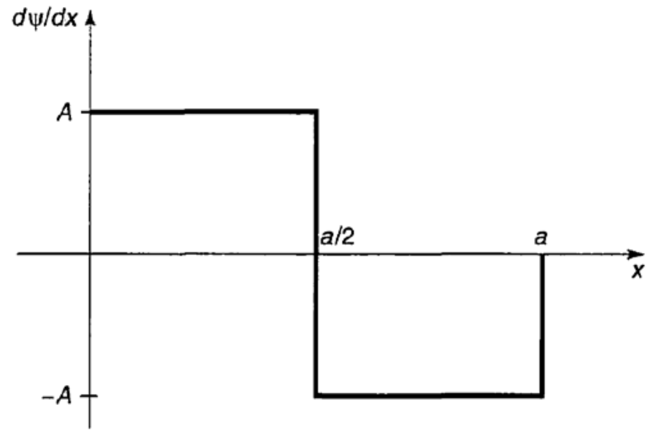
$$\frac{d\psi}{dx} = \begin{cases} A, & \text{if } 0 < x < a/2, \\ -A, & \text{if } a/2 < x < a, \\ 0, & \text{otherwise,} \end{cases}$$



The derivative of a step function is a Dirac delta. Number in front is the jump:

$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta(x - a/2) + A\delta(x - a)$$

$$\langle H \rangle = -\frac{\hbar^2 A}{2m} \int [\delta(x) - 2\delta(x - a/2) + \delta(x - a)]\psi(x)\,dx$$

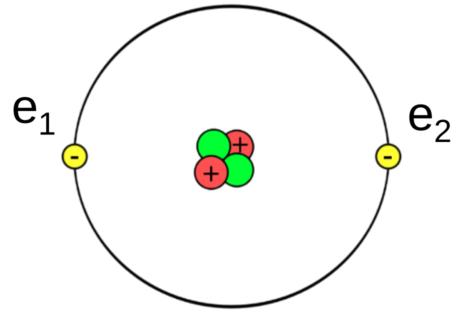
$$= -\frac{\hbar^2 A}{2m}[\psi(0) - 2\psi(a/2) + \psi(a)] = \frac{\hbar^2 A^2 a}{2m} = \boxed{\frac{12\hbar^2}{2ma^2}}$$

The exact result is:

$$E_{gs} = \pi^2\hbar^2/2ma^2$$

Variational theorem holds because $12 > \pi^2$

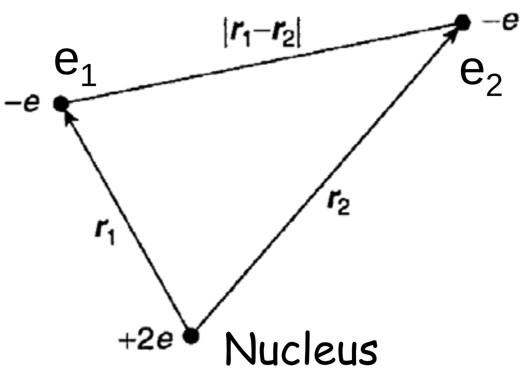
8.2 The Ground State of Helium



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

This problem cannot be solved exactly because of the e-e repulsion. However, we know the ground state energy experimentally:

$$E_{gs} = -78.975 \text{ eV} \quad \text{(experimental)}$$



If we neglect the e-e repulsion, the problem can be solved but energy is 8x(-13.6 eV) = -109 eV (as shown in a lecture in Ch 5), a bit far from the exact result: Qualitatively ok, quantitatively not enough. NOTE: dropping a term in the Hamiltonian is not variational, this is why -109 < -78.975

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

To improve on the discrepancy between -109 eV and -78.975 eV, we will use a variational method, employing the **same wave function** $\psi_0(\mathbf{r}_1,\mathbf{r}_2)$ that solves the problem exactly **when e-e neglected (Ch. 5)**.

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

Note we have NO variational parameter here, yet it is still a variational problem. We will still get an upper bound on the energy.

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

with

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

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

E_1 = -13.6 eV

where

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

The double integral can be done, see book. The result is:

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

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

Considerable quantitative improvement!

Note that -109 eV was the result of neglecting e-e, i.e. a different Hamiltonian. Not surprising -109 eV is below -79 eV. Note also that when the complete problem -- with e-e repulsion included -- is treated variationally, then the result, -75 eV, is ABOVE -79 eV as it must.

We can do even better, by introducing a variational parameter Z that mimics "screening" effects: each electron should see a reduced nuclear charge because the core electrons are in between. Then, let us now try:

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

and optimize Z after calculating $\langle H \rangle$. Note we never "play" with *H*, that is fixed. We "play" with the trial wavefunction.

How do we do the calculation of ‹*H*›? First rewrite exactly the Hamiltonian, without modifying it:

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

$$+ \frac{e^2}{4\pi\epsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

The unperturbed wave functions are those of the hydrogen atom:

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

Z^3 Z

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}$$

Then:

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

No Z dependence in Vee, but wave function has Z. Repeat calculation and you get $-5ZE_1/4$.

We finally find:

$$\langle H \rangle = \left[2Z^2 - 4Z(Z-2) - (5/4)Z\right] E_1 = [-2Z^2 + (27/4)Z]E_1$$

Now we must optimize with respect to *Z*:

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

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

The optimal *Z* being less than 2 makes sense. It is like an effective "screened" charge: one electron often sees the nucleus plus the other electron in between.

The final answer is then:

$$\langle H\rangle = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 = -77.5 \text{ eV}$$

In summary, once the full *H* is considered then our approx. must be an upper bound:

-75 eV	$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$
-77.5 eV	$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$
-78.975 eV	Experimental