Light and Atoms

In SI units, the microscopic Maxwell equations are

$$\nabla \cdot B = 0 \qquad \nabla \times E + \dot{B} = 0 \tag{1}$$

$$\nabla \cdot E = \frac{\rho}{\epsilon_0} \qquad \nabla \times B = \mu_0 J + \frac{\dot{E}}{c^2}. \tag{2}$$

The scalar and vector potentials give E & B as

$$\vec{E} = -\nabla\phi - \dot{A} \quad \text{and} \quad \vec{B} = \vec{\nabla} \times \vec{A} \tag{3}$$

which imply the homogeneous equations (1).

These potentials ϕ/c and $\vec{A}$ form a 4-vector

$$A^\mu = \begin{pmatrix} \phi/c \\ \vec{A} \end{pmatrix}. \tag{4}$$

Under the gauge transformation

$$A'^\mu(x) = A^\mu(x) + \partial^\mu \lambda(x) \tag{5}$$

the fields $\vec{E}$ and $\vec{B}$ do not change.

In the Coulomb gauge (also known as the radiation gauge)

$$\vec{\nabla}\cdot\vec{A} = 0 . \tag{6}$$

To get there, we set $\Delta\lambda \equiv \nabla\cdot\nabla\lambda = -\nabla\cdot A$ so that

$$\vec{\nabla}\cdot\vec{A}' = \nabla\cdot A + \nabla\cdot\nabla\lambda = \nabla\cdot A - \nabla\cdot A = 0. \tag{7}$$

Then Gauss's law gives

$$\nabla\cdot E = -\nabla\cdot\nabla\phi = \frac{\rho}{\epsilon_0} \tag{7}$$

whence

$$\phi(\vec{x},t) = \frac{1}{4\pi\epsilon_0}\int d^3y\,\frac{\rho(\vec{y},t)}{|\vec{x}-\vec{y}|} \tag{8}$$

since

$$-\Delta_x \frac{1}{|\vec{x}-\vec{y}|} = 4\pi\,\delta^{(3)}(\vec{x}-\vec{y}) . \tag{9}$$

In Coulomb's gauge and where $\rho = \vec{J} = \phi = 0$, the identity $\vec{\nabla}\times(\vec{\nabla}\times\vec{A}) = \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) - \Delta\vec{A} = -\Delta\vec{A}$ and Maxwell's equations (1-2) imply that $\vec{\nabla}\times\vec{B} = -\Delta\vec{A} = \frac{\dot{E}}{c^2} = -\frac{\ddot{A}}{c^2}$ or

$$\left(\Delta - \frac{1}{c^2}\partial_0^2\right)\vec{A}(x,t) = 0 . \tag{10}$$

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 (10) 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 $\vec{k}$

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

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

These are the polarization vectors.

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

$$\vec{A}(\vec{x},t) = \sum_{k} \sum_{r=1}^{2} \left(\frac{\hbar}{2\epsilon_0 V \omega_k} \right)^{\frac{1}{2}} \Big[\vec{\epsilon}_r(\vec{k}) a_r(\vec{k},t) e^{i\vec{k}\cdot\vec{x}} + \vec{\epsilon}_r^{\,*}(\vec{k})\, a_r^{\dagger}(\vec{k},t)\, e^{-i\vec{k}\cdot\vec{x}} \Big]. \quad (27)$$

Often we use real polarization vectors $\vec{\epsilon}$ to represent linearly polarized fields.

For $\vec{A}(\vec{x},t)$ to satisfy the wave equation (10)

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

we need

$$-k^2 a_r(\vec{k},t) - \frac{\ddot{a}_r(k,t)}{c^2} = 0 \quad (29)$$

or

$$\ddot{a}_r(\vec{k},t) = -(kc)^2 a_r(\vec{k},t). \quad (30)$$

Thus

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

with

$$\omega_k = kc, \quad k = |\vec{k}|. \quad (32)$$

The hamiltonian for $\vec{E}$ and $\vec{B}$ is

$$H_{0F} = \int d^3x \left(\frac{\epsilon_0}{2} \vec{E}^2(\vec{x},t) + \frac{1}{2\mu_0} \vec{B}^2(\vec{x},t) \right). \quad (33)$$

If we substitute (27) for $\vec{A}(\vec{x},t)$ into (33) and use

$$\vec{E} = -\dot{\vec{A}} \quad \& \quad \vec{B} = \vec{\nabla} \times \vec{A} \quad (34)$$

then after some churning we find

$$H_{0F} = \sum_{\vec{k}} \sum_{r=1}^{2} \hbar \omega_k \left[a_r^\dagger(\vec{k})\, a_r(\vec{k}) + \tfrac{1}{2} \right] \quad (36)$$

by using the commutation relations

$$[a_r(\vec{k}), a_{r'}(\vec{k}')] = \delta_{\vec{k},\vec{k}'} \delta_{r,r'} \quad (37)$$

and

$$[a_r(\vec{k}), a_{r'}(\vec{k}')] = 0 \quad (39)$$

which implies that

$$[a_r^\dagger(\vec{k}), a_{r'}^\dagger(k')] = 0 . \quad (40).$$

The hamiltonian for a particle of charge q and mass m in a field $(\phi/c, \vec{A})$ is

$$H_M = \frac{1}{2m}\left[\vec{p} - q\vec{A}(\vec{x},0)\right]^2 + q\phi(\vec{x},0) \qquad (40)$$

If the particle has spin $\frac{1}{2}$, then we add to H the term $-q/m\, \vec{S}\cdot\vec{B}(\vec{x},0)$ with $\vec{S} = \hbar\vec{\sigma}/2$.

The scalar potential $\phi(x,0)$ is fixed by (8), and so for an electron about a proton

$$H_M = H_{0M} + V$$

where

$$H_{0M} = \frac{p^2}{2m} - \frac{q^2}{4\pi\epsilon_0|\vec{x}|} = \frac{p^2}{2m} - \frac{\alpha\hbar c}{|\vec{x}|} \qquad (41)$$

in which $\alpha = e^2/\hbar c \approx 1/137$ is the fine-structure constant and V is

$$V = -\frac{q}{m}\vec{A}(\vec{x},0)\cdot\vec{p} + \frac{q^2\vec{A}^2(x,0)}{2m}. \qquad (43)$$

Note that in the Coulomb gauge $\nabla\cdot A = 0$ and so

$$A\cdot p = p\cdot A. \qquad (44)$$

We will use

$$V = -\frac{q}{m} \vec{A}(\vec{x},0)\cdot\vec{p} \tag{45}$$

to approximate the transition

$$|i, n_r(k)\rangle \rightarrow |f, n_r(k)-1\rangle. \tag{46}$$

With H_{0f} given by (36) and H_{0m} by (41), the operator

$$V_I(t) = e^{i(H_{0m}+H_{0f})t/\hbar}\, V\, e^{-i(H_{0m}+H_{0F})t/\hbar} \tag{47}$$

is hard to compute, but we only need it between the states of the transition (46) which are eigenstates of $H_{0m}+H_{0f}$. Thus

$$\begin{aligned}\langle f, n_r(k)-1|\, V_I(t)\, |i, n_r(k)\rangle &= e^{i(E_f+\hbar\omega(n-1))t/\hbar}\langle f, n_r(k)-1|V|i, n_r(k)\rangle e^{-i(E_i+n\hbar\omega)t/\hbar}\\ &= e^{i(E_f-E_i-\hbar\omega)t/\hbar}\langle f, n_r(k)-1|V|i, n_r(k)\rangle.\end{aligned} \tag{48}$$

Now the field $\vec{A}(\vec{x},0)$ is linear in $a_r(k)$, and

$$\langle n_r(k)-1|\, a_r(k)\, |n_r(k)\rangle = \sqrt{n_r(k)}\,. \tag{49}$$

So by using the Fourier series (27) for $\vec{A}(\vec{x},0)$, we get

$$\langle f, n_n(k)-1 | V | i, n_n(k) \rangle = \left(\frac{\hbar}{2\epsilon_0 V \omega_k}\right)^{1/2} \sqrt{n_n(k)} \left(-\frac{q}{m}\right)$$

$$\times \langle f | e^{i\vec{k}\cdot\vec{x}} \vec{\epsilon}_n(k)\cdot\vec{p} | i \rangle. \qquad (50)$$

The amplitude then is

$$\langle f, n-1 | S(t,0) | i, n \rangle = -\frac{q}{m}\sqrt{n}\left(\frac{\hbar}{2\epsilon_0 V \omega_k}\right)^{\frac{1}{2}} \int_0^t e^{i(E_f - E_i - \hbar\omega)t'/\hbar} dt'$$

$$\times \left(\frac{-i}{\hbar}\right) \langle f | e^{i\vec{k}\cdot\vec{x}} \vec{\epsilon}_n(k)\cdot\vec{p} | i \rangle. \qquad (51)$$

$$= \frac{i}{\hbar}\frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V \omega_k}\right)^{\frac{1}{2}} \sqrt{n} \langle f | e^{ik\cdot x} \vec{\epsilon}_n(k)\cdot\vec{p} | i \rangle$$

$$\times \frac{e^{i(E_f - E_i - \hbar\omega)t/\hbar} - 1}{i(E_f - E_i - \hbar\omega)/\hbar} \qquad (52)$$

$$= \frac{q}{m}\left(\frac{\hbar n}{2\epsilon_0 V \omega_k}\right)^{\frac{1}{2}} \langle f | e^{ik\cdot x} \vec{\epsilon}\cdot p | i \rangle \frac{e^{i(E_f - E_i - \hbar\omega)t/\hbar} - 1}{E_f - E_i - \hbar\omega}. \qquad 53$$

The probability then is

$$P(t) = \frac{q^2}{m^2}\frac{\hbar n}{2\epsilon_0 V\omega_k}\left|\langle f|e^{ik\cdot x}\epsilon\cdot p|i\rangle\right|^2 \frac{4\sin^2[(E_f-E_i-\hbar\omega)t/2\hbar]}{(E_f-E_i-\hbar\omega)^2} \tag{54}$$

Now since

$$\lim_{t\to\infty}\frac{\sin^2(E_f-E_i-\hbar\omega)t/2\hbar}{(E_f-E_i-\hbar\omega)^2} = \frac{\pi t}{2\hbar}\delta(E_f-E_i-\hbar\omega) \tag{55}$$

$P(t)$ is

$$P(t) = \pi t\frac{q^2}{m^2}\frac{n}{\epsilon_0 V\omega_k}\left|\langle f|e^{ik\cdot x}\epsilon\cdot p|i\rangle\right|^2\delta(E_f-E_i-\hbar\omega_k) \tag{56}$$

and so the transition rate w is

$$\hat{w} = \frac{dP}{dt} = \pi\frac{q^2}{m^2}\frac{n}{\epsilon_0 V\omega_k}\left|\langle f|e^{ik\cdot x}\epsilon\cdot p|i\rangle\right|^2\delta(E_f-E_i-\hbar\omega). \tag{57}$$

Now $q^2 = \alpha\hbar c\, 4\pi\epsilon_0$, where $\alpha = e^2/\hbar c$, so

$$\hat{w} = \frac{4\pi^2\alpha\hbar c\, n}{m^2 V\omega_k}\left|\langle f|e^{ik\cdot x}\epsilon\cdot p|i\rangle\right|^2\delta(E_f-E_i-\hbar\omega) \tag{58}$$

Now by (41)
$$[x_i, H_{0m}] = [x_i, \frac{\vec{p}^{\,2}}{2m}] = \sum_{ij}[x_i,p_j]\frac{p_j}{2m}+\frac{p_j}{2m}[x_i,p_j]$$
$$= \frac{i\hbar}{m}p_i. \tag{59}$$

So

$$[\vec{x}, H_{0m}] = \frac{i\hbar}{m}\,\vec{p}. \tag{60}$$

Using this commutator as a formula for $\vec{p}$ in (58), we find

$$\hat{w} = \frac{4\pi^2 \alpha \hbar c\, n_r}{m^2 V \omega_k} |\langle f| e^{ik\cdot x} [\vec{\epsilon}\cdot\vec{x}, H_{0m}] \frac{m}{i\hbar} |i\rangle|^2 \delta(E_f - E_i - \hbar\omega) \tag{61}$$

At optical frequencies $\lambda \approx 500\,nm$ whereas in atomic hydrogen

$$\langle n\ell m| r |n\ell m\rangle = \frac{a_0}{2}\left[3n^2 - \ell(\ell+1)\right]. \tag{62}$$

So

$$\langle |k\cdot x|\rangle \sim \frac{2\pi}{\lambda}\frac{3}{2}a_0 n^2 \tag{63}$$

$$\sim 10\frac{a_0}{\lambda}n^2 \sim \frac{.5}{500}n^2 \sim \frac{n^2}{1000}. \tag{64}$$

This estimate is the basis of the "dipole approximation" in which the exponential $\exp(ik\cdot x)$ is expanded in powers of $k\cdot x$

$$e^{ik\cdot x} = 1 + i\,k\cdot x + \frac{1}{2}(i k\cdot x)^2 + \frac{(ik\cdot x)^3}{3!} + \dots \tag{65}$$

and only the term 1 is kept.

In this dipole approximation, Eq. (61) gives

$$\hat{W} = \frac{4\pi^2 \alpha c m_r}{\hbar V \omega_k} |\langle f| [\vec{\epsilon}\cdot\vec{x}, H_{om}] |i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega) \quad (66)$$

in which the matrix element is

$$\langle f| \vec{\epsilon}\cdot\vec{x} \, H_{om} |i\rangle - \langle f| H_{om} \, \vec{\epsilon}\cdot\vec{x} |i\rangle$$

$$= (E_i - E_f) \langle f| \vec{\epsilon}\cdot\vec{x} |i\rangle . \quad (67)$$

Thus apart from an integration over ω and a summation over final states

$$\hat{W} = \frac{4\pi^2 \alpha c m_r}{\hbar V \omega_k} (E_f - E_i)^2 \, |\langle f| \vec{\epsilon}\cdot\vec{x} |i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega) \quad (68)$$

which involves the dipole moment

$$\vec{D}_{fi} = q \langle f| \vec{x} |i\rangle \quad (69)$$

of the atom.

Because of the δ-function in (68) $\hat{W}$ also is

$$\hat{w} = \frac{4\pi^2 \alpha c m_r (\hbar\omega_{fi})^2}{\hbar V \omega_k} |\langle f| \vec{\epsilon}\cdot\vec{x} |i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

$$= \frac{4\pi^2 \alpha \hbar c m_r \omega_{fi}}{V} |\langle f| \vec{\epsilon}\cdot\vec{x} |i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega). \quad (70)$$

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

$$\vec{\epsilon}_r(\hat{k}) \cdot \vec{x} = z \qquad (70a)$$

which commutes with L_z

$$[z, L_z] = 0 \qquad (70b)$$

it follows that $m_f = m_i$. (71)

But if $\epsilon_r(\hat{k}) = \hat{x}$ 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 since parity rules out $l_f = l_i$, we have the rule

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

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

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

$$= \int \sum_f 4\pi^2\alpha\hbar c\, m_n\, \omega_{fi}\,\frac{1}{V}\,|\langle f|\epsilon_r(k)\cdot x|i\rangle|^2$$

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

So

$$\int w\, d\omega = \sum_f 4\pi^2 \alpha c\, m_r (\vec{h})\, W_{fi} \frac{1}{V} |\langle f | \epsilon_r(h) \cdot x | i \rangle|^2 \qquad 76$$

But

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

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

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

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

This is the Thomas-Reiche-Kuhn sum rule.

So the rate w integrated over ω is

$$\int w \, d\omega = \frac{2\pi^2}{m} \alpha \hbar c m_n \frac{1}{V} . \qquad 82$$

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

$$\int \sigma(\omega) d\omega = \frac{2\pi^2 \alpha \hbar c n}{m V} \frac{1}{\frac{nc}{V}}$$

$$= \frac{2\pi^2 \alpha \hbar}{m}$$

is the absorption x-section $\sigma(\omega)$ integrated over $d\omega$.