

Chapter 13. Molecular Structure and Energy Levels for Polyatomic Molecules

Valence bond (VB) theory

A localized view: A bond is formed with e-pairs between bonding atoms.

Valence shell electron pair repulsion (VSEPR) model:
ligands and lone pairs repel each other.

CO₂

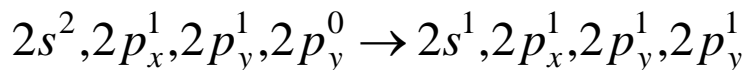
SO₂

H₂O:

Hybrid orbitals

CH₄ is tetrahedral, but electronic configuration of C(2s²2p_x¹2p_y¹) suggests divalence.

Promotion and hybridization:



$$\Psi_h = s \pm p_x \pm p_y \pm p_z \quad (\text{total of 4})$$

(109.5°)

The 4 sp^3 hybrid orbitals are equivalent and responsible for the shape of CH_4 .

Other hybrid orbitals:

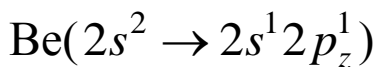
sp ,

sp^2 ,

sp^3

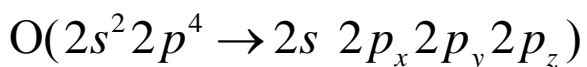
Hybrid orbitals are orthonormal.

BeH_2 :



The two sp orbitals make BeH_2 linear.

H_2O :



The four sp^3 orbitals accommodate 2 lone pairs and 2 bonds with H, making H_2O bent.

Molecular orbital (MO) theory

Dilocalized view: electrons are placed in delocalized MOs.

Walsh diagram

Let's look at H₂A system.

$$\Psi_{MO} = c_1 1s(H_a) + c_2 1s(H_b) \\ + c_3 2s(A) + c_4 2p_x(A) + c_5 2p_y(A) + c_6 2p_z(A)$$

Walsh diagram

At linear geometry

At bent geometry

Explains why BeH₂ is linear and H₂O is bent.

Hückel theory

π system in conjugated molecules (alternating single and double bonds), such as $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, benzene, etc.

Hückel approximation:

- i. Only π MOs are treated and molecular frame is fixed by σ bonds.
- ii. Coulomb integrals (α) are set equal.
- iii. Overlap integrals (S) are set to zero.
- iv. Resonance integrals (β) are equal for neighbors, but zero for non-neighbors.

Ethene:

Secular determinant:

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

Orbital energies

$$E = \alpha \pm \beta$$

Total energy (π electrons) is

$$E = 2(\alpha + \beta) = 2\alpha + 2\beta \quad (\text{no extra stabilization})$$

Butadiene: $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

Secular determinant:

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

Energies are

$$E = \alpha \pm 1.62\beta, \quad \alpha \pm 0.62\beta$$

Total energy:

$$E = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

$$E_{\pi} = 4\alpha + 4\beta$$

Delocalization energy: extra stabilization energy due to delocalization ($E - E_{\pi} = 0.48\beta$).

Benzene:

Secular determinant:

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

Orbital energies

$$E = \alpha \pm 2\beta, \alpha \pm \beta, \alpha \pm \beta$$

Total energy

$$\begin{aligned} E &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned}$$

Delocalization energy is 2β (app. -150 kJ/mol), aromatic stability.

What about $C_6H_6^+$?

$$\begin{aligned} E &= 2(\alpha + 2\beta) + 3(\alpha + \beta) \\ &= 5\alpha + 7\beta \end{aligned}$$

Delocalization energy is 2β .

Band theory for solids

Conductors: conducting and valence bands overlap.

Insulators: large band gap between the bands.

Semiconductors: small band gap between the bands.