

GENERAL CHEMISTRY

Chapter 3

Molecular Geometry and Bonding Theories

Dr. Huỳnh Kỳ Phương Hạ

Office: 112 B2 Building

Phone: 38650484

Email: hkpha@hcmut.edu.vn

Chemical Bonds, Lewis Symbols, and the Octet Rule

Chemical bond: attractive force holding two or more atoms together.

Electrostatic force: positive charge – negative charge

Covalent bond results from sharing electrons between 2 atoms.

Usually found between nonmetals. (nucleus – electron – nucleus)

Ionic bond results from the transfer of electrons from a metal to a nonmetal. ($M^+ - X^-$) $M \rightarrow$ cation, $X \rightarrow$ anion

Metallic bond: attractive force holding pure metals together. (M^+ sharing electron of entire system)

Hydrogen bond is a **special type of attractive interaction** (perhaps a variation of a dipole-dipole bond) that exists between an **electronegative atom** and a hydrogen atom bonded to another **electronegative atom** (N, O, F). $X \cdots H-X$

Lewis Symbols

- As a pictorial understanding of where the valence electrons are in an atom, we represent the electrons as dots around the symbol for the element.
- The number of electrons available for bonding are indicated by unpaired dots.
- These symbols are called Lewis symbols.
- We generally place the electrons one four sides of a square around the element symbol.

Lewis Symbols

Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
Li	[He]2s ¹	Li·	Na	[Ne]3s ¹	Na·
Be	[He]2s ²	·Be·	Mg	[Ne]3s ²	·Mg·
B	[He]2s ² 2p ¹	·B·	Al	[Ne]3s ² 3p ¹	·Al·
C	[He]2s ² 2p ²	·C·	Si	[Ne]3s ² 3p ²	·Si·
N	[He]2s ² 2p ³	·N·	P	[Ne]3s ² 3p ³	·P·
O	[He]2s ² 2p ⁴	·O·	S	[Ne]3s ² 3p ⁴	·S·
F	[He]2s ² 2p ⁵	·F·	Cl	[Ne]3s ² 3p ⁵	·Cl·
Ne	[He]2s ² 2p ⁶	·Ne·	Ar	[Ne]3s ² 3p ⁶	·Ar·

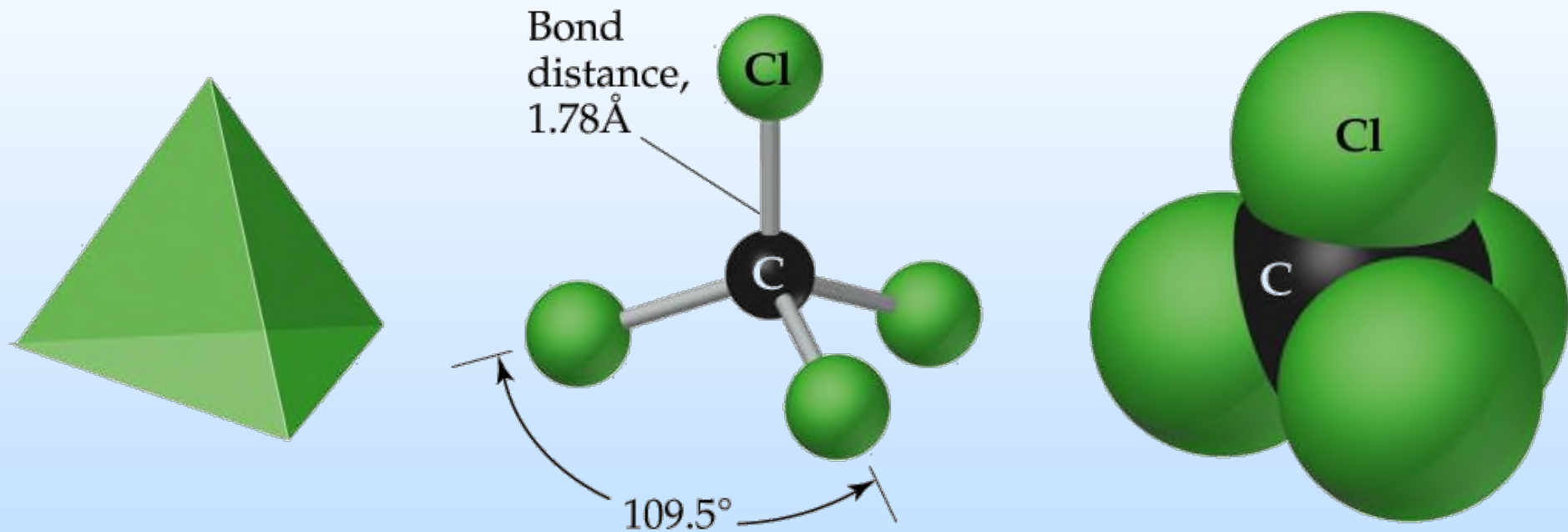
The Octet Rule

- **All noble gases except He has an s^2p^6 configuration.**
- **Octet rule:** atoms tend to gain, lose, or share electrons until they are surrounded by 8 valence electrons (**4 electron pairs**).
- **H: 2 e (He)**
- **Caution:** there are many exceptions to the octet rule.
- **Main group: ns np**

Molecular Shapes

- **Lewis structures** give atomic connectivity: they tell us which atoms are physically connected to which. However, do not show their overall shape)
- **A molecule's shape** is determined by its bond angles.
- Consider CCl_4 : experimentally we find all Cl-C-Cl bond angles are 109.5° .
 - Therefore, the molecule cannot be planar. (90°)
 - All Cl atoms are located at the vertices of a tetrahedron with the C at its center.

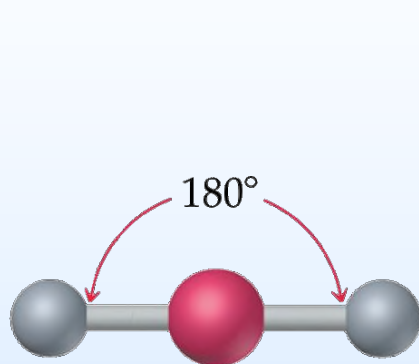
Molecular Shape of CCl_4



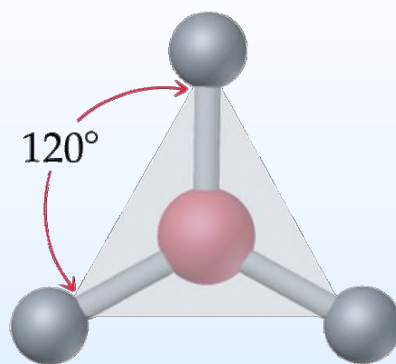
VSEPR Theory

- In order to predict molecular shape, we assume the valence electrons around central atom repel each other. Therefore, the molecule adopts which ever 3D geometry minimized this repulsion.
- Stable: low energy \rightarrow symmetric
- We call this process **Valence Shell Electron Pair Repulsion (VSEPR)** theory.
- There are simple shapes for AB_2 and AB_3 molecules (see page 347).

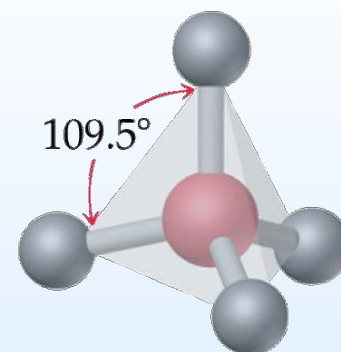
Molecular Shape: Five Fundamental Geometries



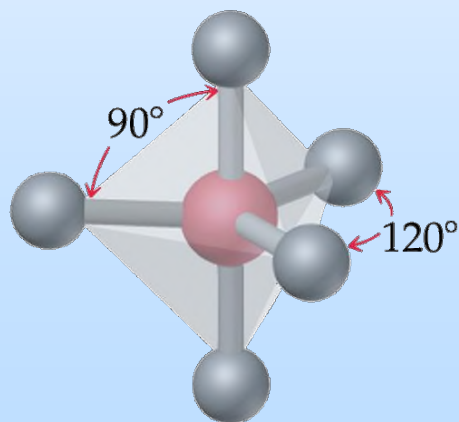
Linear



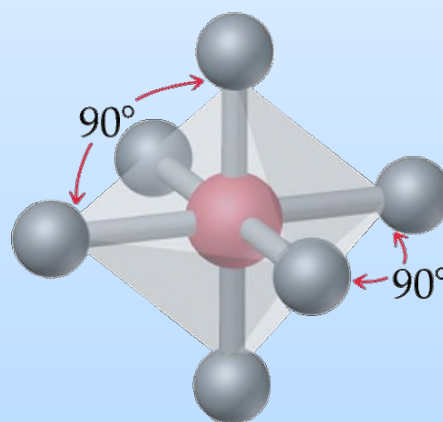
Trigonal planar



Tetrahedral



Trigonal bipyramidal



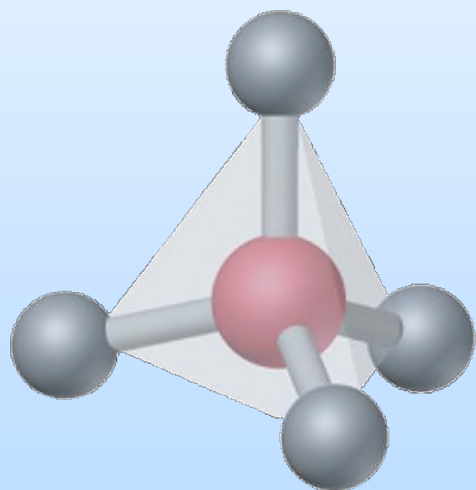
Octahedral

Total pairs of valence electron

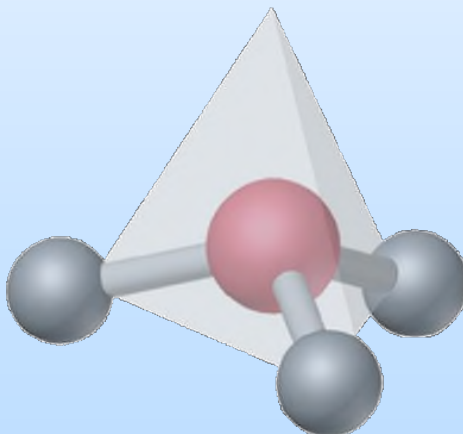
- When considering the **geometry about the central atom** (electron domain geometry), we consider all electrons
- Electron around central atom A: 2 groups
 - electron pair that share or connect to B: bonding pairs
 - electron pair just belong to atom A: lone pair or non-bonding
- Electron domain geometry
- When naming the molecular geometry, we focus only on the **positions of the atoms**. (bonding pair)
- electron pair: empty space/nothing there, moving
- Lone pair: no atom → empty or nothing

Naming Molecular Geometry

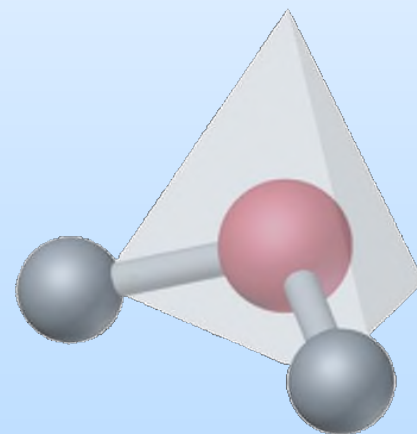
- When considering the geometry about the central atom, we consider all electrons (lone pairs and bonding pairs).
- When naming the molecular geometry, we focus only on the positions of the atoms.



Tetrahedral



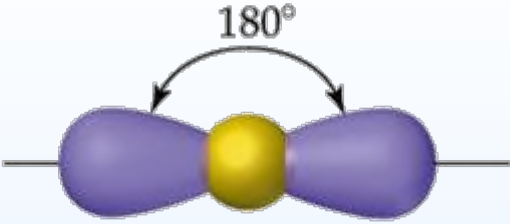
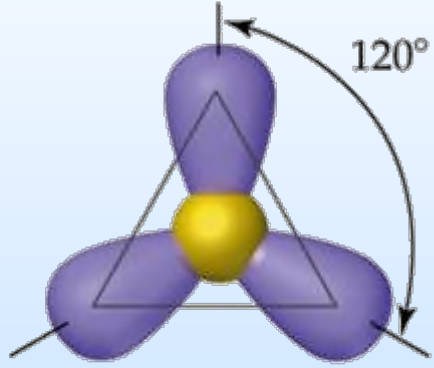
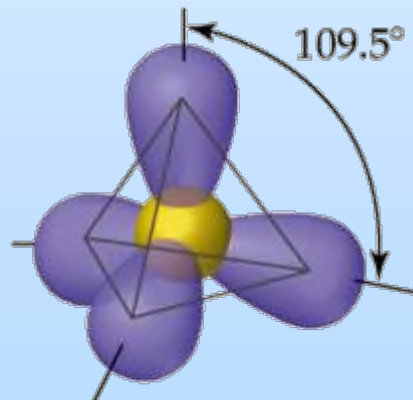
Trigonal pyramidal

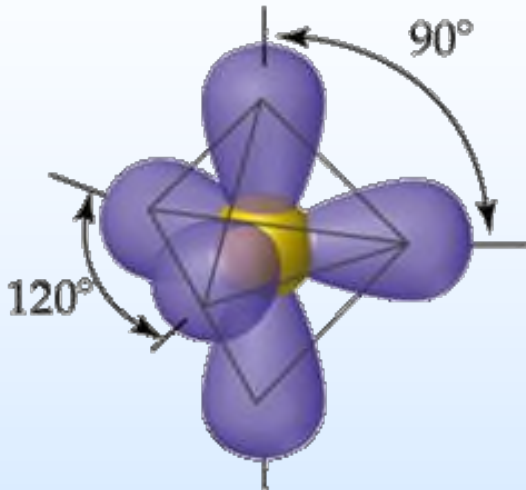
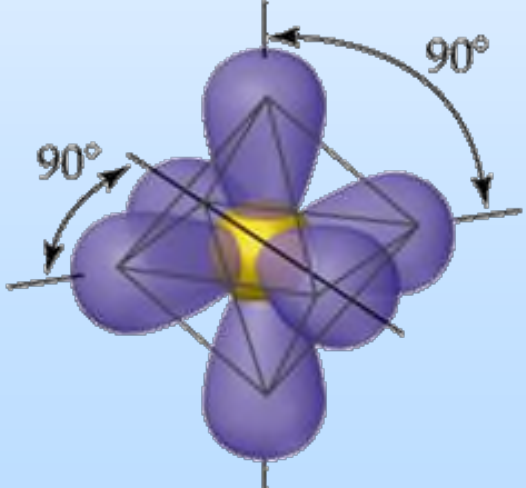


Bent

VSEPR Model

- We define the electron domain geometry by the positions in 3D space of *ALL* electron pairs (bonding or non-bonding).
- The electrons adopt an arrangement in space to minimize e^- - e^- pair repulsion. (symmetric arrangement)
- To determine the shape of a molecule, we distinguish between lone pairs (or non-bonding pairs, those not in a bond) of electrons and bonding pairs (those found between two atoms).

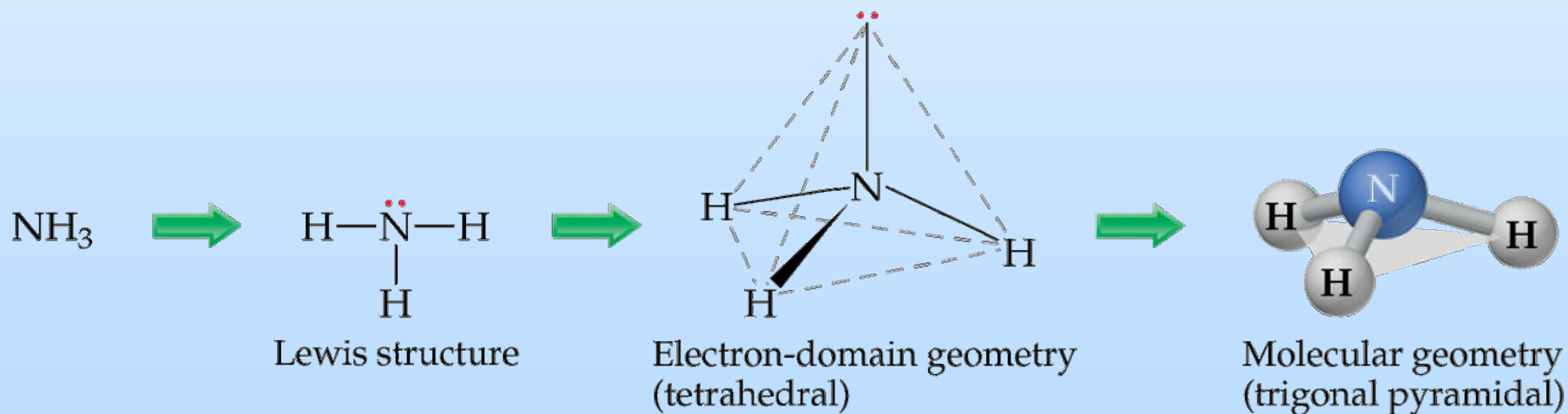
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

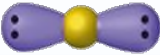
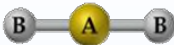
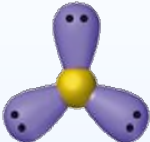
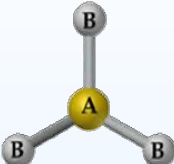
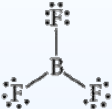
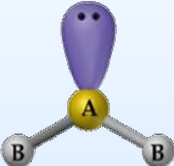

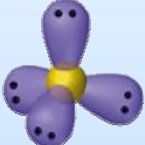
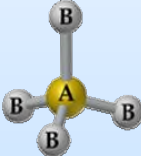
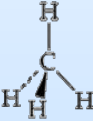
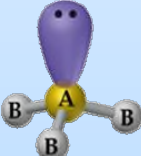

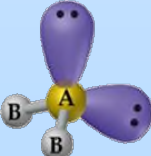

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°


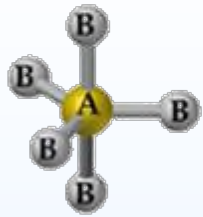
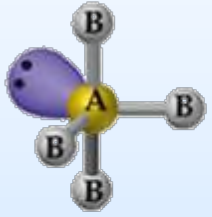
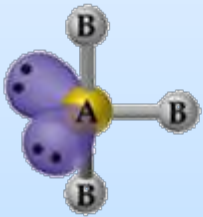
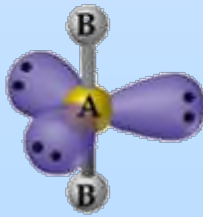
VSEPR Model


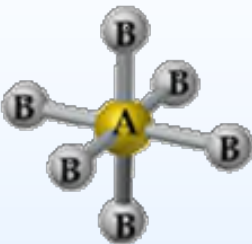
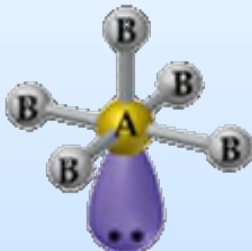
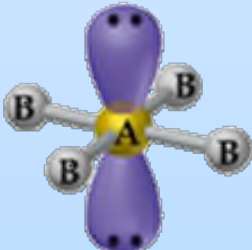
To determine the electron pair geometry (e domain):

- draw the Lewis structure,
- count the total number of electron pairs around the central atom,
- arrange the electron pairs in one of the above geometries to minimize e^-e^- repulsion, and count multiple bonds as one bonding pair.



Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
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

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

Practice

- Molecular shape and bonding angle:

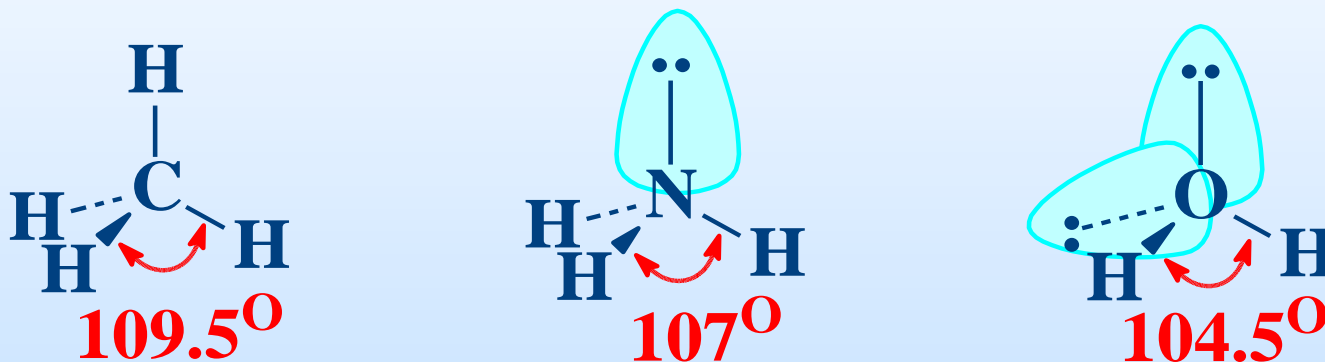
BeF ₂	CS ₂	PH ₃	H ₂ O	ClO ₂
BCl ₃	CH ₄	NO ₂ ⁺	SO ₂	ClO ₂ ⁻
	CO ₃ ²⁻	NO ₂	SO ₃	ClO ₃ ⁻
		NO ₂ ⁻	SO ₃ ²⁻	ClO ₄ ⁻
		NH ₄ ⁺	SO ₄ ²⁻	
			H ₃ O ⁺	

The Effect of Nonbonding Electrons

- We determine the electron pair geometry only looking at electrons. (electron domain)
- We name the molecular geometry by the positions of atoms. (bonding pair)
- We ignore lone pairs in the molecular geometry.
- All the atoms that obey the octet rule have tetrahedral electron pair geometries.

The Effect of Nonbonding Electrons on Bond Angles

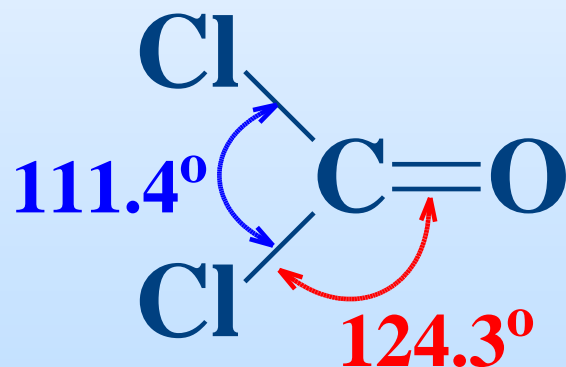
- By experiment, the H-X-H bond angle decreases on moving from C to N to O:



- Since electrons in a bond are attracted by two nuclei, they do not repel as much as lone pairs.
- Therefore, the bond angle decreases as the number of lone pairs increase.

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

- Similarly, electrons in multiple bonds repel more than electrons in single bonds.



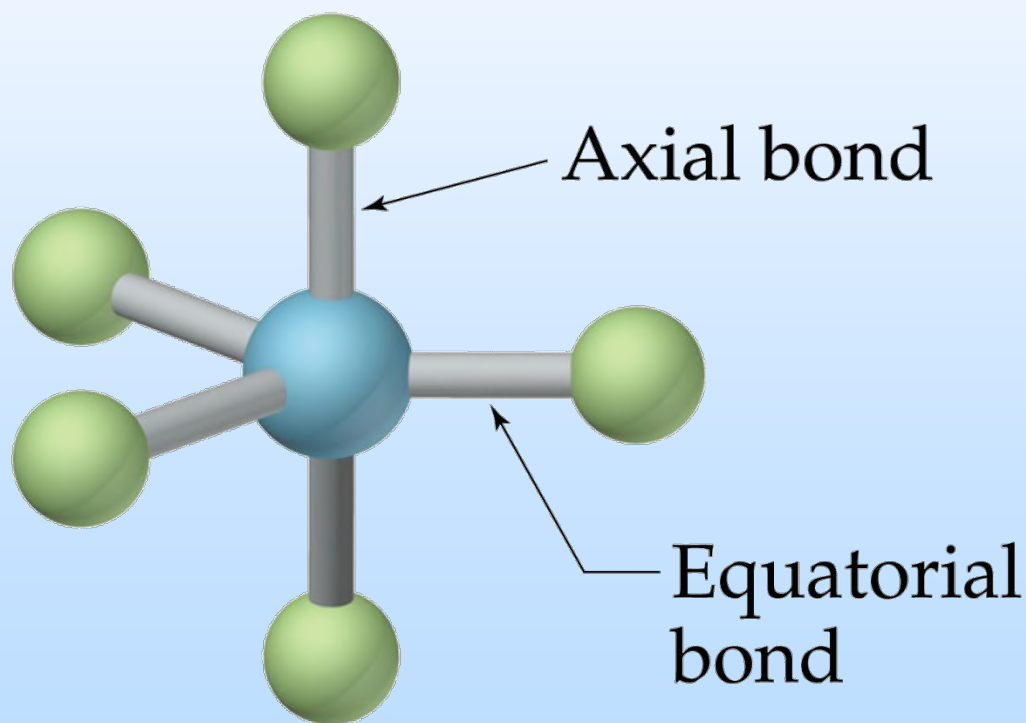
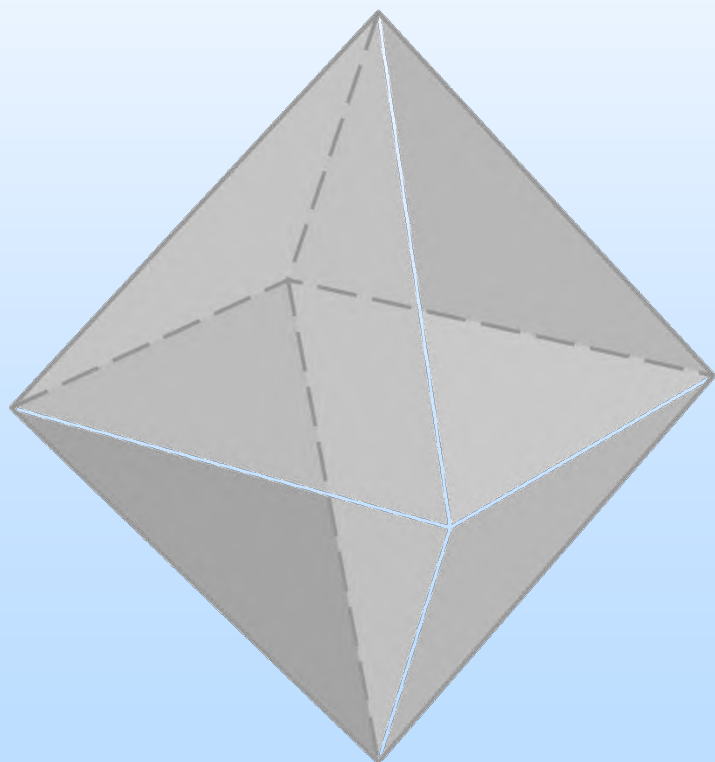
- Single e repel less than a bonding pair/full pair \rightarrow bond angle become bigger NO_2 : $\text{ONO} > 120^\circ$ $\text{NO}_2 > \text{NO}_2^-$

Molecules with Expanded Valence Shells

- Atoms that have expanded octets have AB_5 (trigonal bipyramidal) or AB_6 (octahedral) electron pair geometries.
- For trigonal bipyramidal structures there is a plane containing three electron pairs. The fourth and fifth electron pairs are located above and below this plane.
- For octahedral structures, there is a plane containing four electron pairs. Similarly, the fifth and sixth electron pairs are located above and below this plane.

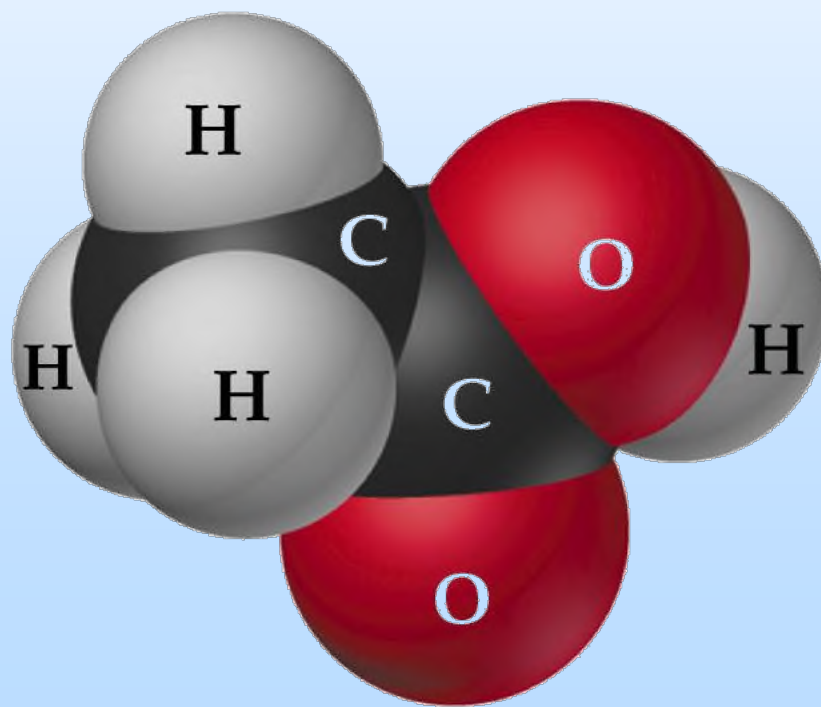
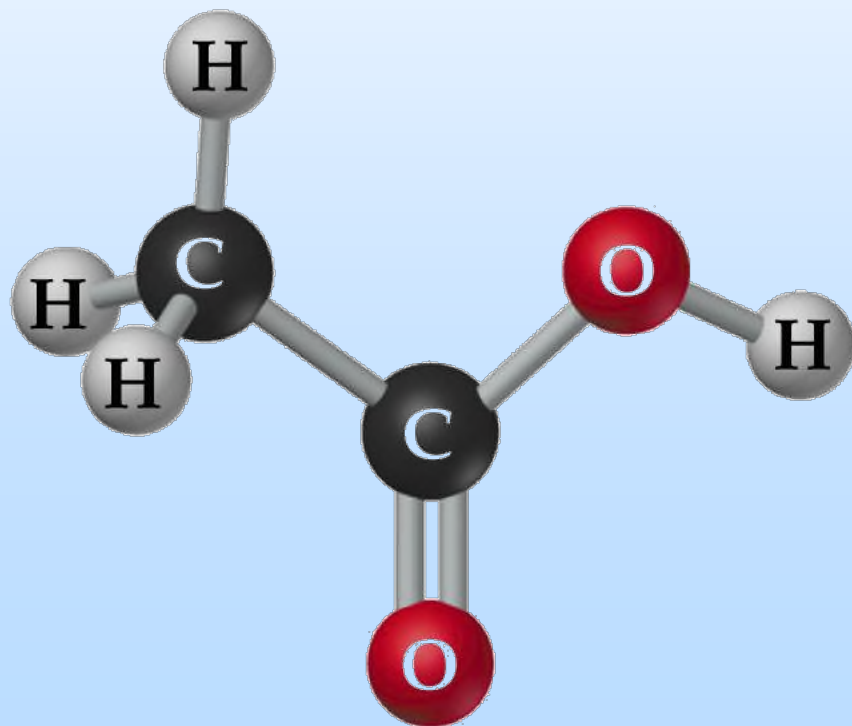
Molecules with Expanded Valence Shells

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



Shapes of Larger Molecules

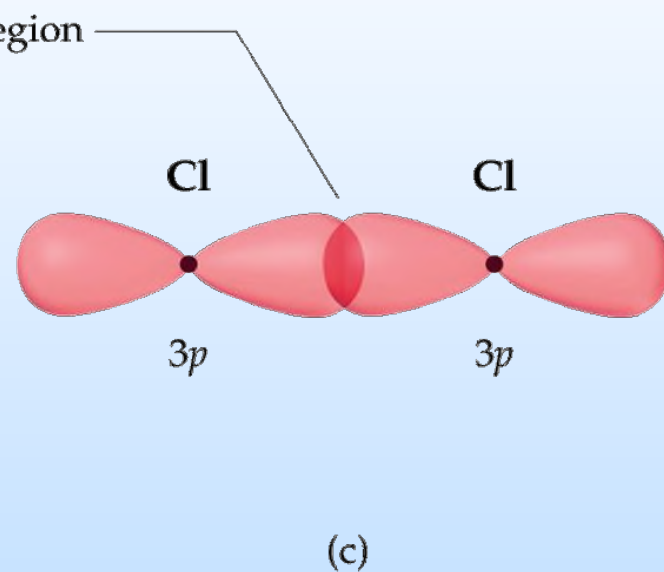
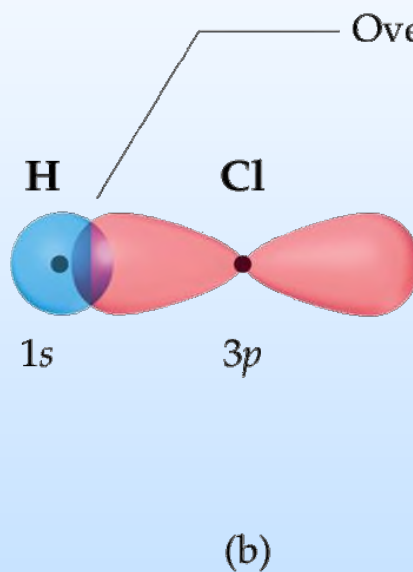
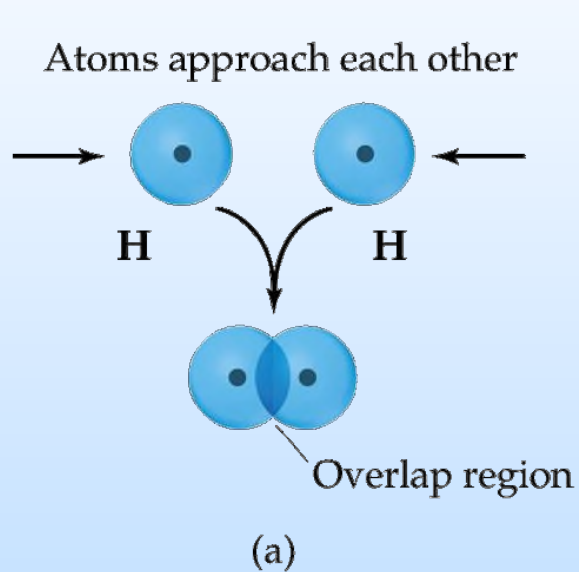
- In acetic acid, CH_3COOH , there are three central atoms (surrounded by at least 2 atoms).
- We assign the geometry about each central atom separately.



Covalent Bonding and Orbital Overlap

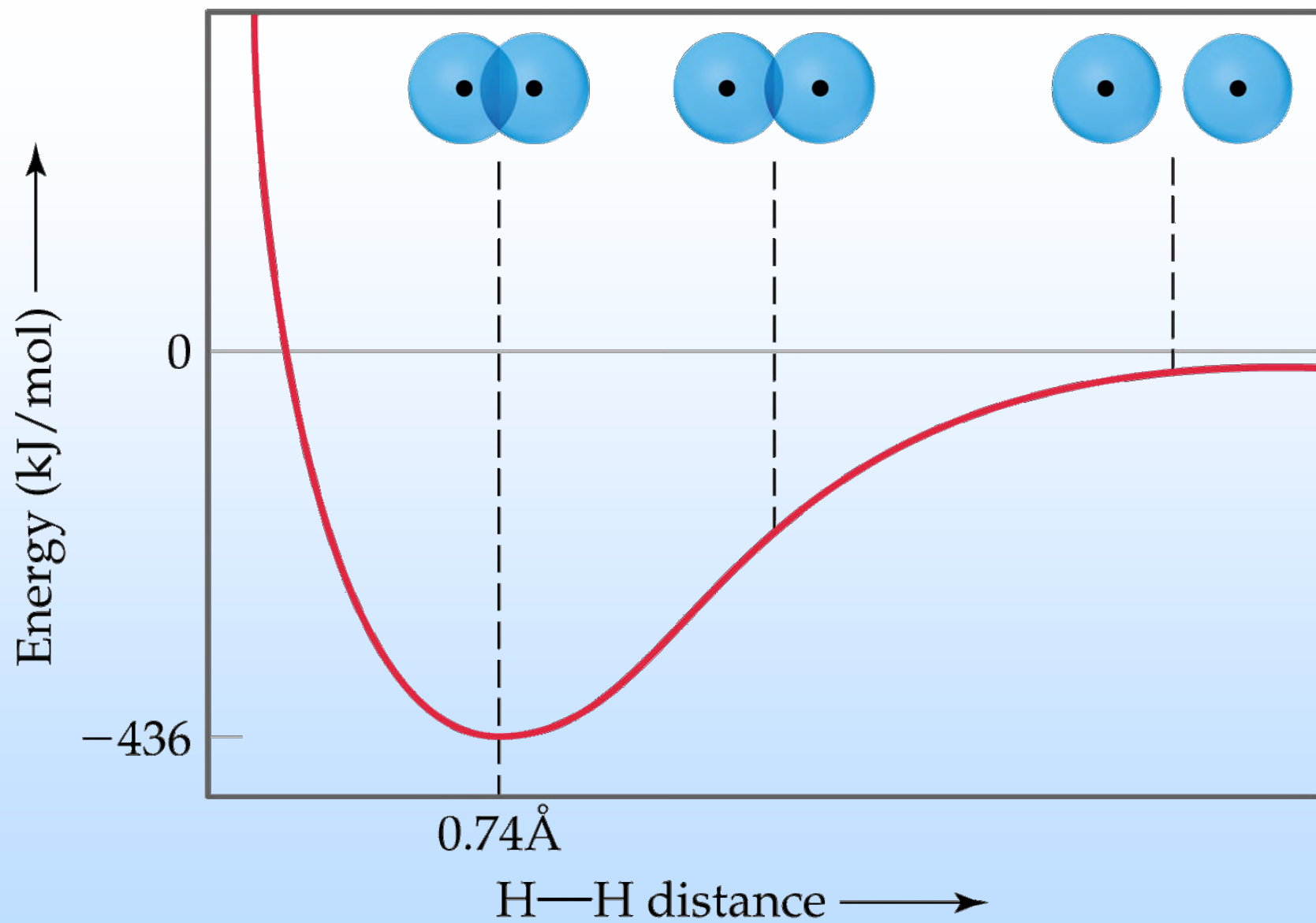
- Lewis structures and VSEPR do not explain how a bond forms.
- How the atom can share the electron
- How do we account for shape in terms of quantum mechanics?
- What are the orbitals that are involved in bonding?
- We use Valence Bond Theory:
 - Bonds form when orbitals on atoms overlap.
 - There are two electrons of opposite spin in the orbital overlap.

Covalent Bonding Illustration



Covalent Bonding and Orbital Overlap Mechanism

- As two nuclei approach each other their atomic orbitals overlap.
- As the amount of overlap increases, the energy of the interaction decreases. (share electron → more stable config.)
- At some distance the minimum energy is reached.
- The minimum energy corresponds to the bonding distance (or bond length).
- As the two atoms get closer, their nuclei begin to repel and the energy increases.
- At the bonding distance, the attractive forces between nuclei and electrons just balance the repulsive forces (nucleus-nucleus, electron-electron).



Hybrid Orbitals

- Atomic orbitals can mix or **hybridize** in order to adopt an appropriate geometry for bonding.
- Hybridization is determined by the electron domain geometry.

sp Hybrid Orbitals

- Consider the BeF_2 molecule (experimentally known to exist):

sp Hybrid Orbitals

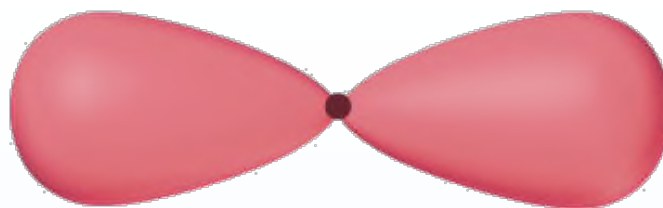
- Be has a $1s^2 2s^2$ electron configuration.
- There is no unpaired electron available for bonding.
- We conclude that the atomic orbitals are not adequate to describe orbitals in molecules.
- We know that the F-Be-F bond angle is 180° (VSEPR theory).
- We also know that one electron from Be is shared with each one of the unpaired electrons from F.

sp Hybrid Orbitals

- We assume that the Be orbitals in the Be-F bond are 180° apart.
 - We could promote an electron from the $2s$ orbital on Be to the $2p$ orbital to get two unpaired electrons for bonding.
 - BUT the geometry is still not explained. ($2s$ and $2p$: overlap with F)
- We can solve the problem by allowing the $2s$ and one $2p$ orbital on Be to mix or form a hybrid orbital..
- The hybrid orbital comes from an s and a p orbital and is called an sp hybrid orbital.
- The lobes of sp hybrid orbitals are 180° apart.



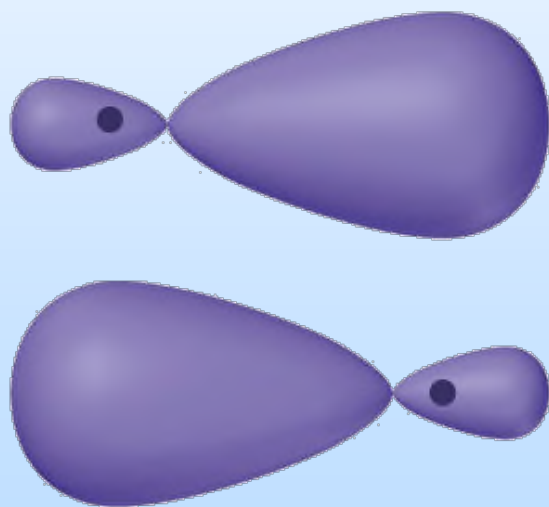
s orbital



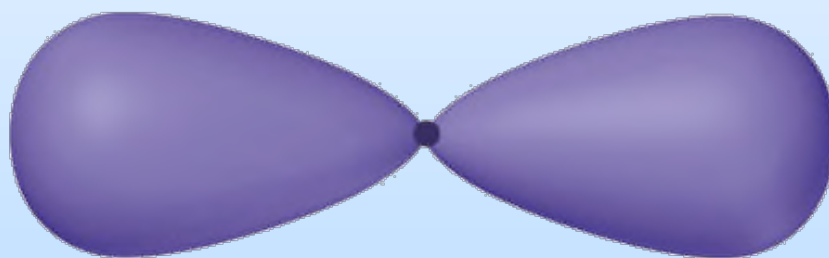
p orbital



Hybridize



Two *sp* hybrid orbitals



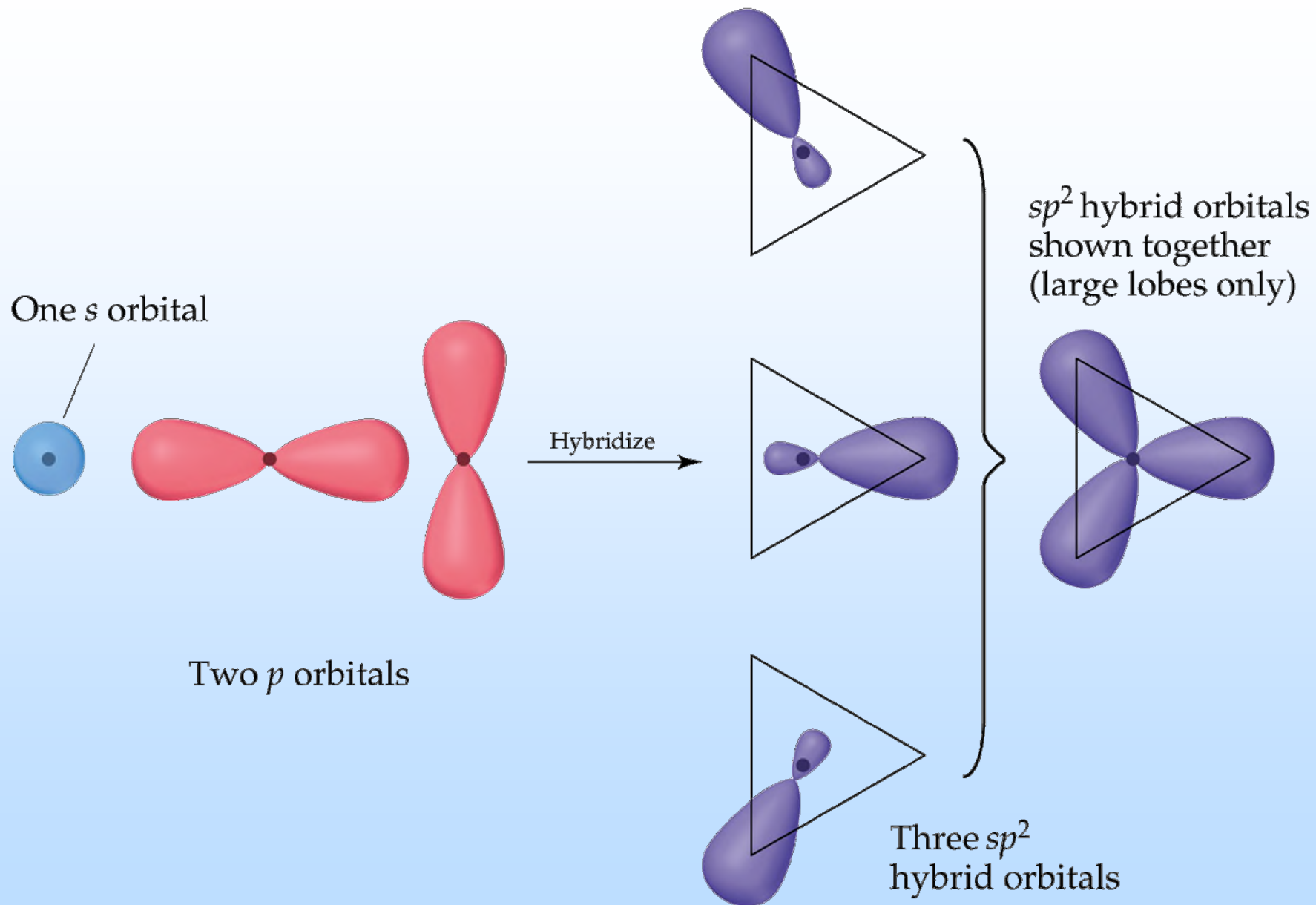
sp hybrid orbitals shown together
(large lobes only)

sp Hybrid Orbitals

- Since only one of the Be $2p$ orbitals has been used in hybridization, there are two unhybridized p orbitals remaining on Be.
- If hybridization: s and p_x , so p_y and p_z remaining (unhybridized), perpendicular to 2 sp hybrid orbital (x -axis)

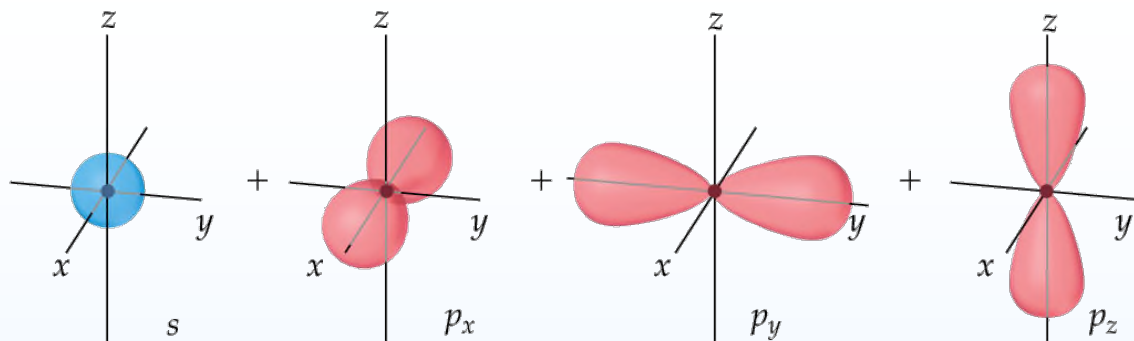
sp^2 Hybrid Orbitals

- *Important:* when we mix n atomic orbitals we must get n hybrid orbitals.
- sp^2 hybrid orbitals are formed with one s and two p orbitals. (Therefore, there is one unhybridized p orbital remaining.)
- The large lobes of sp^2 hybrids lie in a trigonal plane.
- All molecules with trigonal planar electron pair geometries have sp^2 orbitals on the central atom.

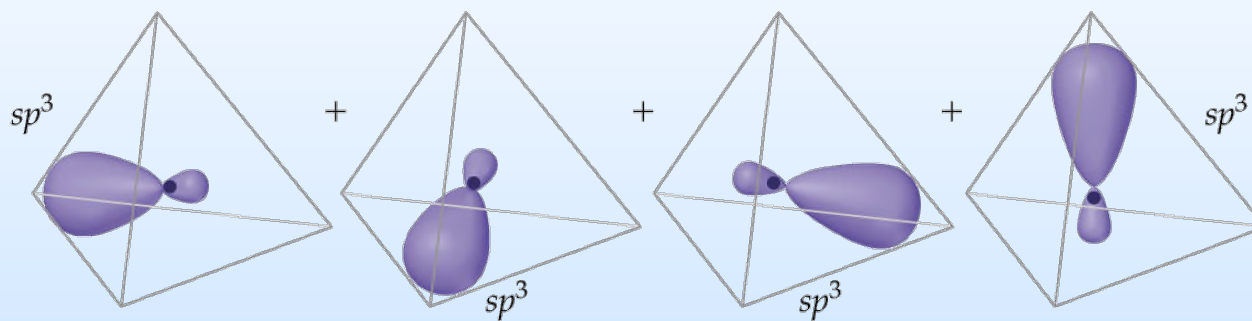


sp^3 Hybrid Orbitals

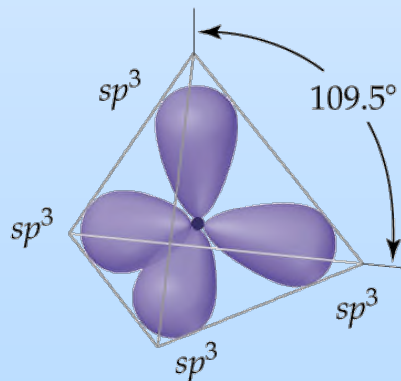
- sp^3 Hybrid orbitals are formed from one s and three p orbitals. Therefore, there are four large lobes.
- Each lobe points towards the vertex of a tetrahedron.
- The angle between the large lobes is 109.5° .
- All molecules with tetrahedral electron pair geometries are sp^3 hybridized.



Hybridize to form four sp^3 hybrid orbitals



Shown together (large lobes only)



VB & VSEPR

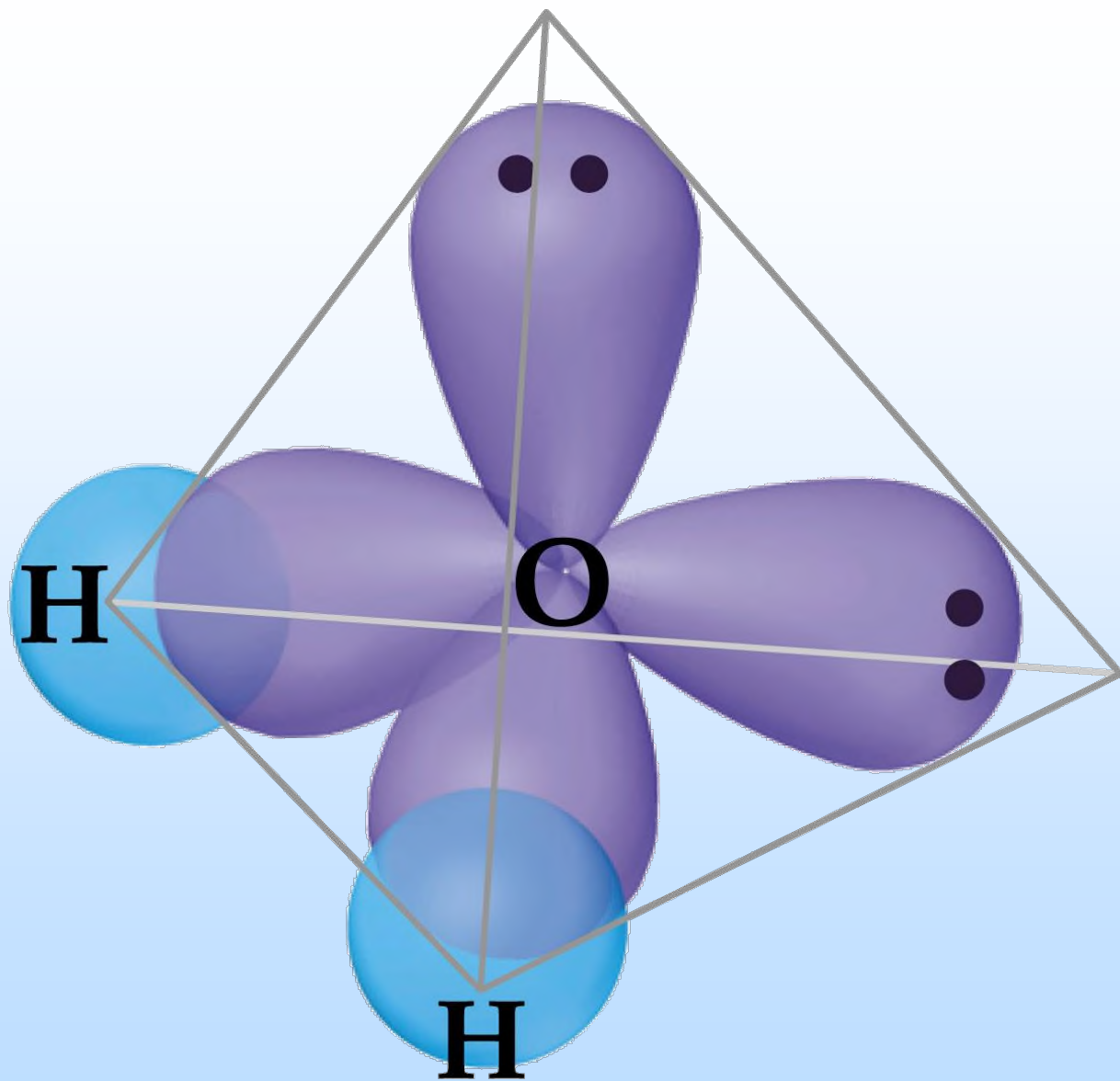
- **VSEPR:** *only* explain the shape
- **VB:** explain the mechanism (share electron)+explain the shape of molecules :
- The same: VSEPR: trigonal planar Hybridization: sp^2

Total pairs y	Electron domain geometry	Hybridization
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

Practice

- Hybridization of central atoms:

BeF ₂	CS ₂	PH ₃	H ₂ O	ClO ₂
BCl ₃	CH ₄	NO ₂ ⁺	SO ₂	ClO ₂ ⁻
	CO ₃ ²⁻	NO ₂	SO ₃	ClO ₃ ⁻
		NO ₂ ⁻	SO ₃ ²⁻	ClO ₄ ⁻
		NH ₄ ⁺	SO ₄ ²⁻	
			H ₃ O ⁺	

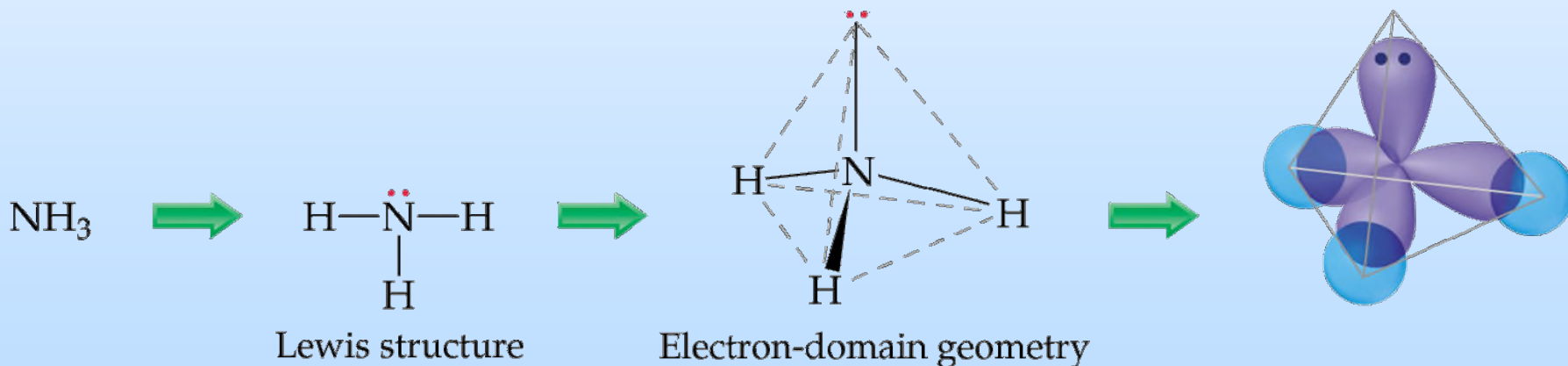


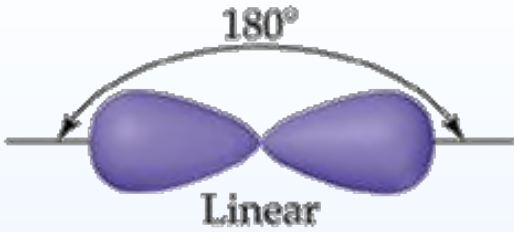
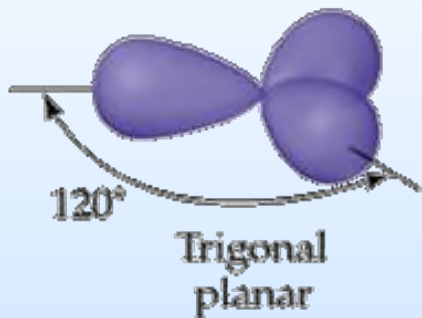
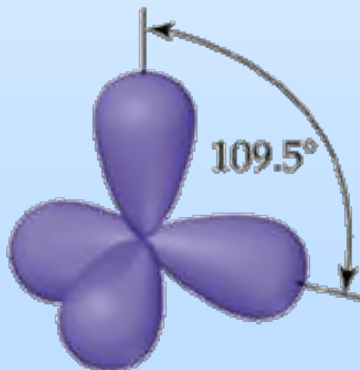
Hybridization Involving d Orbitals

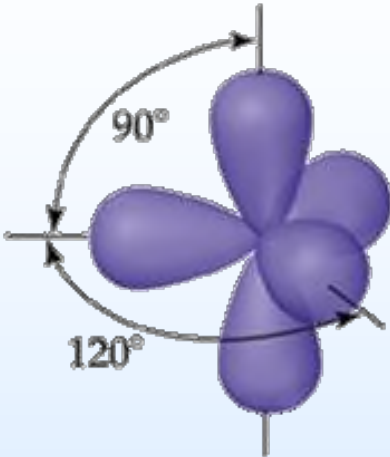
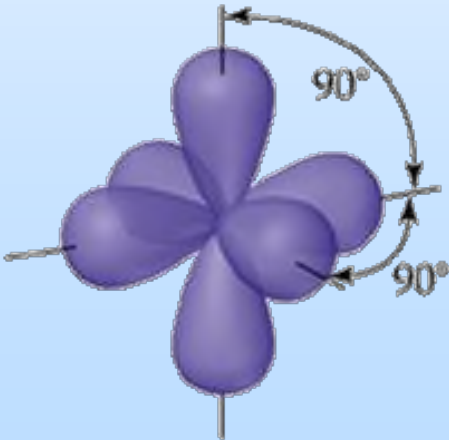
- Since there are only three p -orbitals, trigonal bipyramidal and octahedral electron domain geometries must involve d -orbitals.
- Trigonal bipyramidal electron domain geometries require sp^3d hybridization.
- Octahedral electron domain geometries require sp^3d^2 hybridization.
- Note the electron domain geometry from VSEPR theory determines the hybridization.

Hybrid Orbitals - Summary

1. Draw the Lewis structure (total pairs from formulae).
2. Determine the electron domain geometry with VSEPR.
3. Specify the hybrid orbitals required for the electron pairs based on the electron domain geometry.
4. Total pairs = electron domain = hybridization



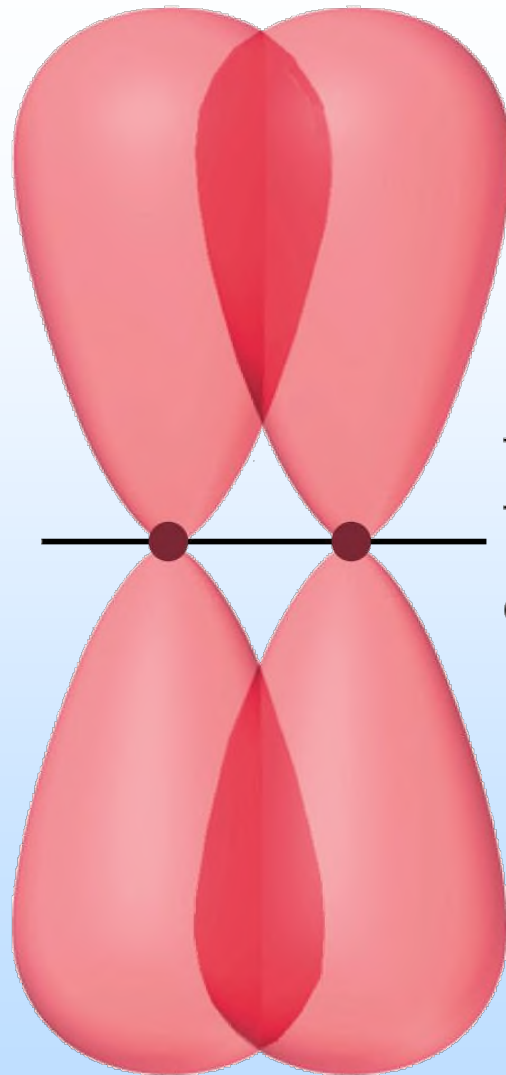
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	 <p>Linear</p>	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 <p>Trigonal planar</p>	BF_3, SO_3
s, p, p, p	Four sp^3	 <p>Tetrahedral</p>	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p, p, p, d	Five sp^3d	 <p>Trigonal bipyramidal</p>	PF_5 , SF_4 , BrF_3
s, p, p, p, d, d	Six sp^3d^2	 <p>Octahedral</p>	SF_6 , ClF_5 , XeF_4 , PF_6^-

Multiple Bonds

- σ -Bonds: electron density lies on the axis between the nuclei.
- Strongest, first bond, only one (one axis between two)
- All single bonds are σ -bonds. (First bond formed between two atom is σ)
- 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.
- Often, the p -orbitals involved in π -bonding come from unhybridized orbitals.

π bond



Internuclear
axis

p

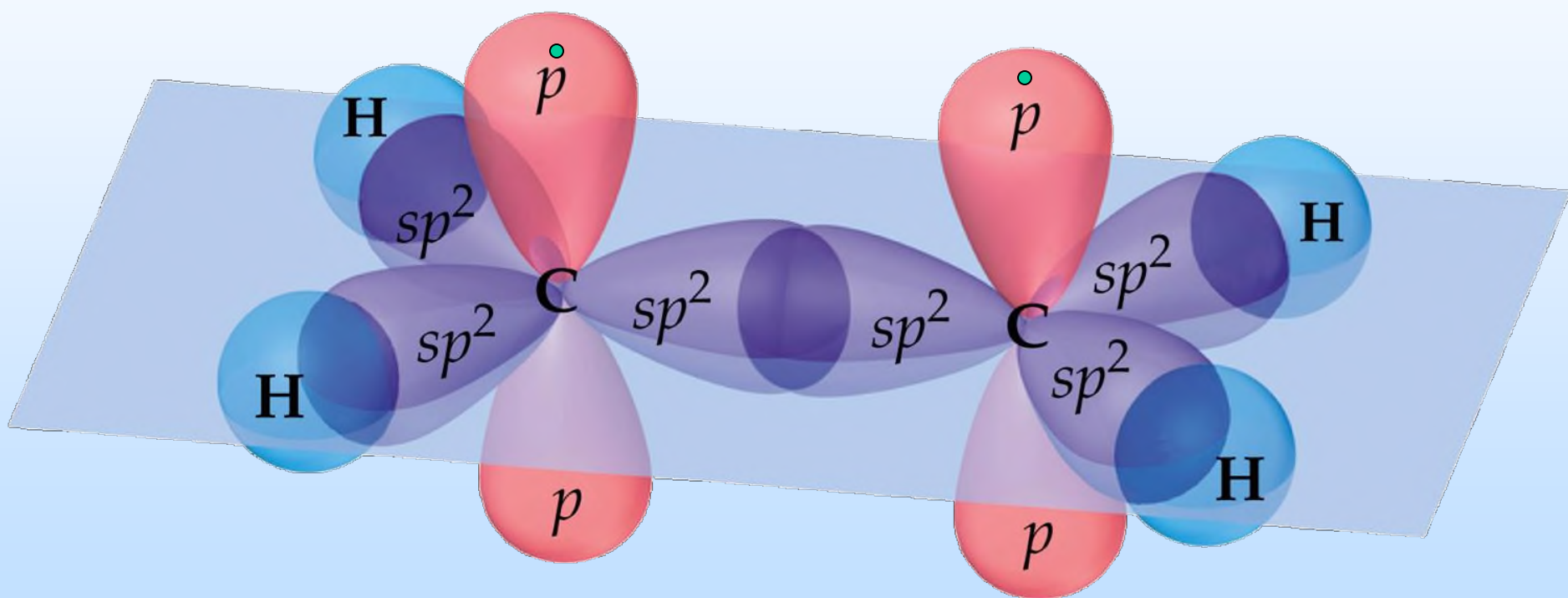
p

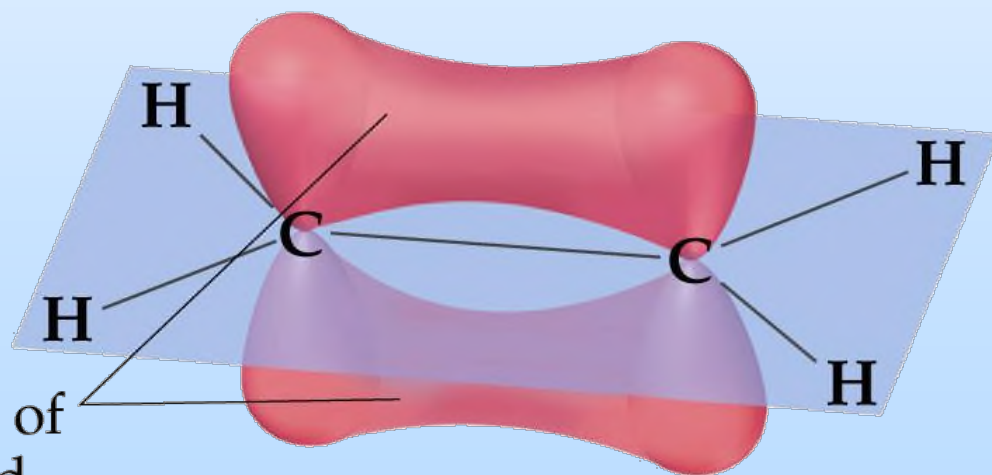
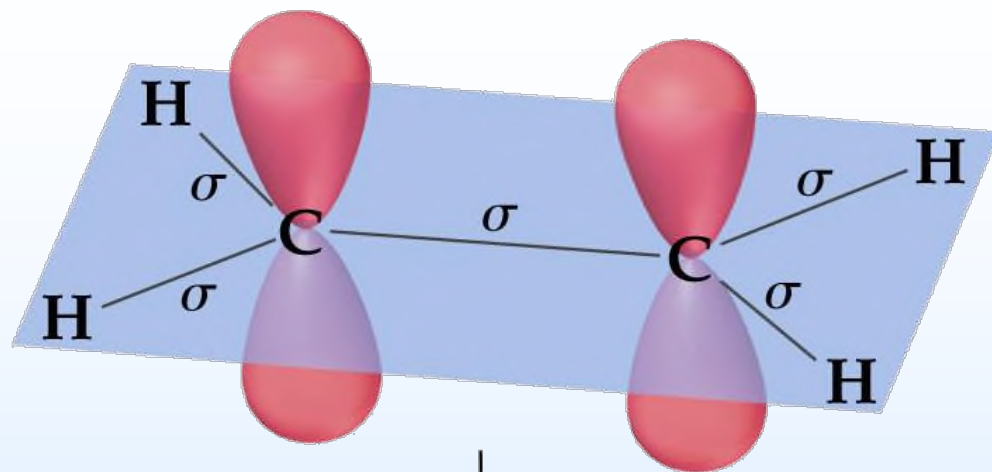
Multiple Bonds

Ethylene, C_2H_4 , has: $\text{H}_2\text{C}=\text{CH}_2$

- 3 atoms around each C (2 H and 1 C),
- C: 4 bonds (no lone pair) and 3 atoms, therefore:
- three σ - and one π -bond;
- both C atoms sp^2 hybridized;
- both C atoms with trigonal planar electron pair and molecular geometries.

Ethylene



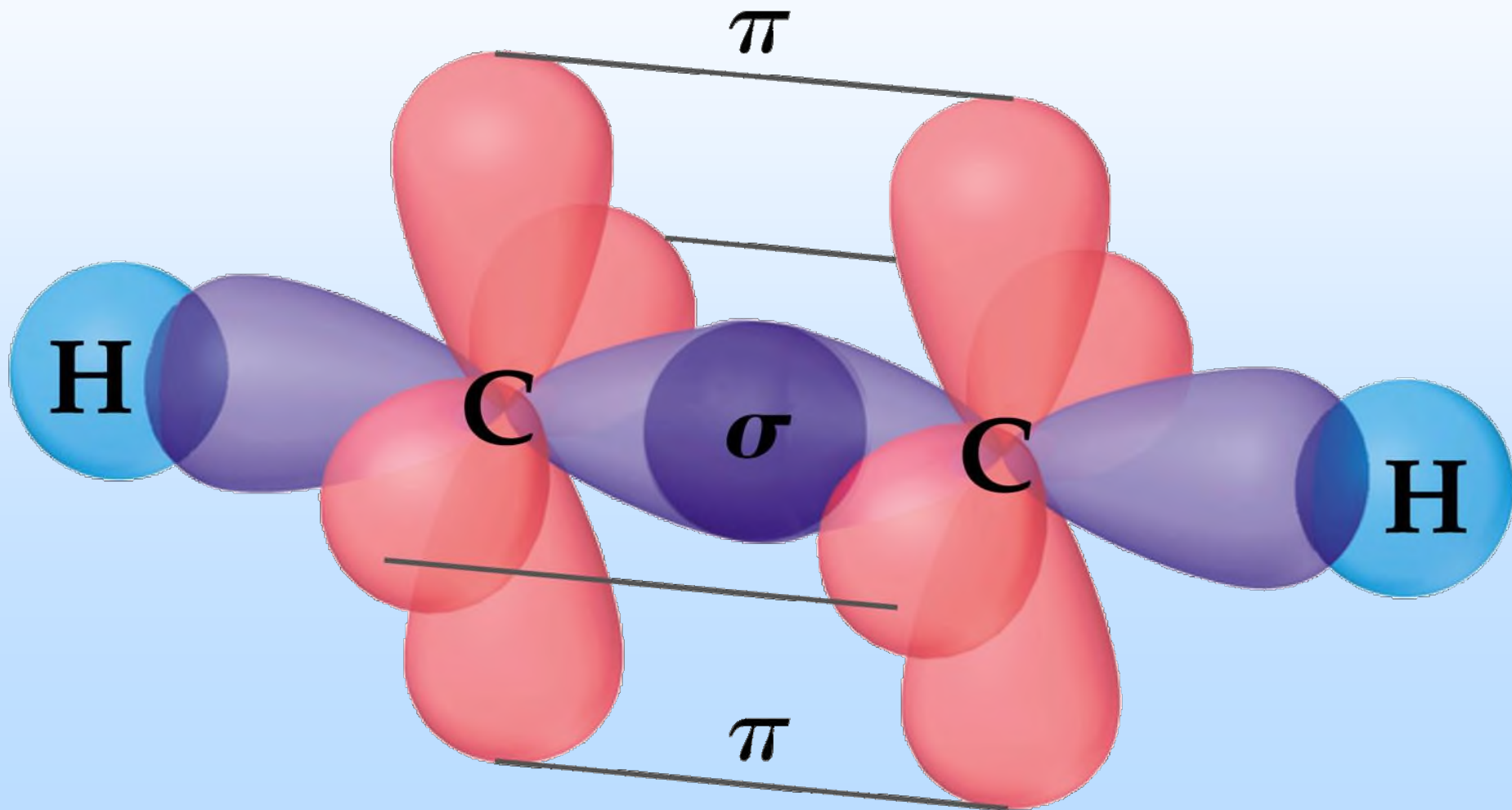


Two lobes of
one π bond

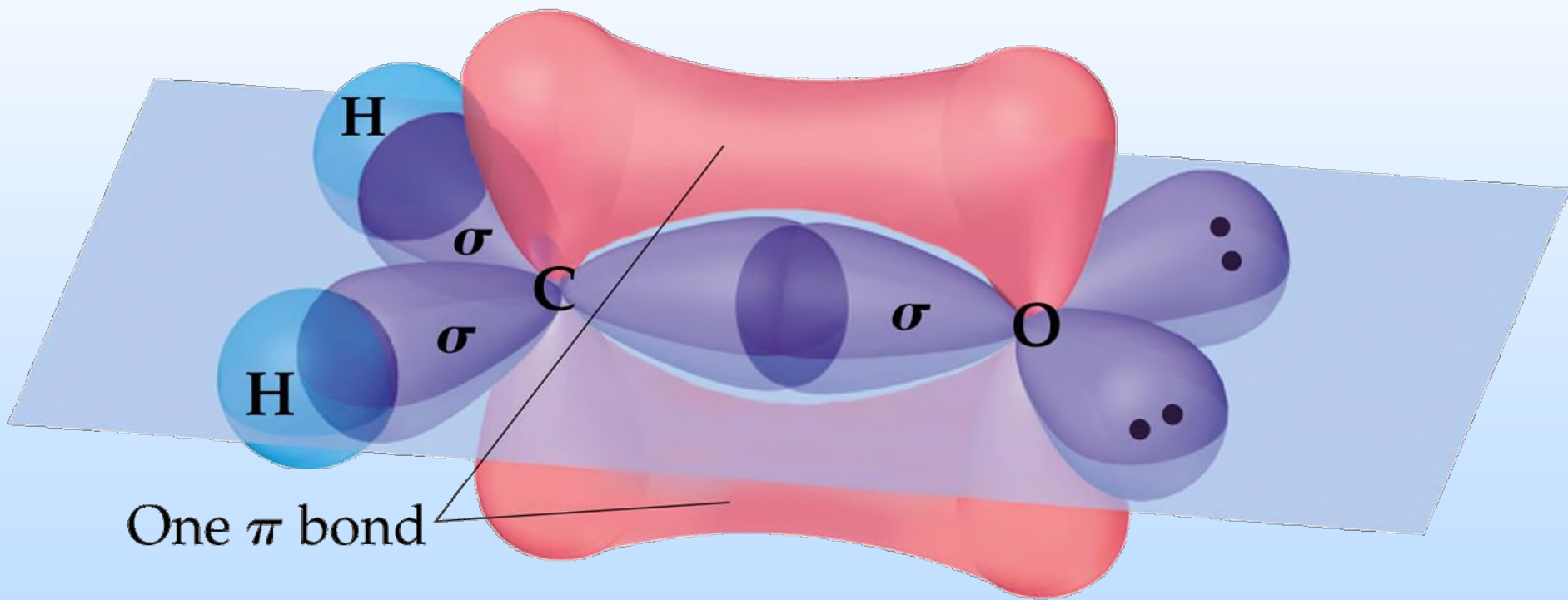
Multiple Bonds

- Consider acetylene, C_2H_2 $\text{HC}\equiv\text{CH}$
 - Around each C: 2 atoms 1 C and 1 H \rightarrow sp
 - the electron pair geometry of each C is linear;
 - therefore, the C atoms are sp hybridized;
 - the sp hybrid orbitals form the C-C and C-H σ -bonds;
 - there are two unhybridized p -orbitals;
 - both unhybridized p -orbitals form the two π -bonds;
 - one π -bond is above and below the plane of the nuclei;
 - one π -bond is in front and behind the plane of the nuclei.
- When triple bonds form (e.g. N_2) one π -bond is always above and below and the other is in front and behind the plane of the nuclei.

Acetylene



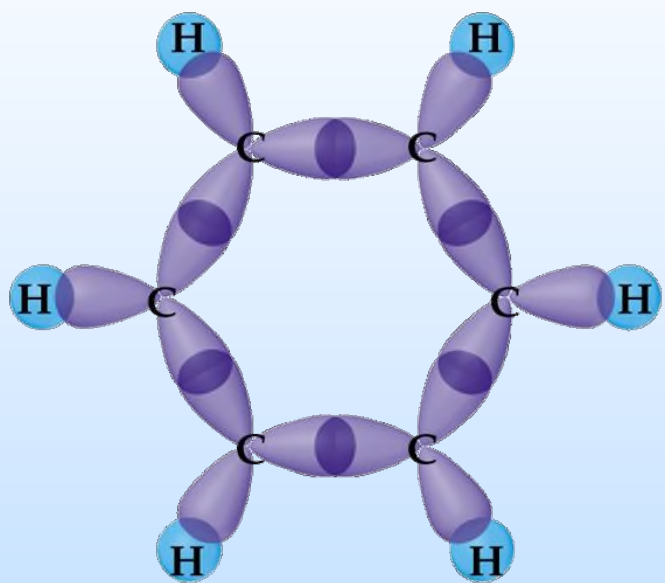
π -Bonds



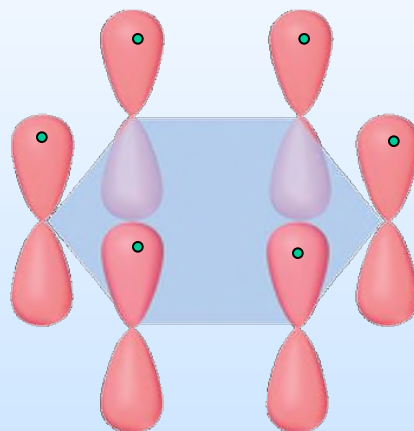
Delocalized π Bonding

- So far all the bonds we have encountered are localized between two nuclei. (position is fixed)
- In the case of benzene: C_6H_6
 - there are 6 C-C σ bonds, 6 C-H σ bonds,
 - each C atom is sp^2 hybridized,
 - and there are 1 unhybridized p orbitals on each C atom.
 - 6 unhybridized p orbitals in total

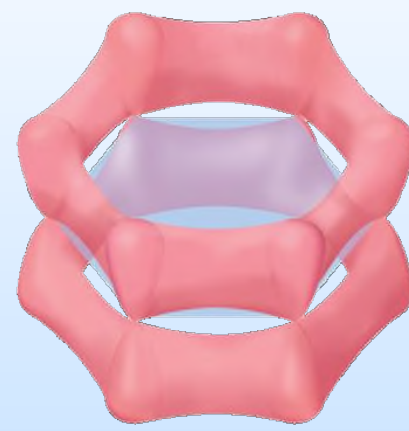
Delocalized π Bonding



(a) σ bonds



(b) $2p$ atomic orbitals



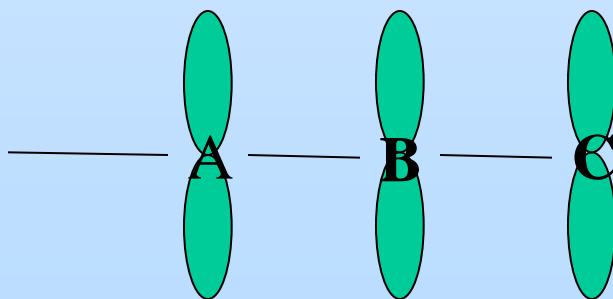
(c) Delocalized π bonds

Delocalized π Bonding

- In benzene there are two options for the 3 π bonds
 - localized between C atoms or
 - delocalized over the entire ring (i.e. the π electrons are shared by all 6 C atoms).
- Experimentally, all C-C bonds are the same length in benzene.
- Therefore, all C-C bonds are of the same type (recall single bonds are longer than double bonds).

Multiple Bonds - General Conclusions

- Every two atoms share at least 2 electrons. (form bond)
- Two electrons between atoms on the same axis as the nuclei are σ bonds.
- σ -Bonds are always localized.
- If two atoms share more than one pair of electrons, the second and third pair form π -bonds.
- When resonance structures are possible, delocalization is also possible. (CO_3^{2-}) $p - \sigma - \pi$ $\pi - \sigma - \pi$



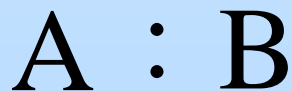
Molecular Shape and Molecular Polarity

- When there is a difference in electronegativity between two atoms, then the bond between them is polar.
- It is possible for a molecule to contain polar bonds, but not be polar.
- For example, the bond dipoles in CO_2 cancel each other because CO_2 is linear.

Bonding polarity

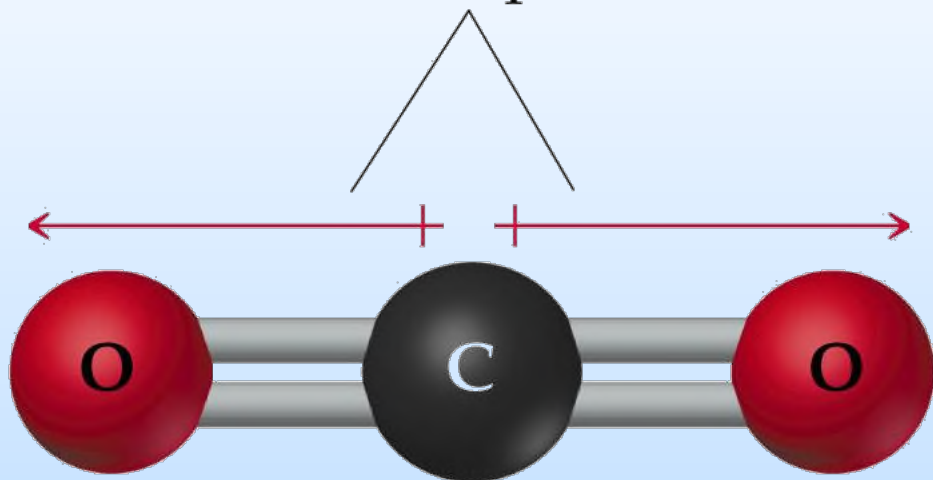
- Non-polar bond: Br_2 , $\text{CH}_3\text{-CH}_3$ (A, B: identical)
- When there is a difference in electronegativity between two atoms
- 2 “ends” of the bond: dipole, polar \rightarrow dipole moment

$$\mu = Qr$$

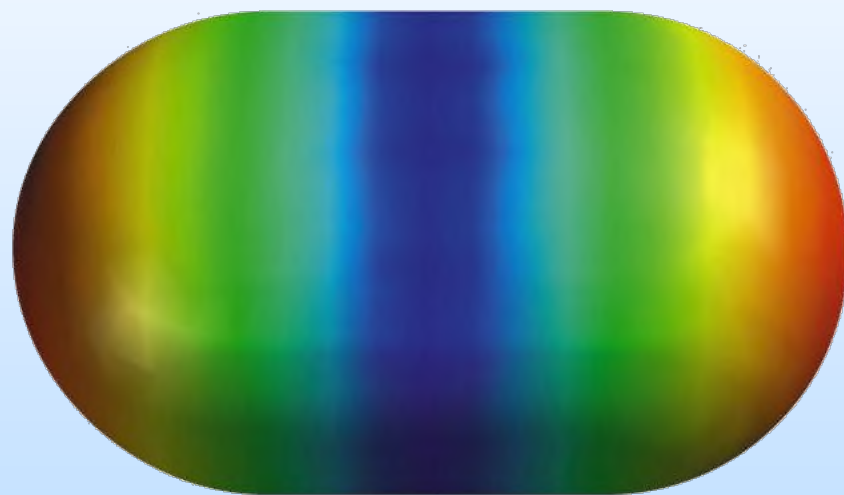


Carbon Dioxide

Bond dipoles



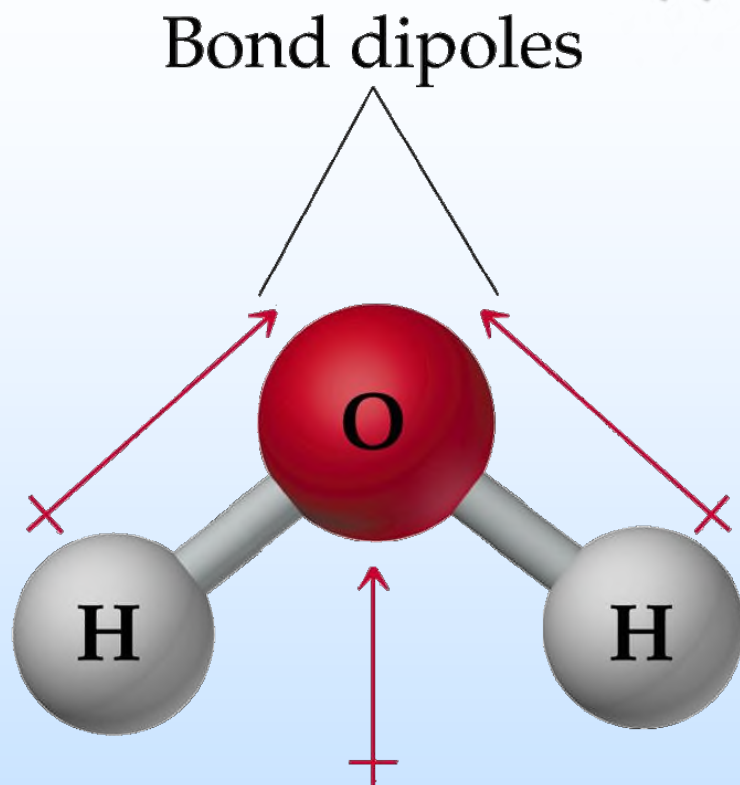
Overall dipole moment = 0



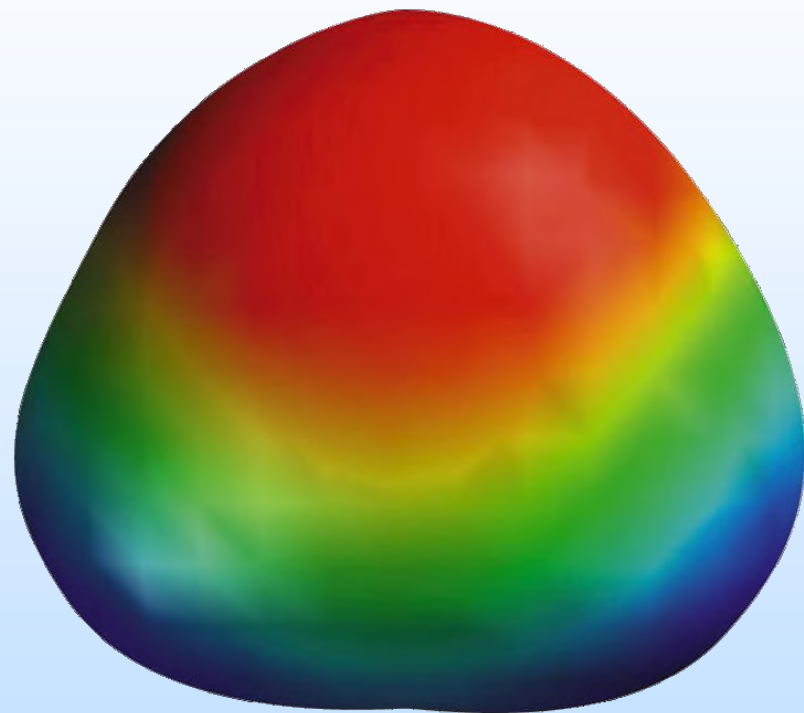
Molecular Polarity of H₂O

- In water, the molecule is not linear and the bond dipoles do not cancel each other.
- Therefore, water is a polar molecule.
- The overall polarity of a molecule depends on its molecular geometry
- Dipole moment of molecule = Σ dipole moment of bonding : 0 \rightarrow nonpolar, not 0 \rightarrow polar
- moment: vector

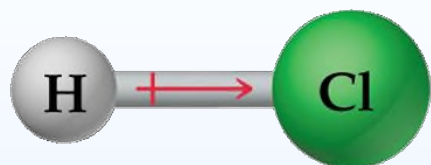
Water



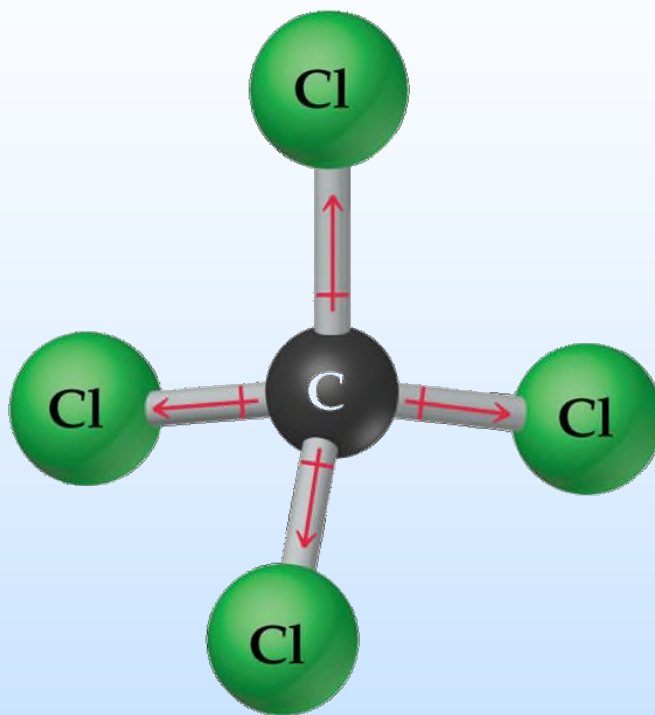
Overall
dipole
moment



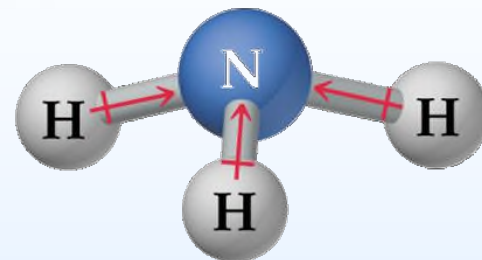
Molecular Polarity



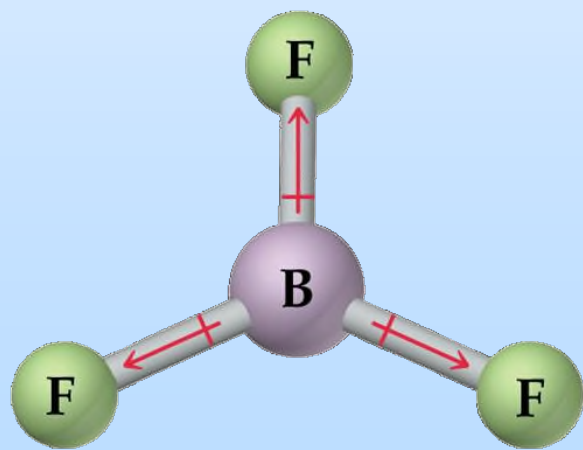
Polar



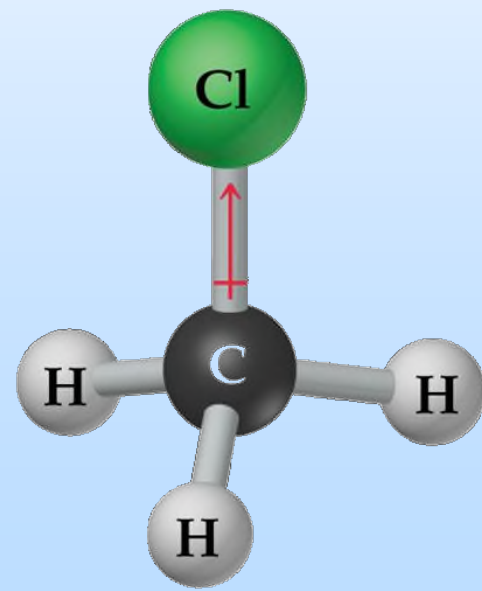
Nonpolar



Polar



Nonpolar



Polar

Dipole Moments

- Consider HF:
 - The difference in electronegativity leads to a polar bond.
 - There is more electron density on F than on H.
 - Since there are two different “ends” of the molecule, we call HF a dipole.

- **Dipole moment**, μ , is the magnitude of the dipole:

$$\mu = Qr$$

where Q is the magnitude of the charges.

- Dipole moments are measured in *debyes*, D.

Practice

- Polarity of the following molecules

	CS ₂	PH ₃	H ₂ O	ClO ₂
	CH ₄	COS	SO ₂	
	cis-CHCl=CHCl		SO ₃	
	BeF ₂			
	BCl ₃			

Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Strengths of Covalent Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

Molecular Orbitals

- Some aspects of bonding are not explained by Lewis structures, VSEPR theory and Valence Bond theory (hybridization). (E.g. why does O_2 interact with a magnetic field?; Why are some molecules colored?)
- For these molecules, we use **Molecular Orbital (MO)** Theory.
- Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in molecular orbitals.

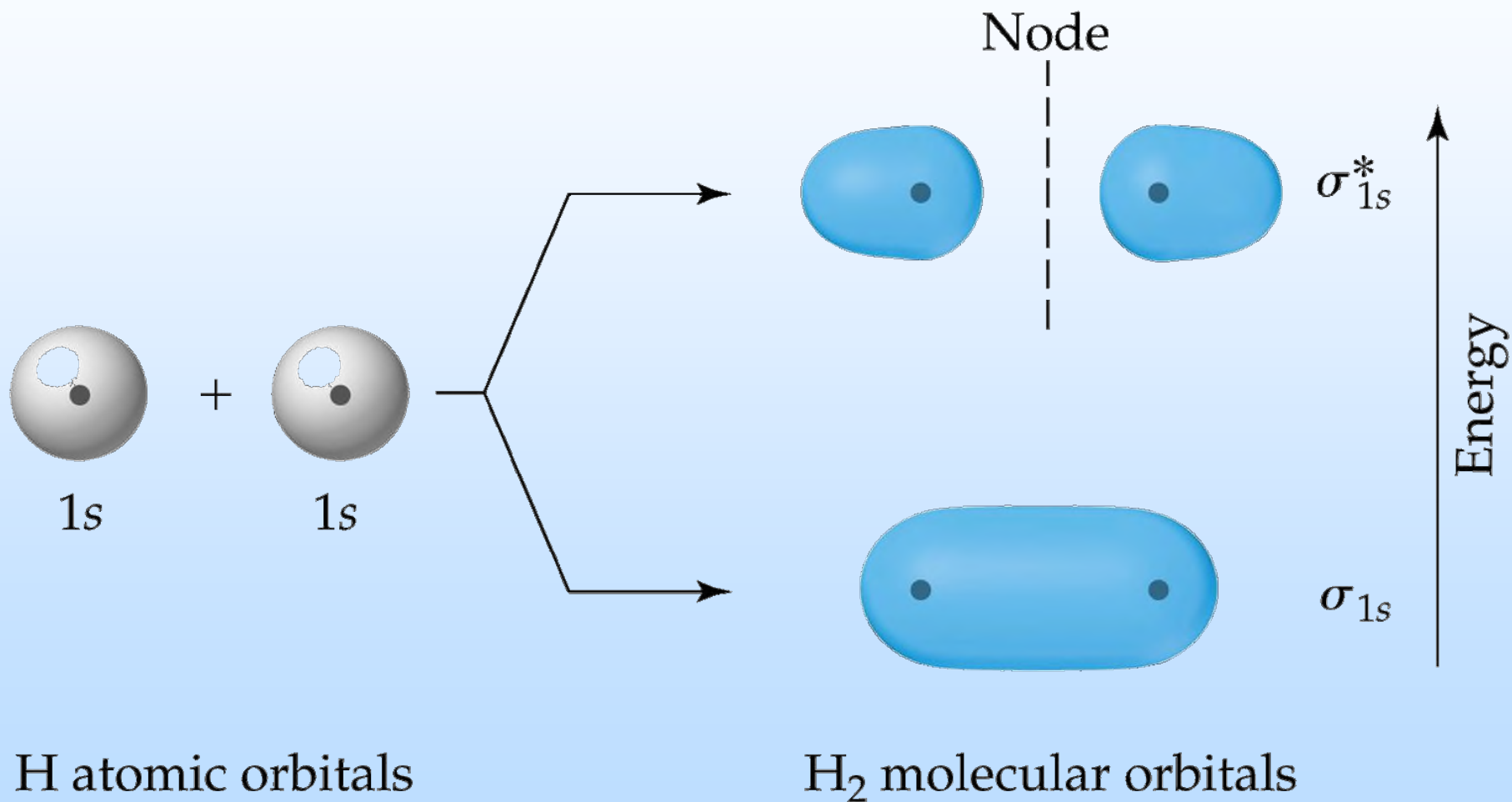
MO Theory

- Valence Bond: molecule is the combination of separate atoms, connect the atom by overlapping the orbital
- Molecular orbitals: single system (multi nuclei, multi e)
 - each contain a maximum of two electrons;
 - have definite energies;
 - can be visualized with contour diagrams;
 - are associated with an entire molecule.
- When two AOs overlap, two MOs form.

The Hydrogen Molecule

- Therefore, $1s$ (H) + $1s$ (H) must result in two MOs for H_2 :
 - one has electron density between nuclei (bonding MO);
 - one has little electron density between nuclei (antibonding MO).
- MOs resulting from s orbitals are σ MOs.
- σ (bonding) MO is lower energy than σ^* (antibonding) MO.

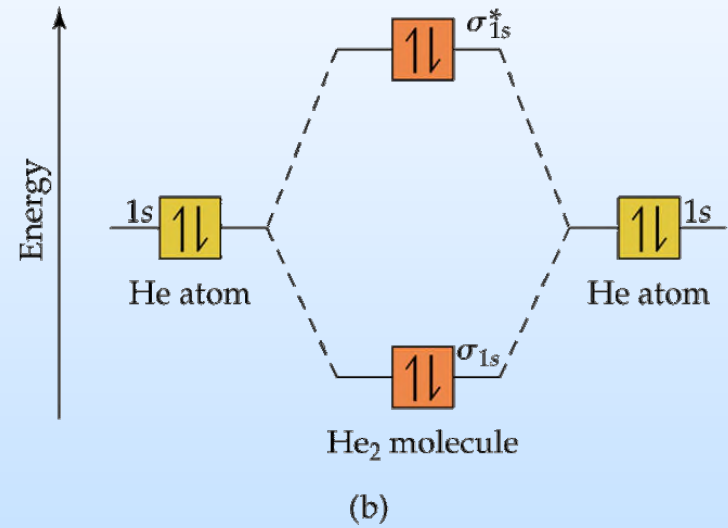
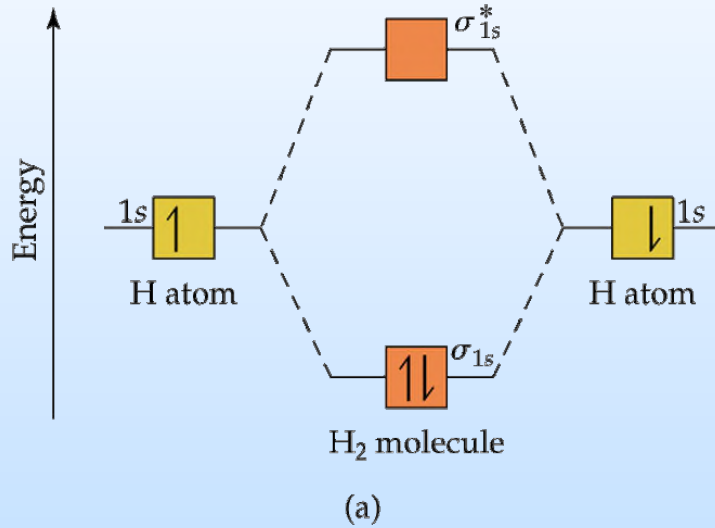
The Hydrogen Molecule



The Hydrogen Molecule

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

The Hydrogen Molecule



Bond Order

- Define

$$\text{Bond order} = \frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons})$$

- Bond order = 1 for single bond.
 - Bond order = 2 for double bond.
 - Bond order = 3 for triple bond.
 - Fractional bond orders are possible.
 - For H_2
 - $\text{Bond order} = \frac{1}{2} (2 - 0) = 1$
- Therefore, H_2 has a single bond.

Bond Order

- For He_2

$$\text{Bond order} = \frac{1}{2} (2 - 2) = 0$$

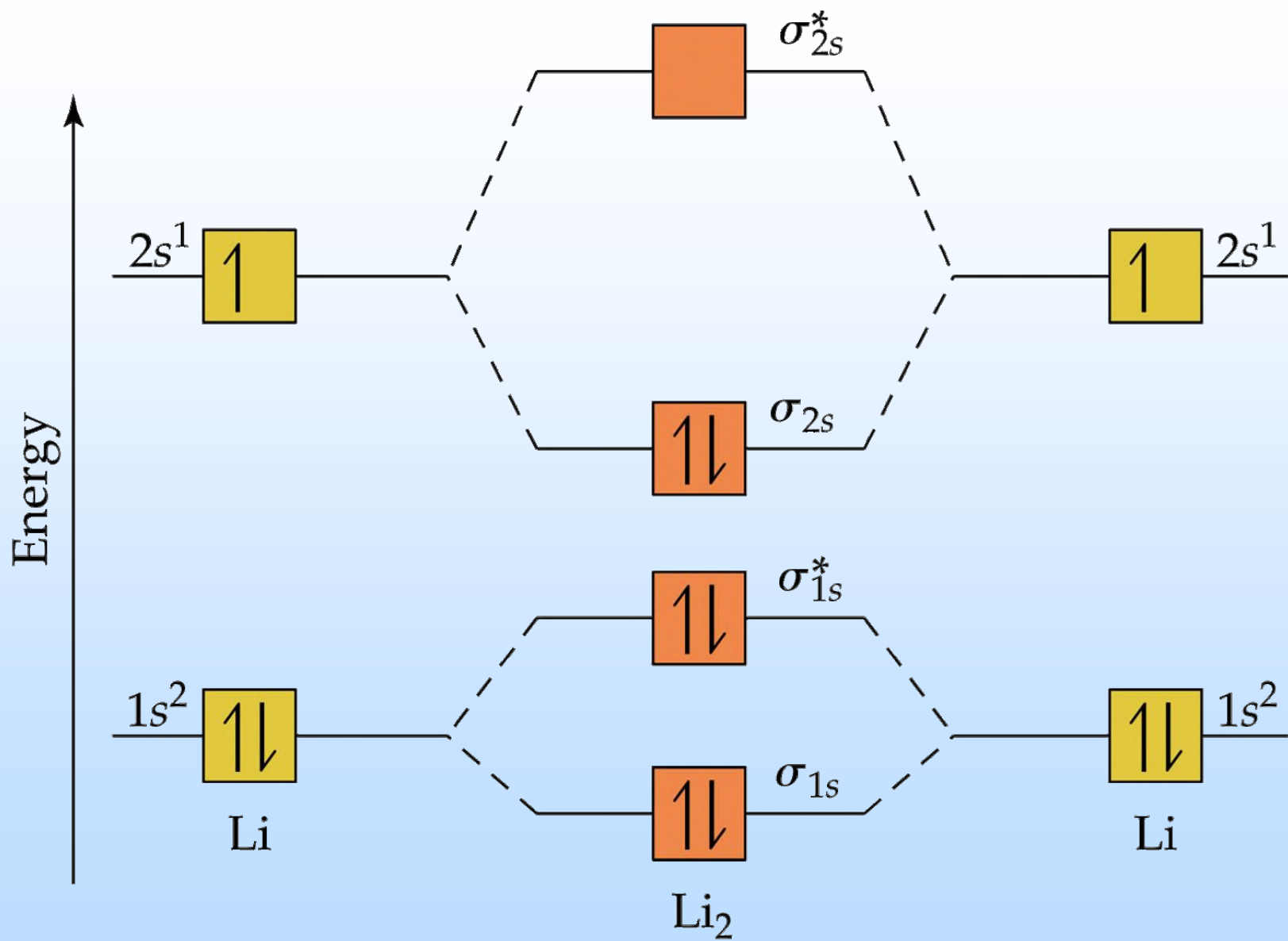
- Therefore He_2 is not a stable molecule

Second-Row Diatomic Molecules

- We look at homonuclear diatomic molecules (e.g. Li_2 , Be_2 , B_2 etc.).
- AOs combine according to the following rules:
 - The number of MOs = number of AOs;
 - AOs 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.

Molecular Orbitals for Li_2 and Be_2

- Each $1s$ orbital combines with another $1s$ orbital to give one σ_{1s} and one σ_{1s}^* orbital, both of which are occupied (since Li and Be have $1s^2$ electron configurations).
- Each $2s$ orbital combines with another $2s$ orbital, two give one σ_{2s} and one σ_{2s}^* orbital.
- The energies of the $1s$ and $2s$ orbitals are sufficiently different so that there is no cross-mixing of orbitals (i.e. we do not get $1s + 2s$).



Molecular Orbitals for Li_2 and Be_2

- There are a total of 6 electrons in Li_2 :
 - 2 electrons in σ_{1s} ;
 - 2 electrons in σ_{1s}^* ;
 - 2 electrons in σ_{2s} ; and
 - 0 electrons in σ_{2s}^* .

$$\text{Bond order} = \frac{1}{2}(4 - 2) = 1$$

- Since the $1s$ AOs are completely filled, the σ_{1s} and σ_{1s}^* are filled. We generally ignore core electrons in MO diagrams.

Molecular Orbitals for Li_2 and Be_2

- There are a total of 8 electrons in Be_2 :
 - 2 electrons in σ_{1s} ;
 - 2 electrons in σ_{1s}^* ;
 - 2 electrons in σ_{2s} ; and
 - 2 electrons in σ_{2s}^* .

$$\text{Bond order} = \frac{1}{2}(4 - 4) = 0$$

- Since the bond order is zero, Be_2 does not exist.

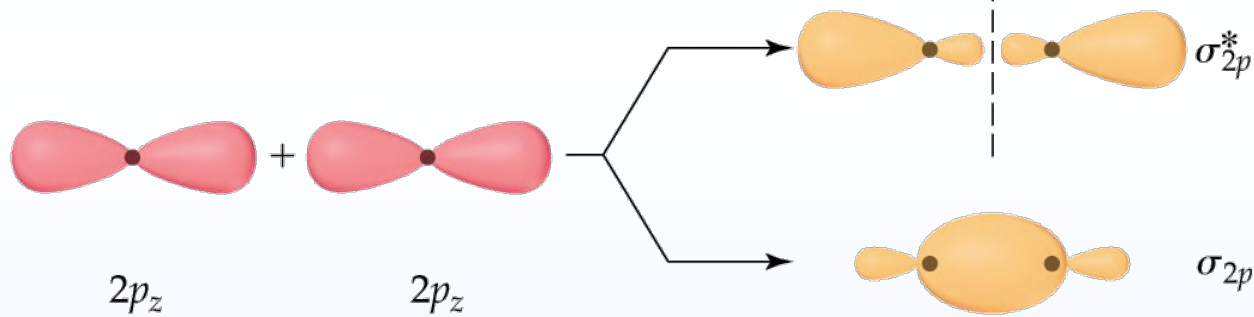
Molecular Orbitals from 2p Atomic Orbitals

- 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 (i.e. σ type orbital);
 - sideways so that the resulting MO has electron density above and below the axis between nuclei (i.e. π type orbital).

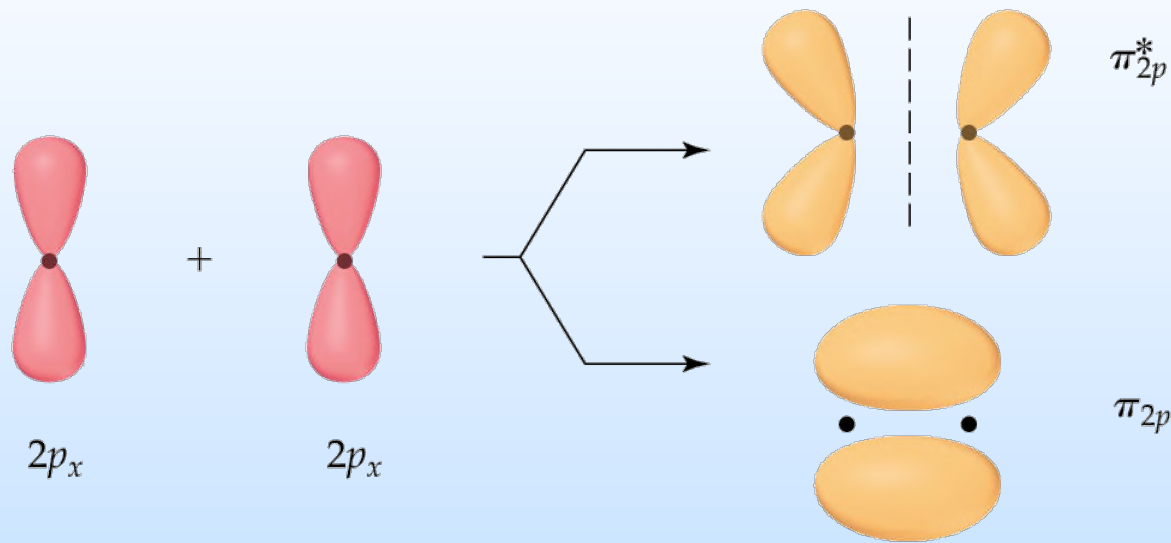
Molecular Orbitals from 2p Atomic Orbitals

- The six p -orbitals (two sets of 3) must give rise to 6 MOs:
 - σ , σ^* , π , π^* , π , and π^* .
 - Therefore there is a maximum of 2 π bonds that can come from p -orbitals.
- The relative energies of these six orbitals can change.

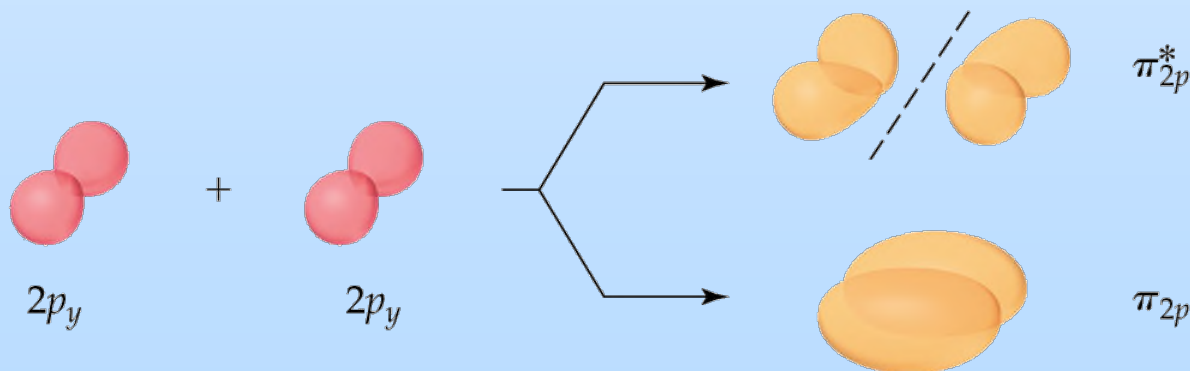
(a)



(b)



(c)

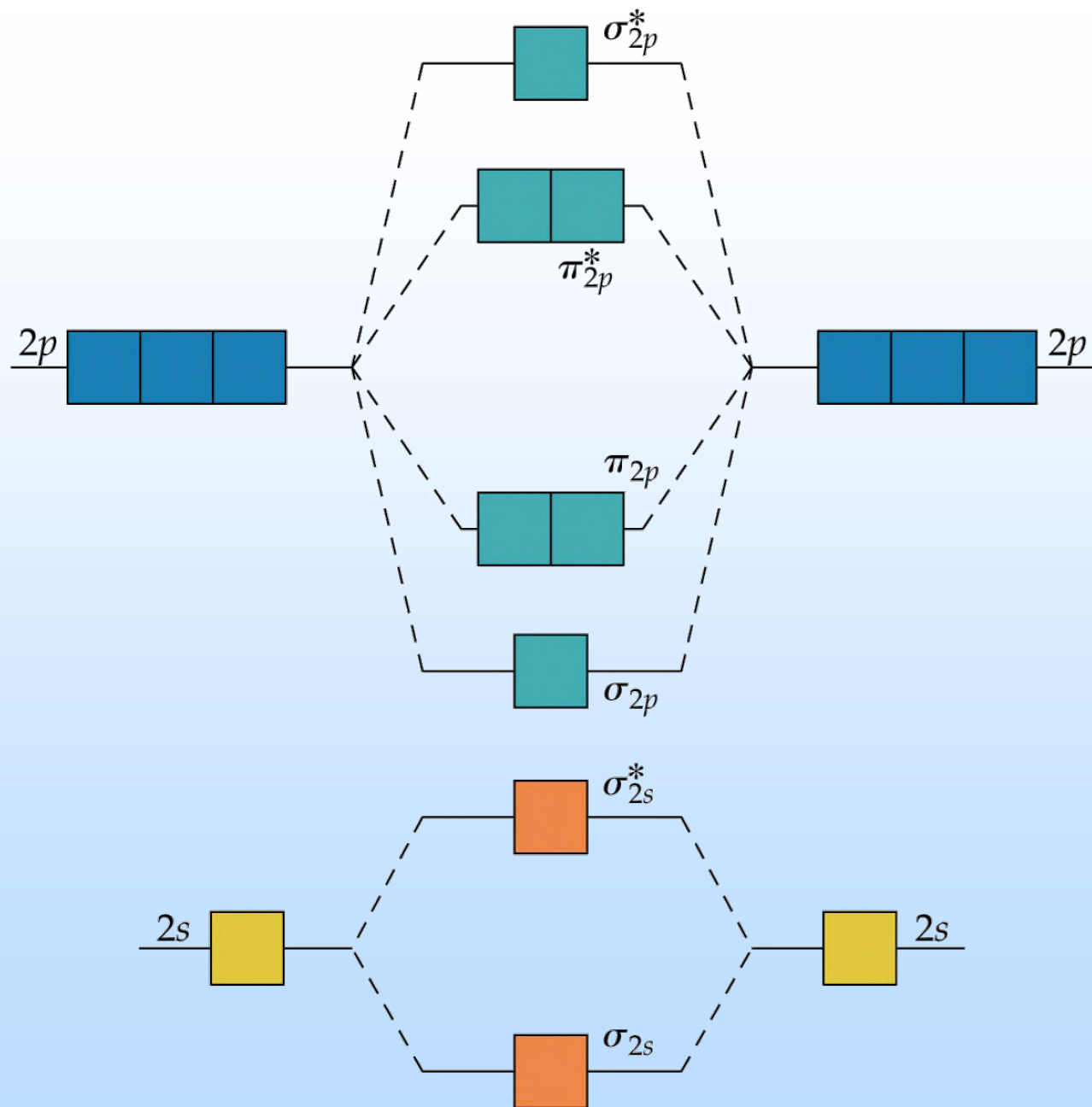


Molecular Orbitals from 2p Atomic Orbitals

Configurations for B₂ Through Ne₂

- 2s Orbitals are lower in energy than 2p orbitals so σ_{2s} orbitals are lower in energy than σ_{2p} orbitals.
- There is greater overlap between 2p_z orbitals (they point directly towards one another) so the σ_{2p} is MO is lower in energy than the π_{2p} orbitals.
- There is greater overlap between 2p_z orbitals so the σ^*_{2p} is MO is higher in energy than the π^*_{2p} orbitals.
- The π_{2p} and π^*_{2p} orbitals are doubly degenerate.

Energy



Configurations for B₂ Through Ne₂

- As the atomic number decreases, it becomes more likely that a 2s orbital on one atom can interact with the 2p orbital on the other.
 - As the 2s-2p interaction increases, the σ_{2s} MO lowers in energy and the σ_{2p} orbital increases in energy.
- For B₂, C₂ and N₂ the σ_{2p} orbital is higher in energy than the π_{2p} .
- For O₂, F₂ and Ne₂ the σ_{2p} orbital is higher in energy than the π_{2p} .

Configurations for B₂ Through Ne₂

- Once the relative orbital energies are known, we add the required number of electrons to the MOs, taking into account Pauli's exclusion principle and Hund's rule.
 - As bond order increases, bond length decreases.
 - As bond order increases, bond energy increases.

Configurations for B₂ Through Ne₂

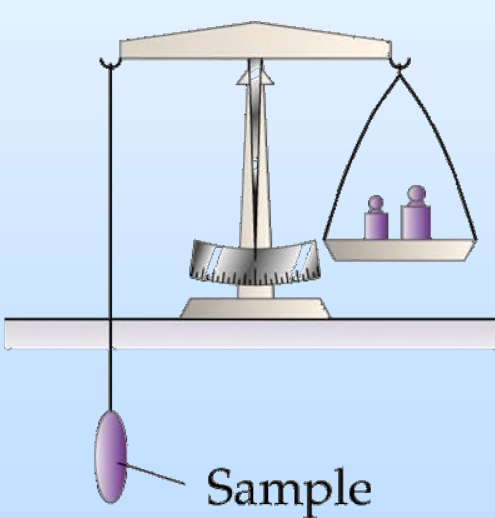
	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*	<div>□</div>	<div>□</div>	<div>□</div>	<div>□</div>	<div>□</div>	<div>↑↓</div>
π_{2p}^*	<div>□ □</div>	<div>□ □</div>	<div>□ □</div>	<div>↑ ↑</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>
σ_{2p}	<div>□</div>	<div>□</div>	<div>↑↓</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>
π_{2p}	<div>↑ ↑</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>
σ_{2s}^*	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>
σ_{2s}	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Electron Configurations and Molecular Properties

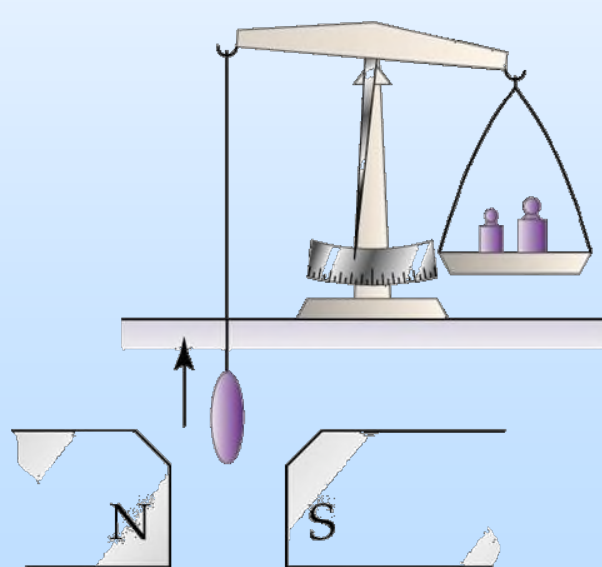
- Two types of magnetic behavior:
 - **paramagnetism** (unpaired electrons in molecule): strong attraction between magnetic field and molecule;
 - **diamagnetism** (no unpaired electrons in molecule): weak repulsion between magnetic field and molecule.
- Magnetic behavior is detected by determining the mass of a sample in the presence and absence of magnetic field:

Electron Configurations and Molecular Properties

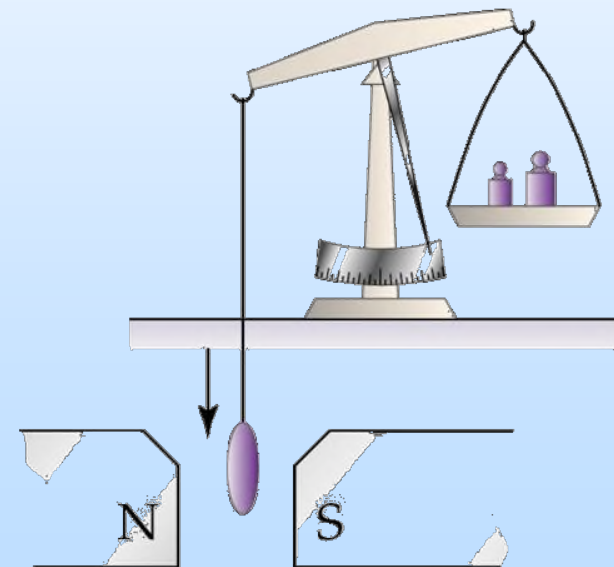
- large increase in mass indicates paramagnetism,
- small decrease in mass indicates diamagnetism.



(a)



(b)



(c)

Electron Configurations and Molecular Properties

- Experimentally O_2 is paramagnetic.
- The Lewis structure for O_2 shows no unpaired electrons.
- The MO diagram for O_2 shows 2 unpaired electrons in the π^*_{2p} orbital.
- Experimentally, O_2 has a short bond length (1.21 Å) and high bond dissociation energy (495 kJ/mol). This suggests a double bond.

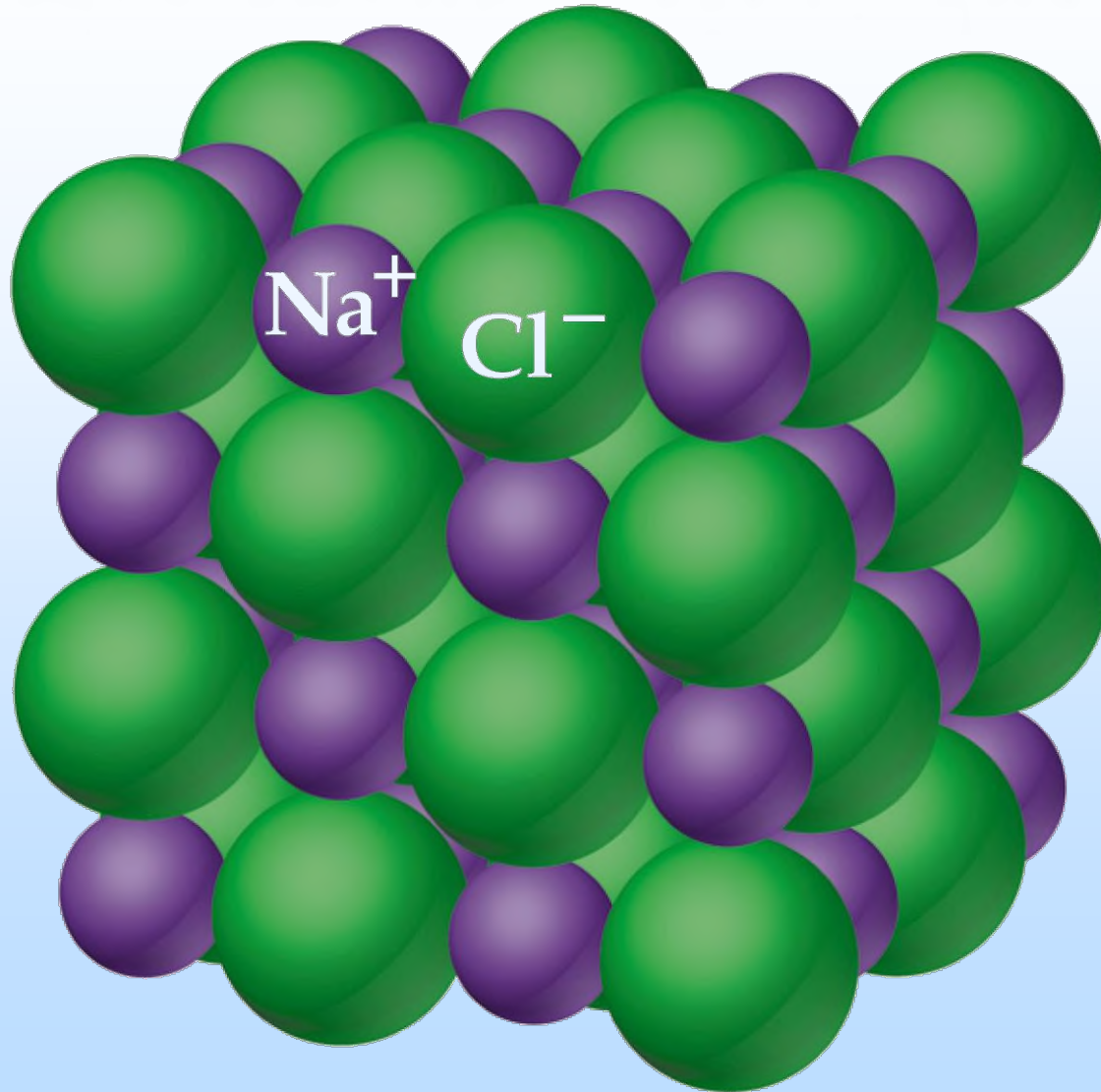
Electron Configurations and Molecular Properties

The MO diagram for O_2 predicts both paramagnetism and the double bond (bond order = 2).

Ionic Bonding

- The reaction is violently exothermic.
- **We infer that the NaCl is more stable than its constituent elements. Why?**
- Na has lost an electron to become Na^+ and chlorine has gained the electron to become Cl^- . Note: Na^+ has an Ne electron configuration and Cl^- has an Ar configuration.
- **That is, both Na^+ and Cl^- have an octet of electrons surrounding the central ion.**

Ionic Bonding Arrangement



Energetics of Ionic Bond Formation

- **Lattice energy:** the energy required to completely separate an ionic solid into its gaseous ions.
- Lattice energy depends on the charges on the ions and the sizes of the ions:

$$E_l = \kappa \frac{Q_1 Q_2}{d}$$

κ is a constant ($8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$), Q_1 and Q_2 are the charges on the ions, and d is the distance between ions.

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
LiCl	834	SrCl ₂	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

Ionic Bonding

- | Anions and cations are held together by *opposite charges* (+ and -)
- | Ionic compounds are called **salts**.
- | Simplest ratio of elements in an ionic compound is called the formula unit.
- | The bond is formed through the **transfer of electrons** (lose and gain)
- | Electrons are transferred **to achieve noble gas configuration**.

Ionic Bonding

- | Metal – ne \rightarrow cation (+)
- | Non-metal + ne \rightarrow anion (-)
- | Held together by opposite charge
- | Bond not fixed position
- | Delocalized

- | NaCl : Na - Cl

Ionic Compounds

- 1) Also called **SALTS**
- 2) Made from: a **CATION** with an **ANION** (or literally from a metal combining with a nonmetal)

Ionic Bonding



The metal (sodium) tends to lose its one electron from the outer level.

The nonmetal (chlorine) needs to gain one more to fill its outer level, and will accept the one electron that sodium is going to lose.

Ionic Bonding



Note: Remember that NO DOTS are now shown for the cation!

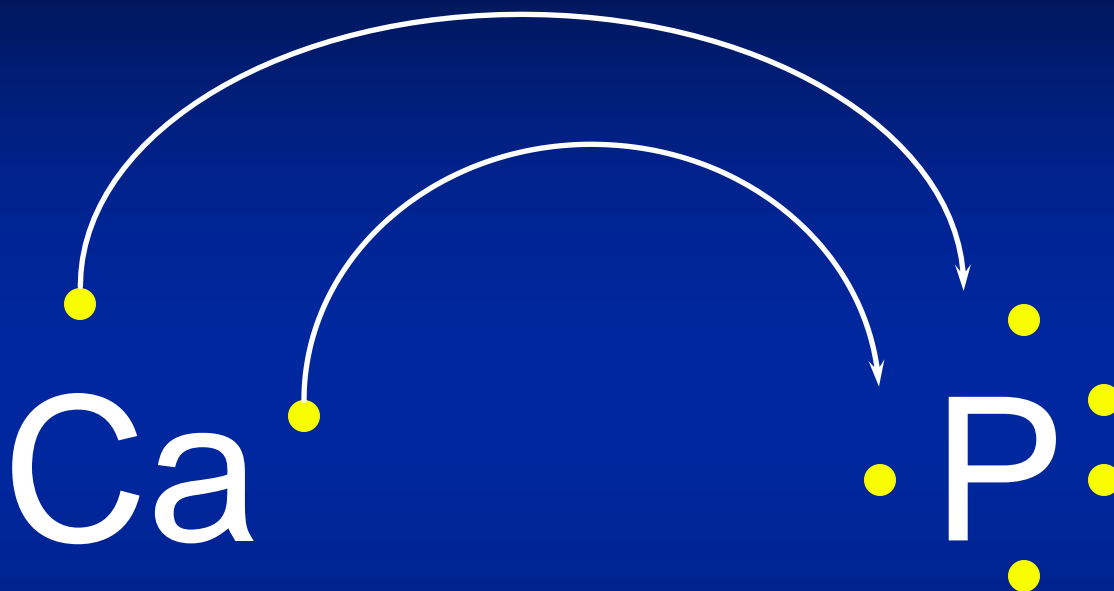
Ionic Bonding

Lets do an example by combining calcium and phosphorus:



- | All the electrons must be accounted for, and **each** atom will have a noble gas configuration (which is stable).

Ionic Bonding



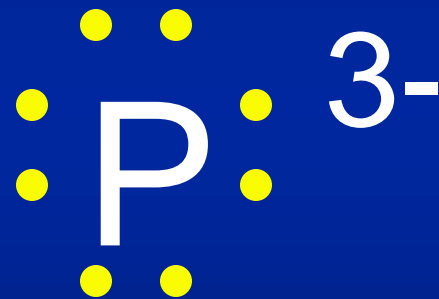
Ionic Bonding



Ionic Bonding

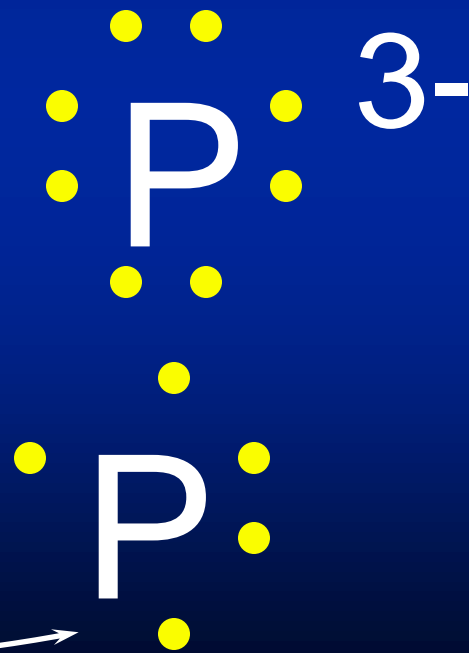


Ionic Bonding



Ionic Bonding

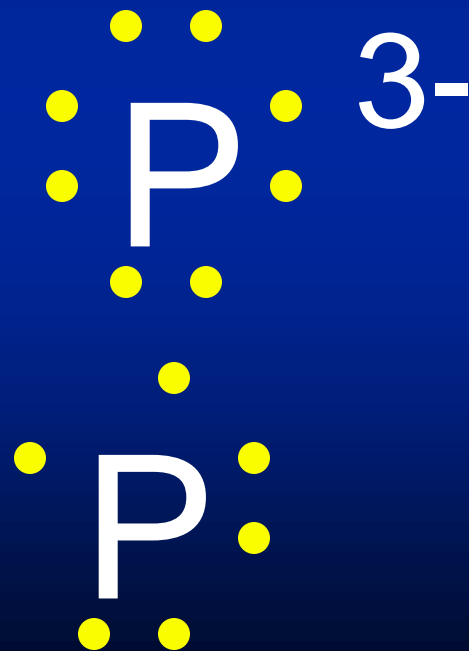
Ca^{2+}



Ca



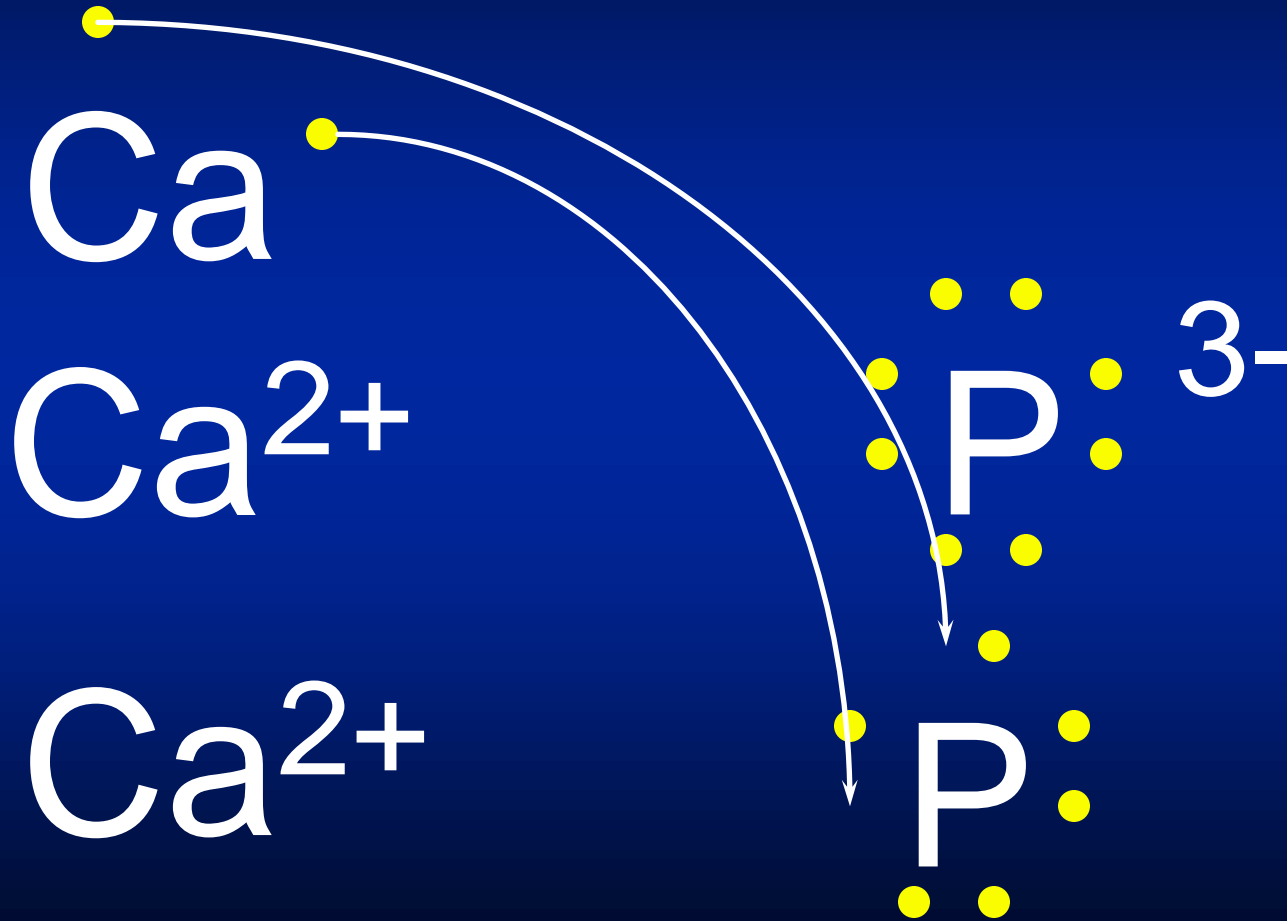
Ionic Bonding



Ionic Bonding



Ionic Bonding



Ionic Bonding



Ionic Bonding



This is a **chemical formula**, which shows the kinds and numbers of atoms in the smallest representative particle of the substance.

For an ionic compound, the smallest representative particle is called a:

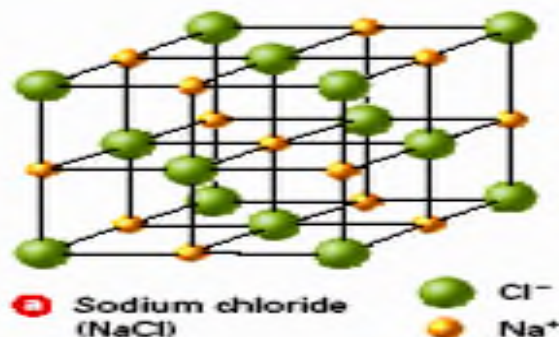
Formula Unit (not a molecule)

Properties of Ionic Compounds

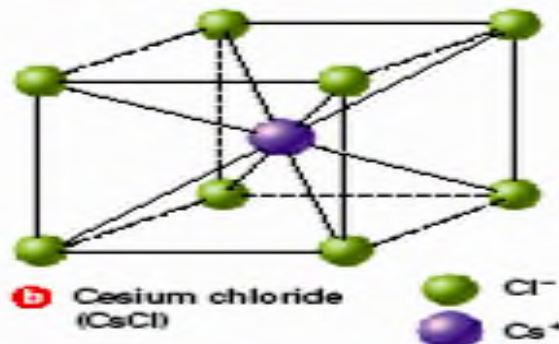
1. Crystalline solids - a regular repeating arrangement of ions in the solid:
2. NaCl: ratio (not molecule)
 - Ions are strongly bonded together.
 - Structure is rigid.
2. High melting points
1. Coordination number- number of ions of opposite charge surrounding it

Figure 7.10 Crystalline Structures of Ionic Compounds - Page 198

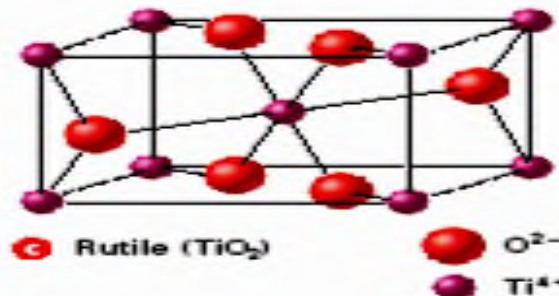
Coordination Numbers:



Both the sodium and chlorine have 6



Both the cesium and chlorine have 8



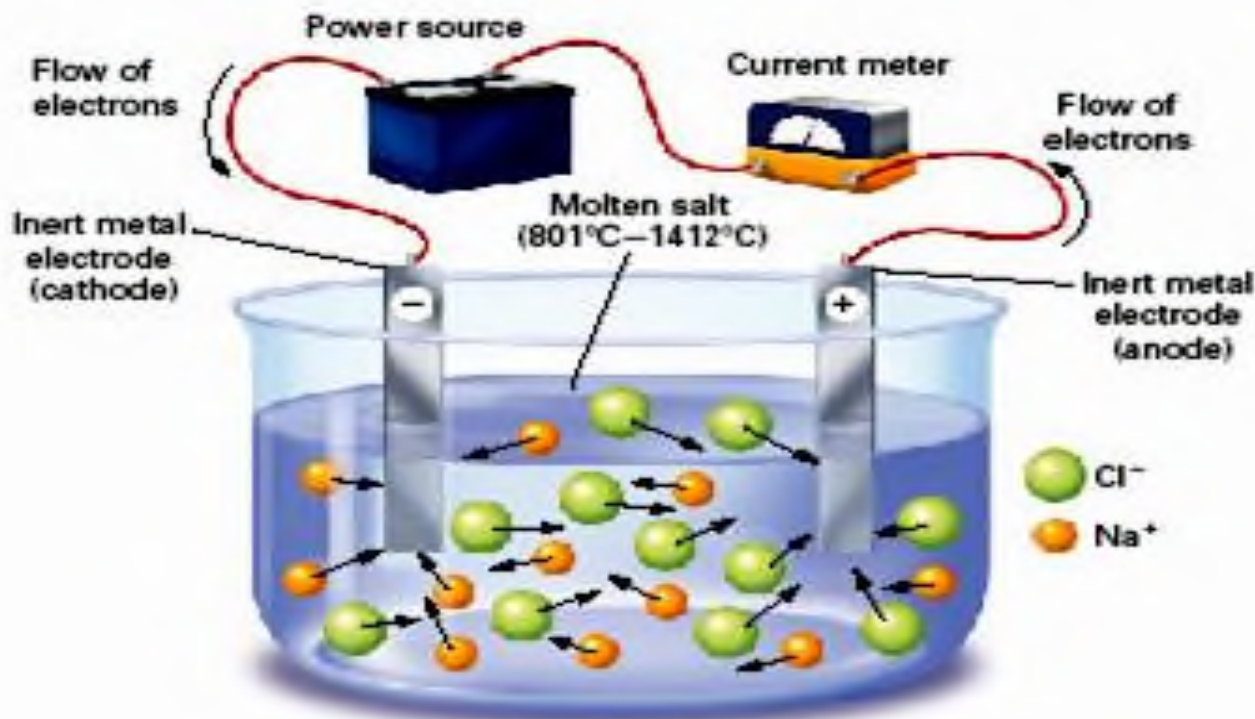
Each titanium has 6, and each oxygen has 3

Do they Conduct?

- | Conducting electricity means allowing charges to move.
- | In a solid, the ions are locked in place.
- | Ionic solids are insulators.
- | When melted, the ions can move around.
- 3. Melted ionic compounds conduct.
 - NaCl: must get to about 800 °C.
 - Dissolved in water, they also conduct (free to move in aqueous solutions)

Figure 7.11 Electrical Conductivity of Molten Sodium Chloride

The ions are free to move when they are **molten** (or in **aqueous solution**), and thus they are able to conduct the electric current.

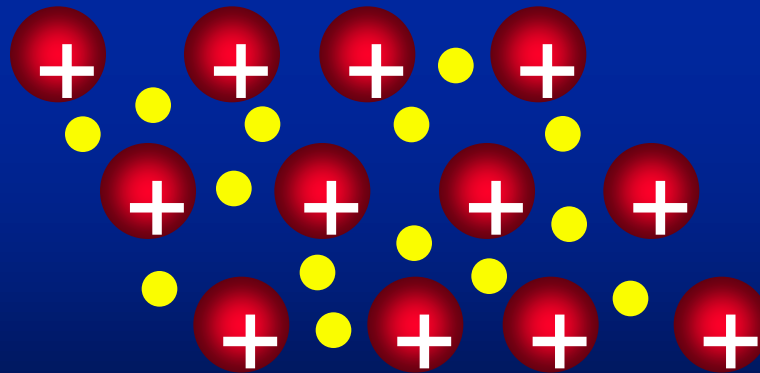


Metallic Bonds are...

- | How metal atoms are held together in the solid.
- | Metals hold on to their valence electrons very weakly.
- | Metal – ne \rightarrow metal cation
- | Think of them as positive ions (cations) floating in a sea of electrons: Fig. 7.12, p.201

Sea of Electrons

- | Electrons are free to move through the solid.
- | Metals conduct electricity.

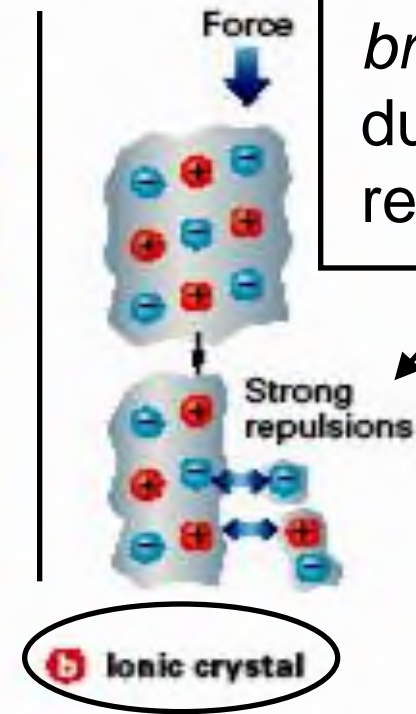
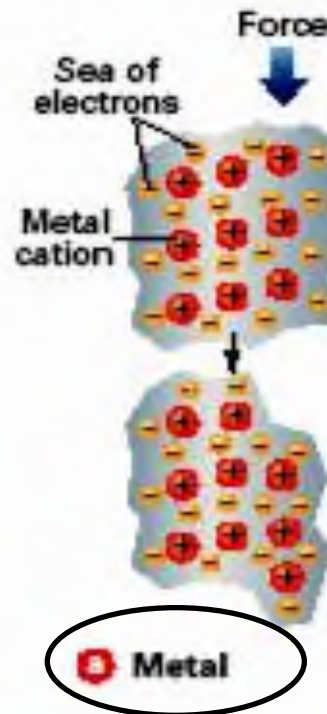
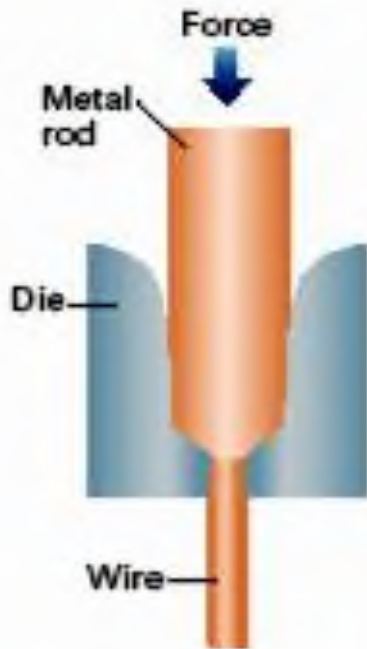


Metals are Malleable

- | Hammered into shape (bend).
- | Also ductile - drawn into wires.
- | Both malleability and ductility explained in terms of the *mobility* of the valence electrons

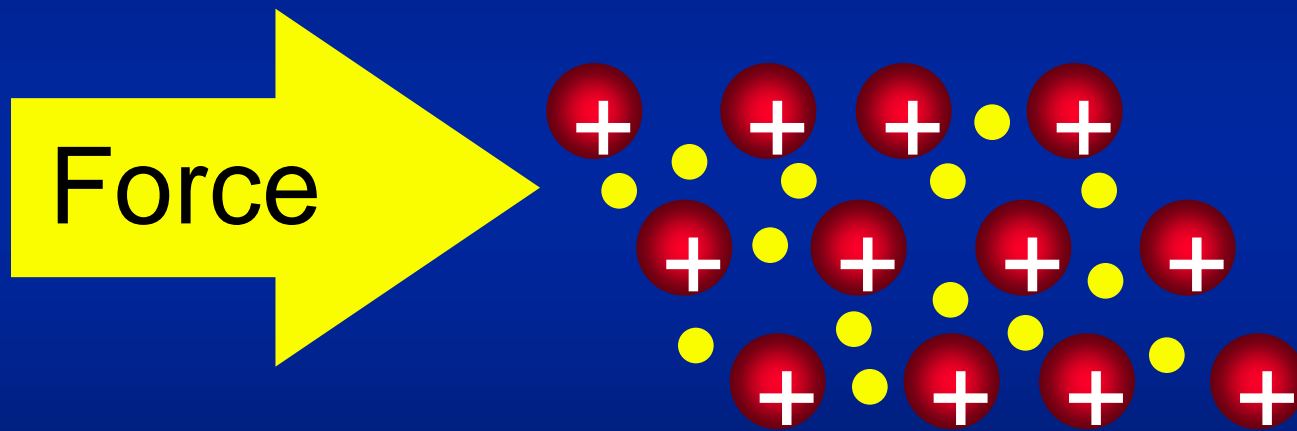
Due to the mobility of the valence electrons, metals have:

1) Ductility and 2) Malleability



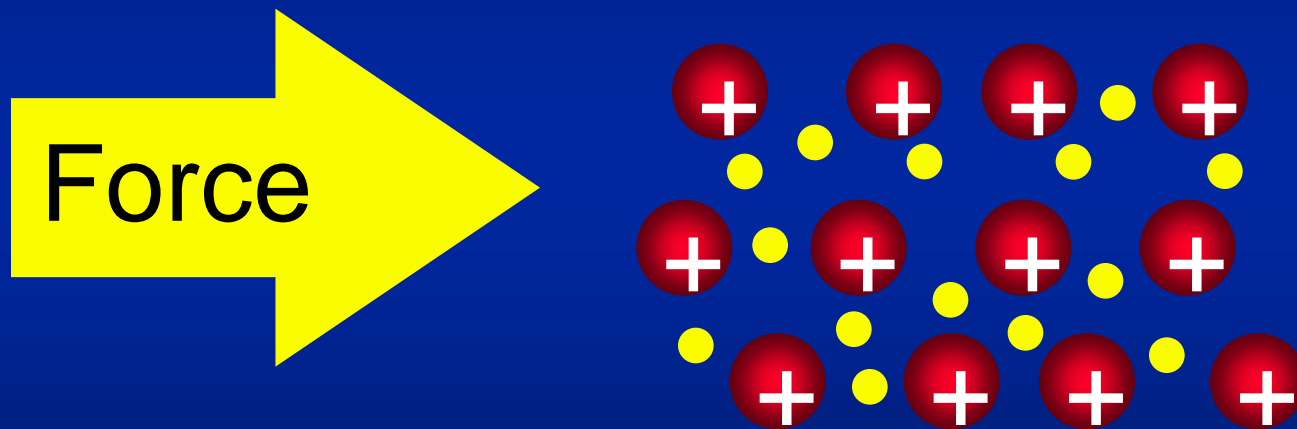
Notice that the **ionic crystal breaks** due to ion repulsion!

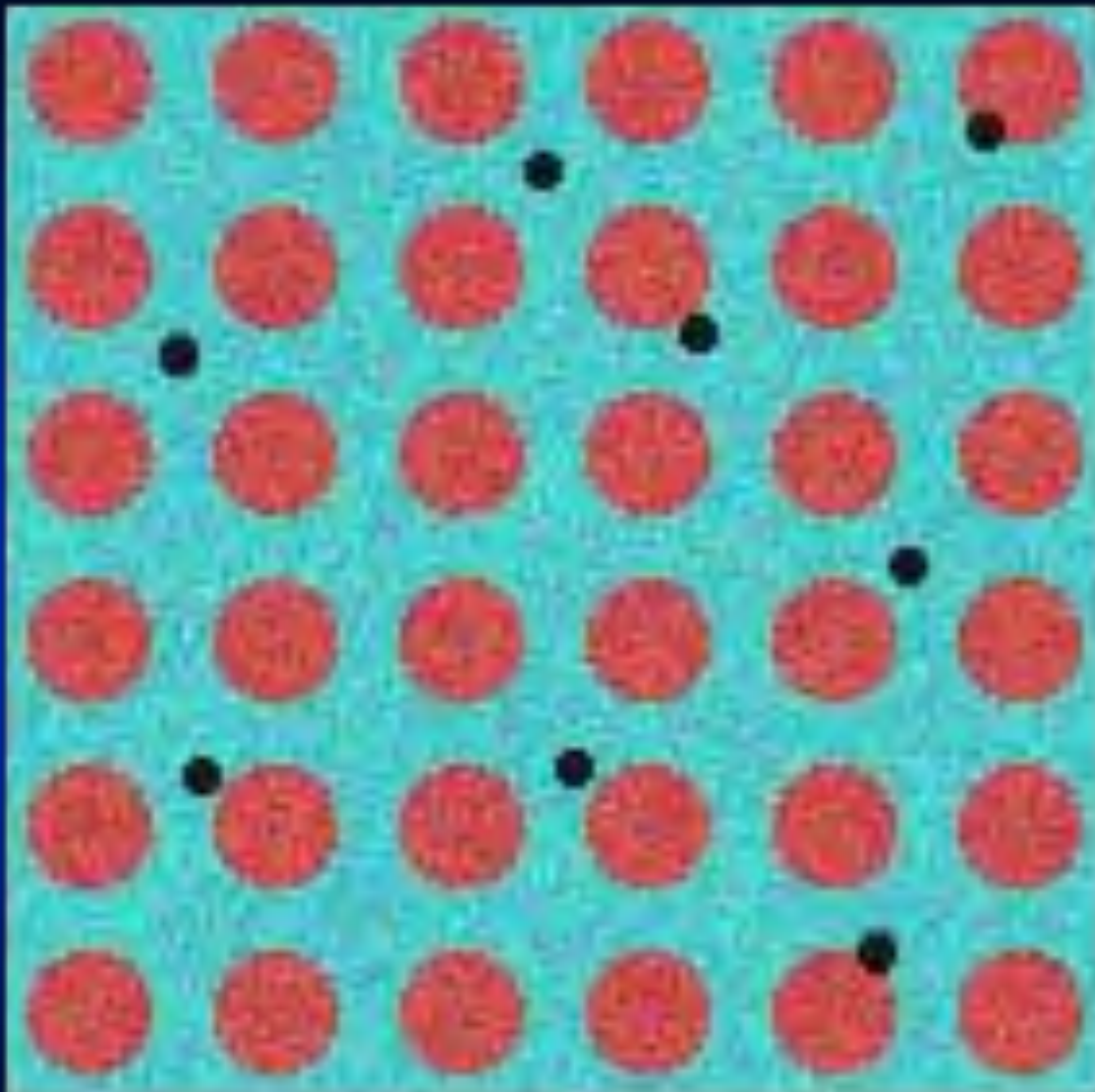
Malleable



Malleable

- | Mobile electrons allow atoms to slide by, sort of like ball bearings in oil.





Crystalline structure of metal

- | If made of *one kind of atom*, metals are among the simplest crystals; very compact & orderly
- | Note Fig. 7.14, p.202 for types:
 1. Body-centered cubic:
 - every atom (except those on the surface) has 8 neighbors
 - Na, K, Fe, Cr, W

Crystalline structure of metal

2. Face-centered cubic:

- every atom has 12 neighbors
- Cu, Ag, Au, Al, Pb

3. Hexagonal close-packed

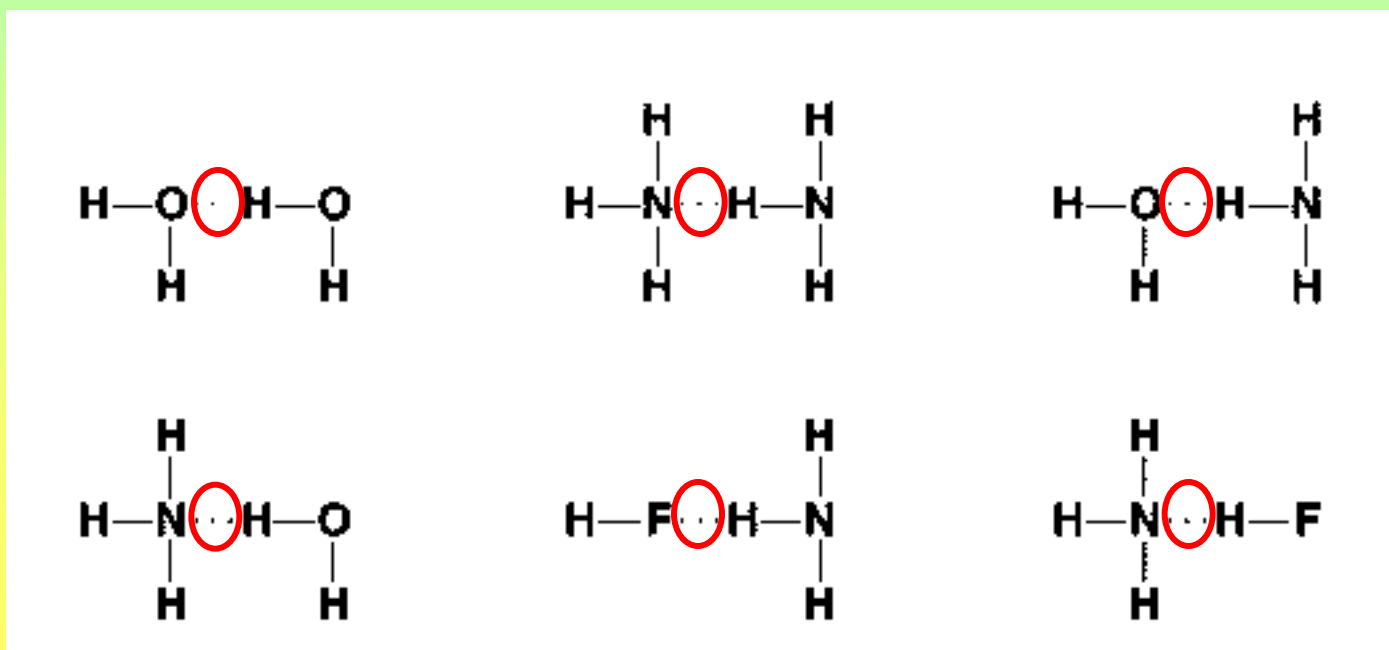
- every atom also has 12 neighbors
- different pattern due to hexagonal
- Mg, Zn, Cd

Hydrogen Bond

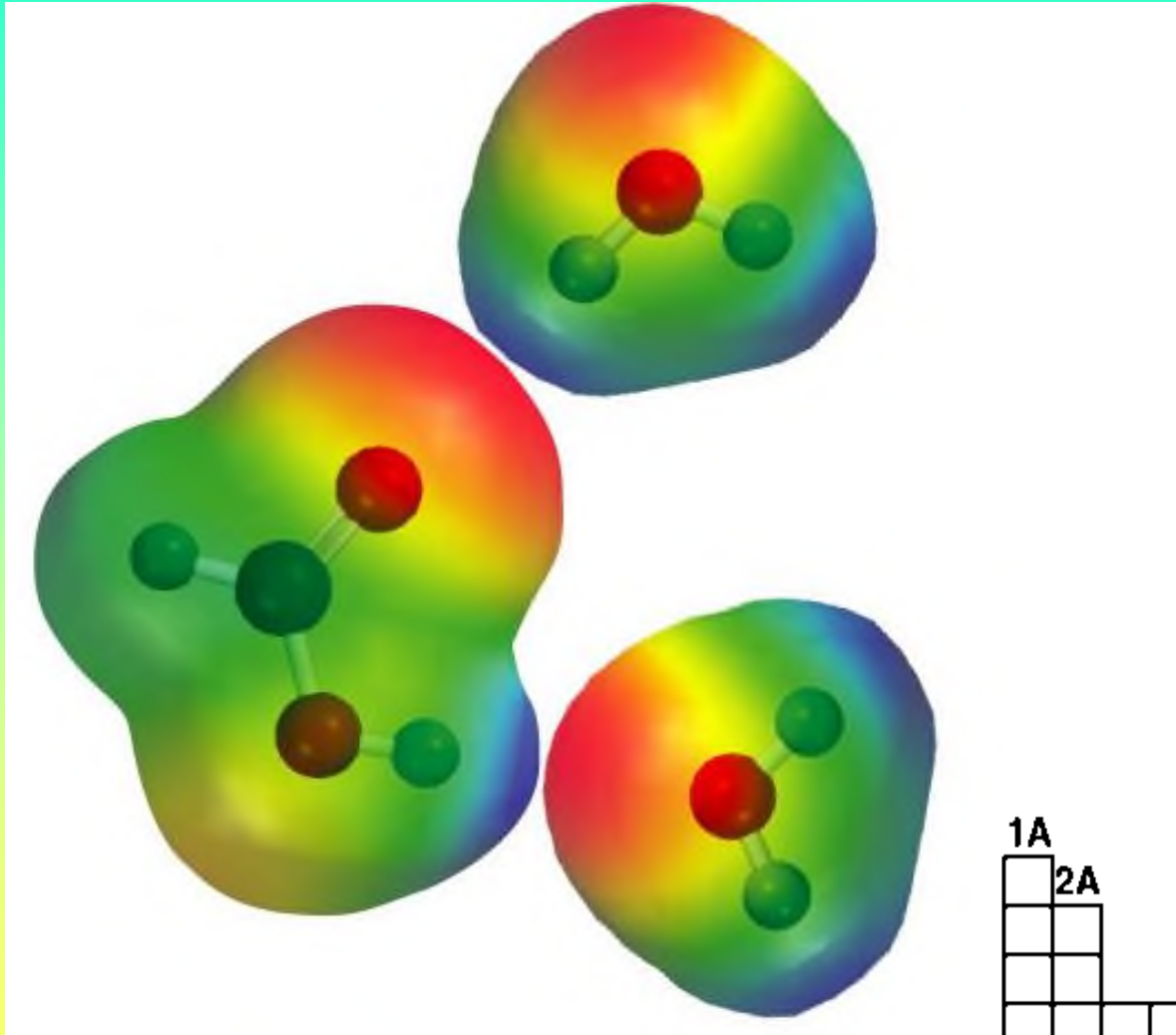
The **hydrogen bond** is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom. **IT IS NOT A BOND.**



A & B are N, O, or F



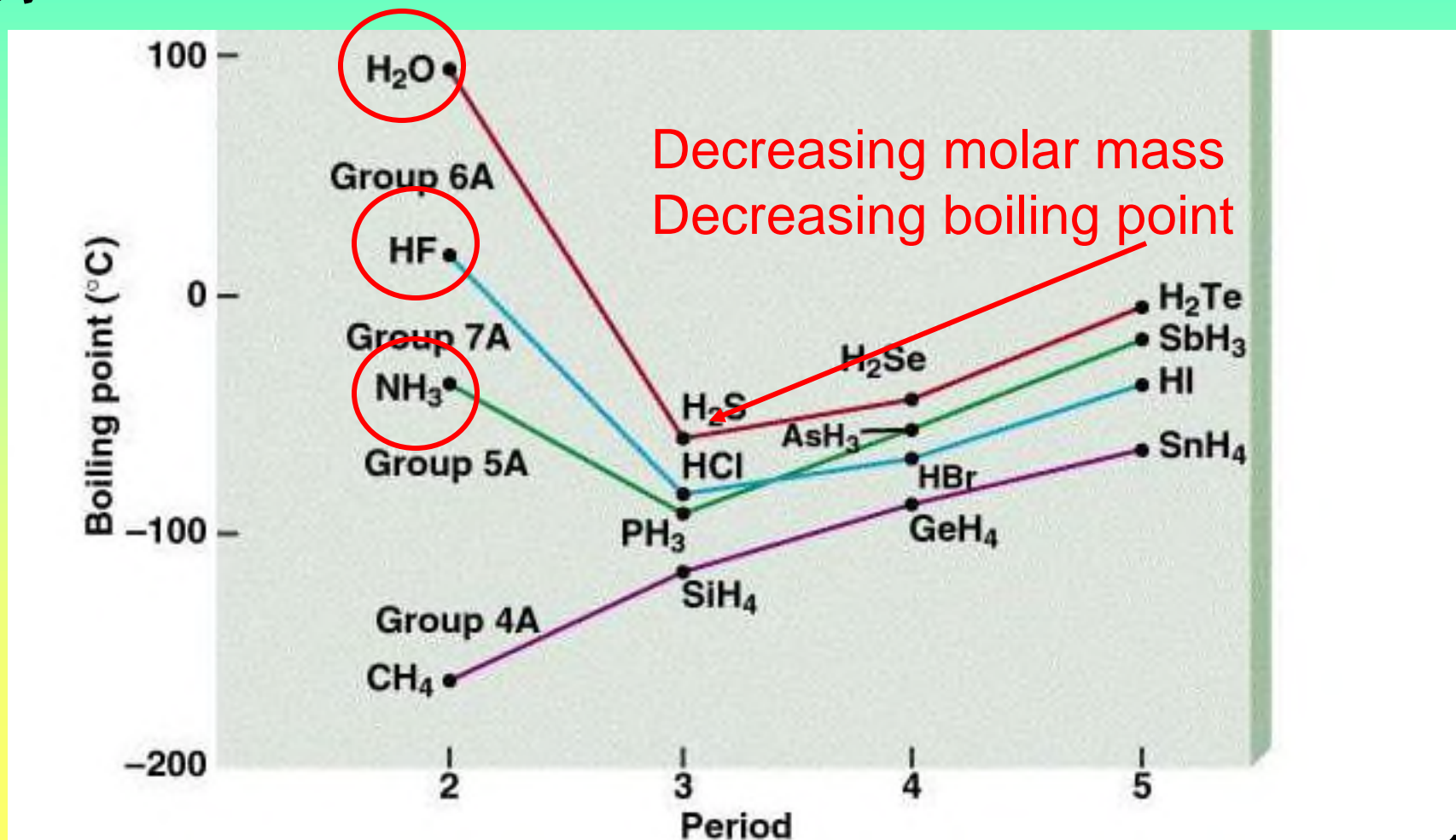
Hydrogen Bond

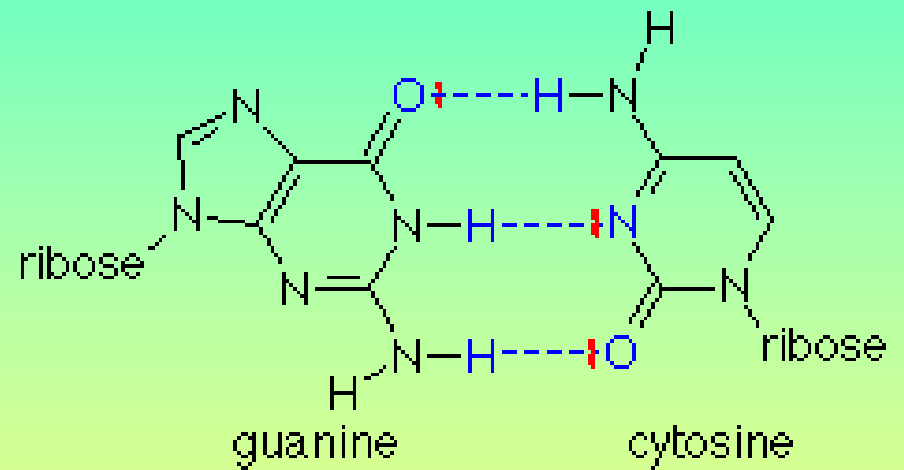
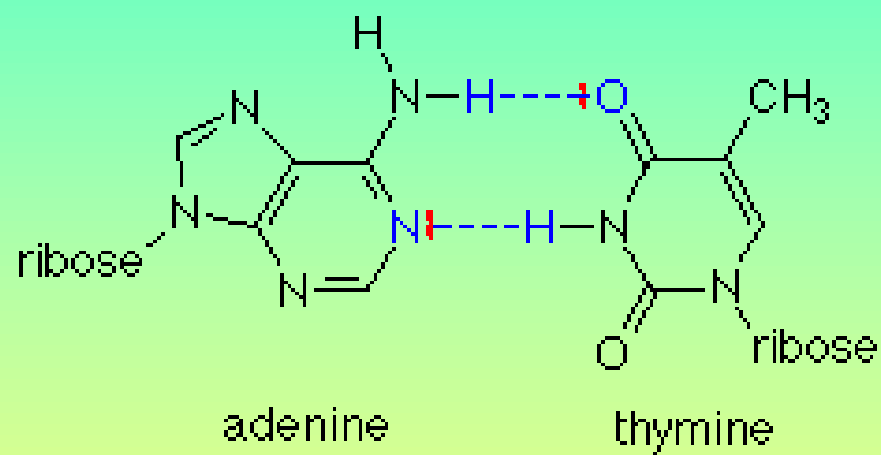


1A																	8A
2A																	
</																	



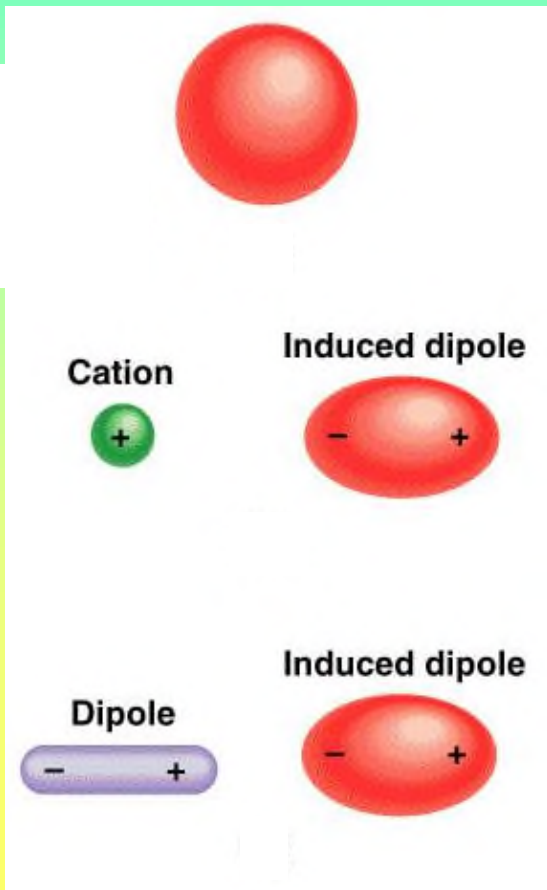
Why is the hydrogen bond considered a “special” dipole-dipole interaction?





Van der Waals forces/London forces

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules



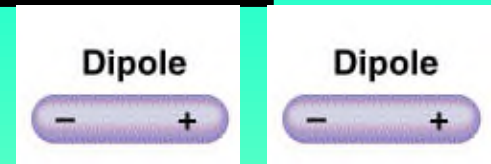
- **two molecules: polar – polar: dipole – dipole interaction**
- **Two molecules: non-polar: any instant in time: electron moving: generate dipole: induced dipole**

ion-induced dipole interaction

dipole-induced dipole interaction

Induced dipole – induced dipole

Van der Waals forces/London forces

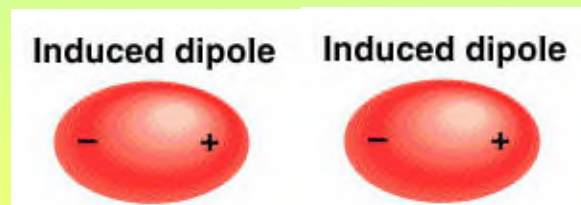


Polar: HCl: always have two ends, (permanent) dipole

Cl₂: non-polar, electron are not fixed at any position, move → break the sym. → generate dipole (temporary)

Overall, molecule is still non-polar

At any instant in time, molecule is polar → induced dipole (temporary)

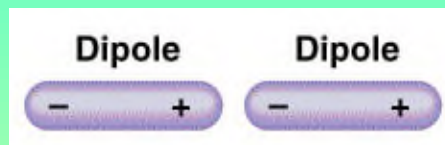


- Dipole – dipole (polar – polar)
- Dispersion (induced dipole – induced dipole): nonpolar
- Induced (polar – nonpolar) (dipole- induced dipole)

Types of Van der Waals Forces

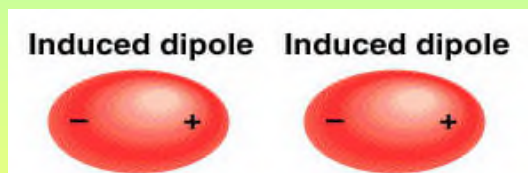
1. Keesom Interactions

interactions between two permanent dipoles and are temperature dependent.



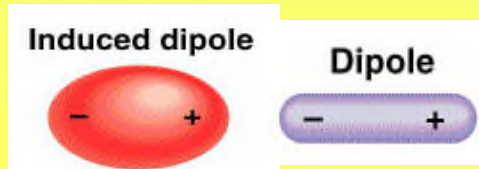
2. Debye Forces

interactions between permanent dipoles and induced dipoles.



3. London Dispersion Forces

interactions between an induced dipole and an atom/molecule.



Dispersion Forces Continued

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted (break the sym → dipole)

Polarizability increases with:

- greater number of electrons
- more diffuse electron cloud



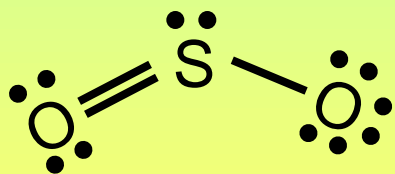
Dispersion forces usually increase with molar mass.

Melting Points of Similar Nonpolar Compounds	
Compound	Melting Point (°C)
CH ₄	-182.5
CF ₄	-150.0
CCl ₄	-23.0
CBr ₄	90.0
CI ₄	171.0

TABLE 11.2



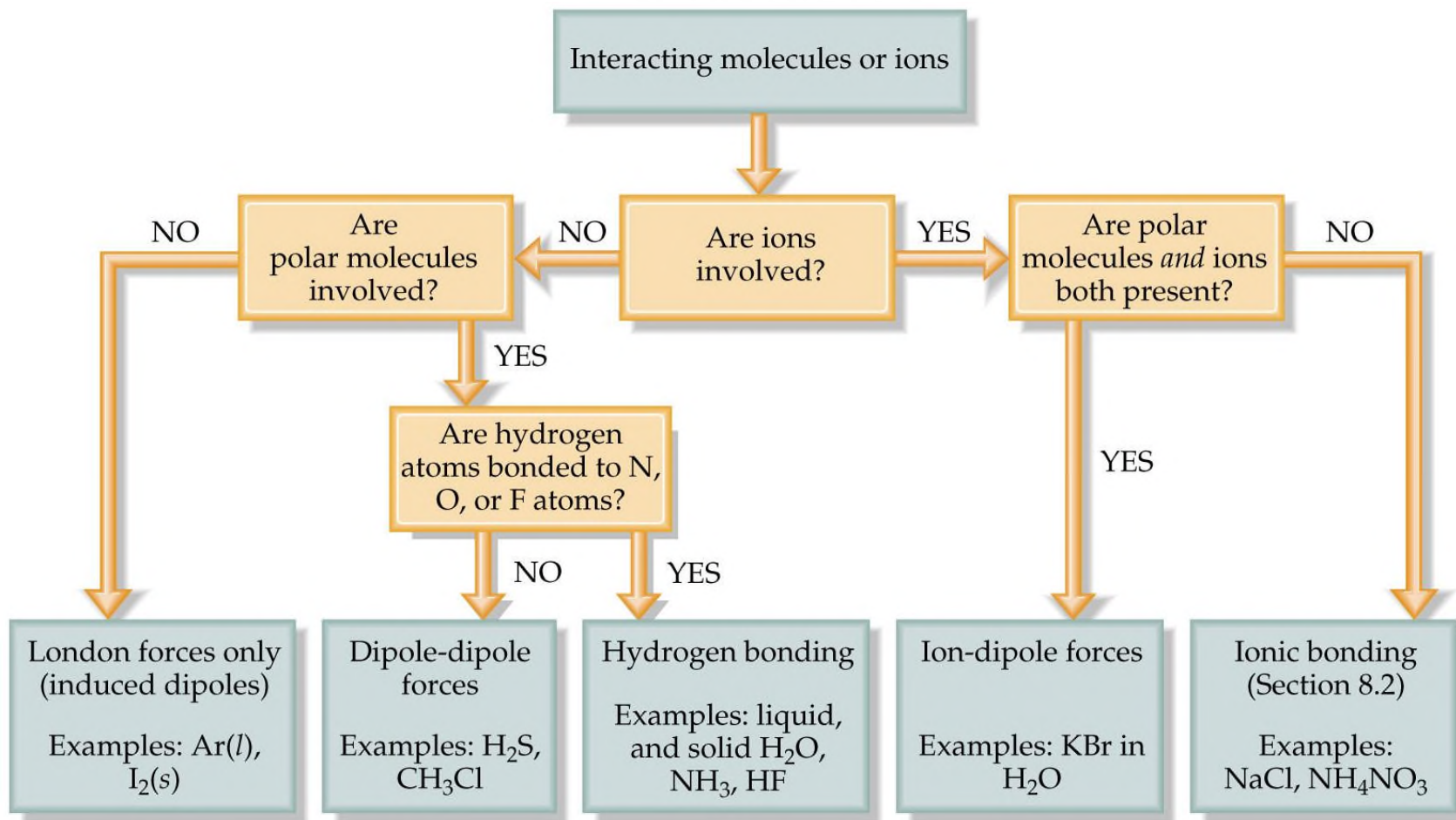
What type(s) of intermolecular forces exist between each of the following molecules?



Comparing Intermolecular Forces

- Dispersion forces are found in all substances.
 - Their strength depends on molecular shapes and weights.
- Dipole-dipole forces add to the effect of dispersion forces.
 - They are found only in polar substances.
- H-bonding is a special case of dipole-dipole interactions.
 - Strongest of the intermolecular forces involving neutral species.
 - Most important for hydride compounds (NH_3 , H_2O , etc.).
- Ion-dipole forces are interactions between ionic and polar molecules.
 - Ion-dipole are stronger than H-bonds.
- Covalent bonds are stronger than any of these reactions.

Intermolecular Forces Chart



van der Waals forces