QM Variational Examples Feb10

Variational Principle

$$E_\phi = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

Example 1

$$H = \frac{p^2}{2m} + V(x)$$

let $V(x)$ to be infinite square well situated at $x = a, x = -a$
We find a trial $\phi(x)$. Our trial function is better if it satisfy:

1. Symmetric
2. No nodes
3. Vanished at $x = \pm a$
   Try using trial function
   $\phi(x) = N(x-a)(x+a)$ for $x \leq a$, $\phi(x) = 0$ for $x > a$
   $\langle\phi|\phi\rangle = \int \mid \phi(x) \mid^2 \, dx = 1 \implies \text{fixes } N$
   $\langle\phi|H|\phi\rangle = \int \frac{\hbar^2}{2m} |\frac{d\phi}{dx}|^2 + V(x) \mid \phi(x) \mid^2 \, dx$
   Compute $E_\phi = \frac{\alpha\hbar^2}{ma^2}$ (find α)
   Find the exact $E_0 = \alpha_0 \frac{\hbar^2}{ma^2}$

Example 2: Helium Atom

$$H = -\frac{\hbar^2}{2m}\Delta_1 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2m}\Delta_2 - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

A digression on spin, statistics and symmetrization of identical particles in QM

In $d = 3$ space $+1$ time dimension, all identical particles come in two types:

Fermions	Bosons
Half integer spins	integer spins
Electrons ...	Photons, Gluons...

Fermions	Bosons
Fermi-Dirac Statistics	Bose_Einstein Statistics
Symmetric under exchange	Anti-Symmetric under exchange

Note:
$\vec{R}_i = (r_i m_{s_i})$ where r_i is position, m_{s_i} is the spin quantum number S_z if needed
Any wave function for N identical bosons:

$$\Psi_B(\vec{R}_1\vec{R}_2\ldots\vec{R}_i\ldots\vec{R}_j\ldots\vec{R}_N) = \Psi_B(\vec{R}_1\vec{R}_2\ldots\vec{R}_j\ldots\vec{R}_i\ldots\vec{R}_N)$$

Which is **Symmetric** under particle exchange.
Any wave function for N identical fermions:

$$\Psi_B(\vec{R}_1\vec{R}_2\ldots\vec{R}_i\ldots\vec{R}_j\ldots\vec{R}_N) = -\Psi_B(\vec{R}_1\vec{R}_2\ldots\vec{R}_j\ldots\vec{R}_i\ldots\vec{R}_N)$$

Which is **Anti-Symmetric** under particle exchange, and this anti-symmetry causes the **Pauli exclusion principle**.

Back to our Helium Problem

$$H = H_1 + H_2 + H_{12}$$

As a first step ignore H_{12}
We can try using Hydrogen ground state wave function
$\psi_{100}(\vec{r_1})\psi_{100}(\vec{r_2})$. However, this breaks our symmetry. So we have to change our spin state in combination with our wave function

$$\Psi = \psi_{100}(\vec{r_1})\psi_{100}(\vec{r_2})(\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}})$$

where

$$\psi_{100}(\vec{r}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$

This implies

$$\Psi(\vec{r_1}\vec{r_2}) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

Using Variational Method

$$\langle\Psi|(H_1+H_2)|\Psi\rangle = 2\left(-\frac{m(Ze^2)^2}{2\hbar^2}\right) \approx -108.8\text{eV}$$

Where the measured data is $E=-78.6\text{eV}$

- Note our variational method is **not** larger because we didn't account for H_{12}.
- Note, we can introduce a variational parameter. The variation parameter we can change is Z. This is because an electron will create a partial shielding for the other electron.