Lecture 10

Variational Methods

This is a powerful method for approximating lowest or highest energy states and their eigenvalues.

The method is based on the following 2 Theorems:

Theorem 1: Assume E is the lowest eigenvalue of a Hamiltonian H. Then for any $|\psi\rangle$

$$\boxed{\begin{array}{l} * \ \langle\psi|H|\psi\rangle \geq E \\ * \ \text{if } \langle\psi|H|\psi\rangle = E \ \text{ then} \\ \quad H|\psi\rangle = E|\psi\rangle \end{array}}$$

Theorem 2

Let P be an orthogonal projection on a finite dimensional subspace of the Hilbert space

Let

$$PHP\,|\tilde{\psi}_n\rangle = \tilde{E}_n|\tilde{\psi}_n\rangle$$

with

$$\tilde{E}_1 \le \tilde{E}_2 \le \tilde{E}_3 \cdots \le \tilde{E}_n$$

Also assume

$$H\,|\psi_n\rangle = E_n\,|\psi_n\rangle$$

$$E_1 \le E_2 \le E_3 \cdots$$

Then

$$E_m \le \tilde{E}_m \qquad 1 \le m \le N$$

and if $E_m = \tilde{E}_m$

$$H\,|\tilde{\psi}_m\rangle = E_m\,|\psi_m\rangle$$

The proof of Theorem 1

is surprisingly elementary

Assume $H|\psi_n\rangle = E_n|\psi_n\rangle$

$E_1 \leq E_2 \leq E_3 \cdots$

$$\langle\psi|H|\psi\rangle = \sum_{mn} \langle\psi|\psi_m\rangle\langle\psi_m|H|\psi_n\rangle \times \langle\psi_n|\psi\rangle$$

since $|\psi_n\rangle$ is an eigenstate

of H

$$\langle\psi_m|H|\psi_n\rangle = E_n\langle\psi_m|\psi_n\rangle$$
$$= E_n\delta_{mn}$$

using this in the above

gives

$$\langle\psi|H|\psi\rangle = \sum \langle\psi|\psi_m\rangle E_m\langle\psi_m|\psi\rangle$$

$$= \sum_m |\langle\psi|\psi_m\rangle|^2 E_m$$

$$\langle\psi|H|\psi\rangle = \sum |\langle\psi|\psi_m\rangle|^2 E_m$$

$$(E_1 \leq E_m)$$

$$\leq \sum |\langle\psi|\psi_m\rangle|^2 E_1$$

$$= E_1 \sum |\langle\psi|\psi_m\rangle|^2$$

$$= E_1$$

This gives the first part of theorem 1. For the second part assume $\langle\psi|H|\psi\rangle = E_1$

$$0 = \langle\psi|H|\psi\rangle - E_1 =$$

$$= \langle\psi|H|\psi\rangle - E_1\langle\psi|\psi\rangle$$

$$= \sum_n |\langle\psi|\psi_n\rangle|^2 (E_n - E_1)$$

since $E_n \geq E_1$ $|\langle\psi|\psi_n\rangle|^2 = 0$ unless $E_n = E_1$

$$\boxed{\begin{aligned} \therefore\ |\psi\rangle &= \sum_{E_m = E_1} |\psi_m\rangle\langle\psi_m|\psi\rangle \\ H|\psi\rangle &= \sum_{E_m = E_1} E_1 |\psi_m\rangle\langle\psi_m|\psi\rangle \\ &= E_1|\psi\rangle \end{aligned}}$$

the completes the proof of theorem 1

the way that this is used is to assume a trial wave function that depends on parameters $\alpha_1 \cdots \alpha_N$

$$\Psi_{\alpha_1 \, \alpha_N}(x)$$

where

$$\int |\Psi_{\alpha_1 \, \alpha_N}(x)|^2 \, dx = 1$$

define

$$E(\alpha_1 \, \alpha_N) = \langle \Psi_{\alpha_1 \, \alpha_N} | H | \Psi_{\alpha_1 \, \alpha_N} \rangle$$
$$\geq E_1$$

since this inequality holds for all $\vec{\alpha}$, is holds for the $\vec{\alpha}_{min}$ that minimizes $E(\alpha_1 \, \alpha_N)$

To use this find $\vec{\alpha}$ satisfying

$$\frac{\partial}{\partial \alpha_j} E(\tilde{\alpha}_1 \ \tilde{\alpha}_n) = 0 \qquad j = 1 \cdots N$$

$$\frac{\partial^2}{\partial \alpha_i \partial \alpha_j} E(\tilde{\alpha}_1 \ \tilde{\alpha}_n) > 0$$

i.e. it is a matrix with positive eigenvalues

then

(1) $E(\tilde{\alpha}_1 \ \tilde{\alpha}_n)$ is the approximate lowest energy

(2) $\varphi(\tilde{\alpha}_1 \ \tilde{\alpha}_n)$ is the approximate wave function

Proof of Theorem 2

* solve

$$PHP|\tilde{\Psi}_n\rangle = \tilde{E}_n|\tilde{\Psi}_n\rangle \qquad 1 \le n \le N$$

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle$$

* assume

$$\tilde{E}_1 \le \tilde{E}_2 \cdots \le \tilde{E}_N$$

$$E_1 \le E_2 \qquad \le E_N \le \cdots$$

step 1

* from the ordinary variational principle we have $E_1 \le \tilde{E}_1$

and if $E_1 = \tilde{E}_1$ $|\tilde{\psi}_1\rangle$ is an eigenstate of H with eigenvalue E_2

step 2

Let $|\chi\rangle = c_1 |\tilde{E}_1\rangle + c_2 |\tilde{E}_2\rangle$

choose c_1 and c_2

so

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

(2) $\langle \chi | \psi_1 \rangle = 0$

It follows

By construction

$|\chi\rangle = P|\chi\rangle$

$$\langle \chi | H | \chi \rangle = \langle \chi | P H P | \chi \rangle$$

since $\langle \psi_1 | \chi \rangle = 0$

$$\langle \chi | H | \chi \rangle = \sum_{n=2}^{\infty} |\langle \chi | \psi_n \rangle|^2 E_n$$

$$= \sum_{n=2}^{\infty} \underbrace{|\langle \chi | \psi_n \rangle|^2}_{\geq 0} \left[\underbrace{(E_n - E_2)}_{\geq 0} + E_2 \right]$$

$$\geq E_2$$

on the other hand

$$\langle \chi | P H P | \chi \rangle = |c_1|^2 \tilde{E}_1 + |c_2|^2 \tilde{E}_2$$

$$= |c_1|^2 (\tilde{E}_1 + \tilde{E}_2 - \tilde{E}_2) + |c_2|^2 \tilde{E}_2$$

$$= |c_1|^2 \underbrace{(\tilde{E}_1 - \tilde{E}_2)}_{\leq 0} + \tilde{E}_2$$

$$\leq \tilde{E}_2$$

$$\therefore \quad E_2 \leq \langle \chi | H | \chi \rangle = \langle \chi | P H P | \chi \rangle \leq \tilde{E}_2$$

If $E_2 = \tilde{E}_2 \Rightarrow c_1 = 0$ or $\tilde{E}_1 = \tilde{E}_2$

and $\langle \chi | \psi_n \rangle = 0$ unless $E_n = E_2$

for $n \geq 2$

$$H | \chi \rangle = \sum_{cn} E_n | \psi_n \rangle \langle \psi_n | \chi \rangle$$

$$= \sum_{n=2}^{\infty} E_n | \psi_n \rangle \langle \psi_1 | \chi \rangle$$

but the terms in the sum with $E_n \neq E_2$ vanish $\Rightarrow$

$$H|\chi\rangle = E_2|\chi\rangle$$

where $|\chi\rangle$ is a linear combination of terms with eigenvalue E_2

This argument can be repeated

$$|\chi\rangle = \sum_{n=1}^{K} c_n |\tilde{\psi}_n\rangle$$

choose c_n so $\langle\chi|\chi\rangle = 1$ and $\langle\psi_n|\chi\rangle = 0$ for all $n < K$.

Then we still have

$$\langle\chi|H|\chi\rangle = \langle\chi|PHP|\chi\rangle$$

on the left hand side of this equation we have

$$\langle \chi | H | \chi \rangle = \sum_{n=1}^{\infty} \langle \chi | \Psi_n \rangle E_n \langle \Psi_n | \chi \rangle$$

since $\langle \chi | \Psi_n \rangle = 0$ for $n < k$ by construction

$$= \sum_{n=k}^{\infty} |\langle \chi | \Psi_n \rangle|^2 (E_n - E_k + E_k) =$$

$$= E_k \langle \chi | \chi \rangle + \sum_{n=k}^{\infty} \underbrace{|\langle \chi | \Psi_n \rangle|^2}_{\geq 0} \underbrace{(E_n - E_k)}_{\geq 0}$$

it follows that

$$\boxed{\begin{array}{l} E_k \leq \langle \chi | H | \chi \rangle \text{ and} \\ \text{if } E_k = \langle \chi | H | \chi \rangle \text{ then} \\ \langle \chi | \Psi_n \rangle = 0 \text{ for all } n \\ \text{with } E_n > E_k \end{array}}$$

next consider the right side of this equation

$$\langle \chi | H | \chi \rangle = \langle \chi | PHP | \chi \rangle =$$

$$\sum_{n=1}^{K} \langle \chi | \tilde{\varphi}_n \rangle \tilde{E}_n \langle \tilde{\varphi}_n | \chi \rangle =$$

$$\tilde{E}_k \sum |\langle \chi | \tilde{\varphi}_n \rangle|^2 + \sum |\langle \chi | \tilde{\varphi}_n \rangle|^2 (\tilde{E}_n - \tilde{E}_k) =$$

$$\tilde{E}_k + \sum \underbrace{|\langle \chi | \tilde{\varphi}_n \rangle|^2}_{\geq 0} \underbrace{(\tilde{E}_n - \tilde{E}_k)}_{\leq 0}$$

This means

$$\langle \chi | H | \chi \rangle = \langle \chi | PHP | \chi \rangle \leq \tilde{E}_k$$

and if this is equal to $\tilde{E}_k$ then $|\langle \chi | \tilde{\varphi}_n \rangle| = 0$ all $n < k$ with $\tilde{E}_n < \tilde{E}_k$

putting everything togethe

$$E_k \leq \langle \chi | H | \chi \rangle = \langle \chi | PHP | \chi \rangle \leq \tilde{E}_k$$

If $\tilde{E}_k = E_k$ then the above equation has all $=$ signs

Then we have

$$|\chi\rangle = \sum_{n=0}^{\infty} |\psi_n\rangle\langle\psi_n|\chi\rangle =$$

$$\sum_{n=k}^{\infty} |\psi_n\rangle\langle\psi_n|\chi\rangle$$

since $\langle\psi_n|\chi\rangle = 0$ for $n < k$ by construct

$$\sum_{n=k}^{n_{max}} |\psi_n\rangle\langle\psi_n|\chi\rangle$$

the only terms in the sum are eigenstat of H with eigenvalue E_k

$$\therefore H|\chi\rangle = E_k|\chi\rangle$$

This completes the proof of the second variational theorem

Application - Hydrogen ground state

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right) - \frac{Ze^2}{r}$$

$$\mu = \text{reduced mass} = \frac{m_e m_p}{m_e + m_p}$$

step 1

choose a variational wave function

$$\psi_e(\vec{r}) = N(\alpha)\, e^{-\alpha r}\, Y_{00}$$

$$1 = \int |\psi_e(\vec{r})|^2 \, d^3r =$$

$$= \int_0^\infty r^2 dr \, N(\alpha)^2 e^{-2\alpha r} \underbrace{\int \frac{1}{4\pi} \sin\theta \, d\theta \, d\phi}_{1}$$

To solve this problem we have to compute integrals of the fa.

$$\int_0^\infty r^n e^{-2\alpha r} dr = \qquad u = 2\alpha r$$

$$\int_0^\infty \frac{1}{(2\alpha)^{n+1}} u^n e^{-u} du =$$

$$\frac{1}{(2\alpha)^{n+1}} \int_0^\infty u^{(n+1)-1} e^{-u} du =$$

$$\boxed{\frac{1}{(2\alpha)^{n+1}} \Gamma(n+1) = \frac{n!}{(2\alpha)^{n+1}}}$$

using this identity gives

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

$$= N(\alpha)^2 \frac{2!}{(2\alpha)^3}$$

This gives

$$N(\alpha)^2 = \frac{(2\alpha)^3}{2}$$

$$N(\alpha) = \frac{(2\alpha)^{3/2}}{\sqrt{2}} = 2\alpha^{3/2}$$

so we consider the trial wave function

$$\boxed{\psi(r) = 2\alpha^{3/2} e^{-\alpha r} Y_{00}(\theta \phi)}$$

where in this case α is a variational parameter.

step 2: compute the expectation value of the Hamiltonian in the variational wave function

The integrals that we need are

(1) $$e^{-\alpha r}\frac{d^2}{dr^2}e^{-\alpha r} = \alpha^2 e^{-2\alpha r}$$

$$-\frac{\hbar^2}{2m}N(\alpha)^2\int_0^\infty r^2\alpha^2 e^{-2\alpha r}\,dr$$

$$-\frac{\hbar^2}{2m}N(\alpha)^2\alpha^2\frac{2!}{(2\alpha)^3}$$

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

$$-\frac{\hbar^2}{2m}N(\alpha)^2(-2\alpha)\int_0^\infty\frac{r^2}{r}e^{-2\alpha r}\,dr$$

$$\frac{\hbar^2\alpha}{m}N(\alpha)^2\frac{1!}{(2\alpha)^2}$$

(3) $$-\frac{\hbar^2}{2m}(-\ell(\ell+1))\int_0^\infty r^2\frac{1}{r^2}e^{-2\alpha r}\,dr\;N(\alpha)^2$$

$$\frac{\hbar^2}{2m}\ell(\ell+1)\frac{1}{2\alpha}N(\alpha)^2$$

(4) $$-Ze^2\int\frac{r^2}{r}e^{-2\alpha r}\,dr\;N(\alpha)^2$$

$$-Ze^2\frac{1!}{(2\alpha)^2}N(\alpha)^2$$

we all all of these terms up to get the expectation value of H

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

$$-\frac{\hbar^2}{2m} N(\alpha)^2 \frac{2\alpha^2}{(2\alpha)^3} + \frac{\hbar^2}{m} N(\alpha)^2 \frac{\alpha}{(2\alpha)^2}$$

$$+ \frac{\hbar^2}{2m} N(\alpha)^2 \frac{\ell(\ell+1)}{2\alpha} - \frac{Ze^2 N(\alpha)^2}{(2\alpha)^2}$$

where $N(\alpha)^2 = 4\alpha^3$ — using this in the above gives

$$= -\frac{\hbar^2}{m}\frac{\alpha^2}{2} + \frac{\hbar^2}{m}\alpha^2 + \frac{\hbar^2}{m}\ell(\ell+1)\alpha^2 - Ze^2\alpha$$

$$= \frac{\hbar^2}{m}\left(\frac{1}{2} + \ell(\ell+1)\right)\alpha^2 - Ze^2\alpha$$

step 3 — find the minimum of $\langle \psi(\alpha) | H | \psi(\alpha) \rangle$ as a function of α

$$0 = \frac{d}{d\alpha}\langle \psi(\alpha) | H | \psi(\alpha) \rangle =$$

$$0 = \frac{2\hbar^2}{m}\left(\ell(\ell+1) + \frac{1}{2}\right)\alpha - Ze^2$$

and we also have

$$\frac{d^2}{d\alpha^2} \langle \psi(\alpha) | H | \psi(\alpha) \rangle = \frac{2\hbar^2}{m} \left(\ell(\ell+1) + \tfrac{1}{2} \right) > 0$$

so this function has a minimum at

$$\alpha_* = \frac{Ze^2 m}{2\hbar^2 \left(\ell(\ell+1) + \frac{1}{2} \right)}$$

next we use this to calculate the minimum value of $\langle \psi(\alpha) | H | \psi(\alpha) \rangle$

$$E(\alpha^*) = \frac{\hbar^2}{m} \alpha^2 \left(\tfrac{1}{2} + \ell(\ell+1) \right) - Ze^2 \alpha$$

$$= \frac{\hbar^2}{m} \frac{Z^2 e^4 m^2}{4\hbar^4} \frac{1}{\ell(\ell+1) + \frac{1}{2}} - \frac{Z^2 e^4 m}{2\hbar^2 \left(\ell(\ell+1) + \frac{1}{2} \right)}$$

$$= \frac{Z^2 e^4 m}{\hbar^2} \left(\frac{1}{4} - \frac{1}{2} \right) \frac{1}{\left(\ell(\ell+1) + \frac{1}{2} \right)} =$$

$$\boxed{= - \frac{Z^2 e^4 m}{2\hbar^2} \frac{1}{2\ell(\ell+1) + 1}}$$

This is the exact binding energy for the ground state ($\ell = 0$)

we can use α^* to construct the variational wave function - for $l=0$ we get

$$\boxed{\begin{aligned}\Psi(\bar{r}) &= \Psi_{\alpha^*}(r)\,Y_{00} = \\ &(2\alpha^*)^{3/2}\, e^{-\alpha^* r}\,\frac{1}{\sqrt{4\pi}} = \\ &\left(\frac{2Ze^2m}{\hbar^2}\right)^{3/2} e^{-\frac{Ze^2m}{\hbar^2}r}\,\frac{1}{\sqrt{4\pi}}\end{aligned}}$$