Lecture 13

The variational principle

The variational principle let you get an **upper bound** for the ground state energy when you can not directly solve the Schrödinger's equation.

How does it work?

(1) Pick any normalized function ψ .

(2) The ground state energy E_{gs} is

$$\boxed{E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle}$$

3) Some choices of the trial function ψ will get your E_{gs} that is close to actual value.

The ground state of Helium

Two electrons orbiting the nucleus with charge Z=2.

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\frac{\overset{Z=2}{2}}{r_1} - \frac{e^2}{4\pi\epsilon_0}\frac{\overset{Z=2}{2}}{r_2}$$

$$+ \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\bar{r}_1 - \bar{r}_2|} \longleftarrow \text{Electron-electron repulsion term}$$

(ignoring fine structure and smaller corrections).

Experimental result: $E_{gs} = -78.975\,eV$

Our task: use variational principle to get as close as possible to experimental result.

If we ignore term

$$\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{|\bar{r}_1-\bar{r}_2|}$$

our problem reduces to two independent Hydrogen-like hamiltonians with Z=2. In this case, the solution for the ground state is just a product of two hydrogen ground state wave functions with Z=2.

$$\psi_0(\vec{r}_1,\vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3}\,e^{-2(r_1+r_2)/a} \qquad (1)$$

The energy is just the sum of two hydrogen-like energies with Z=2:

$$E_n = \frac{Z^2 E_1}{n^2} \qquad n=1,\ Z=2 \qquad E_{100} = 4E_1,$$

$$E_1 = -13.6\ \text{eV} \qquad \Rightarrow$$

$$E_{He} = 2E_{100} = 8E_1 = -109\ \text{eV}.$$

Rather far from experiment value of -79eV.

To get a better approximation, we apply variational principle with trial function (1).

We need to calculate the expectation value $\langle\psi_0|H|\psi_0\rangle$.

$$H = \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\,\frac{}{r_1} - \frac{e^2}{4\pi\epsilon_0}\,\frac{2}{r_2}}_{\text{Hydrogen-like } H_0} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{|\bar{r}_1-\bar{r}_2|}}_{V_{ee}}$$

$$\boxed{H_0\psi_0 = 8E_1\psi_0} \quad \Rightarrow$$

$$H\psi_0 = (H_0+V)\psi_0 = (8E_1 + V_{ee})\psi_0$$

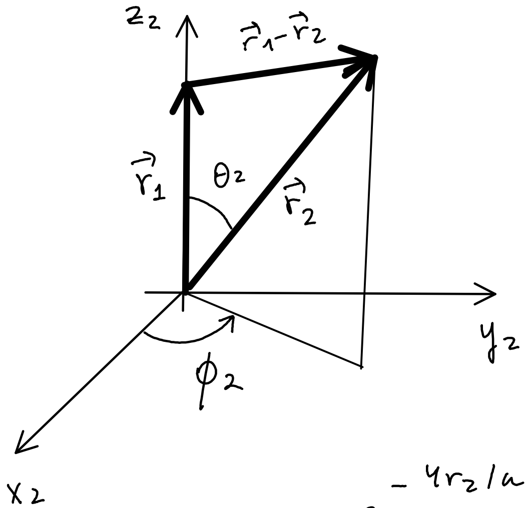
$$\langle\psi_0|H|\psi_0\rangle = 8E_1\overset{1}{\cancel{\langle\psi_0|\psi_0\rangle}} + \langle\psi_0|V_{ee}|\psi_0\rangle$$

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

$$\langle V_{ee} \rangle = \langle \psi_0 | V_{ee} | \psi_0 \rangle$$

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

We calculate $\vec{r}_2$ integral first, we orient our coordinate system so z_2 is along $\vec{r}_1$.



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

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2$$

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

Integral over ϕ_2 gives 2π.

Integral over θ_2 is

$$\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} d\theta_2 = \left.\frac{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}{r_1 r_2}\right|_0^\pi$$

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

$$= \frac{1}{r_1 r_2}\left((r_1+r_2) - |r_1-r_2| \right) = \begin{cases} \frac{1}{r_1 r_2}[r_1+r_2 - r_1 + r_2] & r_2<r_1 \\ \frac{1}{r_1 r_2}[r_1+r_2 + r_1 - r_2] & r_2>r_1 \end{cases}$$

$$= \begin{cases} \frac{2}{r_1} & \text{if} \quad r_2<r_1 \\ \frac{2}{r_2} & \text{if} \quad r_2>r_1 \end{cases}$$

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

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

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0}\left(\frac{8}{\pi a^3}\right) \int \left[1 - \left(1+\frac{2r_1}{a}\right) e^{-4r_1/a} \right] e^{-4r_1/a} \times$$

$$r_1 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$$

Angular integrals give 4π, integral over r_1 gives $\frac{5a^2}{128}$.

$$\langle V \rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5}{2} E_1 = 34 \text{ eV}$$

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

Much closer to -79 eV!
We can do even better!