Application of Time-Dependent Perturbation Theory to Electromagnetic Radiation

In class and on the spectroscopy handout we derived the expression for the contribution of an excited state as the result of a perturbation:

$$C_\beta(t) = -\frac{i}{\hbar}\int_{t_0}^{t} e^{i/\hbar(E_\beta^0 - E_\alpha^0)t''} H'_{\beta\alpha}\; dt''$$

where $H'_{\beta\alpha} = \int_{\text{space}} (\psi_\beta^0)^* \hat{H}'(t)(\psi_\alpha^0)d\tau$.

We stated (with some illustrations of the nature of the vector potential $\vec{A}$) that

$$H' = -\frac{e}{2mc}(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) \qquad \text{where}$$

$$\vec{A} = A_0 \cos(kz - \omega t)\vec{i} \qquad \omega = 2\pi\nu \quad \text{note: } A_0 = 2a_0 \text{ of Bohm's treatment}$$

for a plane electromagnetic wave with its electric field in the x-direction and traveling in the z-direction.

We wanted to "fill in the steps" for derivations which led to two results:

$$\text{I.}\quad |C_\beta|^2 = \frac{e^2}{m^2c^2}\; A_0^2\; |Q_{\beta\alpha}|^2 \frac{\sin^2\left[(E_\beta - E_\alpha - h\nu)\frac{t - t_0}{2\hbar}\right]}{(E_\beta - E_\alpha - h\nu)^2}$$

for radiation of a single frequency ν.

where $\qquad Q_{\beta\alpha} = \int_{\text{space}} \psi_\alpha^0 \hat{p}_x e^{ikz}\psi_\beta^0 d\tau$

and:

$$\text{II.}\qquad |C_\beta|^2 = \frac{2\pi e^2}{m^2 c\hbar^2}\;\frac{I(\nu_0)}{\omega_0^2}\;|Q_{\beta\alpha}|^2 (t - t_0)$$

for a small spread of frequencies centered around ν_0 with intensity $I(\nu)$.

To derive I we substitute H' into the formula for C_β:

$$C_\beta = -\frac{i}{\hbar}\int_{t_0}^{t} e^{i/\hbar(E_\beta - E_\alpha)t''}dt''\int\left(-\frac{e}{2mc}\right)\left[(\psi_\beta^0)^*\left(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A}\right)\right]\psi_\alpha^0 d\tau$$

since $\vec{A}$ for our plane wave is in the x direction but is only a function of z, $\vec{p}_{op}\cdot\vec{A} = \vec{A}\cdot\vec{p}_{op}$ and

$$C_\beta = \frac{ie}{2m\hbar c}\int_{t_0}^{t} e^{i/\hbar(E_\beta - E_\alpha)t''}dt'' \int (\psi_\beta^0)^*(2A_0\cos(kz-\omega t)\hat{p}_x)\psi_\alpha^0 d\tau$$

expanding $2\cos(kz - \omega t) = e^{i(kz-\omega t)} + e^{-i(kz-\omega t)}$ with $\omega_{\beta\alpha} = (E_\beta - E_\alpha)/\hbar$

$$C_\beta = \frac{ieA_0}{2\hbar mc}\left[\int_{t_0}^{t} e^{i(\omega_{\beta\alpha}-\omega)t''}dt''\int(\psi_\beta^0)^* e^{+ikz}\,\hat{p}_x\,\psi_\alpha^0\,d\tau\right.$$

$$\left.+\int_{t_0}^{t} e^{i(\omega_{\beta\alpha}+\omega)t''}dt''\int(\psi_\beta^0)^* e^{-ikz}\,\hat{p}_x\psi_\alpha^0\,d\tau\right]$$

Completing the time integrations:

$$C_\beta = \frac{eA_0}{2\hbar mc}\left[\frac{1}{(\omega_{\beta\alpha}-\omega)}\left(e^{i(\omega_{\beta\alpha}-\omega)t} - e^{i(\omega_{\beta\alpha}-\omega)t_0}\right)\int(\psi_\beta^0)^* e^{ikz}\,\hat{p}_x\psi_\alpha^0 d\tau\right.$$

$$\left.+\frac{1}{(\omega_{\beta\alpha}+\omega)}\left(e^{i(\omega_{\beta\alpha}+\omega)t} - e^{i(\omega_{\beta\alpha}+\omega)t_0}\right)\int(\psi_\beta^0)^* e^{-ikz}\,\hat{p}_x\psi_\alpha^0\,d\tau\right]$$

If $E_\beta > E_\alpha$ (absorption) then only the first term will be important [check denominator] and if we are dealing with emission $\omega_{\beta\alpha} < 0$, the second term is dominant. Since we will be after $\left|C_\beta\right|^2 = C_\beta^* C_\beta$, the first and second terms are complex conjugates for the cases with $|\omega_{\beta\alpha}|$ and $-|\omega_{\beta\alpha}|$ as the transition energies. Thus, treating the first term in absorption ($\omega_{\beta\alpha} > 0$) will lead to identical transition probabilities as the second term in stimulated emission ($\omega_{\beta\alpha} < 0$), i.e., equal probability of absorption and stimulated emission.

$$C_\beta = \frac{eA_0}{2\hbar mc}\,\frac{e^{i(\omega_{\beta\alpha}-\omega)t_0}}{(\omega_{\beta\alpha}-\omega)}\left[e^{i(\omega_{\beta\alpha}-\omega)(t-t_0)} - 1\right]\underbrace{\int(\psi_\beta^0)^* e^{ikz}\,\hat{p}_x\,\psi_\alpha^0 d\tau}_{Q_{\beta\alpha}}$$

$$\left|C_\beta\right|^2 = \frac{e^2A_0^2}{4\hbar^2m^2c^2}\,\frac{\left[2-2\cos[(\omega_{\beta\alpha}-\omega)(t-t_0)]\right]}{(\omega_{\beta\alpha}-\omega)^2}\left|Q_{\beta\alpha}\right|^2$$

$$\left|C_\beta\right|^2 = \frac{e^2 A_0^2}{2\hbar^2 m^2 c^2} \frac{\left[1-\cos((\omega_{\beta\alpha}-\omega)(t-t_0))\right]}{(\omega_{\beta\alpha}-\omega)^2} \left|Q_{\beta\alpha}\right|^2$$

$$\left|C_\beta\right|^2 = \frac{e^2 A_0^2}{\hbar^2 m^2 c^2} \frac{\sin^2\left[\frac{(\omega_{\beta\alpha}-\omega)(t-t_0)}{2}\right]}{(\omega_{\beta\alpha}-\omega)^2} \left|Q_{\beta\alpha}\right|^2$$

Note $1-\cos x = 2\sin^2\frac{x}{2}$

with $\omega_{\beta\alpha} = \frac{E_\beta - E_\alpha}{\hbar}$, etc. This is just the first result we set out to prove.

To get result II we consider a range of incident frequencies with amplitudes $A_0(\nu)$ (this defines the "band") and integrate, over all frequencies in the band, the probability that radiation at single frequency ν caused a transition.

$$\int\left|C_\beta\right|^2 d\nu = \frac{e^2\left|Q_{\beta\alpha}\right|^2}{\hbar^2 m^2 c^2} \int_{-\infty}^{\infty} A_0^2(\nu) \frac{\sin^2\left[(\omega_{\beta\alpha}-\omega)\frac{t-t_0}{2}\right]}{(\omega_{\beta\alpha}-\omega)^2} d\nu$$

$$= \frac{e^2 \left|Q_{\beta\alpha}\right|^2}{2\pi\hbar^2 m^2 c^2} \int_{-\infty}^{\infty} \frac{A_0^2(\nu)\sin^2\left[(\omega_{\beta\alpha}-\omega)\frac{t-t_0}{2}\right]}{(\omega_{\beta\alpha}-\omega)^2} d\omega$$

from applied math $\lim_{L\to\infty}\frac{\sin^2 LX}{2LX^2} = \frac{\pi\delta(x)}{2}$ where $\delta(x)$ is the *Dirac* delta such that

$$\int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0).$$

For $t - t_0$ long compared to $(\omega_{\beta\alpha}-\omega)^{-1}$ (about 10^{-15} sec or less) the Dirac delta limit is approximately satisfied and

$$\int\left|C_\beta\right|^2 d\nu = \frac{e^2 \left|Q_{\beta\alpha}\right|^2}{2\hbar^2 \pi m^2 c^2} \int_{-\infty}^{\infty} A_0^2(\nu)(t-t_0) \frac{\sin^2\left[(\omega_{\beta\alpha}-\omega)\frac{t-t_0}{2}\right]}{(t-t_0)(\omega_{\beta\alpha}-\omega)^2} d\omega$$

$$\left|C_\beta\right|^2 = \frac{e^2 \left|Q_{\beta\alpha}\right|^2}{2\pi\hbar^2 m^2 c^2} A_0^2(\nu_0)(t-t_0)\frac{\pi}{2} = \frac{e^2 \left|Q_{\beta\alpha}\right|^2}{4\,\hbar^2 m^2 c^2} A_0^2(\nu_0)(t-t_0)$$

where ν_0 is the value of ν such that "x" = $(\omega_{\beta\alpha} - \omega) = 0$, i.e., $\nu_0 = \nu_{\beta\alpha}$ the transitions freq. Using an expression from classical electrodynamics relating the intensity of the wave to its electric field (via the Poynting vector).

$$I(\nu) = \frac{c|\mathcal{E}|^2}{4\pi} = \frac{A_0^2\omega^2}{8\pi c}$$

$$A_0^2 = \frac{8\pi c I(\nu)}{\omega^2}$$

$$\left|C_\beta\right|^2 = \frac{2\pi e^2 \left|Q_{\beta\alpha}\right|^2}{\omega_0^2 m^2 c \hbar^2}\; I(\nu_0)(t - t_0)$$

which is result II!!

To get the probability per unit time per intensity we divide by $I(\nu_0)(t - t_0)$

$$P_{\beta\leftarrow\alpha} = \frac{2\pi e^2}{\omega_{\beta\alpha}^2 m^2 c \hbar^2} \left|Q_{\beta\alpha}\right|^2$$