THE VARIATIONAL PRINCIPLE

At this point, we must have convinced ourselves that there are few quantum problems that we can solve completely. However, there are methods (perturbation theory, WKB...) that allow us to say something about complex systems. The variational principle offers us the way to find an <u>upper bound</u> to the ground energy of a system, without the need to know the solutions of the time-independent Schroedinger's equation. It is very simple: it states that given a generic state ψ, we have:

$$E_{\substack{\text{ground}\\\text{state}}} \leq \langle \psi | H | \psi \rangle$$

The proof is quite trivial: the (unknown!) solutions of Schroedinger's equation (i.e., the eigenfunctions of H) form a complete set, hence:

generic state

$$\psi = \sum_n c_n \psi_n$$

← eigenstate of H

Let us take the eigenstates ψ_n orthonormal

Since ψ is normalized, we have $\sum_n |c_n|^2 = 1$.

Finally:

$$\langle \psi | H | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| H \middle| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle$$

$$= \sum_n E_n |c_n|^2 \geq E_{\substack{\text{ground}\\\text{state}}} \cdot \sum |c_n|^2 = E_{\substack{\text{ground}\\\text{state}}}$$

$E_{\text{ground state}}$ is smallest among E_n: $E_{\substack{\text{ground}\\\text{state}}} \leq E_n \;\; \forall n$

Let us solve a traditional problem: ground state of Helium. To first order, it is an hydrogen atom with two protons:

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

Our trial function ψ will be built using the solutions of the hydrogen Hamiltonian:

$\psi = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$

Let us note that, if we discarded the e-e repulsion term $\propto \frac{1}{|r_1 - r_2|}$, ψ is <u>already</u> an eigenstate of the rest of the Hamiltonian, with eigenvalue:

$$E = \underbrace{8}_{\text{2 electrons, and } E \text{ of each electron is } \propto Z^2} E_1 \qquad \text{where } E_1 = -13.6\text{ eV}$$

Hence, $E = -109$ eV, quite far from experimental value : -78.975 eV.

Let us calculate the contribution of the electron interaction term:

$$\langle\psi|\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec{r}_1-\vec{r}_2|}|\psi\rangle =$$

remember : $\psi_{100}(\vec{r}) = \sqrt{\frac{Z^3}{\pi a^3}}\, e^{-\frac{Zr}{a}}$, a = Bohr radius

$$= \int d^3\vec{r}_1\, d^3\vec{r}_2 \left(\frac{e^2}{4\pi\varepsilon_0}\right)\cdot\left(\frac{8}{\pi a^3}\right)^2 e^{-\frac{4(r_1+r_2)}{a}} \cdot \frac{1}{|\vec{r}_1-\vec{r}_2|}$$

note that I replaced $Z = 2$ in the above expression.

Finally:

$$\int dr_2\, d\theta_2\, d\varphi_2\, \sin\theta_2 \cdot r_2^2\, e^{-\frac{4r_2}{a}} \cdot \frac{1}{(r_1^2+r_2^2-2r_1r_2\cos\theta_2)^{1/2}} =$$

$$= 2\pi \cdot \int r_2^2 e^{-\frac{4r_2}{a}} dr_2 \cdot \frac{1}{r_1 r_2}\left[(r_1^2+r_2^2-2r_1r_2\cos\theta_2)^{1/2}\right]_0^{\pi}$$

$$= 2\pi \cdot \int dr_2\, \frac{r_2}{r_1}\, e^{-\frac{4r_2}{a}} \underbrace{(r_1+r_2-|r_1-r_2|)}_{\substack{2r_2 \text{ if } r_1>r_2 \\ 2r_1 \text{ if } r_1<r_2}} =$$

$$= \frac{4\pi}{r_1}\int_0^{r_1} r_2^2\, e^{-4r_2/a}\, dr_2 + 4\pi\int_{r_1}^{\infty} r_2\, e^{-4r_2/a}\, dr_2$$

From this point on, the integrals are straightforward, but tedious (need to integrate polynomials times exponentials ...). Ultimately, we shall obtain:

$$\langle V_{EE} \rangle = \langle \psi | \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \psi \rangle = \frac{5}{4a} \cdot \frac{e^2}{4\pi\varepsilon_0} = -\frac{5}{2} E_1 = 34 \text{ eV}$$

Finally:

$$E = 8E_1 + \langle V_{EE} \rangle = -109 + 34 \text{ eV} = -75 \text{ eV}$$

already quite close to experimental measurement

We can do better if we treat Z as a variational parameter. Note that we will NOT modify the Hamiltonian, but we will rewrite it in a more convenient form, given our choice of trial wave function.

Trial wave

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1 + r_2)/a}$$

Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} \right) + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

re-arrange

$$= -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) +$$

$$+ \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

We do this because the trial function is an eigenstate of the Hamiltonian with Z, with eigenenergy $2Z^2 E_1$, while it is not an eigenstate of the Hamiltonian with the terms $\frac{2}{r_1}$ and $\frac{2}{r_2}$.

Therefore, we obtain:

$$\langle \psi | H | \psi \rangle = 2Z^2 E_1 + 2(Z-2) \frac{e^2}{4\pi\varepsilon_0} \cdot \left\langle \frac{1}{r} \right\rangle + \langle V_{EE} \rangle$$

We know these terms:

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}$$ (if the charge were 1, we would obtain the Bohr radius)

$$\langle V_{EE} \rangle = \frac{5}{4a} \cdot \frac{e^2}{4\pi\varepsilon_0} \longrightarrow \frac{5Z}{8a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5Z}{4} E_1$$

old value, when we had 2 instead of Z

replace Z=2 we did before with generic Z by multiplying by $\frac{Z}{2}$

Final result:

$$\langle \psi | H | \psi \rangle = \left[2Z^2 - 4Z(Z-2) - \frac{5}{4}Z \right] E_1$$

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

The expression above must be $\geq E_{\text{ground state}}$ <u>for any value of Z</u>: let us minimize it:

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

It makes sense physically: the presence of the other electron partially shields the charge of the nucleus, which thus appear having $Z < 2$.

If we now calculate $\langle H \rangle$, we obtain:

$$\langle H \rangle = \left(-2Z^2 + \frac{27}{4}Z \right) E_1 = -77.5 \text{ eV}$$

within 2% of the correct answer!