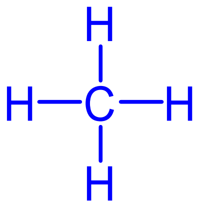
Shapes of Molecules

A. Molecular Geometry

- Lewis structures provide us with the number and types of bonds around a central atom, as well as any NB electron pairs. They do not tell us the 3-D structure of the molecule.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

CH_4 as drawn conveys no 3-D information (bonds appear like they are 90° apart)

- The Valence Shell Electron Pair Repulsion Theory (**VSEPR**), developed in part by Ron Gillespie at McMaster in 1957, allows us to predict 3-D shape. This important Canadian innovation is found worldwide in any intro chem course.

- VSEPR theory has four assumptions

  1. Electrons, in pairs, are placed in the valence shell of the central atom
  2. Both bonding and non-bonding (NB) pairs are included
  3. Electron pairs repel each other → maximum separation.
  4. NB pairs repel more strongly than bonding pairs, because the NB pairs are attracted to only one nucleus

- To be able to use VSEPR theory to predict shapes, the molecule first needs to be drawn in its Lewis structure.

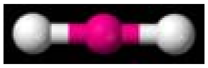
- VSEPR theory uses the **AXE** notation (m and n are integers), where m + n = number of *regions of electron density* (sometimes also called *number of charge clouds*).

$$AX_mE_n$$

1. Molecules with no NB pairs and only single bonds

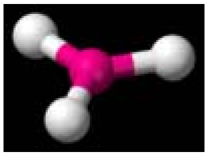
- We will first consider molecules that do not have multiple bonds nor NB pairs around the central atom (n = 0).

- Example: $BeCl_2$



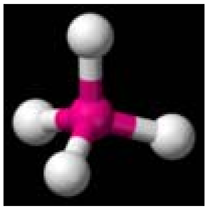
  - Molecule is **linear** (180°)

- Example: BF_3



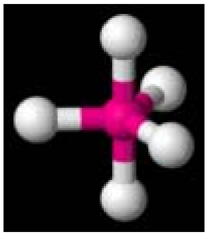
  - Molecule is **trigonal (or triangular) planar** (120°)

- Example: CH_4



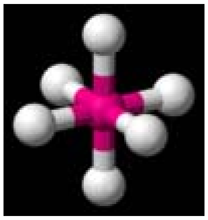
  - Molecule is **tetrahedral** (109.5°)

- Example: PF_5



  - Molecule is **trigonal bipyramidal** (90° and 120°). There are three X atoms in a planar triangle and two axial atoms, one above and one below the central atom.

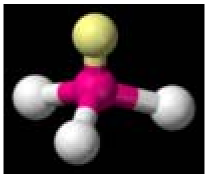
- Example: SF_6

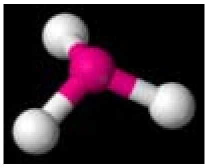


  - Molecule is **octahedral** (all 90°)

2. Molecules with ≥ 1 NB pairs and only single bonds

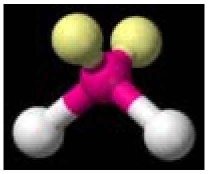
- The geometry of the *regions of electron density* is roughly the same as what we see when no NB pairs are involved.
- However, the shape of the molecule is determined by looking at only the bonding pairs, NOT the non-bonding pairs.
- Example: NH_3

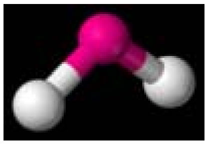




  - There are four regions of electron density (m + n = 4), and the electronic arrangement is still tetrahedral.
  - Yet, the shape of the molecule (look at bonding pairs only) is **trigonal pyramidal**. Angles < 109.5° (why?)

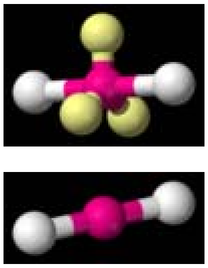
- Example: H_2O





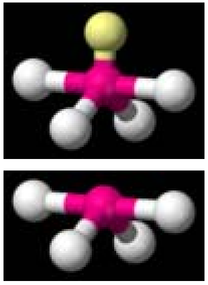
  - Electronic arrangement is tetrahedral. Shape of molecule = **bent**

- Example: XeF_2 (or I_3^-)



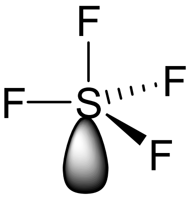
  - o Electronic arrangement is trigonal bipyramid. Shape of molecule = **linear**

- Example: SF_4

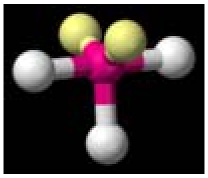


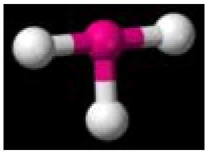
  - o Electronic arrangement is trigonal bipyramidal. Shape of molecule = **see saw**

Why is this better than triganol pyramid?



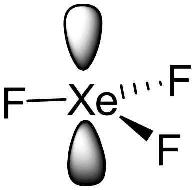
Example: XeF_3^+



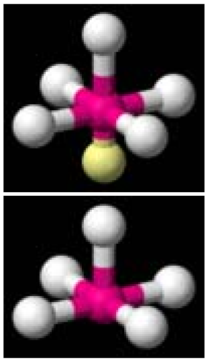


- o Electronic arrangement is trigonal bipyramidal.
  Shape of molecule = **T-shaped**

Why is this better than triganol planar?

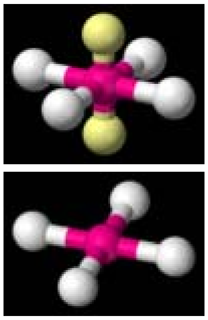


- Example: XeF_5^+



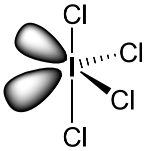
o Electronic arrangement is octahedral.
Shape of molecule = **Square pyramidal**

- Example: ICl_4^-

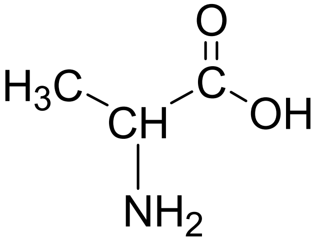


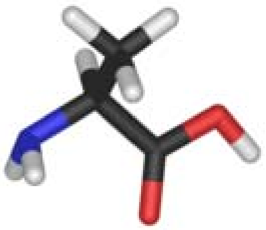
  - o Electronic arrangement is octahedral.
    Shape of molecule = **Square planar**

Why is this better than?



- Example: the amino acid alanine
  - o There can be more than one “central atom”

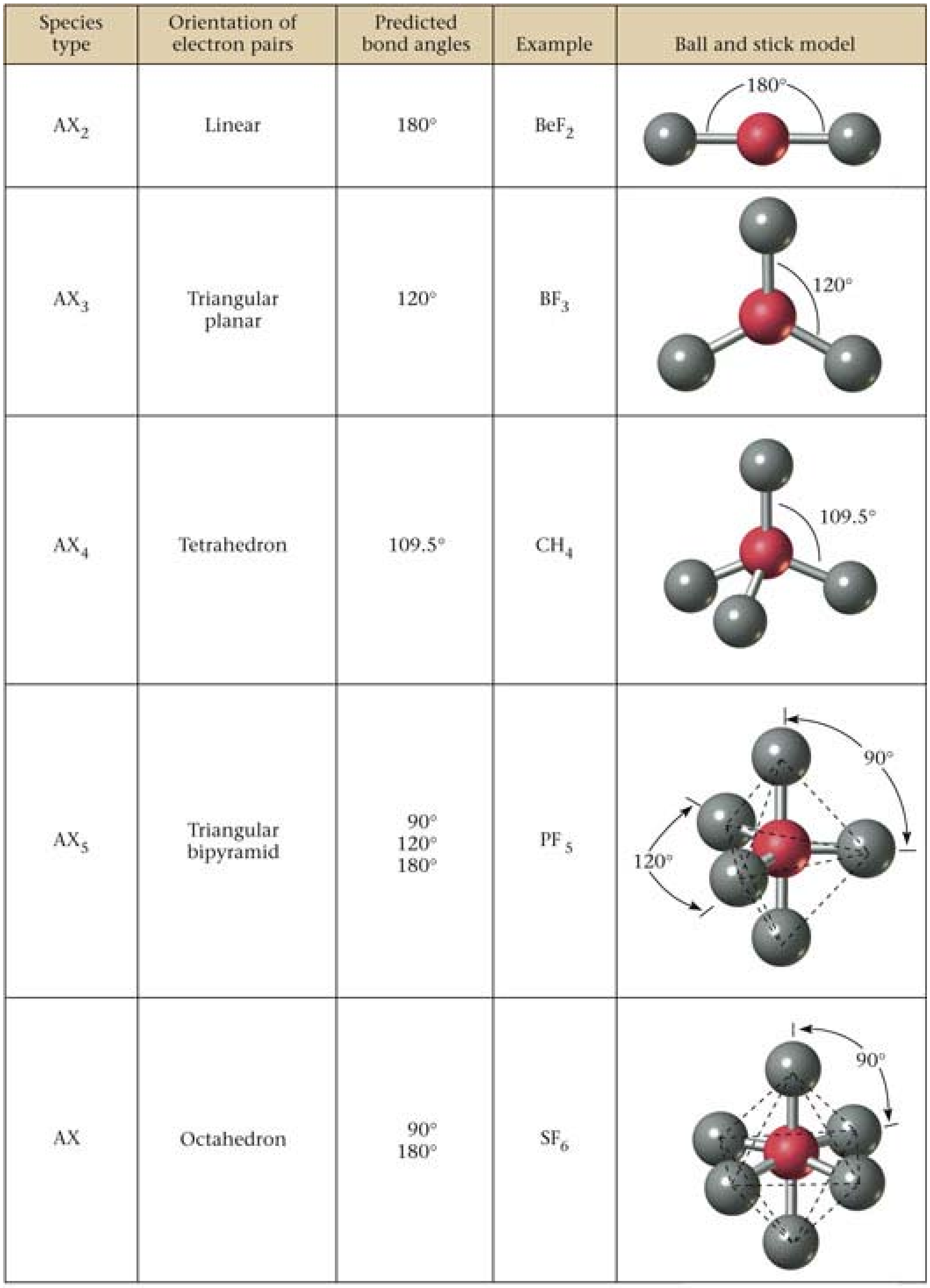




3. Molecules with double or triple bonds

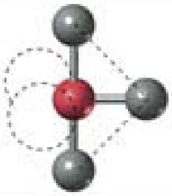
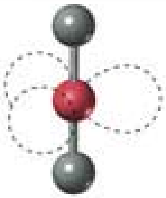
- These are quite simple: treat multiple bonds as single bonds, and the AXE system still works. *i.e.* a multiple bond is still considered to be **one region** of electron density.
- Examples: predict the shapes of CO_2, C_2H_4, and NO_2^-

Summary

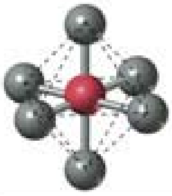
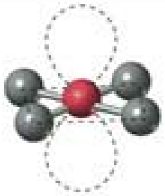


Species type	Orientation of electron pairs	Predicted bond angles	Example	Ball and stick model
AX_2	Linear	180°	BeF_2	
AX_3	Triangular planar	120°	BF_3	
AX_4	Tetrahedron	109.5°	CH_4	
AX_5	Triangular bipyramid	90° 120° 180°	PF_5	
AX	Octahedron	90° 180°	SF_6	

5 ELECTRON PAIRS

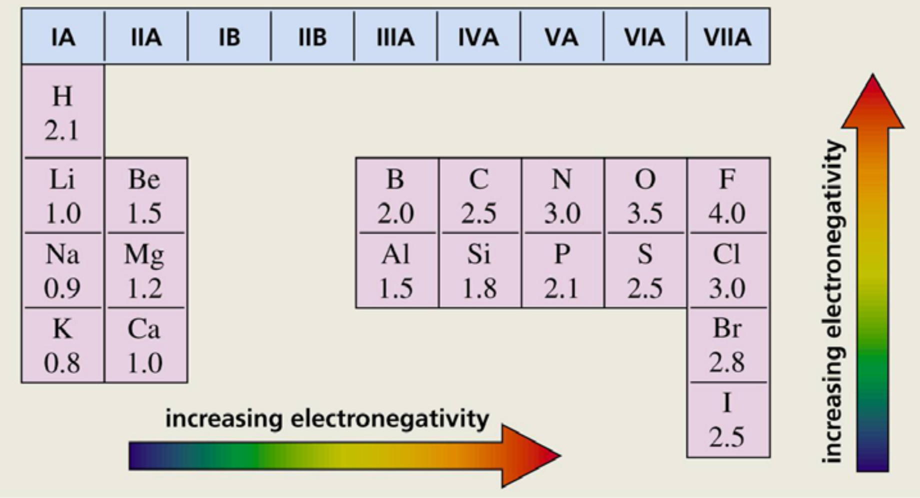
Species type	Structure	Description	Example	Bond angles
AX_5		Triangular bipyramidal	PF_5	90°, 120°, 180°
AX_4E		See-saw	SF_4	90°, 120°, 180°
AX_3E_2		T-shaped	ClF_3	90°, 180°
AX_2E_3		Linear	XeF_2	180°

6 ELECTRON PAIRS

AX_6		Octahedral	SF_6	90°, 180°
AX_5E		Square pyramidal	ClF_5	90°, 180°
AX_4E_2		Square planar	XeF_4	90°, 180°

B. Molecular Polarity

- Recall that electronegativity is a relative measurement of an atom's ability to attract a bonding electron pair to itself.



IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

- Differences in electronegativity between two covalently bonded atoms result in a polar covalent bond, and atoms have a partial negative or partial positive charge.

- These bonds are said to have dipole moments, which can be experimentally quantified. If placed in an electric field, the molecule will rotate and line up to the field.

- The greater the bond polarity, the greater the dipole moment. However, can we say that a molecule with a polar bond must also be a polar molecule? Not necessarily!

- Note: The overall polarity of a molecule depends on its geometry and the presence of polar bonds.
    - The presence of polar bonds does not necessarily imply that the molecule is polar. This is because the bond dipole moments can cancel out (no net dipole moment).
    - Think of the bond dipoles as vectors, and if the sum of all of the vectors is zero, the molecule is not polar.

- Examples:

CO_2 H_2O

BF_3 NH_3

CCl_4 $CFCl_3$

SF_4 SF_6

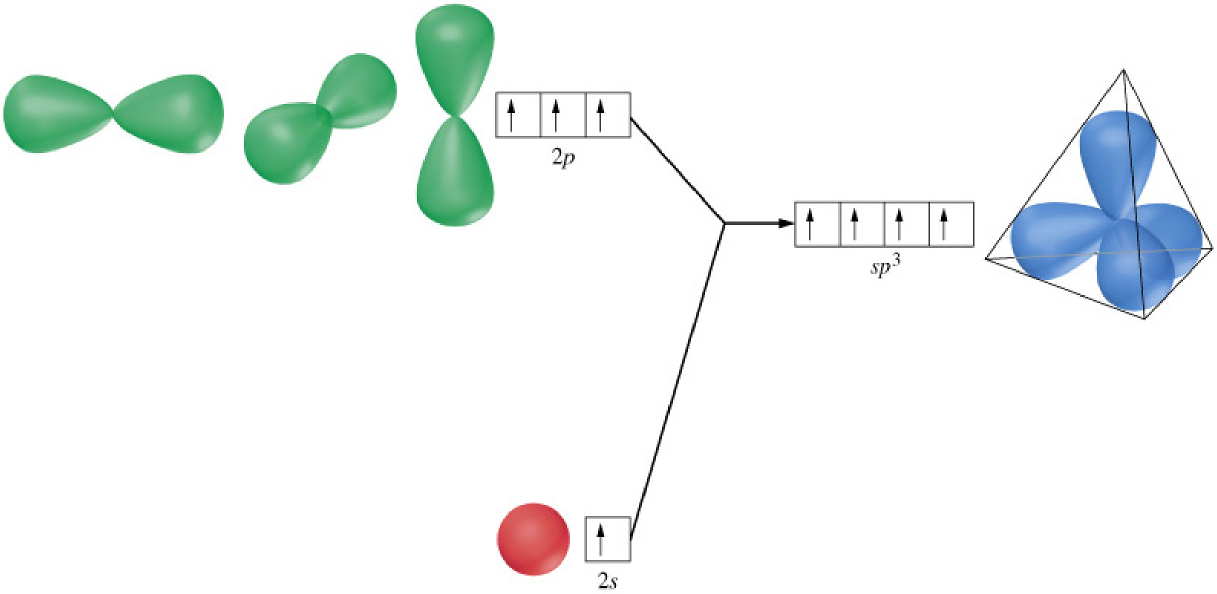
- Notice that non-polar molecules are highly symmetrical, allowing the bond dipole moments to cancel out.

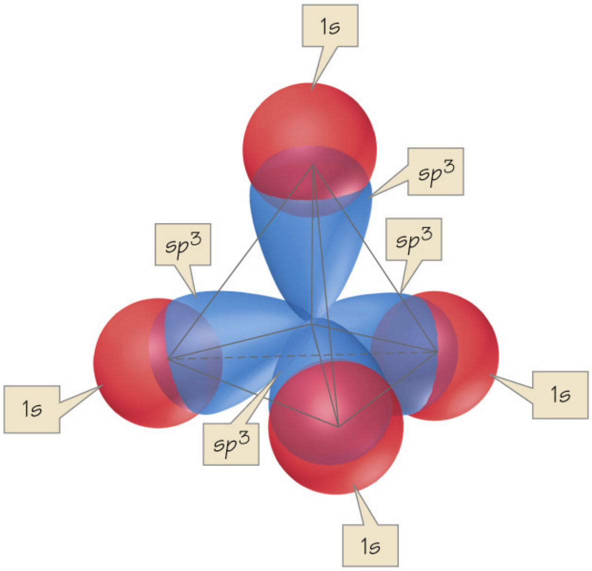
- In a set of resonance structures, the overall polarity is averaged out over the resonance structures. For example, CO_3^{2-} and SO_4^{2-} are non-polar (no net dipole moment).

C. Hybridization (Compounds with Single Bonds)

- How does molecular shape relate to the orbitals in the valence shell?
- Consider methane, CH_4, which uses the valence electrons in the 2*s*, $2p_x$, $2p_y$, and $2p_z$ orbitals. These electrons must become unpaired prior to making bonds with H.
- Recall the shapes of the *s* and *p* orbitals.
- If we used these orbitals to bond with the H atoms, we would get this structure. Yet, we know that the proper structure from VSEPR theory is tetrahedral. This structure shown is clearly incorrect!
- How do we explain this?

- Before bonding to H atoms, the one 2*s* and three 2*p* atomic orbitals are mixed and rearranged to give a new set of four equivalent (same energy) “hybrid” atomic orbitals (*sp*^{3}) arranged at tetrahedral angles of 109.5°.



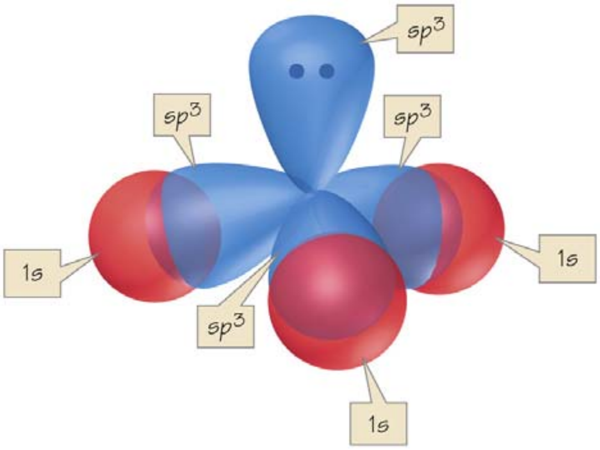


- Each new hybrid orbital around the C contains one electron.
- After each pairs up with one electron from H, the orbitals contain an electron pair.

- The single bond formed by the *direct, head-on overlap* of orbitals is a sigma bond (σ).

- Note: hybrid orbitals can also contain NB pairs, for example, in ammonia and water. These also have tetrahedral electronic arrangements and are sp^3.

- NH_3, which has a tetrahedral electronic arrangement, contains three σ bonds. Its shape is trigonal pyramidal.



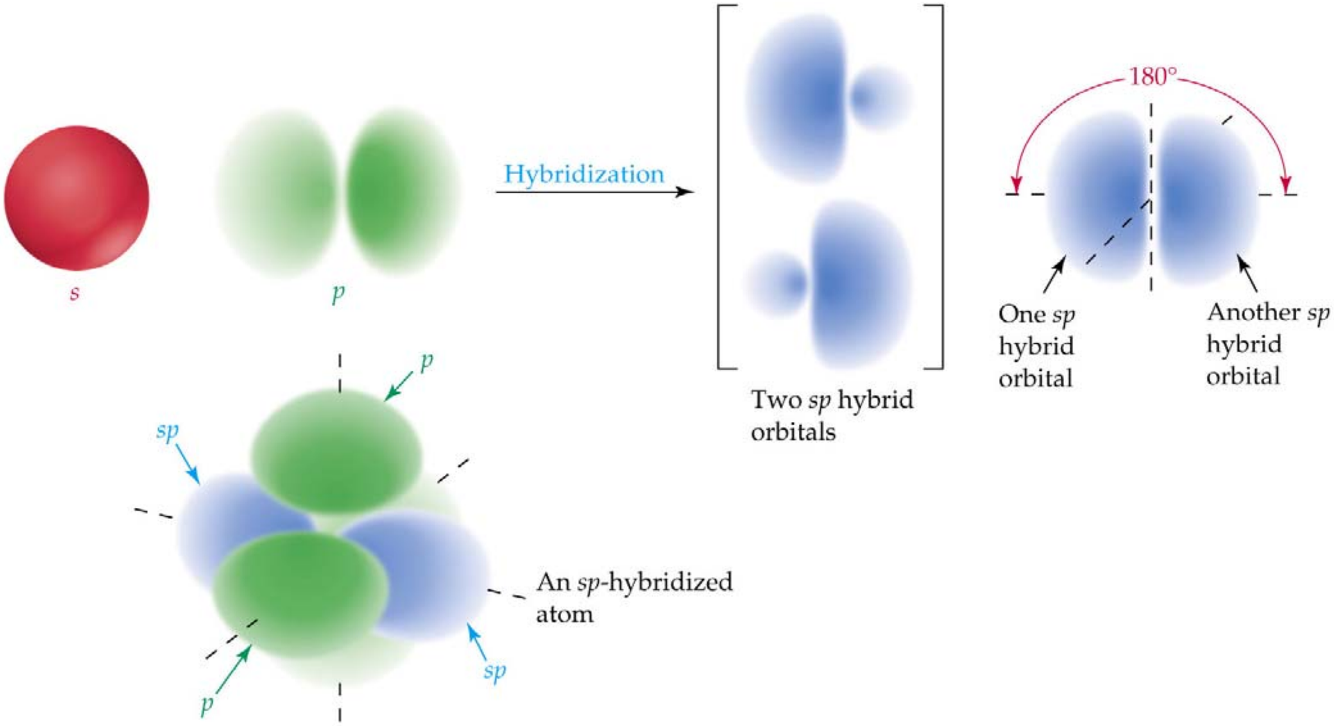
- sp^3 hybridization is just one possibility. Five major hybridization types form the VSEPR structures, and these types are summarized in this table (details follow).

Regions of e^- density	Atomic orbitals	Hybrid orbitals	Electronic arrangement
2	one *s*, one *p*	two *sp*	linear
3	one *s*, two *p*	three sp^2	trigonal planar
4	one *s*, three *p*	four sp^3	tetrahedral
5	one *s*, three *p*, one *d*	five sp^3d	trigonal bipyramidal
6	one *s*, three *p*, one *d*	six sp^3d^2	octahedral

  - *Regions of electron density*: an NB pair, a single bond, or a multiple bond each constitute one region.
  - *Electronic arrangement* may not equate to molecular shape if there is at least an NB pair present.

1. *sp* hybridization

- The combination of one *s* and one *p* results in the formation of two *sp* orbitals. These two hybrid orbitals are 180° apart.

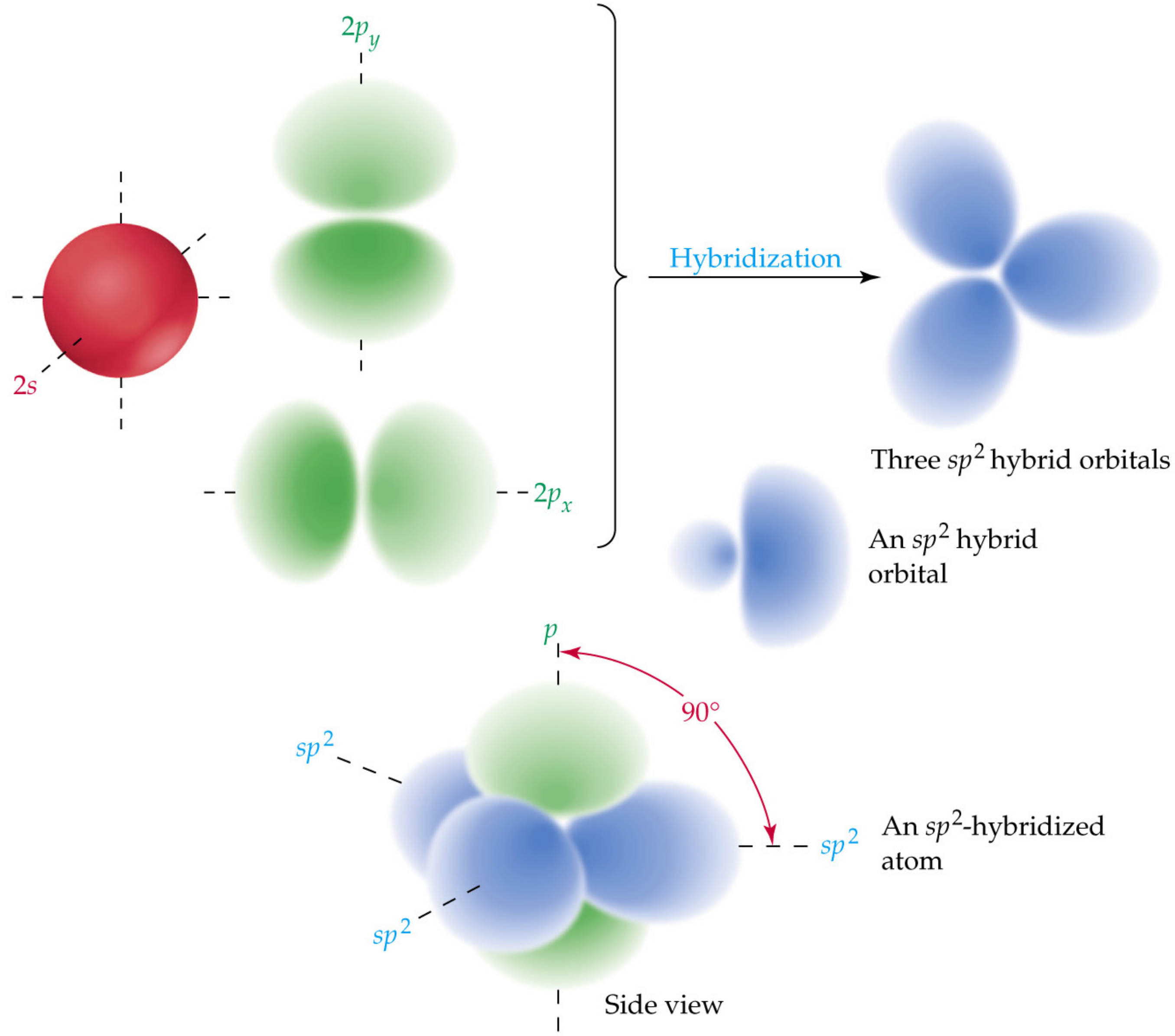


- Where we have used only one of the *p* orbitals, there must be two *p* orbitals remaining. (Recall there are three *p* orbitals). We'll see later on that these leftover orbitals are used when there is multiple bonding.

- The two leftover *p* are 90° to each other and the *sp* hybrids.

2. *sp*^{2} hybridization

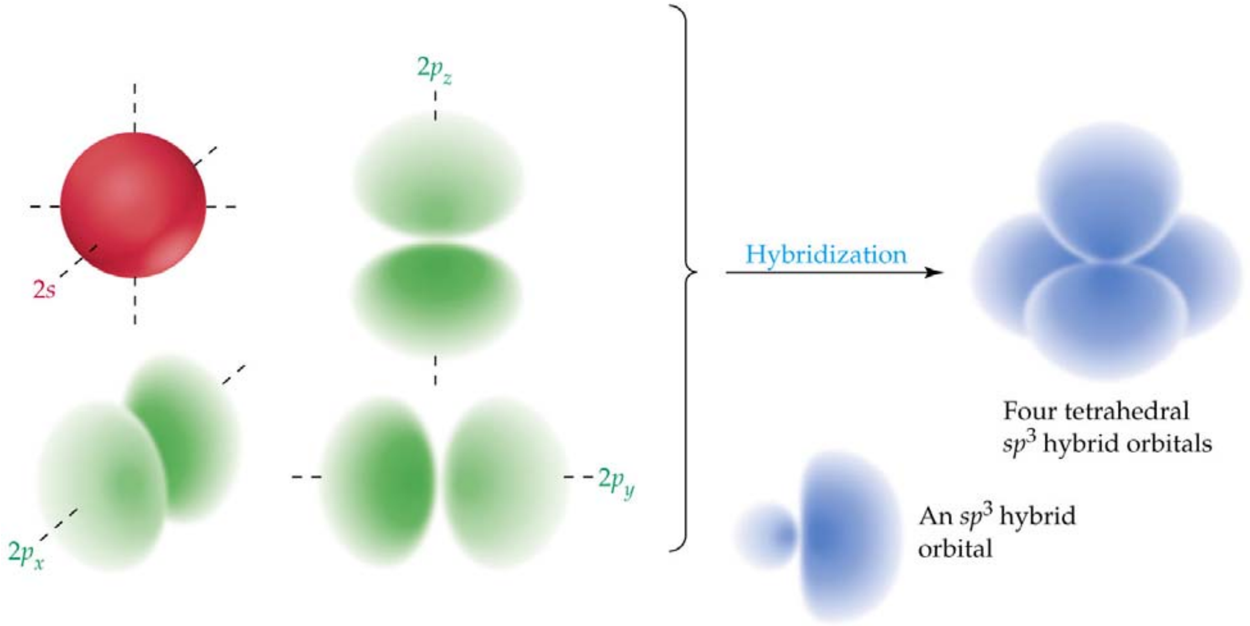
- One *s* + two *p* = three *sp*^{2} orbitals 120° apart.



- There is one leftover *p* orbital remaining, since we started with three *p* orbitals and used two of them for hybridization.

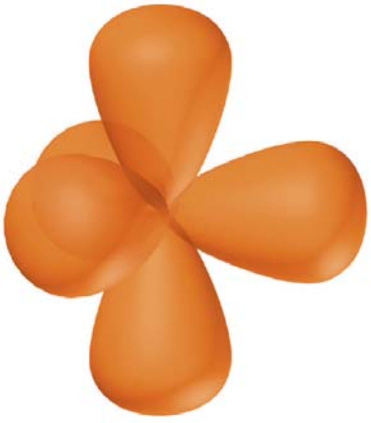
3. sp^3 hybridization

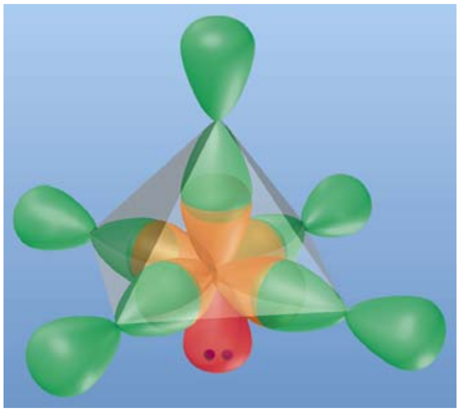
- One s + three p = four sp^3 orbitals 109.5° apart.
- There are no leftover p orbitals. Also see diagram on p. 12.



4. Others: sp^3d and sp^3d^2 hybridization

- One s + three p + one d = five sp^3d orbitals
- One s + three p + two d = six sp^3d^2 orbitals

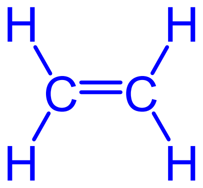




IF_5 (sq. pyramidal)

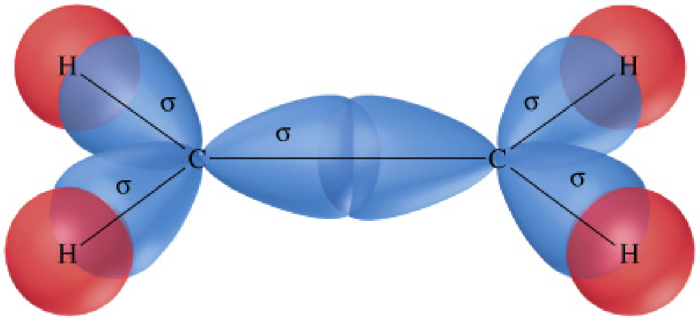
D. Hybridization (Compounds with Multiple Bonds)

- How do we assign hybridization to compounds containing multiple bonds? The same way! We still examine the number of regions of electron density (table on page 13).

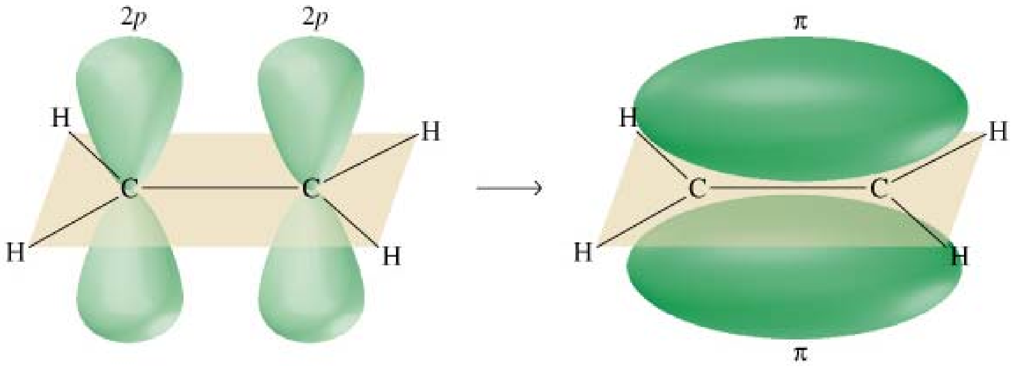


- Consider ethene. Each carbon has an AX_3 configuration (sp^2-hybridized). Remember to count double bonds as one region. Each C also has a remaining *p* orbital (see p. 15).

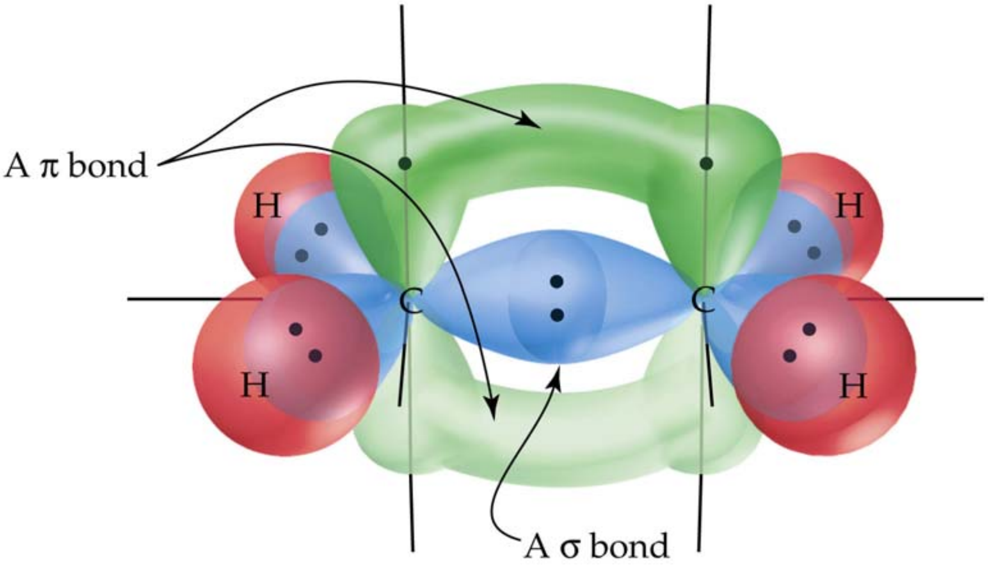
- Recall that σ bonds are formed by the direct overlap of orbitals, which result in single bonds. Where do double bonds come from?
  - The first bond in the double bond comes from a regular single bond caused by direct overlap (*i.e.* a σ bond)



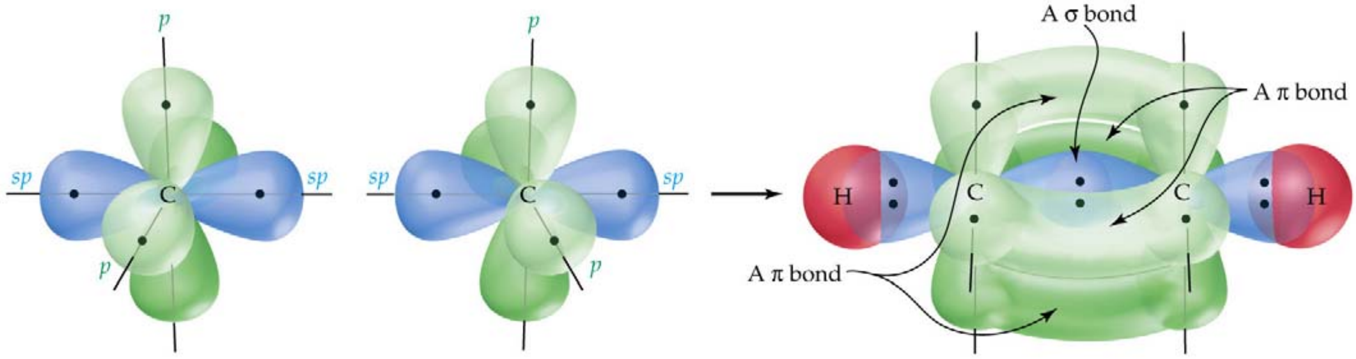
- The second bond comes from the *sideways overlap* of the leftover *p* orbitals to give a pi (π) bond. This is 90° to the plane defined by the trigonal-planar σ bonds. The π bond is both above and below the plane (2 lobes).



- Our structure therefore appears like this… note that π bonds involve a sideways overlap, so bond rotation is not possible.



- How about a triple bond? Example: acetylene $H{-}C{\equiv}C{-}H$
  - Carbon atoms are *sp*-hybridized, and each has two remaining *p* orbitals 90° to each other (see p. 14)
  - The first bond in the triple bond originates from the direct overlap of *sp* orbitals (σ bond)
  - Both the second and the third bonds in the triple bond are π bonds originating from the sideways overlap of the remaining *p* orbitals. These two π bonds are 90° apart.



- Example: assign the hybridizations and the number of π bonds present in the molecule acetone