Variational calculation for Helium

Recall the variational principle. See Chapter 7 of the textbook. The variational theorem for a Hermitian operator $H$ with the smallest eigenvalue $E_0$ states that for any normalized $|\psi\rangle$ we have

$$E_0 \leq \langle \psi | H | \psi \rangle .$$

Given a Hamiltonian the method consists in starting with a clever and tractable guess for the so-called trial wave function with one (or more) free (variational) parameters. Normalize the wave function and evaluate $\langle \psi | H | \psi \rangle$. This yields a function of the variational parameters. Find the value of the parameters that minimizes this function and this is the variational estimate for the ground state energy.

In Helium we place the two electrons in a $1s$-like state with the spatial part being symmetric (both electrons are in the same state) and the spin part in the antisymmetric spin singlet. So we write the spatial part of the wave function as

$$\phi(\vec{r}_1) \phi(\vec{r}_2)$$

where we will determine the functional form of $\phi_0$ using the variational approach$^1$. We try a form inspired by the $1s$ state of the hydrogen atom which is exponentially decaying:

$$\phi(r) = \frac{1}{\sqrt{4\pi}} 2\alpha^{3/2} e^{-\alpha r} .$$

This is normalized and has one variational parameter $\alpha$ which controls the spatial extent of the wave function. The angular part is a constant, i.e., $\ell = 0$. The Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m} \nabla^2_1 - \frac{\hbar^2}{2m} \nabla^2_2 - \frac{Zq^2}{|\vec{r}_1|} - \frac{Zq^2}{|\vec{r}_2|} + \frac{q^2}{|\vec{r}_1 - \vec{r}_2|}$$

where the first two terms correspond to the kinetic energies of the two electrons and the last term is the Coulombic repulsion between the two electrons. For Helium the nuclear charge $Z = 2$. We need to evaluate $\langle \Psi | H | \Psi \rangle$. The first term we need is

$$\int d^3r_1 \int d^3r_2 \phi^*(\vec{r}_1) \phi^*(\vec{r}_2) \left( -\frac{\hbar^2}{2m} \nabla^2_1 \right) \phi(\vec{r}_1) \phi(\vec{r}_2) .$$

Since the operator only involves the first coordinate $\vec{r}_1$ the integral over $d^3r_2$ yields 1 since $\phi(\vec{r}_2)$ is normalized. We are left with

$$\int d^3r_1 \left( -\frac{\hbar^2}{2m} \nabla^2_1 \right) \phi(\vec{r}_1)$$

$^1$Note that the actual wave function will not be of this form and can depend upon $|\vec{r}_1 - \vec{r}_2|$ which cannot be written as a product of a function of $\vec{r}_1$ and $\vec{r}_2$ separately. However, we choose the product form for calculational convenience. If we want a better approximation to the ground state energy we can use other forms of the wave function.
and this is the same calculation as the kinetic energy of the electron in the hydrogen atom
and we find \( \frac{h^2 \alpha^2}{2m} \); this must be multiplied by a factor of 2 for the kinetic energy of the
second electron which involves identical integrals.\(^2\) Now for the potential energies. For
the attractive energy of the first electron and the nucleus we have

\[
\int d^3r_1 \int d^3r_2 \phi^*(\vec{r}_1) \phi^*(\vec{r}_2) \left( -\frac{Zq^2}{r_1} \right) \phi(\vec{r}_1) \phi(\vec{r}_2).
\]

Again the \( d^3r_2 \) integral yields 1 and we are left with

\[
\int d^3r_1 \phi^*(\vec{r}_1) \left( -\frac{Zq^2}{r_1} \right) \phi(\vec{r}_1)
\]

which can be done since this is spherically symmetric and yields \( -\alpha Zq^2 \); this should
also be multiplied by 2 for the contribution from the other electron.

The interaction energy is much harder to calculate (Please see the next page if you
are mathematically curious) and yields \( 5q^2\alpha/8 \). Together we have

\[
E(\alpha) = \frac{h^2 \alpha^2}{m} - q^2\alpha \left( 2Z - \frac{5}{8} \right).
\]

Minimizing with respect to \( \alpha \) we obtain\(^3\)

\[
\alpha^* = \frac{mq^2}{\hbar^2} \left( Z - \frac{5}{16} \right).
\]

The minimum energy is given by \( E(\alpha = \alpha^*) \) and is

\[
E_g = -\frac{mq^4}{\hbar^2} \left( Z - \frac{5}{16} \right)^2.
\]

Recall that the ground state of the hydrogen atom is given by

\[
E_0 = -\frac{mq^4}{2\hbar^2}.
\]

Thus we write our estimate of the ground state energy is

\[
E_g = -2E_0 \left( Z - \frac{5}{16} \right)^2.
\]

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\(^2\)Observe that when the Hamiltonian involves a single-particle term, i.e., depends on the coordinates of
one of the particles only, the expectation value involves a three-dimensional integral over the coordinates
of that particle only. Which of the terms in the Hamiltonian is not single-particle?

\(^3\) \[
\frac{2h^2 \alpha}{m} - q^2 \left( 2Z - \frac{5}{8} \right) \bigg|_{\alpha=\alpha^*} = 0
\]
If we had just naively used the 1s hydrogen atom energy except with nuclear charge \( Z \), each electron would have an energy \(-E_0 \times Z^2\) and so for two electrons we would have \(-2E_0Z^2\). Instead the nuclear charge is reduced from \( Z = 2 \) to a lower value thanks to the shielding effect of the other electron.

What is measured is not the ground state energy but the ionization energy. This is the energy required to remove the most weakly bound electron from the atom. It is given by the difference \( E_{\text{ion}} - E_{\text{atom}} \).

First the energy of the helium ion. A singly ionized Helium atom looks like a hydrogen atom with a nuclear charge 2. The latter has an energy \(-4E_0\).

We have computed the energy of the atom Thus the ionization energy is \( 2E_0(2-(5/16))^2 - 4E_0 = E_0(217/128 \text{ which yields } 23.05 eV \text{ compared to the observed value of } 24.59 eV \).

S. Chandrasekhar and G, Herzberg used 10 variational parameters and later 18. Later T. Kinoshita used 39 and later 80 parameters.

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**Calculation of the interaction energy for the Helium atom with the simplest variational ansatz**

The trial wave function is given by

\[
u(\vec{r}) = \frac{1}{\sqrt{4\pi}} 2\alpha^{3/2} e^{-\alpha r}.
\]

We need to evaluate the six-dimensional integral

\[
I \equiv \int d^3 r_1 \int d^3 r_2 |u(\vec{r}_1)|^2 \frac{q^2}{|\vec{r}_1 - \vec{r}_2|} |u(\vec{r}_2)|^2.
\]

There are many ways of doing this integral. Here is one: We use the fact that the (three-dimensional) Fourier transform of the Coulomb potential is \( 4\pi/k^2 \), a very important result:

\[
\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \int \frac{d^3 k}{(2\pi)^3} \frac{4\pi}{k^2} e^{i\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)}.
\]

Substituting this in the integral and changing the orders of integration

\[
I = \int \frac{d^3 k}{(2\pi)^3} \frac{4\pi q^2}{k^2} \int d^3 r_1 |u(\vec{r}_1)|^2 e^{i\vec{k} \cdot \vec{r}_1} \int d^3 r_2 |u(\vec{r}_2)|^2 e^{-i\vec{k} \cdot \vec{r}_2}.
\]

Clearly, we need we need the Fourier transform of \(|u(\vec{r})|^2\) which occurs twice:

\[
\int d^3 r_1 e^{i\vec{k} \cdot \vec{r}_1} \alpha^3 \pi e^{-2\alpha r_1}.
\]

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\(^4\)One way of convincing yourself of this is to Fourier transform the equation

\[
\nabla^2 \left( \frac{1}{r} \right) = -4\pi \delta(\vec{r}).
\]

\(^5\)Since we can change \( \vec{r}_2 \to -\vec{r}_2 \) the sign of the argument in the exponential does not matter.
Using \[ \int d\Omega \, e^{i\vec{k} \cdot \vec{r}_1} \equiv \int_0^\pi d\theta \, \sin \theta \int_0^{2\pi} d\phi \, e^{i\vec{k} \cdot \vec{r}_1} = 4\pi \frac{\sin(kr_1)}{kr_1} \]

we have

\[ \int d^3r_1 \, e^{i\vec{k} \cdot \vec{r}_1} \frac{\alpha^3}{\pi} e^{-2\alpha r_1} = \int_0^\infty dr \, r^2 \frac{4\alpha^3}{kr_1} \frac{\sin(kr_1)}{kr_1} e^{-2\alpha r_1} = \frac{16\alpha^4}{(4\alpha^2 + k^2)^2}. \]

So we finally need the integral\(^6\)

\[ \int \frac{d^3k}{(2\pi)^3} \frac{4\pi q^2}{k^2} \left( \frac{16\alpha^4}{(4\alpha^2 + k^2)^2} \right)^2 = \frac{5}{8} q^2 \alpha. \]

\(^6\)The angular part of this integral is \(4\pi\) since the integrand is independent of angles and so we need an integral over \(k\) only that can be done using Mathematica if you wish.