

HELIUM ATOM: ELECTRON-ELECTRON INTERACTION

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.11.

The crude model of the helium atom ignored the interaction between the two electrons. As a result, the ground state energy of -109 eV as predicted by the model was quite far off the measured value of -78.975 eV. One way of computing a correction to the model is to take the interaction-free wave function and use it to calculate the mean value of the interaction term. That is, we take the ground state wave function to be

$$(1) \quad \psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)$$

The two functions on the RHS aren't quite the same as the hydrogen ground state functions, however. Recall that the ground state of hydrogen is

$$(2) \quad \psi_{100H} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

where a is the Bohr radius:

$$(3) \quad a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

The e^2 in the denominator comes from the interaction energy between the single electron in hydrogen and the single proton in the nucleus. For helium, each electron interacts with the two protons in the nucleus, so the 'Bohr radius for helium' has a factor of $2e^2$ in place of the e^2 for hydrogen. Thus we must replace e^2 by $2e^2$ to get the helium wave function:

$$(4) \quad \psi_{100He} = \frac{1}{\sqrt{\pi \left(\frac{a}{2}\right)^3}} e^{-2r/a}$$

giving:

$$(5) \quad \psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

We can now use this function to calculate the mean value of the interaction term $\frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$. That is, we want the integral:

$$(6) \quad \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{\pi a^3} \right)^2 \int \int e^{-4(r_1+r_2)/a} \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Isolating the mean value factor and expanding the modulus term in the denominator, we get, if we take \mathbf{r}_1 to be along the z axis:

$$(7) \quad \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \left(\frac{8}{\pi a^3} \right)^2 \int \int e^{-4(r_1+r_2)/a} \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}}$$

Each integration element has the form

$$(8) \quad d^3\mathbf{r}_i = r_i^2 \sin \theta_i dr_i d\theta_i d\phi_i$$

so we get

$$(9) \quad \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \left(\frac{8}{\pi a^3} \right)^2 \int e^{-4(r_1+r_2)/a} \frac{r_1^2 \sin \theta_1 r_2^2 \sin \theta_2 dr_1 d\theta_1 d\phi_1 dr_2 d\theta_2 d\phi_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}}$$

The two ϕ_i integrals just give a factor of $4\pi^2$, so we can do those and then the integral over θ_2 . This gives

$$(10) \quad \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \frac{512}{a^6} \int_0^{r_1} r_1 r_2^2 \sin \theta_1 e^{-4(r_1+r_2)/a} dr_2 d\theta_1 dr_1 +$$

$$(11) \quad \frac{512}{a^6} \int_{r_1}^{\infty} r_1^2 r_2 \sin \theta_1 e^{-4(r_1+r_2)/a} dr_2 d\theta_1 dr_1$$

We can now do the remaining integrals in the order r_2 , θ_2 and r_1 , where the r_2 integral is done in two parts: the first from 0 to r_1 and the second from r_1 to ∞ . The result is

$$(12) \quad \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle = \frac{5}{4a}$$

The correction to the energy is then

$$(13) \quad \Delta E = \frac{5}{4a} \frac{e^2}{4\pi\epsilon_0} = 5.4497 \times 10^{-18} \text{ Joules} = 34 \text{ eV}$$

This adjusts the model energy to $-109 + 34 = -75$ eV which is much closer to the experimental value of -78.975 .

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