Lecture #21

Time-dependent perturbation theory

So far, we considered **quantum static**, as all our potentials did not depend on time. Therefore, our time dependence was trivial and always the same:

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

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

$\psi(\vec{r})$ satisfies $H\psi(\vec{r}) = E\psi(\vec{r})$

If we want to consider transitions (quantum jumps) between different energy levels, we need to introduce **quantum dynamics**. We will focus on the particular important problem: the emission and absorption of radiation by an atom. As a particular useful technical application, we will discuss **how lasers work**.

Two-level systems

We start with a quantum system that has only two orthonormal states, ψ_a and ψ_b, that are eigenstates of the unperturbed Hamiltonian.

$$H^0\psi_a = E_a\psi_a\,; \quad H^0\psi_b = E_b\psi_b\,; \quad \langle\psi_a|\psi_b\rangle = \delta_{ab}.$$

Of course, any state can be expressed as the linear combination of these two states.

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

($t = 0$)

If there is no time-dependent perturbation, the time evolution of such state is described by

$$\psi(t) = c_a\psi_a e^{-iE_at/\hbar} + c_b\psi_b e^{-iE_bt/\hbar}$$

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

Now, we turn on the time-dependent perturbation, described by the Hamiltonian H'. The resulting wave function can still be represented as the superposition of our two unperturbed functions, since they make a complete set, but the coefficients c now depend on time:

$$\psi(t) = c_a(t)\psi_a e^{-iE_at/\hbar} + c_b(t) e^{-iE_bt/\hbar}.$$

What happens during the transition between these two energy levels?

If the system was originally in state a, then $c_a(t=0)=1$ and $c_b(t)=0$ since the $|C_a|^2$ and $|C_b|^2$ are the corresponding probabilities that measurement of energy will give results E_a and E_b . As a result of the transition at time t, $c_a(t)=0$ and $c_b(t)=1$.

Our mission: to determine the coefficients $c_a(t)$ and $c_b(t)$.

First, we derive the equations for $c_a(t)$ and $c_b(t)$. To accomplish that, we substitute the wave function

$$\psi(t) = c_a(t)\psi_a e^{-iE_at/\hbar} + c_b(t) e^{-iE_bt/\hbar}$$

into the Schrödinger equation $H\psi = i\hbar \frac{\partial \psi}{\partial t}$

with the Hamiltonian $H = H^0 + H'(t)$.

$$(H^0 + H')\left(c_a\psi_a e^{-iE_at/\hbar} + c_b\psi_b e^{-iE_bt/\hbar}\right)$$

$$= i\hbar \frac{\partial}{\partial t}\left(c_a\psi_a e^{-iE_at/\hbar} + c_b\psi_b e^{-iE_bt/\hbar}\right)$$

$$c_a \underbrace{H^0\psi_a}_{=E_a\psi_a} e^{-iE_at/\hbar} + c_b \underbrace{H^0\psi_b}_{=E_b\psi_b} e^{-iE_bt/\hbar}$$

cancel → $E_a\psi_a$; these two terms cancel ← $-iE_bt/\hbar$

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

$$= i\hbar\left(-\frac{iE_a}{\hbar}\right)\psi_a e^{-iE_at/\hbar} + i\hbar\left(-\frac{iE_b}{\hbar}\right)\psi_b e^{-iE_bt/\hbar}$$

$$+ i\hbar \dot{c}_a\psi_a e^{-iE_at/\hbar} + i\hbar \dot{c}_b\psi_b e^{-iE_bt/\hbar}$$

$\dot{c}_a = \frac{\partial c_a}{\partial t}$

Note that ψ_a and ψ_b do not depend on time, as they are eigenstates of the unperturbed Hamiltonian H_0.

$$c_a H' \psi_a e^{-iE_a t/\hbar} + c_b H' \psi_b e^{-iE_b t/\hbar} = i\hbar \dot{c}_a \psi_a e^{-iE_a t/\hbar} + i\hbar \dot{c}_b \psi_b e^{-iE_b t/\hbar}$$

Next step: separate this equation into two, one containing $\dot{c}_a$ and another one containing $\dot{c}_b$. To get the first equation for $\dot{c}_a$, multiply this equation on the left by ψ_a^* and integrate, i.e. take inner product with ψ_a. Use inner product designations. Then, use orthogonality of the ψ_a and ψ_b wave functions. Introduce the following designations:

$$\boxed{H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle} \qquad i, j \equiv a, b$$

Class exercise: derive equation for $\dot{c}_a$.

$$c_a \underbrace{\langle \psi_a | H' | \psi_a \rangle}_{H'_{aa}} e^{-iE_a t/\hbar} + c_b \underbrace{\langle \psi_a | H' | \psi_b \rangle}_{H'_{ab}} e^{-iE_b t/\hbar}$$

$$= i\hbar \dot{c}_a \underbrace{\langle \psi_a | \psi_a \rangle}_{1} e^{-iE_a t/\hbar} + i\hbar \dot{c}_b \cancel{\langle \psi_a | \psi_b \rangle}^{=0} e^{-iE_b t/\hbar}$$

$$i\hbar \dot{c}_a e^{-iE_a t/\hbar} = c_a H'_{aa} e^{-iE_a t/\hbar} + c_b H'_{ab} e^{-iE_b t/\hbar}$$

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

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

introduce "transition frequency" $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

(assume $E_b \geq E_a$) $\omega_0 \geq 0$

$$\boxed{\dot{c}_a = -\frac{i}{\hbar}\left\{ c_a H'_{aa} + c_b H'_{ab} e^{-i\omega_0 t}\right\}}$$

To get the equation for $\dot{c}_b$, take inner product with ψ_b. The resulting equation is:

$$\dot{c}_b = -\frac{i}{\hbar}\left\{ c_b H'_{bb} + c_a H'_{ba} e^{i\omega_0 t}\right\}$$

For most cases, the diagonal matrix elements of the perturbation Hamiltonian H' are zero:

$$H'_{aa} = 0, \quad H'_{bb} = 0 \qquad (1).$$

The resulting equations become:

$$\boxed{\begin{aligned} \dot{c}_a &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \\ \dot{c}_b &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \end{aligned}}$$

These equations are exact for the cases where (1) is true as we made no approximations so far. However, there are very few problems which can be solved exactly. If the perturbation is small, we can use time-dependent perturbation theory.

Time-dependent perturbation theory

We take the perturbation H'(t) to be small. We start with our system in the ground state, ψ_a. Therefore, the values of the coefficients are the following:

$$c_a(0) = 1 \quad \text{and} \quad c_b(1) = 0.$$

(0: time $t=0$)

Zeroth-order

If there is no perturbation, then our system just stays in this state forever. Therefore, our **zeroth-order** is (superscript $^{(0)}$ designates order) :

$$c_a^{(0)} = 1 \quad \text{and} \quad c_a^{(1)} = 0.$$

First order

To get the **first-order** approximation for the coefficients $c_a(t)$ and $c_b(t)$, we take our zeroth-order values and substitute them into right side of the equations that we have just derived.

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \Rightarrow \frac{dc_a^{(1)}}{dt} = 0 \Rightarrow \boxed{c_a^{(1)}(t) = 1}$$

replace by $\dot{c}_a^{(1)}$

plug in $\boxed{c_b^{(0)} = 0}$

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

$\dot{c}_b$ replaced by $\frac{d\dot{c}_b^{(1)}}{dt}$

plug in $\boxed{c_a^{(0)} = 1}$

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

Second order

To get second-order approximation, repeat the same thing: plug in your first-order result

$$c_a^{(1)}(t) = 1$$

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

into the right size of the general form of the equations for coefficients c:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab}\, e^{-i\omega_0 t}\, c_b \quad \text{(plug in first-order above)}$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba}\, e^{i\omega_0 t}\, c_a \quad \text{(plug in first-order above)}$$

$$\frac{d\dot{c}_a^{(2)}}{dt} = -\frac{i}{\hbar} H'_{ab}\, e^{-i\omega_0 t}\left\{-\frac{i}{\hbar}\int_0^t H'_{ba}(t')\, e^{i\omega_0 t'}\, dt'\right\} \quad (c_b^{(1)})$$

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

zeroth-order ↗

$$c_b^{(2)}(t) = c_b^{(1)}(t) \quad (\text{since } c_a^{(1)}(t) = 1).$$

Higher orders

To get $(n+1)^{th}$ order, plug in the results from the n^{th} order into the equations …. again. Note that the orders are counted in the perturbation potential:

Zeroth order contain no matrix elements of H';
First-order contains one matrix elements of H';
Second-order contains two of them , and so on.

Now it is time to make an example of the perturbation. We will pick the sinusoidal perturbation owing to its relevance to real problems.

Sinusoidal perturbation

We take the time-dependent perturbation to be

$$H'(\vec{r},t) = \underbrace{V(\vec{r})}_{\text{does not depend on time}} \underbrace{\cos(\omega t)}_{\text{time dependence}}$$

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

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

Our system starts in state a. **Our goal is to find transition probability into state b.** We will do it as a class exercise together. Our calculations are limited to first order only. As before, we assume diagonal terms of H' to be zero.

First, let's determine what is it we need to find. Our system was initially in state a, so the transition probability is simply the probability to find it in a state b:

Step 1. $$P_{a\to b}(t) = |C_b(t)|^2 \approx |C_b^{(1)}(t)|^2$$

Substitute perturbation H' into our first-order expression for the $c_b(t)$ and integrate over time t. Recall that $\cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right)$.

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

(V_{ba}: does not depend on time)

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

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

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

The answer is quite cumbersome, so we can make the following simplification:

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

assuming the "driving" frequency ω is close to the transition frequency ω_0. This is reasonable since the probability of the transition with the perturbations at other frequencies not in the immediate vicinity of ω_0 is small. This approximation allows us to drop the second term in our result (2) on the previous page.

Step 2.

Drop the second term in our solution and write the simplified expression for the transition probability that contains only **sin** function (i.e. no **exp**).

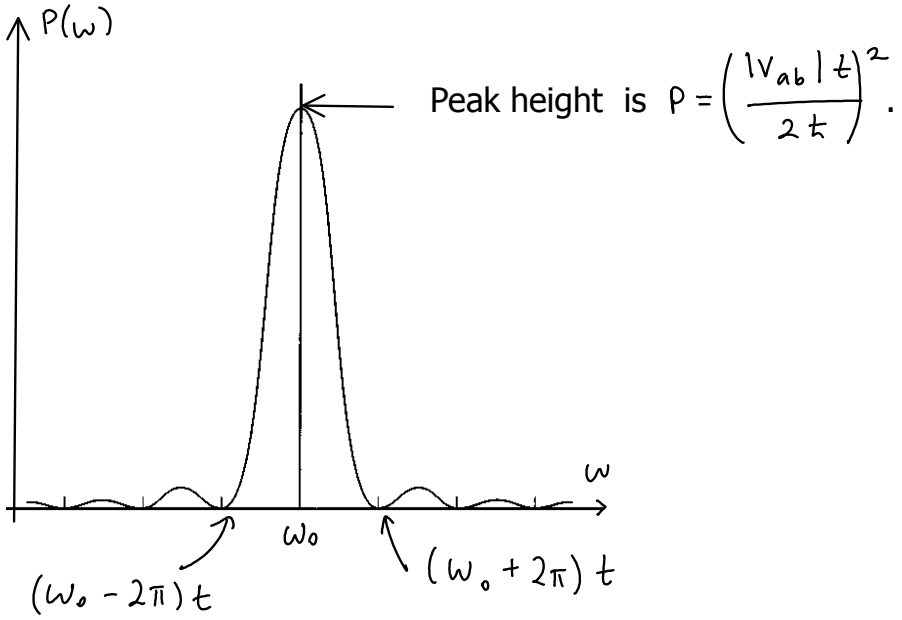
$$C_b(t) \approx -\frac{V_{ba}}{2\hbar}\,\frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega} =$$

$$= -\frac{iV_{ba}}{\hbar}\,\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left\{\frac{e^{i(\omega_0-\omega)t/2}-e^{-i(\omega_0-\omega)t/2}}{2i}\right\}$$

$$= -\frac{iV_{ba}}{\hbar}\,\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\,\sin\{(\omega_0-\omega)t/2\}$$

$$P_{a\to b}(t) = \underbrace{|C_b(t)|^2}_{C_b^*(t)\,C_b(t)} \approx \frac{|V_{ba}|^2}{\hbar}\,\frac{\sin^2\{(\omega_0-\omega)t/2\}}{(\omega_0-\omega)^2}$$

To analyze this answer, we first plot the transition probability as a function of the driving frequency ω.



This confirms our earlier assumption that the transition probability is negligible if the driving frequency is far from the natural frequency ω_0. As we see, the peak of the transition probability is at the natural frequency and quickly falls off.

Next, we plot the **transition probability as a function of time**. The transition probability oscillate sinusoidally. The interesting consequence is that to maximize the chance of transition, you need to turn the perturbation off after time

$$t = \pi/|\omega_0 - \omega|$$

rather than keeping the perturbation on for longer periods of time. Note that this "flopping" is not artifact of the perturbation theory but is also present in the exact solution.