Hence

$$\boxed{F_{fi}(q) = \sum_{l=0}^{n-1} a_{nl0}\sqrt{2l+1}\, i^l \int_0^\infty dr\, r^2 j_l(qr) \times R^*_{nl}(r) R_{10}(r)}$$

8.3. Semi-Classical Treatment of Electromagnetic Radiation: The interaction of Bound states of charged particles with Photons

Up to present we have dealt with the interaction of matter with matter, we have not included the interaction of matter with electromagnetic radiation. For example the emission or absorption of photons by atoms. A consistent quantum mechanical treatment of the matter as well as electromagnetic radiation would require the generalization of our quantum mechanical postulates to the special relativistic Maxwell equations governing the time evolution of the E-M field as well as the generalization of the quantum theory to deal with systems that have an infinite number of degrees of freedom (fields). As a compromise we will consider the matter as quantized, i.e. governed by the dynamics of Schrödinger's equation but the electromagnetic radiation as classical except to recognize that a monochromatic e-m wave with frequency ω of energy E is comprised of N photons, the quanta of the e-m field, with $N = E/\hbar\omega$. (This is a technical compromise, as one can show in QED that it is a coherent state with an infinite number of photons that approaches the classical Maxwell field. However we will ignore such technical points in our semi-classical treatment.)

Consider a bound system such as an atom in the presence of an electromagnetic field. We will assume the atom is in a region of space far away from the (classical) sources of the radiation and that the E-M field is described by (externally controlled) classical potentials $\vec{A}(\vec{r},t)$ and $\phi(\vec{r},t)$.

The bound system evolves in time according to the Schrödinger equation

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

with the Hamiltonian

$$H = \frac{1}{2m}(\vec{P} - q\vec{A})^2 + q\phi + V$$

with the interaction with $\vec{A}$ and ϕ determined by the gauge principle and $V = V(\vec{R})$ the potential responsible for the binding of the atomic system. As already stated $\vec{A}(\vec{R},t)$, $\phi(\vec{R},t)$ are external classical e-m potentials. In the $\{|\vec{r}\rangle\}$ basis we have the usual Schrödinger wave equation (with spin if applicable)

$$i\hbar \frac{\partial}{\partial t}\psi(\vec{r},t) = H(\vec{r},t)\psi(\vec{r},t) \quad \text{and}$$

$$H(\vec{r},t) = \frac{1}{2m}\left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}(\vec{r},t)\right)^2 + q\phi(\vec{r},t) + V(\vec{r}).$$

The electric and magnetic fields are given by

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\phi(\vec{r},t) - \frac{1}{c}\frac{\partial \vec{A}(\vec{r},t)}{\partial t}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A}(\vec{r},t).$$

Since we are considering the atomic system to be in a region of space far away from the classical sources of the e-m radiation, we will treat $\vec{A}, \phi$ as being determined by Maxwell's equations in a source free region of space. On the other hand these external fields interact with the above atom whose evolution is governed by Schrödinger's equation which we shall treat according to time dependent perturbation theory. Thus we consider the terms involving $\vec{A}$ & ϕ as perturbations on the binding potential V

$$H = H_0(\vec{r}) + H'(\vec{r},t)$$

with
$$H_0 = \frac{1}{2m}\vec{P}^2 + V(\vec{r})$$
and
$$H' = -\frac{q}{2m}\left[\vec{P}\cdot\vec{A}(\vec{r},t) + \vec{A}(\vec{r},t)\cdot\vec{P}\right] + \frac{q^2}{2m}\vec{A}^2(\vec{r},t) + q\phi(\vec{r},t)$$

According to Dirac perturbation theory the transition probability for the atom to be in the final state $|\varphi_f\rangle$ at time t when initially in the state $|\varphi_i\rangle$ at time t_0, where $|\varphi_n\rangle$ are the eigenstates of H_0

$$H_0|\varphi_i\rangle = E_i|\varphi_i\rangle$$

$$H_0|\varphi_f\rangle = E_f|\varphi_f\rangle$$

which we assume we know, is just given by the 1st order expression

$$P_{fi}(t,t_0) = \left|\frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, e^{i\omega_{fi}t_1}\langle\varphi_f|H'(t_1)|\varphi_i\rangle\right|^2$$

for $f \neq i$ (page -1143-) with $\omega_{fi} = \frac{E_f - E_i}{\hbar}$.

Since $H'(t)$ depends on $\vec{A}$ & ϕ we must determine their form in this source free region of space. Recall the form of Maxwell's equations for no sources

$$1)\quad \vec{\nabla}\cdot\vec{E} = 0$$

$$2)\quad \vec{\nabla}\times\vec{E} + \frac{1}{c}\frac{\partial\vec{B}}{\partial t} = 0 \implies \vec{E} = -\vec{\nabla}\phi - \cancel{\frac{1}{c}}\frac{\partial\vec{A}}{\partial t}$$

$$3)\quad \vec{\nabla}\cdot\vec{B} = 0 \implies \vec{B} = \vec{\nabla}\times\vec{A}$$

$$4)\quad \vec{\nabla}\times\vec{B} - \frac{1}{c}\frac{\partial\vec{E}}{\partial t} = 0$$

$(\frac{1}{c^2})$

So

$$4)\quad \vec{\nabla}\times\vec{B} - \frac{1}{c}\frac{\partial\vec{E}}{\partial t} = 0$$

$(1/c^2)$

$$\Rightarrow \vec{\nabla}\times\vec{\nabla}\times\vec{A} - \frac{1}{c}\frac{\partial}{\partial t}\left(-\vec{\nabla}\phi - \cancel{\frac{1}{c}}\frac{\partial\vec{A}}{\partial t}\right)$$

$(1/c^2)$

$$\Rightarrow -\nabla^2\vec{A} + \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) + \frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\phi + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0$$

$1/c^2$

and 1) $\vec{\nabla}\cdot\vec{E} = 0$

$$\Rightarrow -\nabla^2\phi - \cancel{\frac{1}{c}}\frac{\partial}{\partial t}\vec{\nabla}\cdot\vec{A} = 0$$

Choose <u>Coulomb</u> <u>gauge</u> $\boxed{\vec{\nabla}\cdot\vec{A} \equiv 0}$

Then 1) $\Rightarrow$ $\nabla^2\phi=0$ and since there are no sources $\Rightarrow$ $\boxed{\phi=0.}$

Then 4) becomes

$$\boxed{\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\nabla^2\right)\vec{A}(\vec{r},t)=0}$$

Wlog the real plane wave solution to this wave equation is given by

$$\vec{A}(\vec{r},t)=\vec{A}_0\, 2\cos(\vec{k}\cdot\vec{r}-\omega t)$$
$$=\vec{A}_0\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)}+e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

with $\omega=|\vec{k}|c$ and $\vec{A}_0$ a constant polarization vector.

$$\vec{\nabla}\cdot\vec{A}=0 \Rightarrow \boxed{\vec{k}\cdot\vec{A}_0=0}$$

Thus $\vec{A}_0$ and so $\vec{A}(\vec{r},t)$ is orthogonal to $\vec{k}$. Now the electric and magnetic fields are

$$\vec{E}(\vec{r},t) = -\cancel{\frac{1}{c}}\frac{\partial \vec{A}}{\partial t}$$

$$= \frac{i\omega}{\cancel{c}}\vec{A}_0\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} - e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A}$$

$$= i\vec{k}\times\vec{A}_0\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} - e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right],$$

Thus $\vec{B}(\vec{r},t) = \frac{1}{c}\hat{k}\times\vec{E}(\vec{r},t)$ and

so $\vec{B}\cdot\vec{E} = 0 = \vec{k}\cdot\vec{E} = \vec{k}\cdot\vec{B}$, hence

$\vec{k}, \vec{E}, \vec{B}$ are mutually orthogonal.

The energy flux in the e-m wave is given by the Poynting vector $\vec{S}$

$$\vec{S}(\vec{r},t) = \frac{\cancel{c}\,1}{4\pi\mu_0}\vec{E}(\vec{r},t)\times\vec{B}(\vec{r},t) = \frac{1}{\mu_0 c}|\vec{E}|^2\hat{k}$$

$$= \frac{\omega}{4\pi\mu_0}|\vec{A}_0|^2\vec{k}\left[2 - e^{2i(\vec{k}\cdot\vec{r}-\omega t)} - e^{-2i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

The time averaged Poynting vector is

$$\langle \vec{S} \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, \vec{S}(\vec{r},t)$$

$$= \frac{2\omega}{2\mu_0} |\vec{A}_0|^2 \vec{k} \,.$$

For plane waves it is independent of $\vec{r}$. Recall the energy flux in the wave is just the energy per unit time through the area with normal $\vec{k}$, that is

$$\langle \vec{S} \rangle = \frac{\text{energy in e-m wave}}{\text{time} \times \text{transverse area}} \,.$$

According to our semi-classical view of the e-m wave this (up to now classical) wave is composed of photons each carrying energy $\hbar\omega$. Thus the flux of photons is just

$$J_\gamma = \frac{\text{number of photons}}{\text{time} \times \text{transverse area}}$$

$$= \frac{1}{\text{energy per photon}} \; \frac{\text{total energy in e-m wave}}{\text{time} \times \text{transverse area}}$$

$$= \frac{1}{\hbar\omega} |\langle \vec{S} \rangle|$$

$\langle \vec{S} \rangle = c \langle u \rangle \hat{k}$

Thus
$$J_\gamma = \frac{2|\vec{k}|}{\cancel{2\pi}\hbar}|\vec{A}_0|^2 .$$

As well the density of photons in the wave is just ~~related~~ related to the energy density in the e-m wave in ~~a~~ similar manner

$$\vec{B}^2 = \frac{1}{c^2}\vec{E}^2$$

$$u(\vec{r},t) = \cancel{\frac{1}{8\pi}}\left(\epsilon_0\vec{E}^2 + \frac{1}{\mu_0}\vec{B}^2\right)\frac{1}{2} = \epsilon_0 \vec{E}^2$$

$$= \frac{\text{energy in e-m wave}}{\text{Volume}}$$

The time averaged energy density is

$$\langle u \rangle = \frac{1}{8\pi}\frac{1}{2}\left(\langle \vec{E}^2\rangle \epsilon_0 + \langle \vec{B}^2 \rangle \frac{1}{\mu_0}\right) = \epsilon_0 \langle \vec{E}^2 \rangle$$

$$= 2\frac{\omega^2}{c^2}\frac{1}{\mu_0}\frac{|\vec{A}_0|^2}{\cancel{2\pi}} .$$

Thus the photon density in the wave is

$$\rho_\gamma \equiv \frac{\text{\# of photons}}{\text{Volume}} = \frac{1}{\text{energy per photon}} \; \frac{\text{Total energy in e-m wave}}{\text{Volume}}$$

$$= \frac{1}{\hbar\omega}\langle u \rangle = \frac{2\omega}{\cancel{2\pi}\hbar c^2 \mu_0}|\vec{A}_0|^2$$

Thus we find

$$\boxed{|\vec{A}_0|^2 = \frac{\cancel{2\pi}\hbar c^2\mu_0}{2\omega}\rho_\gamma}$$

with $\rho_\gamma = \frac{n_\gamma}{\Omega}$, with $n_\gamma = \#$ of photons in Ω, Ω = volume

For a single photon in our box $n_\gamma = 1$

$$\Rightarrow \boxed{|\vec{A}_0|^2 = \frac{1}{\Omega}\frac{2\pi\hbar c^2\mu_0}{2\omega} \quad \left(\text{for a single photon}\right)}.$$

We are now prepared to determine the effect of this e-m wave on the atomic system. According to the time dependent perturbation theory formula (page -1197-) for the transition probability we must evaluate

$\langle\psi_f|H'(t)|\psi_i\rangle$ with in the Coulomb gauge

$$H'(t) = -\frac{q}{2m}[\vec{P}\cdot\vec{A} + \vec{A}\cdot\vec{P}] + \frac{q^2}{2m}\vec{A}^2.$$

Since the effects of $q\vec{A}$ are small we shall consider only the first order contributions in $q\vec{A}$, thus we ignore the $\frac{q^2\vec{A}^2}{2m}$ term. So we have

$$\langle \varphi_f | H'(t) | \varphi_i \rangle = -\frac{q}{2m} \langle \varphi_f | \vec{P}\cdot\vec{A} + \vec{A}\cdot\vec{P} | \varphi_i \rangle$$

$$= -\frac{q}{2m}\int d^3r \left\{ \varphi_f^*(\vec{r})\,\frac{\hbar}{i}\vec{\nabla}\cdot\left(\vec{A}\,\varphi_i(\vec{r})\right) + \varphi_f^*(\vec{r})\,\vec{A}\cdot\frac{\hbar}{i}\vec{\nabla}\varphi_i(\vec{r}) \right\}$$

We can integrate the first term by parts, dropping the surface term since the φ_n are bound states, to obtain

$$= -\frac{q\hbar}{2mi}\int d^3r \left[\varphi_f^*(\vec{r})\,\vec{\nabla}\varphi_i(\vec{r}) - \left(\vec{\nabla}\varphi_f^*(\vec{r})\right)\varphi_i(\vec{r}) \right] \cdot \vec{A}(\vec{r},t)$$

$$= -q\int d^3r\, \vec{J}_{em}(\vec{r})_{fi} \cdot \vec{A}(\vec{r},t)$$

where the <u>electromagnetic current</u>

matrix element is (actually charge $q\vec{J}_{em\,fi}$ flux)

$$\vec{J}_{em}(\vec{r})_{fi} = \frac{\hbar}{2im}\left[\varphi_f^*(\vec{r})\vec{\nabla}\varphi_i(\vec{r}) - (\vec{\nabla}\varphi_f(\vec{r}))^*\varphi_i(\vec{r})\right]$$

Substituting the plane wave solution for $\vec{A}(\vec{r},t)$, we obtain

$$\langle\varphi_f|H'(t)|\varphi_i\rangle = -q\int d^3r\,\vec{J}_{em\,fi}(\vec{r})\cdot\vec{A}_0 \times \left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right].$$

This yields the transition probability for $f\neq i$

$$P_{fi}(t,t_0) = \left|\frac{1}{i\hbar}(-q)\int d^3r\,\vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0 \times \left[e^{i\vec{k}\cdot\vec{r}}\int_{t_0}^{t} dt_1\, e^{i(\omega_{fi}-\omega)t_1} + e^{-i\vec{k}\cdot\vec{r}}\int_{t_0}^{t} dt_1\, e^{i(\omega_{fi}+\omega)t_1}\right]\right|^2$$

Recalling that

$$\int_{t_0}^{t} dt_1\, e^{i(\omega_{fi}\pm\omega)t_1} = \frac{e^{i(\omega_{fi}\pm\omega)t} - e^{i(\omega_{fi}\pm\omega)t_0}}{i(\omega_{fi}\pm\omega)}$$

$$= e^{i(\omega_{fi}\pm\omega)\left(\frac{t+t_0}{2}\right)} \frac{\sin\left[(\omega_{fi}\pm\omega)\left(\frac{t-t_0}{2}\right)\right]}{\left(\frac{\omega_{fi}\pm\omega}{2}\right)}$$

we find for $f\neq i$

$$P_{fi}(t,t_0) = \frac{q^2}{\hbar^2}\Big|\int d^3r\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0 \times$$

$$\times\Big\{ e^{i\vec{k}_0\cdot\vec{r}} e^{i(\omega_{fi}-\omega)\left(\frac{t+t_0}{2}\right)} \frac{\sin\left[(\omega_{fi}-\omega)\left(\frac{t-t_0}{2}\right)\right]}{\left(\frac{\omega_{fi}-\omega}{2}\right)}$$

$$+ e^{-i\vec{k}_0\cdot\vec{r}} e^{i(\omega_{fi}+\omega)\left(\frac{t+t_0}{2}\right)} \frac{\sin\left[(\omega_{fi}+\omega)\left(\frac{t-t_0}{2}\right)\right]}{\left(\frac{\omega_{fi}+\omega}{2}\right)}\Big\}\Big|^2$$

writing out the square we find the expression

$P_{fi}(t,t_0) =$

$$\frac{q^2}{\hbar^2}\left(\frac{\sin\left[\left(\frac{\omega_{fi}-\omega}{2}\right)(t-t_0)\right]}{\left(\frac{\omega_{fi}-\omega}{2}\right)}\right)^2 \left|\int d^3r\, e^{i\vec{k}_0\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2$$

$$+\frac{q^2}{\hbar^2}\left(\frac{\sin\left[\left(\frac{\omega_{fi}+\omega}{2}\right)(t-t_0)\right]}{\left(\frac{\omega_{fi}+\omega}{2}\right)}\right)^2 \left|\int d^3r\, e^{-i\vec{k}_0\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2$$

$$+\frac{q^2}{\hbar^2}\,\frac{\sin\left[\left(\frac{\omega_{fi}-\omega}{2}\right)(t-t_0)\right]}{\left(\frac{\omega_{fi}-\omega}{2}\right)}\;\frac{\sin\left[\left(\frac{\omega_{fi}+\omega}{2}\right)(t-t_0)\right]}{\left(\frac{\omega_{fi}+\omega}{2}\right)}\times$$

$$\times\Big[e^{i\omega(t+t_0)}\int d^3r\, e^{-i\vec{k}_0\cdot\vec{r}}\,\vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\int d^3r'\, e^{-i\vec{k}_0\cdot\vec{r}'}\,\vec{J}_{em}(\vec{r}')_{fi}\cdot\vec{A}_0$$

$$+e^{-i\omega(t+t_0)}\int d^3r\, e^{+i\vec{k}_0\cdot\vec{r}}\,\vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\int d^3r'\, e^{+i\vec{k}_0\cdot\vec{r}'}\,\vec{J}_{em}(\vec{r}')_{fi}\cdot\vec{A}_0\Big]$$

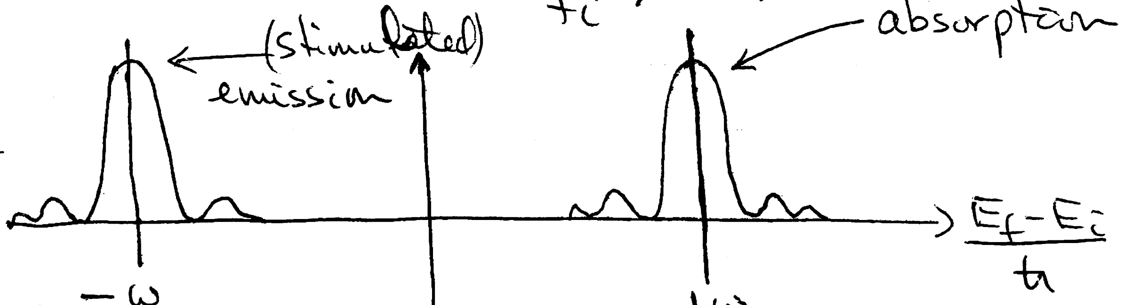
Using the fact that

$$\frac{\sin\left[\frac{\omega_{fi}\pm\omega}{2}(t-t_0)\right]}{\left(\frac{\omega_{fi}\pm\omega}{2}\right)}$$

is strongly peaked about $\omega = \mp\omega_{fi}$

The transition probability is determined by values of ω close to $\pm\omega_{fi}$.

In the case that the external E-M wave has $\omega > 0$ with $|\omega - \omega_{fi}| << |\omega_{fi}|$ we have that $\omega_{fi} > 0$.



i.e. (for $t - t_0 = T$ long enough we have no overlap of sinc functions), so atom looses or gains energy to or from E-M field; $|\omega - \omega_{fi}|$ is small only when $\omega_{fi} > 0$, $\omega_{fi} \simeq +\omega$.

Then $E_f > E_i$, hence the atom has made a transition from a lower energy state $|\varphi_i\rangle$ to a higher energy state $|\varphi_f\rangle$. This can only occur by "absorbing" a photon of energy $\hbar\omega = E_f - E_i$. Thus for $\omega_{fi} > 0$ we have absorption of a photon by the atom and its consequent excitation.

Since the "diffraction" functions are peaked only at the vanishing of their frequency argument, we have that $\mathcal{P}_{fi}$ is given predominantly by the first term on the RHS of page -1207-

$$\boxed{\begin{aligned} \mathcal{P}_{fi}(t,t_0)\Big|_{\text{absorption}} &= \frac{q^2}{\hbar^2}\left(\frac{\sin\left[\frac{(\omega-\omega_{fi})}{2}(t-t_0)\right]}{\left(\frac{\omega-\omega_{fi}}{2}\right)}\right)^2 \times \\ &\times \left|\int d^3r\, e^{i\vec{k}_0\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2 \\ \text{for } |\omega-\omega_{fi}| &\ll |\omega_{fi}|,\ \omega_{fi}>0. \end{aligned}}$$

On the other hand if $\omega>0$ is such that $|\omega+\omega_{fi}| \ll |\omega_{fi}|$, then from the diagram above we have that $\omega_{fi}<0$, thus $E_f<E_i$. The atom has made a transition from a higher energy level to a lower energy level, and this can only occur with the emission of a photon of energy $\hbar\omega = E_i - E_f$. So $\omega_{fi}<0$ corresponds to emission of a photon by the atom, the transition probability is predominantly given by the

Second term on the RHS of page -1207-

$$\boxed{P_{fi}(t,t_0)\Big|_{\text{(stimulated emission)}} = \frac{q^2}{\hbar^2}\left(\frac{\sin\left[\frac{(\omega+\omega_{fi})}{2}(t-t_0)\right]}{\left(\frac{\omega+\omega_{fi}}{2}\right)}\right)^2 \times \left|\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2 \text{ for } |\omega+\omega_{fi}| \ll |\omega_{fi}|,\ \omega_{fi}<0.}$$

Thus we see that an atom can give up or absorb energy from an E-M field, which depends on the phase relation between the atom and the E-M field. That is waiting long enough for the interaction to occur $\delta T = t - t_0$ becomes large enough so that the emission and absorption cross terms in P_{fi} vanish. Then (no overlap) we recall that

$$\lim_{T\to\infty} \frac{1}{T}\left[\frac{\sin\left[\left(\frac{\omega\pm\omega_{fi}}{2}\right)T\right]}{\left(\frac{\omega\pm\omega_{fi}}{2}\right)}\right]^2 = 2\pi\delta(\omega\pm\omega_{fi})$$

$$= 2\pi\hbar\,\delta(E_f - E_i \pm \hbar\omega),$$

Hence the <u>transition rate</u>

$$R_{fi} \equiv \frac{1}{T} P_{fi}(t, t_0) \; ; \text{ for}$$

absorption or emission becomes

$$R_{fi}\Big|_{\text{absorption}} = \frac{2\pi}{\hbar}\left| q\int d^3r\, e^{i\vec{k}_0\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2 \times \delta(E_f - E_i - \hbar\omega)$$

$$R_{fi}\Big|_{\text{emission}} = \frac{2\pi}{\hbar}\left| q\int d^3r\, e^{-i\vec{k}_0\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\right|^2 \times \delta(E_f - E_i + \hbar\omega)$$

i.e.

$$R_{fi}\Big|_{\substack{\text{abs.}\\ \text{emis.}}} = \frac{2\pi}{\hbar}\left| q\int d^3r\, \vec{J}_{em}(\vec{r})_{fi}\cdot\vec{A}_0\, e^{\pm i\vec{k}_0\cdot\vec{r}}\right|^2 \delta(E_f - E_i \mp \hbar\omega)$$

This is just <u>Fermi's Golden Rule</u> for emission or absorption of a photon.

We can further simplify these expressions by exploiting the transversality of the e-m field. That is, $\vec{A}_0 \cdot \vec{k} = 0$. The photon has two states of polarization, orthogonal to $\vec{k}$, thus

$$\vec{A}_0 = A_0 \, \vec{\epsilon}(\vec{k}, \lambda) \quad , \quad \lambda = 1, 2$$

where $\vec{\epsilon}(\vec{k}, \lambda)$ are 2 orthonormal polarization vectors $\perp$ to $\vec{k}$:

$$\vec{\epsilon}(\vec{k}, \lambda) \cdot \vec{\epsilon}(\vec{k}, \lambda') = \delta_{\lambda\lambda'}$$

$$\vec{k} \cdot \vec{\epsilon}(\vec{k}, \lambda) = 0 .$$

Hence $\hat{k}, \vec{\epsilon}(\vec{k}, 1), \vec{\epsilon}(\vec{k}, 2)$ form an orthonormal set of basis vectors

$$\sum_{\lambda=1}^{2} \epsilon_i(\vec{k}, \lambda)\, \epsilon_j(\vec{k}, \lambda) = \delta_{ij} - \hat{k}_i \hat{k}_j .$$

The absorption and emission transition rates can be written as

$$R_{fi}\Big|_{\substack{\text{abs.}\\ \text{emis.}}} = \frac{2\pi}{\hbar} \left| qf \int d^3r \, \vec{J}_{em}(\vec{r})_{fi} \cdot \vec{\epsilon}(\vec{k}, \lambda) A_0 e^{\pm i \vec{k} \cdot \vec{r}} \right|^2 \times \delta(E_f - E_i \mp \hbar\omega)$$

for a particular polarization λ, and energy of the final state.

Writing out the electromagnetic current matrix element, we can further simplify this expression,

$$\vec{J}_{em}(\vec{r})_{fi} = \frac{\hbar}{2im}\left(\varphi_f^*(\vec{r})\vec{\nabla}\varphi_i(\vec{r}) - (\vec{\nabla}\varphi_f^*(\vec{r}))\varphi_i(\vec{r}) \right)$$

Hence integrating by parts we find

$$\int d^3r\, e^{\pm i\vec{k}\cdot\vec{r}}\, \vec{J}_{em}(\vec{r})_{fi} \cdot \vec{\epsilon}(\vec{k},\lambda)$$

$$= \frac{\hbar}{2im}\int d^3r\, e^{\pm i\vec{k}\cdot\vec{r}}\, \vec{\epsilon}(\vec{k},\lambda)\cdot\left[\varphi_f^*\vec{\nabla}\varphi_i - (\vec{\nabla}\varphi_f^*)\varphi_i\right]$$

$$= \frac{\hbar}{2im}\int d^3r\, e^{\pm i\vec{k}\cdot\vec{r}}\, \vec{\epsilon}(\vec{k}\lambda)\cdot \varphi_f^*\vec{\nabla}\varphi_i\,(2)$$

$$+ \frac{\hbar}{2im}\int d^3r\, \underbrace{\left(\vec{\nabla}e^{\pm i\vec{k}\cdot\vec{r}}\right)}_{= e^{\pm i\vec{k}\cdot\vec{r}}(\pm i\vec{k})}\cdot\vec{\epsilon}(\vec{k},\lambda)\, \varphi_f^*\varphi_i$$

where we have dropped the surface term in the parts integration.

Since $\vec{k}\cdot\vec{\varepsilon}(\vec{k},\lambda)=0$, this last term vanishes, so

$$= \frac{\hbar}{im}\vec{\varepsilon}(\vec{k};\lambda)\cdot\int d^3r\, e^{\pm i\vec{k}\cdot\vec{r}}\varphi_f^*(\vec{r})\vec{\nabla}\varphi_i(\vec{r})$$

and we find

$$\boxed{\begin{aligned} R_{fi}\Big|_{\substack{\text{abs.}\\ \text{emis.}}} &= \frac{2\pi}{\hbar}\left|\frac{q\hbar}{im}\int d^3r\,\varphi_f^*(\vec{r})\vec{\nabla}\varphi_i(\vec{r})\cdot\vec{\varepsilon}(\vec{k},\lambda)A_0\times e^{\pm i\vec{k}\cdot\vec{r}}\right|^2\delta(E_f-E_i\mp\hbar\omega) \\ &= \frac{2\pi}{\hbar}\left|\frac{q}{m}\int d^3r\left(\varphi_f^*(\vec{r})\vec{P}\varphi_i(\vec{r})\right)\cdot\vec{\varepsilon}(\vec{k},\lambda)A_0\,e^{\pm i\vec{k}\cdot\vec{r}}\right|^2\times\delta(E_f-E_i\mp\hbar\omega)\end{aligned}}$$

For atomic transitions we can estimate the volume of integration $\int d^3r$ by the size of the atom $R\simeq Za_0=\frac{Z\hbar}{mc\alpha}$.

Hence

$$kR=\frac{\omega}{c}R\simeq\frac{\hbar\omega}{mc^2}\frac{Z}{\alpha}.$$

Since $mc^2 \approx 0.5\,\text{MeV}$ for an electron and $\alpha \approx \frac{1}{137}$ while $\hbar\omega \approx 10\,\text{eV}$ for typical atomic energy level transitions we'll find

$$kR \approx \frac{10\,\text{eV}}{\frac{1}{2}\times 10^6\,\text{eV}} Z(137) \approx 2.8\times 10^{-3} Z \ll 1$$

Hence, it is plausible to expand

$$e^{\pm i\vec{k}\cdot\vec{r}} \approx 1 \pm i\vec{k}\cdot\vec{r} \approx 1$$

(i.e. the γ wavelength $= \lambda = \frac{2\pi}{k} \gg R =$ size of atom, so $\vec{A}_0 e^{\pm i\vec{k}\cdot\vec{r}} \approx$ constant, across atom, and only consider 1 since $kR \ll 1$,

This is called the dipole approximation since then

$$R_{fi}^{\text{Dipole}}\Big|_{\substack{\text{abs.}\\ \text{emis.}}} = \frac{2\pi}{\hbar}\left|\frac{q}{m}\overbrace{\left(\int d^3r\, \varphi_f(\vec{r})\vec{P}\varphi_i(\vec{r})\right)}^{\langle\varphi_f|\vec{P}|\varphi_i\rangle}\cdot\vec{\epsilon}(\vec{k},\lambda)A_0\right|^2 \times\delta(E_f-E_i\mp\hbar\omega)$$

$$= \frac{2\pi}{\hbar}\left|\frac{q}{m}\langle\varphi_f|\vec{P}|\varphi_i\rangle\cdot\vec{\epsilon}(\vec{k},\lambda)A_0\right|^2 \times\delta(E_f-E_i\mp\hbar\omega)$$

Further, recall that $H_0 = \frac{1}{2m}\vec{P}^2 + V(r)$,
so

$$[H_0, X^i] = \frac{1}{2m}[\vec{P}^2, X^i] = \frac{\hbar}{im} P^i$$

$\Rightarrow$

$$\boxed{\vec{P} = \frac{im}{\hbar}[H_0, \vec{R}]}.$$

Hence

$$\langle \varphi_f | \vec{P} | \varphi_i \rangle = \frac{im}{\hbar} \langle \varphi_f | [H_0, \vec{R}] | \varphi_i \rangle$$

$$= \frac{im}{\hbar}(E_f - E_i) \langle \varphi_f | \vec{R} | \varphi_i \rangle$$

The matrix element of $\vec{P}$ is proportional to the <u>dipole matrix element</u>; that is the matrix element of $\vec{R}$.

Since $E_f - E_i = \mp \hbar\omega$ for $\left\{\begin{matrix}\text{abs.} \\ \text{emiss.}\end{matrix}\right\}$,
we find

$$R_{fi}^{\text{Dipole}}\Big|_{\substack{\text{abs.}\\ \text{emis.}}} = \frac{2\pi}{\hbar}(q\omega)^2 |A_0|^2 \left| \langle \varphi_f | \vec{R} | \varphi_i \rangle \cdot \vec{\epsilon}(k, \lambda) \right|_\lambda^2$$

$$\times \delta(E_f - E_i \mp \hbar\omega)$$

Using $q = \frac{e}{\cancel{c}}$ and $\alpha = \frac{e^2}{\hbar c}$ we have

$$\boxed{R_{fi}^{Dipole}\Big|_{\substack{abs.\\ emis.}} = \frac{2\pi\alpha\omega^2}{\cancel{c}} 4\pi\epsilon_0 c\, |A_0|^2 \left| \vec{\epsilon}(\hbar,\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i \mp \hbar\omega)}$$

This is Fermi's Golden Rule in the dipole approximation for the emission or absorption of a photon by an atom. The photon has definite energy ω and polarization λ while the atom has initial energy E_i and final energy E_f (with $E_f - E_i = \mp\hbar\omega$ expressing ~~overall~~ energy conservation).

As before, suppose one final state particle is in the continuum. Then we must sum over the number of states in the energy resolution of the detector. This yields for an absorption process

$$\delta R_{fi}^{Dipole}\Big|_{abs.} = \int dn\, R_{fi}^{Dipole}\Big|_{abs}$$

$$\delta R_{fi}^{Dipole}\Big|_{abs.} = \int dE_f \, \frac{\partial n}{\partial E_f} \, R_{fi}^{Dipole}\Big|_{abs.}$$

$$= \frac{2\pi\alpha\omega^3}{\overset{4\pi\epsilon_0 c}{\cancel{c}}} |A_0|^2 \left| \vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle \right|^2 \Bigg|_{E_f = E_i + \hbar\omega}.$$

$$\frac{\partial n(E_f)}{\partial E_f}$$

The incident flux of photons was given by (page -1202-)

$$J_{in} = J_\gamma = \frac{2|\vec{k}|}{\cancel{2\pi}\hbar\mu_0}|A_0|^2 = \frac{2\omega}{\cancel{2\pi}\hbar c\mu_0}|A_0|^2.$$

Hence the differential cross-section for absorption is given by

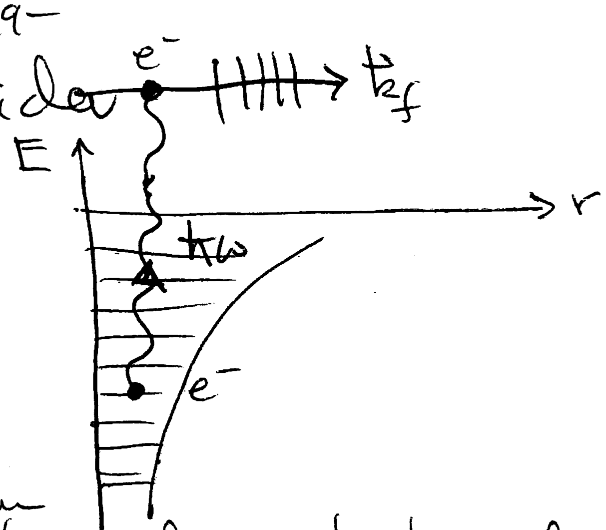
$$d\sigma_{fi}^{Dipole}\Big|_{abs.} = \frac{\delta R_{fi}^{dipole}\big|_{abs}}{J_\gamma}$$

same in both units.

$$= (2\pi)^2 \alpha \hbar\omega \frac{\partial n}{\partial E_f} \left| \vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle \right|^2 \Bigg|_{E_f = E_i + \hbar\omega}$$

independent of A_0.

As an example concider



Photoionization:

Suppose the external E-M pumps enough energy into the atom to liberate an electron from its bound state into the continuum. Since the electron is in the continuum, we must sum over the e^- states within the resolution of the detector. So

$$d\sigma_{fi}^{\text{Dipole}}\Big|_{abs} = (2\pi)^2 \alpha \hbar\omega \frac{\partial n}{\partial E_f} \left| \vec{\epsilon}(\vec{k},\lambda)\cdot\langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2$$

$$E_f = E_i + \hbar\omega.$$

Now the final electron is in a plane wave state, so

$$\varphi_f(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}_f\cdot\vec{r}}$$

(assume plane wave dominates matrix el. though not eigenstate of H_0)

with $E_f = \frac{\hbar^2 k_f^2}{2m}$. As usual for plane waves, the density of final states is

−1170− $$\frac{\partial n}{\partial E_f} = d\Omega_f \frac{\Omega}{(2\pi\hbar)^3} m\hbar k_f \quad , \text{ where}$$

−1163− $$dn = \frac{L^3}{(2\pi)^3} d^3k = \left(\frac{L}{2\pi}\right)^3 d\Omega_f \, k^2 \frac{dk}{dE} dE$$

we have not included the spin of the electron since the interaction is spin independent. Hence we find

$$\left.\frac{d\sigma_{fi}^{Dipole}}{d\Omega_f}\right|_{abs.} = \frac{\alpha}{2\pi}\frac{m\omega k_f}{\hbar}\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\int d^3r\,\vec{r}\,e^{-i\vec{k}_f\cdot\vec{r}}\times\varphi_i(\vec{r})\right|^2\Bigg|_{\frac{\hbar^2k_f^2}{2m}=E_i+\hbar\omega}$$

As another example, consider the de-excitation of an atom with the emission of a photon. Recalling the dipole approximation golden Rule transition rate, we have

$$\left.R_{fi}^{Dipole}\right|_{emis.} = \frac{2\pi\alpha\omega^2}{\cancel{c}}\,4\pi\epsilon_0 c\,|A_0|^2\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2\times\delta(E_f-E_i+\hbar\omega).$$

insert -1220'- to -1220'''-

Since we are interested in the emission of a single photon(*) when the atom makes the $|\varphi_i\rangle\rightarrow|\varphi_f\rangle$ transition, we use (page -1203-) the relation

(*) This is spontaneous emission (really should quantized values)

Note that for the atom in the presence of an external electromagnetic field, we have by our semi-classical viewpoint that $|A_0|^2$ is related to the photon number density or, more appropriately, the classical energy density of the wave

$$|A_0|^2 = \frac{\cancel{2\pi}\hbar c^2\mu_0}{2\omega}\rho_\gamma \qquad \text{(page -1203-)}$$

$$= \frac{\cancel{2\pi}\,\omega^2\mu_0}{\cancel{c^2}}\langle u\rangle\frac{\mu_0 c^2}{2\omega^2} \qquad \text{(page -1202-)}.$$

Hence the emission rate is

$$R\Big|^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{2\pi\alpha\omega^2 /4\pi\epsilon_0 c}{\cancel{c}}\;\frac{\cancel{2\pi}\hbar c^2\mu_0}{2\omega}\rho_\gamma\left|\vec{\epsilon}(k,\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times\delta(E_f - E_i + \hbar\omega)$$

$$\underset{\text{OK}}{=} 4\pi^2\alpha\,(\underbrace{\hbar\omega\rho_\gamma}_{=\langle u\rangle} c)\left|\vec{\epsilon}(k,\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times\delta(E_f - E_i + \hbar\omega)$$

$$= 4\pi^2\alpha\langle u\rangle c\left|\vec{\epsilon}(k,\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times\delta(E_f - E_i + \hbar\omega).$$

Thus the atom, when stimulated by the classical electromagnetic field, gives up energy to the field (in the form of photons with $\hbar\omega$ energy). Even though we have derived this result for the stimulated case, we can imagine that after the atom de-excites it gives up one additional photon when there were no photons present to start with. This is just the spontaneous emission of a γ by the atom (decay of atom by spontaneous emission). Since there is just one photon present $\rho_\gamma = \frac{1}{\Omega}$ in the above formula to obtain the spontaneous emission case

$$R_{fi}^{\text{Dipole}}\Big|_{\text{ems}} = \frac{4\pi^2 \alpha \hbar \omega c}{\Omega} \left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega).$$

To be correct, we should "quantize" the electromagnetic field as we did the atom. This can be done by considering the "field" as an infinite collection of point mechanical particles and then apply the rules of Q.M. to them (i.e. this is Quantum Field Theory and in the case of E-M field Quantum Electrodynamics QED). Then H_0 will contain an additional unperturbed photon energy piece. Hence the atomic level wavefunctions are not stationary states of H_0 anymore, we need also the photon wavefunctions, hence we can have transition between atomic states. The interaction Hamiltonian H' is still of the same $\vec{J}_{emfi} \cdot \vec{A}$ form and we obtain the same result as we will below when we apply Fermi's Golden Rule to this QED system. That is the QED calculation reduces to our $P_\gamma = \frac{1}{\Omega}$ condition in the stimulated emission rate formula for the spontaneous emission case we next study.

$$|\vec{A}_0|^2 = |A_0|^2 = \frac{1}{\Omega}\,\frac{\cancel{2}\pi\hbar c^2}{\cancel{2}\omega}\,.$$

Hence the "spontaneous" emission rate of the atom is

$$R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = \frac{(2\pi)^2\alpha\hbar\omega c}{\Omega}\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega)\,.$$

Now the energy of the emitted photon is

$$E_\gamma = \hbar\omega = \hbar|\vec{k}|c = \hbar kc\,,\quad \text{so}$$

$$R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = \frac{(2\pi)^2\alpha E_\gamma c}{\Omega}\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i + E_\gamma)\,.$$

Further, the emitted photon in the final state of the system is in the continuum, hence we must sum over the number of γ-states in the resolution of the detector. The density of final states for the photon is

$$\frac{\partial n}{\partial E_\gamma} = d\Omega_\gamma \frac{\Omega}{(2\pi)^3} \underbrace{g(E_\gamma)}_{=\sum_{\lambda=1}^{2}} k^2 \frac{\partial k}{\partial E_\gamma} ,$$

Since $E_\gamma = \hbar k c$; $\frac{\partial k}{\partial E_\gamma} = \frac{1}{\hbar c}$, so

$$\boxed{\frac{\partial n}{\partial E_\gamma} = d\Omega_\gamma \frac{\Omega}{(2\pi\hbar)^3} \frac{E_\gamma^2}{c^3} \sum_{\lambda=1}^{2} .}$$

Summing over the energy resolution of the detector, we get

$$\delta R_{fi}^{Dipole}\Big|_{emis.} = \int dE_\gamma \frac{\partial n}{\partial E_\gamma} R_{fi}^{Dipole}\Big|_{emis.}$$

$$= d\Omega_\gamma \int dE_\gamma \, \delta(E_f - E_i + E_\gamma) \frac{\Omega}{(2\pi\hbar)^3} \frac{E_\gamma^2}{c^3} \times$$

$$\times \sum_{\lambda=1}^{2} \frac{(2\pi)^2 \alpha E_\gamma c}{\Omega} \left| \vec{\epsilon}(\vec{k},\lambda) \cdot \langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2$$

$$= d\Omega_\gamma \frac{\alpha}{2\pi} \frac{E_\gamma^3}{\hbar^3 c^2} \sum_{\lambda=1}^{2} \left| \vec{\epsilon}(\vec{k},\lambda) \cdot \langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2 \Bigg|_{E_\gamma = E_i - E_f}$$

$$= d\Omega_\gamma \frac{\alpha}{2\pi} \frac{(E_i - E_f)^3}{\hbar^3 c^2} \sum_{\lambda=1}^{2} \epsilon_i(\hat{k},\lambda)\,\epsilon_j(\hat{k},\lambda) \times$$

$$\times \langle \varphi_f | X^i | \varphi_i \rangle \langle \varphi_f | X^j | \varphi_i \rangle^* \Big|_{E_\gamma = E_i - E_f}$$

Recall that $\sum_{\lambda=1}^{2} \epsilon_i(\hat{k},\lambda)\epsilon_j(\hat{k},\lambda) = \delta_{ij} - \hat{k}_i \hat{k}_j$

$$= \delta_{ij} - \frac{k_i k_j}{\vec{k}^2}$$

$\Rightarrow$

$$\delta R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = d\Omega_\gamma \frac{\alpha}{2\pi} \left(\frac{E_i - E_f}{\hbar}\right)^3 \frac{1}{c^2} \left(\delta_{ij} - \hat{k}_i \hat{k}_j\right) \times$$

$$\times \langle \varphi_f | X^i | \varphi_i \rangle \langle \varphi_f | X^j | \varphi_i \rangle^* \Big|_{E_\gamma = E_i - E_f}.$$

The <u>total</u> <u>rate</u> for the emission process is found by integrating over all angles for the emitted photon, using

$$\int_{4\pi} d\Omega_\gamma\, \delta_{ij} = 4\pi\, \delta_{ij} \quad \text{and}$$

$$\int_{4\pi} d\Omega_\gamma \hat{k}_i \hat{k}_j = C\delta^{ij},$$
↑ constant

since for $i \neq j$ the integral vanishes by symmetry (i.e. summing over all directions of vectors cancels, when $i=j$, summing the same quantity over all angles.)

To find the constant, take the ij trace

$$\int_{4\pi} d\Omega_\gamma \underbrace{\hat{k}_i \hat{k}_i}_{=1} = C\delta_{ii} = 3C$$

$$\Rightarrow \quad 4\pi = 3C \Rightarrow C = \frac{4\pi}{3}.$$

So $\int_{4\pi} d\Omega_\gamma \hat{k}_i \hat{k}_j = \frac{4\pi}{3}\delta_{ij}$, hence we find

the total rate

$$\Gamma^{\text{Dipole}}_{fi \text{ emis.}} \equiv \int_{4\pi} d\Omega_\gamma \, \delta R^{\text{Dipole}}_{fi}\Big|_{\text{emis.}}$$

$$= \frac{\alpha}{2\pi}\left(\frac{E_i - E_f}{\hbar}\right)^3 \frac{1}{c^2}\left(4\pi - \frac{4\pi}{3}\right)\delta_{ij} \langle \varphi_f | X^i | \varphi_i \rangle \times$$
$$\times \langle \varphi_f | X^j | \varphi_i \rangle^*$$

$$\boxed{\Gamma^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{4}{3}\alpha\left(\frac{E_i - E_f}{\hbar}\right)^3 \frac{1}{c^2}\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 .}$$

We can further simplify the matrix element by expanding x, y, z in terms of spherical polar coordinates

$$\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 = \langle\varphi_f|X^i|\varphi_i\rangle\langle\varphi_f|X^i|\varphi_i\rangle^*$$

$$= \langle\varphi_f|X^i|\varphi_i\rangle\langle\varphi_i|X^i|\varphi_f\rangle$$

$$= \langle\varphi_f|X|\varphi_i\rangle\langle\varphi_i|X|\varphi_f\rangle + \langle\varphi_f|Y|\varphi_i\rangle\langle\varphi_i|Y|\varphi_f\rangle$$

$$+ \langle\varphi_f|Z|\varphi_i\rangle\langle\varphi_i|Z|\varphi_f\rangle$$

Defining $X_\pm \equiv \frac{1}{\sqrt{2}}(X \pm iY)$, this becomes

$$\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 = \langle\varphi_f|X_+|\varphi_i\rangle\underbrace{\langle\varphi_i|X_-|\varphi_f\rangle}_{=\langle\varphi_f|X_+|\varphi_i\rangle^*}$$

$$+ \langle\varphi_f|X_-|\varphi_i\rangle\langle\varphi_i|X_+|\varphi_f\rangle^*$$

$$+ \langle\varphi_f|Z|\varphi_i\rangle\underbrace{\langle\varphi_i|Z|\varphi_f\rangle}_{=\langle\varphi_f|Z|\varphi_i\rangle^*}$$

So $|\langle\varphi_f|\vec{R}|\varphi_i\rangle|^2 = |\langle\varphi_f|X_+|\varphi_i\rangle|^2$

$$+|\langle\varphi_f|X_-|\varphi_i\rangle|^2 + |\langle\varphi_f|Z|\varphi_i\rangle|^2.$$

Now introducing spherical coordinates

$$Z = r\cos\theta = \sqrt{\frac{4\pi}{3}}\, r Y_1^0(\theta,\varphi)$$

$$X_\pm = \frac{1}{\sqrt{2}} r\sin\theta\, e^{\pm i\varphi} = \mp\sqrt{\frac{4\pi}{3}}\, r Y_1^{\pm 1}(\theta,\varphi)$$

we have

$$|\langle\varphi_f|\vec{R}|\varphi_i\rangle|^2 = \frac{4\pi}{3}\Big\{ |\langle\varphi_f|rY_1^1(\theta,\varphi)|\varphi_i\rangle|^2$$

$$+|\langle\varphi_f|rY_1^{-1}(\theta,\varphi)|\varphi_i\rangle|^2$$

$$+|\langle\varphi_f|rY_1^0(\theta,\varphi)|\varphi_i\rangle|^2\Big\}$$

$$= \frac{4\pi}{3}\sum_{m=-1}^{+1} |\langle\varphi_f|rY_1^m(\theta,\varphi)|\varphi_i\rangle|^2 .$$

Then the total rate for photon emission becomes

$$\Gamma^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{16\pi}{9}\alpha\left(\frac{E_i-E_f}{\hbar}\right)^3 \frac{1}{c^2}\sum_{m=-1}^{+1} |\langle\varphi_f|rY_1^m(\theta,\varphi)|\varphi_i\rangle|^2$$

For initial and final hydrogenic atom bound states we have

$$|\varphi_i\rangle = |n_i, l_i, m_i\rangle$$

$$|\varphi_f\rangle = |n_f, l_f, m_f\rangle \quad \text{with the}$$

corresponding bound state energies

$$E_i = -\frac{mc^2\alpha^2 Z^2}{2n_i^2}, \quad E_f = -\frac{mc^2\alpha^2 Z^2}{2n_f^2}$$

yielding

$$E_i - E_f = \frac{mc^2\alpha^2 Z^2}{2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

As well, since we do not detect the final state hydrogen atom azimuthal quantum number we must sum over these states. Also we do not specify the initial hydrogen atom azimuthal quantum number, hence we must average over these. This implies

$$\Gamma_{fi}^{\text{Dipole}}_{\text{emis.}} = \frac{2\pi}{9}\,\frac{\alpha^7 m^3 c^4 Z^4}{\hbar^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)^3$$

$$\sum_{m=-1}^{+1}\ \underbrace{\sum_{m_f=-l_f}^{+l_f}}_{\text{sum over final m-q\#}} \underbrace{\left(\frac{1}{2l_i+1}\right)\sum_{m_i=-l_i}^{+l_i}}_{\text{average initial m-q\#}} \left|\langle n_f, l_f, m_f | r Y_1^m(\theta,\varphi) | n_i, l_i, m_i\rangle\right|^2$$

Now we can write

$$\langle n_f, l_f, m_f | r Y_1^m(\theta,\varphi) | n_i, l_i, m_i \rangle$$

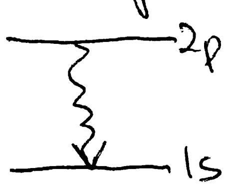
$$= \langle n_f, l_f | r | n_i, l_i \rangle \langle l_f, m_f | Y_1^m(\theta,\varphi) | l_i, m_i \rangle$$

So we finally obtain the <u>total</u> <u>dipole</u> <u>transition rate</u>

$$\Gamma_{fi\ \text{emis.}}^{\text{Dipole}} = \frac{2\pi}{9} \frac{\alpha^7 m^3 c^4 Z^6}{\hbar^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^3 |\langle n_f, l_f | r | n_i, l_i \rangle|$$

$$\times \sum_{m=-1}^{+1} \sum_{m_f=-l_f}^{+l_f} \left(\frac{1}{2l_i+1} \right) \sum_{m_i=-l_i}^{+l_i} |\langle l_f, m_f | Y_1^m(\theta,\varphi) | l_i, m_i \rangle|^2 .$$

<u>example</u>: Hydrogen 2p - 1s transition rate



$$R_{10} = \frac{1}{\sqrt{2}} \left(\frac{2Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} e^{-Zr/a_0} \left(\frac{Zr}{a_0} \right)$$

$$\Rightarrow \langle 1s | r | 2p \rangle = \frac{1}{\sqrt{6}} \frac{2^8}{3^4} \left(\frac{a_0}{Z} \right)$$

& recall $\frac{a_0}{Z} = \frac{1}{\alpha Z} \left(\frac{\hbar}{mc} \right)$.

The angular integral becomes

$$\langle 1s | Y_1^m | 2p \rangle = \int d\Omega \, Y_0^0 Y_1^m Y_{l_i}^{m_i}$$

$$= \frac{1}{\sqrt{4\pi}} (-1)^m \int Y_1^{-m\,*} Y_{l_i}^{m_i} \, d\Omega$$

$$= \frac{(-1)^m}{\sqrt{4\pi}} \delta_{l_i,1} \delta_{m_i,-m} .$$

(This is a selection rule for Electric dipole transitions, Only $l=1$, the p-state, can decay via the dipole mode to 1s state.)

So

$$\underbrace{\frac{1}{2l_i+1}}_{2+1} \sum_{m_i=-1}^{+1} \sum_{m_f=0} \sum_{m=-1}^{+1} \delta_{m_i,-m} = \frac{1}{3} \sum_{m_i=-1}^{+1} = \frac{1}{3} \cdot 3 = 1$$

So

$$\Gamma_{2p \to 1s} = \frac{2\pi}{9} \frac{Z^6 \alpha^7 m^3 c^4}{\hbar^3} \underbrace{\left(\frac{1}{1} - \frac{1}{2^2} \right)^3}_{\left(\frac{3}{4} = \frac{3}{2^2} \right)^3} \left(\frac{1}{\sqrt{6}} \frac{2^8}{3^4} \left(\frac{a_0}{Z} \right) \right)^2 \times \frac{1}{4\pi}$$

$$= \frac{2\pi}{9} \frac{Z^6 \alpha^7 m^3 c^4}{\hbar^3} \left(\frac{3^3}{2^6} \right) \frac{1}{6} \frac{2^{16}}{3^8} \underbrace{\left(\frac{a_0}{Z} \right)^2}_{= \left(\frac{1}{\alpha Z} \right)^2 \left(\frac{\hbar}{mc} \right)^2} \frac{1}{4\pi}$$

$$= \left(\frac{2}{3} \right)^8 Z^4 \alpha^5 \left(\frac{mc^2}{\hbar} \right)$$

So the $2p \to 1s$ total transition rate is

$$\boxed{\Gamma_{2p\to 1s} = \left(\frac{3}{8}\right)^8 Z^4 \alpha^5 \left(\frac{mc^2}{\hbar}\right)}$$

Suppose we have N-atoms in the initial state $|\varphi_i\rangle$. Γ_{fi}^{Dipole} is the transition rate $= \dfrac{\text{probability of transition}}{\text{unit time}}$. The number of atoms dN that make the transition in time dt is

$$dN = -N\Gamma_{fi}^{Dipole}\, dt$$

$$\Rightarrow \quad N = N_0 e^{-\Gamma_{fi}^{Dip.} t} \equiv N_0 e^{-\frac{t}{\tau}}.$$

$$\tau = \text{mean lifetime} = \frac{1}{\Gamma_{fi}^{Dipole}}.$$

For $2p \to 1s$ we have for H-atom

$$\Gamma_{2p\to 1s} = 6.3\times 10^{8}\ \text{sec}^{-1}$$

$$\Rightarrow \boxed{\tau_{2p\to 1s} = 1.6\times 10^{-9}\ \text{sec.}}$$

If the atom can decay to many states we must sum over these to find the total rate, then

$$dN = -N \sum_f^i \Gamma_{fi}^{Dipole}\, dt$$

so (to lowest order in α) $\Rightarrow$

$$N = N_0 e^{-\left(\sum_f^i \Gamma_{fi}^{Dip.}\right)t} \equiv N_0 e^{-\frac{t}{\tau}}$$

$$\Rightarrow \quad \boxed{\tau = \frac{1}{\sum_f^i \Gamma_{fi}^{Dip.}}}$$

add transition rates to find lifetime.

8.4. The Formal Theory of Scattering

So far we have been working to lowest order in time-dependent perturbation theory. Many times it's necessary to determine the transition probability in higher orders. As well, it is often useful to have a formal expression for the exact solution, as in the case of potential scattering with the L-S equation, so that symmetry