Equations - Quantum Chem 3

Atomic Term Symbols

$^{2S+1}L_J$ - Generalized Term Symbol (J=0 is forbidden)

$S = \sum_i^n s$; s $\epsilon \{\frac{1}{2}, -\frac{1}{2}\}$

2S+1 = Multiplicity; $(2S+1)_{poss}$ = 1,2,3,4… ie singlet, doublet, triplet, quartet, …

$N_{det} = \binom{k}{n} = \frac{k!}{n!(k-n)!}$ k=#spin orbitals, n=num electrons = (2L+1)(2S+1) {for specific L/S}

$m_L = \sum_i^n m_l^i$; $L \geq m_L \geq -L$; $l \geq m_l \geq -l$; $m_l \, \epsilon \, \mathbb{Z}$

$m_s = \sum_i^n m_s^i$; $S \geq m_S \geq -S$

L_{poss} = 0, …, max(m_L) {corresponding to S, P, D as the L in term symbol}

S_{poss} = 0, …, max(m_S)

These are used to determine all possible term symbols (not including the J value)

$L + S \geq J \geq |L - S|$

Type equation here.

Hund's Rules of stability

1) Largest S
2) For same levels of S, then the largest L
3) For same levels of S and L
    a. If the shells are less than half full, the lowest J is most stable
    b. If the shells are more than half full, the largest J is most stable

Hund's Rule of Maximum Multiplicity states that *for a given electron configuration, the term with maximum multiplicity falls lowest in energy*

Bonding

σ MO

$\psi_\sigma = \psi_{s,A} + \psi_{s,B}$ $\psi_{\sigma^*} = \psi_{s,A} - \psi_{s,B}$

$\psi_\sigma = \psi_{s,A} + \psi_{p_{z,B}}$ $\psi_{\sigma^*} = \psi_{s,A} - \psi_{p_{z,B}}$

π MO

$\psi_\pi = \psi_{p_{x,A}} + \psi_{p_{x,B}}$ $\psi_{\pi^*} = \psi_{p_{x,A}} - \psi_{p_{x,B}}$

$\psi_\pi = \psi_{p_{y,A}} + \psi_{p_{y,B}}$ $\psi_{\pi^*} = \psi_{p_{y,A}} - \psi_{p_{y,B}}$

Hybridization

sp³

$$\psi_{h_1} = \frac{1}{\sqrt{4}}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})$$
$$\psi_{h_2} = \frac{1}{\sqrt{4}}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})$$
$$\psi_{h_3} = \frac{1}{\sqrt{4}}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})$$
$$\psi_{h_4} = \frac{1}{\sqrt{4}}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})$$

sp²

$$\psi_{h_1} = \psi_s + \sqrt{2}\psi_{p_x}$$
$$\psi_{h_2} = \psi_s + \sqrt{\frac{3}{2}}\psi_{p_x} - \sqrt{\frac{1}{2}}\psi_{p_y}$$
$$\psi_{h_3} = \sqrt{\frac{1}{2}}(\psi_s - \psi_{p_z})$$

sp

$$\psi_{h_1} = \psi_s + \sqrt{2}\psi_{p_z}$$
$$\psi_{h_2} = \psi_s - \sqrt{2}\psi_{p_z}$$