Chapter 10 Molecular Geometry (Ch9 Jespersen, Ch10 Chang)

The arrangement of the atoms of a molecule in space is the molecular geometry.

This is what gives the molecules their shape.

Molecular shape is only discussed when there are *three or more* atoms connected (diatomic shape is obvious).

Molecular geometry is essentially based upon five basic *geometrical structures*, and can be predicted by the **v**alence **s**hell **e**lectron **p**air **r**epulsion model (VSEPR).

The VSEPR Method

This method deals with electron domains, which are regions in which it is *most likely* to *find* the *valence electrons*.

This includes the: -bonding pairs (located between two atoms, bonding domain), and

-nonbonding pairs or lone pairs (located principally on one atom, nonbonding domain).

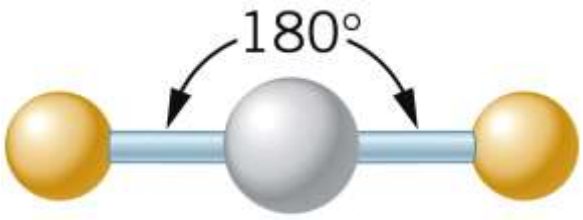
(Note for bonding domains, they contain **all** the electrons shared between two atoms – so a multiple bond is considered as one domain).

The best arrangement of a given number of electron domains (charge clouds) is the one that *minimizes* the *repulsions* among the *different domains*.

The arrangement of electron domains about the central atom of a molecule is called its electron-domain geometry (or electronic geometry).

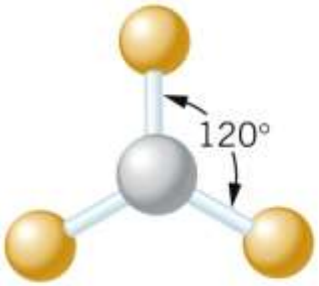
The **five** basic geometrical structures are linear, trigonal planar (planar triangular), tetrahedral, trigonal bipyramid and octahedral.

Linear

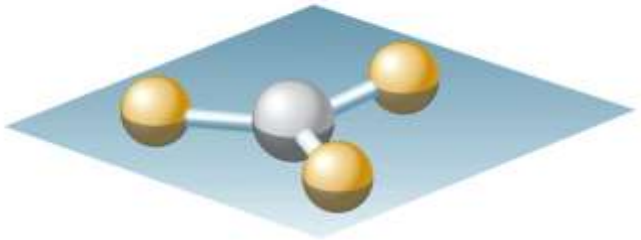


A linear molecule

Trigonal Planar



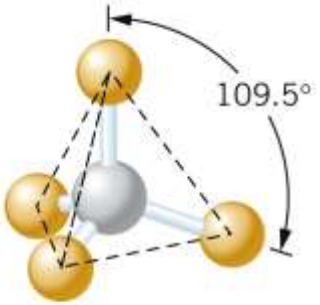
A planar triangular molecule



Another view showing how all the atoms are in the same plane

Tetrahedral

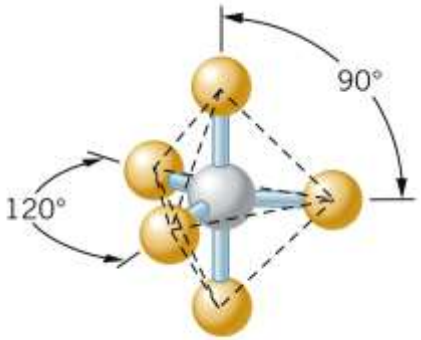
A tetrahedron



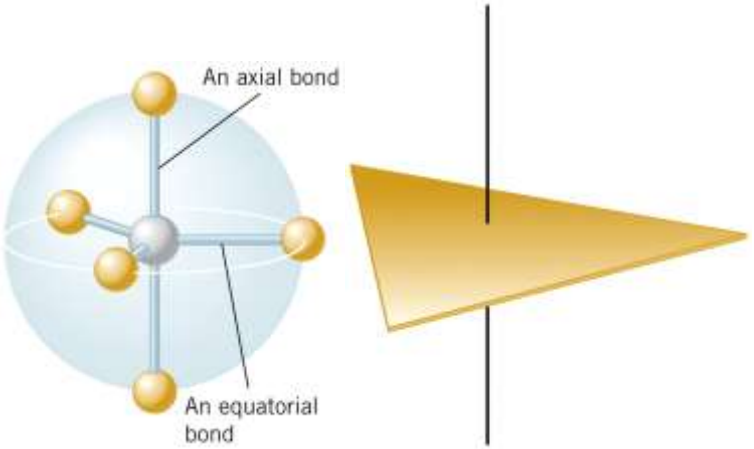
A tetrahedral molecule

Trigonal Bipyramid

A trigonal bipyramid

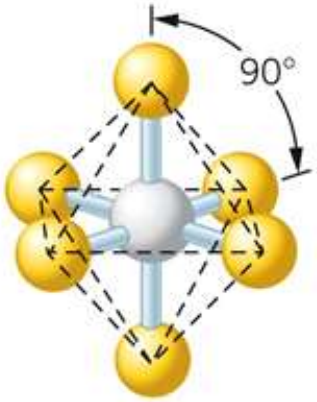


A trigonal bipyramidal molecule

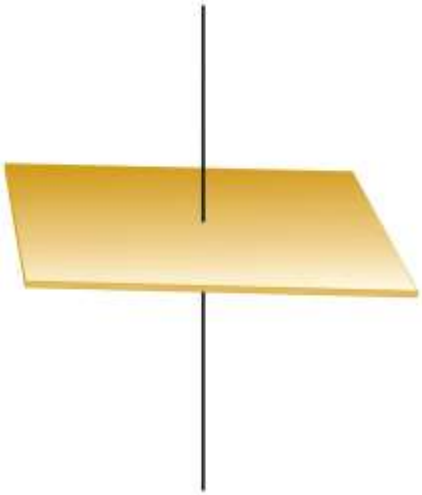


Octahedral

An octahedron



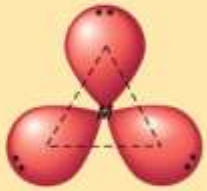
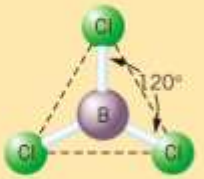
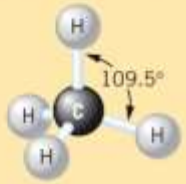
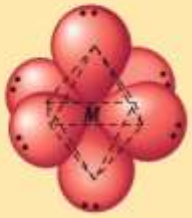
An octahedral molecule



The *number* and *type* of electron domains control the geometry; the number and type of electron domains is obtained from the Lewis structure.

There are **two** general situations – either the central atom (which controls the geometry) has non-bonding electrons (*lone pairs*), or it does not.

If the central atom does NOT have lone pairs, then the following shapes are produced for molecules of the general form **AB_2**, **AB_3**, **AB_4**, **AB_5** and **AB_6**.

Number of Domains	Shape		Example	
2		Linear	$BeCl_2$	
3		Planar triangular	BCl_3	
4		Tetrahedral (A tetrahedron is pyramid shaped. It has four triangular faces and four corners.)	CH_4	
5		Trigonal bipyramidal (This figure consists of two three-sided pyramids joined by sharing a common face—the triangular plane through the center.)	PCl_5	
6		Octahedral (An octahedron is an eight-sided figure with *six* corners. It consists of two square pyramids that share a common square base.)	SF_6	

If the central atom **does** have lone pairs, it is slightly more complicated.

We describe such systems as $\mathbf{AB_nE_m}$ where E = lone pairs.

So it is **essential** to know if the central atom has lone pairs (or not).

1. Generate the correct Lewis structure.
2. Count the **total** number of electron domains (*atoms and lone pairs*) around the *central* atom.
3. Arrange them in a way to minimize repulsions (1of the 5 basic geometrical structures).
4. Describe the molecular geometry in terms of the angular arrangement of the bonded ATOMS (**not** the domains – you cannot "*see*" the shape of the lone pairs).

Remember that a double or triple bond is counted as one electron domain when predicting geometry.

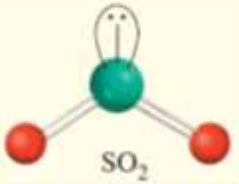
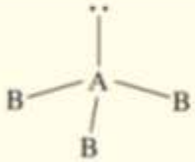
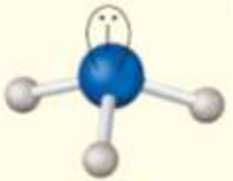
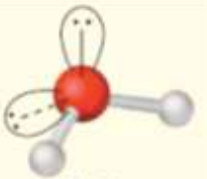
(# of electron domains) = (# of atoms bonded to central atom) + (# of nonbonding pairs on the central atom)

= B + E

B = atoms attached to the central atom.

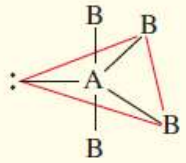
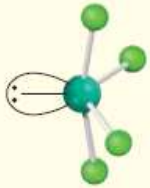
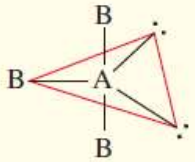
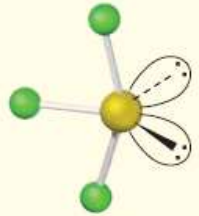
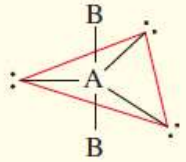
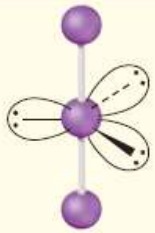
E = lone pairs on A.

For **AB_2E**, and then **AB_3E** and **AB_2E_2** (*three* and then *four* domains)

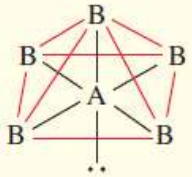
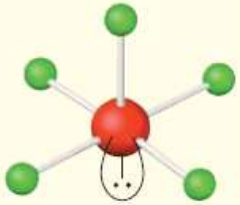
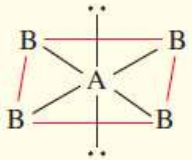
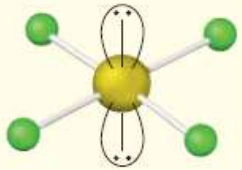
Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB_2E	3	2	1	Trigonal planar	Bent	 SO_2
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AB_2E_2	4	2	2	Tetrahedral	Bent	 H_2O

Notice that the *overall* molecular shape is **different** than the "*based on basic geometric structure*" shape.

For **AB_4E**, **AB_3E_2** and **AB_2E_3** (five domains)

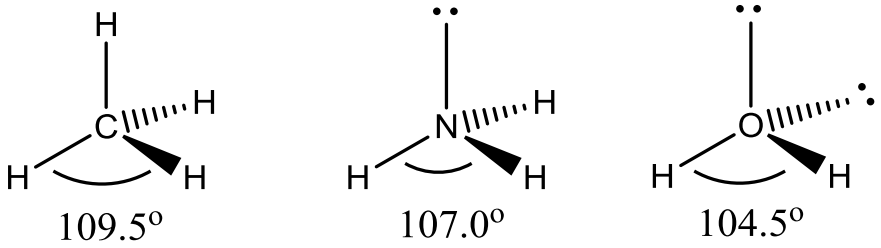
Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AB_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3^-

For **AB_5E** and **AB_4E_2** (six domains)

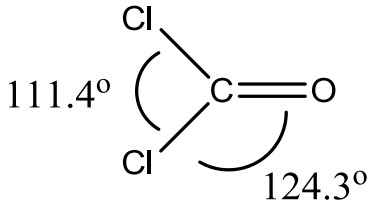
Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AB_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

The effect of nonbonding electrons and multiple bonds on bond angles

Electron domains for nonbonding electron pairs exert **greater** *repulsive* forces (than single bonds) on adjacent electron domains and thus tend to compress the bond angles.



Electron domains for multiple bonds exert a **greater** *repulsive* force on adjacent electron domains than do single bonds.



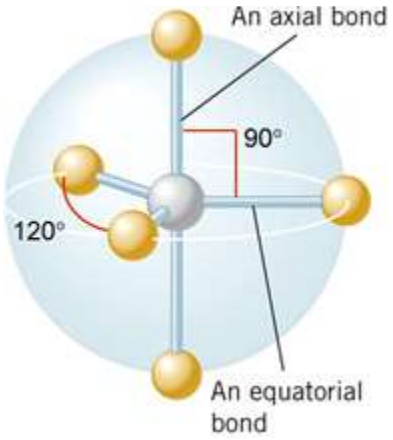
Molecules with expanded valence shells

Atoms from the third period (and beyond) can have **more** than *four pairs* of *electrons* around them.

Five electron domains give rise to trigonal bipyramidal electron domain geometries.

Trigonal bipyramidal structures have *three* electron domains in the equatorial position, and *two* in the axial positions. Axials have three 90° interactions while equatorial positions have only two.

Therefore the bulkier domains (i.e. lone pairs, not bonds) will prefer to be in the *equatorial* position.



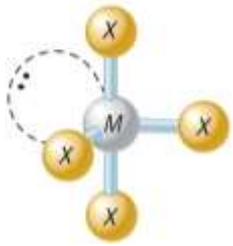
Six electron domains give rise to octahedral geometries.

All electron domains are at 90° to four other electron domains (all positions are equivalent).

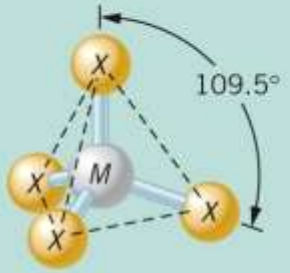
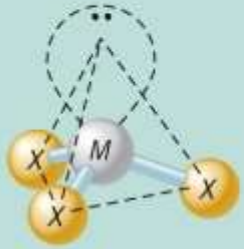
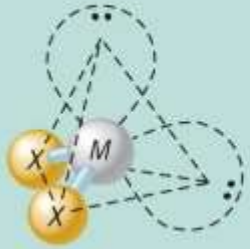
In summary:

Number of Electron Domains	Electronic Geometry	Nonbonding Pairs	Molecular Geometry	Examples
2	Linear	0 (AB_2)	Linear	CO_2, HCN
3	Trigonal Planar	0 (AB_3) 1 (AB_2E)	Trigonal Planar Bent	BCl_3 O_3, SO_2
4	Tetrahedral	0 (AB_4) 1 (AB_3E) 2 (AB_2E_2)	Tetrahedral Trigonal Planar Bent	CH_4 NH_3 H_2O
5	Trigonal Bipyramid	0 (AB_5) 1 (AB_4E) 2 (AB_3E_2) 3 (AB_2E_3)	Trigonal Bipyramid See-saw T-shaped Linear	PCl_5 SF_4 BrF_3 I_3^-
6	Octahedral	0 (AB_6) 1 (AB_5E) 2 (AB_4E_2)	Octahedral Square Pyramid Square Planar	SF_6 $XeOF_4$, BrF_5 XeF_4

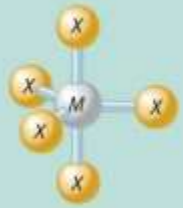
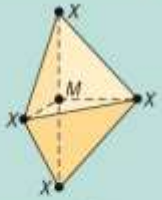
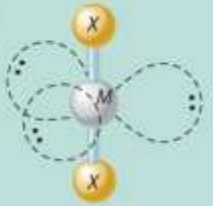
(*See-saw* is sometimes referred to as *Distorted Tetrahedral*).



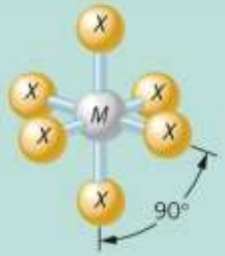
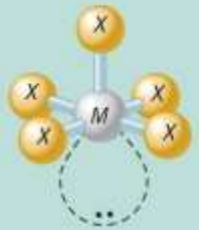
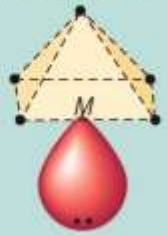
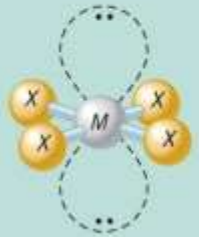
For **4** total electron domains:

Number of Bonding Domains	Number of Nonbonding Domains	Structure	
4	0		**Tetrahedral** (example, CH_4) All bond angles are 109.5°.
3	1		**Trigonal pyramidal** (pyramid shaped) (example, NH_3)
2	2		**Nonlinear, bent** (example, H_2O)

For **5** total electron domains:

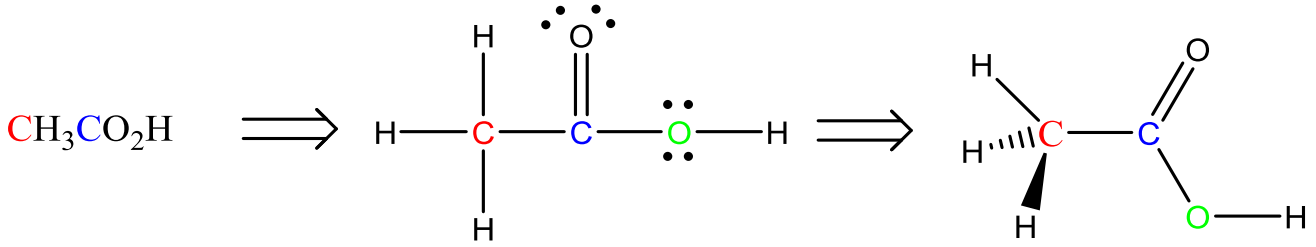
Number of Bonding Domains	Number of Nonbonding Domains	Structure	
5	0		**Trigonal bipyramidal** (example, PCl_5)
4	1		**Distorted tetrahedral**  (example, SF_4)
3	2		**T-shaped** (example, ClF_3)
2	3		**Linear** (example, I_3^-)

For **6** total electron domains:

Number of Bonding Domains	Number of Nonbonding Domains	Structure	
6	0		**Octahedral** (example, SF_6) All bond angles are 90°.
5	1		**Square pyramidal**  (example, BrF_5)
4	2		**Square planar** (example, XeF_4)

Molecules with more than one central atom

We can describe the geometry of *each* "central atom".



So here the 1st **C** is *tetrahedral* (4 bonding domains)

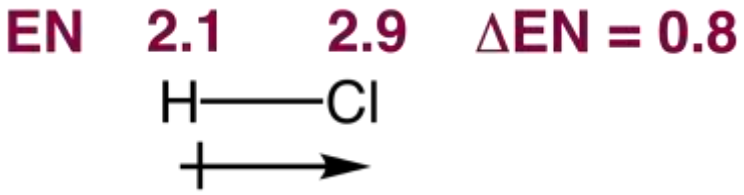
The 2nd **C** is *trigonal planar* (3 bonding domains)

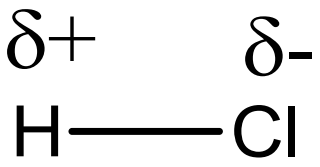
The **O** is *bent* (2 bonding and 2 non-bonding domains)

Polarity in Polyatomic Molecules

When two atoms of *different* electronegativity are connected, there is **unequal** sharing of the electron density, and this creates a polar covalent bond.

One end is partially positive, the other is partially negative. (The symbol δ means a small amount).





The shift in electron density is indicated by a crossed arrow, pointing in the direction of the shift (towards the more electronegative atom).

Each polar bond has an associated Dipole moment (μ):

$$\mu = Q \times r$$

r = distance between charges

Q = magnitude of charge

Unit is the Debye, D.

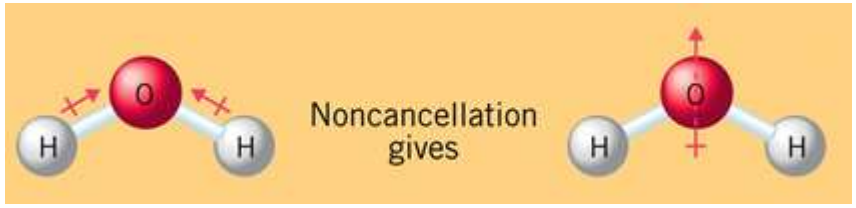
For diatomic molecules:

Polar molecules have different elements connected, e.g. HCl, CO, NO.

Nonpolar molecules have the same elements connected, e.g. H_2, O_2, F_2.

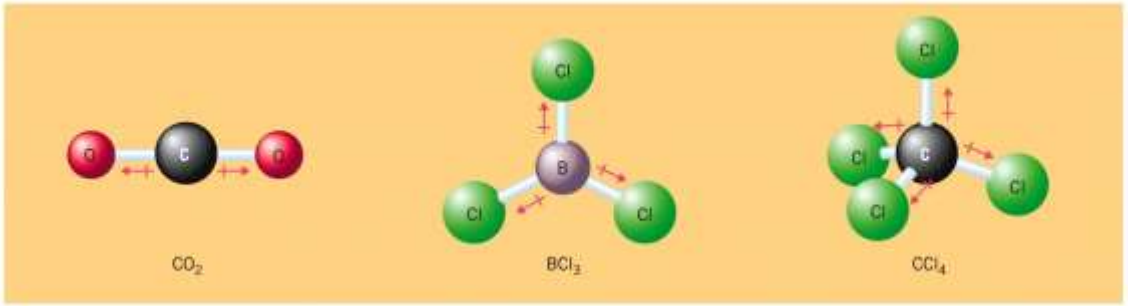
For polyatomic molecules, we also have to consider the molecular geometry.

We must consider the *combination* of *all* of the *individual* bond dipoles to determine the **net** overall **molecular** dipole.



Sometimes the *individual* dipoles will cancel each other out, which generates a molecule with **no** dipole moment (even though it contains *individual* polar bonds).

E.g.

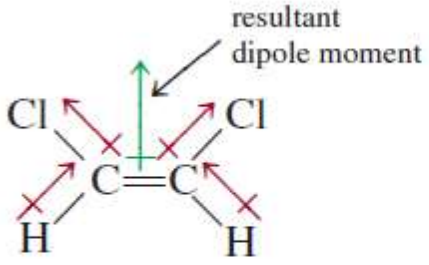


Dipole moments of Some Polar Molecules

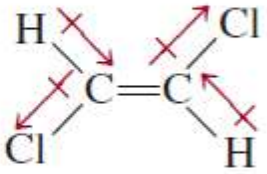
Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H_2O	Bent	1.87
H_2S	Bent	1.10
NH_3	Trigonal pyramidal	1.46
SO_2	Bent	1.60

Dipole moments (which can be measured) can distinguish between very similar structures.

E.g.



cis-dichloroethylene
$\mu = 1.89$ D



trans-dichloroethylene
$\mu = 0$

Covalent Bonding

There are two different theories (approaches/perspectives) that are used to explain covalent bonding.

They are Valence Bond Theory (VB theory) and Molecular Orbital Theory (MO theory).

Essentially they are atomic and molecular perspectives of covalent bonding.

Valence-bond theory – the electrons in a molecule occupy *atomic* orbitals of the individual *atoms*.

In valence-bond theory, we assume that bonds form via the pairing of unpaired electrons in valence-shell atomic orbitals.

The *electrons* can *pair* when their *atomic orbitals overlap*.

"Overlap" means that a portion of the *atomic orbitals* from each *atom* occupy the *same region* of *space*; or

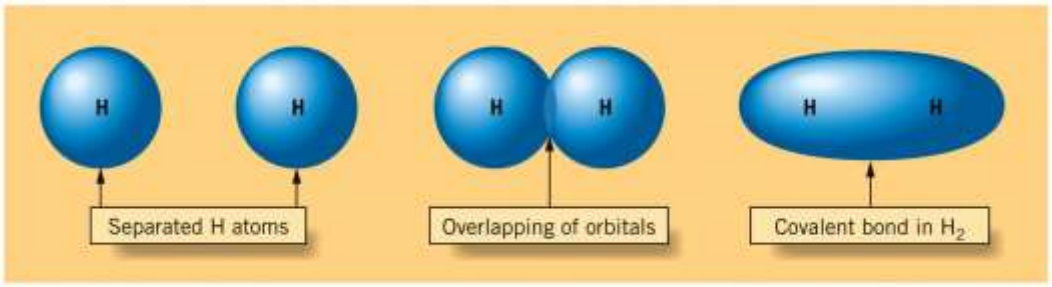
Overlap = interaction/interference of wavefunctions.

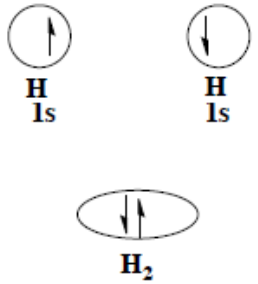
If the atomic orbitals overlap end over end we call it σ bonding (forming σ-bonds).

If the atomic orbitals overlap side by side we call it π bonding (forming π-bonds).

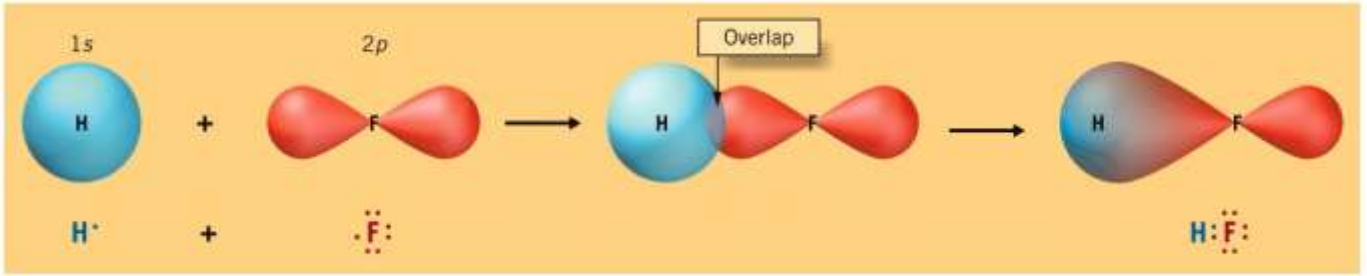
When orbitals on two atoms overlap, the two electrons of *opposite* spin are involved in the orbital overlap.

For **H_2**:

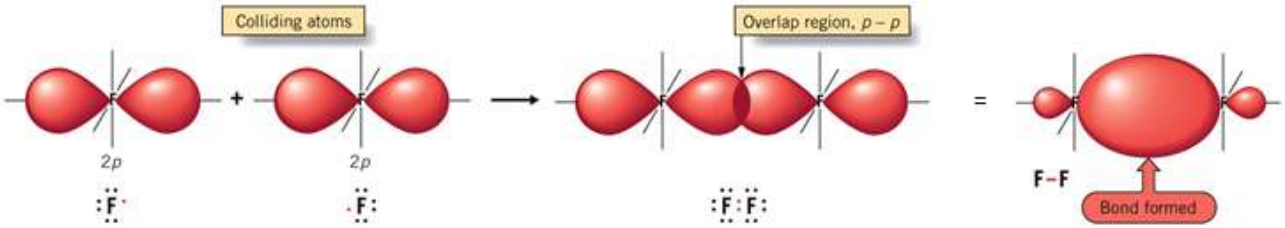




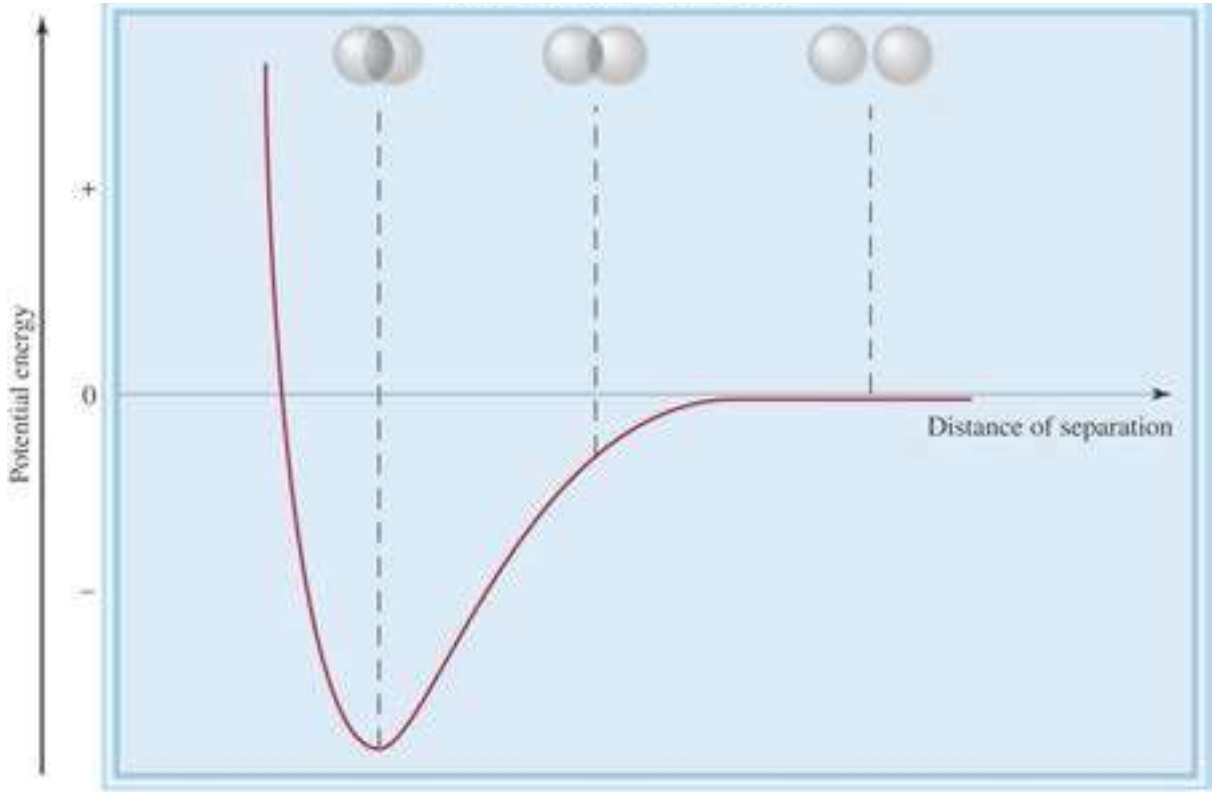
For **H-F**:

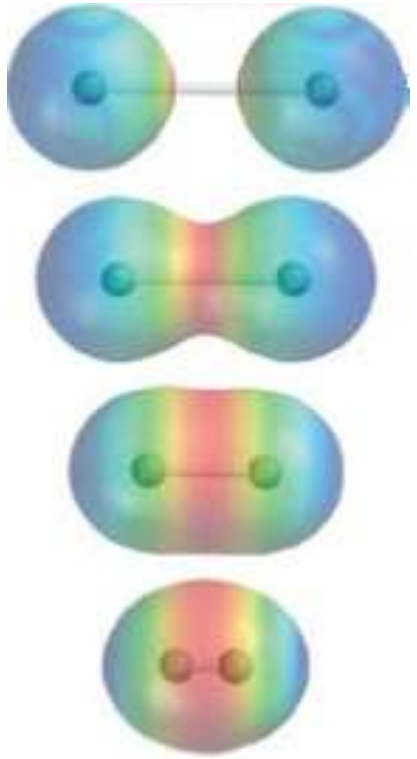


For **F_2**:



To get them to overlap, the atoms must approach each other in space:





The *lowest* energy distance of separation is called the Bond Length.

Lewis theory basically says two electrons make a covalent bond; VB theory says *which* two electrons (and in doing so explains different bond strengths/energies) – but it still **does not** explain tetrahedral geometries.

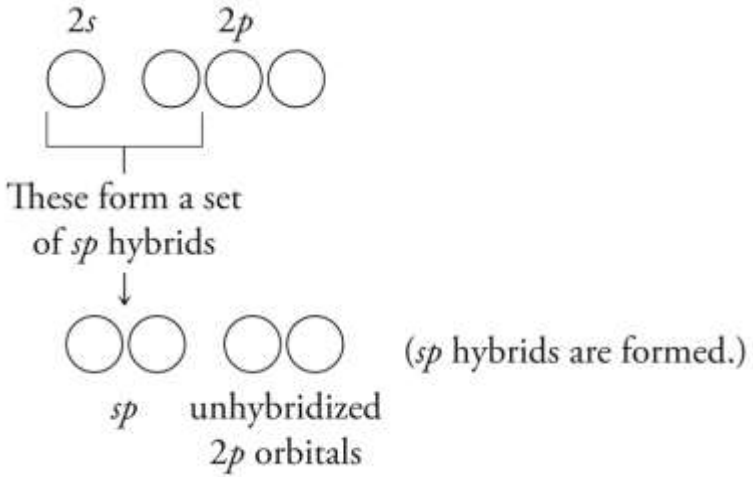
This prompted the idea of Hybrid Atomic Orbitals. (*Hybrid* = mixture).

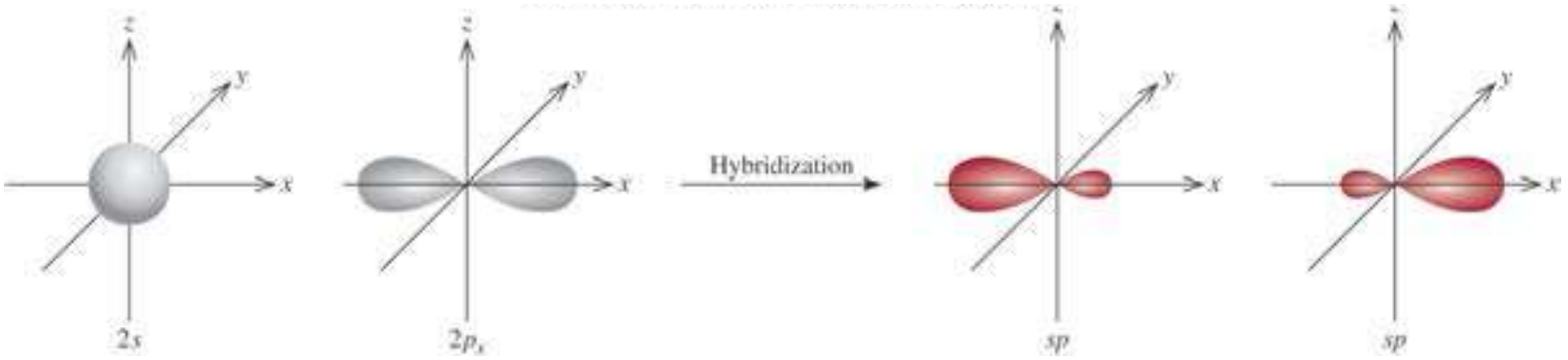
Hybrid atomic orbitals are the mathematical combination of wavefunctions on the **same** *atom* to form a new set of **equivalent** wavefunctions called *hybrid atomic wavefunctions*.

The mixing of ***n*** atomic orbitals **always** results in ***n*** hybrid orbitals.

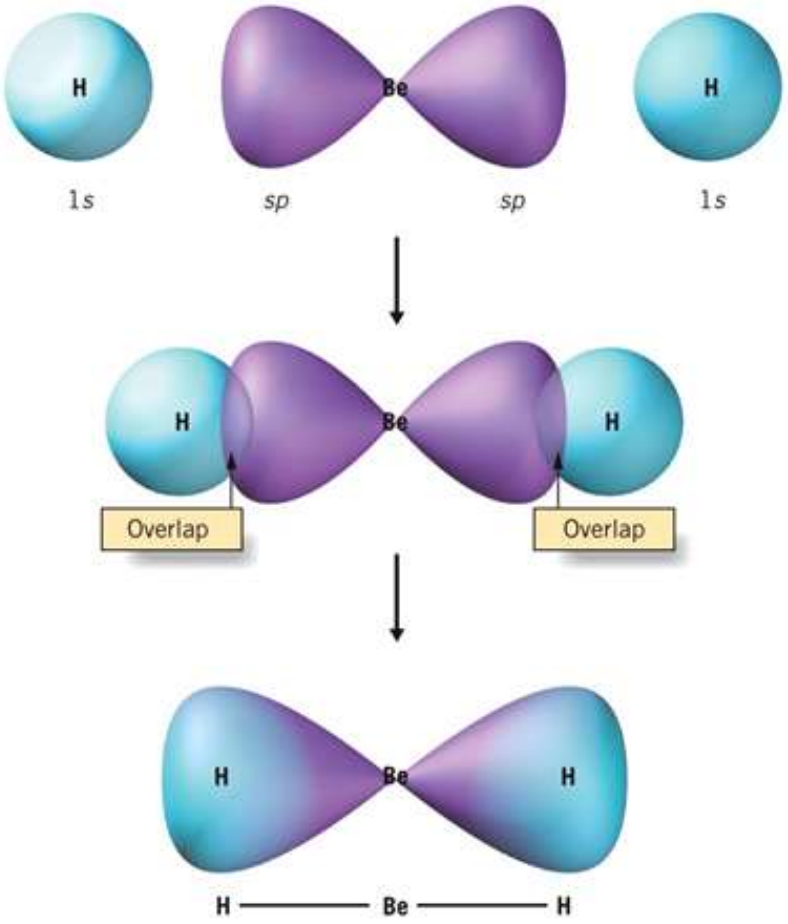
sp hybrids

s + **p** = *two* **sp** hybrid orbitals, leaving *two* unhybridized **p**-orbitals.





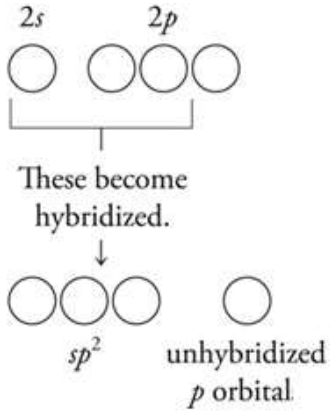
Examples: **C** in **C**O_2, **C** in H**C**N, **Be** in BeH_2.

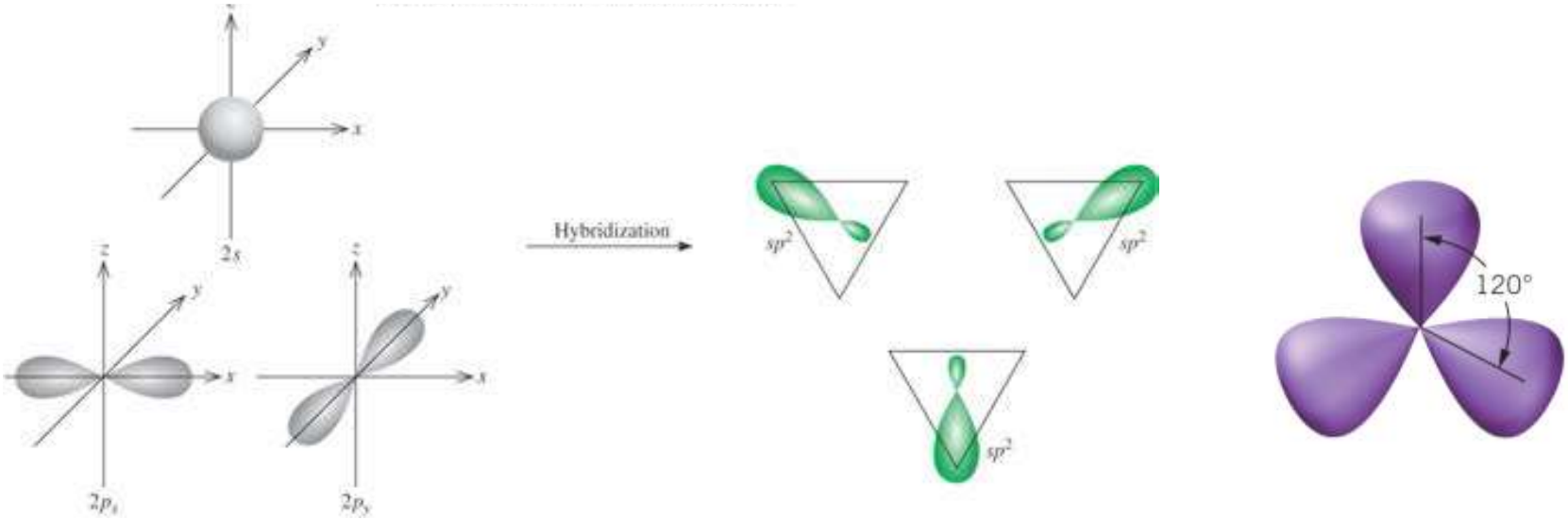


Linear central atom with bond angles of **180°**.

sp^2 hybrids

s + **p** + **p**= *three* $\mathbf{sp^2}$ hybrid orbitals, leaving *one* unhybridized **p**-orbital.

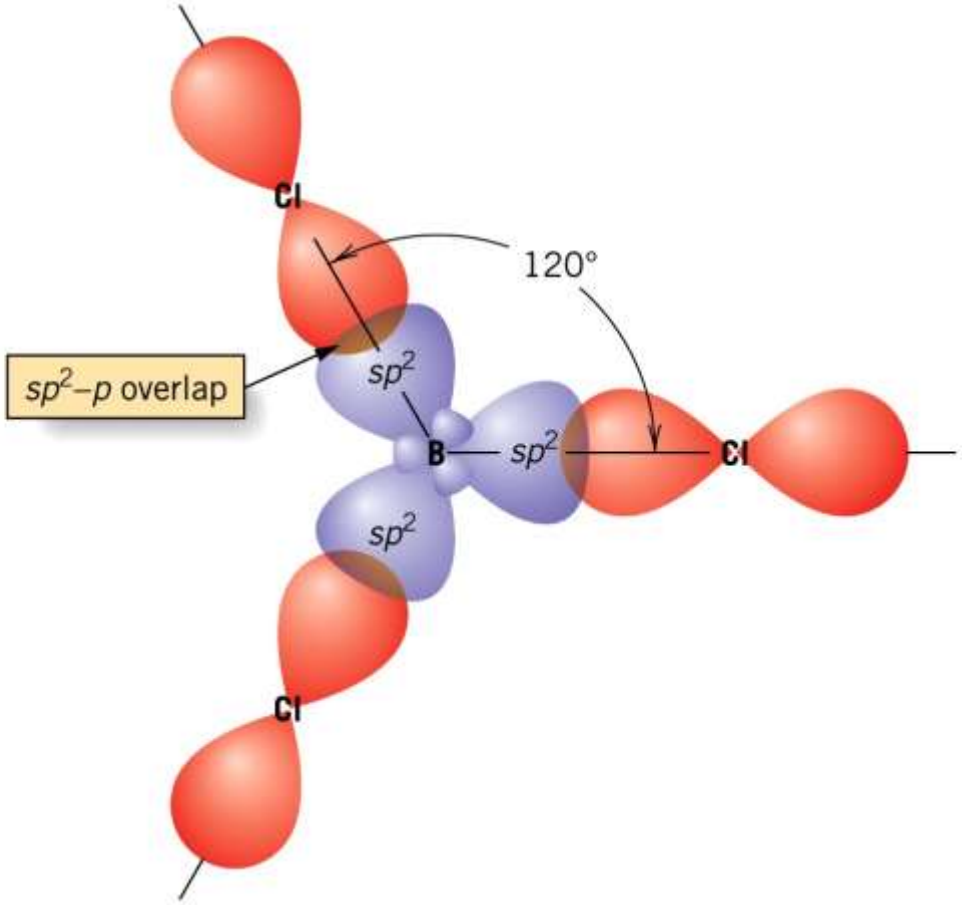




Trigonal planar central atom, with bond angles of $\mathbf{120^o}$.

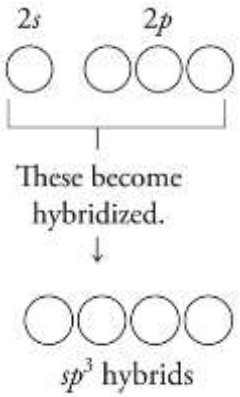
Examples: **B** in BCl_3, **N** in $\mathbf{N}O_2^-$.

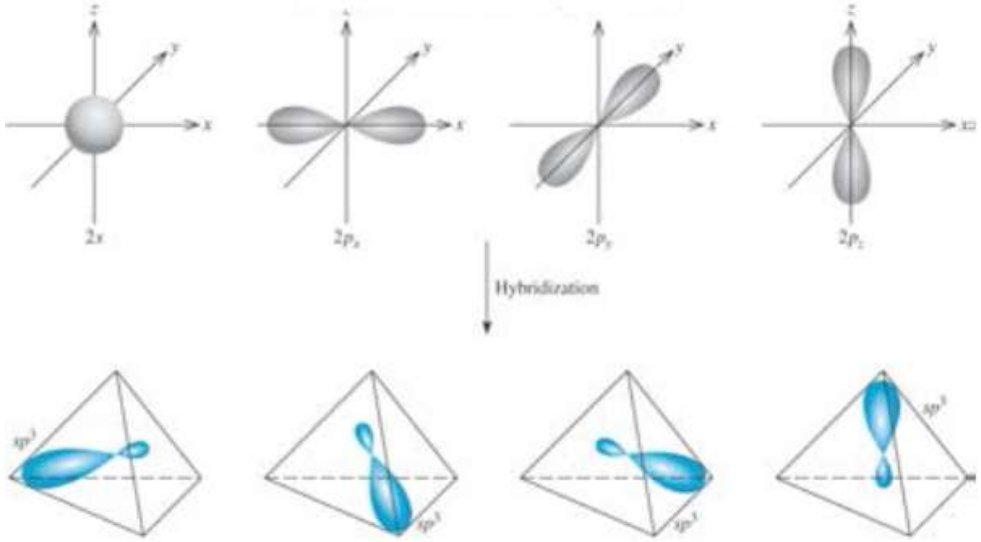
sp^2 hybrid orbital

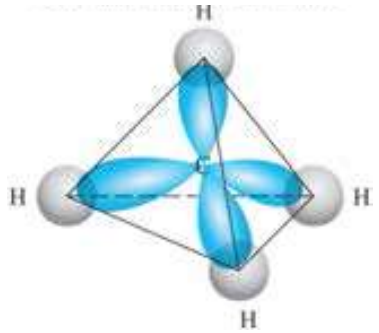


sp^3 hybrids

s + **p** + **p** + **p** = *four* $\mathbf{sp^3}$ hybrid orbitals

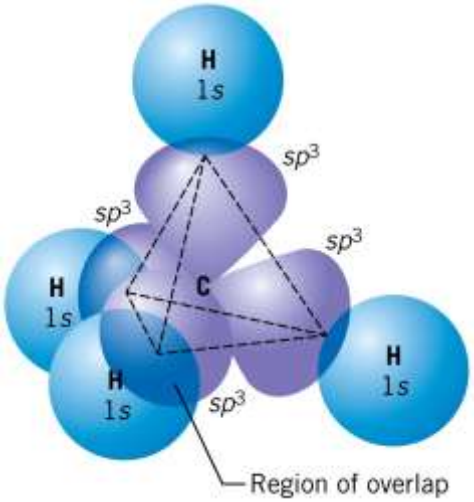


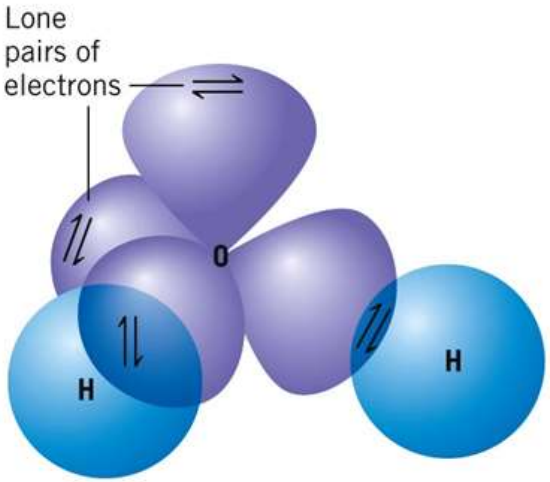


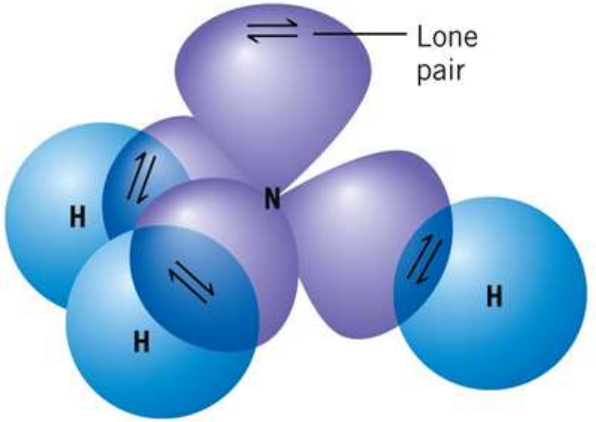


Tetrahedral central atom with bond angles of **109.5**°.

Examples: **C** in CH_4, **N** in NH_3, **O** in H_2O.

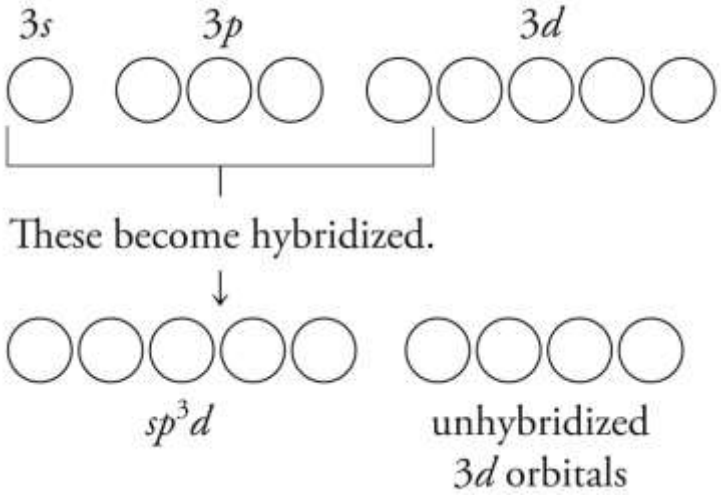


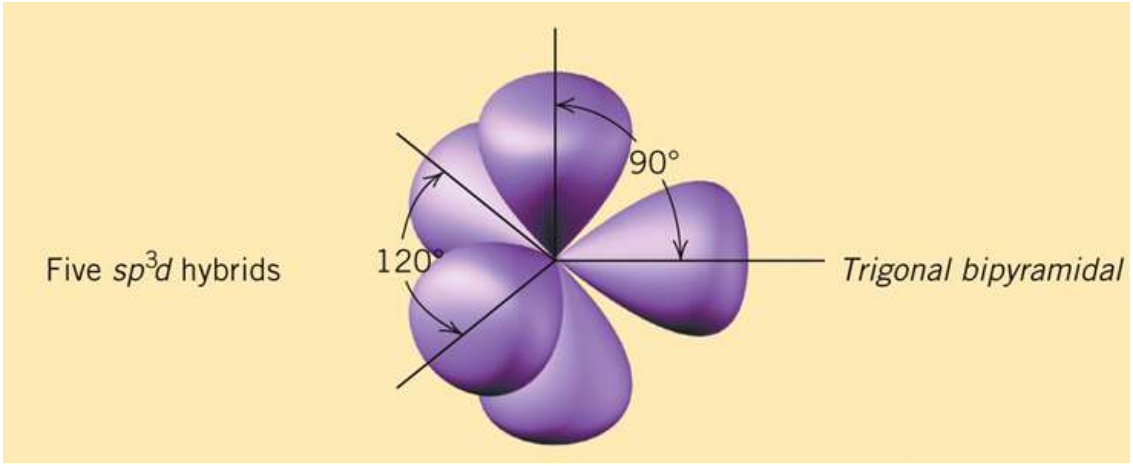




sp^3d hybrids

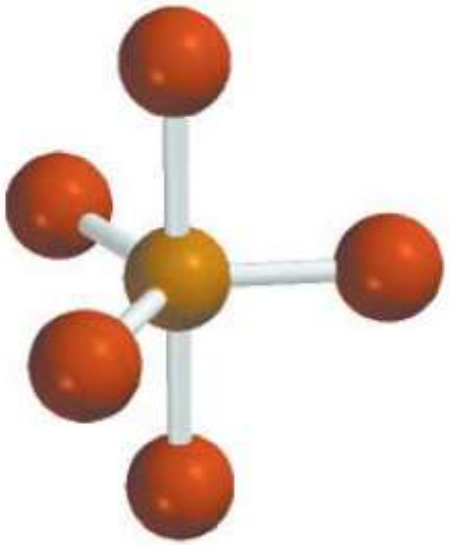
s + **p** + **p** + **p** + **d** = *five* **sp^3d** hybrid orbitals, leaving *four* unhybridized **d**-orbitals.



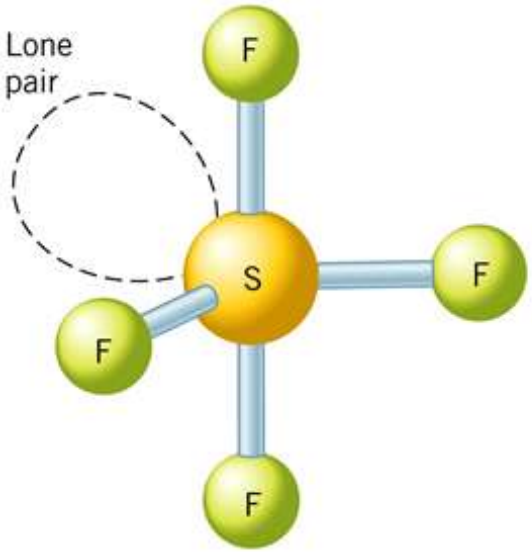


Trigonal bipyramidal central atom with bond angles of **90^o** and **120^o**.

Examples: **P** in PBr_5, **S** in SF_4.



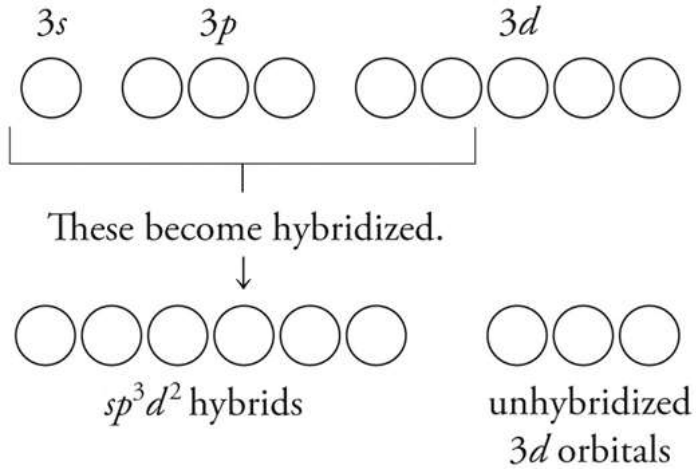
PBr_5

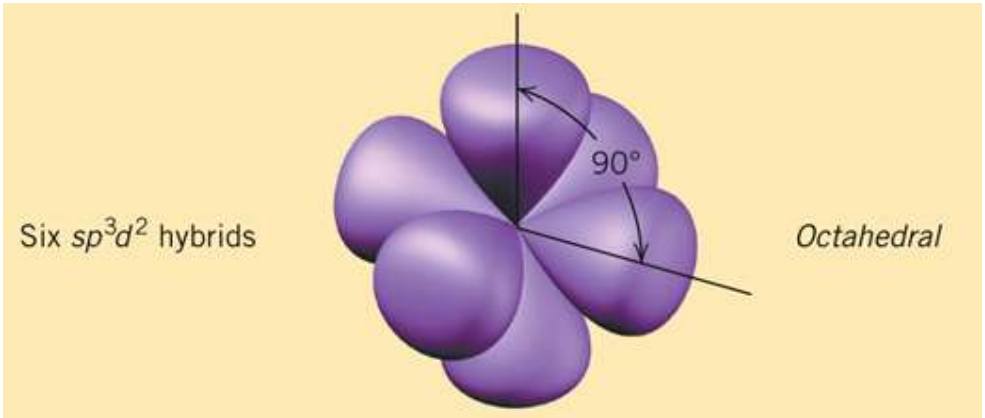


SF_4

sp^3d^2 hybrids

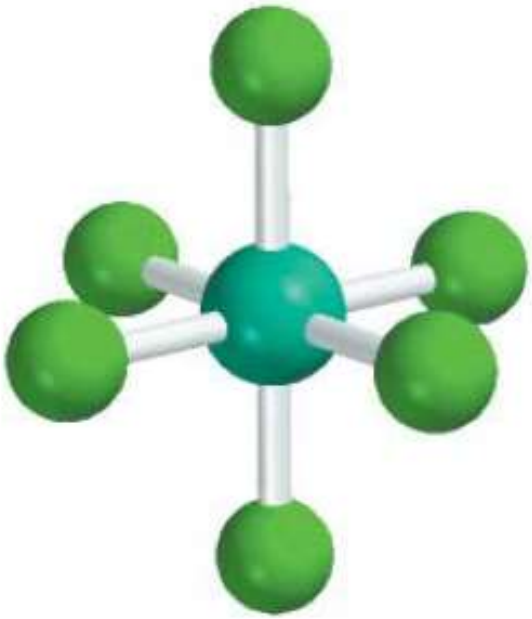
s + **p** + **p** + **p** + **d** + **d**= *six* $\mathbf{sp^3d^2}$ hybrid orbitals, leaving *three* unhybridized **d**-orbitals.



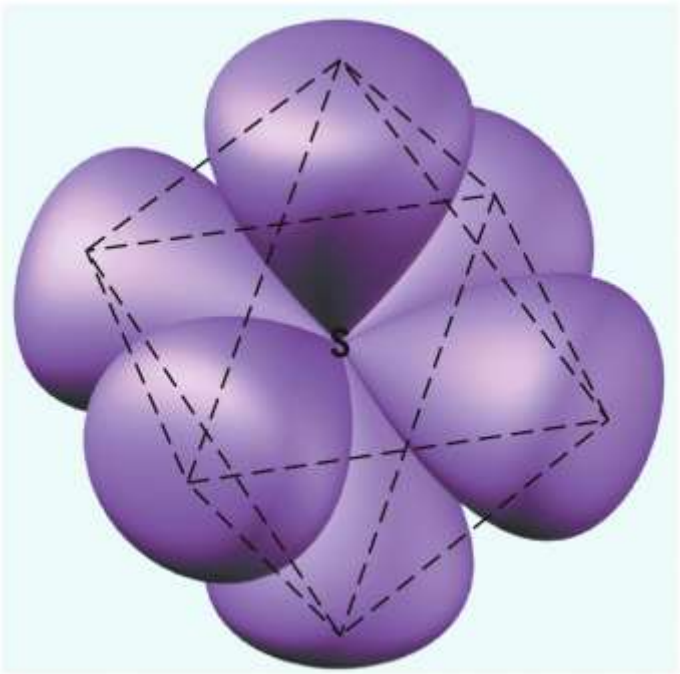


Octahedral central atom with bond angles of $\mathbf{90^o}$.

Examples: **S** in SF_6.



SF_6



Summary

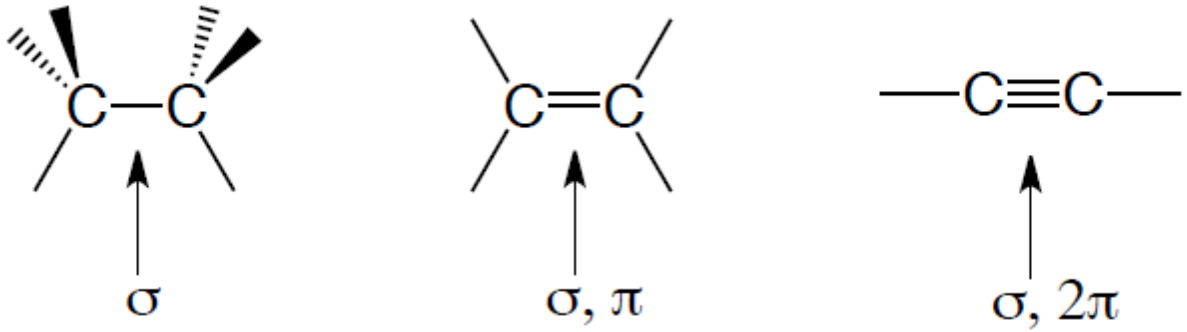
Electron Domains	Hybrid	Atomic Orbitals Used	Electron Geometry
2	sp	s + p	Linear Bond angles 180°
3	sp^2	s + p + p	Trigonal planar Bond angles 120°
4	sp^3	s + p + p + p	Tetrahedral Bond angles 109.5°
5	sp^3d	s + p + p + p + d	Trigonal Bipyramidal Bond angles 90° and 120°
6	sp^3d^2	s + p + p + p + d + d	Octahedral Bond angles 90°

Number of electron domains = connected atoms plus lone pairs = number of hybrid orbitals

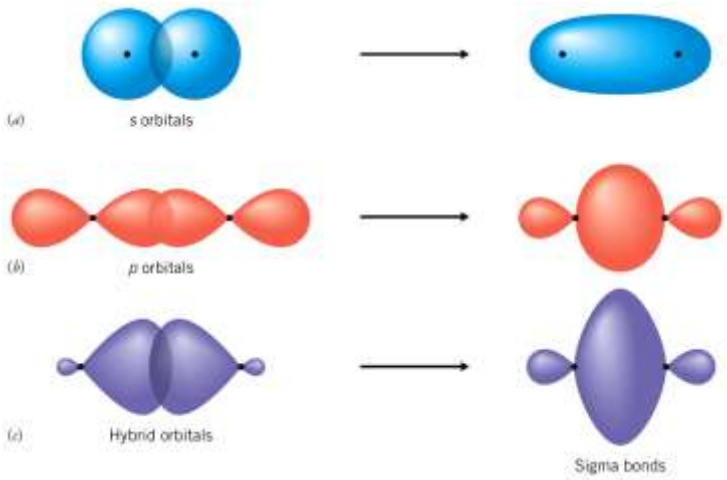
Multiple Bonds

All single bonds are sigma bonds.

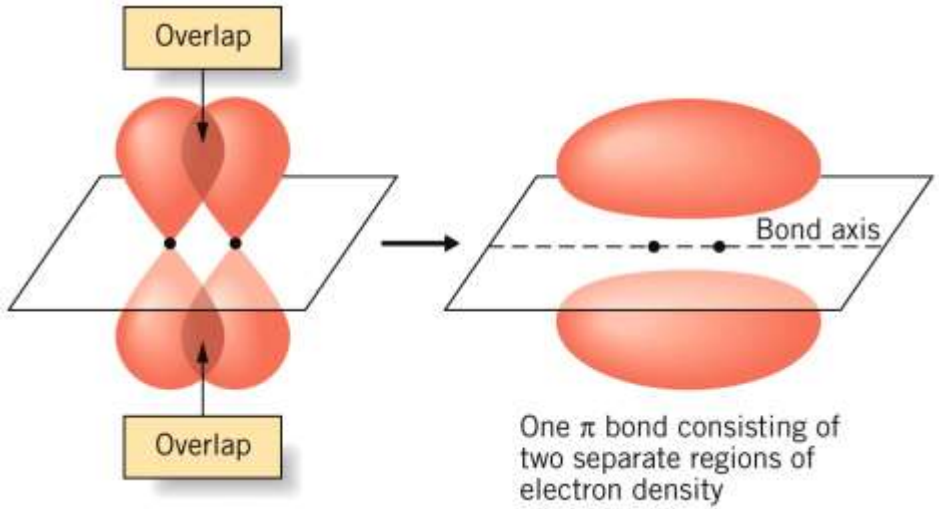
All multiple bonds contain one sigma bond, and the *remaining* bonds are pi bonds.



Sigma (σ) bonding is end over end overlap of two orbitals, resulting in an interaction (bonding/electron density) ***along*** the *internuclear* axis.



Pi (π) bonding is the sideways overlap
of adjacent p orbitals,
resulting in an interaction (bonding/electron density)
above and ***below*** the *internuclear* axis.



π bonding **cannot** occur *alone*.

It only forms *once* a sigma bond *already exists* between the two atoms.

E.g. Ethene, $CH_2=CH_2$.

Each Carbon is sp^2 hybridized (3 sp^2 and a p).

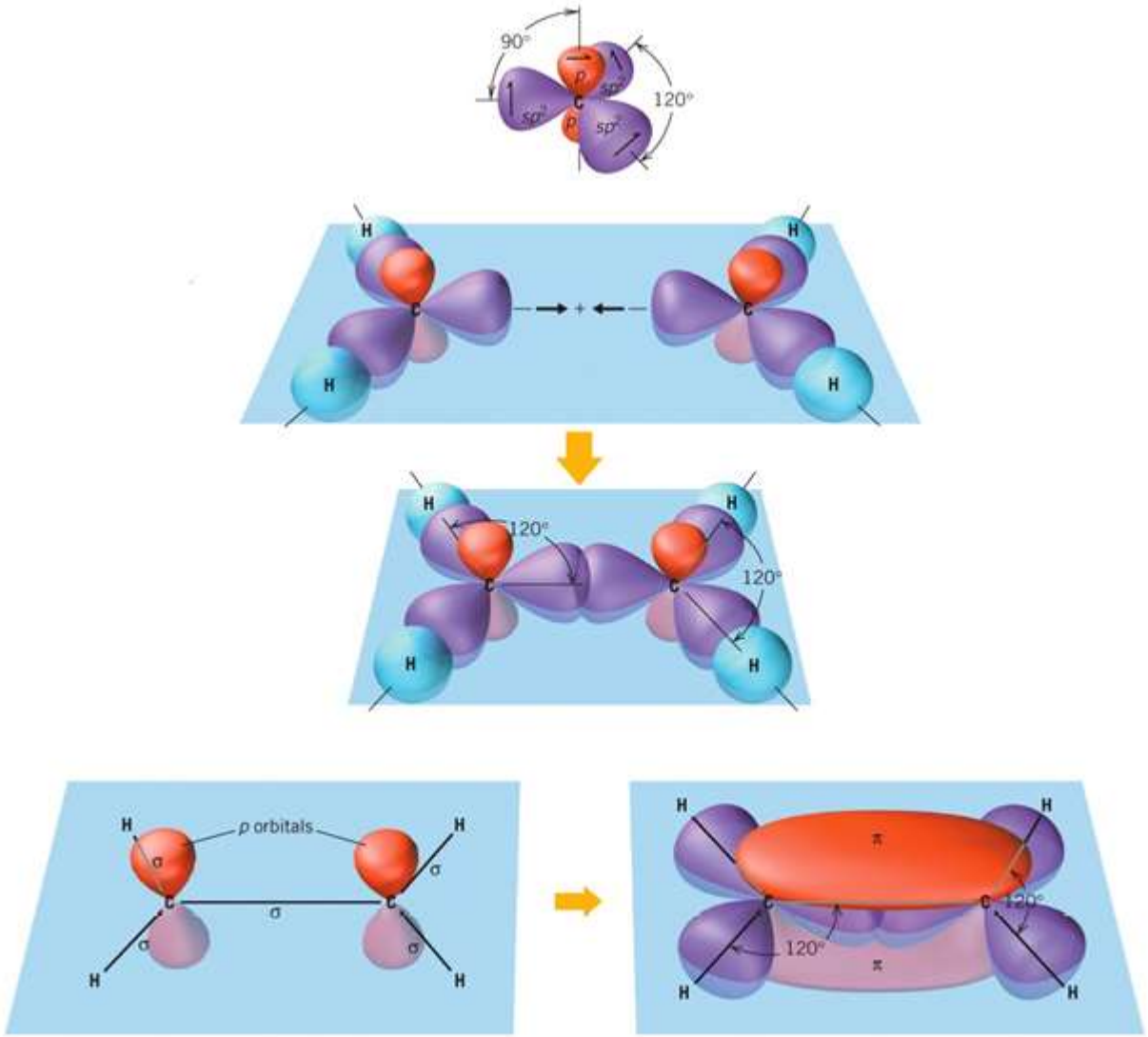
The **C**-**H** bonds are (**H**)s-(**C**)sp^2 overlap.

The **C**-**C** bond is (**C**)sp^2-(**C**)sp^2 overlap.

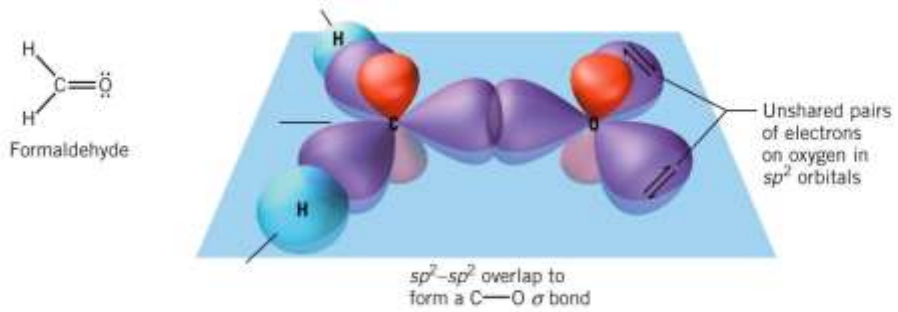
These are all the **sigma** bonds.

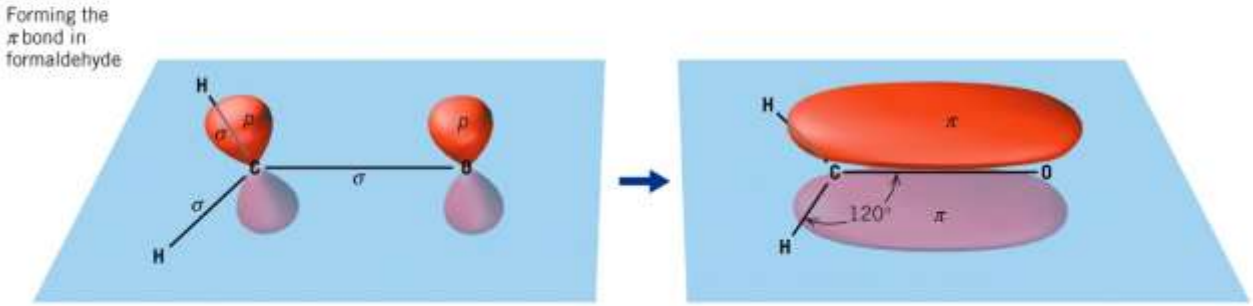
The **pi** bonding is from *sideways overlap* of the two (**C**)p-(**C**)p orbitals.

The *sum* of the σ and π bonding gives the complete bonding picture.



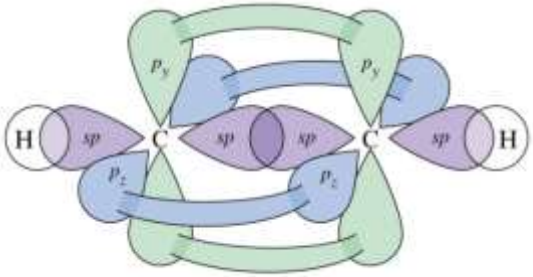
Bonding picture for Formaldehyde:

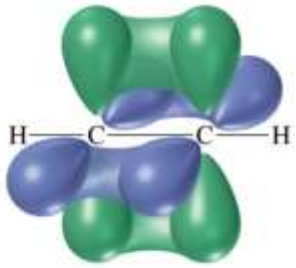




Bonding picture for Acetylene, C_2H_2:

$$H-C\equiv C-H$$





Molecular Orbital (MO) Theory

There is also an *alternative* to VB Theory to describe bonding in molecules – Molecular Orbital Theory.

A molecular *orbital* is a mathematical function that describes the *wave-like behavior* of an *electron* in a molecule.

The molecular orbital is associated with the *entire* molecule.

Molecular orbitals form from the *overlap* of *atomic* orbitals.

Overlap of *n atomic* orbitals results in *n molecular* orbitals.

Sigma interaction of *two* AO's generates *two* MO's, one is bonding and one is anti-bonding.

We call these the σ and σ* molecular orbitals.

To discuss these interactions we need to recall:

Electrons are waves.

Waves have associated wavefunctions, ψ.

When overlapping/interacting waves, they interfere with each other.

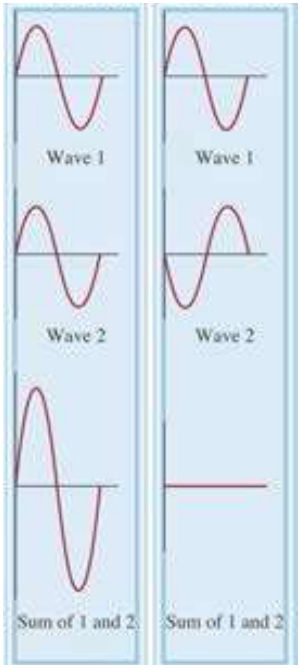
Depending on the wavefunctions, this can be *constructive* or *destructive*.

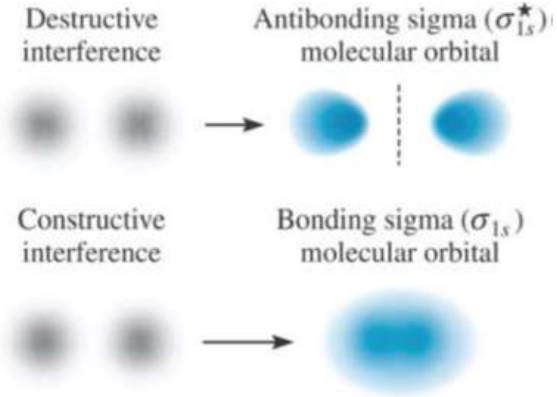
Wave functions have an associated sign of wave function (*up* or *down*).

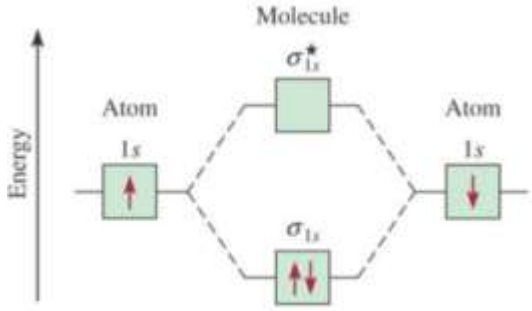
When interfering/interacting:

Constructive interference = same sign.

Destructive interference = opposite sign.





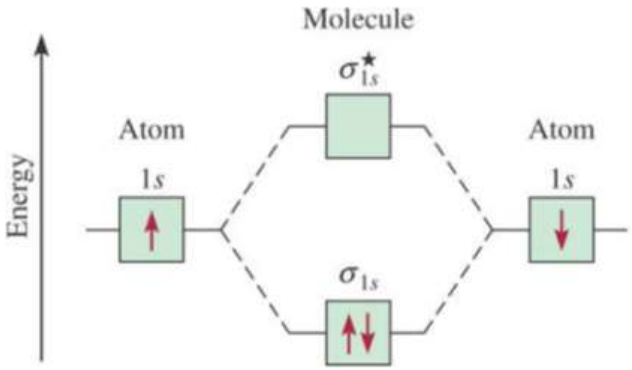


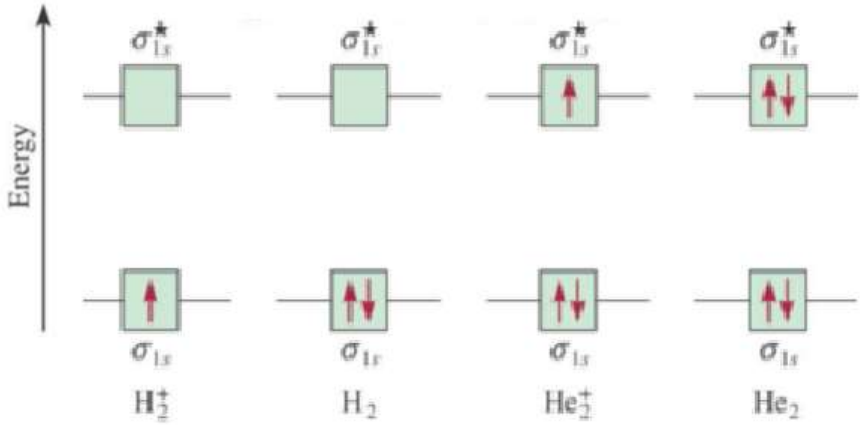
The molecular orbital diagram shows *why* it is better for the two electrons to interact (bond) than stay isolated and apart (not interacting) – they achieve a *lower energy*.

The *interaction* of AO's *produces* MO's.

The **total** energies of the AO's = **Total** energies of MO's, but we care about the electron energies (*Lower* is *better*).

For example, if we consider four different simple diatomic species (H_2^+, H_2, He_2^+ and He_2), all produced via 1s-1s interaction:





The only difference is the number of electrons for each species.

But this difference produces difference bonding results (*electronic energies*).

We can pretend that ***anti**-bonding cancels bonding*.

The lowest energy (*most stable*) is **H_2**; the highest energy (*least stable*) is **He_2**.

We can quantify this discussion of "*how much bonding*" using Bond Order.

$$\textbf{Bond Order} = \frac{1}{2}\textbf{(number of } \textbf{\textit{bonding}} \textbf{ electrons} - \textbf{number of } \textbf{\textit{antibonding}} \textbf{ electrons)}$$

Bond order of 1 = Single bond

2 = Double bond

3 = Triple bond.

Be aware that it is possible to have non-integer bond orders, e.g. $1\frac{1}{3}$, $2\frac{1}{2}$.

Bond order of H_2 $= \frac{1}{2}(2 - 0) = 1.$

Bond order of He_2 $= \frac{1}{2}(2 - 2) = 0.$ *Predict* the two He's to NOT be connected.

Second-Row Diatomic Molecules

We can extend our MO theory to more larger, more complicated molecules.

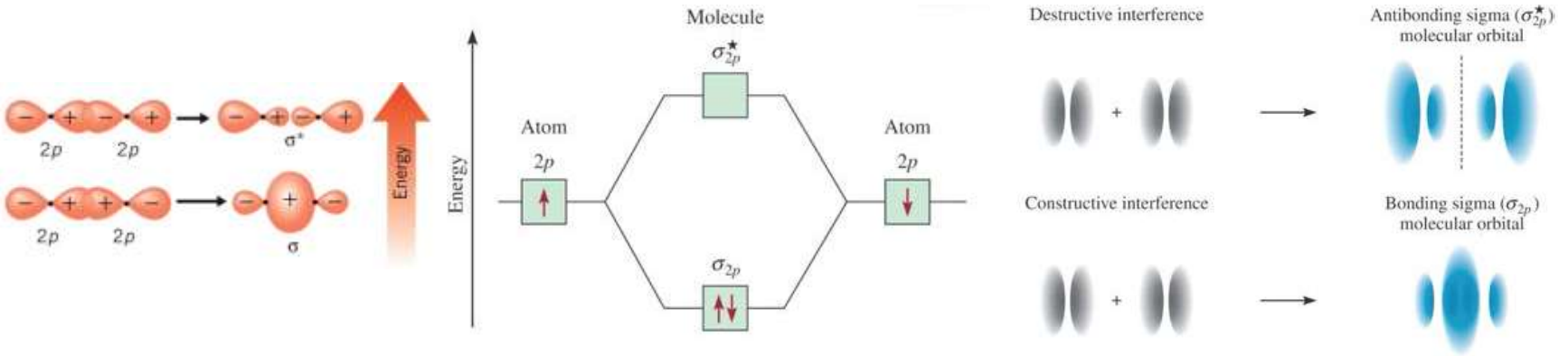
If we look at the second row elements, and consider homonuclear diatomics – these will be bonding/interacting using the **2s** and three **2p** orbitals.

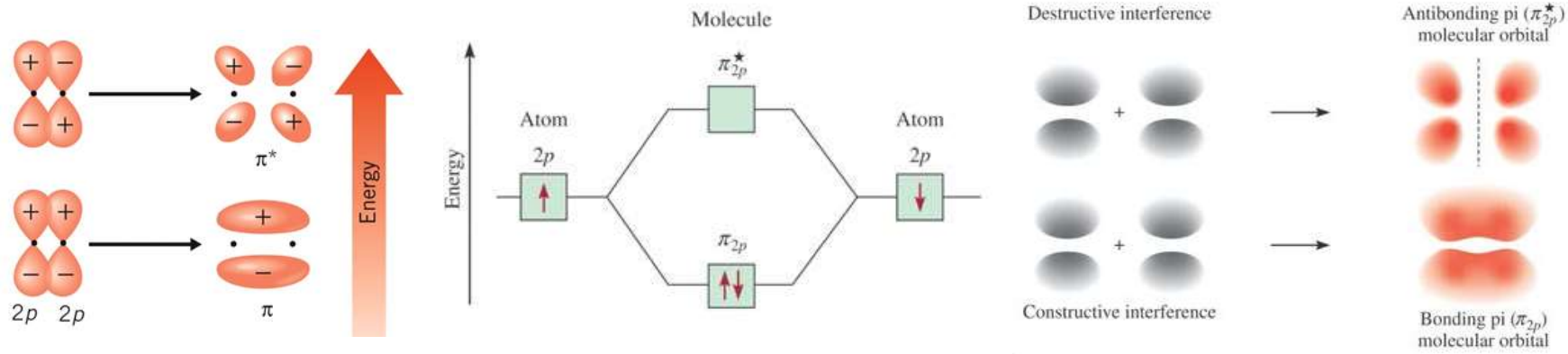
Atomic orbitals *interact most effectively* with other atomic orbitals of similar energy and shape.

So we see **1s** interact with **1s**, 2s interact with 2s, 2p interact with 2p, etc.

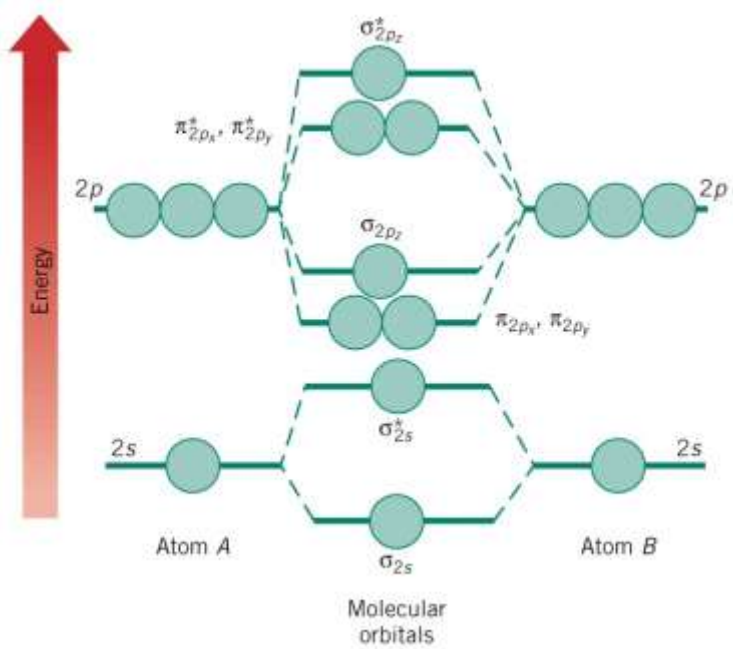
We already talked about how p orbitals can interact in *either* or *both* σ and π fashion, and this can lead to sigma (σ and σ*) MO's, and pi (π and π*) MO's.

σ and π MO's from **2p-2p** interactions



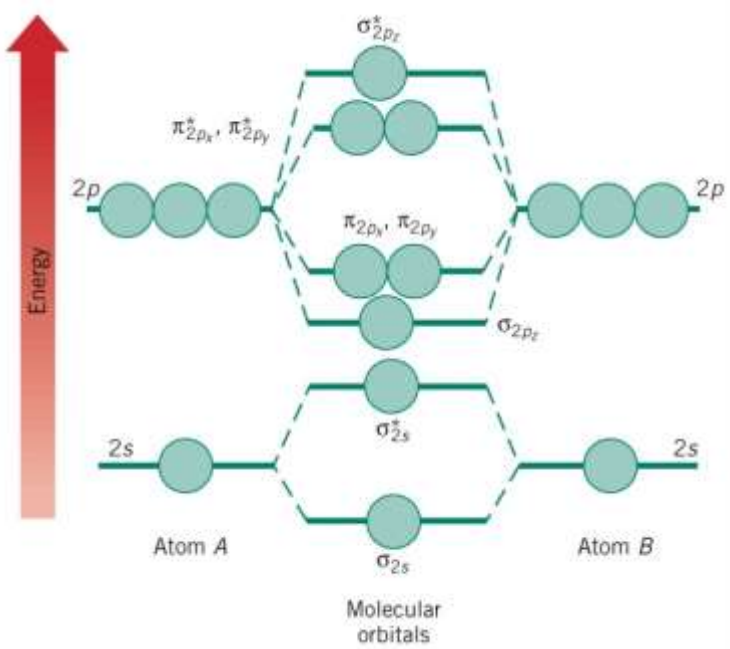


So we can *construct* the MO diagram for the (*valence* shell of the *homonuclear*) diatomic second row molecules:



For $\mathbf{Li_2}$ to $\mathbf{N_2}$
$\boldsymbol{\sigma_{2p}}$ is *above* $\boldsymbol{\pi_{2p}}$.

Notice the difference ⇐ here ⇒



For $\mathbf{O_2}$ to $\mathbf{Ne_2}$
$\boldsymbol{\sigma_{2p}}$ is *below* $\boldsymbol{\pi_{2p}}$.

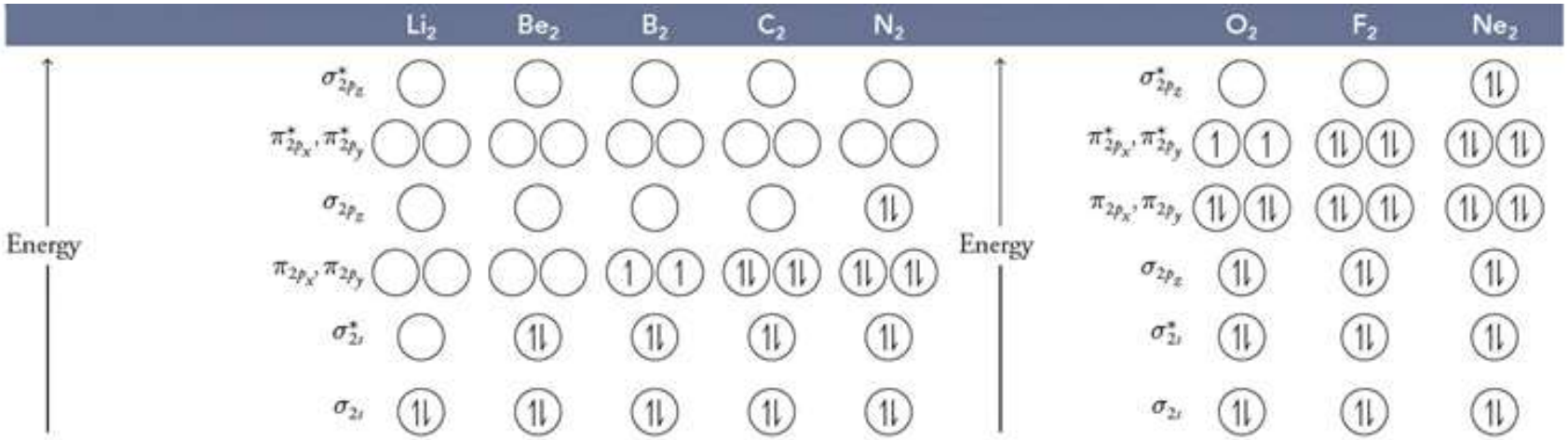
So now that we have our levels, we just need to occupy them with the *appropriate* number of electrons, obeying our previously established Aufbau/Pauli/Hund rules.

1. Electrons fill the *lowest* energy orbitals that are available.

2. No more than 2 electrons (with *paired* spins) per orbital.

3. When there are degenerate orbitals, single electrons enter all the orbitals (*spin aligned*) **before** pairing starts.

If we apply this to our 2nd row homonuclear diatomics:



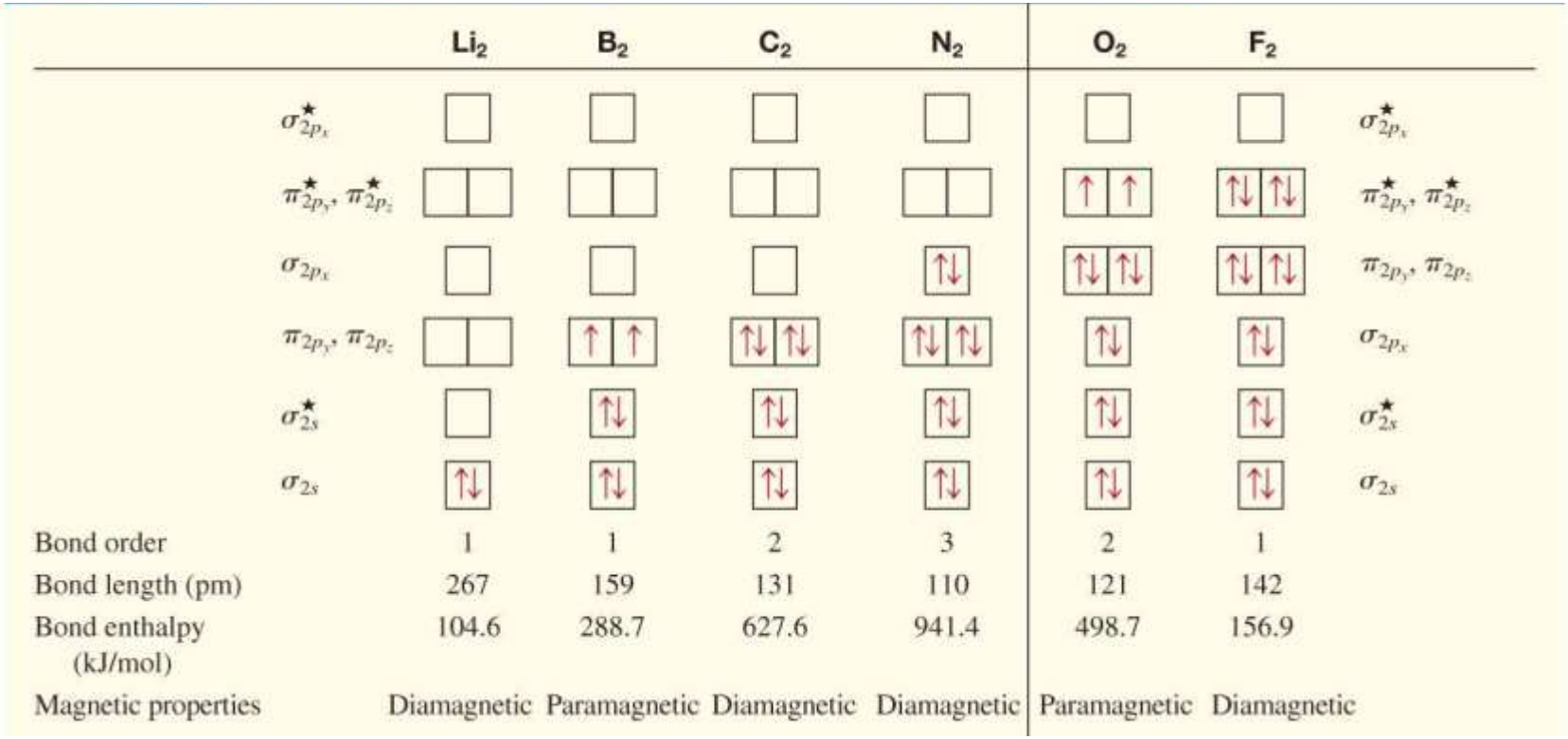
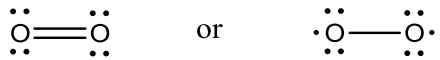
	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Number of Bonding Electrons	2	2	4	6	8	8	8	8
Number of Antibonding Electrons	0	2	2	2	2	4	6	8
Bond Order	1	0	1	2	3	2	1	0
Bond Energy (kJ/mol)	110	—	300	612	953	501	129	—
Bond Length (pm)	267	—	158	124	109	121	144	—

This description was actually a big success for MO theory, since it correctly *explains* / *predicts* the experimentally observed magnetic properties of these compounds.

Magnetic Properties

Paramagnetic – attracted to a magnetic field – unpaired electrons.

Diamagnetic – weakly repelled by a magnetic field – paired electrons.



MO theory *correctly* predicts **O_2** to be paramagnetic, and to have a bond order of **2**, (O=O double bond), whereas VB theory *incorrectly* would predict: