Radiation and matter

We handle the interaction of radiation and matter *semiclassically*:

- the radiation field classically,
- the matter quantum mechanically,
- OK, if there is large number of photons in the volume $\approx \lambda^3$,
- in the case of the spontaneous emission we impose a fictive field equivalent with the quantum theory.

The vector potential $\boldsymbol{A}$ of the classical radiation field can always be chosen to satisfy the transverse condition: $\nabla \cdot \boldsymbol{A} = 0$. The electric and magnetic field are obtained from the vector potential as

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla \times \boldsymbol{A}. \end{aligned}$$

The energy flux —energy/unit area/unit time— is

$$c\mathcal{U} = \frac{c}{2}\left(\frac{E_{\max}^2}{8\pi} + \frac{B_{\max}^2}{8\pi}\right).$$

For a monochromatic plane wave we have

$$\boldsymbol{A} = A_0\hat{\boldsymbol{\epsilon}}\left[e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}-i\omega t} + e^{-i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}+i\omega t}\right],$$

where $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{\epsilon}}$ are the directions of the propagation and polarization of the plane wave. Due to the transverse condition

$$\nabla \cdot \boldsymbol{A} = 0$$

we have $\hat{\boldsymbol{\epsilon}} \perp \hat{\boldsymbol{n}}$. The energy flux is then

$$c\mathcal{U} = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2.$$

A particle in the radiation field has the mechanical momentum

$$\begin{aligned} \left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 &= \boldsymbol{p}^2 - \frac{e}{c}\boldsymbol{p}\cdot\boldsymbol{A} - \frac{e}{c}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{c^2}\boldsymbol{A}^2 \\ &= \boldsymbol{p}^2 - 2\frac{e}{c}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{c^2}\boldsymbol{A}^2, \end{aligned}$$

since due to the transvers condition

$$\boldsymbol{p}\cdot\boldsymbol{A} = \boldsymbol{A}\cdot\boldsymbol{p}.$$

The Hamiltonian of an electron in the field is now

$$\begin{aligned} H &= \frac{1}{2m_e}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\phi(\boldsymbol{x}) \\ &\approx \frac{\boldsymbol{p}^2}{2m_e} + e\phi(\boldsymbol{x}) - \frac{e}{m_e c}\boldsymbol{A}\cdot\boldsymbol{p}, \end{aligned}$$

when we drop off the term $|\boldsymbol{A}|^2$. Now

$$\begin{aligned} &-\left(\frac{e}{m_e c}\right)\boldsymbol{A}\cdot\boldsymbol{p} \\ &= -\left(\frac{e}{m_e c}\right)A_0\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p} \\ &\quad\times\left[e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}-i\omega t} + e^{-i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}+i\omega t}\right]. \end{aligned}$$

Earlier we saw that in the case of the harmonic potential

$$V(t) = \mathcal{V}e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t}$$

transitions are possible if

$$\begin{aligned} \omega_{ni} + \omega \approx 0 &\quad \text{or} \quad E_n \approx E_i - \hbar\omega \\ \omega_{ni} - \omega \approx 0 &\quad \text{or} \quad E_n \approx E_i + \hbar\omega, \end{aligned}$$

or

$$\begin{aligned} e^{i\omega t} &\longleftrightarrow \text{stimulated emission} \\ e^{-i\omega t} &\longleftrightarrow \text{absorption.} \end{aligned}$$

Absorption

In the case of the radiation field,

$$\mathcal{V}_{ni}^\dagger = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}\right)_{ni}$$

is the matrix element corresponding to the absorption. The transition rate is then

$$\begin{aligned} w_{i\to n} &= \frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}|A_0|^2|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad\times\delta(E_n - E_i - \hbar\omega). \end{aligned}$$

We should note that

- if the final states $|n\rangle$ form a continuum we integrate weighing with the state density $\rho(E_n)$.
- if the final states $|n\rangle$ are discrete they, nevertheless, are not ground states so that their energy cannot be extremely accurate.
- collisions can broaden the energy levels.
- the incoming radiation is not usually completely monochromatic.

So we write the δ-function as

$$\delta(\omega - \omega_{ni}) = \lim_{\gamma\to 0}\left(\frac{\gamma}{2\pi}\right)\frac{1}{[(\omega-\omega_{ni})^2 + \gamma^2/4]}.$$

We define the absorption cross section:

$$\sigma_{\text{abs}} = \frac{\text{(energy/unit time) absorbed by the atom } (i\to n)}{\text{energy flux of the radiation field}}.$$

Since in every absorption process the atom absorbs the energy $\hbar\omega$, we have

$$\begin{aligned} \sigma_{\text{abs}} &= \frac{\hbar\omega w_{i\to n}}{\frac{1}{2\pi}\frac{\omega^2}{c}A_0^2} \\ &= \frac{\hbar\omega\frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}|A_0|^2|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2}{\frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2} \\ &\quad\times\delta(E_n - E_i - \hbar\omega) \\ &= \frac{4\pi^2\hbar}{m_e^2\omega}\left(\frac{e^2}{\hbar c}\right)|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad\times\delta(E_n - E_i - \hbar\omega). \end{aligned}$$

Here $e^2/\hbar c$ is the fine structure constant $\alpha \approx 1/137$.
In order the absorption to be possible the energy quantum $\hbar\omega$ of the radiation must be of the order of the energy level spacing:

$$\hbar\omega \approx \frac{Ze^2}{(a_0/Z)} \approx \frac{Ze^2}{R_{\text{atom}}},$$

when Z is the atomic number. Now

$$\frac{c}{\omega} = \frac{\lambda}{2\pi} \approx \frac{c\hbar R_{\text{atom}}}{Ze^2} \approx \frac{137 R_{\text{atom}}}{Z}$$

or

$$\frac{R_{\text{atom}}}{\lambda} \approx \frac{Z}{2\pi 137} \ll 1.$$

We expand the exponential function in the expression for the cross section as the power series

$$e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}} = 1 + i\frac{\omega}{c}\hat{\boldsymbol{n}}\cdot\boldsymbol{x} + \cdots.$$

Now

$$\frac{\omega}{c}\langle\hat{\boldsymbol{n}}\cdot\boldsymbol{x}\rangle \approx \frac{\omega}{c}R_{\text{atom}} \approx \frac{Z}{137 R_{\text{atom}}}\,R_{\text{atom}} = \frac{Z}{137},$$

so it is usually enough if we keep only the term 1. We have then the so called *electric dipole approximation*. Thus in the electric dipole approximation

$$\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \longrightarrow \hat{\boldsymbol{\epsilon}}\cdot\langle n|\boldsymbol{p}|i\rangle.$$

We choose

$$\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{x}} \text{ and } \hat{\boldsymbol{n}} \parallel \hat{\boldsymbol{z}}.$$

Let the states $|n\rangle$ be the solutions of the problem

$$H_0|n\rangle = E_n|n\rangle,\ H_0 = \frac{\boldsymbol{p}^2}{2m_e} + e\phi(\boldsymbol{x})$$

Because

$$[x, H_0] = \frac{i\hbar p_x}{m_e},$$

we have

$$\begin{aligned}\langle n|p_x|i\rangle &= \frac{m_e}{i\hbar}\langle n|[x,H_0]|i\rangle \\ &= i m_e\omega_{ni}\langle n|x|i\rangle.\end{aligned}$$

Since x is a superposition of the spherical tensors $T^{(1)}_{\pm1}$ we get the selection rules

$$\begin{aligned}m' - m &= \pm1 \\ |j' - j| &= 0, 1.\end{aligned}$$

If we had

- $\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{y}}$, the same selection rules were valid.
- $\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{z}}$, we should have $m' = m$, because $z = T^{(1)}_0$.

In the dipole approximation the absorption cross section is

$$\sigma_{\text{abs}} = 4\pi^2\alpha\omega_{ni}|\langle n|x|i\rangle|^2\delta(\omega - \omega_{ni}).$$

Integration gives

$$\int \sigma_{\text{abs}}(\omega)\,d\omega = \sum_n 4\pi^2\alpha\omega_{ni}|\langle n|x|i\rangle|^2.$$

The oscillator strength is defined as follows:

$$f_{ni} \equiv \frac{2m_e\omega_{ni}}{\hbar}|\langle n|x|i\rangle|^2.$$

One can show that it satisfies so called *Thomas-Reiche-Kuhn's sum rule*:

$$\sum_n f_{ni} = 1.$$

We see that

$$\int \sigma_{\text{abs}}(\omega)\,d\omega = \frac{4\pi^2\alpha\hbar}{2m_e} = 2\pi^2 c\left(\frac{e^2}{m_e c^2}\right).$$

This is known as the oscillator sum rule of classical electrodynamics.

Photoelectric effect
The initial state $|i\rangle$ is atomic but the final state $|n\rangle$ is in the continuum formed by the plane waves $|\boldsymbol{k}_f\rangle$. In the absorption cross section we have now to weigh the function $\delta(\omega_{ni} - \omega)$ with the final state density $\rho(E_n)$:

$$\begin{aligned}\sigma_{\text{abs}} &= \frac{4\pi^2\hbar}{m_e^2\omega}\alpha|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad\times\rho(E_n)\delta(E_n - E_i - \hbar\omega).\end{aligned}$$

Under the periodic boundary conditions in the L-sided cube we have

$$\langle\boldsymbol{x}'|\boldsymbol{k}_f\rangle = \frac{e^{i\boldsymbol{k}_f\cdot\boldsymbol{x}'}}{L^{3/2}},$$

where

$$k_i = \frac{2\pi n_i}{L},\ n_i = 0, \pm1, \pm2, \ldots.$$

When $L \to \infty$, the variable n, defined via the relation

$$n^2 = n_x^2 + n_y^2 + n_z^2,$$

can be considered continuous. Then the volume in the solid angle $d\Omega$ bounded by the surfaces $n' = n$ and $n' = n + dn$ is $n^2\,dn\,d\Omega$.
The final state energy is

$$E = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2}{2m_e}\frac{n^2(2\pi)^2}{L^2}.$$

The number of states with the wave vector $\boldsymbol{k}_f$ in the interval $(E, E + dE)$ and in the solid angle is

$$\begin{aligned}n^2\,d\Omega\frac{dn}{dE}\,dE &= \left(\frac{L}{2\pi}\right)^3\left(\boldsymbol{k}_f^2\right)\frac{dk_f}{dE}\,d\Omega\,dE \\ &= \left(\frac{L}{2\pi}\right)^3\frac{m_e}{\hbar^2}k_f\,dE\,d\Omega.\end{aligned}$$

The differential cross section is now

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2\alpha\hbar}{m_e^2\omega}|\langle\boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2\frac{m_e k_f L^3}{\hbar^2(2\pi)^3}.$$

Example Emission of an electron from the innermost shell.
The wave function of the initial state is approximately like the one of the hydrogen ground state provided we substitute $a_0 \longrightarrow a_0/Z$:

$$\langle \boldsymbol{x}'|i\rangle \approx \left(\frac{Z}{a_0}\right)^{3/2} e^{-iZr/a_0}.$$

The matrix element is now

$$\begin{aligned}
&\langle \boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \\
&= \hat{\boldsymbol{\epsilon}}\cdot\int d^3x'\,\frac{e^{-i\boldsymbol{k}_f\cdot\boldsymbol{x}'}}{L^{3/2}}e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}'} \\
&\times(-i\hbar\nabla)\left[e^{-Zr/a_0}\left(\frac{Z}{a_0}\right)^{3/2}\right].
\end{aligned}$$

Integrating by parts and noting that due to the transversal condition $\hat{\boldsymbol{\epsilon}}\cdot\hat{\boldsymbol{n}}=0$ we have

$$\hat{\boldsymbol{\epsilon}}\cdot\left[\nabla e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}'}\right]=0.$$

We get

$$\begin{aligned}
&\langle \boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \\
&= \frac{\hbar\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f}{L^{3/2}}\int d^3x' e^{i(\boldsymbol{k}_f-\frac{\omega}{c}\hat{\boldsymbol{n}})\cdot\boldsymbol{x}'}\psi_{\text{atom}}(\boldsymbol{x}').
\end{aligned}$$

Thus the matrix element is proportional to the Fourier transform of the atomic wave function with the respect of the variable

$$\boldsymbol{q}=\boldsymbol{k}_f-\left(\frac{\omega}{c}\right)\hat{\boldsymbol{n}}.$$

As the final result we can write the differential cross section as

$$\frac{d\sigma}{d\Omega}=32e^2k_f\frac{(\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f)^2}{m_ec\omega}\frac{Z^5}{a_0^5}\frac{1}{\left[(Z/a_0)^2+q^2\right]^4}.$$

If now $\hat{\boldsymbol{\epsilon}}\parallel\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{n}}\parallel\hat{\boldsymbol{z}}$, the differential cross section can be written using the polar angle θ, the azimuthal angle ϕ and the relations

$$\begin{aligned}
\boldsymbol{k}_f &= k_f(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta)\\
(\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f)^2 &= k_f^2\sin^2\theta\cos^2\phi\\
q^2 &= k_f^2-2k_f\frac{\omega}{c}\cos\theta+\left(\frac{\omega}{c}\right)^2.
\end{aligned}$$