# Lecture 13

## Time-dependent perturbation theory



The kind of problem we want to study is as follows. Suppose we have a Hamiltonian $H_0$ and we know its eigenfunctions ~~and~~ $\psi_n(x)$ and eigenvalues $E_n$:

$$H_0\psi_n(x) = E_n\psi_n(x).$$

Now we consider $H = H_0 + \lambda W(x,t)$ where $\lambda$ is a small parameter and $W(x,t)$ is a time-dependent perturbation with the property $W(x,t) = 0$ for $t < 0$.

At $t > 0$, the solutions of the Schrödinger equation are $\psi(t)$ satisfying:

$$(H_0 + \lambda W)\psi(t) = i\hbar \frac{d}{dt}\psi(t)$$

Suppose we look for the particular solution which starts out as an energy eigenstate at $t = 0$:

$$\psi(t)\Big|_{t=0} = \psi_k \quad \text{for some fixed } k.$$

Then we measure the energy at time $t$ and ask what is the <u>probability</u> that $\psi(t)$ is in the eigenstate $\psi_m$.

Clearly this is given by

$$P_{km} = |\langle \psi_m | \psi(t) \rangle|^2$$

$$= \left| \int d^3x \; \psi_m^*(x) \psi(x,t) \right|^2$$

Note that in the presence of the time-dependent perturbation $\lambda W(x,t)$, energy is not conserved. So at $t > 0$, "energy eigenstate of H" has no meaning. However "energy eigenstate of $H_0$" always has a meaning. So our question, in words, is: "what is the probability that a perturbation $\lambda W(x,t)$ will take an eigenstate $\psi_n$ of $H_0$ at time $t = 0$ to another eigenstate $\psi_m$ of $H_0$ at time $t$?"

Since $\psi_n$ form a complete set of states, we can always write

$$\psi(x,t) = \sum_n c_n(t) \psi_n(x)$$

for any $\psi(x,t)$, with $c_n(t) =$

$$\int d^3x \; \psi_n^*(x) \psi(x,t).$$

Hence $P_{km} = |c_m(t)|^2$ where the k-dependence enters when we impose a boundary condition: $c_m(0) = \delta_{mk}$.

Insert this expansion into the time-dep Schrödinger eqn:

$$i\hbar \frac{d}{dt}\left(\sum_n c_n(t)\psi_n\right) = \left(H_0 + \lambda W(t)\right)\sum_n c_n(t)\psi_n$$

$$= \sum_n c_n(t) E_n \psi_n$$

$$+ \lambda \sum_n c_n(t)\; W(t)\psi_n$$

Multiply by $\psi_m^*$ and integrate in $x$ to get:

$$i\hbar \frac{dc_m}{dt} = E_m c_m(t) + \lambda \sum_n W_{mn} c_n(t)$$

where $\quad W_{mn} = \int W(x,t)\, \psi_m^* \psi_n \; d^3x$

$$\equiv \langle \psi_m | W | \psi_n \rangle$$

The above is a set of coupled linear differential equations of first order for $c_n(t)$. The off-diagonal elements $W_{mn}$ couple the different equations.

Notice now that if $W = 0$ (equivalently $\lambda = 0$) then we just have

$$i\hbar \frac{dc_m}{dt} = E_m c_m(t)$$

$$\Rightarrow \quad c_m(t) = b_m e^{-\frac{iE_m t}{\hbar}}$$

where $b_m$ are constants determined by the initial conditions.

If $\lambda$ is very small then we expect $c_m(t)$ will take a similar form as above with $b_m$ varying in time:

$$c_n(t) = b_n(t) e^{-i\frac{E_n}{\hbar}t}$$

Accordingly we make this substitution in the diff. eqn for $c_n(t)$ to get:

$$i\hbar\left(\dot{b}_m - \frac{iE_m}{\hbar}\right)e^{-i\frac{E_m}{\hbar}t}$$

$$= E_m b_m e^{-i\frac{E_m t}{\hbar}} + \lambda \sum_n W_{mn} b_n(t) e^{-i\frac{E_n}{\hbar}t}$$

Dividing throughout by $e^{-iE_m t/\hbar}$ and cancelling out common terms on both sides, we get:

$$i\hbar \frac{d}{dt} b_m = \lambda \sum_n e^{\frac{i}{\hbar}(E_m - E_n)t} W_{mn} b_n(t)$$

$$= \lambda \sum_n e^{i\omega_{mn}t} W_{mn} b_n(t)$$

where $\omega_{mn} = \dfrac{E_m - E_n}{\hbar}$.

So far we have not made any approximation. Now we assume

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

$$= \sum_{k=0}^{\infty} \lambda^k b_n^{(k)}(t)$$

Then we find:

$$i\hbar \frac{db_m^{(0)}}{dt} = 0 \qquad \text{(as expected!)}$$

$$i\hbar \frac{db_m^{(1)}}{dt} = \sum_n e^{i\omega_{mn}t} W_{mn} b_n^{(0)}$$

$$\vdots$$

$$i\hbar \frac{db_m^{(r)}}{dt} = \sum_n e^{i\omega_{mn}t} W_{mn} b_n^{(r-1)}$$

Now let us solve the first nontrivial equation:

$$b_m^{(1)}(t) = \sum_n \frac{b_n^{(0)}}{i\hbar} \int^t e^{i\omega_{mn}t'} W_{mn}(t')\, dt'$$

We need boundary conditions to get a unique solution. Suppose as we initially said, $\Psi(0) = \Psi_k$ for a fixed $k$.

Then $b_k^{(0)} = 1$, $b_n^{(0)} = 0$ for $n \neq k$.

ie $b_n^{(0)} = \delta_{kn}$

Hence $$b_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{mk}t} W_{mk}(t)\, dt$$

It follows that to this order,

$$\begin{aligned} C_m(t) &= b_m(t)\, e^{-\frac{i}{\hbar}E_m t} \\ &= \left(b_m^{(0)} + \lambda b_m^{(1)}(t)\right) e^{-\frac{i}{\hbar}E_m t} \\ &= \left(\delta_{mk} + \lambda b_m^{(1)}(t)\right) e^{-\frac{i}{\hbar}E_m t} \end{aligned}$$

And $\Psi(x,t) = \sum_{m} C_m(t) \Psi_m(x)$

The probability we want to compute is

$$P_{km} = |C_m(t)|^2 = |b_m(t)|^2$$

If we choose $m \neq k$ then $b_m^{(0)} = 0$ while $b_m^{(1)}(t) =$ has been determined above. So

$$P_{km} = \lambda^2 |b_m^{(1)}(t)|^2$$

$$= \frac{\lambda^2}{\hbar^2} \left| \int_0^t e^{i\omega_{mk}t'} W_{mk}(t')\,dt' \right|^2$$

to lowest order in $\lambda$.

Note that the validity of this approximation depends both on $\lambda$ being small and the time interval $(0,t)$ not growing too large. For large $t$ we may need to keep corrections $b_m^{(2)}$, $b_m^{(3)}$ etc.

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Now suppose the perturbation is sinusoidal:

$$W(x,t) = \tilde{W}(x)\,\sin\omega t$$

for some externally chosen $\omega$.

Then

$$\int_0^t e^{i\omega_{mk}t'}\,W_{mk}(t')\,dt'$$

$$= \tilde{W}_{mk}\int_0^t e^{i\omega_{mk}t'}\,\sin\omega t'\,dt'$$

$$= \frac{\tilde{W}_{mk}}{2i}\int_0^t \left[e^{i(\omega_{mk}+\omega)t'} - e^{+i(\omega_{mk}-\omega)t'}\right]dt'$$

$$= +\frac{\tilde{W}_{mk}}{2}\left[\frac{1-e^{i(\omega_{mk}+\omega)t}}{\omega+\omega_{mk}} - \frac{1-e^{i(\omega_{mk}-\omega)t}}{\omega_{mk}-\omega}\right]$$

So $$b_m^{(1)}(t) = \frac{\tilde{W}_{mk}}{2i\hbar}\left[\frac{1-e^{i\omega_+ t}}{\omega_+} - \frac{1-e^{i\omega_- t}}{\omega_-}\right]$$

where $\omega_\pm = \omega_{mk}\pm\omega$

Then with the other assumptions above $(m\neq k)$ we have

$$P_{km} = \frac{|\lambda\tilde{W}_{mk}|^2}{4\hbar^2}\left|\frac{1-e^{i\omega_+ t}}{\omega_+} - \frac{1-e^{i\omega_- t}}{\omega_-}\right|^2$$

Similarly for a $\cos\omega t$ type perturbation,

$$P_{km} = \frac{|\lambda\tilde{W}_{mk}|^2}{4\hbar^2}\left|\frac{1-e^{i\omega_+ t}}{\omega_+} + \frac{1-e^{i\omega_- t}}{\omega_-}\right|^2$$

Let us now focus on $\psi_k$, $\psi_m$ corresponding to discrete energy levels. Then

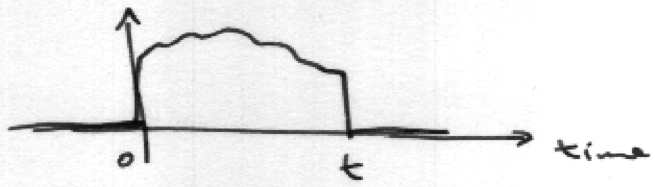
$$P_{km} = \frac{|\lambda \tilde{W}_{km}|^2}{4\hbar^2} \left| \frac{1-e^{i\omega_+ t}}{\omega_+} \pm \frac{1-e^{i\omega_- t}}{\omega_-} \right|$$

is a physical probability. We see that it is a function of $\omega$ (for fixed $\omega_{km}$, ie the system is fixed and the perturbation frequency varied). Now $P_{km}$ can be re-written:

$$P_{km} = \frac{|\lambda \tilde{W}|^2}{4\hbar^2} \left| e^{i\omega_+ t/2} \frac{\sin \frac{\omega_+ t}{2}}{\frac{\omega_+}{2}} \pm \frac{e^{i\omega_- t/2} \sin \frac{\omega_- t}{2}}{\frac{\omega_-}{2}} \right|^2$$

The first term attains its maximum modulus of $t$ as $\omega_+ \to 0$ while the second term does the same if $\omega_- \to 0$. These are called "resonant frequencies": when the frequency $\omega$ of the perturbation is equal to $\pm$ the Bohr frequency $\omega_{km} = \frac{E_k - E_m}{\hbar}$ of the two levels.

Since the integral we evaluated is from 0 to t, we don't care about $W(t)$ before or after that. So we may as well imagine $W(t)$ to be of the form:




In the interval it could be constant as a special case: a step-fn perturbation in time. This would be like the Cos perturbation at $\omega = 0$. Then $\omega_+ = \omega_- = \omega_{mk}$ and:

$$P_{km} = \frac{|\lambda \tilde{W}_{mk}|^2}{\hbar^2} \left| \frac{1 - e^{i\omega_{mk} t}}{\omega_{mk}} \right|^2$$

$$= \frac{|\lambda \tilde{W}_{mk}|^2}{\hbar^2} \cdot \left[ \frac{\sin \omega_{mk} t/2}{\omega_{mk}/2} \right]^2$$

So far we have not said whether the final state m is part of a discrete spectrum of states or a continuum. The formula above is the same for both but in the latter case $P_{km}$ is not directly observable as ~~the transition~~ it is a "probability density": we need to sum over final states in an interval.

Now resonance will be significant if the other (non-resonant) term remains small, ie: near ~~$\omega_+$~~ $\omega_+ \to 0$, the term

$$e^{i\omega_- t/2} \frac{\sin \omega_- t/2}{\omega_-/2}$$ is small and near

$\omega_- \to 0$ the term $e^{i\omega_+ t/2} \dfrac{\sin \omega_+ t/2}{\omega_+/2}$ is small.

The magnitude of these terms is bounded because $\left| e^{i\omega_\pm t/2} \sin \omega_\pm t/2 \right| \leq 1$

Hence near the resonance $\omega_+ \to 0$, we have

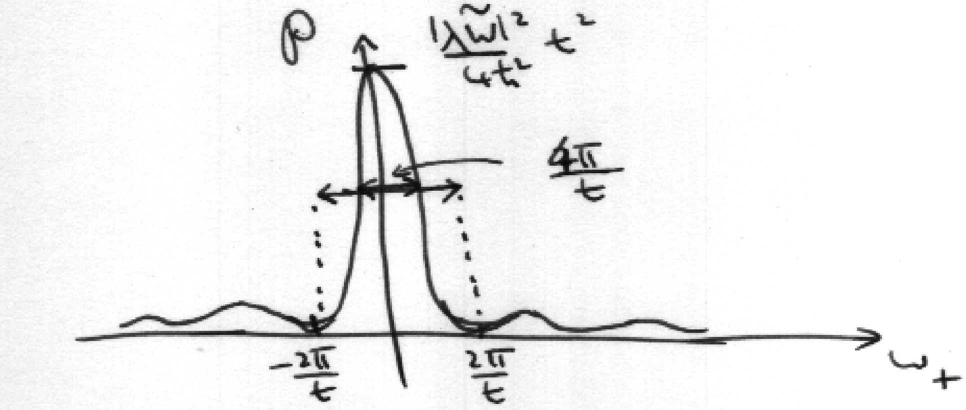
$$|\quad|^2 \to \left| t \pm e^{i\omega_- t/2} \frac{\sin \omega_- t/2}{\omega_-/2} \right|^2$$

~~ie $t \to$~~

So if $t \gg \frac{1}{\omega} \sim \frac{1}{\omega_{km}}$, we can neglect the second term. So for $\omega_+ \simeq 0$ we can write:

$$P_{km} = \frac{|\lambda \tilde{V}_{km}|^2}{4\hbar^2} \left[ \frac{\sin \omega_+ t/2}{\omega_+/2} \right]^2$$

For a fixed ~~time~~ duration, if we plot $P_{km}$ as a function of $\omega_+$ we get:




The distance between two consecutive zeroes of $P_{km}$ around $\omega_+ \simeq 0$ is $\frac{4\pi}{t}$. This is called the "resonance width".

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Now suppose the final state lies in a continuous spectrum. Instead of labelling the state by m (as in $\Psi_m(t)$, $E_m$), we label it by a continuous parameter. As a concrete example, if the final states are those of a free particle then they are labelled by $\vec{p}$. Now $P_{km}$ is replaced by

$$\Delta P_{k,\vec{p}} = \int_\Delta d^3\vec{p} \; P_{k,\vec{p}}$$

Some region in $\vec{p}$-space, eg detector resolution.

calculated as above.

In the above case we can re-express the $\vec{p}$ integral as an integral over energy:

$$E = \frac{\vec{p}^{\,2}}{2m} \Rightarrow dE = \frac{p}{m} dp$$

So $\quad d^3p = p^2 \, dp \, d\Omega$

$$= p \, d\Omega . \, m \, dE$$

$$= m\sqrt{2mE} \, d\Omega \, dE$$

So $d^3p \quad \rightarrow \rho(E) \, dE \quad$ (we use $\int d\Omega = 4\pi$)

where $\rho(E) = 4\pi m \sqrt{2mE}$ is the density of states of energy $E$ and angular direction $\Omega$.

Thus:
$$\Delta P_{k,E} = \int_\Delta dE \, \rho(E) \, P_{k,E}$$

We will assume this formula holds for any continuous set of final states, where the particle is not necessarily free and therefore $\rho(E) \neq 4\pi m \sqrt{2mE}$ in general. In each case one needs to find $\rho(E)$ to compute the RHS.

Note that in the above, we have assumed the initial state $\Psi_k$ to be normalisable, ie in the discrete spectrum of $H_0$.