Time-dependence and transitions between states

When $V \neq V(t)$ the time dependence of the wave function is trivial and can the solution of the time-dependent Schrödinger equation can be written as a linear combination (we derived it last semester)

$$\Psi(\vec{r},t) = \sum_k c_k \psi_k(\vec{r})\, e^{-\frac{iE_k t}{\hbar}}$$

where ψ_k, E_k satisfy the stationary Schrödinger equation:

$$H\psi_k = E_k \psi_k$$

Note that the average energies and the respective probabilities are constant in the case when $V \neq V(t)$

If we want to allow for transitions (jumps) between energy levels there must be explicit time dependence in the potential. If we have $V = V(t)$ then we deal with quantum dynamics

Oftentimes the time-dependent portion of the potential is in some sense "small". Think, for example of a hydrogen atom disturbed slightly by a charged fast particle that passes by at a relatively large distance. While the solution of the SE in general case is very difficult, treating the time-depending potential as a perturbation can simplify the problem.

Before we introduce the time-dependent perturbation theory it is instructive to consider simple time-dependent systems and understand their time evolution.

Let us begin with a two-level system. Suppose there are just two states of the Hamiltonian H^0:

$$H^0\psi_1 = E_1\psi_1 \qquad H^0\psi_2 = E_2\psi_2 \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij}$$

Any state of this system can be expressed as a linear combination of ψ_1 and ψ_2. If there is no time-dependent perturbation the wave function is

$$\Psi(t) = c_1\psi_1 e^{-\frac{iE_1t}{\hbar}} + c_2\psi_2 e^{-\frac{iE_2t}{\hbar}} \qquad |c_1|^2 + |c_2|^2 = 1$$

If we now suppose that there is a time-dependent perturbation, $H'(t)$, the coefficients c_a and c_b become functions of time

$$\Psi(t) = c_1(t)\,\psi_1 e^{-\frac{iE_1t}{\hbar}} + c_2(t)\,\psi_2 e^{-\frac{iE_2t}{\hbar}}$$

If we want to know everything about the system, we need to determine $c_1(t)$ and $c_2(t)$. Since the magnitudes of $c_1(t)$ and $c_2(t)$ are, in general, no longer constant we can see that the probabilities of "finding" the system in each state change with time. If, for instance, $c_1(0) = 1$ and $c_2(0) = 0$ and $c_1(t=\tau) = 0$ and $c_2(t=\tau) = 1$ then we can report a complete transition from ψ_1 to ψ_2.

Now let us solve for $c_1(t)$ and $c_2(t)$. $\Psi(t)$ must satisfy the TDSE:

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad \text{with} \qquad H = H^0 + H'(t)$$

Plugging the linear combination in place of $\Psi(t)$ gives:

$$c_1 e^{-\frac{iE_1t}{\hbar}} H^0\psi_1 + c_2 e^{-\frac{iE_2t}{\hbar}} H^0\psi_2 + c_1 e^{-\frac{iE_1t}{\hbar}} H'\psi_1 + c_2 e^{-\frac{iE_2t}{\hbar}} H'\psi_2 =$$

$$= i\hbar\left[\dot{c}_1\psi_1 e^{-\frac{iE_1t}{\hbar}} + \dot{c}_2\psi_2 e^{-\frac{iE_2t}{\hbar}} + c_1\psi_1\left(-\frac{iE_1}{\hbar}\right)e^{-\frac{iE_1t}{\hbar}} + c_2\psi_2\left(-\frac{iE_2}{\hbar}\right)e^{-\frac{iE_2t}{\hbar}}\right]$$

Here we assume that $H'(t)$ does not contain any derivatives with respect to t.

After cancelling some terms we obtain

$$c_1 e^{-\frac{iE_1t}{\hbar}} H'\psi_1 + c_2 e^{-\frac{iE_2t}{\hbar}} H'\psi_2 = i\hbar \left[\dot{c}_1 \psi_1 e^{-\frac{iE_1t}{\hbar}} + \dot{c}_2 \psi_2 e^{-\frac{iE_2t}{\hbar}} \right]$$

by making the inner product with $\langle \psi_1 |$ and $\langle \psi_2 |$ we get two equations

$$c_1 \langle \psi_1 | H' | \psi_1 \rangle e^{-\frac{iE_1t}{\hbar}} + c_2 \langle \psi_1 | H' | \psi_2 \rangle e^{-\frac{iE_2t}{\hbar}} = i\hbar \dot{c}_1 e^{-\frac{iE_1t}{\hbar}}$$

$$c_1 \langle \psi_2 | H' | \psi_1 \rangle e^{-\frac{iE_1t}{\hbar}} + c_2 \langle \psi_2 | H' | \psi_2 \rangle e^{-\frac{iE_2t}{\hbar}} = i\hbar \dot{c}_2 e^{-\frac{iE_2t}{\hbar}}$$

or simply

$$\begin{pmatrix} H'_{11} & H'_{12} e^{-i\omega_{21} t} \\ H'_{21} e^{i\omega_{21} t} & H'_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix}$$

where $H'_{ij} = \langle \psi_i | H'(t) | \psi_j \rangle$

and $\omega_{21} = \frac{E_2 - E_1}{\hbar}$

The above matrix equation is completely equivalent to the TDSE. Typically, H'_{ii} (diagonal elements) vanish due to symmetry.

Time-dependent perturbation theory

Suppose the total Hamiltonian is of the form

$$H(\vec{r},t) = H^{\circ}(\vec{r}) + \lambda H'(\vec{r},t)$$

where λ is a small parameter

Let the time-dependent eigenstates of H° be

$$\Psi_n(\vec{r},t) = \varphi_n(\vec{r})\, e^{-i\omega_n t} \qquad H^{\circ}\varphi_n = E_n^{(0)}\varphi_n = \hbar\omega_n\varphi_n$$

Suppose at time $t>0$ the system is in the state

$$\Psi(\vec{r},t) = \sum_n c_n(t)\,\Psi_n(\vec{r},t) = \sum_n c_n(t)\,\varphi_n(\vec{r})\, e^{-i\omega_n t}$$

Let us now determine coefficients $c_n(t)$. $\Psi(\vec{r},t)$ is a solution of

$$i\hbar\frac{\partial\Psi}{\partial t} = \left(H^{\circ} + \lambda H'\right)\Psi$$

Substituting the above expansion and operating from the left by $\langle\varphi_k|$ we get

$$i\hbar\frac{dc_k}{dt} = \lambda\sum_n \langle k|H'|n\rangle c_n \qquad (*)$$

This is an infinite (in general) sequence of coupled equations for $\{c_k(t)\}$. In the limit $\lambda\to 0$, c_k are all constants. It is therefore possible to seek solution in the form

$$c_k(t) = c_k^{(0)} + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \ldots$$

Substituting this series into $(*)$ and equating terms of equal powers in λ we get:

$$\lambda^0: \quad i\hbar\dot{c}_k^{(0)} = 0 \qquad\qquad \lambda^2: \quad i\hbar\dot{c}_k^{(2)} = \sum_n H'_{kn} c_n^{(1)}$$

$$\lambda^1: \quad i\hbar\dot{c}_k^{(1)} = \sum_n H'_{kn} c_n^{(0)} \qquad \ldots$$

The lowest order equations for $C_n^{(0)}$ indicate that these coefficients are all constant in time. They are the initial values of $\{C_n(t)\}$

Let us now focus on the problem when the initial state of the system is $\Psi_e(\vec{r},t)$. As $t \to -\infty$

$$\Psi(\vec{r},t) \to \Psi_e(\vec{r},t) = \sum_n \delta_{ne} \Psi_n(\vec{r},t)$$

and $C_n^{(0)}(-\infty) = \delta_{ne}$

Substituting this into the equation for λ^1 we obtain

$$i\hbar \dot{C}_k^{(1)}(t) = \sum_n H'_{kn} C_n^{(0)}(-\infty) = H'_{ke}$$

For $k \neq e$ $\quad C_k^{(0)}(-\infty) = 0$, so

$$C_k^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} H'_{ke}(t')\, dt' \qquad k \neq e$$

If the time dependence is factorable, then

$$H'(\vec{r},t) = \mathcal{H}'(r) f(t)$$

then

$$H'_{ke}(t) = \langle \Psi_k | H'(\vec{r},t) | \Psi_e \rangle = \langle \Psi_k | \mathcal{H}'(\vec{r}) | \Psi_e \rangle e^{i\omega_{ke} t} f(t)$$

$$= \mathcal{H}'_{ke}\, e^{i\omega_{ke} t} f(t)$$

where $\omega_{ke} \equiv \dfrac{E_k^{(0)} - E_e^{(0)}}{\hbar}$ and $\mathcal{H}'_{ke} = \langle \Psi_k | \mathcal{H}'(r) | \Psi_e \rangle$

Then the explicit form of $C_k^{(1)}(t) = \dfrac{\mathcal{H}'_{ke}}{i\hbar} \displaystyle\int_{-\infty}^{t} e^{i\omega_{ke} t'} f(t')\, dt$

These coefficients determine the effect of the perturbation on the initial state Ψ_e. The probability of transition from Ψ_e to Ψ_k is

$$P_{k \leftarrow e}^{(1)}(t) = |C_k^{(1)}|^2 = \left| \frac{\mathcal{H}'_{ke}}{\hbar} \right|^2 \left| \int_{-\infty}^{t} e^{i\omega_{ke} t'} f(t')\, dt' \right|^2$$

The usual convention is to write the initial state on the right and the final state on the left:

$$\langle \text{final} \,|\, H' \,|\, \text{initial} \rangle$$

and often time indexes i and f are used, i.e.

$$\mathcal{H}'_{fi} \quad , \quad P_{f \to i}$$

In case if we need to go to second order the solution for $c_n^{(2)}(t)$ can also be obtained in a similar manner:

$$c_k^{(2)}(t) = \frac{1}{(i\hbar)^2} \sum_m \mathcal{H}'_{km} \mathcal{H}'_{me} \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \, e^{i\omega_{km} t' + i\omega_{me} t''} f(t') f(t'')$$

Example: kicked oscillator

Suppose a simple harmonic oscillator is prepared in its ground state at $t = -\infty$. It is perturbed by a weak time-dependent potential

$$H'(t) = -eEx\, e^{-\frac{t^2}{\tau^2}}$$

What is the probability of finding it in the first excited state at $t = +\infty$?

$$P_{1 \leftarrow 0}(t) = |c_1^{(1)}(t)|^2 = \left| \frac{1}{i\hbar} \int_{-\infty}^{t} dt' \, e^{i\omega_{10} t'} e^{-\frac{t'^2}{\tau^2}} \mathcal{H}'_{10} \right|^2$$

$$\mathcal{H}'_{10} = -eE \underbrace{\langle 1 | x | 0 \rangle}_{\sqrt{\frac{\hbar}{2m\omega}}} = -eE \sqrt{\frac{\hbar}{2m\omega}}$$

Using the identity

$$\int_{-\infty}^{+\infty} dt' \, e^{i\omega t' - \frac{t'^2}{\tau^2}} = \sqrt{\pi}\,\tau\, e^{-\frac{\omega^2\tau^2}{4}}$$

we obtain

$$P_{1\leftarrow 0}(t=+\infty) = \frac{\pi e^2 E^2 \tau^2}{2m\hbar\omega} e^{-\frac{\omega^2\tau^2}{2}}$$

Note that the probability is maximized when $\tau \sim \frac{1}{\omega}$

Also note that there will be no transitions to other states because $\langle n | x | 0 \rangle \propto \delta_{0,n-1}$