Chemical Bonding

What holds things together?

100% covalente

100% iônica

Ligações

A : B

A : B

A^{+} $:B^{-}$

ΔEN crescente

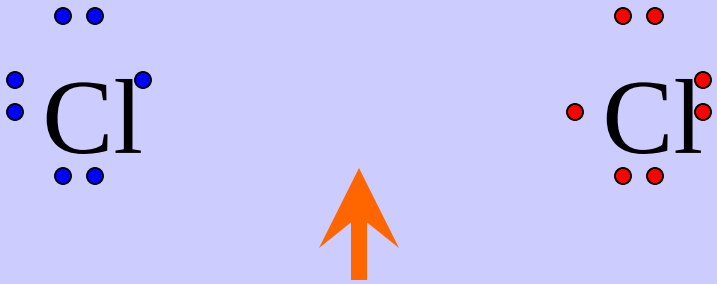
Transferência

polaridade crescente

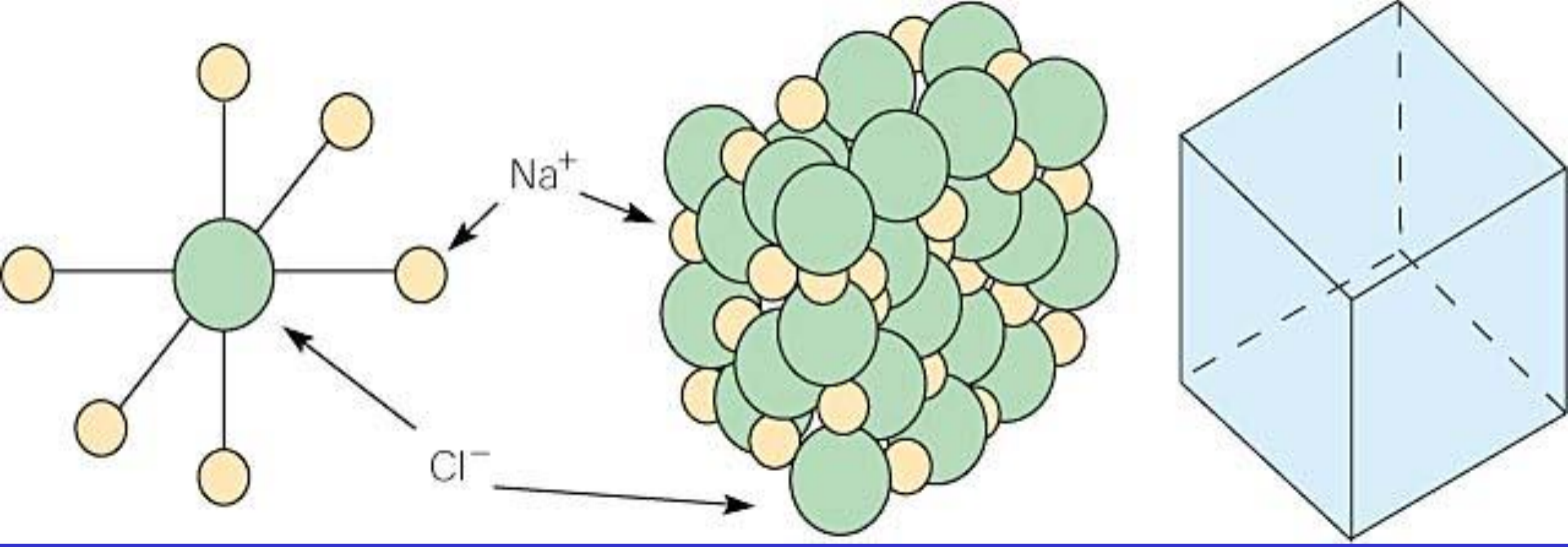
NaCl This is the formation of an **ionic bond**.

electron transfer
and the formation of ions

Cl_2 This is the formation of a **covalent bond**.



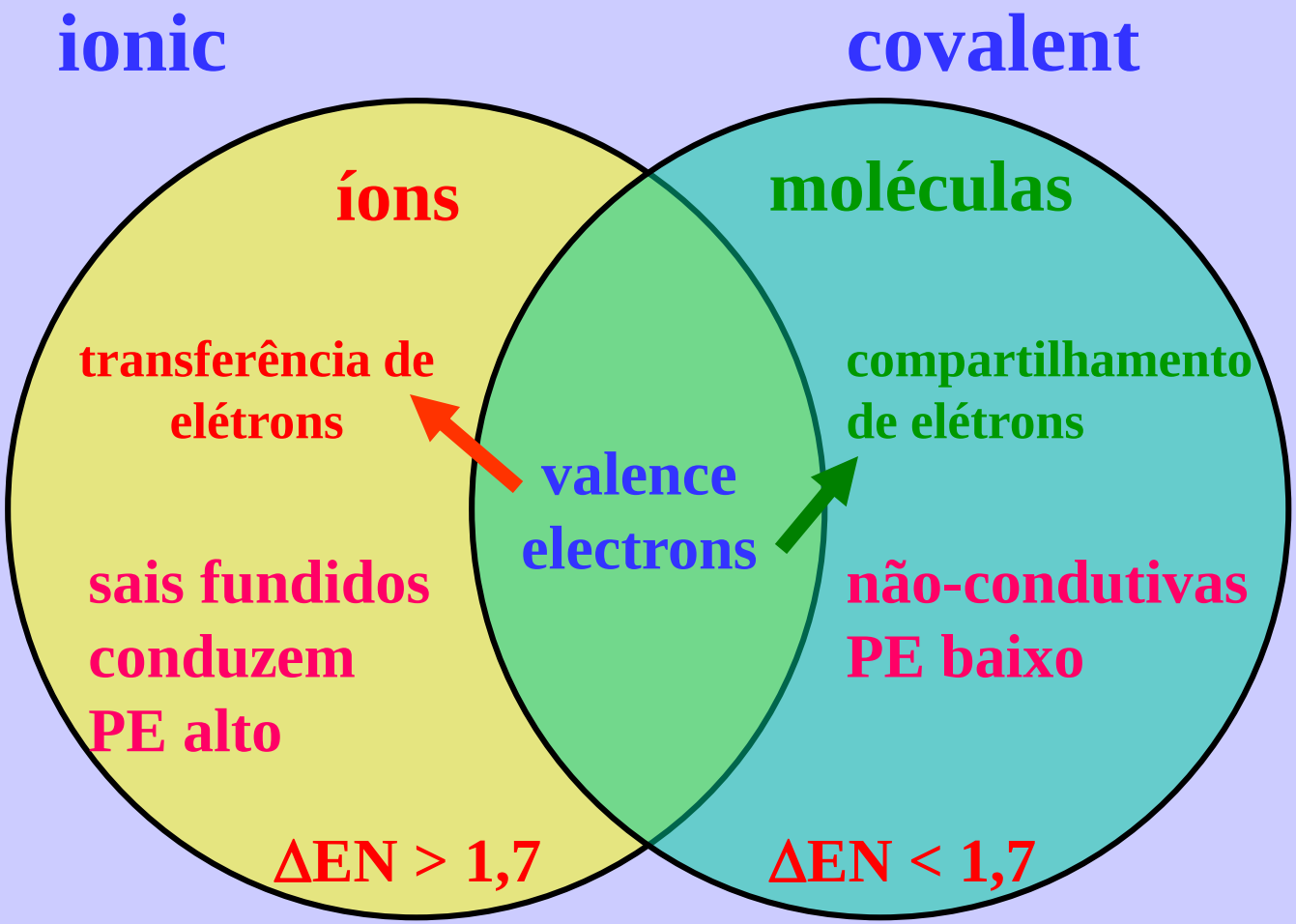
sharing of a pair of electrons
and the formation of molecules



- Sodium chloride crystals are composed of sodium and chlorine ions held together by electrostatic attraction. Each sodium ion is surrounded by six chlorine ions, and each chlorine ion is surrounded by six sodium ions. A crystal builds up like this, giving the sodium chloride crystal a cubic structure.

- You can clearly see the cubic structure of these ordinary table salt crystals because they have been magnified about ten times.

Comparison of Bonding Types



Bonding

Can we explain the melting point behavior across a period?

- involves the valence electrons or outermost shell (or highest shell) electrons
- for group A elements - the group number tells how many valence electrons

How many valence electrons on N?

Group 5A → 5 valence electrons

Let's examine the melting point of compounds across two periods.

Qual é a tendência?

Conductivity - high **Conductivity - low**

Chlorides of Period 2							
compound	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	Cl_2
melting point	610	415	-107	-23	-40	-121	-102
Chlorides of Period 3							
compound	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_6	Cl_2
melting point	801	714	193	-69	-112	-51	-102

high low

CRC *Handbook of Chemistry and Physics*, 1995

Eletronegatividade

The electronegativity difference - $\Delta EN = EN_{alta} - EN_{baixa}$

Cloretos do Período 2							
composto	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	Cl_2
ΔEN	2.2	1.6	1.1	0.6	0	0.6	0
Cloretos do Período 3							
composto	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_6	Cl_2
ΔEN	2.2	1.9	1.6	1.3	1.0	0.6	0

diferença grande

diferença pequena

Using electronegativities to determine bond type

$\Delta EN > 1.7$ ionic bond - transfer

$\Delta EN < 1.7$ covalent bond - sharing

O fundamento físico da energia de rede cristalina é a atração eletrostática entre cátions e ânions:

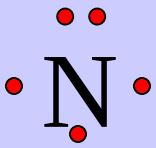
$$E = k \frac{Q_{cation} Q_{anion}}{r}$$

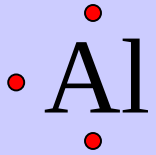
onde r representa a distância entre os íons.

Quanto maior a energia de rede cristalina, maiores os pontos de fusão e de ebulição do composto.

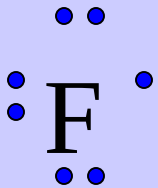
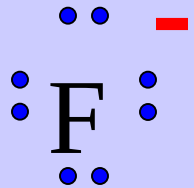
Bonding…

- Lewis dot structures show the valence electrons around at atom and for most molecules and compounds a complete octet for the elements



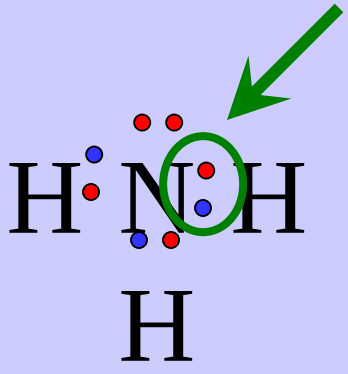


- most monatomic ions have an electron configuration of noble gases

$1s^2\underline{2s^2 2p^5}$  + e^- →  $1s^2\underline{2s^2 2p^6}$ Ne

Some more sharing examples

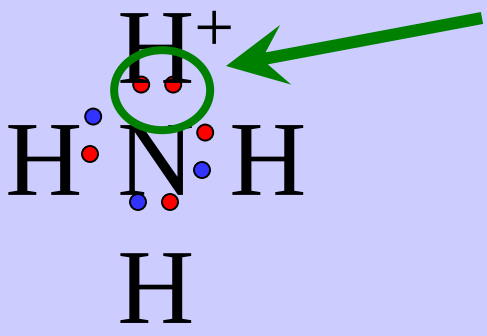
NH_3



normal covalent bond (each atom supplies an electron)

NH_4^+

$NH_3 + H^+ \rightarrow NH_4^+$

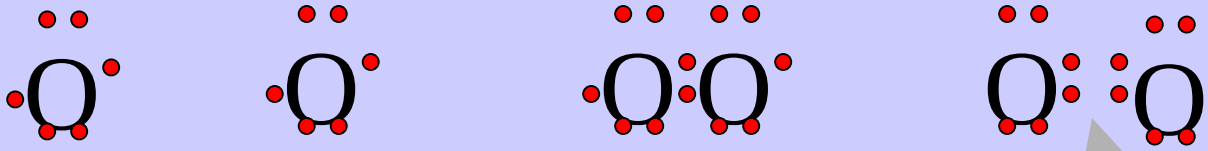


coordinate covalent bond (the pair of electrons from the same atom)

More sharing examples

O_2

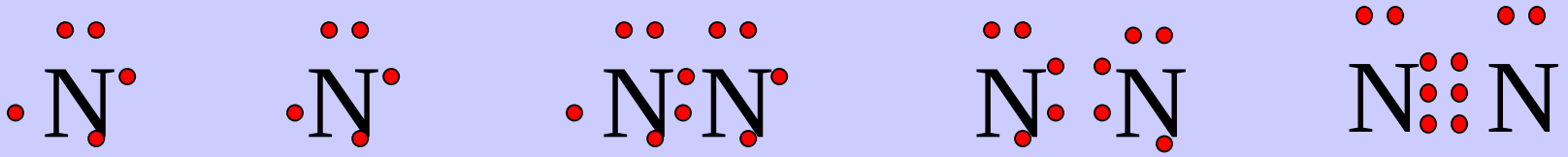
Share until octet is complete.



double bond (2 pairs)

N_2

octet complete



triple bond (3 pairs)

Is the sharing of electrons in molecules always equal?

non-polar bond

X : Y ΔEN = 0

Which element is more electronegative?

$EN_Y > EN_X$

X : Y ΔEN = 0.3

X : Y ΔEN = 0.6

polar bond

X : Y ΔEN = 0.9

$0 < EN < 1.7$

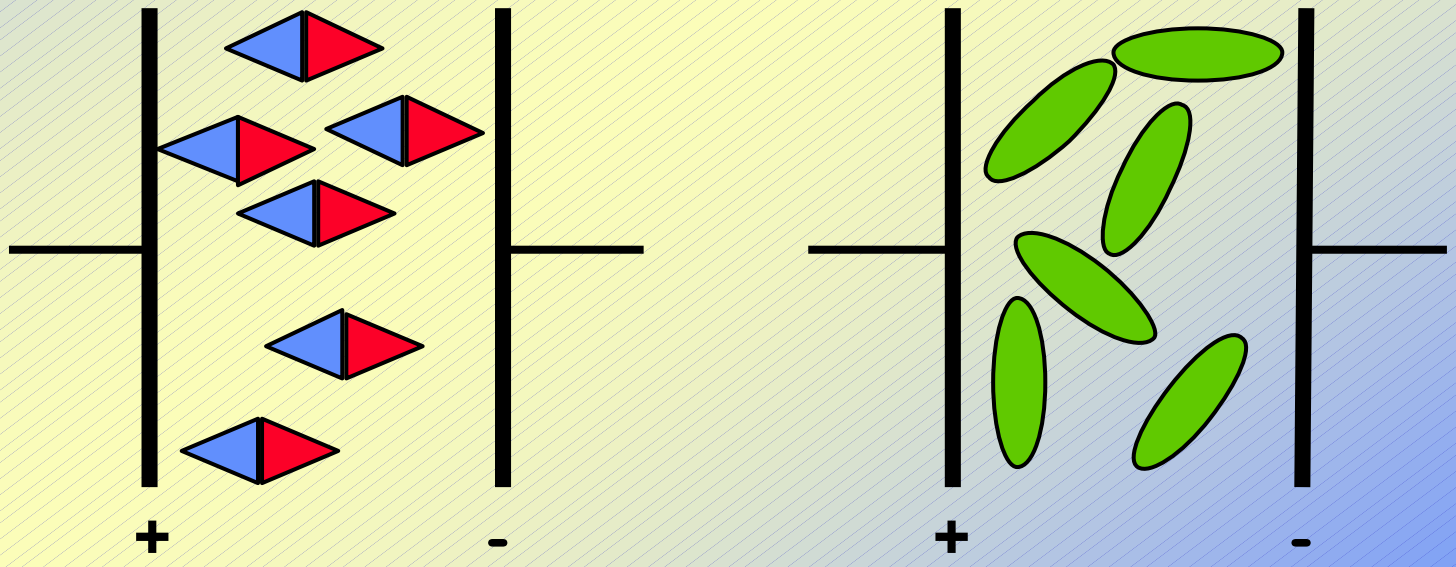
X : Y ΔEN = 1.2

increasing polarity of bond

Direction of electron migration

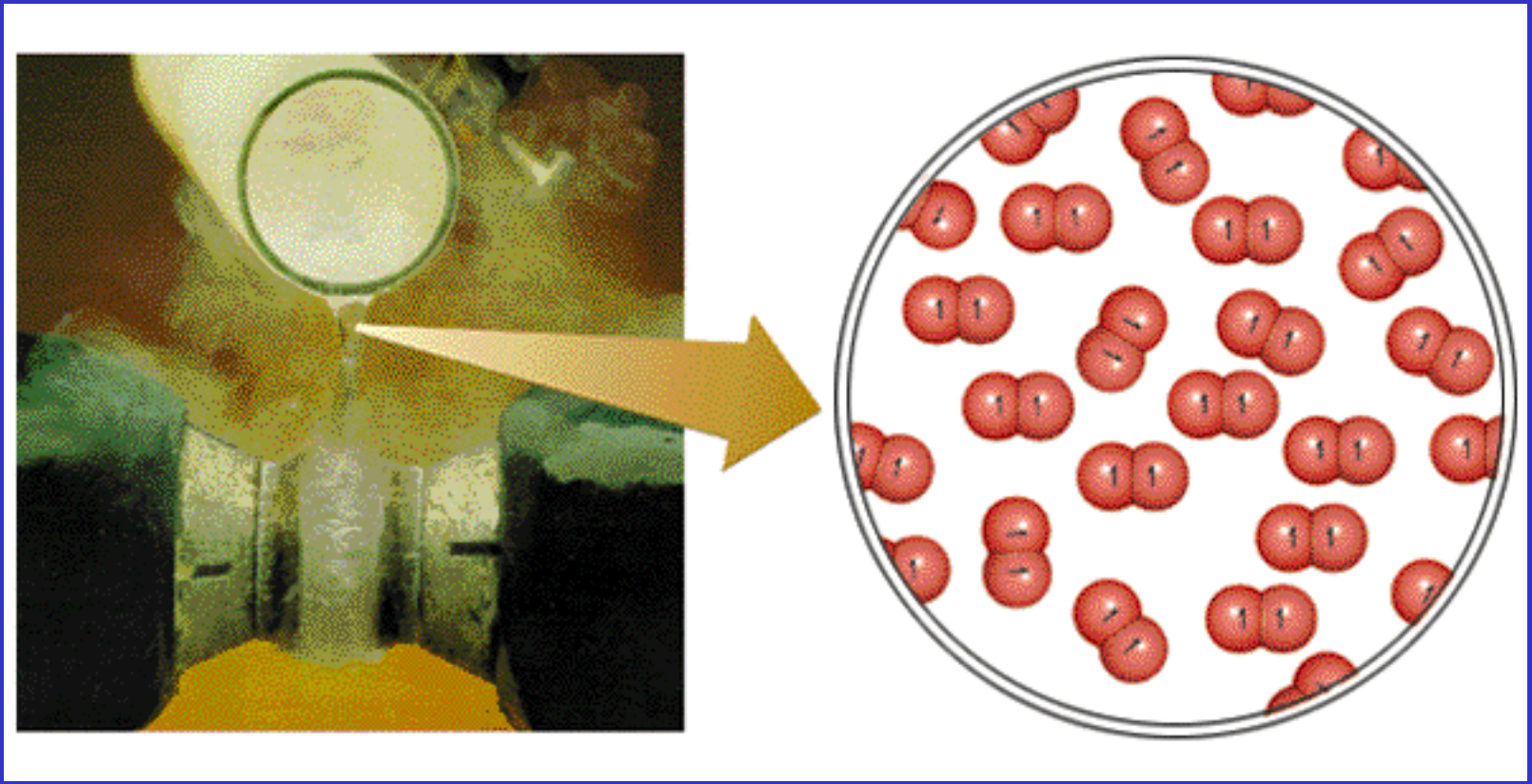
Dipole moment

This property can be measured by placing molecules in an electrical field. Polar molecules will align when The field is on. Nonpolar molecules will not.



Second-Row Diatomic Molecules

Electron Configurations and Molecular Properties



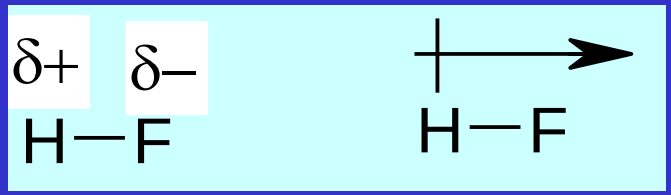
Polar and nonpolar molecules

Polarity is an important property of molecules.

- It affects physical properties such as melting point, boiling point and solubility.
- Chemical properties also depend on polarity.
- **Dipole moment**, μ, is a quantitative measure of the polarity of a molecule.

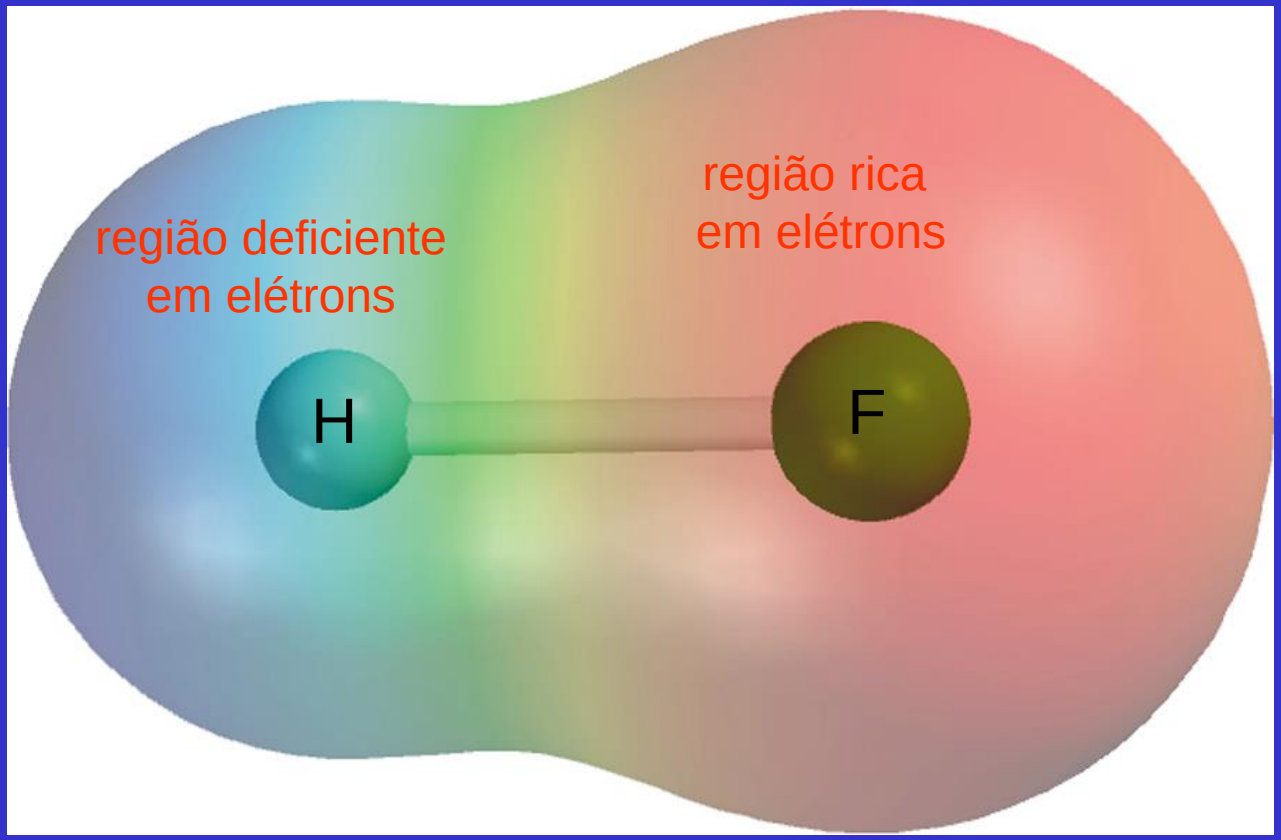
Polarity of Molecules

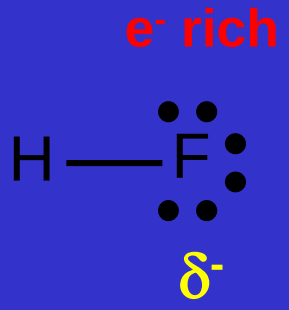
- To determine if a molecule is polar, you need to know two things:
  - polarity of the bonds in a molecule
  - how the bonds are arranged
- A molecule is considered polar if its center of negative and positive charge do not coincide.



- Polar molecules have a dipole (a vector quantity)
- If these dipoles act equally and in opposition to each other, the dipoles cancel-out and the molecule is considered nonpolar.

Ligação covalente polar ou ligação polar *é uma ligação covalente que apresenta maior densidade eletrônica ao redor de um dos dois átomos.*





Polarity of Molecules

Dipole Moments of Polyatomic Molecules

Two simple rules to help determine molecular polarity (most of the time)

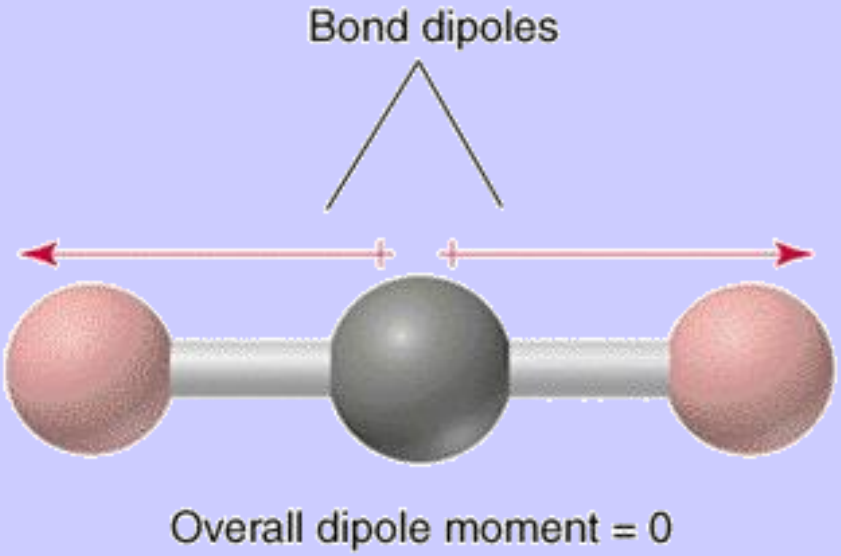
- **If there are lone pairs on the central atom – the molecule is polar.**
- **If there are more than one type of bonds on the central atom – the molecule is polar.**

Polarity of Molecules

Dipole Moments of Polyatomic Molecules

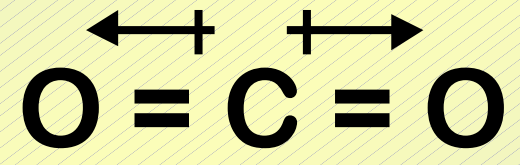
Example:

CO_2, each C-O dipole is canceled because the molecule is linear.



Polar and nonpolar molecules

Most bonds between atoms of dissimilar elements in a molecule are polar. That does not mean that the molecule will be polar.



Electronegativities:
Oxygen = 3.5
Carbon = 2.5
Difference 1.0
(polar bond)

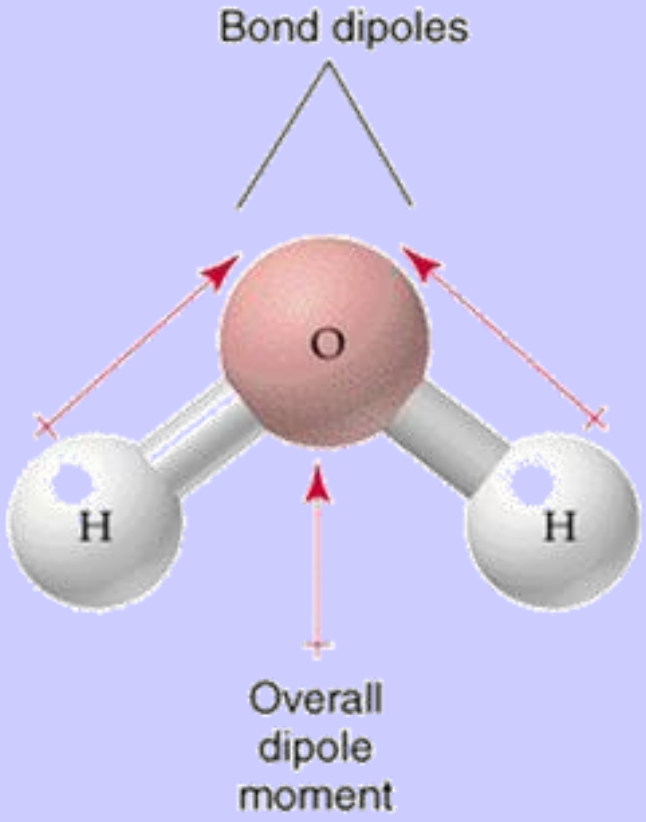
The electronegativity values
Show that the C-O bond would be polar with electrons
Being pulled towards the oxygens. However, due to
The geometry, the pull happens in equal and opposite directions.

Polarity of Molecules

Dipole Moments of Polyatomic Molecules

Example:

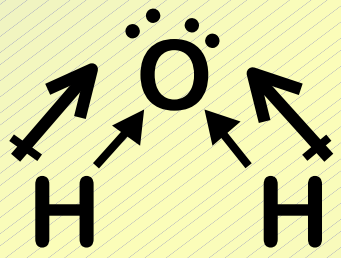
H_2O, the H-O dipoles do not cancel because the molecule is bent.



Polar and nonpolar molecules

For a molecule to be polar, the effects of bond polaritymust not cancel out.

One way is to have a geometry that is not symmetrical like in water.

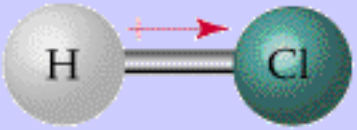


Electronegativity difference = 1.3

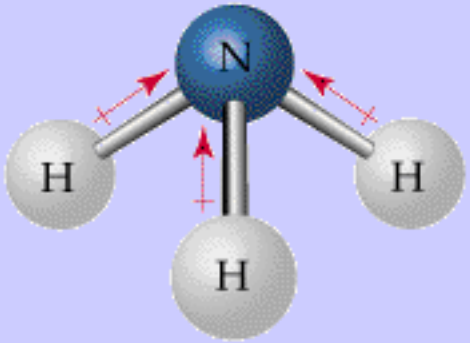
Here, the effects of the polar bonds do not canceled so the molecule is polar.

Polarity of Molecules

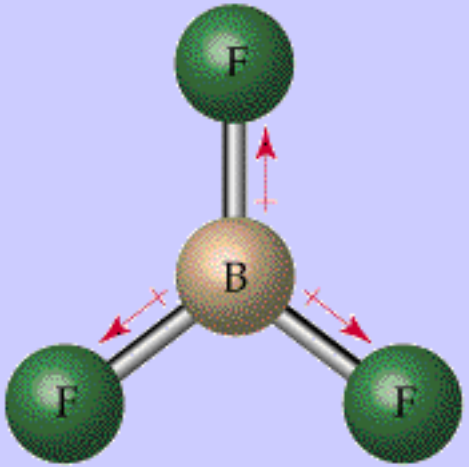
Dipole Moments of Polyatomic Molecules



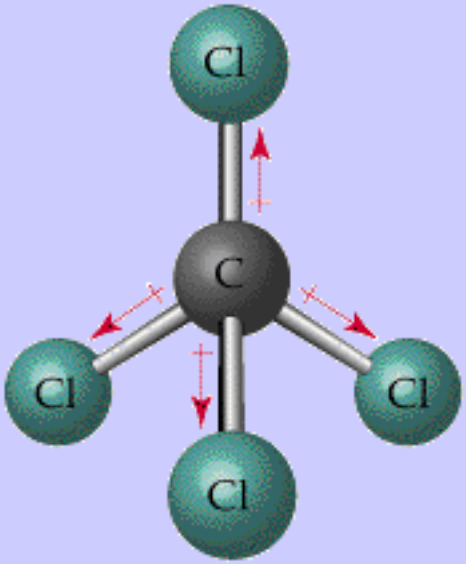
Polar



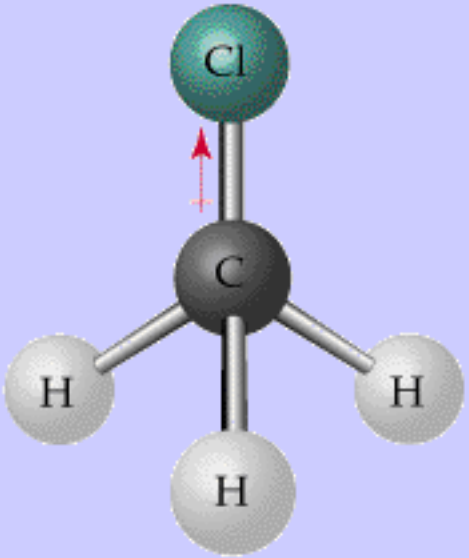
Polar



Nonpolar



Nonpolar



Polar

Polar and nonpolar molecules

A molecule is nonpolar if the central atom is symmetrically substituted by identical atoms.

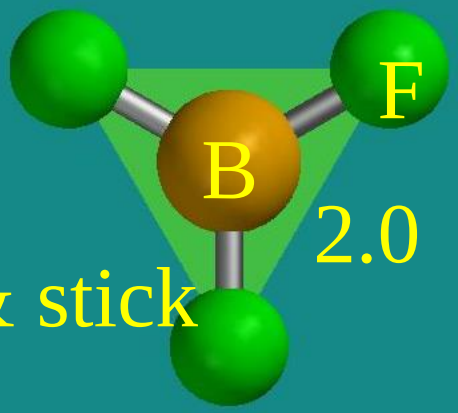
CO_2, CH_4 , CCl_4

A molecule will be polar if the geometry is not symmetrical.

H_2O, NH_3, CH_2Cl_2

The degree of polarity is a function of the number and type of polar bonds as well as the geometry.

BF_3 – a planar molecule

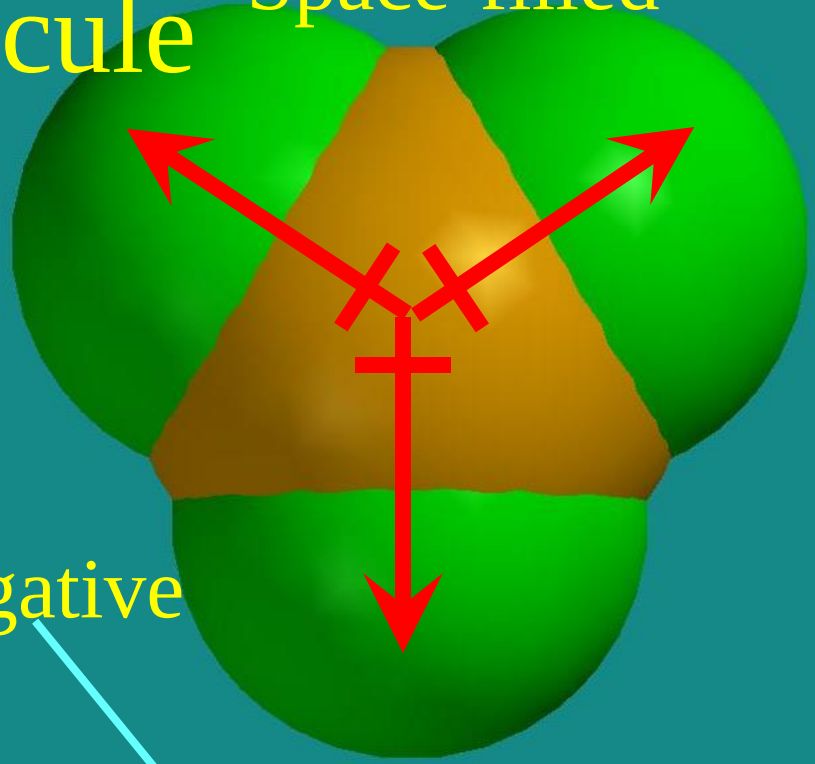


4.0

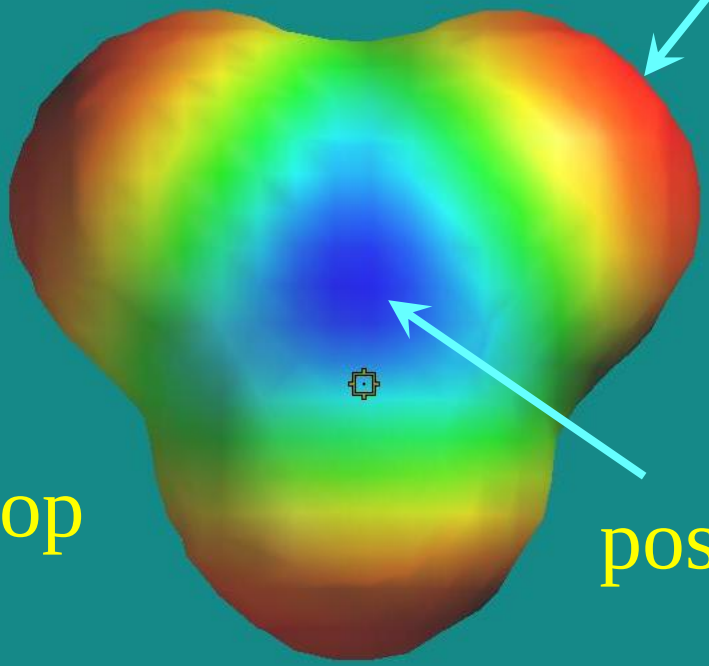
2.0

Ball & stick

Space-filled

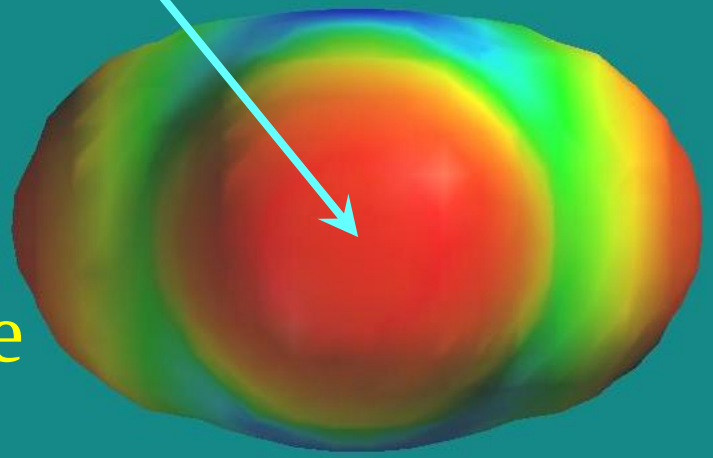


negative



positive

top

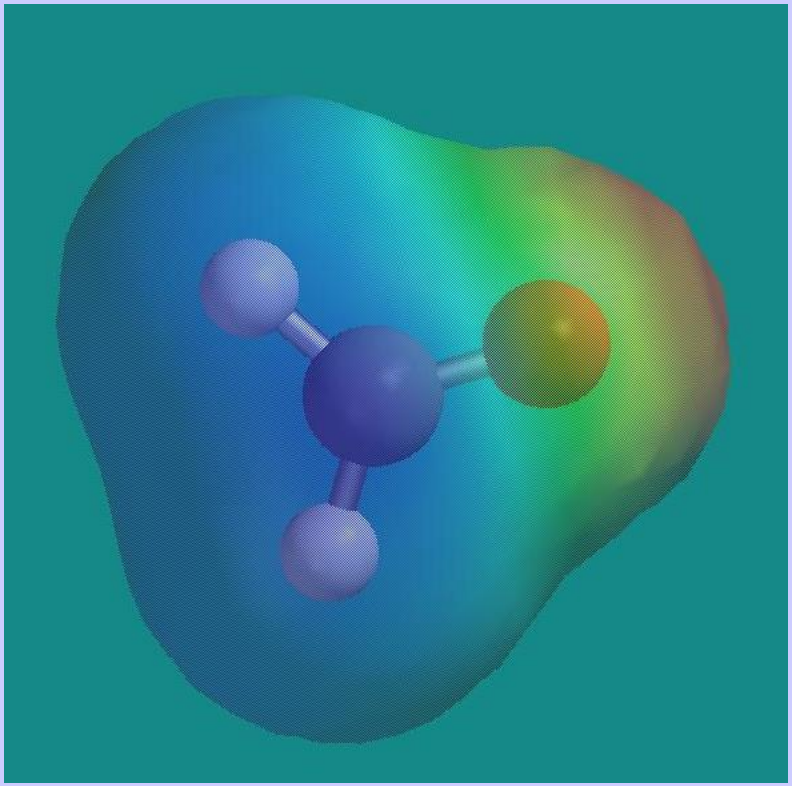


side

Electrostatic potential maps

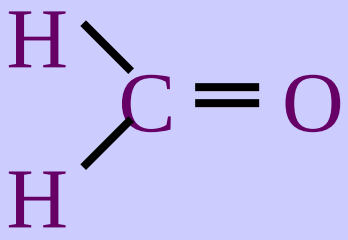
Spartan ‘02

Here is the electrostatic potential map for H_2CO.



blue – positive red - negative

Show the electron migration on this planar molecule.



How is this molecule different than BF_3?

Geometrias de moléculas e de poli-íons

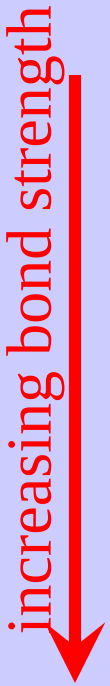
- Molecules and polyatomic ions are not all ‘flat’ structures.
- Many have a three dimensional arrangement that helps account for their various chemical and physical properties.
- Several models are used to help predict and describe the geometries for these species.
- One model is called the Valence Shell Electron Pair Repulsion model (VSEPR)

Bond Energy

Is breaking a bond an endothermic or exothermic process?

$$X_2 + \text{energy} \rightarrow X + X$$

F_2	single bond	BE = 142 kJ/mole
O_2	double bond	BE = 494
N_2	triple bond	BE = 942



http://wulfenite.fandm.edu/Data%20/Table_6.html

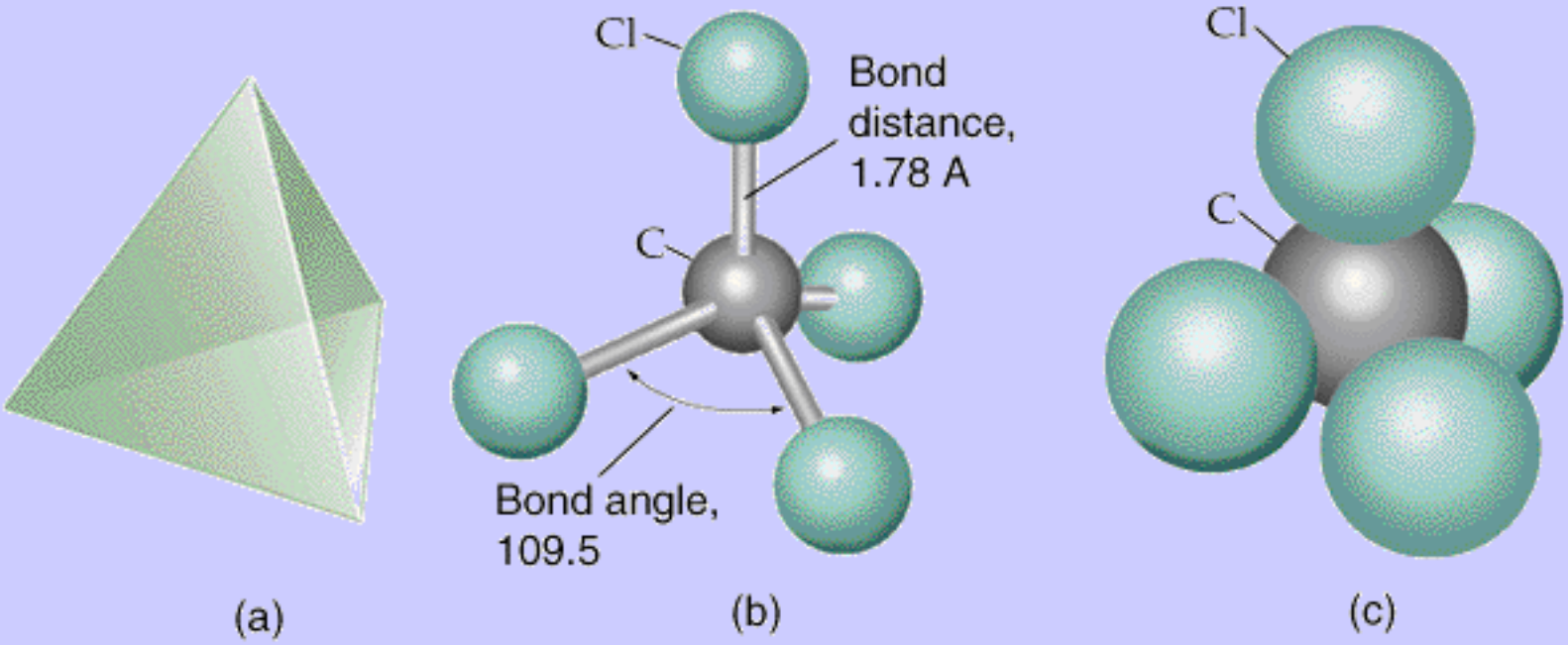
Molecular Shapes

Molecular Shapes are determined by:

***Bond Distance* – Distance between the nuclei of two bonded atoms along a straight line.**

***Bond Angle* – The angle between any two bonds containing a common atom.**

Molecular Shapes



Molecular Shapes

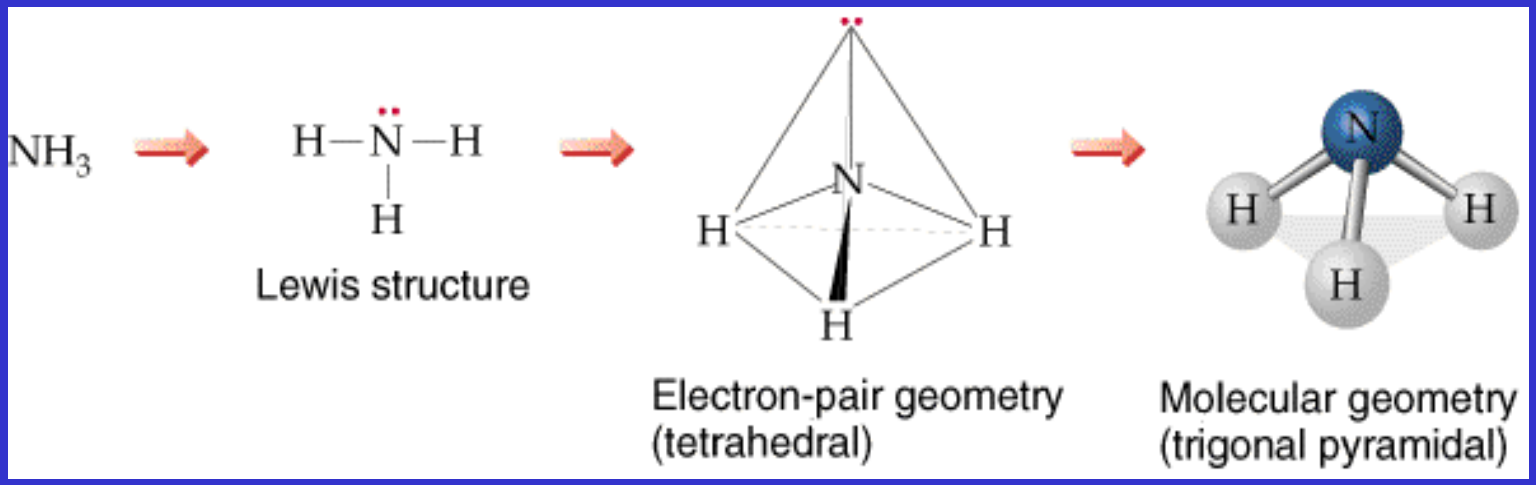
Valence Shell Electron Pair Repulsion Theory (VSEPR)

- **VSEPR theory is based on the idea that electrostatic repulsion of the electrons are reduced to a minimum when the various regions of high electron density assume positions as far apart as possible.**

The VSEPR Model

Predicting Molecular Geometries

- draw the Lewis structure
- count the total number of bonding regions and lone pairs around the central atom
- arrange the bonding regions and lone pairs in one of the standard geometries to minimize e^--e^- repulsion
- multiple bounds count as a single bonding region



Molecular Shapes

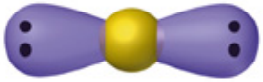
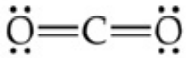
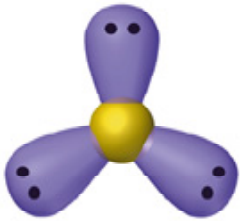
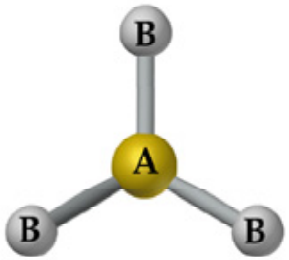
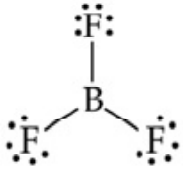
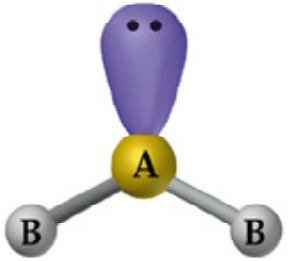
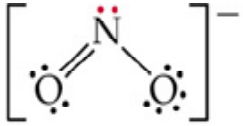
Valence Shell Electron Pair Repulsion Theory (VSEPR)

Common configurations for saturated molecules.

Regions of Density	Shape	Bond Angle
2 (AX_2)	Linear	180°
3 (AX_3)	Trigonal Planar	120°
4 (AX_4)	Tetrahedral	109.5°
5 (AX_5)	Trigonal Bipyramidal	90° / 120°
6 (AX_6)	Octahedral	90°

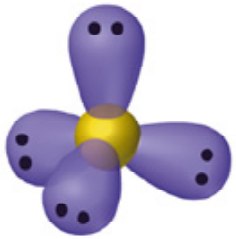
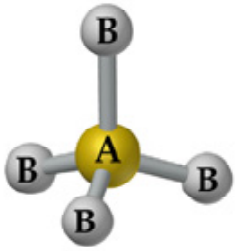
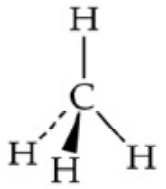
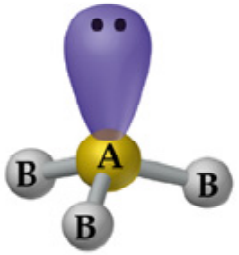
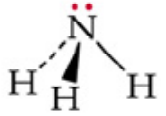
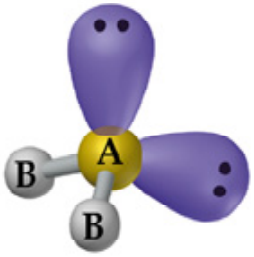
The VSEPR Model

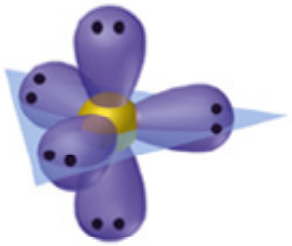
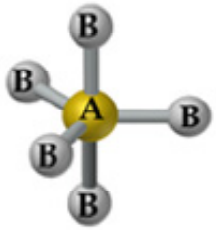
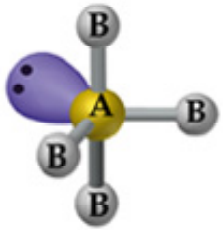
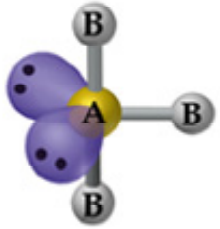
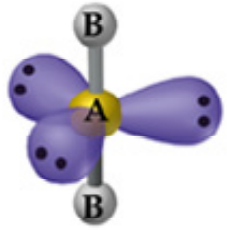
Predicting Molecular Geometries

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

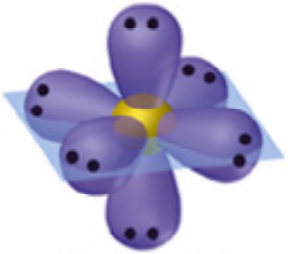
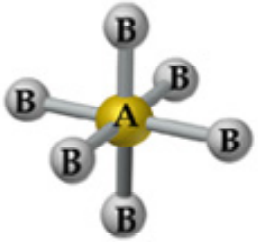
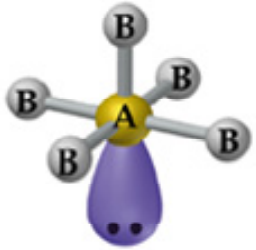
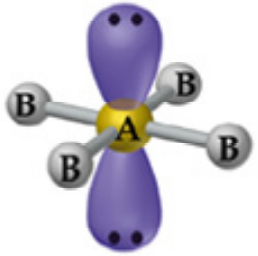
The VSEPR Model

Predicting Molecular Geometries

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

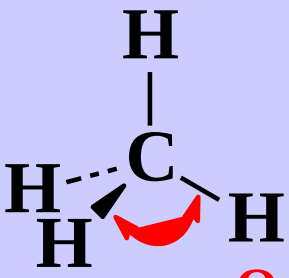
The VSEPR Model : Molecules with Expanded Valence Shells

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

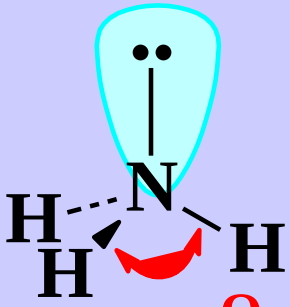
The VSEPR Model

Factors Effecting Bond Angles

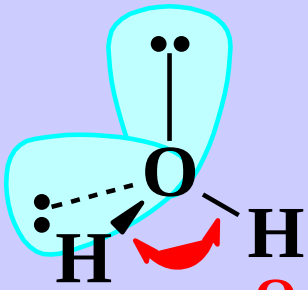
- **The bond angle decreases as the number of lone pairs on the central atom increases.**



109.5°



107°



104.5°

The VSEPR Model

Factors Effecting Bond Angles

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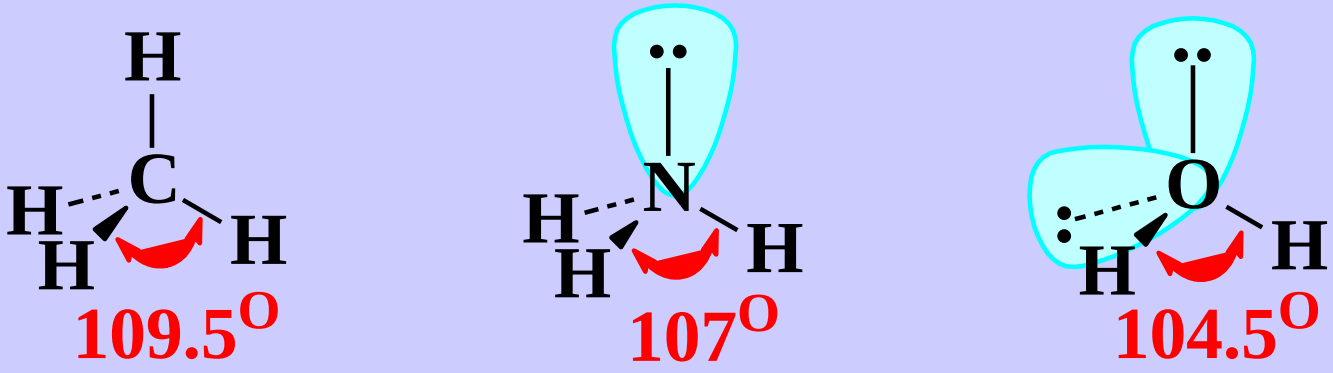
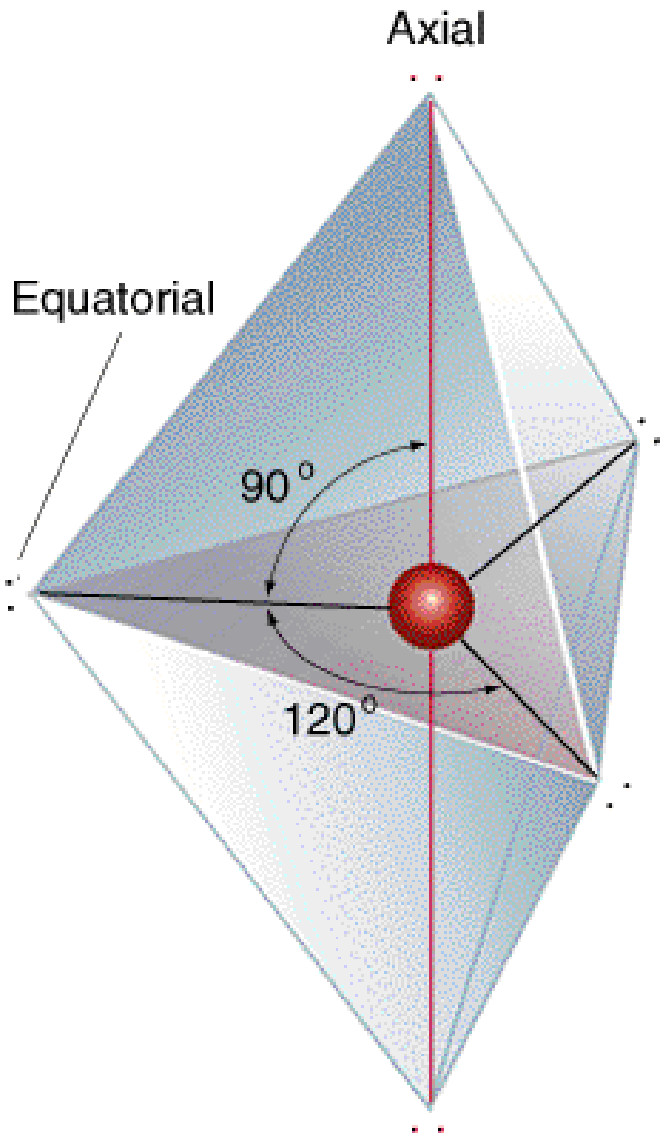


- **Lone pairs take-up more space, therefore they push-back the chemical bonds.**

The VSEPR Model



To minimize e^-–e^- repulsion, lone pairs are always placed in equatorial positions.

VSEPR model

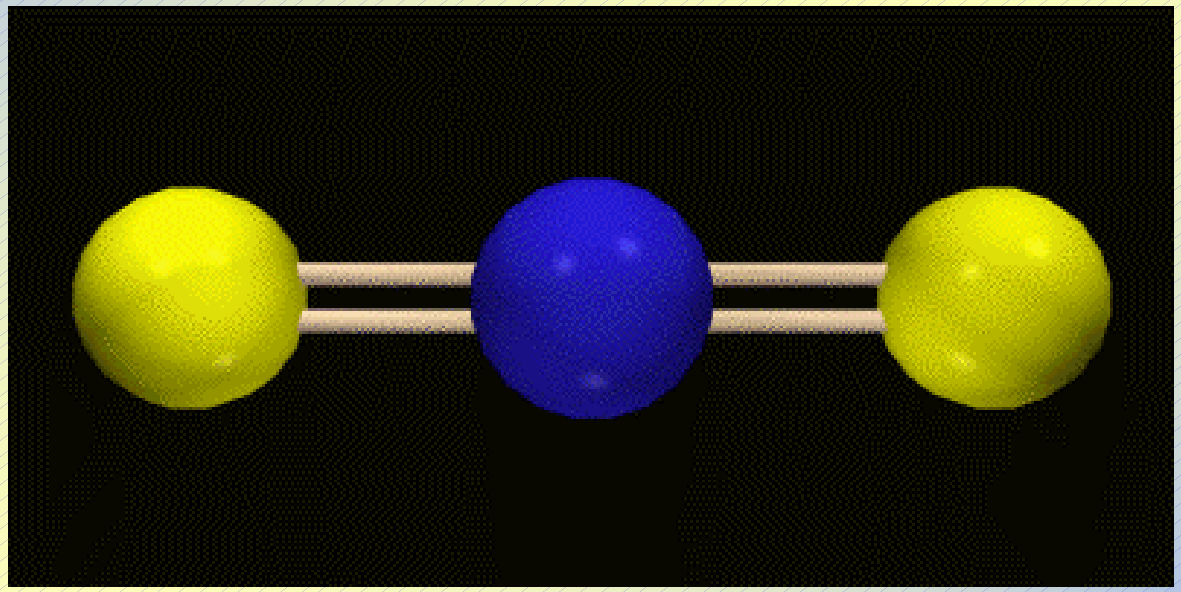
According to this model, for main group elements, electron pairs will be as far apart from each other as possible.

This occurs in three dimensional space.

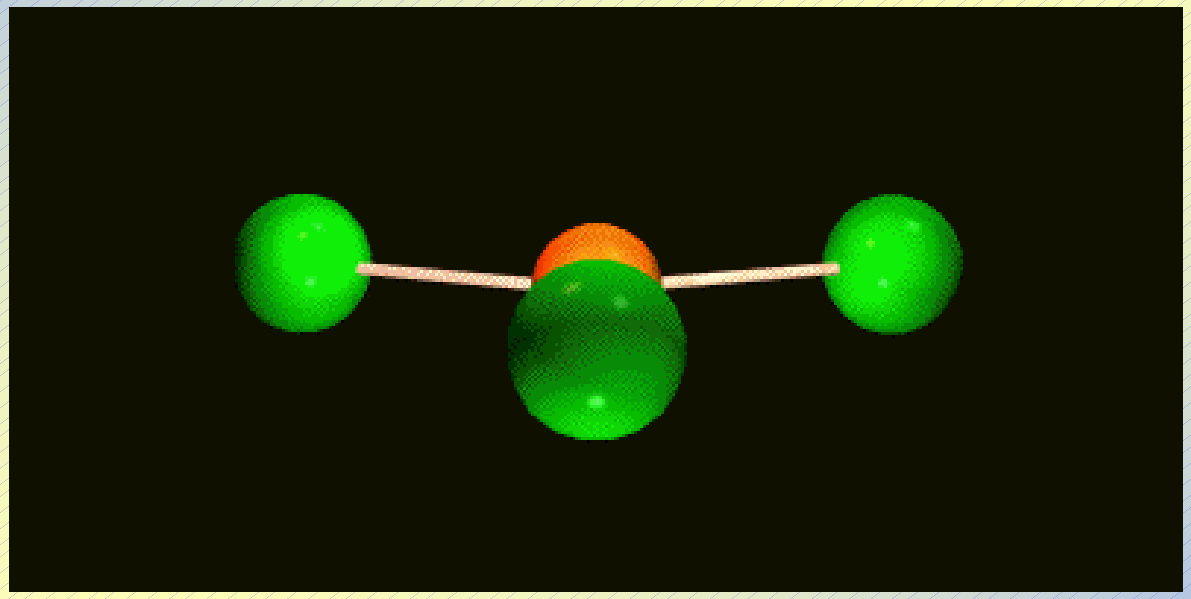
Both bonded and unshared pairs will occupy space with unshared pairs taking up more space.

The geometry is based on the total number of electron pairs - total coordination number.

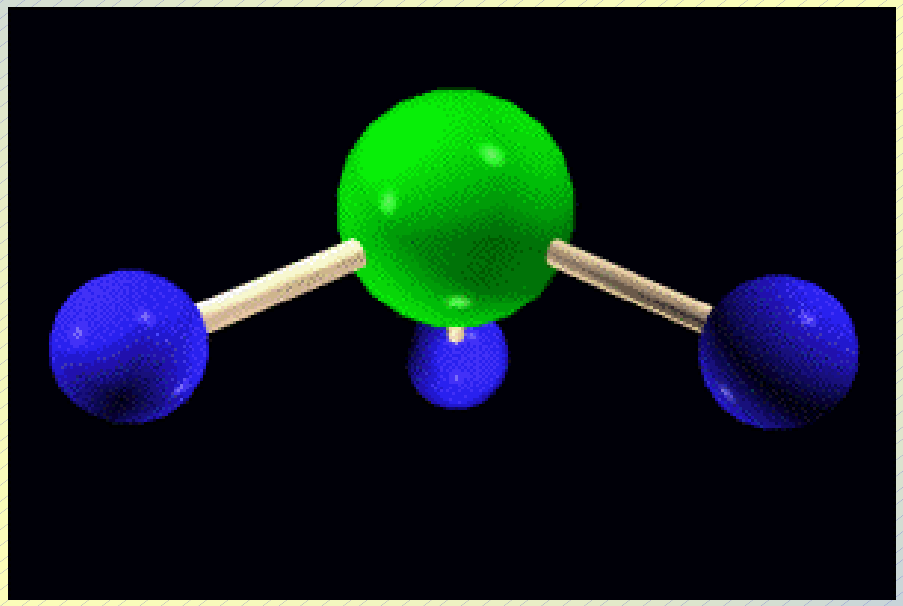
Linear - CO_2



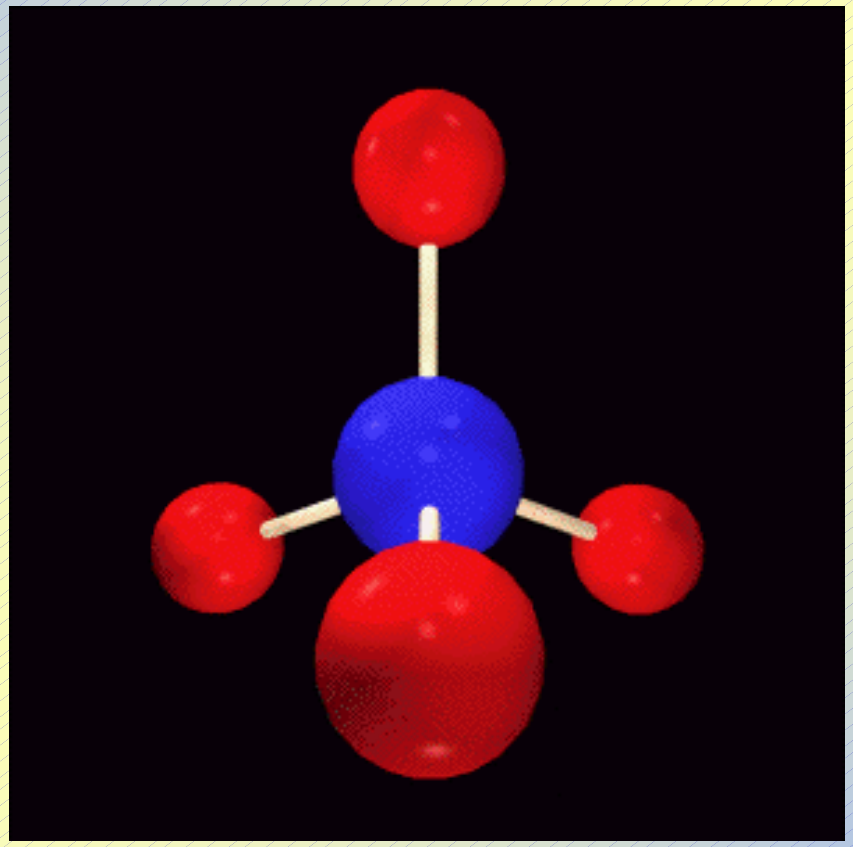
Trigonal planar, BCl_3



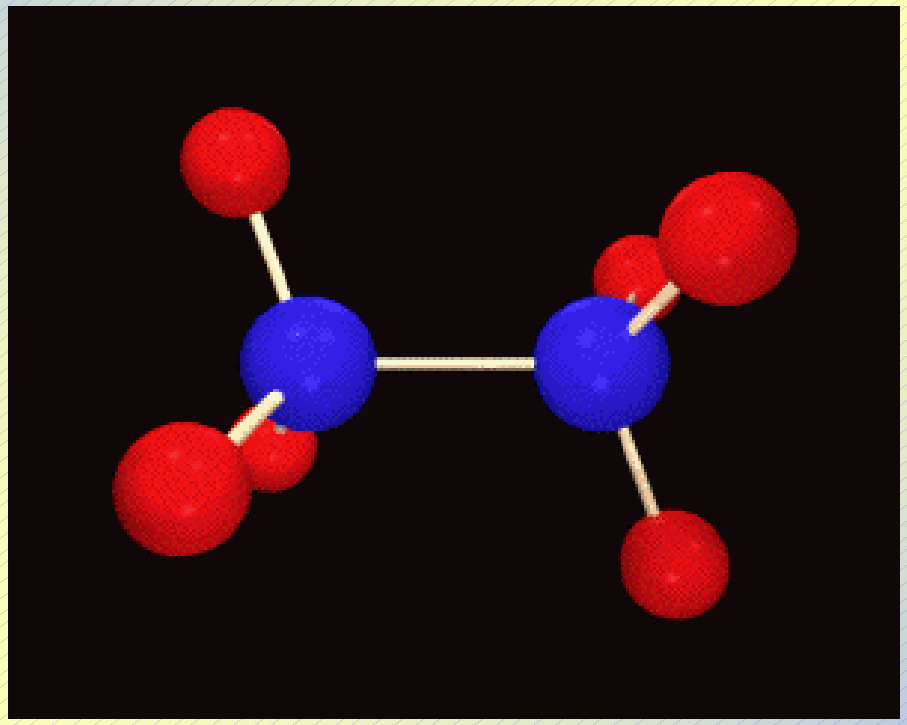
Pyramidal, NH_3



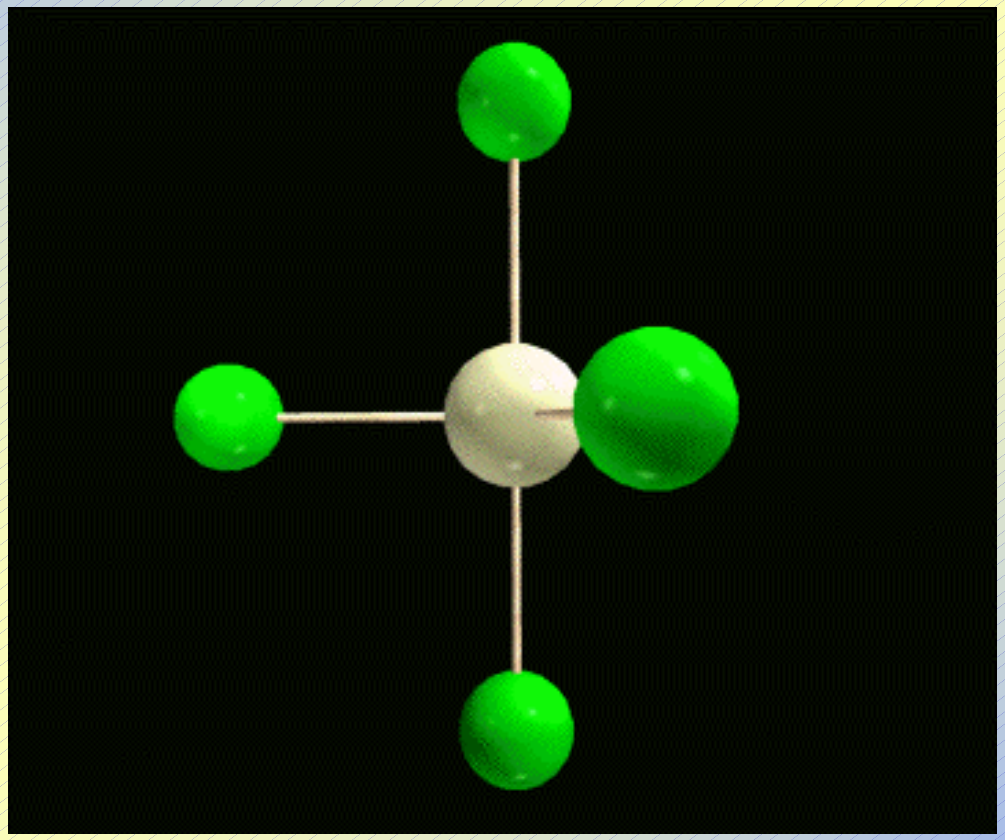
Tetrahedral, CH_4



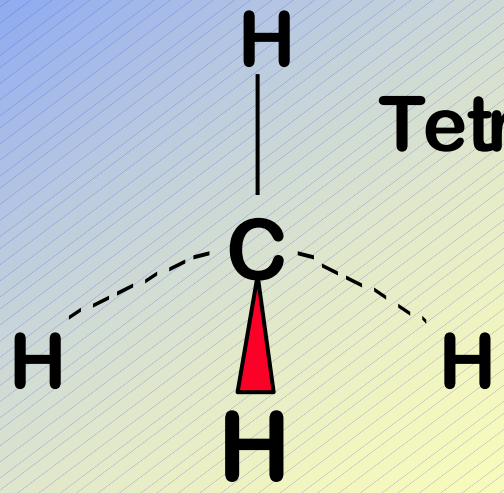
Ethane



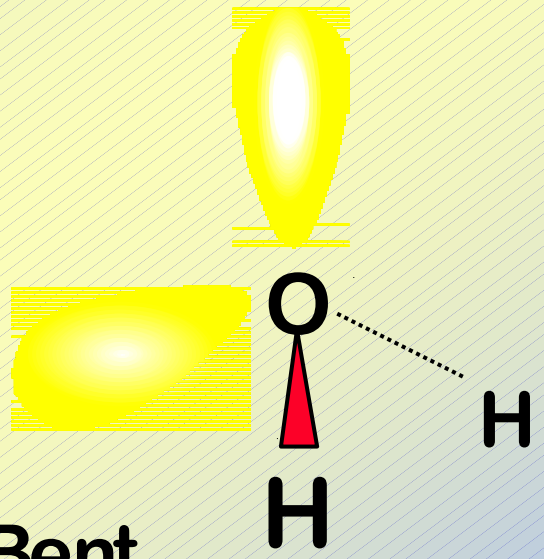
Trigonal bipyramidal



Molecular geometries based on tetrahedral

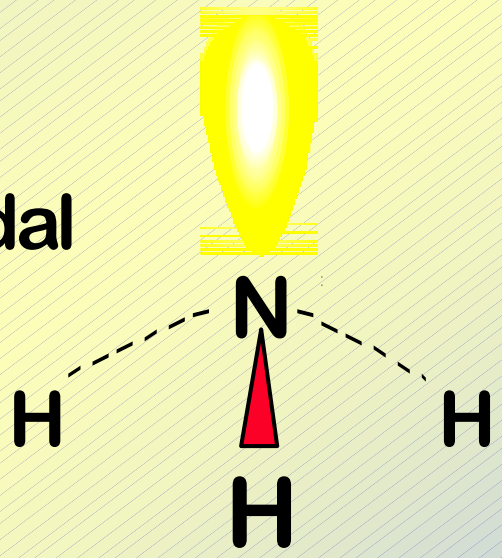


Tetrahedral



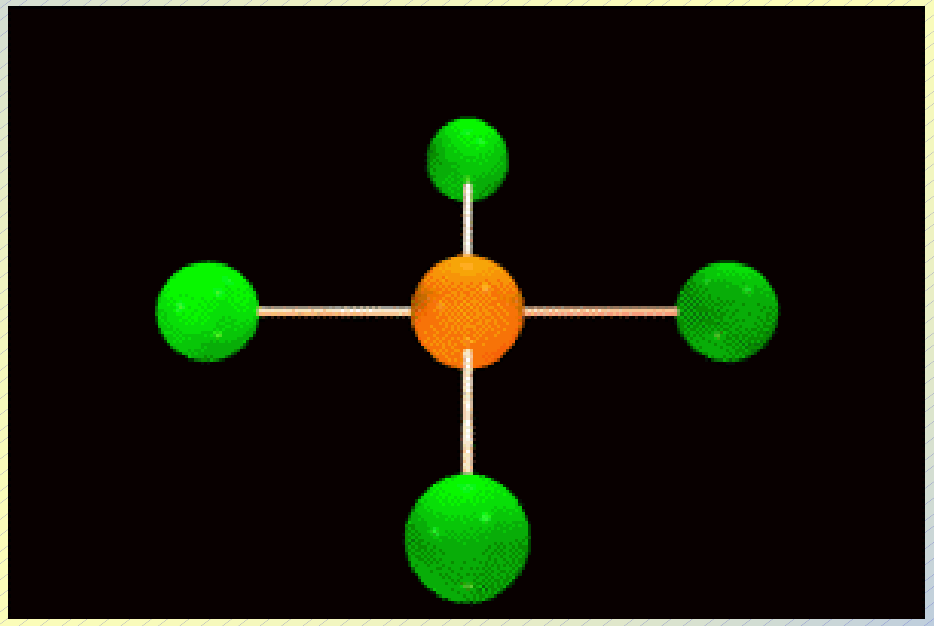
Bent

Pyramidal

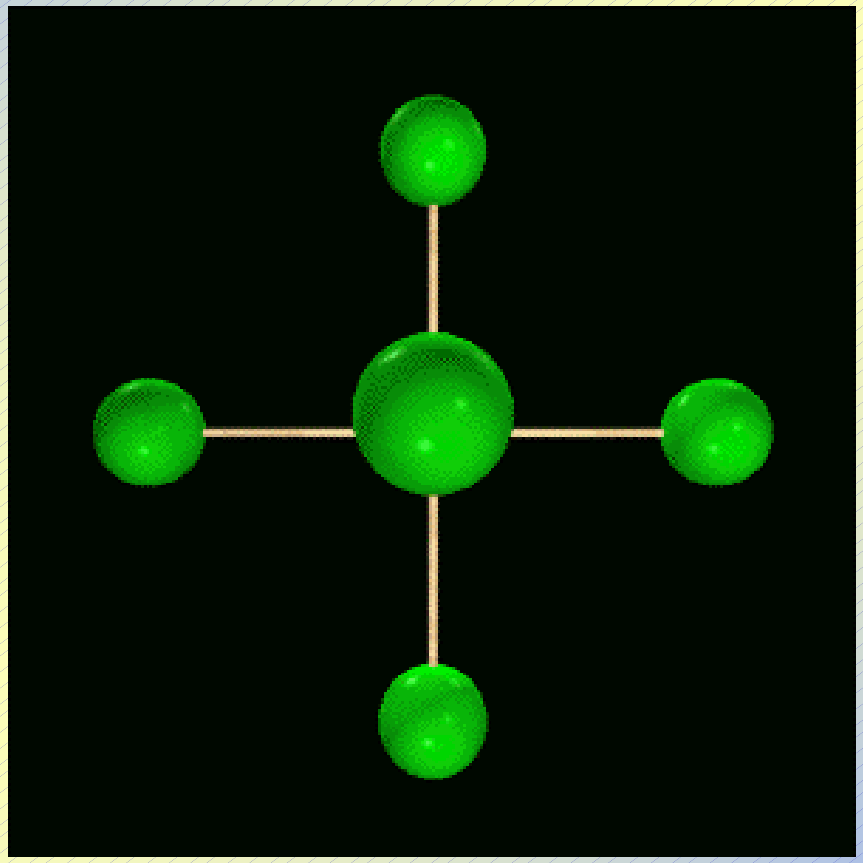


Bent and pyramidal are actually tetrahedral but some of the electron pairs are not bonded.

Square planar



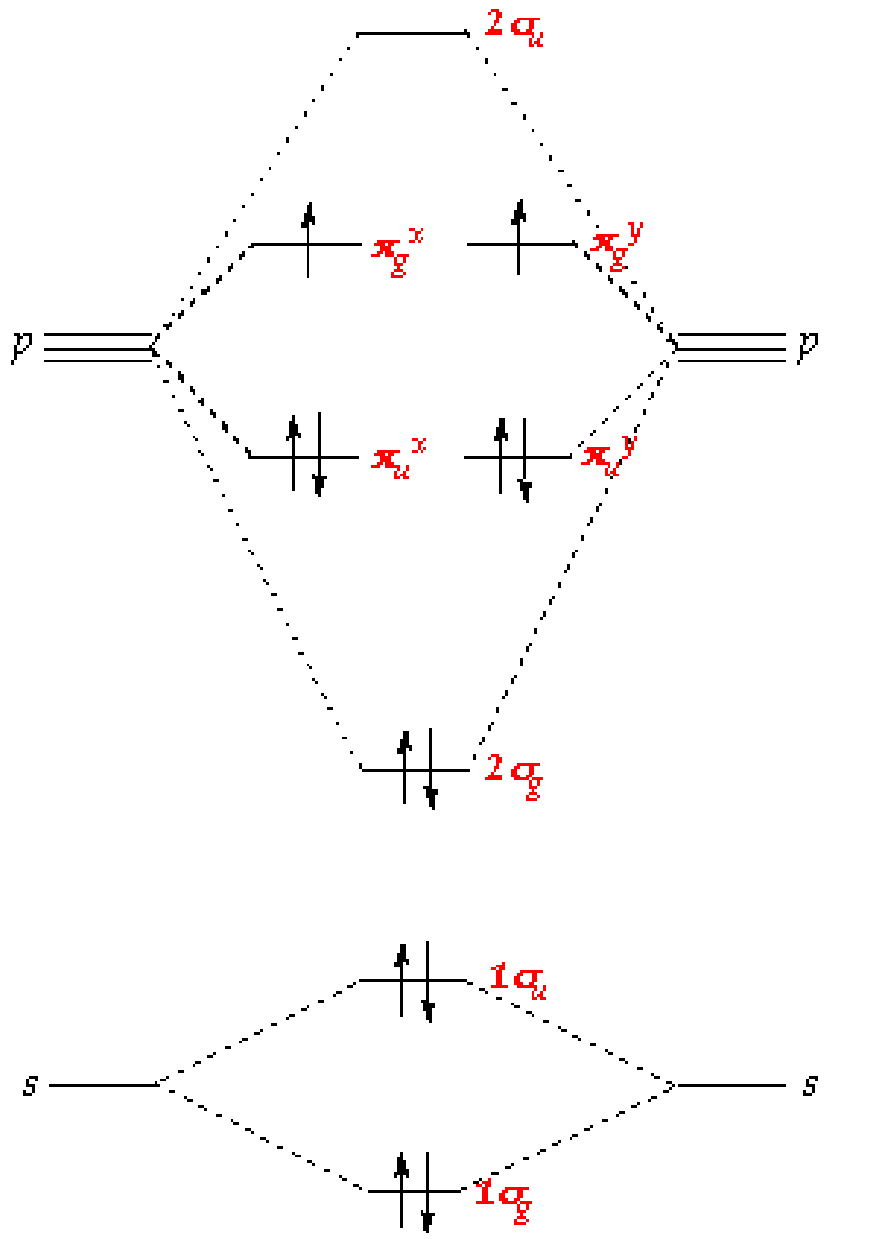
Octahedral



Covalent Bonding and Orbital Overlap

- **Lewis structures and VSEPR do not explain how a bond forms.**
- **VSEPR predicts the shape of a molecule, but it does not explain how the molecule is put together.**
- **One method to explain bonding would be *Valence Bond Theory*:**
  - **Bonds form when atomic orbitals on atoms overlap.**
  - **Two electrons are shared by the orbital overlap.**

- Oxigênio (O_2)é paramagnético

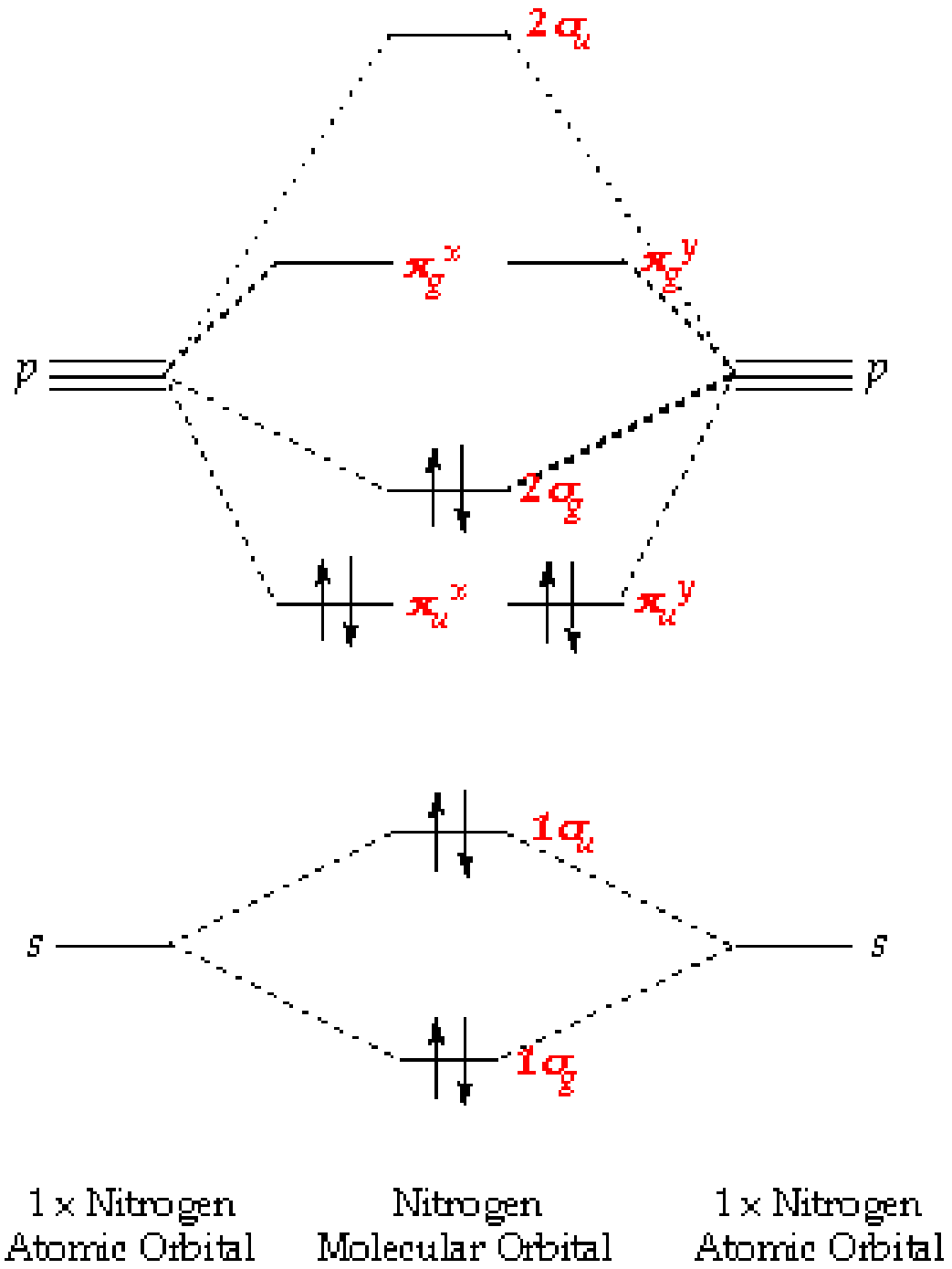


Oxigênio

O: s^2p^4

distribuição dos elétrons na camada de valência

- orbitais atômicos se combinam, gerando orbitais moleculares
- a molécula tem 12 elétrons, dois a mais do que o nitrogênio.
- esses dois elétrons extras estão situados em um par de orbitais π_g degenerados.



Nitrogênio

N: s^2p^3

distribuição dos elétrons na camada de valência

LCAO: orbitais moleculares

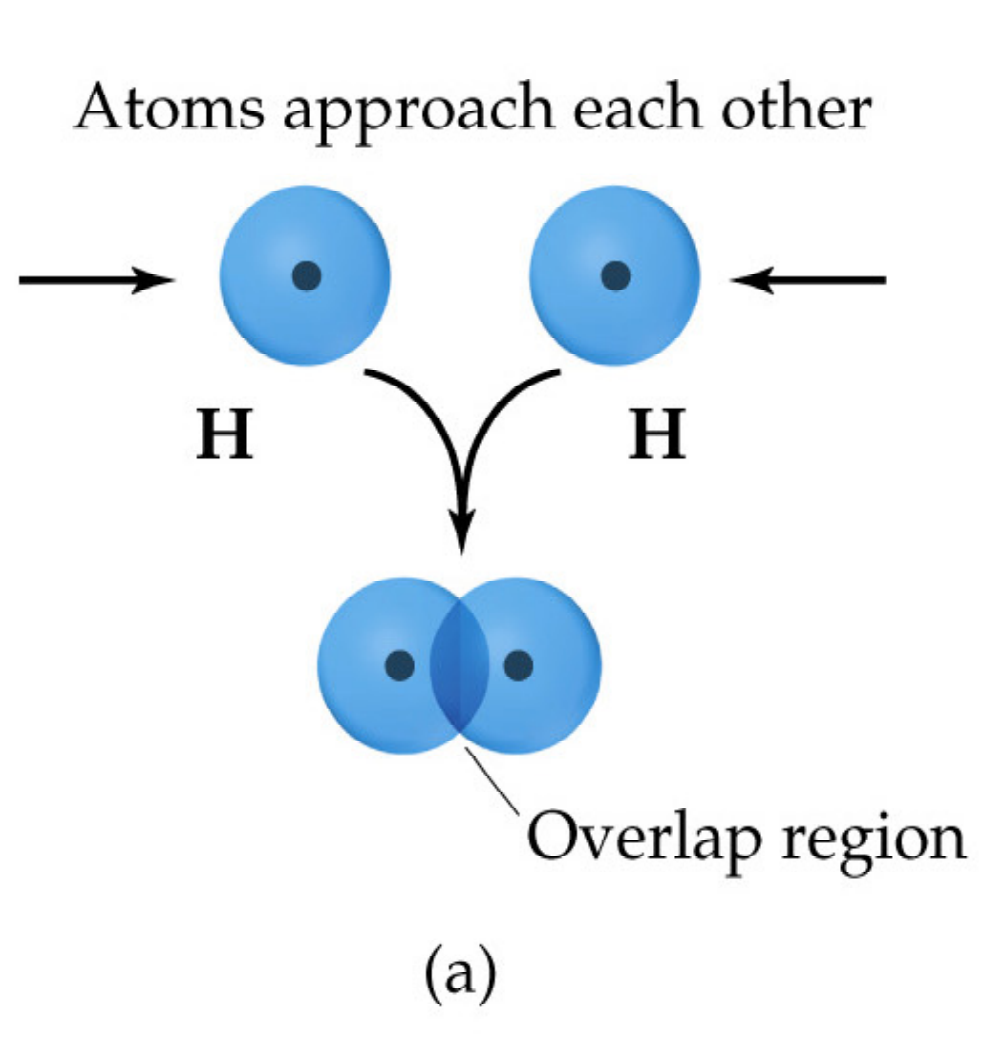
$2\pi_g$ orbital is occupied by two electrons to give a total bond order of three (g = gerade; u = ungerade).

N≡N

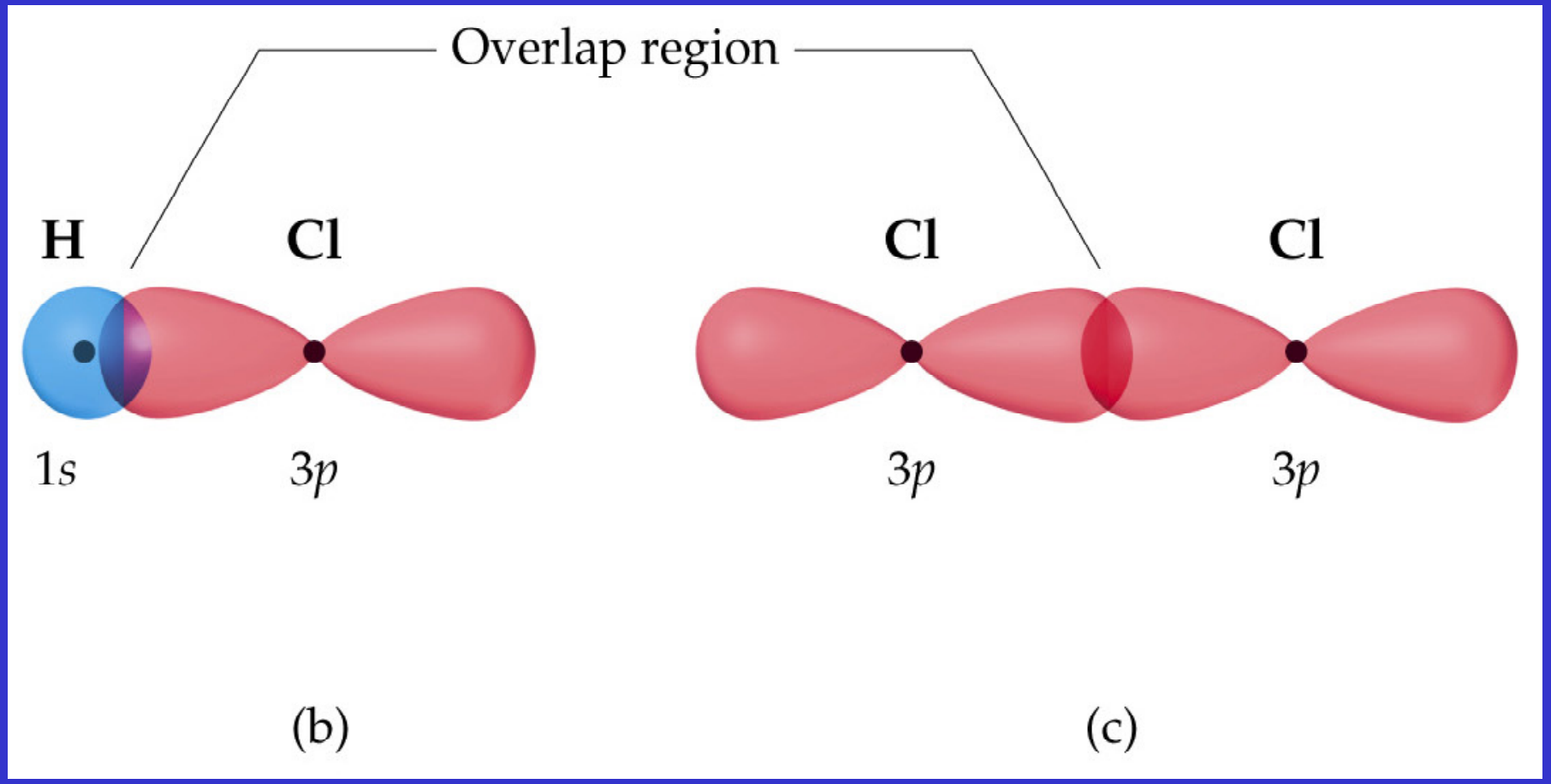
Lewis structure

orbital approach tells us that there is one σ and two π.

Covalent Bonding and Orbital Overlap



Covalent Bonding and Orbital Overlap



Hybrid Orbitals

sp Hybrid Orbitals

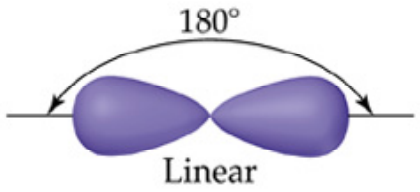
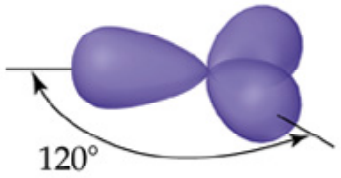
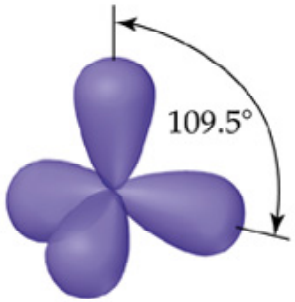
- **Consider BeF_2**

  - **Be has a $1s^2 2s^2$ electron configuration.**
  - **There is no unpaired electron available for bonding.**
  - **We could promote and electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding.**

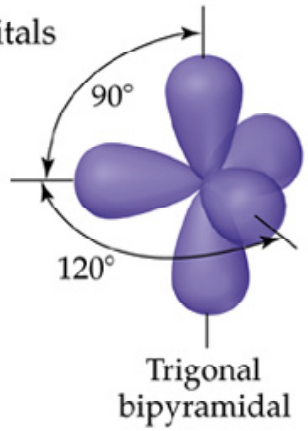
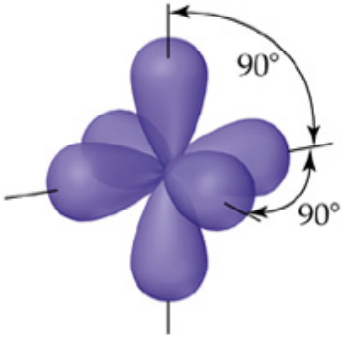
- **The F-Be-F bond angle is 180° (VSEPR theory).**

  - **BUT the geometry is still not explained.**

Hybrid Orbitals

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,*p*	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,*p*,*p*	Three sp^2	 Trigonal planar	BF_3, SO_3
s,*p*,*p*,*p*	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Hybrid Orbitals

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
	e of hybrid orbitals		
s,*p*,*p*,*p*,*d*	Five sp^3d	 Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,*p*,*p*,*p*,*d*,*d*	Six sp^3d^2	 Octahedral	SF_6, ClF_5, XeF_4, PF_6^-

Hybrid Orbitals

Summary

To assign hybridization:

- **draw a Lewis structure**
- **assign the electron pair geometry using VSEPR theory**
- **from the electron pair geometry, determine the hybridization**

Hybrid Orbitals

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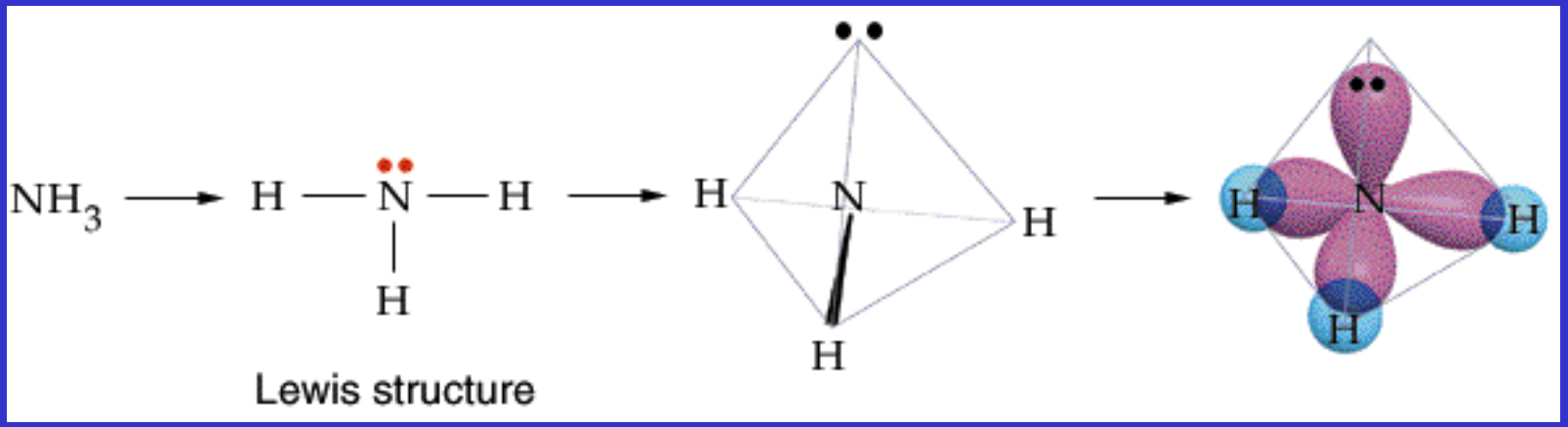
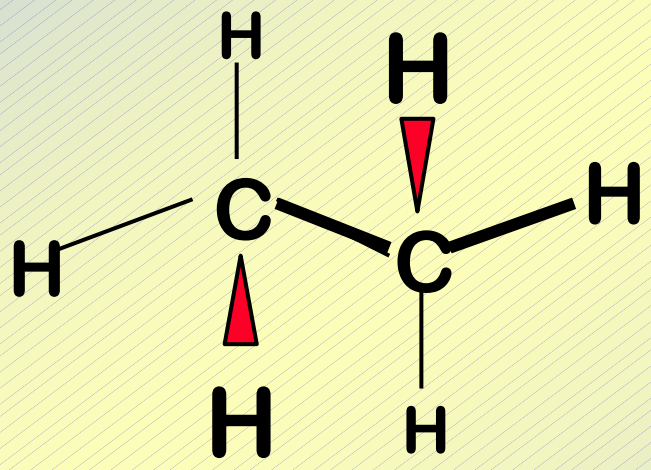
- **assign the electron pair geometry using VSEPR theory**
- **from the electron pair geometry, determine the hybridization**



Molecular geometry



As molecules get larger, the rules regarding molecular geometry still hold.

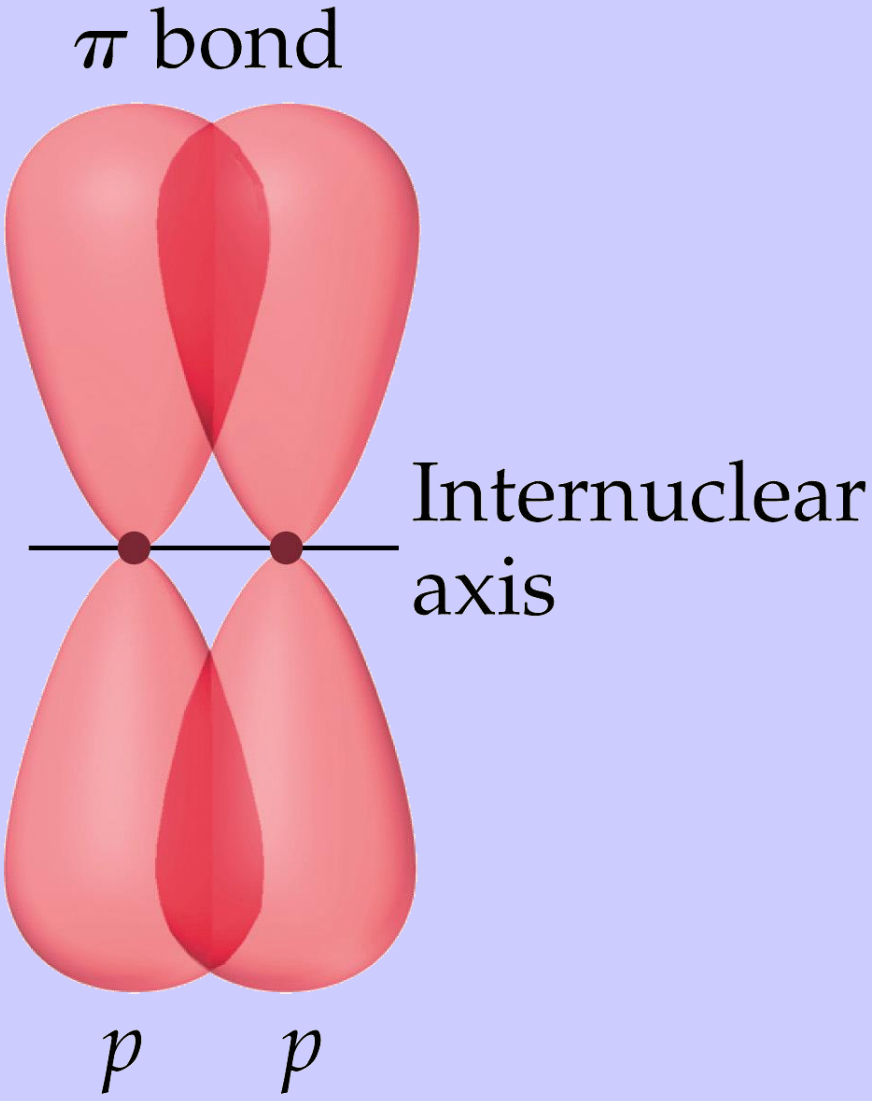
Multiple Bonds

σ-Bonds **- electron density lies on the axis between the nuclei.**

π-Bonds **- electron density lies above and below the plane of the nuclei.**

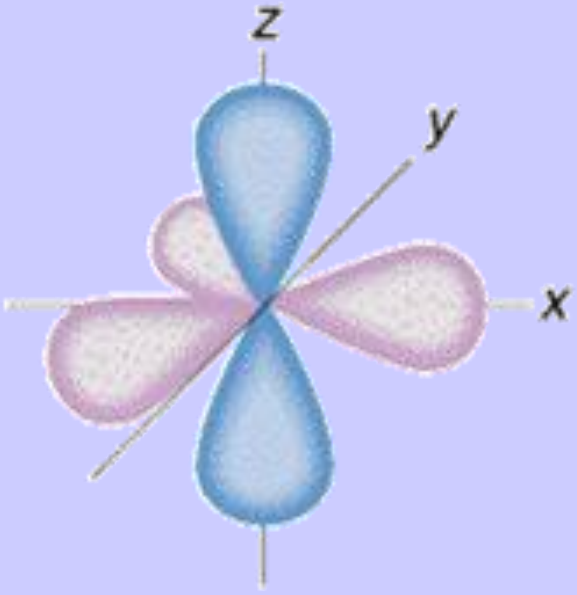
- **A double bond consists of one σ-bond and one π-bond**
- **A triple bond has one σ-bond and two π-bonds**
- **π-bonds come from unhybridized p orbitals.**

Multiple Bonds



Multiple Bonds

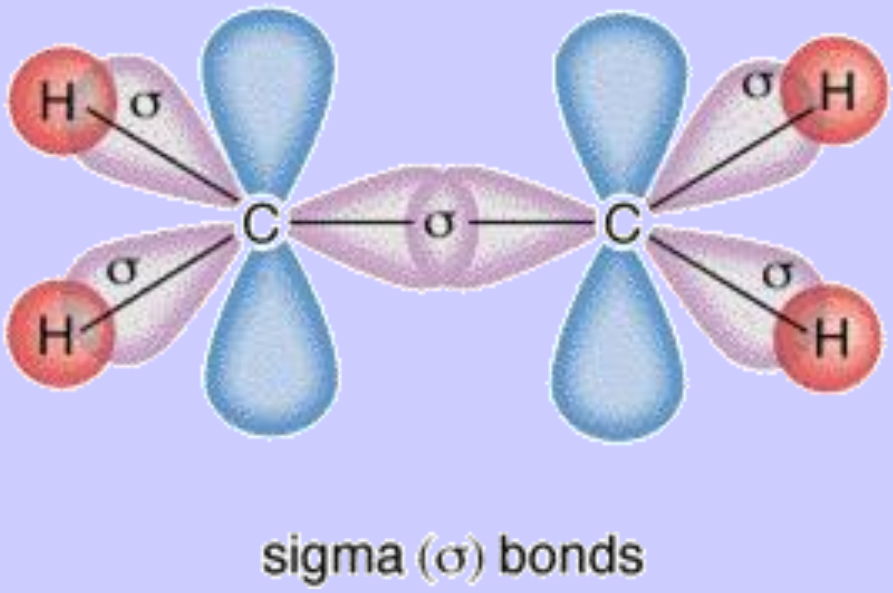
Ethylene, C_2H_4



the set of orbitals $sp^2 + p$

Multiple Bonds

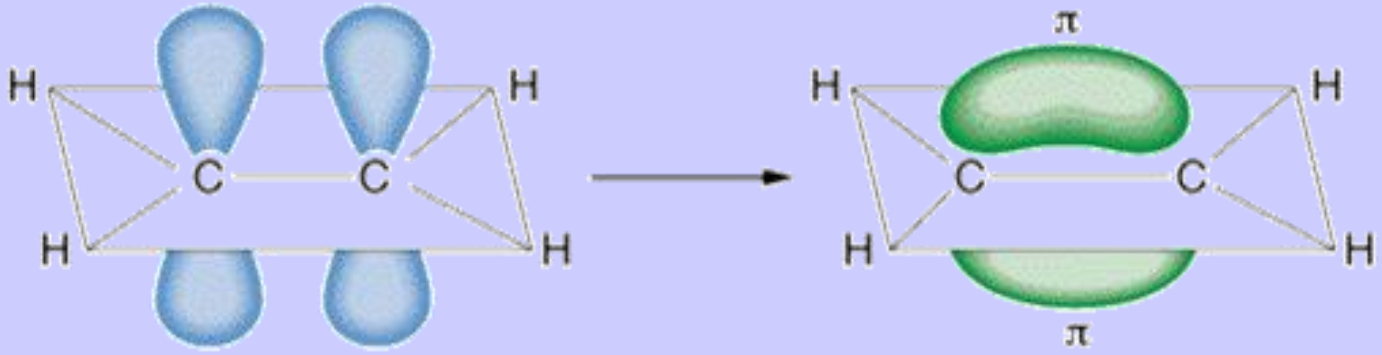
Ethylene, C_2H_4



sigma (σ) bonds

Multiple Bonds

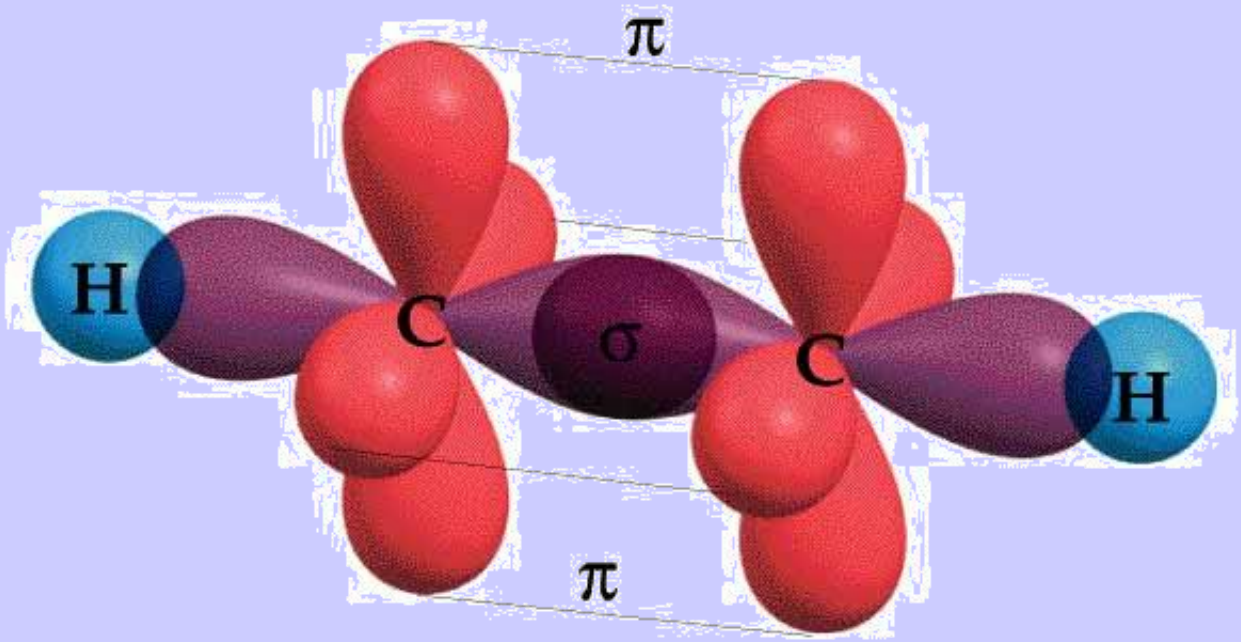
Ethylene, C_2H_4



overlap of *p* orbitals leading to pi (π) bond

Multiple Bonds

Acetylene, C_2H_2



Molecular Orbitals

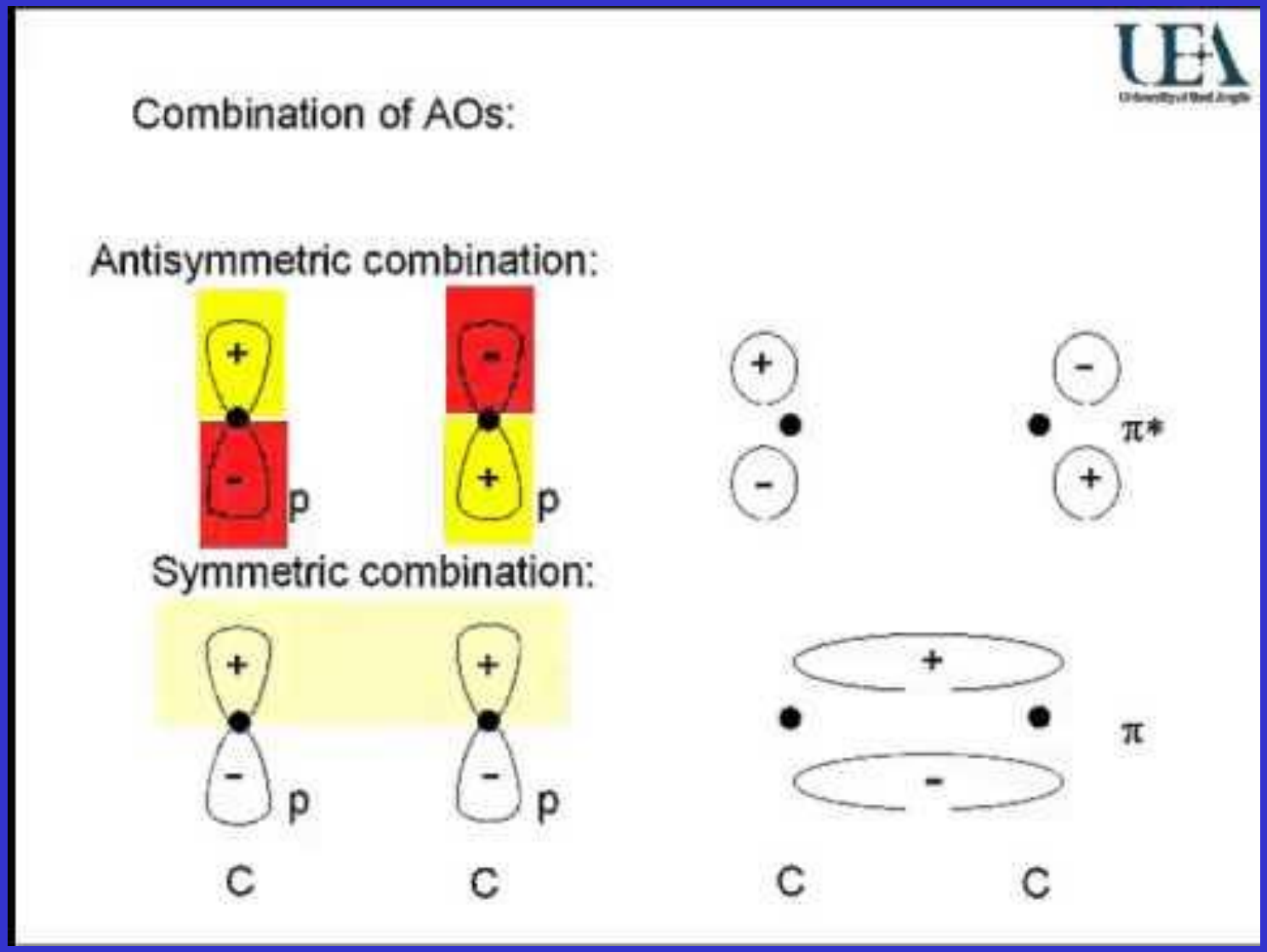
- **Some aspects of bonding are not explained by Lewis structures, VSEPR theory and hybridization.**
- **For these molecules, we use *Molecular Orbital Theory* (MO theory).**
- **Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in molecular orbitals.**

Molecular Orbitals

The Hydrogen Molecule

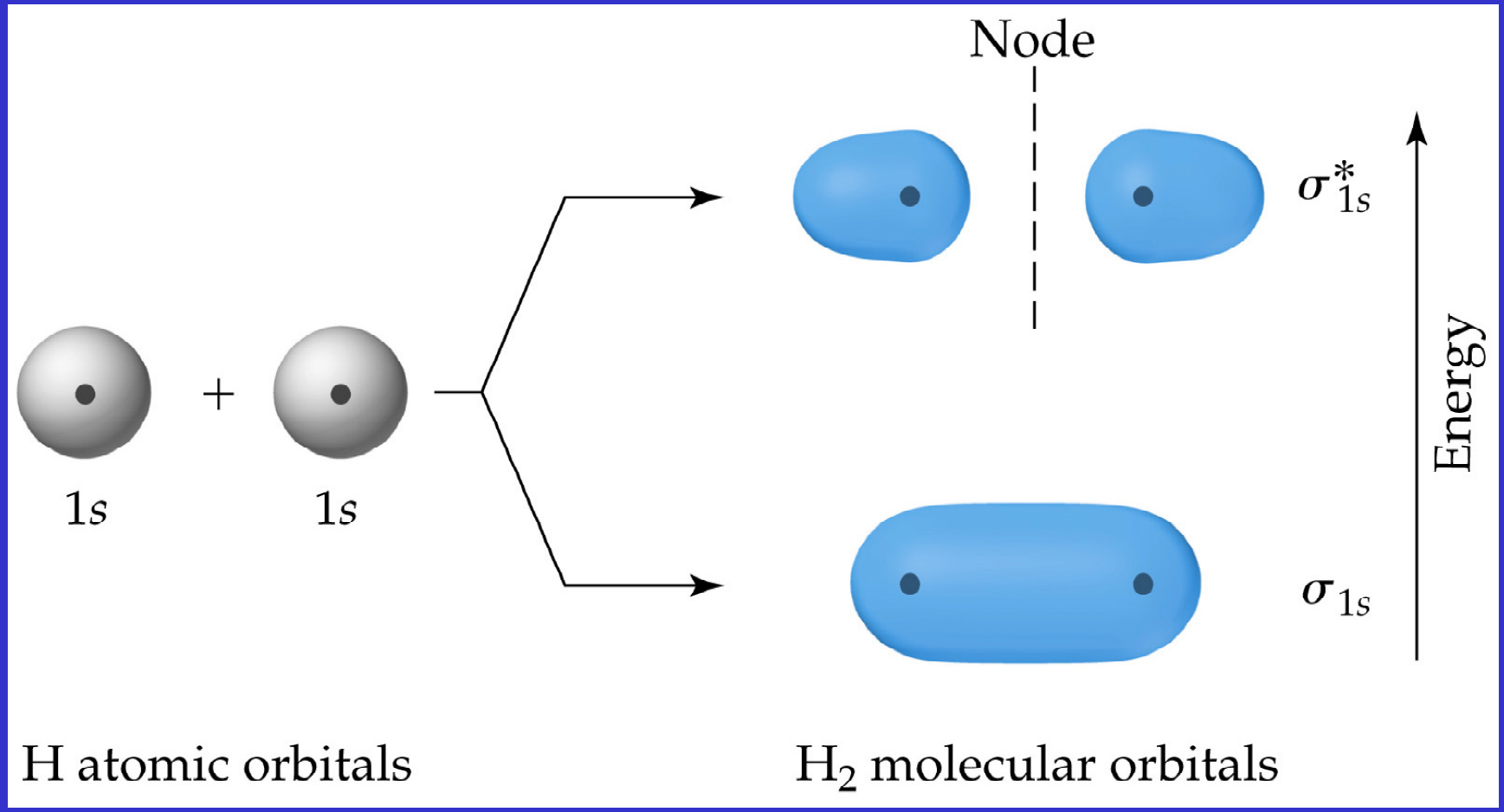
- **When two AOs overlap two MO's form.**
- **One molecular orbital has electron density between nuclei (σ, bonding MO);**
- **One molecular orbital has little electron density between nuclei (σ^*, antibonding MO).**

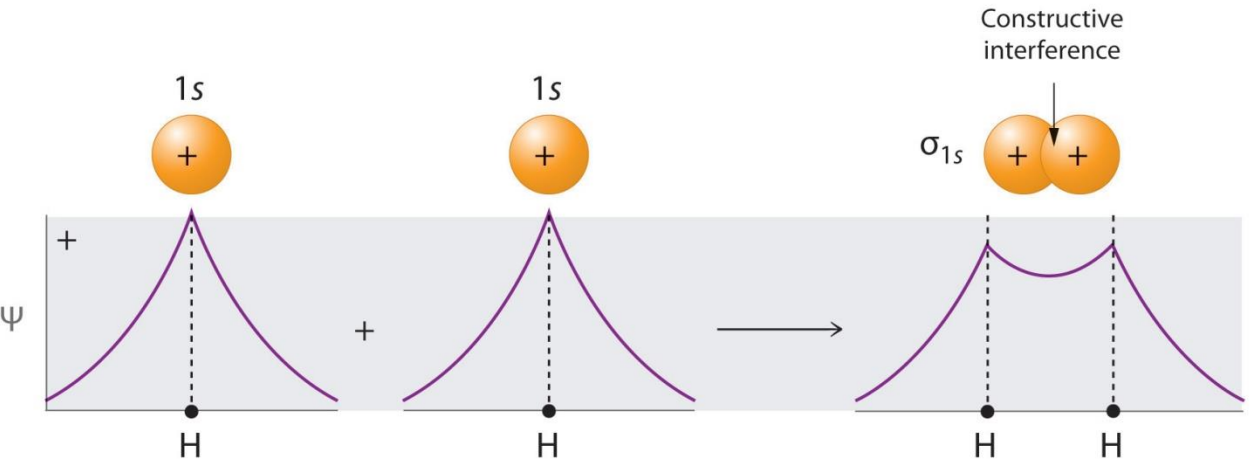
as combinações simétrica (+) e antissimétrica (-) de A e B.



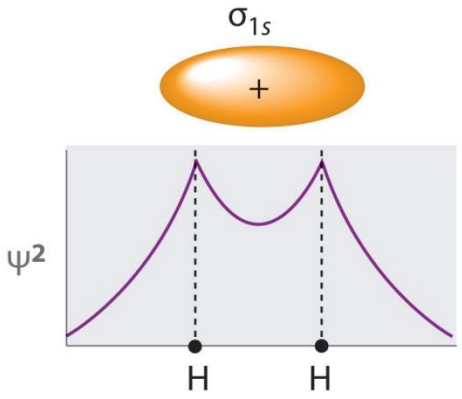
Molecular Orbitals

The Hydrogen Molecule

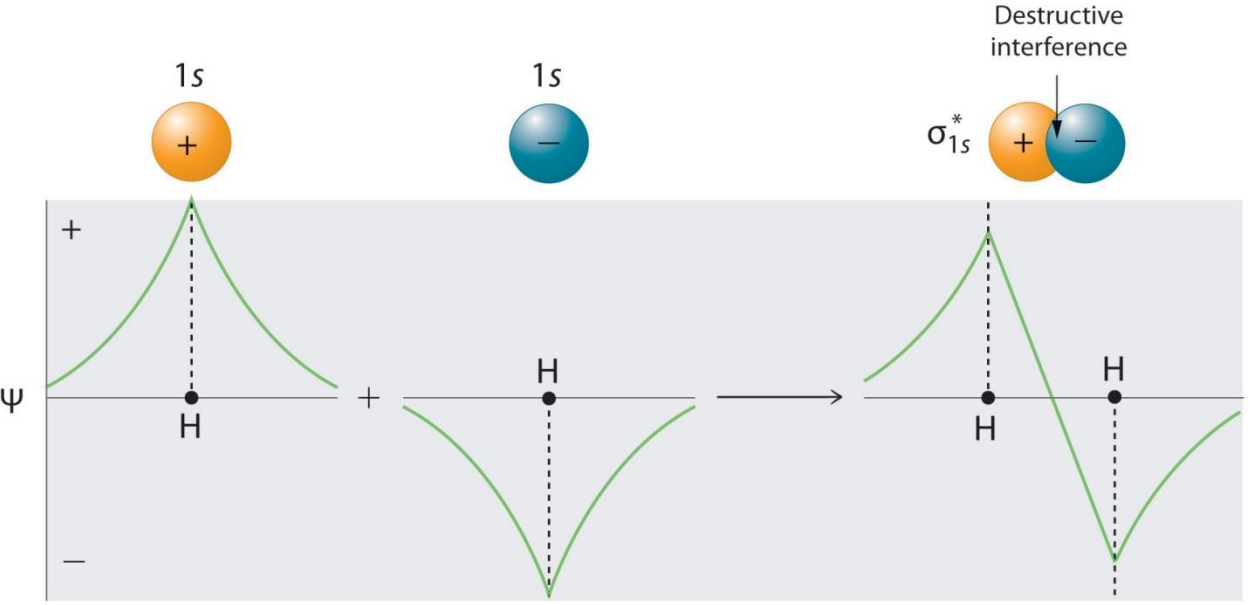




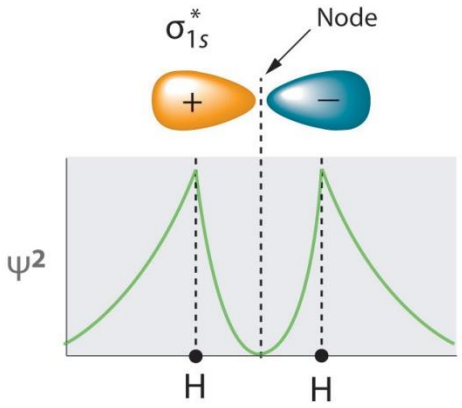
(a) Wave functions combined for σ_{1s}



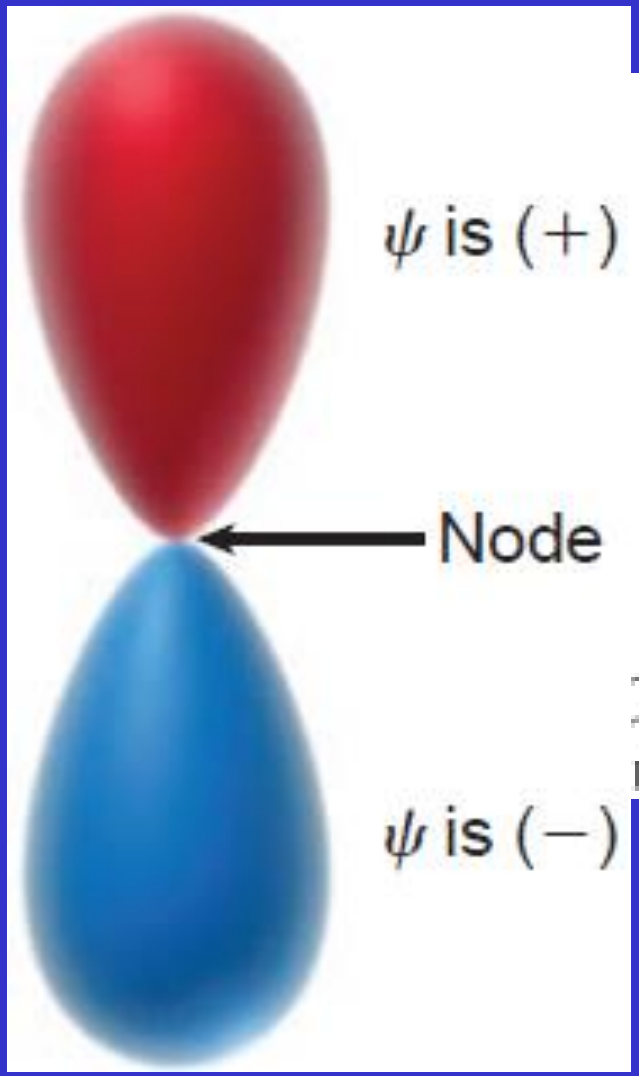
(b) Bonding probability density



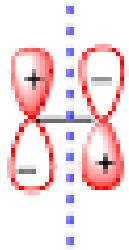
(c) Wave functions combined for σ^*_{1s}



(d) Antibonding probability density



Increasing Energy of Orbitals



π* (Antibonding molecular orbital)

π (Bonding molecular orbital)

Total Number of π-electrons = 2
Total Number of π-orbitals = 2
Both electrons will occupy the lowest energy MO, i.e., BMO

Molecular Orbitals

Bond Order

Bond Order = ½(bonding electrons - antibonding electrons).

Bond order = 1 for single bond.

Bond order = 2 for double bond.

Bond order = 3 for triple bond.

Bond order for H_2 = ½(bonding electrons - antibonding electrons)

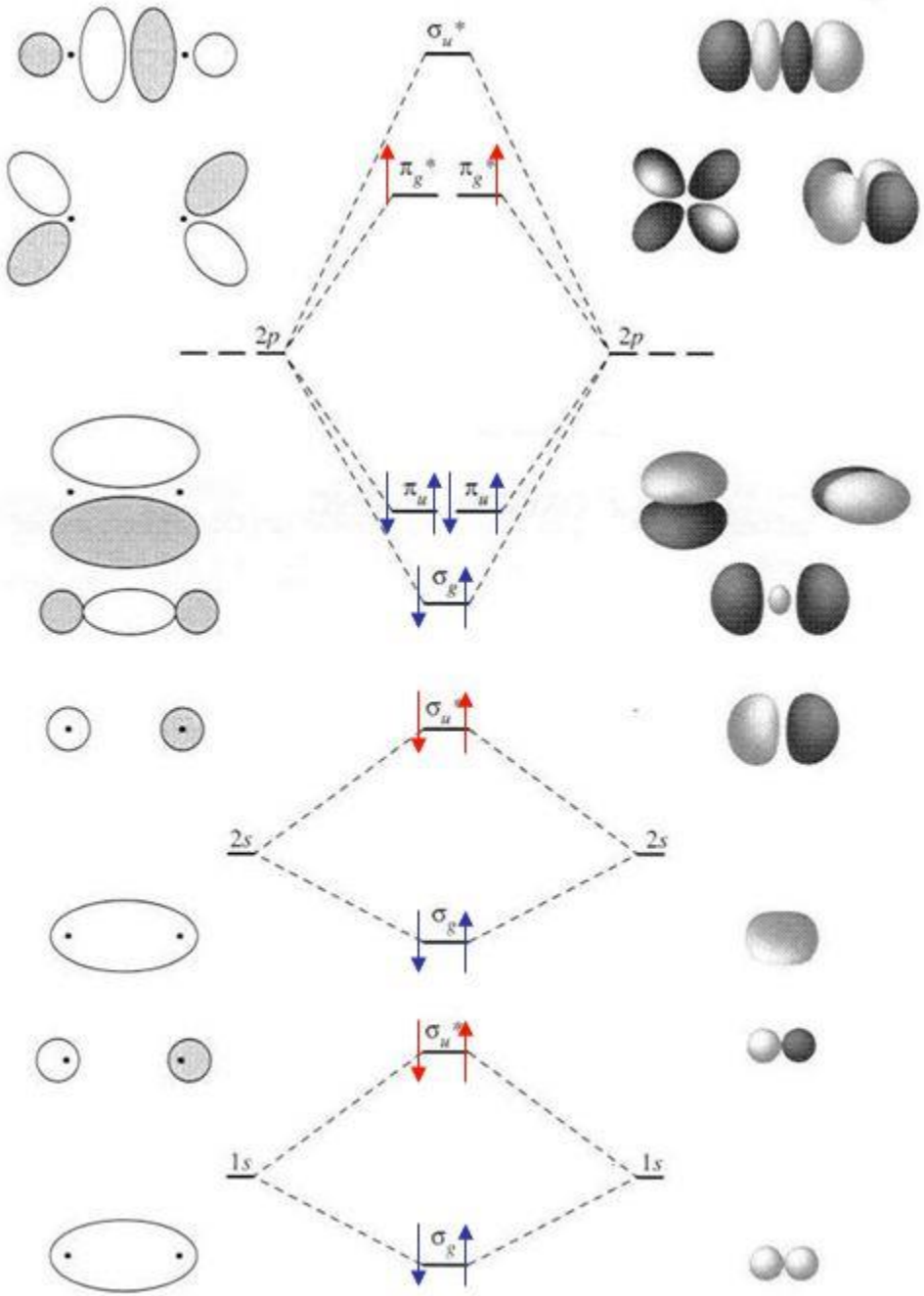
= ½(2 - 0) = 1.

Therefore, H_2 has a single bond.

Bond order for He_2 = ½(bonding electrons - antibonding electrons)

= ½(2 - 2) = 0.

Therefore He_2 is not a stable molecule.



O_2 (2 x 8e)

1/2 (10 - 6) = 2

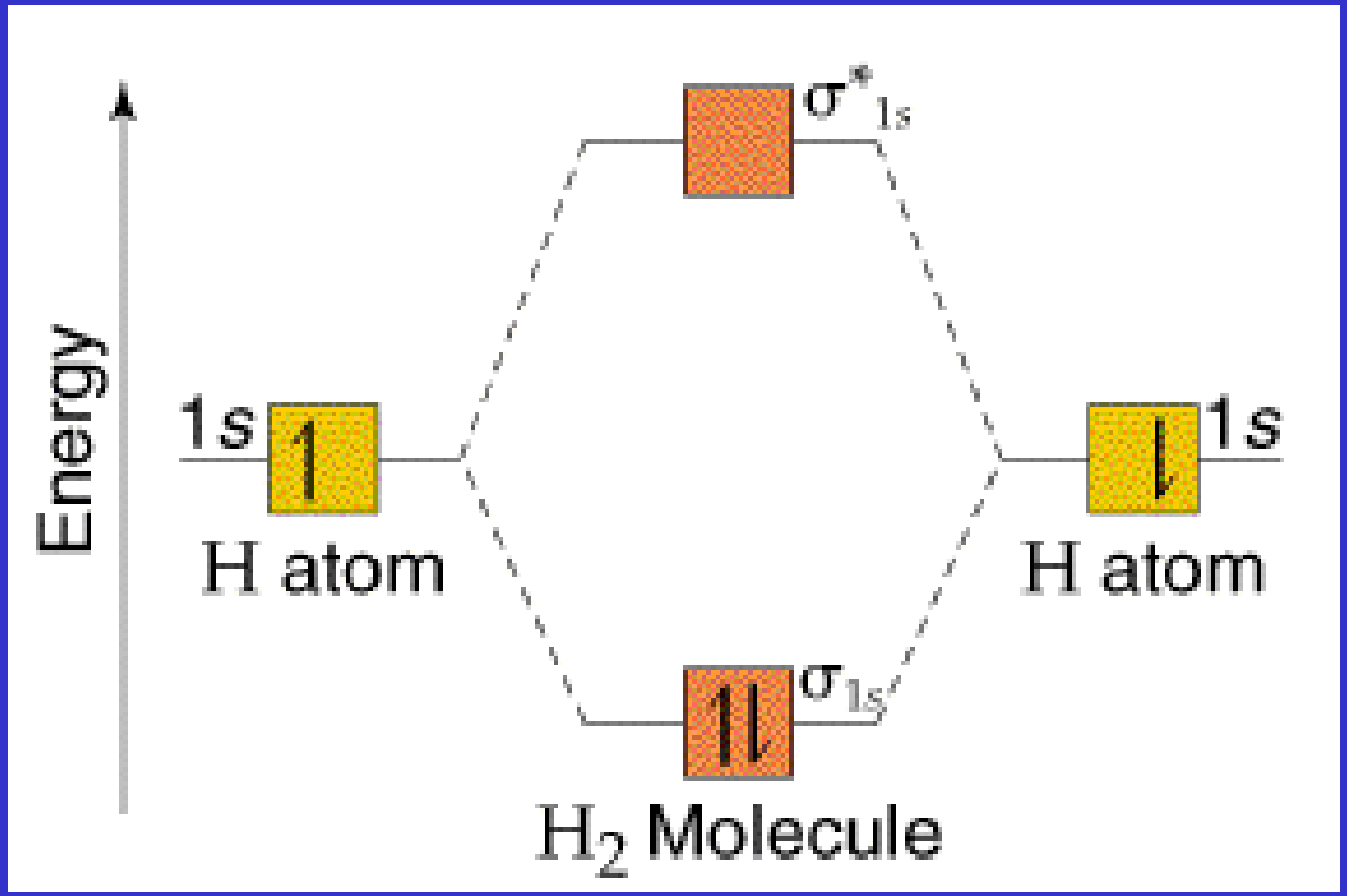
A double bond

Or counting only *valence* electrons:
1/2 (8 - 4) = 2

Note subscripts
g and *u*
symmetric/antisymmetric
upon *i*

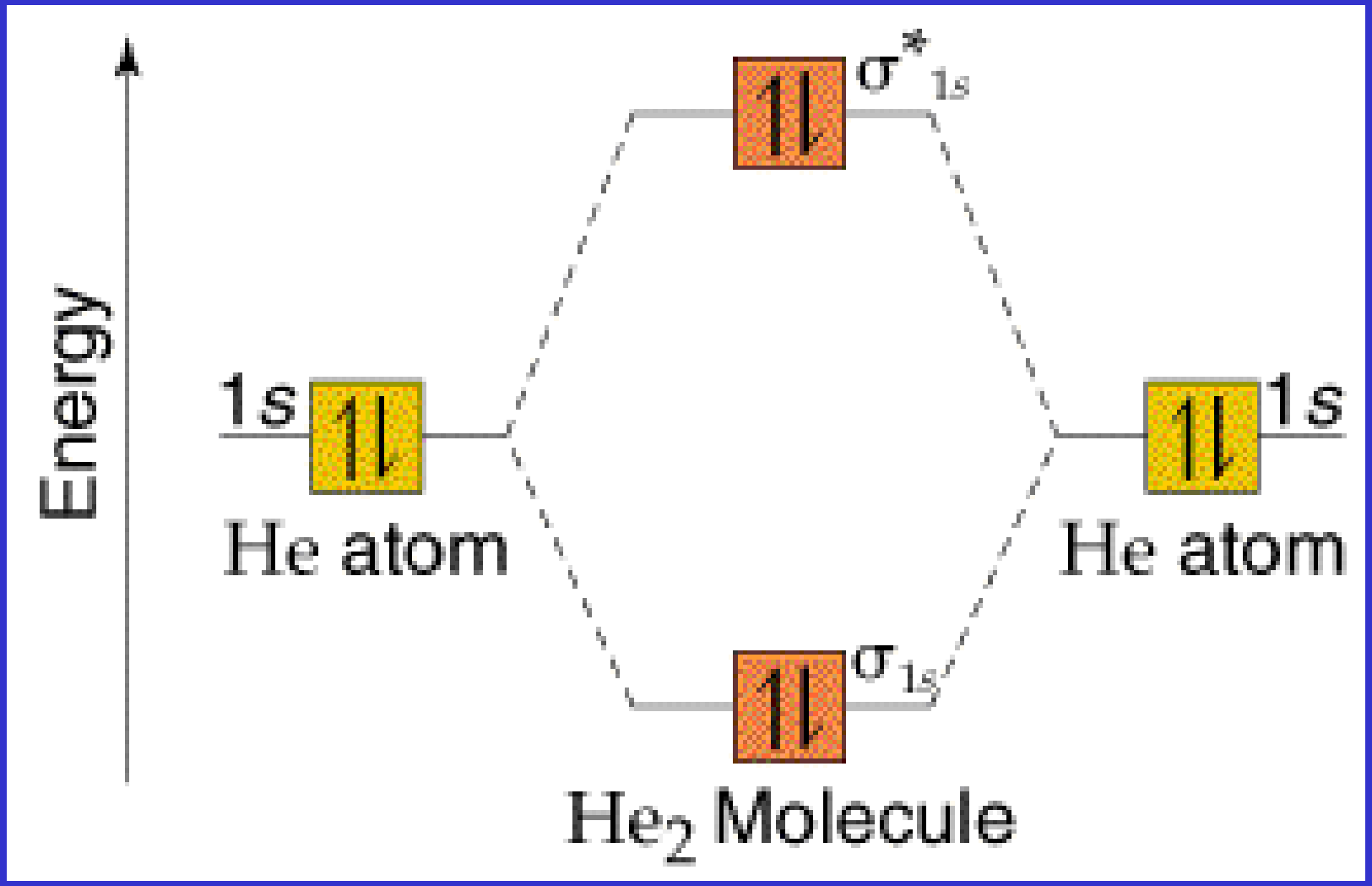
Molecular Orbitals

The Hydrogen Molecule

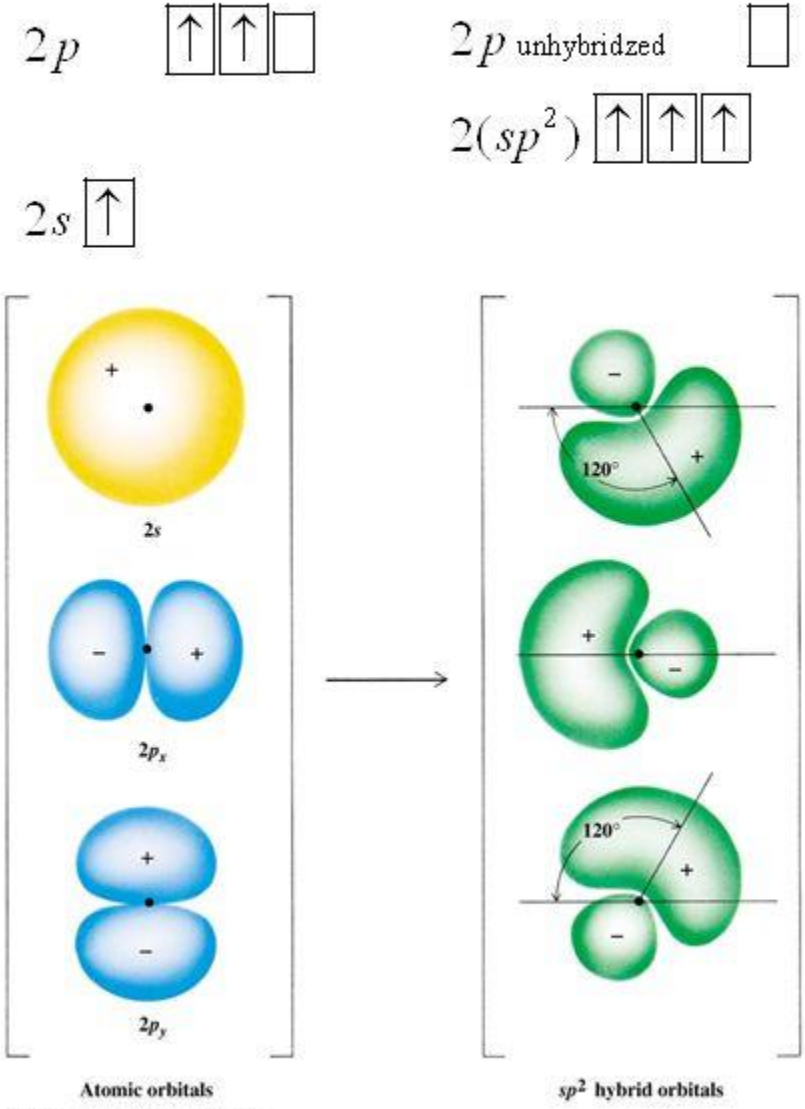


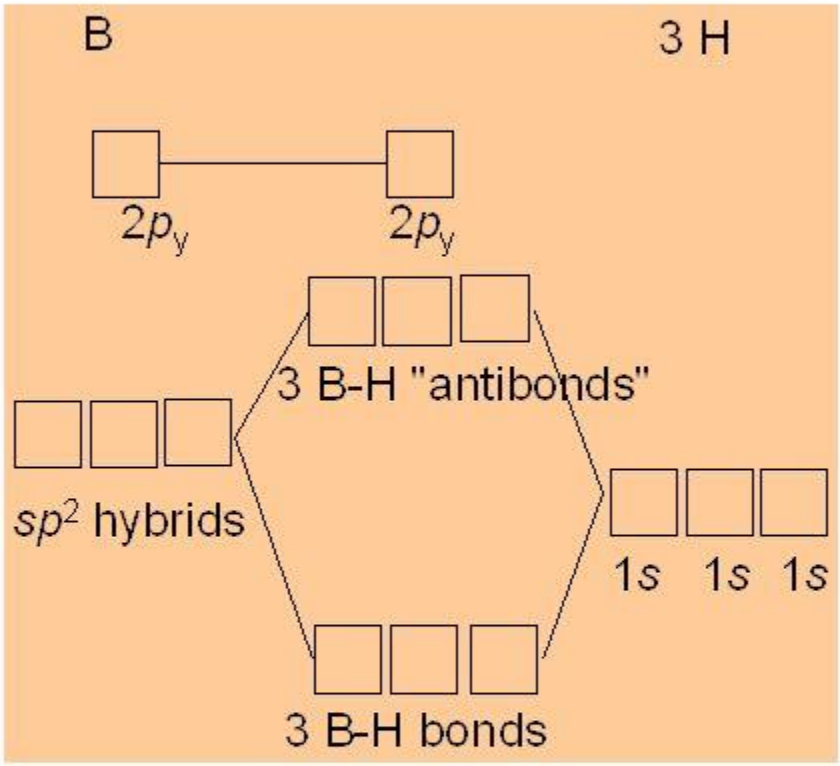
Molecular Orbitals

The Helium Molecule



BH_3 and sp^2 hybridization





- BH_3 is trigonal planar with three equal B—H bonds
- To get this shape, we need to combine the 2*s* with **two** 2*p* AO's to generate three equivalent **hybrid atomic orbitals**
- Combination with the H *1s* leads to bonding and anti-bonding molecular orbitals, which are **localized molecular orbitals pointing to the corners of a triangle**

Molecular Orbitals

The Hydrogen Molecule

- **MO diagram shows the energies and electrons in an orbital.**
- **The total number of electrons in all atoms are placed in the MO's starting from lowest energy (σ_{1s}) and ending when you run out of electrons.**
- **Note that electrons in MO's have opposite spins.**
- **H_2 has two bonding electrons.**
- **He_2 has two bonding electrons and two antibonding electrons.**

Second-Row Diatomic Molecules

AO's combine according to the following rules

- **The number of MO's equals the number of AO's**
- **AO's of similar energy combine**
- **As overlap increases, the energy of the MO decreases;**

- Pauli: each MO has at most two electrons

- Hund: for degenerate orbitals, each MO is first occupied singly.

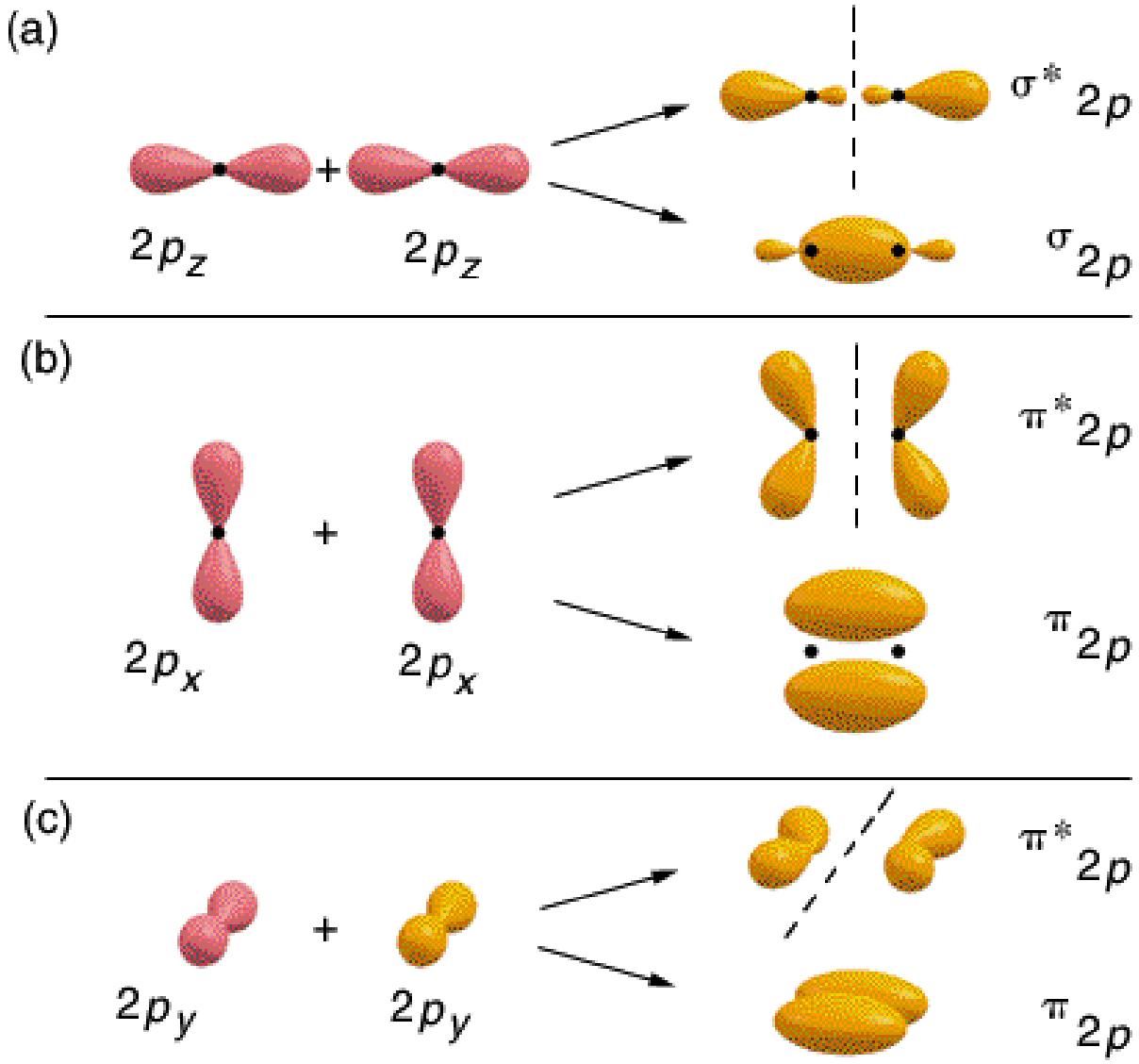
Second-Row Diatomic Molecules

Molecular Orbitals from 2*p* Atomic Orbitals

- There are two ways in which two *p* orbitals overlap
  - end-on so that the resulting MO has electron density on the axis between nuclei (σ orbital)
  - sideways so that the resulting MO has electron density above and below the axis between nuclei (π orbital).
- The *p*-orbitals must give rise to 6 MO's:
  - one σ and two π orbitals
  - one σ* and two π*orbitals
- The relative energies of these σ and π orbitals can change.

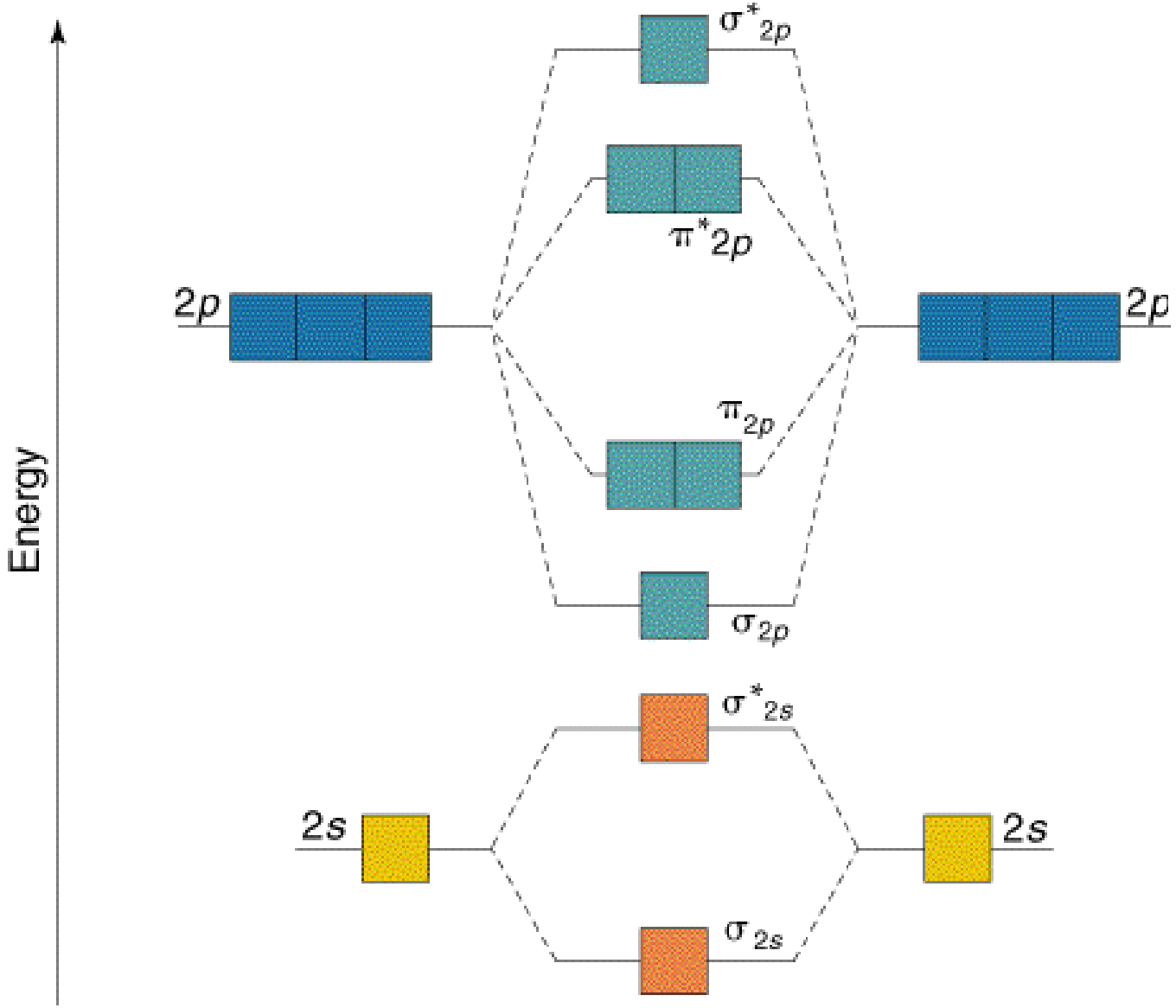
Second-Row Diatomic Molecules

Molecular Orbitals from 2*p* Atomic Orbitals



Second-Row Diatomic Molecules

Electron Configurations for B_2 through Ne_2



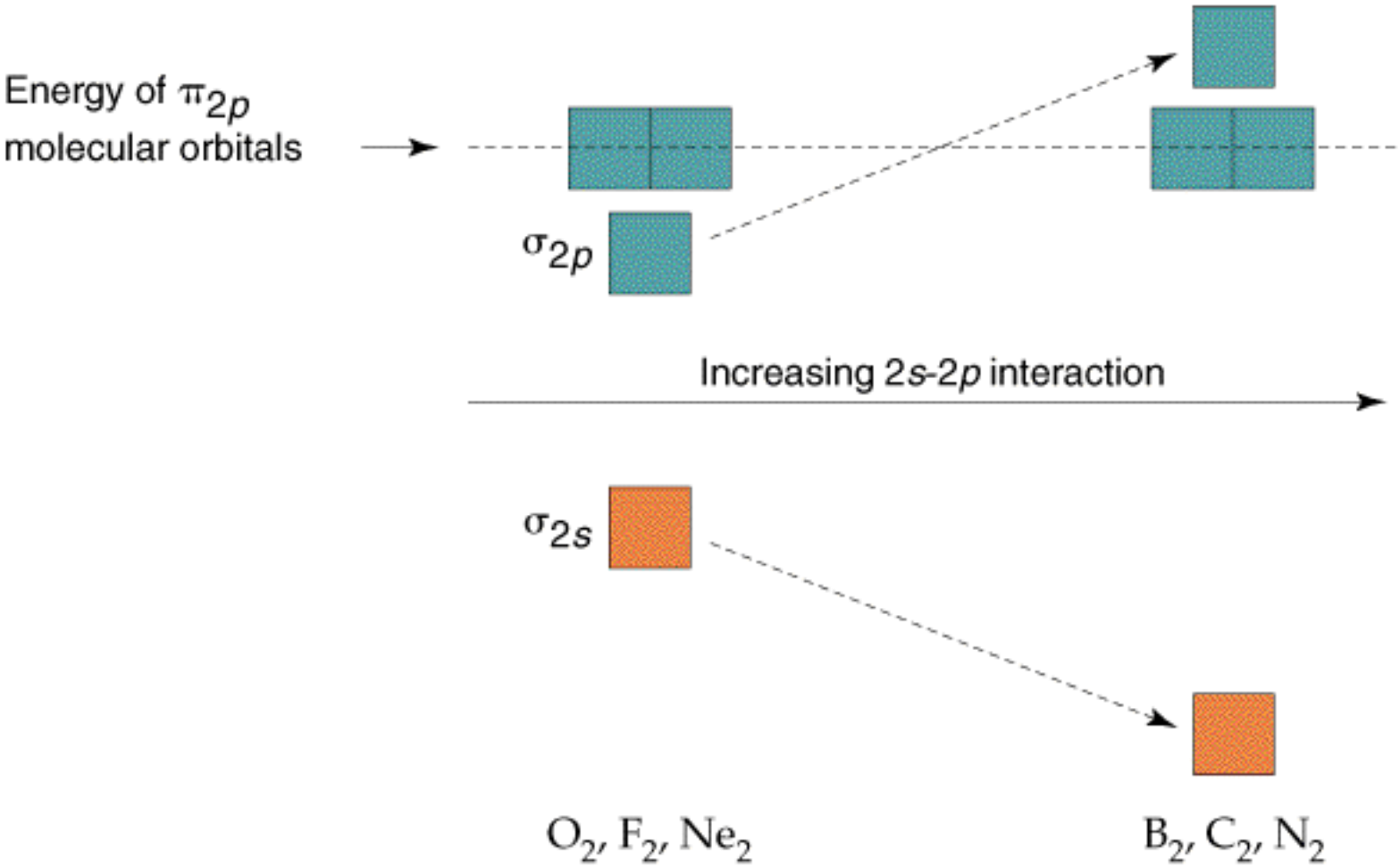
Second-Row Diatomic Molecules

Electron Configurations for B_2 through Ne_2

- As the atomic number decreases, it becomes more likely that a 2*s* orbital can interact with the 2*p* orbital.
  - As the 2*s*-2*p* interaction increases, the σ_{2s} MO decreases in energy and the σ_{2p} orbital increases in energy.
- For B_2, C_2 and N_2 the σ_{2p} orbital is higher in energy than the π_{2p}.
- For O_2, F_2 and Ne_2 the σ_{2p} orbital is lower in energy than the π_{2p}.

Second-Row Diatomic Molecules

Electron Configurations for B_2 through Ne_2



Second-Row Diatomic Molecules

Electron Configurations and Molecular Properties

Two types of magnetic behavior:

- **Paramagnetism, unpaired electrons in molecule**
- **Diamagnetism, no unpaired electrons in molecule**

Second-Row Diatomic Molecules

Electron Configurations for B_2 through Ne_2