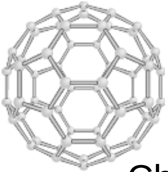
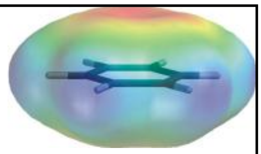



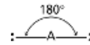
Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

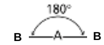
Chapter 10

Valence shell electron pair repulsion (VSEPR) model:

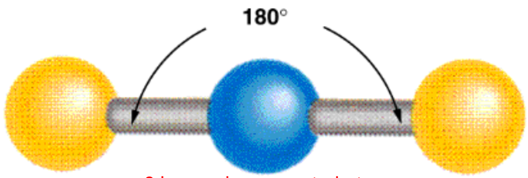
Predict the geometry of the molecule from the electrostatic repulsions between the electron (bonding and nonbonding) pairs.

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear





Beryllium Chloride



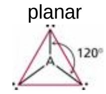
0 lone pairs on central atom

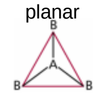
:Cl—Be—Cl:

2 atoms bonded to central atom

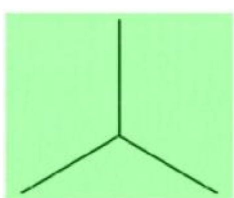
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar

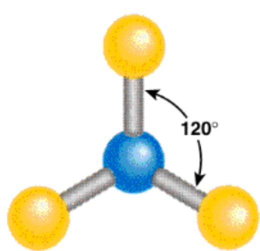




Boron Trifluoride

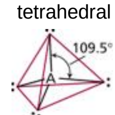


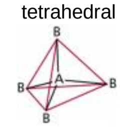
Planar



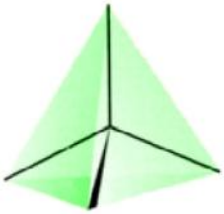
VSEPR

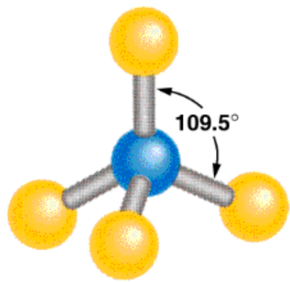
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral





Methane

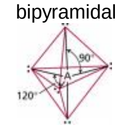




7

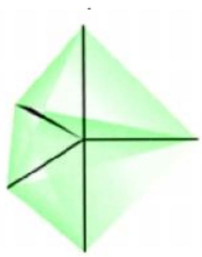
VSEPR

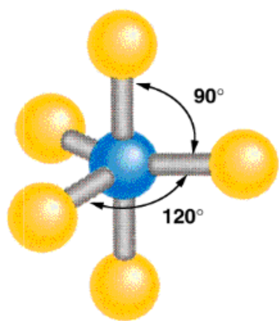
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal



8

Phosphorus Pentachloride

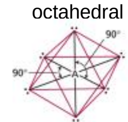


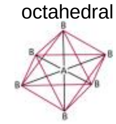


9

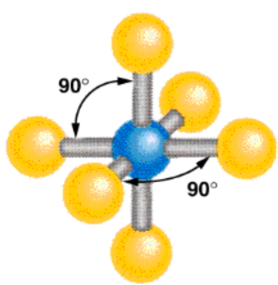
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_6	6	0	octahedral	octahedral





Sulfur Hexafluoride



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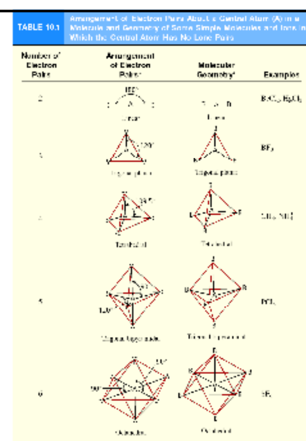
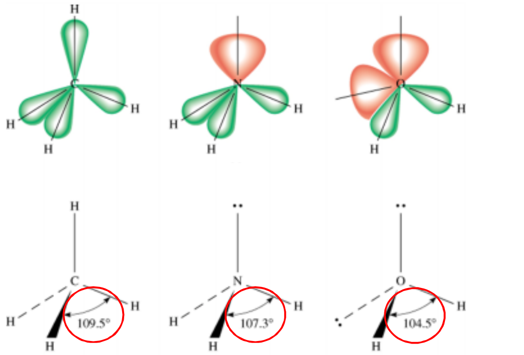


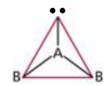
12

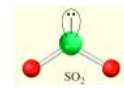


lone-pair vs. lone pair repulsion > lone-pair vs. bonding pair repulsion > bonding-pair vs. bonding pair repulsion

VSEPR

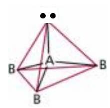
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_3	3	0	trigonal planar	trigonal planar
AB_2E	2	1	trigonal planar	bent

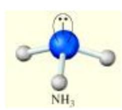




VSEPR

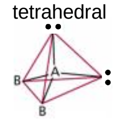
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal

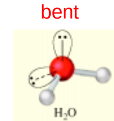




VSEPR

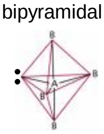
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal
AB_2E_2	2	2	tetrahedral	bent

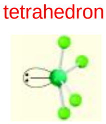




VSEPR

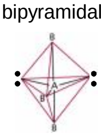
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron

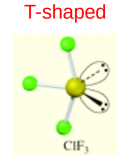




VSEPR

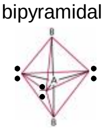
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AB_3E_2	3	2	trigonal bipyramidal	T-shaped

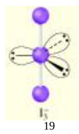




VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AB_3E_2	3	2	trigonal bipyramidal	T-shaped
AB_2E_3	2	3	trigonal bipyramidal	linear

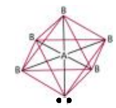


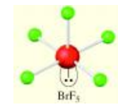


19

VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_6	6	0	octahedral	octahedral
AB_5E	5	1	octahedral	square pyramidal

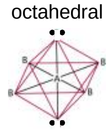


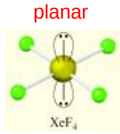


20

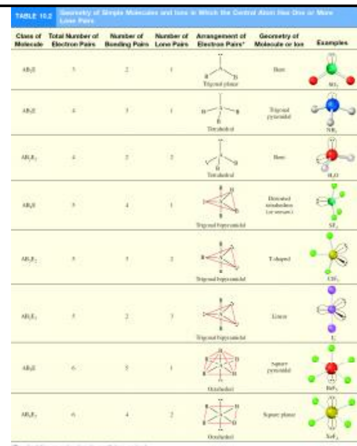
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_6	6	0	octahedral	octahedral
AB_5E	5	1	octahedral	square pyramidal
AB_4E_2	4	2	octahedral	square planar





21

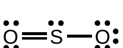


22

Predicting Molecular Geometry

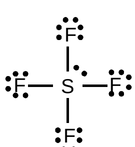
1. Draw Lewis structure for molecule.
2. Count number of lone pairs on the central atom and number of atoms bonded to the central atom.
3. Use VSEPR to predict the geometry of the molecule.

What are the molecular geometries of SO_2 and SF_4?



AB_2E

bent

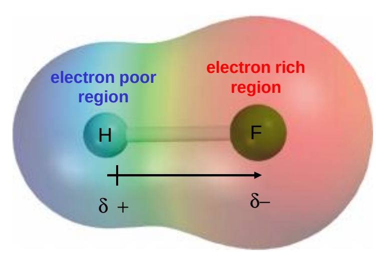


AB_4E

distorted tetrahedron

23

Dipole Moments and Polar Molecules



$\mu = Q \times r$

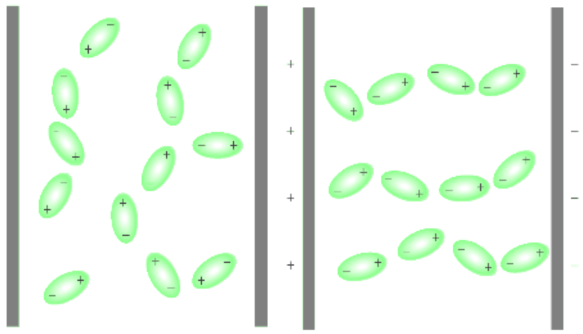
Q is the charge

r is the distance between charges

$1\ D = 3.36 \times 10^{-30}\ C\ m$

24

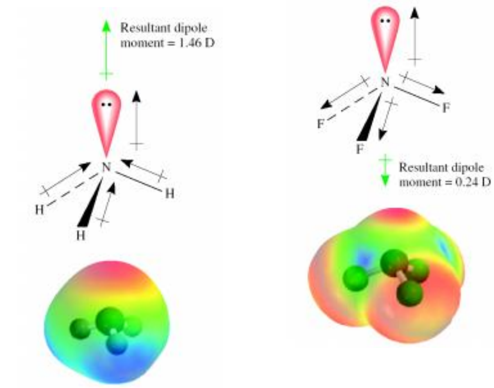
Behavior of Polar Molecules



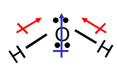
field off

field on

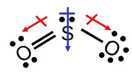
Bond moments and resultant dipole moments in NH_3 and NF_3.



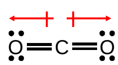
Which of the following molecules have a dipole moment?
H_2O, CO_2, SO_2, and CF_4



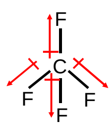
dipole moment
polar molecule



dipole moment
polar molecule

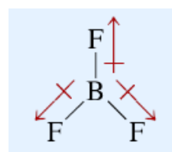


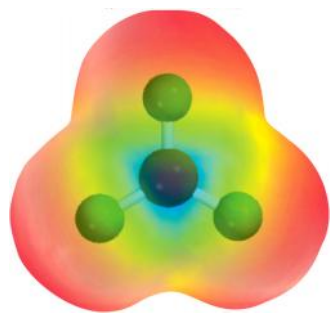
no dipole moment
nonpolar molecule



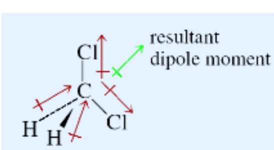
no dipole moment
nonpolar molecule

Does BF_3 have a dipole moment?





Does CH_2Cl_2 have a dipole moment?



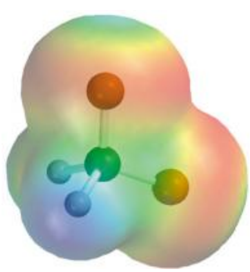
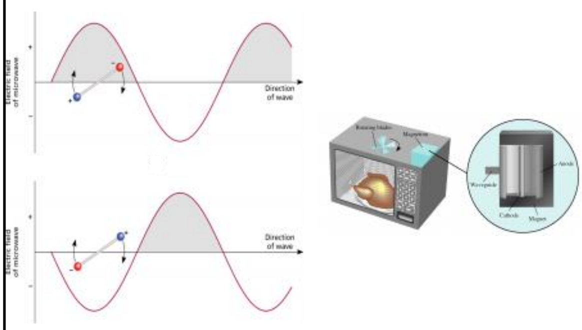


TABLE 10.3 Dipole Moments of Some Polar Molecules

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

Chemistry In Action: Microwave Ovens



31

How does Lewis theory explain the bonds in H_2 and F_2?

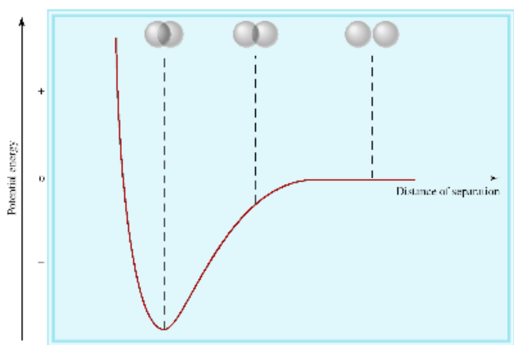
Sharing of two electrons between the two atoms.

	Bond Enthalpy	Bond Length	Overlap Of
H_2	436.4 kJ/mol	74 pm	2 1*s*
F_2	150.6 kJ/mol	142 pm	2 2*p*

Valence bond theory – bonds are formed by sharing of e^- from overlapping **atomic** orbitals.

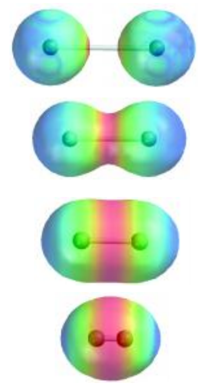
32

Change in Potential Energy of Two Hydrogen Atoms as a Function of Their Distance of Separation



33

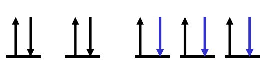
Change in electron density as two hydrogen atoms approach each other.



34

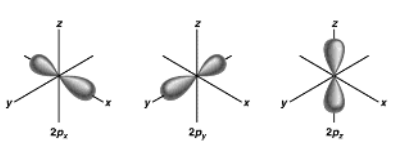
Valence Bond Theory and NH_3

N – $1s^22s^22p^3$



3 H – $1s^1$

If the bonds form from overlap of 3 2*p* orbitals on nitrogen with the 1*s* orbital on each hydrogen atom, what would the molecular geometry of NH_3 be?



If use the 3 2*p* orbitals predict 90º

Actual H-N-H bond angle is 107.3º

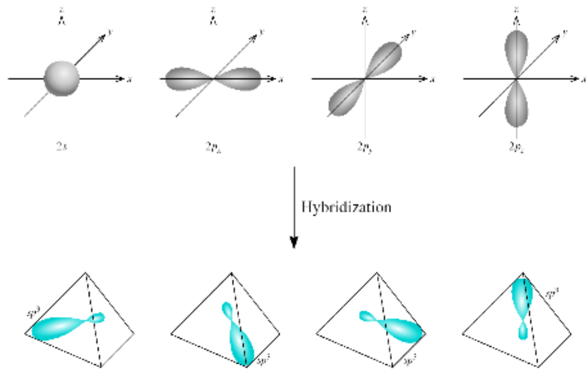
35

Hybridization – mixing of two or more atomic orbitals to form a new set of hybrid orbitals.

1. Mix at least 2 nonequivalent atomic orbitals (*e.g.* s and p). Hybrid orbitals have very different shape from original atomic orbitals.
2. Number of hybrid orbitals is equal to number of pure atomic orbitals used in the hybridization process.
3. Covalent bonds are formed by:
   a. Overlap of hybrid orbitals with atomic orbitals
   b. Overlap of hybrid orbitals with other hybrid orbitals

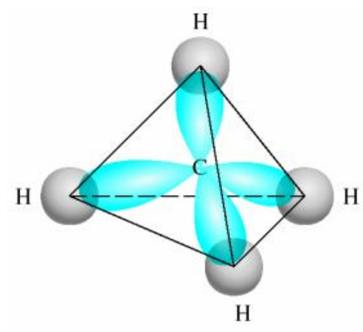
36

Formation of *sp*³ Hybrid Orbitals



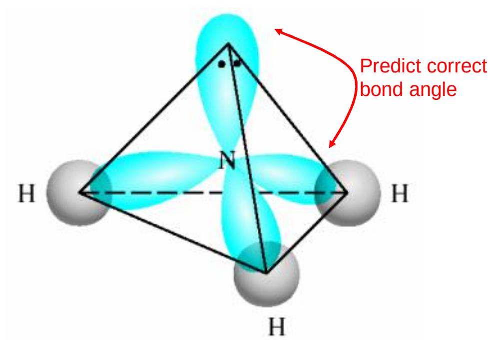
37

Formation of Covalent Bonds in CH_4



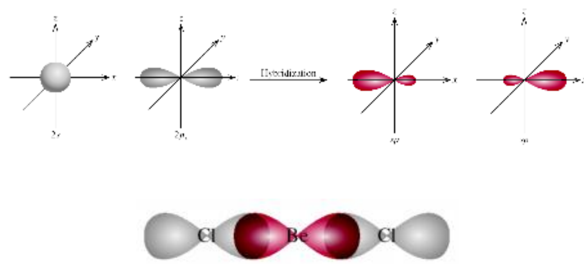
38

*sp*³-Hybridized N Atom in NH_3



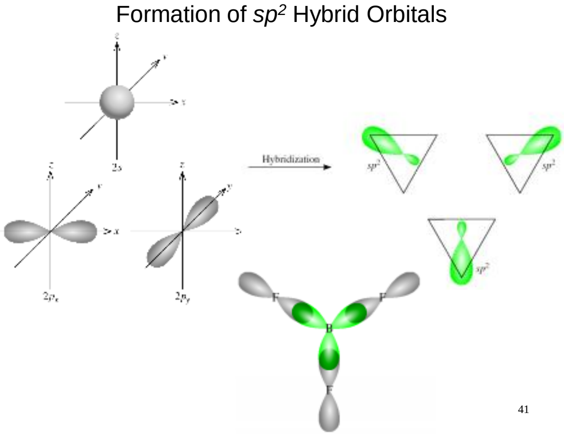
39

Formation of *sp* Hybrid Orbitals



40

Formation of *sp*² Hybrid Orbitals



41

How do I predict the hybridization of the central atom?

1. Draw the Lewis structure of the molecule.
2. Count the number of lone pairs AND the number of atoms bonded to the central atom

# of Lone Pairs + # of Bonded Atoms	Hybridization	Examples
2	sp	$BeCl_2$
3	sp^2	BF_3
4	sp^3	CH_4, NH_3, H_2O
5	sp^3d	PCl_5
6	sp^3d^2	SF_6

42

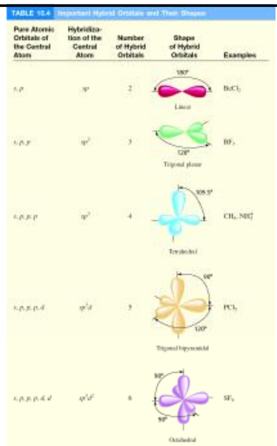
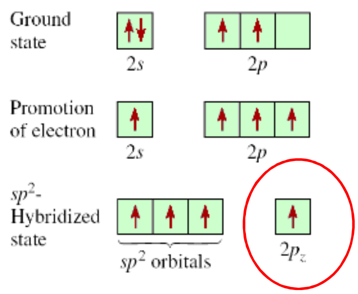


TABLE 10.4 Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	sp	2	Linear (180°)	$BeCl_2$
s, p, p	sp^2	3	Trigonal planar (120°)	BF_3
s, p, p, p	sp^3	4	Tetrahedral (109.5°)	CH_4, NH_4^+
s, p, p, p, d	sp^3d	5	Trigonal bipyramidal (90°, 120°)	PCl_5
s, p, p, p, d, d	sp^3d^2	6	Octahedral (90°)	SF_6

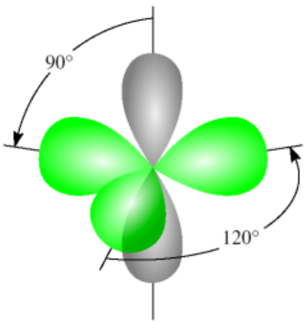
43

sp^2 Hybridization of Carbon



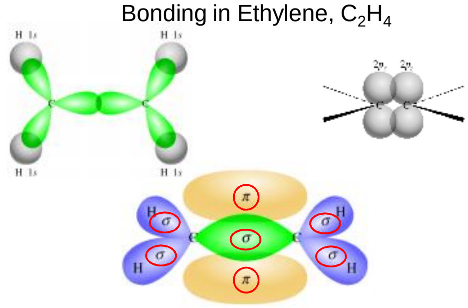
44

Unhybridized $2p_z$ orbital (gray), which is perpendicular to the plane of the hybrid (green) orbitals.



45

Bonding in Ethylene, C_2H_4

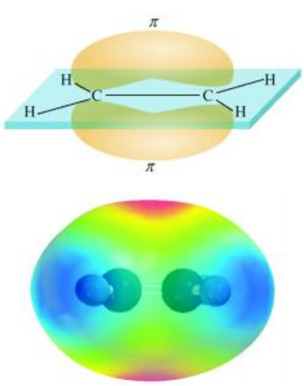


Sigma bond (σ) – electron density between the 2 atoms

Pi bond (π) – electron density above and below plane of nuclei of the bonding atoms

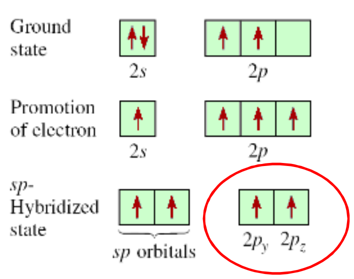
46

Another View of π Bonding in Ethylene, C_2H_4



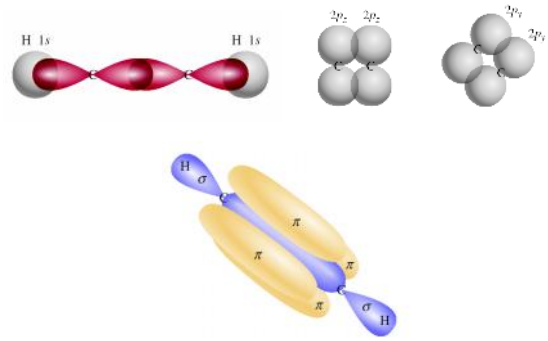
47

sp Hybridization of Carbon

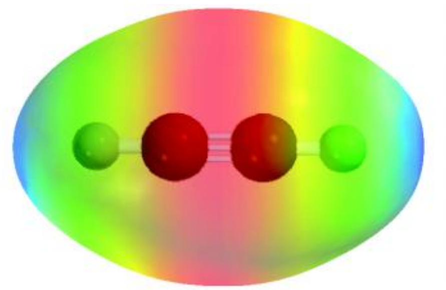


48

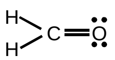
Bonding in Acetylene, C_2H_2



Another View of the Bonding in Ethylene, C_2H_4

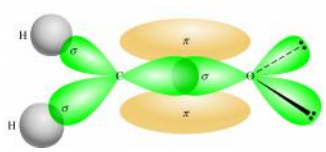


Describe the bonding in CH_2O.



C – 3 bonded atoms, 0 lone pairs
C – sp^2

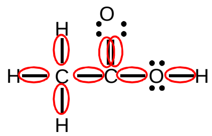
CH_2O



Sigma (σ) and Pi Bonds (π)

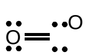
Single bond	1 sigma bond
Double bond	1 sigma bond and 1 pi bond
Triple bond	1 sigma bond and 2 pi bonds

How many σ and π bonds are in the acetic acid (vinegar) molecule CH_3COOH?



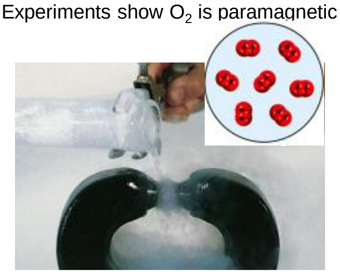
σ bonds = 6 + 1 = 7
π bonds = 1

Experiments show O_2 is paramagnetic



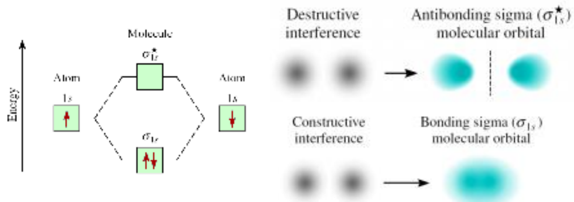
No unpaired e[-]

Should be diamagnetic



Molecular orbital theory – bonds are formed from interaction of atomic orbitals to form **molecular** orbitals.

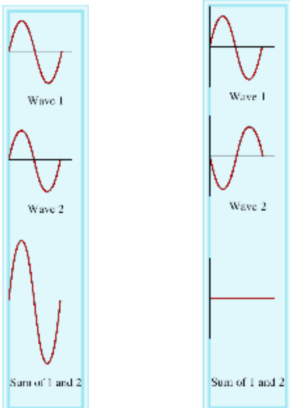
Energy levels of bonding and antibonding **molecular** orbitals in hydrogen (H_2).



A ***bonding molecular orbital*** has lower energy and greater stability than the atomic orbitals from which it was formed.

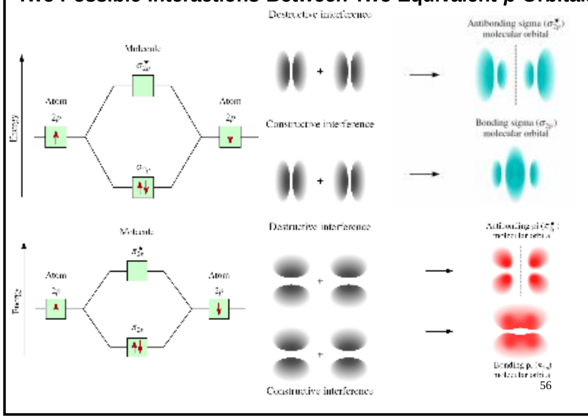
An ***antibonding molecular orbital*** has higher energy and lower stability than the atomic orbitals from which it was formed.

Constructive and Destructive Interference



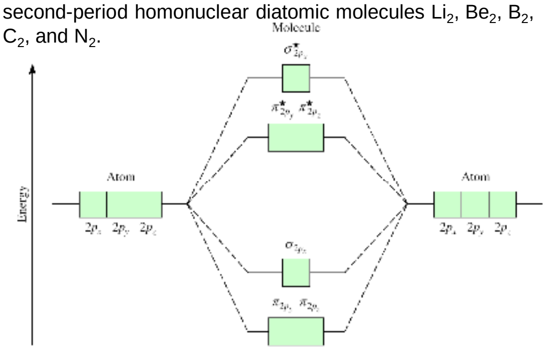
55

Two Possible Interactions Between Two Equivalent *p* Orbitals



56

General molecular orbital energy level diagram for the second-period homonuclear diatomic molecules Li_2, Be_2, B_2, C_2, and N_2.



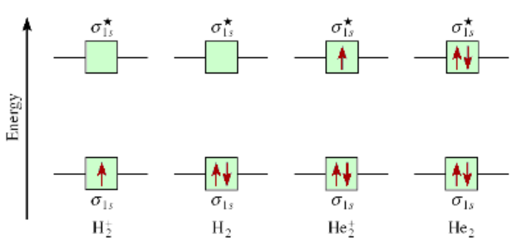
57

Molecular Orbital (MO) Configurations

1. The number of molecular orbitals (MOs) formed is always equal to the number of atomic orbitals combined.
2. The more stable the bonding MO, the less stable the corresponding antibonding MO.
3. The filling of MOs proceeds from low to high energies.
4. Each MO can accommodate up to two electrons.
5. Use Hund's rule when adding electrons to MOs of the same energy.
6. The number of electrons in the MOs is equal to the sum of all the electrons on the bonding atoms.

58

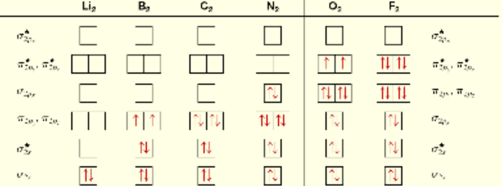
$$\textbf{bond order} = \frac{1}{2}\left(\text{Number of electrons in bonding MOs} - \text{Number of electrons in antibonding MOs}\right)$$



bond order	½	1	½	0

59

TABLE 10.5 Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*



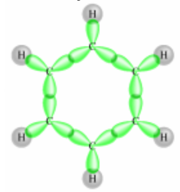
	Li_2	B_2	C_2	N_2	O_2	F_2
Bond order	1	1	2	3	2	1
Bond length (pm)	267	159	131	110	121	142
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic

*For simplicity the σ_{1s} and σ^*_{1s} orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O_2 and F_2, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z}.

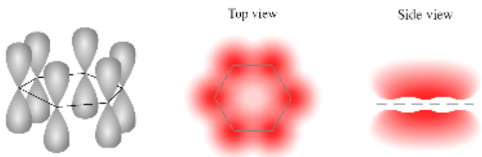
60

Delocalized molecular orbitals are not confined between two adjacent bonding atoms, but actually extend over three or more atoms.

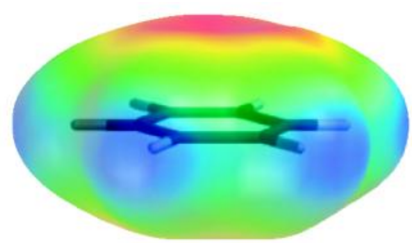
Example: Benzene, C_6H_6



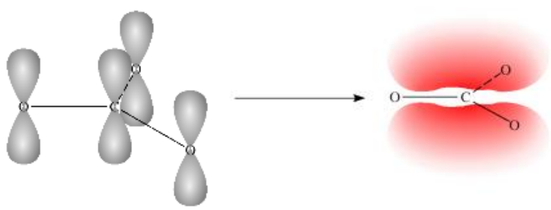
Delocalized π orbitals



Electron density above and below the plane of the benzene molecule.



Bonding in the Carbonate Ion, CO_3^{2-}



Chemistry In Action: Buckyball Anyone?