

Exercise 10.1 The Ground State of the Helium Atom

a) We can write the denominator as

$$|\mathbf{x}_1 - \mathbf{x}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta} \quad (1)$$

Hence

$$\begin{aligned} \int \frac{d\Omega}{|\mathbf{x}_1 - \mathbf{x}_2|} &= \int_0^{2\pi} d\phi \int_{-1}^1 d\cos \theta \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}} \\ &= -\frac{2\pi}{r_1r_2} \left[\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta} \right]_{-1}^1 \\ &= \frac{2\pi}{r_1r_2} [-|r_1 - r_2| + (r_1 + r_2)] \\ &= \frac{4\pi}{\max(r_1, r_2)} \end{aligned}$$

b) Substituting in the explicit form of the wavefunction ψ_{100} into Δ , we arrive at the following

$$\Delta E = \frac{e^2}{\pi^2} \left(\frac{Z}{a_0} \right)^6 \int_0^\infty dr_1 r_1^2 e^{-2Zr_1/a_0} \int_0^\infty dr_2 r_2^2 e^{-2Zr_2/a_0} \int d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}. \quad (2)$$

We can use the result of the previous question for the angular part of the integration,

$$\int d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} = (4\pi)^2 \frac{1}{\max(r_1, r_2)}. \quad (3)$$

Hence,

$$\Delta E = (4\pi)^2 \frac{e^2}{\pi^2} \left(\frac{Z}{a_0} \right)^6 \int_0^\infty dr_1 r_1^2 e^{-2Zr_1/a_0} \int_0^\infty dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{1}{\max(r_1, r_2)}. \quad (4)$$

We note that this integral is symmetric in r_1 and r_2 . We can split the integration region of r_2 into $r_2 < r_1$ and $r_2 > r_1$ and carry out the integration accordingly.

$$\begin{aligned} \Delta E &= \frac{e^2}{\pi^2} \left(\frac{Z}{a_0} \right)^6 (4\pi)^2 \int_0^\infty dr_1 r_1^2 e^{-2Zr_1/a_0} \left[\int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{1}{r_1} + \int_{r_1}^\infty dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{1}{r_2} \right] \\ &= \frac{e^2}{\pi^2} \left(\frac{Z}{a_0} \right)^6 (4\pi)^2 \frac{5}{128} \left(\frac{a_0}{Z} \right)^5 \\ &= \frac{5}{8} \frac{Ze^2}{a_0} \end{aligned} \quad (5)$$

For $Z = 2$, we obtain

$$\Delta E = 34\text{eV}. \quad (6)$$

Exercise 10.2 The Excited States of the Helium Atom

We can write the wavefunctions of the electrons as a product of the radial and angular parts

$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_{lm}(\theta, \phi). \quad (7)$$

Using this and the expansion of $1/|\mathbf{x}_1 - \mathbf{x}_2|$, we have

$$K_{nl} = e^2 \int r_1^2 dr_1 d\Omega_1 r_2^2 dr_2 d\Omega_2 R_{10}(r_1)R_{nl}(r_2)R_{10}(r_2)R_{nl}(r_1) \frac{\min(r_1, r_2)^l}{\max(r_1, r_2)^{l+1}} Y_{00}^*(\Omega_1)Y_{l0}^*(\Omega_2)Y_{00}(\Omega_2)Y_{l0}(\Omega_1) \frac{4\pi}{2l'+1} \sum_{m=-l'}^{l'} Y_{l'm}(\Omega_1)Y_{l'm}^*(\Omega_2). \quad (8)$$

We note that $Y_{00} = Y_{00}^* = 1/\sqrt{4\pi}$ such that the angular integration becomes

$$\int d\Omega_1 d\Omega_2 \frac{1}{4\pi} \sum_{m=-l'}^{l'} Y_{l0}(\Omega_1)Y_{l'm}(\Omega_1)Y_{l0}^*(\Omega_2)Y_{l'm}^*(\Omega_2) = \frac{1}{4\pi} \delta_{l'l} \delta_{m0}, \quad (9)$$

where we have used

$$Y_{lm} = (-1)^{-m} Y_{l,-m}^*, \quad (10)$$

and the orthogonality relation for the special harmonics to evaluate the angular integration

$$\int d\Omega Y_{lm}^* Y_{l'm'} = \delta_{ll'} \delta_{mm'}. \quad (11)$$

Thus the exchange term becomes

$$K_{nl} = \frac{e^2}{2l+1} \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 R_{10}(r_1)R_{nl}(r_2)R_{10}(r_2)R_{nl}(r_1) \frac{\min(r_1, r_2)^l}{\max(r_1, r_2)^{l+1}}. \quad (12)$$

The radial part of the wavefunction is given by

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3} \right\}^{1/2} e^{-Zr/na_0} \left(\frac{2Zr}{na_0} \right)^l L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right), \quad (13)$$

where $L_{n+l}^{2l+1}(r)$ are the associated Laguerre polynomials

$$L_{n+l}^{2l+1}(x) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{[(n+l)!]^2 x^k}{(n-l-1-k)!(2l+1+k)!k!}. \quad (14)$$

Due to the characteristics of the Laguerre polynomials, which has $n-l-1$ nodes, $R_{n,n-1}$ has no nodes. It therefore follows that $K_{n,n-1} > 0$. By explicit computation it can be shown that $K_{n,1}$ is 0 for other values of l as well. This correction means that the energy of the triplet state lies lower than that for the singlet state and is therefore energetically more favourable.

This makes sense since the antisymmetric spatial wavefunction (corresponding to the symmetric triplet spin state) must have lower energy due to the smaller electron-electron interaction. This is known as the orthohelium state.