

Exercise 10.1 The Ground State of the Helium Atom

Neglecting the effects of spin-orbit interaction and the motion of the nucleus, the Hamiltonian of the Helium atom can be written as

$$H = \frac{1}{2m} \mathbf{p}_1^2 + \frac{1}{2m} \mathbf{p}_2^2 - \frac{Ze^2}{|\mathbf{x}_1|} - \frac{Ze^2}{|\mathbf{x}_2|} + \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|}, \quad (1)$$

where \mathbf{x}_1 and \mathbf{x}_2 denote the distance of electron 1 and electron 2, respectively, from the nucleus and Z is the atomic number of Helium. We can treat this in the framework of perturbation theory, with the electron-electron interaction (the final term in the Hamiltonian above) as the perturbation.

a) Show that

$$\int \frac{d\Omega}{|\mathbf{x}_1 - \mathbf{x}_2|} = \frac{4\pi}{\max(r_1, r_2)}, \quad (2)$$

for the integral over solid angle $d\Omega = \sin\theta d\theta d\phi$, with $r_i \equiv |\mathbf{x}_i|$.

b) Compute the energy shift for the ground state due to the electron-electron interaction, given by

$$\Delta E = e^2 \int d^3x_1 d^3x_2 \frac{|\psi_{100}(\mathbf{x}_1)|^2 |\psi_{100}(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|}, \quad (3)$$

where

$$\psi_{100}(\mathbf{x}) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \quad (4)$$

with the Bohr radius $a_0 = \frac{\hbar^2}{me^2}$.

Exercise 10.2 The Excited States of the Helium Atom

The correction to excited energy states of the Helium atom for singlet and triplet states in first-order perturbation theory is given by

$$\begin{aligned} \Delta E_{nl} &= \frac{1}{2} e^2 \int d^3x_1 \int d^3x_2 \frac{|\psi_{100}(\mathbf{x}_1)\psi_{nl0}(\mathbf{x}_2) \pm \psi_{nl0}(\mathbf{x}_1)\psi_{100}(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \\ &= e^2 \left[\int d^3x_1 d^3x_2 \frac{|\psi_{100}(\mathbf{x}_1)|^2 |\psi_{nl0}(\mathbf{x}_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \right. \\ &\quad \left. \pm \int d^3x_1 d^3x_2 \frac{\psi_{100}^*(\mathbf{x}_1)\psi_{nl0}^*(\mathbf{x}_2)\psi_{100}(\mathbf{x}_2)\psi_{nl0}(\mathbf{x}_1)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right] \\ &= J_{nl} \pm K_{nl}. \end{aligned} \quad (5)$$

where \mathbf{x}_1 and \mathbf{x}_2 denote the distances of electron 1 and electron 2, respectively, from the nucleus. Note that we are considering the case where one electron remains in the (1s) state while the other one is excited to a (nl) state. J_{nl} characterizes the electrostatic interaction of the two charge distributions $|\psi_{100}(\mathbf{x}_1)|^2$ and $|\psi_{nl0}(\mathbf{x}_2)|^2$, while K_{nl} is known as the exchange term and arises from the antisymmetrisation of the wavefunction that is required by the Pauli principle. Which of these splittings is the more energetically favourable for an electron to occupy? Show this for the limited case of $l = n - 1$.

You may find the following relations useful. Consider two vectors \mathbf{x}_1 and \mathbf{x}_2 , with spherical coordinates (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) and separated by an angle γ , defined by

$$\cos \gamma \equiv \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2). \quad (6)$$

The inverse of the difference between the two vectors can be expanded in terms of Legendre polynomials

$$|\mathbf{x}_1 - \mathbf{x}_2|^{-1} = \sum_{l'=0}^{\infty} P_{l'}(\cos \gamma) \frac{\min(r_1, r_2)^{l'}}{\max(r_1, r_2)^{l'+1}}. \quad (7)$$

The addition theorem for spherical harmonics allows us to express Legendre polynomials in terms of spherical harmonics

$$P_{l'}(\cos \gamma) = \frac{4\pi}{2l'+1} \sum_{m=-l'}^{l'} Y_{l'm}(\theta_1, \phi_1) Y_{l'm}^*(\theta_2, \phi_2). \quad (8)$$

You may also want to make use of the orthogonality of the spherical harmonics in this computation.