Helium ($Z=2$)

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

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

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

energies	single particle states
$E_1 = -54.4\text{ eV}$	$u_{100}\chi_+$, $u_{100}\chi_-$
$E_2 = -13.6\text{ eV}$	$u_{2lm}\chi_+$, $u_{2lm}\chi_-$ w/ $\begin{cases} l=0 & m=0 \\ l=1, & m=-1,0,1 \end{cases}$

ground state of helium: $E^0_{gnd} = -108.8\text{ eV}$

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

$$= \underbrace{u_{100}(\vec{r}_1)\,u_{100}(\vec{r}_2)}_{\text{sym'c in space}}\ \underbrace{\frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right)}_{\text{anti-symmetric in spin}} \Rightarrow \text{total spin} = 0,\ \vec{S} = \vec{S}_1 + \vec{S}_2$$

spin $\frac{1}{2}$ ⊗ spin $\frac{1}{2}$ = (spin 1) ⊕ (spin 0)

$\uparrow\uparrow$

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

$\downarrow\downarrow$

First excited state of helium

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

Both electrons can now be aligned

orthohelium

$$\frac{1}{\sqrt{2}}\left(u_{100}(\vec{r}_1)\,u_{21m}(\vec{r}_2) - u_{21m}(\vec{r}_1)\,u_{100}(\vec{r}_2)\right)$$

antisym in space

sym in spin

$$\chi_+^{(1)}\chi_+^{(2)}$$

or

$$\chi_-^{(1)}\chi_-^{(2)}$$

or

$$\frac{1}{\sqrt{2}}\left[\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)}\right]$$

total spin 1

or

parahelium

$$\frac{1}{\sqrt{2}}\left(u_{100}(\vec{r}_1)\,u_{21m}(\vec{r}_2) + u_{21m}(\vec{r}_1)\,u_{100}(\vec{r}_2)\right)$$

$$\frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right)$$

total spin 0

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

But interactions $\Rightarrow$ ortho < para

(expt ~ -58 eV)