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:

$$H^0 \psi_a = E_a \psi_a \qquad H^0 \psi_b = E_b \psi_b \qquad \langle \psi_a | \psi_b \rangle = \delta_{ab}$$

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

$$\Psi(t) = c_a \psi_a e^{-\frac{iE_a t}{\hbar}} + c_b \psi_b e^{-\frac{iE_b t}{\hbar}} \qquad |c_a|^2 + |c_b|^2 = 1$$

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

$$\Psi(t) = c_a(t) \psi_a e^{-\frac{iE_a t}{\hbar}} + c_b(t) \psi_b e^{-\frac{iE_b t}{\hbar}}$$

If we want to know everything about the system, we need to determine $c_a(t)$ and $c_b(t)$. Since the magnitudes of $c_a(t)$ and $c_b(t)$ 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, $c_a(0) = 1$ and $c_b(0) = 0$ and $c_a(t=\tau) = 0$ and $c_b(t=\tau) = 1$ then we can report a complete transition from ψ_a to ψ_b.

Now let us solve for $c_a(t)$ and $c_b(t)$. $\Psi(t)$ 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:

$$c_a e^{-\frac{iE_a t}{\hbar}} H^0 \psi_a + c_b e^{-\frac{iE_b t}{\hbar}} H^0 \psi_b + c_a e^{-\frac{iE_a t}{\hbar}} H' \psi_a + c_b e^{-\frac{iE_b t}{\hbar}} H' \psi_b =$$

$$= i\hbar \left[\dot{c}_a \psi_a e^{-\frac{iE_a t}{\hbar}} + \dot{c}_b \psi_b e^{-\frac{iE_b t}{\hbar}} + c_a \psi_a \left(-\frac{iE_a}{\hbar}\right) e^{-\frac{iE_a t}{\hbar}} + c_b \psi_b \left(-\frac{iE_b}{\hbar}\right) e^{-\frac{iE_b t}{\hbar}} \right]$$

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

After cancelling some terms we obtain

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

by making the inner product with $\langle \psi_a |$ and $\langle \psi_b |$ we get two equations

$$c_a \langle \psi_a | H' | \psi_a \rangle e^{-\frac{iE_a t}{\hbar}} + c_b \langle \psi_a | H' | \psi_b \rangle e^{-\frac{iE_b t}{\hbar}} = i\hbar \dot{c}_a e^{-\frac{iE_a t}{\hbar}}$$

$$c_a \langle \psi_b | H' | \psi_a \rangle e^{-\frac{iE_a t}{\hbar}} + c_b \langle \psi_b | H' | \psi_b \rangle e^{-\frac{iE_b t}{\hbar}} = i\hbar \dot{c}_b e^{-\frac{iE_b t}{\hbar}}$$

or simply

$$\begin{pmatrix} H'_{aa} & H'_{ab} e^{-i\omega_{ba} t} \\ H'_{ba} e^{i\omega_{ba} t} & H'_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = i\hbar \begin{pmatrix} \dot{c}_a \\ \dot{c}_b \end{pmatrix}$$

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

and $\omega_{ba} = \frac{E_b - E_a}{\hbar}$

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