Chapter 9: Molecular Geometry and Bonding Theories

9.1 Molecular Shapes
- Lewis structures do not indicate shape of molecule
- bond angles – angles made by the lines joining the nuclei of the atoms in the molecule; determines shape of molecule along with bond length
- AB_n molecule, A is central atom bonded to n B atoms

9.2 The VSEPR Model
- best arrangement of a given number of electron pairs is one that minimizes the repulsion among them

9.2.1 Predicting Molecular Geometries
- two types of valence shell electron pairs 1)bonding pairs and 2)nonbonding pairs
- electron-pair geometry – arrangement of electron pairs about the central atom of an AB_n
- molecular geometry – arrangement of atoms in space
- when describing shapes give molecular geometry rather than electron-pair geometry
- steps to predict molecular geometries with VSEPR
- 1) sketch Lewis structure of the molecule or ion
- 2) count total number of electron pairs around central atom and arrange to minimize electron-pair repulsion
- 3) describe molecular geometry in terms of angular arrangement of the bonding pairs
- 4) double or triple bond counts as one bonding pair

9.2.2 The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles
- bond angles decrease as number of nonbonding electron pairs increase
- nonbonding electron pairs exert greater repulsive forces on adjacent electron pairs → compress angles between bonding pairs
- electrons in multiple bonds exert a greater repulsive force on adjacent electron pairs than do single bonds

9.2.3 Molecules with Expanded Valence Shells
- most stable electron-pair geometry for five electron pairs is trigonal bipyramid
    - two geometrically distinct electron pairs – axial pairs and equatorial pairs
    - equatorial pairs feel less repulsion than axial pairs
    - nonbonding pairs always equatorial
- most stable electron-pair geometry for six electron pairs is octahedron
- all angles are 90 or 190 degrees

9.2.4 Molecules with More than One Central Atom

9.3 Polarity of Molecules
- polar if centers of negative and positive charge do not coincide
- "δ+" and "δ-" used to indicate partial positive and negative charges
- or an arrow that shows a shift in electron density
- polar molecules align themselves in an electric field
- dipole – two electrical charges of equal magnitude but opposite sign are separated by a distance
- dipole moment – size of dipole, μ
    - if equal magnitude, Q+ and Q-, separated by a distance r then dipole moment is product of Q and r
    - $\mu = Qr$
    - unit = debyes (D) = 3.34×10^{-30} columb-meters (C-m)
    - charge of molecules measured in units of electronic charge e, 1.60×10^{-19} C. and distance Å
    - dipole moments provide information about charge distributions in molecules

9.3.1 Dipole Moments of Polyatomic Molecules

- bond dipole – dipole moment due only to the two atoms bonded together
- bond dipoles and dipole moments are vector quantities
- overall dipole moment of a polyatomic molecule is sum of its bond dipoles

9.4 Covalent Bonding and Orbital Overlap
- VSEPR does not explain why bonds exist between atoms
- Valence-bond theory – extension of Lewis's notion of electron-pair bonds
- In Lewis theory, covalent bonding occurs when atoms share electrons
- Valence-bond theory, covalent bonding occurs when valence atomic orbital of one atom merges with that of another atom
    - Orbitals are said to overlap
- as distance between the atoms decreases, the overlap between their 1s orbitals increases
- increase in electron density → decrease in potential energy of system
- strength of bond increases →decrease in energy
- as atoms come close together → energy increases rapidly
    - increase due to electrostatic repulsion between nuclei
    - observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) balanced by repulsive forces of like charges (electron-electron and nucleus-nucleus)

9.5 Hybrid Orbitals
9.5.1 sp Hybrid Orbitals
- hybrid orbitals – orbitals formed by mixing two or more atomic orbitals on an atom
    - formed by hybridization
- promotes one s electron to the p orbital

9.5.2 sp^2 and sp^3 Hybrid Orbitals
- mixing one 2s and 2p orbitals yields two equivalent sp hybrid orbitals that point in opposite directions
- s orbital can mix with all three p orbitals which form sp^3 hybrid orbitals
- each sp^3 hybrid orbital has a large lobe that points toward a vertex of a tetrahedron

9.5.3 Hybridization Involving d Orbitals
- mix one s orbital, three p orbitals, and one d orbital → five sp^3d orbitals
- mix one s orbital, three p orbitals, and two d orbitals → siz sp^3d^2 hybrid orbitals (directed toward vertices of an octahedron
    - corresponds to notion of expanded valence shells

9.5.4 Summary
- predicting hybrid orbitals:
- 1) draw Lewis structure for molecule or ion
- 2) determine the electron-pair geometry using the VSEPR model
    - 3) specify hybrid orbitals needed to accommodate electron pairs based on their geometrical arrangement

9.6 Multiple Bonds
- internuclear axis – line joining nuclei
- sigma bonds (σ) – overlap of two s orbitals, s and p orbital, two p orbitals, p orbital with sp hybrid
- pi bond – overlap of two p orbitals oriented perpendicularly to the internuclear axis
    - covalent bond in which the overlap regions lie above and below the internuclear axis
    - no probability of finding electron on internuclear axis
    - pi bonds weaker than sigma bonds
- single bonds are sigma bonds, double bond consists of one sigma bond and one pi bond, triple bond consists of one sigma bond and two pi bonds
- cannot experimentally observe a pi bond directly

- pi bonds create rigidity in molecules
    - double and triple bonds are more common in molecules with small atoms

9.6.1 Delocalized pi bonding
- localized bonding – sigma and pi electrons are associated totally with the two atoms that form the bond
- delocalized molecules have pi bonds and more than one resonance structure

9.6.2 General Conclusions
- 1) in every bond at least one pair of electrons is localized in space between atoms in a sigma bond. Appropriate set of hybrid orbitals used to form sigma bonds between atom and neighbors determined by observed geometry of the molecule
- 2) electrons in sigma bonds are localized in region between two bonded atoms and do not make a significant contribution to the bonding between any other atom
- 3) when atoms share more than one pair of electrons, additional pairs are pi bonds
- 4) molecules with two or more resonance structures can have pi bonds that extend over more than two bonded atoms

9.7 Molecular Orbitals
- molecular orbital theory – another way to describe bonding in molecules
- electrons allowed in energy states called molecular orbitals

9.7.1 the Hydrogen Molecule
- when two atomic orbitals overlap, two molecular orbitals form
- bonding molecular orbital – the lower energy orbital concentrates charge density in the region between the nuclei
- antibonding molecular orbital – excludes electrons form the region between the nuclei
- atomic orbitals cancel each other in the antibonding molecular orbital
    - excludes electrons from region that bonds have to be formed
    - electron repelled from boning region
- sigma molecular orbitals – orbitals formed from the combination of bonding and antibonding molecular orbitals
- energy-level diagram (molecular orbital diagram) – shows the interaction between two 1s orbitals to form σ_{1s} and σ_{1s}^* molecular orbitals

9.7.2 Bond Order
- $$\text{bond order} = \frac{1}{2}\left(\text{no. bonding electrons - no. antibonding electrons}\right)$$
- an bond order of 1 = a single bond
- bond order of 2 = double bond
- bond order of 3 = triple bond
- ½, 3/2 or 5/2 also possible
    - bond order of 0 = no bond

9.8 Second-Row Diatomic Molecules
- homonuclear diatomic molecules – composed of two identical atoms
- 1) number of molecular orbitals formed = number of atomic orbitals combined
- 2) atomic orbitals combine most effectively with other atomic orbitals of similar energy
- 3) effectiveness of combining atomic orbitals proportional to overlap with one another
- 4) each molecular orbital can have up to 2 electrons (pauli exclusion principle)
- 5) Hund's Rule

9.8.1 Molecular Orbitals for Li_2 and Be_2
- core electrons usually do not contribute significantly to bonding in molecule formation

- in Be_2 there is an equal number of bonding and antibonding electrons so bond order equals 0 therefore Be_2 does not exist
- Li_2 has a bond order of 1 = 1 single bond

9.8.2 Molecular Orbitals from 2p Atomic Orbitals
- p orbitals that are perpendicular to the internuclear axis form pi molecular orbitals
- head to head 2p orbitals form σ_{2p} and $\sigma_{2p}*$ orbitals
- overlap sideways forms $\pi_{2p}*$ and π_{2p} orbitals
- σ_{2p} lower in energy than π_{2p}
- $\sigma_{2p}*$ higher energy than $\pi_{2p}*$

9.8.3 Electron Configurations for B_2 Through Ne_2
- 1) 2s atomic orbitals lower than 2p atomic orbitals
- 2) σ_{2p} lower in energy than π_{2p} and $\sigma_{2p}*$ higher energy than $\pi_{2p}*$
- 3) both π_{2p} and $\pi_{2p}*$ molecular orbitals are doubly degenerate, there are two degenerate molecular orbitals of each type
- For B_2, C_2, and N_2 the σ_{2p} molecular orbital is above the π_{2p} molecular orbitals in energy. For O_2, F_2, and Ne_2 the σ_{2p} molecular orbital below the π_{2p} molecular orbitals

9.8.4 Electron Configurations and Molecular Properties
- paramagnetism – attraction of unpaired electrons in a magnetic field
- diamagnetism – substances with no unpaired electrons are weakly repelled in magnetic field
    - weaker than paramagnetism
- test for paramagnetism and diamagnetism is to weigh substance without presence of magnetic field and then with a magnetic field
    - substance will appear to weigh more in paramagnetic in magnetic field, or would appear to weigh less if diamagnetic