

HELIUM ATOM USING THE VARIATIONAL PRINCIPLE

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We can use the variational principle to work out some real-world situations. The first of these is an analysis of the ground state of the helium atom. The problem with helium is that it is a three-body problem (the nucleus and two electrons), and it is well-known that there is no closed-form solution to the general three-body problem in mechanics (classical or quantum). The full hamiltonian for helium is

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

Here we are using two independent spatial coordinates \mathbf{r}_1 and \mathbf{r}_2 , one for each electron. The terms in the square brackets are the interaction terms between the electron and the nucleus (the latter with charge $2e$, hence the factors of 2), and between the two electrons. Except for the last term, the hamiltonian is separable, but this last term renders the situation unsolvable in closed form. Ignoring this term gives a ground state energy of $E = -108.8$ eV while the experimental value is -78.975 eV.

To apply the variational principle, we can use the test function ψ_0 which is just the product of two ground state hydrogen wave functions, adjusted for a nuclear charge number of $Z = 2$. We've already worked out this problem (although we didn't call it the variational principle at the time) and found that the correction to the energy from this interaction term comes out to

$$\Delta E = \frac{5}{4a} \frac{e^2}{4\pi\epsilon_0} \quad (2)$$

which is about $+34$ eV, so the new estimate is about $E = -74.8$ eV.

A more accurate estimate can be obtained by making the nuclear charge Z seen by each electron a parameter in a variational model. The rationale behind this is that the electrons shield each other to some extent from the full charge on the nucleus, so we'd expect the effective value of Z to be somewhat less than 2. From the general form for the wave function:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) Y_l^m(\theta, \phi) \quad (3)$$

and the form of the Bohr radius a :

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad (4)$$

where the e^2 in the denominator is the product of the two charges, so it goes over to Ze^2 for a hydrogen-like atom, we can see that the ground state of a hydrogen-like atom ($nlm = 100$) is

$$\psi_{100} = \frac{Z^{3/2}}{\sqrt{\pi a^3}} e^{-Zr/a} \quad (5)$$

Therefore the combined wave function is

$$\psi_0 = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \quad (6)$$

$$= \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a} \quad (7)$$

This function is an eigenfunction of the hamiltonian of an atom with nuclear charge Ze ignoring the electron-electron interaction, that is

$$H_Z = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z}{r_1} + \frac{Z}{r_2} \right] \quad (8)$$

The energy eigenvalue is

$$E_Z = 2Z^2 E_1 \quad (9)$$

where E_1 is the ground state energy of hydrogen (the 2 comes from the fact there are 2 electrons). We can rewrite 1 as

$$H = H_Z + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \quad (10)$$

The correction due to the electron-electron interaction is the same as before, except we're using a general value of Z rather than $Z = 2$ that was assumed in 2. We therefore need to replace a by $a \rightarrow 2a/Z$. The e^2 factor results from the charges on the electrons, so it doesn't change. Therefore

$$\Delta E_Z = \frac{5Z}{8a} \frac{e^2}{4\pi\epsilon_0} \quad (11)$$

All that's left are the two terms containing $Z - 2$. The first of these works out to

$$\frac{e^2 (Z - 2)}{4\pi\epsilon_0} \left\langle \psi_0 \left| \frac{1}{r_1} \right| \psi_0 \right\rangle = \frac{e^2 (Z - 2)}{4\pi\epsilon_0} \left\langle \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \left| \frac{1}{r_1} \right| \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \right\rangle \quad (12)$$

$$= \frac{e^2 (Z - 2)}{4\pi\epsilon_0} \left\langle \psi_{100}(\mathbf{r}_1) \left| \frac{1}{r_1} \right| \psi_{100}(\mathbf{r}_1) \right\rangle \langle \psi_{100}(\mathbf{r}_2) | \psi_{100}(\mathbf{r}_2) \rangle \quad (13)$$

$$= \frac{e^2 (Z - 2)}{4\pi\epsilon_0} \left\langle \frac{1}{r_1} \right\rangle \quad (14)$$

since the ψ_{100} functions are normalized. The quantity $\langle 1/r_1 \rangle$ is the average of the reciprocal of the electron's distance from the nucleus calculated using the single electron wave function, and this is something we've worked out before, for hydrogen., where we got:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{an^2} \quad (15)$$

This was worked out for $Z = 1$, so this time we replace $a \rightarrow a/Z$ and take $n = 1$ to get

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad (16)$$

The term with r_2 gives the same result, so we get

$$\langle \psi_0 | H | \psi_0 \rangle = 2Z^2 E_1 + \frac{2e^2 (Z - 2) Z}{4\pi\epsilon_0 a} + \frac{5Z}{8a} \frac{e^2}{4\pi\epsilon_0} \quad (17)$$

From the Bohr energy formula:

$$E_n = -\frac{1}{n^2} \frac{me^4}{2\hbar^2 (4\pi\epsilon_0)^2} = -\frac{1}{2n^2 a} \frac{e^2}{4\pi\epsilon_0} \quad (18)$$

we can write 17 as

$$\langle H \rangle = 2Z^2 E_1 - 4Z(Z - 2) E_1 - \frac{5Z}{4} E_1 \quad (19)$$

$$= \left[-2Z^2 + \frac{27Z}{4} \right] E_1 \quad (20)$$

We can now minimize $\langle H \rangle$ with respect to Z by taking the derivative and setting to zero to get

$$-4Z + \frac{27}{4} = 0 \quad (21)$$

$$Z_{min} = \frac{27}{16} = 1.6875 \quad (22)$$

This gives an effective nuclear charge of a bit less than 2, which is reasonable. Using $E_1 = -13.6$ eV, this value of Z gives

$$\langle H \rangle = -77.45625 \text{ eV} \quad (23)$$

We can use the same method to find the ground state energies of similar atoms, such as the negative hydrogen ion or singly ionized lithium. We can follow the same derivation if we define ζ to be the nuclear charge number ($\zeta = 1$ for hydrogen and $\zeta = 3$ for lithium). Then 10 becomes

$$H = H_Z + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z-\zeta}{r_1} + \frac{Z-\zeta}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \quad (24)$$

This gives us

$$\langle H \rangle = \left(2Z^2 - 4Z(Z-\zeta) - \frac{5Z}{4} \right) E_1 \quad (25)$$

$$= \left(-2Z^2 + \frac{16\zeta - 5}{4} Z \right) E_1 \quad (26)$$

The derivative gives us

$$Z_{min} = \zeta - \frac{5}{16} \quad (27)$$

For the H^- ion, we get $Z_{min} = 0.6875$ and $\langle H \rangle_{min} = -12.86$ eV. For Li^+ , we get $Z_{min} = 2.6875$ and $\langle H \rangle_{min} = -196.45$ eV.

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