

Chapter Ten

Bonding Theory and Molecular Structure

VSEPR notation: AX_3E

Angular

2,4,6-Trinitrotoluene (TNT, an explosive)
2,4-Dinitroaniline (used to make dyes)
2,4,5-Trichlorophenol (a fungicide)

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Molecular Geometry

- Molecular geometry** is simply the **shape** of a molecule.
- Molecular geometry is described by the geometric figure formed when the atomic nuclei are joined by (imaginary) straight lines.
- Molecular geometry is found **using** the Lewis structure, but the Lewis structure itself does **NOT** necessarily represent the molecule's shape.

A carbon dioxide molecule is **linear**.

A water molecule is **angular or bent**.

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VSEPR

- Valence-Shell Electron-Pair Repulsion (VSEPR)** is a simple method for determining geometry.
- Basis: pairs of valence electrons in bonded atoms repel one another.
- These mutual repulsions push electron pairs as far from one another as possible.

When the electron pairs (bonds) are as far apart as they can get, what will be the B-A-B angle?

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Electron-Group Geometries

- An **electron group** is a collection of valence electrons, localized in a region around a central atom.
- One electron group:
 - an unshared pair of valence electrons or
 - a bond (single, double, or triple)
- The repulsions among electron groups lead to an orientation of the groups that is called the **electron-group geometry**.
- These geometries are based on the **number** of electron groups:

Electron groups	Electron-group geometry
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

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A Balloon Analogy

- Electron groups repel one another in the same way that balloons push one another apart.
- When four balloons, tied at the middle, push themselves apart as much as possible, they make a **tetrahedral** shape.

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VSEPR Notation

- In the VSEPR notation used to describe molecular geometries, the central atom in a structure is denoted as **A**, terminal atoms as **X**, and the lone pairs of electrons as **E**.
- The H_2O molecule would therefore carry the designation AX_2E_2 .

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VSEPR Notation

- For structures with no lone pairs on the central atom (AX_n), the molecular geometry is the same as the electron-group geometry.
- When there are lone pairs, the molecular geometry is *derived from* the electron-group geometry.
- In either case, the electron-group geometry is the *tool* we use to obtain the molecular geometry.

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Table 10.1 (Part 1) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
2	Linear	0	AX_2	$X-A-X$ Linear	180°	$BeCl_2$	
3	Trigonal planar	0	AX_3		120°	BF_3	
3	Trigonal planar	1	AX_2E		120°	SO_2	

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Table 10.1 (Part 2) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	0	AX_4		109.5°	CH_4	
4	Tetrahedral	1	AX_3E		109.5°	NH_3	

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Table 10.1 (Part 3) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	2	AX_2E_2		109.5°	H_2O	
5	Trigonal bipyramidal	0	AX_5		$90^\circ, 120^\circ, 180^\circ$	PCl_5	

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Table 10.1 (Part 4) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	1	AX_4E		$90^\circ, 120^\circ, 180^\circ$	SF_4	
5	Trigonal bipyramidal	2	AX_3E_2		$90^\circ, 180^\circ$	ClF_3	

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Table 10.1 (Part 5) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	3	AX_2E_3		180°	XeF_2	
6	Octahedral	0	AX_6		$90^\circ, 180^\circ$	SF_6	





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Table 10.1 (Part 6) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
6	Octahedral	1	AX_5E_1	 Square pyramidal	90°	BrF_5	
6	Octahedral	2	AX_4E_2	 Square planar	90°	XeF_4	

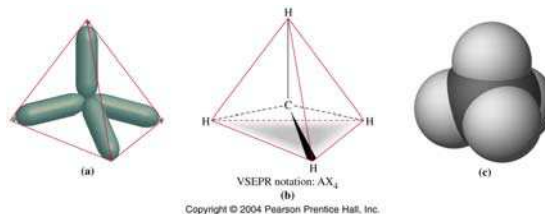
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Example 10.1

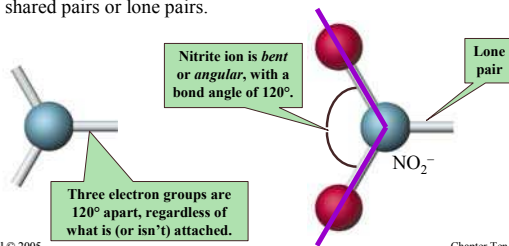
Use the VSEPR method to predict the shape of the nitrate ion.

Structures with No Lone Pairs

- AX_2 : both the electron-group geometry and the molecular geometry for two electron groups is *linear*.
- AX_3 : these molecules have a *trigonal planar* geometry.
- AX_4 : these molecules have a *tetrahedral* geometry.
- AX_5 : these molecules have a *trigonal bipyramidal* geometry.
- AX_6 : these molecules have an *octahedral* geometry.
- The AX_5 and AX_6 require an expanded valence shell and, therefore, the central atom is a third-period or higher element.

Geometry of Methane**Structures with Lone Pairs**

- Electron groups on the central atom repel one another, whether they are shared pairs or lone pairs.
- However, the geometry of the *molecule* is found using the bonded atoms.

**Some Structures with Lone Pairs**

- AX_2E : these molecules have an electron-group *trigonal planar* geometry, but a *bent* molecular geometry.
- AX_2E_2 : these molecules have an electron-group *tetrahedral* geometry, but a *bent* molecular geometry.
- AX_3E : these molecules have an electron-group *tetrahedral* geometry, but a *trigonal pyramidal* molecular geometry.
- AX_4E : these molecules have an electron-group *trigonal bipyramidal* geometry, but a *seesaw* molecular geometry.
- AX_4E_2 : these molecules have an electron-group *octahedral* geometry, but a *square planar* molecular geometry.

19

Molecular Geometry of Water

Is the water molecule tetrahedral?

No; its electron groups are tetrahedrally arranged. The molecule is _____.

VSEPR notation: AX_2E_2

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20

Example 10.2

Use the VSEPR method to predict the molecular geometry of XeF_2 .

Example 10.3

Use the VSEPR method to describe, as best you can, the molecular geometry of the nitric acid molecule, HNO_3 .

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21

Polar Molecules and Dipole Moments

- A **polar bond** (Chapter 9) has separate centers of positive and negative charge.
- A **molecule** with separate centers of positive and negative charge is a **polar molecule**.
- The **dipole moment** (μ) of a molecule is the product of the magnitude of the charge (δ) and the distance (d) that separates the centers of positive and negative charge.

$$\mu = \delta d$$
- A unit of dipole moment is the **debye (D)**.
- One debye (D) is equal to 3.34×10^{-30} C m.

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Polar Molecules in an Electric Field

An electric field causes polar molecules to align with the field.

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23

Example 10.4

Explain whether you expect the following molecules to be polar or nonpolar.

(a) $CHCl_3$ (b) CCl_4

Example 10.5 A Conceptual Example

Of the two compounds NOF and NO_2F , one has $\mu = 1.81$ D and the other has $\mu = 0.47$ D. Which dipole moment do you predict for each compound? Explain.

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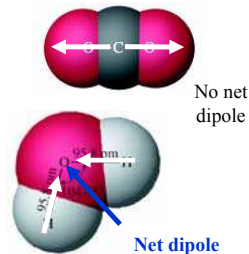
Bond Dipoles and Molecular Dipoles

- A polar covalent bond has a **bond dipole**; a separation of positive and negative charge centers in an individual bond.
- Bond dipoles have both a **magnitude** and a **direction** (they are **vector** quantities).
- Ordinarily, a polar molecule must have polar bonds, **BUT** ... polar bonds are not sufficient.
- A molecule may have polar bonds and be a **nonpolar** molecule – **IF** the bond dipoles cancel.

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Bond Dipoles and Molecular Dipoles

- CO₂ has polar bonds, but is a linear molecule; the bond dipoles cancel and it has no net dipole moment ($\mu = 0$ D).
- The water molecule has polar bonds also, but is an **angular** molecule.
- The bond dipoles do **not** cancel ($\mu = 1.84$ D), so water is a **polar** molecule.



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Molecular Shapes and Dipole Moments

To predict molecular polarity:

1. Use electronegativity values to predict bond dipoles.
2. Use the VSEPR method to predict the molecular shape.
3. From the molecular shape, determine whether bond dipoles cancel to give a nonpolar molecule, or combine to produce a resultant dipole moment for the molecule.

Note: Lone-pair electrons can also make a contribution to dipole moments.

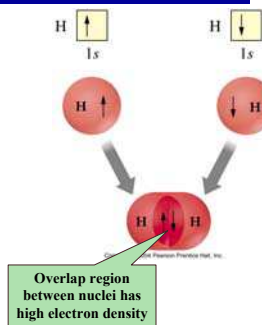
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Atomic Orbital Overlap

- **Valence Bond (VB)** theory states that a covalent bond is formed when atomic orbitals (AOs) overlap.
- In the overlap region, electrons with opposing spins produce a high electron charge density.
- In general, the more extensive the overlap between two orbitals, the stronger is the bond between two atoms.

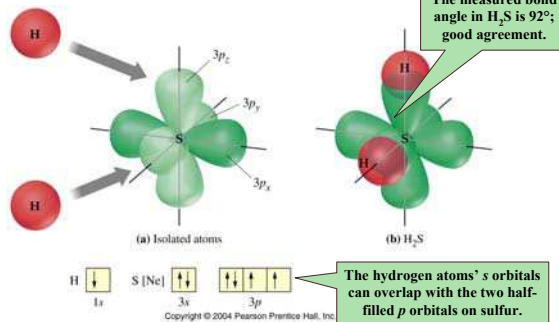


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Bonding in H₂S



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Important Points of VB Theory

- Most of the electrons in a molecule remain in the same orbital locations that they occupied in the separated atoms.
- Bonding electrons are **localized** in the region of AO overlap.
- For AOs with directional lobes (such as *p* orbitals), maximum overlap occurs when the AOs overlap **end to end**.
- VB theory is not without its problems ...

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Hybridization of Atomic Orbitals

VB theory: carbon should have just **two** bonds, and they should be about 90° apart. [He] $\uparrow\downarrow$ \uparrow \uparrow \uparrow
 $2s$ $2p$
 But CH₄ has **four** C—H bonds, 109° apart.

- We can **hybridize** the four orbitals holding valence electrons; mathematically combine the wave functions for the 2*s* orbital and the three 2*p* orbitals on carbon.
- The four AOs combine to form four new **hybrid** AOs.
- The four hybrid AOs are degenerate (same energy) and each has a single electron (Hund's rule).

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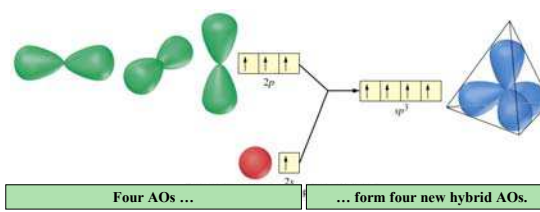
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sp³ Hybridization

- Hybridizing one *s* orbital with three *p* orbitals gives rise to four hybrid orbitals called **sp³** orbitals.
- The number of hybrid orbitals is equal to the number of atomic orbitals combined.
- The four hybrid orbitals, being equivalent, are about 109° apart.

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The sp³ Hybridization Scheme

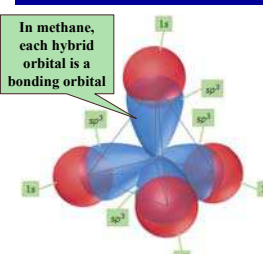


Four AOs ... form four new hybrid AOs.

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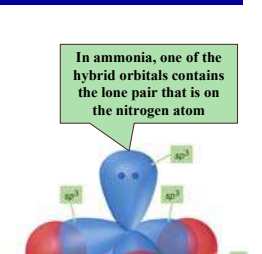
Methane and Ammonia

In methane, each hybrid orbital is a bonding orbital



Four sp³ hybrid orbitals: tetrahedral
Four electron groups: tetrahedral
Coincidence? Hardly.

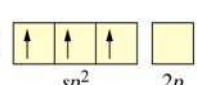
In ammonia, one of the hybrid orbitals contains the lone pair that is on the nitrogen atom



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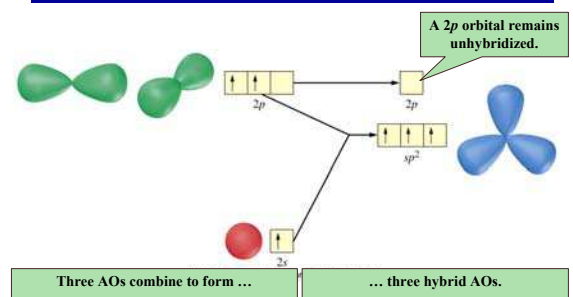
sp² Hybridization

- Three **sp²** hybrid orbitals are formed from an *s* orbital and two *p* orbitals.
- The empty *p* orbital remains unhybridized. It may be used in a multiple bond.
- The **sp²** hybrid orbitals are in a plane, 120° apart.
- This distribution gives a **trigonal planar** molecular geometry, as predicted by VSEPR.

sp² hybridization in B: [He] 

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The sp² Hybridization Scheme in Boron



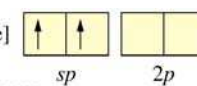
Three AOs combine to form ... three hybrid AOs.

A 2p orbital remains unhybridized.

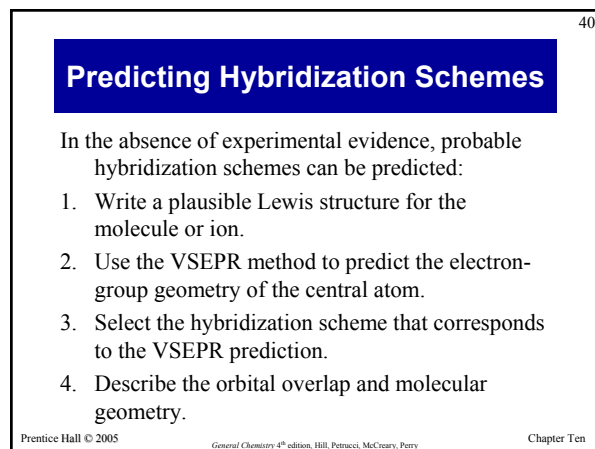
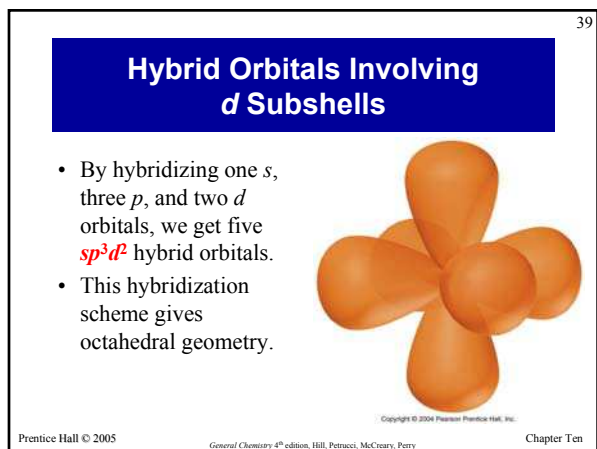
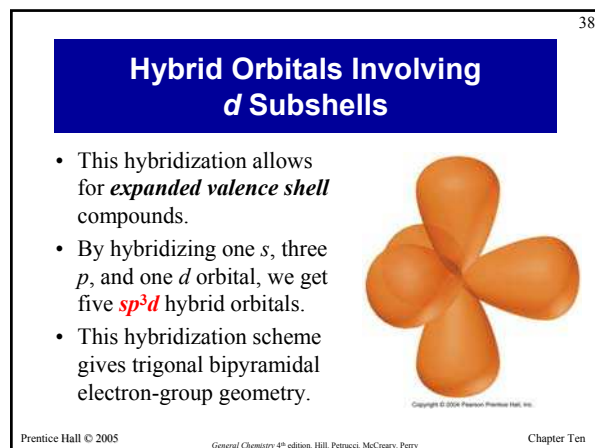
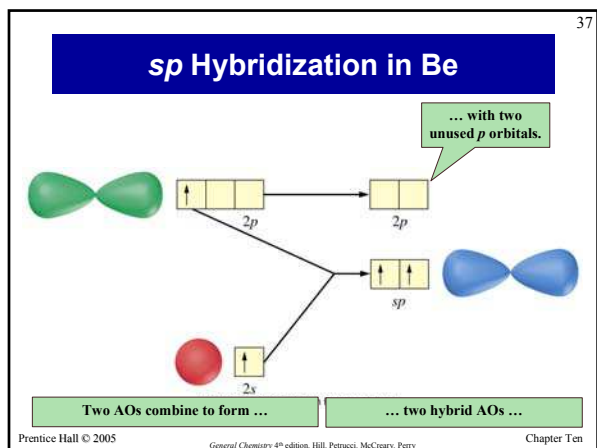
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sp Hybridization

- Two **sp** hybrid orbitals are formed from an *s* orbital and a *p* orbital.
- Two empty *p* orbitals remain unhybridized; the *p* orbitals may be used in a multiple bond.
- The **sp** hybrid orbitals are 180° apart.
- The geometry around the hybridized atom is **linear**, as predicted by VSEPR.

sp hybridization in Be: [He] 

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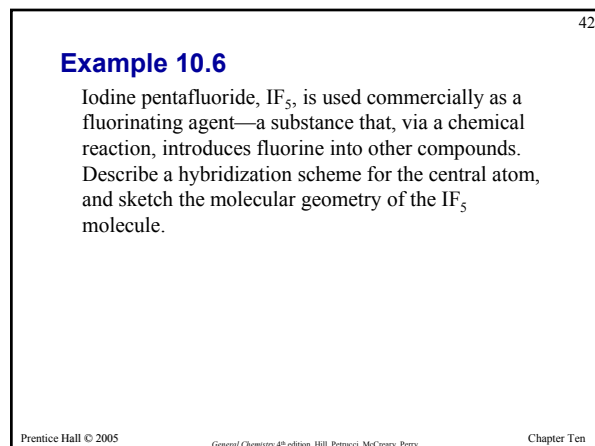
41

Table 10.2 Hybrid Orbitals and Their Geometric Orientation

Hybrid Orbitals	Geometric Orientation	Example
<i>sp</i>	Linear	BeCl ₂
<i>sp²</i>	Trigonal planar	BF ₃
<i>sp³</i>	Tetrahedral	CH ₄
<i>sp³d</i>	Trigonal bipyramidal	PCl ₅
<i>sp³d²</i>	Octahedral	SF ₆

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Hybrid Orbitals and Multiple Covalent Bonds

43

- Covalent bonds formed by the end-to-end overlap of orbitals are called **sigma (σ) bonds**.
- All single bonds are sigma bonds.
- A bond formed by parallel, or side-by-side, orbital overlap is called a **pi (π) bond**.
- A double bond is made up of **one** sigma bond and **one** pi bond.
- A triple bond is made up of **one** sigma bond and **two** pi bonds.

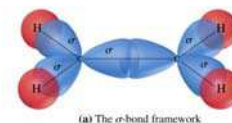
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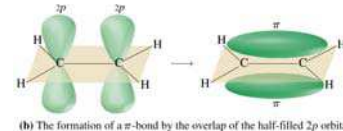
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VB Theory for Ethylene, C₂H₄

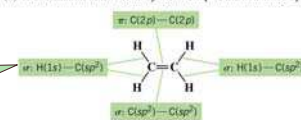
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π -bond has **two lobes** (above and below plane), but is **one bond**. Side overlap of $2p-2p$.



The hybridization and bonding scheme is described by listing each bond and its overlap.



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Example 10.7

Formic acid, HCOOH, is the simplest carboxylic acid.

- Predict a plausible molecular geometry for this molecule.
- Propose a hybridization scheme for the central atoms that is consistent with that geometry.
- Sketch a bonding scheme for the molecule.

45

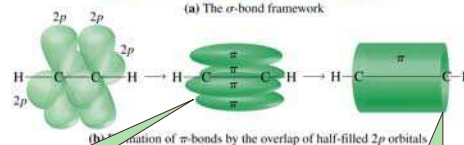
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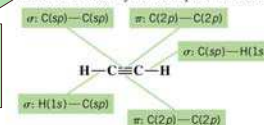
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VB Theory: Acetylene

46



Two π -bonds (above and below, and front and back) from $2p-2p$ overlap ...



... form a cylinder of π -electron density around the two carbon atoms.

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Geometric Isomerism

47

- **Geometric isomers** are isomers that differ only in the geometric arrangement of certain substituent groups.
- Two types of geometric isomers include:
 - **cis**: substituent groups are on the same side
 - **trans**: substituent groups are on opposite sides
- *cis*- and *trans*- compounds are distinctly different in both physical and chemical properties.
- Usually formed across double bonds and in square planar compounds.

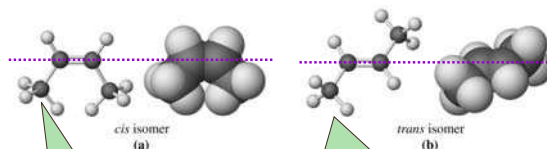
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Geometric Isomerism in 2-Butene

48



Groups are on the **same side** of the double bond: **cis-isomer**

Groups are on **opposite sides** of double bond: **trans-isomer**

n-Butane does not have these isomers; why not??

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Example 10.8 A Conceptual Example

Is it possible to write a unique structural formula for 1,2-dichloroethene if we are told that the molecule is nonpolar?

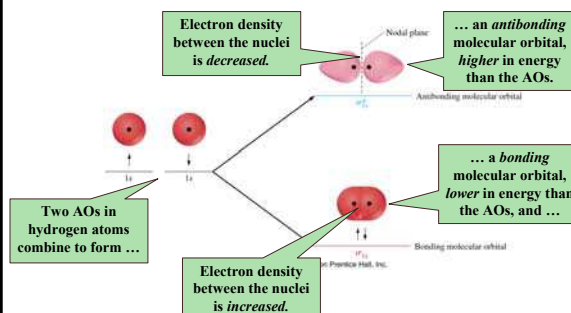
Molecular Orbitals

- An alternative scheme to VB theory uses molecular orbitals.
- A **molecular orbital (MO)** is a mathematical description of the region in a **molecule** where there is a high probability of finding electrons.
- **Molecular orbitals** are to molecules as _____ are to atoms.
- In MO theory, molecular orbitals are formed by the combination of atomic orbitals.

Characteristics of Molecular Orbitals

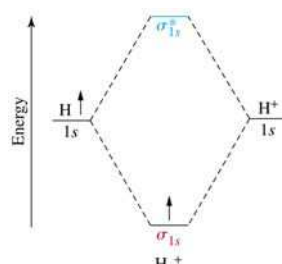
- Two atomic orbitals combine => two molecular orbitals result.
- Of each pair of molecular orbitals, one is a **bonding** molecular orbital.
 - The bonding orbital is at a **lower** energy than the separate atomic orbitals.
 - Electrons in a bonding orbital **increase** the stability of the molecule.
- The second orbital is an **antibonding** orbital.
 - The antibonding orbital is at a **higher** energy than the AOs.
 - Electrons in an antibonding orbital **decrease** the stability of the molecule.

Types of Molecular Orbitals

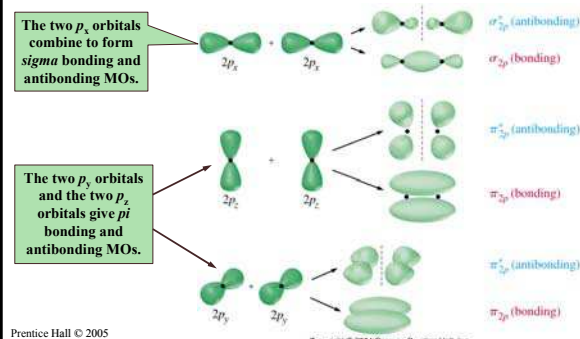


Example 10.9 A Conceptual Example

Molecular orbital theory allows for species with a one-electron bond. What does the term “one-electron bond” signify? Cite an example of such a bond.



Homonuclear Diatomic Molecules of the Second-Period Elements



Molecular Orbital Diagrams

Just like AOs: there are some irregularities in the filling order ...

Electrons fill MOs in the same way that AOs are filled – lowest energy to highest energy.

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Example 10.10 A Conceptual Example

When an electron is removed from a N_2 molecule, forming an N_2^+ ion, the bond between the N atoms is weakened. When an O_2 molecule is ionized to O_2^+ , the bond between the O atoms is strengthened. Explain this difference.

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Bonding in Benzene

- In 1865, Kekulé proposed that benzene (C_6H_6) has a *cyclic* structure, with a hydrogen atom attached to each carbon atom. Alternating single and double bonds join the carbon atoms.

- Modern view: there are two resonance hybrids of benzene.
- The pi-electrons are not localized between any particular carbon atoms, but are *delocalized* among all six carbon atoms.

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The σ -Bonding Framework

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Computer-Generated Structure of Benzene

Sigma bond between carbon atoms

Donut-shaped pi-cloud above ...


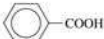




... and below the plane of sigma bonds.

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Aromatic Compounds

- Many of the first benzene-like compounds discovered had pleasant odors, hence the name *aromatic* was applied to the compounds.
- Today an **aromatic compound** is one that has a ring structure and bonding characteristics related to those of benzene (more in Chapter 23).
- All organic compounds that are not aromatic are called **aliphatic compounds**.

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TABLE 10.3 Some Representative Aromatic Compounds		
Name	Structure	Typical Use(s)
Aniline		Starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
Benzoic acid		Food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
Bromobenzene		Starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
Nitrobenzene		Starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
Phenol		Disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
Toluene		Solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

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Cumulative Example

Methyl isocyanate (MIC), used in the manufacture of pesticides and polymers, is a carbon–hydrogen–oxygen–nitrogen compound with a molecular mass of 57.05 u; it is 5.29% H by mass. The nitrogen in a 0.7500-g sample of the compound is converted to $\text{NH}_3(\text{g})$, which is neutralized by passing it into 50.00 mL of 0.2800 M $\text{H}_2\text{SO}_4(\text{aq})$. After neutralization of the $\text{NH}_3(\text{g})$, the excess $\text{H}_2\text{SO}_4(\text{aq})$ requires 36.49 mL of 0.4070 M $\text{NaOH}(\text{aq})$ for complete neutralization. Indicate hybridization for the central atoms in the methyl isocyanate molecule, and draw a sketch of the molecule with appropriate bond angles.