ELECTRONIC STATES OF LINEAR MOLECULES

ANALOGOUS CLASSIFICATION TO THE RUSSELL-SAUNDERS TERMS FOR ATOMS

UNIQUE MOLECULAR AXIS = z AXIS (ALONG THE BOND)

THE COMBINING ATOMIC ORBITALS IN MO HAVE THE SAME VALUE OF m_l COMPONENT OF ANGULAR MOMENTUM OPERATOR

EACH MO : QUANTUM NUMBER $\lambda = |m_l|$

MO	m_l	λ	AO
σ	0	0	s, p_z, d_{z^2}
π	± 1	1	p_x, p_y, d_{xz}, d_{yz}
δ	± 2	2	$d_{xy}, d_{x^2-y^2}$

↖ NUMBER OF NODAL PLANES

MOLECULAR TERMS

$$M_L = m_{l_1} + m_{l_2} + \dots + m_{l_n}$$

$\Lambda = |M_L|$: $^{2S+1}\Lambda$

$\Lambda = 0\ 1\ 2\ 3$

$\Sigma\ \Pi\ \Delta\ \Phi$

FOR MOLECULES WITH CENTER OF SYMMETRY

g (gerade) u (ungerade)

Σ^+ SYMMETRIC FUNCTION WITH RESPECT TO REFLECTION IN ANY PLANE CONTAINING THE MOLECULAR AXIS

Σ^- ANTISYMMETRIC

IF SPIN-ORBIT INTERACTION IS IMPORTANT:

$^{2S+1}\Lambda_\Omega$

$\Omega = \Lambda + S, \Lambda + S - 1, \dots |\Lambda - S|$

EXAMPLES:

$H_2 : (\sigma_g^b)^2 \quad (\equiv (\sigma_g 1s)^2 \equiv (1\sigma_g)^2)$

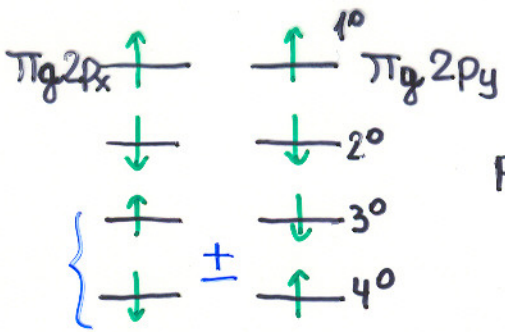
MO: $\sigma \quad M_L = m_{l_1} + m_{l_2} = 0 + 0 = 0 \Rightarrow \Sigma$

$m_{s_1} = \frac{1}{2} \quad m_{s_2} = -\frac{1}{2} \Rightarrow M_S = m_{s_1} + m_{s_2} = \frac{1}{2} - \frac{1}{2} = 0 \quad S = 0$

$^1\Sigma$ (FOR ALL CLOSED SHELLS)

$O_2 : \underbrace{(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4}_{\text{CLOSED SHELLS}} (\pi_g^* 2p)^2$ $\Rightarrow$ MOLECULAR TERM

$^1\Sigma$



(HUND'S RULE)

$P_x, P_y \Rightarrow P_{+1}, P_{-1}$

$m_{l_1} + m_{l_2} = 1 - 1 = 0 \Rightarrow \Sigma$

1° $M_S = \frac{1}{2} + \frac{1}{2} = 1$
2° $M_S = -\frac{1}{2} - \frac{1}{2} = -1$ } $S = 1$
3° $M_S = \frac{1}{2} - \frac{1}{2} = 0$
4° $M_S = -\frac{1}{2} + \frac{1}{2} = 0$ } $S = 0$

$^3\Sigma$ GROUND STATE
$^1\Sigma$

SINGLE ELECTRON APPROXIMATION $\Rightarrow$ MO (SYMMETRY!)

WHAT IS THE NEXT STEP?

— ELECTRON CONFIGURATION (ENERGY SCHEME)

$\Downarrow$ CALCULATIONS

$$\Psi_{MOL} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) \dots & \varphi_1(N) \\ \vdots & & \\ \varphi_N(1) & \varphi_N(2) \dots & \varphi_N(N) \end{vmatrix}$$

ALSO SYMMETRY!

— VARIATIONAL PRINCIPLE

— HARTREE-FOCK EQUATIONS FOR THE OPTIMAL MO's AND BEST ENERGY

— PRACTICAL REALIZATION: H-F-R EQUATIONS

$$MO_i = \sum_j c_{ij} \chi_{ij}$$ ← BASIS SET

FOR EXAMPLE

SCF MO LCAO

χ_{ij} = AO's

EACH χ: H-F
SLATER
GAUSSIAN
HYDROGENIC ATOM

$$\sum_i (F_{ij} - ES_{ij}) c_{ij} = 0 \quad j=1,\dots$$

F_{ii} - COULOMB INTEGRALS

F_{ij} - RESONANCE INTEGRALS

(4 CENTER INTEGRALS IF 4 FUNCTIONS OF $\langle ij||kl\rangle$ ARE LOCALIZED ON 4 VARIOUS ATOMS)

SEMI-EMPIRICAL APPROACH (BETTER RESULTS FROM THOSE OBTAINE WITHIN SCF MO LCAO

F_{ij} - ADJUSTED, S_{ij} - EVALUATED

BUT FOR $i \neq j$ $F_{ij} = 0$ IF ATOMS ARE NOT BONDED

} HÜCKEL

APPROXIMATIONS:

$H_{ii} \cong -IP$

$H_{ij} = \frac{1}{2} F (H_{ii} + H_{jj}) S_{ij}$ (ALGEBRAIC AV)

$H_{ij} = -F \sqrt{H_{ii} H_{jj}} S_{ij}$ (GEOMETRIC AV)

$H_{ij} = F \left(H_{ii} H_{jj} / \frac{1}{2} (H_{ii} + H_{jj}) \right) S_{ij}$ (HARMONIC AV.)

POINT GROUP THEORY

TRANSPARENCES:

QMVI
QMVI-pt2
} FROM PHYS 330A

SELECTION RULES FOR THE NON-VANISHING MATRIX ELEMENTS

THEOREM: ψ_{Γ_i} – BASIS OF IRREDUCIBLE REPRESENTATION $\Gamma_i \neq A_1$

$$\int \psi_{\Gamma_i} \, dV = 0$$

INTEGRATION OVER THE WHOLE SPACE

$$\int \psi_{\Gamma_i} \, dV = \int \hat{R} \psi_{\Gamma_i} \, dV =$$

THE RESULT OF INTEGRATION IS INDEPENDENT OF THE COORDINATE SYSTEM

$$\hat{R}\psi_{\Gamma_i} = \underbrace{\sum_j}_{\text{COMPLETE SET}} |\psi_{\Gamma_j}\rangle \underbrace{\langle \psi_{\Gamma_j} | R | \psi_{\Gamma_i} \rangle}_{D_\Gamma(\hat{R})_{ji}}$$

$D_\Gamma(\hat{R})_{ji}$ MATRIX REPRESENTATION

$$= \sum_j D_\Gamma(\hat{R})_{ji} \int \psi_{\Gamma_j} \, dV$$

$$\sum_{\hat{R} \in G} \int \psi_{\Gamma_i} \, dV = \sum_{\hat{R}} \sum_j D_1^*(\hat{R})_{11} \, D_\Gamma(\hat{R})_{ji} \int \psi_{\Gamma_j} \, dV$$

1 FOR FULLY SYMMETRIC REPR. (CHARACTER = DIAGONAL ELEMENT)

ORTHOGONALITY THEOREM:

$$\sum_{\hat{R} \in G} D_m(\hat{R})^*_{ij} \, D_n(\hat{R})_{kl} = \frac{h}{l_m} \delta_{ik} \delta_{jl} \delta_{mn}$$

↖ DIMENSION OF REPRESENTATION

$$\Rightarrow h \int \psi_{\Gamma_i} \, dV = h \delta_{\Gamma 1} \int \psi_{\Gamma_j} \, dV$$

BUT $\Gamma_{\Gamma_i} \neq \Gamma_{A_1}$ THEREFORE

$$\int \psi_{\Gamma_i} \, dV = 0$$

EXAMPLES:

1. $\int p_x dV = 0$ FOR D_3, $p_x \in E \neq A_1$

$p_x = x f(r)$ – ANTISYMMETRIC

FOR EACH $+ p_x dV$ THERE IS $- p_x dV$

2. $\int \underbrace{(s + p_x)}\, dV \neq 0$ FOR D_3: $s \to A_1$, $p_x \to$

$\Downarrow$

$\Gamma = A_1 + E$

SELECTION RULES FOR

$$\int \psi_{\gamma_i} \hat{F} \psi_{s_j} dV \neq 0$$

$\psi_{\gamma_i} \to \Gamma_\gamma$, $\hat{F} \to$ SCALAR OPERATOR, $\psi_{s_j} \to \Gamma_s$

IF $\Gamma_\gamma \times \Gamma_s$ CONTAINS IRR. REPRESENTATION A_1

IN GENERAL:

$$\int \psi_{\gamma_i} \hat{F} \psi_{s_j} dV \neq 0$$

$\psi_{\gamma_i} \to \Gamma_\gamma$, $\hat{F} \to \Gamma_F$, $\psi_{s_j} \to \Gamma_s$

IF

$$\Gamma_\gamma \times \Gamma_F \times \Gamma_s \in A_1$$

OTHERWISE IT VANISHES

EXAMPLE: ELECTRIC DIPOLE TRANSITIONS

$$\int \psi_{\gamma_i} \vec{r} \psi_{\gamma_j} dV$$

IF $\mathcal{J} \in G$

$\vec{r} \xrightarrow{\hat{\mathcal{J}}} -\vec{r} : \Gamma_u$

$\hat{\mathcal{J}}(\psi_{\gamma_i}, \psi_{\gamma_j}) = \psi_{\gamma_i} \psi_{\gamma_j} \Rightarrow \Gamma_g \Rightarrow u \times g = u \neq A_1$!

THE SAME SYMMETRY

$g \not\to g$ $u \not\to u$ FORBIDDEN

TRANSITION AMPLITUDE $= 0$