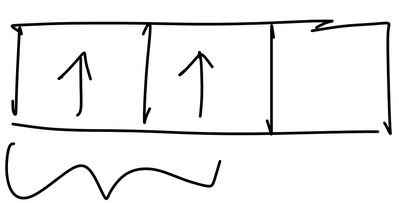
P1. Electron configuration of C6: $1s^2\ 2s^2\ 2p^2$

($1s^2\ 2s^2$ → filled)

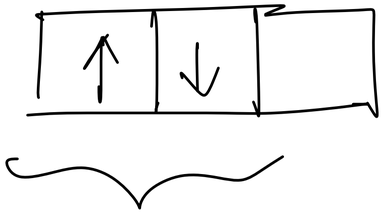
Both the outer e^- have same $l = 1$.

Two possibilities for $2p^2$:



$M_S = 1$

OR



$M_S = 0$

When spins are parallel, χ_{spin} → symmetric

$\Rightarrow$ for $\psi = \phi_{space}\,\chi_{spin}$ to be antisymmetric,

ϕ_{space} → anti-symmetric.

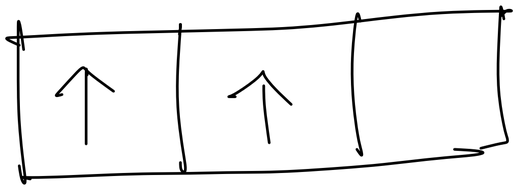
$\Rightarrow$ $|\phi_{space}|^2$ is sizable when the two e^-s are away from each other, leading to reduced coulomb repulsion between the e^-s.

$\Rightarrow$ less +ve contribution to total energy.

When the spins are anti-parallel, ϕ_{space} is symmetric, the configuration with the two e^-s very close is non-zero $\Rightarrow$ relatively larger coulomb repulsion $\Rightarrow$ more +ve contribution to total energy

Thus $\uparrow\uparrow$ configuration is energetically favourable

P2. In C_6 since the two outermost e⁻s are unpaired, only their s and l values contribute to total S and L.

$2p^2 \equiv$ 

For both the e⁻s.

$$s_i = \frac{1}{2} \quad \& \quad l_i = 1$$

$$\Rightarrow \quad S = \Sigma s_i \equiv 0, 1$$

$$\& \; L = \Sigma l_i = 0, 1, 2$$

$\Rightarrow$ Possible states:

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^1S	^1P	^1D	:	^3S	^3P	^3D
✓	×	✓		×	✓	×

with J values ranging from 0 to 3.

Noting $S = 0, 1$

$S = 0$ → anti-symmetric

$S = 1$ → symmetric

$L = 0, 1, 2$ → symmetric

$L = 1$ → antisymmetric

[2]

The anti-symmetry of the wf.

$\Rightarrow$ $S = 0$ with $L = 0, 2$ & $S = 1$ with $L = 1$ are allowed

$\therefore$ allowed states: $^1S_0, {}^1D_2, {}^3P_{0,1,2}$ (total 15 states)

P_3. In the thomas-fermi model, the momenta of the particle ranges from $0 \to p_F$

Total K.E., $E_1 = \sum_{i=1}^{N} \frac{p_i^2}{2} \equiv \int \frac{dN}{\downarrow} \frac{p^2}{2}$

$\downarrow$ # of particles with momentum p

$$dN = 2 \times \frac{4\pi p^2 dp\, d^3r}{h^3}$$

$\swarrow$ spin degeneracy

$$= \frac{1}{\pi^2} p^2 dp\, d^3r \quad ; \quad \hbar = 1$$

$$\Rightarrow E_1 = \frac{1}{2\pi^2}\int d^3r \int_0^{k_F} k^4 = \frac{1}{10\cdot\pi^2}\int d^3r\, k_F^5$$

$$\text{or} \quad E_1 = \frac{1}{10\pi^2}\int d^3r \,(3\pi^2\rho)^{5/3} = \frac{3}{10}(2\pi^2)^{2/3}\int d^3r\, \rho^{5/3} \quad -(1)$$

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By defn: $E_2 = -\sum_i \frac{Z}{r_i} = -Z\int d^3r \,\frac{\rho(r)}{r}$ $\quad -(2)$

& $E_3 = \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} = \frac{1}{2}\int d^3r\, d^3r' \,\frac{\rho(r)\,\rho(r')}{|\vec{r}-\vec{r}'|}$

$$= -\frac{1}{2}\int d^3r\, \rho(r)\,\phi_e(r) \quad -(3)$$

where $\phi_e = -\int d^3r' \,\frac{\rho(r')}{|r-r'|}$ is

potential due to e^- at r.

Noting that net potential at r,

$$\phi = \phi_e + Z/r \qquad -(4)$$

we have

$$E_3 = +\frac{1}{2} Z \int d^3r \frac{\rho(r)}{r} - \frac{1}{2} \int d^3r \, \rho(r) \phi(r)$$

$$= -E_2/2 - \frac{1}{2} \int d^3r \, \rho(r) \phi(r) \qquad -(5)$$

using $\frac{1}{2}(3\pi^2 \rho)^{2/3} = \phi$, for neutral atom.

$$\Rightarrow E_3 = -\frac{E_2}{2} - \frac{(3\pi)^{2/3}}{4} \int d^3r \, \rho^{5/3} \qquad -(6)$$

$$E_3 = -\frac{E_2}{2} - \frac{5}{6} E_1 \qquad -(7)$$

Virial Thm for central potential

$$T = -U/2$$

$$\Rightarrow \quad E_1 = -\frac{E_2+E_3}{2} \qquad -(8)$$

From (7) & (8) we get

$$E_3 = -\frac{E_2}{2} + 5/6\left(\frac{E_2+E_3}{2}\right)$$

$$E_3(1-5/12) = E_2(5/12-1/2) = E_2(-1/12)$$

$$7/12\, E_3 = -E_2/12 \Rightarrow \boxed{E_3 = -1/7\, E_2}$$

P4

$$K = \sum_{\lambda,\mu} \langle \psi_\lambda(q_{r_i})\, \psi_\mu(q_{r_j}) \left| \frac{1}{r_{ij}} \right| \psi_\mu(q_{r_i})\, \psi_\lambda(q_{r_j}) \rangle$$

$$= \sum_{\lambda,\mu} \int dq_{r_i}\, dq_{r_j}\; \psi_\lambda^*(q_{r_i})\, \psi_\mu^*(q_{r_j})\, \frac{1}{r_{ij}}\, \psi_\mu(q_{r_i})\, \psi_\lambda(q_{r_j})$$

Notring. $\dfrac{\delta \psi_\lambda^*(q_{r_i})}{\delta \psi_\alpha^*(q_{r_k})} = \delta_{\lambda\alpha}\, \underbrace{\delta(q_{r_i} - q_{r_k})}_{\downarrow \Delta_{ik}} \cdot \phi \dfrac{\delta \psi_\lambda(q_{r_i})}{\delta \psi_\alpha^*(q_{r_k})} = 0$

$$\frac{\delta K}{\delta \psi_\alpha^*(q_{r_k})} = \sum_{\lambda,\mu} \int dq_{r_i}\, dq_{r_j} \Big\{ \delta_{\lambda\alpha} \Delta_{ik}\, \psi_\mu^*(q_{r_j}) + \psi_\lambda^*(q_{r_i})\, \delta_{\mu\alpha} \Delta_{jk} \Big\} \frac{1}{r_{ij}}$$

$$\psi_\kappa(q_{r_i})\, \psi_\lambda(q_{r_j})$$

$$\frac{\delta K}{\delta \psi_\alpha^*(q_R)} = \sum_\mu \int dq_j \; \psi_\mu^*(q_j) \frac{1}{r_{Rj}} \psi_\mu(q_R) \psi_\alpha(q_j) + \sum_\lambda \int dq_i \; \psi_\lambda^*(q_i) \frac{1}{r_{iR}} \psi_\alpha(q_i) \psi_\lambda(q_R)$$

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where we have used properties of δ under sum and integration.

In the 2nd term, if we identify i with j and λ with μ as they are dummy indices & $\frac{1}{r_{Rj}} = \frac{1}{r_{jR}}$ we get.

$$\frac{\delta K}{\delta \psi_\alpha^*(q_R)} = 2 \sum_\mu \langle \psi_\mu(q_j) | \frac{1}{r_{jR}} | \psi_\alpha(q_j) \rangle \psi_\mu(q_R) \; //$$

P5.

The transition amplitude in dipole approxn; $M_{ba} = \langle \psi_b | \underbrace{\hat{\epsilon}\cdot\vec{D}}_{\text{spin-independent}} | \psi_a \rangle$

Since, $\psi = \underbrace{\phi}_{\text{space}} \underbrace{\chi}_{\text{spin}}$ 2

$$\langle \psi_b | \hat{\epsilon}\cdot\vec{D} | \psi_a \rangle = \underbrace{\langle \chi_b | \chi_a \rangle}_{\delta_{ab}} \langle \phi_b | \hat{\epsilon}\cdot\vec{D} | \phi_a \rangle$$

where a and b are m_s values.

$\Rightarrow$ the m_s value does not change. //