9.3. 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

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

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

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

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

Since we are considering the atomic system to be in a region of space far away from the classical sources of the ext 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 -9.15-) 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) $\vec{\nabla}\cdot\vec{E} = 0$

2) $\vec{\nabla}\times\vec{E} + \frac{\partial\vec{B}}{\partial t} = 0 \Longrightarrow \vec{E} = -\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}$

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

4) $\vec{\nabla}\times\vec{B} - \frac{1}{c^2}\frac{\partial\vec{E}}{\partial t} = 0$

So

4) $\vec{\nabla}\times\vec{B} - \frac{1}{c^2}\frac{\partial\vec{E}}{\partial t} = 0$

$$\Rightarrow \vec{\nabla}\times\vec{\nabla}\times\vec{A} - \frac{1}{c^2}\frac{\partial}{\partial t}\left(-\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}\right)$$

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

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

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

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

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

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

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

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

$$\vec{S}(\vec{r},t) = \vec{E}(\vec{r},t)\times\vec{B}(\vec{r},t) = \frac{\;}{\mu_0 c}\;\hat{k}$$
$$= \frac{\omega}{\;}|\vec{A}_0|^2\vec{k}\left[2 - e^{2i(\vec{k}\cdot\vec{r}-\omega t)} - e^{-2i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

The time averaged Poynting vector is

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

$$= [\text{illegible}]\, |\vec{A}_0|^2 \vec{k} \,.$$

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

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

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

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

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

Thus
$$J_\gamma = \frac{2|\vec{k}|}{\mu_0 \hbar} |\vec{A}_0|^2 .$$

As well the density of photons in the wave is just related to the energy density in the e-m wave in a similar manner $(\vec{B}^2 = \frac{1}{c^2}\vec{E}^2)$

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

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

The time averaged energy density is

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

$$\frac{1}{c}\langle \vec{S} \rangle \cdot \hat{k} = 2\frac{\omega^2}{c^2}\frac{|\vec{A}_0|^2}{\mu_0}$$

Thus the photon density in the wave is

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

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

Thus we find

$$\boxed{|\vec{A}_0|^2 = \frac{4\pi \hbar c^2}{2\omega}\, \rho_\gamma}$$

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

For a <u>single photon</u> in our box $\underline{n_\gamma = 1}$

$$\Rightarrow \quad \boxed{|\vec{A}_0|^2 = \frac{1}{\Omega}\,\frac{4\pi \hbar c^2}{2\omega} \quad \left(\text{for a single photon}\right)}.$$

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 -9.__-) for the transition probability we must evaluate

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

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

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

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

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

where the <u>electromagnetic</u> <u>current</u>

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

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

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

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

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

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

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 $f \neq i$

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

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

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

writing out the square we find the expression

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

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

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

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

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

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

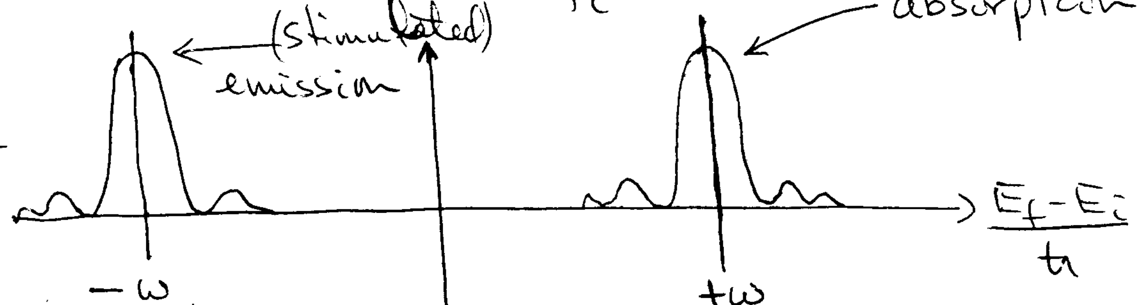
Using the fact that

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

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 sine functions, so atom looses or gains energy to or from E-M field!

$|\omega - \omega_{fi}|$ is small only when $\omega_{fi} > 0$, $\omega_{fi} \cong +\omega$.

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 δP_{fi} is given predominantly by the first term on the RHS of page -?-

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

for $|\omega-\omega_{fi}| \ll |\omega_{fi}|$, $\omega_{fi} > 0$.

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 - ? -

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

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. (no overlap) Then we recall that

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

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

Hence the transition rate

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

absorption or emission becomes

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

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

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i.e.

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

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

We can further simplify these expression by exploiting the ~~tr~~ 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

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

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

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

and we find

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

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

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

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

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

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

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

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 dipole matrix element, 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

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

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

Using $g = 1$ and $\alpha = \frac{e^2}{4\pi\hbar c}$ we have

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

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

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

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

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

$$\frac{\partial n(E_f)}{\partial E_f} \times 4\pi\epsilon_0 c$$

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

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

Hence the differential cross-section for absorption is given by

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

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

independent of A_0.