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Quantum Mechanics: Time-dependent Perturbation Theory

Time-dependent weak disturbance of a system

When a system experiences a *static*, weak disturbance, we studied that the phenomenon can be studied using time-independent perturbation theory. Broadly speaking, what happens is that the energy levels of the system are slightly modified, and so are the energy eigenstates. The change is not drastic, and the essential character of the system is not changed. But what happens when the weak disturbance is varying with time? An atom interacting with a radiation field, is a good example of this. Radiation is like a time-varying field. While studying the Bohr's model of atom we are taught that an atom makes a transition from energy level n_1 to n_2, when radiation of frequency $\omega = (E_{n_2} - E_{n_1})/\hbar$ falls on it. However, no underlying theory is provided for it. In the following we will study the time-dependent perturbation theory, which is the right tool to study such a phenomenon.

Let us suppose that there is a system with a known Hamiltonian $\hat{H}_0$, whose dynamics can also by solved. The time-dependent Schrdinger equation describes the dynamics of any state of this system:

$$i\hbar\frac{\partial}{\partial t}|\psi^0(t)\rangle = \hat{H}_0|\psi^0(t)\rangle.$$

Let us assume that there is a weak time-dependent perturbation on the system, characterized by a time-dependent potential $\hat{V}(t)$. We would know the effect of the disturbance exactly if we could solve the full Schrdinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = (\hat{H}_0 + \hat{V}(t))|\psi(t)\rangle.$$

Such an equation, in general, cannot be solved exactly. However, we will take advantage of the fact that $\hat{V}(t)$ represents a weak disturbance on the system, and its effect would be small. The undisturbed original dynamics of the system is known to us, and we will not be bothered with it in the following analysis. In such a situation the *interaction picture* or the *Dirac picture* comes in useful. In the interaction picture, the undisturbed dynamics is hidden, whereas the dynamics due to the interaction is treated explicitly. The time dependence of the state in the Schrdinger picture is

$$|\psi(t)\rangle = e^{-i[\hat{H}_0+\hat{V}(t)]t/\hbar}|\psi(0)\rangle.$$

On the other hand, the state in the interaction picture is defined as

$$|\psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar}|\psi(t)\rangle.$$

The equation of motion for $|\psi(t)\rangle_I$ can be worked out to give

$$i\hbar\frac{d|\psi(t)\rangle_I}{dt} = \hat{V}_I(t)|\psi(t)\rangle_I, \qquad (1)$$

where $\hat{V}_I(t)$ is the perturbation term, in the interaction picture, given by

$$\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{V}e^{-i\hat{H}_0 t/\hbar}.$$

The advantage here is that the explicit time evolution of the interaction picture state is governed only by the perturbation term.

Equation (1) is a first order differential equation, and its formal solution can be written as

$$|\psi(t)\rangle_I = |\psi(t_0)\rangle_I + \frac{1}{i\hbar}\int_{t_0}^{t} \hat{V}_I(t')|\psi(t')\rangle_I dt'. \tag{2}$$

We call it a formal solution, and not a real solution, because $|\psi(t)\rangle_I$ on the LHS is given by the expression on RHS which has an integral involving $|\psi(t)\rangle_I$ itself. Such an integral equation can be solved *iteratively* by successively substituting the expression for $|\psi(t)\rangle_I$ on the LHS back into the integral on the RHS. After successive substitutions, the equation looks like

$$\begin{aligned}|\psi(t)\rangle_I = &|\psi(t_0)\rangle_I + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\hat{V}_I(t')|\psi(t_0)\rangle_I \\ &+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\hat{V}_I(t')\hat{V}_I(t'')|\psi(t_0)\rangle_I + \ldots\end{aligned} \tag{3}$$

Approximate solutions up to successive orders of accuracy can be obtained by terminating the series successively retaining larger number of terms on the RHS. For certain situation, retaining the first two terms on the RHS, and ignoring the rest, may suffice. That will be called the first order approximation.

First order approximation

Let us assume that the unperturbed Hamiltonian $\hat{H}_0$ has a set of eigenstates such that

$$\hat{H}_0|n'\rangle = E_{n'}|n'\rangle,$$

and also assume that at time 0 the system is in one of the eigenstates of $\hat{H}_0$, namely $|m\rangle$. So that initial state, at time t_0, will evolve to (in the Schrödinger picture) $|\psi(t_0)\rangle = e^{-i\hat{H}_0 t_0}|m\rangle$. In the interaction picture the same state would look like

$$|\psi(t_0)\rangle_I = e^{i\hat{H}_0 t/\hbar}|\psi(t_0)\rangle = |m\rangle. \tag{4}$$

This shows the advantage in using the interaction picture - the known time evolution via the the unperturbed Hamiltonian is hidden. Substituting (4) in (3), and retaining only terms up to first order in $\hat{V}_I$, we get

$$|\psi(t)\rangle_I = |m\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\hat{V}_I(t')|m\rangle.$$

We are interested in finding the probability that at a later time t, the system is found in another eigenstate of $\hat{H}_0$, namely $e^{-i\hat{H}_0 t/\hbar}|n\rangle$. The probablilty amplitude for such a transition can be calculated by

$$\begin{aligned}\langle n,t|\psi(t)\rangle = \langle n|\psi(t)\rangle_I &= \langle n|m\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\langle n|\hat{V}_I(t')|m\rangle \\ &= \delta_{nm} + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\langle n|e^{i\hat{H}_0 t'/\hbar}\hat{V}e^{-i\hat{H}_0 t'/\hbar}|m\rangle \\ &= \delta_{nm} + \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{i(E_n-E_m)t'/\hbar}\langle n|\hat{V}(t')|m\rangle\end{aligned} \tag{5}$$

Using this we can calculate the probability that the system will make a transition to another energy eigenstate $|n\rangle$ as

$$P_{mn}(t) = \left| \frac{1}{\hbar} \int_{t_0}^{t} dt' e^{i(E_n - E_m)t'/\hbar} \langle n|\hat{V}(t')|m\rangle \right|^2 . \tag{6}$$

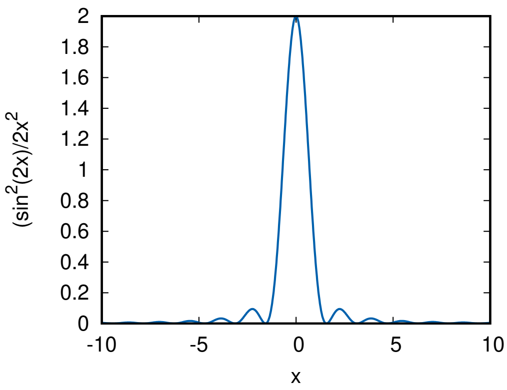
One thing that is obvious from the above expression is that if there is no perturbation, the system will continue to remain in the eigenstate $|m\rangle$ it was in, to begin with.

Static disturbance suddenly switched on

Let us first consider a static perturbation $\hat{V}$ suddenly switched on at time $t_0 = 0$. In this situation (6) reduces to

$$\begin{aligned} P_{mn}(t) &= \left| \frac{1}{\hbar} \int_{0}^{t} dt' e^{i(E_n - E_m)t'/\hbar} \langle n|\hat{V}|m\rangle \right|^2 \\ &= \frac{1}{\hbar^2} \left(\frac{\sin(\omega_{nm} t/2)}{\omega_{nm}/2} \right)^2 |V_{nm}|^2 , \end{aligned} \tag{7}$$

where $\omega_{nm} = (E_n - E_m)/\hbar$. The function $\frac{\sin^2 xt}{x^2 t}$ is plotted in the figure. For larger values of t, is becomes narrower and taller. In order to see what happens at long times, it is useful to recall the limit of the following function



The function $\frac{\sin^2 xt}{x^2 t}$ *plotted for* $t = 2$.

$$\lim_{t\to\infty} \frac{\sin^2 xt}{\pi x^2 t} = \delta(x),$$

where $\delta(x)$ is the familiar Dirac delta function. One can then calculate the probability per unit time that the system makes a transition to another eigenstate $|n\rangle$, which is the transition rate

$$\Gamma_{mn} = \lim_{t\to\infty} \frac{P_{mn}(t)}{t} = \frac{2\pi}{\hbar} \delta(E_n - E_m) |V_{nm}|^2 .$$

The physical meaning of this relation is that if there is a static weak perturbation which is suddenly switched on, it can cause transition between states of the system which have *same energy*. It cannot cause transition between states of different energy. In many physical problems, like scattering, there is a continuous set of eigenstates (momentum states in the case of scattering) into which the system can make a transition. In such a case it is useful to calculate the transition rate from a given initial state $|m\rangle$ to all possible final energy eigenstates. In such situations the energy levels may be degenerate with a density of states $\rho(E_n)$. This transition rate is given by

$$\sum_n \Gamma_{mn} = \frac{2\pi}{\hbar} \int dE_n \rho(E_n) \delta(E_n - E_m) |V_{nm}|^2 = \frac{2\pi}{\hbar} \rho(E_m) |V_{nm}|^2 .$$

The above two relations are extremely useful in various physical situations, and are known as *Fermi golden rule*.

Periodic disturbance

Next we look at the interesting scenario where the external perturbation is periodically varying in time. This situation would describe an electron in an atom interacting with a monochromatic radiation. Typically the potentian for light-matter interaction is

$$\hat{V}(t) = \hat{V}_0 e^{-i\omega t} + \hat{V}_0^\dagger e^{i\omega t},$$

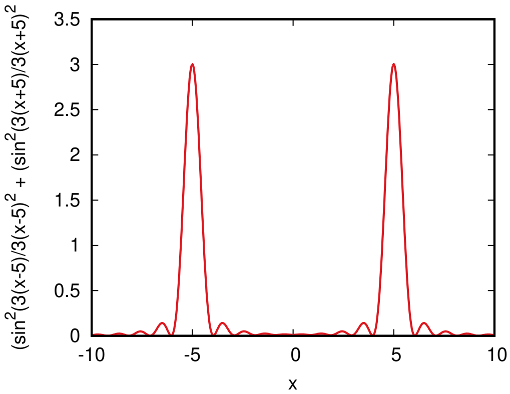
where ω is the frequency of the oscillating field. Inserting this in (6), we get

$$\begin{aligned} P_{mn}(t) &= \left| \frac{1}{\hbar} \int_0^t dt' e^{i(\omega_{nm}-\omega)t'/\hbar} \langle n|\hat{V}_0|m\rangle + e^{i(\omega_{nm}+\omega)t'/\hbar} \langle n|\hat{V}_0^\dagger|m\rangle \right|^2 \\ &= \frac{1}{\hbar^2} \left(\frac{\sin((\omega-\omega_{nm})t/2}{(\omega-\omega_{nm})/2} \right)^2 |V_{0nm}|^2 + \frac{1}{\hbar^2} \left(\frac{\sin(\omega+\omega_{nm})t/2}{(\omega+\omega_{nm})/2} \right)^2 \left|V_{0\,nm}^\dagger\right|^2, \end{aligned} \tag{8}$$

where we have ignored the cross terms as the overlap between them is negligible, as can be seen from the plot of this function, in the figure. Following the procedure in the preceding section, we find that the transition rate, from the state $|m\rangle$ to $|n\rangle$, in the long time limit, has the form

$$\Gamma_{mn} = \frac{2\pi}{\hbar} \left(\delta(\omega-\omega_{nm})|V_{0nm}|^2 + \delta(\omega+\omega_{nm})|V_{0\,nm}^\dagger|^2 \right).$$

The above relation involves two Dirac delta functions, centered at $\omega = \pm\omega_{nm}$. It implies that a transition from energy level E_m to E_n can take place only when the frequency of the oscillating field is equal to ω_{nm}. This is the quantum mechanical explanation of the assumption in Bohr's model of atom which says that an electron makes a transition from one energy level to the other by absorbing a photon of frequency ω_{nm}. Here the second delta function has no contribution. However, there can be a situation where $E_m > E_n$, and ω_{nm} is negative. In this case the first term does not contribute, but the second term does. This case represents the phenomenon of *stimulated emission*, where the system makes a transition from a higher energy level to a lower energy level, due to interaction with radition of frequency $(E_m - E_n)/\hbar$.



The function $\frac{\sin^2(x-5)t}{(x-5)^2 t} + \frac{\sin^2(x+5)t}{(x+5)^2 t}$ *plotted for* $t = 3$.

A few comments can be made here. In general, time-dependent perturbations cause transition between different states of the system, unlike static perturbations. It may appear that the matrix elements $|V_{0nm}|$ play little role here. However it should be emphasized the these matrix elements play the most important role. They decide whether a transition between two levels is allowed or not. We know that in atoms there are often *forbidden transitions* - they are forbidden simply because the matrix element $|V_{0nm}|$ for those two states is zero. In atomic transitions for example, $|V_{0nm}|$ govern the *selection rules*. Most often $\hat{V}_0$ does not involve the spin. So $\langle n|\hat{V}_0|m\rangle$ will be zero if the states $|m\rangle, |n\rangle$ have different spins.