Name: ____ Period: _______

Hybrid Atomic Orbitals

Directions: This activity discusses hybrid atomic orbitals, which are the basis for the valence bond theory. Part A introduces σ (sigma) and π-bonds. Part B describes sp, sp^2 , and sp^3 hybrid atomic orbitals and their shapes. Part C discusses sp^3d and sp^3d^2 hybrid atomic orbitals, which are for molecules with expanded octets.

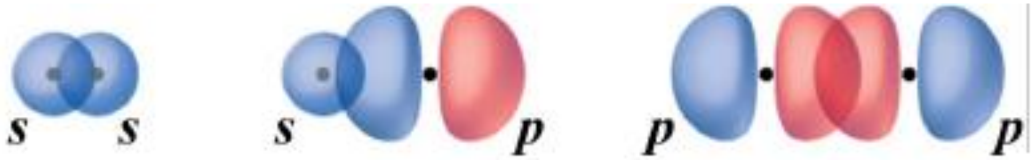
Part A: Introduction of σ and π bonds (Sigma and Pi Bonds)

A covalent bond forms when the orbitals of two separate atoms overlap, allowing the shared electrons to occupy orbitals in both atoms as shown below.

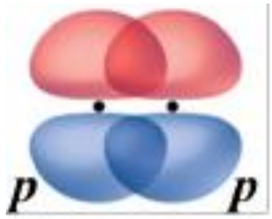
The **Valence Shell Electron Pair Repulsion theory (VSEPR)** states that the electron groups around an atom will position themselves as far as possible from each other around a central atom. **Hybrid Atomic Orbital** theory is a framework that we can use to explain how these two ideas can both be true. Keep in mind that the atomic orbitals that we have discussed previously (s, p, d, and f) are mathematical probability functions. Like all mathematical functions, these can be added and subtracted to yield new functions that represent the same total distribution.

Before considering the details of the Hybrid Atomic Orbital Theory, it is important to understand the ways that these atomic orbitals can overall to form bonds. There are two different ways that these atomic orbitals can overlap, producing two different types of bonds: sigma bonds (σ-bonds) and pi bonds (π-bonds).

A σ-bond is formed when orbitals overlap in the space between the nuclei of two atoms. This type of overlap is a result of the following orbital combinations: two s-orbitals, one s- and one p-orbital, and two end-to-end p-orbitals. These three bonds are shown in the figure below. Hybridized orbitals (discussed in Part B) also overlap along the internuclear axis, and so also form σ-bonds.



A π-bond forms when orbitals overlap outside of the space between the nuclei. This overlap arises from the side-to-side overlap of two unhybridized p-orbitals, as shown in the figure below. Importantly, π-bonds prevent rotation around the internuclear axis since rotating the p-orbitals independently of each other will decrease the overlap of the orbitals.



When analyzing the bonds in a molecule, every bond will be composed of one σ-bond. Only double and triple bonds will be composed of π-bonds.

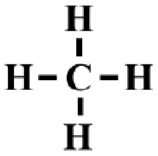
Type of bond	Number of σ-bonds	Number of π-bonds
Single	1	0
Double	1	1
Triple	1	2

Practice
Identify all of the types of bonds in the molecule acetic acid (CH_3CO_2H).

Example #1
Identify all the types of bonds in the most stable resonance structure of the ion OCN^{-1}.

Part B: Atomic Orbital Hybridization in Period 2 Elements

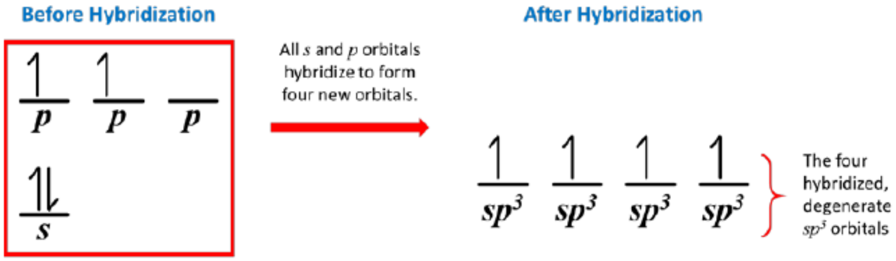
Consider a methane (CH_4) molecule. In this molecule, we anticipate that each of the carbon's 4 valence electrons will be shared with one of the hydrogen atoms.



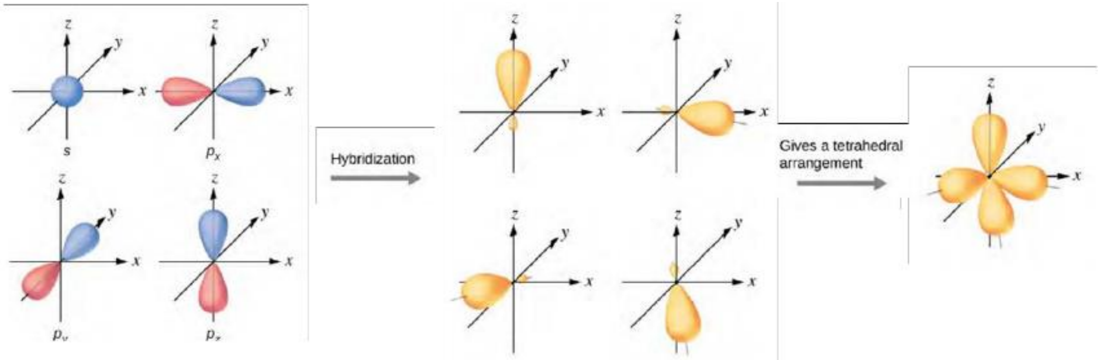
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-H} \\ | \\ \mathrm{H} \end{array}$$

Yet we predict the electron configuration for carbon should be $1s^2 2s^2 2p^2$, meaning that only two of the carbon's valence electrons are unpaired. Based on this, we would expect two of the electrons to be available for sharing with H, so the molecule CH_2 would form. However, because the carbon would prefer to have a full valence shell, the s and p orbitals combine to form 4 energetically equivalent <u>hybrid</u> orbitals. (A more accurate way to state this is that it is more energetically favorable for the carbon to have a full valence shell). This allows each valence electron to occupy an orbital by itself and therefore be available to form a bond with a hydrogen atom.

In the case of CH_4, because one s- and three p- orbitals combine to form four new orbitals, we call the hybrid orbitals sp^3 orbitals. Each valence electron in the carbon atom can reside in one of the energetically-equivalent sp^3 orbitals, as shown below.

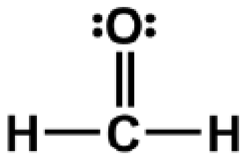


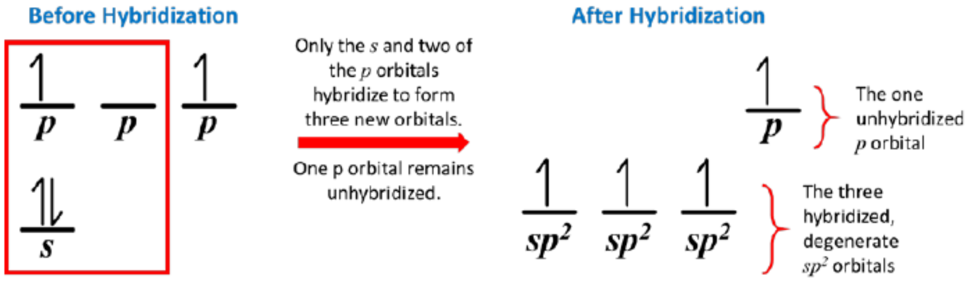
When these four new orbitals form, they take on a tetrahedral arrangement, as shown in the figure below.



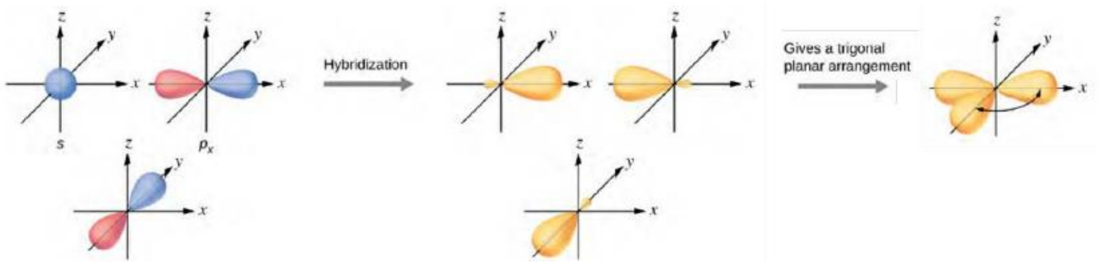
The four hybrid orbitals are positioned around the nucleus as far away from each other as possible, as predicted by VSEPR. In addition, when the orbitals hybridize the electron density shifts from being equally distributed on either side of the nucleus to being located mostly on one side of the nucleus. This favors bond formation, because it means the electrons can spend more time in the space between two atoms rather than on the opposite side of the central atom.

Now consider a formaldehyde molecule (CH_2O). When there are three electron groups around the central atom, three atomic orbitals hybridize to form three sp^2 hybrid orbitals. Three out of four of carbon's valence electrons reside in one of the degenerate sp^2 orbitals. Carbon's fourth valence electron resides in the one unhybridized p-orbital and is shared with oxygen in a π-bond, which creates a double bond. Since the p-orbitals' electron density in a π-bond extends above and below the axis between the bonded atoms, the second electron pair is spatially separated from the first electron pair (which resides in the internuclear space).

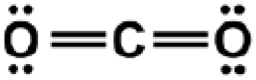




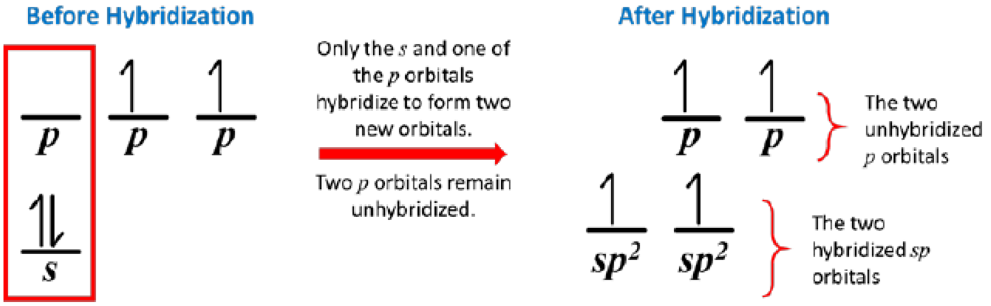
When these three new orbitals form, they take on a trigonal planar arrangement, as shown in the figure below. The unhybridized p-orbital is oriented perpendicular to these, in the z-direction.



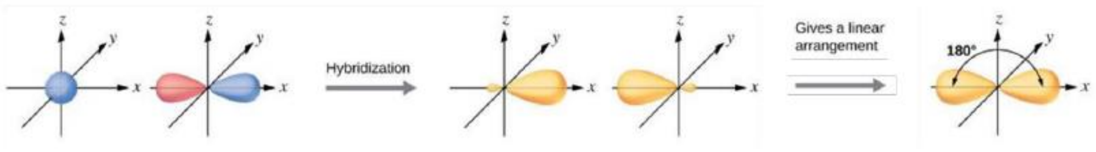
Now consider a carbon dioxide molecule (CO_2). Where there are two electron groups around the central atom, two atomic orbitals hybridize to form two sp hybrid orbitals. Two out of four of carbon's valence electrons reside in one of the degenerate sp orbitals.



Carbon's third and fourth valence electrons reside in the two unhybridized p-orbitals. These two unhybridized p-orbitals can either form one triple bond (one σ-bond and two π-bonds) or two double bonds (one σ-bond and one π-bond in each bond). In the case of CO_2, each p-orbital forms one double bond with each oxygen atom.



When these two new orbitals form, they take on a linear arrangement, as shown in the figure below. The unhybridized p-orbitals are oriented along the z- and y-axes.



Practice
How will the atomic orbitals of the carbon in hydrogen cyanide (HCN) hybridize?

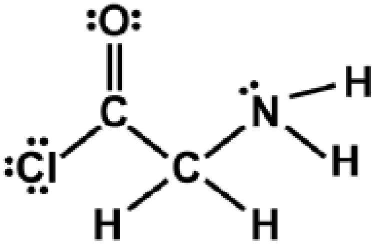
Example #2
How will the atomic orbitals of the central oxygen atom in ozone (O_3) hybridize?

Hybrid atomic orbitals allow us to predict the approximate shape of complex molecules. This is especially important in biological systems where most of the constituent elements are small and likely exhibit hybridization. The hybridization of each central atom can be determined by evaluating the number of lone pairs, σ-bonds and π-bonds that surround the atom. Terminal atoms are assumed to not hybridize.

# Sigma Bonds + # Lone Pairs	Hybridization	# Pi Bonds
4	sp^3	0
3	sp^2	1
2	sp	2

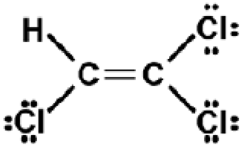
Practice
Give the hybridization that occurs for each of the internal atoms in acetic acid.

Example #3
Give the hybridization that occurs for each of the internal atoms in the following molecule:



Because the hybrid atomic orbitals correspond to VSEPR molecular shapes, the structure of the molecule can be estimated by this method.

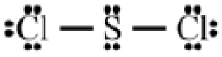
Example #4
What angle do you expect will exist between the H-C-C bond in trichloroethylene ($CHClCCl_2$)?



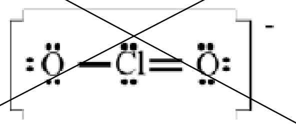
Part D: Extra Practice

For each of the following molecules, predict the hybridization that occurs at each inner atom.

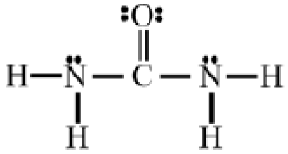
1. Sulfur dichloride (SCl_2)



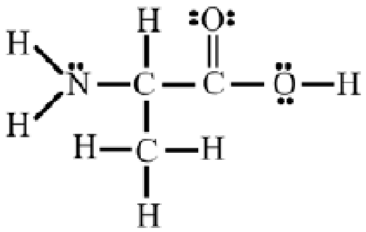
~~2. Chlorite ion (ClO_2^-)~~



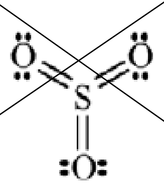
3. Urea ($(NH_2)_2CO$)



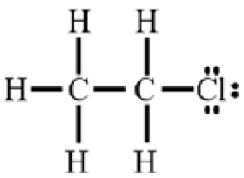
4. Alanine ($H_2NC(CH_3)COOH$)



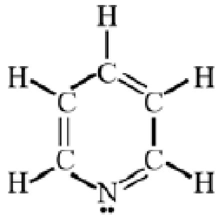
~~5. Sulfur trioxide (SO_3)~~



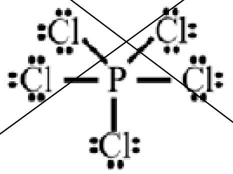
6. Chloroethane (C_2H_5Cl)



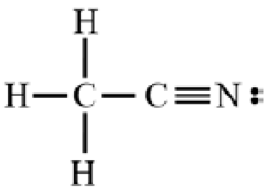
7. Pyridine (C_5H_5N)



~~8. Phosphorus pentachloride (PCl_5)~~



9. Acetonitrile (H_3CCN)



10. Vitamin C