Time-dep. Perturbation theory

Time dep. Schrodinger Eqn (S.E.)

$$H \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

for H indep of time $\rightarrow$ separable soln $\Psi(\vec{r},t) = \psi(\vec{r}) e^{-iEt}$

$H_0 \psi_n = E_n \psi_n$ eigenvalue eqn for energy eigenstates

this is our unperturbed system.

We consider two levels of the system, as before so that:

$$\Psi(\vec{r},t) = c_a(t)\, \psi_a(\vec{r}) e^{-iE_a t/\hbar} + c_b(t)\, \psi_b(\vec{r}) e^{-iE_b t/\hbar}$$

$$= c_a \Psi_a + c_b \Psi_b$$

$$= c_a e^{-iE_a t/\hbar} |a\rangle + c_b e^{-iE_b t/\hbar} |b\rangle$$

Now add t-dep. part of hamiltonian:

$$H = H_0 + \underbrace{H'(t)}_{\text{will contain our applied field.}}$$

Even though our H is different, we make the assumption that the new state can still be described as a linear superposition of ψ_a, ψ_b.

- If only two levels, this is exact.

$$H\Psi = (H_0 + H')(c_a \Psi_a + c_b \Psi_b) = i\hbar c_a \frac{\partial \Psi_a}{\partial t} + i\hbar c_b \frac{\partial \Psi_b}{\partial t}$$

$$+ i\hbar (\dot{c}_a \Psi_a + \dot{c}_b \Psi_b)$$

Now we want to isolate $\dot{c}_a$, multiply through from left by ψ_a^* then integrate, use orthogonality: $\langle a|b\rangle = 0$

$$c_a e^{-iE_a t/\hbar} \langle a|H'|a\rangle + c_b e^{-iE_b t/\hbar} \langle a|H'|b\rangle = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

re arrange

$$\dot{c}_a = -\frac{i}{\hbar}\left(c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \right)$$

similarly

$$\dot{c}_b = -\frac{i}{\hbar}\left(c_a H'_{ba} e^{+i(E_b - E_a)t/\hbar} + c_b H'_{bb} \right)$$

let $\omega_{ab} = (E_b - E_a)/\hbar = \omega_o$ for 2-level system

General case (> 2 levels) can be written in matrix form:

$$i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \\ \vdots \\ \dot{C}_n \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} e^{-i\omega_{12} t} & \cdots \\ H_{21} e^{+i\omega_{12} t} & H_{22} & \\ \vdots & \vdots & \ddots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{pmatrix}$$

set of coupled diff. eqns.

off diag. terms transfer probability (=population for an ensemble)

- often diag terms = 0, many others = 0 by selection rules

Now make approximations.

Assume at $t=0$ $C_a = 1$

Put lower order of appx on RHS: assume diag = 0 $H_{aa} = H_{bb} = 0$

0th $\quad C_a^{(0)}(t) = 1 \quad C_b^{(0)}(t) = 0$

1st $\quad \dot{C}_a^{(1)} = 0 \rightarrow C_a^{(1)} = 1$

$$\dot{C}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_o t} \rightarrow C_b^{(1)} = -\frac{i}{\hbar}\int_0^t H'_{ba}(t') e^{i\omega_o t'} dt'$$

2nd $\quad \dot{C}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_o t} \underbrace{\left(\frac{-i}{\hbar}\right)\int_0^t H_{ba}(t') e^{i\omega_o t'} dt'}_{C_b^{(1)}}$

integrate this

$\rightarrow 1 - (\text{stuff})$ to account for depletion of a state.

More orders: effectively higher powers of H' (= E-field) $\rightarrow$ Nonlinear optics

Now gradually be more specific about perturbation:

- sudden
- sinusoidal here $\quad H'(\vec{r},t) = V(\vec{r})\cos(\omega t)$

$$H'_{ab} = V_{ab}\cos\omega t$$

calculate 1st order coeff $c_b(t)$

$$c_b(t) \approx -\frac{i}{\hbar}V_{ba}\int_0^t \cos(\omega t')\, e^{i\omega_0 t'}dt' =$$

$$= -\frac{i}{2\hbar}V_{ba}\int_0^t \left(e^{i(\omega+\omega_0)t'} + e^{i(\omega_0-\omega)t'}\right)dt'$$

$$= -\frac{i}{2\hbar}V_{ba}\left(\frac{e^{i(\omega+\omega_0)t}-1}{i(\omega+\omega_0)} + \frac{e^{i(\omega_0-\omega)t}-1}{i(\omega_0-\omega)}\right)$$

standard rearrangement: factor out $e^{i(\,)t/2}$, convert to sinc

$$c_b(t) = -\frac{i}{\hbar}V_{ba}\left(\frac{e^{i(\omega+\omega_0)t/2}\sin((\omega+\omega_0)t/2)}{\omega+\omega_0} + \frac{e^{i(\omega_0-\omega)t/2}\sin((\omega_0-\omega)t/2)}{\omega_0-\omega}\right)$$

For $\omega \approx \omega_0$, keep only second term (= "rotating wave approx")

- example: $\omega = \omega_0$ (limit)

$$c_b(t) \to -\frac{i}{\hbar}V_{ba}\left[\frac{e^{i\omega_0 t}\sin\omega_0 t}{2\omega_0} + \frac{t}{2}\right] = -\frac{i V_{ba}}{2\hbar\omega_0}\left(e^{i\omega_0 t}\sin\omega_0 t + \omega_0 t\right)$$

as $\omega_0 t >> 1$ 2nd term dominates

$|c_b(t)|^2 \equiv$ transition probability

Yield actually oscillates - this is a real effect, though outside our approximation.

> For 2-level system, can solve coupled eqns directly.

→ coherent oscillation of population w/ Rabi flopping freq.

$$\omega_r = \tfrac{1}{2}\sqrt{(\omega-\omega_0)^2 + |V_{ab}|^2/\hbar^2}$$

from solution of the "optical Bloch" eqns.

EM interaction

$$\vec{E} = E_0 \cos(\omega t)\,\hat{z}$$

from electric dipole interaction,

$$H' = -qE_0 z \cos(\omega t)$$

we are assuming $\lambda \gg a_0$ $\quad \lambda \simeq 500\,nm \quad a_0 \sim 1\,Å$

using $\mu = q\langle b|z|a\rangle$ = dipole moment,

$$V_{ab} = -\mu_{ab} E_0 = -\mu E_0$$

Now we can write the transition probability as

$$P_{a\to b}(t) = \frac{|\mu|^2 E_0^2}{\hbar^2} \frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}$$

$E_0^2 \propto$ energy density: $\quad u = \frac{1}{2}\varepsilon_0 E_0^2$

but we will illuminate w/ a broad range of ω

$$u \to \rho(\omega)\,d\omega$$

and integrate over $\Delta\omega$ around ω_0 (so that rot wave appx is valid)

$$P_{a\to b}(t) = \frac{2}{\varepsilon_0\hbar^2}|\mu|^2 \int_{\omega_0-\frac{1}{2}\Delta\omega}^{\omega_0+\frac{1}{2}\Delta\omega} \rho(\omega) \frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}\,d\omega$$

for small t, yield $\propto t^2$, but for large t, width is narrow.

in fact, the fcn approaches a $\delta(\omega-\omega_0)$

Pick out $\rho(\omega_0)$. then extend range of integral

$$\to \frac{2}{\varepsilon_0\hbar^2}|\mu|^2 \rho(\omega_0) \int^{\infty} \frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}\,d\omega$$

let $x = (\omega_0 - \omega)t/2$ $\quad dx = (-t/2)\,d\omega$

$$\rightarrow + \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} \frac{(t/2)^2}{(t/2)}\, dx = \frac{\pi t}{2}$$

Together,

$$P_{a\to b}(t) = \underbrace{\frac{\pi |\mu|^2 \rho(\omega_0)}{\varepsilon_0 \hbar}}_{\text{rate: } W_{ab}} t$$ linear in time.

Angle average (unpolarized light, incident from all directions or atom orientation)

$\rightarrow \frac{1}{3}$ factor

$$\therefore \quad W_{ab} = \frac{\pi}{3} \frac{|\mu|^2}{\varepsilon_0 \hbar} \rho(\omega_0)$$

Fermi's Golden rule:

can have both a range of input ω ($\rho(\omega)$) or a spread or continuous range of final states.

$\therefore$ generalize transition rate using

$$\lim_{t\to\infty} \frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2 t/2} \rightarrow \delta(\omega_0 - \omega)$$

not squared.

$$W_{i\to f} = \frac{2\pi}{\hbar^2} \int d\omega_f \, |\langle f | H' | i \rangle|^2 \delta(\omega_f - \omega_i)$$ Fermi's Golden rule.

When final states are continuous in range

$\rightarrow$ use density of states.