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

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

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

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

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

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 $\quad c_n^{(0)}(-\infty) = \delta_{ne}$

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

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

If the time dependence is factorable, then

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

then

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

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

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

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

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

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

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:

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

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 $\langle n | x | 0 \rangle \propto \delta_{0,n-1}$