CHEMISTRY

an atoms-focused approach

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Chapter 5

Bonding Theories

Explaining Molecular Geometry

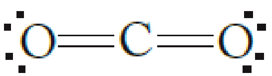
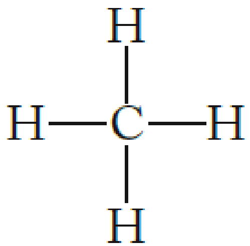
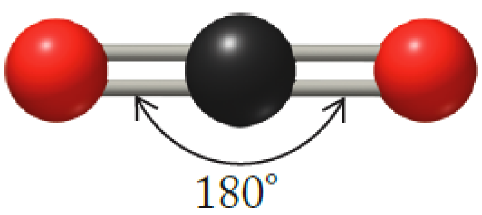
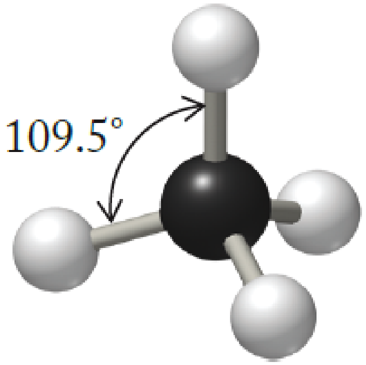
Chapter Outline

- 5.1 Molecular Shape
- 5.2 Valence-Shell Electron-Pair Repulsion Theory (VSEPR)
- 5.3 Polar Bonds and Polar Molecules
- 5.4 Valence Bond Theory and Hybrid Orbitals
- 5.5 Molecules with Multiple Central Atoms
- 5.6 Chirality and Molecular Recognition
- 5.7 Molecular Orbital Theory

Molecular Shape

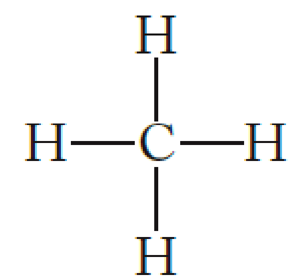
- Chemical/physical properties related to molecular shape.
  - Lewis Structures
    - Show atoms and bonds, but not spatial orientations (3-D)
  - Molecular Models
    - Show orientations and bond angles; help us understand physical and chemical properties

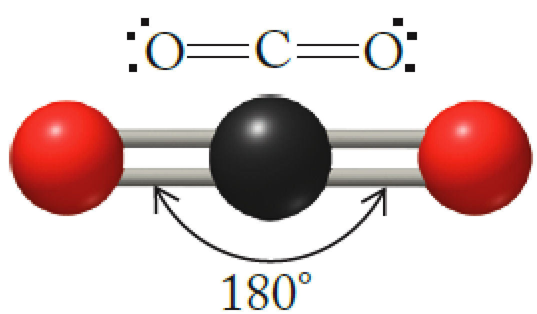
Lewis Structures vs. Models

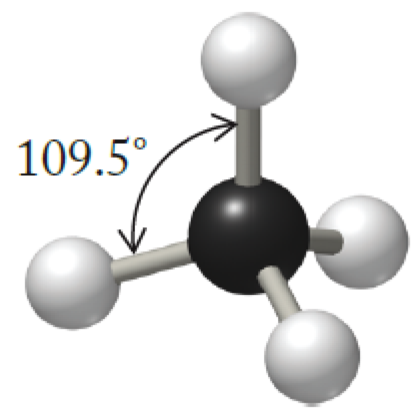
Compound:	Carbon dioxide	Methane
Molecular formula:	CO_2	CH_4
Lewis structure:		
Ball-and-stick model and bond angles:		

Molecular Shape

- Bond Angle:
  - Angle (in degrees) defined by lines joining the centers of two atoms to the center of a third atom to which they are covalently bonded
  - Not always predictable from Lewis structures







Chapter Outline

- 5.1 Molecular Shape
- 5.2 Valence-Shell Electron-Pair Repulsion Theory (VSEPR)
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Valence Shell Electron Pair Repulsion Theory (VSEPR)

- VSEPR Theory
  - A model predicting that the arrangement of valence electron pairs around a central atom minimizes repulsion to produce the lowest energy orientation
- Electron(ic) Geometry
  - 3-dimensional arrangement of bonding e^- pairs <u>and</u> lone pairs electrons about a central atom
- Molecular Geometry
  - 3-dimensional arrangement of atoms in a molecule

VSEPR: Electronic Geometry

- To determine electronic geometry:
  - Draw Lewis structure (see Chapter 8)
  - From Lewis structure, determine steric number (SN):

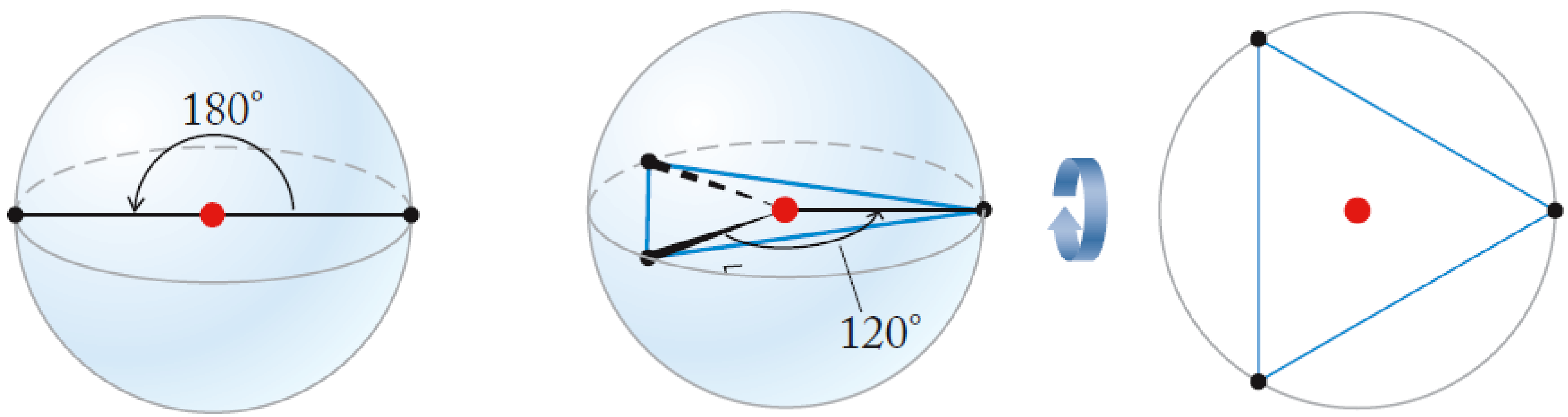
$$SN = \begin{pmatrix} \text{number of atoms} \\ \text{bonded to central atom} \end{pmatrix} + \begin{pmatrix} \text{number of lone pairs} \\ \text{on central atom} \end{pmatrix}$$

  - Determine optimal spatial arrangement of electron pairs (bonding + nonbonding) to minimize repulsion

Molecular Geometry: Central Atom with No Lone Pairs

- Molecular Geometry = Electronic Geometry
- Determine Steric Number (SN):
  - SN = 2 (two atoms bonded to central atom)
    - geometry = linear
  - SN = 3 (three atoms bonded to central atom)
    - geometry = trigonal planar
  - SN = 4 → tetrahedral
  - SN = 5 → trigonal bipyramidal
  - SN = 6 → octahedral

Central Atom with No Lone Pairs



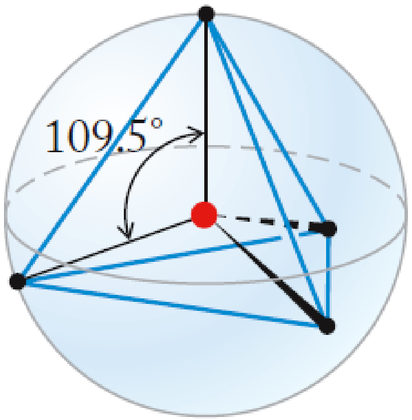
Linear SN = 2

(a)

Trigonal planar SN = 3

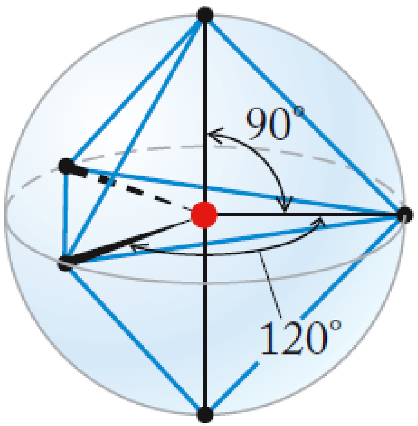
(b)

Central Atom with No Lone Pairs



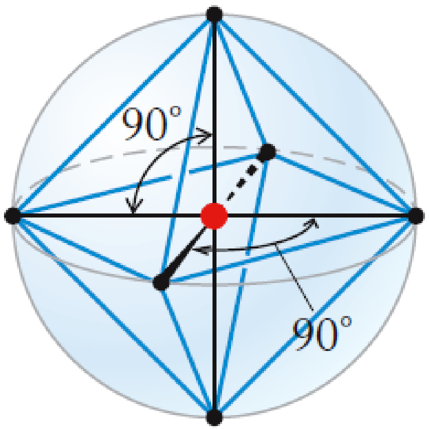
Tetrahedral SN = 4

(c)



Trigonal bipyramidal SN = 5

(d)



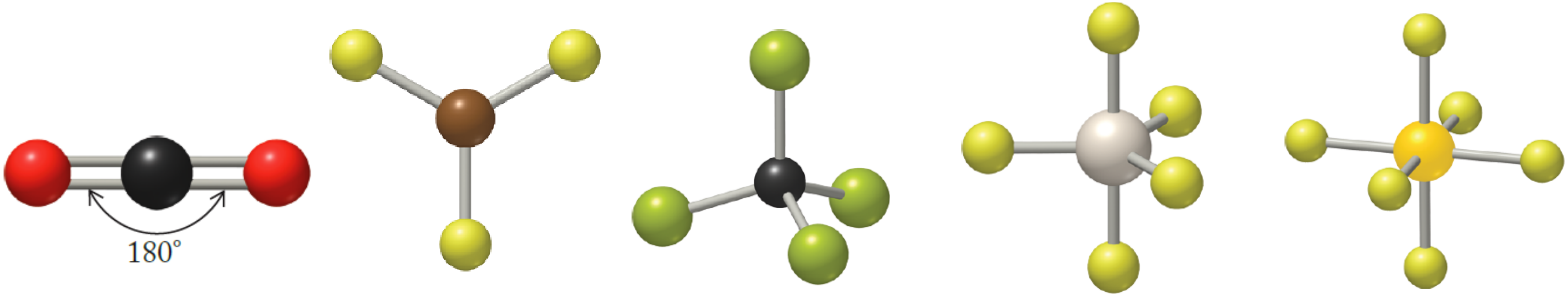
Octahedral SN = 6

(e)

Geometric Forms

- Examples:

CO_2 BF_3 CCl_4 PF_5 SF_6



Practice: Molecular Geometry (No Lone Pairs)

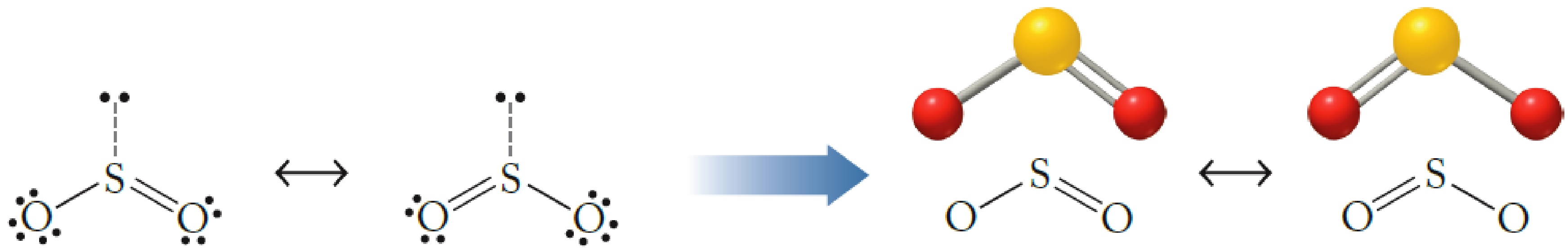
- Determine the molecular geometry of: a) H_2CO (C is central atom)

  b) CH_4

  - Collect and Organize:
  - Analyze:
  - Solve:
  - Think about It:

Central Atoms with Lone Pairs

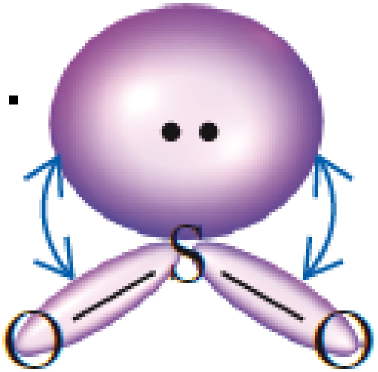
- Molecular Geometry ≠ Electronic Geometry
  - Replace bonding pair(s) with lone pair(s)
- Example: SO_2 (SN = 3)
  - Three electron pairs (2 bonding + 1 lone pair)



(a) Electron-pair geometry = trigonal planar

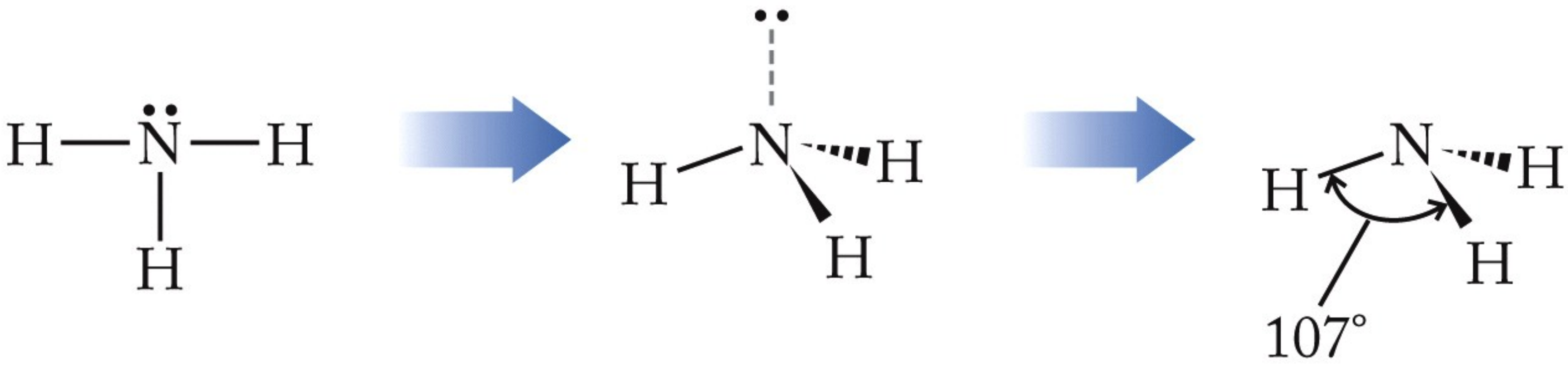
(b) Molecular geometry = bent

Central Atoms with Lone Pairs



- Bond angles less than predicted.
- Electron group repulsion!
  - Lone pair – Lone pair = Greatest repulsion
  - Lone pair – Bonding pair
  - Bonding pair – Bonding pair = Least repulsion
    - Mulitple bonds > single bonds

Molecular Geometry: SN = 4



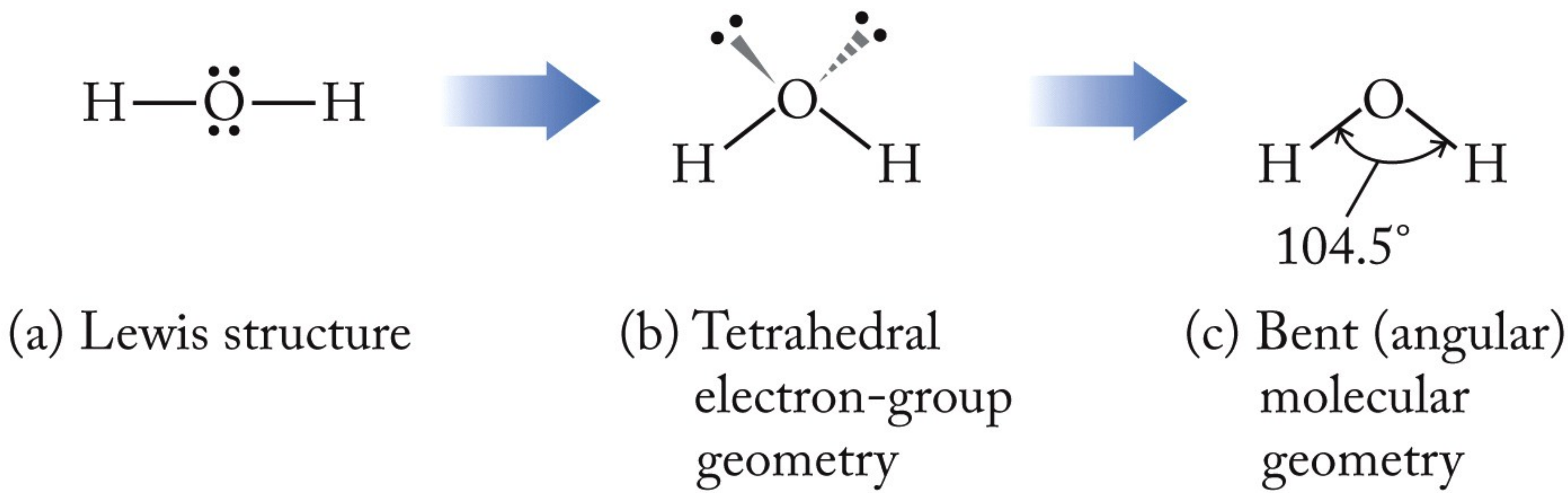
(a) Lewis structure

(b) Tetrahedral electron-group geometry

(c) Trigonal pyramidal molecular geometry

Note: Bond angles decrease as # of lone pairs increases.

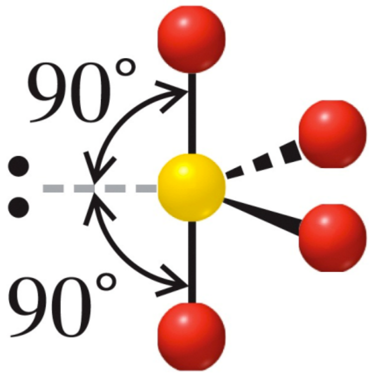
Molecular Geometry: SN = 4



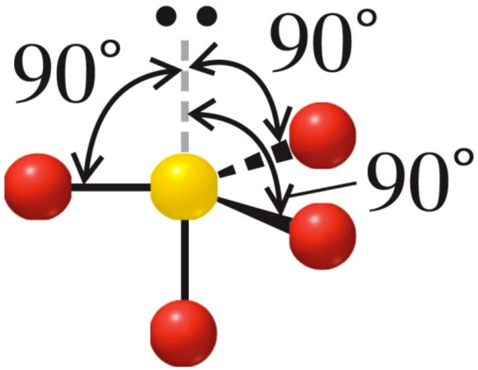
Two lone pairs = greater repulsion, decreased bond angle.

Molecular Geometry: SN = 5

With SN = 5, we see there are two distinctly different positions.

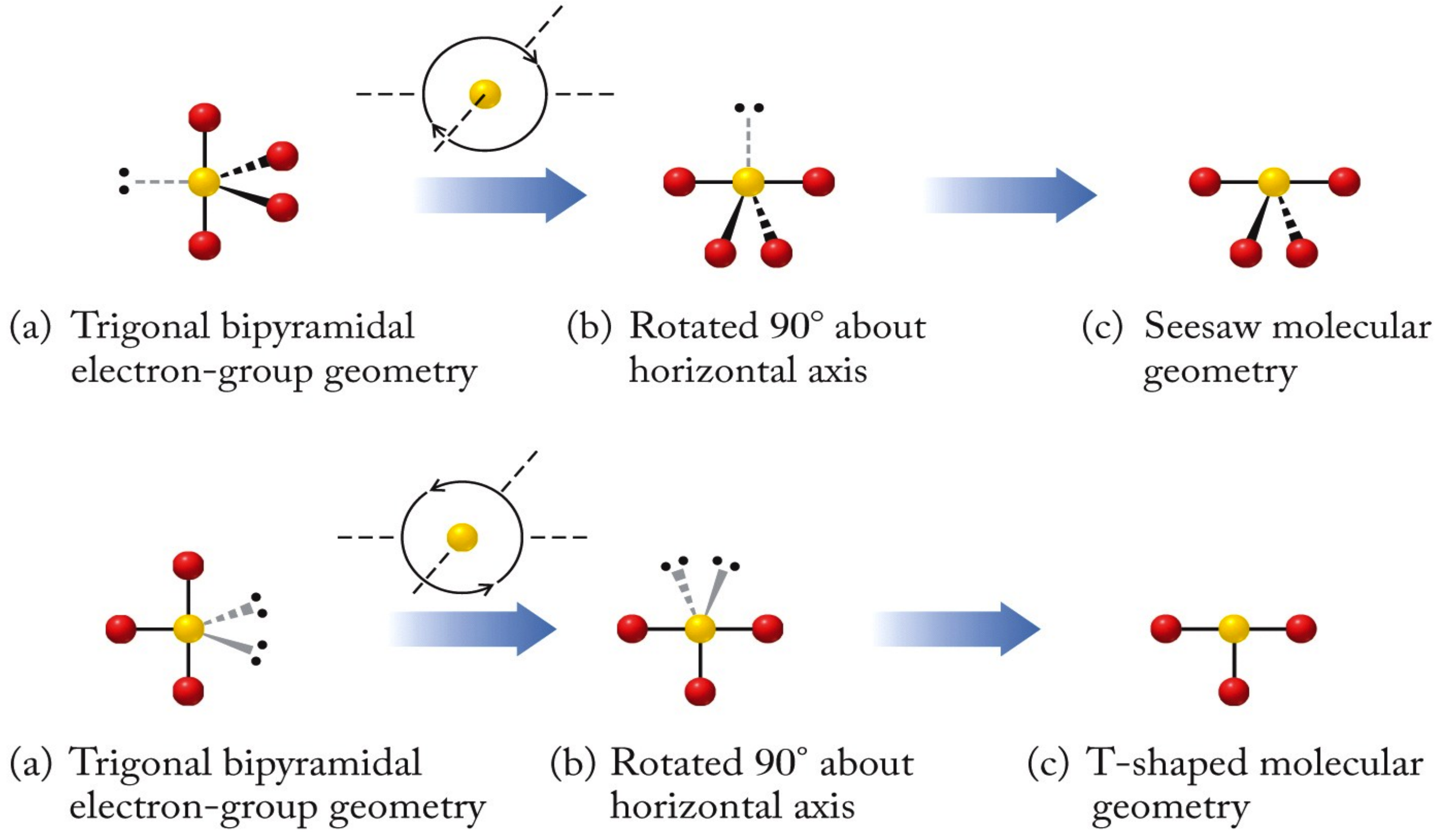


Equatorial lone pair



Axial lone pair

Molecular Geometry: SN = 5



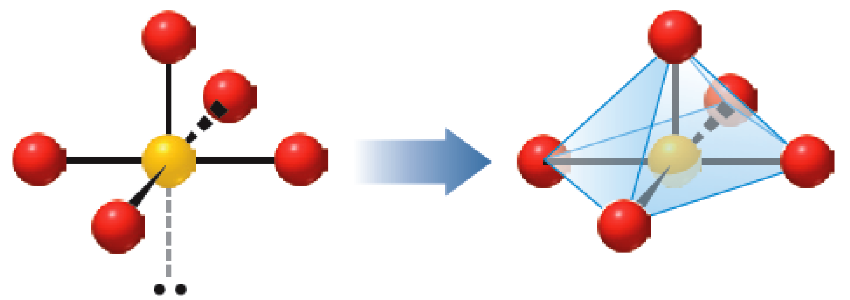
Note: Lone pairs occupy equatorial positions.

Molecular Geometry: SN = 6

Note:

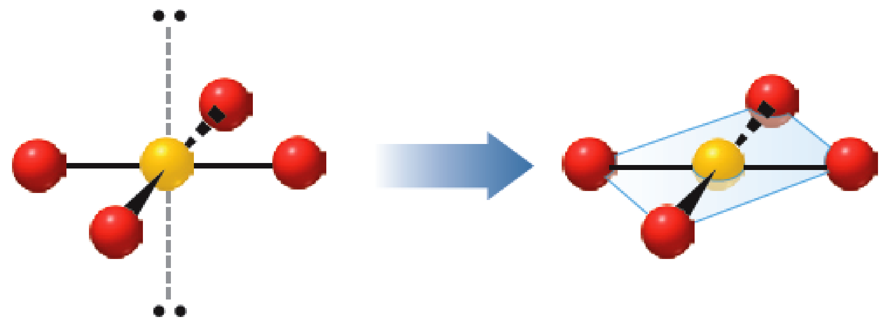
– bond angles = 90°

(geometries with more than 2 lone pairs possible)



(a) Octahedral electron-group geometry

(b) Square pyramidal molecular geometry



(a) Octahedral electron-group geometry

(b) Square planar molecular geometry

Practice: Molecular Geometry

What are the molecular geometries of the ions SCN^- and NO_2^-?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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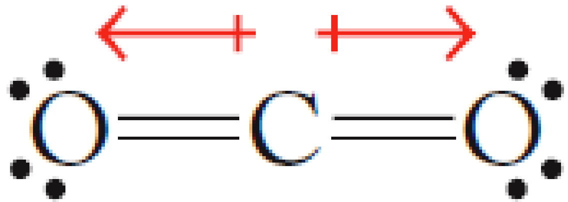
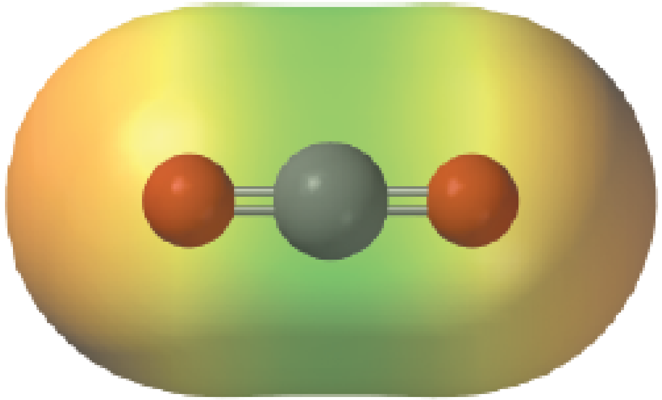
Polar Bonds and Polar Molecules

- Requirements for Polar Molecule:
  - 1. Polar bonds (i.e., covalent bonds between atoms with ΔEN).
  - 2. Nonuniform distribution of polar bonds.





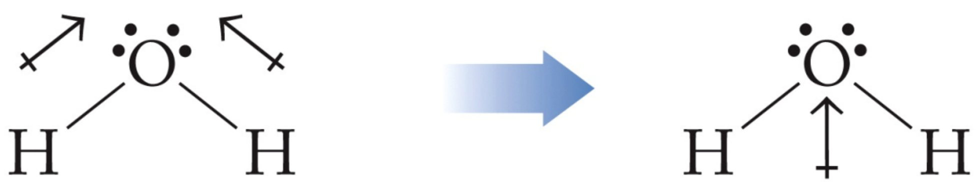
Polar Bonds and Polar Molecules

- Exactly symmetric molecules are not polar

- Molecules with unshared electron pairs will almost always be polar

Polar Molecules

- Bond Dipole:
  - Separation of electrical charge created when atoms with different EN form a covalent bond



- Polar Molecule:
  - Sum of bond dipole vectors > zero

Measuring Polarity

- Dipole Moment (μ): A quantitative expression of the polarity of a molecule.

  Units = *debyes* (D); 1 D = 3.34×10^{-30} coul·m)

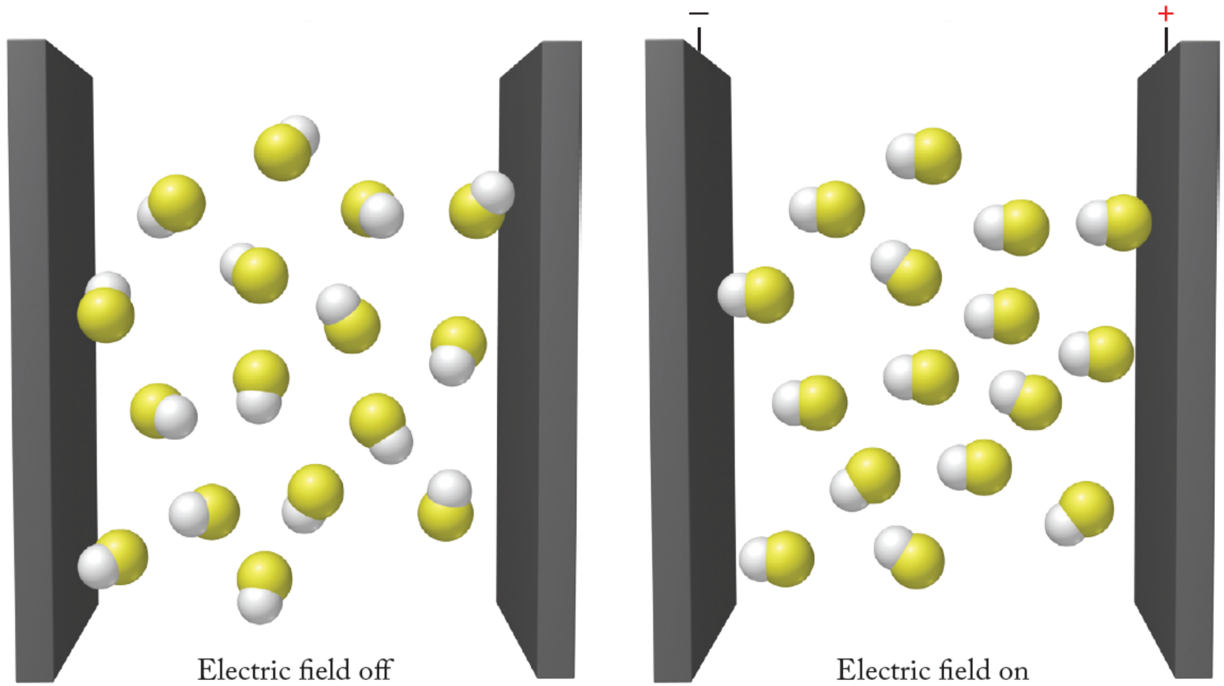
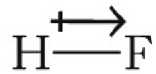
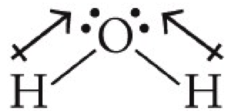
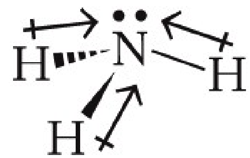
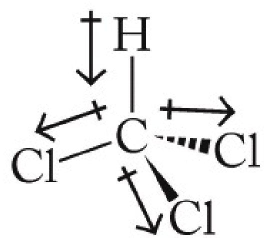
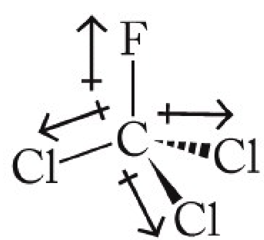


TABLE 5.2 Permanent Dipole Moments of Several Polar Molecules

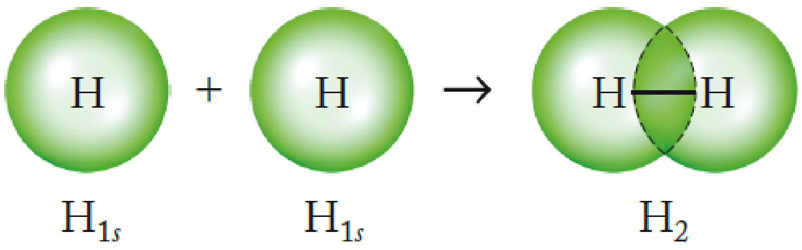
Formula	Structure with Bond Dipole(s)	Direction of Overall Dipole	Dipole Moment (debyes)
HF		$\mapsto$	1.91
H_2O		$\uparrow$	1.85
NH_3		$\uparrow$	1.47
$CHCl_3$		$\downarrow$	1.04
CCl_3F		$\uparrow$	0.45

Chapter Outline

Atomic Orbitals and Bonds

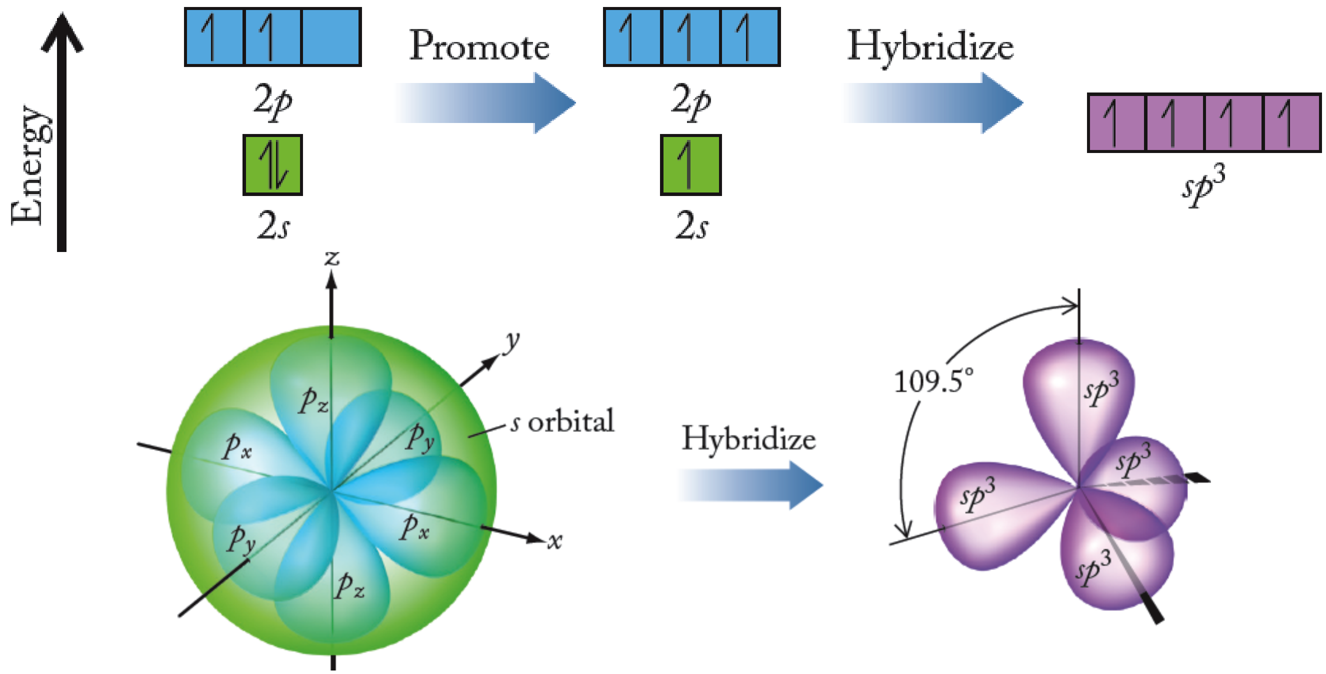
- Valence Bond Theory (Linus Pauling)
  - Quantum mechanics-based model
  - Covalent bond = overlap of orbitals
- Sigma (σ) Bond:
  - Covalent bond having highest electron density between the two atoms along the bond axis.

Overlap of 1*s* orbitals



Hybridization: *sp*^{3} Orbitals

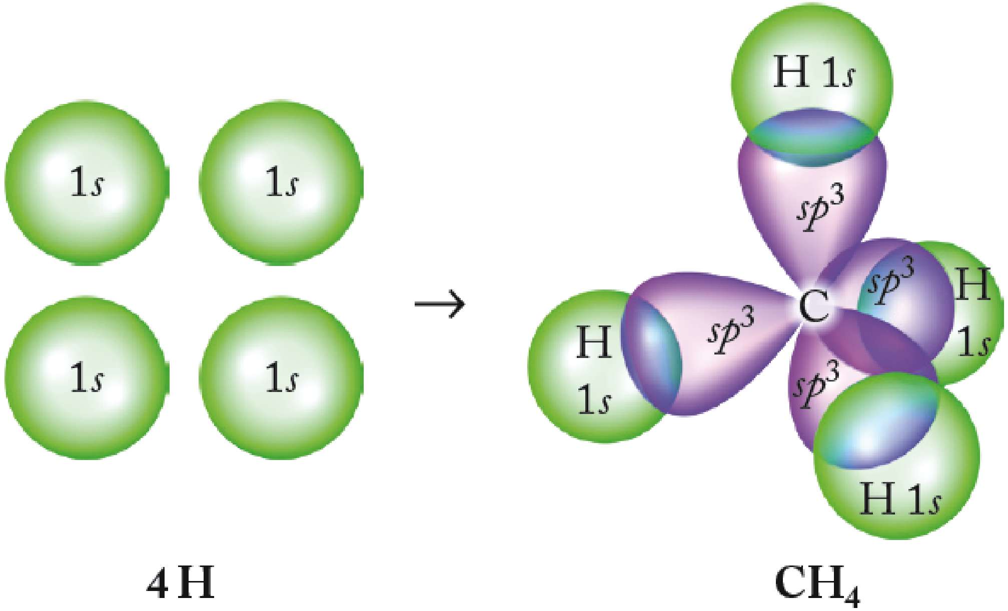
- Hybridization: Mixing of atomic orbitals to generate new sets of equivalent orbitals that form covalent bonds with other atoms



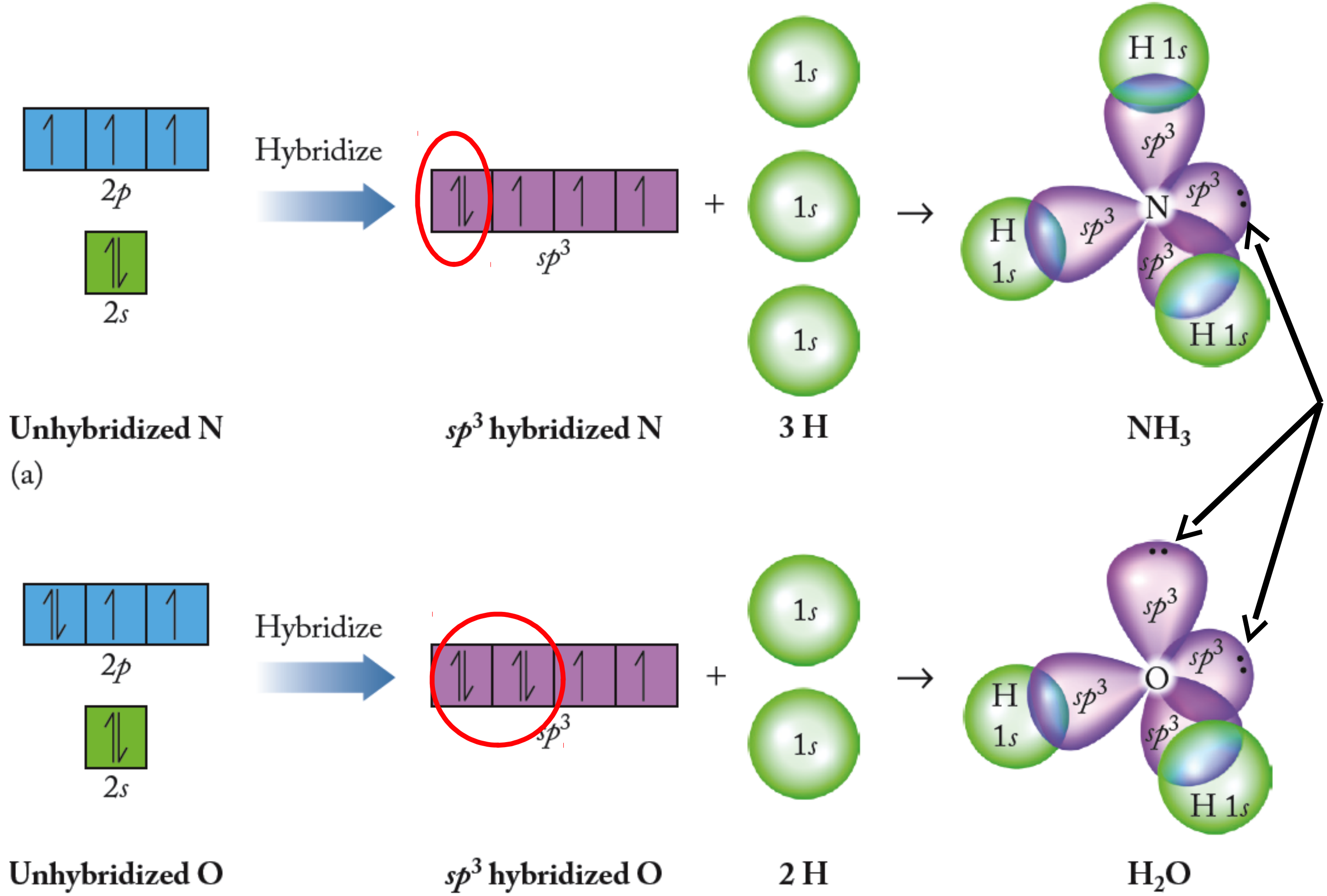
Tetrahedral Sigma Bonds

- Tetrahedral orientation of sp^3 hybridized orbitals = tetrahedral molecular geometry

Overlap of 1*s* with sp^3 orbitals →

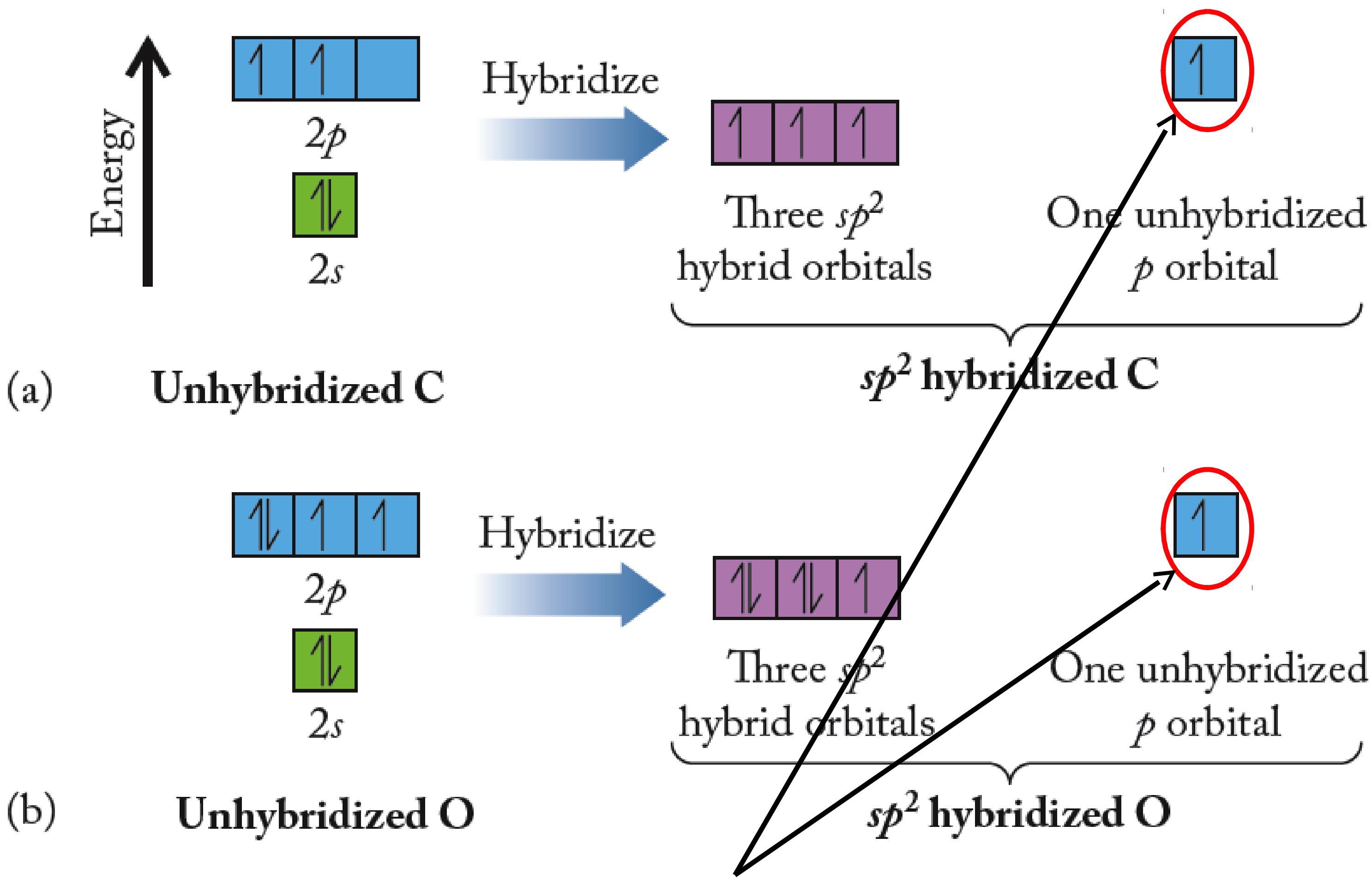


Other sp^3 Examples



Note: lone pairs (non-bonding)

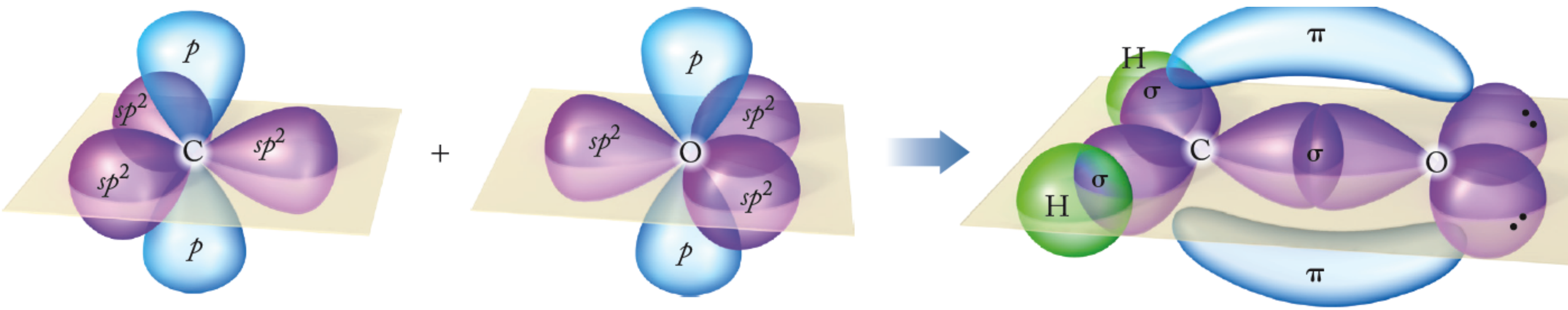
Trigonal Planar: *sp*² Hybridization



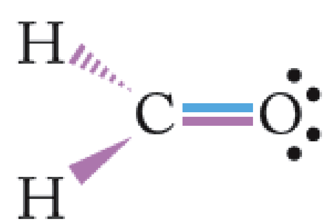
Unhybridized *p* orbitals – form double bonds.

sp^2 Hybridization

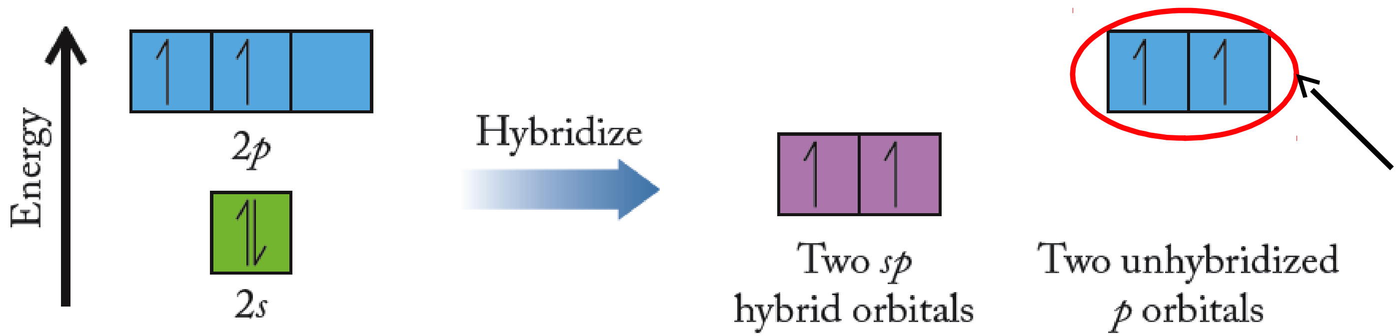
- Pi (π) Bond:
  - Electron density is concentrated above / below the bonding axis.



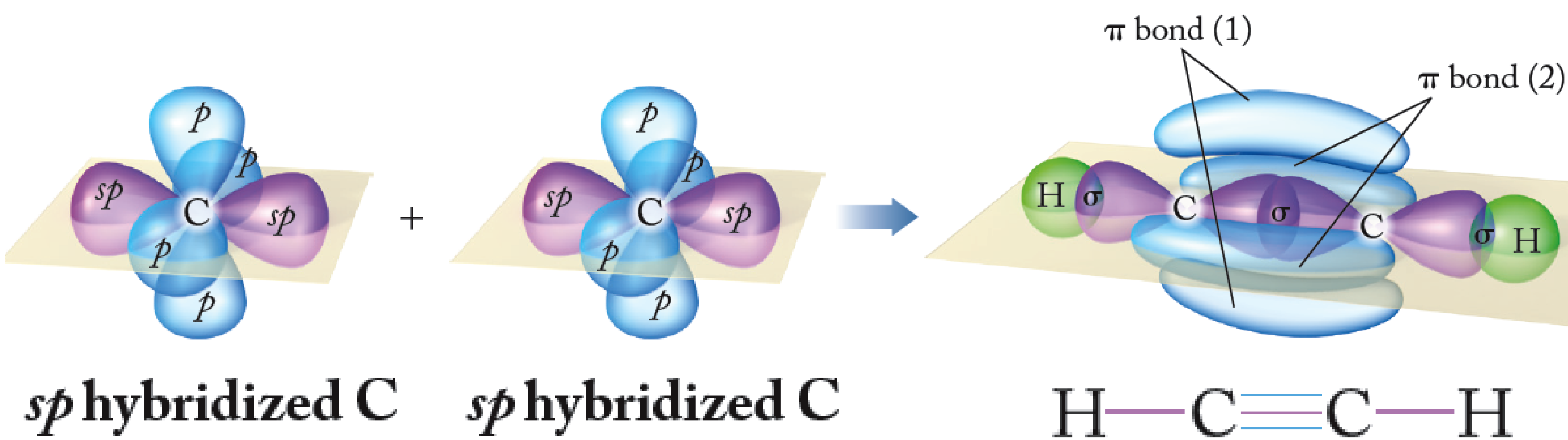
sp^2 hybridized C sp^2 hybridized O



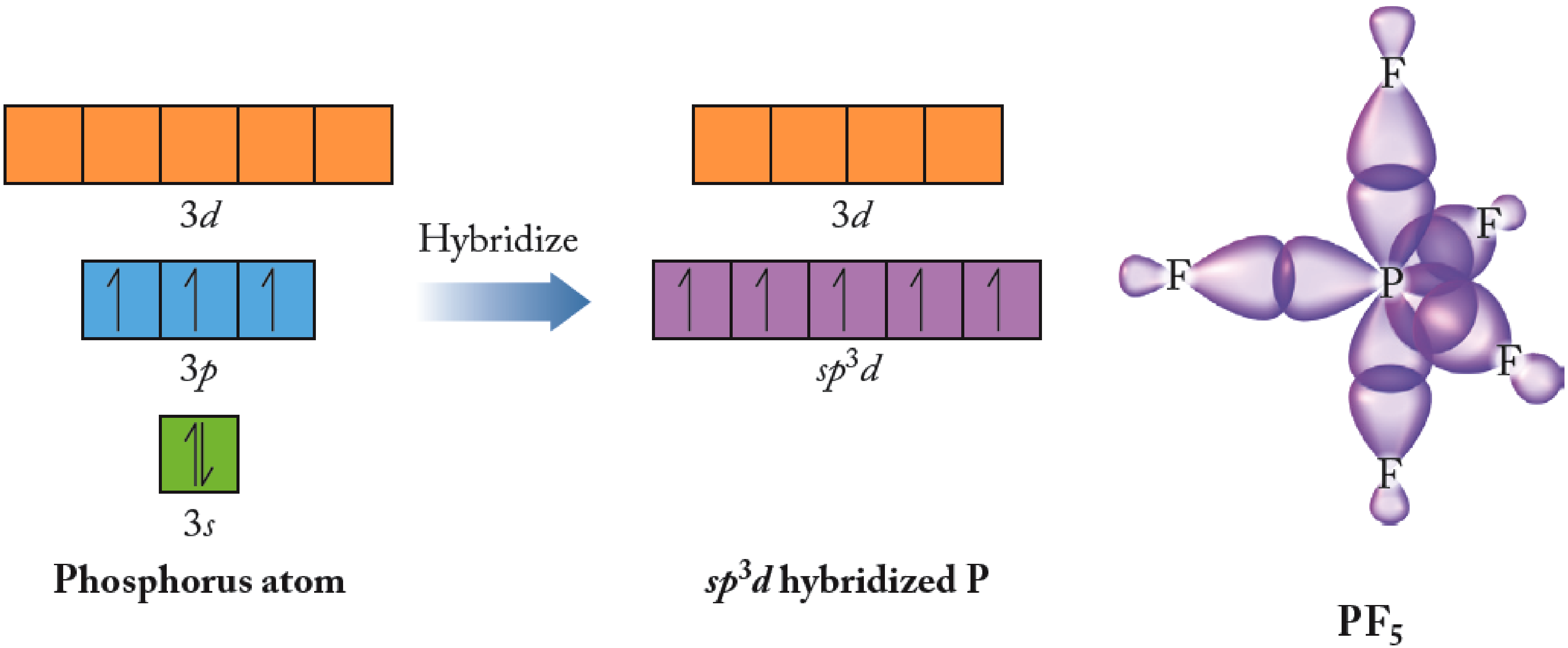
Linear: *sp* Hybridization



form triple bond (one σ and two π bonds)



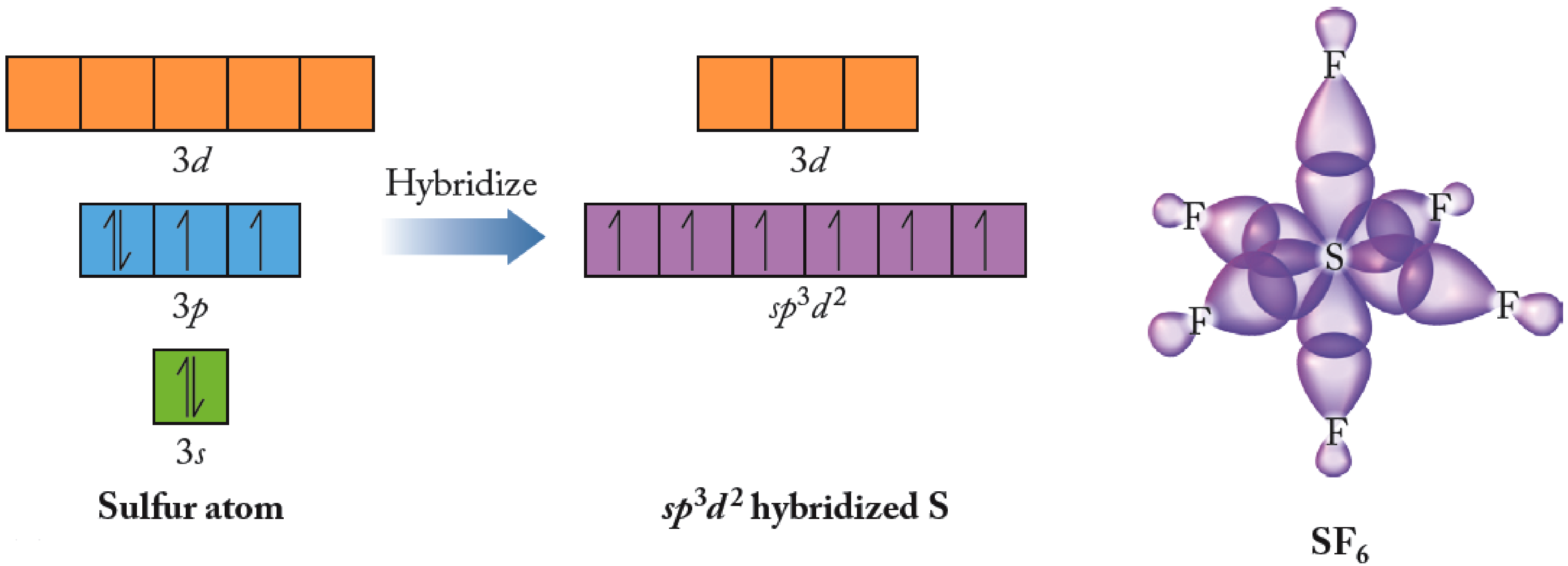
Trigonal Bipyramidal: *sp*³*d* Hybridization



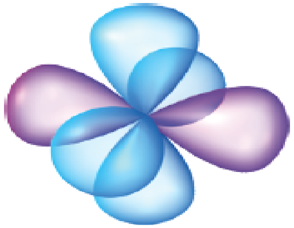
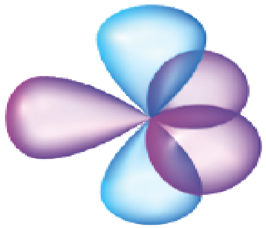
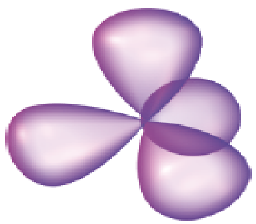
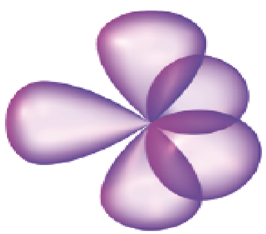
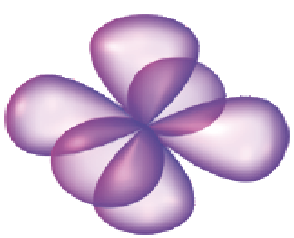
Formed by mixing one *s*, one *d*, and three *p* orbitals.

Example: PF_5 – five sigma bonds.

Octahedral: sp^3d^2 Hybridization



Formed by mixing one *s*, two *d*, and three *p* orbitals. Example: SF_6 – six sigma bonds.

Hybridization	Orientation of Hybrid Orbitals	Number of σ bonds	Molecular Geometrics	Angles Between Hybrid Orbitals
sp		2	Linear	180°
sp^2		3 2	Trigonal planar Bent	120°
sp^3		4 3 2	Tetrahedral Trigonal pyramidal Bent	109.5°
sp^3d		5 4 3 2	Trigonal bipyramidal Seesaw T-shaped Linear	90°, 120°, 180°
sp^3d^2		6 5 4	Octahedral Square pyramidal Square planar	90°, 180°

Practice: Hybrid Orbitals

What are the hybridizations of the central atoms of the ions: SCN^- and NO_2^-?

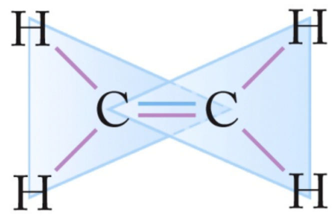
- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

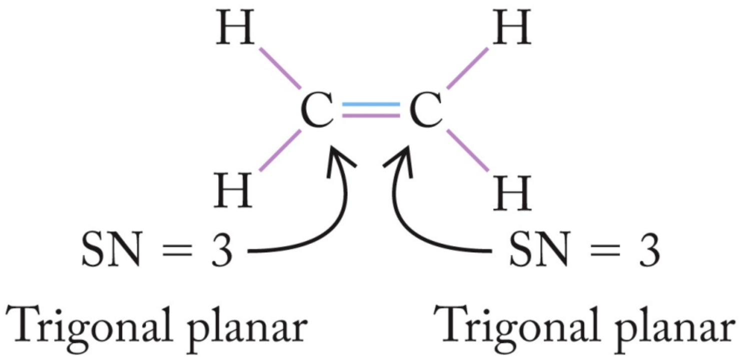
Chapter Outline

Molecular Recognition

- Molecular Recognition:
  - Process by which molecules interact with other molecules in living tissues to produce a biological effect
  - Example: Ethylene (ripening agent)

All atoms in same plane.

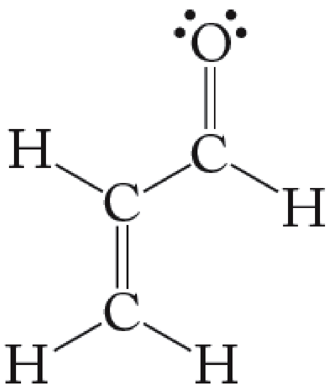




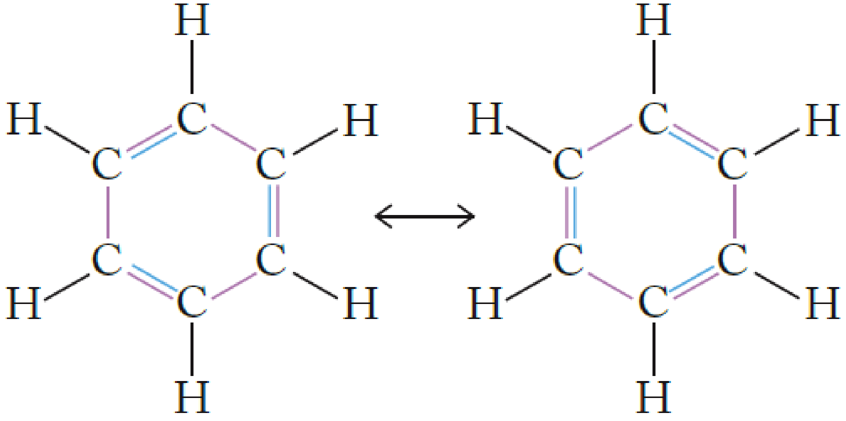
Delocalization of Electrons

- **Delocalization:** Spreading of electrons in alternating single and double bonds over three or more atoms in a molecule

a)

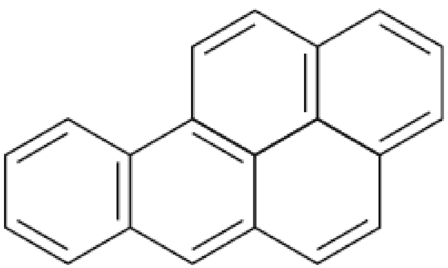


b)

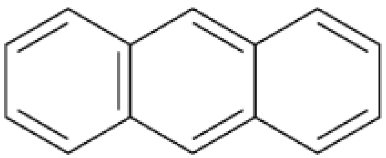


Aromatic Compounds

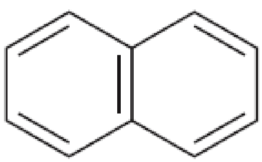
- Aromatic Compound:
  - A cyclic, planar compound with delocalized π electrons above and below the plane of the molecule
  - Example – Polycyclic Aromatic Hydrocarbons (PAH)
    - Planar shape may allow intercalation in DNA



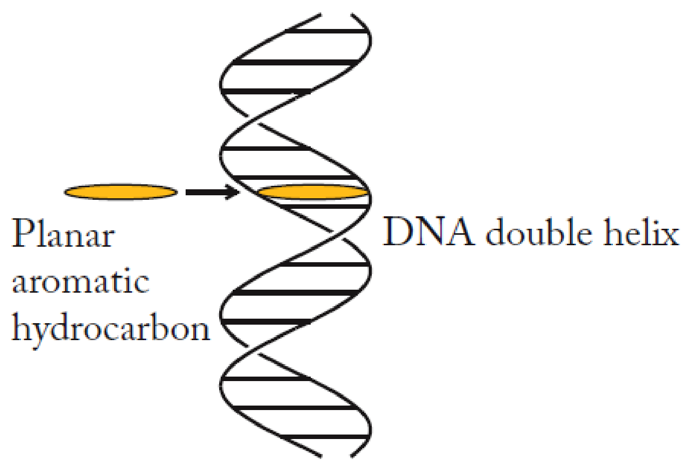
Benzo[*a*]pyrene



Anthracene



Naphthalene



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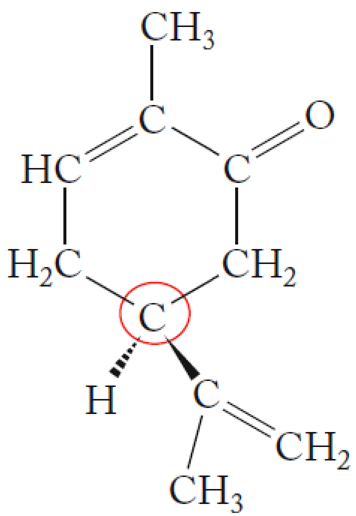
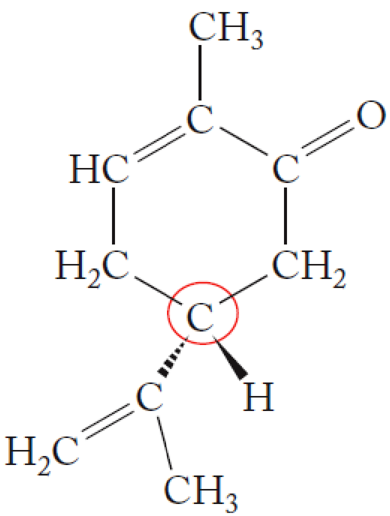
- 5.4 Valence Bond Theory and Hybrid Orbitals
- 5.5 Molecules with Multiple Central Atoms
- 5.6 Chirality and Molecular Recognition
- 5.7 Molecular Orbital Theory

Isomerism

- Isomers: Compounds with same molecular formula but with atoms arranged differently in 3-dimensional space



(a) (+)-Carvone
(caraway)

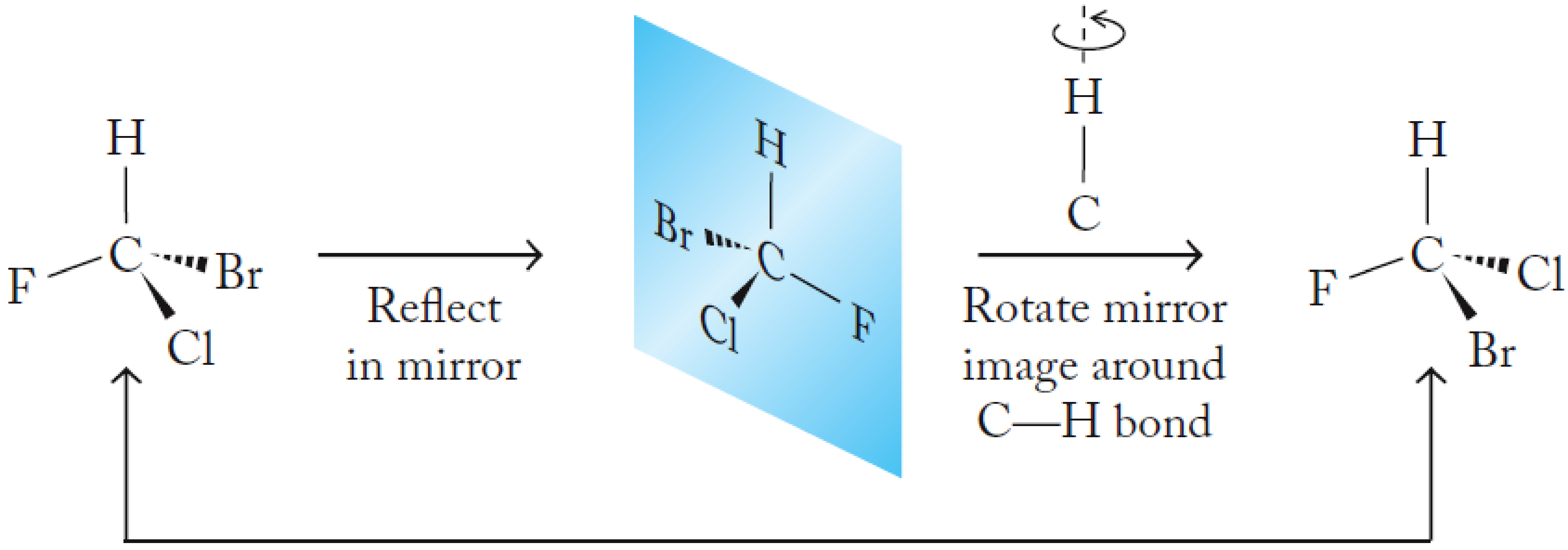


(b) (−)-Carvone
(spearmint)

Optical isomers

Optical Isomers = Chirality

- Chirality: Property of a molecule that is not superimposable on its mirror image



Chapter Outline

- 5.1 Molecular Shape
- 5.2 Valence-Shell Electron-Pair Repulsion Theory (VSEPR)
- 5.3 Polar Bonds and Polar Molecules
- 5.4 Valence Bond Theory and Hybrid Orbitals
- 5.5 Molecules with Multiple Central Atoms
- 5.6 Chirality and Molecular Recognition
- 5.7 Molecular Orbital Theory

Molecular Orbital (MO) Theory

- Based on mixing of atomic orbitals of similar shapes and energies to form molecular orbitals (MOs) that belong to the molecule as a whole.
  - The number of MOs formed is equal to the number of atomic orbitals combined
  - MOs represent discrete energy states; orbitals spread out over entire molecule

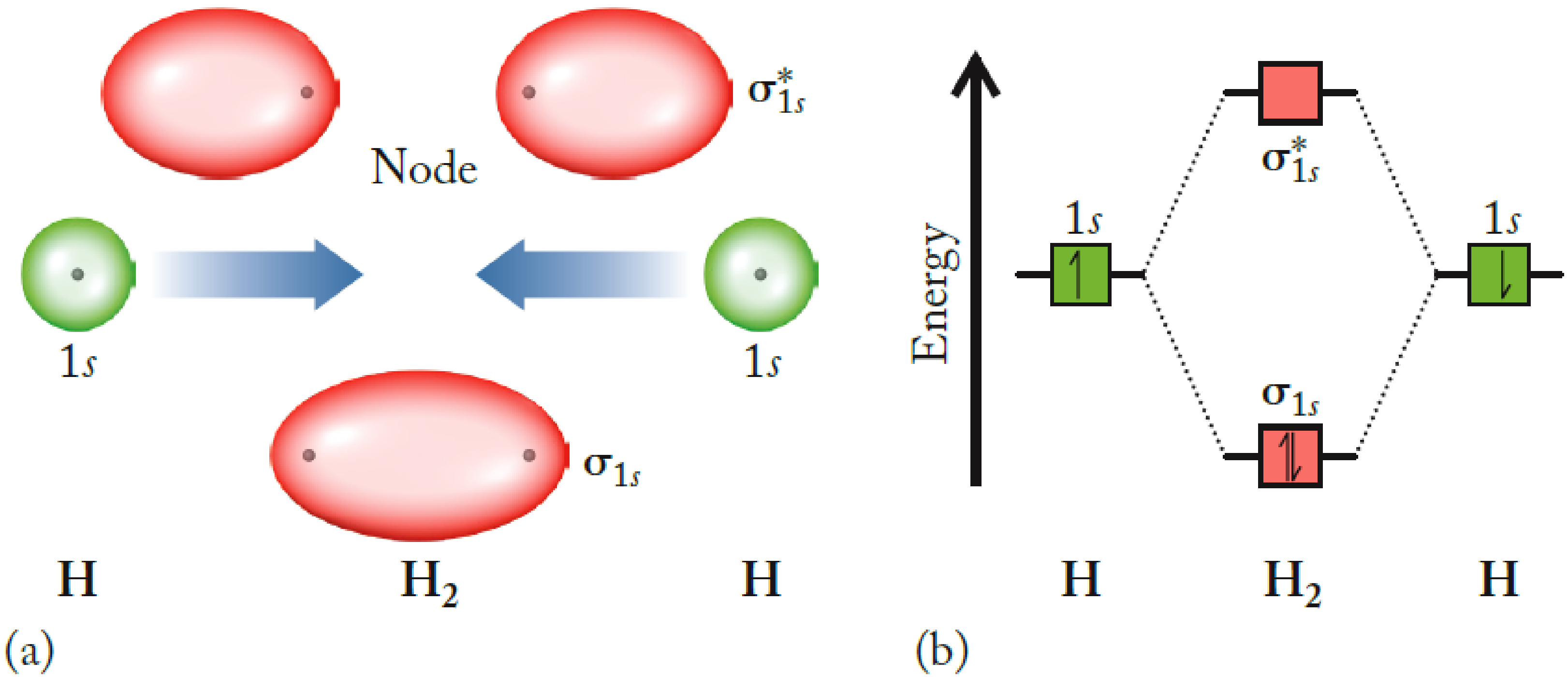
Types of Molecular Orbitals

- Bonding Orbitals:
  - Region of increased electron density between nuclear centers that hold atoms together
  - Are lower in energy (more stable) than atomic orbitals from which they are formed
- Antibonding Orbitals:
  - Regions of electron density that destabilize the molecule because they do not increase electron density between nuclear centers
  - Less stable than atomic orbitals from which they are formed

Molecular Orbital Diagram

- MO Diagram:
  - Energy level diagram for showing the relative energies and electron occupancy of the MOs for a molecule
- Sigma (σ) Bond:
  - Covalent bond with the highest electron density along the bond axis
- Pi (π) Bond:
  - Formed by mixing of atomic orbitals not oriented along the bonding axis in a molecule

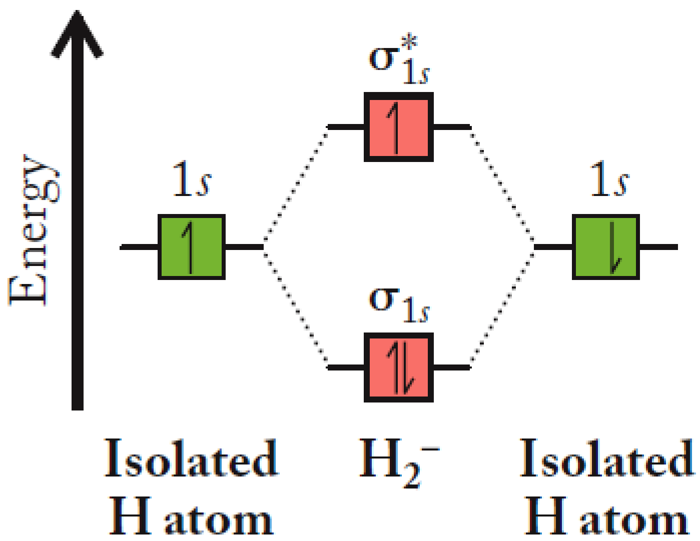
Molecular Orbital Diagram: H_2

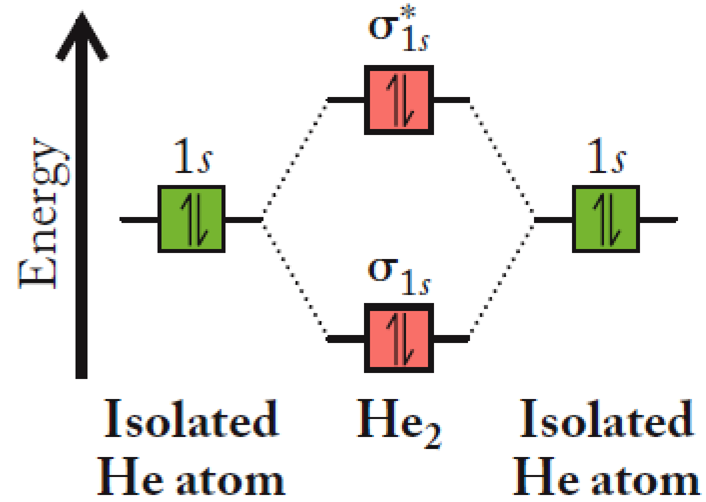


- The two 1*s* orbitals mix to yield two sigma MOs (1 bonding / 1 antibonding).

Bond Order and Stability

Bond Order = 1/2 (# bonding e$^-$ – # antibonding e$^-$)





Bond order in H_2^- = ½ (Stable)

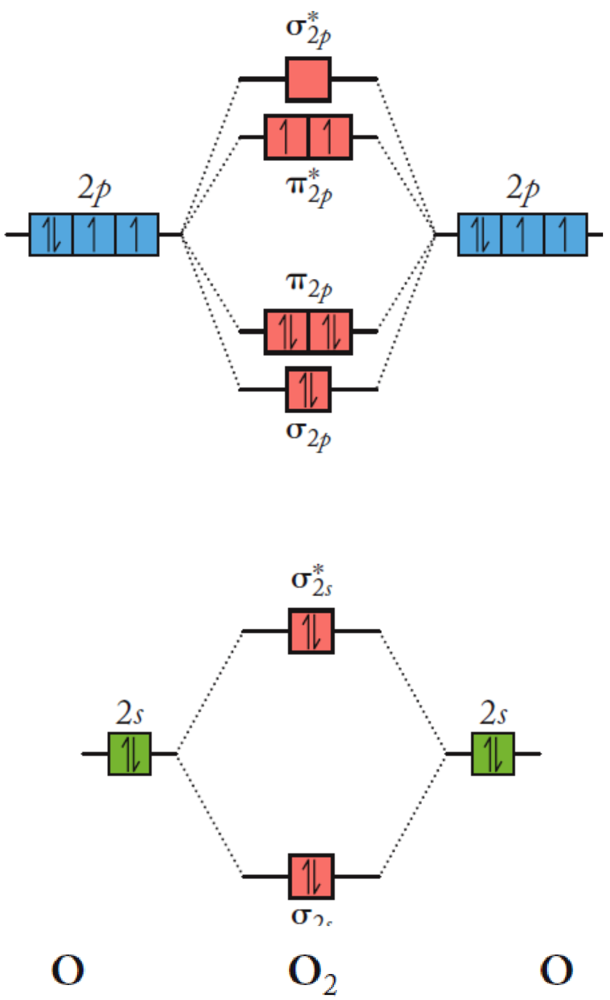
Bond order in He_2 = 0 (Not Stable)

MO Guidelines

1. The total # of MOs = the # of AOs orbitals mixed.
2. Orbitals with similar energy/shape mix more effectively than do those of different energy/shape.
3. Orbitals of different *n* (different sizes/energies) result in less effective mixing.
4. A MO can accommodate two electrons.
5. Electrons fill MO diagrams according to Hund's rule.

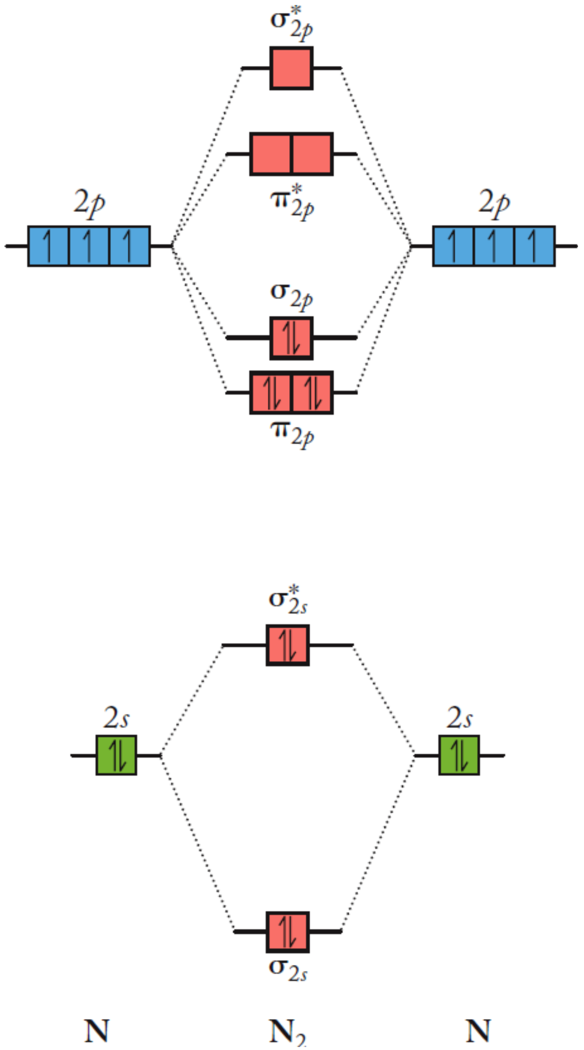
MO Scheme for O_2

- Electron configuration for O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$
- Bond order = ½ (8 – 4) = 2
  - O_2 has two bonds
  - O_2 has two unpaired electrons in π_{2p}^*



MO Scheme for N_2

- Electron configuration for N_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4$
- Bond order = ½ (8 – 2) = 3
  - N_2 has three bonds.
  - N_2 has no unpaired electrons.

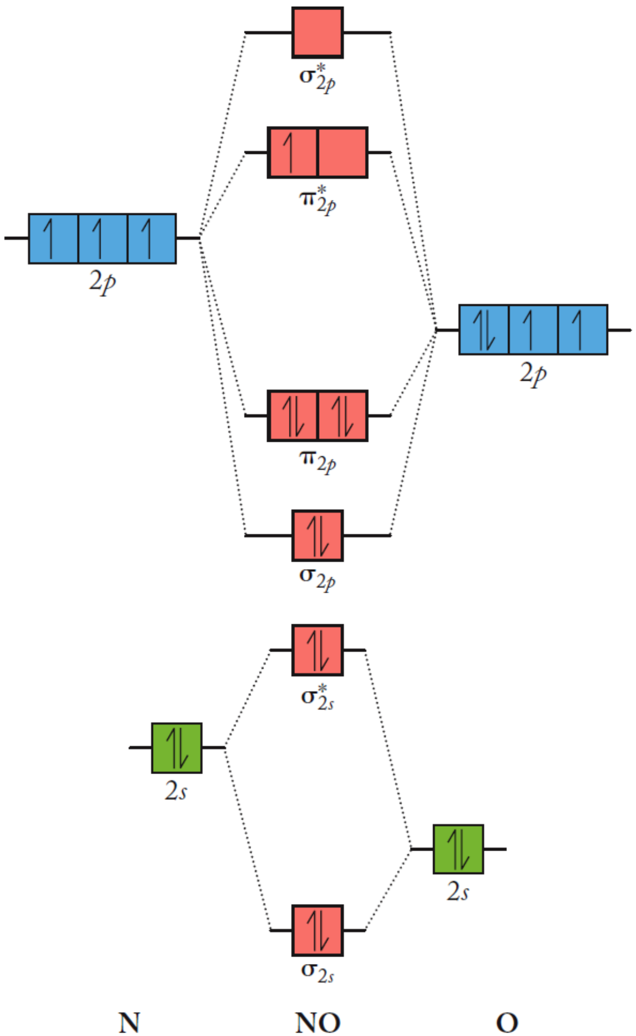


Paramagnetism vs. Diamagnetism

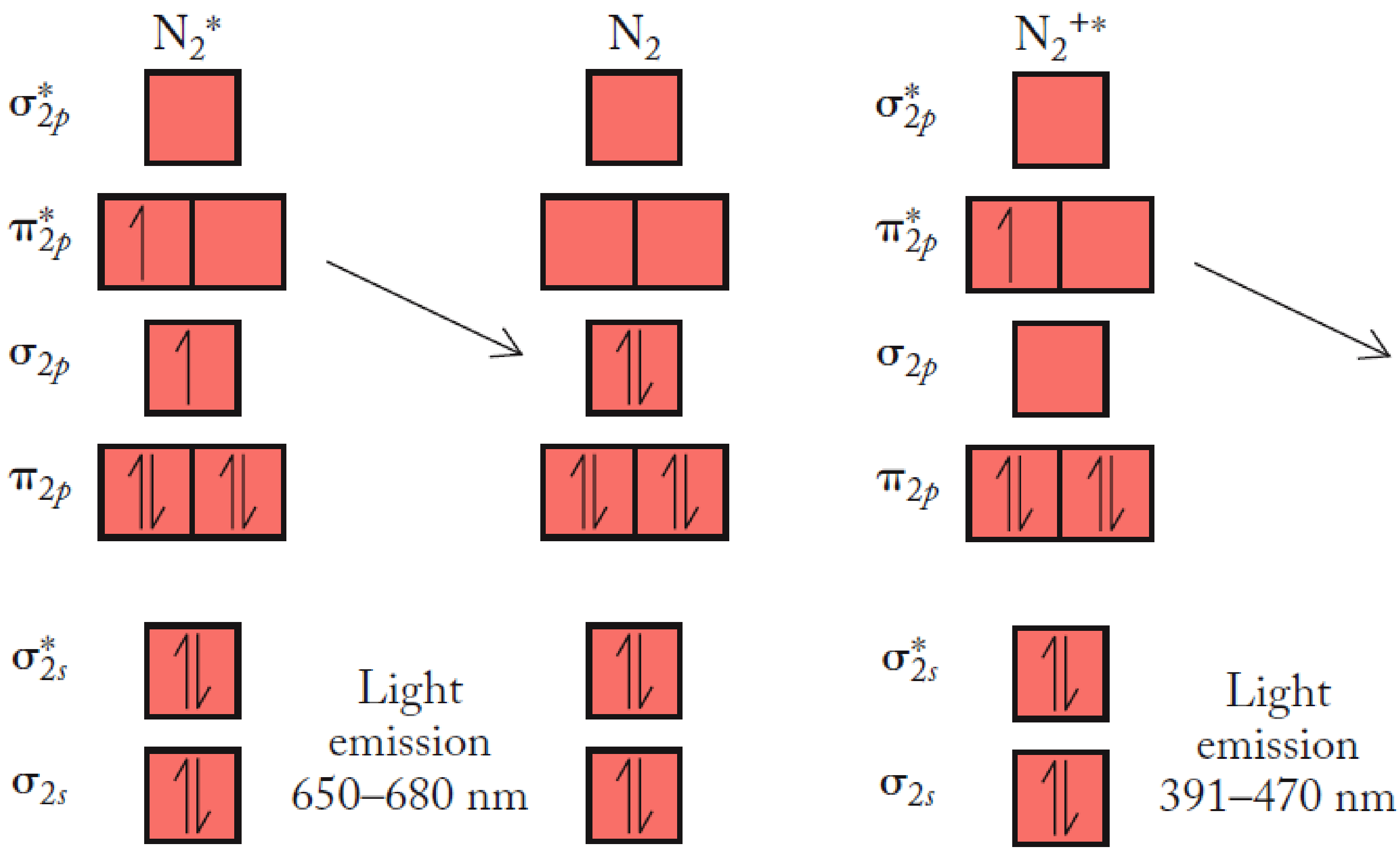
- Paramagnetism:
  - Atoms or molecules having unpaired electrons are attracted to magnetic fields
  - Example: O_2
- Diamagnetism:
  - Atoms or molecules having all paired electrons are repelled by magnetic fields
  - Example: N_2

MO for NO

- Z_{eff} alters MO diagram; atomic orbitals for O are lower in energy.
- Odd electron in π^*_{2p} , closer in energy to the 2*p* atomic orbitals of N atom.
- Bond order = ½ (8 – 3) = 2.5



MO for N_2, N_2^+: Emission Spectra



Crimson red

Blue-violet

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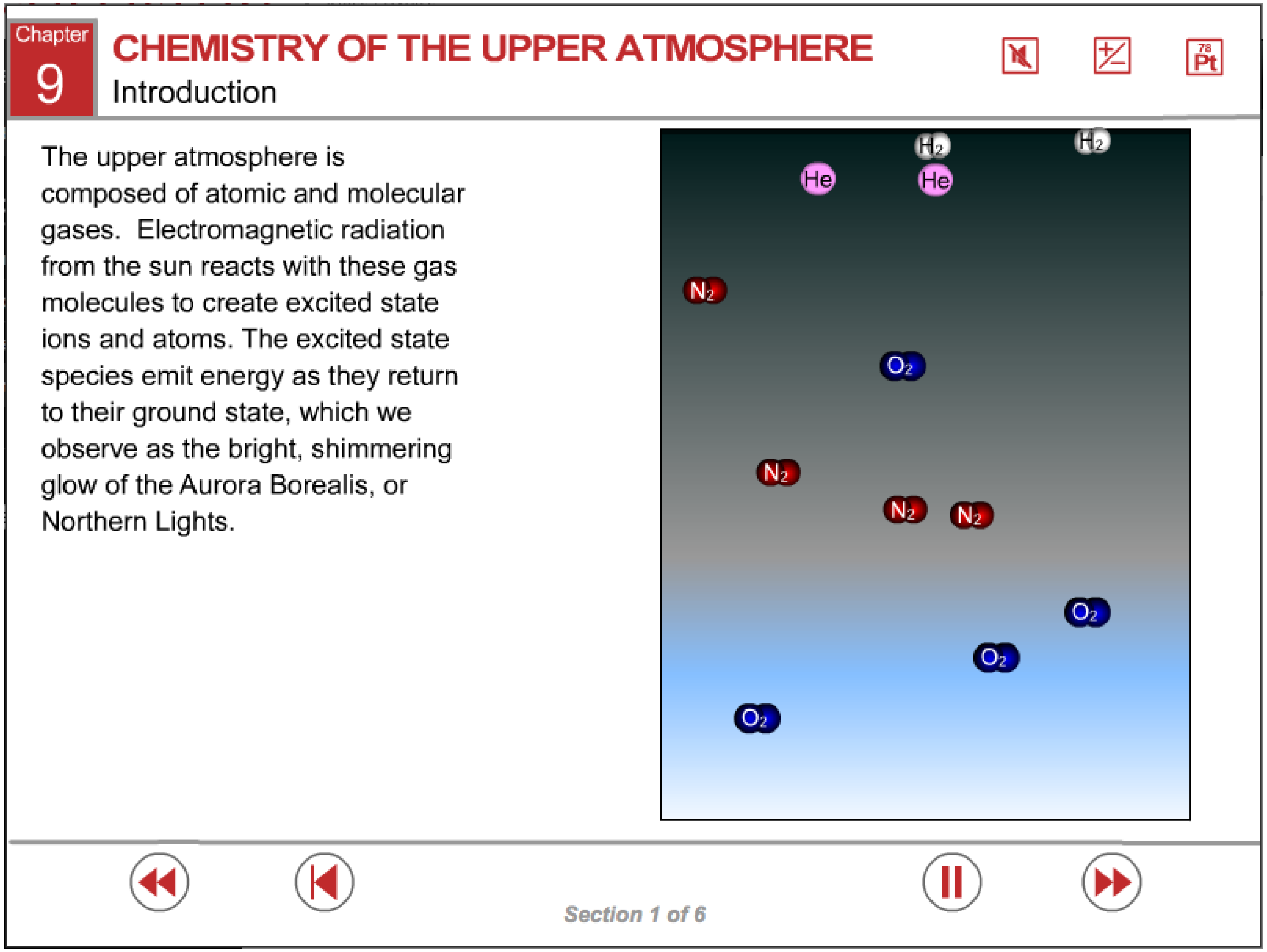

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This concludes the Lecture PowerPoint presentation for Chapter 5

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