

Oct. 20, 1999

Parity

- **Parity**- Molecular orbitals of homonuclear diatomics are labeled **u, g** depending on their behavior under inversion.

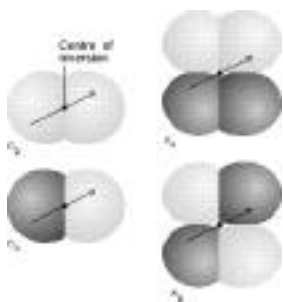
u=odd (ungerade)

g=even (gerade)

g_xg=g

u_xu=g

u_xg=u



Term Symbols

- Term symbols for linear molecules are constructed similarly to atoms. Except, must pay attention to total orbital angular momentum about internuclear axis, \hbar

$$2S+1 \quad \text{g,u}$$

- The value of Λ is the sum of λ for individual electrons in molecule.

$$\Lambda = 0, 1, 2, \dots \quad \text{orbital; } \Lambda = 0$$

$$\Lambda = 1, 2, \dots \quad \text{orbital; } \Lambda = \pm 1$$

$$\Lambda = 2, 3, \dots \quad \text{orbital; } \Lambda = \pm 2$$

Rules and Examples

1) H_2^+

One electron in a σ_g orbital. $\Lambda = 0, S = 1/2$

Term symbol is $^2\Sigma_g^+$

2) For any closed shell homonuclear diatomic,

$\Lambda = 0, S = 0$; g parity so the term symbol is: $^1\Sigma_g^+$

3) Consider O_2 : 2 electrons in 2 π^* orbital.

$\Lambda = 1, -1; \Lambda = 0; S = 1, g_{xg} = g$

Rules- cont.

- For Σ terms, a \pm superscript denotes behavior of the wavefunction under reflection in a plane containing the nuclei. (see Figure 14.36)
- For H_2^+ , complete term symbol is $^2\Sigma_g^+$
- For O_2 , complete term symbols is $^3\Sigma_g^-, ^1\Sigma_g^+, ^3\Sigma_g^-, ^1\Delta_g, ^3\Pi_g^-, ^1\Pi_g, ^3\Pi_g^-, ^1\Pi_g$

Heteronuclear Diatomics

- 1) When Z_A and Z_B are close, then the MO's of heteronuclear diatomics are similar to the MO's of homonuclear diatomics.

Example: CO

– Energies will follow those of C_2 .

- Molecular orbital electronic configuration:

$$(1s)^2(2s)^2(2p)^4(3s)^2$$

$$b = (8-2)/2 = \underline{\quad}$$

Heteronuclear Diatomics- cont.

- 2) When Z_A and Z_B are of very different electronegativities, then the MO's will have a very different energy scheme.

$$\psi = c_A A + c_B B$$

$$\text{nonpolar bond: } |c_A|^2 = |c_B|^2$$

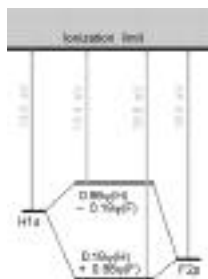
$$\text{pure ionic bond: } |c_A|^2 = 0; |c_B|^2 = 1$$

Example: HF

HF- polar bond-electron pair closer to F atom resulting in a permanent dipole moment.

$$= c_H H + c_F F$$

Bonding orbital is mainly F_{2p}
Antibonding orbital is mainly H_{1s}



Variation Principle

- If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy.
- The arbitrary wavefunction is called a **trial wavefunction**.
 - **Basis set** is a given set of atomic orbitals that are used to construct the trial wavefunctions
- The procedure is to vary the coefficients in trial wavefunction to minimize energy. The best coefficients for the MO's will be obtained in this way.

General Method

$$\psi = c_A \phi_A + c_B \phi_B$$

Trial wavefunction

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$

Search for coefficients that minimize E.

$$\frac{\partial E}{\partial c_A} = 0; \quad \frac{\partial E}{\partial c_B} = 0$$

$$\begin{aligned} 2d &= (c_A A + c_B B)^2 d \\ &= c_A^2 A^2 d + c_B^2 B^2 d + 2c_A c_B ABd \\ &= c_A^2 A + c_B^2 B + 2c_A c_B S \end{aligned}$$

$$\begin{aligned} H \psi &= (c_A A + c_B B)H(c_A A + c_B B)d \\ &= c_A^2 AHA + c_B^2 BHB + c_A c_B AHB + c_A c_B BHA \\ &= c_A^2 A + c_B^2 B + 2c_A c_B S \end{aligned}$$

=Coulomb integral-energy of electron occupying A
=resonance integral- vanishes if there is no overlap

Solve for Energy

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{c_A^2 A + c_B^2 B + 2c_A c_B S}{c_A^2 A + c_B^2 B + 2c_A c_B S}$$

Find minimum energy: Differentiate E with respect to c_A and c_B and set equal to 0.

$$\begin{cases} (A - E)c_A + (-ES)c_B = 0 \\ (-ES)c_A + (B - E)c_B = 0 \end{cases} \quad \begin{vmatrix} A - E & -ES \\ -ES & B - E \end{vmatrix} = 0$$

Secular Equations

Solution if the determinant of coefficients is 0.

Secular Determinant

Solve secular determinant to get energies.

Example- Homonuclear Diatomic

$$c_A = c_B \text{ and } A = B = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

$$\begin{vmatrix} -E & -ES \\ -ES & -E \end{vmatrix} = (-E)^2 - (-ES)^2 = 0$$

$$E_{\pm} = \frac{\pm}{1 \pm S}$$

The two roots give the energies of bonding and antibonding molecular orbitals formed from atomic orbitals. According to variation principle these roots are best energies for given basis set.

To get c_A and c_B , solve the secular equation by plugging in energies to get the ratio c_A/c_B . Then normalize.

Wavefunctions

$$c_A = \frac{1}{2(1+S)^{1/2}} \quad \text{for } E_+$$

$$c_B = \frac{1}{2(1-S)^{1/2}} \quad \text{for } E_-$$

$$+ = \frac{A+B}{2(1+S)^{1/2}} \quad \text{Bonding orbital}$$

$$- = \frac{A-B}{2(1-S)^{1/2}} \quad \text{Antibonding orbital}$$

Example 2- Heteronuclear Diatomic

$$S = 0 \quad (\text{common approximation})$$

$$\begin{vmatrix} A-E & \\ & B-E \end{vmatrix} = (A-E)(B-E) - ()^2 = 0$$

$$= \frac{1}{2} \arctan \frac{2| |}{B-A}$$

$$- = -A \sin + B \cos$$

$$E_- = A - \cot$$

$$+ = A \cos + B \sin$$

$$E_+ = B + \cot$$

Strongest bonding and antibonding effects occur when two contributing orbitals have similar energies.

Example- Calculate the MO's of HF

- Consider Ionization Energies:

$$\begin{array}{l} H_{1s}: 13.6\text{eV} = B \\ F_{2s}: 40.2\text{eV} \\ F_{2p}: 18.6\text{eV} = A \end{array} \quad \left. \vphantom{\begin{array}{l} H_{1s} \\ F_{2s} \\ F_{2p} \end{array}} \right\} \text{Closest in energy}$$

- Given $\epsilon = -1.0\text{eV}$; Neglect F_{2s} orbital.

$$= \frac{1}{2} \arctan \frac{2| |}{B-A} = \frac{1}{2} \arctan \frac{2(1)}{-13.6 - (-18.6)} = 10.9^\circ$$

$$E_- = A - \cot = -18.8\text{eV} \quad - = 0.98 \quad H - 0.19 \quad F$$

$$E_+ = B + \cot = -13.4\text{eV} \quad + = 0.19 \quad H - 0.98 \quad F$$