

WS 9: The Valence Bond Model and Hybridization

The Lewis theory of the chemical bond and its extension VSEPR, assume that each bonding electron pair is located between the two bonded atoms. From Chapter 6, we know that electrons are not located at precise positions but are spread over a region defined by the atomic orbitals they occupy. Our task is to see how to combine the Lewis approach with the description of a molecule in terms of orbitals. We will use **Valence Bond Theory** (VBT) for this.

DEFINITION: Valence-bond theory is a description of bond formation in terms of merging of atomic orbitals in the valence shells of neighboring atoms and of pairing of the spins of the electrons that occupy these orbitals.

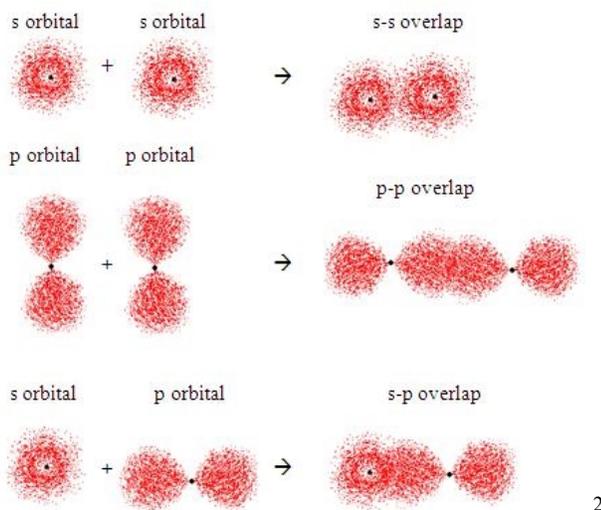
Types of bonds in VBT:

There are two types of bonds that we consider in valence bond theory: the sigma bond (σ) and the pi bond (π).

- Sigma bonds are skeletal bonds
- They hold molecules together and are stronger than pi bonds
- Pi bonds represent multiple bonds
 - They consist of a sigma bond and p-orbital overlap.

Let's consider **overlap between pure atomic orbitals** with 1s orbitals and 2p orbitals. The sigma bond (σ), or sigma type overlap occurs when the orbitals lie along the inter-nuclear axis, the line that joins two atoms.

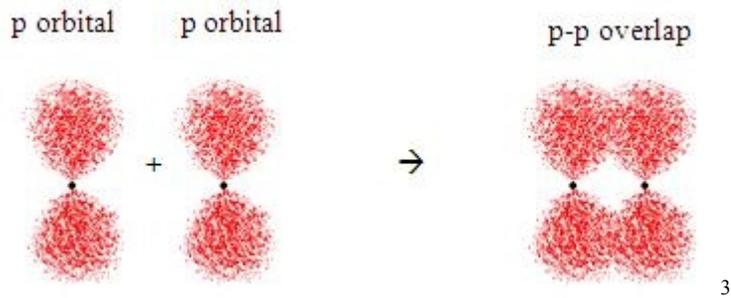
- The following overlaps form a σ bond: s-p, s-s, p-p (end to end). The sigma bond is usually a single bond or a skeletal bond.¹



¹ Atkins page 337

² https://sites.google.com/site/ed350201003/_/rsrc/1287654375409/Task/sigma.JPG

- A multiple bond consists of a σ bond and one or two π bonds. The side-to-side overlap of two p orbitals forms a π bond.
 - The two lobes of a π bond lie on either side of the axis. To achieve side-to-side overlap, the p orbitals must be aligned.



- This means that the molecule is not free to rotate about a multiple bond axis as it is about a single bond axis.
 - A π bond is weaker than a σ bond because its overlap is not as efficient.
 - A single bond consists of one σ bond between two atoms; a double bond consists of a σ bond and one π bond between two atoms; a triple bond consists of a σ bond and two π bonds between two atoms.

Drawing the bond:

Draw a 2p_x orbital

Draw a 2p_z orbital

Draw a 1s orbital.

Draw a 2p_x orbital with 1 electron overlapping a 1s orbital with 1 electron forming a σ bond

Draw two 2p_x orbitals with 1 electron each showing σ bond

Draw two 2p_z orbitals with one electron each showing π bond

³ https://sites.google.com/site/ed350201003/_/rsrc/1287654452021/Task/pi.JPG

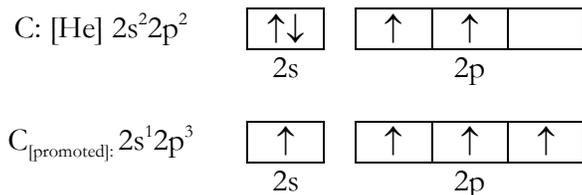
Notice that the two 2p_x orbitals overlap on the inter-nuclear axis, while the two 2p_z orbitals form a plane of electron density above and below the inter-nuclear axis.

Part 2: The fundamental basis of Valence Bond Theory;

Valence bond theory states that a bond forms when two atomic orbitals come close enough together that they overlap. Orbitals inter-penetrate, but the term overlap is commonly used.

- Overlap implies that the atoms share electrons.
- Each bond contains at most two electrons with their spins paired (opposed).
- A high degree of overlap means that a strong bond is formed.
- Atomic orbitals with directional character (those that point in a certain direction) overlap better than those with no directional character.
 - We say they overlap more efficiently or there is a greater degree of overlap.

An attempt to explain the bonding in the CH₄ (methane) molecule provides an example of the need for hybridization. The promoted, or excited, configuration of C permits the formation of four equal C—H bonds.



If we examine the un-hybridized orbitals of carbon, we see a problem.

- A bond that would result from the overlap of a half-filled 2p orbital on carbon with a half-filled orbital on the hydrogen (1s) would have a bond angle of 90°.
- The filled 2s orbital on carbon would not form a bond at all.
- These bonds would disagree in two ways with the experimental results for the bonding on methane.

In methane, the four bonds are the same; the bonds we have just formed differ from each other because they use different orbital overlap to form the bonds.

- One bond forms via 2s–1s overlap while three other bonds form via 2p–1s overlap. Also, the just predicted bond angles are 90°, compared to the bond angles of 109.5°.
- **However, we can combine the four pure atomic orbitals to produce four equivalent hybrid orbitals. THIS IS THE BASIS OF HYBRIDIZATION.**

Hybridization: Combining or mixing atomic orbitals to create a new orbital that has properties of the atomic orbital. These new orbitals have the molecular shape and angle suitable for bonding in VBT.

Notice that hybridization is used after we know the bond angles, which VSEPR theory can often predict.

HOW DOES IT WORK?

In the process of hybridization, pure atomic orbitals are combined (mathematically mixed) to produce hybrid orbitals that have the correct geometry for the resulting molecule. The hybridization of a species can be predicted by starting from the Lewis structure.

There are as many hybrid orbitals as there are total electron pairs on the central atom. This implies that there is conservation of orbitals.

What goes in must come out.

Recall that the total number of electron pairs is found by adding the number of lone pairs to number of bonding pairs. The pure atomic orbitals are used in order of increasing energy. Thus, if the total number of electron pairs is two, and one s and one p orbital are combined or hybridized to form two sp hybrid orbitals. If an s and two p orbitals hybridize (three atomic orbitals), they form three sp²-hybridized orbitals.

Table 1: Electron Domain Geometry

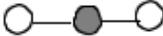
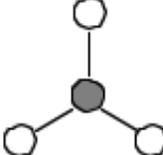
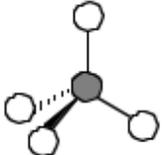
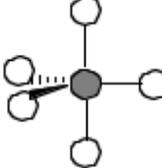
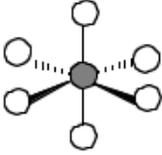
No. Eln. Pairs	2	3	4	5	6
	Linear	Trigonal planar	Tetrahedral, tetrahedron	Trigonal bipyramidal	Octahedron
Electron pair geometry					
Bond angles	180°	120°	109.5°	120° equatorial 90° axial	90°

Table 2: Hybridized orbitals, geometries, and angles

Number of lone pairs and bonds	Hybridization	Geometry of hybrid	Bond angles
2	sp	linear	180°
3	sp ²	Trigonal planar	120°
4	sp ³	tetrahedral	109.5°
5	sp ³ d	trigonal bipyramidal	120°, 90°
6	sp ³ d ²	octahedral	90°

When hybrid orbitals are formed, those that are to hold lone pairs are full, while those that are to form bonds have one electron. The exception is the coordinate covalent bond. Whenever we consider the origin of bonding, we must assess whether the overall outcome of a series of changes is a net lowering of energy. In carbon, not only is the energy of promotion or formation of hybridized orbitals very small and for bonds are formed in place of the two bonds of the un-promoted electrons in the pure orbitals, but the sigma bonds are stronger than in the absence of hybridization because the hybrid orbitals are strongly directional and have a large overlap with the orbitals of the neighboring atoms.

- Energy is lowered with hybridization
- Sigma overlap is stronger in the hybridized molecule than in the un-hybridized molecule
- Hybridized are directional and have good overlap.

The properties of hybrid orbitals depend on the properties of the pure atomic orbitals that were combined to form them. Consider the direction of the orbital. A p orbital points along a line

on an axis (xyz). Thus, if an s orbital is combined with a p orbital the two sp hybrids formed must also point along a line. In similar fashion, sp² orbitals are confined to a plane; they are made from 2 p orbitals interacting with an s orbital all in the same plane; they must be flat. When three p orbitals and an s orbital interact, the result is a three-dimensional structure because each of the p orbitals lies on a different axis orthogonal to each other. Therefore, the four sp³ orbitals are three-dimensional. When the number of bonds pairs totals five or six, d orbitals must be included in the hybridization scheme, since the mixing orbitals are s, p, and d atomic orbitals. This makes the hybrid orbitals sp³d and sp³d² respectively.

TAKE AWAY:

- The hybrid orbitals are like atomic orbitals as they are considered mathematical functions
- Energy of the orbitals is lowered with hybridization
- Sigma overlap is stronger in the hybridized molecule than in the un-hybridized molecule
- Hybridized are directional and have good overlap.
- The total number of atomic orbitals mixed equals the number of hybrid orbitals made
- There are 5 types of hybrid orbitals
 - They correspond to VSEPR shapes
- Lone pairs must go in hybrid orbitals to minimize repulsions.
- Hybridization creates bi-lobe orbitals with one side being larger than the other
- These orbitals have direction and angle, and characteristics of the mixed atomic orbitals.

Building the hybrid scheme

1. Draw the most plausible Lewis structure for the species; include formal charge
 - a. For each central atom, count the total number of bonds and lone pairs. These are the regions of electron density or electron domains.
 - b. The total number of electron domains determines the electron domain geometry based on VSEPR and the number of hybrid orbitals needed for that geometry.

Use the following information to determine the hybridization of the central atom:

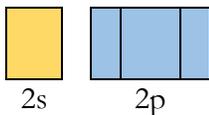
1. Write the ground state orbital diagram of the central atom (subtracting or adding electrons to account for the charge, if any, of the species.
 - a. You don't have to add any electrons yet; it is the number of atomic orbitals available that is important.
2. Each electron domain represents one hybrid orbital needed. For each hybrid orbital need, one atomic orbital is used. 2 electron domains = 2 hybrid orbitals = 2 atomic orbitals.
3. Consider the n-level for the central atom. All n=2 atoms have only s and p orbitals to hybridize, while n=3 and above have s, p, and d orbitals to use.
4. Form the hybrid orbitals needed. Fill with the valence electrons, one electron per orbital.
 - a. Keep in mind that if the atom has lone pairs, those lone pair electrons must go in hybrid orbitals.
 - b. If the formal charge is a negative value, add that number to the electron total to be used; if it is positive, remove electrons accordingly.
5. Overlap two half-filled orbitals, one from a terminal (out side) atom and one from the central atom for each bond.

6. Overlap one half-filled p orbital on a bonding atom with one half filled p orbital on a central atom to form each π bond.
- a. π bonds are made from un-hybridized orbitals.

Example C in methane

Sp^3

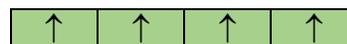
C: [He]
 $2s^2 2p^2$



The atomic orbitals available to hybridize are in $n = 2$ and are 2s and 3-2p orbitals

Carbon has a valence of 4, and the formal charge is zero. We would use 4 atomic orbitals to make 4 hybrid orbitals. Each hybrid orbital is $\frac{1}{4}$ s character and $\frac{3}{4}$ p character.

4 equal sp^3 orbitals, notice that yellow and blue make green.



Pulling it all together?

Table 3: Bond order and types of bonds used

Bond order	Concepts Equivalent To Bond Order	
	Lewis theory	Valence bond theory
1	Single bond	One σ bond
2	Double bond	One σ bond and one π bond
3	Triple bond	One σ bond and two π bonds

In the table below, fill in the types of atomic and hybrid orbitals used for electron domain geometry.

Formula	Example	No. of regions			Electron-domain geometry	Central atom's n and types of orbitals Use RED for regions of electron density(EDG) Use AO for atomic orbitals Use HO for hybrid orbitals
		lone	bonding	total		
AX_2	$BeCl_2$	0	2	2	linear	<ul style="list-style-type: none"> $n=2$, Two RED = 2 AO used to make 2 HO The HO made are two $2sp$ orbitals I use the 2s and one of the three 2p orbitals, two HO orbitals needed to make two $2sp$ orbitals; two unused 2 p orbitals remain for π overlap (double or triple bonds, or not used at all.

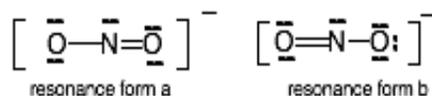
Formula	Example	No. of regions			Electron-domain geometry	Central atom's n and types of orbitals Use RED for regions of electron density(EDG) Use AO for atomic orbitals Use HO for hybrid orbitals
		lone	bonding	total		
AX_3	BF_3	0	3	3	trigonal planar	
	SO_2	1	2	3	trigonal planar	
AX_4	CF_4	0	4	4	tetrahedral	
AX_3E	NF_3	1	3	4	tetrahedral	

Formula	Example	No. of regions			Electron-domain geometry	Central atom's n and types of orbitals Use RED for regions of electron density(EDG) Use AO for atomic orbitals Use HO for hybrid orbitals
		lone	bonding	total		
AX_2E_2	OF_2	2	2	4	tetrahedral	
AX_5	PCl_5	0	5	5	trigonal bipyramidal	
AX_4E	SF_4	1	4	5	trigonal bipyramidal	
AX_3E_2	ClF_3-	2	3	5	trigonal bipyramidal	
AX_2E_3	XeF_2	3	2	5	trigonal bipyramidal	

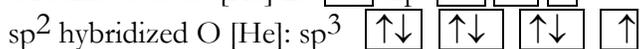
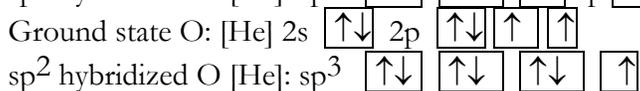
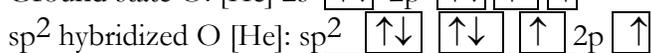
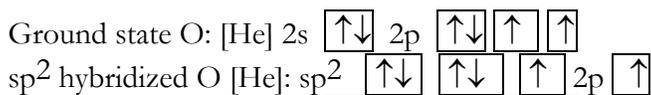
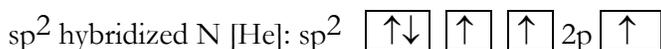
Formula	Example	No. of regions			Electron-domain geometry	Central atom's n and types of orbitals Use RED for regions of electron density(EDG) Use AO for atomic orbitals Use HO for hybrid orbitals
		lone	bonding	total		
AX_6	SF_6	0	6	6	octahedral	
AX_5E	BrF_5	1	5	6	octahedral	
AX_4E_2	XeF_4	2	4	6	octahedral	

How to do a hybridization scheme for a molecule.

Consider the nitrite ion NO_2^-
Following the steps listed above,



1. Draw the best lewis structure for nitrite.
2. determine the regions of electron density around the atoms of interest. For example, nitrogen has three regions of electron density: 2 bonding regions and 1 lone pair.
3. Determine the electron geometry: Triangular planar for the oxygen and nitrogen, one oxygen could be considered sp^3 .
Now we consider the electron configuration and how electrons are distributed in hybridization.
4. sp^2 hybridization on N
5. Ground state N: [He] 2s



Bond Descriptions

Structure A = N (sp^2)—O (2p) N (sp^2)—O (sp^2)

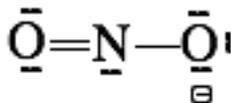
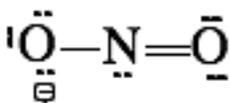
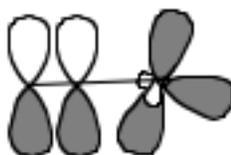
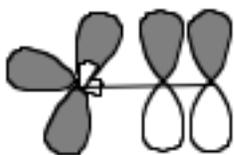
Structure B = N (sp^2)—O (sp^2) N (sp^2)—O (2p)

In Structure A, the π bond forms between N and O#2. In Structure B, the π bond forms between N and O #1.

Valence bond theory, strictly applied, still does not explain resonance structures. The problem is transferred from lines between atoms to pictures of p orbitals. Notice also that the number of boxes (or lines) represents the numbers of orbitals and the grouping of the boxes represents their relative energies. In the un-hybridized atom, the boxes form distinct groups for the s, p (and d-but not for these atoms) orbitals. After hybridization, the boxes form two groups consisting of hybridized orbitals at an energy that is broadly the average of the contributing orbitals, and the unused p- (or d) orbitals. These orbitals can have electrons, or can be un occupied.

Structure A

Structure B

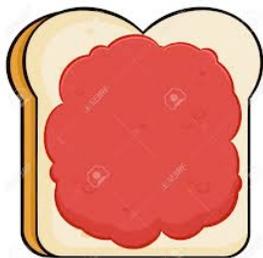


What about resonance?

What is the difference between localized and delocalized bonds?

Localized bonds between two nuclei localizes the electron density in that region of the molecule and no other. This could be a single bond, a double bond or, a triple bond.

Delocalized bonds result in un-hybridized orbitals sharing electrons over a larger extent of the molecule. The bonds are delocalized because the electrons in each of the $p\pi$ (peepie) system are shared with all the other $p\pi$ orbitals in the system.



I think toast and jam! Toast with a blob of jam is localized! Spread the jam, now it is delocalized. The electron density (jam) is spread all over the toast. It does not belong to any one part.

Delocalized Electrons: Resonance



This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.



If we look at nitrate, we see that the four $p\pi$ orbitals (3 from oxygen and 1 from nitrogen) are used to build the π -system to hold the electrons that are being delocalized. The top picture shows a localized system. The bottom shows the delocalized system. A localized system would not support resonance. We know that the structure for nitrate is best described with resonance structures (there are 3). This would support a delocalized system. The atoms share the 6 electrons in the $p\pi$'s.

Questions to help you think.

1. For the following molecules (OF_2 , XeF_2 , BrF_3):
 - a) Draw the Lewis structure.
 - b) Determine the electron domains about the central atom.
 - c) What is the expected hybridization of each molecule.
 - d) What is the molecular geometry?
 - e) Predict the bond angle(s).

Put your answers in the chart on the below

	OF_2	XeF_2	BrF_3
Lewis structure			
# of RED			
# of AO			
# of HO			

	OF ₂	XeF ₂	BrF ₃
What is the hybridization of central atom?			
What is the molecular geometry?			
What are the Bond angles around central atom?			
What is the hybridization scheme for central atom?			

2. Which type of atomic orbitals of the central atom mix to form hybrid orbitals in SiClH₃ (which is central, Si or Cl?) and Cl₂O (one Cl is central)

3. For the molecule hydrogen sulfide:
- Draw the Lewis structure.
 - Determine the electron domains about the sulfur atom.
 - Predict the bond angles $\angle\text{HSH}$.
 - What is the molecular geometry?
 - What is the expected hybridization of hydrogen sulfide.
 - Draw a bonding description for hydrogen sulfide.
 - Show the hybridization scheme for the molecule.
4. Use partial orbital diagrams to show how the atomic orbitals of the central atom lead to hybrid orbitals in IF_4^- and GeCl_4 .
5. Predict the shape, state the hybridization of the central atom and give the ideal bond angle(s) and any expected deviation for: IF_4^+ , BiF_3^{2-} , BrO_3^- , AsCl_4^- .
6. The compound 2,6-dimethylpyrazine gives chocolate its odor and is used in flavorings. A valid Lewis structure is shown below.
- Which atomic orbitals mix to form the hybrids of N?

- b) In what type of hybrid orbital does the lone pairs of N reside? Is the hybridization of each C in a CH_3 group the same as that of each C in the ring? Explain?
- c) How many localized π bonds are present?
- d) How many delocalized π bonds are present?
- e) How many σ bonds are present?

