}}) = 0$$

and from the wave equation we get:

$$\frac{1}{c^2} \ddot{a}_{\vec{k}} + k^2 a_{\vec{k}} = 0 \quad \Rightarrow \quad \vec{a}_{\vec{k}} \sim e^{-i \underbrace{kc}_{\omega_k} t}$$

ω_k → frequency.

for $a^*_{\vec{k}} \sim e^{+i\omega_k t}$

(in general we should take a linear combination of harmonics with positive and negative ch ω_k. but the final result will stay the same if under $\sum_{\vec{k}}$ in the terms with $+\omega_k$ change sign in $\vec{k} \to -\vec{k}$ and to make simple relabeling).

Total Energy: $E = \frac{1}{8\pi} \int (E^2 + H^2)\, dr =$

$$\frac{1}{8\pi} \int \left(\frac{1}{c^2} \dot{A}^2 + [\vec{\nabla} \times \vec{A}]^2 \right) dr$$

Sub in $\vec{E}$ Fourier series for $\vec{A}$ and will use $\delta_{\vec{k}\vec{k}'} = \frac{1}{V}\int e^{i\vec{r}(\vec{k}-\vec{k}')}\,d\vec{r}$

$$\Downarrow$$

$$\underline{E} = \frac{c^2}{2}\sum_{\vec{k}}\left\{\frac{1}{c^2}\dot{\vec{a}}_{\vec{k}}\cdot\dot{\vec{a}}_{-k} + \frac{2}{c^2}\dot{\vec{a}}_{\vec{k}}\dot{\vec{a}}^{*}_{\vec{k}} + \frac{1}{c^2}\dot{\vec{a}}^{*}_{k}\dot{\vec{a}}^{*}_{-k} + \right.$$

$$+\left([\vec{k}\times\vec{a}_k]\cdot[\vec{k}\times\vec{a}_{-\vec{k}}]\right) + 2\left([\vec{k}\times\vec{a}_{\vec{k}}]\cdot[\vec{k}\times\vec{a}^{*}_{+\vec{k}}]\right)$$

$$\left. + \left([\vec{k}\,\vec{a}^{*}_{\vec{k}}]\cdot[\vec{k}\cdot\vec{a}^{*}_{-\vec{k}}]\right)\right\}$$

① = -④
③ = -⑥
② = ⑤

Using $\dot{a}_k = -i\omega_k a_k$

$\dot{a}^{*}_k = i\omega_k a^{*}_k$ and rewriting terms with vector products as:

$$\cancel{\left([\vec{k}\times\vec{a}_k]\cdot[\vec{k}\times\vec{a}_{-k}]\right)} = \left([\vec{a}_k\times\underbrace{[\vec{k}\times\vec{a}_{-k}]}_{\perp k}]\cdot\vec{k}\right)$$

$$\cancel{A\times[B\times C] = B\cdot(A\cdot C) - C\cdot(A\cdot B)}$$

$$\left([\vec{k}\times\vec{a}(\vec{k})]\cdot[\vec{k}\times\vec{a}_{-\vec{k}}]\right) = \cancel{\vec{k}\cdot(\vec{a}_k\cdot\vec{a}_{-k})\vec{k} - \vec{a}_{-k}\cdot(\vec{a}_k\cdot k)\cdot k}$$

$$= \varepsilon_{ijn}\,k_j\,a(k)_n\cdot\varepsilon_{iem}\,k_e\,a(-k)_m =$$

$$= \left(\delta_{je}\delta_{nm} - \delta_{jm}\delta_{ne}\right)k_j a(k)_n\cdot k_e\left(a(-k)_m\right) =$$

$$= k_e\,a(k)_n\cdot k_e\,a(-k)_n - \underbrace{k_m\,a(k)_e\cdot k_e\,a(-k)_m}_{0}$$

$$= k^2\,\vec{a}_k\cdot\vec{a}_{-k}$$

we find that $\frac{1}{c^2}\ddot{\vec{a}}_k \dot{\vec{a}}_{-k} = \frac{-1}{c^2}\omega_k^2 \vec{a}_k \cdot \vec{a}_{-k} =$

$$= -k^2 \vec{a}_k \cdot \vec{a}_{-k}$$

will cancel the 4^{th} term

Similarly the 3^{rd} term will cancel the last term

leading to:

$\frac{2}{c^2}\ddot{\vec{a}}_k \dot{\vec{a}}_k^* = 2k^2 |\vec{a}_k|^2 \Rightarrow ② \cdot ⑤ \to \frac{c^2 k^2 \cdot 4}{2} = 2\omega_k^2$

$⑤ = 2k^2 |\vec{a}_k|^2$

$$E = 2\sum_k \omega_k^2 |\vec{a}_{\vec{k}}|^2 , \qquad \omega_k = kc$$

now we introduce two real quantities:

$$\begin{cases} \vec{Q}_k = \vec{a}_k + a_k^* \\ \dot{Q}_k = i\omega_k (\vec{a}_k^* - \vec{a}_k) \end{cases}$$

inverse relations read

$$\vec{a}_k = \frac{1}{2}\left(\vec{Q}_k - \frac{\dot{\vec{Q}}_k}{i\omega_k}\right), \quad \vec{a}_k^* = \frac{1}{2}\left(\vec{Q}_k + \frac{\dot{\vec{Q}}_k}{i\omega_k}\right)$$

in the new variables the energy will be

$$E = \frac{1}{2}\sum_{\vec{k}} \left(\dot{\vec{Q}}_{\vec{k}}^2 + \omega_k \vec{Q}_k^2\right)$$

As the consequence of $(\vec{a}_k \cdot \vec{k}) = 0 \to (\vec{Q}_k \cdot \vec{k}) = 0$

$\vec{Q}_{\vec{k}} = (Q_{\vec{k},1}, Q_{\vec{k},2})$ - two component = polarisations

$$\vec{Q}_{\vec{k}} = \sum_{\alpha=1,2} \vec{e}_{\vec{k},\alpha} Q_{\vec{k},\alpha}$$

generalised coordinate of the Harmonic oscillator representing E.F.

↳ polarisation unit vectors

$$\vec{e}_{\vec{k},\alpha} \cdot \vec{e}_{\vec{k},\alpha'} = \delta_{\alpha\alpha'}$$

e.g. if $\vec{k} \parallel z$ then $\vec{e}_{\vec{k},1} \parallel x$

$\vec{e}_{\vec{k},2} \parallel y$

$$E = \frac{1}{2} \sum_{\alpha=1,2} \sum_{\vec{k}} \underbrace{\left(\dot{Q}^2_{\vec{k},\alpha} + \omega_k^2 Q^2_{\vec{k},\alpha} \right)}$$

$\parallel$

Harmonic oscillator.

each field Harmonic with $\vec{k}$, ω_k and α is represented by an oscillator. the mass of the oscillators is set to 1, which means that the generalised momenta $P_{\vec{k},\alpha} = \dot{Q}_{\vec{k},\alpha}$

We have then the Hamilton function of the E.M. field:

$$H = \frac{1}{2} \sum_{\alpha=1,2} \sum_{\vec{k}} \left\{ P_{\vec{k},\alpha}^2 + \omega_k^2 Q_{\vec{k},\alpha}^2 \right\}$$

And the field equations takes the form of the canonical Hamilton equations of classical mechanics:

$$\begin{cases} \dot{Q}_{\vec{k},\alpha} = \dfrac{\partial H}{\partial P_{\vec{k},\alpha}} \\ \dot{P}_{\vec{k},\alpha} = -\dfrac{\partial H}{\partial Q_{\vec{k},\alpha}} \end{cases}$$

the 1st equation is equivalent to the definition of generalised momentum and the second renders

$$\begin{cases} \dot{P}_{\vec{k},\alpha} = -\omega_k^2 Q_{\vec{k},\alpha} \\ \ddot{Q}_{\vec{k},\alpha} + \omega_k^2 Q_{\vec{k},\alpha} = 0 \end{cases}, \text{ or}$$

$$Q_{\vec{k},\alpha} \to a_{\vec{k},\alpha} \to \vec{A} \to \begin{cases} \vec{E} \\ \vec{H} \end{cases}.$$

General Q.M. scheme to introduce operators

$\hat{P}_{\vec{k},\alpha}$ and $\hat{Q}_{\vec{k},\alpha}$ obeying kanonical comutation relations.

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

and Hamiltoniah reads:

$$\hat{H} = \frac{1}{2} \sum_{\alpha=1,2}' \sum_{\vec{k}} \left\{ \hat{P}^2_{\vec{k},\alpha} + \omega_k^2 \hat{Q}^2_{\vec{k},\alpha} \right\}.$$

The problem of finding eigenvalues and eigenstates of $\hat{H}$ is reduced to that of a system of non-interacting oscillators.

define $|N_{\vec{k},\alpha}\rangle$ - wave function of $\vec{k},\alpha$ - oscillators with the quantum number $N_{\vec{k},\alpha}$ the Composite wave function can be writen as

$$\psi_{\dots, N_{\vec{k},\alpha}, \dots} = \left| \dots, N_{\vec{k},\alpha}, \dots \right\rangle = \prod_{\vec{k}} \prod_{\alpha} \left| N_{\vec{k},\alpha} \right\rangle$$

$N_{\vec{k},\alpha} = 0, 1, 2, \dots$

$N_{\vec{k},\alpha}$ = ~~occupation numbers.~~

↳ quantum numbers. (not occupation).

Ground (vacuum state):

$$N_{\vec{k},\alpha} = 0 \quad \text{for all } \vec{k}, \alpha$$

$\{ \dots, N_{k,\alpha}, \dots \}$ ← quantum numbers.

(defines the state of the field)

2nd quantisation

$$E_{\dots, N_{\vec{k},\alpha}, \dots} = \sum_{\vec{k}} \sum_{\alpha} \left(\hbar \omega_k \left[N_{\vec{k},\alpha} + \frac{1}{2} \right] \right)$$

$$E_0 = E_{\dots 0 \dots} = \sum_{\vec{k}} \sum_{\alpha} \frac{\hbar \omega_k}{2}$$

if one d.o.f. $N_{\vec{k},\alpha} = 1$, then $E_1 = E_0 + \hbar \omega_k$

Transition into such an excited state may be interpreted as emergence (creation) of a E.M. field quantum = photon. So, increase of $N_{\vec{k},\alpha}$ by a unity is a creation of a new particle - photon with frequency ω_k and polarisation α. The concept of a field quantum as a particle was introduced by Einstein in 1905 (photoeffect) in this work it is assumed the quatum propertice (particle-like) are also assined to light itself.

To make the formalism closer to the Harmonic oscillator math we introduce operators of creation and annihilation.

$$\hat{B}_{\vec{k},\alpha} = \sqrt{\frac{\omega_k}{2\hbar}} \left(\hat{Q}_{\vec{k},\alpha} - \frac{\hat{P}_{\vec{k},\alpha}}{i\omega_k} \right)$$

$$\hat{B}^{+}_{\vec{k},\alpha} = \sqrt{\frac{\omega_k}{2\hbar}} \left(\hat{Q}_{\vec{k},\alpha} + \frac{\hat{P}_{\vec{k},\alpha}}{i\omega_k} \right).$$

Inverse relations:

$$\hat{Q}_{\vec{k},\alpha} = \sqrt{\frac{\hbar}{2\omega_k}} \left[\hat{B}^{+}_{\vec{k},\alpha} + \hat{B}^{+}_{\vec{k},\alpha} \right]$$

$$\hat{P}_{\vec{k},\alpha} = i \sqrt{\frac{\hbar\omega_k}{2}} \left(\hat{B}^{+}_{\vec{k},\alpha} - \hat{B}_{\vec{k},\alpha} \right)$$

Commutators:

$$\left[\hat{B}_{\vec{k},\alpha}, \hat{B}^{+}_{\vec{k}',\alpha'} \right] = \delta_{\vec{k},\vec{k}'} \delta_{\alpha\alpha'}$$

$$\left[\hat{B}_{\vec{k},\alpha}, \hat{B}_{\vec{k}',\alpha'} \right] = 0$$

$$\left[\hat{B}^{+}_{\vec{k},\alpha}, \hat{B}^{+}_{\vec{k}',\alpha'} \right] = 0$$

in terms of $\hat{B}$'s the field Hamiltonian takes the form:

$$\hat{H} = \sum_{\vec{k},\alpha} \hbar\omega_k \left[\hat{B}^{+}_{\vec{k},\alpha} \hat{B}_{\vec{k},\alpha} + \frac{1}{2} \right].$$

and in analogy to the simple harmonic oscilator we have:

$$\hat{B}_{\vec{k},\alpha} \left| \dots, N_{\vec{k},\alpha}, \dots \right\rangle = \sqrt{N_{\vec{k},\alpha}} \left| \dots, N_{\vec{k},\alpha} - 1, \dots \right\rangle$$

↳ annihilation

$$\hat{B}^{+}_{\vec{k},\alpha} \left| \dots, N_{\vec{k},\alpha} \dots \right\rangle = \sqrt{N_{\vec{k},\alpha} + 1} \left| \dots, N_{\vec{k},\alpha} + 1, \dots \right\rangle$$

↳ creation

$$\hat{B}^{+}_{\vec{k},\alpha} \hat{B}_{\vec{k},\alpha} \cdot \left| \dots, N_{\vec{k},\alpha}, \dots \right\rangle = N_{\vec{k},\alpha} \left| \dots, N_{\vec{k},\alpha}, \dots \right\rangle$$

↳ operator of the photon number

The vacuum state follows from the equation:

$$\hat{B}_{\vec{k},\alpha} |0,\dots,0,\dots\rangle = 0$$

Other operators of observables:

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

$$\hat{\vec{a}}^{+}_{\vec{k}} \to \sum_{\alpha} \vec{e}_{\vec{k},\alpha} \sqrt{\frac{\hbar}{2\omega_k}}\, \hat{B}^{+}_{\vec{k},\alpha}$$

see page (36)

Vector potential operator:

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

$\hat{E}$ and $\hat{H}$ can be expressed through $\hat{A}$

We may also speak about the ~~pha~~ wave function of a photon if a photon has momentum $\hbar\vec{k}$, and polarisation α its ~~wave function~~ state may be denoted as $|\vec{k},\alpha\rangle$ with $\langle \vec{k}',\alpha' | \vec{k},\alpha \rangle = \delta_{\vec{k}\vec{k}'}\delta_{\alpha\alpha'}$.

The photon has two polarisation states, which in own representation may be presented as

$$|\updownarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad |\leftrightarrow\rangle \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

↳ y-polarisation ↳ x-polarisation.

Superposition holds:

$$|\nearrow\rangle = a|\uparrow\rangle + b|\leftrightarrow\rangle$$

$$|a|^2 + |b|^2 = 1$$

Vacuum state:

$$E_0 = \sum_{\vec{k}} \sum_{\alpha} \frac{\hbar k c}{2} = 2 \frac{\hbar c}{2} \frac{V}{(2\pi)^3} \int_0^\infty 4\pi k \cdot k^2 dk \to \infty$$

↙ intrinsic inconsistency of the theory

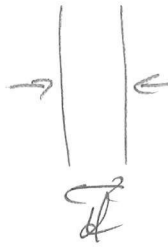
But in the final results on measureble quantities only the Energy differences enter.

Note that $\left[\hat{N}_{\vec{k},\alpha}, \hat{E}/\hat{H}\right] \neq 0 \Rightarrow$ in the vacuume state $|0\rangle$ $\hat{E}$, and $\hat{H}$ have no definite value, only their $\langle\hat{E}\rangle/\langle\hat{H}\rangle = 0$.

$\hat{E}$ and $\hat{H}$ fluctuate in vacuum state and e.g. interaction of of an electron in an atom with these fluctuations is the reason for the spontaneous transitions from excited to ground state, which in turn gives rise to the finite width of the spectral lines. (to be discussed Later).

§ Casimir Effect (1948).

two metal plates in the vacuume experiense attractive forces.



reason confinement of vacuum fluctuations.

Let's discuss the effect in 1d case.

Unconfined case:

$$E_0 = \sum_k \frac{\hbar\omega_k}{2}\Big| = \frac{L}{2\pi}\int_{-\infty}^{+\infty} \frac{\hbar\omega_k}{2}\,dk = \frac{L\hbar c}{2\pi}\int_0^{\infty} k\,dk$$
$L\to\infty$

if the field is confined in space between $x=0$, d then the vector potential

$\vec{A}(0/d)=0$

$$\vec{A} = \sqrt{\frac{4\pi c^2}{d}}\sum_k \left(\vec{a}_k e^{ikx} + \vec{a}_k^* e^{-ikx}\right)$$

$x=0 \Rightarrow a_k + a_k^* = 0 \Rightarrow \vec{a}_k = -\vec{a}_k^*$

$x=d \Rightarrow \sin kd = 0$, or $k = \frac{\pi n}{d}$, $n = 1,2,3,\ldots$

$n=0$ render $A=0$ for any x, an $n<0$ do not introduce new states.

Now Energy of zero-point is

$$E = \sum_k \frac{\hbar\omega_k}{2} = \sum_{n=1}^{\infty} \frac{\hbar c}{2}\frac{\pi}{a} n$$

difference in the energy densities (linear)

$$\mathcal{E} = \frac{E}{d} - \frac{F_0}{L} = \frac{\hbar c \pi}{2d^2} \sum_{n=1}^{\infty} n - \frac{\hbar c}{2\pi} \int_0^{\infty} k\, dk$$

is called the Casimir energy.

To estimate $\mathcal{E}$ let's introduce a regularizing function $e^{-\nu k}$ under the sums: and after calculations pass with $\nu \to 0$:

$$\mathcal{E} = \lim_{\nu \to 0} \left\{ \frac{\hbar c \pi}{2d^2} \sum_{n=1}^{\infty} e^{-\frac{\pi}{d} n \nu} \cdot n - \frac{\hbar c}{2\pi} \int_0^{\infty} e^{-\nu k} k\, dk \right\}$$

$$\left[\sum_{n=1}^{\infty} f(n) = \int_0^{\infty} f(x)\, dx - \frac{f'(0)}{12} + \frac{f'''(0)}{720} + \dots \right.$$

↳ Euler – Maclaurin formula

$$\left. \right]$$

$$\frac{\hbar c \pi}{2d^2} \sum_{n=1}^{\infty} e^{-\frac{\pi}{d} n \nu} \cdot n \underset{\sim}{\overset{\hbar c \pi}{2d^2}} \int_0^{\infty} e^{-\frac{\pi}{d} x \nu} \cdot x\, dx = \frac{\hbar c \pi}{24 d^2} \left[e^{-\frac{\pi}{d} x \nu} \cdot x \right]' \Big|_{x=0}$$

$$\frac{\pi}{d} x = \kappa$$

$$dx = \frac{d\kappa\, d\kappa}{\pi}$$

$$x = \frac{d\kappa}{\pi}$$

$$= \frac{\hbar c \pi}{2d^2} \frac{d^2}{\pi^2} \int_0^{\infty} e^{-\kappa \nu} \kappa\, d\kappa - \frac{\hbar c \pi}{24 d^2} \left(x \left(-\frac{\pi}{d} \nu \right) \cdot e^{-\frac{\pi}{d} x \nu} + e^{-\frac{\pi}{d} x \nu} \right) \Big|_{x=0}$$

$$= \frac{\hbar c}{2\pi} \int_0^{\infty} e^{-\kappa \nu} \kappa\, d\kappa - \frac{\hbar c \pi}{24 d^2} \Big|_{\nu \to \infty}$$ and integrals cancel out.

So $\varepsilon = -\frac{\pi \hbar c}{24 d^2}$

↳ attractive interation with the force

$$\boxed{F = \left| -\frac{d(\varepsilon d)}{d d} \right| = \frac{\pi \hbar c}{24 d^2}}$$

For the 3d case we obt

$$\varepsilon = \frac{1}{d} \sum_{\alpha=1,2} \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{+\infty} dk_y \sum_{n=1}^{\infty}{}' \frac{\hbar c}{2} \sqrt{k_x^2 + k_y^2 + \left(\frac{\pi n}{d}\right)^2}$$

$$- \sum_{\alpha=1,2}{}' \frac{1}{(2\pi)^3} \iiint_{-\infty}^{+\infty} d^3k \, \frac{\hbar c}{2} \sqrt{k_x^2 + k_y^2 + k_z^2} =$$

. . . . .

$$\varepsilon = -\frac{\hbar c \pi^2}{720 d^4} \quad , \quad p = 3$$

the force / area is

$$\boxed{f = \frac{\hbar c \pi^2}{240 a^4}}$$

§. Theory of light emission and adsorption.

Consider a system "atom + E.M. field".

under name "atom" we will understan a particle in (mol., ion, atom, etc.) ground or exited state, and will focus on the interaction of a single electron of the atom (this electron is called optical electrone)

The full Hamiltonian: $\hat{H} = \hat{H}_a + \hat{H}_{ph}$

$$\hat{H}_a = \frac{\hat{p}^2}{2m} + \hat{U}$$

↳ potential energy of the interaction of the optical electron with the rest stuff in the atom (other electrons and nucleus).

$$\hat{H}_{ph} = \sum_{\vec{k},\alpha} \hbar\omega_k \left(\hat{B}^+_{\vec{k},\alpha} \hat{B}_{\vec{k},\alpha} + \tfrac{1}{2} \right)$$ - E.M. field Hamiltonian.

From the classical Electrodynamics introducing E.M. field with the gauge $\varphi = 0$, $\operatorname{div}\vec{A} = 0$ is performed by replacing $\vec{p} \to \vec{p} - \frac{e\hat{A}}{c}$, e - is the charge of the particle.

$$\Rightarrow \hat{H}_a \Rightarrow \frac{1}{2m}\left[\hat{p} - \frac{e}{c}\hat{A}\right]^2 + \hat{U} = \hat{H}_a + \hat{V}$$

where $$\hat{V} = -\frac{e}{2mc}\left(\hat{A}\hat{p} + \hat{p}\hat{A}\right) + \frac{e^2}{2mc^2}\hat{A}^2$$

$$\operatorname{div}\hat{A} = 0$$

$$\hat{p}\hat{A}\psi = -i\hbar\vec{\nabla}\cdot\hat{A}\,\psi = -i\hbar(\vec{\nabla}\cdot\hat{A})\,\psi + \hat{A}(-i\hbar\vec{\nabla})\,\psi$$

$$= \hat{A}\hat{p}\psi \Rightarrow$$

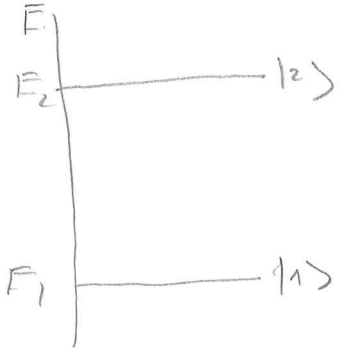
$$\left[\hat{p}, \hat{A}\right] = 0$$

and the operator of interaction

$$\hat{V} = -\frac{e}{mc}\hat{A}\hat{p} + \frac{e^2}{2mc^2}\hat{A}^2$$ which will be

treated as the perturbation to $\hat{H}_0 = \hat{H}$

Lets consider an atom with two selected states $|1\rangle$ and $|2\rangle$ with the corresponding energies E_1, E_2 :



The E.M. Field is given by the states

$|\dots, N_{\vec{k},\alpha}, \dots\rangle$ with the energy

$E_{\dots, N_{\vec{k},\alpha}, \dots}$.

Lets consider initial state

$$|i\rangle = |2\rangle \cdot |\dots, N_{\vec{k},\alpha}, \dots\rangle \;, \quad E_i^{(0)} = E_2 + E_{\dots, N_{\vec{k},\alpha}, \dots}$$

and the final state:

$$|f\rangle = |1\rangle\, |\dots, N'_{\vec{k},\alpha}, \dots\rangle \;, \quad E_f^{(0)} = E_1 + E_{\dots, N'_{\vec{k},\alpha}, \dots}$$

We are interested in the creation of just one electron when $N'_{\vec{k},\alpha} = N_{\vec{k},\alpha} + 1$, and all the rest occupation numbers stay unchanged.

So $E_f^{(0)} = E_1 + E_{\dots, N_{k,\alpha}, \dots} + \hbar\omega_k$.

This is so-called one photon transitions.

Transition probability per unit time is calculated according

$$\omega_{i\to f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{V} | i \rangle \right|^2 \delta\left(E_f^{(0)} - E_i^{(0)}\right)$$

Expressin $\hat{\vec{A}}$ via $\hat{B}^+$ and $\hat{B}$ we have.

$$\langle f | \hat{V} | i \rangle = -\frac{e}{mc} \langle f | \hat{A}\hat{p} | i \rangle + \frac{e^2}{2mc^2} \langle f | \hat{A}^2 | i \rangle$$

$$\langle f | \hat{A}\hat{p} | i \rangle = \sum_{\vec{k},\alpha'} \sqrt{\frac{2\pi\hbar c^2}{\omega_{k'} V}} \Big[\langle 1 | e^{i\vec{k}'\vec{r}} (\vec{e}_{\vec{k}',\alpha'} \cdot \vec{p}) | 2 \rangle \times$$

$$\langle \dots, N_{k,\alpha}+1, \dots | \hat{B}_{\vec{k}',\alpha'} | \dots, N_{k,\alpha}, \dots \rangle +$$

$$\langle 1 | e^{-i\vec{k}'\vec{r}} (\vec{e}_{\vec{k}',\alpha'} \cdot \hat{p}) | 2 \rangle \langle \dots, N_{\vec{k},\alpha}+1, \dots | \hat{B}^+_{\vec{k}',\alpha'} | \dots N_{\vec{k},\alpha} \dots \rangle \Big]$$

According to the rules on $\hat{B}$ and $\hat{B}^+$ we obtaine

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

$$\langle \dots, N_{k,\alpha}+1, \dots | \hat{B}^+_{k',\alpha'} | \dots, N_{k,\alpha}, \dots \rangle = \delta_{kk'} \delta_{\alpha\alpha'} \sqrt{N_{k,\alpha}+1}$$

Now

$$\langle f | \hat{A}\hat{p} | i \rangle = \langle 1 | e^{-ikr} (e_{k,\alpha} \hat{p}) | 2 \rangle \times \sqrt{\frac{2\pi\hbar^2 c^2}{V\omega_k} (N_{k,\alpha}+1)}$$

on the other hand we get

$$\langle f|\hat{A}^2|i\rangle = 0.$$

$$E_f^{(0)} - E_i^{(0)} = E_1 - E_2 + \hbar\omega_k$$

Collecting terms together we obtaine for the trans. prob. / time with the photon emission expression.

$$\omega_{i\to f}^{(+)} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi\hbar c^2}{V\omega_k}\left[N_{\vec{k},\alpha}+1\right]\left|\langle 1|e^{-i\vec{k}\vec{r}}(\vec{e}_{k\alpha}\hat{p})|2\rangle\right|^2 \times$$

$$\delta(E_1 - E_2 + \hbar\omega)$$

For the process of adsorption the initial state is $|1\rangle$ with energy E_1 and the field with the amplitude $|\dots, N_{k,\alpha}, \dots\rangle$ and energy $E_{\dots, N_{k,\alpha}, \dots}$. Final state is for atom $|2\rangle$, E_2 and field $|\dots, N_{k,\alpha}-1, \dots\rangle$; and $E_{\dots, N_{k,\alpha}-1, \dots}$

The result of such transition is photon annihilatie $(\omega_k, \vec{k}, \alpha)$

we may show that

$$\left|\langle 2|e^{ikr}(e_{k,\alpha}\cdot\hat{p})|1\rangle\right|^2 = \left|\langle 1|e^{-ikr}(e_{k,\alpha}\cdot\hat{p})|2\rangle\right|^2 \equiv$$

$$|p_{12}|^2.$$

and $$\omega_{i\to f}^{(-)} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi\hbar c^2}{V\omega_k} N_{\vec{k},\alpha}\,|p_{12}|^2\,\delta(E_2 - E_1 + \hbar\omega_k)$$

Before we turn our atention to the calculation of the emission intensities, let's us consider equilibrium state of "atom + field" at temperature T, which is the case of black body radiation.

Probability that atom is in states $|1\rangle$ or $|2\rangle$ are given by:

$$P_1 = \frac{e^{-E_1/T}}{\sum_n' e^{-E_n/T}}, \quad P_2 = \frac{e^{-E_2/T}}{\underbrace{\sum_u' e^{-E_n/T}}_{\text{partition function}}}$$

in equilibrium we have a detailed ballance condition.

$$P_2 \omega_{i\to f}^{(+)} = P_1 \omega_{i-1}^{(-)}, \quad \text{substituting}$$

$\omega_{i-1}^{(\pm)}$ with $N_{\vec{k},\alpha} \to \overline{N_{\vec{k},\alpha}}$ we get

$$P_2 \left(\overline{N_{\vec{k},\alpha}} + 1\right) = P_1 \overline{N_{\vec{k},\alpha}} \quad \text{or}$$

$$1 + \frac{1}{\overline{N_{\vec{k},\alpha}}} = \frac{P_1}{P_2}$$

$$= e^{\frac{E_2 - E_1}{T}} \quad \text{since } E_2 - E_1 = \hbar\omega_k$$

we find that

$$\overline{N_{\vec{k},\alpha}} = \frac{1}{e^{\frac{\hbar\omega_k}{T}} - 1} \to \text{Planck formular.}$$

The full energy of the field — vacuum energy is

$$E - E_0 = \sum_{\vec{k}}' \sum_{\alpha} \hbar\omega_k \overline{N_{\vec{k},\alpha}} = 2\frac{V}{(2\pi)^3} \int_0^\infty \frac{4\pi k^2 \hbar\omega_k}{e^{\frac{\hbar\omega_k}{T}} - 1} dk$$

$$K \to \frac{\omega_K}{c}, \quad dk = \frac{d\omega}{c}$$

$$4\pi \frac{\omega^2}{c^3} \hbar\omega \, d\omega$$

$$= \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega \quad \text{or for energy density}$$

$$\frac{E - E_0}{V} = \int_0^\infty u_\omega(\omega, T) d\omega$$

$$u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$

↳ spectral energy density

This is the Planck formula obtained in 1900.

Now lets calculate the intensity of emission and adsorption

if $\omega_{i\to f}^{(\pm)}$ multiply by $\hbar\omega_K$ and $\sum_{\vec{K},\alpha}$ then we obtaine rates of energy emition "+" and "−" adsorption.

$$\frac{dE}{dt}^{(\pm)} = \sum_{\vec{K},\alpha}{}' \omega_{i\to f}^{(\pm)} \hbar\omega_K =$$

$$= \frac{V}{(2\pi)^3} \int d\vec{k} \sum_\alpha \omega_{i\to f}^{(\pm)} \hbar\omega_K =$$

$$= \sum_\alpha{}' \int d\Omega \frac{V}{(2\pi)^3} \int_0^\infty dk \, k^2 \omega_{i\to f}^{(\pm)} \hbar\omega_K$$

$d\Omega$ - solid angle in $\vec{k}$ space.

let's us introduce emission/adsorption intensitye $\left(\frac{E}{t}\right)$ as total energy of given polarisation (emitted/adsorbed) by the atom per solid angle and time:

$$I^{(\pm)}_{\vec{k},\alpha} = \frac{V}{(2\pi)^3} \int_0^\infty dk\, k^2\, \omega^{(\pm)}_{i\to f}\, \hbar\omega_k =$$

$$\Rightarrow$$

$$I^{+}_{\vec{k},\alpha} = \frac{V}{(2\pi)^3} \int_0^\infty dk\, k^2 \hbar\omega_k \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{2\pi\hbar c^2}{V\omega_k} \times \left(N_{\vec{k},\alpha}+1\right) |P_{12}|^2 \times$$

$$\delta\left(E_1 - E_2 + \hbar\omega_k\right) =$$

using $k = \frac{\omega_k}{c}$, and the presence of δ

$$= \frac{e^2\hbar}{(2\pi)m^2} \int_0^\infty dk\, k^2 \left|P_{12}\right|^2 \left(N_{\vec{k},\alpha}+1\right) \delta\left(E_1 - E_2 + \hbar kc\right) =$$

$$= \frac{e^2\hbar}{(2\pi)m^2\hbar c}\left[\frac{E_2 - E_1}{\hbar c}\right]^2 |P_{12}|^2 \left(N_{\vec{k},\alpha}+1\right) =$$

$$= \frac{e^2}{2\pi m^2 c^3}\underbrace{\left[\frac{E_2 - E_1}{\hbar}\right]}_{\omega}{}^2 |P_{12}|^2 \left(N_{k,\alpha}+1\right) = \frac{e^2\omega^2}{2\pi m^2 c^3}|P_{12}|^2\left(N_{\vec{k},\alpha}+1\right)$$

$\omega \to$ frequency of the transition

Similarly:

$$I^{(-)}_{\vec{k},\alpha} = \frac{e^2\omega^2}{2\pi m^2 c^3}|P_{12}|^2 N_{\vec{k},2}$$

if the field is in the ground state, i.e. $N_{\vec{K},\alpha} = 0$

$\Rightarrow I^{(-)}_{\vec{K},\alpha} = 0$

Emission however does exist in this case and has a name of spontaneous emission

$$I^{(+)}_{K,\alpha} = \frac{e^2\omega^2}{2\pi m^2 c^2} |p_{12}|^2$$

due to the fluctuations of $\vec{E}, \vec{H}$ $\langle \Delta E \rangle \neq 0$

this ensure interaction of the electron with E.M. field which is the reason for spontaneous quantum transitions.

$N_{\vec{K},\alpha}$ in $I^{(+)}_{\vec{K},\alpha}$ gives rise to induced light emission, in the base of the laser function.

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§. Electric dipole emission. Selection rules.

let investigate in more details $I^{cn}_{\vec{K},\alpha}$ focusing on

$|p_{12}|$. we will be interested in the regim $\lambda \geq 100\text{nm}$ which includes visible light. This will significantly Simplify expression for $|p_{12}|$. Wave functions which will be used to calculate $|p_{12}|$ are different from zero for distances $\sim 1\text{Å}$

Therefore $\vec{k}\cdot\vec{r}$, which enters $e^{-i\vec{k}\vec{r}}$ is small

$\vec{k}\cdot\vec{r} \approx kr = \frac{2\pi a}{\lambda} \sim 10^{-3}$ this allows to use

$e^{-i\vec{k}\cdot\vec{r}} = 1 - i\,\vec{k}\cdot\vec{r} + \dots$

$$P_{12} = \langle 1 | e^{-i\vec{k}\vec{r}} (\vec{e}_{\vec{k},\alpha}\cdot\hat{p}) | 2 \rangle \approx$$

$$\langle 1 | (\vec{e}_{\vec{k},\alpha}\hat{p}) | 2 \rangle - i \langle 1 | (\vec{k}\cdot\vec{r})\cdot(\vec{e}_{\vec{k},\alpha}\hat{p}) | 2 \rangle + \dots$$

(for $\lambda \sim 1\text{Å}$ (X-rays) we must calculate this matrix element exactly.)

$$P_{12} \approx \langle 1 | \vec{e}_{\vec{k},\alpha}\cdot\hat{p} | 2 \rangle = \vec{e}_{\vec{k},\alpha} \langle 1 | \hat{p} | 2 \rangle =$$

$$= \vec{e}_{\vec{k},\alpha} \langle 1 | m\dot{\hat{r}} | 2 \rangle = \langle 1 | m \frac{\hat{r}\hat{H}_a - \hat{H}_a\hat{r}}{i\hbar} | 2 \rangle$$

$$\langle 1 | \hat{r}\hat{H}_a | 2 \rangle = \langle 1 | \hat{r} | 2 \rangle E_2$$

$$\langle 1 | \hat{H}_a\hat{r} | 2 \rangle = \sum_n \langle 1 | \hat{H}_a | n \rangle \langle n | \hat{r} | 2 \rangle = \sum_n E_n \langle 1 | n \rangle \langle n | \hat{r} | 2 \rangle$$

$$= \sum_n E_n \delta_{1n} \langle n | \hat{r} | 2 \rangle = E_1 \langle 1 | \hat{r} | 2 \rangle$$

So $$\langle 1 | \hat{p} | 2 \rangle = \frac{m}{i\hbar}(E_2 - E_1)\langle 1 | \vec{r} | 2 \rangle = m\frac{\omega}{i} r_{12}$$

r_{12}: matrix element of the $\hat{r}$

Let's introduce dipole moment operator

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

So, now we have

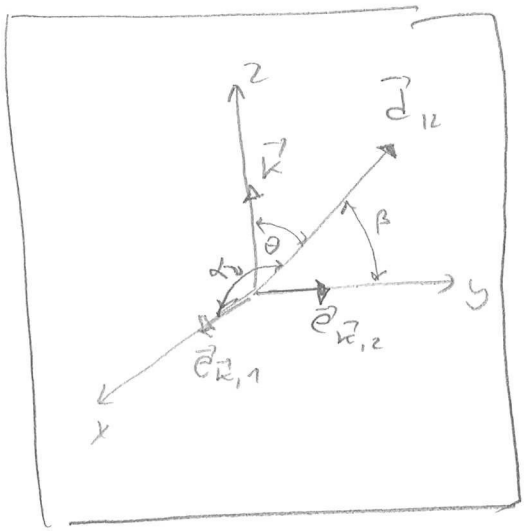
$$P_{12} = \frac{m\omega}{ie} \vec{d}_{12} \cdot \vec{e}_{\vec{k},e}$$

$$I^{en}_{\vec{k},\alpha} = \frac{\omega^4}{2\pi c^3} \left| \vec{d}_{12} \cdot \vec{e}_{\vec{k},\alpha} \right|^2 \rightarrow \text{dipole emission related to dipole transitions.}$$

$$I^{sp}_{\vec{k}} = \sum_{\alpha} I^{sp}_{\vec{k},\alpha} = \frac{\omega^4}{2\pi c^3} \left\{ \left| \vec{d}_{12} \vec{e}_{\vec{k},1} \right|^2 + \left| \vec{d}_{12} \vec{e}_{\vec{k},2} \right| \right\} =$$

$$= \frac{\omega^4}{2\pi c^3} \left| \vec{d}_{12} \right|^2 \left(\cos^2\alpha + \cos^2\beta \right)$$

$$= \frac{\omega^4}{2\pi c^3} \left| \vec{d}_{12} \right|^2 \left(1 - \cos^2\theta \right)$$



$$d^2 = d^2 \left(\cos^2\alpha + \cos^2\beta + \cos^2\theta \right)$$

let's integrate this over angles

to obtaine total emission per unit time

$$I^{sp}(\omega) = \int d\Omega \, I^{sp}_{\vec{k}} = \frac{\omega^4}{2\pi c^3} \left| \vec{d}_{12} \right|^2 \int d\Omega \sin^2\theta = \frac{\omega^4}{2\pi c^3} \left| \vec{d}_{12} \right|^2 \frac{4\pi}{3} =$$

$$= \frac{4}{3} \frac{\omega^4}{c^3} \left| \vec{d}_{12} \right|^2$$

this expression is similar to that of a classical case, where d_{12} is replaced by the Fourier component of the classical dip. moment?

if $\vec{d}_{12} = 0$ no dipolar emission which may happen for certaine $|1\rangle$ and $|2\rangle \Rightarrow$ dictates selection rule for (dipolar) transitions.

as an example let's us conside 1d oscillator.

$x_{12} = \langle 1 | x | 2 \rangle$, where $\langle 1 | = \langle n |$, $|2\rangle = |n'\rangle$

$$x_{12} = \sqrt{\frac{\hbar}{2m\omega}} \langle n | \hat{b}^+ + \hat{b} | n' \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left\{ \sqrt{n'+1}\,\delta_{n,n'+1} + \sqrt{n'}\,\delta_{n,n'-1} \right\}$$

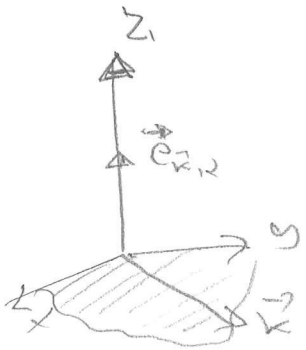
$x_{12} \neq 0$ for $\boxed{n' = n \pm 1}$!

dipolar transition are possible for adjacent levels only!

the case of electron in centro-symmetric field e.g. H atom.

$$|1\rangle = |n, l, m\rangle = R_{n,l}(r)\, Y_{l,m}(\theta, \varphi)$$

$$|2\rangle = |n', l', m'\rangle = R_{n',l'}(r)\, Y_{l',m'}(\theta, \varphi)$$



Consider photon which is polarised along $\hat{z}$:

$$P_{12} = \frac{m\omega}{i} \vec{e}_{k,a} \cdot \vec{r}_{12} = \frac{m\omega}{i} z_{12}$$

$$z_{12} = \langle 1|\hat{z}|2\rangle = \langle n\ell m|\, r\cos\theta\,|n'\ell'm'\rangle$$

$$= \int_0^\infty r^2 R_{n,\ell}(r)\, r\, R_{n',\ell'}(r)\, dr \;\cdot$$

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{\ell,m}(\theta,\varphi)\cos\theta\, Y_{\ell',m'}\sin\theta\, d\varphi\, d\theta =$$

$$= \underbrace{R}_{\neq 0} \int_0^{2\pi} \frac{e^{-im\varphi}}{\sqrt{2\pi}} \frac{e^{-im'\varphi}}{\sqrt{2\pi}}\, d\varphi \int_0^{\pi} \sin\theta\, \Theta_{\ell,m}(\theta)\cos\theta\, \Theta_{\ell',m'}(\theta)\, d\theta$$

where we used $Y_{\ell,m}(\theta,\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}}\Theta_{\ell,m}(\theta)$

$$\Theta_{\ell,m}(\theta) = (-1)^m \sqrt{\frac{2\ell+1}{2}\frac{(\ell-m)!}{(\ell+m)!}}\, P_\ell^m(\cos\theta).$$

↓ associated Legendre polynomial

It is easy to check using explicite expressions for $P_\ell^m(x)$ that

$$\cos\theta\,\Theta_{\ell m}(\theta) = \underbrace{\sqrt{\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}}}_{A_{\ell,m}}\cdot\Theta_{\ell-1,m} + \underbrace{\sqrt{\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}}}_{B_{\ell,m}}\Theta_{\ell+1,m}$$

Next using condition of orthonormality of spherical harmonics we obtain:

$$z_{12} = R\,\delta_{m'm}\left(A_{\ell,m}\,\delta_{\ell-1,\ell'} + B_{\ell,m}\,\delta_{\ell+1,\ell'}\right)$$

$$\boxed{m' = m\ ,\quad \ell' = \ell \pm 1}$$

now in the case of $\vec{k} \parallel z$, consider the case circular polarised light with the polarisation vectors

$$\vec{e}_{\vec{k},\pm} = \frac{1}{\sqrt{2}} \left[\vec{e}_{\vec{k},1} \pm i \vec{e}_{\vec{k},2} \right] = \frac{1}{2} \left[\cancel{\quad} \right]$$

$\vec{e}_{\vec{k},1} \parallel x$

$\vec{e}_{\vec{k},2} \parallel y$

"+" corresponds to the right circular polarisation, while

"−" corresponds to the left circular polarisation.

now we are after the matrix element

$$\langle 1 | \vec{e}_{\vec{k},\pm} \cdot \vec{r} | 2 \rangle = \langle 1 | \frac{\hat{x} \pm i\hat{y}}{\sqrt{2}} | 2 \rangle$$

$$= \frac{1}{\sqrt{2}} \left\langle n, l, m \left| r \sin\theta \, e^{\pm i\varphi} \right| n', l', m' \right\rangle =$$

$$= \frac{R}{\sqrt{2}} \overset{\text{defined as above}}{\rightarrow} \int_0^{2\pi} d\varphi \, \frac{e^{-im\varphi}}{\sqrt{2\pi}} e^{\pm i\varphi} \frac{e^{im'\varphi}}{\sqrt{2\pi}} \cdot \int_0^{\pi} \sin\theta \, \Theta_{l,m}(\theta) \cdot \sin\theta \, \Theta_{l',m'}(\theta) d\theta$$

$$\sin\theta \, \Theta_{l,m}(\theta) = A'_{l,m} \, \Theta_{l-1,m-1}(\theta) + B'_{l,m} \, \Theta_{l+1,m-1}(\theta)$$

$$A'_{l,m} = \sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}} \; ; \; B'_{l,m} = -\sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}}$$

From the condition of orthogonality of $\Theta_{\ell,m}(\theta)$

$\Rightarrow$

$$\langle 1 | \vec{e}_{\vec{k},+} \cdot \vec{r} | 2 \rangle = \frac{R}{\sqrt{2}} \delta_{m', m-1} \left(A'_{\ell,m} \delta_{\ell-1, \ell'} + B'_{\ell,m} \delta_{\ell+1, \ell'} \right)$$

$$\langle 1 | \vec{e}_{\vec{k},-} \cdot \vec{r} | 2 \rangle = \frac{R}{\sqrt{2}} \delta_{m', m+1} \left(A'_{\ell',m'} \delta_{\ell, \ell'-1} + B'_{\ell',m'} \delta_{\ell, \ell'+1} \right)$$

$\Downarrow$

$|P_{12}| \neq 0$ when $m' = m \pm 1$ and $\ell' = \ell \pm 1$

Together for linear and circular polarisations we have

$$\boxed{\begin{array}{c} m' = m,\ m \pm 1;\quad \ell' = \ell \pm 1 \\ \Delta m = 0,\ \pm 1;\quad \Delta \ell = \pm 1 \end{array}}$$

selection rules for dipolar light emission.

Δm reflects the conservation of the k_z projection component of L of the combined system "atom + field".

Photon angular momentum is $\hbar$, ~~for~~

For linear polarised light $\parallel z$, atom looses angular momentum with $L_z = 0$, $\Delta m = 0$.

For the circular polarised light L_z for photon is $\pm \hbar$ accordingly also changes the L_z for atom.

Taking into account higher order terms we can make

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§ life time of excited states of atoms.

the expressions obtained so far show that the spectral lines are infinitely thin, e.g. the atom emit on a certaine frequency.

$$\omega = \frac{E_2 - E_1}{\hbar} \Rightarrow e^- \text{ can be in } |2\rangle \text{ for } t \to \infty$$

This does not correspond to reality and excited states are only quasistationary finite lifetime.

Reason: interaction of e^- with zero-point vacuume fluctuations. in classical terms e^- interacts withe the field which it emits - so-called emission reaction

Finite life time → spread of the spectral lines.

Let is sketch the reason why spectral line is spreaded:

Expand wave function of an atom as

$$\psi(q,t) = \sum_n C_n e^{-\frac{i}{\hbar} E_n t} \psi_n(q) \quad \text{/ unperturbed solutions.}$$

For simplicity consider atom with two levels.

ground state $|1\rangle = \psi_1$, and excited state.

$$|2\rangle = \psi_2$$

in a system with N atoms

$N_2 = N |c_2|^2$ → is the number of atoms in excited states. As the result of light emission we may write the following phenomenological equation:

$$\frac{dN_2}{dt} = -N_2 w_{2\to 1}$$

↳ prob. of transition per unit time

$$\Rightarrow N_2 = N_2(0) \cdot e^{-\gamma t} \quad ; \quad \gamma = w_{2-1} \;/\; \text{decay constant.}$$

$$\Rightarrow |c_2|^2 \sim e^{-\gamma t} \quad \text{and}$$

$$c_2 \sim e^{-\gamma t/2}$$

$$\Rightarrow \psi_2(q,t) \sim e^{-\frac{i}{\hbar} E_2 t - \frac{\gamma_2}{2} t} \psi_2(q) \to 0 \text{ as } t \to \infty$$

this means no stationary states different then the ground exist!

life time of the excited state

$$\tau_2 = \frac{1}{\gamma_2} = \frac{1}{w_{2\to 1}}$$

emission intensity without state relaxation was given by term $\sim \delta(E_f - E_2)$.

Now if we consider the quasistationary state, in the expression for $w_{i\to f}$ istead of the δ-function we will obtain the following expression:

$E_n \to E_n - i\hbar\gamma_n/2$

$$\delta(E_f - E_i) \to \frac{\gamma/2\pi\hbar}{\omega_{fi}^2 + \left(\frac{\gamma}{2}\right)^2}$$

(and γ_n is the probability of transition from state $|n\rangle$ to lower energy states.)

where $\omega_{fi} = \frac{E_f - E_i}{\hbar}$ and $\gamma = \gamma_f + \gamma_i$

$\omega_{2f}^2 +$

To estimate $\gamma \sim \frac{I_e^{SP}}{\hbar\omega} = \frac{4}{c}\frac{\omega^2}{c^3\hbar}|\vec{d}_{12}|^2$

$d_{12} \sim ea$ ↳ size of atom $a \sim a_B = \frac{\hbar^2}{mc^2}$

$$\Rightarrow \frac{\gamma}{\omega} \sim \frac{\omega^2}{c^3\hbar} e^2 a^2$$

$$\hbar\omega \sim \frac{e^2}{a}$$

$$\omega \sim \frac{e^2}{\hbar a}$$

$$\frac{\gamma}{\omega} \sim \left(\frac{e^2}{\hbar a}\right)^2 \frac{e^2 a^2}{c^3\hbar} = \left(\frac{e^2}{\hbar c}\right)^3 \approx \alpha^3 \approx \left(\frac{1}{137}\right)^3$$

$\frac{\gamma}{\omega} \sim 10^{-7}$, for $\omega \sim 10^{15}\,s^{-1} \to \tau \sim 10^{-8}\,s$

if dipole transition are forbiden then life time will increas by a factor of $\left(\frac{\delta}{a}\right)^2$ which may be estimated to give

$$\tau \sim 10^{-2}\,s.$$

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§. Variational method.

this method is based on the following statement for E_0 of a certaine $\hat{H}$ (not possible to solve)

$$E_0 \leq \langle\psi|\hat{H}|\psi\rangle \quad \text{, for any } \psi \text{ such that}$$

$$\langle\psi|\psi\rangle = 1$$

Proof: assum $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$$|\psi\rangle = \sum_{n=0}^{\infty} C_n |n\rangle \quad , \quad \sum_n |C_n|^2 = 1$$

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{n'=0}^{\infty} C_{n'}^* \langle n'| \hat{H} \sum_n C_n |n\rangle =$$

$$= \sum_{n'n=0}^{\infty} C_{n'}^* C_n E_n \langle n'|n\rangle =$$

$$\sum_{n',n=0}^{\infty} C_{n'}^* C_n E_n \delta_{nn'} = \sum_{n=0} E_n |C_n|^2 \geq E_0 \sum_{n=0}^{\infty} |C_n|^2 \geq$$

$$\geq E_0 \; !$$

Select certain trial function

$$\psi(q; \underbrace{a_1, \ldots, a_n}_{\text{variational parameters}})$$