

Helium ($Z=2$)

Single particle energies $E_n = -\frac{4(Ryd)}{n^2} = -\frac{(54.4 \text{ eV})}{n^2}$

$$U(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [u_{A_1}(\vec{r}_1) u_{A_2}(\vec{r}_2) - u_{A_2}(\vec{r}_1) u_{A_1}(\vec{r}_2)]$$

$$u_A(\vec{r}) = u_{nlm} m_s = u_{nlm}(r, \theta, \phi) \chi_{m_s}$$

energies

$$E_1 = -54.4 \text{ eV}$$

single particle state

$$u_{100} \chi_+$$

$$u_{100} \chi_-$$

$$E_2 = -13.6 \text{ eV}$$

$$\begin{array}{l} u_{2lm} \chi_+ \\ u_{2lm} \chi_- \end{array} \quad \text{w/ } \begin{cases} l=0 & m=0 \\ l=1 & m=-1, 0, 1 \end{cases}$$

ground state of helium = $E_{\text{grd}}^0 = -108.8 \text{ eV}$

$$\frac{1}{\sqrt{2}} [u_{100}(r_1) \chi_+^{(1)} u_{100}(r_2) \chi_-^{(2)} - u_{100}(r_1) \chi_-^{(1)} u_{100}(r_2) \chi_+^{(2)}]$$

$$= u_{100}(\vec{r}_1) u_{100}(\vec{r}_2) \frac{1}{\sqrt{2}} [\chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)}]$$

spin's in spin

and -symmetric in spin

$$\Rightarrow \text{total spin} = 0$$

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$\text{spin } \frac{1}{2} \otimes \text{spin } \frac{1}{2} = (\text{spin } 1) \oplus (\text{spin } 0)$$

$$\uparrow \uparrow$$

$$\frac{1}{\sqrt{2}} (\uparrow \uparrow + \downarrow \downarrow)$$

$$\downarrow \downarrow$$

$$\frac{1}{\sqrt{2}} (\uparrow \downarrow - \downarrow \uparrow)$$

First excited state of Helium

77-2

$$E = E_1 + E_2 = -54.4 + 13.6 = -68.0 \text{ eV}$$

Both electrons can now be aligned

Orthohelium

$$\frac{1}{\sqrt{2}} \left(u_{100}(\vec{r}_1) u_{200}(\vec{r}_2) - u_{200}(\vec{r}_1) u_{100}(\vec{r}_2) \right)$$

anti Sym in space

sym in spin

$$\begin{aligned} & \left(\chi_+^{(1)} \chi_+^{(2)} \right. \\ & \quad \text{or} \\ & \quad \chi_-^{(1)} \chi_-^{(2)} \\ & \quad \text{or} \\ & \quad \left. \frac{1}{\sqrt{2}} [\chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)}] \right) \end{aligned}$$

total spin 1

parahelium

$$\frac{1}{\sqrt{2}} \left(u_{100}(\vec{r}_1) u_{200}(\vec{r}_2) + u_{200}(\vec{r}_1) u_{100}(\vec{r}_2) \right) \quad \frac{1}{\sqrt{2}} \left(\chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)} \right)$$

total spin 0

Unperturbed Hamiltonian: all these states ($2 \times 8 = 16$) are degenerate

But interactions $\Rightarrow$ ortho < para

(expt $\sim -58 \text{ eV}$)