Light and Atoms

In our unmagnetized Lorentz–Heaviside units, Maxwell’s equations are \((4, 4, 2)\):

\[
\mathbf{\nabla} \cdot \mathbf{E} = 4\pi \rho \\
\mathbf{\nabla} \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi \mathbf{j}}{c}
\]

\[
\mathbf{\nabla} \cdot \mathbf{B} = 0 \\
\mathbf{\nabla} \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}.
\]

The scalar \(\phi\) and vector \(\mathbf{A}\) potentials give \(\mathbf{E}\) and \(\mathbf{B}\) as

\[
\mathbf{E} = -\mathbf{\nabla} \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}
\]

and

\[
\mathbf{B} = \mathbf{\nabla} \times \mathbf{A}
\]

which imply the two homogeneous equations (2).

The gauge fields \((\phi, \mathbf{A})\) form a 4-vector

\[
\mathbf{A}^\mu = \begin{pmatrix} \phi \\ \mathbf{A} \end{pmatrix}
\]

and under the gauge transformation

\[
\mathbf{A}'_{\mu}(x) = \mathbf{A}_\mu(x) + \partial_{\mu} \lambda(x)
\]

the fields \(\mathbf{E}\) and \(\mathbf{B}\) are unchanged.
In the Coulomb gauge
\[ \nabla \cdot \mathbf{A} = 0 \]
and so by Gauss's law
\[ \nabla \cdot \mathbf{E} = -\nabla^2 \phi = -\Delta \phi = 4\pi \rho, \]
So one can solve for the scalar potential \( \phi \)
\[ \phi(x,t) = \int \frac{d^3y}{|x-y|} \rho(y,t) \]
\[ \Rightarrow \Delta x \frac{1}{|x-y|} = 4\pi \delta^{(3)}(x-y). \]
In the absence of charges and currents, the "free" electromagnetic vector potential in the Coulomb gauge is transverse
\[ \nabla \cdot \mathbf{A} = 0 \]
and obeys the wave equation
\[ \square A(x) = \Delta A(x) - \frac{i}{c^2} \frac{\partial^2}{\partial t^2} A^2 = 0. \]
The basic solutions of the wave equation (12) are
\[ A(x',t) = \vec{A}_0 \, e^{i(k \cdot x - \omega t)} \]
and
\[ \vec{A} = -\omega^2 \vec{A} \]
and
\[ \Delta \vec{A} = -\vec{n} \cdot \vec{A} \]
and so (13) solves (12) if
\[ -\vec{n}^2 + \frac{\omega^2}{c^2} = 0 \]
So \( w = \hbar \omega \) where \( \hbar = |\vec{k'}| \).
Because of the Coulomb gauge condition (7), we need
\[ 0 = \nabla \cdot A = \vec{n} \cdot \vec{A}_0 = 0 \]
So \( \vec{A}_0 \) must be a vector perpendicular to \( \vec{n} \).
Box quantization: We imagine the radiation inside a large box of side $L$ and volume $V = L^3$.

We impose periodic boundary conditions:

$$\overrightarrow{A}(0, y, z, t) = \overrightarrow{A}(L, y, z, t).$$

So we set:

$$A(x, t) = \epsilon_n(\overrightarrow{p}) e^{i(\overrightarrow{p} \cdot \overrightarrow{x} - \omega t)}$$

with $\omega = \hbar c$, $\overrightarrow{p} \cdot \epsilon_r(\overrightarrow{p}) = 0$, and

$$\overrightarrow{p} = \frac{2\pi}{L} (n, m_1, m_2)$$

where $m_1, m_2, m_3 = 0, \pm 1, \pm 2, \ldots$.

The two vectors $\epsilon_r(\overrightarrow{p})$ are $\pm$ to each other and $\perp \overrightarrow{p}$.

$$\epsilon_r(\overrightarrow{p}) \cdot \epsilon_r(\overrightarrow{p}) = \delta_{rr}$$

$$\overrightarrow{p} \cdot \epsilon_r(\overrightarrow{p}) = 0.$$

There are the polarization vectors.
We now expand the gauge field $A^2(x, t)$ as a Fourier series

$$A^2(x, t) = \sum_{k \in \mathbb{Z}} \sum_{n} \frac{1}{2} \left( \frac{\hbar c^2}{\sqrt{\omega k}} \right)^{1/2} \left[ E_n(k) \phi_n(k, t) e^{-i k \cdot x} \right]$$

$$+ E_n^*(k) \phi_n^*(k, t) e^{i k \cdot x}$$

Here $\hbar = \frac{h}{2\pi}$ is Planck's constant.

Often one uses real polarization vectors $\phi$, which represent linearly polarized fields.

If $A$ is to satisfy the wave equation (11)

$$0 = \Box A = \Delta A - \frac{1}{c^2} \ddot{A}$$

then we need

$$-\hbar^2 \ddot{A} - \frac{1}{c^2} \dddot{A} = 0$$

or

$$\dddot{A} = -\left(\frac{\hbar c}{\omega k}\right)^2 \ddot{A}$$

which is

$$\phi_n(k, t) = \phi_n(k) e^{-i \omega k t}$$

with

$$\omega k = \hbar c$$
The energy of $E$ and $B$ fields in

\[ H_0 = \frac{1}{8\pi} \int [E(x, t)^2 + B(x, t)^2] \, d^3x. \]

Now we substitute the Fourier expansion (27) into (3)

\[ E = -\frac{1}{c} \nabla A \] (empty space) \n
\[ B = \nabla \times A \]

and then puts the resulting expressions for $E$ and $B$ into (33), then one finds

\[ H_0 = \sum_k \frac{\hbar}{2} \hbar \omega_k [a_k^+ a_k + \frac{1}{2}] \]

in which we used the commutation relation

\[ [a_k, a_k^+] = \hbar \delta_{kk'} \]

to find

\[ a_k a_k^+ a_{k'} a_{k'} = a_k^+ a_k a_{k'} a_{k'} + 1. \]

The "annihilation" operators all commute

\[ [a_k, a_{k'}] = 0. \]

and the adjoint of this equation implies that the creation operators do too \[ [a^+, a^+] = 0. \]
That is,

\[ \{a^\dagger_r (\hbar^2), a^\dagger_r (\hbar^1)\} = 0. \]

So we now have our hamiltonian for how light interacts with atoms:

\[
H_0 = \sum \text{tw } \left( a^\dagger_r (\hbar) a_r (\hbar) + \frac{1}{2} \right) \\
+ \frac{\vec{p}^2}{2m} - e^2 \frac{1}{r} = H_0^{EM} + H_0^{AT}
\]

for a single electron around a fixed proton and

\[
V = -\frac{e}{mc} A(x, t) \cdot \vec{p} + \frac{e^2}{2mc^2} A(x, t)
\]

The term \( V \) comes from the expansion of

\[
\frac{1}{2m} (\vec{p} - \frac{e}{c} \vec{A})^2 = \frac{\vec{p}^2}{2m} - \frac{e}{2mc} \vec{p} \cdot \vec{A} - \frac{e^2}{2mc} \frac{\vec{A}^2}{2mc^2}
\]

with the Coulomb-gauge condition \( \nabla \cdot A = 0 \) which implies

\[
\vec{p} \cdot \vec{A} = \frac{\hbar}{i} \nabla \cdot \vec{A}, \quad \frac{\hbar}{i} \nabla \times \vec{A} = \vec{A} \times \vec{p},
\]
Absorption of a photon by an atom is the transition

\[ |i, m_i(x)\rangle \rightarrow |f, m_f(x)\rangle \] 45

in which the photon number \( m_f(x) \) drops by 1 as the atom absorbs a photon of type \( \overline{\gamma} \) in and the electron rises from the initial state \( i \) to the final state \( f \).

The main part of \( V \) for this process is

\[ V = -\frac{e}{mc} \vec{A}(x,t) \cdot \vec{p} \] 46

and in the interaction picture it is

\[ V_{int}(t) = -\frac{e}{mc} \vec{A}(x,t) \cdot \vec{p} e^{-i\hbar \Omega t/\hbar} \]

where \( \hbar \Omega = \frac{\hbar}{2m} - \frac{e^2}{r} \) 47

in which \( \hbar \Omega \) is

\[ \hbar \Omega = \frac{p^2}{2m} - \frac{e^2}{r} \] 48

The field \( \vec{A}(x,t) \) given by (27) when the \( a \)'s and \( a^+ \)'s have the harmonic and dependence of eq. (31) already is in the EM interaction picture as

\[ \exp(i \hbar \Omega t/\hbar) A(x,0) \exp(-i \hbar \Omega t/\hbar) \]

\[ \vec{A}(x,t) = \sum_k \left( \frac{\hbar c^2}{W_k V} \right)^{1/2} \exp(i \hbar x/k - i \hbar c x/\lambda) \left[ \epsilon_n(h) e^{-i a_k(x/\lambda)} + \epsilon_{n}(h) a^+_k(x/\lambda) e^{+i a_k(x/\lambda)} \right] \] 49
That is,

\[ A_{\perp}(x,t) = e^{-iH_{0}t/H} A_{\perp}(x,0) e^{iH_{0}t/H}, \quad (50) \]

where

\[ H_{0} = \sum_{k\nu} \frac{T_{kk}}{m_{\nu}} \left[ a_{\nu}^{\dagger}(k) a_{\nu}(k) + \frac{1}{2} \right]. \tag{51} \]

Now

\[ 14, t \rangle_{\Sigma} = \frac{1}{T} \left\{ e^{-i\int_{0}^{t} V_{\perp}(x, t') dt'} \right\} 14, 0 \rangle_{\Sigma}, \tag{52} \]

so

\[ 14, m_{\nu}(k), t \rangle_{\Sigma} = \left( 1 - \frac{i}{\hbar} \int_{0}^{t} V_{\perp}(x, t') dt' \right) 14, m_{\nu} = 1 \tag{53} \]

to lowest order. The amplitude for the\ntransition \( 14, m_{\nu} = 1 \rightarrow 14, m_{\nu} = 0 \) is

\[ \langle \bar{f}, m_{\nu}(k), t \rangle_{\Sigma} = \left( 1 - \frac{i}{\hbar} \int_{0}^{t} V_{\perp}(x, t') dt' \right) 14, m_{\nu} = 0 \]

\[ = -\frac{i}{\hbar} \int_{0}^{t} e^{iE_{k}t'/\hbar} \left( \frac{-e}{mc} \right)^{3/2} \langle \bar{f}, m_{\nu} = 1 \rangle_{\Sigma} e^{-iE_{k}t'/\hbar} \]

\[ = -\frac{i}{\hbar} \left( \frac{-e}{mc} \right) \left( \frac{\hbar c^{2}}{w_{k} V} \right)^{1/2} \langle \bar{f}, m_{\nu} = 1 \rangle_{\Sigma} e^{-iE_{k}t'/\hbar} \int_{0}^{t} e^{-i\omega_{k} t'} dt' \quad \text{because} \]

\[ \langle \bar{f}, m_{\nu} = 1 \rangle_{\Sigma} A(x, t), p e^{i\xi_{n}(n) \cdot \vec{p}} e^{i(\bar{E}_{n} - E_{n})t'/\hbar} \]

\[ < f_{m = 1, e} A(x, t), p e^{i\xi_{n}(n) \cdot \vec{p}} < f_{m = 1}, e > = < f_{m = 1} A_{\perp}(x, t), p e^{i\xi_{n}(n) \cdot \vec{p}} e^{i(\bar{E}_{n} - E_{n})t'/\hbar} >. \tag{55} \]
The usual harmonic oscillator rules

\[ a_n(k) |m(k)\rangle = \sqrt{m_n(k)} |m_n(k) - 1\rangle \]

apply. So

\[ \langle f, m-1| i, m\rangle_2 = \frac{i\hbar}{\hbar mc} \left( \frac{\hbar c^2}{\omega_k V} \right)^{1/2} \langle f, \psi_n(\tilde{r}), \tilde{p}(i) \rangle \]

\[ \exp \left[ \frac{i (E_f - E_i - \hbar \omega_k) t}{\hbar} \right] \left[ \frac{E}{E_f - E_i - \hbar \omega_k} + 1 \right] \]

\[ \langle f, n-1| i, m\rangle_2 = \frac{e}{mc} \left( \frac{\hbar c^2}{\omega_k V} \right)^{1/2} \langle f, \psi_n(\tilde{r}), \tilde{p}(i) \rangle \]

\[ \exp \left[ \frac{i (\omega_{k_f} - \omega_k) t}{\hbar} \right] \left[ \frac{E}{E_f - E_i - \hbar \omega_k} + 1 \right] \]

So as before (Sec. 5.6), the probability is

\[ P_{sf}(t) = \left( \frac{e}{mc} \right)^2 \frac{\hbar c^2}{\omega_k V} \left( \frac{1}{4} \right)^2 \frac{\hbar \omega_k}{(E_f E_i - \hbar \omega_k)^2} \]

\[ \times \frac{E}{E_f - E_i - \hbar \omega_k} \]
And since

\[
\lim_{t \to \infty} \frac{1}{(E_f - E_i - tw_c)^2} \frac{\sin^2 \left( \frac{E_f - E_i - tw_c}{2t} \right)}{2t} = \frac{\pi \delta(E_f - E_i - tw_c)}{2t}
\]

we have

\[
P(i, n \rightarrow f(n - 1)) = \frac{2\pi t |V|^2 \delta(E_f - E_i - tw_c)}{\hbar}
\]

\[
= \frac{2\pi t}{\hbar} \left( \frac{e}{mc} \right)^2 \frac{\hbar c^2}{w_c V} \left| \langle f | \left( e, \epsilon_c \right); p \rangle \right|^2 \delta(E_f - E_i - tw_c).
\]

The transition rate \( W \) then is

\[
W_{i \to f(n)} = \frac{dP}{dt} = \frac{2\pi}{\hbar} \left( \frac{e}{mc} \right)^2 \frac{\hbar c^2}{w_c V} \left| \langle f | \left( e, \epsilon_c \right); p \rangle \right|^2 \delta(E_f - E_i - tw_c)
\]

Now what do we do with the matrix element? First, we assume that

\[
\lambda \gg \alpha
\]

so that

\[
\delta \rightarrow 1,
\]

This is true for visible light which is
a few hundred nanometers while now \( \frac{\text{in}}{\text{mm}} \).

So we now have

\[
\langle f | e^\dagger \cdot p l l | i \rangle = \langle f l | p^\dagger l l \rangle
\]

But

\[
\hat{L} \cdot \hat{H}_0 = \frac{i \hbar \cdot p}{m}
\]

so

\[
\langle f l | p^\dagger l l \rangle = \frac{m}{i \hbar} \langle f l | \hat{L} \cdot [x, \hat{H}_0] l l \rangle
\]

\[
= \frac{m}{i \hbar} \langle f l | \hat{L} \cdot (E_i - \hat{E}_f) l l \rangle
\]

\[
= i \frac{\hbar}{m} \omega_f \cdot \langle f l | x^2 l l \rangle
\]

This is called the dipole approximation,

So now

\[
\hat{W} = \frac{2 \pi}{\hbar} \left( \frac{e}{mc} \right)^2 \hbar c^2 \frac{m^2 \omega_f^2}{W_n V} | \langle E_f | (x) \rangle \cdot \langle f l | x l l \rangle |^2
\]

\[
\times \delta (E_f - E_i - \hbar \omega_k)
\]

which we must sum over final states

\[
W = \int \rho(E_f) dE_f
\]
If \( \ell \) \( \ell \) = \( \hat{\ell} \), then since
\[
\hat{\ell} \cdot \hat{\ell} = \hat{\ell}
\]
which commutes with \( L_z \)
\[
[\hat{\ell}, L_z] = 0
\]
It follows that \( m_F = m_i \).

But \( \hat{\ell} \cdot \hat{\ell} = \hat{x} \) or \( \hat{y} \), then
since \( \hat{x} \) and \( \hat{y} \) are linear combinations
of \( Y_i \) and \( \bar{Y}_i \) (A.5.7), \( m_F \) must change by \( \pm 1 \)
\[
m_F = m_i \pm 1.
\]
Also, since under reflections \( \hat{x} \rightarrow -\hat{x} \),
the parity must also change; so if \( \ell \) \( \ell \) is
odd, then \( \ell \) \( \ell \) is even, and vice versa.

Furthermore, since \( \hat{x} \) is a linear combination
of \( Y_i \)'s, \( \ell \) behaves as an \( l = 1 \) object.
\[
\ell_F = \ell_i \pm 1.
\]
These electron rules apply to atomic hydrogen
-treated non-relativistically, but similar
selection rules apply more generally. Let us consider

\[ \langle i | \{ \epsilon \cdot x, \epsilon \cdot x, H_0 \} | i \rangle \]

\[ = \langle i | \epsilon \cdot x (\{ \epsilon \cdot x, H_0 \} - \{ H_0 \cdot \epsilon \cdot x \} \} | i \rangle \]

\[ = 2 \epsilon i \langle i | (\{ \epsilon \cdot x \}^2) | i \rangle - 2 \langle i | \epsilon \cdot x H_0 \epsilon \cdot x | i \rangle \]

\[ = \sum_\mathcal{M} \left[ 2 \epsilon \langle i | \epsilon \cdot x | \text{M}_\mathcal{M} \rangle | \epsilon \cdot x | i \rangle \right. \]

\[ - 2 \epsilon n \langle i | \epsilon \cdot x | \text{M}_\mathcal{M} \rangle \langle \epsilon \cdot x | i \rangle \left. \right] \]

\[ = 2 \sum_\mathcal{M} \left( \mathcal{E}_i - \mathcal{E}_n \right) \left| \langle i | \epsilon \cdot x | \text{M}_\mathcal{M} \rangle \right|^2. \quad 74 \]

5. If \( | i \rangle = | 0 \rangle \) is the ground state — \( | 11/2 \rangle \) for the hydrogen atom — then

\[ \int \omega \omega \omega = \int \omega \rho(\mathcal{E}_f) d\mathcal{E}_f d\mathcal{W}_k \]

\[ = \int \sum_\mathcal{M} \frac{2 \pi}{\hbar} \left( \frac{\mathcal{E}_f}{m c} \right)^2 \hbar^2 c \mathcal{E}_f \mathcal{W}_k^2 \left| \langle \mathcal{M}_\mathcal{M} | \epsilon \cdot x | i \rangle \right|^2 \]

\[ \delta \left( \mathcal{E}_f - \mathcal{E}_i - \hbar \mathcal{W}_k \right) d\hbar \mathcal{W}_k \frac{1}{\hbar} \quad 75 \]
\[ \int w \, dw = \sum F \frac{2\pi}{\hbar^2} \left( \frac{e}{c} \right)^2 \frac{m \hbar c^2}{\gamma} \left\langle \frac{\hbar}{i} l [\varepsilon(\lambda) \cdot \lambda] \right\rangle \]
So the rate $\sigma$ integrated over $w$ is
\[ \int \sigma(w) \, dw = \frac{\pi}{m} \frac{(\frac{e}{c})^2 \frac{m}{k} \frac{\hbar c^2}{V}}{\frac{k}{V}}. \]

Physicists usually divide rates by the incident flux $F$ which is the density of incoming particles times their speed. Here
\[ F = \frac{nc}{V}. \]

So,
\[ \int \sigma(w) \, dw = \frac{\pi}{m} \left( \frac{e}{c} \right)^2 \frac{m}{k} \frac{\hbar c^2}{V} \frac{1}{\frac{nc}{V}} \]
\[ = \frac{\pi \frac{\hbar c^2}{k} \frac{1}{m c}}{\frac{nc}{V}} = 2\pi \frac{\hbar c^2}{n mc^2}, \]

which is (5.7.26) derived from QED, rather than semi-classically.