Lecture 22: Time Dependent Perturbation

$\hat{H} = \hat{H}_0 + \hat{H}_1(t)$

Assume $\hat{H}_0$ has been completely solved.

$$\hat{H}_0 |E_n^0\rangle = E_n^0 |E_n^0\rangle$$

We cannot write time evolution operator for full Hamiltonian as

$$\hat{U}(t) = \exp\left(\frac{-i}{\hbar}\hat{H}t\right)$$

However we do know $|E_n^0(t)\rangle = e^{-iE_nt/\hbar}|E_n^0(0)\rangle$.

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ " $|E_n^0\rangle$

Exploiting this let

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

and put into $i\hbar\frac{\partial}{\partial t}|\psi\rangle = \left(\hat{H}_0 + \hat{H}_1(t)\right)|\psi\rangle$

let $\omega_n \equiv E_n^0/\hbar$

$$\sum\left(i\hbar\dot{C}_n + C_nE_n^0\right)e^{-i\omega_nt}|E_n^0\rangle =$$

$$\sum\left(C_n\hat{H}_1 + C_nE_m^0\right)e^{-i\omega_nt}|E_n^0\rangle$$

apply $\langle E_f^0|$ on left,

$$i\hbar\dot{C}_f = \sum_n C_n\, e^{+i\omega_{fn}t}\langle E_f^0|\hat{H}_1|E_n^0\rangle$$

where $\omega_{fn} \equiv \frac{1}{\hbar}\left(E_f^0 - E_n^0\right)$

System of equations for $C_n(t)$ with initial conditions $C_n(0) = \delta_{ni}$ cannot be solved exactly.

Perturbation theory: $\hat{H} = \hat{H}_0 + \underline{\underline{\lambda}}\,\hat{H}'$

let

$$C_n(t) = C_n^{(0)}(t) + \lambda C_n^{(1)}(t) + \lambda^2 C_n^{(2)}(t) + \cdots$$

then

$$\left(\dot{C}_f^{(0)} + \underline{\lambda}\,\dot{C}_f^{(1)} + \cdots\right) = \frac{-i}{\hbar} \sum \left(C_n^{(0)} + \underline{\lambda}\, C_n^{(1)} + \cdots\right) e^{i\omega_{fn}t} \langle E_f^0 | \underline{\lambda} \hat{H}_1 | E_n^0 \rangle$$

order by order in λ:

$$\lambda^0: \qquad C_f^{(0)} = \delta_{fi}$$

$$\lambda^1: \quad \dot{C}_f^{(1)} = \frac{-i}{\hbar} \sum C_n^{(0)} e^{i\omega_{fn}t} \langle E_f | \hat{H}_1 | E_n^0 \rangle$$

then using $C_n^{(0)}(0) = \delta_{ni}$ we get

$$\dot{C}_f^{(1)} = \frac{-i}{\hbar} e^{-i\omega_{fi}} \langle E_f^0 | \hat{H}_1 | E_i^0 \rangle$$

integrating,

$$\boxed{C_f^{(1)}(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t dt' e^{i\omega_{fi}t'} \langle E_f^0 | \hat{H}_1 | E_i^0 \rangle}$$

first order result for $i \to f$ transition

Example: H-atom in classical field

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

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

Exitation amplitude is

$$C^{(1)}_{1s\to 2p} = \frac{-i}{\hbar}\int_0^\infty dt\, e^{i\omega t}\langle 2p|\hat{H}_1|1s\rangle$$

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

$$C^{(1)}_{1s\to 2p} = \frac{-ie\mathcal{E}_0}{\hbar}\langle 2p|z|1s\rangle \int_0^\infty dt\, e^{i\omega t} e^{-t/\tau}$$

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

space integral $\quad z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}Y_{10}$

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

$$R_{10} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\ ; \quad R_{21} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$$

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

$$= a_0\frac{1}{\sqrt{2}\sqrt{3}}\left(\frac{2}{3}\right)^5 \underbrace{\int_0^\infty x^4 e^{-x}dx}_{4! = 2^3\cdot 3} = \underbrace{\sqrt{\frac{2}{3}}\frac{2^7}{3^4}}_{\equiv A} a_0$$

$$|A|^2 = \frac{2^{15}}{3^9} \doteq 1{,}66$$

radial integral (RI) $= \sqrt{\frac{2}{3}}\frac{2^7}{3^4}a_0 = A\ a\_0$

$$C^{(1)}_{1s\to 2p} = -i\frac{e\mathcal{E}_0}{\hbar}\left(\frac{\tau}{1-i\omega\tau}\right)\frac{1}{\sqrt{3}}\,A\,a_0$$

$$\left|C^{(1)}_{1s\to 2p}\right|^2 = \left(\frac{e\mathcal{E}_0 a_0}{\hbar}\right)^2 \frac{A^2}{3}\left[\frac{\tau^2}{1-(\omega\tau)^2}\right]$$

note <u>resonance</u> when $\omega\tau = \left(\frac{E_{2p}-E_{1s}}{\hbar}\right)\tau = 1$

check $[e\mathcal{E}_0 a_0] = [\text{energy}]$

so $\left(\frac{e\mathcal{E}_0 a_0 \tau}{\hbar}\right)$ is dimensionless

In general, dipole selection rules are

$\Delta l = 0$

$\Delta m = 0, \pm 1$

since photon may be emitted in any direction.

<u>Fermi's Golden Rule</u> Applying perturbation theory to photon-atom interaction,

$$C_{fi}' = \frac{-i}{\hbar}\int_0^T dt\, e^{i\omega_{fi}t}\,\langle f|\hat{H}_1|i\rangle$$

states are direct product

$$|\psi\rangle = |\text{electron}\rangle \otimes |\text{photon}\rangle = |n\,l\,m_l\,\tfrac{1}{2}m_s\rangle\,|\vec{k},\lambda\rangle$$

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

↳ contains $\hat{a}_{\vec{k}\lambda}, \hat{a}^{+}_{\vec{k}\lambda}$ operators

free field operator,

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

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

$$\hat{a}(t) = \hat{a}(0)\,e^{-i\omega t} \quad \text{annihilates photon}$$
$$\hat{a}^{+}(t) = \hat{a}^{+}\,e^{+i\omega t} \quad \text{creates photon}$$

To leading order in α, omit $|\hat{\vec{A}}|^2$ term.
Time dependence of $\hat{\vec{A}}$ can be included in ω_{fi}:

$$\hbar\omega_{fi} = E_{n_f} - E_{n_i} \pm \hbar\omega \qquad \text{take + for photon emission}$$

What remains is $\hat{\vec{A}}(\vec{r},0)$.
For more rigorous treatment see "interaction picture" discussed in textbook.

time integral

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

Then

$$|C_{fi}^{(1)}|^2 = \frac{1}{\hbar^2}\left|\langle f|\hat{H}_1|i\rangle\right|^2 \frac{\sin^2(\omega T/2)}{(\omega/2)^2}$$

$\lim T \to \infty$ $\quad \frac{1}{\pi}\frac{\sin^2(\omega T/2)}{T(\omega/2)^2} = \delta\left(\frac{\omega}{2}\right) = 2\hbar\,\delta(E_f - E_i + \hbar\omega)$

$$\delta(g(x)) = \frac{\delta(x-x_0)}{\left|\frac{dg}{dx}\right|_{x_0}} \quad \text{(Appendix C.11)}$$

δ-function ensures energy conservation. Picks out correct $E_\gamma = \hbar ck$ in expansion of $\hat{\vec{A}}$.

$$|C_{fi}^{(1)}|^2 = \frac{2\pi}{\hbar}\, T\,\delta(E_f - E_i + \hbar\omega)\left|\langle f|\hat{H}_1|i\rangle\right|^2$$

(dimensionless)

Transition rate is the <u>probability per unit time</u> times density of photon states in phase space.

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

with $E = \hbar ck$

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

V cancels $\frac{1}{\sqrt{V}}$ factors in $\vec{A}$ box normalization

Differential decay rate

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

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

Energy integral ensures $E_\gamma = E_f - E_i$ giving
Fermi's Golden Rule:

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

Rate is independent of time so R^{-1} = lifetime of state. For $N(0)$ excited atoms at $t=0$,

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