Lecture 13

Feynman Hellmann Theorem

<u>Assume</u>

$$\boxed{H(\alpha)|\psi(\alpha)\rangle = E(\alpha)|\psi(\alpha)\rangle}$$

where α represents parameters that appear in the Hamiltonian.

Then

$$\langle\psi(\alpha)|\frac{\partial H}{\partial\alpha_i}(\alpha)|\psi(\alpha)\rangle =$$

$$\frac{\partial E}{\partial\alpha_i}(\alpha)\langle\psi(\alpha)|\psi(\alpha)\rangle$$

If $\langle\psi(\alpha)|\psi(\alpha)\rangle = 1$ then

$$\boxed{\langle\psi(\alpha)|\frac{\partial H}{\partial\alpha_i}(\alpha)|\psi(\alpha)\rangle = \frac{\partial E(\alpha)}{\partial\alpha}}$$

Proof:

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

using the chain rule

$$\frac{\partial \langle \Psi(\alpha)|}{\partial \alpha_i} \underbrace{(H(\alpha) - E(\alpha))|\Psi(\alpha)\rangle}_{0} +$$

$$\langle \Psi(\alpha)| \left(\frac{\partial H(\alpha)}{\partial \alpha_i} - \frac{\partial E(\alpha)}{\partial \alpha_i} \right) |\Psi(\alpha)\rangle +$$

$$\left(\langle \frac{\partial \langle \Psi(\alpha)|}{\partial \alpha_i} \underbrace{(H(\alpha) - E(\alpha))|\Psi(\alpha)\rangle}_{0} \right)^*$$

Thus as long as $H(\alpha) = H^+(\alpha)$

and $|\Psi(\alpha)\rangle$ is an eigenstate

of $H(\alpha)$ with eigenvalue $E(\alpha)$

the only remaining term

is the middle term

$$\langle \Psi(\alpha)| \frac{\partial H}{\partial \alpha_i}(\alpha) |\Psi(\alpha)\rangle = \frac{\partial E}{\partial \alpha}(\alpha) \langle \Psi(\alpha)|\Psi(\alpha)\rangle$$

This completes the proof

of the theorem

example

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r}$$

$$= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$$

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

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

we can use any of the above forms of the Hamiltonian

(1) compute $\langle \psi(\alpha) | p^2 | \psi(\alpha) \rangle$

$$\frac{\partial H}{\partial m} = -\frac{p^2}{2m^2} \qquad p^2 = -2m^2\frac{\partial H}{\partial m}$$

$$\langle \psi | p^2 | \psi \rangle = -2m^2 \langle \psi | \frac{\partial H}{\partial m} | \psi \rangle$$

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

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

* compute $\langle \psi(\alpha) | V | \psi(\alpha) \rangle$

$$\frac{\partial H}{\partial Z} = -\frac{e^2}{r}$$

$$Z\frac{\partial H}{\partial Z} = -\frac{Ze^2}{r} = V$$

$$\langle \psi | V | \psi \rangle = Z \langle \psi | \frac{\partial H}{\partial Z} | \psi \rangle =$$

$$Z\,\frac{\partial E}{\partial Z} = -\frac{2Z^2 e^4 m}{2\hbar^2}\frac{1}{(n+l+m)^2}$$

* compute $\langle \psi | \frac{1}{r^2} | \psi \rangle$

$$\frac{\partial H}{\partial l} = -\frac{\hbar^2}{2m}\left(-\frac{2l+1}{r^2}\right)$$

$$\langle \psi | \frac{1}{r^2} | \psi \rangle = \frac{2m}{\hbar^2}\frac{1}{(2l+1)}\langle \psi | \frac{\partial H}{\partial l} | \psi \rangle$$

$$\frac{2m}{\hbar^2}\frac{1}{(2l+1)}\left(-\frac{Z^2 e^4 m}{2\hbar^2}\right)(-2)\frac{1}{(n+l+1)^3}$$

$$\frac{2m^2 Z^2 e^4}{\hbar^4}\frac{1}{(2l+1)}\frac{1}{(n+l+1)^3}$$

Another similar theorem is called the Virial theorem

This theorem related to expectation value of the kinetic and potential energy in eigenstates of the Hamiltonian for potentials of the form

$V(r) = \alpha r^n$

consider

$$H = \frac{p^2}{2m} + \alpha r^n$$

$$[\bar{p} \cdot \bar{r}, H] =$$

$$[\bar{p}, H] \cdot \bar{r} + \bar{p} \cdot [\bar{r}, H]$$

for the Hamiltonian above

$$[\bar{p}, H] = -i\alpha\hbar \bar{\nabla}(r^n)$$

$$[r, H] = \frac{1}{2m}[\bar{r}, p^2] = \frac{i\hbar}{2m} 2\bar{p}$$

putting these together

gives

$$[\bar{p}\cdot\bar{r}, H] = -i\alpha\hbar\, \bar{r}\cdot\bar{\nabla}(r^n) + \frac{2i\hbar}{2m}\bar{p}\cdot\bar{p}$$

$$= i\hbar\left(-n\alpha r^n + \frac{p^2}{m}\right)$$

evaluating this commutator

in eigenstate of H gives

$$0 = (E-E)\langle\psi|\bar{p}\cdot\bar{r}|\psi\rangle =$$

$$= i\hbar\left(-n\alpha r^n + \frac{p^2}{m}\right)$$

canceling the $i\hbar$ and

using

$$V = \alpha r^n \quad ; \quad T = KE = \frac{p^2}{2m}$$

this becomes

$$0 = -n\langle\psi|V|\psi\rangle + 2\langle\psi|T|\psi\rangle$$

$$\boxed{2\langle\psi|T|\psi\rangle = n\langle\psi|V|\psi\rangle}$$

This can be combined with energy conservation

$$\langle\psi|H|\psi\rangle = E = \langle\psi|T|\psi\rangle + \langle\psi|V|\psi\rangle$$

$$2\langle\psi|T|\psi\rangle = n\langle\psi|V|\psi\rangle$$

This can be used to express the expectation value of T and V in terms of the energy eigenvalue E

$$E = \langle\psi|T|\psi\rangle + \frac{2}{n}\langle\psi|T|\psi\rangle$$

$$= \left(1+\frac{2}{n}\right)\langle\psi|T|\psi\rangle$$

$$\boxed{\langle\psi|T|\psi\rangle = \left(\frac{n}{n+2}\right)E}$$

$$E = \frac{n}{2}\langle\psi|V|\psi\rangle + \langle\psi|V|\psi\rangle$$

$$= \left(1+\frac{n}{2}\right)\langle\psi|V|\psi\rangle$$

$$\boxed{\langle\psi|V|\psi\rangle = \frac{2}{n+2}E}$$

For $n=-1$ (one electron atom)

$$\langle\psi|V|\psi\rangle = 2E = -2\langle\psi|T|\psi\rangle$$

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

which agrees with the result of using the Hellmann Feynman theorem.

The advantage of both of these theorems is that the results do not require performing an integration — they give useful information on the energy is distributed in terms of potential and kinetic terms

Rayleigh Schrodinger perturbation theory

Assume

$$H = H_0 + V$$

where H_0 is simple to solve and V is "small".

Rayleigh Schrodinger perturbation theory constructs solutions to the eigenvalue problem

$$H|\Psi\rangle = E|\Psi\rangle$$

starting with solutions of

$$H_0|\Psi^0\rangle = E^0|\Psi^0\rangle$$

and constructing correction is powers of the small interaction V.

In order to keep track of powers of V we replace H by

$$H(\lambda) = H_0 + \lambda V$$

(eventually we will let $\lambda \to 1$)

the starting approximation is the unperturbed solution

$$H_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle$$

where we can choose the $|\psi_n^0\rangle$ for different n to be orthogonal. Next we assume the solutions to

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

can be represented as a series in powers of V

$$|\Psi_n\rangle = |\Psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\Psi_n^m\rangle$$

$$E_n = E_n^0 + \sum_{m=1}^{\infty} \lambda^m E_n^m$$

substituting these expansions in the Schrodinger equation gives

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\Psi_n^m\rangle + V \sum_{m=0}^{\infty} \lambda^{m+1} |\Psi_n^m\rangle =$$

$$\sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} \lambda^{k+\ell} |\Psi_n^k\rangle E_n^\ell$$

In the second term let $m' = m+1$ and in the third term let $m = k+\ell$

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\Psi_n^m\rangle + \sum_{m'=1}^{\infty} \lambda^{m'} V |\Psi_n^{m'-1}\rangle =$$

$$\sum_{m=0}^{\infty} \sum_{k=0}^{m} \lambda^m |\Psi_n^k\rangle E_n^{m-k}$$

equating equal power of λ gives the following relations

$$\boxed{\begin{aligned} &H_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle \qquad m=0 \\ &H_0 |\psi_n^m\rangle + V|\psi_n^{m-1}\rangle = \qquad m>0 \\ &\sum_{k=0}^{m} |\psi_n^k\rangle E_n^{m-k} \end{aligned}}$$

The $m=0$ equation is satisfied by assumption. It is useful to write the second equation in the form

$$(H_0 - E_n^0)|\psi_n^m\rangle - |\psi_n^0\rangle E^m =$$
$$-V|\psi_n^{m-1}\rangle + \sum_{k=1}^{m-1} |\psi_n^k\rangle E_n^{m-k}$$

all of the term on the right side of this equation involve $|\psi_n^k\rangle\ E_n^k$ for $k<m$.

observations

(1) If $|\psi_n^m\rangle$ is a solution to the equation on the last page, so is

$$|\psi_n^m\rangle + \eta |\psi_n^0\rangle$$

where η is an arbitrary constant

* This ambiguity can be avoided by requiring

$$\boxed{\langle \psi_n^m | \psi_n^0 \rangle = 0 \quad \text{all } m > 0}$$

(2) With this assumption

$$|\psi_n\rangle = |\psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\psi_n^m\rangle$$

both $|\psi_n\rangle$ and $|\psi_n^0\rangle$ cannot both be normalized to 1 unless

$$\left\| \sum_{m=1} \lambda^m |\psi_n^m\rangle \right\| = 0$$

we choose normalization s.

$$\boxed{\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}}$$

This means that once we find $|\Psi\rangle$ it must be re-normalized:

$$\boxed{|\Psi\rangle \to |\Psi\rangle / \langle\Psi|\Psi\rangle^{1/2}}$$

given $\langle\Psi_n^0|\Psi_m^0\rangle = \delta_{mn}$ $\langle\Psi_n^0|\Psi_n^k\rangle = 0$ $k>0$

we can solve the equation for $|\Psi_n^m\rangle$, E_n^m.

we start by considering the case $m=1$

$$(H_0 - E_n^0)|\Psi_n^1\rangle - E_n^1|\Psi_n^0\rangle =$$

$$-V|\Psi_n^0\rangle$$

To find E_n^1 multiply by $\langle\Psi_n^0|$

$$\underbrace{\langle\Psi_n^0|(H_0 - E_n^0)|\Psi_n^1\rangle}_{0} - E_n^1\langle\Psi_n^0|\Psi_n^0\rangle =$$

$$-\langle\Psi_n^0|V|\Psi_n^0\rangle$$

This gives

$$\boxed{E_n^1 = \langle \psi_n^0 | V | \psi_n^0 \rangle}$$

$$E = E_n^0 + \langle \psi_n^0 | V | \psi_n^0 \rangle + \cdots$$

(to get this we used $\langle \psi_n^0 | \psi_n^0 \rangle = 1$)

next multiply both sides by $\langle \psi_m^0 |$ $\quad m \neq n$

$$(E_m^0 - E_n^0)\langle \psi_m^0 | \psi_n^1 \rangle - \overbrace{\langle \psi_m^0 | E_n^1 | \psi_n^0 \rangle}^{0 \quad m \neq n}$$

$$= -\langle \psi_m^0 | V | \psi_n^0 \rangle$$

this gives

$$\langle \psi_m^0 | \psi_n^1 \rangle = -\frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_m^0 - E_n^0}$$

$$= \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

since

$\langle \psi_m^0 | \psi_n^0 \rangle = 0 \quad n \neq m$ we get

$$\boxed{\begin{aligned} |\psi_n^1\rangle &= \sum_m |\psi_m^0\rangle\langle \psi_m^0 | \psi_n^1 \rangle \\ &= \sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_0^n - E_0^m} \end{aligned}}$$

Now we know E_n^1 $|\Psi_n^1\rangle$. We use this information to calculate E_n^2 and $|\Psi_n^2\rangle$

the starting point is

$$(H_0 - E_n^0)|\Psi_n^2\rangle - E_n^2|\Psi_n^0\rangle =$$
$$-V|\Psi_n^1\rangle + |\Psi_n^1\rangle E_n^1$$

as in the $m=1$ case

first multiply by $\langle\Psi_n^0|$ —

$\langle\Psi_n^0|H_0 - E_n^0|\Psi_n^2\rangle = 0 \Longrightarrow$

$$-E_n^2 = -\langle\Psi_n^0|V|\Psi_n^1\rangle + \underbrace{\langle\Psi_n^0|\Psi_n^1\rangle}_{0} E_n^1$$

$$E_n^2 = \langle\Psi_n^0|V|\Psi_n^1\rangle =$$
$$\sum_{m\neq n}\frac{\langle\Psi_n^0|V|\Psi_m^0\rangle\langle\Psi_m^0|V|\Psi_n^0\rangle}{E_n^0-E_m^0}$$
$$= \sum_{m\neq n}\frac{|\langle\Psi_n^0|V|\Psi_m^0\rangle|^2}{E_n-E_m}$$

note that if E_n^0 is the ground state the first order correction is negative (consistent with variational method)

We can also compute the second order wave function using $\langle \psi_m^0 |$ $m \neq n$

$$\langle \psi_m^0 | (H_0 - E_n^0) | \psi_n^2 \rangle - \overbrace{E \langle \psi_m^0 | \psi_n^0 \rangle}^{0}$$

$$- \langle \psi_m^0 | V | \psi_m^1 \rangle + E_n^1 \langle \psi_m^0 | \psi_n^1 \rangle =$$

$$(E_m^0 - E_n^0) \langle \psi_m^0 | \psi_n^2 \rangle =$$

$$-\sum_{k \neq n} \frac{\langle \psi_m^0 | V | \psi_k^0 \rangle \langle \psi_n^0 | V | \psi_n^0 \rangle}{(E_n^0 - E_n^0)}$$

$$- \langle \psi_n^0 | V | \psi_n^0 \rangle \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n - E_m}$$

dividing by the $(E_n^0 - E_m^0)$ give an expression for $\langle \psi_m^0 | \psi_n^2 \rangle$

$$\langle \psi_m^0 | \psi_n^2 \rangle = \frac{1}{(E_n^0 - E_m^0)} \left\{ \sum_{k \neq n} \frac{\langle \psi_m^0 | V | \psi_k^0 \rangle \langle \psi_k^0 | V | \psi_n^0 \rangle}{(E_n - E_m)(E_n - E_k)} - \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle \langle \psi_n^0 | V | \psi_n^0 \rangle}{(E_n - E_m)^2} \right\}$$

this can be used to expand

$$|\psi_n^2\rangle = \sum_{m \neq n} |\psi_m^0\rangle \underbrace{\langle \psi_m^0 | \psi_n^2 \rangle}_{\text{above}}$$

while it is possible to continue to any order, normally the first order energy is enough.

If $\langle \psi_n^0 | V | \psi_n^0 \rangle = 0$ then the second order energy should be good approximation assuming V is small.