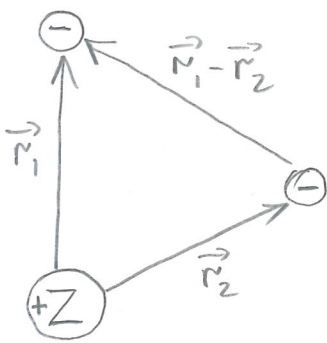


Variational method applied to the helium atom

Let us consider the ground state of a two-electron system - the helium-like atom. If we assume the nucleus to be very heavy we can neglect its motion (fixed nucleus). Then the Hamiltonian of this system can be written as (in SI units)

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

where Z is the charge of the nucleus. From the experiment it is known that the ground state energy of He ($Z=2$) is



$$E^{\text{exp}} = -2.904 \text{ hartree} = -78.98 \text{ eV}$$

If we ignore, for the moment, the interelectron interaction, $V_{ee} = \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$,

then we end up with a Hamiltonian that nicely separates into two hydrogen-like Hamiltonians:

$$H = \underbrace{-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2 Z}{4\pi\epsilon_0 r_1}}_{H_1} + \underbrace{-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2 Z}{4\pi\epsilon_0 r_2}}_{H_2}$$

The solution of such a simplified problem is known to us:

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \Psi_{100}(Z\vec{r}_1) \Psi_{100}(Z\vec{r}_2) = \frac{1}{\pi a^3} e^{-\frac{(r_1+r_2)}{a}} \quad a = \frac{a_0}{Z}$$

where $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ - Bohr radius.

The corresponding energy is $E = 2E_1^{(Z=2)} = 4 \text{ hartree} = -109 \text{ eV}$ when $Z=2$.

(recall that for a Hydrogen-like atom $E_n^{(Z)} = -\frac{1}{a^2} \frac{\hbar^2}{2m} \frac{1}{n^2}$)

A question one might ask immediately when a product $\psi_{100}(Zr_1)\psi_{100}(Zr_2)$ is employed as an approximate wave function is: The two electrons are identical particles. Does this form satisfy the Pauli principle? The answer is yes. In general, the wave function depends on both the spatial and spin coordinates. So we can write our trial wave function as

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{s}_1, \vec{s}_2) = \psi_0(\vec{r}_1, \vec{r}_2) \chi(\vec{s}_1, \vec{s}_2)$$

Notice that our choice of ψ_0 is such that it is symmetric under the permutation $\vec{r}_1 \leftrightarrow \vec{r}_2$. We can then assume that χ is antisymmetric under $\vec{s}_1 \leftrightarrow \vec{s}_2$, which indeed takes place if we choose a spin-triplet:

$$\chi = \frac{1}{\sqrt{2}} (|\uparrow_1\rangle |\downarrow_2\rangle - |\downarrow_1\rangle |\uparrow_2\rangle) = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \beta_1 \alpha_2)$$

The total wave function (spatial + spin) is then antisymmetric with respect to permuting two electrons.

Since the Hamiltonian does not depend on spin at all we can drop the spin part of the wave function from further consideration. The summation over spin variables when evaluating the expectation values is trivial and just gives unity in this case.

Now the energy value of -109 eV is obviously quite far from the exact He energy (-79 eV). We can improve the result of the independent electron

approximation by including the interelectron interaction.

Note that

$$(H - V_{ee})\psi_0 = 2E_1^{(2)}\psi_0 \quad \text{or} \quad H\psi_0 = (2E_1^{(2)} + V_{ee})\psi_0.$$

Therefore

$$\langle H \rangle = 2E_1^{(2)} + \langle V_{ee} \rangle$$

If we do not vary ψ_0 (which, in principle, can be done, but requires more effort) then the application of the variational method becomes particularly simple as we just need to evaluate $\langle V_{ee} \rangle$:

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{\pi a^3}\right)^2 \iint e^{-\frac{(r_1+r_2)}{a}} \frac{1}{|\vec{r}_1 - \vec{r}_2|} e^{-\frac{(r_1+r_2)}{a}} d\vec{r}_1 d\vec{r}_2$$

While this integral may look difficult at first glance, it can actually be evaluated. Let us express $|\vec{r}_1 - \vec{r}_2|$ as

$$|\vec{r}_1 - \vec{r}_2| = \sqrt{(\vec{r}_1 - \vec{r}_2)^2} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}$$

where θ_2 is the angle between \vec{r}_1 and \vec{r}_2 . Hence,

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{\pi a^3}\right)^2 \int e^{-\frac{2r_1}{a}} \left(\underbrace{\int \frac{e^{-\frac{2r_2}{a}}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} d\vec{r}_2}_{I(r_1)} \right) d\vec{r}_1$$

The integral over \vec{r}_2 can be computed as follows:

$$I = \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{e^{-\frac{2r_2}{a}}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} r_2^2 \sin\theta_2 d\phi_2 d\theta_2 dr_2$$

The integration over θ_2 yields:

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

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

$$= \begin{cases} \frac{2}{r_1}, & r_2 < r_1 \\ \frac{2}{r_2}, & r_1 < r_2 \end{cases}$$

So the integral over \vec{r}_2 becomes

$$I = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} e^{-\frac{2r_2}{a}} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-\frac{2r_2}{a}} r_2 dr_2 \right) = \frac{\pi a^3}{r_1} \left[1 - \left(1 + \frac{r_1}{a}\right) e^{-\frac{2r_1}{a}} \right]$$

Going back to $\langle V_{ee} \rangle$ we get:

$$\begin{aligned} \langle V_{ee} \rangle &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{\pi a^3} \right) \int \left[1 - \left(1 + \frac{r_1}{a}\right) e^{-\frac{2r_1}{a}} \right] e^{-\frac{2r_1}{a}} r_1 \sin\theta_1 d\phi_1 d\theta_1 dr_1 = \\ &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{\pi a^3} \right) 4\pi \int_0^{\infty} \left[r_1 e^{-\frac{2r_1}{a}} - \left(r_1 + \frac{r_1^2}{a}\right) e^{-\frac{4r_1}{a}} \right] dr_1 = \\ &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{\pi a^3} \right) 4\pi \frac{5a^2}{32} = \frac{5}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) \end{aligned}$$

Now since

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \Rightarrow \frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0} = \frac{\hbar^2}{mZa}$$

on the other hand $E_1^{(Z)} = -\frac{\hbar^2}{2m} \frac{1}{a^2} \Rightarrow \frac{1}{a^2} = -\frac{2m}{\hbar^2} E_1^{(Z)}$

With that we have

$$\langle V_{ee} \rangle = \frac{5}{8} \frac{\hbar^2}{mZa^2} = -\frac{5}{4Z} E_1^{(Z)}$$

For the expectation value of H we obtain

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

In the case of He atom ($Z=2$) it gives:

$$\langle H \rangle = \frac{11}{8} E_1^{(Z=2)} = -\frac{11}{4} \text{hartree} = -2.75 \text{hartree} \approx -75 \text{eV}$$

Now this is much closer to the exact result (-79eV) than the number we obtained with the independent electron approximation (-109eV)

The next improvement we can make is by varying the wave function so that it corresponds to some "effective" nuclear charge ζ (rather than Z) seen by the electrons

$$\Psi_1(\vec{r}_1, \vec{r}_2) = \frac{\zeta^3}{\pi a_0^3} e^{-\frac{\zeta(r_1+r_2)}{a_0}}$$

ζ is going to be a variational parameter, which we can adjust by minimizing the total energy. Note that the Hamiltonian of the system can be written as

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

The expectation value of H with function Ψ_1 is

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

$\left\langle \frac{1}{r} \right\rangle_{\text{loo}}$ is known to be equal to $\frac{\zeta}{a_0}$ (this can be found in almost any QM textbook)

$$\begin{aligned} \langle V_{ee} \rangle &= \frac{5\zeta}{8a_0} \left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5}{4\zeta} E_1^{(\zeta)} = -\frac{5}{4\zeta} \frac{\zeta^2}{Z^2} E_1^{(Z)} = \\ &= -\frac{5}{4} \frac{\zeta}{Z^2} E_1^{(Z)} \end{aligned}$$

With that we have

$$\begin{aligned} \langle H \rangle &= \left[2 \frac{\zeta^2}{Z^2} - \frac{4\zeta(\zeta-Z)}{Z^2} - \frac{5}{4} \frac{\zeta}{Z^2} \right] E_1^{(Z)} = \\ &= \left[2\zeta^2 - 4\zeta(\zeta-Z) - \frac{5}{4}\zeta \right] \frac{E_1^{(Z)}}{Z^2} \end{aligned}$$

The minimum of the energy takes place when

$$\frac{\partial \langle H \rangle}{\partial \zeta} = 0 \Rightarrow 4\zeta - 8\zeta + 4Z - \frac{5}{4} = 0$$

$$4Z - \frac{5}{4} = 4\zeta \Rightarrow \zeta = Z - \frac{5}{16}$$

For He atom ($Z=2$) $\zeta = \frac{27}{16} \approx 1.69$

$$\begin{aligned} \langle H \rangle &= \left[-2\zeta^2 + 4\zeta Z - \frac{5}{4}\zeta \right] \frac{E_1^{(2)}}{Z^2} = \left[-2\zeta + 4Z - \frac{5}{4} \right] \zeta \frac{E_1^{(2)}}{Z^2} = \\ &= \left[-2\left(Z - \frac{5}{16}\right) + 4Z - \frac{5}{4} \right] \left(Z - \frac{5}{16}\right) \frac{E_1^{(2)}}{Z^2} = \frac{(5-16Z)^2}{128} \frac{E_1^{(2)}}{Z^2} \end{aligned}$$

Again we put $Z=2$ for He atom and get

$$\langle H \rangle = \frac{729}{128} \frac{E_1^{(2)}}{Z^2} = -2.848 \text{ hartree} = -77.5 \text{ eV}$$

This value is very close to the exact energy (-79 eV)

We have just shown that even with a relatively simple trial wave function the variational method can give good estimates of the total energy, provided that the trial wave function is capable of mimicking the proper physical behavior of the exact wave function.