

Spin of two electron system

1 electron : $\Psi_{n, l, m_l, m_s}(\vec{r}, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \chi_{m_s}$

2 electron : $\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1, \vec{r}_2) \chi(l_1, l_2)_{S, m_s}$

$\Delta L = \Delta L_1 + \Delta L_2$; $L = L_1 + L_2, L_1 + L_2 - 1, \dots, |L_1 - L_2|$

$\Delta S = \Delta S_1 + \Delta S_2$; $S = |S_1 + S_2|, \dots, |S_1 - S_2|$
 $= 1, 0$

$m_s = -1, 0, 1$ for $S = 1$

$m_s = 0$ for $S = 0$

∴ We already have a hint that $\chi(l_1, l_2)$

will be: $\chi_{0,0}$; $\chi_{1,+}$; $\chi_{1,0}$; $\chi_{1,-}$

singlet

triplet

We have already seen that if a Hamiltonian is indifferent to exchange of coordinates of two electrons then the eigen states must be symmetric or anti-symmetric w.r.t exchange of electrons. $\therefore P_{12} \Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \pm \Psi_{\pm}(\vec{r}_1, \vec{r}_2)$

We have also seen that if the Hamiltonian is completely separable in the coordinates of the two electrons then the two particle wave fun can be written in terms of products of 1 particle wave fun. As we did for the He atom

$H_0 = H_{e1} + H_{e2} = \left[-\frac{\hbar^2}{2m} \nabla_1^2 + V(r_1) \right] + \left[-\frac{\hbar^2}{2m} \nabla_2^2 + V(r_2) \right]$

after neglecting the interaction term $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$
 Now since H_0 does not involve spin or has no term which couples the spins of the two electrons, H_0 is then trivially separable in the spin of the electron.

Therefore at the zeroth order $\Psi(r_1, r_2)$ can be written in terms of products of the 1 particle wavefunctions:

$$\phi_1(r_1) \chi_{\frac{1}{2}, \frac{1}{2}}^{(1)}, \phi_1(r_1) \chi_{\frac{1}{2}, -\frac{1}{2}}^{(1)}, \phi_2(r_1) \chi_{\frac{1}{2}, \frac{1}{2}}^{(1)}, \phi_2(r_1) \chi_{\frac{1}{2}, -\frac{1}{2}}^{(1)}$$

and similarly for electron 2 such that $\Psi(r_1, r_2)$ is antisymmetric.

We have already seen also that $\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)]$

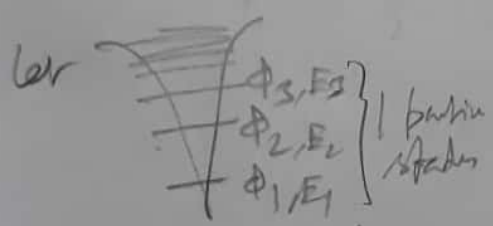
naturally satisfies the Pauli's Exclusion Principle.

However, since Pauli Exclusion principle must be valid for the total wavefunction which comprises of the space and the spin part, $\Psi(r_1, r_2)$ must also be antisymmetric.

$$\therefore \Psi(r_1, r_2) = \Psi(r_1, r_2) \chi(1, 2)$$

$$(\text{antisymmetric}) = (\text{sym}) \times (\text{antisym}) \quad \text{--- 1}$$

$$(\text{antisym}) \times (\text{sym}) \quad \text{--- 2}$$



Let $\chi_{\frac{1}{2}, \frac{1}{2}} \rightarrow \alpha; \chi_{\frac{1}{2}, -\frac{1}{2}} \rightarrow \beta$

If 2e are both in ϕ_1 : $\Psi(r_1, r_2) = \phi_1(r_1)\phi_1(r_2)$: sym.

(Ground state) \therefore Antisymmetric $\chi(1, 2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

\downarrow
 $\left[\begin{matrix} \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, -\frac{1}{2} \end{matrix} \right] \otimes \left[\begin{matrix} \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, -\frac{1}{2} \end{matrix} \right] \rightarrow \chi_{2 \times 2}$

If 1e is in ϕ_1 the other in ϕ_2 : $\Psi(r_1, r_2)$ can be Ψ_+ or Ψ_-

(1st excited state) These $\chi(1, 2)$ have antisymmetric and symmetric respectively.

Possible total wavefunctions Ψ : (4 options):

$$\frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] = \Psi_+ \chi_-$$

$$\frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1)] \times \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \end{cases} = \Psi_- \chi_+ \\ = \Psi_- \chi_2$$

$$\frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] = \Psi_- \chi_+$$

$$\hat{S}_z \chi_- = (S_+^1 + S_+^2) \chi_- = \frac{1}{\sqrt{2}} [(+1-1) \alpha(1) \beta(2) - (-1+1) \alpha(2) \beta(1)]$$

$$= 0$$

$$\hat{S}_z \chi_H = \chi_{+1} \quad (\text{a.u. } \hbar=1)$$

$$\hat{S}_z \chi_{+2} = -\chi_{+2}$$

$$\hat{S}_z \chi_{+3} = 0$$

$$S^2 \chi_- = [S_+^1 + S_+^2 + 2S_1 S_2] \chi_- = \left[\frac{3}{4} \times 2 + 2(S_x^1 S_x^2 + S_y^1 S_y^2 + S_z^1 S_z^2) \right] \chi_-$$

$$= \left[\frac{3}{2} + 2 \times \frac{1}{2} (S_+^1 + S_-^1) \frac{1}{2} (S_+^2 + S_-^2) + \dots \right] \chi_- = 0 \Rightarrow S=0$$

$$S^2 \chi_{+1} = 2 \chi_{+1} \Rightarrow S=1$$

$$S^2 \chi_{+2} = 2 \chi_{+2} \Rightarrow S=1$$

$$S^2 \chi_{+3} = 2 \chi_{+3} \Rightarrow S=1$$

$$\chi_- = \chi_{0,0} \quad \text{singlet}$$

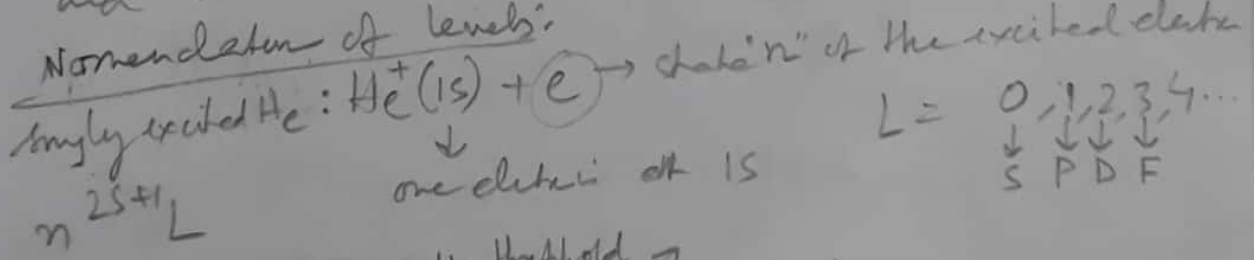
$$\chi_{+1} = \chi_{1,1} \quad \text{triplet}$$

$$\chi_{+2} = \chi_{1,0} \quad \text{triplet}$$

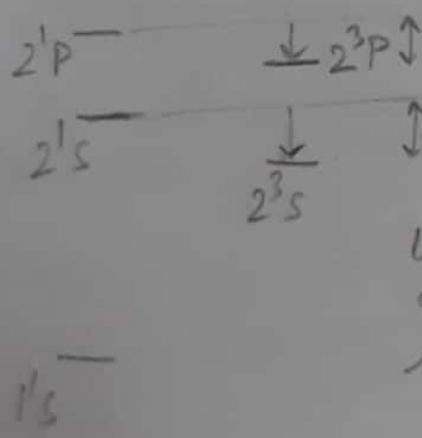
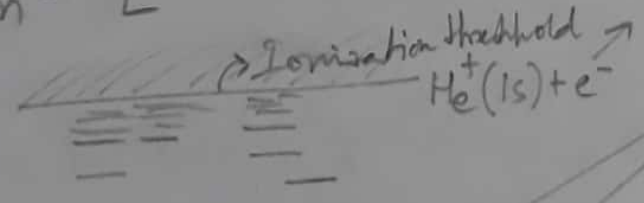
$$\chi_{+3} = \chi_{1,0} \quad \text{triplet}$$

∴ If the electrons are at different spatial wavefunctions the two electron wavefunction will separate out into a singlet and three spin triplets. Ground state is necessarily a singlet.

Nomenclature of levels:



$L = 0, 1, 2, 3, 4, \dots$
 $\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$
 $S \quad P \quad D \quad F$



Split of singlet and triplet states for same n and L is due to the spin:

The symmetric spatial wavefunction allow electrons to come close arbitrarily to each other, leading to average higher repulsion. Whereas the antisymmetric wavefunction does not allow electrons to come infinitesimally close hence lower repulsion. \rightarrow exchange force (Pauli's)

If we start with zero order wave fun

$$\psi_0^{(0)}(r_1, r_2) = \psi_{1s}(r_1) \psi_{1s}(r_2)$$

$$\stackrel{6s}{=} \frac{z^3}{\pi} e^{-z(r_1+r_2)}$$

$$E_n = -\frac{1}{2} \frac{z^2}{n^2}$$

$$E_0^{(0)} = E_{1s} + E_{1s} = -z^2 \text{ a.u.}$$

$$= -4 \text{ a.u. against } E_0^{\text{exp}} = -2.9 \text{ a.u.}$$

Ionization potential = 2 a.u. against $I^{\text{exp}} = 0.9 \text{ a.u.}$

\Rightarrow In effect Z should be increased to reflect the effect of the interaction term $\frac{1}{r_{12}}$

$$\Rightarrow V(r) = -\frac{Z-S}{r} = -\frac{z_c}{r}, \quad S \rightarrow \text{shielding of nuclear charge.}$$

$$E_0^{(0)} = -(Z-S)^2 = -z_c^2 = E_0^{\text{exp}} \text{ at } \underline{S = 0.3}$$

Z_c can also be variationally obtained after considering the full Hamiltonian including $1/r_{12}$

$$E[\Phi] = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}; \quad \Phi = \frac{z_c^3}{\pi} e^{-z_c(r_1+r_2)}$$

$$E[\Phi] = \langle \Phi | \left(-\frac{\nabla_{r_1}^2}{2} - \frac{z}{r_1} - \frac{\nabla_{r_2}^2}{2} - \frac{z}{r_2} + \frac{1}{r_{12}} \right) | \Phi \rangle \text{ in a.u.}$$

$$\langle \Phi | \nabla_{r_i}^2 | \Phi \rangle = z_c^2, \quad \langle \Phi | \frac{1}{r_1} | \Phi \rangle = z_c, \quad \langle \Phi | \frac{1}{r_{12}} | \Phi \rangle = \frac{5}{8} z_c$$

$$\therefore E[\Phi] = E(z_c) = z_c^2 - 2z z_c + \frac{5}{8} z_c$$

$$\Rightarrow \frac{\partial E[\Phi]}{\partial z_c} = 2z_c - 2z + \frac{5}{8} = 0 \Rightarrow z_c = z - \frac{5}{16}$$

for ground state works remarkably well!

	$E_0^{(0)}$	with Z_c	exp
H^-	-1	-0.473	-0.528
He	-4	-2.848	-2.903
Li^+	-9	-7.222	-7.28
CH^+	-36	-32.35	-32.41

More accurately $v(r) = -\frac{Z}{r} + S(r)$
Such that $v(r) \rightarrow -\frac{Z}{r}$ as $r \rightarrow 0$

$$v(r) \rightarrow -\frac{1}{r} \text{ as } r \rightarrow \infty$$