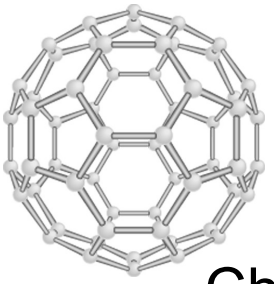
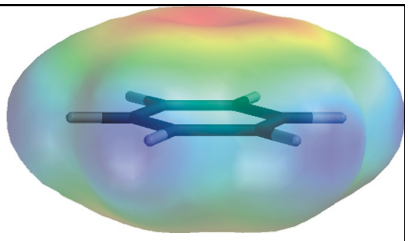




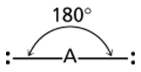
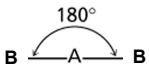
# Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

*Chapter 10*



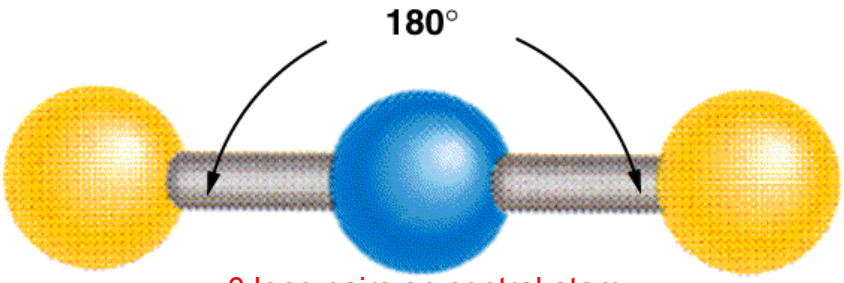
***Valence shell electron pair repulsion*** (VSEPR) model:

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

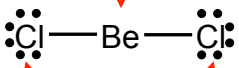
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear   | linear   |

2

## Beryllium Chloride



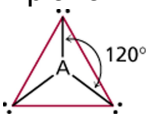
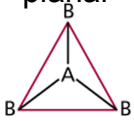

0 lone pairs on central atom




2 atoms bonded to central atom

3

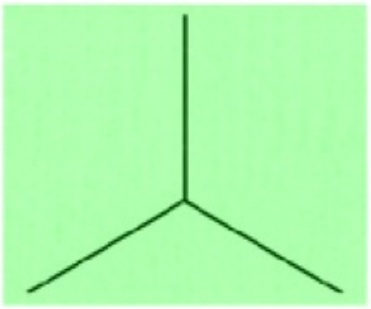
## VSEPR

| 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  |

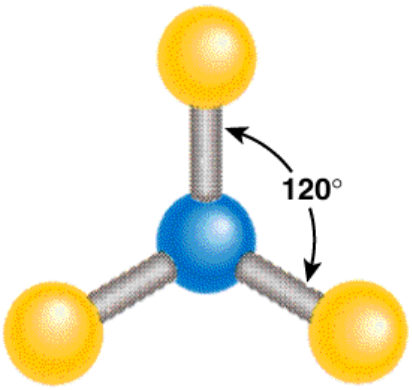


4

## Boron Trifluoride



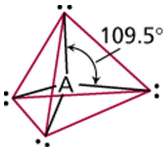
Planar

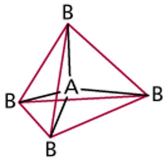



5

## VSEPR

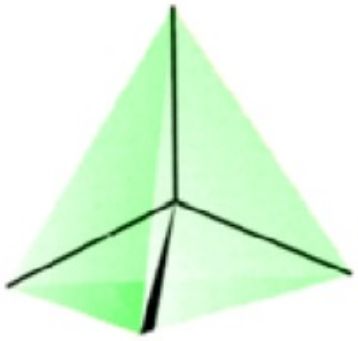
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |



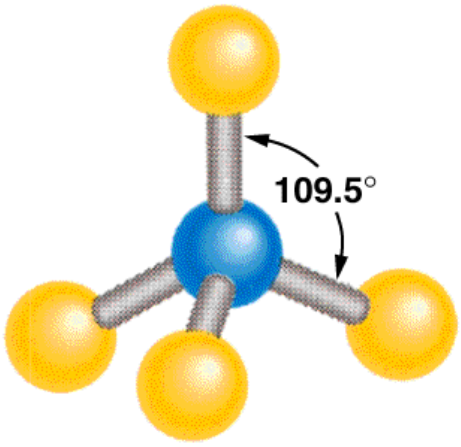




6

## Methane



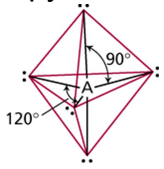
Tetrahedral

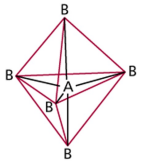



7

## VSEPR

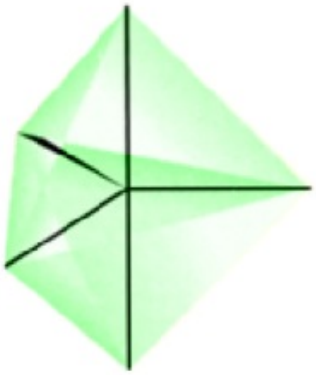
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_5$ |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



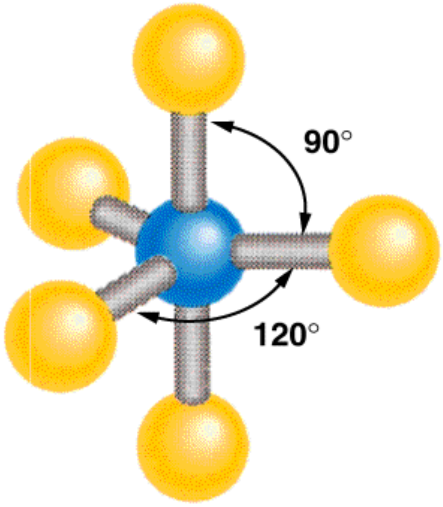




8

## Phosphorus Pentachloride



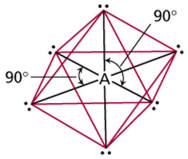
Trigonal bipyramidal

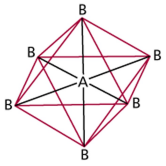



9

## VSEPR

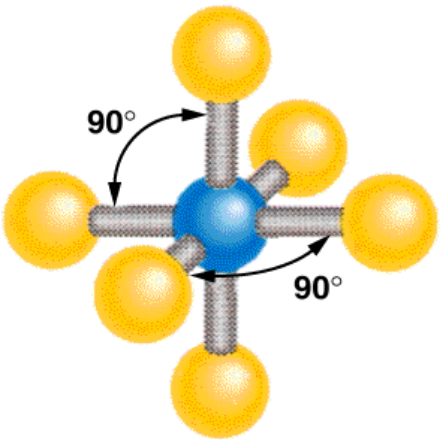
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_5$ |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



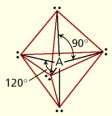
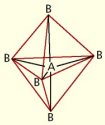
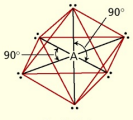
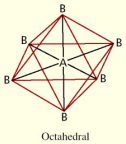
# Sulfur Hexafluoride

Octahedral



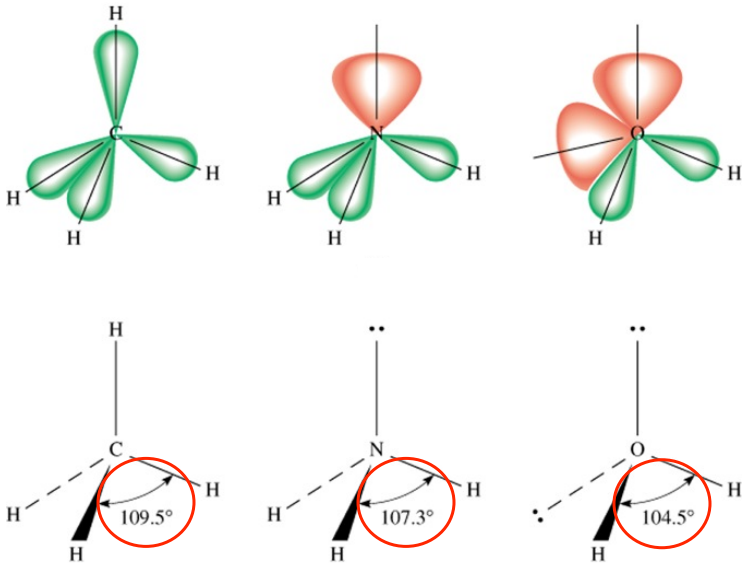

11

**TABLE 10.1** Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

| Number of Electron Pairs | Arrangement of Electron Pairs* | Molecular Geometry* | Examples |
|---|---|---|---|
| 2 |  Linear | B—A—B Linear | $BeCl_2$, $HgCl_2$ |
| 3 |  Trigonal planar |  Trigonal planar | $BF_3$ |
| 4 |  Tetrahedral |  Tetrahedral | $CH_4$, $NH_4^+$ |
| 5 |  Trigonal bipyramidal |  Trigonal bipyramidal | $PCl_5$ |
| 6 |  Octahedral |  Octahedral | $SF_6$ |

*The colored lines are used only to show the overall shapes; they do not represent bonds.

12

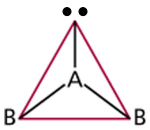


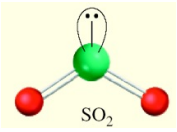

lone-pair vs. lone pair repulsion > lone-pair vs. bonding pair repulsion > bonding-pair vs. bonding pair repulsion

13

## 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 |

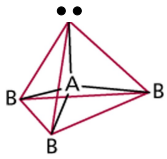


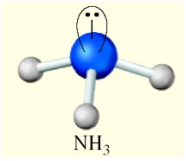




14

## 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 |

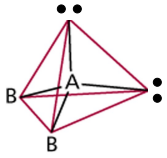


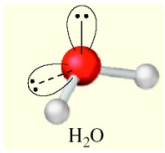




15

## 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 |

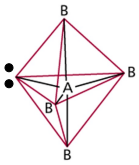


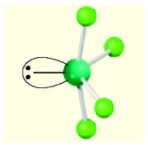




16

## 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 |

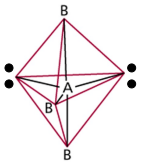


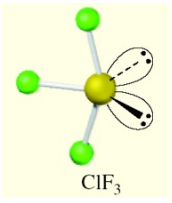



17

## 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 |

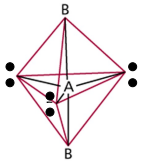


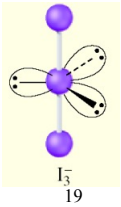




18

## 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 |

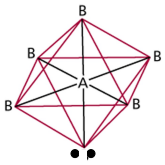


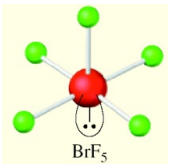




19

## 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 |

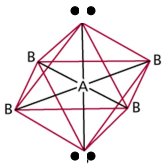


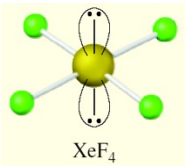




20

# 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

**TABLE 10.2** Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

| Class of Molecule | Total Number of Electron Pairs | Number of Bonding Pairs | Number of Lone Pairs | Arrangement of Electron Pairs* | Geometry of Molecule or Ion | Examples |
|---|---|---|---|---|---|---|
| $AB_2E$ | 3 | 2 | 1 | Trigonal planar | Bent | $SO_2$ |
| $AB_3E$ | 4 | 3 | 1 | Tetrahedral | Trigonal pyramidal | $NH_3$ |
| $AB_2E_2$ | 4 | 2 | 2 | Tetrahedral | Bent | $H_2O$ |
| $AB_4E$ | 5 | 4 | 1 | Trigonal bipyramidal | Distorted tetrahedron (or seesaw) | $SF_4$ |
| $AB_3E_2$ | 5 | 3 | 2 | Trigonal bipyramidal | T-shaped | $ClF_3$ |
| $AB_2E_3$ | 5 | 2 | 3 | Trigonal bipyramidal | Linear | $I_3^-$ |
| $AB_5E$ | 6 | 5 | 1 | Octahedral | Square pyramidal | $BrF_5$ |
| $AB_4E_2$ | 6 | 4 | 2 | Octahedral | Square planar | $XeF_4$ |

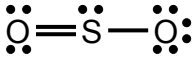
*The colored lines are used to show the overall shape, not bonds.

22

# Predicting Molecular Geometry

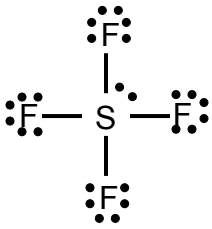
1. Draw Lewis structure for molecule.
2. Count number of lone pairs on the central atom and number of atoms bonded to the central atom.
3. Use VSEPR to predict the geometry of the molecule.

What are the molecular geometries of $SO_2$ and $SF_4$?



$AB_2E$

bent

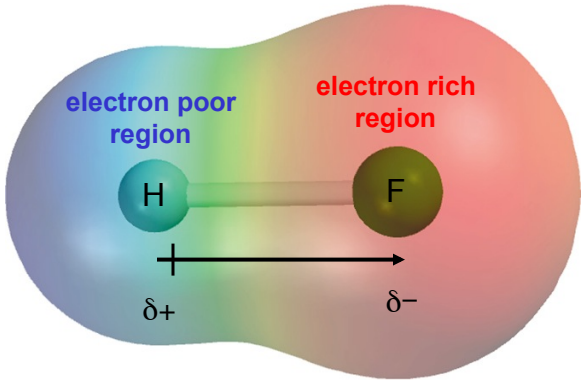


$AB_4E$

distorted tetrahedron

23

# Dipole Moments and Polar Molecules




$\mu = Q \times r$

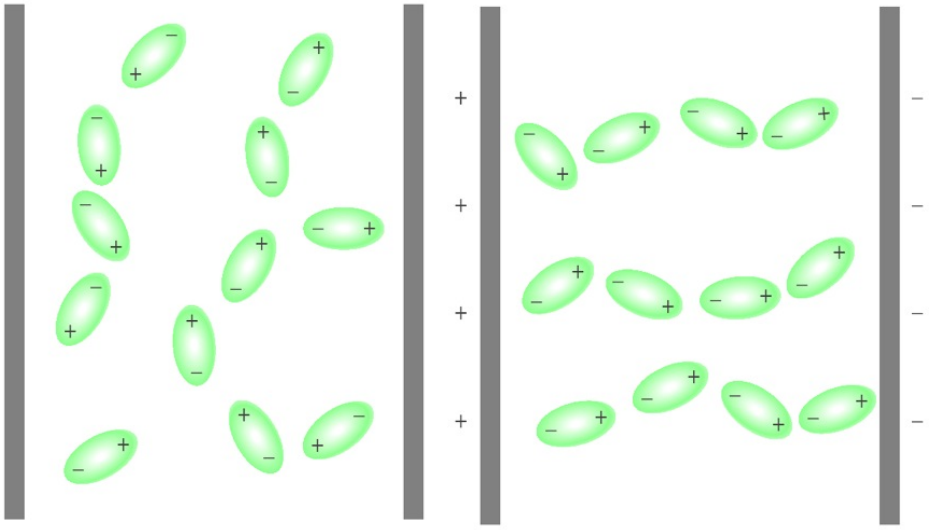
$Q$ is the charge

$r$ is the distance between charges

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

24

## Behavior of Polar Molecules



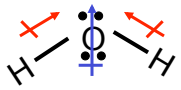
field off

field on

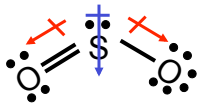
25

## Which of the following molecules have a dipole moment?

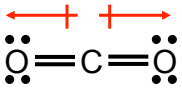
$H_2O$, $CO_2$, $SO_2$, and $CF_4$



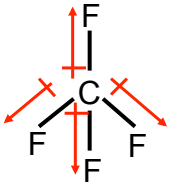
dipole moment
polar molecule



dipole moment
polar molecule



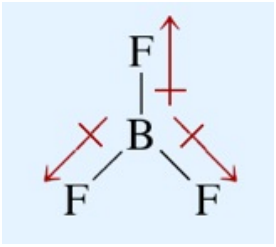
no dipole moment
nonpolar molecule

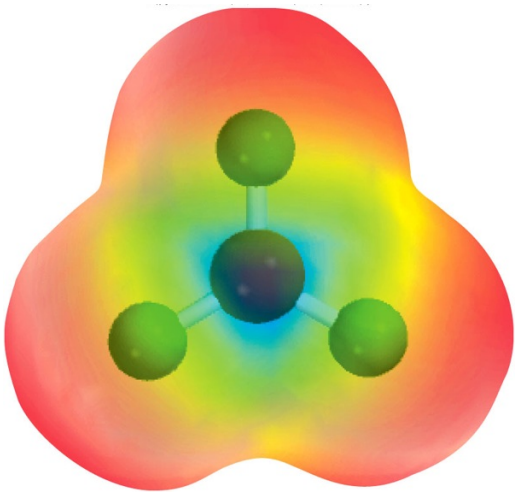


no dipole moment
nonpolar molecule

26

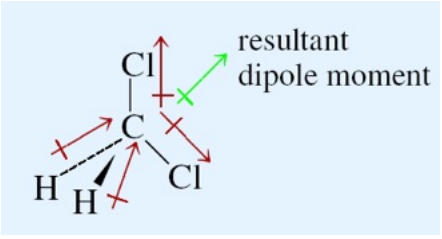
Does $BF_3$ have a dipole moment?

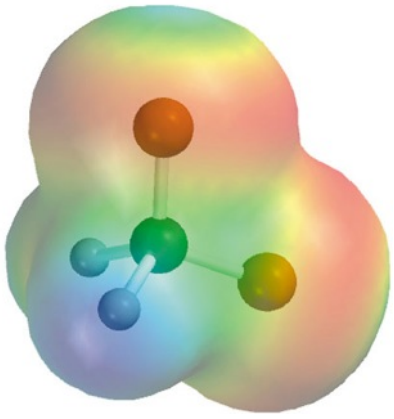


27

Does $CH_2Cl_2$ have a dipole moment?



28

**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 |

29

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

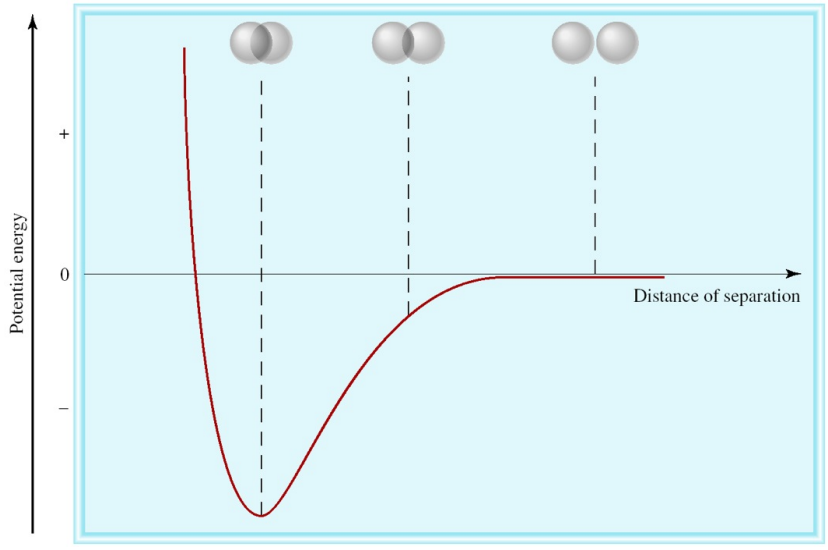
Sharing of two electrons between the two atoms.

| | 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.

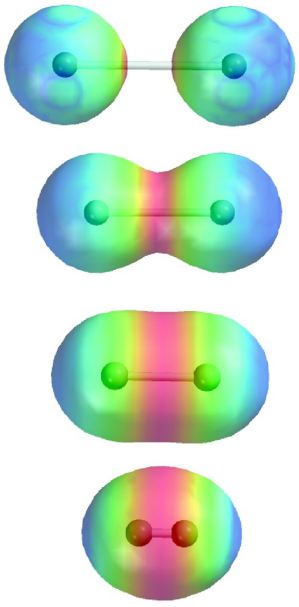
30

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




31

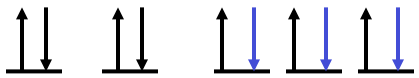
## Change in electron density as two hydrogen atoms approach each other.



32

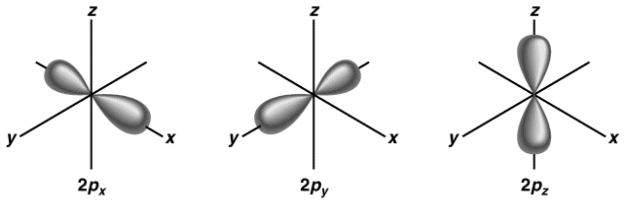
## Valence Bond Theory and $NH_3$

N – $1s^2 2s^2 2p^3$



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 90°

Actual H-N-H bond angle is 107.3°

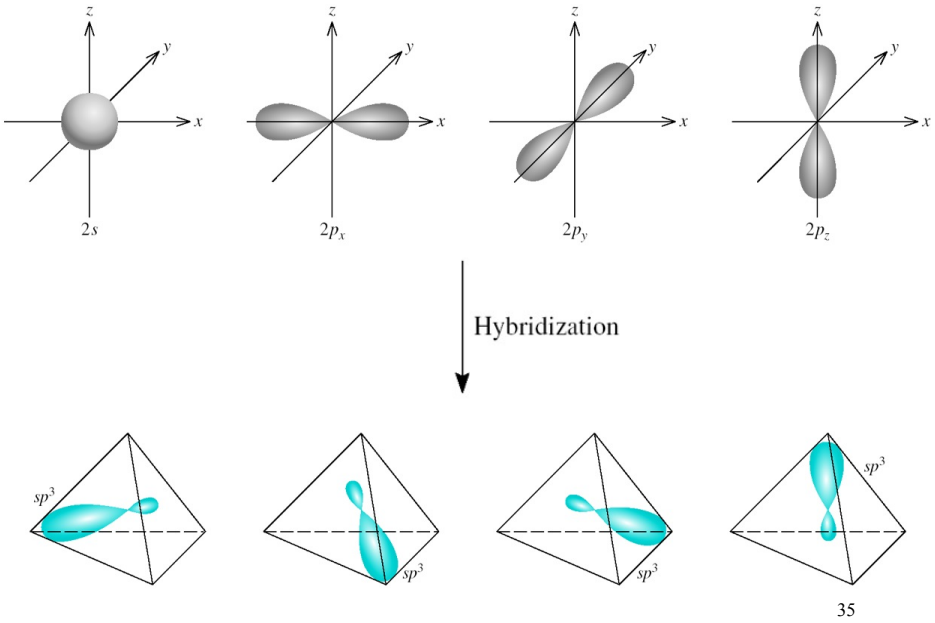
33

## **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

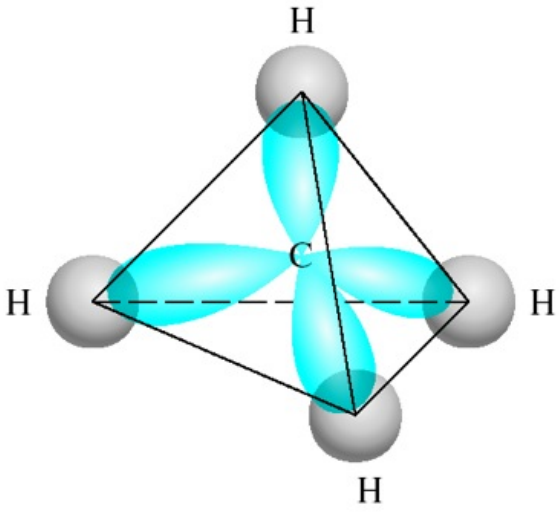
34

## Formation of $sp^3$ Hybrid Orbitals



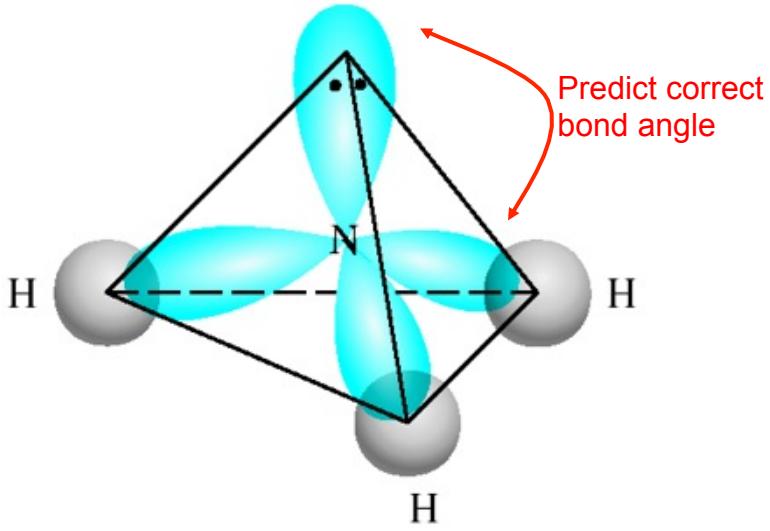

35

## Formation of Covalent Bonds in $CH_4$



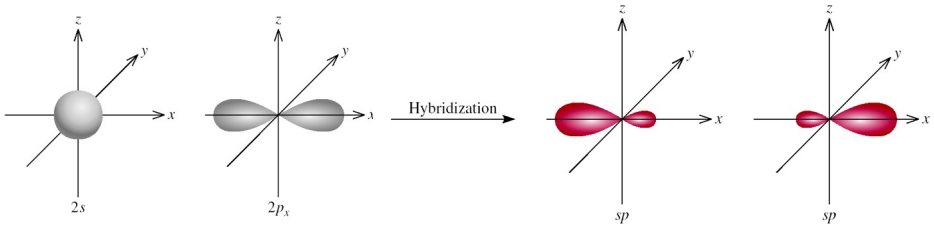

36

## $sp^3$-Hybridized N Atom in $NH_3$




37

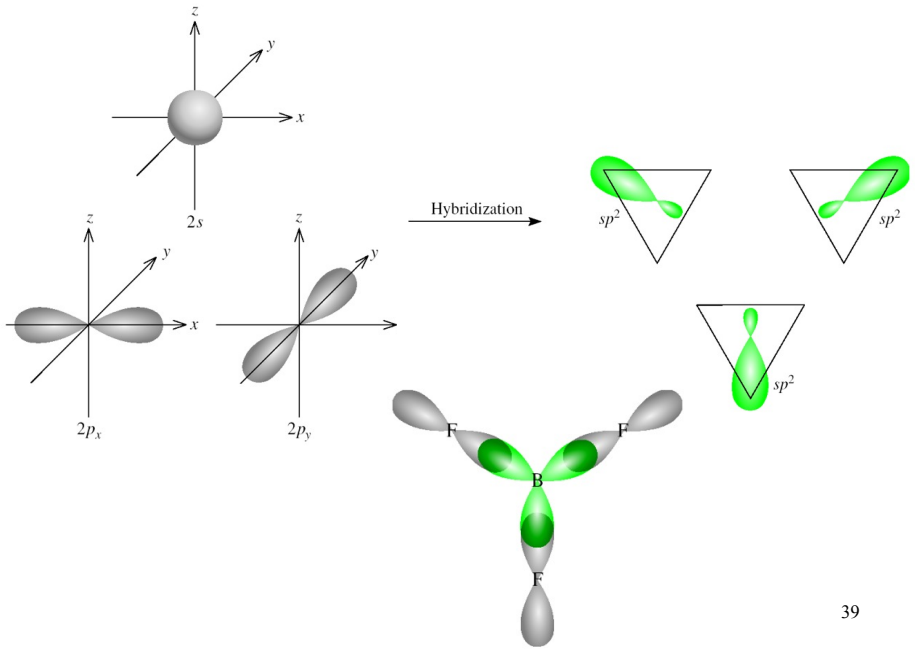
## Formation of *sp* Hybrid Orbitals





38

## Formation of $sp^2$ Hybrid Orbitals




39

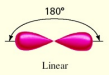
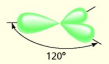
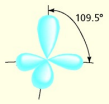
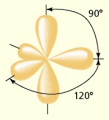
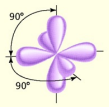
How do I predict the hybridization of the central atom?

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 | $sp^3d^2$ | $SF_6$ |

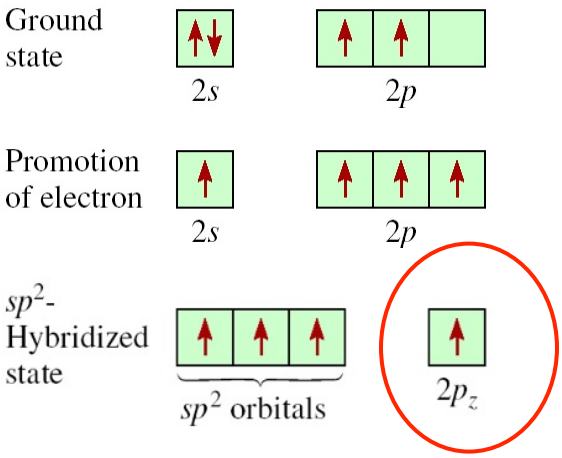
40

**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 | $BeCl_2$ |
| *s*, *p*, *p* | $sp^2$ | 3 |   Trigonal planar | $BF_3$ |
| *s*, *p*, *p*, *p* | $sp^3$ | 4 |   Tetrahedral | $CH_4$, $NH_4^+$ |
| *s*, *p*, *p*, *p*, *d* | $sp^3d$ | 5 |   Trigonal bipyramidal | $PCl_5$ |
| *s*, *p*, *p*, *p*, *d*, *d* | $sp^3d^2$ | 6 |   Octahedral | $SF_6$ |

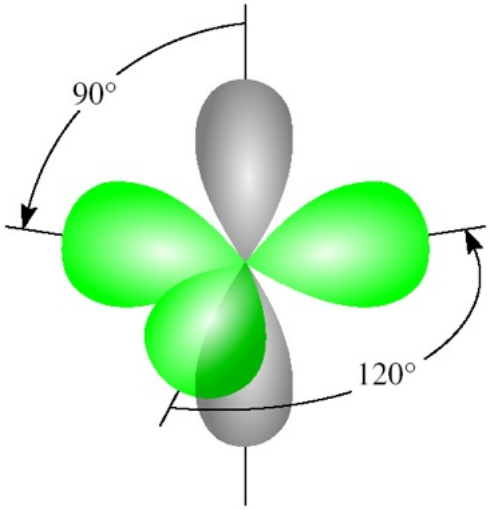
41

## $sp^2$ Hybridization of Carbon



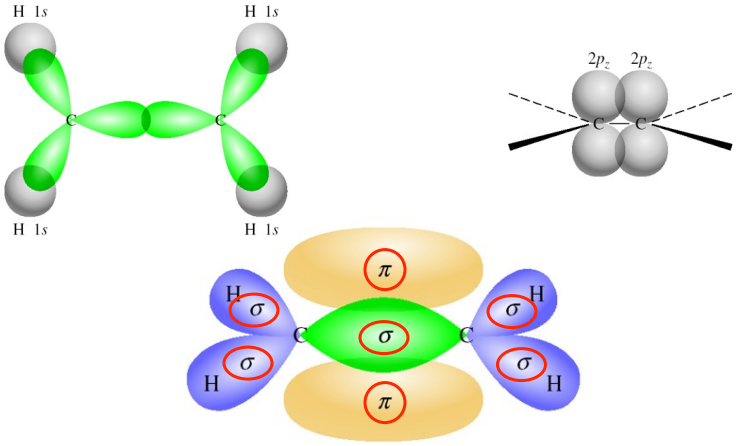

42

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




43

## Bonding in Ethylene, $C_2H_4$

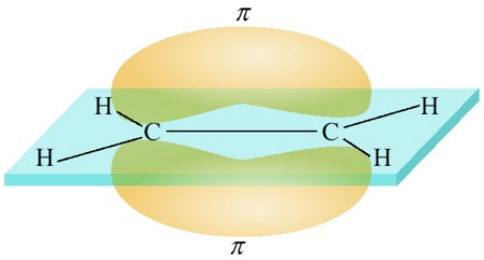


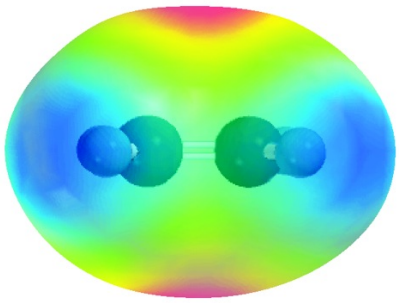

Sigma bond (σ) – electron density between the 2 atoms

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

44

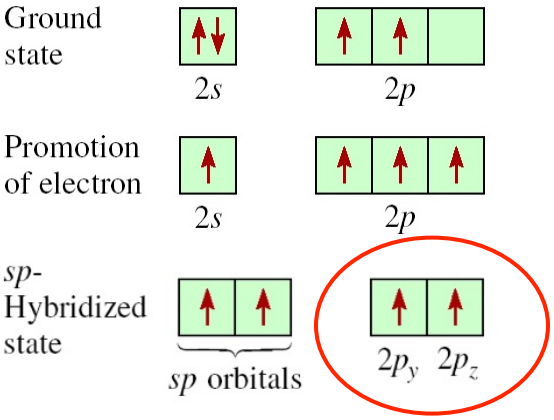
## Another View of π Bonding in Ethylene, $C_2H_4$



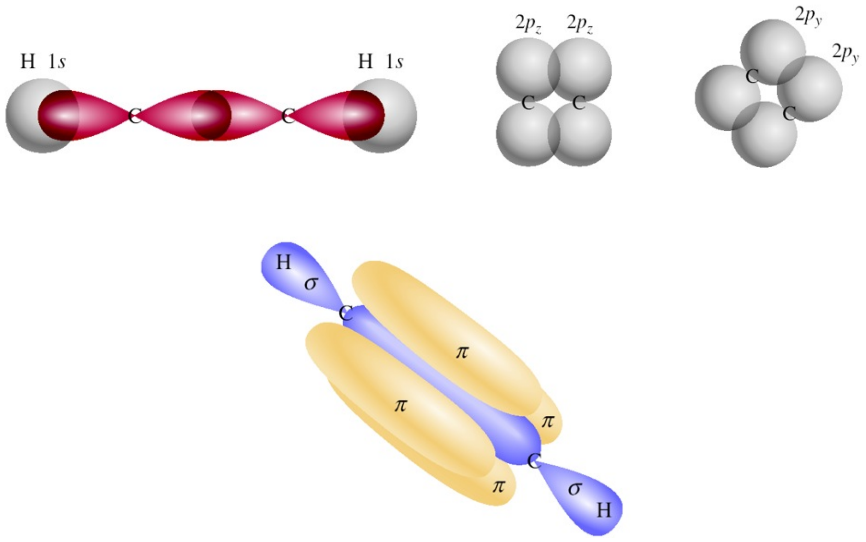
45

## *sp* Hybridization of Carbon



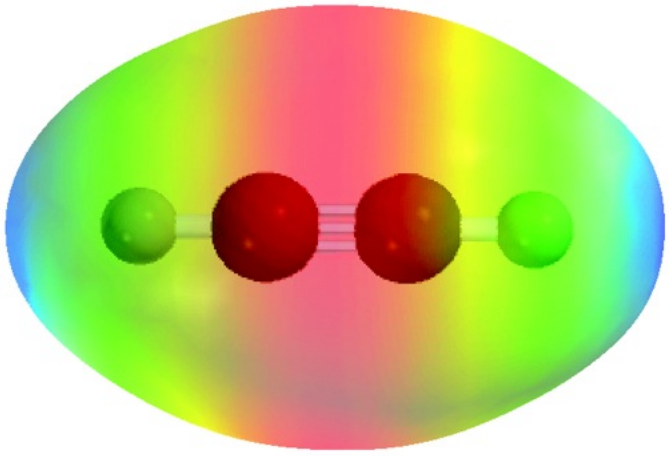

46

## Bonding in Acetylene, $C_2H_2$



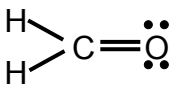

47

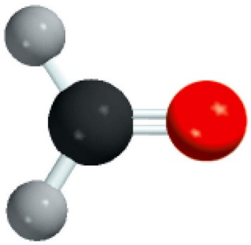
## Another View of the Bonding in Ethylene, $C_2H_4$



48

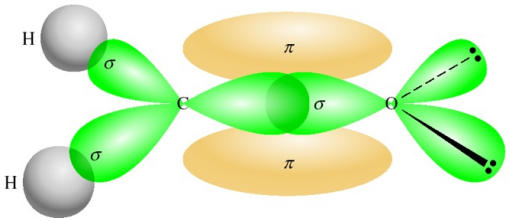
Describe the bonding in $CH_2O$.





$CH_2O$

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

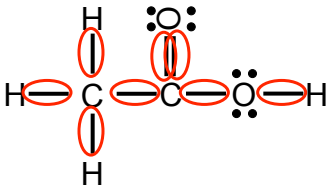



49

## 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

50

Experiments show $O_2$ is paramagnetic

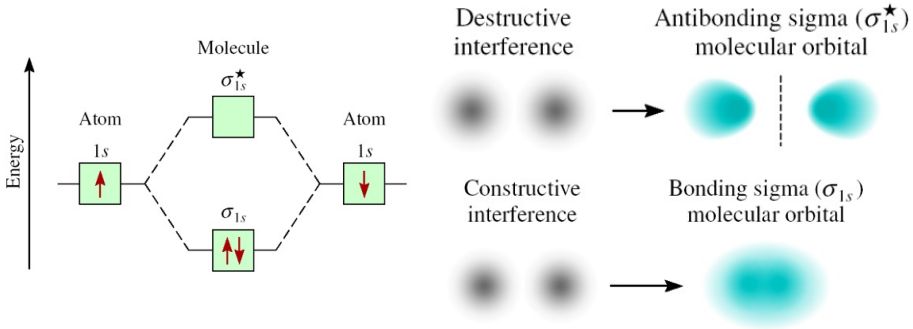
No unpaired $e^-$

Should be diamagnetic

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

51

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

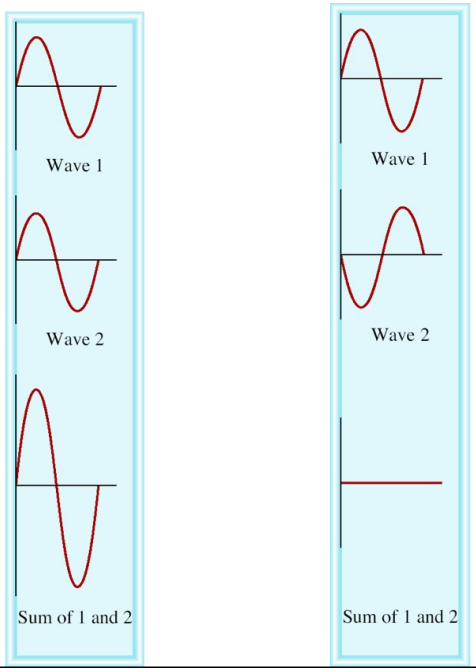



A ***bonding molecular orbital*** has lower energy and greater stability than the atomic orbitals from which it was formed.

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

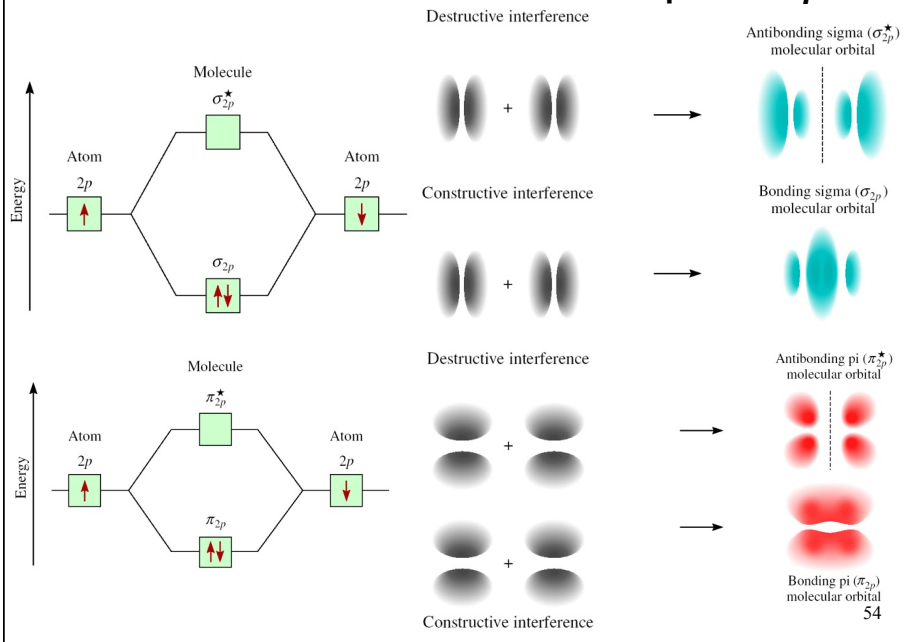
52

## Constructive and Destructive Interference



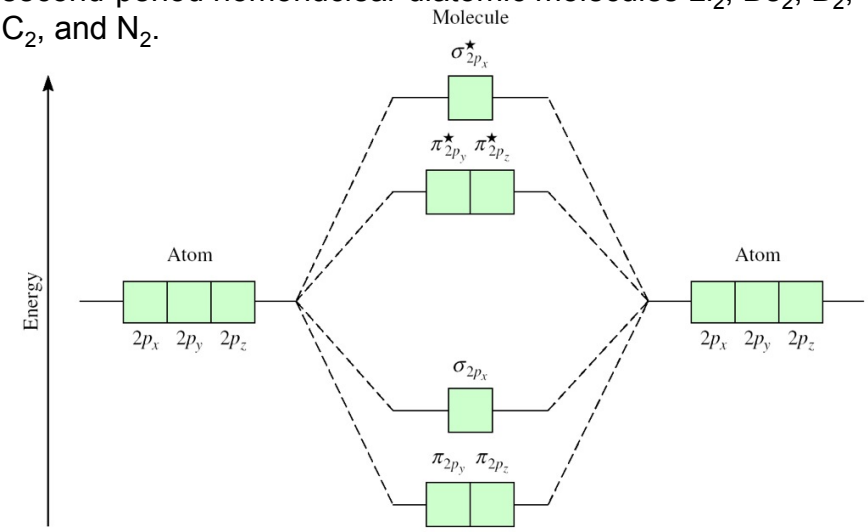

53

## Two Possible Interactions Between Two Equivalent *p* Orbitals




54

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



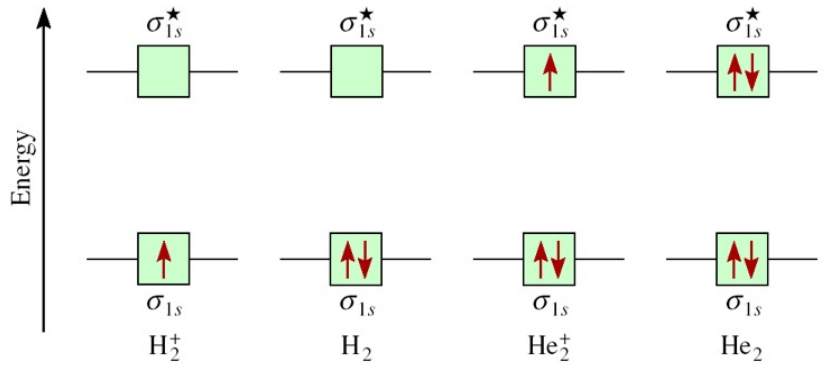

55

## 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.

56

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




| | $H_2^+$ | $H_2$ | $He_2^+$ | $He_2$ |
|---|---|---|---|---|
| bond order | ½ | 1 | ½ | 0 |

57

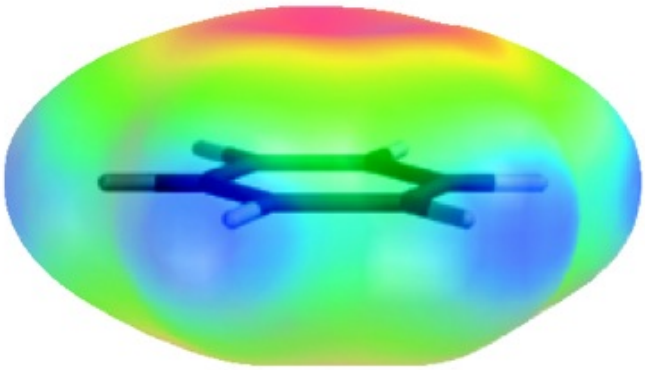
**TABLE 10.5** Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*

| | $Li_2$ | $B_2$ | $C_2$ | $N_2$ | $O_2$ | $F_2$ | |
|---|---|---|---|---|---|---|---|
| $\sigma^{\star}_{2p_x}$ | □ | □ | □ | □ | □ | □ | $\sigma^{\star}_{2p_x}$ |
| $\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$ | □□ | □□ | □□ | □□ | ↑↑ | ↑↓ ↑↓ | $\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$ |
| $\sigma_{2p_x}$ | □ | □ | □ | ↑↓ | ↑↓ ↑↓ | ↑↓ ↑↓ | $\pi_{2p_y}, \pi_{2p_z}$ |
| $\pi_{2p_y}, \pi_{2p_z}$ | □□ | ↑ ↑ | ↑↓ ↑↓ | ↑↓ ↑↓ | ↑↓ | ↑↓ | $\sigma_{2p_x}$ |
| $\sigma^{\star}_{2s}$ | □ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | $\sigma^{\star}_{2s}$ |
| $\sigma_{2s}$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | $\sigma_{2s}$ |
| 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 $\sigma_{1s}$ and $\sigma^{\star}_{1s}$ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for $O_2$ and $F_2$, $\sigma_{2p_x}$ is lower in energy than $\pi_{2p_y}$ and $\pi_{2p_z}$.

58

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



59