LECTURE #12

FOR ANY ATOM MORE COMPLICATED THAN HYDROGEN, WE CANNOT SOLVE THE SCHRODINGER EQUATION EXACTLY. HENCE, WE NEED APPROXIMATION TECHNIQUES. THE FIRST THAT WE WILL CONSIDER IS THE VARIATIONAL PRINCIPLE

VARIATIONAL PRINCIPLE: WITH A REASONABLE GUESS FOR THE GROUND STATE WAVEFUNCTION, AN UPPER BOUND CAN BE CALCULATED FOR THE GROUND STATE ENERGY E_{gs}

PICK ANY NORMALIZED WAVEFUNCTION ψ

$$E_{gs} \le \langle \psi | H | \psi \rangle = \langle H \rangle$$

PROOF: $\underbrace{\psi = \sum_n c_n \psi_n}_{\text{SINCE } \psi_n \text{ ARE COMPLETE}}$ WITH $H\psi_n = E_n \psi_n$

SINCE ψ IS NORMALIZED,

$$1 = \langle \psi | \psi \rangle = \langle \sum_m c_m \psi_m \,|\, \sum_n c_n \psi_n \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$$

MEANWHILE,

$$\langle H \rangle = \langle \sum_m c_m \psi_m \,|\, H \sum_n c_n \psi_n \rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

BUT, THE GROUND STATE ENERGY IS THE SMALLEST EIGENVALUE.

$$\Rightarrow E_{gs} \le E_n$$

$$\therefore \langle H \rangle \ge E_{gs} \sum_n |c_n|^2 = E_{gs}$$ ← VARIATIONAL PRINCIPLE

THE STRATEGY IS TO GUESS $\psi(\alpha)$, WHICH DEPENDS ON SOME PARAMETER(S) α, AND CALCULATE:

$$\frac{d}{d\alpha}\langle H\rangle = 0$$

TO FIND THE MINIMUM. THE MINIMUM VALUE OF $\langle H\rangle$ REPRESENTS AN UPPER BOUND ON E_{gs}.

EXAMPLE: 1-D DELTA-FUNCTION WELL:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\,\delta(x)$$

A NICE GUESS ("TRIAL WAVEFUNCTION") IS A GAUSSIAN:

$$\psi(x) = Ae^{-bx^2}$$

FIRST DETERMINE A THROUGH NORMALIZATION:

$$1 = |A|^2\int_{-\infty}^{\infty} e^{-2bx^2}dx = |A|^2\sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$$

NEXT CALCULATE $\langle H\rangle = \langle T\rangle + \langle V\rangle$

$$\langle T\rangle = -\frac{\hbar^2}{2m}|A|^2\int_{-\infty}^{\infty} e^{-bx^2}\underbrace{\frac{d^2}{dx^2}\left(e^{-bx^2}\right)}_{\underbrace{\frac{d}{dx}\left(-2bx\,e^{-bx^2}\right)}_{\left(4b^2x^2e^{-bx^2}-2b\,e^{-bx^2}\right)}}dx$$

$$\therefore \langle T\rangle = \frac{\hbar^2}{m}|A|^2 b\int_{-\infty}^{\infty}(1-2bx^2)\,e^{-2bx^2}dx$$

NOTE: $\int_{-\infty}^{\infty} x^2 e^{-ax^2}\,dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

$$\therefore \langle T \rangle = \frac{\hbar^2}{m}|A|^2 b\left(\sqrt{\frac{\pi}{2b}} - 2b\left(\frac{1}{4b}\right)\sqrt{\frac{\pi}{2b}}\right)$$

$\sqrt{\frac{2b}{\pi}}$ (NORMALIZATION)

$$\therefore \langle T \rangle = \frac{\hbar^2}{2m} b$$

$$\langle V \rangle = -\alpha |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\delta(x)\,dx = -\alpha |A|^2 = -\alpha\sqrt{\frac{2b}{\pi}}$$

$$\therefore \langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}$$

MINIMIZE: $\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4}$

$$\therefore \langle H \rangle_{min} = \frac{\hbar^2}{2m}\left(\frac{2m^2\alpha^2}{\pi\hbar^4}\right) - \alpha\sqrt{\frac{2}{\pi}}\sqrt{\frac{2m^2\alpha^2}{\pi\hbar^4}} = \frac{m\alpha^2}{\pi\hbar^2} - \frac{2m\alpha^2}{\pi\hbar^2} = -\frac{m\alpha^2}{\pi\hbar^2}$$

RECALL: THE EXACT RESULT: $E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$

SO, THE APPROXIMATE VALUE IS INDEED SLIGHTLY HIGHER THAN E_{gs} SINCE $\pi > 2$

VARIATIONAL PRINCIPLE IS VERY POWERFUL AND EASY TO USE. TO FIND THE GROUND STATE ENERGY OF COMPLICATED MOLECULES, PHYSICAL CHEMISTS WRITE DOWN A TRIAL WAVEFUNCTION WITH A LARGE NUMBER OF ADJUSTABLE PARAMETERS, CALCULATE $\langle H \rangle$, AND THEN TWEAK THE PARAMETERS TO GET THE LOWEST POSSIBLE VALUE.

LET'S TRY HELIUM:

HELIUM: 2 ELECTRONS, 2 PROTONS, 2 NEUTRONS

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

IF WE IGNORE THE $e^- - e^-$ REPULSION, THE HAMILTONIAN SPLITS INTO TWO INDEPENDENT HYDROGEN HAMILTONIANS (WITH NUCLEAR CHARGE $2e$). IN THIS CASE, THE EXACT SOLUTION IS THE PRODUCT OF TWO HYDROGENIC WAVE FUNCTIONS:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1 + r_2)/a}$$

AND $E_{gs} = 8E_1 = 8(-13.6\,eV) = -109\,eV$

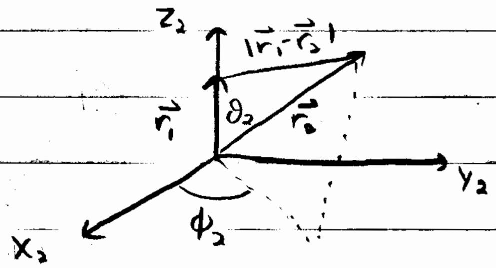
BUT THE EXPERIMENTAL VALUE IS $E_{gs} = -79\,eV$

SO, WE NEED TO ACCOUNT FOR THE $e^- - e^-$ INTERACTION.

LET'S TRY VARIATIONAL PRINCIPLE WITH ψ_0 AS OUR TRIAL WAVE FUNCTION:

$$H\psi_0 = (8E_1 + V_{ee})\psi_0 \Rightarrow \langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

WHERE $\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4(r_1 + r_2)/a}}{|\vec{r}_1 - \vec{r}_2|}\, d^3\vec{r}_1\, d^3\vec{r}_2$



LAW OF COSINES:
$|\vec{r}_1 - \vec{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}$

PERFORM THE $\vec{r}_2$ INTEGRAL FIRST:

$$I_2 = \int \frac{e^{-4r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} r_2^2 \sin\theta_2 \, dr_2 \, d\theta_2 \, d\phi_2$$

ϕ_2 INTEGRAL IS 2π

θ_2 INTEGRAL IS: $\displaystyle\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} d\theta_2 = \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1 r_2}\Bigg|_0^\pi$

$$= \frac{1}{r_1 r_2}\left(\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right)$$

$$= \frac{1}{r_1 r_2}\left((r_1+r_2) - |r_1 - r_2|\right) = \begin{cases} 2/r_1 & \text{IF } r_2 < r_1 \\ 2/r_2 & \text{IF } r_2 > r_1 \end{cases}$$

$$\therefore I_2 = 4\pi\left(\frac{1}{r_1}\int_0^{r_1} e^{-4r_2/a} r_2^2 \, dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2 \, dr_2\right)$$

$$\rightarrow \frac{\pi a^3}{8 r_1}\left[1 - \left(1 + \frac{2r_1}{a}\right)e^{-4r_1/a}\right]$$

$$\therefore \langle V_{ee}\rangle = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{8}{\pi a^3}\right)\int\left[1-\left(1+\frac{2r_1}{a}\right)e^{-4r_1/a}\right]e^{-4r_1/a} r_1 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$$

ANGULAR INTEGRALS ARE 4π

r_1 INTEGRAL IS: $\displaystyle\int_0^\infty \left[r_1 e^{-4r_1/a} - \left(r_1 + \frac{2r_1^2}{a}\right)e^{-8r_1/a}\right] dr_1 = \frac{5a^2}{128}$

$$\therefore \langle V_{ee}\rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5}{2}E_1 = 34\,\text{eV} \qquad \left(E_1 = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{2a}\right)$$

$$\therefore \langle H\rangle = -109\,\text{eV} + 34\,\text{eV} = -75\,\text{eV}$$

THIS IS CLOSE TO EXPERIMENT (−79 eV), BUT WE CAN DO BETTER:

WE NEED A MORE REALISTIC TRIAL WAVEFUNCTION THAT SOMEHOW ACCOUNTS FOR THE INFLUENCE OF THE OTHER ELECTRON.

EACH e^- REPRESENTS A CLOUD OF NEGATIVE CHARGE THAT PARTIALLY SHIELDS THE NUCLEUS, SO THE OTHER e^- SEES AN EFFECTIVE NUCLEAR CHARGE Z THAT IS LESS THAN 2.

$\Rightarrow$ NEW TRIAL WAVEFUNCTION: $\psi_1(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$

THIS WAVEFUNCTION IS AN EIGENSTATE OF THE HYDROGENIC HAMILTONIAN WITH NUCLEAR CHARGE Z. THEREFORE, LET'S WRITE THE HELIUM HAMILTONIAN AS:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)$$
$$+ \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

$$\therefore \langle H \rangle = 2Z^2 E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

WHERE $\langle \frac{1}{r} \rangle$ IS THE EXPECTATION VALUE OF $\frac{1}{r}$ IN THE HYDROGENIC GROUND STATE ψ_{100} WITH NUCLEAR CHARGE Z

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad \text{(SEE PROBLEM 6.12 OF GRIFFITHS)}$$

$\langle V_{ee} \rangle$ IS THE SAME AS BEFORE EXCEPT NOW WE WANT ARBITRARY Z INSTEAD OF $Z=2$

$$\Rightarrow \text{MULTIPLY } a \text{ BY } \frac{2}{Z} \Rightarrow \langle V_{ee} \rangle = \frac{5Z}{8a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5Z}{4} E_1$$

$$\therefore \langle H \rangle = 2Z^2E_1 + 2(Z-2)\underbrace{\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{Z}{a}}_{-2ZE_1} - \frac{5}{4}ZE_1$$

$$\therefore \langle H \rangle = \left(2Z^2 - 4Z(Z-2) - \frac{5}{4}Z\right)E_1 = \left(-2Z^2 + \frac{27}{4}Z\right)E_1$$

MINIMIZE $\langle H \rangle$:

$$\frac{d}{dZ}\langle H \rangle = \left(-4Z + \frac{27}{4}\right)E_1 = 0 \Rightarrow Z = \frac{27}{16} = 1.69$$

THIS IS REASONABLE SINCE WE WOULD EXPECT SCREENING TO REDUCE THE EFFECTIVE NUCLEAR CHARGE BELOW 2.

PLUGGING $Z = \frac{27}{16}$ INTO $\langle H \rangle$ YIELDS:

$$\langle H \rangle = \left[-2\left(\frac{27}{16}\right)^2 + \left(\frac{27}{4}\right)\left(\frac{27}{16}\right)\right](-13.6\,eV) = -77.5\,eV$$

WE ARE NOW WITHIN 2% OF THE EXPERIMENTAL VALUE.

IF DESIRED, EVEN GREATER ACCURACY CAN BE ACHIEVED WITH MORE COMPLICATED TRIAL WAVEFUNCTIONS WITH MORE ADJUSTABLE PARAMETERS.