Lecture 18

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).

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

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:

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

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

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

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 $\langle\psi_0|H|\psi_0\rangle$.

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

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

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

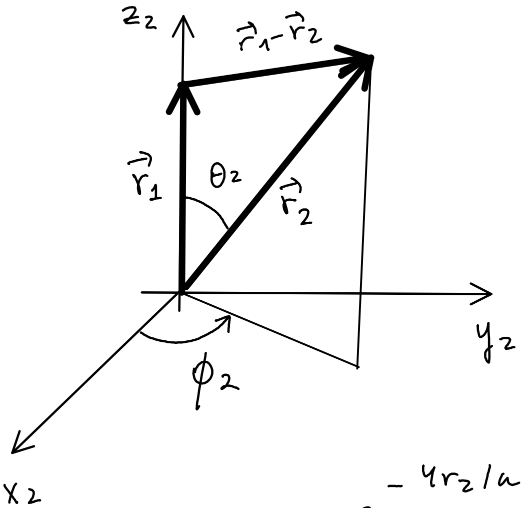
$$\langle\psi_0|H|\psi_0\rangle=8E_1\underbrace{\langle\psi_0|\psi_0\rangle}_{1}+\langle\psi_0|V_{ee}|\psi_0\rangle$$

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

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

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

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

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

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

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

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

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

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

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

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

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!

The ground state of Helium: how to improve the result?

Our initial trial function was:

$$\psi_0 = \frac{8}{\pi a^3} e^{-\overset{\swarrow Z}{2}(r_1+r_2)/a}$$

Now, we take

$$\boxed{\psi_0 = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}}$$

and take Z to be a parameter. We re-write the Hamiltonian as

$$H = \underbrace{\boxed{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)}}_{H_0}$$

our ψ_0 is eigenfunction of this Hamiltonian

$$+ \underbrace{\frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2}\right)}_{H_1} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\bar{r}_1 - \bar{r}_2|}}_{V_{ee}}$$

Note, that we did not change our Hamiltonian (we are not allowed to do that in the variational method). We just added and subtracted

$$\frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right).$$

We now calculate the expectation value

$$\langle\psi_0|H|\psi_0\rangle = \langle\psi_0|H_0|\psi_0\rangle + \langle\psi_0|H_1|\psi_0\rangle + \langle\psi_0|V_{ee}|\psi_0\rangle.$$

with our "new" trial function

$$\psi_0 = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a} \equiv \underbrace{\psi_{100}(\bar{r}_1)\,\psi_{100}(\bar{r}_2)}_{\text{with charge } Z}$$

$$\langle\psi_0|H_0|\psi_0\rangle = \langle\psi_0|E_0\psi_0\rangle = 2E_1\frac{Z^2}{1^2}\overbrace{\langle\psi_0|\psi_0\rangle}^{1}$$

$$= 2E_1 Z^2$$

Note: if Z=2 $\quad\langle H_0\rangle = 2E_1\cdot 2^2 = 8E_1$ as before.

$$\langle\psi_0|H_1|\psi_0\rangle = \langle\psi_0|\frac{e^2}{4\pi\epsilon_0}\frac{Z-2}{r_1}|\psi_0\rangle + \langle\psi_0|\frac{e^2}{4\pi\epsilon_0}\frac{Z-2}{r_2}|\psi_0\rangle$$

$$= \frac{e^2}{4\pi\epsilon_0}(Z-2)\iint\psi^*_{100}(\vec r_1)\psi^*_{100}(\vec r_2)\frac{1}{r_1}\psi_{100}(\vec r_1)\psi_{100}(\vec r_2)\,d^3\vec r_1\,d^3\vec r_2$$

$$+\frac{e^2}{4\pi\epsilon_0}(Z-2)\iint\psi^*_{100}(\vec r_1)\psi^*_{100}(\vec r_2)\frac{1}{r_2}\psi_{100}(\vec r_1)\psi_{100}(\vec r_2)\,d^3\vec r_1\,d^3\vec r_2$$

$$= \frac{e^2}{4\pi\epsilon_0}(Z-2)\Big\{\underbrace{\int\psi^*_{100}(\vec r_1)\frac{1}{r_1}\psi_{100}(\vec r_1)\,d^3\vec r_1}_{\langle\psi_{1s}|\frac{1}{r}|\psi_{1s}\rangle\equiv\langle\frac{1}{r}\rangle_{1s}}\;\underbrace{\int\psi^*_{100}(\vec r_2)\psi_{100}(\vec r_2)\,d^3\vec r_2}_{\substack{1\\(\text{normalized})}}$$

$$+\underbrace{\int\psi^*_{100}(\vec r_1)\psi_{100}(\vec r_1)\,d^3\vec r_1}_{=1}\;\underbrace{\int\psi^*_{100}(\vec r_2)\frac{1}{r_2}\psi^*_{100}(\vec r_2)\,d^3\vec r_2}_{\langle\frac{1}{r}\rangle_{1s}}\Big\}$$

$$= 2\frac{e^2}{4\pi\epsilon_0}(Z-2)\left\langle\frac{1}{r}\right\rangle_{1s}$$

We need to calculate $\quad\left\langle\frac{1}{r}\right\rangle_{1s}\equiv\langle\psi_{1s}|\frac{1}{r}|\psi_{1s}\rangle$

$$\psi_{1s} = \sqrt{\frac{Z^3}{\pi a_0^3}}\,e^{-Zr/a_0}$$

where a_0 is the Bohr radius $\quad a_0\equiv\dfrac{4\pi\epsilon_0}{me^2}\hbar^2$

Note: $\quad a = \dfrac{4\pi\epsilon_0}{me^2Z}\hbar^2 = \dfrac{a_0}{Z}$ since $e^2\to e^2Z$ for H-like atoms.

$$\left\langle \frac{1}{r} \right\rangle_{1s} = \frac{Z^3}{\pi a_0^3} \int_0^\infty e^{-2Zr/a_0} \frac{1}{r} r^2 \, dr \underbrace{\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$= \frac{4\pi Z^3}{\pi a_0^3} \underbrace{\int_0^\infty e^{-2Zr/a_0} r \, dr}_{\frac{a_0^2}{4Z^2}} = \frac{4\cancel{\pi} Z^{\cancel{3}}}{\cancel{\pi} a_0^{\cancel{3}}} \frac{\cancel{a_0^2}}{4\cancel{Z^2}} = \frac{Z}{a_0}$$

We already calculated the third term:

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) \quad \text{(previous result)}$$

For our new trial function, $a \to 2a_0/Z$

$$\langle V_{ee} \rangle = \frac{5}{4a_0} \frac{Z}{2} \frac{e^2}{4\pi\epsilon_0} = \frac{5Z}{8a_0} \frac{e^2}{4\pi\epsilon_0}$$

Putting it all together, we get

$$\langle H \rangle = 2E_1 Z^2 + 2(Z-2)Z \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} + \frac{5Z}{8} \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$$

For convenience, let's express all terms via E_1:

$$E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$$

$$a_0 = \frac{4\pi\epsilon_0}{me^2} \hbar^2 = \left(\frac{e^2}{4\pi\epsilon_0} \right)^{-1} \frac{\hbar^2}{m} \implies$$

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} = \frac{e^2}{4\pi\epsilon_0} \frac{e^2}{4\pi\epsilon_0} \frac{m}{\hbar^2} = -2E_1$$

$$\langle H \rangle = 2E_1 Z^2 - 4E_1 (Z-2)Z - \frac{5}{4} Z E_1$$

$$= E_1 \left(2Z^2 - 4Z^2 + 8Z - \frac{5}{4} Z \right) = E_1 \left(-2Z^2 + \frac{27}{4} Z \right)$$

Therefore, for any Z

$$\langle H \rangle \geq E_{gs}$$

We yet the lowest upper bound when $\langle H \rangle$ is minimized, i.e. $\frac{d\langle H \rangle}{dZ} = 0$.

Class exercise: minimize $\langle H \rangle$. Find Z and get the lowest upper bound for E_{gs} (i.e. a number in eV).

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

$$Z = \frac{27}{16} = 1.69$$

$$\langle H \rangle = E_1 \left(-2Z^2 + \frac{27}{4} Z \right) = -13.6 \left(-2 \cdot (1.69)^2 + \frac{27}{4} 1.69 \right)$$

$$\langle H \rangle = -77.5 \text{ eV}$$

Even closer to the experimental value -79.0 eV!

Summary: variational method

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

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

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

If you picked a function with a parameter, minimize the resulting expression for $\langle H \rangle$. Substitute resulting value of the parameter into $\langle H \rangle$ to get lowest upper bound on E_{gs}.