TIME-DEPENDENT PERTURBATION THEORY

At this point, we must have forgotten that Schroedinger's equation says:

$$\underset{\substack{\uparrow\\ \text{operator}}}{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Only when H does not explicitly depend on t we can separate the equation and find stationary states $|\psi(t)\rangle$ such that:

$$|\psi(t)\rangle = e^{-iEt/\hbar}|\psi\rangle \quad \text{and} \quad \underset{\text{operator}}{H}|\psi\rangle = \underset{\text{eigenvalue}}{E}|\psi\rangle$$

There are very few cases that can be solved, when H depends on t. But what if the time-dependent part of the Hamiltonian is <u>small</u> compared to the rest? I can use the methods of perturbation theory.

Let us assume that H^0 is a nice, time-independent Hamiltonian, with eigenstates ψ_n^0 and eigenvalues E_n^0. Then:

$$H\psi_n^0 = E_n^0\psi_n^0 \quad \text{and} \quad \psi_n^0(t) = e^{-iE_n^0 t/\hbar}\psi_n^0$$

Suppose that I turn on a small time-dependent perturbation, $\lambda H'(t)$.

The <u>question</u> I want to answer is: what is the probability that my quantum system, in state ψ_n^0 <u>before</u> I turned on the perturbation, is now in state ψ_m^0, $m \neq n$?

Let us use again an expansion in orders of λ:

$$(H^0 + \lambda H'(t))\psi_n(t) = i\hbar\frac{\partial\psi_n}{\partial t}$$

where: $\psi_n(t) = \psi_n^0(t) + \lambda\psi_n^1(t) + \lambda^2\psi_n^2(t) + \ldots$

NOTE: ψ is a function of $\vec{r}$: $\psi(t)$ means <u>$\psi(\vec{r}, t)$</u> <u>everywhere in these notes</u>

We collect the like-powers of λ:

$$\lambda^0 : \qquad H^0 \psi_n^0 = i\hbar \frac{\partial \psi_n^0}{\partial t}$$ satisfied: it is the original, unperturbed problem

$$\lambda^1 : \qquad H^0 \psi_n^1 + H^1 \psi_n^0 = i\hbar \frac{\partial \psi_n^1}{\partial t}$$

Let us stop here. We can now exploit the fact that the states ψ_n^0 are a complete set, meaning that any state of our system, including $\psi_n^1(t)$, can be written as a linear combination of $\psi_n^0(t)$. However, this time the coefficients are, in general, time-dependent:

$$\psi_n^1(t) = \sum_\ell a_{n\ell}(t)\, \psi_\ell^0(t)$$

Let us replace this expression above, and apply the time-derivative on the right side of the equation:

$$H^0 \cancel{\sum_\ell a_{n\ell}(t)\, \psi_\ell^0(t)} + H^1 \psi_n^0(t) = i\hbar \sum_\ell \dot{a}_{n\ell}(t)\, \psi_\ell^0(t) + i\hbar \cancel{\sum_\ell a_{n\ell}(t) \frac{\partial \psi_\ell^0(t)}{\partial t}}$$

⊛ this is Schroedinger's equation on unperturbed states!

Let us now calculate the product with $\langle \psi_j^0 |$. In other words, multiply by $\psi_j^{0*}(t)$ and integrate over $\vec{r}$:

$$\int d^3\vec{r}\; \psi_j^{0*}(\vec{r},t)\, H^1(t)\, \psi_n^0(\vec{r},t) = i\hbar \sum_\ell \dot{a}_{n\ell} \underbrace{\int d^3\vec{r}\; \psi_j^{0*}(\vec{r},t)\, \psi_n^0(\vec{r},t)}_{\delta_{jn}\,!}$$

remember: $\psi_n^0(\vec{r},t) = \underline{\underline{e^{-iE_n^0 t/\hbar}}}\, \psi_n^0(\vec{r})$

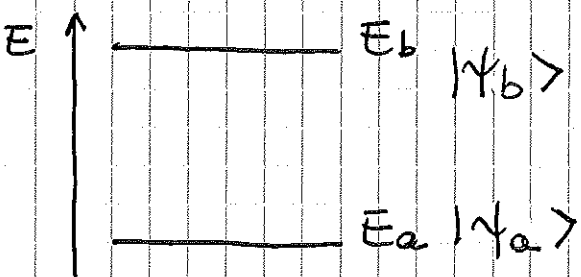
Finally:

$$\dot{a}_{nj} = -\frac{i}{\hbar}\, e^{i(E_j^0 - E_n^0)t/\hbar} \cdot \int d^3\vec{r}\; \psi_j^{0*}(\vec{r})\, H^1(\vec{r},t)\, \psi_n^0(\vec{r})$$

The probability of the transition $n \to j$ is proportional to $|a_{nj}(t)|^2$.

We solved the problem of finding the probability with which, starting in state $\psi_n^0(t)$, we may find ourselves in state $\psi_j^0(t)$, after the intervention of a time-dependent perturbation. This is what happened: we were in state $\psi_n^0(t)$, eigenstate of Hamiltonian H^0; a perturbation $\lambda H'(t)$ is turned on, which modified our state by adding a component $\psi_n^1(t)$, which contains state $\psi_j^0(t)$ with a coefficient $a_{nj}(t)$; now I turn off the perturbation, and am once again in a systems governed by the unperturbed Hamiltonian H^0. The probability that now I am in state $\psi_j^0(t)$, at first order, is $|a_{nj}(t)|^2$.

Let us do a concrete example: a two-state system:



$$H^0|\psi_{a,b}\rangle = E^0_{a,b}|\psi_{a,b}\rangle$$ unperturbed case

$$|\psi_{a,b}(t)\rangle = e^{-iE_{a,b}t/\hbar}\,|\psi_{a,b}(0)\rangle$$

This being a 2-state system, any generic state can be written as a linear combination:

$$|\psi\rangle = c_a|\psi_a\rangle + c_b|\psi_b\rangle$$

In the unperturbed case, the time evolution is simply:

$$|\psi(t)\rangle = c_a e^{-iE_at/\hbar}|\psi_a(0)\rangle + c_b e^{-iE_bt/\hbar}|\psi_b(0)\rangle$$

If now I perturb H^0, the only difference is that c_a and c_b become functions of t:

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

Let us plug this expression into Schroedinger's equation:

$$\left(H^0 + \lambda H'(t)\right)|\psi(t)\rangle = i\hbar\frac{\partial|\psi(t)\rangle}{\partial t}$$

We obtain (let me save space and use C_a for $C_a(t)$; let me also take $\lambda=1$: let us just keep in mind that $H' \ll H^0$, although, here, we will find exact solution):

$$\cancel{C_a e^{-iE_at/\hbar} H^0 |\psi_a\rangle} + \cancel{C_b e^{-iE_bt/\hbar} H^0 |\psi_b\rangle} + C_a e^{-iE_at/\hbar} H'|\psi_a\rangle + C_b e^{-iE_bt/\hbar} H'|\psi_b\rangle =$$

$$= i\hbar \dot{C}_a e^{-iE_at/\hbar} |\psi_a\rangle + \cancel{C_a E_a e^{-iE_at/\hbar} |\psi_a\rangle} + i\hbar \dot{C}_b e^{-iE_bt/\hbar} |\psi_b\rangle + \cancel{C_b E_b e^{-iE_bt/\hbar} |\psi_b\rangle}$$

⊗ unperturbed Schroedinger's equation: $|\psi_{a,b}\rangle$ are eigenstates of H^0.

Let us now apply $\langle\psi_a|$ and $\langle\psi_b|$:

$$\langle\psi_a|: \quad C_a e^{-iE_at/\hbar} \langle\psi_a|H'|\psi_a\rangle + C_b e^{-iE_bt/\hbar} \langle\psi_a|H'|\psi_b\rangle = i\hbar \dot{C}_a e^{-iE_at/\hbar}$$

$$\langle\psi_b|: \quad C_a e^{-iE_at/\hbar} \langle\psi_b|H'|\psi_a\rangle + C_b e^{-iE_bt/\hbar} \langle\psi_b|H'|\psi_b\rangle = i\hbar \dot{C}_b e^{-iE_bt/\hbar}$$

Typically, $\langle\psi_a|H'|\psi_a\rangle = 0$ and $\langle\psi_b|H'|\psi_b\rangle = 0$.

Then:

$$\begin{cases} \dot{C}_a(t) = \dfrac{-i}{\hbar} \langle\psi_a|H'|\psi_b\rangle \cdot e^{-i\omega t} \, C_b(t) \\[2ex] \dot{C}_b(t) = -\dfrac{i}{\hbar} \langle\psi_b|H'|\psi_a\rangle \, e^{i\omega t} \, C_a(t) \end{cases} \qquad \omega = \frac{E_b - E_a}{\hbar}$$

System of two first-order differential equations, solvable with initial conditions (I need two IC: let us take $C_a(t=0)$ and $C_b(t=0)$).

IMPORTANT NOTE: solution still valid exactly, we have not done any approximation yet (hence it looks different from the $\dot{a}_{nj}(t)$ we found earlier, which instead is valid only at first order)