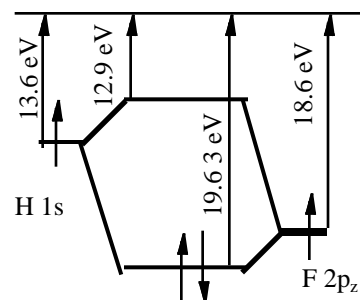


## Heteronuclear Diatomic Molecules

- Molecules formed from different atoms: The electron distribution in the covalent bonds is no longer evenly shared between the two atoms, because it is energetically favorable for the electron pair to reside closer to one nucleus than to the other. This means that the chemical bond is polarized.
- Example:  $\text{H}^+ - \text{F}^-$  electron pair is located closer to the F nucleus than to the H nucleus.
- Polar Bonds consist of two electrons of opposite spin in one orbital of the form:  $\psi = C_A \psi(A) + C_B \psi(B)$  where  $C_A$  differs from  $C_B$
- The proportion of atomic orbital  $\psi(A)$  in the MO is given by  $C_A^2$  and that of atomic orbital  $\psi(B)$  is given by  $C_B^2$
- In a pure ionic bond, one of the coefficients is 0 and the other is 1.

- The atomic orbital with the lower energy makes the larger contribution to the bonding molecular orbital. The atomic orbital with the higher energy makes the larger contribution to the antibonding orbital.
- Example H - F



H:  $1s^1$

F:  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

$1 \psi = 0.33 \psi(\text{H}) + 0.94 \psi(\text{F})$

$2 \psi = 0.94 \psi(\text{H}) - 0.33 \psi(\text{F})$

Partial Charge on F (88%)

### Variation Principle:

- A systematic way to find the coefficients  $C_A$  and  $C_B$  in the linear combinations of atomic orbitals is to use the variation principle. "If an arbitrary wave function is used to calculate the energy, then the value calculated is never less than the true energy".
- The lowest energy conditions define the MO coefficients.
- For an A - B molecule, the MO is given by:  

$$\psi = C_A \psi_A + C_B \psi_B$$
 Then  $C_A$  and  $C_B$  are calculated through the Secular Equations:

$$\begin{aligned} (H_{AA} - E) C_A + (H_{AB} - ES) C_B &= 0 \\ (H_{BA} - ES) C_A + (H_{BB} - E) C_B &= 0 \end{aligned}$$

Where  $H_{AA}$ ,  $H_{BB}$  are the Coulomb Integrals,  $H_{AB}$  is the Resonance Integral and  $S$  is the Overlap Integral. (derivation next slides ...)

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

We want to find  $C_A$  and  $C_B$  such that  $E$  is minimized:

This condition is equivalent to:  $\frac{\partial E}{\partial C_A} = 0$        $\frac{\partial E}{\partial C_B} = 0$

$$\begin{aligned} \int \psi^* \psi d\tau &= \int (C_A \psi_A^* + C_B \psi_B^*) (C_A \psi_A + C_B \psi_B) d\tau \\ &= C_A^2 \int \psi_A^* \psi_A d\tau + C_B^2 \int \psi_B^* \psi_B d\tau + 2C_A C_B \int \psi_A^* \psi_B d\tau \\ &= C_A^2 + C_B^2 + 2SC_A C_B \end{aligned}$$

$$\begin{aligned} \int \psi^* H \psi d\tau &= \int (C_A \psi_A^* + C_B \psi_B^*) H (C_A \psi_A + C_B \psi_B) d\tau \\ &= C_A^2 \int \psi_A^* H \psi_A d\tau + C_B^2 \int \psi_B^* H \psi_B d\tau + 2C_A C_B \int \psi_A^* H \psi_B d\tau \\ &= C_A^2 \alpha_A + C_B^2 \alpha_B + 2\beta C_A C_B \end{aligned}$$

$$E = \frac{\alpha_A C_A^2 + \alpha_B C_B^2 + 2C_A C_B \beta}{C_A^2 + C_B^2 + 2C_A C_B S}$$

Then the secular equations are obtained by equating the partial derivatives of E with respect to  $C_A$  and  $C_B$  to zero. To solve the secular equations, one writes the secular determinant:

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$

If the secular determinant is equal to zero then the secular equations have a solution, which is given by:  
 $(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0$

The solutions to this equation are generally cumbersome but are enlightening in two specific cases:

- Homonuclear Diatomic Molecules:  $\alpha_A = \alpha_B = \alpha$   
 $(\alpha - E)^2 - (\beta - ES)^2 = 0$

$$E_+ = \frac{\alpha + \beta}{1 + S} \quad \psi_+ = \frac{1}{2(1 + S)}^{1/2} (\psi_A + \psi_B) \quad \text{Bonding Orbital}$$

$$E_- = \frac{\alpha - \beta}{1 - S} \quad \psi_- = \frac{1}{2(1 - S)}^{1/2} (\psi_A - \psi_B) \quad \text{Antibonding Orbital}$$

- Heteronuclear Diatomic Molecules & Negligible Overlap:  $S=0$   
 $(\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$   
 It is practical to express the solutions in trigonometric fashion using the variable  $\theta$  such that:  $\tan(2\theta) = 2\beta / (\alpha_A - \alpha_B)$

- $$E_{(1)} = E_A - \cot \theta \quad \psi_{(1)} = -\sin(\theta) \psi(A) + \cos(\theta) \psi(B)$$

$$E_{(2)} = E_B + \cot \theta \quad \psi_{(2)} = +\cos(\theta) \psi(A) + \sin(\theta) \psi(B)$$

Note that as the difference in energy between the two atomic orbitals increases, the value of  $\theta$  decreases, and the difference in energy between the molecular and the atomic orbital decreases. Bonding and antibonding effects become small.

$\Rightarrow$  The strongest bonding and antibonding effects are observed when the atomic orbitals have very similar energies.

- Example: H - F

$$E_H = -2.0 \text{ eV} \quad E_F = -E_i(\text{H}) = -13.6 \text{ eV} \quad E_F = -E_i(\text{F}_{2p_z}) = -18.6 \text{ eV}$$

$$\tan(2\theta) = -0.8 \quad \Rightarrow \quad \theta = -19.33^\circ$$

$$E_{(1)} = -19.3 \text{ eV} \quad \psi_{(1)} = 0.33 \psi(A) + 0.94 \psi(\text{F}_{2p_z}) \quad \text{Bonding}$$

$$E_{(2)}^* = -12.9 \text{ eV} \quad \psi_{(2)} = 0.94 \psi(A) - 0.33 \psi(\text{F}_{2p_z}) \quad \text{Antibonding}$$

### Treatment of Conjugated Molecules and Metals

- Molecular Orbital Theory can also deal with very large molecules and extended aggregates of atoms. Two examples will be covered here: Conjugated Molecules and Solids.
- Conjugated Molecules: alternation of single and double bonds

  - Treats orbitals separately from orbitals.
  - orbitals form a framework that determines molecular shape.
  - All C atoms are treated identically  $\Rightarrow$  all Coulomb integrals are equivalent (all denoted by  $H_{ii}$ ).

Examples:  $\text{CH}_2=\text{CH}_2$  (ethylene),  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  (butadiene),  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$  (hexatriene), benzene, cyclobutadiene,  $-(\text{CH}=\text{CH})_n-$  poly(acetylene).

- Strategy:

Molecular Orbitals are written as linear combinations of  $C_{2p}$  atomic orbitals

Find the LCAO MO coefficients and MO energies using the Variation Principle (Secular Determinant approach)

- Ethylene  $H_2C_{(A)}=C_{(B)}H_2$

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0 \quad = C_A (C_{2p}) + C_B (C_{2p})$$

- Hexatriene  $C_{(A)}H_2=C_{(B)}H-C_{(C)}H=C_{(D)}H-C_{(E)}H=C_{(F)}H_2$

$$\begin{vmatrix} \alpha - E & \beta_{AB} - ES_{AB} & \beta_{AC} - ES_{AC} & \beta_{AD} - ES_{AD} & \beta_{AE} - ES_{AE} & \beta_{AF} - ES_{AF} \\ \beta_{BA} - ES_{BA} & \alpha - E & \beta_{BC} - ES_{BC} & \beta_{BD} - ES_{BD} & \beta_{BE} - ES_{BE} & \beta_{BF} - ES_{BF} \\ \beta_{CA} - ES_{CA} & \beta_{CB} - ES_{CB} & \alpha - E & \beta_{CD} - ES_{CD} & \beta_{CE} - ES_{CE} & \beta_{CF} - ES_{CF} \\ \beta_{DA} - ES_{DA} & \beta_{DB} - ES_{DB} & \beta_{DC} - ES_{DC} & \alpha - E & \beta_{DE} - ES_{DE} & \beta_{DF} - ES_{DF} \\ \beta_{EA} - ES_{EA} & \beta_{EB} - ES_{EB} & \beta_{EC} - ES_{EC} & \beta_{ED} - ES_{ED} & \alpha - E & \beta_{EF} - ES_{EF} \\ \beta_{FA} - ES_{FA} & \beta_{FB} - ES_{FB} & \beta_{FC} - ES_{FC} & \beta_{FD} - ES_{FD} & \beta_{FE} - ES_{FE} & \alpha - E \end{vmatrix} = 0$$

$$= C_A (C_{2p}) + C_B (C_{2p}) + C_C (C_{2p}) + C_D (C_{2p}) + C_E (C_{2p}) + C_F (C_{2p})$$

In actuality, two approaches are used which vary with the ultimate goal : 1) Computational Approach of each Overlap and Resonance Integrals (ab-initio or empirical) or 2) Huckel Approximations.

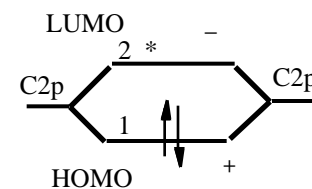
Huckel Approximation:

- All Overlap Integrals are set to 0
- All Resonance Integrals between non-neighbors are set to 0
- All remaining Resonance Integrals are set to

Ethylene: Carbon:  $1s^2 2s^2 2p^2$

" $2p_z$ " e for bond and  
 $2p_x$  e for bond

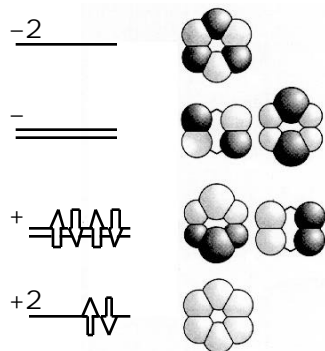
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$



### Benzene

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

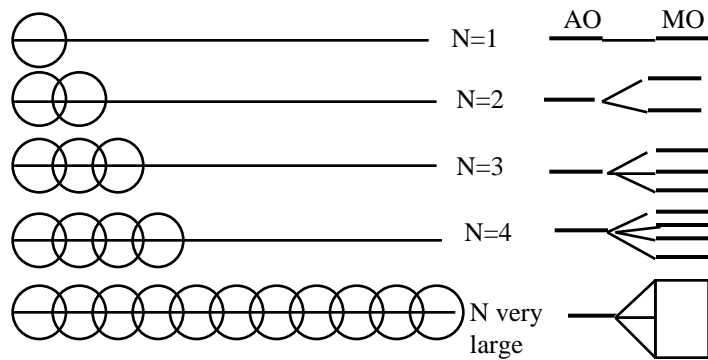
The roots of the secular determinant are  $E = +2\beta$ ,  $-2\beta$ ,  $+\beta$ ,  $-\beta$ ,  $+\beta$ ,  $-\beta$ . Two pairs of MO have the same energy, they are called degenerate orbitals.



- We define the electron binding energy  $E_d$  as the sum of the energies of each electron.
- The added stabilization of conjugated systems is called the delocalization energy,  $E_d$ . It is obtained by comparing for the same number of electrons, the electron-bonding energy of the molecule of interest to that of ethylene.
- For ethylene (2 electrons)  $E_d = 2(+\beta)$   
For butadiene (4 electrons)  $E_d = 4(+\beta) + 0.48\beta$   $E_d = 0.48\beta$   
For benzene (6 electrons)  $E_d = 6(+\beta) + 8\beta$   $E_d = 2\beta$  ( $-150$  kJ/mol)
- The highly negative delocalization energy for benzene explains the “aromatic stability” (higher temperature stability of organic materials containing such structures).

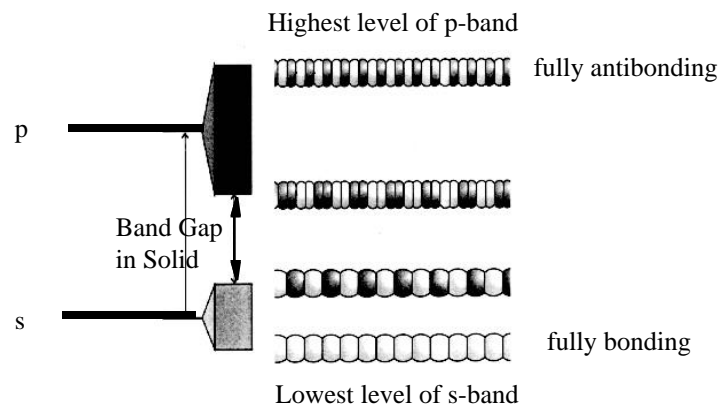
## Band Theory of Solids

- The extreme case of delocalization is that of a solid in which atoms lie in a three dimensional array and take part in a bonding that spreads throughout the entire sample.



- Bands formed from the overlap of s atomic orbitals are called s-bands, these formed from the p atomic orbitals are the p-bands.
- When the s-band and the p-band do not overlap, then the energy domain between these bands is called the band gap. The band gap is the energy domain for which no orbital exist.

### Band Formation



When  $N$  atoms are added together in a line, there are  $N$  atomic orbitals, each contributing a  $2s$  electron in the case of  $\text{Na}$  for example. The  $N$  molecular orbitals cover a band of finite width and the secular determinant (using Huckel approximation) is:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \dots & 0 \\ \beta & \alpha - E & \beta & 0 & \dots & 0 \\ 0 & \beta & \alpha - E & \beta & \dots & 0 \\ 0 & 0 & \beta & \alpha - E & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \alpha - E \end{vmatrix} = 0$$

are now the  $s$ ,  $s$  resonance integral. The roots of such an equation are given by:

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{N+1} \quad \text{for } k = 1, 2, 3, \dots, N$$

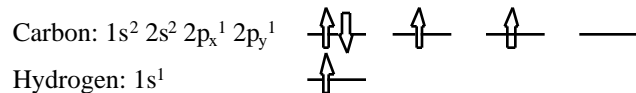
Note that when  $N$  becomes infinitely large:

1.  $E_{k+1} - E_k$  becomes infinitely small
2.  $E_N - E_1$  approaches 4

## Concept of Electron Promotion and Hybridization

- When examining the electronic configuration of Carbon and Hydrogen atoms, it is difficult to understand the structure and properties of molecules such as methane ( $\text{CH}_4$ ), ethylene ( $\text{C}_2\text{H}_4$ ) and acetylene ( $\text{C}_2\text{H}_2$ ).

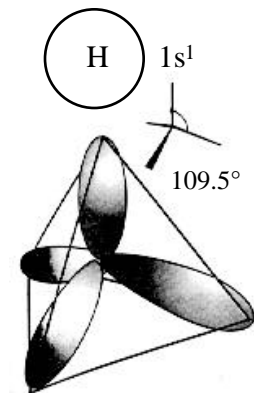
For example, the 4 C-H bonds of methane have identical properties. However, they cannot be made by the same types of electrons, and in principle their energy should be different.



- To make four identical bonds, one needs to first promote an electron from the  $2s^2$  orbital to the empty  $2p_z^1$  orbital and subsequently hybridize the resulting orbitals

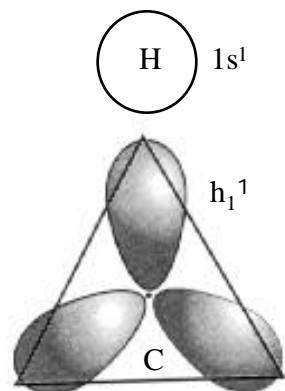
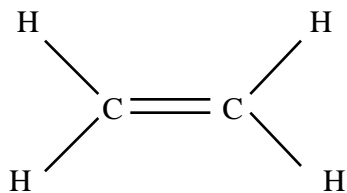
- Electron Promotion:  
 $1s^2 2s^2 2p_x^1 2p_y^1$  transformed into  $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$
- Hybridization ( $sp^3$ )  
 $2s^1 2p_x^1 2p_y^1 2p_z^1$  transformed into  $h_1^1 h_2^1 h_3^1 h_4^1$  where:  
 $h_1 = s + p_x + p_y + p_z$   
 $h_2 = s - p_x - p_y - p_z$   
 $h_3 = s - p_x + p_y - p_z$   
 $h_4 = s + p_x - p_y - p_z$

As a result of constructive and destructive interferences between its various components, each hybridized orbital consists of a big lobe pointing in one corner of a regular tetrahedron (which will be used to make a MO with a H 1s AO). Each of these hybridized orbitals is orthogonal to the other three (zero overlap).



### Other Hybridization Schemes

- sp<sup>2</sup> Hybridization**  
 Similarly, one can form 3 Hybrid sp<sup>2</sup> orbitals by the superposition of one s orbital with two p orbitals.  
 $h_1 = s + (2)^{1/2} p_y$   
 $h_2 = s + (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$   
 $h_3 = s - (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$   
 Each bond is at 120° from the preceding one.



- sp Hybridization**  
 Similarly, one can form 2 hybrid sp orbitals by the superposition of one s orbital with one p orbital.

$$h_1 = s + p_z$$

$$h_2 = s - p_z$$

These bonds are at 180° from each other and in the case of acetylene will form a bond on one side with a 1s electron of a H atom and on the other side with the other carbon atom hybridized orbital.

