Lecture #13

Although the variational principle is powerful and particularly useful in quantum chemistry, it suffers from a few limitations:

(1) You never know how close you are to E_{gs}; rather, you just know an upper bound for E_{gs}

(2) You don't know how close your test wave function is to the actual wave function

(3) In most cases, you can only find an upper bound for E_{gs}; the excited state energies remain unknown.

Consequently, other approximation methods are needed:

Nondegenerate Time-Independent Perturbation Theory

Suppose we know the stationary state solutions to the Sch. Eq. for some potential:

$$H^{\circ}\psi_n^{\circ} = E_n^{\circ}\psi_n^{\circ}$$

Now we perturb the potential slightly.

i.e., $H = H^{\circ} + \lambda H'$ This just keeps track of the order of the correction (we will set it equal to 1 later)

We want to find the new solutions:

$$H\psi_n = E_n\psi_n$$

WE WILL APPROXIMATE THESE SOLUTIONS BY BUILDING ON THE KNOWN EXACT SOLUTIONS TO THE UNPERTURBED CASE.

TO BEGIN, WE WRITE ψ_n AND E_n AS POWER SERIES IN λ:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

E_n^1, ψ_n^1 ARE FIRST ORDER CORRECTIONS

E_n^2, ψ_n^2 ARE SECOND ORDER CORRECTIONS

$\therefore$ THE SCH. EQ. THEN BECOMES:

$$(H^0 + \lambda H^1)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$

TERMS OF ORDER λ^0: $\quad H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad$ (WE KNEW THAT)

ORDER λ^1: $\quad H^0 \psi_n^1 + H^1 \psi_n^0 = E_n^1 \psi_n^0 + E_n^0 \psi_n^1$

ORDER λ^2: $\quad H^0 \psi_n^2 + H^1 \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

FIRST ORDER THEORY: TAKE INNER PRODUCT OF ORDER λ^1 WITH ψ_n^0:

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H^1 | \psi_n^0 \rangle = E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{=1} + E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

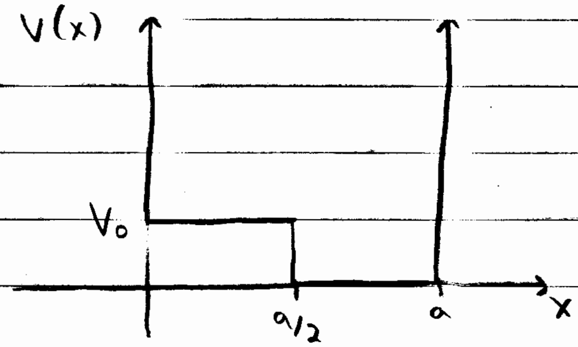
SINCE H^0 IS HERMITIAN,

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$\therefore$ $\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}$

i.e., THE FIRST ORDER CORRECTION TO THE ENERGY IS THE EXPECTATION VALUE OF THE PERTURBATION, IN THE UNPERTURBED STATE.

FOR EXAMPLE, CONSIDER THE FOLLOWING POTENTIAL:



PERTURBED INFINITE POTENTIAL WELL IN 1-D

$$H' = \begin{cases} V_0 , & 0 < x < a/2 \\ 0 , & \text{OTHERWISE} \end{cases} \qquad \psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$\therefore \quad E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2V_0}{a}\left(\frac{a}{4}\right) = \frac{V_0}{2}$$

i.e., TO FIRST ORDER, ALL ENERGY LEVELS ARE LIFTED BY $\frac{V_0}{2}$

WITH PERTURBATION THEORY, WE CAN ALSO FIND CORRECTIONS TO THE WAVEFUNCTIONS. TO FIRST ORDER,

REWRITE THE ORDER λ^1 EQUATION: $(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$

SINCE ψ_n^0 ARE COMPLETE, WE CAN EXPRESS ψ_n^1 AS:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0$$

COEFFICIENTS FOR THE CORRECTION TO THE WAVEFUNCTION FOR THE nth STATE

OMIT THE REDUNDANT TERM

$$\therefore \sum_{m\neq n} (E_m^\circ - E_n^\circ) c_m^{(n)} \psi_m^\circ = -(H' - E_n')\psi_n^\circ$$

TAKE INNER PRODUCT WITH ψ_ℓ°:

$$\sum_{m\neq n} (E_m^\circ - E_n^\circ) c_m^{(n)} \langle \psi_\ell^\circ | \psi_m^\circ \rangle = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle + E_n' \langle \psi_\ell^\circ | \psi_n^\circ \rangle$$

IF $\ell = n$, WE RECOVER THE FIRST ORDER ENERGY CORRECTION.

IF $\ell \neq n$, $\langle E_\ell^\circ - E_n^\circ \rangle c_\ell^{(n)} = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle$

$$\Rightarrow \quad c_m^{(n)} = \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ}$$

$$\therefore \boxed{\psi_n' = \sum_{m\neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{(E_n^\circ - E_m^\circ)} \psi_m^\circ}$$

THIS EQUATION IS OKAY AS LONG AS THERE ARE NO DEGENERATE ENERGY LEVELS. IN THAT CASE, YOU NEED DEGENERATE PERTURBATION THEORY

<u>SECOND ORDER THEORY</u>: TAKE INNER PRODUCT OF ORDER λ^2 WITH ψ_n°:

$$\langle \psi_n^\circ | H^\circ | \psi_n^2 \rangle + \langle \psi_n^\circ | H' | \psi_n' \rangle$$
$$= E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle + E_n' \langle \psi_n^\circ | \psi_n' \rangle + E_n^2 \underbrace{\langle \psi_n^\circ | \psi_n^\circ \rangle}_{=1}$$

AGAIN EXPLOIT HERMITICITY OF H°:

$$\langle \psi_n^\circ | H^\circ | \psi_n^2 \rangle = \langle H^\circ \psi_n^\circ | \psi_n^2 \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle$$

$$\therefore\ E_n^2 = \langle \psi_n^\circ | H' | \psi_n' \rangle - E_n' \langle \psi_n^\circ | \psi_n' \rangle$$

BUT, $\langle \psi_n^\circ | \psi_n' \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^\circ | \psi_m^\circ \rangle = 0$

$$\therefore\ E_n^2 = \langle \psi_n^\circ | H' | \psi_n' \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^\circ | H' | \psi_m^\circ \rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle \langle \psi_n^\circ | H' | \psi_m^\circ \rangle}{E_n^\circ - E_m^\circ}$$

$$\therefore\ \boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^\circ | H' | \psi_n^\circ \rangle|^2}{E_n^\circ - E_m^\circ}}$$