

## Phys 487 Discussion 10 – Time-Dependent PT with 2-State Systems

Same formula summary as last week : Consider a system with Hamiltonian  $H(t) = H^{(0)} + H'(t)$ , where  $\{E_n^{(0)}, |n^{(0)}\rangle\}$  are the known eigen-values/states of the “unperturbed” time-independent part  $H^{(0)}$ . We can express any time-dependent state  $|\Psi(t)\rangle$  of this system as a superposition of the unperturbed states  $|n^{(0)}\rangle$  with amplitudes  $c_n(t)$  :

$$|\Psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t} |n^{(0)}\rangle \quad \text{where} \quad i\hbar \dot{c}_f(t) = \sum_n H'_{fn} e^{i\omega_{fn} t} c_n(t)$$

- $\omega_{fn} \equiv (E_f^{(0)} - E_n^{(0)}) / \hbar$
- $H'_{fn} \equiv \langle f^{(0)} | H' | n^{(0)} \rangle$

If  $H'$  is *very small* compared to  $H_0$ , we can obtain an approximate solution for the amplitudes  $c_n(t)$  by expanding them in powers of this smallness  $\rightarrow$  this is **time-dependent perturbation theory**. We find

$$c_f(t) \approx \delta_{fi} + \frac{1}{i\hbar} \int_{t_0}^t dt' H'_{fi}(t') e^{i\omega_{fi} t'}$$

at 1<sup>st</sup> order in  $H' \ll H_0$ , given the initial state  $|\Psi(t_0)\rangle = |i^{(0)}\rangle$ .

$\omega_{fi}$  is called the **transition frequency** for going from initial state  $i$  (at time  $t_0$ ) to final state  $f$  (at time  $t$ );  $c_f(t)$  is called the **transition amplitude** for this  $i \rightarrow f$  transition. The **transition probability** that we are usually trying to calculate is, as usual, the magnitude<sup>2</sup> of the corresponding amplitude :

$$P_{i \rightarrow f} = |c_f(t)|^2$$

### Problem 1 : Two-state hydrogen atom in electric field

*adapted from Griffiths 9.1<sup>1</sup>*

Systems with only two independent states are excellent sandboxes for playing around with time-dependent potentials since you can readily write down *all* the matrix elements of  $H'_{fn}$ . Let's take a specific case:

A hydrogen atom is placed in a time-dependent electric field  $\vec{E} = E(t)\hat{z}$ . **Ignore spin** throughout.

- (a) Calculate all four matrix elements  $H'_{ij}$  of the perturbation  $H' = eEz$  between the ground state ( $n = 1$ ) and the quadruply degenerate first excited states ( $n = 2$ ).
- (b) Show that the diagonal elements  $H'_{ii}$  of the perturbation are both zero for all five states.

► **NOTE:** There is only one integral to be done here, if you exploit oddness with respect to  $z$ ; only one of the  $n = 2$  states is “accessible” from the ground state by a perturbation of this form, and therefore the system functions as a two-state configuration — assuming transitions to higher excited states can be ignored.

- (c) It is very commonly the case that the diagonal elements  $H'_{ii}$  of a time-dependent perturbation are zero. In this case, the exact differential equations

$$i\hbar \dot{c}_f(t) = \sum_n H'_{fn} e^{i\omega_{fn} t} c_n(t)$$

<sup>1</sup> **Q1 (a)** Hints: You must calculate  $H'_{21}$  for the four different energy eigenstates of hydrogen with principal quantum number  $n=2$ . What are these four  $n=2$  states? ... A complete hydrogen wavefunction needs 3 quantum numbers (when spin is ignored) ...  $|nlm\rangle$  ... the four degenerate  $n=2$  states are  $|200\rangle$ ,  $|21+1\rangle$ ,  $|210\rangle$ , and  $|21-1\rangle$  ... How do you calculate  $H'_{21}$ ? Remember that it's called a “transition **matrix element**”, that should help ... the formula is at the top! ...  $H'_{21} = \langle 2lm | H' | 100 \rangle = \langle 2lm | eEz | 100 \rangle$  ... You will need the hydrogen wavefunctions, so consult the 486 formula sheet ... **Answer:** The only non-zero matrix element is  $\langle 210 | H' | 100 \rangle = -2^8 / (3^5 \sqrt{2}) eEa_0$ . ... Wait, that was  $H'_{21}$ , what about  $H'_{12}$ ? You don't have to calculate it explicitly if you remember a property of all Hamiltonians ... The important property starts with H ... Hermitian!  $\rightarrow H'_{21} = H'_{12}^*$  which here is just  $H_{12}$ .

for the two coefficients  $c_a(t)$  and  $c_b(t)$  (using Griffiths' notation for two states) reduce to two coupled differential equations without summation signs. Show that the above reduces to these two in the case  $H'_{ii} = 0$ :

$$\boxed{\dot{c}_a = \frac{1}{i\hbar} H'_{ab} e^{-i\omega_0 t} c_b} \quad \& \quad \boxed{\dot{c}_b = \frac{1}{i\hbar} H'_{ba} e^{i\omega_0 t} c_a} \quad \text{with} \quad \omega_0 \equiv \omega_{ba} = \omega_b - \omega_a$$

(hardly seems worth defining a new variable!)

These are Eq. 9.13 in Griffiths; most of his chapter 9 is based on this pair of equations.

**NOTATION CHANGE** : We will henceforth stop placing a superscript <sup>(0)</sup> on the states and energies of the unperturbed system. Reason? We are ALWAYS referring to the states of the unperturbed system in time-dependent PT, so there is no reason to flag it with such notation. As we mentioned in class, the goal of time-dependent PT is quite different from that of time-independent PT.

- $t$ -indep. PT : calculate changes to the eigenenergies & eigenstates of  $H_0$  produced by the perturbation  $H'$
- $t$ -dep. PT : calculate transition probabilities caused by  $H'$  between states of the unperturbed system  $H_0$

### Problem 2 : Rabi flopping frequency

*adapted from Griffiths 9.7*

A rare example of a system that can be solved exactly is the important case of a two-state problem with a sinusoidal oscillating potential. The system is often an atom or a molecule, with two states of particular interest or relevance ; the perturbation usually comes from an incident electromagnetic wave whose frequency  $\omega$  is tuned to the transition frequency  $\omega_{ab} = (E_a - E_b)/\hbar$  between the two states.

Here is a simplified expression for the sinusoidal perturbation  $V(\vec{r}) \cos(\omega t)$ . after it is applied to a system with two states  $a$  and  $b$  in the case that the driving frequency  $\omega$  is very close to the transition frequency  $\omega_{ab}$  : (see <sup>2</sup>)

$$H'_{ba} = \frac{V_{ba}}{2} e^{-i\omega t}, \quad H'_{ab} = \frac{V_{ab}}{2} e^{i\omega t}, \quad H'_{aa} = H'_{bb} = 0 \quad \text{with} \quad V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle.$$

(a) Solve the two coupled equations you obtained in problem 1(c) using the initial conditions  $c_a(0) = 1$  and  $c_b(0) = 0$  (i.e. the system starts in state  $a$  at time  $t = 0$ ). Express your results for  $c_a(t)$  and  $c_b(t)$  in terms of

$$\omega_r \equiv \frac{1}{2} \sqrt{(\omega - \omega_{ab})^2 + (|V_{ab}|/\hbar)^2}, \quad \text{called the **Rabi flopping frequency**. Answers in footnote<sup>3</sup>.$$

(b) Determine the transition probability  $P_{a \rightarrow b}(t)$  and show that it never exceeds 1. Confirm that  $|c_a(t)|^2 + |c_b(t)|^2 = 1$  at all times. (What would it mean if that were *not* true? Ask if you're not sure!)

(c) Check that  $P_{a \rightarrow b}(t)$  reduces to the perturbation theory result

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \approx \frac{|V_{ab}|^2 \sin^2[(\omega_{ab} - \omega)t/2]}{(\omega_{ab} - \omega)^2}$$

when the perturbation is "small", and state precisely what small *means* in this context, as a constraint on  $V$ .

(d) At what time does the system first return to its initial state?

<sup>2</sup> Griffiths §9.1.3 shows how the approximation  $\omega \approx \omega_0 \equiv \omega_{ba}$  is applied.

<sup>3</sup> **Q2** (a)  $c_a(t) = e^{i\left(\frac{\omega - \omega_0}{2}\right)t} \left[ \cos(\omega_r t) + i \frac{(\omega_0 - \omega)}{2\omega_r} \sin(\omega_r t) \right]$  &  $c_b(t) = \frac{V_{ba}}{2i\hbar\omega_r} e^{i\left(\frac{\omega_0 - \omega}{2}\right)t} \sin(\omega_r t)$

(b)  $P_{a \rightarrow b}(t) = |c_b(t)|^2 = \frac{|V_{ba}|^2}{4\hbar^2\omega_r^2} \sin^2(\omega_r t)$  (d) when  $c_b(t)$  first = 0 again  $\rightarrow$  at  $t = \frac{\pi}{\omega_r}$