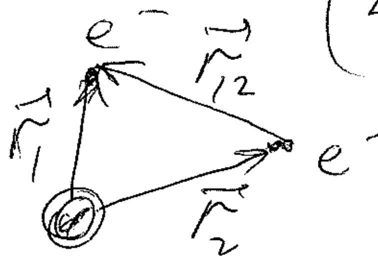
PH 457/557 QM

The Helium atom

(Lecture # 23)



$2p + 2n \Leftarrow Z = 2$

$$H = \underbrace{\frac{P_1^2}{2m} - \frac{\overset{Z}{2}e^2}{4\pi\varepsilon_0 r_1}}_{H_1} + \underbrace{\frac{P_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_2}}_{H_2} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{H'}$$

$H_1 + H_2 = H_0$; H' ← perturbation

$$E_n = -\frac{E_I}{n^2} \cdot Z^2$$

$$H_{1,2}\Psi(\vec{r}_{1,2}) = E_n \Psi(\vec{r}_{1,2})$$

$$\Psi : a_0 \to \frac{a_0}{Z} \Rightarrow \Psi_{100}(r,\theta,\varphi) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Zr}{a_0}}$$

Now $H_0 \Psi(\vec{r}_1, \vec{r}_2) = E^{(0)}_{n_a, n_b} \Psi(\vec{r}_1, \vec{r}_2) \Rightarrow$

$$E^{(0)}_{n_a,n_b} = E_{n_a} + E_{n_b} = -\overset{4}{Z^2} E_I \cdot \left(\frac{1}{n_a^2} + \frac{1}{n_b^2}\right)$$

$\Downarrow$

e^- are identical

$\Downarrow$ most general form

$$\Psi(\vec{r}_1, \vec{r}_2)_{S/A} = \frac{1}{\sqrt{2}}\left(\Psi_{n_a l_a m_a}(\vec{r}_1)\Psi_{n_b l_b m_b}(\vec{r}_2) \pm \Psi_{n_a l_a m_a}(\vec{r}_2) \cdot \Psi_{n_b l_b m_b}(\vec{r}_1)\right) \Rightarrow |\Psi\rangle = |\Psi_{spatial}\rangle\,|\Psi_{spin}\rangle$$ so

need to pair these up with

$S = 1 \Leftarrow$ triplet $\to$ S

$$\begin{cases} |11\rangle = |++\rangle \\ |10\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\ |1-1\rangle = |--\rangle \end{cases}$$

$S = 0 \Leftarrow$ singlet $\Rightarrow$ A or

$$|00\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$$

Ground state!

$\uparrow\downarrow$ $1s^2$ $\qquad {}^1S_0$: $S=0$, $L=0$, $J=0$ (2)

$n_a = n_b = 1$
$l_a = l_b = 0 \Rightarrow \psi_{spatial} = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) \Rightarrow$
$m_a = m_b = 0$

only (S) is possible

$$|\psi^{SA}_{1s\,1s}\rangle_{total} \doteq \underbrace{\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)}_{(S)} \underbrace{\frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right)}_{(A)} \text{"}|00\rangle\text{"}$$

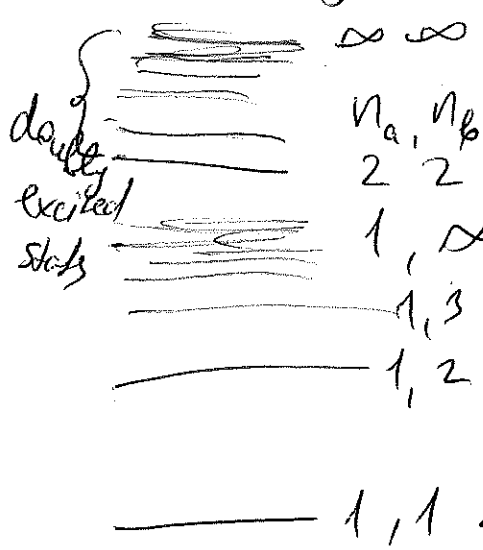
(A)

the only choice

$\Downarrow$

total spin $S=0 \Leftrightarrow M_S = \underbrace{M_{S_1}}_{1/2} + \underbrace{M_{S_2}}_{-1/2} = 0$

non-degenerate, $E_{11} = -4E_I(1+1) =$
$= -8E_I = -108.8\,eV$



double ionization level

energy need to remove/free up both e^-

single ionization level

Exp. value is $-79.0\,eV$

Need to account for H'!

$$E^{(1)}_{1s,1s} = \langle \psi^{SA}_{1s,1s} | H' | \psi^{SA}_{1s,1s} \rangle = \langle \psi^{S}_{1s,1s} | \cdot$$

$$\cdot \langle 00 | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi^{S}_{1s,1s} \rangle |00\rangle = \langle \psi^{S}_{1s,1s} | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi^{S}_{1s,1s} \rangle$$

③

$$\underbrace{\langle 00|00\rangle}_{=1} = \iint \psi^*_{100}(\vec{r}_1)\psi^*_{100}(\vec{r}_2)\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\psi_{100}(\vec{r}_2)\cdot$$

$$\cdot\,\psi_{100}(r_1)\,d^3\vec{r}_1\,d^3\vec{r}_2 = J_{1s,1s} = \frac{5}{4}\frac{e^2}{4\pi\varepsilon_0 a_0} = 34\,eV$$

$J_{1s,1s}$ ↑ direct integral (Coulomb interaction between the electrons)

So $E = E^{(0)}_{11} + J_{1s,1s} \approx \underline{-75\,eV}$

↑ ground state

↑ closer to expt, but not great

nucleus–e^- interaction

$$\frac{\dfrac{4e^2}{4\pi\varepsilon_0 r}}{\dfrac{e^2}{4\pi\varepsilon_0 r}} \sim 4$$

e^-–e^- interaction

↑ e^-–e^- interaction only 4x smaller than nucleus–e^- interaction ⇒ perturbation is not so small!

⇑ can get much closer using variational method

$Z \to Z_{eff}$ (accounts for nuclear screening)

Now let's look at the 1st excited state ⇒

$\downarrow$ 2s

$\uparrow$ 1s

$$E^{(0)}_{1,2} = -4E_I\left(\frac{1}{1^2}+\frac{1}{2^2}\right) = -5E_I = -68\,eV$$

$$|\psi^{SA}_{1s,2s}\rangle = |\psi^{S}_{1s,2s}\rangle|00\rangle \leftarrow \text{singlet state}$$

$$|\psi^{S}_{1s,2s}\rangle = \frac{1}{\sqrt{2}}\left(\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) + \psi_{200}(\vec{r}_1)\psi_{100}(\vec{r}_2)\right)$$

or

$$|\psi^{AS}_{1s,2s}\rangle = |\psi^{A}_{1s,2s}\rangle|1M\rangle \quad M = 1,0,-1 \leftarrow \text{triplet state}$$

$|\psi^{A}_{1s,2s}\rangle$: same as ↗ but with "−"

H' matrix is diagonal $\Rightarrow$ energy corrections $\Rightarrow$

$$E^{(1)}_{1s,2s} = \langle \psi^{SA}_{1s,2s} | H' | \psi^{SA}_{1s,2s} \rangle$$ and

$$E^{(1)}_{1s,2s} = \langle \psi^{AS}_{1s,2s} | H' | \psi^{AS}_{1s,2s} \rangle$$

(H' doesn't act on the spin states!)

$$E^{(1)}_{1s,2s} = \frac{1}{\sqrt{2}} \iint \left(\psi^*_{100}(\vec{r}_1)\psi^*_{200}(\vec{r}_2) \pm \psi^*_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1) \right) \cdot \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \cdot \frac{1}{\sqrt{2}} \left(\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) \pm \psi_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1) \right) \cdot d^3\vec{r}_1 d^3\vec{r}_2 =$$

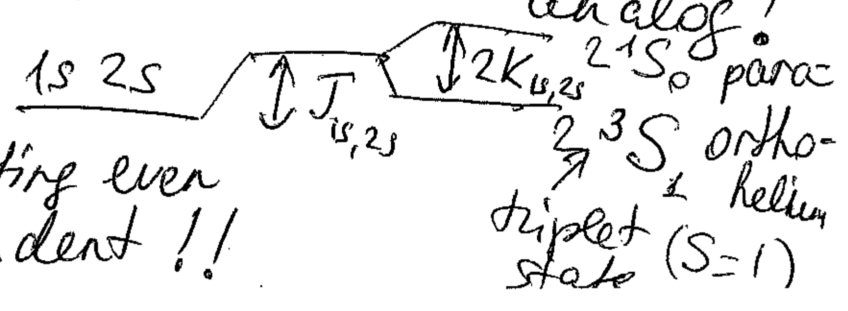
$$= \underbrace{\iint |\psi_{100}(\vec{r}_1)|^2 \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} |\psi_{200}(\vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2}_{= J_{1s,2s}} \pm$$

direct integral $\rightarrow$ $= J_{1s,2s}$ $\leftarrow$ Coulomb interaction of e^-_{1s} & e^-_{2s}

$$\pm \underbrace{\iint \psi^*_{100}(\vec{r}_1)\psi^*_{200}(\vec{r}_2) \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \psi_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1) d^3\vec{r}_1 d^3\vec{r}_2}_{= K_{1s,2s}}$$

(responsible for ferromagnetism!) $= K_{1s,2s}$ $\leftarrow$ exchange integral $\Leftarrow$ no classical analog!

$$= \underbrace{J_{1s,2s} \pm K_{1s,2s}}$$ $\Rightarrow$



Spin-dependent energy splitting even though H' is spin-independent!!