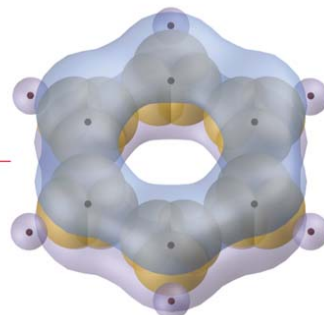
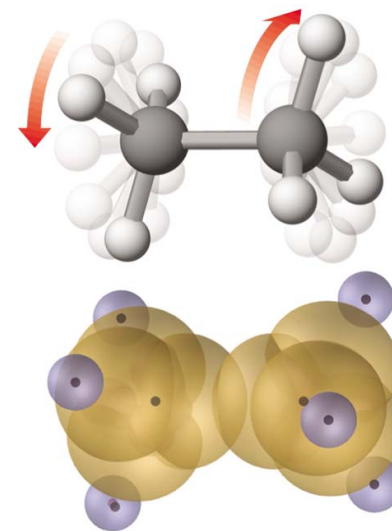
 σ and π bonding in benzene

Model of bonding in benzene

© 2003 Thomson - Brooks/Cole

(a) Free rotation can occur around the axis of a single (σ) bond.

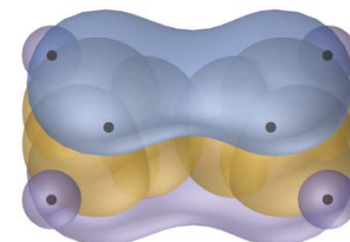
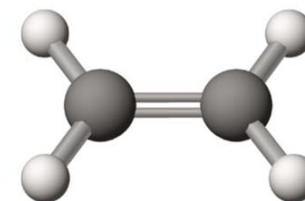
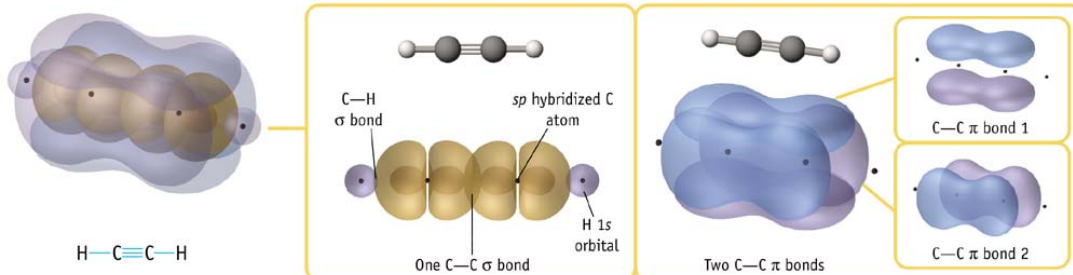
CHEMISTRY 2000

Topic #1: Bonding – VB Theory

Fall 2020

Dr. Susan Findlay

See Exercises 5.3 to 5.5

(b) In contrast, rotation is severely restricted around double bonds because doing so would break the π bond, a process generally requiring a great deal of energy.



Valence Bond Theory vs. MO Theory

- There are two major models for bonding theory:
 - We've spent the last 2-3 weeks introducing ourselves to **molecular orbital theory** – in which atomic orbitals are combined to make molecular orbitals in which electrons reside. From a computational perspective, MO calculations are much simpler than the alternative, and there are several very good software packages that allow just about anyone to build models and use MO theory to predict their properties. Even organic chemists. 😊
 - The alternative is **valence bond theory**. In valence bond theory, the orbitals on each atom are first “hybridized” so that they can then be combined to make localized bonds. This is more computationally difficult than molecular orbital theory – particularly for larger molecules. I don't know of any software packages that will let the “lay chemist” do valence bond calculations.
- While some chemists like to mix VB theory into their MO theory (or MO theory into their VB theory), it's not good practice. Because you are likely to encounter VB terminology at some point in future chemistry courses (or MCATs), we will take a brief look at VB theory.



Valence Bond Theory vs. MO Theory

- VB Theory begins with two steps:
 - hybridization (*where necessary to get atomic orbitals that "point at each other"*)
 - combination of hybrid orbitals to make bonds with electron density localized between the two bonding atoms
- Key differences between MO and VB theory:
 - MO theory has electrons distributed over whole molecule
 - VB theory localizes an electron pair between two atoms
 - MO theory combines AOs on DIFFERENT atoms to make MOs (*LCAO*)
 - VB theory combines AOs on the SAME atom to make hybridized atomic orbitals (*hybridization*)
 - In MO theory, the symmetry (or antisymmetry) of the molecule must be retained in each orbital.
 - In VB theory, all orbitals must be viewed simultaneously to see retention of the molecule's symmetry.



Valence Bond Theory and Hybridization (BeH_2)

- The VB picture of a molecule derives directly from its molecular geometry. Consider (again) the simplest triatomic: BeH_2 .

- BeH_2 is a _____ molecule with equal Be–H bond lengths. Thus, according to VB theory, Be would need two atomic orbitals of equal energy that are _____ apart. Using only s and p orbitals, this is not possible:



Valence Bond Theory and Hybridization (BeH_2)

- Now, Be has two hybrid atomic orbitals of equal energy that are _____ apart. Each of these can combine with a $1s$ orbital on one of the hydrogen atoms to make a σ bond:



Valence Bond Theory and Hybridization (BH_3)

- BH_3 would be a _____ molecule with equal B–H bond lengths. Thus, B would need three AOs of equal energy that are _____ apart. Again, we can't do this using only s and p orbitals.
- We form three sp^2 orbitals from the $2s$ and two $2p$ orbitals:



Valence Bond Theory and Hybridization (BH_3)

- **The empty $2p$ orbital doesn't participate in hybridization, giving a B atom with one $2p$ orbital and three $2sp^2$ orbitals.** *Note that the energy of an sp^2 orbital is closer to the p energy because it has more 'p character' than 's character'.*
- Now, B has three hybrid atomic orbitals of equal energy that are _____ apart. Each of these can combine with a $1s$ orbital on one of the hydrogen atoms to make a σ bond:



Valence Bond Theory and Hybridization (CH₄)

- CH₄ is a _____ molecule with equal C–H bond lengths. Thus, C would need four atomic orbitals of equal energy that are _____ apart.
- We form four *sp*³ orbitals from the 2*s* and three 2*p* orbitals:



Valence Bond Theory and Hybridization (CH₄)

- Now, C has four hybrid atomic orbitals of equal energy that are _____ apart. Each of these can combine with a 1s orbital on one of the hydrogen atoms to make a σ bond:



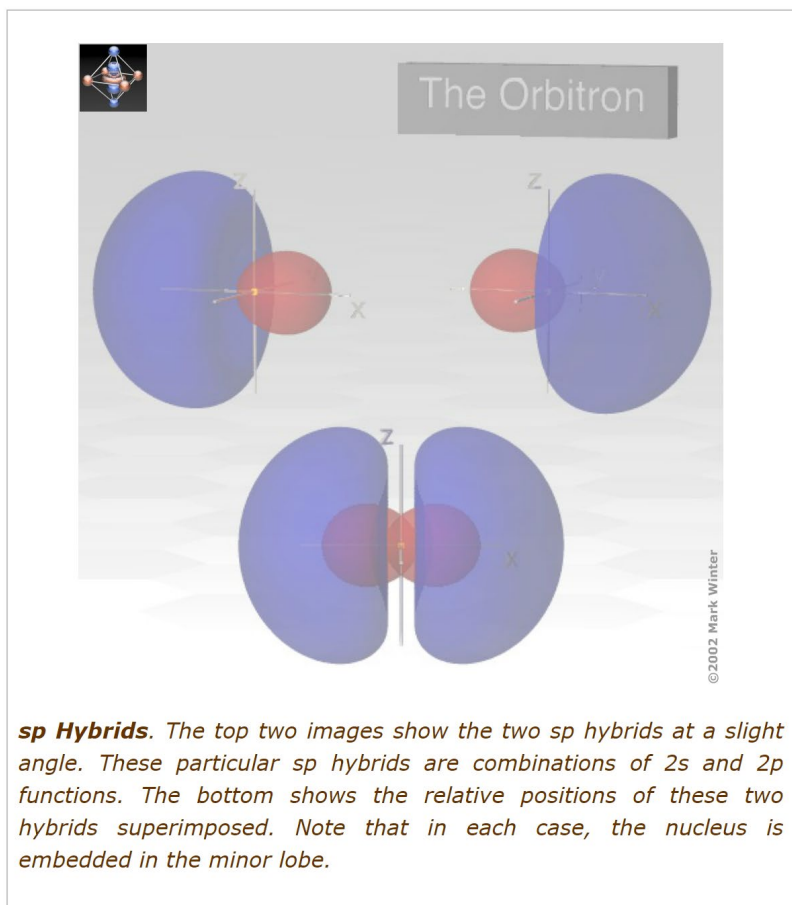
Valence Bond Theory in Short

- Atoms are typically only hybridized if it's necessary to give the observed geometry and bond lengths. As such, terminal atoms are not typically hybridized (since you can just use a p orbital).
- **Electron Group Geometry determines hybridization:**
 - Linear (180°) = sp ($s+p$ with two leftover p orbitals)
 - Trigonal planar (120°) = sp^2 ($s+p+p$ with one leftover p orbital)
 - Tetrahedral (109.5°) = sp^3 ($s+p+p+p$ with no leftover p orbitals)
- Hybrid orbitals have σ symmetry and combine with each other (or other σ -symmetric atomic orbitals) to make σ bonds in which two electrons are localized between two atoms.
- π bonds for double or triple bonds are made by combining the "leftover" π -symmetric p orbitals (just like we did in MO theory).

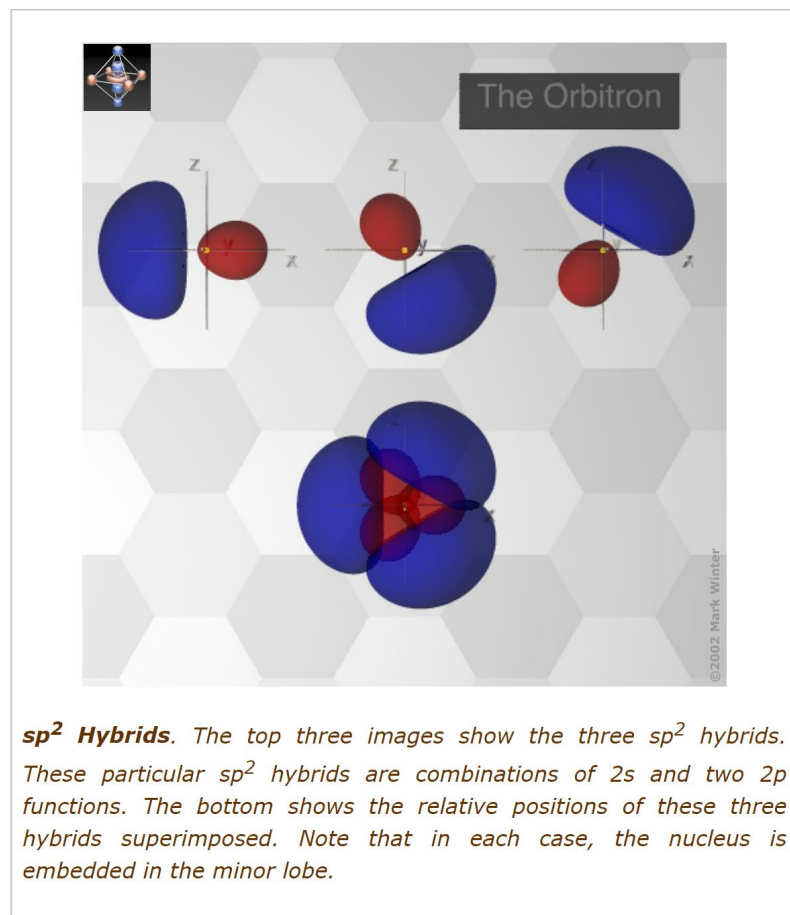
Valence Bond Theory in Short

- <http://winter.group.shef.ac.uk/orbitron/AO-hybrids/index.html> has nice pictures of each type of hybrid atomic orbital:

Atomic hybrid orbitals: sp

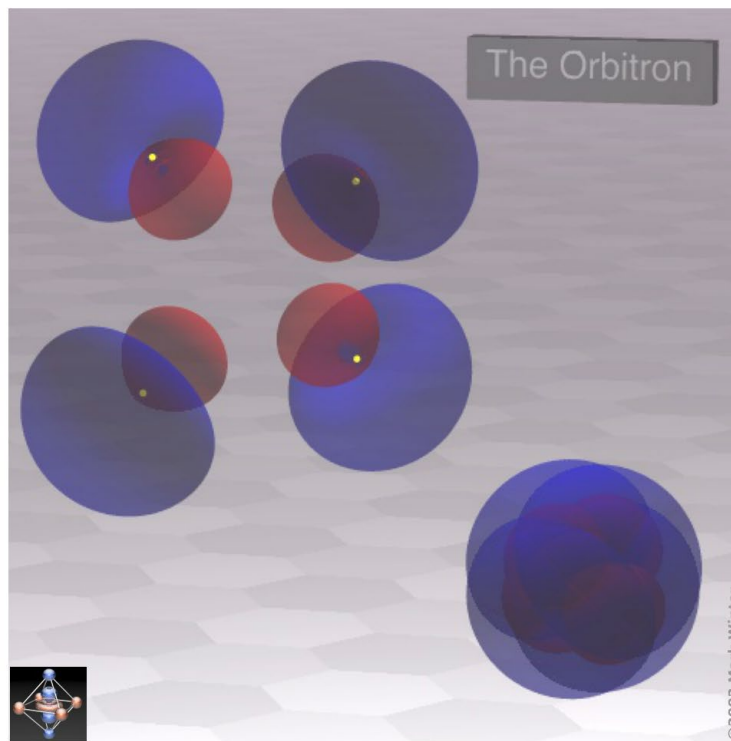


Atomic hybrid orbitals: sp^2



Valence Bond Theory in Short

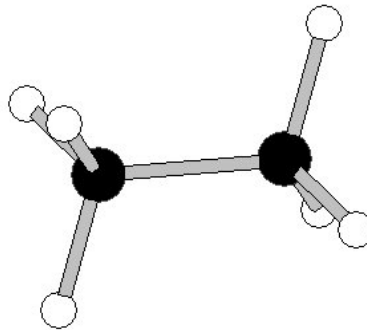
Atomic hybrid orbitals: sp^3



sp^3 Hybrids. The top four images show the four sp^3 hybrids. These particular sp^3 hybrids are combinations of $2s$ and three $2p$ functions. The bottom shows the relative positions of these four hybrids superimposed. Note that in each case, the nucleus is embedded in the minor lobe.

VB Theory for Larger Molecules: Ethane

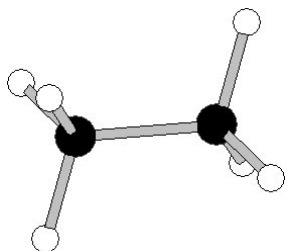
- The Lewis structure for ethane (C_2H_6) is:
- According to VSEPR theory, each carbon atom is _____ and therefore ____ hybridized. A three-dimensional picture of ethane looks like:



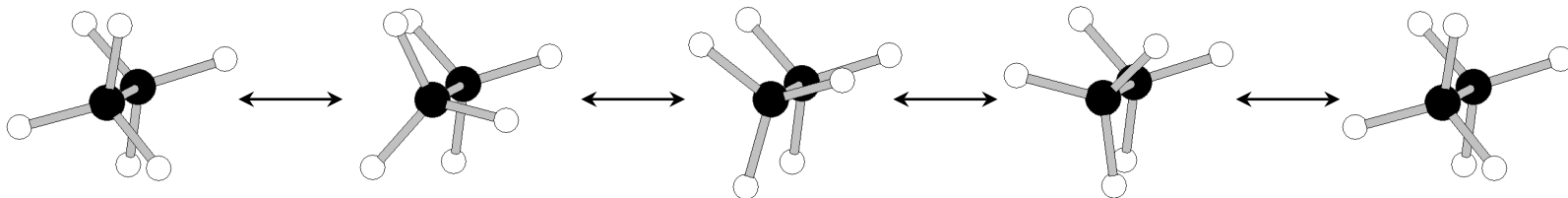
To make things easier for those of us who aren't artists, we use wedges and dashes to indicate 3-dimensional shape. A wedge indicates that an atom is coming out of the page toward you. A series of dashes indicates that an atom is going into the page away from you.

VB Theory for Larger Molecules: Ethane

- The bonding in ethane can be explained using sp^3 hybridization of each carbon atom and $1s$ orbitals on each hydrogen.
 - Each C–H σ bond is due to combination of an sp^3 orbital from C and an s orbital from H.
 - The C–C σ bond is due to combination of sp^3 orbitals from each C.



- Because the C–C bond is a σ bond, it can be rotated freely without breaking. Ethane is therefore not limited to one conformation. It can rotate freely between them:



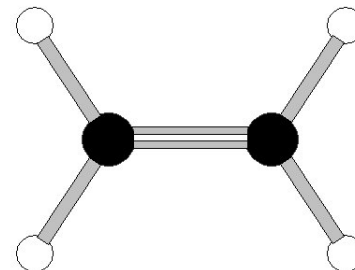
VB Theory for Larger Molecules: Ethene

- The Lewis structure for ethene (C_2H_4) is:

- According to VSEPR theory, each carbon atom is _____ and therefore _____ hybridized. A three-dimensional picture of ethene looks like:



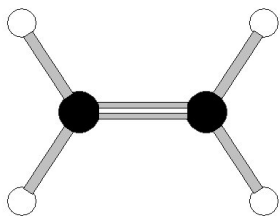
or



Ethene is flat so it's easiest to draw a top-view. If we wanted to draw a side-view, we'd use wedges and dashes.

VB Theory for Larger Molecules: Ethene

- The bonding in ethene can be explained using sp^2 hybridization of each carbon atom and $1s$ orbitals on each hydrogen.

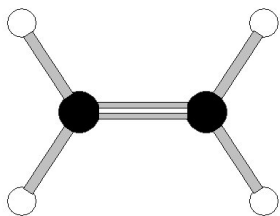


- Each C–H σ bond is due to combination of an sp^2 orbital from C and an s orbital from H.
- The C–C σ bond is due to combination of sp^2 orbitals from each C.
- The C–C π bond is due to combination of p orbitals from each C.



VB Theory for Larger Molecules: Ethene

- Why is ethene flat?



- The only way that the π bond can form is if the two p orbitals are lined up (same symmetry):



- If we rotate the C-C bond by 90° , the C-H σ bonds are farther apart, but the p orbitals are **orthogonal** and therefore do not overlap at all. Thus, there is no π bond:
- Since ethene would be much less stable without the π bond, the CH_2 fragments are forced to be **coplanar**, making the molecule flat. In other words, rotating around the C=C bond would require **BREAKING** the π bond – which requires a fair amount of energy. As such, π bonds always make a molecule more rigid.

VB Theory for Larger Molecules: Ethyne

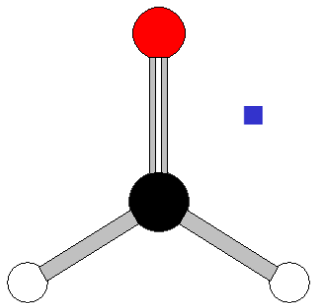
- The Lewis structure for ethyne (C_2H_2) is:



- According to VSEPR theory, each carbon atom is **linear** and therefore *sp* hybridized:
 - Each C–H σ bond is due to combination of an *sp* orbital from C and a $1s$ orbital from H.
 - The C–C σ bond is due to combination of *sp* orbitals from each C.
 - The C–C π bonds are due to combination of $2p$ orbitals from each C.

VB Theory for Larger Molecules: CH₂O

- The Lewis structure for formaldehyde (CH₂O) is:



- According to VSEPR theory, the carbon atom is **trigonal planar** and therefore *sp*² hybridized:
 - Each C–H σ bond is due to combination of an *sp*² orbital from C and a 1*s* orbital from H.
 - The C–O σ bond is due to combination of an *sp*² orbital from C and a 2*p* orbital from O. (*You could hybridize O too, but it's unnecessary.*)
 - The C–O π bond is due to combination of 2*p* orbitals from C and O.
 - The lone pairs on O are its two remaining AOs (2*s* and a 2*p*).

VB Theory for Larger Molecules: HCN

- The Lewis structure for hydrogen cyanide (HCN) is:
- According to VSEPR theory, the carbon atom is **linear** and therefore *sp* hybridized:
 - The C–H σ bond is due to combination of an *sp* orbital from C and a $1s$ orbital from H.
 - The C–N σ bond is due to combination of an *sp* orbital from C and a $2p$ orbital from N. (*You could hybridize N too, but it's unnecessary.*)
 - The C–N π bonds are due to combination of $2p$ orbitals from C and N.
 - The lone pair on N is its remaining atomic orbital ($2s$).

