MOLECULAR SHAPES AND STRUCTURES

VSEPR Model

VSEPR: Valence-Shell Electron-Pair Repulsion method

Bond angle: angle between two atoms bonded to a central atom.

⇩

Regions of electron like to be
as far away as possible from the others.

Regions of electron density

Four regions of electron density around an atom:

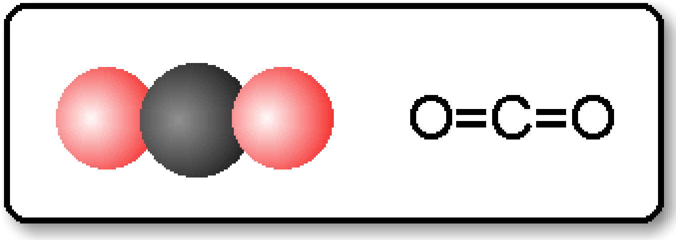
—

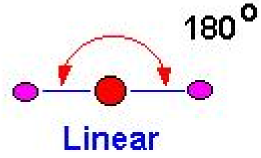
=

≡

•• Lone Pair

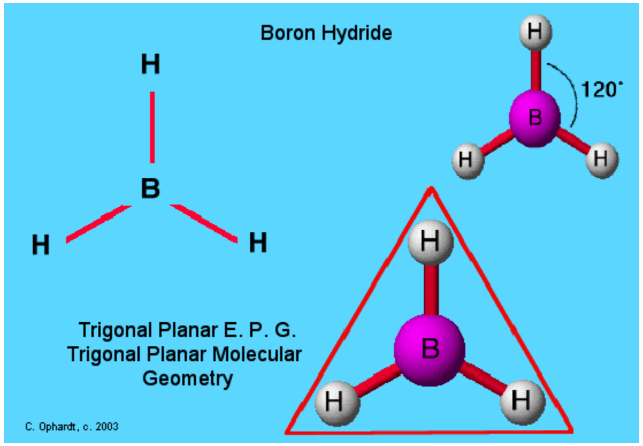
Bond Angles & Geometric Structures



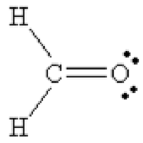


Linear molecules

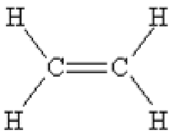
2 regions



Formaldehyde

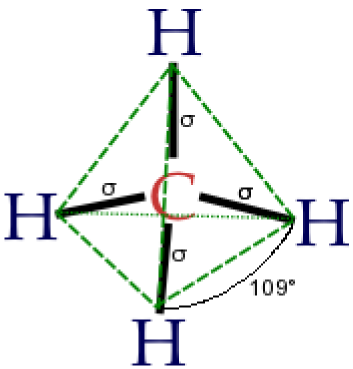


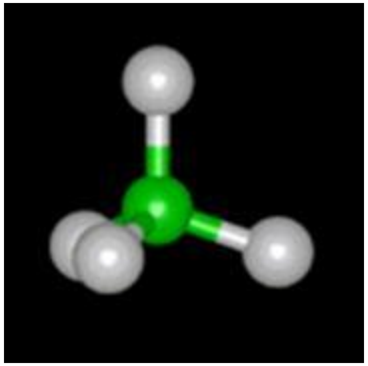
Ethylene



Trigonal planar molecules

3 regions

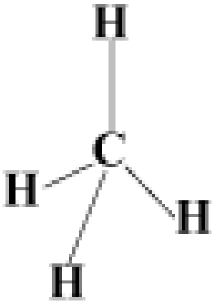




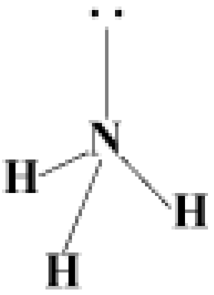
Tetrahedral arrangement

4 regions

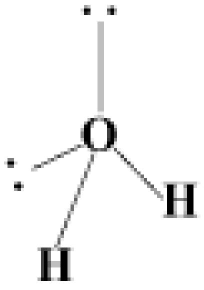
Tetrahedral Electron Pair Geometry
(Molecular Geometry-Shape)



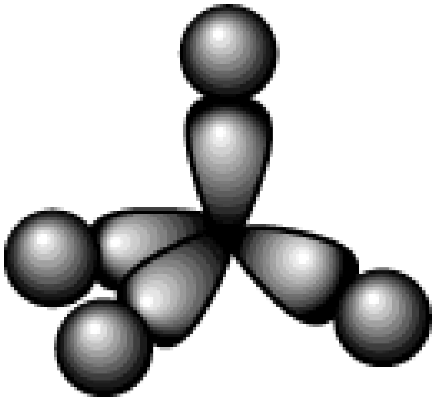
Methane (CH_4)



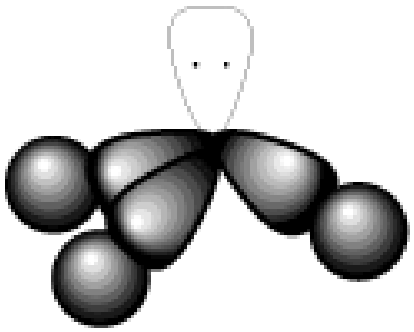
Ammonia (NH_3)



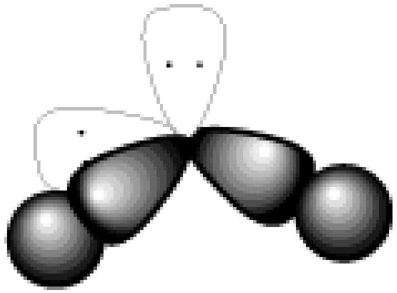
Water (H_2O)



Tetrahedral

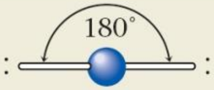
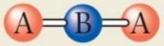
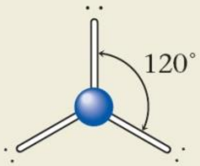
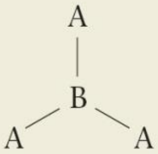
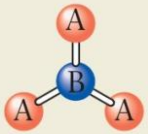
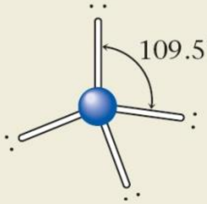
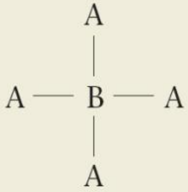
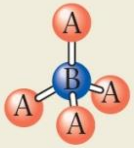
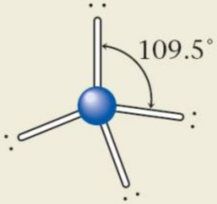
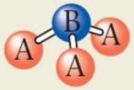
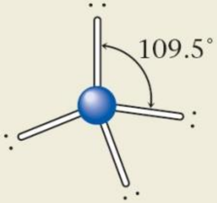
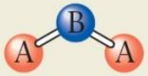


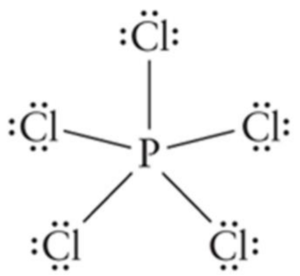
Trigonal Pyramidal



Bent (V-Shaped)

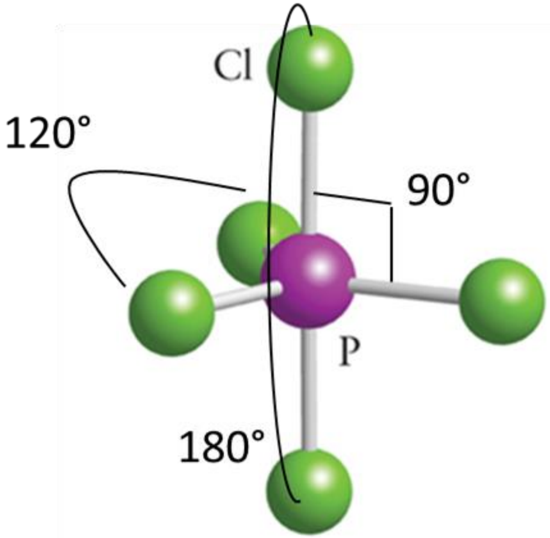
Table 12.4 Arrangements of Electron Pairs and the Resulting Molecular Structures for Two, Three, and Four Electron Pairs

Case	Number of Electron Pairs	Bonds	Electron Geometry (Arrangement)	Ball-and-Stick Model	Angle Between Pairs	Molecular Geometry (Shape)	Partial Lewis Structure	Ball-and-Stick Model	Example
1	2	2	Linear		180°	Linear	A—B—A		BeF_2
2	3	3	Trigonal planar (triangular)		120°	Trigonal planar (triangular)			BF_3
3	4	4	Tetrahedral		109.5°	Tetrahedral			CH_4
4	4	3	Tetrahedral		109.5°	Trigonal pyramid			NH_3
5	4	2	Tetrahedral		109.5°	Bent or V-shaped			H_2O

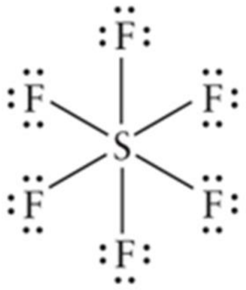


Phosphorus pentachloride, PCl_5

PF_5 has 5 electron regions, therefore it has a **Trigonal bipyramidal** shape of electron regions.

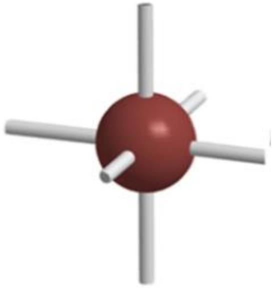


90° , 120°, 180°



Sulfur hexafluoride, SF_6

SF_6 has 6 electron regions, therefore it has a **Octahedral** shape of electron regions.



Octahedral

90°

Electron Pair Shapes (Geometry)

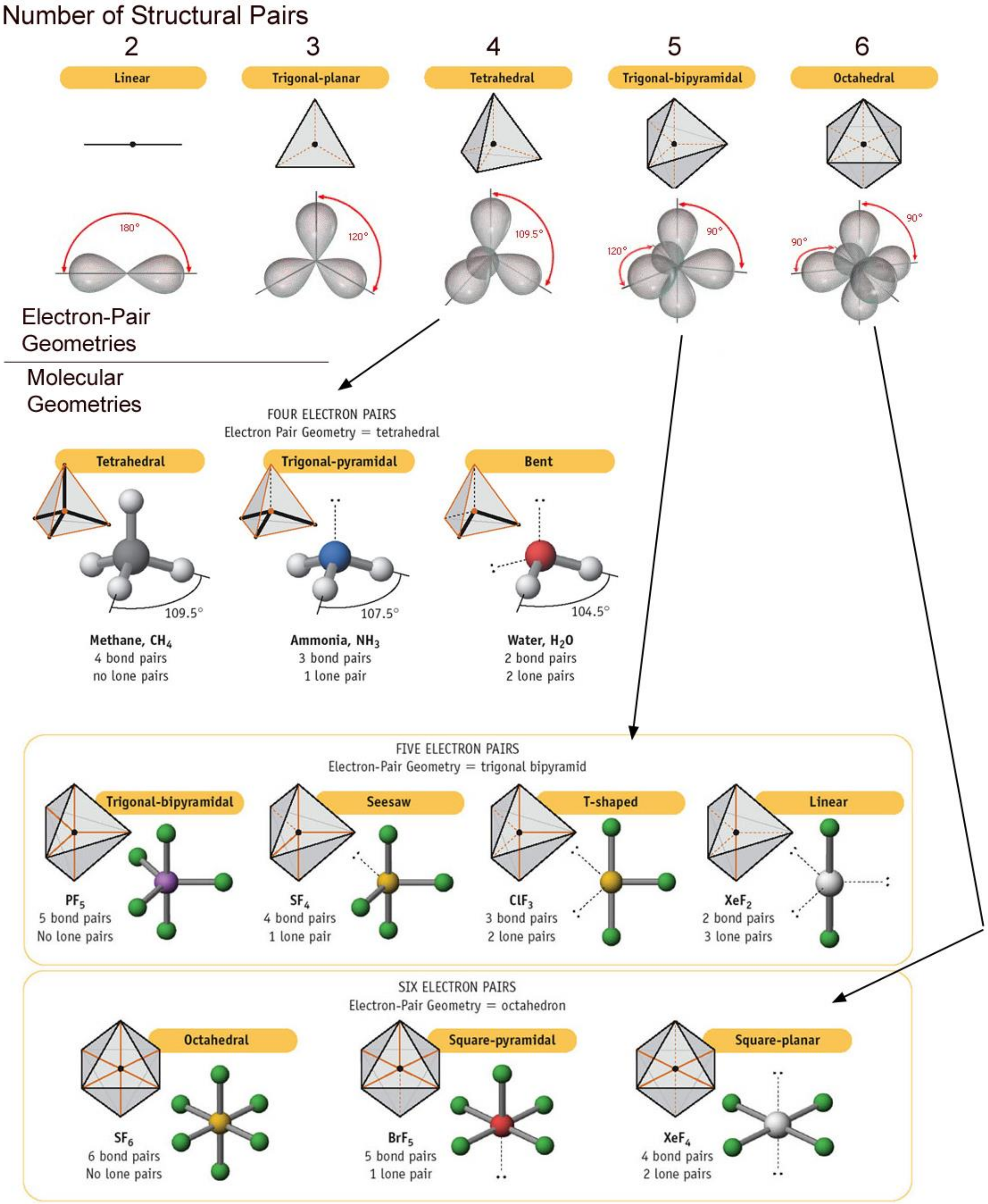
Linear

Trigonal bipyramidal

Trigonal planer

Octahedral

Tetrahedral



Number of Structural Pairs

2	3	4	5	6
Linear	Trigonal-planar	Tetrahedral	Trigonal-bipyramidal	Octahedral

Electron-Pair Geometries

Molecular Geometries

FOUR ELECTRON PAIRS
Electron Pair Geometry = tetrahedral

Tetrahedral
Methane, CH_4
4 bond pairs
no lone pairs

Trigonal-pyramidal
Ammonia, NH_3
3 bond pairs
1 lone pair

Bent
Water, H_2O
2 bond pairs
2 lone pairs

FIVE ELECTRON PAIRS
Electron-Pair Geometry = trigonal bipyramid

Trigonal-bipyramidal
PF_5
5 bond pairs
No lone pairs

Seesaw
SF_4
4 bond pairs
1 lone pair

T-shaped
ClF_3
3 bond pairs
2 lone pairs

Linear
XeF_2
2 bond pairs
3 lone pairs

SIX ELECTRON PAIRS
Electron-Pair Geometry = octahedron

Octahedral
SF_6
6 bond pairs
No lone pairs

Square-pyramidal
BrF_5
5 bond pairs
1 lone pair

Square-planar
XeF_4
4 bond pairs
2 lone pairs

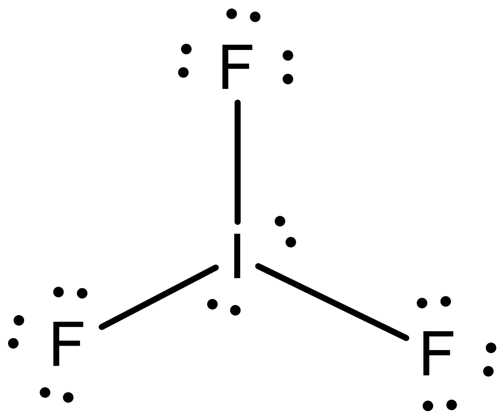
Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, (3) VSEPR formula, and (4) VSEPR molecular shape name.

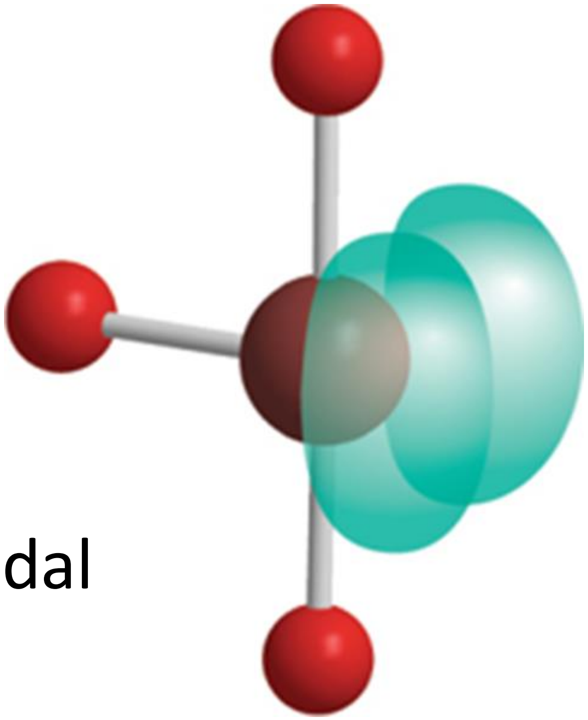
IF_3

Valence electrons: 4(7) = 28

"T" shaped

(1)





(2) 5 electron groups = trigonal bipyramidal

(3) AX_3E_2

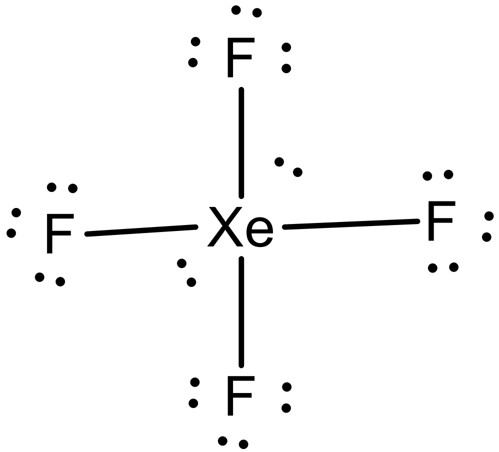
Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, (3) VSEPR formula, and (4) VSEPR molecular shape name.

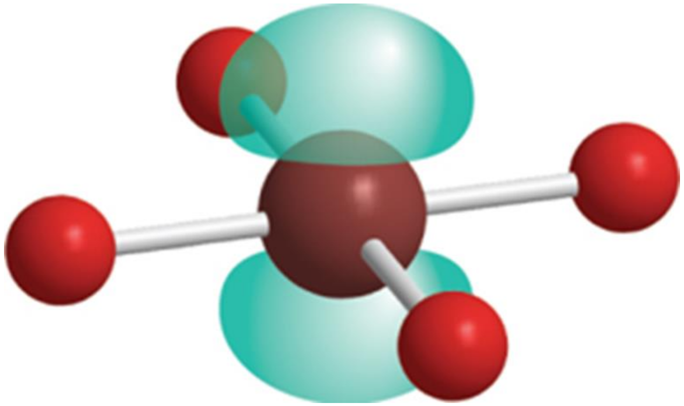
XeF_4

Valence electrons: 1(8) + 4(7) = 36

(4) Square planar

(1)





(2)6 electron groups = octahedral

(3)AX_4E_2

The basic VSEPR model

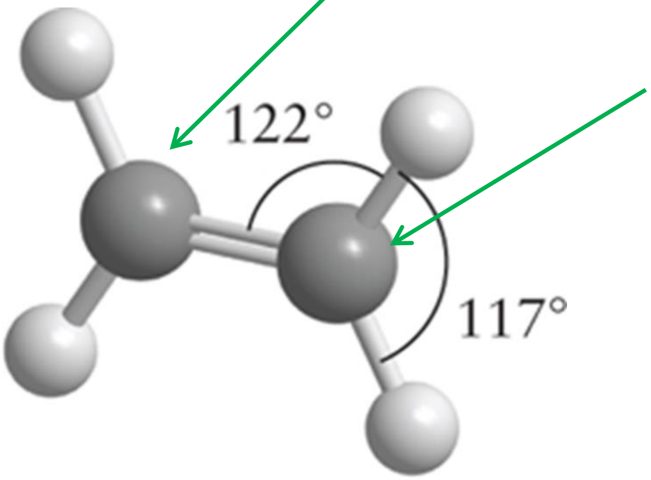
When there is more than one central atom, we consider the bonding about each atom independently.

Ethene, C_2H_4

Lewis Diagram

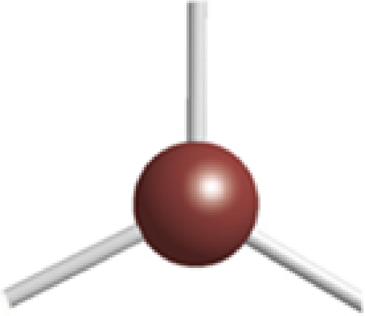
Trigonal planar

Trigonal planar



Ethene, C_2H_4

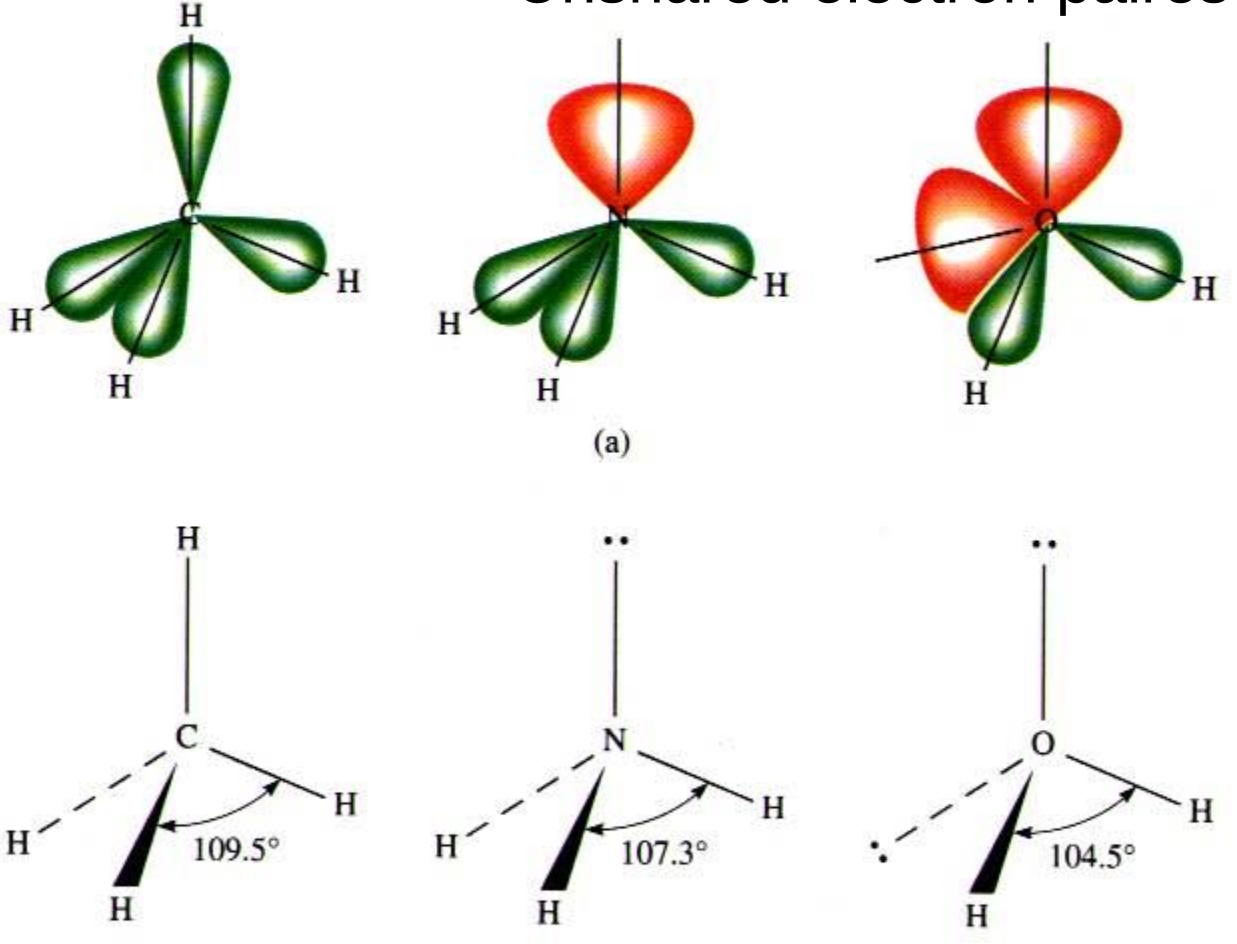
VSEPR 3D shape



Trigonal planar

Tetrahedral Electron Pair Geometry

Unshared electron paires

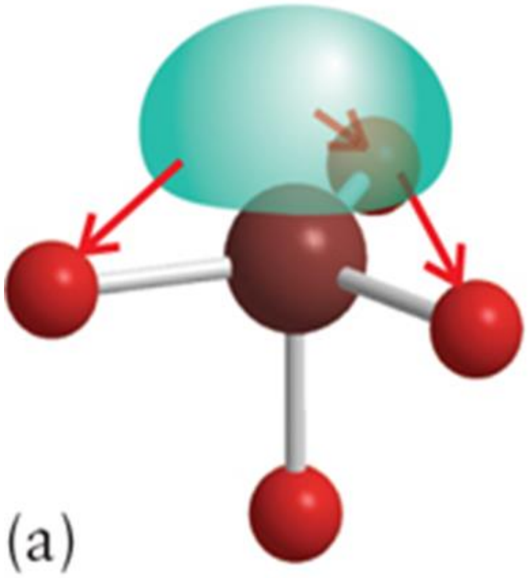


CH_4 NH_3 H_2O

lone pair repulsions energies follow as:

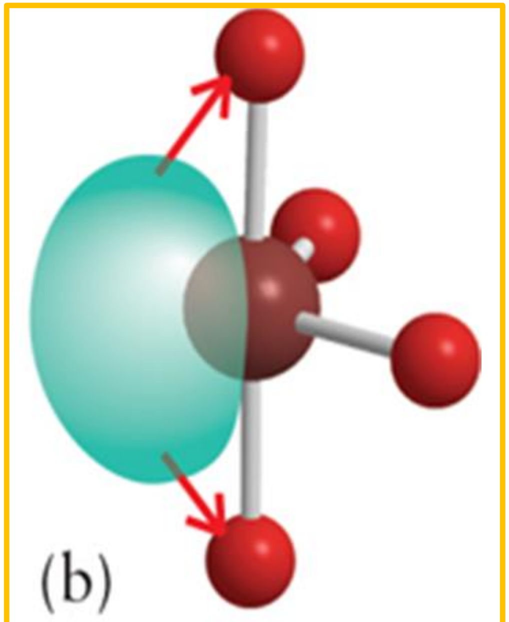
lone pair-lone pair > **lone pair-atom** > **atom-atom**

This lone pair has
3 neighbors at 90°



trigonal bipyramidal

This lone pair has
2 neighbors at 90°

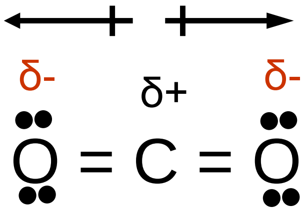


The one with the least amount of repulsion.

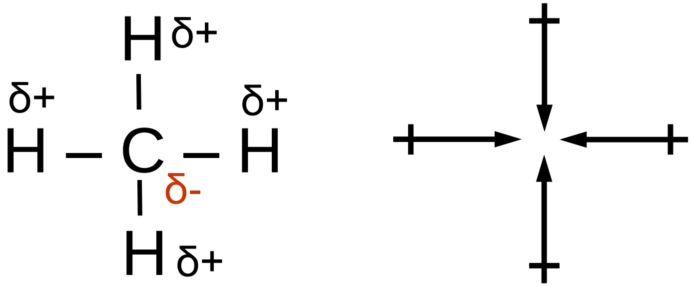
See-Saw

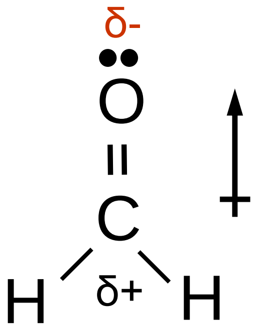
Polarity

1. It has polar bonds.
2. Centers of δ+ and δ- lie at different places (sides).

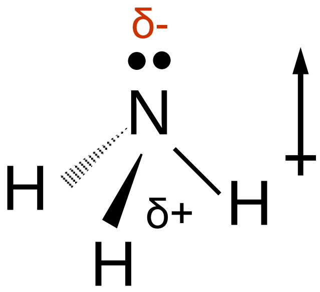


nonpolar molecule





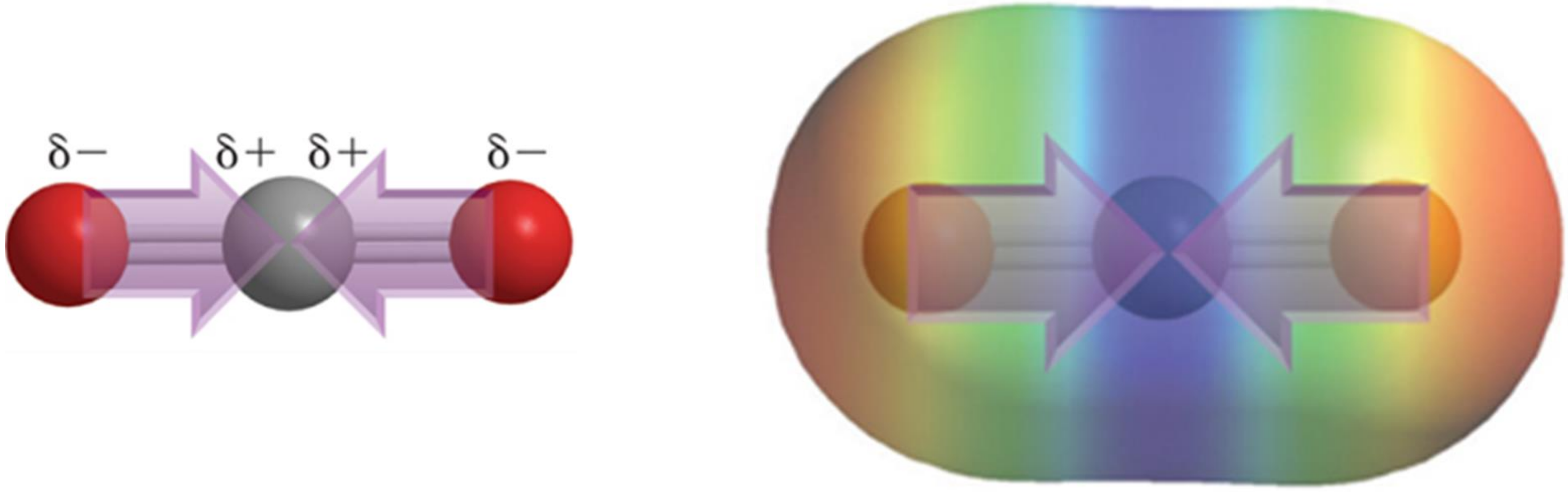
polar molecule



Some of the consequences of molecular shape

Electrostatic potential diagram (Elpot) for CO_2.

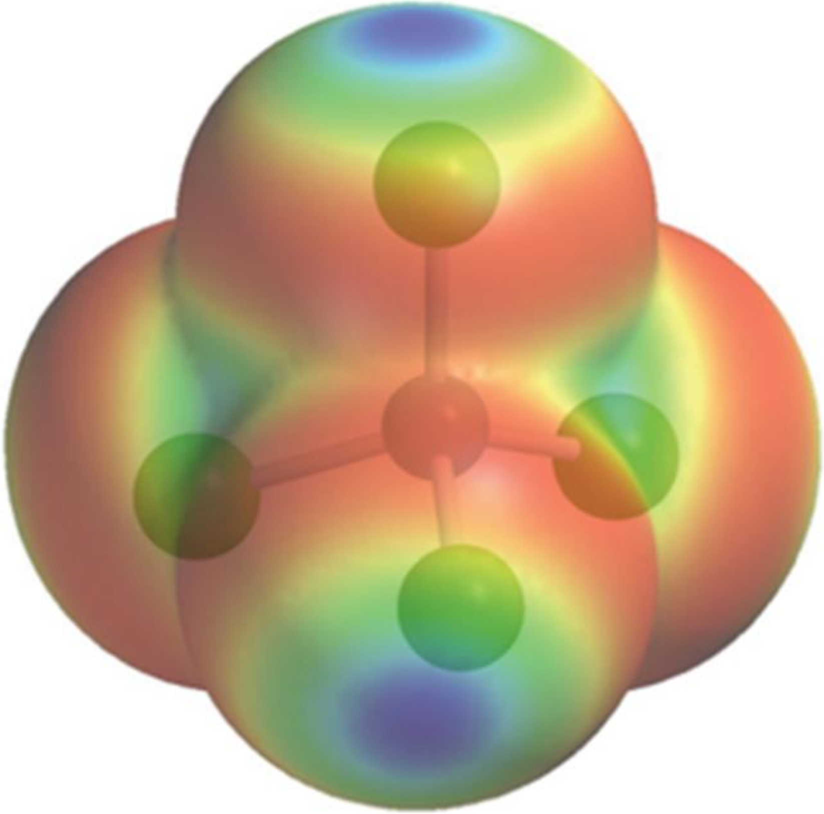
The negative charge converges on the positive center, so the molecule is nonpolar.



Carbon dioxide, CO_2

Some of the **consequences** of molecular shape

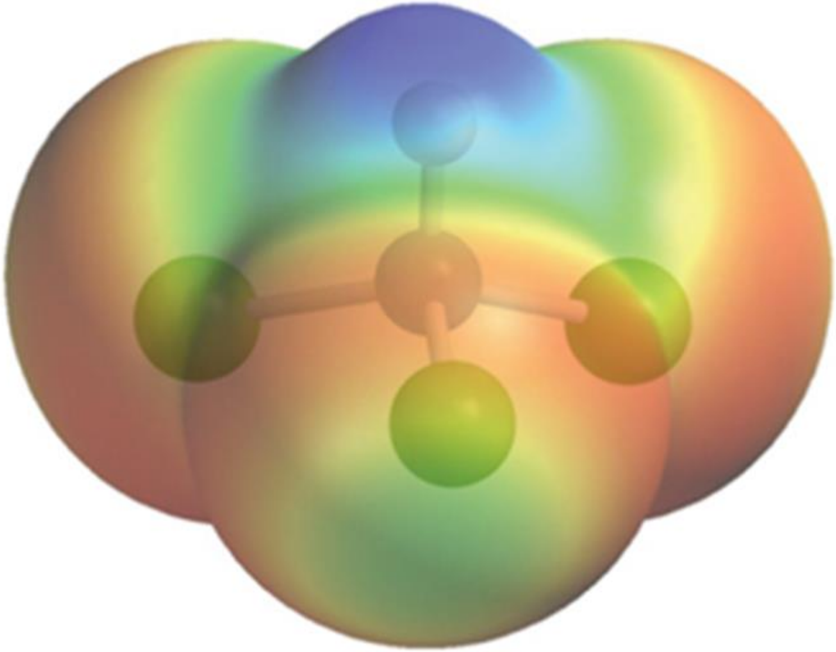
Changing one atom.



CCl_4

Symmetric dipole = Non-polar

Asymmetric dipole = Polar



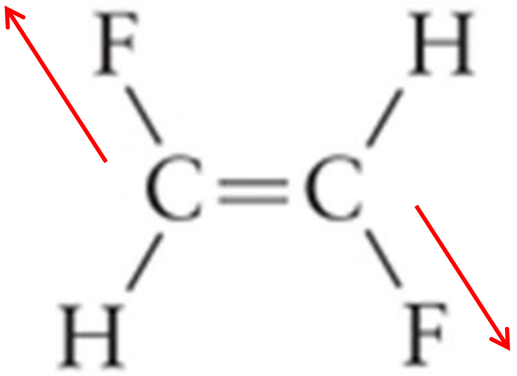
$CHCl_3$

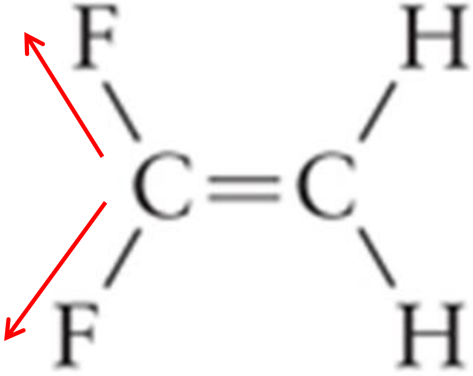
Some of the **consequences** of molecular shape

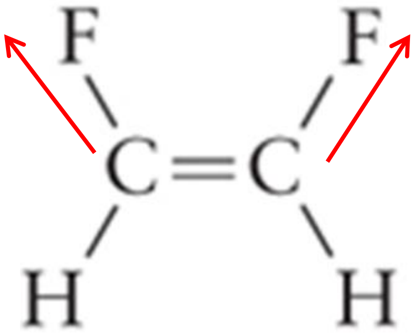
Double or triple bonds fix atoms into a position.

directional dipoles

Opposing dipoles





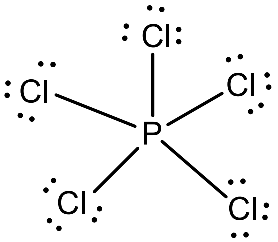


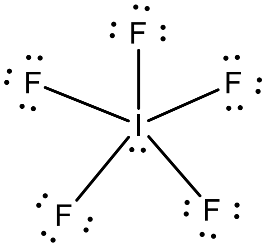
Symmetric dipole = Non-polar

Asymmetric dipole = Polar

Self-test 4.5B Predict whether (a) PCl_5, (b) IF_5 is polar or nonpolar.

(1) Draw the Lewis structure.





(2) Assign the electron arrangement.

trigonal bipyramidal

octahedral

(3) Identify the VSEPR formula.

AX_5

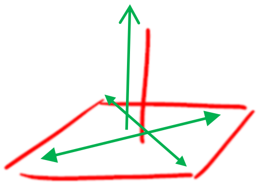
AX_5E

(4) Name the molecular shape.

trigonal bipyramidal

square pyramidal

(5) Identify the polarity.

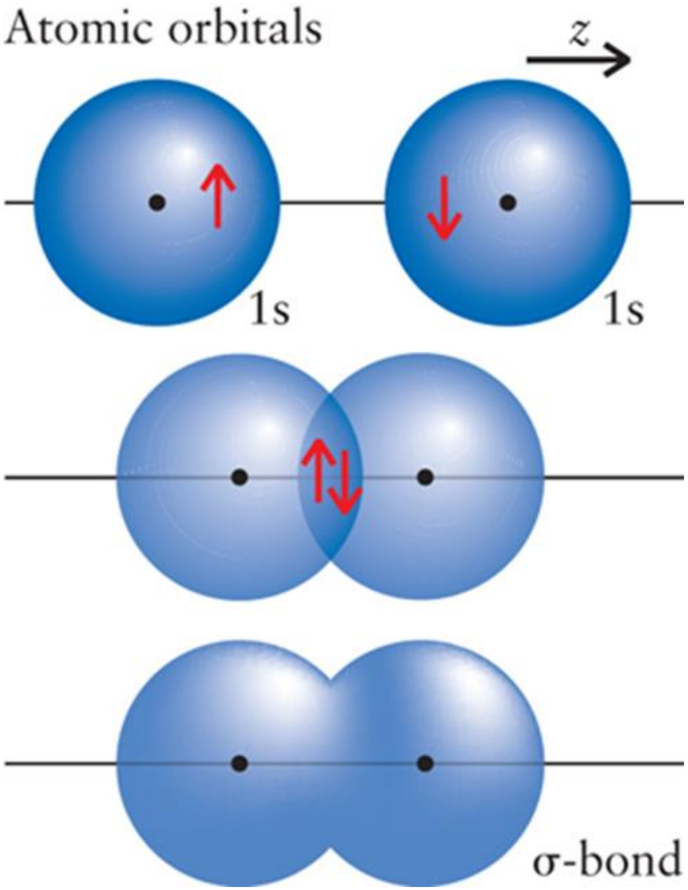


Asymmetric dipole polar

Symmetric dipole nonpolar

Types of bonds in Valence-Bond Theory

Sigma Bonds



The simplest molecule of all is H_2.

A "ground-state" hydrogen atoms has one electron in a 1s-orbital.

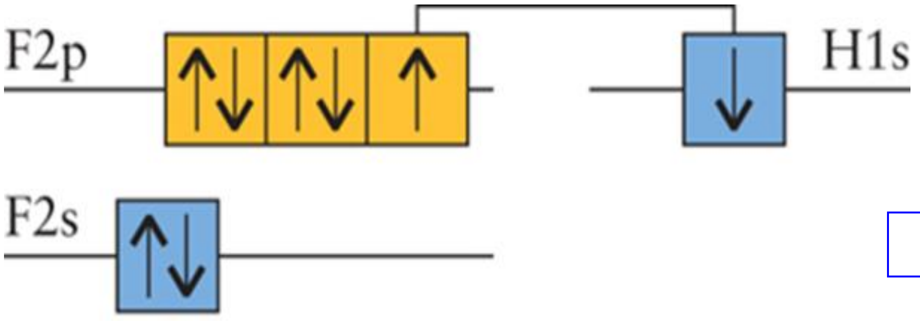
As two H atoms come together, their 1s-electrons pair (denoted ↑↓) begin to overlap.

The resulting sausage-shaped distribution of electrons density is between the nuclei, and called a "σ-bond" (a sigma bond) .

Types of bonds in Valence-Bond Theory

F has an unpaired electron atom in the $2p_z$-orbital. Hydrogen has an unpaired electron in the 1s-orbital.

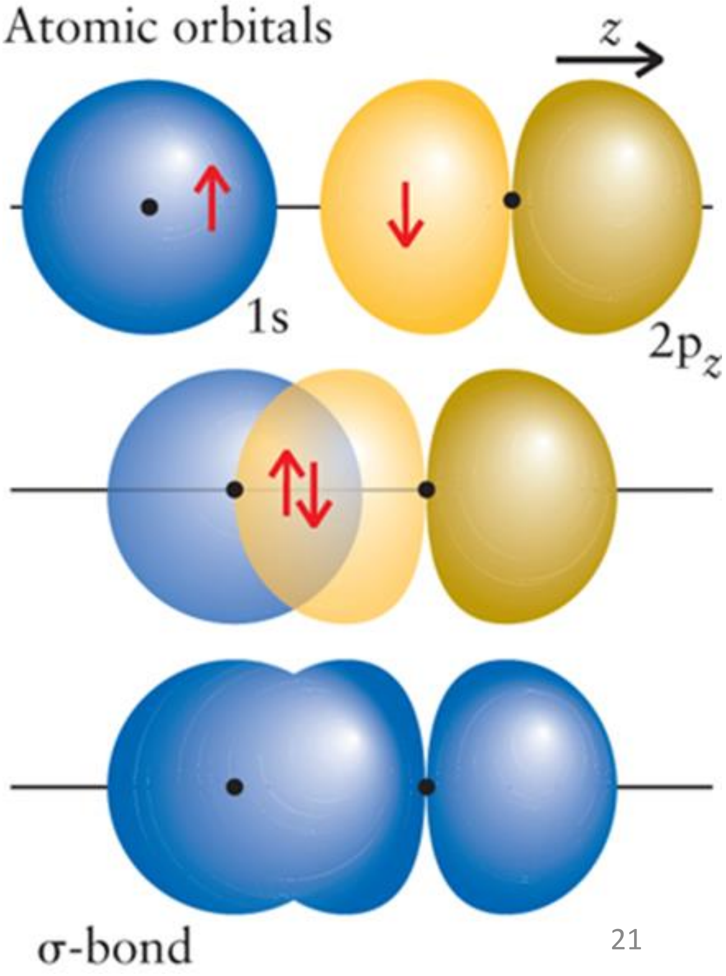
The orbitals overlap and merge into a cloud that spreads over both atoms



Hydrogen fluoride, HF

Sigma Bonds

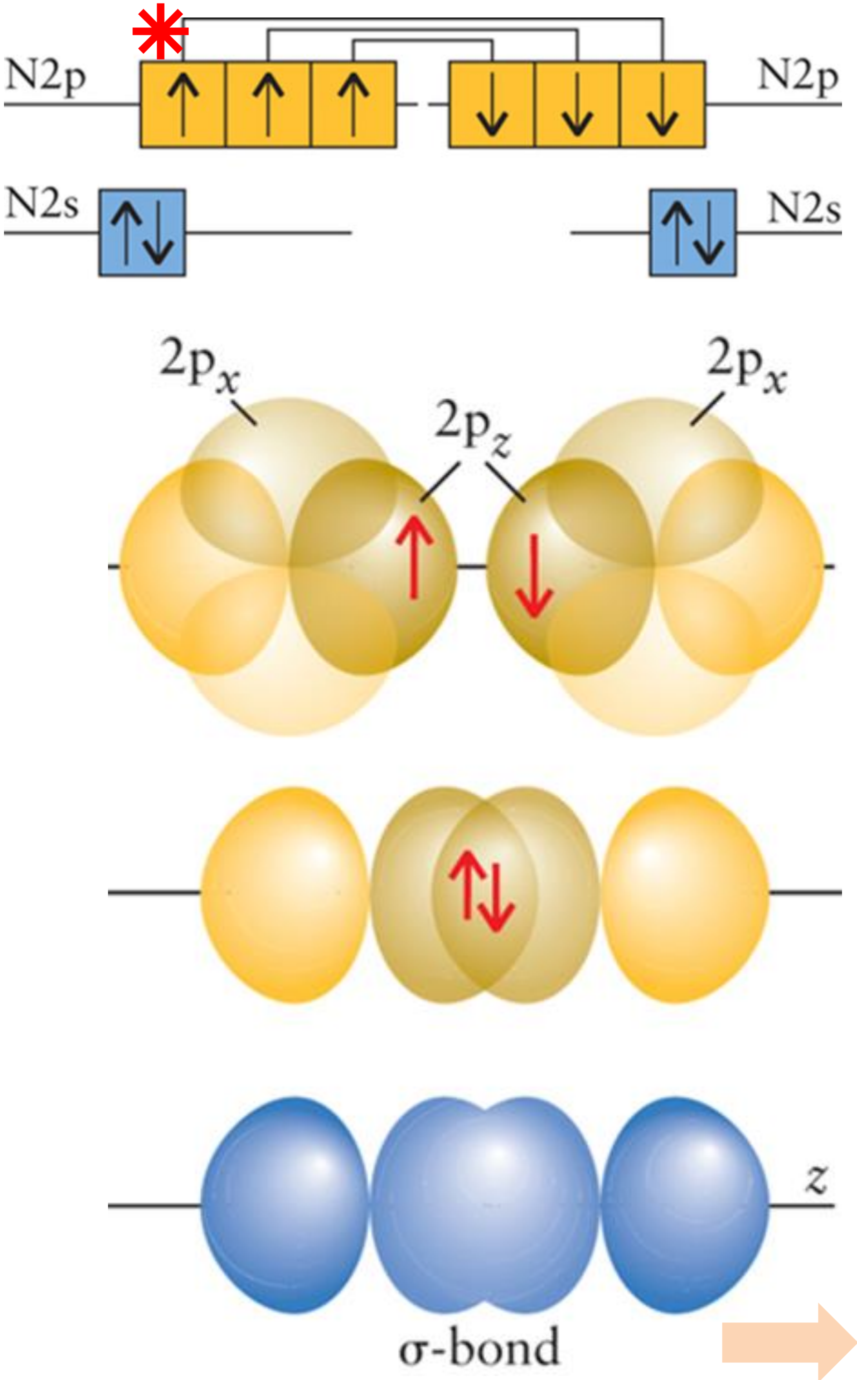
H F



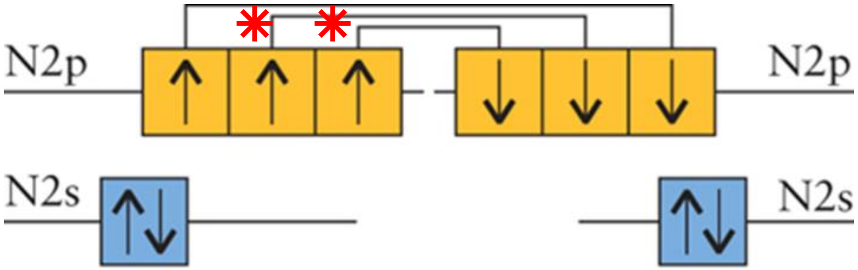
A different type of bond in a nitrogen molecule, N_2.

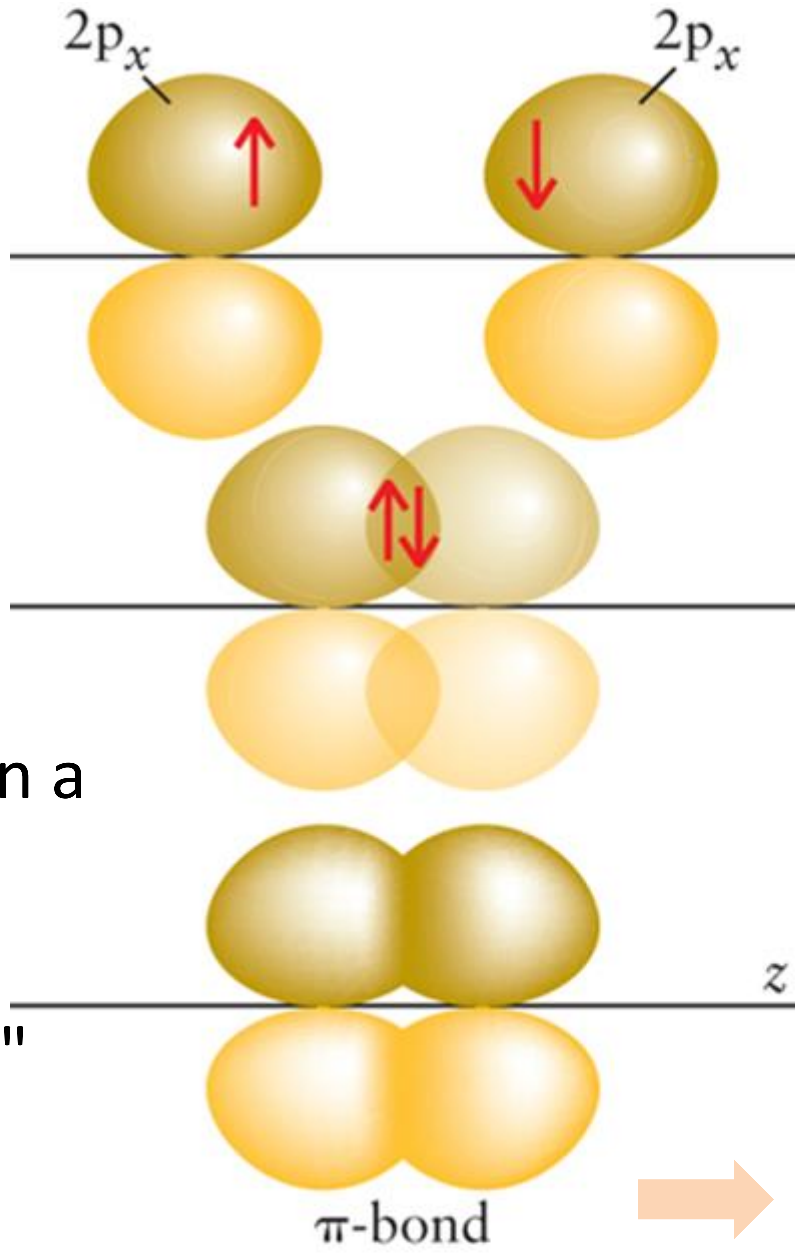
There is a single electron in each three 2p-orbitals.

*However, due to **bond angles**, only one of the three orbitals overlaps end-to-end to form a **σ-bond**



A different type of bond in a nitrogen molecule, N_2.

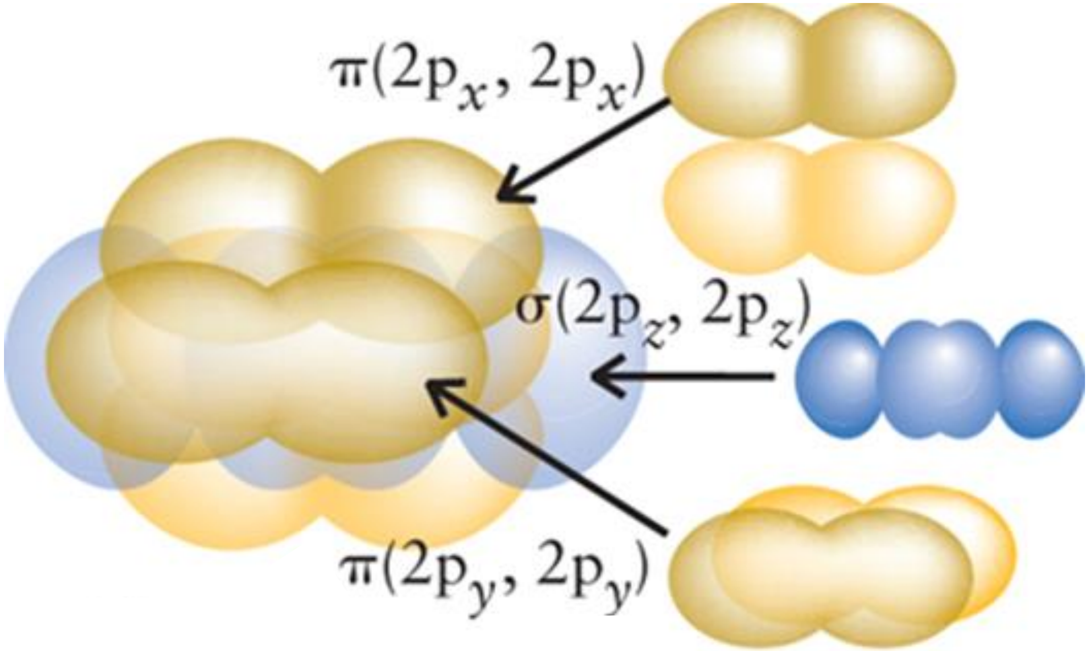




The other two 2p-orbitals (*$2p_x$ and *$2p_y$) are perpendicular to the internuclear axis.

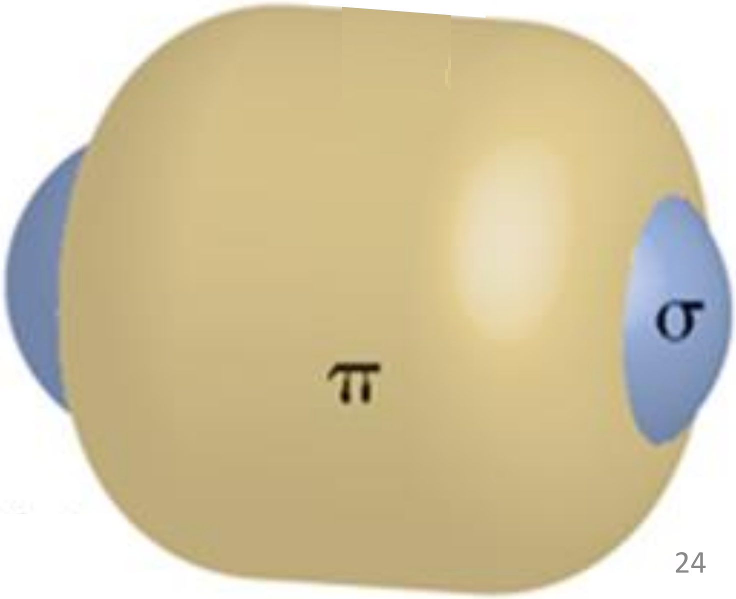
These p-orbitals can overlap only in a side-by-side arrangement.

This overlap results in a "**π-bond**."

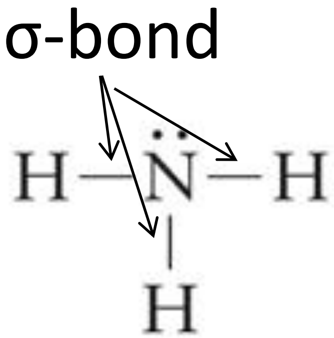


N_2

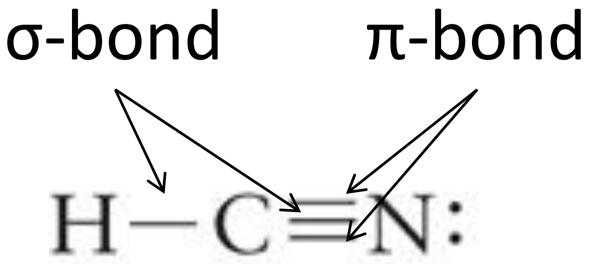
Two π-bond merge forming a long doughnut-shaped cloud surrounding the σ-bond cloud, resembling a **cylindrical hot dog**.



Self-test 4.6B How many σ-bonds and how many π-bonds are there in (a) NH_3 and (b) HCN?


σ-bond

3 @ σ-bond
1 lone pair

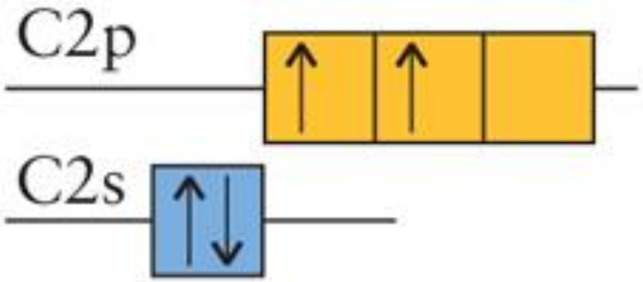

σ-bond π-bond

2 @ σ-bond
2 @ π-bond

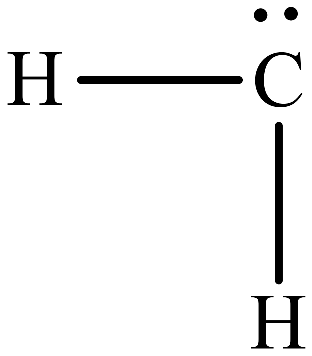
Valence-bond theory :
A single bond is a σ-bond.
A double bond is a σ-bond plus one π-bond.
A triple bond is a σ -bond plus two π -bonds.

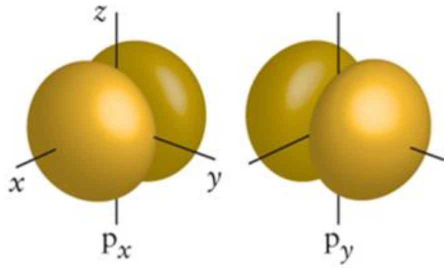
Difficulties with polyatomic molecules in VB theory.

A carbon atom has an electron configuration [He]$2s^22p_x^{\,1}2p_y^{\,1}$ with four valence electrons.

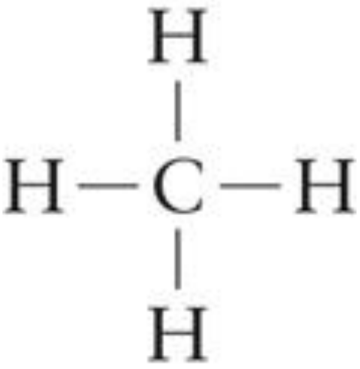


It looks as though a carbon atom should have a valence of 2 and form only two perpendicular bonds.





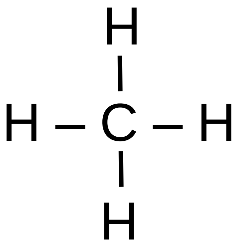
However, it always has a valence of 4 (it is commonly "tetravalent").



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

Hybridization - sp^3

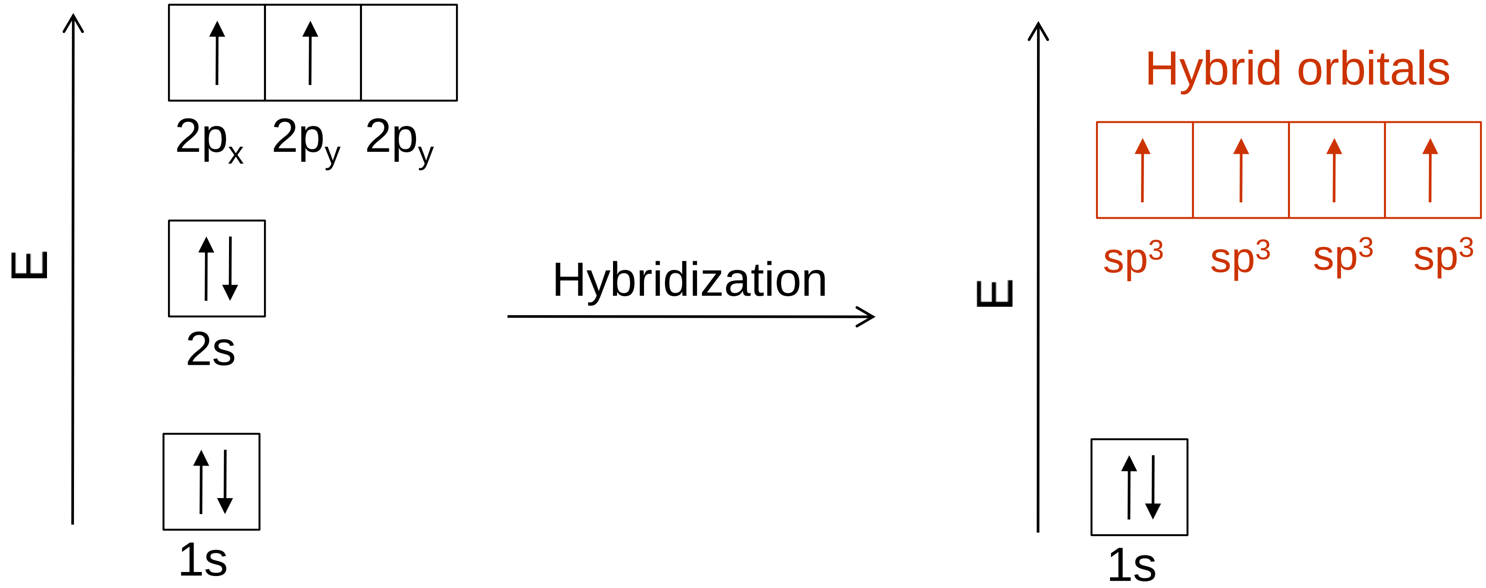
CH_4



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

Four single bonds (δ bonds) - Tetrahedral (109.5º)

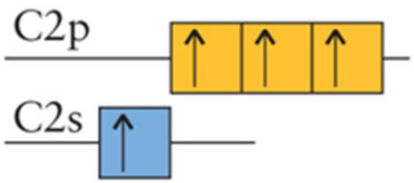
C (6)

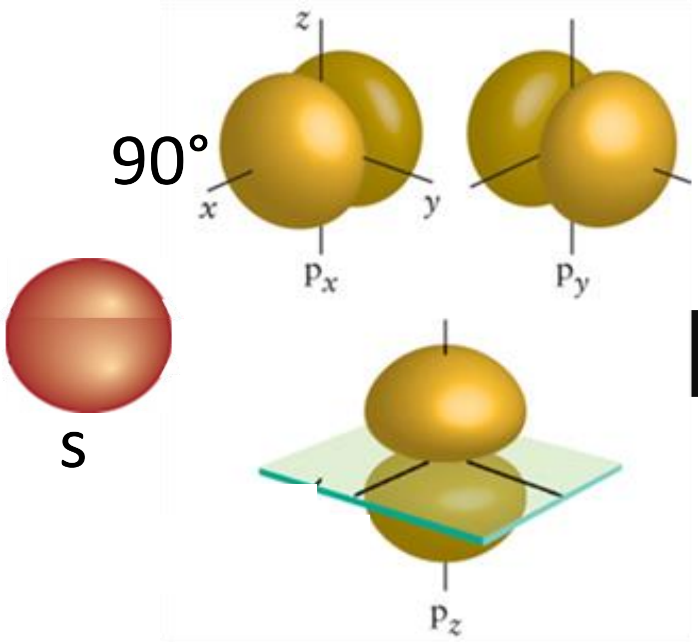


One electron is promoted (relocated) to a higher-energy orbital.

What about the bond angles?

The 90° bond angles of our original orbitals do not match our observed 109.5° bond angles.





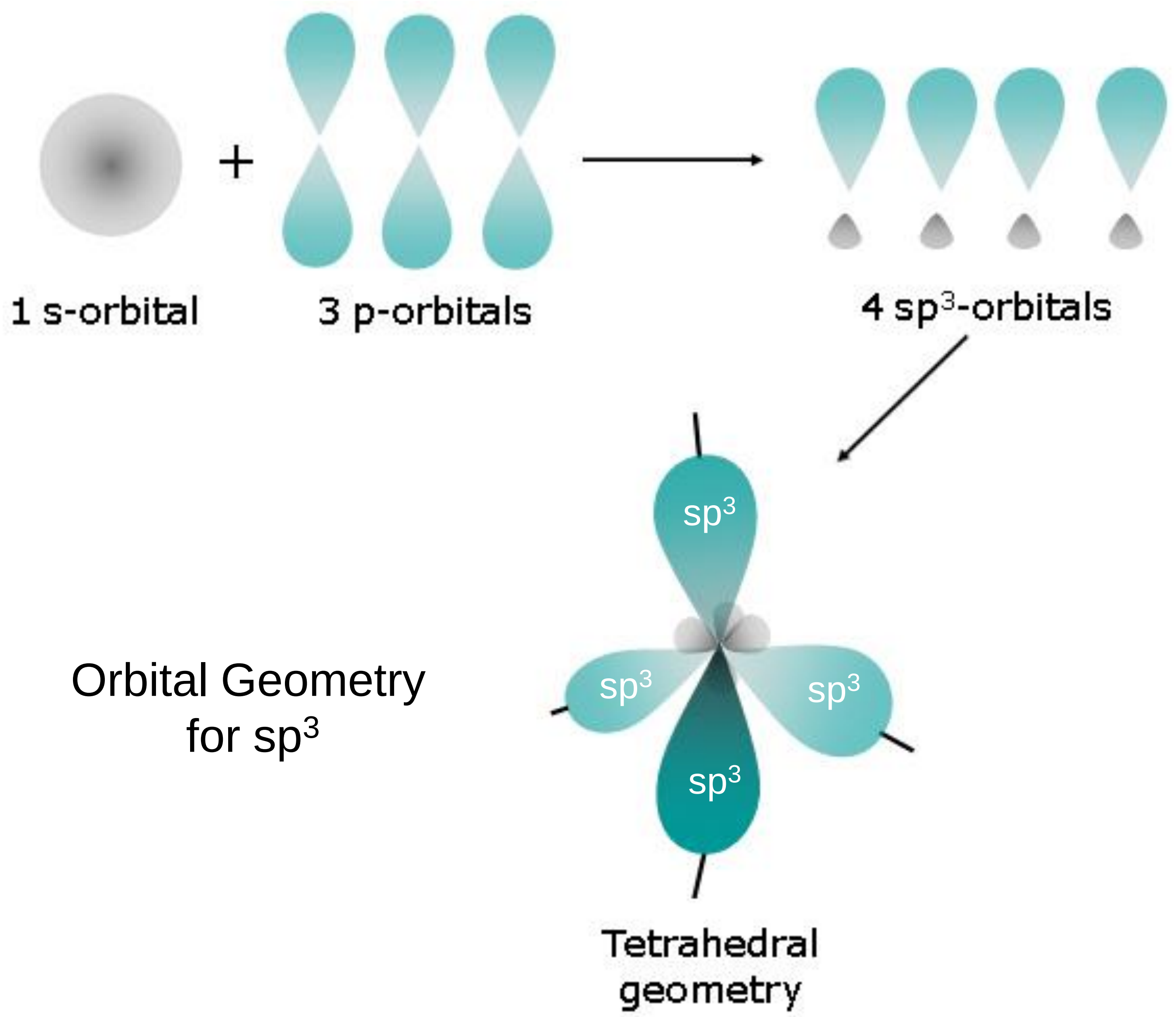
?

Correct number of orbital

Shape of the orbitals is wrong

Merging these two ideas together → Correct view

Hybridization - sp^3

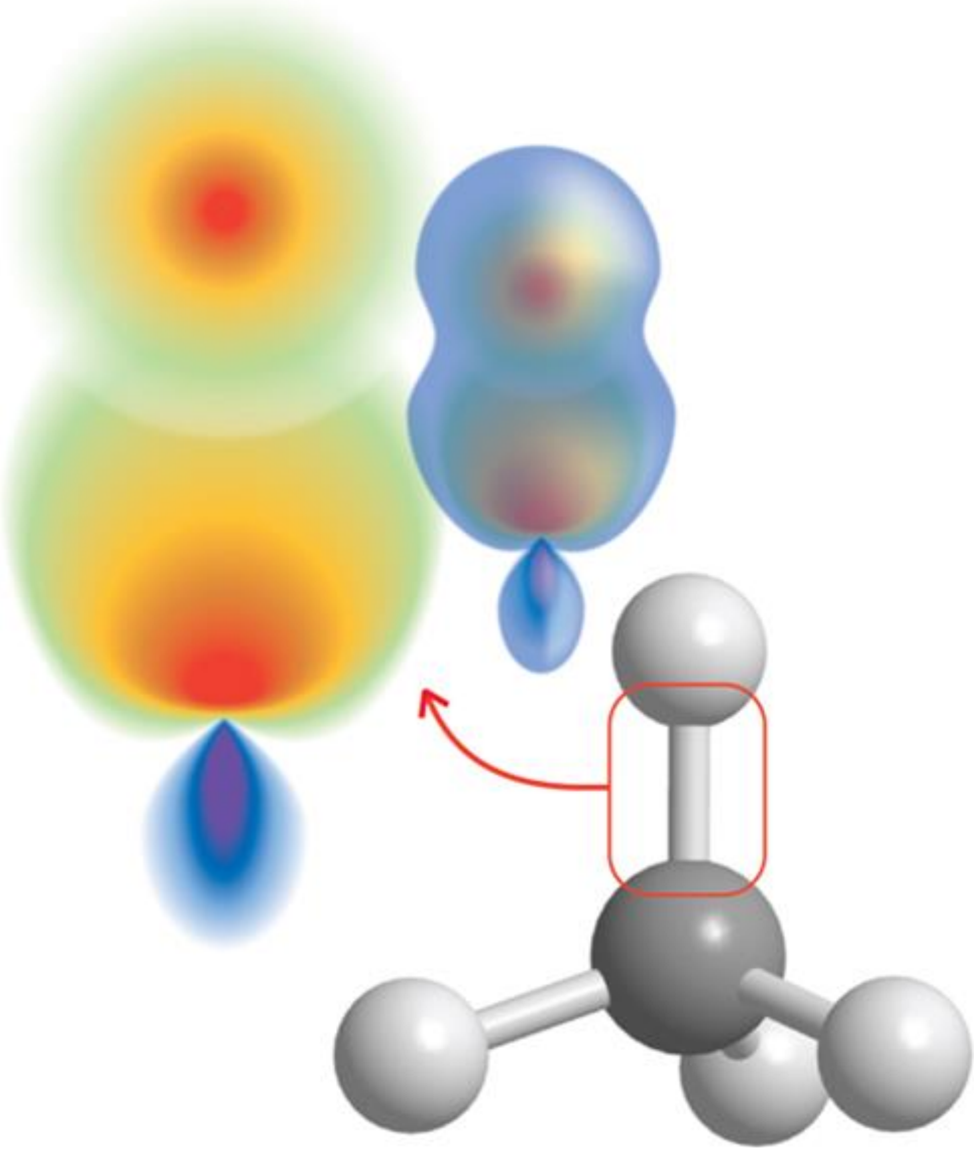


Orbital Geometry
for sp^3

These new patterns are called **hybrid orbitals**.

The wavefunctions overlap (with either positive or negative amplitudes) and constructively reinforced each other. →

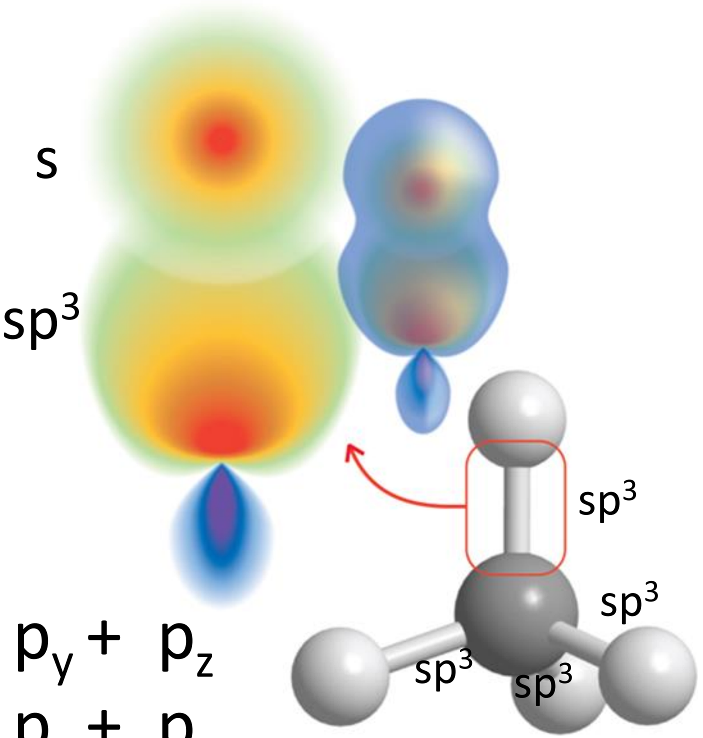
Wavefunctions have the opposite signs, the overall amplitude is reduced and might cancel. →



4 new hybrid orbitals

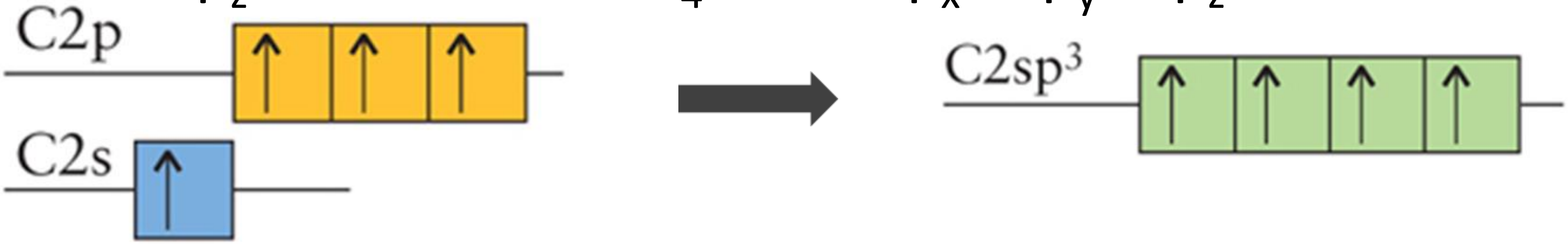
Hybrid orbital names

Each of the four hybrid orbitals, designated h_n. Each of the four hybrid orbital is formed from a linear **combinations** of the four original atomic orbitals:



s
p_x
p_y
p_z

$h_1 = s + p_x + p_y + p_z$
$h_2 = s + p_x + p_y + p_z$
$h_3 = s + p_x + p_y + p_z$
$h_4 = s + p_x + p_y + p_z$



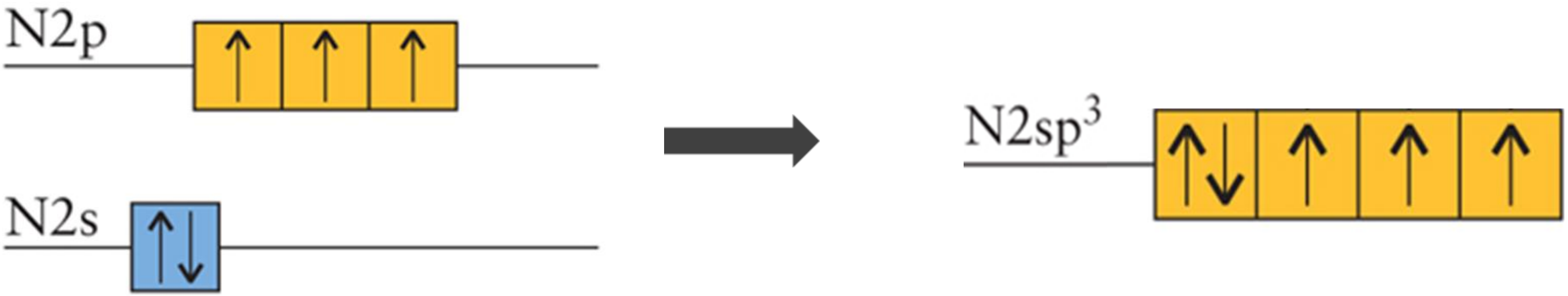
s p_x p_y p_z → sp^3 sp^3 sp^3 sp^3

Atomic orbitals

Hybrid orbitals

For every sigma bond we need a hybrid orbital.

3 @ σNsp^3 , H1s



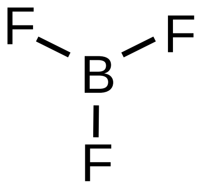
s p_x p_y p_z → sp^3 sp^3 sp^3 sp^3

Atomic orbitals

Hybrid orbitals

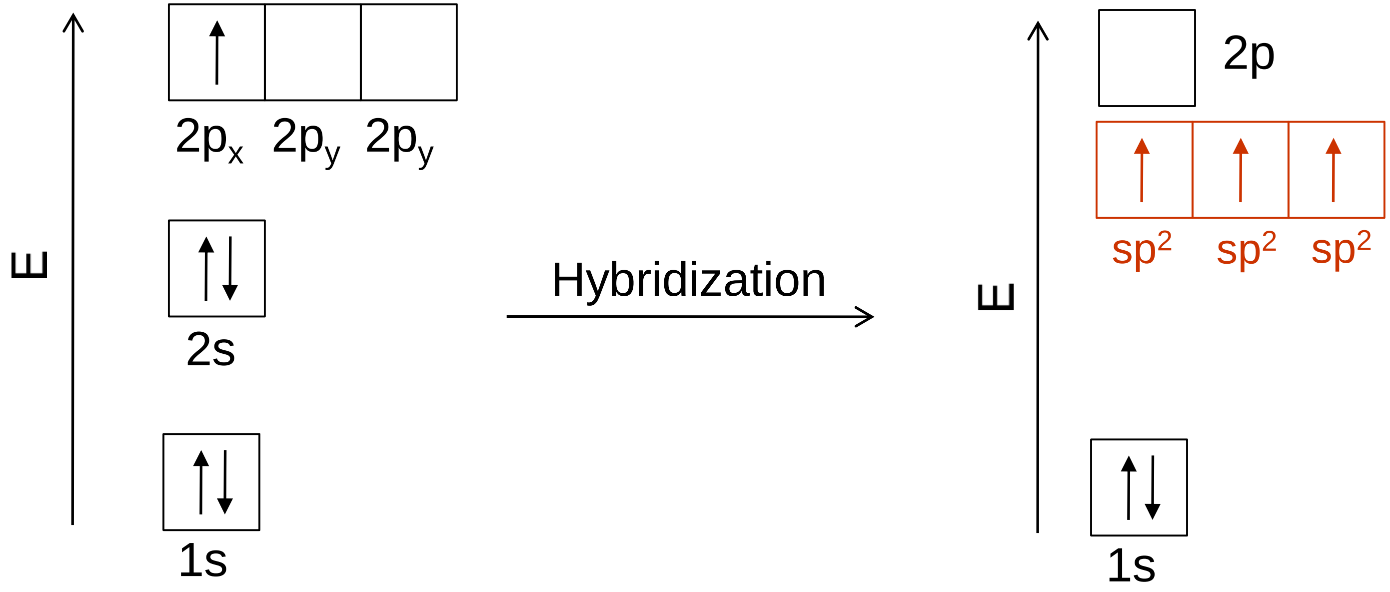
Hybridization - sp^2

BF_3



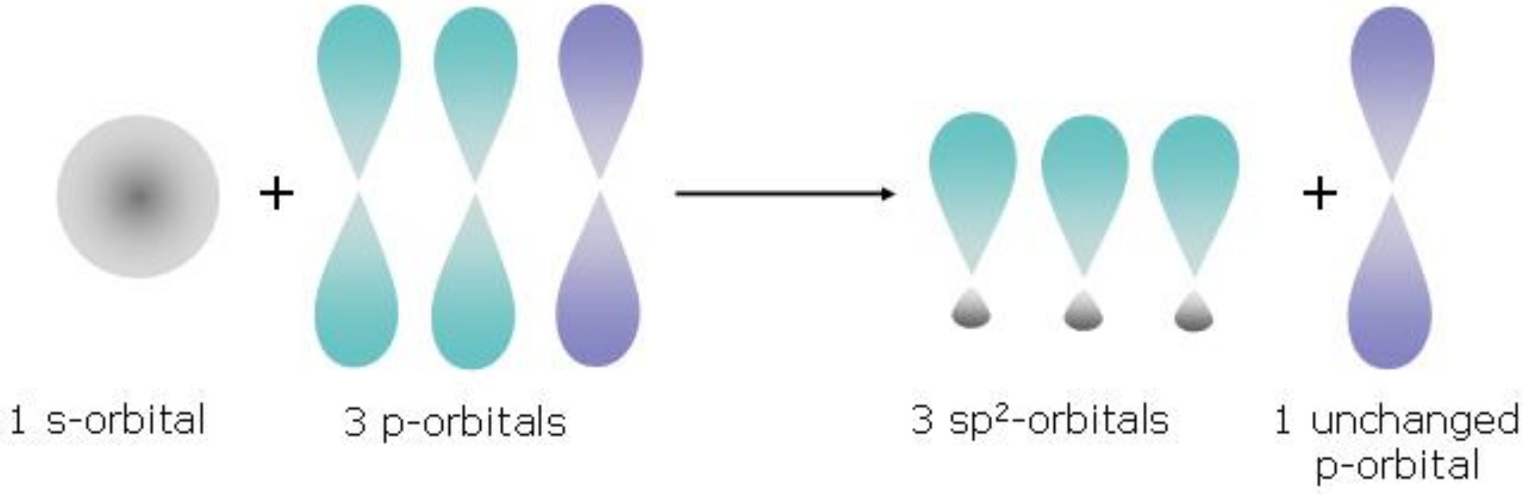
Three single bonds (δ bonds) - Trigonal Planar (120º)

B (5)

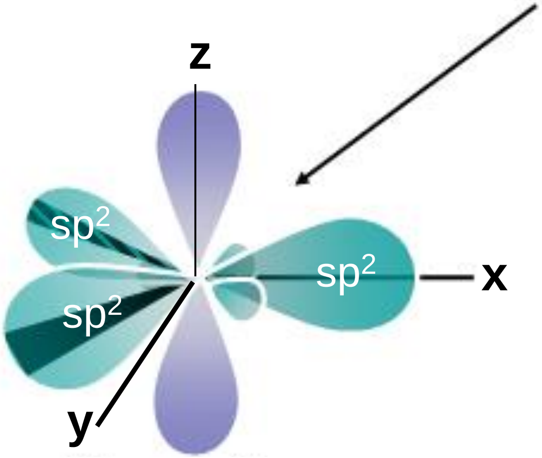


One electron is promoted (relocated) to a higher-energy orbital.

Hybridization - sp^2



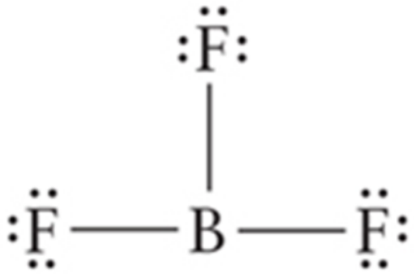
Orbital Geometry for sp^2



Trigonal Planar geometry

Hybridization - sp^2

sp^2 hybrid orbitals



only 3 sigma bonds form, one p-bond is not hybridized.

$$h_1 = s + 2^{½} p_y$$

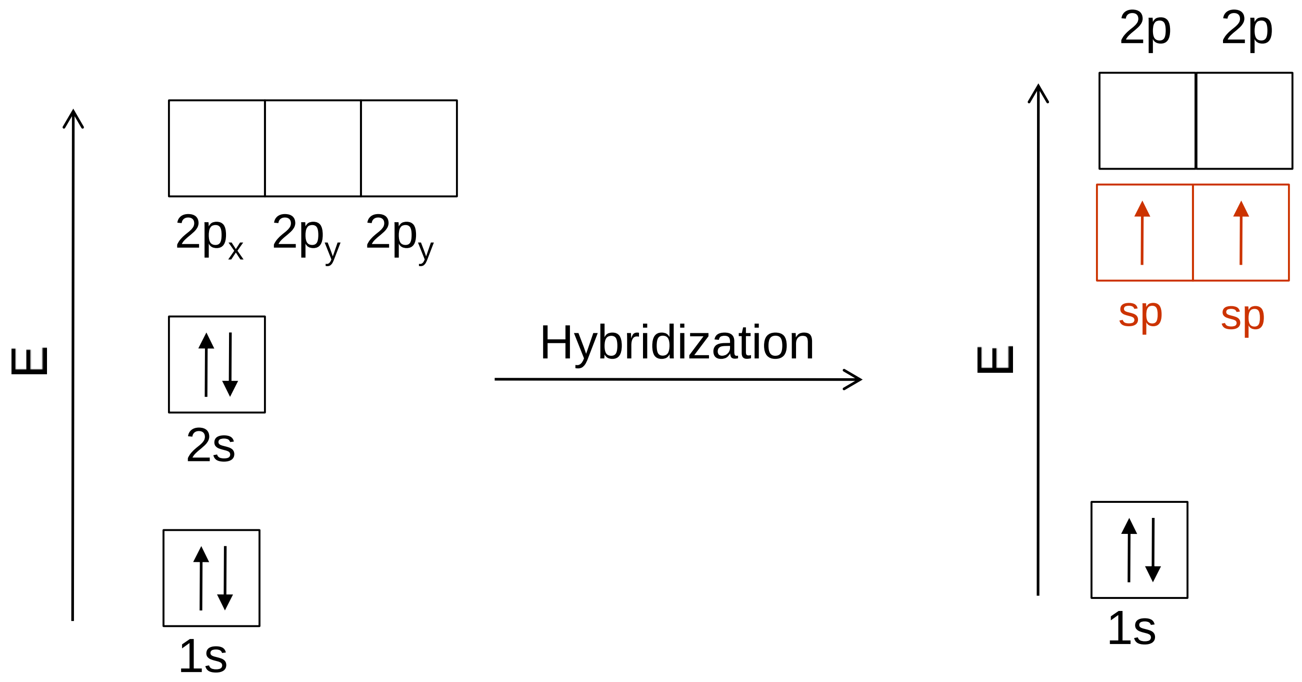
$$h_2 = s + \left(\frac{3}{2}\right)^{½} p_x - \left(\frac{1}{2}\right)^{½} p_y$$

$$h_3 = s + \left(\frac{3}{2}\right)^{½} p_x - \left(\frac{1}{2}\right)^{½} p_y$$

Hybridization - sp

$BeCl_2$ Cl–Be–Cl Two single bonds (δ bonds) - Linear (180º)

Be (4)



E

$2p_x$ $2p_y$ $2p_y$

2s

1s

Hybridization

E

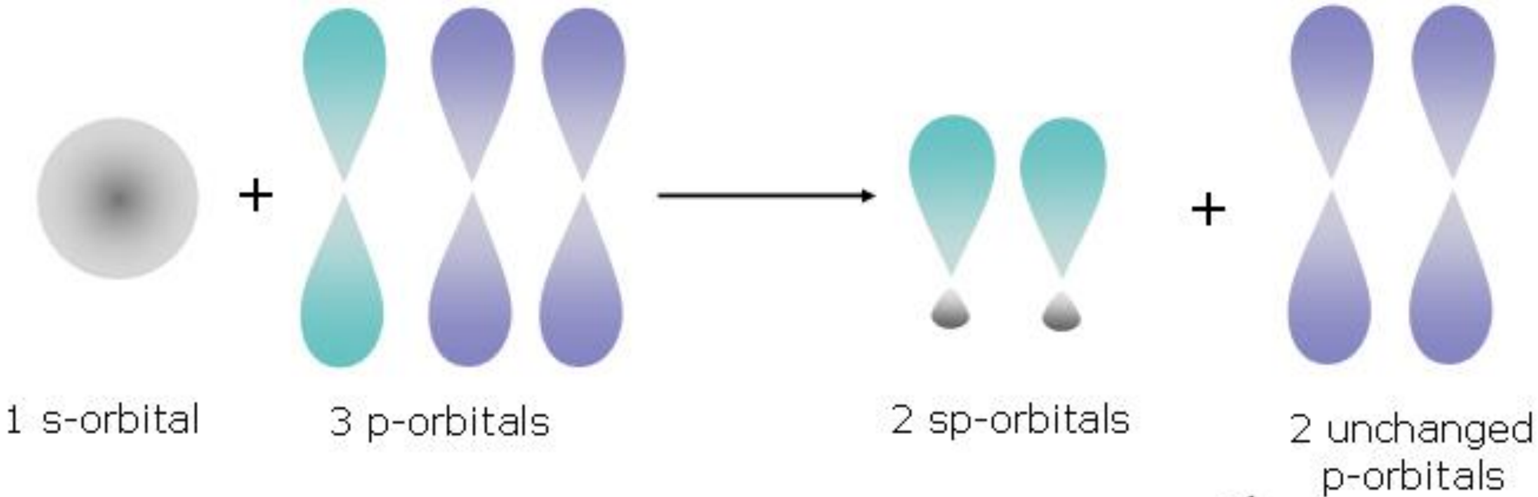
2p 2p

sp sp

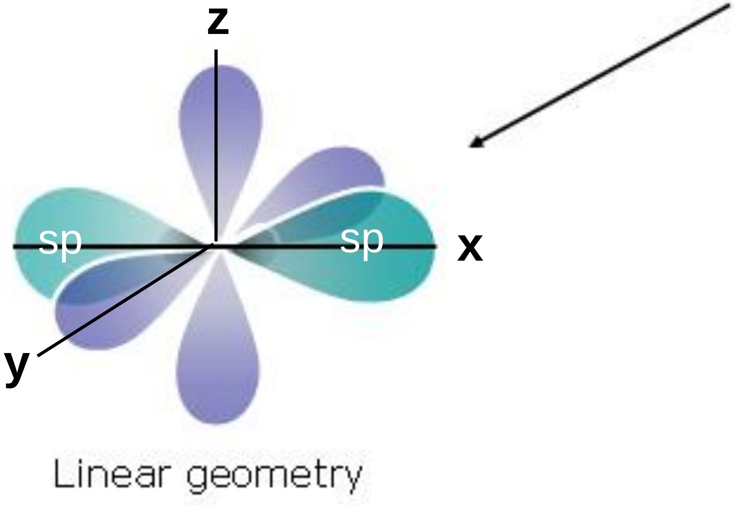
1s

One electron is promoted (relocated) to a higher-energy orbital.

Hybridization - sp

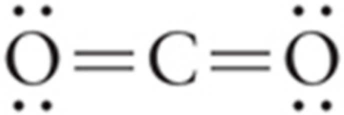


Orbital Geometry for sp



Hybridization - sp

sp hybrid orbitals

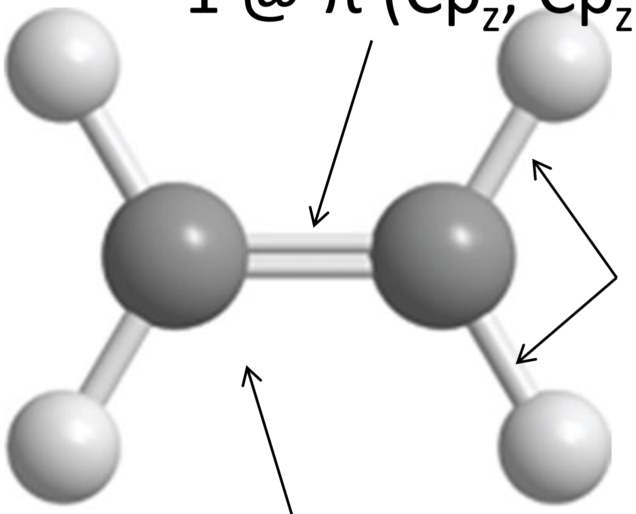


$O=C=O$

only 2 sigma bonds form, and two p-bond are not hybridized.

$h_1 = s + p_x$
$h_2 = s - p_x$

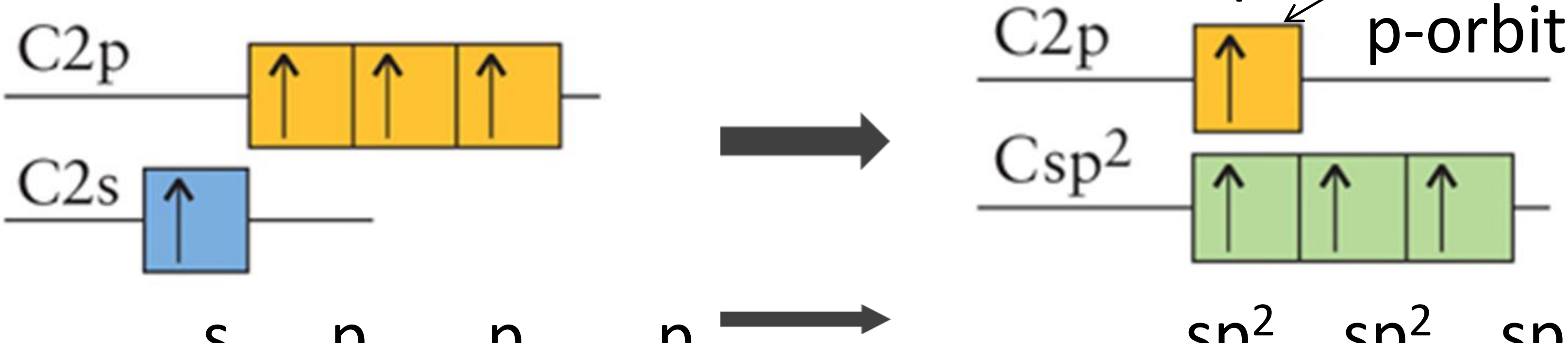
Self-test 4.7B Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2 .



1 @ π (Cp_z, Cp_z)

4 @ σ (Csp^2, H1s)

1 @ σ (Csp^2, Csp^2)



p

unhybridized p-orbital

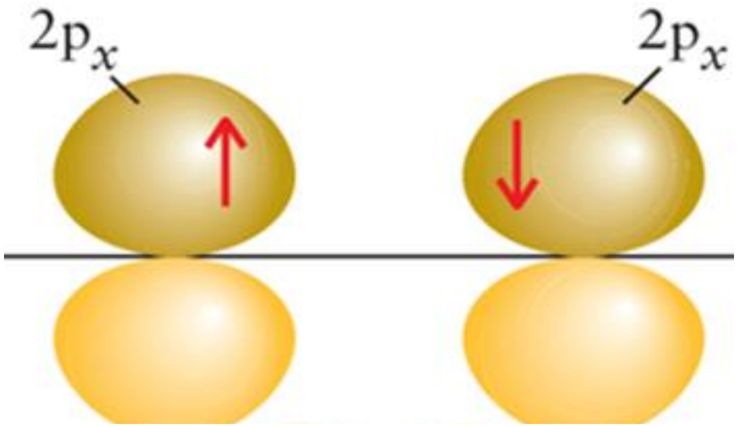
s p_x p_y p_z

Atomic orbitals

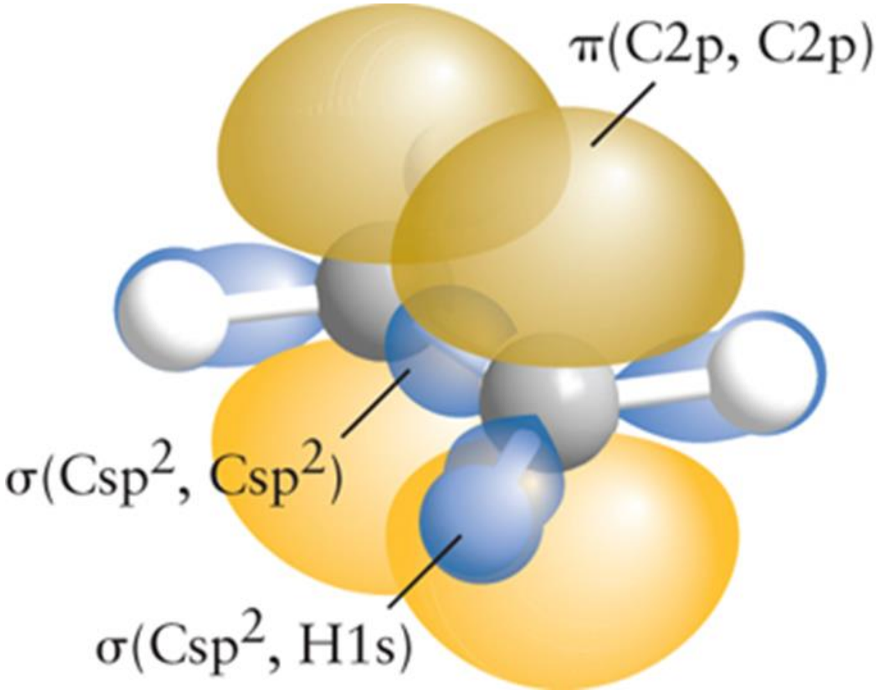
sp^2 sp^2 sp^2

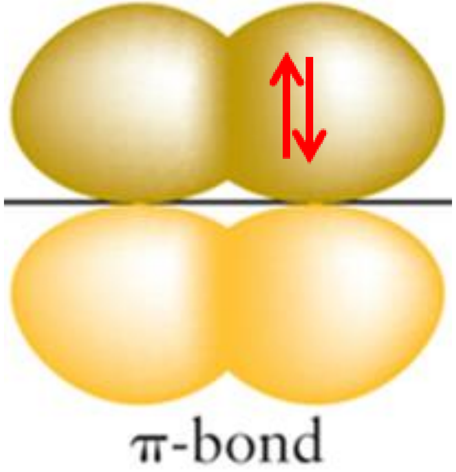
Hybrid orbitals

The unhybridized 2p-orbital, is perpendicular to the C-C plane.



The electrons in the two unhybridized 2p-orbitals form a π-bond through side-by-side overlap.

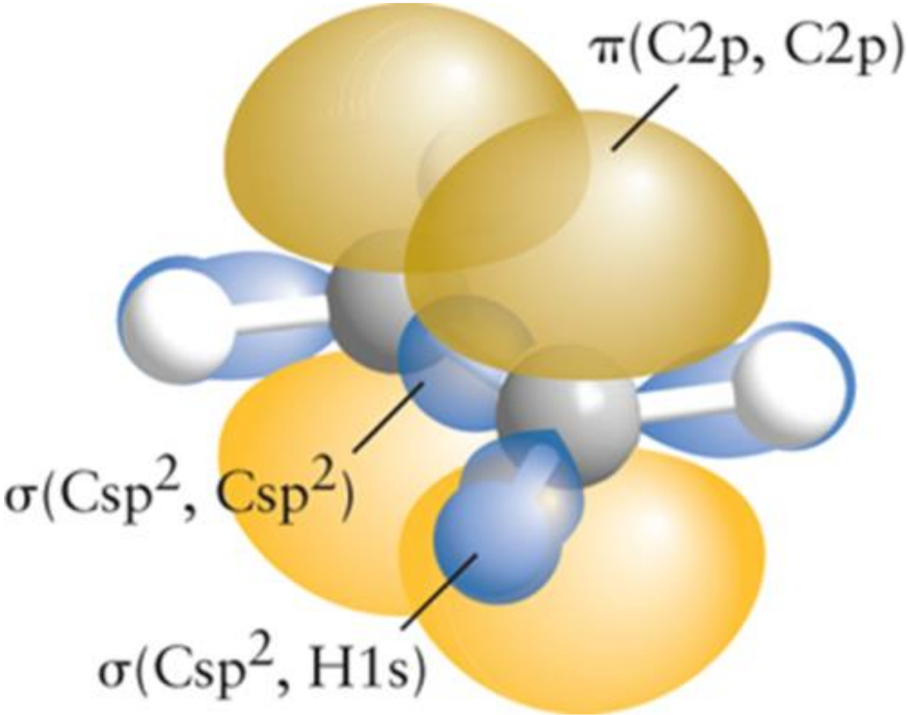




π-bond spin-pairing

Double bond properties

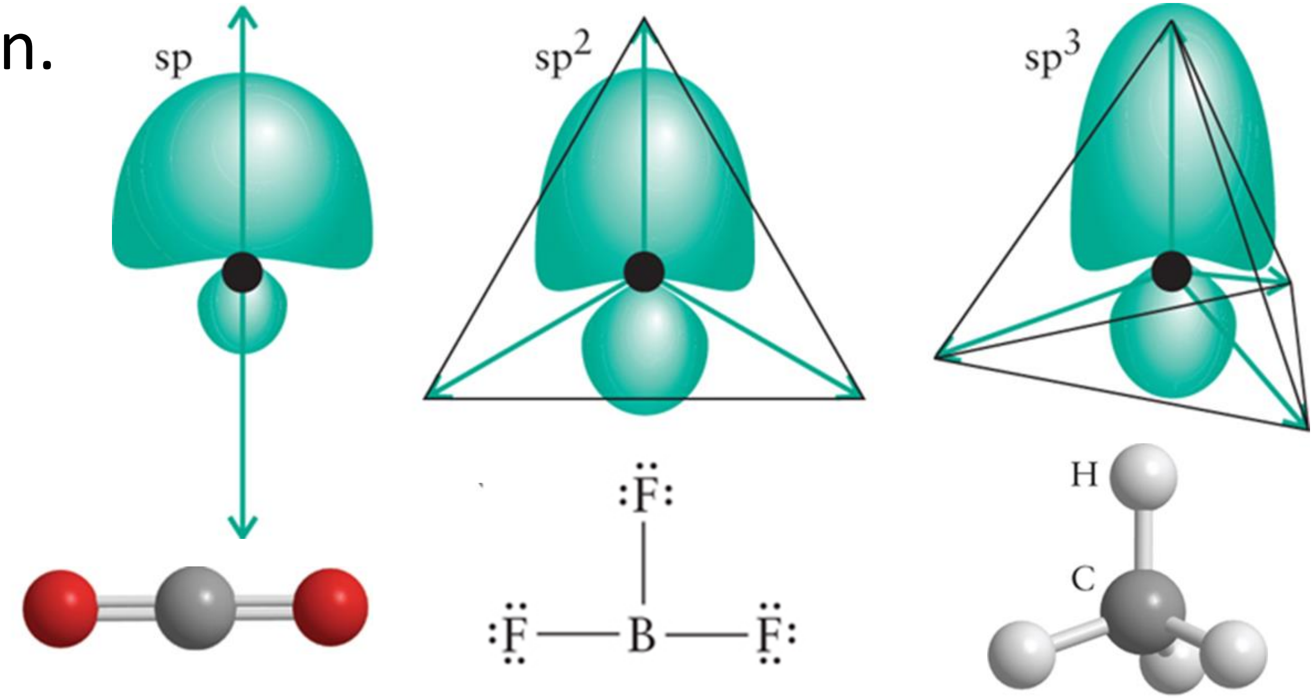
Double bond prevents one part of a molecule from rotating around another.



The **π-bonds** of ethene, hold the entire molecule flat.

Rotation around the C-C bond is prohibited.

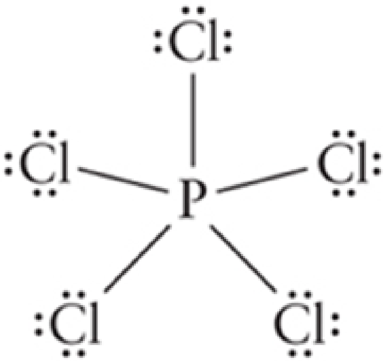
hybridization orbitals showing the amplitude of a single wavefunction.



2 σ-bonds
linear

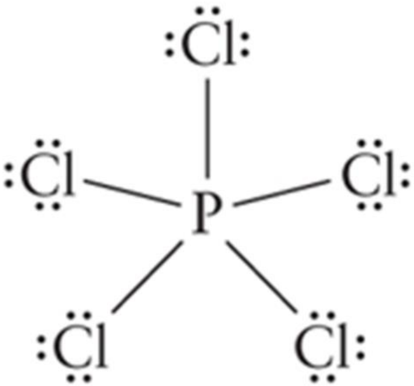
3 σ-bonds
trigonal planar

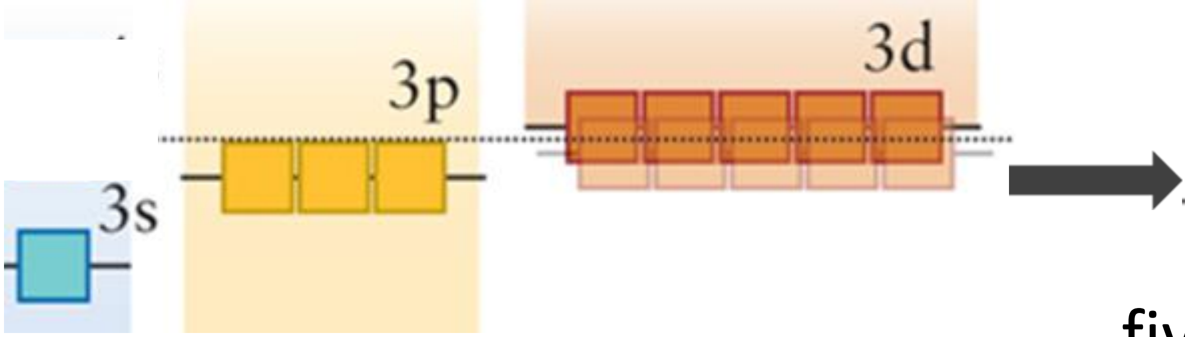
4 σ-bonds
tetrahedral



How do we account of 5 σ-bonds in trigonal bipyramidal or 6 σ-bonds in octahedral compounds?

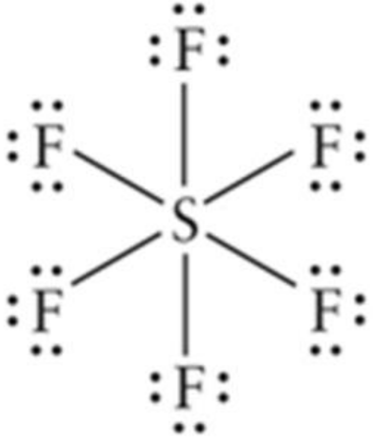
Trigonal bipyramidal have five electron pairs, so one d-orbital along with the valence s- and p-orbitals of the atom.

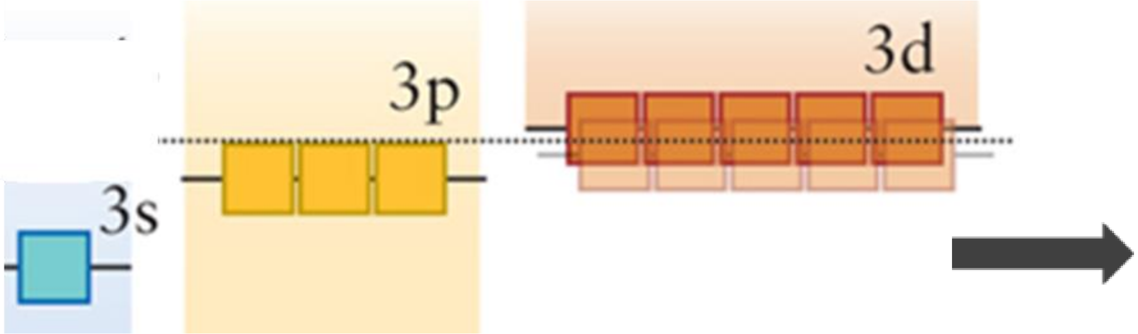


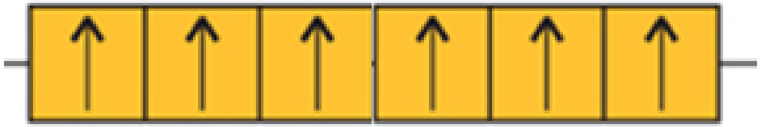


five sp^3d hybrid orbitals

six electron pairs, in an octahedral, use two d-orbitals in addition to the valence s- and p-orbitals to form.







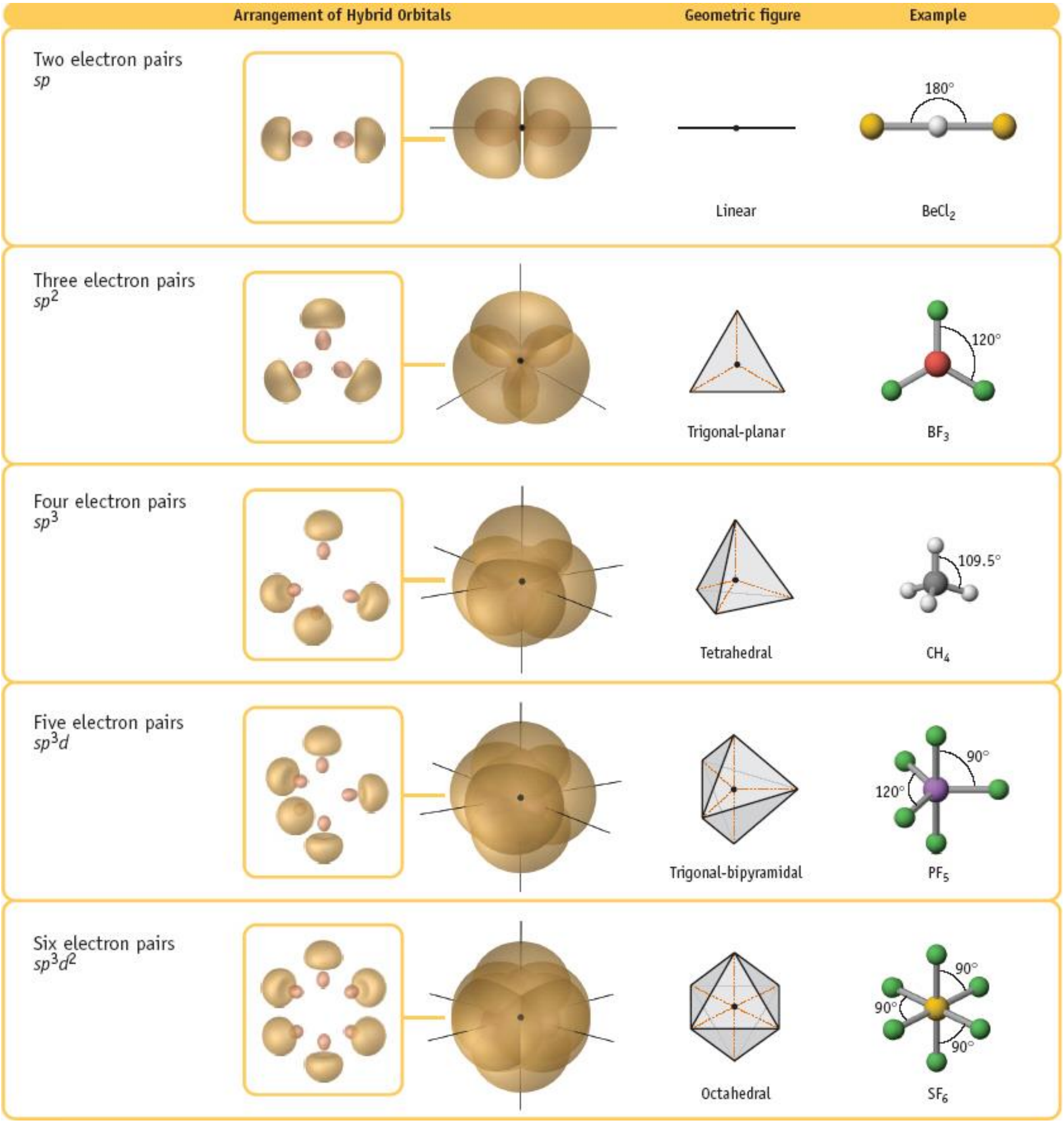
six sp^3d^2 hybrid orbitals

Summery

Number of electron regions = Number of hybrid orbitals

Molecular Geometry	Number of electron regions	Hybridization of central atom	Number of hybrid orbitals
Linear	2	sp	2
Trigonal Planar	3	sp^2	3
Tetrahedral	4	sp^3	4
Trigonal Bipyramidal	5	sp^3d	5
Octahedral	6	sp^3d^2	6

Summery



Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs *sp*	Linear	$BeCl_2$
Three electron pairs *sp*^{2}	Trigonal-planar	BF_3
Four electron pairs *sp*^{3}	Tetrahedral	CH_4
Five electron pairs *sp*^{3}*d*	Trigonal-bipyramidal	PF_5
Six electron pairs *sp*^{3}*d*^{2}	Octahedral	SF_6

Summery

To Find the hybridization of the central atom:

1. Draw the Lowis structure.

2. Determine the electron regions around the central atom.

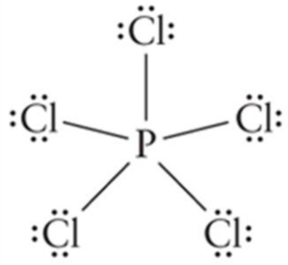
3. Identify the molecular shape (molecular geometry)

4. # of electron regions = # of hybrid orbitals

5. Construct the hybrid orbitals, starting with s-orbital, and proceeding to the p- and d-orbitals.

EXAMPLE 4.5 Sample exercise: Assigning a hybridization scheme for phosphorous in PCl_5 ?

1. Draw the Lewis structure.

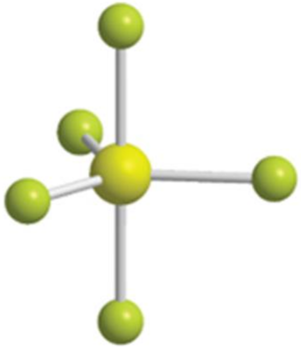


2. Determine the electron regions around the central atom.

Trigonal bipyramidal

3. Identify the molecular shape.

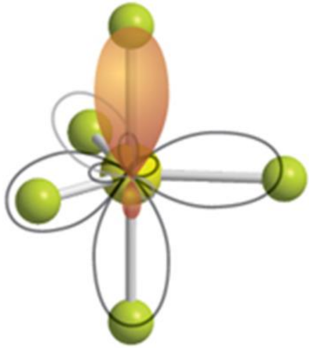
Trigonal bipyramidal



4. Select the same number of atomic orbitals as there are hybrid orbitals.

5

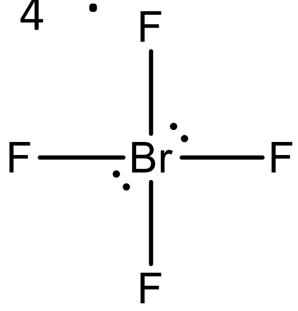
5. Construct the hybrid orbitals, starting with the s-orbital, then p- and d-orbitals.



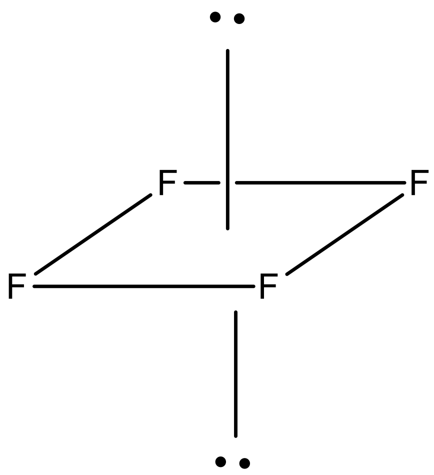
five sp^3d hybrid orbitals

EXAMPLE 4.5 Sample exercise: Assigning a hybridization scheme for bromine in BrF_4^- ?

1. Draw the Lewis structure.



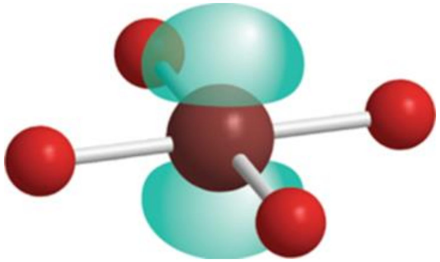
2. Determine the electron regions around the central atom.



octahedral

3. Identify the molecular shape.

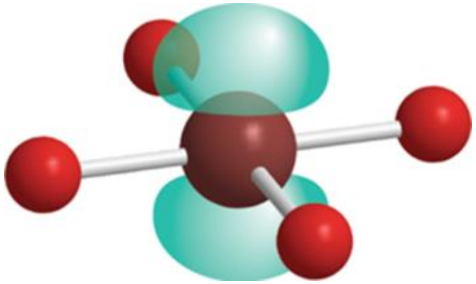
Square planar



4. Select the same number of atomic orbitals as there are hybrid orbitals.

6

5. Construct the hybrid orbitals, starting with the s-orbital, then p- and d-orbitals.



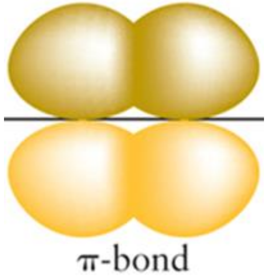
6 sp^3d^2 hybrid orbitals

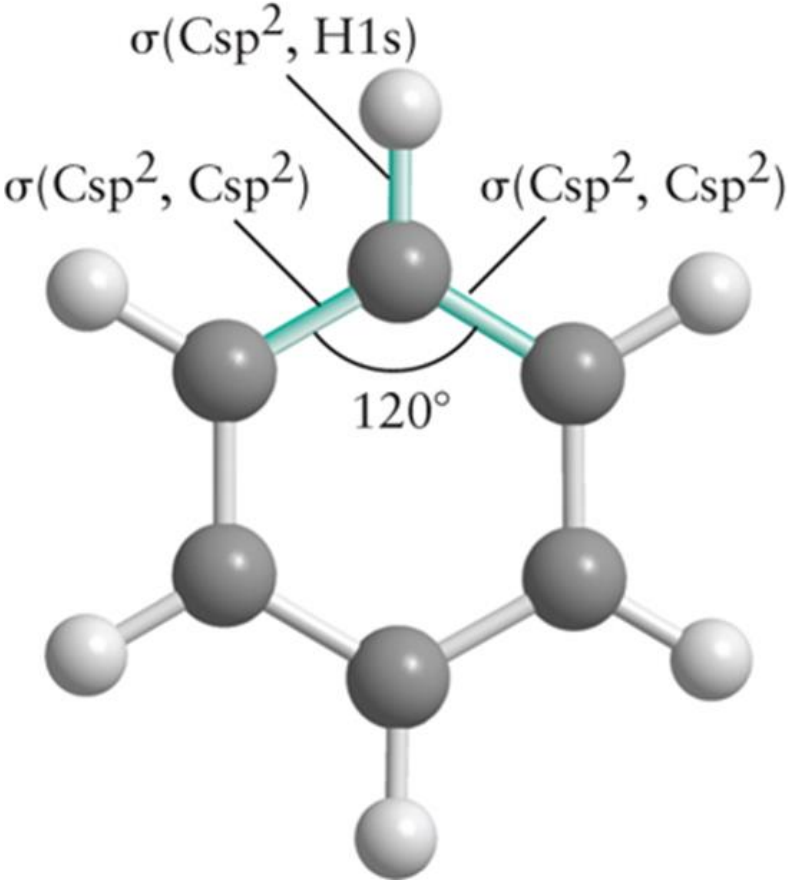
Characteristics of Multiple Bonds

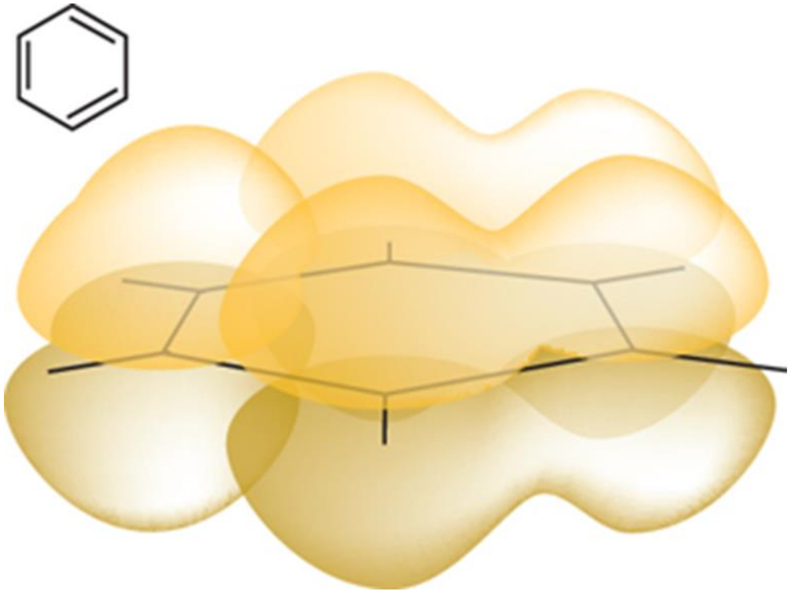
Atoms of the Period 2 elements C, N, and O readily form double bonds (especially oxygen).

However, double bonds are rarely found between atoms of elements in Period 3 and later periods, because the atoms are so *large* and *bond lengths consequently are so great* that it is difficult for their p-orbitals to take part in effective side-by-side overlap.

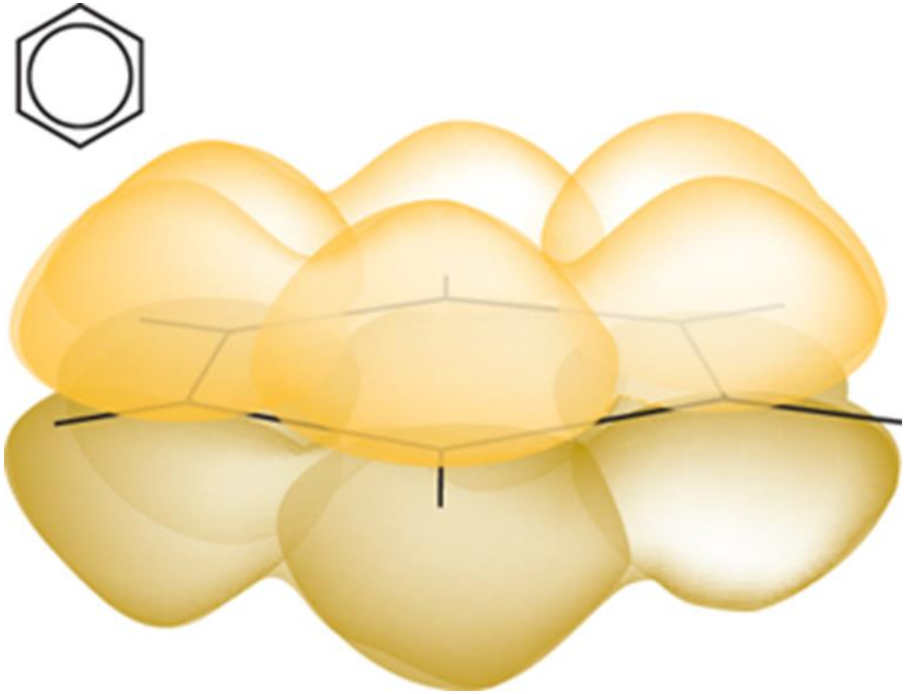
In benzene, the C and H atoms all lie in the same plane, and carbons join forming a ring.





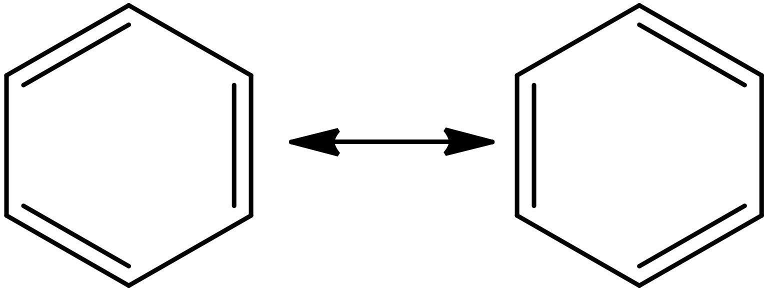


The Kekulé structures of benzene show 6 hybridized sp^2 carbon atoms.



Since every carbon neighbor has a π-bond, there are two or **resonance hybrid** structures.

The electrons are **spread around the entire ring** through the **π-bonds** .



Molecular Orbital Theory

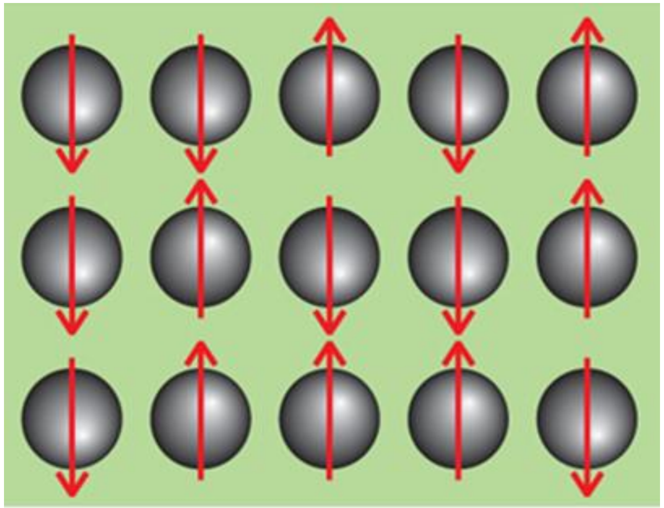
Lewis's theory of the chemical bond was brilliant, but it was little more than **guesswork** inspired by insight.

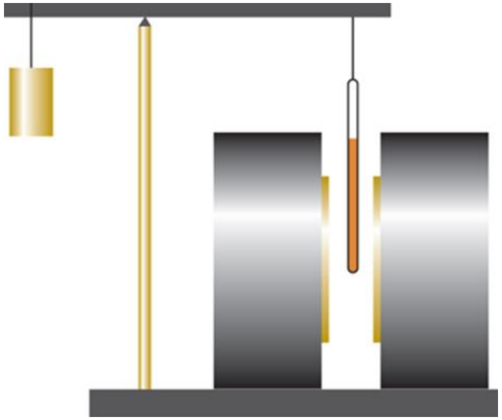
Valence-bond theory explained electron pairs in terms of **spin-pairing** but it could not explain the properties of some molecules.

Molecular orbital theory, based on quantum mechanics and was introduced in the late 1920s by Mulliken and Hund, has proved to be **the most successful theory of the chemical bond**: it overcomes all the deficiencies of Lewis's theory and is easier to use in calculations than valence-bond theory (still use orbital box, σ-bonds & π-bonds).

Lewis and valence-bond theory, describe O_2 as having all electrons paired. However, oxygen is a **paramagnetic**, a property of **unpaired electrons**; whereas *diamagnetic* have *paired* e^- *'s*.

Horseshoe magnet





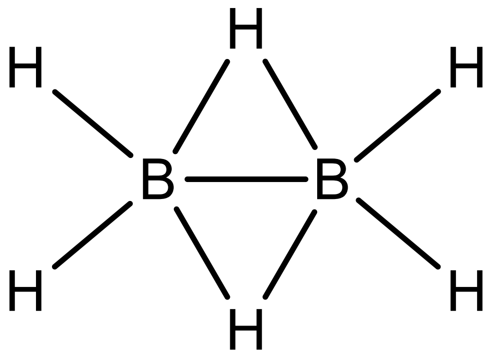
A Gouy balance is used to observe magnetic properties

Lewis's theory fails to account for the compound **diborane**, B_2H_6, that bursts into flame on contact with air.

The problem is that diborane has only **12 valence electrons** instead of the 14 electrons it should have.

VB theory can only give an awkward explanation for the structures electron-deficiency.

Bridging Hydride



Unknown at the time

Molecular Orbitals

In molecular orbital theory, electrons occupy orbitals called molecular orbitals that **spread throughout** the **entire molecule**.

Lewis and valence-bond models of molecules **localizes** the electrons on atoms or between pairs of atoms.

Molecular Orbitals

We start with the simplest molecule, H_2, and extend the same principles to more complex molecules and solids.

In every case, **molecular orbitals are built by adding** together-the technical term is superimposing-**atomic orbitals** belonging to the valence shells of the atoms in the molecule.

For H_2 is $\psi = \psi_{A1s} + \psi_{B1s}$

A is atom A
B is atom B
1s is the 1s-orbital for hydrogen

Molecular Orbitals

A is atom A
B is atom B
1s-orbital for hydrogen

$$\psi = \psi_{A1s} + \psi_{B1s}$$

ψ is called the linear combination of atomic orbitals or LCAO.

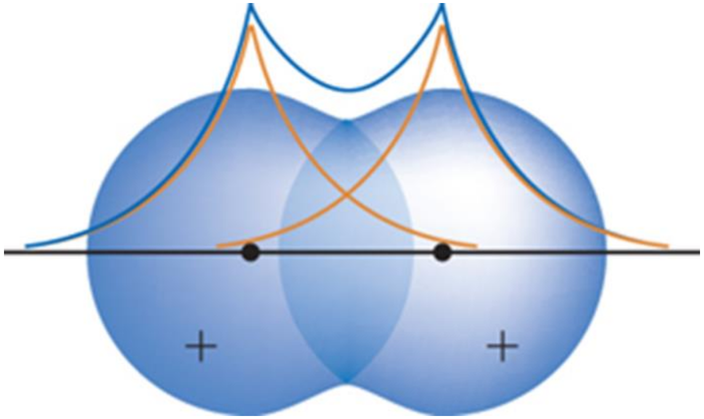
The term LCAO-MO is a molecular orbital formed from a linear combination of atomic orbitals.

To note: a MO contains no electrons, it’s just an overlap of wavefunctions (superimposing).

Molecular Orbitals

bonding

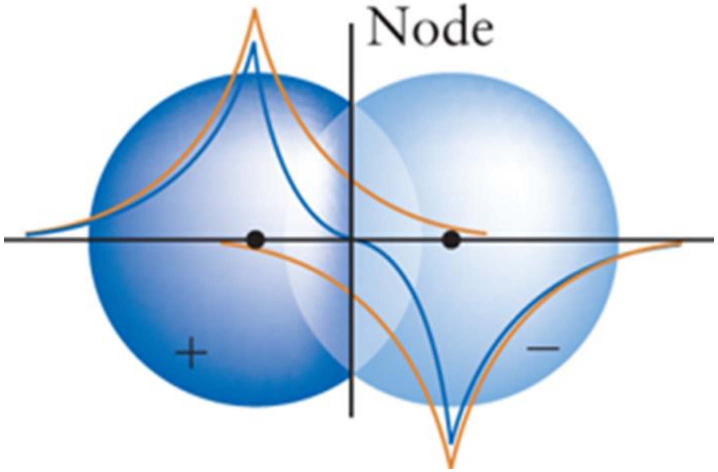
constructive interference



$$\psi = \psi_{A1s} + \psi_{B1s}$$

antibonding

deconstructive interference



$$\psi * = \psi_{A1s} - \psi_{B1s}$$

LCAO-MO's

A note on good practice: the negative sign really represents the reverse of a positive (so a peak becomes a trough and vice versa), resulting in a node in the wavefunction.

The relative energies of the original atomic orbitals and the bonding (ψ) and antibonding ($\psi *$) molecular orbitals.

$$\psi * = \psi_{A1s} - \psi_{B1s}$$

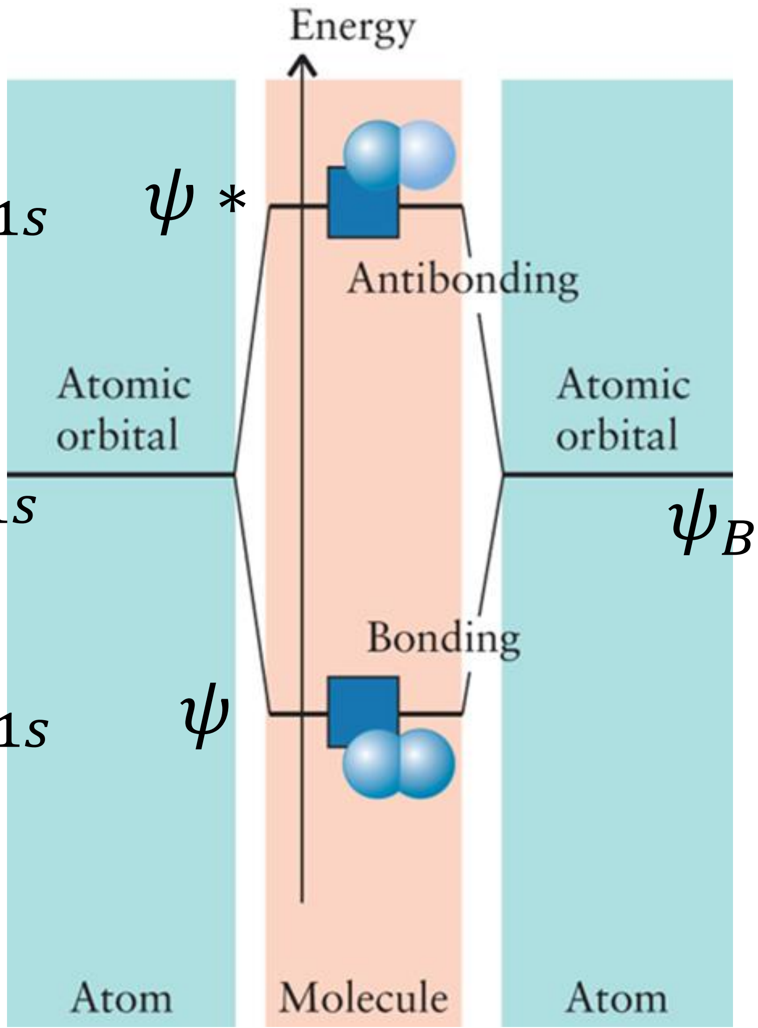
$\psi *$

ψ_{A1s}

ψ_{B1s}

$$\psi = \psi_{A1s} + \psi_{B1s}$$

ψ



Atomic orbitals that interfere destructively, give rise to antibonding molecular orbitals.

Molecular orbitals form when atomic orbitals interfere constructively.

Diatomic Molecules

Molecular orbitals (MO) are built from valence-shell atomic orbitals (AO) *and* for every AO produces a MO.

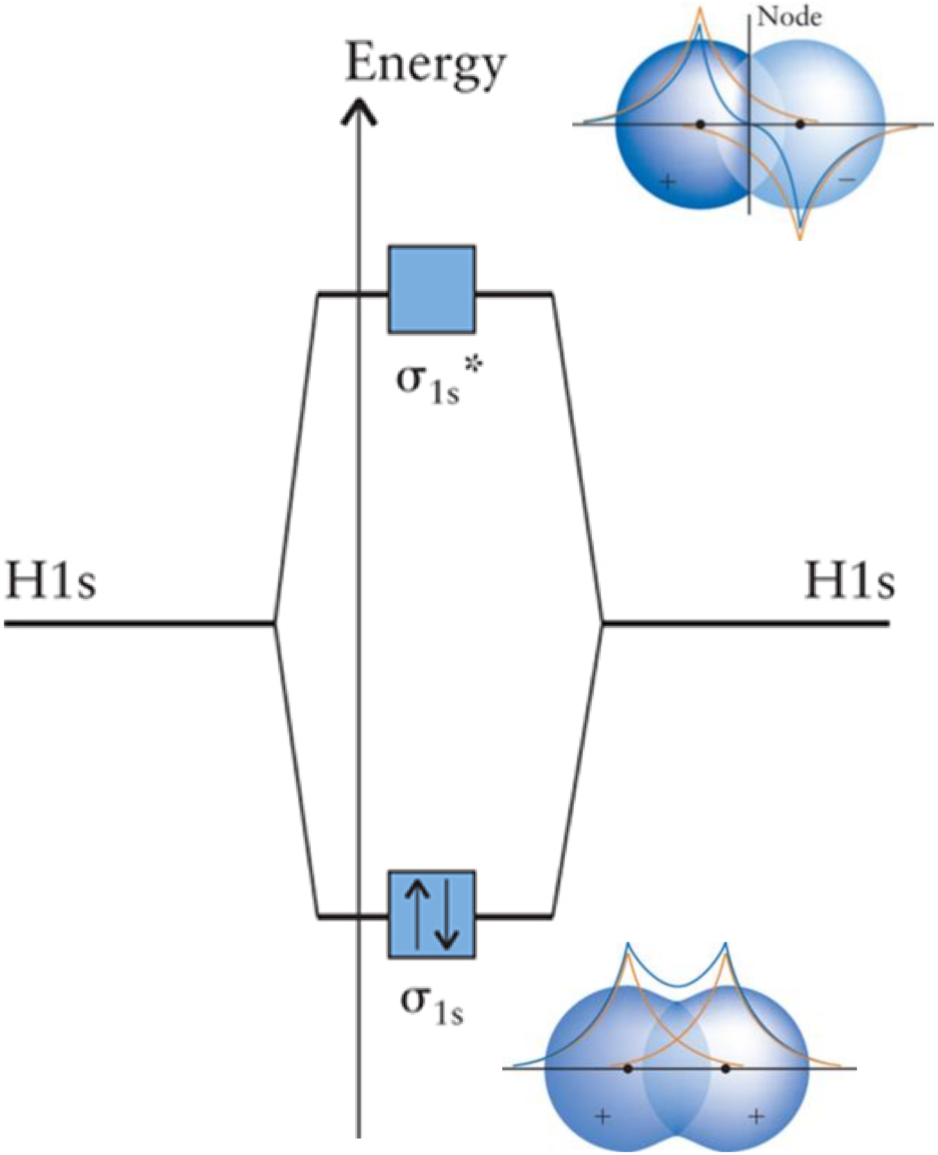
Place valence electrons, using a building-up principle for atoms (aufbau).

1) Electrons start in the lowest-energy MO;

2) Pauli exclusion principle: each MO can accommodate up to two electrons, and spin-paired if together;

3) Hund's rule: If more than one molecular orbital of the same energy exists, electrons enter them singly and adopt parallel spins.

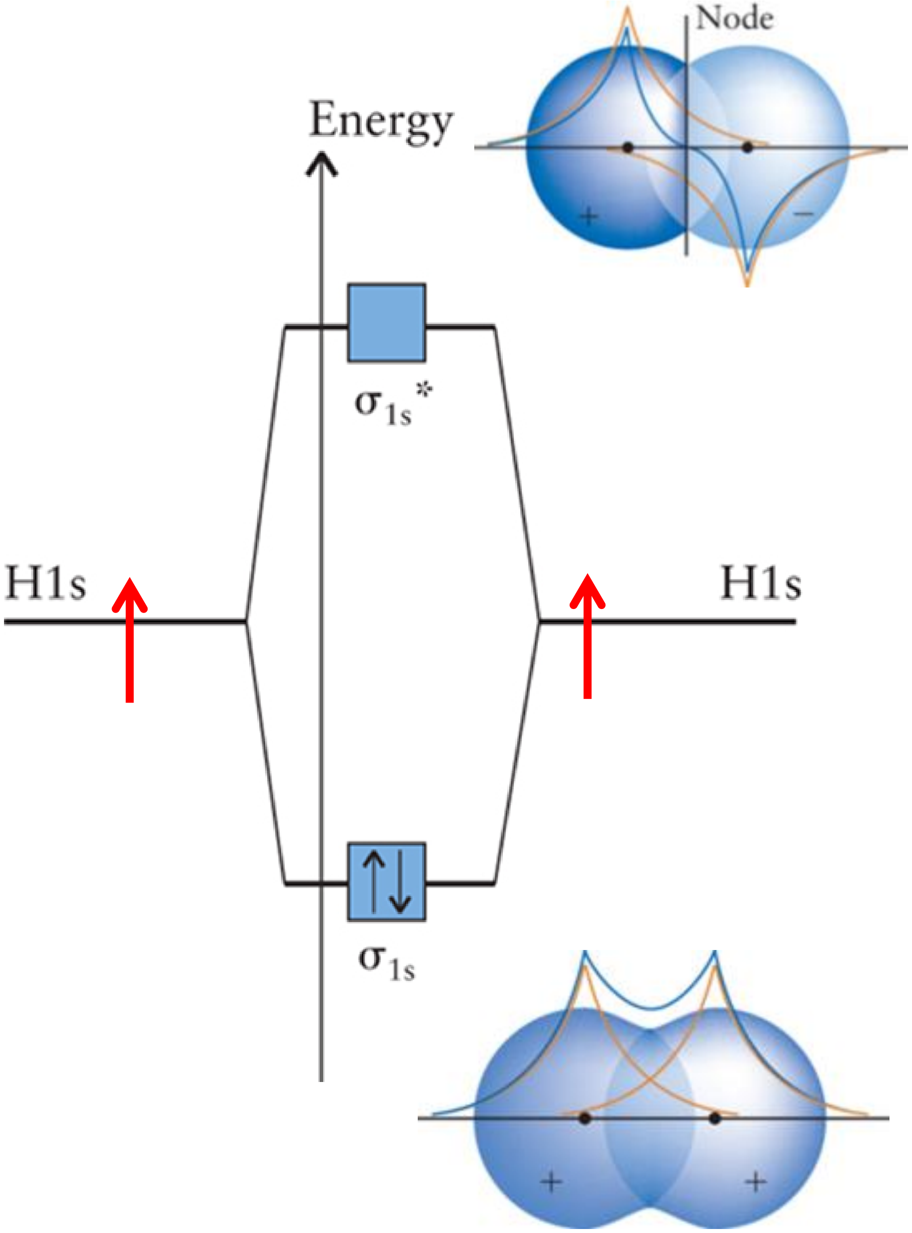
“N” atomic orbitals combine to give “N” molecular orbitals.



H_2, has **two** 1s-orbitals (one on each atom) that merge to form **two** molecular orbitals.

Notation: bonding orbital is σ_{1s} and antibonding orbital is σ_{1s}*.

The σ indicates we have built a "σ-orbital," *a cylinder-shaped orbital*.



Both electrons occupy the bonding σ_{1s} orbital (the lower-energy orbital).

A pair of electrons is the maximum allowed per orbital.

One huge difference between Lewis's theory and VB theory, is that MO theory allows a single electron bond to hold a molecule together (of course with half the strength of an electron-pair).

Homonuclear diatomic molecules of Period 2 elements

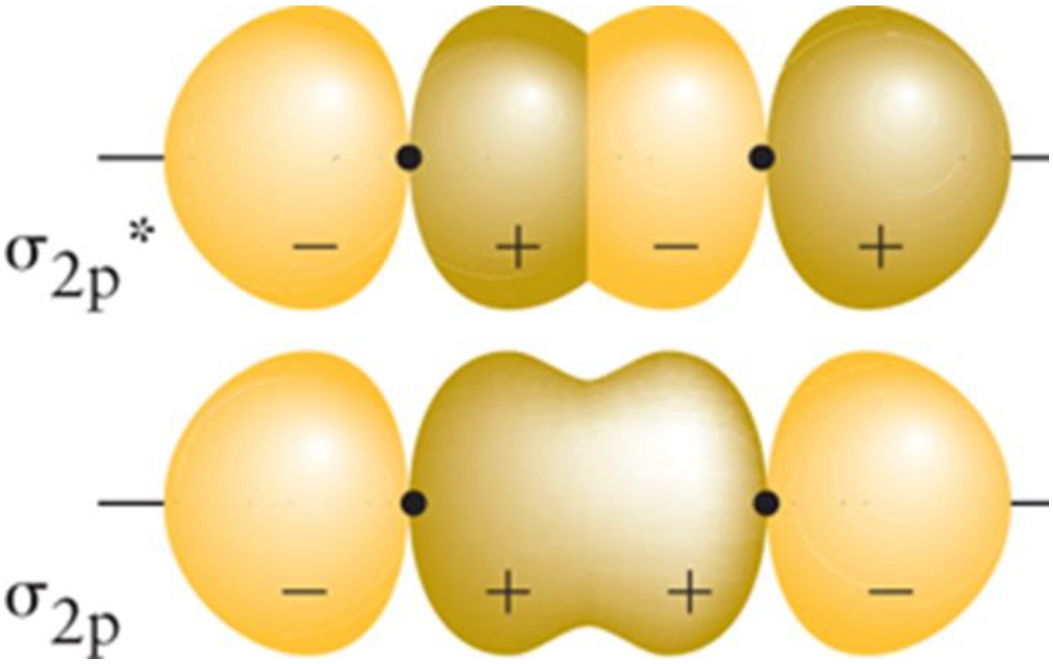
Building MO energy-level diagrams start with the **valence-shell** atomic orbitals from each atom.

If 2 atoms have both **2s-** and **2p-orbitals** valence shells for a total of ***eight*** **atomic orbitals** we end with ***eight*** **molecular orbitals**.

Therefore, # of AO’s = # of MO’s.

Orientation of p-orbitals

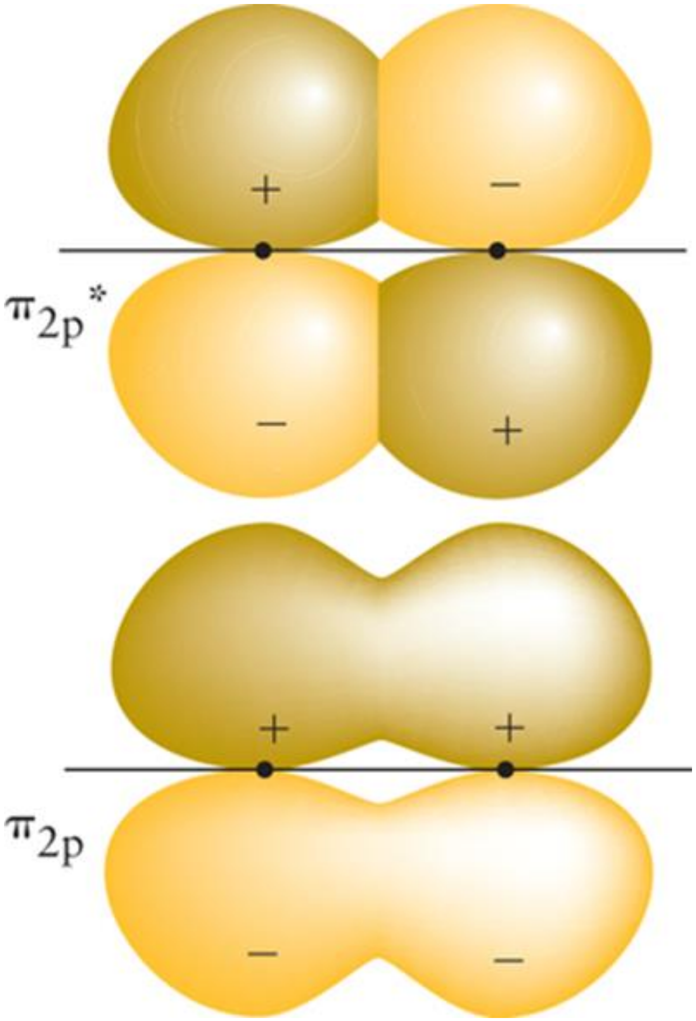
If the two 2p-orbitals are **directed toward each other**, along the internuclear axis, they will form a bonding σ-orbital. The 2 AO's will produce the 2 MO's shown.



σ*-antibonding

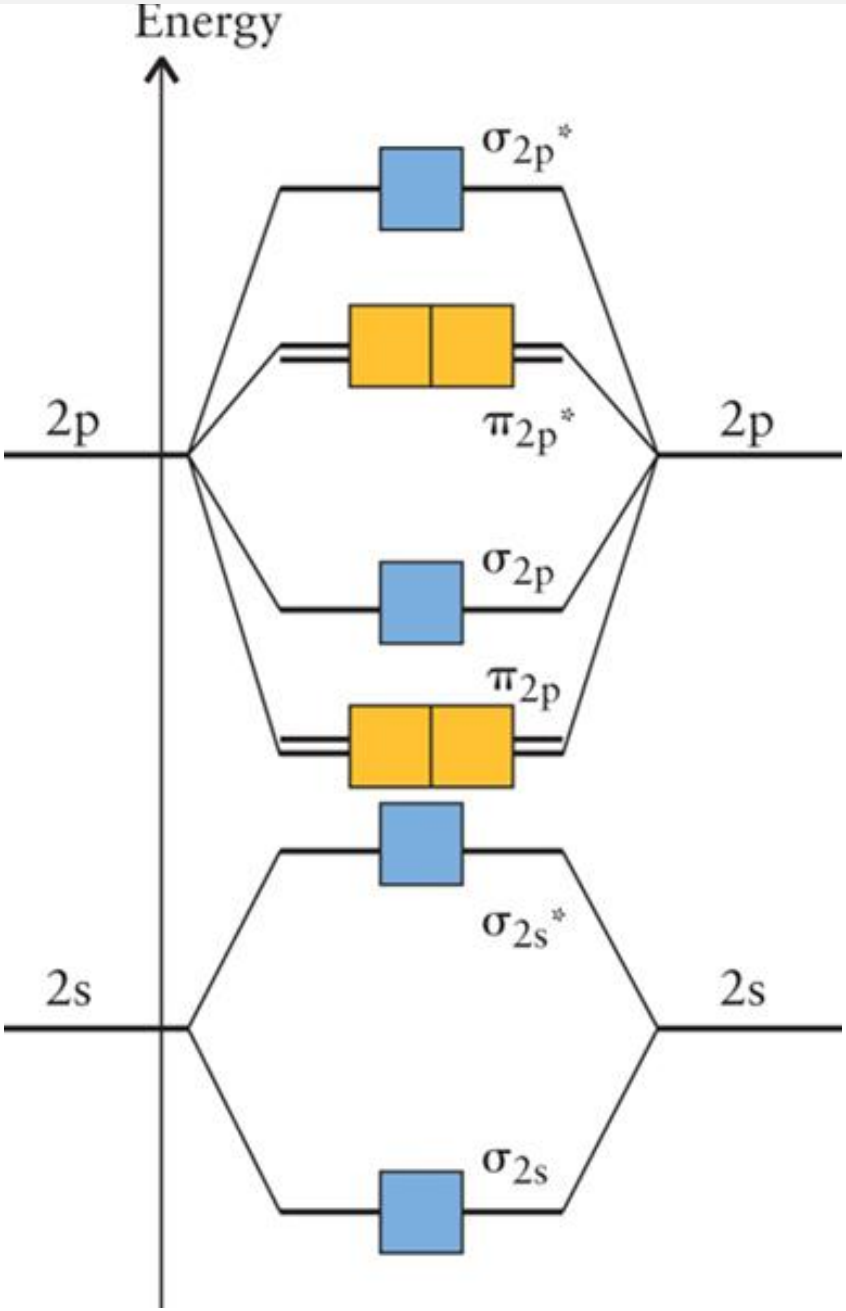
σ-bonding

Orientation of p-orbitals



Perpendicular p-orbitals, along the internuclear axis, overlap side by side to form bonding and antibonding “π-orbitals”.

Different MO diagrams for Period 2 elements.



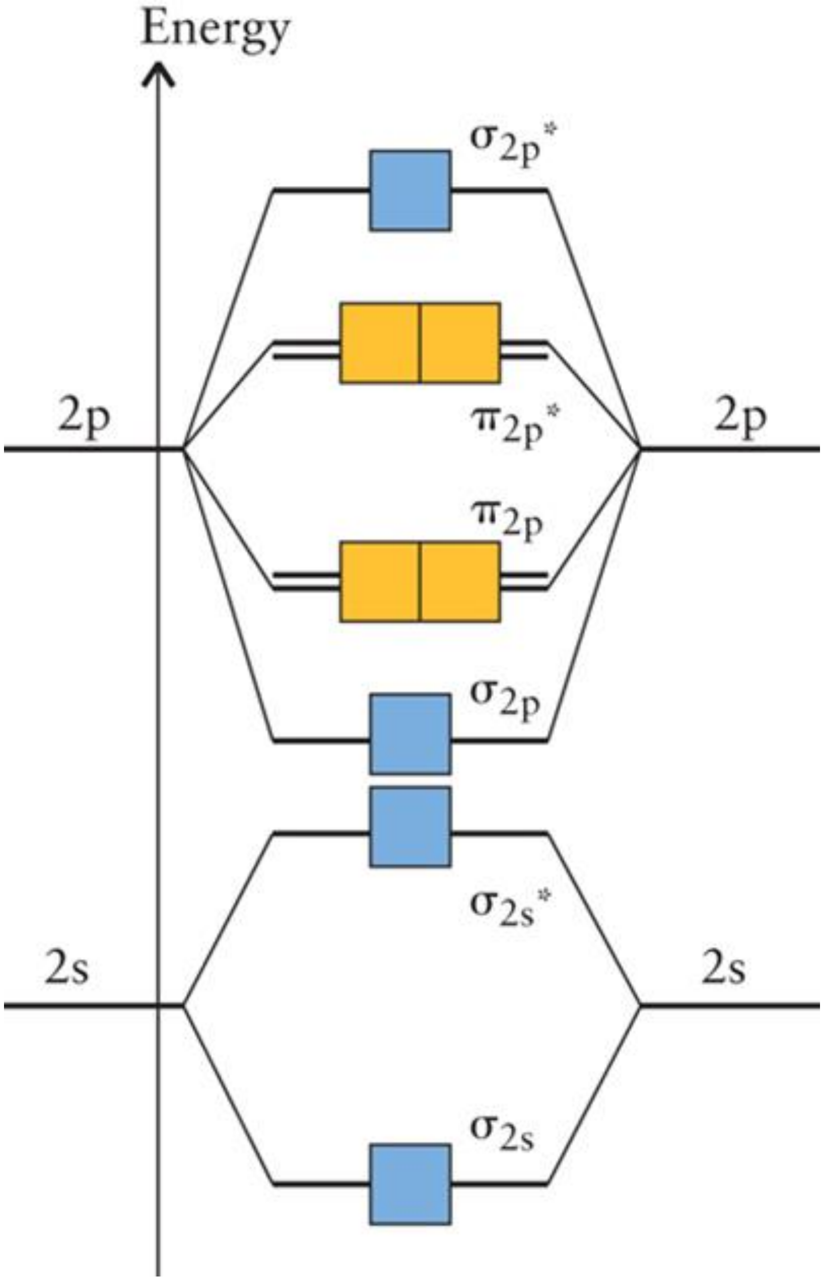
Diatomic molecules **Li_2 through N_2**, have fewer electrons in their 2p-orbitals, while the 2s-orbitals have more electrons.

Since the σ_{2p} is the first bond to form, it is populated with electrons so this orbital is raised in energy compared to the emptier π_{2p}-orbital.

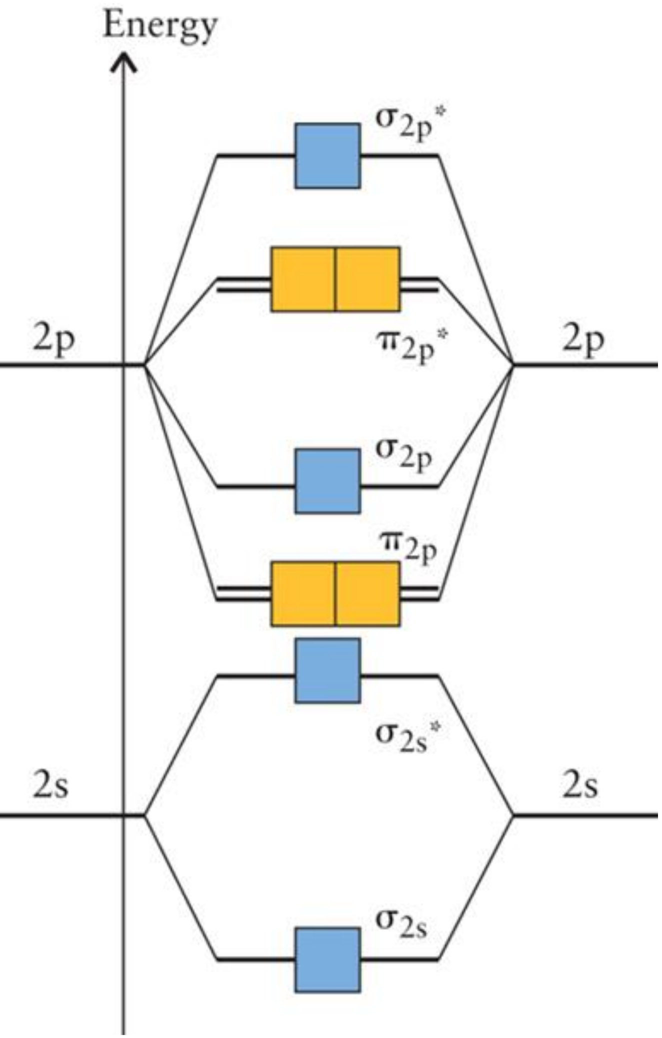
Different MO diagrams for Period 2 elements.

O_2 and F_2 diatomic molecules have a greater number of electrons in their 2p-orbitals than earlier period diatomic molecules.

A greater number of electrons will occupy the π_{2p}-orbital raising them compared to the σ_{2p}-orbital.

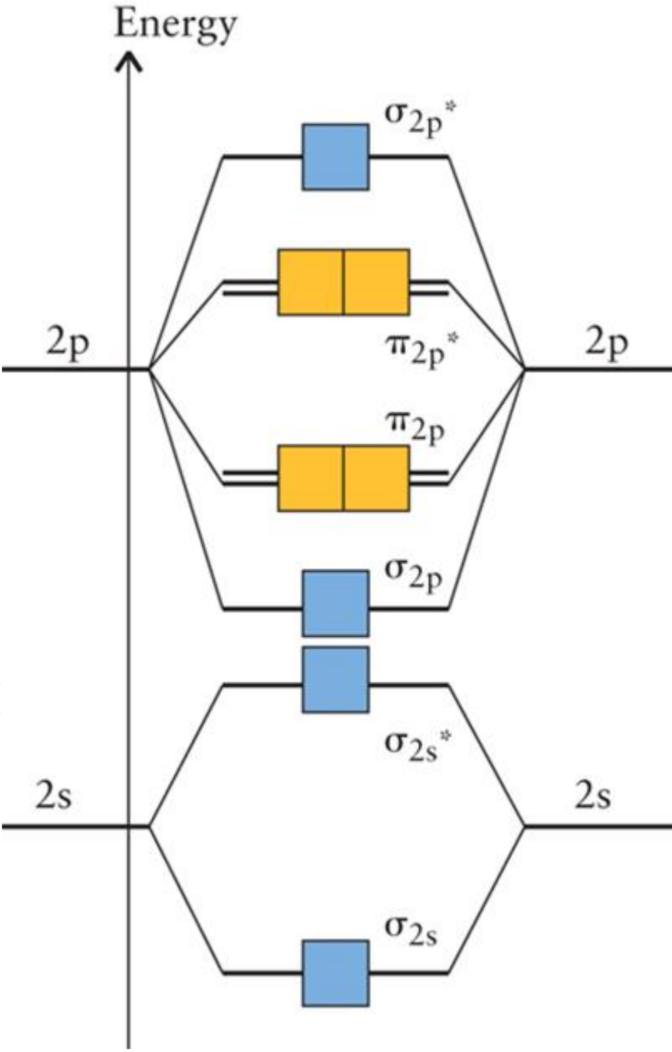


Different MO diagram for the Period 2 elements.



Energy differences between the two MO diagrams is due to shielding.

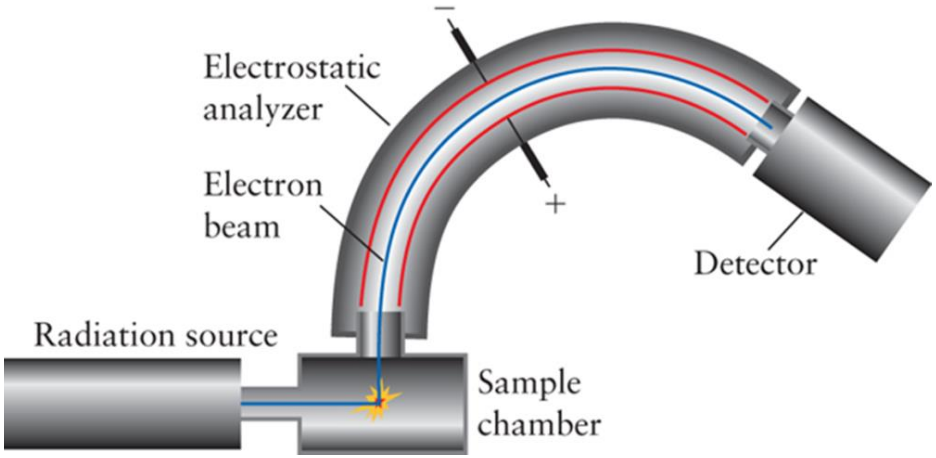
It is hard to predict without detailed calculation where the last orbitals will lie.



Li_2 through N_2

O_2 and F_2

UV or X-ray



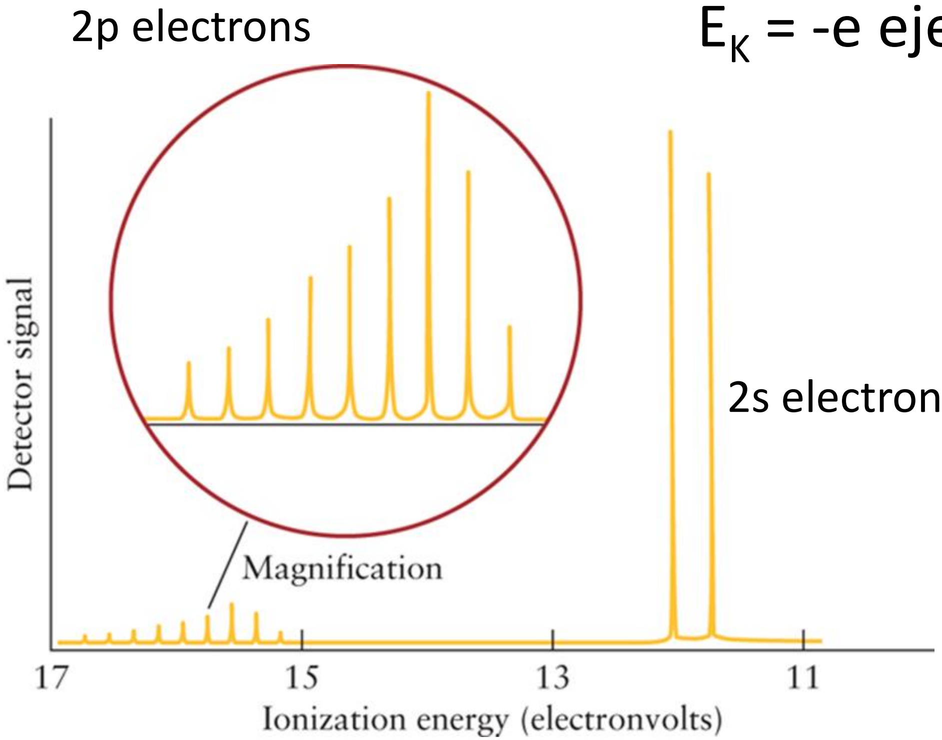
The energies of orbitals are probed directly with UV or even X-ray photoelectric spectroscopy (PES). Photons ($h\upsilon$) of known energy collide and eject electrons from a sample.

$$h\upsilon - E_{orbital} = E_k$$

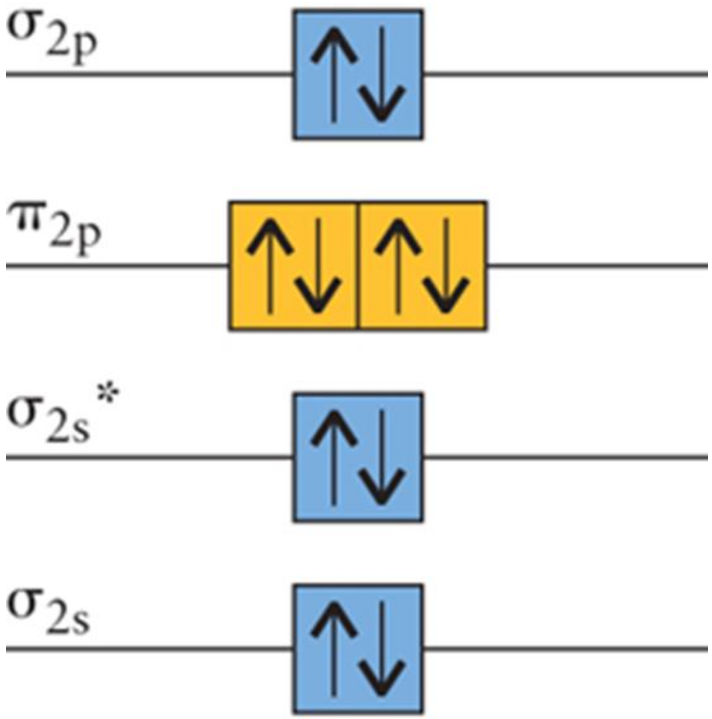
E_K = -e ejected

From the speed, we can calculate the kinetic energy of the electrons and so obtain the energy of the orbital from which they came.

$$E_K = \frac{1}{2}mv^2$$



N_2



At first sight, the molecular orbital description of N_2 looks quite different from the Lewis description (:NΞN:). In fact, they are closely related when we compare their bond order.

Bond order = ½ × (number of electrons in bonding orbitals
- number of electrons in antibonding orbitals

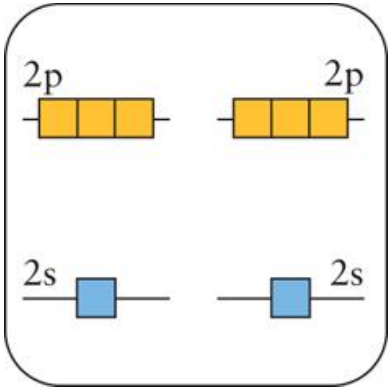
$$b = ½ \times (N - N^*)$$

BO for N_2 = ½ (8 - 2) = 3, the same for Lewis's model.

Example 4.7 Deduce the ground-state electron configuration of the fluorine molecule and calculate its bond order.

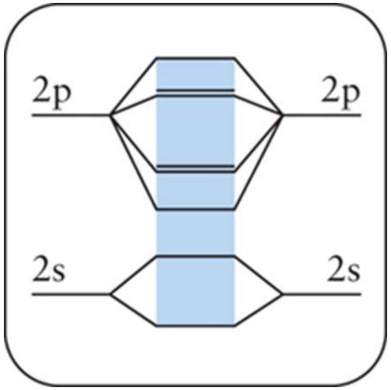
The Lewis structure of F_2 is F-F so we expect a bond order of 1.

Identify the valence atomic orbitals.

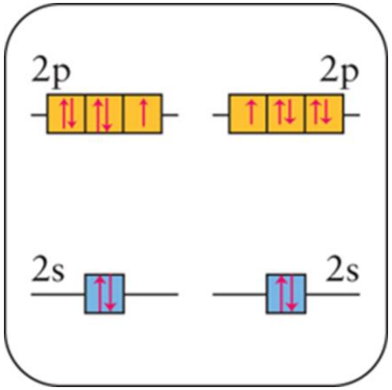


Each atom contributes a 2s-orbital and three 2p-orbitals, for a total of 8 orbitals.

Construct the molecular orbital energy level diagram.

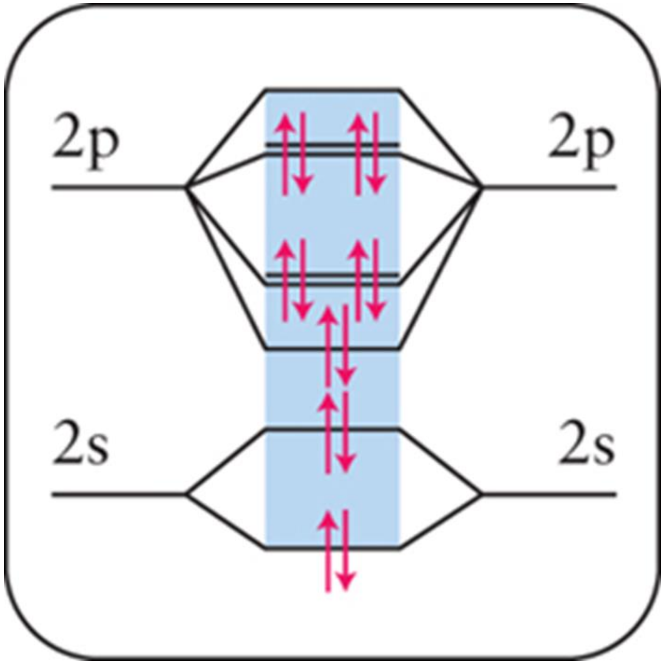


Count the valence electrons.



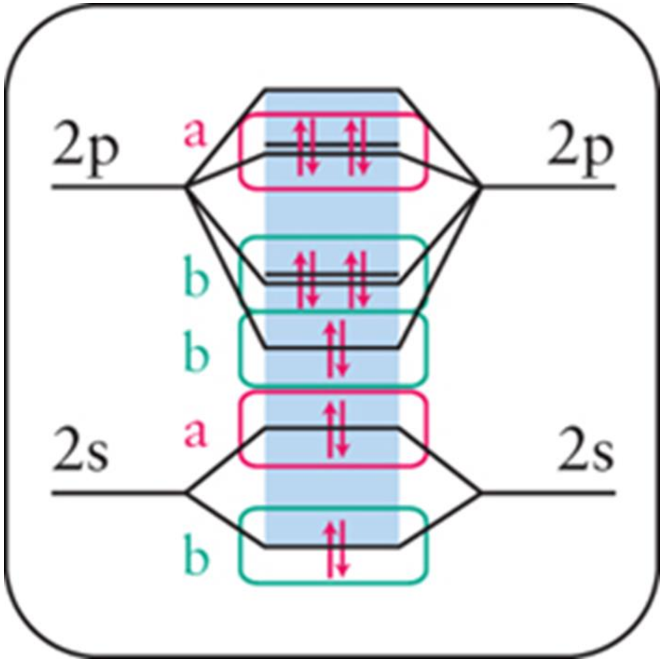
2 × 7 = 14

Construct the electron configuration.



Fill the orbitals in order of increasing

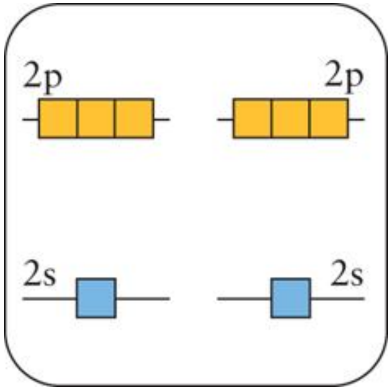
Determine the bond order



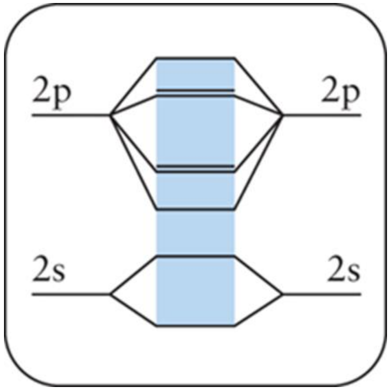
Diamagnetic all electrons are paired.

The bond order for F_2 = ½ (8 - 6) = 1.

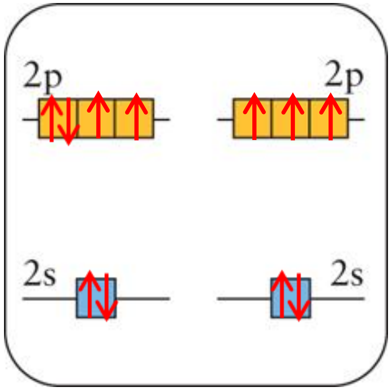
Self-test 4.10B Suggest a configuration for the O_2^+ ion and state its bond order.



Identify the valence atomic orbitals.



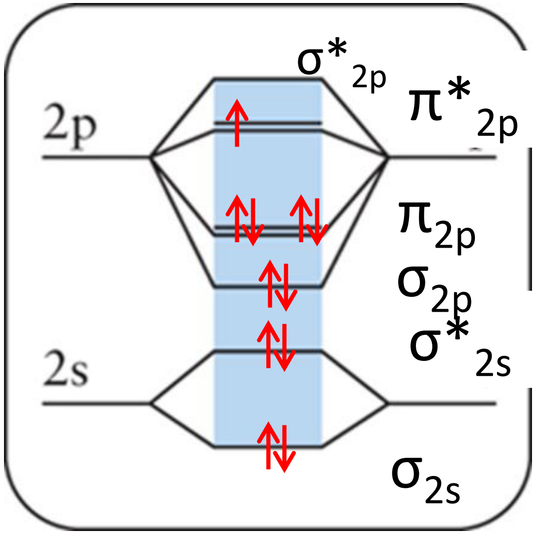
Construct the molecular orbital energy level diagram.



Count the valence electrons.

O_2^+: 6 + 6 – 1 = 11

Construct the electron configuration.



Determine the bond order

The bond order for O_2^+ = ½ (8 - 3) = 2.5

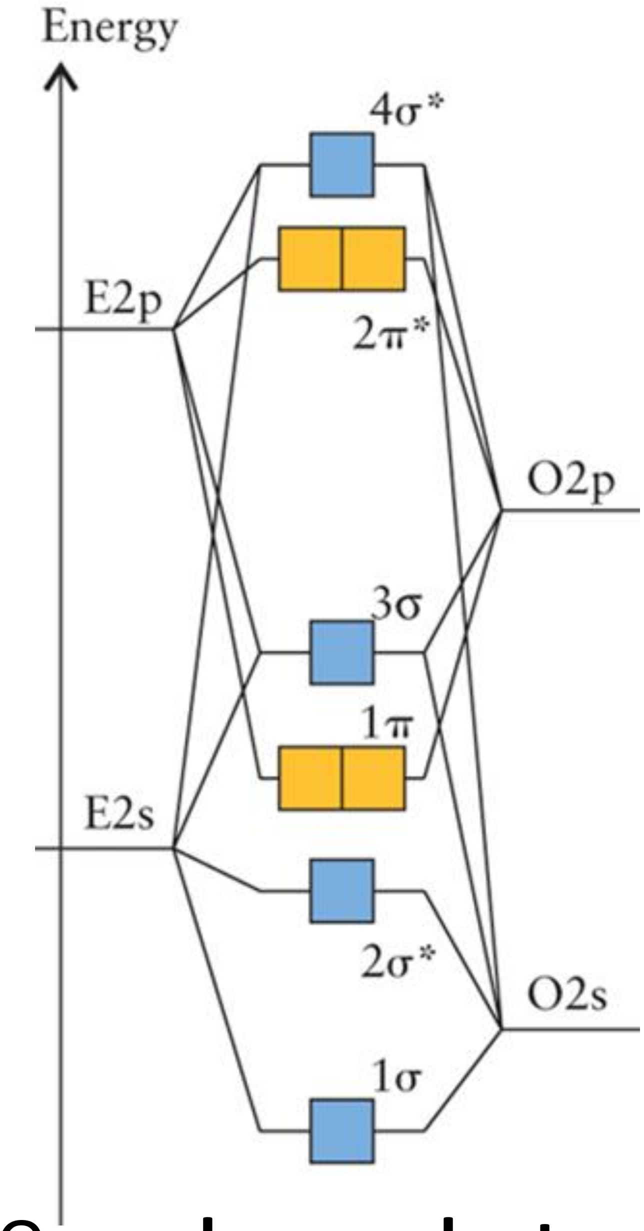
Paramagnetic, at least one MO has an unpaired electron.

Bonding in Heteronuclear Diatomic Molecules

The bond in a heteronuclear diatomic **polar,** molecule, has unequal sharing of electrons.

$$\psi = c_A\psi_A + c_B\psi_B$$

The more electronegative element has lower energy, so it's atomic orbitals are lower energy, dominating the molecular orbitals with **greater electron density**, since their electrons are closer to that atom.



E = N, for NO

polar covalent

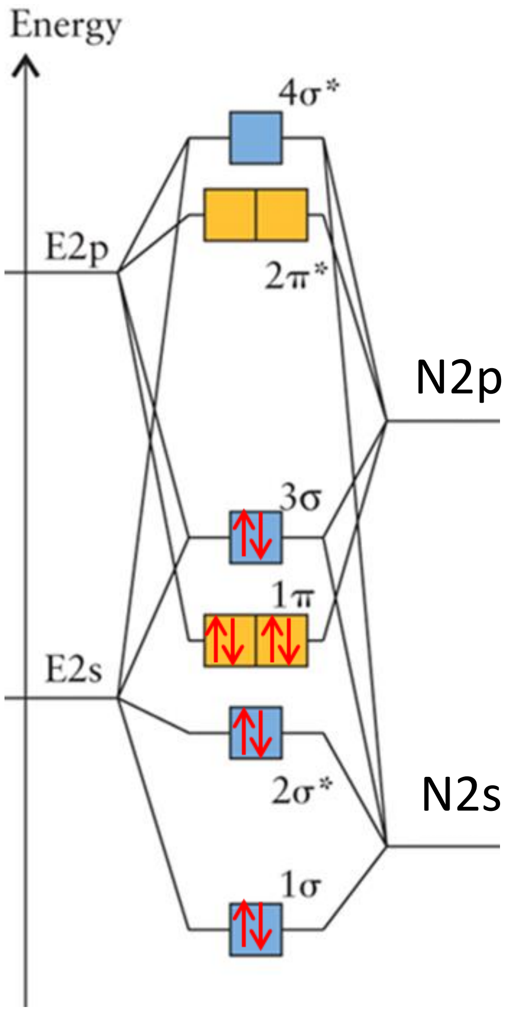
Self-test 4.11B Write the configuration of the ground state of the cyanide ion, CN^-, assuming that its molecular orbital energy-level diagram is the same as that for NO.

Count the valence electrons.

CN^- : 4 + 5 + 1 = 10

Construct the electron configuration.

$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$



The bond order for CN^- = ½ (8 - 2) = 3

diamagnetic

Orbitals in Polyatomic Molecules

Remember:

Unlike Lewis's theory or Valance bond theory, molecular orbitals spread over the entire molecule helping to bind the **whole molecule**, not just an individual pair of atoms.

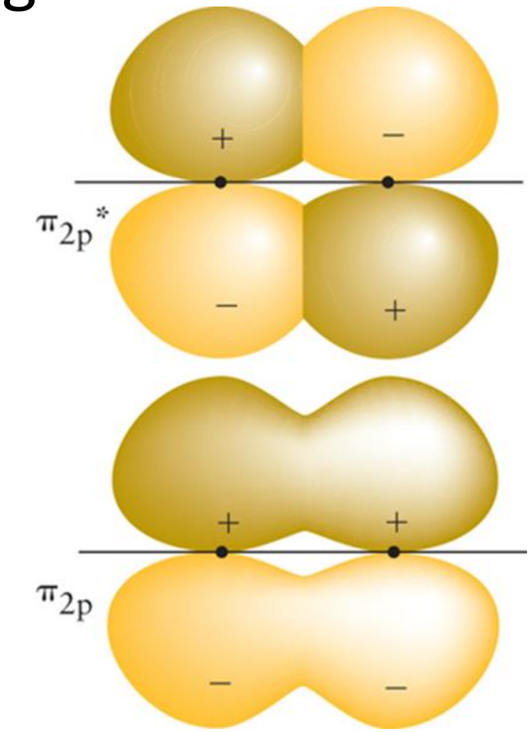
Viewing molecular orbitals as spread out over the entire molecule produces quit a complex bonding model.

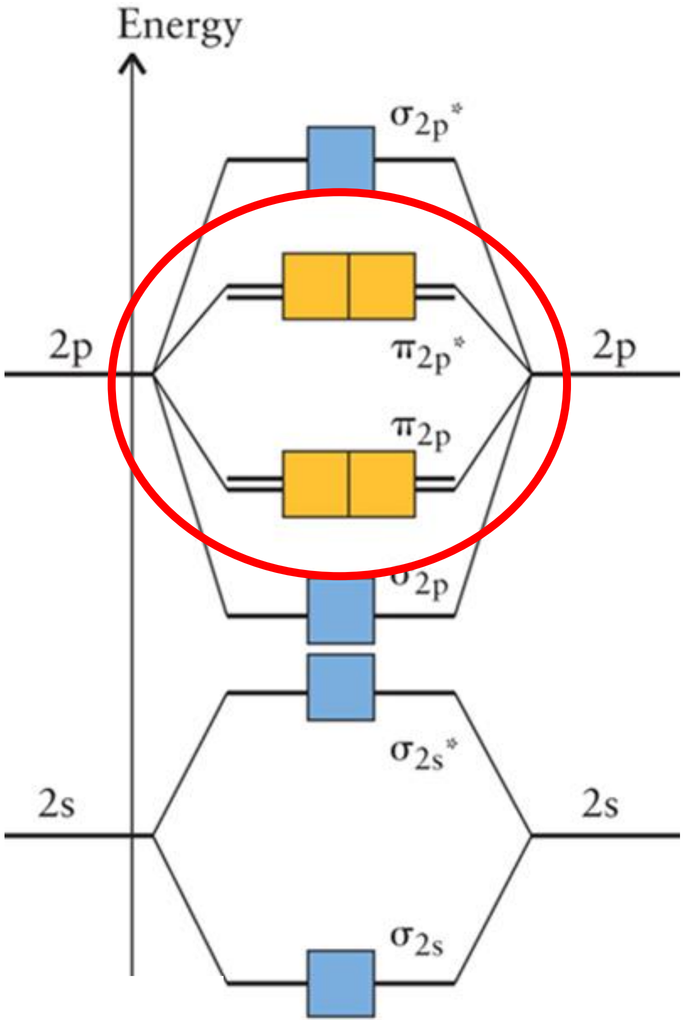
Orbitals in Polyatomic Molecules

Remember that in MO theory, for every bonding orbital there is an antibonding orbital.

Placing 2 e^- in a bonding orbital and 2 e^- in a antibonding orbital, results in a bond order = 0

Antibonding orbitals are destructive, pushing the bonds apart.



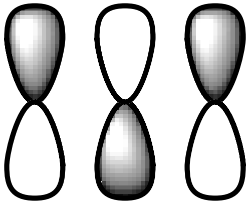


There is third type of molecular orbital is a **non-bonding orbital**.

Orbitals in Polyatomic Molecules

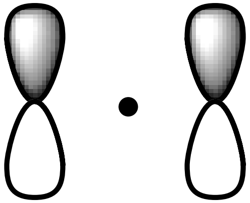
3 atoms have 3 molecular orbitals and 3 possible bonding modes.

2 nodes



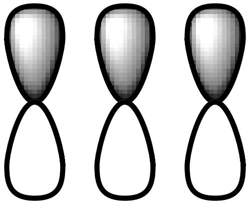
antibonding

1 nodes



nonbonding

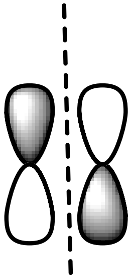
0 nodes



bonding

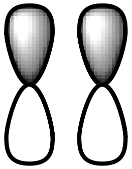
2 atoms have two molecular orbitals and 2 bonding possibilities

1 node



antibonding

0 nodes



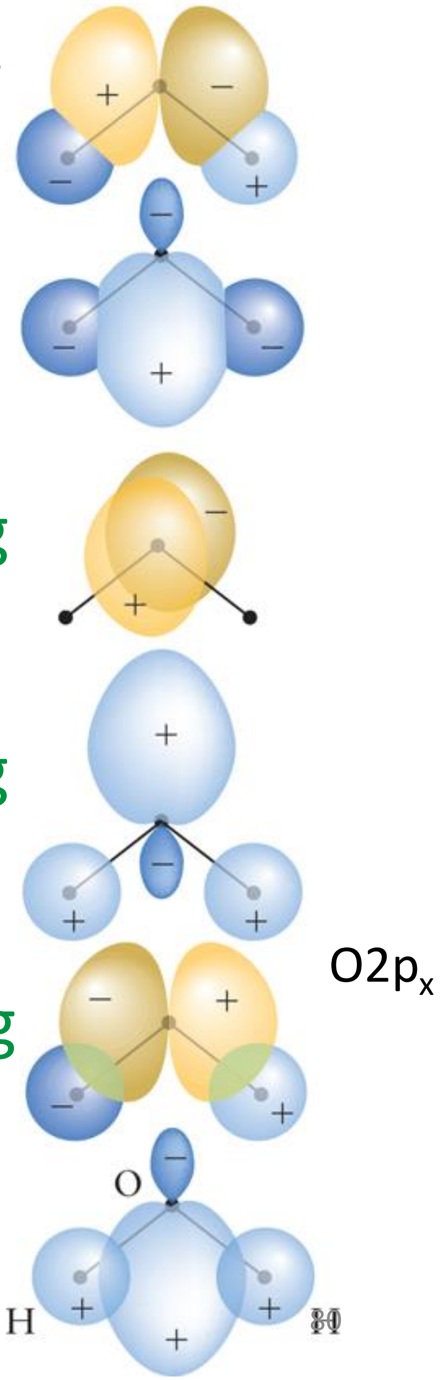
bonding

Water has 6 atomic orbitals (one O2*s*, three O2*p*, and two H1*s*).

2 of oxygen's orbitals are occupied with lone pairs which are purely O2p_x-orbital.

No nodes is fully bonding and contributes to holding all the atoms together.

One or more nodes is antibonding and pushes atoms apart.



antibonding
2 nodes

antibonding
2 nodes

nonbonding
0 nodes

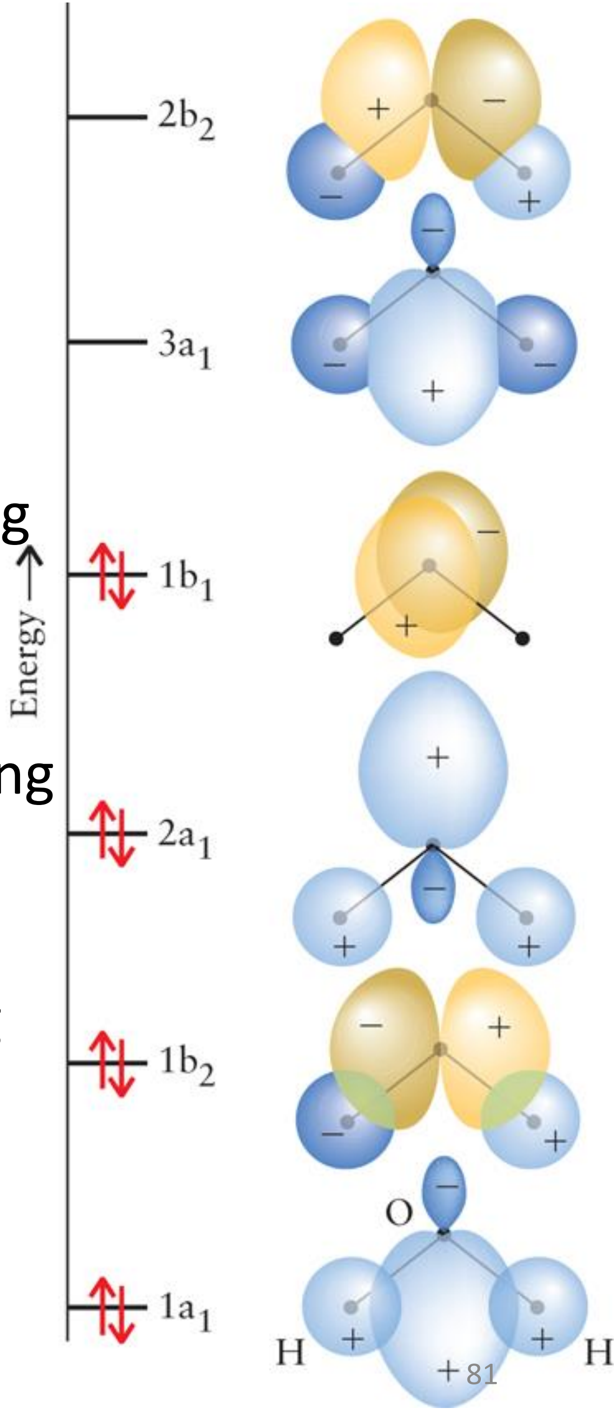
antibonding
2 nodes

nonbonding
0 nodes

bonding
0 nodes

What's **strikingly different** between this and Valance Bond theory is here eight electrons work in unison holding water together, the $1a_1$ contributes the most to the overall binding.

Valance bond theory is like taking an X-ray of your body and saying your foot is held there by a bone. MO theory would say the foot is held in place by your entire body including muscles, veins, skin, bones, etc.



nonbonding
0 nodes

antibonding
2 nodes

nonbonding
0 nodes

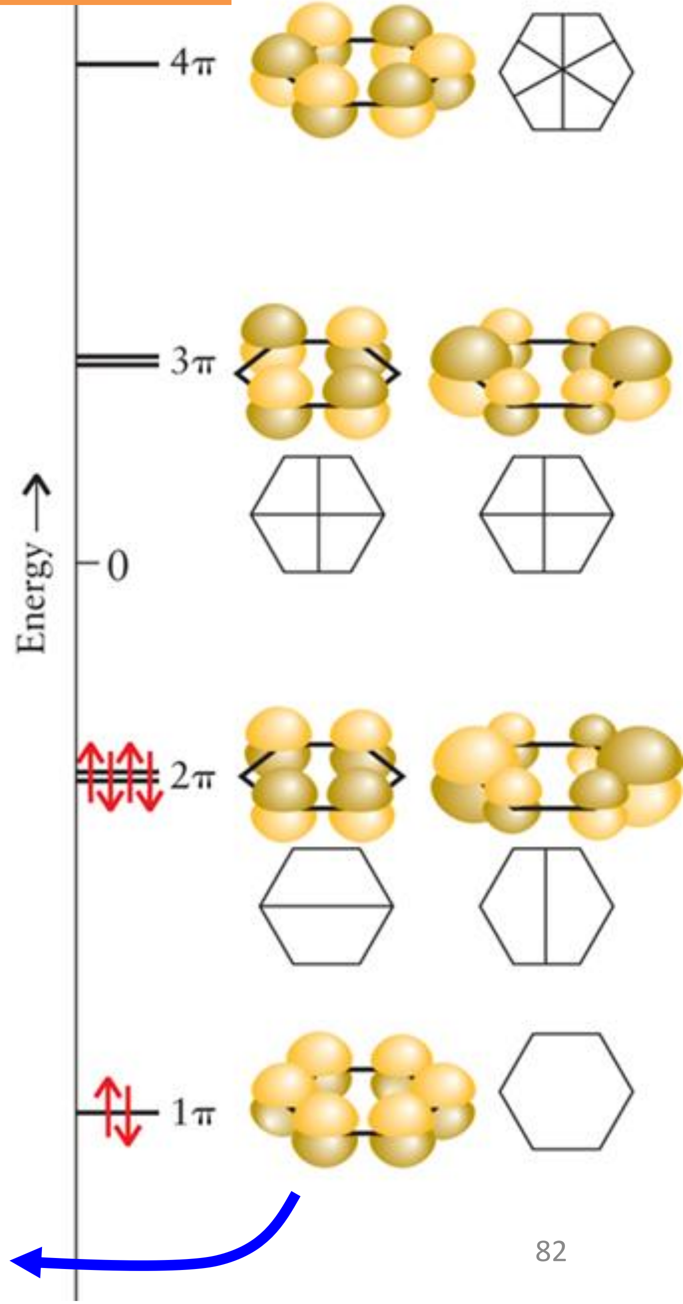
bonding
0 nodes

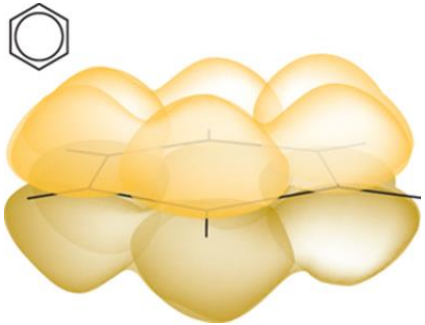
Benzene C_6H_6, is a polyatomic, aromatic compound.

Here are a few of benzene's **thirty** molecular orbital.

Below, there are no nodes, all orbitals are bonding, the e^-'s are free to move between orbitals; electrons on one side of the benzene ring migrate to the other side, by hopping to the adjacent orbitals, and so forth.

Benzene

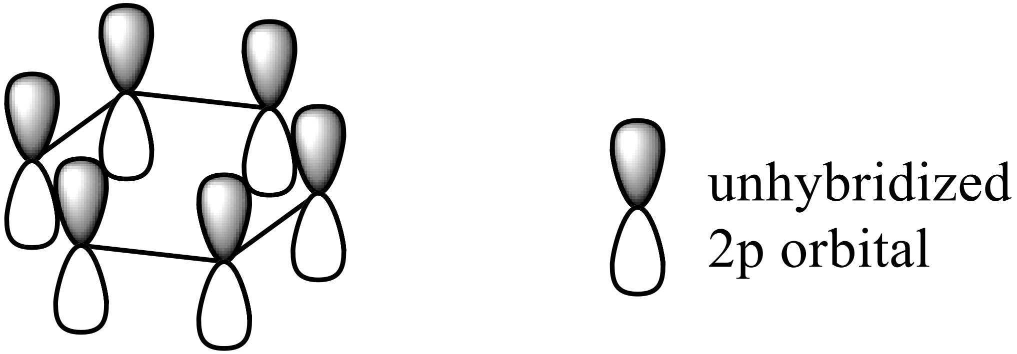




MO is different than VB theory

Aromatic or delocalization is such an important topic in chemistry, often to get the point across to students, it’s a common mistake to mix Valance bond theory with Molecular orbital theory.

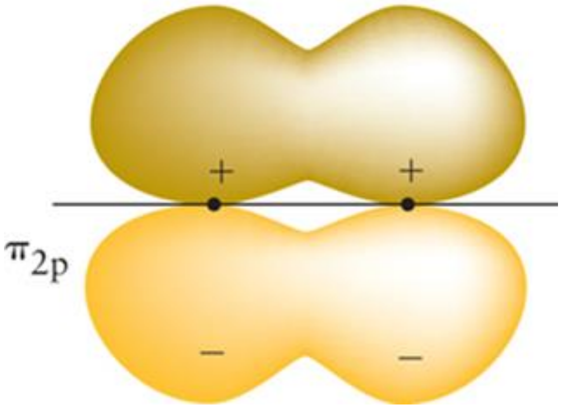
VB theory describes aromaticity using **individual** sp^2 **hybridized** orbitals.



MO is different than VB theory

MO theory is different. Granted, they look similar, it's important to remember they are different.

The big difference is seen in polyatomic molecules where **MO theory** talks about "***sets***" of orbitals, and the lowest energy set, is bonding, holds the molecule together with just 2 electrons.

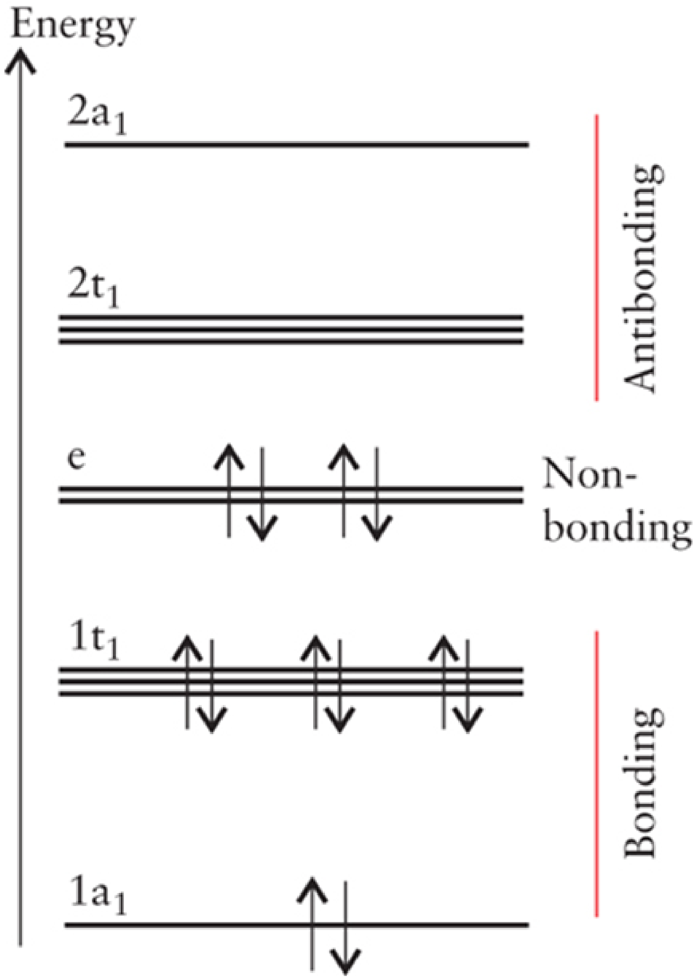


Hypervalent compounds

In valence bond theory, hybridized the central atom to sp^3d for PF_5 or sp^3d^2 for SF_6 for expanded octets.

However, the d-orbitals of *phosphorus* and *sulfur* lie at ***relatively high energies.*** The MO diagram for SF_6 **does not involve *d-orbitals***.

The 12 electrons occupy the lowest six orbitals, are either bonding or nonbonding, so bind all the atoms together without d-orbitals.

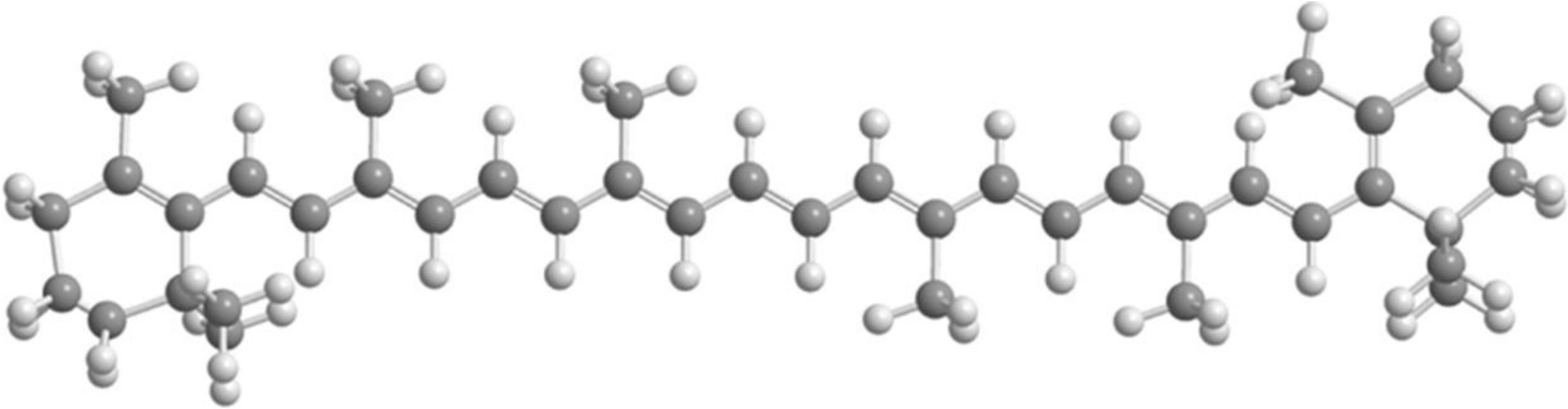


4 valence orbitals for S,
6 orbitals for F,
for a total of 10 atomic orbitals.

Colors

The presence of highly delocalized electrons in the large molecules found in the petals of flowers and in fruit and vegetables is largely responsible for their colors.

Because many carbon atoms contribute p-orbitals to the π-system of these molecules, there are **many** molecular orbitals.



β-carotene, has a **highly delocalized π-system**

Colors

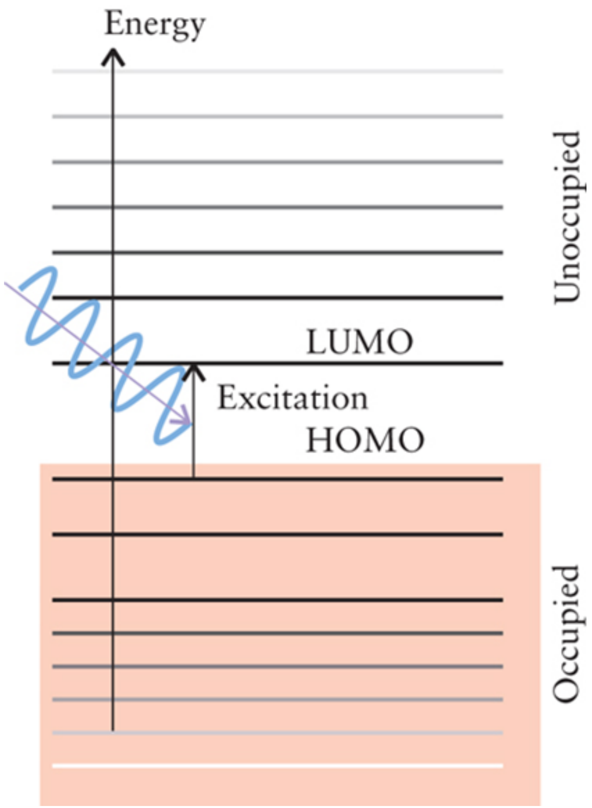
#AO's = #MO's so in large molecules there are many MO's

Electrons in a π-system are like a particle in a one-dimensional box.

Because the "box" is very large, the energy levels are very close together.

The highest occupied molecular orbital (HOMO) is very close in energy to the lowest unoccupied molecular orbital (LUMO).

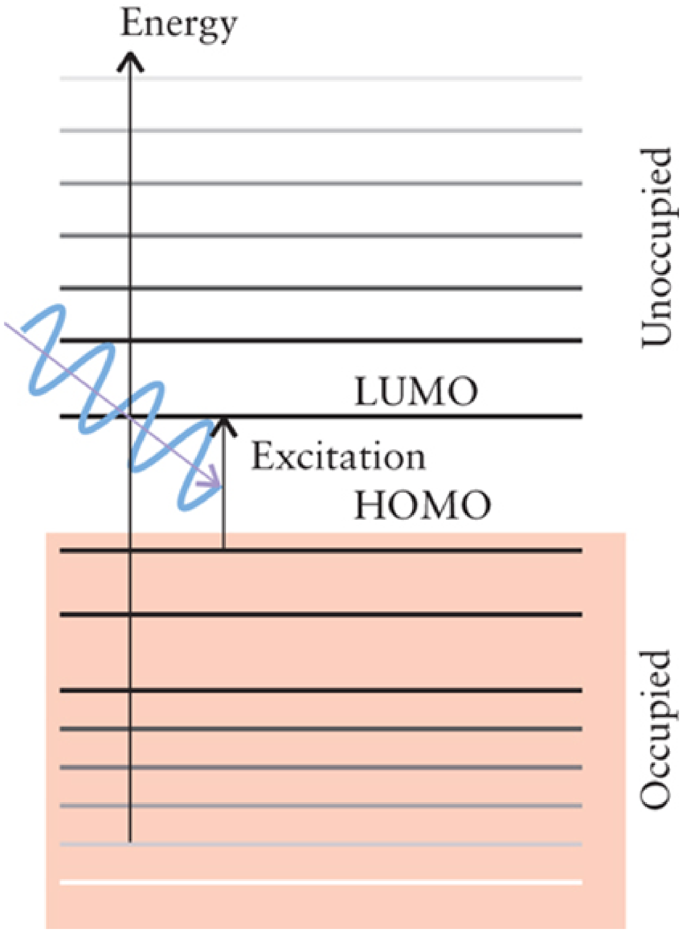
As a result, it takes very little energy to excite an electron from a HOMO to a LUMO.



Colors

Photons of visible light have enough energy to excite the electrons across this energy gap, and the absorption of these photons results in the colors that we perceive.

This is what happens for the red color of lycopene and orange in β-carotene.



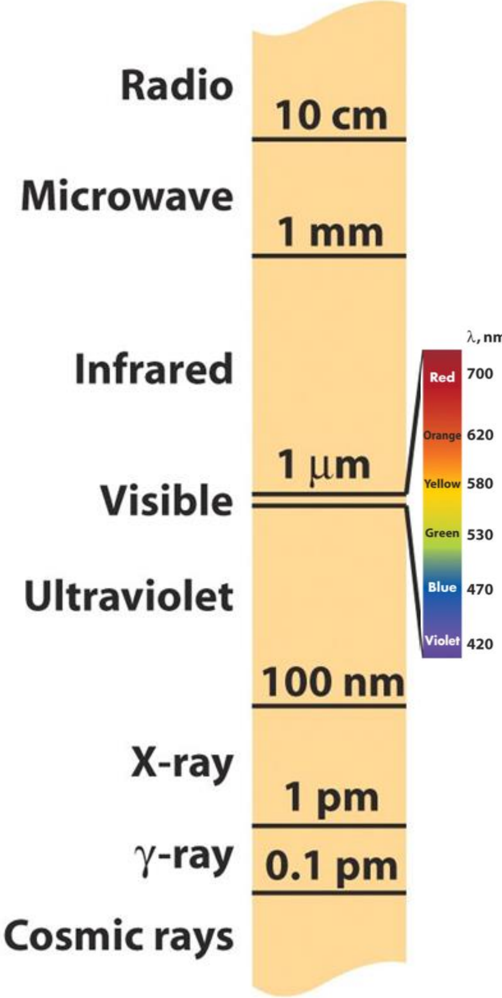
Ultraviolet and Visible Spectroscopy

All the colors of vegetation around us arise from the selective *absorption* and *reflection* of visible light.

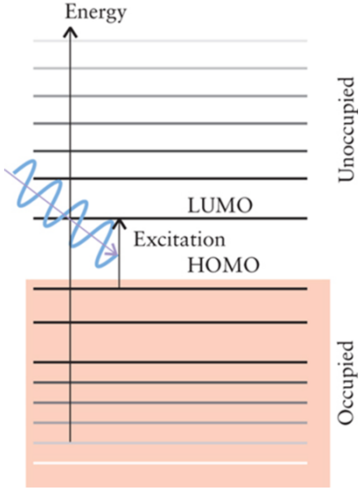
Our eyes are only sensitive to the visible spectrum of while honeybee’s can see in both the ultraviolet and visible electromagnetic radiation spectrum.

visible vision
λ in μm

X-ray vision
λ in pm

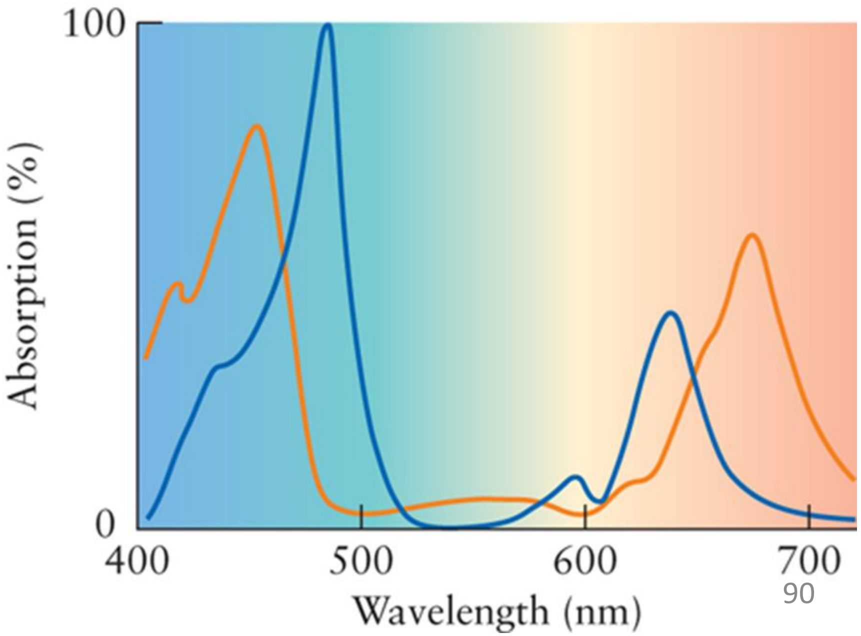


When electromagnetic radiation falls on a molecule, the electrons in the molecule can be excited to a higher energy state.



If an electron "absorbs" incoming radiation, thereby becoming excited, we refer to this as an **absorption**.

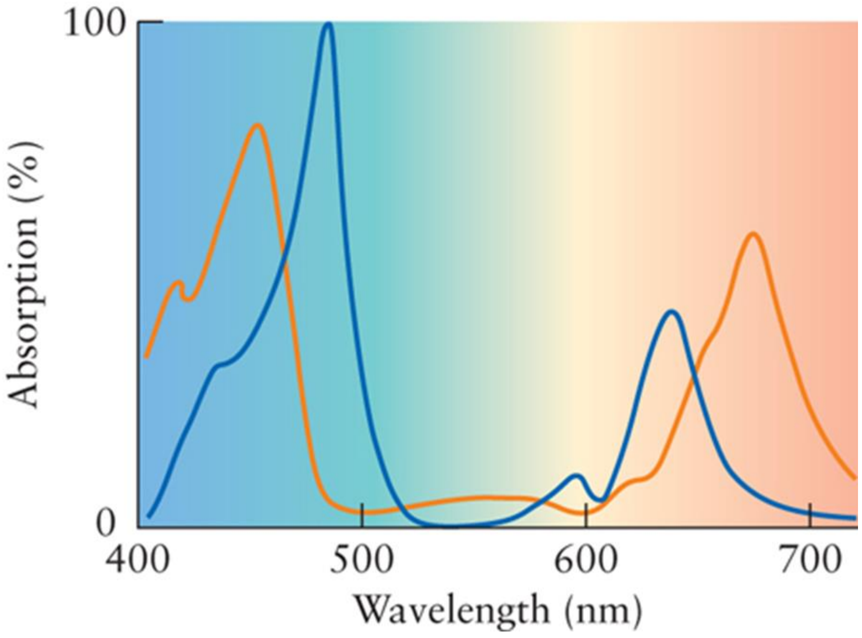
We can monitor the frequencies absorbed which gives us information about the electronic energy levels of molecules.



The **absorption spectrum** of two types of chlorophyll. Chlorophyll a is shown in red, and chlorophyll b in blue.

We notice both chlorophyll absorb **blue** and **red** wavelengths of light.

The color **not absorbed**: **Green**. The reason why leaves look green.



Chromophores

One feature of visible and ultraviolet spectra is the ability to identify special characteristic of molecules, for instance the different types of bonds present.

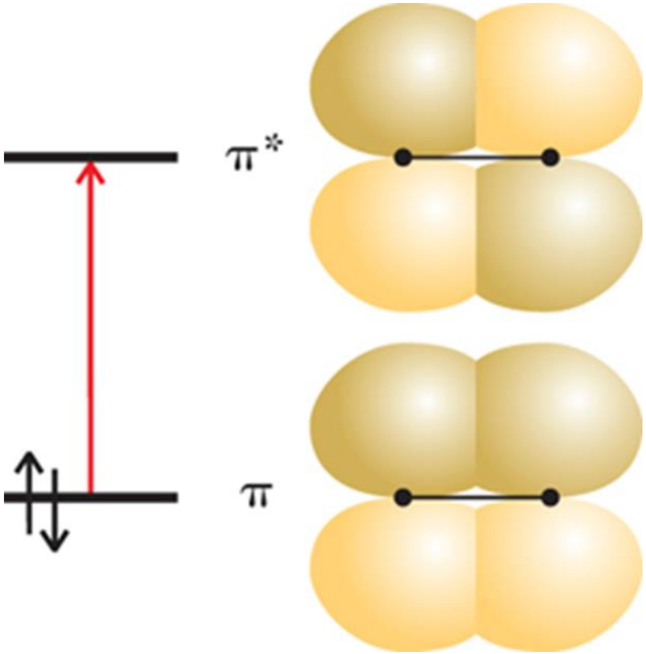
Some groups of atoms are called **chromophores**, from the Greek words for "color bringer. "

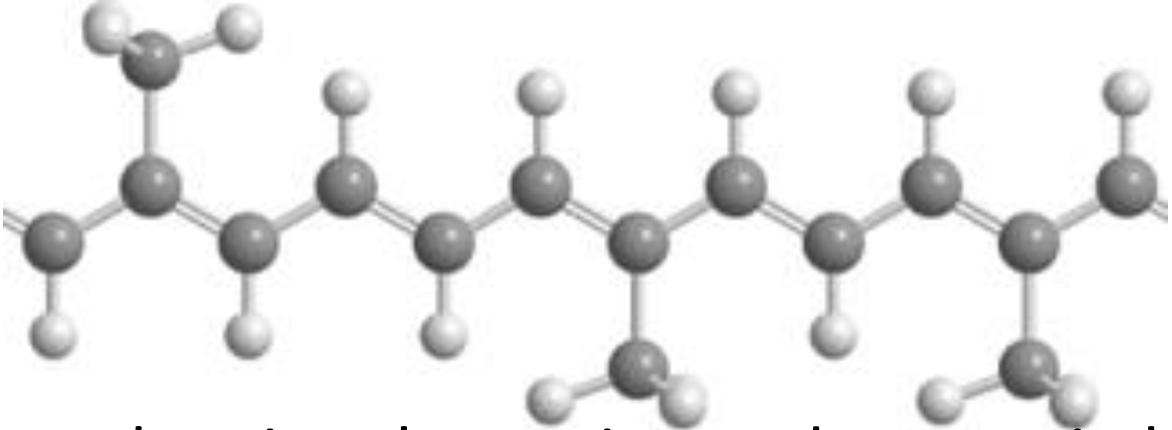
An important chromophore is a carbon-carbon double bond because it has an electronic transition (absorption) that takes place near 160 nm, close to the UV spectrum.

Chromophores

Excitation takes place, and is known as a **π to π*** transition.

These orbitals are part of the "**conjugated** "double bonding occurs in the compound carotene which is partly responsible for the color of carrots, mangoes, and persimmons.

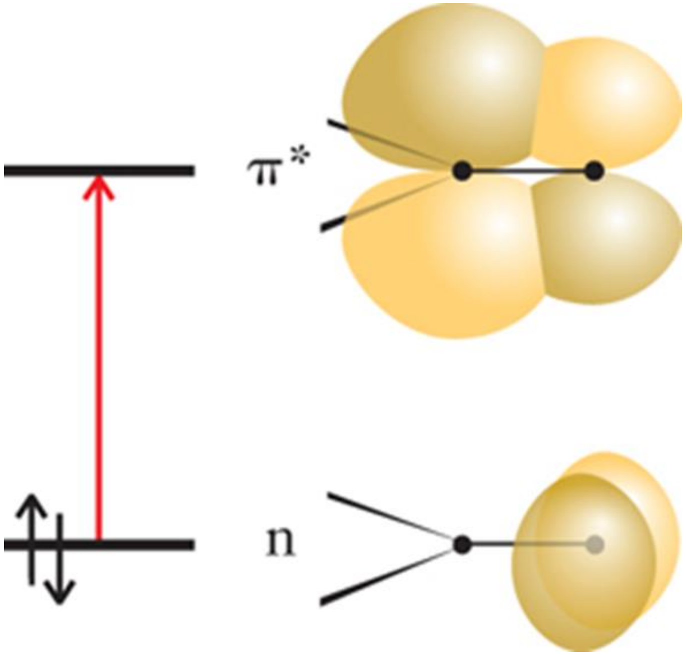




A portion showing the conjugated system in lycopene

The carbonyl group, >C=O, is another chromophore and absorbs at about 280 nm.

The lone-pair electron on the oxygen atom, a "nonbonding" electron is excited into the empty anti bonding π*-orbital of the C=O double bond. This transition is therefore called an **n-π*** (n to pi star) transition.



A d-metal ion may also be responsible for color. Two types of transitions may be involved.

In one, called a **d-to-d transition**, an electron is excited from a d-orbital of one energy to a d-orbital of higher energy.

In a second type of transition involving d-orbitals, called a **charge-transfer** transition, electrons migrate from the atoms attached to the metal into the metals d-orbitals or vice versa. This transfer of charge can result in very intense absorption; it is responsible, for instance, for the deep purple of permanganate ions, MnO_4^- .