

## Lecture #6: Molecular Structure: VB & MO Theory

You are strongly advised to attend these lectures since they involve many transparencies which are not presented on-line.

### I. VB Theory (cont'd)

#### A. Hybridization

#### B. Resonance

### II. MO Theory

### I. VB Theory (Cont'd)

#### A. Hybridization (LCAO on the same atom → new atomic orbitals)

Valence Bond Theory  
Covalent bond forms when two atomic orbitals overlap. Hybridization is used to prepare new atomic orbitals for optimal overlap (strongest bonds).

How use VB-theory to describe orbital overlap consistent w VSEPR

*SP hybrid orbitals* - i.e MgCl<sub>2</sub> molecules formed by heating MgCl<sub>2</sub> salt.

Lewis structure = Cl-Mg-Cl, e-domain geo is linear,

Mg electron config: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup> Orbital config: [Ne]  $\begin{array}{c} \uparrow\uparrow \\ 3s \\ \uparrow\uparrow\uparrow \\ 3p \end{array}$

energy needed to promote electron: [Ne]  $\begin{array}{c} \uparrow \\ 3s \\ \uparrow\uparrow\uparrow \\ 3p \end{array}$

Cl has [Ne]3s<sup>2</sup>3p<sup>5</sup>, so the p orbitals open to bonding

Thus initially in principle Mg 3s/3p forms bond with Cl 3p

Bonds are equal so mixing of 3s & 3p orbitals = hybridization

leads to 2 sp orbitals.

The good overlap lowers energy to offset e-promotion energy.

Illustrate Cl P orbitals overlapping the two sp orbitals of Mg

*Hybrid orbitals w nonbonding e-*

i.e. H<sub>2</sub>O: Lewis structure H-<sup>⋅</sup>O-<sup>⋅</sup>H 4-electron domains, thus 4 = sp<sup>3</sup> superscripts add (# hybrid orbitals = # atomic orbitals)

Note O-atom config: [He]  $\begin{array}{c} \uparrow\uparrow \\ 2s \\ \uparrow\uparrow\uparrow \\ 2p \end{array}$  → [He]  $\begin{array}{c} \uparrow \\ 2s \\ \uparrow\uparrow\uparrow \\ 2p \end{array}$

→ [He]  $\begin{array}{c} \uparrow\uparrow\uparrow \\ sp^3 \end{array}$  2 orbitals for bonding to H

SP hybrid - 2 e-domains linear

SP<sup>2</sup> hybrid - 3 e-domains, trigonal planar

sp<sup>3</sup> hybrid - 4 e-domain, tetrahedral

sp<sup>3</sup>d hybrid - 5 e-domain, trigonal bipyramidal

sp<sup>3</sup>d<sup>2</sup> hybrid - 6 e-domain, octahedral

*Steps for determining hybrid orbitals* - 1. write lewis structure, 2. Determine e-domain geometry 3. From the # of e-domain determining hybrid orbitals noting # superscripts = # e-domains. 4. For nonbonding electrons, still may fill the orbitals

i.e. determine hybrid orbitals & draw geo of SF<sub>4</sub>

Draw lewis structure of SF<sub>4</sub>, note 5-e domains, thus sp<sup>3</sup>d

### B. Resonance

Resonance (hybrid) = expressing a wavefn as a superposition (LC) of wavefn corresponding to a variety of structures.

For example: HCl wave fn is a resonance hybrid of covalent & ionic wavefn:  $\psi = \psi_{cov} + \lambda \psi_{ion}$

$\psi_{cov} = \psi_{H1s}(1)\psi_{Cl2pz}(2) + \psi_{H1s}(2)\psi_{Cl2pz}(1)$ ,  $\psi_{ion} = \psi_{Cl2pz}(1)\psi_{Cl2pz}(2)$

$\psi$  is a trial wavefunction in which SE is solved yielding  $E$ .  $\lambda$  is varied until  $E$  is lowerd ( $E \geq$  to true  $E$ ) and correspond  $\psi$  is best  $\psi$ . This is **variation Theorem**.

The fraction of  $\psi_{\text{ion}}$  contributions is proportional to  $\lambda^2$ .

Resonance lowers energy relative to individual component wavefns ( $\psi_{\text{cov}}$  &  $\psi_{\text{ion}}$ ): the is **resonance stabilization**. -> i.e. for Benzene 2 resonance structures stabilize  $E$

### III. Molecular Orbitals

*In VB Theory – Occupied atomic orbitals were allowed to merge (overlap).*

*In M.O. Theory – A linear combination is formed from atomic orbitals with all electrons removed, then electrons are added (“poured into”) the resultant molecular orbitals.*

Electrons do not belong to particular bonds - first remove **all** e- from MOs from LC of A orbitals, then fill in electrons to bonding, antibonding & nonbonding orbitals. VB theory does good job **with ground state** geometry, but to describe **excited state** and understand certain properties as **paramagnetism** we need to invoke Molecular Orbital (MO) theory.

#### A. LCAO

*Intro: molecular orbitals from s atomic orbitals*

MO Theory says that MOs are a LCAO, then we fill these MO with electrons to get an electron configuration for a molecule, just as we filled e for atomic orbitals to get e-configurations. Hunds rules, Pauli exclusion principle, and orbital conservation hold.

*Hydrogen Molecule*

Linear combination of 1s orbitals yields 2 MOs: bonding MO & antibonding (e-density increase/decrease):

e-density increased for bonding thus more stable than sep atoms, but anti bonding e are repelled from internuc axis region thus less stable separate atoms.

e-density in symmetric wrt to axis thus **sigma molecular orbitals** ( $\sigma_{1s}$  and  $\sigma^*_{1s}$ ).

MO energy level diagram

Note that  $\text{H}_2$  forms stable molecule whereas  $\text{He}_2$  doesn't.

#### Bond Order

Molecular stability may be determined from the Bond Order = ? (# e in Bonding orbitals - #e in antibonding orbitals)

BO for  $\text{H}_2$  = ? (2-0) = 1, BO for  $\text{He}_2$  = ? (2-2) = 0. Compute the BO for  $\text{H}_2^-$  (answer = ? ).

What's the electron config for  $\text{H}_2^-$  :  $\sigma_{1s}^2 \sigma^*_{1s}^1$