Chapter 9 Time-Dependent Perturbation Theory

9.1 Two-Level Systems

Just two states of the (unperturbed) system,

$H_0 \psi_a = E_a \psi_a$, and $H_0 \psi_b = E_b \psi_b$

$\langle \psi_a | \psi_b \rangle = \delta_{ab}$

Any state can be expressed as a linear combination of them. $t=0$

$\Psi(0) = c_a \psi_a + c_b \psi_b$.

In the absence of any perturbation

$\Psi(t) = c_a \psi_a e^{-i\frac{E_a}{\hbar}t} + c_b \psi_b e^{-i\frac{E_b}{\hbar}t}$

$|c_a|^2 + |c_b|^2 = 1$.

9.1.1 The Perturbed System

Turn on a time-dependent perturbation $H'(t)$

Since ψ_a and ψ_b constitute a complete set, the wave function $\Psi(t)$ can still be expressed as a linear combination of them.

$\Psi(t) = c_a(t) \psi_a e^{-i\frac{E_a}{\hbar}t} + c_b(t) \psi_b e^{-i\frac{E_b}{\hbar}t}$

$\Psi(t)$ satisfy the time-dependent Schrödinger eq

→ solve $c_a(t)$ and $c_b(t)$

$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$, where $H = H_0 + H'(t)$

$$\Rightarrow c_a[H_0\psi_a] e^{-i\frac{E_a}{\hbar}t} + c_b[H_0\psi_b] e^{-i\frac{E_b}{\hbar}t} + c_a[H'\psi_a] e^{-i\frac{E_a}{\hbar}t} + c_b[H'\psi_b] e^{-i\frac{E_b}{\hbar}t}$$

$$= i\hbar[\dot{c}_a \psi_a e^{-i\frac{E_a}{\hbar}t} + \dot{c}_b \psi_b e^{-i\frac{E_b}{\hbar}t} + c_a\psi_a(-i\frac{E_a}{\hbar}) e^{-i\frac{E_a}{\hbar}t} + c_b\psi_b(-i\frac{E_b}{\hbar}) e^{-i\frac{E_b}{\hbar}t}]$$

$$\Rightarrow c_a[H'\psi_a] e^{-i\frac{E_a}{\hbar}t} + c_b[H'\psi_b] e^{-i\frac{E_b}{\hbar}t} = i\hbar[\dot{c}_a \psi_a e^{-i\frac{E_a}{\hbar}t} + \dot{c}_b \psi_b e^{-i\frac{E_b}{\hbar}t}]$$

($\langle \psi_a | \psi_b \rangle = \delta_{ab}$)

$$\begin{cases} c_a \langle \psi_a | H' | \psi_a \rangle e^{-i\frac{E_a}{\hbar}t} + c_b \langle \psi_a | H' | \psi_b \rangle e^{-i\frac{E_b}{\hbar}t} = i\hbar \dot{c}_a e^{-i\frac{E_a}{\hbar}t} \\ c_a \langle \psi_b | H' | \psi_a \rangle e^{-i\frac{E_a}{\hbar}t} + c_b \langle \psi_b | H' | \psi_b \rangle e^{-i\frac{E_b}{\hbar}t} = i\hbar \dot{c}_b e^{-i\frac{E_b}{\hbar}t} \end{cases}$$

$$\Rightarrow \begin{cases} \dot{c}_a = -\frac{i}{\hbar}[c_a H'_{aa} + c_b H'_{ab} e^{-i\frac{(E_b - E_a)}{\hbar}t}] \\ \dot{c}_b = -\frac{i}{\hbar}[c_b H'_{bb} + c_a H'_{ba} e^{i\frac{E_b - E_a}{\hbar}t}] \end{cases}$$

where $\boxed{H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle}$ is defined

Typically, $H'_{aa} = H'_{bb} = 0$.

The equation simplify:

$$\boxed{\begin{aligned} \dot{c}_a &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \\ \dot{c}_b &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \end{aligned}}$$ where $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$. [9.13]

(We'll assume that $E_b \geq E_a$, so $\omega_0 \geq 0$).

9.1.2 Time-Dependent Perturbation Theory

If H' is "small", we can solve Eq 9.13 by a process of successive approximations

Suppose the particle starts out in the lower state:

$c_a(0) = 1$, $c_b(0) = 0$.

- Zeroth Order:

$c_a^{(0)}(t) = 1$, $c_b^{(0)}(t) = 0$.

- First Order: insert in Eq 9.13

$\frac{dc_a}{dt} = 0 \Rightarrow c_a^{(1)}(t) = 1$.

$\frac{dc_b}{dt} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \Rightarrow \boxed{c_b^{(1)} = -\frac{i}{\hbar}\int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'}$

- Second Order: $P_{a\to b}(t) = |c_b^{(1)}(t)|^2$

$\frac{dc_a}{dt} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} (-\frac{i}{\hbar}) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \Rightarrow$

$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} [\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt''] dt'$.

$c_b^{(2)}(t) = c_b^{(1)}(t)$.

9.1.3 Sinusoidal Perturbations

$\boxed{H'(\vec{r}, t) = V(\vec{r}) \cos(\omega t)}$

$H'_{ab} = V_{ab} \cos(\omega t)$ where $V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle$

To first order

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

$$= -\frac{iV_{ba}}{2\hbar} \int_0^t [e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'}] dt'$$

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

* When driving frequencies (ω) that are very close to the transition frequency (ω_0), ~~so that the second~~

$\omega_0 + \omega \gg |\omega_0 - \omega|$

the second term dominates:

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

The transition probability

the probability a particle which started out in the state ψ_a will be found, at time t, in the state ψ_b — is

$$P_{a\to b}(t) = |c_b(t)|^2 \cong \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}.$$

9.2 Emission and Absorption of Radiation

9.2.1 Electromagnetic Waves

An atom, in the presence of a passing light wave

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

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

$H'_{ba} = \wp E_0\cos(\omega t)$ where $\wp \equiv q\langle\psi_b|z|\psi_a\rangle$

Typically, ψ is an even or odd function of z; in either case $z|\psi|^2$ is odd, and integrates to zero. $\Rightarrow$ the diagonal matrix elements of H' vanish.

$V_{ba} = -\wp E_0$

9.2.2 Absorption, Stimulated Emission and Spontaneous Emission

$$P_{a\to b}(t) = \left(\frac{|\wp|E_0}{\hbar}\right)^2\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$ ~~the atom absorbs en~~

the atom absorbs energy $E_b - E_a = \hbar\omega_0$.

$$P_{b\to a}(t) = |c_a(t)|^2 = \left(\frac{|\wp|E_0}{\hbar}\right)^2\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

light amplification by stimulated emission of radiation

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9.2.3 Incoherent Perturbations

The energy density in an e-m wave is $u = \frac{\epsilon_0}{2}E_0^2$

$$P_{b\to a}(t) = \frac{2u}{\epsilon_0\hbar^2}|\wp|^2\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

$$P_{b\to a}(t) = \frac{2}{\epsilon_0\hbar^2}|\wp|^2\int_0^\infty \rho(\omega)\left\{\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}\right\}d\omega$$
$$\cong \frac{2|\wp|^2}{\epsilon_0\hbar^2}\rho(\omega_0)\int_0^\infty\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}d\omega$$

$\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}dx = \pi$ $\quad \cong \frac{\pi|\wp|^2}{\epsilon_0\hbar^2}\rho(\omega_0)t.$

transition rate ($R \equiv \frac{dP}{dt}$)

$$R_{b\to a} = \frac{\pi}{\epsilon_0\hbar^2}|\wp|^2\rho(\omega_0)$$

↳ the perturbing wave is coming in along the x-direction and polarized in the z-direction

? An atom bathed in radiation coming from all directions, and with all possible polarizations.

$|\wp|^2 \Rightarrow |\hat{n}\cdot\vec{\wp}|^2$. $\quad \vec{\wp} = q\langle\psi_b|\vec{r}|\psi_a\rangle$

- Polarization:

$$(\hat{n}\cdot\vec{\wp})^2_p = \frac{1}{2}[(\hat{i}\cdot\vec{\wp})^2 + (\hat{j}\cdot\vec{\wp})^2]$$
$$= \frac{1}{2}(\wp_x^2 + \wp_y^2)$$
$$= \frac{1}{2}\wp^2\sin^2\theta.$$

where θ is the angle between $\vec{\wp}$ and the direction of propagation

- Propogation direction:

$$(\hat{n}\cdot\vec{\wp})^2_{pp} = \frac{1}{4\pi}\int\left[\frac{1}{2}\wp^2\sin^2\theta\right]\sin\theta\, d\theta\, d\phi$$
$$= \frac{\wp^2}{4}\int_0^\pi \sin^3\theta\, d\theta$$
$$= \frac{\wp^2}{3}.$$

So the transition rate for stimulated emission from state b to state a, under the influence of incoherent, unpolarized light incident for all directions, is

$$R_{b\to a} = \frac{\pi}{3\epsilon_0\hbar^2}|\wp|^2\rho(\omega_0)$$

where $\vec{\wp}$ is the matrix element of the electric dipole moment between the two states and $\rho(\omega)$ is the energy density in the fields, per unit frequency, evaluated at $\omega_0 \equiv (E_b - E_a)/\hbar$.

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9.3.3 Selection Rules

The calculation of spontaneous emission rates has been reduced to a matter of evaluating matrix elements of the form $\langle \psi_b | \vec{r} | \psi_a \rangle$

Suppose systems like hydrogen. $\langle n'l'm' | \vec{r} | nlm \rangle$

- Selection rules involving m and m':

$[L_z, z] = 0$

$0 = \langle n'l'm' | [L_z, z] | nlm \rangle = \langle n'l'm' | (L_z z - z L_z) | nlm \rangle$

$= \langle n'l'm' | [(m'\hbar) z - z(m\hbar)] | nlm \rangle$

$= (m'-m)\hbar \langle n'l'm' | z | nlm \rangle$.

So unless $m' = m$, the matrix elements of z are always zero.

$\langle n'l'm' | [L_z, x] | nlm \rangle = \langle n'l'm' | (L_z x - x L_z) | nlm \rangle$

$= (m'-m)\hbar \langle n'l'm' | x | nlm \rangle$

$= i\hbar \langle n'l'm' | y | nlm \rangle$

$\Rightarrow (m'-m) \langle n'l'm' | x | nlm \rangle = i \langle n'l'm' | y | nlm \rangle$

$\Rightarrow (m'-m) \langle n'l'm' | y | nlm \rangle = -i \langle n'l'm' | x | nlm \rangle$

$(m'-m)^2 \langle n'l'm' | x | nlm \rangle = i(m'-m) \langle n'l'm' | y | nlm \rangle$

$= \langle n'l'm' | x | nlm \rangle$

Hence unless $(m'-m)^2 = 1$, the matrix elements of x & y are always zero.

No transitions occur unless $\Delta m = \pm 1$ or 0.

— SELECTION RULE for m

- Selection rules involving l and l':

$[L^2, [L^2, \vec{r}]] = 2\hbar^2 (\vec{r} L^2 + L^2 \vec{r})$.

$\langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle = 2\hbar^2 \langle n'l'm' | (\vec{r} L^2 + L^2 \vec{r}) | nlm \rangle$

$\cancel{= 2\hbar^4 [l(l+1) + l'(l'+1)] \langle n'l'm' | \vec{r} | nlm \rangle}$

$\cancel{= \hbar^4 [l'}$

$\rightarrow 2\hbar^2 \langle n'l'm' | (\vec{r} L^2 + L^2 \vec{r}) | nlm \rangle$

$= 2\hbar^4 [l(l+1) + l'(l'+1)] \langle n'l'm' | \vec{r} | nlm \rangle$

$\rightarrow \langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle$

$= \langle n'l'm' | (L^2 [L^2, \vec{r}] - [L^2, \vec{r}] L^2) | nlm \rangle$

$= \hbar^2 [l'(l'+1) - l(l+1)] \langle n'l'm' | (L^2 \vec{r} - \vec{r} L^2) | nlm \rangle$

$= \hbar^4 [l'(l'+1) - l(l+1)]^2 \langle n'l'm' | \vec{r} | nlm \rangle$.

$\Rightarrow$ Either $2[l(l+1) + l'(l'+1)] = [l'(l'+1) - l(l+1)]^2$.

Or else $\langle n'l'm' | \vec{r} | nlm \rangle = 0$.

But $[l'(l'+1) - l(l+1)] = (l'+l+1)(l'-l)$

and $2[l(l+1) + l'(l'+1)] = (l'+l+1)^2 + (l'-l)^2 - 1$

$\Rightarrow [(l'+l+1)^2 - 1][(l'-l)^2 - 1] = 0$

The first factor cannot be zero (unless $l' = l = 0$)

No transitions occur unless $\Delta l = \pm 1$

— SELECTION RULE for l.