

# Chemistry 2000 Slide Set 8: Valence bond theory

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# MO theory: a recap

- A molecular orbital is a one-electron wavefunction which, in principle, extends over the whole molecule.
- Two electrons can occupy each MO.
- MOs have nice connections to a number of experiments, e.g. photoelectron spectroscopy, Lewis acid-base properties, etc.
- However, correlating MO calculations to **bond** properties is less straightforward.

# Valence-bond theory

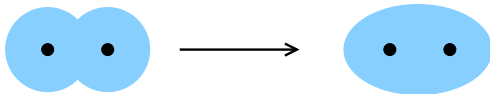
- Valence-bond (VB) theory takes a **different** approach, designed to agree with the chemist's idea of a chemical bond as a shared pair of electrons between two **particular** atoms.
- Bonding is described in terms of overlap between orbitals from adjacent atoms.
- This “overlap” gives a two-electron bond wavefunction, **not** a one-electron molecular orbital.  
**There are no molecular orbitals in valence-bond theory.**
- The description of bonding in VB theory is a direct counterpart to Lewis diagrams.

## Example: H<sub>2</sub>

- For diatomic molecules, the VB and MO descriptions of bonding are **superficially** similar.
- In VB theory, we start with the Lewis diagram, which for H<sub>2</sub> is



- We need to make a single bond.
- We take one 1s orbital from each H atom, and “overlap” them to make a valence bond:



- Two electrons occupy this valence bond.
- The overlap operation is **not the same** as the linear combinations of LCAO-MO theory.

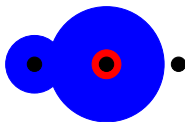
# Polyatomic molecules

- In traditional chemical theory (e.g. Lewis diagrams), a chemical bond consists of one or more pairs of electrons being shared between **two** atoms.
- Valence-bond theory builds two-electron **bond** wavefunctions.
- These wavefunctions should occupy the space **between** two atoms and not extend very far outside this region.  
(Again, think in terms of the lines in a Lewis diagram.)

**Problem:** Atomic orbitals don't necessarily point in the right directions in space, nor are they necessarily confined to the region between two atoms.

**Solution:** Use mixtures of atomic orbitals (“hybrid orbitals”) instead of the AOs themselves.

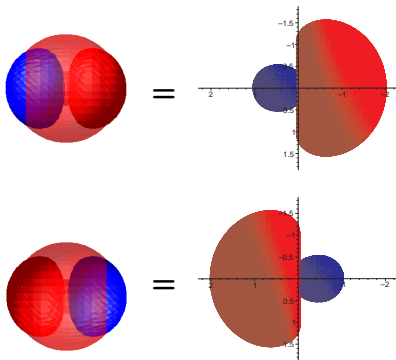
- Suppose that we wanted to make VB wavefunctions for the two Be-H bonds in BeH<sub>2</sub>.
- We can't use a Be 2s orbital to form the valence bonds because this orbital extends into the bonding regions for **both** H atoms:



- Another way to think about this is that a valence bond made between one of the H atoms and the Be atom using the 2s orbital would interfere with the valence bond to the other H atom.

# Hybrid atomic orbitals

- To fix this problem, we add atomic orbitals **on Be** to get **hybrid atomic orbitals** that point towards each of the H atoms, with little extension in the opposite direction.
- Specifically, for a linear molecule, we use **sp hybrids** made by adding (or subtracting) the 2s and 2p<sub>z</sub> atomic orbitals **on the same atom**:



## Hybrid atomic orbitals (continued)

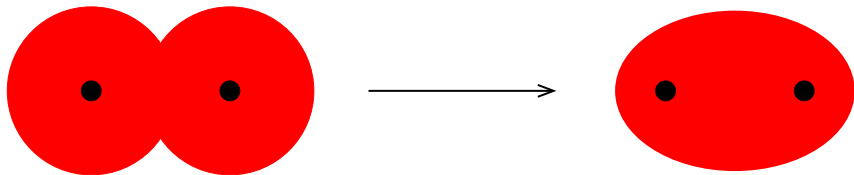
- Once we have the hybrid orbitals, we can overlap them with the H 1s AOs to form two valence bond wavefunctions.

**Notation:** Each of these bonds would be described as  $\text{Be}(\text{sp})\text{-H}(1\text{s})$ .



## Comparing MO and VB theory

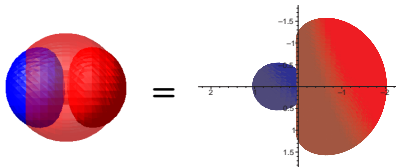
- In MO theory, we make linear combinations of AOs (LCAOs) from **different** atoms to make an MO.



- These MOs extend (in principle) over the whole molecule.

## Comparing MO and VB theory (continued)

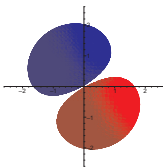
- In VB theory we combine AOs from **one** atom to make **hybrid atomic orbitals**.



- These hybrid orbitals are used to construct a wavefunction for a **shared electron pair** involved in a particular chemical bond.

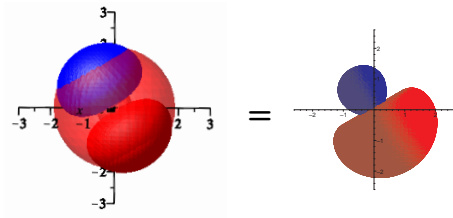
- BH<sub>3</sub> is trigonal planar.
- The s and p orbitals of boron do not point toward the corners of an equilateral triangle.
- We will create a set of hybrid orbitals that do point toward the corners of an equilateral triangle and can thus be used in the VB treatment of BH<sub>3</sub>.
- The 2p orbitals point along the Cartesian axes.
- We will need **two** 2p orbitals to create orbitals that point toward different directions in a plane.
- We will therefore construct **sp<sup>2</sup> hybrids** from the 2s, 2p<sub>x</sub> and 2p<sub>y</sub> atomic orbitals.

- In general, combining two p wavefunctions gives another p wavefunction, but rotated:

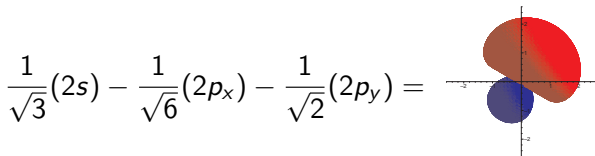
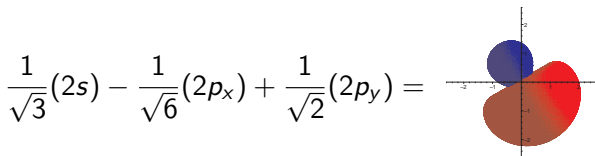
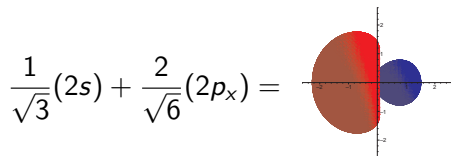
$$-\frac{1}{2}(2p_x) + \frac{\sqrt{3}}{2}(2p_y) =$$


Note:  $-\frac{1}{2}(1, 0, 0) + \frac{\sqrt{3}}{2}(0, 1, 0)$  is a vector that points  $120^\circ$  counter-clockwise from the x axis.

- Adding in an appropriate amount of s character then cancels off most of the wave in one of the lobes:



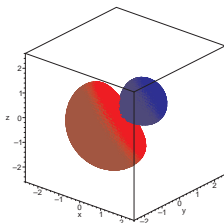
# $sp^2$ hybrids



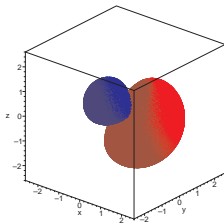
- We now need to make hybrid orbitals that point to the corners of a tetrahedron.
- The idea is exactly as with the trigonal planar geometry, except that we now need our hybrid orbitals to point to directions in the full three-dimensional space.
- We therefore need all three 2p orbitals, resulting in  $sp^3$  hybrids.

# $sp^3$ hybrids

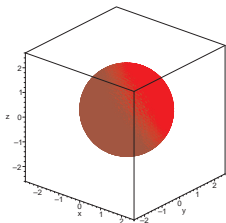
$$\frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) =$$



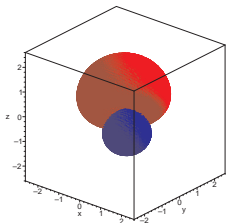
$$\frac{1}{2}(2s - 2p_x - 2p_y + 2p_z) =$$



$$\frac{1}{2}(2s - 2p_x + 2p_y - 2p_z) =$$

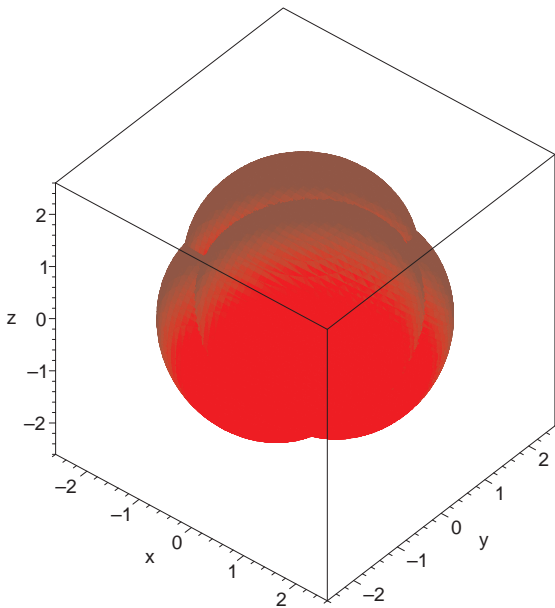


$$\frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) =$$





All four  $sp^3$  hybrids together:



# Hybridization and VSEPR

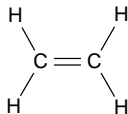
- The VSEPR **electronic geometries** are each uniquely associated with a hybridization state:

Electronic geometry	Hybridization
Linear	$sp$
Trigonal planar	$sp^2$
Tetrahedral	$sp^3$

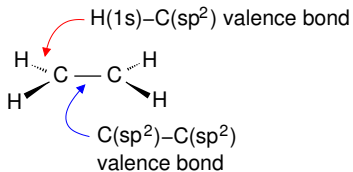
In a lot of cases, this table is all you need to know about VB theory. . .

- Example:  $\text{NH}_3$  has a tetrahedral **electronic geometry**, therefore  $sp^3$  hybridization at N.

# Ethene

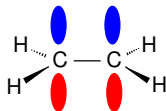


- Trigonal planar carbons  $\implies$   $sp^2$  hybridization
- $sp^2$  hybrids used to make  $\sigma$  bonds to H atoms (with their 1s orbitals) and between the C atoms:



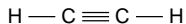
## Ethene (continued)

- This leaves one unused p orbital on each carbon atom:

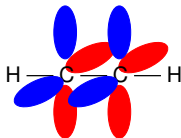


- The overlap of these p orbitals forms a  $\pi$  valence bond.
- VB description of the  $\pi$  bond: C(2p)-C(2p).

# Ethyne

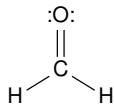


- Linear geometry around each carbon  $\implies$  sp hybridization
- Each carbon atom has two p orbitals left over:

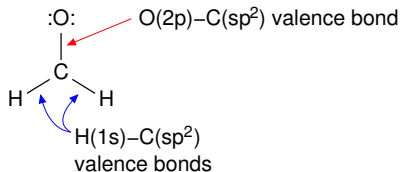


- These p orbitals combine into **two**  $\pi$  bonds.

# Formaldehyde



- Trigonal planar geometry at the carbon atom  $\implies$   $sp^2$  hybridization
- The O atom can form a  $\sigma$  bond using a p orbital.

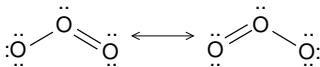


- Why use the O(2p) rather than the O(2s) for bonding?
  - The general assumption in VB theory is that lone pairs go into the lowest-energy AO.

# Formaldehyde

- The carbon atom has one p orbital left over which can combine with the corresponding orbital on O to form the  $\pi$  bond.

# Ozone

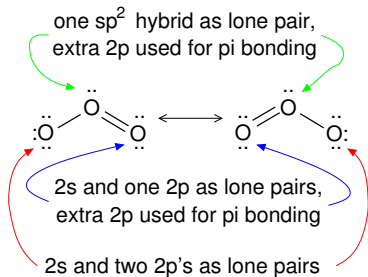


- The sigma framework of ozone is easy:
  - The central O is  $sp^2$  hybridized.
  - One of the  $sp^2$  hybrids contains a lone pair.
  - The other two form  $\sigma$  bonds with one p orbital on each of the terminal O atoms.
- What about the double bond?

Resonance!



- Construct VB wavefunctions corresponding to both of these structures and average these wavefunctions together:



# Shortcomings of VB theory

- A lot of things that fall out naturally in MO theory are hard in VB theory:
  - Explanation of photoelectron spectra
  - Explanation of paramagnetism of  $O_2$
  
- In its simplest form, VB theory only tells us what we already know based on Lewis diagrams and VSEPR.  
It only becomes a predictive theory in its most advanced forms.