Lecture 19

The variational method

Assume $\langle \chi(\alpha) | \chi(\alpha) \rangle = 1$

$\langle \chi(\alpha) | H | \chi(\alpha) \rangle \geq E_0$

E_0 is the lowest eigenvalue of H

if $\langle \chi(\alpha) | H | \chi(\alpha) \rangle = E_0$

then $|\chi(\alpha)\rangle$ is an eigenstate of H with energy E_0

Use:

Let $F(\alpha) = \langle \psi(\alpha) | H | \psi(\alpha) \rangle$

minimize with respect to α

$$\frac{\partial F}{\partial \alpha_i}(\alpha_{min}) = 0$$

$$\frac{\partial^2 F}{\partial \alpha_i \partial \alpha_j}(\alpha_{min})$$ has positive eigenvalues

$$F(\alpha_{min}) \geq E_0$$

The proof is elementary

$$\langle \Psi(\alpha) | H | \Psi(\alpha) \rangle =$$

$$\sum_{n=1}^{\infty} \langle \Psi(\alpha) | \Phi_n \rangle E_n \langle \Phi_n | \Psi(\alpha) \rangle =$$

$$\sum_{n=1}^{\infty} \langle \Psi(\alpha) | \Phi_n \rangle \langle \Phi_n | \Psi(\alpha) \rangle \left(E_0 + \underbrace{(E_n - E_0)}_{\geq 0} \right) =$$

$$E_0 + \sum_{n=1}^{\infty} |\langle \Psi(\alpha) | \Phi_n \rangle|^2 (E_n - E_0) \geq E_0$$

if $\langle \Psi(\alpha) | H | \Psi(\alpha) \rangle = E_0$ then

$$\sum_{n=1}^{\infty} |\langle \Psi(\alpha) | \Phi_n \rangle|^2 (E_n - E_0) = 0$$

$$\sum_{E_n > E_0} |\langle \Psi(\alpha) | \Phi_n \rangle|^2 (E_n - E_0) = 0 \Rightarrow \langle \Psi(\alpha) | \Phi_n \rangle = 0$$

$$|\Psi(\alpha)\rangle = \sum_{(n \text{ with } E_n = E_0)} |\Phi_n\rangle \langle \Phi_n | \Psi(\alpha) \rangle$$

* The normalization is important - otherwise $\langle \Psi(\alpha) | H | \Psi(\alpha) \rangle$ can be any value

Hydrogen Hamiltonian

$$\boxed{\begin{aligned} &\psi(r) = r\,u(r) \\ &-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}u - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}u = Eu \end{aligned}}$$

we can apply the variational method to this

Choose a trial function

$$u(\alpha, r) = re^{-\alpha r}$$

determine the normalization

$$1 = N^2\int_0^\infty r^2 e^{-2\alpha r}\,dr =$$

$$= N^2\left(-\frac{1}{2}\frac{d}{d\alpha}\right)^2\int_0^\infty e^{-2\alpha r}\,d(2\alpha r)\frac{1}{2\alpha}$$

$$= N^2\left(-\frac{1}{2}\frac{d}{d\alpha}\right)^2\frac{1}{2\alpha} = N^2\left(-\frac{1}{2}\frac{d}{d\alpha}\right)\left(-\frac{1}{2}\cdot\frac{1}{2}\frac{-1}{\alpha^2}\right)$$

$$= N^2\left(-\frac{1}{8}\frac{d}{d\alpha}\right)\left(\frac{1}{\alpha^2}\right) = -\frac{(-2)}{8}\frac{1}{\alpha^3}N^2 = \frac{N^2}{4\alpha^3}$$

this can be solved to get

$$N^2 = 4\alpha^3$$

$$N = 2\alpha^{3/2}$$

$$\boxed{u(\alpha, r) = 2\alpha^{3/2}\,re^{-\alpha r}}$$

step 1

calculate $\langle \psi(\alpha) | H | \psi(\alpha) \rangle$

$$\frac{du}{dr} = \frac{d}{dr}\left(2\alpha^{3/2} r e^{-\alpha r}\right) =$$

$$= 2\alpha^{3/2} e^{-\alpha r} - 2\alpha^{5/2} r e^{-\alpha r}$$

$$= 2\alpha^{3/2} e^{-\alpha r}(1 - \alpha r) =$$

$$\frac{d^2u}{dr^2} = 2\alpha^{3/2} e^{-\alpha r}(-\alpha + \alpha^2 r - \alpha)$$

$$= 2\alpha^{3/2} e^{-\alpha r}(\alpha^2 r - 2\alpha)$$

calculating

$$\int_0^\infty u(r)\, H\, u(r)\, dr =$$

$$\int_0^\infty \left(-\frac{\hbar^2}{2m}\left(4\alpha^3 r e^{-2\alpha r}(\alpha^2 r - 2\alpha) - 4\alpha^3 e^{-2\alpha r}\, \ell(\ell+1)\right)\right.$$

$$\left. - \frac{e^2}{4\pi\epsilon_0} r\, 4\alpha^3 e^{-2\alpha r}\right) dr =$$

$$4\alpha^3 \int e^{-2\alpha r}\left[\frac{\hbar^2}{2m}\ell(\ell+1) + r\left(-\frac{\hbar^2}{2m}(-2\alpha) - \frac{e^2}{4\pi\epsilon_0}\right) - \frac{\hbar^2}{2m}\alpha^2 r^2\right]$$

we integrate as before using

$$\int r^n e^{-2\alpha r} = \left(-\frac{1}{2}\frac{d}{d\alpha}\right)^n \frac{1}{2\alpha}$$

$n = 1 \quad \frac{1}{4}\frac{1}{\alpha^2} \qquad n = 2 \quad \frac{1}{4\alpha^3}$

$$4\alpha^3 \frac{1}{2\alpha} \frac{\hbar^2}{2m}(\ell)(\ell+1) + 4\alpha^3\left(\frac{\hbar^2\alpha}{m} - \frac{e^2}{4\pi\epsilon_0}\right)\left(-\frac{1}{2}\frac{1}{2}\frac{-1}{\alpha^2}\right)$$

$$- 4\alpha^3 \frac{\hbar^2}{2m}\alpha^2\left(\frac{1}{4}\alpha^3\right)$$

In terms of powers of α

$$\boxed{\alpha^2\left[\frac{2\hbar^2}{m}(\ell)(\ell+1) + \frac{\hbar^2}{m} - \frac{\hbar^2}{2m}\right] - \frac{e^2}{4\pi\epsilon_0}\alpha}$$

If we differentiate

$$2\alpha\left[\frac{2\hbar^2}{m}\ell(\ell+1) + \frac{\hbar^2}{2m}\right] - \frac{e^2}{4\pi} = 0 \qquad (1)$$

$$\boxed{\alpha_{min} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{2\left[\frac{\hbar^2}{2m} + \frac{2\hbar^2}{m}\ell(\ell+1)\right]}}$$

We note the second derivative of (1) is

$$2\left[\frac{2\hbar^2}{m}\ell(\ell+1) + \frac{\hbar^2}{2m}\right] > 0$$

so α_{min} is a local minimum.

To find the variational approximation to the wave function and energy we must substitute α_{min} in $F(\alpha)$.

$$E_{var} = \alpha_{min}^2 \left[\frac{2\hbar^2}{m} l(l+1) + \frac{\hbar^2}{2m} \right] - \frac{e^2}{4\pi\epsilon_0} \alpha_{min}$$

$$R_{var} = \frac{u_{var}}{r} = 2\alpha_{min}^{3/2} e^{-\alpha_{min} r}$$

$$E_{var} = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \left[\frac{1}{4} \frac{1}{\frac{\hbar^2}{2m} + \frac{2\hbar^2}{m}(l(l+1))} - 2 \frac{1}{\frac{\hbar^2}{2m} + \frac{2\hbar^2}{m} l(l+1)} \right]$$

$$E_{var} = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{4\left(\frac{\hbar^2}{2m} + \frac{2\hbar^2}{m} l(l+1)\right)}$$

for the $l=0$ case

$$\boxed{\begin{aligned} E_{var} &= -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \\ R_{var} &= 2\left(\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{m}{\hbar^2}\right)^{3/2} e^{-\frac{m}{\hbar^2}\frac{e^2}{4\pi\epsilon_0} r} \end{aligned}}$$

which agrees with the exact expressions in chapter 4

(not $\psi_{000} = Y_0^0 R_{000} = \frac{1}{\sqrt{4\pi}} 2\left(\frac{e^2}{4\pi\epsilon_0}\frac{m}{\hbar^2}\right)^{3/2} e^{-\frac{m}{\hbar^2}\frac{e^2}{4\pi\epsilon_0} r}$

$= \frac{1}{\sqrt{\pi}}\left(\frac{e^2}{4\pi\epsilon_0}\frac{m}{\hbar^2}\right)^{3/2} e^{-\frac{m}{\hbar^2}\frac{e^2}{4\pi\epsilon_0} r}$)

There is another variational result that is interesting

Let $H|\psi_n\rangle = E_n|\psi_n\rangle$ and

Let $|\chi_n\rangle$ be any set of

N orthonormal vectors $\langle\chi_n|\chi_m\rangle = \delta_{mn}$.

Let $\Pi_N = \sum_{n=1}^{N} |\chi_n\rangle\langle\chi_n|$ be the projection operator on the space spanned by the N vectors $|\chi_n\rangle$ and consider

$$\Pi H \Pi |\xi_n\rangle = \tilde{E}_n \Pi |\xi_n\rangle \qquad \cdots (*)$$

we label states so

$$E_0 \le E_1 \le E_2 \cdots$$
$$\tilde{E}_0 \le \tilde{E}_1 \le \tilde{E}_2 \cdots$$

The meaning of equation $*$ is

$$|\xi\rangle = \sum |\chi_n\rangle\langle\chi_n|\xi\rangle$$

$$H|\xi\rangle = \sum H|\chi_n\rangle\langle\chi_n|\xi\rangle$$

we want to solve

$$H|\xi\rangle = \sum_n H|\chi_n\rangle\langle\chi_n|\xi\rangle = \tilde{E}\sum|\chi_n\rangle\langle\chi_n|\xi\rangle$$

to solve the multiply by $\langle\chi_m|$ and use the orthogonality

$$\boxed{\sum\left(\langle\chi_m|H|\chi_n\rangle - \tilde{E}\,\delta_{mn}\right)\langle\chi_n|\xi\rangle = 0}$$

This is an eigenvalue problem for the $N\times N$ matrix $\langle\chi_m|H|\chi_n\rangle$.

since $\langle\chi_n|H|\chi_m\rangle = \langle\chi_m|H|\chi_n\rangle^*$ (because $H = H^\dagger$) it has real eigenvalues with are roots of

$$\det\left(\langle\chi_m|H|\chi_n\rangle - \tilde{E}\,\delta_{mn}\right) = 0$$

This gives N eigenvalues and eigenvects

$$|\xi_n\rangle = \sum|\chi_m\rangle\langle\chi_m|\xi_n\rangle$$

$$\Pi H \Pi|\xi_n\rangle = \tilde{E}_n|\xi_n\rangle$$

The second result is

(1) for $n = 1 \cdots N$

$$E_n \leq \tilde{E}_n$$

(2) if $E_n = \tilde{E}_n$ $|\psi_n\rangle = |\xi_n\rangle$ or $|\xi_n\rangle$ is an eigenvector of H with eigenvalue E_n.

The general proof is by mathematical induction - I just give an outline

(1) The ordinary variation principle gives

$$E_1 \leq \tilde{E}_1$$

$\tilde{E}_1 = E_1 \Rightarrow |\xi_1\rangle$ is an eigenstate of H with eigenvalue E_1

(2) Let $|\phi\rangle = c_1 |\xi_1\rangle + c_2 |\xi_2\rangle$

choose c_1 c_2 so

(1) $\langle \phi | \psi_1 \rangle = 0$

(2) $\langle \phi | \phi \rangle = 1$

$$\langle \psi_1 | \phi \rangle = c_1 \langle \psi_1 | \xi_1 \rangle + c_2 \langle \psi_1 | \xi_2 \rangle = 0$$

$$c_2 = -c_1 \frac{\langle \psi_1 | \xi_1 \rangle}{\langle \psi_1 | \xi_2 \rangle}$$

$$|\phi\rangle = c_1 \left(|\xi_1\rangle - |\xi_2\rangle \frac{\langle \psi_1 | \xi_1 \rangle}{\langle \psi_1 | \xi_2 \rangle} \right)$$

$$\langle \phi | \phi \rangle = 1 = c_1^2 \left(1 + \left| \frac{\langle \psi_1 | \xi_1 \rangle}{\langle \psi_1 | \xi_2 \rangle} \right|^2 \right)$$

$$c_1 = \frac{1}{\sqrt{1 + \left| \frac{\langle \psi_1 | \xi_1 \rangle}{\langle \psi_1 | \xi_2 \rangle} \right|^2}}$$

This can be easily done.

(A) note

$$\langle \phi | H | \phi \rangle = \sum_{n=1}^{\infty} \langle \phi | \psi_n \rangle E_n \langle E_n | \phi \rangle$$

but $\langle \psi_1 | \phi \rangle = \langle \phi | \psi_1 \rangle = 0$

$$= \sum_{n=2}^{\infty} |\langle \phi | \psi_n \rangle|^2 \left(E_2 + \underbrace{(E_n - E_2)}_{\text{always non negative}} \right)$$

again since $\langle \phi | \psi_1 \rangle = 0$

$$\sum_{n=2}^{\infty} |\langle \phi | \psi_n \rangle|^2 E_2 = \sum_{n=1}^{\infty} \langle \phi | \psi_n \rangle \langle \psi_n | \phi \rangle E_2 =$$

$$\langle \phi | \phi \rangle E_2 = E_2$$

This means

$$\langle\phi|H|\phi\rangle = E_2 + (\text{non negative})$$

$$\langle\phi|H|\phi\rangle \geq E_2$$

but

$$\langle\phi|H|\phi\rangle = \tilde{E}_1 |\langle\phi|\xi_1\rangle|^2 + \tilde{E}_2 |\langle\phi|\xi_2\rangle|^2$$

$$= \left(\tilde{E}_2 + (\tilde{E}_1 - \tilde{E}_2)\right)|\langle\phi|\xi_1\rangle|^2 + \tilde{E}_2 |\langle\phi|\xi_2\rangle|^2$$

$$= \tilde{E}_2 + \underbrace{(\tilde{E}_1 - \tilde{E}_2)}_{\text{non positive}} \underbrace{|\langle\phi|\xi_1\rangle|^2}_{\text{positive}}$$

$$\langle\phi|H|\phi\rangle \leq \tilde{E}_2$$

$$\therefore \quad \tilde{E}_2 \geq \langle\phi|H|\phi\rangle \geq E_2$$

Or $\tilde{E}_2 \geq E_2$

If $E_2 = \tilde{E}_2$ $\quad \langle\phi|\psi_n\rangle = 0 \quad n > 2$ and

$\langle\phi|\psi_1\rangle = 0$

which requires $|\phi\rangle = \alpha|\psi_2\rangle$.

To proceed by induction

$$|\phi\rangle = \sum_k c_k |\xi_k\rangle$$

choose the c_k so $\langle\phi|\psi_1\rangle = \cdots = \langle\phi|\psi_{k-1}\rangle = 0$

and $\langle\phi|\phi\rangle = 1$

repeating the same argument

gives

$$\tilde{E}_n \geq E_n \qquad n = 1 \cdots N$$

and if

$$\tilde{E}_n = E_n \qquad |\xi_n\rangle \text{ is an eigenstate of } H \text{ with energy } E_n.$$

this means that if you approximate H by projecting on a finite dimensional subspace and solve the eigenvalue problem, the eigenvalues are upper bounds to the exact eigenvalues.

example

potential between quark and antiquark.

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \alpha r - \beta\frac{1}{r}\right)u = Eu$$

As in the case of the Hydrogen atom

$$u = 2\alpha^{3/2} e^{-\alpha r} r$$

example

square well

$$\psi(x) = c\,x(x-a)$$

$$\int_0^a \psi(x)^2\,dx = c^2 \int_0^a x^2(x^2-2ax+a^2)$$

$$= c^2\left(\left(\frac{a^5}{5}\right) - 2a\frac{a^4}{4} + a^2\frac{a^3}{3}\right)$$

$$= c^2 a^5\left(\frac{1}{5} - \frac{1}{2} + \frac{1}{3}\right)$$

$$= c^2 a^5\left(\frac{6-15+10}{30}\right) = c^2\frac{a^5}{30}$$

$$c = \sqrt{\frac{30}{a^5}}$$

$$\psi(x) = \sqrt{\frac{30}{a^5}}\,x(x-a)$$

In this case

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}\sqrt{\frac{30}{a^5}}\cdot 2$$

$$\int \psi(x) H \psi(x)\,dx = -\frac{\hbar^2}{2m}\frac{30}{a^5}\cdot 2\int_0^a (x^2-ax)\,dx$$

$$= -\frac{\hbar^2}{2m}\frac{30}{a^5}\cdot 2\left(\frac{a^3}{3} - \frac{a^3}{2}\right)$$

$$= +\frac{\hbar^2}{2m}\frac{10}{a^2}$$

This is an upper bound on the exact ground state energy

$$E_1 = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2}$$

we note that $\pi^2 = 9.87 < 10$

In this case the variational bound is within about 1.3% of the exact energy

$$\frac{\Delta E_0}{E_0} = \frac{10-\pi^2}{\pi^2} \times 100 = 1.3\%$$

The wave function

$$\sqrt{\frac{30}{a^5}}\, x(x-a) \quad \text{vs} \quad \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

when $x = \frac{a}{2}$ the wave functions have values

$$\sqrt{\frac{30}{a^5}}\left(\frac{a^2}{4}\right) = \frac{1.36}{\sqrt{a}} \; ; \quad \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{2}\right) = \frac{1.41}{\sqrt{a}}$$

we see they both vanish at 0, a and the peak values differ by $\frac{.05}{1.41} \times 100 = 3.5\%$

Note that given this function if we construct a function $\perp$ to this one and find the larger of the eigenvalues of

$$\begin{pmatrix} \langle \chi_1 | H | \chi_1 \rangle & \langle \chi_1 | H | \chi_2 \rangle \\ \langle \chi_2 | H | \chi_1 \rangle & \langle \chi_2 | H | \chi_1 \rangle \end{pmatrix}$$

the larger eigenvalue of this 2x2 matrix is an upper bound on the second eigenvalue.