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 transverse 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,

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

is the matrix element corresponding to the absorption.
Recalling

$$w_{i\to n} = \left(\frac{2\pi}{\hbar}\right)|V_{ni}|^2\delta(E_n - E_i - \hbar\omega),$$

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 weighting 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

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

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

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

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

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

or

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

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

$$\frac{\omega}{c}\langle\hat{\boldsymbol{n}}\cdot\boldsymbol{x}\rangle \approx \frac{\omega}{c}R_{\text{atom}} \approx \frac{\alpha Z}{R_{\text{atom}}}\,R_{\text{atom}} = \frac{Z}{137} \ll 1,$$

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

$$[x, H_0] = [x, f(\mathbf{p})] = i\hbar\frac{\partial f(\mathbf{p})}{\partial p_x} = \frac{i\hbar p_x}{m_e},$$

we have

$$\begin{aligned}
\langle n|p_x|i\rangle &= \frac{m_e}{i\hbar}\langle n|[x, H_0]|i\rangle = -i\frac{m_e}{\hbar}\langle n|xH_0 - H_0x|i\rangle \\
&= \frac{i(E_n - E_i)m_e}{\hbar}\langle n|x|i\rangle = im_e\omega_{ni}\langle n|x|i\rangle.
\end{aligned}$$

Now,

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r} \qquad Y_1^{-1} = (-1)^1 Y_1^{1*}$$

thus,

$$x = \frac{r}{2a}(T_{-1}^1 - T_1^1) \qquad a = \sqrt{\frac{3}{8\pi}}$$

or something like above...

Since x is a superposition of the spherical tensors $T_{\pm 1}^{(1)}$, Wigner-Eckart theorem gives us the selection rules

$$\begin{aligned}
m' = m + q \qquad &\rightarrow \qquad m' = m \pm 1 \\
|j - k| \le j' \le j + k \qquad &\rightarrow \qquad |j - 1| \le j' \le j + 1.
\end{aligned}$$

Otherwise stated

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

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 $z = T_0^{(1)}$.

In the dipole approximation the absorption cross section is

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

i.e. $\sigma_{\rm abs}$ exhibits a sharp δ-like peak around $\omega \approx (E_n - E_i)/\hbar$.
Whenever $E_n > E_i$ and ω_{ni} is positive, then integration gives

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

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

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

This is known as the oscillator sum rule of classical electrodynamics.
Notice: $\hbar$ has disappeared
Notice also:
We did not specify the Hamiltonian in detail

Photoelectric effect
Let us consider photoelectric effect, i.e. emission of an electron due to the radiation field. The initial state $|i\rangle$ is atomic (bound state) but the final state $|n\rangle$ is in the continuum formed by the plane waves $|\boldsymbol{k}_f\rangle$ (provided that the free electron is not too slow).
In the absorption cross section we have to weight the function $\delta(\omega_{ni} - \omega)$ with the final state density $\rho(E_n)$:

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

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

$$k_i = \frac{2\pi n_i}{L}, \;\; n_i = 0, \pm 1, \pm 2, \ldots \quad i = x, y, z.$$

When $L \to \infty$, the variable k_i, thus 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

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

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

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

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

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

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

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

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

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