

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 $c_n(t)$:

$$\boxed{|\Psi(t)\rangle = \sum_n c_n(t) e^{-i\omega_n t} |n^{(0)}\rangle} \quad \text{where} \quad \boxed{i\hbar \dot{c}_f(t) = \sum_n H'_{fn} e^{i\omega_{fn} t} c_n(t)} \quad \begin{aligned} &\bullet \omega_{fn} \equiv (E_f^{(0)} - E_n^{(0)})/\hbar \\ &\bullet H'_{fn} \equiv \langle f^{(0)} | H' | n^{(0)} \rangle \end{aligned}$$

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

$$\boxed{c_f(t) \approx \delta_{fi} + \frac{1}{i\hbar} \int_{t_0}^t dt' H'_{fi}(t') e^{i\omega_{fi} t'}} \quad \text{at 1st order in } H' \ll H_0, \text{ given the initial state } |\Psi(t_0)\rangle = |i^{(0)}\rangle.$$

ω_{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 magnitude² of the corresponding amplitude :

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

Problem 1 : Two-state hydrogen atom in electric field

adapted from Griffiths 9.1¹

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.

- 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 ($n = 2$).
- 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.

- 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

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

¹ **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 ⁽⁰⁾ 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 ω 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 ω is very close to the transition frequency ω_{ab} : (see ²)

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

(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

$$\omega_r \equiv \frac{1}{2} \sqrt{(\omega - \omega_{ab})^2 + (|V_{ab}|/\hbar)^2}, \quad \text{called the **Rabi flopping frequency**. Answers in footnote³.$$

(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?

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

³ **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 $t = \frac{\pi}{\omega_r}$