

Hybrid Orbitals

INTRODUCTION:

Developed by Linus Pauling, the concept of hybrid orbitals was a theory created to explain the structures of molecules in space. The theory consists of combining atomic orbitals (ex: s,p,d,f) into new hybrid orbitals (ex: sp, sp², sp³).

VOCABULARY:

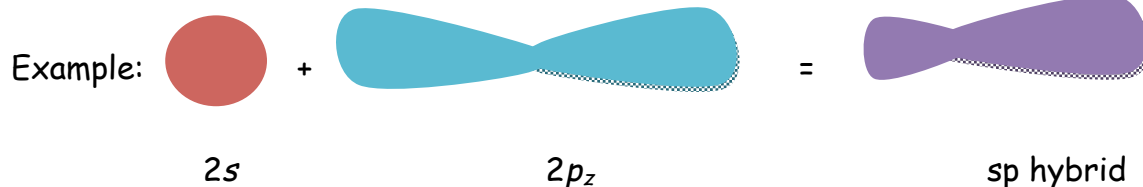
1. Atomic orbital: an expected region of electron density around an atom based on a solution to the Schrödinger wave function. ¹

Example:



The valence electrons of Be will most probably be found in the shaded areas.

2. Hybridization: the combining of solutions to the Schrodinger wave function for atomic orbitals to produce hybrid orbitals. Note: the total number of orbitals available for forming bonds does not change—a new set is simply formed. ²
3. Hybrid orbital: an orbital created by the combination of atomic orbitals in the same atom. ¹



4. Linear sp hybrids: the two hybrid orbitals formed by the mixture of one s and one p orbital. ¹
5. Trigonal sp² hybrids: the three hybrid orbitals formed by the mixture of one s and two p orbitals. ¹
6. Tetrahedral sp³ hybrids: the four hybrid orbitals formed by the mixture of one s and three p orbitals. ¹

DETERMINING HYBRIDIZATION OF ATOMS:

- To determine the hybridization of an atom, count the regions of electron density (bonds and lone pairs) around the atom and match this number with the corresponding hybridization. (Note: this technique does not take into account the changed hybridization that occurs when a molecule is

¹ Vollhardt, P. *Organic Chemistry: Structure and Function*. 5th ed. New York: 2007. 23- 35

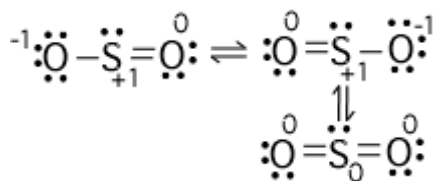
conjugated—this will be discussed under “Note on Conjugation and Hybridization,” because it must always be taken into account to identify the more accurate hybridization)

- An sp hybridized atom has two regions of electron density - Consider the carbon atom of HCN:



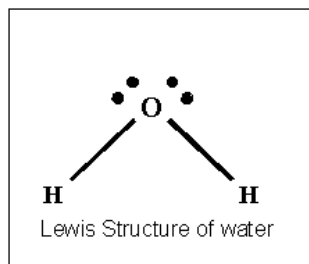
It is important to note that a double or triple bond only counts as ONE region of electron density; the carbon of the HCN therefore has two regions of electron density.

- An sp^2 hybridized atom has three regions of electron density: Consider the sulfur of SO_2



(picture from <http://www.uwosh.edu/>)

- An sp^3 hybridized atom has four regions of electron density: Consider the oxygen atom of water



(picture from <http://employees.csbsju.edu>)

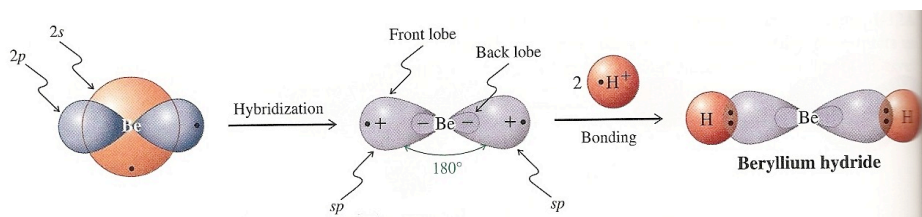
- This same pattern applies for the hybrid orbitals containing d orbitals (dsp^3 , d^2sp^3), but organic chemistry focuses on carbon, which is limited to four bonds/regions of electron density.

DETERMINING GEOMETRY:

Geometry determines hybridization; the geometry of a molecule will be the most energetically favorable arrangement, and this geometry will cause hybridization to accommodate the correct shape.

- sp hybrids: Linear Structures:

- sp hybrids share characteristics evenly between s and p orbitals. The other unhybridized p orbitals remain the same. The front lobes of the sp orbitals point in opposite directions (at 180°). The back lobes also point in opposite directions. A linear structure is created.
- In general: The overlap of the lobes of atoms creates bonds; large front lobes overlap more completely, resulting in a relatively stronger bond.



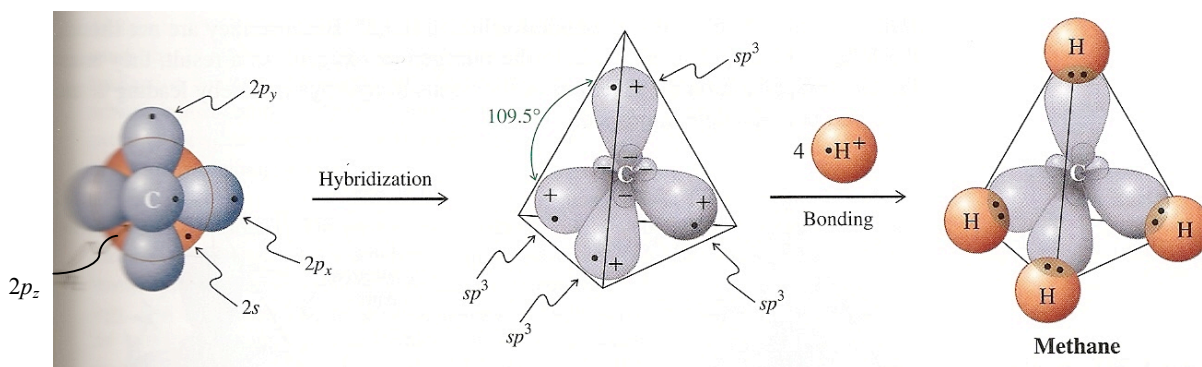
(Figure 1-16 from Vollhardt)

- sp² hybrids: Trigonal Structures:

- The small amount of energy needed to promote an electron from the 2s to one of the 2p levels is compensated by bond formation. The three filled atomic orbitals mix to form three sp² orbitals—each is of 33% s character and 67% p character. The last p orbital stays the same. The front lobes (and their corresponding back lobes) face in opposite directions (at 120° from each other). Electron repulsion therefore creates a trigonal planar geometry.

- sp³ hybrids: Tetrahedral structures:

- The 2s orbital is mixed with all three of the 2p orbitals, creating four hybridized sp³ orbitals. Each of these has 25% s and 75% p character; electron repulsion favors a tetrahedral shape, so the orbitals are 109.5° apart from each other.



(Figure 1-18 from Vollhardt)

- Hybrid orbitals can overlap with any atomic orbital of a different atom to form a bond; this is seen with the substitution of a chlorine atom in place

of a hydrogen atom on methane. They may also contain lone pairs—this explains the geometry of water, which is sp^3 hybridized due to the lone pair, which occupies one of the four hybrid orbitals. Again, the bond angle is slightly distorted due to the electron repulsion of this lone pair.

- Bond angles are distorted because of these changes; typical bond angles of certain hybridization are often increased or decreased due to the relative electronegativities of atoms on a molecule.

Note on Conjugation and Hybridization:

- To accommodate resonance, the hybridization of an atom may change. This change will occur due to the movement of a lone pair into a p orbital, and must be taken into consideration when determining the hybridization of atoms in a molecule. Hybridization will change if:
 - The atom is surrounded by two or more adjacent p orbitals.
 - The atom has a lone pair to move into a p orbital.

Amide molecule—nitrogen looks sp^3 hybridized but it is sp^2 because of conjugation (lone pair goes into a p orbital to have three adjacent, parallel p orbitals).

