Approximation Methods for Helium Atom

Helium Atom Hamiltonian

The Hamiltonian for the two-electron system is given by:

$$H = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |x_1 - x_2|}$$

If we ignore the last term (electron-electron interaction), we have two independent Hydrogen atom Hamiltonians. This allows us to represent the wavefunction of the entire system as:

$$\Psi(x_1, x_2) = \psi_{n_1 l_1 m_1}(x_1) \psi_{n_2 l_2 m_2}(x_2)$$

Using the well-known results of the Hydrogen atom problem, we get the energy of the system for which we are ignoring the interaction term as:

$$E = -Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{Ry}$$

For the ground state ($n_1 = 1, n_2 = 1$), we get the calculated energy:

$$E_0 = -109 \text{ eV}$$

Whereas the experimental value is:

$$E_0 \simeq -79.0 \text{ eV}$$

This shows that ignoring the interaction term is a naive approach.

First order Perturbation

Treating the last term as a perturbation: the perturbative term will be Z times smaller than the unperturbed terms.

$$\frac{\text{Perturbed Element}}{\text{Unperturbed Element}} = \frac{1}{Z}$$

For $Z = 2$, the perturbed term is only 2 times smaller, giving a non-ideal condition for perturbation, this separation of scales is weak, indicating that electron correlation is not a small correction but a substantial part of the physics.

Take the electrons in the hydrogen ground state:

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$$

The Hamiltonian is defined as: $H = H_0 + H_1$, where the perturbation Hamiltonian H_1 is:

$$H_1 = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|x_1 - x_2|}$$

First order perturbation is given as:

$$\Delta E = \langle \Psi | H' | \Psi \rangle = \int d^3 x_1 \int d^3 x_2 \, \Psi^*_{\text{total}}(x_1, x_2) \, H' \, \Psi_{\text{total}}(x_1, x_2)$$

where $\Psi_{\text{total}} = \psi_{100}(x_1)\psi_{100}(x_2)$.

$$\therefore \Delta E = \frac{e^2}{4\pi\epsilon_0} \int d^3 x_1 d^3 x_2 \frac{|\psi_{100}(x_1)|^2 |\psi_{100}(x_2)|^2}{|x_1 - x_2|}$$

We now choose the z-axis of the second particle to lie along the x_1 direction set by first particle.

$$\therefore \text{Angle between the two particles} = \text{Polar angle of the second particle}$$

$$|x_1 - x_2| = \sqrt{(x_1 - x_2)^2} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}$$

$$\Delta E = \frac{8\pi^2 e^2}{4\pi\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int dr_1\, r_1^2 e^{-2Zr_1/a_0} \int dr_2\, r_2^2 e^{-2Zr_2/a_0} \times \int_{-1}^{1} \frac{d(\cos\theta_2)}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}$$

$$\Delta E = \frac{-2\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int dr_1\, r_1^2 e^{-2Zr_1/a_0} \int dr_2\, r_2^2 e^{-2Zr_2/a_0} \times \frac{|r_1 - r_2| - |r_1 + r_2|}{r_1 r_2}$$

Take $r_1 > r_2$ w.l.o.g ; $|r_1 - r_2| - |r_1 + r_2| = -2r_2$

$$\Delta E = \frac{8\pi e^2}{\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_{r_2}^{\infty} dr_1\, r_1 e^{-2Zr_1/a_0} \int_0^{\infty} dr_2\, r_2^2 e^{-2Zr_2/a_0} \Rightarrow \Delta E = \frac{5Z}{4} Ry$$

$$\therefore E_0 \simeq E + \Delta E = \left(-2Z^2 + \frac{5Z}{4}\right) Ry \simeq -74.8\,\text{eV}$$

Hence, we understand that the perturbative approach brings us much closer to the expected value for the ground state.

Variational method
For, $\Psi(x_1, x_2) = \psi(x_1)\psi(x_2)$, we define the wavefunction with a variable α:

$$\psi(x, \alpha) = \sqrt{\frac{\alpha^3}{\pi a_0^3}} e^{-\alpha r/a_0}$$

This approach must at least give the accuracy of perturbation theory for $Z = \alpha$, reassuring its validity.

$$E(\alpha) = \int d^3 x_1\, d^3 x_2\, \Psi^*(x_1)\Psi^*(x_2)\, H\, \Psi(x_1)\Psi(x_2)$$

We define the Hamiltonian for the two-electron system in terms of α as:

$$H = H_\alpha(p_1, r_1) + H_\alpha(p_2, r_2) + \frac{e^2}{4\pi\epsilon_0}\left[(\alpha - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right] + \frac{1}{|x_1 - x_2|}$$

where $H_\alpha = \frac{p^2}{2m} - \frac{\alpha e^2}{4\pi\epsilon_0}\frac{1}{r}$

$$E(\alpha) = -2\alpha^2 Ry + \frac{e^2}{4\pi\epsilon_0}\left[2(\alpha - Z)\int d^3 x \frac{|\psi(x)|^2}{r} + \int d^3 x_1\, d^3 x_2 \frac{|\psi(x_1)|^2 |\psi(x_2)|^2}{|x_1 - x_2|}\right]$$

The calculations of integrals using the calculations of the Perturbation method are as follows:

$$\int d^3 x \frac{|\psi(x)|^2}{r} = 4\pi \frac{\alpha^3}{\pi a_0^3} \int dr \cdot r e^{-2\alpha r/a_0} = \frac{\alpha}{a_0} \quad\text{and}\quad \int d^3 x_1\, d^3 x_2 \frac{|\psi(x_1)|^2 |\psi(x_2)|^2}{|x_1 - x_2|} = \frac{5\alpha}{8a_0}$$

$$\therefore E(\alpha) = \left[-2\alpha^2 + 4(\alpha - Z)\alpha + \frac{5}{4}\alpha\right] Ry$$

The Variational method then finds the minimum of the function described above, to attain an upper bound to the ground state energy.

$$\left.\frac{\partial E}{\partial \alpha}\right|_{\alpha = \alpha^*} = 0 \implies \alpha^* = Z - \frac{5}{16}$$

$$\therefore E(\alpha^*) \simeq -77.5\,\text{eV}$$

Here, we observe that the upper bound closest to the actual result $E_0 \simeq -79.0$ eV is obtained via Variational principle.

Remarks

1. **Assumptions:** In the calculations, we have made the following assumptions:

   - Non-relativistic behaviour of electrons

   - Neglect of spin–orbit and relativistic corrections

   - Spin-singlet ground state, allowing a symmetric spatial wavefunction

   - Infinite nuclear mass (no recoil)

The remaining discrepancy between the variational result and the experimental ground-state energy arises from electron correlation effects not captured by the simple product wavefunction. More accurate treatments, such Hartree–Fock theory with correlation corrections, further reduce this error.

2. **Screening of Charge**: The physical interpretation of the minimum value α^* is described by an phenomena called screening of nuclear charge. When one electron has a higher probability of being closer to the nucleus, the other electron is, on average, pushed to larger radial distances and hence decreasing the net attractive effect of the nucleus on that electron. This phenomena is called Screening of nuclear charge, where the nuclear charge isn't Z, rather the effective nuclear charge is what we get through the Variational Method calculations:

$$Z_{screened} = Z - \frac{5}{16}$$

The reduction 5/16 originates from the electron–electron Coulomb repulsion term $\left\langle \frac{1}{r_{12}} \right\rangle$, whose expectation value contributes a positive energy proportional to α, effectively weakening the nuclear attraction in the variational minimization.