**Name** ________________________________**Chem 162, Section**: _______**Group Number:** ______

# *ALE 14. Valence Bond Theory – Sigma Bonding*

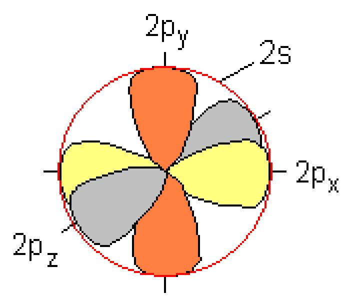
(Reference: Sections 11.1 and 11.2- *Silberberg 5th edition*)

## How do orbitals of neighboring atoms overlap to form a bond?

## The Model: Unhybridized and Hybridized Atomic Orbitals

According to *Valence Bond Theory*, a **sigma bond** is the result of *direct* overlap of the orbitals of adjacent atoms. The overlap of two atomic orbitals results in the formation of a **molecular orbital**—a region of space in the molecule where it is likely to find an electron). The first bond between two atoms is a **σ bond** (sigma bond). The second and third bonds between two atoms (if they exist) are **pi bonds**. (More on π bonds in the next Session.)

For bonding, a second period element has available four valence shell orbitals for bonding: 2*s*, $2p_x$, $2p_y$, and $2p_z$. The 2*s*, $2p_x$, and $2p_y$ orbitals sketched as most probable contours in Cartesian space (with the nucleus at the origin) looks like this:



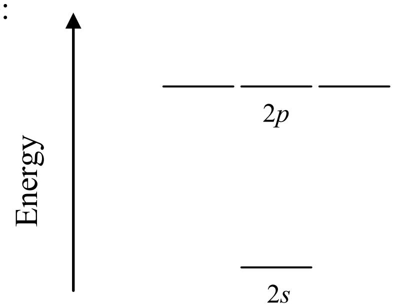

The **2*p* orbitals** are perpendicular to each other. The **2*s* orbital** is spherical in shape, but for simplicity is only shown here drawn in 2-dimensions. Since the two regions of electron density around the central Be atom in $BeCl_2$ are equivalent to each other in energy and are 180° apart from each other, Valence Bond Theory says that Be uses **hybrid orbitals** instead of the unhybridized 2*s*, $2p_x$, $2p_y$, and $2p_z$ orbitals to bond to each of the two Cl's.

### Key Questions

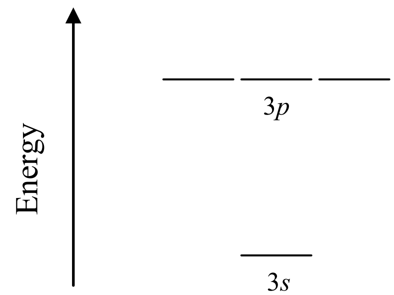
1. Our first example will be of $BeCl_2$. Draw the Lewis structure of $BeCl_2$, and use VSEPR Theory to predict the molecular shape.

2a. Complete the abbreviated orbital diagrams of the valence shell of *ground state* Be and Cl by writing arrows (*e.g.*, ↑ and ↓) to represent the valance electrons.

Be:

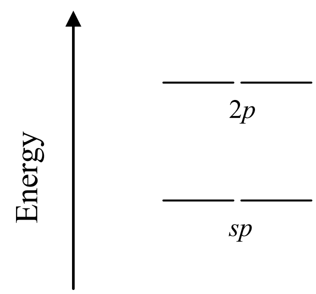



Cl:



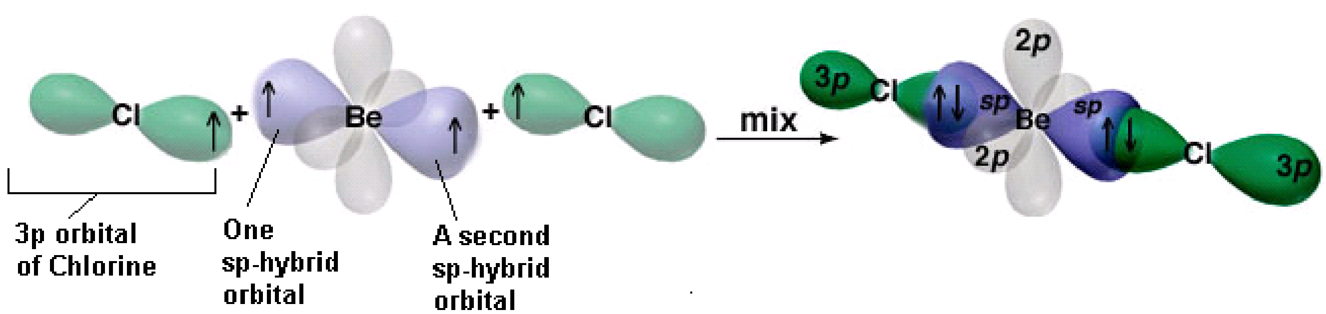

b. How many bonds do the above electron configurations suggest the Be and each Cl want to form? Be: ______ Cl: _______

c. The electron configuration of Be in Question 2a is not at all conducive to bonding! The Be in the Lewis structure has two bonds. This means that there should be two orbitals each with one unpaired electron in it. A 2*s* orbital is not equivalent to a 2*p* orbital, neither in shape nor in energy. Since the two bonds in the Lewis structure are equivalent to each other, the 2*s* orbital combines with one of the 2*p* orbitals to form *two* ***sp*** hybrid orbitals. *Complete the abbreviated orbital diagram of sp-hybridized Be*. (*Hint*: Don't forget to employ Hund's Rule—the most stable arrangement of electrons within orbitals of the same energy occurs when they're all unpaired.




## The Model: Orbitals and Bonding

The two *sp* hybrid orbitals have the same shape (somewhere between that of an *s* and a *p*), have the same energy, but point in opposite directions. Below is a sketch of the orbital overlap that results in σ bonding in $BeCl_2$ is:



**Key Questions**

3. Based on the sketch of $BeCl_2$ in the Model, use Valence Bond Theory to describe each bond between the Be and a Cl. (*i.e.*, What orbital does the Be use and what orbital does the Cl use to form the covalent bond between the two atoms?)

4a. How many *s* orbitals and how many *p* orbitals combined together in order to form the *sp* hybrid orbitals?

# *s* orbitals: ________ # *p* orbitals: ________

b. How many *sp* orbitals are formed when the *s* and *p* orbitals hybridize? Answer:_________

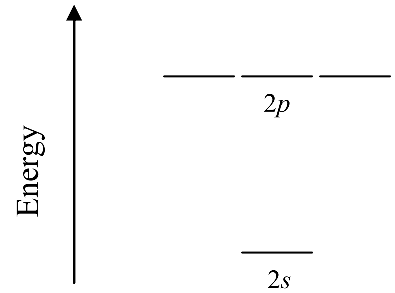
5a. An example of ***sp*$^3$ hybridization** is demonstrated by $NH_3$. Based on the name of the hybrid orbitals, how many *s* orbitals and how many *p* orbitals combine together in order to form the *sp*$^3$ hybrid orbitals?

# *s* orbitals: ________ # *p* orbitals: ________

b. How many *sp*$^3$ orbitals are formed when the *s* and *p* orbitals hybridize? Answer:_______

6a. Draw the Lewis structure of $NH_3$ and use VSEPR Theory to predict what the geometry of *electron density* is around the N.

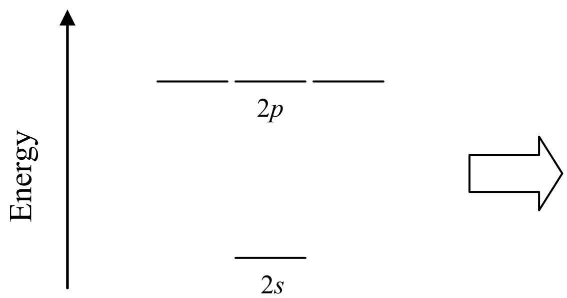
b. Complete the abbreviated ground state orbital diagram of N.




c. If N uses its ***unhybridized*** 2*p* orbitals to overlap with the 1*s* orbitals of the three H's, what would be the measurement of the H—N—H bond angles? Hint: By how many degrees are two *p* orbitals separated from each other?

d. The observed H—N—H bond angle in $NH_3$ is 107.3°. Does the N use unhybridized 2*p* orbitals to overlap with the 1*s* orbitals of the H's? Yes or No (Circle the correct answer.)

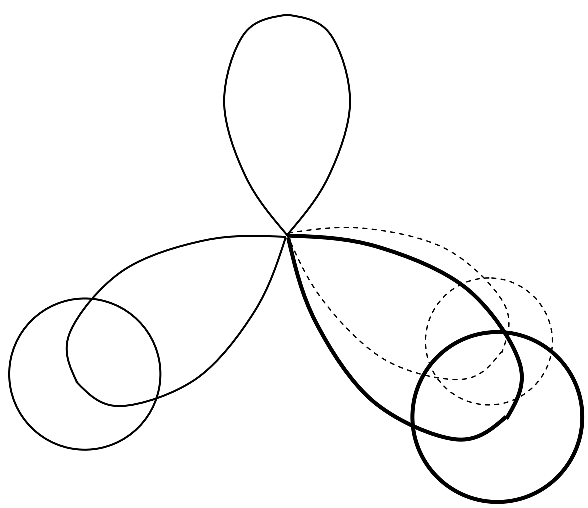
e. Write the abbreviated orbital diagram of N in $NH_3$ before and after hybridizing its 2s and all three of its 2p orbitals.




**Nitrogen before hybridizing** **Nitrogen after hybridizing**

f. In the orbital diagrams of nitrogen, above, what does an orbital with two electrons represent?

g. A sketch of the overlap of orbitals that results in σ bonding in $NH_3$ is shown to the right. (The **bold** curves indicate orbitals coming out of the plane of the paper. The dashed curves orbitals going into the plane of the paper.) Complete the above sketch by drawing arrows to represent electrons in the various regions of electron density. *Label the sketch so that the reader will know what the shapes represent and where the N and three H's are—i.e. label/identify all seven orbitals and indicate where the N and H atoms are located*



7a. Our last example of hybridization is the ***sp*^3^*d* hybridization** of S in $SF_4$. Draw the Lewis structure of $SF_4$.

b. Use VSEPR Theory to predict what the geometry of *electron density* around the S in $SF_4$ is.

c. What is the molecular geometry of $SF_4$ called? (Since the S has a lone pair, in order to minimize repulsions, does the lone pair go on one of the "poles" or does it go on "the equator"?)

d. Write the abbreviated orbital diagrams of the *hybridized* S and an unhybridized F in $SF_4$. (How many hybridized orbitals does S use? How is a lone pair represented in an orbital diagram?)

**Sulfur before hybridizing:** **S: [Ne]**

**Sulfur after hybridizing:** **S: [Ne]**

**Each of the four fluorines:** **F: [He]**

e. Sketch a Valence Bond picture (like the one shown in Question 6g) that shows how the orbitals of sulfur overlap with the orbitals of the four fluorines (Hint: from the orbital diagram of F in Question 7d, what orbital does a F use to bond with S?) in $SF_4$. Orient your sketch so that the reader can see the "see-saw" shape of the $SF_4$ molecule. To show orbitals coming out of the plane of the paper, draw the orbitals **boldly**. To show the orbitals going into the plane of the paper, draw them using dashed curves. Place pairs of arrow in overlap regions and in the lone pair on the S. Label your sketch.

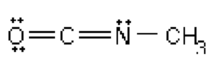
8. Complete the following table, which summarizes the various ways that a central atom can hybridize.

| VSEPR formula | Hybridization | # of Hybrid Orbitals | *Bond Angle* between the orbitals |
|---|---|---|---|
| $AX_2$ | *sp* | 2 | |
| $AX_3$ | | | |
| $AX_4$ | $sp^3$ | | |
| $AX_5$ | $sp^3d$ | | 90, 120 |
| $AX_6$ | | | |

## Exercises

9. What is the hybridization of carbon in each of the following ions. Support your response with the Lewis structure of each ion.

| Ion | Lewis Structure | Hybridization of Carbon |
|---|---|---|
| Carbonate ion: $CO_3^{2-}$ | | |
| Oxalate ion: $C_2O_4^{2-}$ (has a C—C backbone) | | |
| Isocyanato anion: $NCO^-$ | | |

10. Methyl isocyanate,  , is an intermediate in the manufacture of many pesticides. It received notoriety in 1984 when a leak from a manufacturing plant resulted in the death of more than 2000 people in Bhopal, India. (Your instructor was in Bhopal about two months before the leak while on vacation from his job the American Embassy School, New Delhi, where he taught chemistry and biology, 1982-1986.) What is the hybridization, bond angle and geometry of the N atom and the two C atoms in methyl isocyanate? Sketch the shape of the molecule in the space provided

| Element | Hybridization | Bond Angle | Geometry | Isocyante Structure |
|---|---|---|---|---|
| **N** | | | | |
| **Carbon: $CH_3$** | | | | |
| **Carbon: O=C** | | | | |