## Time Dependant Perturbation Theory

$H = H_0 + \lambda H_1(t)$ $\qquad \lambda$ small parameter

$H_0$ independant of time and completely solved

$$H_0 |E_n^0\rangle = E_n^0 |E_n^0\rangle$$

completeness, expand full solution

$$|\psi(0)\rangle = \sum_n C_n(0) |E_n^0\rangle$$

then at time $t$,

$$|\psi(t)\rangle = \sum_n C_n(t) e^{-iE_n^0 t/\hbar} |E_n^0\rangle$$

Schrödinger equation for $|\psi(t)\rangle$

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

then

$$i\hbar \sum_n \left(\dot{C}_n - \frac{iE_n^0}{\hbar} C_n\right) e^{-iE_n^0 t/\hbar} |E_n^0\rangle$$

$$= \sum_n (E_n^0 + \lambda H_1) e^{-iE_n^0 t/\hbar} |E_n^0\rangle$$

$$i\hbar \sum_n \dot{C}_n e^{-iE_n^0 t/\hbar} |E_n^0\rangle = \sum_n \lambda H_1(t) e^{-iE_n^0 t/\hbar} |E_n^0\rangle$$

act on left with bra $\langle E_m^0|$ and $\hbar\omega_{mn} = E_m^0 - E_n^0$

$$\dot{C}_m = \frac{1}{i\hbar} \sum_n C_n(t) \langle E_m^0 | \lambda H_1 | E_n^0\rangle e^{i\omega_{mn} t}$$

perturbation expansion of $C_n(t)$:

$$C_n(t) = C_n^0(t) + \lambda C_n^1(t) + \cdots$$

$$\dot{C}_m^0 + \lambda \dot{C}_m^1 + \cdots = \frac{1}{i\hbar} \sum_n \left[ C_n^0(t) + \lambda C_n^1(t) + \cdots \right] \langle E_m^0 | \lambda H_1 | E_n^0 \rangle e^{i\omega_{mn} t}$$

comparing orders in $\lambda$,

Order $\lambda^0$: $\frac{d}{dt} C_m^0(t) = 0$ $\quad C_m^0$ constant

For initial state $|E_i^0\rangle$ $\quad C_{mi}^0 = \delta_{mi}$
and all higher orders of $C_m^k(0) = 0$

order $\lambda^1$:

$$\lambda \dot{C}_m^1 = \frac{1}{i\hbar} \sum_n C_n^0 \langle E_m^0 | \lambda H_1 | E_n^0 \rangle e^{i\omega_{mn} t}$$

$n$ is "dummy" index & $C_n^0 = \delta_{ni}$. Canceling $\lambda$, and labeling final state $f$ for transition $i \to f$

$$\dot{C}_f^1 = \frac{1}{i\hbar} \langle E_f^0 | H_1(t) | E_i^0 \rangle e^{i\omega_{fi} t}$$

$$\boxed{C_f^1(t) = -\frac{i}{\hbar} \int_0^t dt' \langle E_f^0 | H_1(t') | E_i^0 \rangle e^{i\omega_{fi} t'}}$$

and $C_f(t) = \delta_{fi} + \lambda C_f^1(t) + \cdots$

Example: H atom in classical field

$$\vec{E}(t) = \mathcal{E}_0 \hat{z} e^{-t/\tau}$$

$$\hat{H}_1 = -\vec{\mu}\cdot\vec{E} = e\mathcal{E}_0 z e^{-t/\tau}$$

$$C'_{1s\to 2p} = \frac{-i}{\hbar}\int_0^\infty dt\, e^{i\omega t} \langle 2p|\hat{H}_1|1s\rangle$$

$$\omega = \frac{E_{2p}-E_{1s}}{\hbar} = \left(-\frac{1}{4}+1\right)\frac{1}{2}mc^2\alpha = \frac{3}{8}mc^2\alpha$$

$$C'_{1s\to 2p} = \frac{-ie\mathcal{E}_0}{\hbar}\langle 2p|z|1s\rangle \int_0^\infty dt\, e^{i\omega t} e^{-t/\tau}$$

time integral $\tau\int_0^\infty \frac{dt}{\tau} e^{-\frac{t}{\tau}(1-i\omega\tau)} = \frac{\tau}{1-i\omega\tau}$

Space integral: $z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}\,Y_{10}$

$$\langle \underbrace{2,1,\overset{\Delta m=0}{0}|r\cos\theta|1,0,0}_{\Delta l=1}\rangle = \int_0^\infty R^*_{21}\, r\, R_{10}\, r^2 dr \sqrt{\frac{4\pi}{3}}\int d\Omega |Y_{10}|^2 Y_{00}$$

angular integral $\sqrt{\frac{4\pi}{3}}\int d\Omega |Y_{10}|^2 \frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{3}}$

radial integral $R_{10} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

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

$$\int_0^\infty R^*_{21} r R_{10} r^2 dr = \sqrt{\frac{2}{3}}\left(\frac{1}{a_0}\right)^4 \int_0^\infty r^4 dr\, e^{-3r/2a_0}$$

$$= a_0\sqrt{\frac{2}{3}}\left(\frac{2}{3}\right)^5\int_0^\infty x^4 e^{-x}dx = \sqrt{\frac{2}{3}}\frac{2^7}{3^4}a_0$$

All together: $A \equiv \sqrt{2}\,\frac{2^7}{3^5}$

$$C^{(1)}_{1s\to 2p} = \frac{-ie\mathcal{E}_0}{\hbar} A \, \overset{\hbar/mc\alpha}{a_0} \frac{\tau}{1-i\omega\tau} = \frac{-ie\mathcal{E}_0 A}{mc^2\alpha}\left(\frac{c\tau}{1-i\omega\tau}\right)$$

$$\left|C^{1}_{1s\to 2p}\right|^2 = \left(\frac{e\mathcal{E}_0}{mc^2}\right)^2\left(\frac{A}{\alpha}\right)^2 \frac{(c\tau)^2}{1+(\omega\tau)^2}$$

In general, dipole selection rule are

$\Delta \ell = 1$

$\Delta m = 0, \pm 1$ photons can be emitted in any direction

## Fermi's Golden Rule

Applying perturbation theory to photon-atom interaction, we are interested in the amplitude

$$C_{fi} = \frac{-i}{\hbar}\int_0^T dt\, e^{i\omega_{fi}t}\langle f|\hat{H}_1|i\rangle$$

where states are direct product states:

$$|\psi\rangle = |\text{electron}\rangle \otimes |\text{photon}\rangle, \text{ e.g. } |n\ell m_\ell s m_s\rangle \otimes |\vec{k};\lambda\rangle$$

$$\hat{H}_1(t) = \frac{e}{mc}\vec{A}(t)\cdot\left(\frac{\hbar}{i}\vec{\nabla}\right) + \frac{e^2}{2mc^2}\vec{A}(t)\cdot\vec{A}(t)$$

Where $\vec{A}$ is the free field

$$\vec{A}(\vec{r},t) = \frac{c}{\sqrt{V}}\sum_{\vec{k},\lambda}\sqrt{\frac{2\pi\hbar}{\omega}}\left(\hat{a}(t)\vec{\varepsilon}_\lambda e^{i\vec{k}\cdot\vec{r}} + \hat{a}^\dagger(t)\vec{\varepsilon}_\lambda^{\,*} e^{-i\vec{k}\cdot\vec{r}}\right)$$

$$\equiv \vec{A}^- + \vec{A}^+ \quad \text{where } \pm \text{ refer to } e^{\pm i\omega t}$$

$\hat{a}(t) = \hat{a}(0)e^{-i\omega t}$ annihilation operator

$\hat{a}^\dagger(t) = \hat{a}^\dagger(0)e^{+i\omega t}$ creation operator

To leading order in $\alpha$, we omit $A^2$ term. Then time dependence of $\vec{A}$ can be included in $\omega_{fi}$:

$$\hbar\omega_{fi} = E_{n_f} - E_{n_i} \pm \hbar\omega$$

$E_n$ = electron energy, $\pm\hbar\omega$ for emission (absorption) of photon

What is left is $\vec{A}(\vec{r},0)$. For a more rigorous treatment, see discussion of "interaction picture" in text.

time integral gives energy conservation

$$\int_0^T dt\, e^{i\omega_{fi}t} = \frac{1}{i\omega}\left(e^{i\omega T}-1\right) = \frac{e^{i\omega T/2}}{\omega/2}\sin(\omega T/2)$$

Then $|C_{fi}|^2 = \frac{1}{\hbar^2}\,|\langle f|H_1|i\rangle|^2 \frac{\sin^2(\omega T/2)}{T(\omega/2)^2}\,T$

in limit $T\to\infty$

$$\lim_{T\to\infty} \frac{\sin^2(\omega T/2)}{T(\omega/2)^2} = \pi\,\delta(\omega/2)$$

because, at $\frac{\omega}{2}=0$, ratio $\to\infty$

$\omega/2 \neq 0$, ratio $=0$

and

$$\int_0^\infty \frac{\sin^2\left(\frac{\omega T}{2}\right)}{T(\omega/2)^2}\,d\omega = \int_{-\infty}^{\infty} \frac{\sin^2(\omega T/2)}{\left(\frac{T\omega}{2}\right)^2}\,d\left(\frac{T\omega}{2}\right) = \pi$$

$$\pi\,\delta\left(\frac{\omega}{2}\right) = 2\pi\hbar\,\delta(E_f+\hbar\omega-E_i)$$

enforces energy conservation. Then

$$|C_{fi}|^2 = \frac{2\pi}{\hbar}\,T\,\delta(E_f+\hbar\omega-E_i)\,|\langle f|H_1|i\rangle|^2$$

note, dimensionless.

## Transition rate

physical observable transition rate

rate = probability <u>per unit time</u>.

Photon final states are continuum in phase space. The phase space density $\rho$ is defined by

$$\frac{V d^3k}{(2\pi)^3} = \rho(E_\gamma)\, d\Omega\, dE_\gamma$$

using $E = \hbar c k$,

$$\rho(E_\gamma)\, d\Omega\, dE_\gamma = \left[\frac{V}{(2\pi)^3}\frac{E_\gamma^2}{(\hbar c)^3}\right] d\Omega\, dE_\gamma$$

V cancels factor $\frac{1}{\sqrt{V}}$ in $\vec{A}$.

$$dR = \frac{|C_{fi}|^2}{T} \rho(E_\gamma)\, d\Omega\, dE_\gamma$$

T cancels factor in $|C_{fi}|^2$

$$= \frac{2\pi}{\hbar} \left|\langle f|\hat{H}_1|i\rangle\right|^2 \delta(E_f - E_i)\, \rho(E_\gamma)\, d\Omega\, dE_\gamma$$

Energy integral ensures $E_f = E_i$ giving Golden Rule:

$$\boxed{\frac{dR}{d\Omega_{\vec{k}}} = \left|\langle f|\hat{H}_1|i\rangle\right|^2 \frac{2\pi}{\hbar} \rho(E_\gamma) \qquad \rho(E_\gamma) = \frac{V}{(2\pi)^3} \frac{E_\gamma^2}{(\hbar c)^3}}$$

Note that rate is independent of time so that $R^{-1}$ = lifetime of state.

$$N(t) = N(0)\, e^{-tR}$$