Lecture 40

Proof of variational theorem

\[ H | \psi_n \rangle = E_n | \psi_n \rangle \]

\[ \text{PHP } | \tilde{\psi}_n \rangle = \tilde{E}_n | \tilde{\psi}_n \rangle \]

\[ E_n \leq \tilde{E}_n \]

by induction

(i) \( E_0 \leq \tilde{E}_0 \) already shown

(ii) assume that

\[ P' = \sum_{n=0}^{N} | \tilde{\psi}_n \rangle \langle \tilde{\psi}_n | \rightarrow E_0 \leq \tilde{E}_0 \quad \cdots \quad E_{n-1} \leq \tilde{E}_{n-1} \]

where \( P' \) has \( N+1 \) states, we want to show \( E_n \leq \tilde{E}_n \)

by contradiction assume \( \tilde{E}_n > E_n \)

we can choose linear combination of \( | \psi_0 \rangle \cdots | \psi_n \rangle \) that are \( \perp \) to \( | \psi_0 \rangle \cdots | \psi_{n-1} \rangle \) and \( \text{norm } \gamma = 0 \) : \( \langle \tilde{\psi}_1 | \psi_1 \rangle = 0 \)

\[ \langle \tilde{\psi}_k | \psi_1 \rangle = 0 \quad \text{for } k = 0, 2, \ldots, n-1 \]

\[ \langle \tilde{\psi}_1 | H | \psi_1 \rangle = \sum_{n=0}^{N} \langle \tilde{\psi}_1 | \psi_n \rangle E_n \langle \psi_n | \tilde{\psi}_1 \rangle \]

\[ \geq E_N \sum_{n=0}^{N} | \langle \psi_1 | \psi_n \rangle |^2 = E_n \]
\[ \langle \tilde{\Sigma} l H | \tilde{\Sigma} \rangle \approx E_0 \]

on the other hand

\[ \langle \tilde{\Sigma} l H | \tilde{\Sigma} \rangle = \Sigma c_n c_m \langle \tilde{\Sigma} n H | \tilde{\Sigma} m \rangle = \]

\[ \Sigma c_n c_m \delta_{mn} \tilde{E}_n \leq E_0 \Sigma |c_n|^2 = E_N \]

\[ E_N \leq \langle \tilde{\Sigma} l H | \tilde{\Sigma} \rangle \leq E_0 \]

but

\[ E_N < E_0 \]

This is a contradiction - proving the general result.

Completion of our variational calculation.

\[ H = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{L^2}{r^2} \right) - \frac{Ze^3}{r} \]

\[ |\Psi_n \rangle = 2\alpha^{3/2} e^{-\alpha r} \ell \ell m \rangle \]

\[ \left( \int_0^\infty 4\alpha^3 e^{-2\alpha r} r^2 dr \right) = \int_0^\infty \alpha^4 \left( \frac{1}{2} \frac{d}{dx} \right)^2 e^{-2\alpha x} \frac{2\alpha x dx}{2\alpha} \]

\[ \alpha^3 \frac{4}{8} \frac{d^2}{dx^2} \frac{1}{x} (\frac{2}{\alpha^2}) = 1 \]
\[ \langle \psi_{\alpha} | H | \psi_{\alpha} \rangle = \frac{\hbar^2}{2m} (1+2\epsilon(\ell+1)) \alpha^2 - Z e^2 \alpha = F(\alpha) \]

\[ \frac{d^2 F}{d\alpha^2} = 0 \quad \frac{\hbar^2}{m} (1+2\epsilon(\ell+1)) \alpha = Ze^2 \]

\[ \alpha_c = \frac{\mu Ze^2}{\hbar^2} \frac{1}{1+2\epsilon(\ell+1)} \quad \frac{d^2 F}{d\alpha^2} = \frac{\hbar^2}{m} (1+2\epsilon(\ell+1)) > 0 \]

(\( \ell \) is minimum at \( \alpha_c \))

\[ F(\alpha_c) = \frac{\hbar^2}{2m} (1+2\epsilon(\ell+1)) \left( \frac{\mu Ze^2}{\hbar^2} \frac{1}{1+2\epsilon(\ell+1)} \right)^2 - \frac{Ze^2 \mu Ze^2}{\hbar^2} \frac{1}{1+2\epsilon(\ell+1)} \]

\[ = - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} \frac{1}{1+2\epsilon(\ell+1)} \]

\[ = - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} \frac{1}{1+2\epsilon+2\epsilon^2} \]

Case 1 \( \ell = 0 \)

\[ E \sim F(\alpha_c) = - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} = E_0 \]

\[ \psi = \left( \frac{\mu Ze^2}{\hbar^2} \right)^{3/2} \epsilon^0 \]

These are both exact

Case 2 \( \ell \neq 0 \)

\[ E \sim F(\alpha_c) = - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} \frac{1}{1+2\epsilon+2\epsilon^2} \]

Exact \( 1's \)

\[ - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} \frac{1}{(\ell+1)^2} = - \frac{\mu Ze^2 \epsilon^1}{2\hbar^2} \frac{1}{1+2\epsilon+2\epsilon^2} \]

\[ \psi - \left( \frac{\mu Ze^2 \epsilon^1}{\hbar^2} \frac{1}{1+2\epsilon+2\epsilon^2} \right)^{3/2} \epsilon^0 \left( \frac{\mu Ze^2}{\hbar^2} \right)^{1/2} \frac{1}{1+2\epsilon+2\epsilon^2} \]
the exact binding energy has a smaller denominator (and is negative) so this does give an upper bound.

Time-dependent perturbation theory

\[ H = H_0 + V(t) \]

\[ V(t) \equiv 0 \quad t < 0 \]

\[ H |\psi_n> = E_n |\psi_n> \quad \text{known} \]

What happens to the system in \( t > 0 \)

\[ |\psi(0)> = \sum_{n=0}^{\infty} c_n |\psi_n> \]

\[ |\psi(t)> = \sum_{n=0}^{\infty} c_n(t) e^{-iE_n t/\hbar} |\psi_n> \]

(in the absence of \( V \) the \( c_n \) remain unchanged)

\[ i\hbar \frac{d |\psi>}{dt} = (H_0 + V(t)) |\psi> \rightarrow \]

\[ i\hbar \sum_{n=0}^{\infty} \left( \frac{dc_n}{dt} - i \frac{E_n}{\hbar} c_n(t) \right) e^{-iE_n t/\hbar} |\psi_n> = \]

\[ \sum_{n=0}^{\infty} c_n \left( E_n + V(t) \right) e^{-iE_n t/\hbar} |\psi_n> \]
Left multiply by \( \langle \psi_m | - i \hbar \partial_t \rangle \) not \( E_n \) cancels on both sides of this equation:

\[
\frac{d \psi_m}{dt} e^{-i E_m t / \hbar} = \sum_{n=0}^{\infty} \langle \psi_m | V(t) | \psi_n \rangle e^{-i E_n t / \hbar} e^{-i E_m t / \hbar} \psi_n
\]

Or:

\[
\frac{d \psi_m}{dt} = -i \frac{\hbar}{\hbar} \sum_{n=0}^{\infty} \langle \psi_m | V(t) | \psi_n \rangle e^{i (E_m - E_n) t / \hbar} \psi_n
\]

We define \( \omega_{mn} = \frac{E_m - E_n}{\hbar} \)

This is an infinite set of coupled differential equations, we require \( C_m(0) = \psi_m - \) our initial coefficients \( \rightarrow \) Integration:

\[
C_m(t) = C_m(0) - \frac{i}{\hbar} \int_0^t \sum_{n=0}^{\infty} \langle \psi_m | V(t') | \psi_n \rangle e^{-i E_n t'/\hbar} C_n(t') dt'
\]

This is still an equation because the unknown appears on both the right and the left. It is an infinite set of equations.
Later we will show that if $V$ is reasonably well behaved and $t < \infty$ that this integral equation can be solved by iteration

$$C_m^0(t) = C_m^{(0)}$$

$$C_m^{(k)}(t) = C_m^{(0)} - \frac{i}{\hbar} \int_0^t \sum \langle \psi_m | V(t') | \psi_n \rangle e^{i\omega_{mn} t'} C_n^{(k-1)}(t') \, dt'$$

$$C_m(t) = \lim_{k \to \infty} C_m^{(k)}(t)$$

The strategy is to show that

$$\Sigma \left| C_m^{(k)} - C_m^{(\infty)} \right|^2 \to 0$$

for fixed $t$ as $k \to \infty$. (We do this later.)

(1) First order approximation

$$C_m(t) \approx C_m^{(1)}(t) \equiv C_m^{(0)} - \frac{i}{\hbar} \int_0^t \sum \langle \psi_m | V(t') | \psi_n \rangle e^{i\omega_{mn} t'} C_n^{(0)} \, dt'$$
Assume that the system is in the \( k \)th eigenstate of \( H_0 \) at time \( t = 0 \). This means

\[
  C_n(t) = 1 \quad n = k \\
  C_n(t) = 0 \quad n \neq k
\]

If \( V \) is weak and the probability that it is in the \( m \)th state at time \( t > 0 \) (\( m \neq k \))

\[
  C_m(t) = C_0 - \frac{i}{\hbar} \int_0^t \langle \Psi_m(t') | i \Psi_k > e^{i \omega_{mk} t'} dt'
\]

\[
  P = |\langle \Psi_m | \Psi(t) \rangle|^2 = \\
  = \langle \Psi_m | \sum \Psi_n(t) e^{-iE_n t} \Psi_n \rangle^2 \\
  = |C_m(t) e^{-iE_m t}|^2 = |C_m(t)|^2 \\
  \therefore \quad P = \frac{1}{\hbar^2} \left| \int_0^t \langle \Psi_m(t') | \Psi_k > e^{i \omega_{mk} t'} dt' \right|^2
\]

This is all we can say if we do not know \( V \) — note that

\[
  P \to 0 \quad \text{as} \quad t \to \infty \quad (\text{here} \ n \neq k)
\]
we can say more if we assume
the \( V(t) = \Theta(t) V \) where \( V \) is
independent of \( t = \)

\[
\int_0^t <\psi_m | V(t) | \psi_R> e^{i\omega_{mr}t'} dt' =
\]

\[
<\psi_m | V | \psi_R> \frac{1}{i\omega_{mr}} (e^{i\omega_{mr}t} - 1)
\]

\[
P_{mr} = \frac{1}{\hbar^2} K_{\psi_m | V | \psi_R}^2 \frac{1}{\omega_{mr}} \left( 1 - e^{i\omega_{mr}t} - e^{-i\omega_{mr}t} + 1 \right) =
\]

\[
\frac{1}{\hbar^2 \omega_{mr}^2} K_{\psi_m | V | \psi_R}^2 2 (1 - \cos \omega_{mr}t) =
\]

\[
P_{mr} = \frac{4}{\hbar^2} K_{\psi_m | V | \psi_R}^2 (\sin^2 \frac{\omega_{mr}t}{2}) / \omega_{mr}^2.
\]

This is for a transition to a
single state. Note that
this is sharply peaked when
\( \omega_{mr} \) is small or \( |E_m - E_R| \) is small.
If we sum over all final states and take the limit as $t \to \infty$, we get the probability that this perturbation will cause of decay.

$$P_K \to \frac{2}{m} \frac{\hbar}{V} \left| \langle \psi_m \mid V \mid \psi_K \rangle \right|^2 \frac{\sin^2 \left( \frac{(E_m - E_K) t}{\hbar} \right)}{\left( \frac{(E_m - E_K)}{\hbar} \right)^2}$$

as $t \to \infty$, 

$$\frac{\sin^2 at}{ta^2} \to \frac{\pi}{2} S(a)$$

Proof:

$$\int \frac{\sin^2 at}{a^2} f(a) \, da$$

$\quad v = at \quad dv = da$

$$\int \frac{\sin^2 v}{v^2} \, dv \, f\left( \frac{v}{t} \right) \to f(0) \int \frac{\sin^2 v}{v^2} \, dv = \frac{\pi}{2} f(0)$$

as $t \to \infty \to f(0) + O\left( \frac{1}{t^2} \right)$.

$$P_K \to \frac{2}{m} \frac{\hbar}{V} \langle \psi_m \mid V \mid \psi_K \rangle^2 \frac{\pi}{2} S\left( \frac{E_m - E_K}{\hbar} \right)$$

$$\frac{2\pi}{K} \langle \psi_K \mid V \mid \psi_m \rangle S\left( \frac{E_m - E_K}{\hbar} \right) \langle \psi_m \mid V \mid \psi_K \rangle \ell$$
If we replace
\[ \frac{\hbar}{m} \rightarrow \int dE \rho(E) \]
where \( \rho \) is called the density of states, \( \rho(E) \Delta E = \# \text{ states with energy between } E, E + \Delta E \),

\[ W = \lim_{\hbar \to 0} \frac{d\rho}{dE} \rightarrow \frac{2\pi}{\hbar} |\langle \psi_f | V | \psi_i \rangle|^2 \rho(E) \]

\( W \) is called the transition rate; it is the rate of change of probability — in large \( t \) in first order PT: \( P \sim ct \).

really represents the over all final states with the same energy.

This result is called Fermi's golden rule.
The interaction representation

\[ |\psi(t)\rangle_s = U(t-t_0) |\psi(t_0)\rangle_s \]

\[ |\psi(t)\rangle_H = |\psi(t)\rangle_H \]

\[ |\psi(t)\rangle_I = U^+_o(t) |\psi(t)\rangle_s \]

\[ \frac{d}{dt} |\psi_I(t)\rangle = \left( U^+_o(t) \left( -\frac{i}{\hbar} H_0 - \frac{i}{\hbar} H \right) U_o(t) \right) |\psi_I(t)\rangle_s \]

\[ = -\frac{i}{\hbar} U^+_o(t) V U_o(t) U^+_o(t) |\psi(t)\rangle_s \]

\[ \frac{d}{dt} |\psi_I(t)\rangle = -\frac{i}{\hbar} V(t) |\psi_I(t)\rangle \]

To define

\[ U_I(t,t_0) |\psi_I(t_0)\rangle = |\psi_I(t)\rangle = 0 \]

\[ \frac{dU_I}{dt} = -\frac{i}{\hbar} V(t) U_I(t) \quad U_I(t_0) = I \]

This gives

\[ U_I(t,t_0) = I - \frac{i}{\hbar} \int_{t_0}^{t} V(t') U_I(t') dt' \]

\[ V(t') = U^+_o(t') V U_o(t') = e^{iH_0 t'/\hbar} - i H \frac{t'}{\hbar} \]

We have the same structure as our perturbative equation.
there is a useful trick

\[ U (t, t_t) = 1 - \frac{i}{\hbar} \int_0^t V(t') \, U (t, t_t) + \]

\[ \left\{ -\frac{i}{\hbar} \int_0^t \int_0^t V(t') V(t'') \, dt' \, dt'' \right\} + \cdots \]

we write the second order term of

\[ \left\{ -\frac{i}{\hbar} \right\} \frac{1}{2} \left\{ \int_0^t \int_0^t V(t') V(t'') + \int_0^t \int_{t''}^t V(t') V(t'') \right\} = \]

\[ \left\{ -\frac{i}{\hbar} \right\} \frac{1}{2} \left\{ \int_0^t \int_0^t V(t') V(t'') + \int_0^t \int_{t''}^t V(t') V(t'') \right\} \]

\[ t' > t \quad t'' > t' \]

\[ \left\{ -\frac{i}{\hbar} \right\} \frac{1}{2} \int_0^t \int_0^t \left[ \Theta(t'' - t') V(t') V(t'') + \Theta(t' - t'') V(t') V(t'') \right] \]

\[ \frac{T(V(t') V(t''))} \]

\[ T \text{ is called a time order product} \]

this can be generalized to

\[ U (t, t_t) = 1 + \sum_{n=1}^\infty \left( -\frac{i}{\hbar} \right)^n \frac{1}{n!} \int_0^t \int_0^t T(V(t'), V(t'')) \, dt', \, \, dt'' \]
If $\| V(t_1) \cdot V(t_2) \| \leq V^n$ independent of $t$, it is finite, the norm of the $n$ term in this series is bounded by

$$\left| \frac{1}{n!} \frac{1}{n!} V^n (t-t_0)^n \right| \rightarrow \frac{c^n}{n!} = 0$$

and

$$\| I + \sum_{n=1}^{\infty} \left( \frac{i}{n!} \right)^n \int_{t_0}^{t} \ldots \int_{t_0}^{t} T(V(t_1) \cdot V(t_2)) \, dt \, dt' \|_{\Delta t/n} \leq c$$

where $\Delta t = t-t_0$ — thus unlike bound state perturbation theory the series generated by iterating this equation converges for $V(t)$ with time independent norm and $\| t-t_0 \|$ finite.

The interesting examples of when this does not happen are

$$t-t_0 \rightarrow \infty \quad \| V \| \rightarrow \infty$$