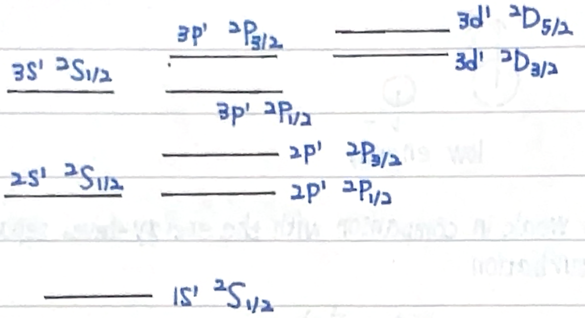
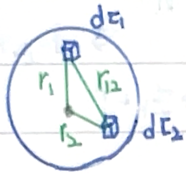
The detailed spectrum of hydrogen



3d'	$^2D_{5/2}$	$E_3 + hc\zeta_{3d}$	$\zeta_{3d} = \frac{\alpha^2 R_\infty}{405}$
	$^2D_{3/2}$	$E_3 - \frac{3}{2}hc\zeta_{3d}$	
3p'	$^2P_{3/2}$	$E_3 + \frac{1}{2}hc\zeta_{3p}$	$\frac{\alpha^2 R_\infty}{81}$
	$^2P_{1/2}$	$E_3 - hc\zeta_{3p}$	
3s'	$^2S_{1/2}$	E_3	
2p'	$^2P_{3/2}$	$E_2 + \frac{1}{2}hc\zeta_{2p}$	$\frac{\alpha^2 R_\infty}{24}$
	$^2P_{1/2}$	$E_2 - hc\zeta_{2p}$	
2s'	$^2S_{1/2}$	E_2	

The Structure of Helium

The helium atom



$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) - \frac{2j_0}{r_1} - \frac{2j_0}{r_2} + \frac{j_0}{r_{12}}$$

where $\frac{e^2}{4\pi\varepsilon_0} = j_0$

the Schrödinger eq for He:

$$-\frac{\hbar^2}{2m_e a_0^2}(\nabla_1'^2+\nabla_2'^2)\psi - \frac{j_0}{a_0}\left(\frac{2}{\frac{r_1}{a_0}} + \frac{2}{\frac{r_2}{a_0}} - \frac{1}{\frac{r_{12}}{a_0}}\right)\psi = \varepsilon E_h \psi$$

(with $\frac{r_1}{a_0} = r_1'$, $\frac{r_2}{a_0} = r_2'$, $\frac{r_{12}}{a_0} = r_{12}'$; $\varepsilon = \frac{E}{E_h}$ Hartree energy)

$$\frac{\hbar^2}{m_e a_0^2} = \frac{j_0}{a_0} = 2hcR_\infty$$

$$-\frac{1}{2}(\nabla_1'^2+\nabla_2'^2)\psi - \left(\frac{2}{r_1'} + \frac{2}{r_2'} - \frac{1}{r_{12}'}\right)\psi = \varepsilon\psi$$

$-\frac{1}{r_{12}'}$: perturbation

use perturbation

$$H^{(0)} = H_1 + H_2 \qquad H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{2j_0}{r_i}$$

$$\Psi(\vec{r}_1,\vec{r}_2) = \psi_{n_1 l_1 m_{l_1}}(\vec{r}_1)\,\psi_{n_2 l_2 m_{l_2}}(\vec{r}_2) \qquad \Rightarrow E = -4hcR_\infty\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$$

writing the actual w.f. as a product of one e^- w.f. is called orbital approximation

$$E^{(1)} = \langle n_1 l_1 m_{l_1}; n_2 l_2 m_{l_2} | \frac{j_0}{r_{12}} | n_1 l_1 m_{l_1}; n_2 l_2 m_{l_2}\rangle = J = j_0 \int |\psi_{n_1 l_1 m_{l_1}}(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_{n_2 l_2 m_{l_2}}(\vec{r}_2)|^2 d\tau_1 d\tau_2$$

J: coulomb integral

Ex:

$$J = j_0\left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_0^{2\pi} \overset{2\pi}{d\varphi_1} \int_0^{2\pi} \overset{2\pi}{d\varphi_2} \int_0^{\pi} \overset{2}{\sin\theta_1\, d\theta_1} \int_0^{\pi} \overset{2}{\sin\theta_2\, d\theta_2} \int_0^\infty \int_0^\infty \frac{e^{-2Z(r_1+r_2)/a_0}}{r_{12}} r_1^2 r_2^2\, dr_1 dr_2$$

$\frac{1}{r_{12}} = \frac{1}{r_1}$ ($r_1 > r_2$), $\frac{1}{r_2}$ ($r_2 > r_1$)

$$= j_0\left(\frac{Z^3}{\pi a_0^3}\right)^2 (4\pi)^2 \int_0^\infty \left(\int_0^{r_2} \frac{r_1^2 e^{-\frac{2Zr_1}{a_0}}}{r_2} dr_1 + \int_{r_2}^\infty \frac{r_1^2 e^{-\frac{2Zr_1}{a_0}}}{r_1} dr_1\right) r_2^2 e^{-\frac{2Zr_2}{a_0}} dr_2$$

$$= j_0\left(\frac{Z^3}{\pi a_0^3}\right)^2 (4\pi)^2 \frac{5}{2^7}\left(\frac{a_0}{Z}\right)^5 = \frac{5}{8} Z \frac{j_0}{a_0}$$

for He, $Z=2$, $1s^2$, $J = \frac{5 j_0}{4 a_0} = 5.45\,aJ = 34.0\ eV$

$$E = \left(-4-4+\frac{5}{2}\right)hcR_\infty = -\frac{11}{2}hcR_\infty = -74.9\,eV \quad (\text{exp}: -78.96\,eV)$$

NO.

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Excited states of He

$1s^1 2s^1$ $\quad \psi_{n_1 l_1 m_{l1}}(\vec{r_1})\,\psi_{n_2 l_2 m_{l2}}(\vec{r_2}) \qquad \psi_{n_2 l_2 m_{l2}}(\vec{r_1})\,\psi_{n_1 l_1 m_{l1}}(\vec{r_2})$

$\qquad\qquad a(1)\,b(2) \qquad\qquad\qquad b(1)\,a(2) \qquad \Rightarrow$ degenerate $=2$

$$H_{11} = \langle a(1)b(2)|H_1+H_2+\frac{\dot{r}_0}{r_{12}}|a(1)b(2)\rangle = E_a+E_b+J$$

$$H_{22} = E_a+E_b+J$$

$$H_{12} = \langle a(1)b(2)|H_1+H_2+\frac{\dot{r}_0}{r_{12}}|a(2)b(1)\rangle$$

$$= (E_a+E_b)\underbrace{\langle a(1)b(2)|a(2)b(1)\rangle}_{0} + \underbrace{\langle a(1)b(2)|\frac{\dot{r}_0}{r_{12}}|a(2)b(1)\rangle}_{\text{exchange integral } K} = H_{21}$$

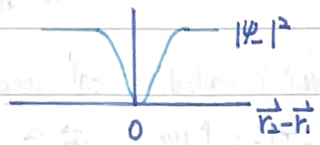
$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} = \begin{vmatrix} E_a+E_b+J-E & K \\ K & E_a+E_b+J-E \end{vmatrix} = 0$$

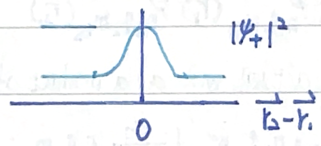
$$\Rightarrow E = E_a+E_b+J\pm K$$

$$\Psi_\pm(1,2) = \frac{1}{\sqrt{2}}\left[a(1)b(2) \pm b(1)a(2)\right]$$

$$\Psi_-(2,1) = \frac{1}{\sqrt{2}}\left[a(2)b(1) - b(2)a(1)\right] = -\frac{1}{\sqrt{2}}\left[a(1)b(2) - b(1)a(2)\right] = -\Psi_-(1,2)$$

$$\Psi_+(2,1) = \Psi_+(1,2)$$





The Pauli Principle

the ground state of He:

$$\Psi(1,2) = \psi_{1s}(\vec{r_1})\psi_{1s}(\vec{r_2})\,\sigma_-(1,2) = \frac{1}{\sqrt{2}}\psi_{1s}(\vec{r_1})\psi_{1s}(\vec{r_2})\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \underbrace{\psi_{1s}(\vec{r_1})\alpha(1)}_{\psi_{1s}^{\alpha}(1)} & \underbrace{\psi_{1s}(\vec{r_1})\beta(1)}_{\psi_{1s}^{\beta}(1)} \\ \psi_{1s}(\vec{r_2})\alpha(2) & \psi_{1s}(\vec{r_2})\beta(2) \end{vmatrix}$$

$\Rightarrow$ two e^- tend to avoid each other

parallel spins tend to avoid one another : spin correlation