Lecture 9

Rayleigh Ritz

**Theorem 1** \[ H = H \geq 0 \]

1. \[ \langle \psi | H | \psi \rangle \geq E_0 \quad \langle \psi | \psi \rangle = 1 \]
2. \[ \langle \psi | H | \psi \rangle = E_0 \quad (H - E_0) | \psi \rangle = 0 \]

**Theorem 2** \[ p = p^2 = p^* \quad H_p = P(H) P_p \]

\[ H | \psi_n \rangle = \varepsilon_n | \psi_n \rangle \quad E_0 \leq \varepsilon_1 \leq \varepsilon_2 \ldots \]

\[ H_p | \psi_{n} \rangle = \overline{E}_n | \psi_{n} \rangle \quad \overline{E}_0 \leq \overline{E}_1 \leq \overline{E}_2 \ldots \]

1. \[ \varepsilon_n \leq \overline{\varepsilon}_n \]
2. \[ \varepsilon_n = \overline{\varepsilon}_n \quad (H - \overline{E}_n) | \overline{\psi}_n \rangle = 0 \]

To prove Theorem 1, let \( | \psi_n \rangle \), \( E_n \) be a complete set of eigenstates of eigenvalues of \( H \):

\[ | \psi \rangle = \sum c_n | \psi_n \rangle \quad c_n = \langle \psi_n | \psi \rangle \quad \sum | c_n |^2 = 1 \]

1. \[ \langle \psi | H | \psi \rangle = \sum | c_n |^2 \varepsilon_n \geq \sum | c_n |^2 E_0 = E_0 \]
2. \[ \langle \psi | (H - E_0) | \psi \rangle = 0 = \sum | c_n |^2 (E_n - E_0) = 0 \]

Since \( E_n - E_0 = 0 \) if \( n \neq 0 \), then \( | c_n |^2 = 0 \) \( \forall \neq 0 \)

\[ \sum | c_n |^2 = | c_0 |^2 = 1 \quad | \psi \rangle = c_0 | \psi_0 \rangle \]

where \( | c_0 | = 1 \).
to prove theorem 2

Let \( |k\rangle = \sum_{x=1}^{k} c_x |\Psi_e\rangle \)

choose \( c_e \) by solving the system of \( k \) equations

\[
\langle \Psi_m | k \rangle = \sum_{x=1}^{k} c_x \langle \Psi_m | \Psi_e \rangle = 0 \quad m = 1, \ldots, k-1
\]

\[
1 = \langle k | k \rangle = \sum_{e=1}^{k} |c_e|^2
\]

by construction \( |k\rangle = P_l |k\rangle \)

\[
\langle k | H | k \rangle = \langle k | H P_l P_l | k \rangle = \sum_{x=1}^{k} |c_e|^2 E_e
\]

\[
= \sum_{e=1}^{k} |c_e|^2 \overline{E_e} = \overline{E_k}
\]

\[
\langle k | H | k \rangle = \sum_{m=1}^{k} \langle k | \Psi_m \rangle E_m \langle \Psi_m | k \rangle
\]

\[
= \sum_{m=1}^{k} \sum_{n=1}^{k} \frac{K_{kn} \Psi_m}{E_n} \overline{E_n}
\]

\[
= \sum_{m=1}^{k} \sum_{n=1}^{k} \frac{K_{kn} \Psi_m}{E_n} \overline{E_n} \geq \sum_{m=1}^{k} \sum_{n=1}^{k} \frac{d_m^2 E_m}{E_k}
\]

\[
\geq \sum_{m=1}^{k} d_m^2 E_m \geq \sum_{m=1}^{k} d_m^2 E_k
\]

\[
\geq E_k
\]

\[
\therefore E_k \leq \langle k | H | k \rangle \leq \overline{E_k}
\]

the proof of the second part of the theorem is left in homework
Example

Consider the Yukawa potential \( V(r) = -\lambda e^{-\alpha r}/r \). We try to find the s wave ground state energy using a trial wave function of the form

\[
\Psi(\beta, r) = N(\beta) e^{-\beta r} Y_0(\hat{r})
\]

\[
\int_0^{\infty} N(\beta)^2 e^{-2\beta r} r^2 dr = 1 =
\]

\[
N(\beta)^2 \frac{1}{4} \frac{d}{d\beta} \int_0^{\infty} e^{-2\beta r} dr = N(\beta)^2 \frac{1}{4} \frac{d}{d\beta} \left( \frac{1}{-2\beta} \right)
\]

\[
\left( \frac{d^2}{d\beta^2} \right) = \frac{d}{d\beta} \left( -\frac{1}{\beta^2} \right) = -\frac{2}{\beta^3}
\]

\[
1 = N(\beta)^2 \frac{1}{4} \frac{2}{\beta^3} \quad N(\beta) = \sqrt{2} \beta^{3/2}
\]

\[
\Psi(\beta, r) = \sqrt{2} \beta^{3/2} e^{-\beta r} Y_0(\hat{r})
\]

This gives a normalized state for any \( \beta \). Calculating the expectation value of the Yukawa Hamiltonian in this state as a function of \( \beta \) gives

\[
E_\beta = \langle \Psi(\beta) | H | \Psi(\beta) \rangle = \frac{1}{2} \beta^3 \int_0^{\infty} e^{-\beta r} \left( \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{\hbar^2}{m} \left( \frac{1}{2} \frac{d}{dr} e^{-\alpha r} \right)^2 - \lambda \frac{e^{-\alpha r}}{r} \right) e^{-\beta r} r^2 dr
\]
\[ L_\beta = 2 \beta^3 \int_0^\infty e^{-2\beta r} \left( -\frac{\kappa_1^2}{2m} \beta^2 + \frac{\kappa_1}{\mu r} \beta - \frac{a_1}{c} r \right) r^2 \, dr \]

\[ = -\frac{\kappa_1^2}{2m} 2 \beta^5 \int_0^\infty e^{-2\beta r} r^2 \, dr + \frac{2 \beta^4}{\mu} \kappa_1 \int_0^\infty e^{-2\beta r} r \, dr \]

\[ - 2 \beta^3 \lambda \int_0^\infty e^{-2\beta r} \, dr \]

\[ = -\frac{\kappa_1^2}{\mu} \beta^5 \left( \frac{1}{4} \frac{d^4}{d\beta^4} \right) \left( \frac{1}{2\beta} \right) + \frac{2 \beta^4}{\mu} \kappa_1 \left( -\frac{1}{2} \frac{d}{d\beta} \right) \left( \frac{1}{2\beta} \right) \]

\[ - 2 \beta^3 \lambda \left( -\frac{1}{2} \right) \frac{d}{d\beta} \left( \frac{1}{2\beta + \alpha} \right) \]

\[ = -\frac{\kappa_1^2}{\mu} \beta^5 \cdot \frac{2}{\beta^3} + \frac{\beta^4 \kappa_1}{2\mu} \frac{1}{\beta^2} - 2 \beta^3 \frac{2}{(2\beta + \alpha)^2} \]

\[ = \beta^3 \left( -\frac{\kappa_1^2}{4\mu} + \frac{\kappa_1}{2\mu} - \frac{2\lambda \beta}{(2\beta + \alpha)^2} \right) \]

Next we minimize this as a function of \( \beta \). This is a rigorous upper bound on the s-wave Yukawa ground state wave functions.

\[ \frac{dE}{d\beta} = 2 \beta \left( \frac{\kappa_1^2}{4\mu} - \frac{2\lambda \beta}{(2\beta + \alpha)^2} \right) + \beta^2 \left( -\frac{2\lambda}{(2\beta + \alpha)^4} + \frac{(2\lambda \beta)(2\beta + \alpha)^2}{(2\beta + \alpha)^4} \right) = 0 \]

Multiply by \( \frac{1}{\beta} (2\beta + \alpha)^3 \)

\[ 0 = 2 \frac{\kappa_1^2}{4\mu} (2\beta + \alpha)^3 - 4 \lambda \beta (2\beta + \alpha)^3 - 2\lambda \beta (2\beta + \alpha) + 4 \lambda \beta^3 = 0 \]

\[ = (4\frac{\kappa_1^2}{4\mu} + 4\lambda) \beta^3 + (\frac{6\kappa_1^2}{\mu} - 4\lambda \frac{\kappa_1}{\mu}) \beta^2 \left( \frac{3\kappa_1^2}{\mu} \alpha^2 - \frac{\kappa_1 \lambda}{\mu} \right) \beta = 0 \]

\[ \frac{\kappa_1^2}{2\mu} \beta^3 \]
This is an odd degree polynomial in $\beta$ so it must change sign and have a real $0$. If $\frac{\partial E}{\partial \beta}(\beta) \equiv 0$ then $E(\beta)$ is minimum:

$$E = E(\beta^*)$$

$$\psi \equiv \sqrt{2} \beta^{3/2} e^{-\beta^r \psi(r)}$$

(In practice $\mu = \frac{1}{2} m_0$, $\alpha = \frac{m_0 c^3}{h}$, $\lambda = \lambda$ is coupling strength)

Born Oppenheimer approximation:

$$H = \sum_{i=3}^{N} \frac{p_i^2}{2m_i} - \frac{u}{|r_i-r_{11}|} - \frac{Z_i e^4}{|r_i-r_{11}|} + \frac{2}{3} \frac{e^4}{|r_i-r_{12}|} + \frac{Z_i Z_j e^4}{|r_i-r_{12}|}$$

Here we treat $r_1$ and $r_2$ as parameter.

Our trial wave function is $\psi(r_1, r_2) \times \chi(r_3), \ldots$ where $\chi$ is square integrable, fixed, and sharply peaked near fixed values of $r_3, r_4$. The exact solutions with $\chi$ treated as fixed is $E(r_1, r_2)$, the BO approximation is realized by minimizing the eigenvalues with respect to $r_1, r_2$. 
Galerkin Methods (Thm 2)

Let $|\phi_n\rangle$ be a basis. Assume a trial function of the form

$$|\psi\rangle = \sum C_n |\phi_n\rangle$$

$$H_{mn} = \langle \phi_m | \phi_n \rangle$$

solve

$$\sum_{n} H_{mn} C_n = \sum E_{mn} C_m$$

$$|\psi^{(n)}\rangle = \sum C^{(n)}_m |\phi_m\rangle$$

$$E^{(n)} = n^{th} eigenvalue of H_{nn}$$

then

$$E^{(n)} \geq E^{(n)}_{exact}$$

giving $N$ variational bounds

by replacing $H$ by a matrix.

Rayleigh–Schrödinger Perturbation Theory

Consider

$$H = H_1 + \lambda H_2 \quad \lambda \ll 1$$

$$H_1 |\psi_n\rangle = E_n |\psi_n\rangle$$

$$H_1 |\psi'_n\rangle = E'_n |\psi'_n\rangle$$
can we write
\[ \lvert \psi_n \rangle = \sum \lambda^m \lvert \psi^{(m)}_n \rangle \]
\[ E_n = \sum \lambda^m E^m_n \]

where
\[ \lvert \psi^{(u)}_n \rangle = \lvert \psi'_n \rangle \]
\[ E^{(u)}_n = E'_n \]

The strategy is pretty simple—we expand both the wave function and energy eigenvalue in powers of \( \lambda \). There are 2 concerns

(1) because the normalization is not fixed (we end up dividing by a normalization constant), we fix a normalization by requiring
\[ \lvert \psi^{(u)}_n \rangle = \lvert \psi'_n \rangle \]

and
\[ \langle \psi^{(m)}_n | \psi^{(1)}_m \rangle = 0 \]

(2) when the final result is obtained, men we normalized to unity.
\[ \begin{align*}
H \sum_{n=0}^{\infty} |\psi_m^{(n)}\rangle \lambda^n &= \sum_{k,l} \lambda^R \sum_{l' \in \mathbb{R}} \langle \psi_m^{(n)} | \psi_{m'}^{(n')} \rangle \\
H \sum_{n=0}^{\infty} |\psi_m^{(n)}\rangle \lambda^n + V \sum_{n'=1}^{\infty} |\psi_m^{(n-1)}\rangle \lambda^{n-1} &= \sum_{k,l} \lambda^R \sum_{l' \in \mathbb{R}} \langle \psi_m^{(n)} | \psi_{m'}^{(n')} \rangle \\
(\ n' = n+1 \quad n' = l+k \ )
\end{align*} \]

Equating coefficients of \( \lambda^n \) gives:

\[ \begin{align*}
\sum_{n=0}^{\infty} |\psi_m^{(n)}\rangle &= E_m |\psi_m^{(n)}\rangle \\
(\text{solution of the unperturbed problem})
\end{align*} \]

\[ \begin{align*}
H |\psi_m^{(n)}\rangle + V |\psi_m^{(n-1)}\rangle &= \sum_{k,l} \lambda^R \sum_{l' \in \mathbb{R}} \langle \psi_m^{(n-2)} | \psi_{m'}^{(n-1)} \rangle \\
it is useful to separate off the first and last term in the sum
\end{align*} \]

\[ \begin{align*}
H |\psi_m^{(n)}\rangle + V |\psi_m^{(n-1)}\rangle &= E_m |\psi_m^{(n)}\rangle - E_m |\psi_m^{(n-1)}\rangle \\
&= \sum_{k,l} \lambda^R \sum_{l' \in \mathbb{R}} \langle \psi_m^{(n-2)} | \psi_{m'}^{(n-1)} \rangle \\
&= \sum_{k,l} \lambda^R \sum_{l' \in \mathbb{R}} \langle \psi_m^{(n-2)} | \psi_{m'}^{(n-1)} \rangle
\end{align*} \]

To find an equation for \( E_m^{(n)} \) multiply the above by \( \langle \psi_m^{(n)} | \)

\[ \begin{align*}
\langle \psi_m^{(n)} | (H_1 - E_m) |\psi_m^{(n)}\rangle + \langle \psi_m^{(n)} | V |\psi_m^{(n-1)}\rangle &= E_m^{(n)}
\end{align*} \]
This gives

\[ E^{(n)}_m = \langle \psi_m | V | \psi^{(n-1)}_m \rangle \]

To get the \( n - m \) correction to the wave function we expand in terms of \( | \psi^{(b)}_k \rangle \) by observing the corrections are \( \perp \) to \( | \psi_m \rangle \)

\[ | \psi^{(m)}_m \rangle = \sum_{k \neq m} C_k | \psi^{(b)}_k \rangle \]

\[ (H_1 - E^{(n)}_m) \sum_{k \neq m} C_k | \psi^{(b)}_k \rangle = -V | \psi^{(n-1)}_m \rangle + \sum_{k \neq m} C_k | \psi^{(n-1)}_m \rangle + \sum_{\alpha=1}^{n} E^{(n-\alpha)}_m | \psi^{(\alpha)}_m \rangle + \sum_{\alpha=1}^{n} E^{(n-\alpha)}_m | \psi^{(\alpha)}_m \rangle \]

left multipled by \( \langle \psi^{(b)}_k | \)

\[ C_{k'} \left( E^{(b)}_{k'} - E^{(b)}_m \right) = -\langle \psi^{(b)}_{k'} | V | \psi^{(n-1)}_m \rangle \]

\[ + \sum_{\alpha=1}^{n-\alpha} E^{(n-\alpha)}_m \langle \psi^{(\alpha)}_m | \psi^{(\alpha)}_m \rangle \]

\[ C_{k'} = \frac{1}{E^{(b)}_{k'} - E^{(b)}_m} \left( \langle \psi^{(n)}_m | V | \psi^{(n-1)}_m \rangle - \sum_{\alpha=1}^{n-\alpha} E^{(n-\alpha)}_m \langle \psi^{(\alpha)}_m | \psi^{(\alpha)}_m \rangle \right) \]

This gives both the approximate wave function and
normally this approximation is useful when \( \lambda \) is small. The most important corrections in that case are the first order corrections:

\[
E_n = E_n^{(0)} + \lambda E_n^{(1)} \\
= E_n^{(0)} + \lambda \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle
\]

\[
\psi_n = \psi_n^{(0)} + \lambda \sum_{k \neq n} \frac{\psi_k^{(0)} < \psi_k^{(0)} | V | \psi_n^{(0)} >}{E_n^{(0)} - E_k^{(0)}}
\]

This works if all of the 0th order eigenvalues are different. Unfortunately one normally chooses \( H_1 \), so it is simple to solve. This often means that \( H_1 \) has a lot of symmetry and a lot of degeneracy. Next we will look at the case of degenerate perturbation theory, but first we consider some examples.

Assume that a hydrogen atom is placed in an electric field in the \( z \) direction. The field causes the proton and electron to experience
in opposite directions, the change in potential energy is 
\[ \Delta E_n = -\langle \Psi_n | -ze^2 | \Psi_n \rangle \]

\[ = -\langle \Psi_n | (r \cos \theta e^2 | \Psi_n \rangle \]

\[ = -\int u_n^2(r) r dr e^2 | \Psi_n \rangle \int Y_{em}(\hat{r}) \cos \theta Y_{em}(\hat{r}) d\Omega \]

while the radial equation determines the strength of this perturbation, the spherical harmonics determine selection rules:

\[ \cos \theta = \sqrt{\frac{4\pi}{3}} Y_{10}(\hat{r}) \]

So,

\[ \int Y_{em}^*(\hat{r}) \cos \theta Y_{em}(\hat{r}) d\Omega = \]

\[ \int Y_{em}(\hat{r}) \sqrt{\frac{4\pi}{3}} Y_{10}(\hat{r}) Y_{em}(\hat{r}) d\Omega \]

Note:

\[ Y_{10}(\hat{r}) Y_{em}(\hat{r}) = \langle \hat{r} | 10 \rangle = \]

\[ = \langle \hat{r} | 10 \rangle \langle 10 | em \rangle \langle em | \hat{r} \rangle \]

Integrating against \( Y_{em}^* \) gives \( \delta_{ej} \delta_{mo} \)

\[ \int Y_{em}^*(\hat{r}) \cos \theta Y_{em}(\hat{r}) d\Omega = \sqrt{\frac{4\pi}{3}} \langle 10 \rangle \langle 10 | em \rangle \langle 10 | em \rangle \]
This gives
\[ \Delta E = \frac{1}{2} \int u_{nt}^2 \langle r \rangle \text{d}r \left( e^2 E \sqrt{\frac{4\pi}{3}} \langle \alpha \text{em} \text{iem} \rangle \right) \]

Degenerate perturbation theory

\[ H_1 \left| \Psi_n^{(o)} \right> = E_n^{(o)} \left| \Psi_n^{(o)} \right> \]

same \( E_n^{(o)} \) for \( m = 1 \ldots N \)

\[ P = \sum_{m=1}^{N} \left| \Psi_m^{(o)} \right> \left< \Psi_m^{(o)} \right| \quad Q = I - P \]

\[ H' = P \Delta H \quad P + P \Delta P \]

\[ V' = 0 \Delta H + P \Delta V + \Delta V \quad P + \Delta V \]

Start by solving

\[ H'_1 \left| \Psi_n^{(o)'} \right> = E_n^{(o)'} \left| \Psi_n^{(o)'} \right> \]

This eigenvalue problem is an \( N \times N \) matrix that can be solved exactly. - Note

1. The \( N \times N \) matrix problem normally lifts the degeneracy

2. The new 0th order solution includes terms to all order in \( \Delta \)

3. The new solution can be used
with $V'$ to start a perturbation theory.