# Example 7.2:

Consider now the attractive delta function. Here we also know the exact result from QM 411: $E_{gs} = -m\alpha^2/2\hbar^2$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$$

Here we will use again the Gaussian trial wave function.
We know already that this is not the exact ground state.

$$\psi(x) = Ae^{-bx^2}$$

The normalization is independent of the Hamiltonian, thus same as Example 7.1:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx = |A|^2\sqrt{\frac{\pi}{2b}} \;\Rightarrow\; A = \left(\frac{2b}{\pi}\right)^{1/4}$$

<T> is the same:

$$\langle T\rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx = \frac{\hbar^2 b}{2m}$$

The only difference between Examples 7.1 and 7.2 arises from <V>:

$$\langle V \rangle = -\alpha |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} \delta(x)\, dx = -\alpha \sqrt{\frac{2b}{\pi}}$$

Adding kinetic and potential: $\langle H \rangle = \dfrac{\hbar^2 b}{2m} - \alpha \sqrt{\dfrac{2b}{\pi}}$

Optimizing b: $\dfrac{d}{db}\langle H \rangle = \dfrac{\hbar^2}{2m} - \dfrac{\alpha}{\sqrt{2\pi b}} = 0 \;\Rightarrow\; b = \dfrac{2m^2\alpha^2}{\pi \hbar^4}$

we arrive to $\langle H \rangle_{\text{min}} = -\dfrac{m\alpha^2}{\pi \hbar^2}$ while exact is $E_{\text{gs}} = -m\alpha^2/2\hbar^2$

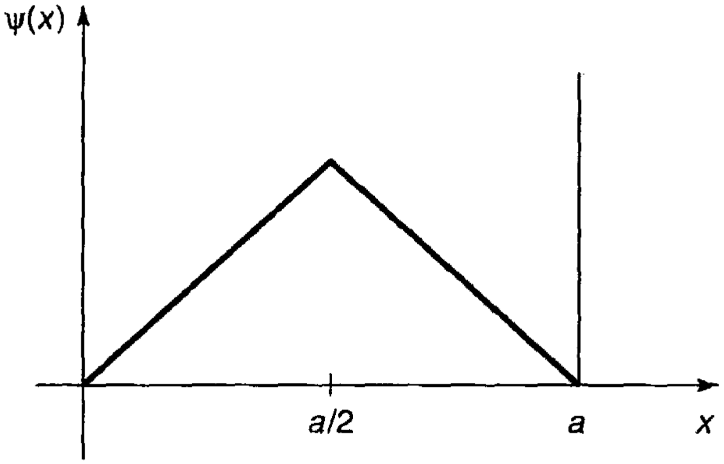
Not perfect but close!

**Note:** If variational state is known to be orthogonal to ground state (e.g. even vs odd), then the upper bound found is for the **first excited state** (see Problem 7.4).

## Example 7.3:

As a wave function you can use anything, including a function with discontinuous first derivatives:

Consider as potential the infinite square well between 0 and a.

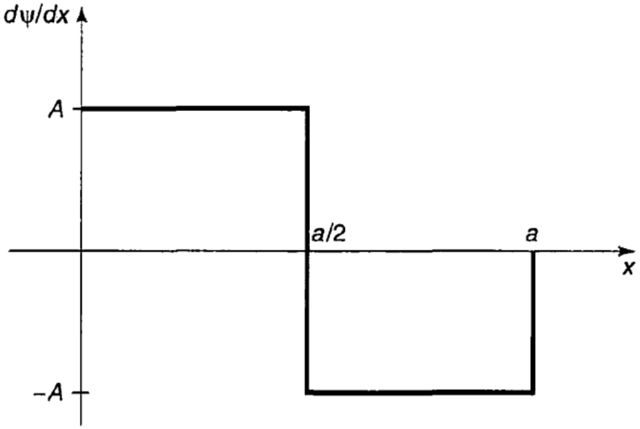



$$\psi(x) = \begin{cases} Ax, & \text{if } 0 \le x \le a/2, \\ A(a-x), & \text{if } a/2 \le x \le a, \\ 0, & \text{otherwise,} \end{cases}$$

$$1 = |A|^2 \left[ \int_0^{a/2} x^2\,dx + \int_{a/2}^{a} (a-x)^2\,dx \right] = |A|^2 \frac{a^3}{12} \Rightarrow A = \frac{2}{a}\sqrt{\frac{3}{a}}$$

The challenge is how to handle <T> that contains a second derivative!

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




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

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

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

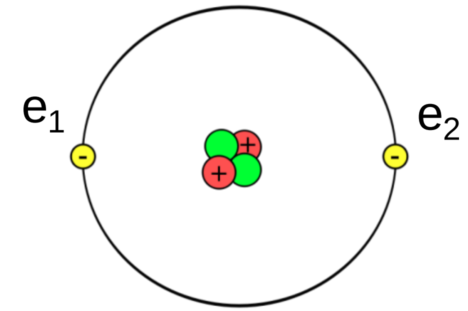
$$= -\frac{\hbar^2 A}{2m}[\psi(0) - 2\psi(a/2) + \psi(a)] = \frac{\hbar^2 A^2 a}{2m} = \boxed{\frac{12\hbar^2}{2ma^2}}$$

The exact result is:

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

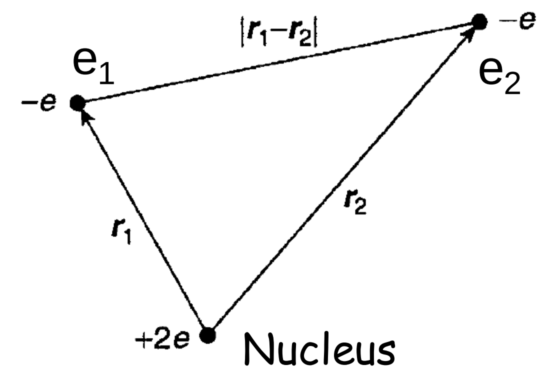
Variational theorem holds because $12 > \pi^2$

# 7.2 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, far from the exact result: Qualitatively ok, quantitatively not enough.

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

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.

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

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

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

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

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:

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

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

Great 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 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 sometimes the other electron is in the way. 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 <H>. 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 H atom:

$Z^3$ $Z$

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

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

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:

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

Now we must optimize with respect to Z:

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

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

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

The final answer is then:

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

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 |