Time Dependent Perturbation Theory

Introduction

Quantum Statics $\rightarrow$ Quantum Dynamics

T.I Schrödinger Eq. $\rightarrow$ Time-Dependent Schrödinger Eq.

$V(\vec{r}) \rightarrow V(\vec{r},t)$

Time-Dependent Schrödinger Equation

$H\Psi = i\hbar \dfrac{\partial \Psi}{\partial t}$ can be solved by separation of variables

$$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-iEt/\hbar} \qquad (1)$$

where $\psi(\vec{r})$ is the solution to $H\psi = E\psi$

With Eq. 1, all probabilities and expectation values are independent of time.

By forming linear combinations of stationary states:

$$\psi(\vec{r},t) = \psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar}$$

These wave functions have interesting time dependence; however, the possible values of their energies, and their respective probabilities are constant.

Neutrino Oscillations p. 122 of Griffiths

Transitions (or Quantum Jumps) require a time-dependent potential

Time-Dependent Perturbation Theory — Two-Level System

Suppose we have a two-state system with unperturbed states:
ψ_a and ψ_b

These are the eigenstates of the unperturbed Hamiltonian, H°.

$$H_0 \psi_a = E_a \psi_a \quad \& \quad H_0 \psi_b = E_b \psi_b \quad \text{where } \langle \psi_a | \psi_b \rangle = \delta_{ab}$$

Any state can be expressed as a linear combination of ψ_a and ψ_b:

$$\Psi(0) = c_a \psi_a + c_b \psi_b \qquad \text{The state at time, } t=0.$$

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

where $|c_a|^2$ = probability of measuring the energy $= E_a$.

$$\langle \Psi(t) | \Psi(t) \rangle = 1 \quad \Rightarrow \quad |c_a|^2 + |c_b|^2 = 1$$

Turn on the perturbation: $V(\vec{r}, t)$, then

$$\Psi(t) = c_a(t)\, \psi_a e^{-iE_a t/\hbar} + c_b(t)\, \psi_b e^{-iE_b t/\hbar} \qquad (2)$$

Solve for $c_a(t)$ & $c_b(t)$ by demanding that $\Psi(t)$ satisfy the time-dependent Schrödinger Equation.

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \text{where } H = H^\circ + H'(t)$$

Time-Dependent Perturbation Theory $\qquad$ Two-Level System

$$c_a\cancel{[H_0^\circ\psi_a]e^{-iE_at/\hbar}} + c_b\cancel{[H_0^\circ\psi_b]e^{-iE_bt/\hbar}} + c_a[H'\psi_a]e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar} =$$

$$= i\hbar\left[\dot{c}_a\psi_a e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar} + \cancel{c_a\psi_a\left(-\frac{iE_a}{\hbar}\right)e^{-iE_at/\hbar}} + \cancel{c_b\psi_b\left(-\frac{iE_b}{\hbar}\right)e^{-iE_bt/\hbar}}\right.$$

and we are left with

$$c_a[H'\psi_a]e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar} =$$

$$= i\hbar\left[\dot{c}_a\psi_a e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar}\right]$$

Isolate $\dot{c}_a$ by taking the inner product $\langle\psi_a|$

$$c_a\langle\psi_a|H'|\psi_a\rangle e^{-iE_at/\hbar} + c_b\langle\psi_a|H'|\psi_b\rangle e^{-iE_bt/\hbar} = i\hbar\dot{c}_a e^{-iE_at/\hbar}$$

Define: $H'_{ij} = \langle\psi_i|H'|\psi_j\rangle$

and multiply by $e^{+iE_at/\hbar}\left(-\frac{i}{\hbar}\right)$, we obtain

$$\dot{c}_a = \frac{-i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab}e^{-i(E_b-E_a)t/\hbar}\right] \qquad \underline{\underline{\text{Eq. 3}}}$$

Similarly, for $\dot{c}_b$ we obtain:

$$\dot{c}_b = \frac{-i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba}e^{i(E_b-E_a)t/\hbar}\right] \qquad \underline{\underline{\text{Eq. 4}}}$$

Problem 9.1 Time-~~In~~Dependent Perturbation Theory

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \qquad \psi_{200} = \frac{1}{\sqrt{8\pi a^3}}\left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

$$\psi_{210} = \frac{1}{\sqrt{32\pi a^3}} \frac{r}{a} e^{-r/2a} \cos\theta \qquad \psi_{21\pm1} = \mp \frac{1}{\sqrt{64\pi a^3}} \frac{r}{a} \sin\theta \, e^{\pm i\phi}$$

$$r\cos\theta \equiv z \quad \& \quad r\sin\theta(\cos\phi \pm i\sin\phi) = x + iy$$

In all cases: $|\psi|^2$ is an even function of z. Thus $\int |\psi|^2 z \, dx\,dy\,dz = 0$

So, $\boxed{H'_{ii} = 0}$

All the above wavefunctions are even in z except for ψ_{210}. odd in z

So, all the $H'_{ij} = 0$ except for $\langle \psi_{100} | H' | \psi_{210} \rangle$

$$\langle \psi_{100} | H' | \psi_{210} \rangle = -eE \frac{1}{\sqrt{\pi a^3}} \frac{1}{\sqrt{32\pi a^3}} \frac{1}{a} \int e^{-r/a} e^{-r/2a} z^2 \, d^3\vec{r}$$

$$\langle \psi_{100} | H' | \psi_{210} \rangle = \frac{-eE}{4\sqrt{2}\,\pi a^4} \underbrace{\int_0^\infty r^4 e^{-3r/2a} dr}_{\left(\frac{2a}{3}\right)^5} \underbrace{\int_0^\pi \cos^2\theta \sin\theta \, d\theta}_{2/3} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$\langle \psi_{100} | H' | \psi_{210} \rangle = -\frac{eE}{4\sqrt{2}\,\pi a^4} 4! \left(\frac{2a}{3}\right)^5 \frac{2}{3} 2\pi = -\left(\frac{2^8}{3^5\sqrt{2}}\right) eEa$$

$H'_{ij} \neq 0$

$$\langle \psi_{100} | H' | \psi_{210} \rangle = -\left(\frac{2^8}{3^5\sqrt{2}}\right) eEa = -0.745 \underbrace{(ea)}_{\text{dipole moment}} E$$

P.E. $= U = -\vec{p}\cdot\vec{E}$ where $\vec{p} \sim e\vec{a}\,(-0.745)$

(0.745)a = characteristic charge separation

Time Dependent Perturbation Theory

$H' = \text{small}$ Two-state system

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

Zeroth Order: No perturbation at all

$$c_a^{(0)}(t) = 1 \qquad c_b^{(0)}(t) = 0$$

First Order:

$$\dot{c}_a^{(1)} = 0 \implies \boxed{c_a^{(1)}(t) = 1}$$

$$\dot{c}_b = \frac{-i}{\hbar} c_a^{(0)} H'_{ba} e^{i\omega_0 t} \implies \dot{c}_b^{(1)}(t) = \frac{-i}{\hbar} H'_{ba} e^{i\omega_0 t}$$

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

Second Order:

$$\dot{c}_a^{(2)}(t) = \frac{-i}{\hbar} c_b^{(1)}(t) H'_{ab} e^{-i\omega_0 t}$$

$$\dot{c}_a^{(2)}(t) = \frac{-i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(\frac{-i}{\hbar} \int_0^t H'_{ba} e^{-i\omega_0 t'} dt' \right)$$

So, $$c_a^{(2)}(t) = c_a^{(1)}(0) - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{-i\omega_0 t''} dt'' \right] dt'$$

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

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

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

Assume that: ① Diagonal matrix elements $V_{ii} = 0$

② Work exclusively in the 1st order approximation.

$$\dot{c}_b(t) = \frac{-i}{\hbar} c_a^{\circ}(0)\, H'_{ba}\, e^{+i\omega_0 t}$$ where $c_a(0) = 1$ $c_b(0) = 0$

and $\omega_0 \equiv \dfrac{E_b - E_a}{\hbar}$

$$c_b(t) \cong \frac{-i}{\hbar}(1)\, V_{ba} \int_0^t \cos\omega t\, e^{i\omega_0 t'}\, dt' + \overset{=0}{c_b^{\circ}(0)}$$

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

$$= \frac{-i V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t'}}{i(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t'}}{i(\omega_0-\omega)} \right]_0^t$$

$$c_b(t) = -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0+\omega} + \frac{e^{i(\omega_0-\omega)t'} - 1}{\omega_0-\omega} \right]$$

Now, let's restrict our attention to:

driving frequencies (ω) <u>close to</u> the transition frequency (ω_0)

So, the 2nd term in the bracket dominates.

Sinusoidal Perturbations

$\omega_0 + \omega >> |\omega_0 - \omega|$ Then: $c_b(t) \cong -\frac{V_{ba}}{2\hbar} e^{\frac{i(\omega_0-\omega)t}{2}} - e^{\frac{-i(\omega_0-\omega)t}{2}}$

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

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

The transition probability for a particle starting in $|\psi_a\rangle$ and found in $\langle\psi_b|$ at a time "t" is:

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

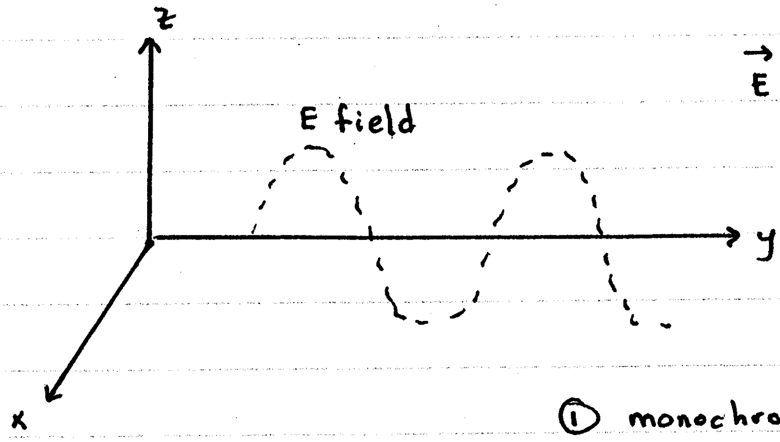
Homework: Problem 9.7 I.I. Rabi's rotating wave approximation.

Light → near the visible frequencies

Atoms → respond to the electric field of em radiation

λ → the wavelength is long compared to the size of the atom.

⇒ so, we can ignore the spatial variations in the field.



$$\vec{E} = E_0 \cos(\omega_0 t)\,\hat{k}$$

① monochromatic

② polarized

Perturbing Hamiltonian

$$H' = -q E_0 z \cos(\omega t)$$

The energy of a charge $-q$ in a static E field $= -q \int \vec{E} \cdot d\vec{r}$

The motion of the charge responds more rapidly than the period of the oscillation.

1st order perturbation ⇒ $H'_{ba} = -\wp E_0 \cos(\omega t)$

where $\wp \equiv q \langle \psi_b | z | \psi_a \rangle$ the off-diagonal matrix element of the z-component of the dipole moment operator, $q\vec{r}$

As a result, $H'_{aa} = H'_{bb} = 0$ $\qquad \vec{\wp} = -q\vec{r}$

Emission and Absorption of Radiation

The interaction of light with matter is described by the sinusoidally variations we studied in the previous section.

$$V_{ba} = -\wp E_0$$

Absorption, Stimulated Emission, and Spontaneous Emission

1. Atom starts in the "lower" state ψ_a and monochromatic, polarized light is shined on it.
2. What is the probability of exciting the atom to a "higher" state ψ_b? ψ_b?

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

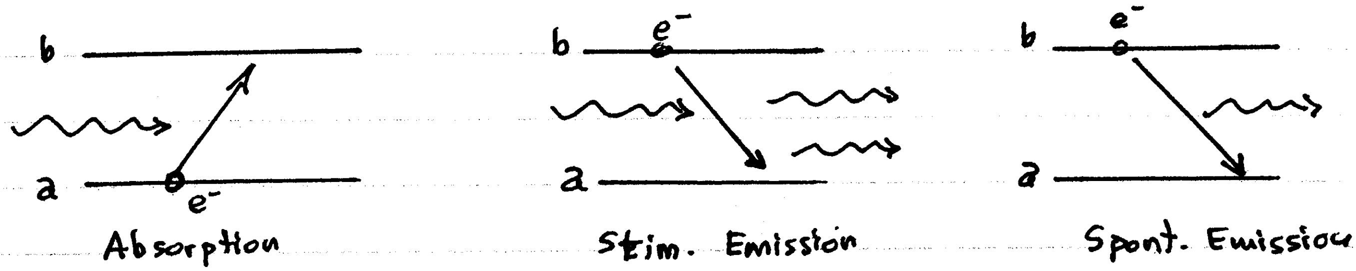
The atom absorbs energy $E_b - E_a = \hbar\omega_0$ from the electromagnetic field.

N.B. We could have started with the atom in the "upper" state $C_a(0)=0$ & $C_b(0)=1$ and calculated $P_{b\to a} = |C_a(t)|^2$ and we would find for stimulated emission:

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

$P_{a\to b} = P_{b\to a}$ "an astonishing result"

Absorption & Emission of Radiation



These are three ways in which light interacts with atoms.

Describe lasers and population inversion.

Spontaneous emission: occurs when an atom in an excited state makes a transition to a lower energy state, thus releasing a photon. However, it does this without interacting with an electromagnetic field (applied or external).
(Perturbation by the ground-state electromagnetic field)

"Zero point" radiation serves to catalyze spontaneous emission. In a sense, there is no such thing as <u>spontaneous emission</u>. It's all <u>stimulated emission</u>.

⇒ Calculate the spontaneous emission rate, and then the natural lifetimes of an excited atomic state.

<u>But first</u> ⇒ Consider the response of an atom to unpolarized, incoherent, non-monochromatic light coming in from all directions

Absorption & Emission of Radiation.

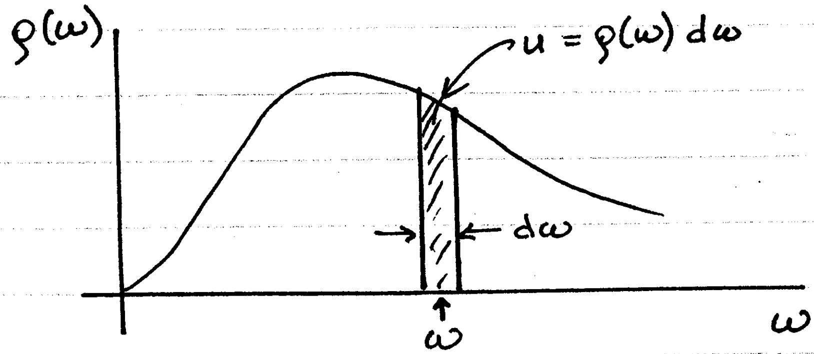
Incoherent Perturbations :

Energy density of an electromagnetic wave $\Rightarrow$ $u = \frac{\varepsilon_0}{2} E_0^2$

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

So, $P_{b\to a}(t) = \frac{2u}{\hbar^2 \varepsilon_0} |\wp|^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$ monochromatic

In many applications, the atomic system is exposed to e.m. waves over a large range of frequencies.



So, $P_{b\to a}(t) = \frac{2}{\varepsilon_0 \hbar^2} |\wp|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2} \right\} d\omega$

$\{\ \}$ $\rightarrow$ is sharply peaked at $\omega = \omega_0$, so, we can write

$$P_{b\to a}(t) \cong \frac{2|\wp|^2}{\varepsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

N.B. $\displaystyle\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx = \pi$ Change variables: $x \equiv (\omega_0 - \omega)\frac{t}{2}$

we find: $$P_{b\to a}(t) \cong \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0)\, t$$

The transition probability is proportional to t.

$\frac{dP}{dt} \equiv$ the transition rate $\Rightarrow$ $R_{b\to a} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$

For atoms: ① e.m. wave in the y-direction
② polarized in the z-direction

What about electromagnetic waves coming from all directions with all possible polarizations?

The energy in the fields $\rho(\omega)$ is equally shared among these different modes.

Instead of $|\wp|^2 \Rightarrow$ we need the average of $|\vec{\wp}\cdot\hat{n}|^2$

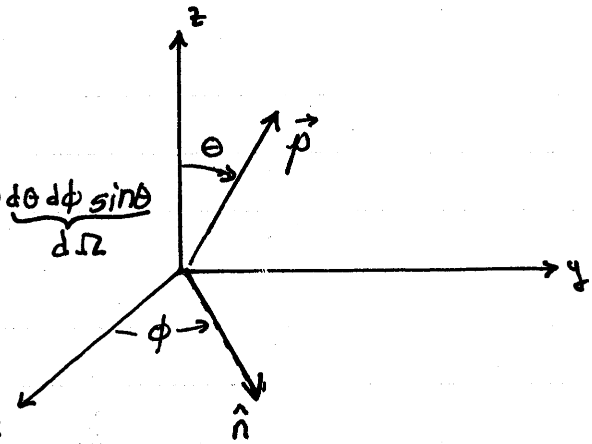
where $\wp \equiv q\langle \psi_b | \vec{r} | \psi_a \rangle$

where the average is over all possible polarizations and all incident directions.

Absorption & Emission of Radiation

$$\vec{p}\cdot\hat{n} = p\sin\theta\,\sin\phi$$

$$\left|\vec{p}\cdot\hat{n}\right|^2_{avg} = \frac{1}{4\pi = \Omega}\int \left|\vec{p}\right|^2 \sin^2\theta\,\sin^2\phi\,\underbrace{d\theta\,d\phi\,\sin\theta}_{d\Omega}$$



$\hat{z}$ = direction of propagation = $\hat{k}$

$\hat{n}$ = polarization = $\cos\phi\,\hat{i} + \sin\phi\,\hat{j}$

$\vec{p} = p\sin\theta\,\hat{j} + p\cos\theta\,\hat{k}$

$$\left|\vec{p}\cdot\hat{n}\right| = \frac{\left|\vec{p}\right|^2}{4\pi}\underbrace{\left(\frac{4}{3}\right)}_{\theta\text{ - integration}}\underbrace{\pi}_{\phi\text{ integration}} = \frac{1}{3}\left|\vec{p}\right|^2$$

Conclusion: the transition rate for stimulated emission from state b to state a is:

$$\boxed{R_{b\to a} = \frac{\pi}{3\varepsilon_0\hbar^2}\left|\vec{p}\right|^2\rho(\omega_0)}$$

Fermi's Golden Rule
Special Case

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