Light and Atoms

In our unrationalized Lorentz-Heaviside units, Maxwell's equations are (4, 4, 2)

$$\nabla \cdot E = 4\pi\rho \qquad \nabla \times B - \frac{1}{c}\dot{E} = \frac{4\pi j}{c} \qquad 1$$

$$\nabla \cdot B = 0 \qquad \nabla \times E + \frac{1}{c}\dot{B} = 0 . \qquad 2$$

The scalar ϕ and vector $\vec{A}$ potentials give E & B as

$$\vec{E} = -\nabla\phi - \frac{1}{c}\dot{A} \qquad 3$$

and

$$\vec{B} = \vec{\nabla} \times \vec{A} \qquad 4$$

which imply the two homogeneous equations (2). The gauge fields $(\phi, \vec{A})$ form a 4-vector

$$A^\mu = \begin{pmatrix} \phi \\ \vec{A} \end{pmatrix} \qquad 5$$

and under the gauge transformation

$$A'_\mu(x) = A_\mu(x) + \partial_\mu \lambda(x) \qquad 6$$

the fields $\vec{E}$ & $\vec{B}$ are unchanged.

In the Coulomb gauge

$$\vec{\nabla} \cdot \vec{A} = 0 \qquad 7$$

and so by Gauss's law

$$\nabla \cdot E = -\nabla^2 \phi = -\Delta \phi = 4\pi \rho . \qquad 8$$

So one can solve for the scalar potential ϕ

$$\phi(x,t) = \int d^3y \, \frac{\rho(y,t)}{|\vec{x}-\vec{y}|} \qquad 9$$

since

$$-\Delta_x \frac{1}{|\vec{x}-\vec{y}|} = 4\pi \delta^{(3)}(\vec{x}-\vec{y}) . \qquad 10$$

In the absense of charges and currents, the "free" electromagnetic vector potential in the Coulomb gauge is transverse

$$\nabla \cdot A = 0 \qquad 11$$

and obeys the wave equation

$$\Box \vec{A}(x) = \Delta \vec{A} - \frac{1}{c^2} \partial_t^2 \vec{A} = 0. \qquad 12$$

The basic solutions of the wave equation (12) are

$$\vec{A}(\vec{x},t) = \vec{A}_0 e^{i(k\cdot x - \omega t)} \qquad 13$$

because then

$$\ddot{\vec{A}} = -\omega^2 \vec{A} \qquad 14$$

and

$$\Delta \vec{A} = -\vec{k}^2 \vec{A} \qquad 15$$

and so (13) solves (12) if

$$-\vec{k}^2 + \frac{\omega^2}{c^2} = 0. \qquad 16$$

So $\omega = kc$ where $k = |\vec{k}|$. 17

Because of the Coulomb-gauge condition (7), we need

$$0 = \nabla \cdot A = i\vec{k}\cdot\vec{A}_0 = 0. \qquad (18)$$

So $\vec{A}_0$ must be a vector $\perp$ to $\vec{k}$.

Box quantization: We imagine the radiation inside a large box of side L and volume

$$V = L^3 \tag{19}$$

We impose periodic boundary conditions

$$\vec{A}(\vec{0}, y, z, t) = \vec{A}(L, y, z, t). \tag{20}$$

So we set

$$A(x,t) = \frac{\epsilon_r(\vec{k})}{\sqrt{V}} e^{i(k\cdot x - \omega t)} \tag{21}$$

with $\omega = kc$, $\vec{k}\cdot\vec{\epsilon}_r(\vec{k}) = 0$, and (22)

$$\vec{k} = \frac{2\pi}{L}(n_1, n_2, n_3) \tag{23}$$

where $n_1, n_2, n_3 = 0, \pm 1, \pm 2$, etc. (24)
The two vectors $\vec{\epsilon}_r(\vec{k})$ are $\perp$ to each other and to $\vec{k}$

$$\epsilon_r(k)\cdot\epsilon_s(k) = \delta_{rs} \tag{25}$$

$$\vec{k}\cdot\vec{\epsilon}_r(\vec{k}) = 0. \tag{26}$$

There are the polarization vectors.

We now expand the gauge field $\vec{A}(x,t)$ as a Fourier series

$$\vec{A}(\vec{x},t) = \sum_k \sum_{r=1}^{2} \left(\frac{hc^2}{V\omega_k}\right)^{1/2} \left[\epsilon_r(k)\, a_r(k,t)\, e^{i\vec{k}\cdot\vec{x}} + \epsilon_r^*(k)\, a_r^+(k,t)\, e^{-i\vec{k}\cdot\vec{x}}\right]. \quad 27$$

Here $h = 2\pi\hbar$ is Planck's constant. Often one uses real polarization vectors ϵ, which represent linearly polarized fields. If A is to satisfy the wave equation (17)

$$0 = \Box A = \Delta A - \frac{1}{c^2}\ddot{A} \quad 28$$

then we need

$$-k^2 a - \frac{1}{c^2}\ddot{a} = 0 \quad 29$$

or

$$\ddot{a} = -(kc)^2 a \quad 30$$

that is

$$a_r(k,t) = a_r(k)\, e^{-i\omega_k t} \quad 31$$

with

$$\omega_k = kc, \quad 32$$

The energy of E & B fields in empty space is

$$H_0 = \frac{1}{8\pi} \int \left[\vec{E}^2(x,t) + \vec{B}^2(x,t) \right] d^3x . \qquad 33$$

If one substitutes the Fourier expansion (27) into (3)

$$\vec{E} = -\frac{1}{c} \dot{\vec{A}} \qquad \text{(empty space)} \qquad 34$$

$$\vec{B} = \vec{\nabla} \times \vec{A} \qquad 35$$

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

$$H_0 = \sum_{\vec{k}} \sum_{r=1}^{2} \hbar\omega_k \left[a_r^+(\vec{k})\, a_r(\vec{k}) + \tfrac{1}{2} \right] . \qquad 36$$

in which we used the commutation relation

$$\left[a_r(\vec{k}), a_s^+(\vec{k}') \right] = \delta_{\vec{k},\vec{k}'}\, \delta_{rs} \qquad 37$$

to find

$$a_r(k)\, a_r^+(k) = a_r^+(k)\, a_r(k) + 1 . \qquad (38)$$

The "annihilation" operators all commute

$$\left[a_r(\vec{k}), a_{r'}(k') \right] = 0 . \qquad 39$$

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

That is,

$$[a^\dagger_r(\vec{k}),\ a^\dagger_{r'}(\vec{k}')] = 0. \qquad 40.$$

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

$$H_0 = \sum_{k,r} \hbar\omega\left(a^\dagger_r(k)a_r(k) + \tfrac{1}{2}\right)$$

$$+ \frac{\vec{p}^{\,2}}{2m} - \frac{e^2}{r} = H_0^{EM} + H_0^{AT} \qquad 41$$

for a single electron around a fixed proton, and

$$V = -\frac{e}{mc}A(\vec{x},t)\cdot p + \frac{e^2}{2mc^2}\vec{A}^2(\vec{x},t) \qquad 42$$

The term V comes from the expansion of

$$\frac{1}{2m}\left(p - \frac{e}{c}A\right)^2 = \frac{\vec{p}^{\,2}}{2m} - \frac{e}{2mc}p\cdot A - \frac{e}{2mc}A\cdot p$$

$$+ \frac{e^2}{2mc^2}\vec{A}^2 \qquad 43$$

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

$$p\cdot A = \frac{\hbar}{i}\nabla\cdot A = \frac{\hbar}{i}A\cdot\nabla = A\cdot p, \qquad 44$$

Absorption of a photon by an atom is the transition

$$|i, n_r(\vec{k})\rangle \to |f, n_r(k)-1\rangle \qquad 45$$

in which the photon number $n_r(k)$ drops by 1 as the atom absorbs a photon of type $\vec{k}, r$ and the electron rises from the initial state i to the final state f.

The main part of V for this process is

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

and in the interaction picture it is

$$V_I(t) = -\frac{e}{mc}\vec{A}(x,t)\cdot e^{iH_0^{AT}t/\hbar}\,\vec{p}\,e^{-iH_0^{AT}t/\hbar} \qquad 47$$

in which H_0^{AT} is

$$H_0^{AT} = \frac{p^2}{2m} - \frac{e^2}{r} \qquad 48$$

The field $\vec{A}(x,t)$ given by (27) where the a's and $a^\dagger$'s have the harmonic time dependence of eq. (31) already is in the EM-interaction picture, $\exp(iH_0^{EM}t/\hbar)A(x,0)\exp(-iH_0^{EM}t/\hbar)$

$$\vec{A}_I(x,t) = \sum_{kr}\left(\frac{hc^2}{\omega_k V}\right)^{\frac{1}{2}}\left[\epsilon_r(k)e^{ik\cdot x-\omega_k t}a_r(k) + \epsilon_r^*(k)a_r^\dagger(k)e^{-i(k\cdot x-\omega t)}\right]. \quad (49)$$

That is,

$$\vec{A}_I(x,t) = e^{iH_0^{EM}t/\hbar} A_I(x,0)\, e^{-iH_0^{EM}t/\hbar}, \qquad (50)$$

where
$$H_0^{EM} = \sum_{k\nu} \hbar\omega_k \left[a_\nu^\dagger(k)a_\nu(k) + \tfrac{1}{2}\right]. \qquad 51$$

Now

$$|\psi,t\rangle_I = T\left\{e^{-\frac{i}{\hbar}\int_0^t V_I(t')dt'}\right\} |\psi,0\rangle_I \qquad 52$$

so

$$|i, n_\nu(k), t\rangle_I = \left(1 - \frac{i}{\hbar}\int_0^t V_I(t')\,dt'\right) |i, n_\nu, 0\rangle_I \qquad 53$$

to lowest order. The amplitude for the transition to $|f, n_\nu(k)-1\rangle$ then is

$$\langle f, n_\nu(k)-1 | i, n_\nu(k), t\rangle_I = -\frac{i}{\hbar} \langle f, n-1| \int_0^t V_I(t')\,dt' |i, n_\nu, 0\rangle$$

$$= -\frac{i}{\hbar}\int_0^t \langle f, n-1|\, e^{iE_f t'/\hbar} \left(-\frac{e}{mc}\right) \vec{A}(x,t)\cdot\vec{p}\, e^{-iE_i t'/\hbar} |i, n_\nu, 0\rangle$$

$$= -\frac{i}{\hbar}\left(-\frac{e}{mc}\right)\left(\frac{hc^2}{\omega_k V}\right)^{\frac{1}{2}} \langle f| e^{i\vec{k}\cdot\vec{x}} \epsilon_\nu(k)\cdot\vec{p}\,|i\rangle \langle n-1|a_\nu(k)|n\rangle$$

$$\int_0^t e^{i(E_f-E_i)t'/\hbar - i\omega_k t'}\,dt' \qquad (54)$$

because

$$\langle f, n-1|\, e^{i(H_0^{AT}+H_0^{EM})t'/\hbar} A(x,0)\cdot p\, e^{-i(H_0^{AT}+H_0^{EM})t'/\hbar} |i,n\rangle = \langle f, n-1| A_I(x,t)\cdot p |i,n\rangle\, e^{i(E_f-E_i)t'/\hbar}, \qquad (55)$$

The usual harmonic-oscillator rules

$$a_r(k)\,|n_r(k)\rangle = \sqrt{n_r(k)}\,|n_r(k)-1\rangle \qquad 56$$

apply. So

$$\langle f, n-1|i, n, t\rangle_I = \frac{ie}{\hbar mc}\left(\frac{hc^2}{\omega_k V}\right)^{\frac{1}{2}}\sqrt{n}\;\langle f|e^{ik\cdot x}\vec{\epsilon}_r(\vec{k})\cdot\vec{p}\,|i\rangle$$

$$\frac{e^{i(E_f-E_i-\hbar\omega_k)t/\hbar}-1}{i(E_f-E_i-\hbar\omega)/\hbar} \qquad 57$$

or

$$\langle f, n-1|i, n, t\rangle_I = \frac{e}{mc}\left(\frac{hc^2}{\omega_k V}\right)^{\frac{1}{2}}\sqrt{n}\;\langle f|e^{ik\cdot x}\epsilon_r(k)\cdot p\,|i\rangle$$

$$\times\;\frac{e^{i(\omega_{fi}-\omega_k)t}-1}{E_f-E_i-\hbar\omega} \qquad 58$$

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

$$P_{i\to f}(t) = \left(\frac{e}{mc}\right)^2\frac{n h c^2}{\omega_k V}\;|\langle f|e^{ik\cdot x}\epsilon_r(k)\cdot p\,|i\rangle|^2\,\frac{4}{(E_f-E_i-\hbar\omega_k)^2}$$

$$\times\;\sin^2(\omega_{fi}-\omega_k)t/2 \qquad 59$$

And since

$$\lim_{t\to\infty} \frac{1}{(E_f - E_i - \hbar\omega_k)^2} \sin^2 \frac{(E_f - E_i - \hbar\omega_k)t}{2\hbar} = \frac{\pi t}{2\hbar}\delta(E_f - E_i - \hbar\omega_k) \tag{60}$$

we have

$$P(i,n \to f\, n-1) = \frac{2\pi t}{\hbar} |V_{fi}|^2 \, \delta(E_f - E_i - \hbar\omega_k)$$

$$= \frac{2\pi t}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{n h c^2}{\omega_k V} |\langle f | e^{ik\cdot x} \epsilon_r(k)\cdot p | i\rangle|^2 \delta(E_f - E_i - \hbar\omega_k), \tag{61}$$

The transition rate w then is

$$w_{ni \to f\, n-1} = \frac{dP}{dt} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{n h c^2}{\omega_k V} |\langle f | e^{ik\cdot x} \epsilon_r(k)\cdot p | i\rangle|^2 \delta(E_f - E_i - \hbar\omega_k) \tag{62}$$

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

$$\lambda >> a_0$$

so that

$$e^{i\vec{k}\cdot\vec{x}} \cong 1 . \tag{63}$$

This is true for visible light which is

a few hundred nanometers while $a_0 \sim \frac{1\,nm}{20}$.

So we now have

$$\langle f | e^{i k_0 \cdot x} \epsilon \cdot p | i \rangle = \epsilon \cdot \langle f | \vec{p} | i \rangle \qquad 64$$

But

$$[\vec{x}, H_0^{AT}] = \frac{i\hbar \vec{p}}{m} \qquad 65$$

so

$$\epsilon \cdot \langle f | \vec{p} | i \rangle = \epsilon \cdot \frac{m}{i\hbar} \langle f | [X, H_0] | i \rangle$$

$$= \epsilon \cdot \frac{m}{i\hbar} (E_i - E_f) \langle f | \vec{x} | i \rangle$$

$$= i \vec{\epsilon} \cdot m \, \omega_{fi} \langle f | \vec{x} | i \rangle \qquad 66$$

This is called the dipole approximation.

So now

$$\hat{W} = \frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^2 \frac{n h c^2}{\omega_k V} m^2 \omega_{fi}^2 \left| \vec{\epsilon}_r(k) \cdot \langle f | \vec{x} | i \rangle \right|^2 \qquad 67$$

$$\times \, \delta(E_f - E_i - \hbar\omega_k)$$

which we must sum over final states

$$W = \int \hat{w} \rho(E_f) \, dE_f \qquad 68$$

If $\epsilon_r(h) = \hat{z}$, then since

$$\vec{\epsilon}_r(u) \cdot \vec{x} = z \qquad 69$$

which commutes with L_z

$$[z, L_z] = 0 \qquad 70$$

it follows that $m_f = m_i$. 71

But if $\epsilon_r(\vec{u}) = \hat{x}$ or $\hat{y}$, then since $\hat{x}$ and $\hat{y}$ are linear combinations of Y_1^1 and Y_1^{-1} (A.5.7), m must change by ±1

$$m_f = m_i \pm 1. \qquad 72$$

Also, since under reflections $\vec{x} \to -\vec{x}$, the parity must also change; so if l_i is odd, then l_f is even, and vice versa.

Further, since $\vec{x}$ is a linear combination of Y_1^m's, it behaves as an $l = 1$ object. So

$$l_f = l_i \pm 1. \qquad 73$$

These selection rules apply to atomic hydrogen treated non-relativistically, but similar selection rules apply more generally.

Let us consider

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

$$= \langle i | \epsilon\cdot x \; (\epsilon\cdot x H_0 - H_0 \epsilon\cdot x) - (\epsilon\cdot x H_0 - H_0 \epsilon\cdot x)\epsilon\cdot x | i \rangle$$

$$= 2E_i \langle i | (\epsilon\cdot x)^2 | i \rangle - 2 \langle i | \epsilon\cdot x \, H_0 \, \epsilon\cdot x | i \rangle$$

$$= \sum_n \Big[2E_i \langle i | \epsilon\cdot x | n \rangle \langle n | \epsilon\cdot x | i \rangle$$

$$- 2E_n \langle i | \epsilon\cdot x | n \rangle \langle n | \epsilon\cdot x | i \rangle \Big]$$

$$= 2 \sum_n (E_i - E_n) \, |\langle i | \epsilon\cdot x | n \rangle|^2 . \qquad 74$$

So if $|i\rangle = |0\rangle$ is the ground state — $|1,0,0\rangle$ for the hydrogen atom — then

$$\int w \, d\omega = \int \hat{w} \, \rho(E_f) \, dE_f \, d\omega_k$$

$$= \int \sum_f \frac{2\pi}{\hbar} \left(\frac{e}{mc}\right)^2 \frac{n h c^2}{\omega_k V} m^2 \omega_{fi}^2 \, |\langle f | \epsilon_r(k)\cdot x | i \rangle|^2$$

$$\delta(E_f - E_i - \hbar\omega_k) \, d\hbar\omega_k \, \frac{1}{\hbar} \qquad 75$$

So

$$\int w\, d\omega = \sum_f \frac{2\pi}{\hbar^2}\left(\frac{e}{c}\right)^2 \frac{n\hbar c^3}{V}\, \omega_{fi}\, |\langle f|\epsilon_r(k)\cdot x|i\rangle|^2 \qquad 76$$

But

$$2\sum_f (E_i - E_f)\, |\langle f|\epsilon_r(k)\cdot x|i\rangle|^2$$

$$= \langle i|[\epsilon\cdot x, [\epsilon\cdot x, H_0]]|i\rangle \qquad 77$$

and

$$[\epsilon\cdot x, H_0] = \frac{i\hbar\, \epsilon\cdot p}{m} \qquad 78$$

and so

$$[\epsilon\cdot x, [\epsilon\cdot x, H_0]] = \frac{i\hbar}{m}[\epsilon\cdot x, \epsilon\cdot p]$$

$$= \frac{i\hbar}{m}\epsilon_i\epsilon_j[x_i, p_j] = \frac{i\hbar}{m}\epsilon_i\epsilon_j\, i\hbar\delta_{ij}$$

$$= -\frac{\hbar^2}{m}\epsilon_i^2 = -\frac{\hbar^2}{m}. \qquad 79$$

So

$$2\sum_f (E_f - E_i)\, |\langle f|\epsilon\cdot x|i\rangle|^2 = \frac{\hbar^2}{m} \qquad 80$$

or

$$\sum_f \frac{2m\omega_{fi}}{\hbar} |\langle f|\epsilon\cdot x|i\rangle|^2 = 1. \qquad 81$$

This is the Thomas-Reiche-Kuhn sum rule.

So the rate w integrated over ω is

$$\int w \, d\omega = \frac{\pi}{m}\left(\frac{e}{c}\right)^2 \frac{n h c^2}{\hbar V} . \qquad 82$$

Physicists usually divide rates by the incident flux F which is the density of incoming particles times their speed. Here

$$F = \frac{nc}{V} . \qquad 83$$

So

$$\int \sigma(\omega) d\omega = \frac{\pi}{m}\left(\frac{e}{c}\right)^2_{\hbar} \frac{n h c^2}{V} \frac{1}{\frac{nc}{V}}$$

$$= \pi \frac{h e^2}{\hbar \, m c} = 2\pi^2 c \left(\frac{e^2}{mc^2}\right), \qquad 84$$

which is (5,7.26) derived from QED, rather than semi-classically.