Time-dependent Perturbation Theory

Note Title

So far we have been dealing with time-independent potential energies:

$$V(\vec{r},t) = U(\vec{r})$$

However, if we want to allow for transitions between different energy levels, we must introduce time-dependent potential.

The following discussion is based on Griffiths section 9.1 and Problem 9.15.

To begin with there are unperturbed time-independent Hamiltonian H^0 and its eigenstates:

$$H^0 \psi_n = E_n \psi_n, \quad \langle \psi_n | \psi_m \rangle = \delta_{nm}.$$

At time $t=0$, we turn on a perturbation $H'(t)$ such that

$$H = H^0 + H'(t)$$

Without the perturbation, the time-dependent wavefunction would be like:

$$\Psi(t) = \sum c_n \psi_n e^{-iE_nt/\hbar}.$$

Now with the time-dependent perturbation, we simply have to make c_n time-dependent:

$$\Psi(t) = \sum_n c_n(t) \psi_n e^{-iE_nt/\hbar}$$

Let's plug this into the Schrödinger Eq.

$$H\Psi(t) = i\hbar \frac{\partial}{\partial t} \Psi(t)$$

$$(H^0 + H')\sum_n c_n(t)\psi_n^0 e^{-iE_nt/\hbar} = i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)\psi_n^0 e^{-iE_nt/\hbar}$$

right side $= i\hbar\sum_n \Big[\dot{c}_n(t)\psi_n^0 e^{-iE_nt/\hbar} + c_n(t)\psi_n^0\left(-\frac{iE_n}{\hbar}\right) e^{-iE_nt/\hbar}\Big]$

$$= i\hbar\sum_n \dot{c}_n(t)\psi_n^0 e^{-iE_nt/\hbar}$$

$$+ \sum_n \cancel{E_n c_n(t)\psi_n^0 e^{-iE_nt/\hbar}}$$

left side $= \sum_n \cancel{E_n c_n(t)\psi_n^0 e^{-iE_nt/\hbar}} + \sum_n c_n(t) H'\psi_n^0 e^{-iE_nt/\hbar}$

left side = right side

$$\Rightarrow \sum_n c_n(t) H'\psi_n^0 e^{-iE_nt/\hbar} = i\hbar\sum_n \dot{c}_n(t)\psi_n^0 e^{-iE_nt/\hbar}$$

$\Rightarrow$ By applying $\langle\psi_m^0|$ both sides, and using

$\langle\psi_m^0|\psi_n^0\rangle = \delta_{mn}$ // H'_{mn}

$$\sum_n c_n(t)\langle\psi_m^0|H'|\psi_n^0\rangle e^{-iE_nt/\hbar}$$

$$= i\hbar\sum_n \dot{c}_n(t)\langle\psi_m^0|\psi_n^0\rangle e^{-iE_nt/\hbar}$$

$$\Rightarrow \dot{c}_m(t)\left(i\hbar e^{-iE_mt/\hbar}\right) = \sum_n c_n(t) H'_{mn} e^{-iE_nt/\hbar}$$

$$\Rightarrow \boxed{\dot{c}_m(t) = -\frac{i}{\hbar}\sum_n c_n(t) H'_{mn} e^{i(E_m-E_n)t/\hbar}}$$

Up to this point, we have not yet used any perturbation theory.

Now we apply the perturbation theory. The strategy is to replace the $c_n(t)$ on the right side by lower order values.

If the system starts out in the state ψ_N, that is $C_N(t=0)=1$ and $C_{m\neq N}(t=0)=0$, up to the 1st order

$$\dot{C}_N(t) \simeq -\frac{i}{\hbar} C_N(t=0) H'_{NN}$$

$$\Rightarrow \underline{C_N(t) \simeq 1 - \frac{i}{\hbar}\int_0^t H'_{NN}(t')dt'}$$

$$\dot{C}_{m\neq N}(t) \simeq -\frac{i}{\hbar} \underbrace{C_N(t=0)}_{=1} H'_{mN} e^{i(E_m-E_N)t/\hbar}$$

$$\Rightarrow \underset{(\neq N)}{C_m}(t) \simeq \underbrace{C_m(0)}_{=0} - \frac{i}{\hbar}\int_0^t H'_{mN} e^{i(E_m-E_N)t'/\hbar} dt'$$

$$= \underline{-\frac{i}{\hbar}\int_0^t H'_{mN} e^{i(E_m-E_N)t'/\hbar} dt'}$$

This is the 1st order perturbation theory

$\boxed{\text{Ex. 1}}$ If H' is constant except that it is turned on at $t=0$, then find the probability of transition from state N to state $M(\neq N)$ at $t\,(>0)$.

$$P_{N\to M}(t) = |C_M(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t H'_{MN} e^{i(E_M-E_N)t'/\hbar} dt'\right|^2$$

$$= \frac{|H'_{MN}|^2}{\hbar^2}\left|\int_0^t e^{i(E_M-E_N)t'/\hbar} dt'\right|^2$$

$$\int_0^t e^{i(E_M-E_N)t'/\hbar} dt' = \frac{e^{i\omega_{MN}t}-1}{i\omega_{MN}}$$

$$\frac{E_M-E_N}{\hbar} \equiv \omega_{MN}$$

$$= 2e^{\frac{i}{2}\omega_{MN}t} \frac{\left(e^{\frac{i}{2}\omega_{MN}t} - e^{-\frac{i}{2}\omega_{MN}t} \right)}{2i\,\omega_{MN}}$$

$$= 2e^{\frac{i}{2}\omega_{MN}t} \cdot \frac{\sin\left(\frac{\omega_{MN}}{2}t\right)}{\omega_{MN}}$$

$$\therefore P_{N\to M}(t) = \frac{|H'_{MN}|^2}{\hbar^2} \cdot 4\frac{\sin^2\left(\frac{\omega_{MN}}{2}t\right)}{\omega_{MN}^2}$$

$$= 4|H'_{MN}|^2 \frac{\sin^2\left(\frac{E_M-E_N}{2\hbar}t\right)^2}{(E_M-E_N)^2}$$

$\boxed{\text{Ex. 2}}$ (Prob. 9.18) In 1D-infinite square well, a particle of mass m is in the ground state

At $t=0$, a brick is dropped into the well, so that the potential becomes

$$V(x) = \begin{cases} V_0, & \text{if } 0 \le x \le \frac{a}{2} \\ 0, & \text{if } \frac{a}{2} \le x \le a \\ \infty, & \text{else} \end{cases}$$

, where $V_0 \ll E_1$

After a time T, the brick is removed, and the energy of the particle is measured. What is the probability of measuring E_2 up to the 1st order perturbation theory?

From above, $N=1$ and $M=2$

$$E_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2, \quad E_2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \cdot 4$$

$$H'_{21} = \langle 2|V(x)|1\rangle = V_0 \int_0^{\frac{a}{2}} \frac{2}{a} \sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{\pi}{a}x\right) dx$$

$$= \frac{V_0}{a} \cdot \int_0^{\frac{a}{2}} \left[\cos\left(\frac{\pi}{a}x\right) - \cos\left(\frac{3\pi}{a}x\right)\right] dx$$

$$= \frac{V_0}{a}\left[\frac{a}{\pi}\sin\left(\frac{\pi}{a}x\right) - \frac{a}{3\pi}\sin\left(\frac{3\pi}{a}x\right)\right]_0^{\frac{a}{2}}$$

$$= \frac{V_0}{\pi}\left[\sin\left(\frac{\pi}{2}\right) - \frac{1}{3}\sin\left(\frac{3\pi}{2}\right)\right]$$

$$= \frac{V_0}{\pi}\left[1 + \frac{1}{3}\right] = \frac{4V_0}{3\pi}$$

$$P_{1\to2} = 4|H'_{21}|^2 \frac{\sin^2\left(\frac{E_2-E_1}{2\hbar}T\right)}{(E_2-E_1)^2}$$

$$= 4\cdot\left(\frac{4V_0}{3\pi}\right)^2 \cdot \frac{\sin^2\left(\frac{\hbar}{4m}\left(\frac{\pi}{a}\right)^2 3T\right)}{\left[\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \cdot 3\right]^2}$$

* Selection rules

From the 1st order, time-dependent perturbation theory above,

$$C_m(t) \simeq -\frac{i}{\hbar}\int_0^t H'_{mn}(t')\, e^{i(E_m-E_n)t'/\hbar}\, dt'$$

So if H'_{mn} is zero, then the probability of making a transition from the initial state n to m is always zero.

This is called selection rules.

For example, atoms exposed to electromagnetic radiations make transitions only if $\Delta l = \pm 1$ and $\Delta m = \pm 1$ or 0.

$\boxed{\text{Ex.3}}$ (related to Prob. 9.1) $(n=1)$

The hydrogen atom in its ground state is exposed to an electric field $\vec{E} = E\hat{z}$ turned on at $t=0$.

Now at a later time t, we want to find the probability that the hydrogen will be in one of the $n=2$ states:

$$|n\,l\,m\rangle = |2\,1\,1\rangle,\ |2\,1\,{-1}\rangle$$
$$|2\,1,0\rangle \text{ and } |2\,0\,0\rangle$$

$$V(\vec{r},t) = \begin{cases} 0 & \text{for } t<0 \\ -q\vec{E}\cdot\vec{r} = eEz & \text{for } t\geq 0, \end{cases}$$

Up to the 1st order time-dependent perturbation theory, which of the four transitions are forbidden?

Initial (N)	$\rightarrow$	final (m)	
$\|1\,0\,0\rangle$	$\rightarrow$	$\|2\,0\,0\rangle$	?
		$\|2\,1\,0\rangle$	?
		$\|2\,1\,{-1}\rangle$	?
		$\|2\,1\,1\rangle$	?

Answer: If H'_{mN} is zero, then the $N \rightarrow m$ transition is forbidden.

$$H'_{mN} = \langle m|\,eEz\,|N\rangle$$

Thus we need to check if $\langle m|\,z\,|N\rangle$ is zero.

$z = r\cos\theta$

$$\langle 200|z|100\rangle = \langle R_{20}|r|R_{10}\rangle\langle Y_0^0|\cos\theta|Y_0^0\rangle$$
$$\langle 210|z|100\rangle = \langle R_{21}|r|R_{10}\rangle\langle Y_1^0|\cos\theta|Y_0^0\rangle$$
$$\langle 21\pm1|z|100\rangle = \langle R_{21}|r|R_{10}\rangle\langle Y_1^{\pm1}|\cos\theta|Y_0^0\rangle$$

Here $\langle Y_0^0|\cos\theta|Y_0^0\rangle \propto \int_0^\pi \cos\theta\sin\theta\, d\theta = 0$

$$\langle Y_1^0|\cos\theta|Y_0^0\rangle \propto \int_0^\pi \cos^2\theta\sin\theta\, d\theta$$
$$= -\int_0^\pi \cos^2\theta\, d\cos\theta$$
$$= \int_{-1}^1 x^2\, dx = \frac{2}{3}$$

$$\langle Y_1^{\pm1}|\cos\theta|Y_0^0\rangle \propto \int_0^\pi \sin\theta\cos\theta\sin\theta\, d\theta$$
$$\times \int_0^{2\pi} e^{\pm i\phi}\, d\phi$$
$$= \int_0^\pi \sin^2\theta\, d(\sin\theta)\cdot\frac{e^{\pm 2\pi i}-1}{\pm i}$$
$$= 0$$

So $\langle 200|z|100\rangle$ and $\langle 21\pm1|z|100\rangle$ are zero. $\Rightarrow$ transitions from $|100\rangle$ to $|200\rangle$ and $|21\pm1\rangle$ are forbidden up to the 1st order perturbation theory in this example.

This is an example of the selection rules.

In this case the allowed state ($|210\rangle$) has $\Delta l = 1$ and $\Delta m = 0$ relative to the initial state of $|100\rangle$