

Chapter 9. Molecular Geometry and Bonding Theories

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Chapter 9. Molecular Geometry and Bonding Theories

Common Student Misconceptions

- Students find it difficult to think in three dimensions. Often, they believe that a square planar arrangement is the best arrangement for the least repulsion of four electron domains.
- Students often confuse the electron domain geometry and the molecular geometry (shape).
- Students need to realize that in order to determine whether a molecule is polar, they need to establish the correct molecular geometry.
- Students need to realize that large molecules with several central atoms do not have easily describable molecular shapes; geometry about each central atom has to be determined individually.
- Students often find it difficult to understand how a molecule with polar bonds can be nonpolar; a review of basic vector algebra to illustrate how the net dipole is derived may be needed.
- Students often attempt to determine polarity of ions.
- Students do not realize that hybridization is related to the electron-domain geometry, not the molecular geometry.
- Students need to realize that in wave mechanics bonding orbitals result from constructive interference and antibonding orbitals form destructive interference.

Teaching Tips

- Simple balloon models can be effectively used in classroom presentations of VSEPR.
- Referring to nonbonded electron pairs, single bonds, and multiple bonds as *regions of electron density* may help relieve any confusion that might arise from treating the various kinds of electron pairs differently.

Lecture Outline¹

9.1 Molecular Shapes^{2,3,4,5,6,7,8,9,10,11,12}

- Lewis structures give atomic connectivity: they tell us which atoms are physically connected to which atoms.
- The shape of a molecule is determined by its **bond angles**.
 - The angles made by the lines joining the nuclei of the atoms in a molecule are the bond angles.
- Consider CCl₄:
 - Experimentally we find all Cl–C–Cl bond angles are 109.5°.
 - Therefore, the molecule cannot be planar.

¹ “Diazepam (valium)” 3-D Model from Instructor’s Resource CD/DVD

² “Carbon Tetrachloride” 3-D Model from Instructor’s Resource CD/DVD

³ Figure 9.2 from Transparency Pack

⁴ Figure 9.3 from Transparency Pack

⁵ “Carbon Dioxide” 3-D Model from Instructor’s Resource CD/DVD

⁶ “Sulfur Dioxide” 3-D Model from Instructor’s Resource CD/DVD

⁷ “Sulfur Trioxide” 3-D Model from Instructor’s Resource CD/DVD

⁸ “Nitrogen Trifluoride” 3-D Model from Instructor’s Resource CD/DVD

⁹ “Chlorine Trifluoride” 3-D Model from Instructor’s Resource CD/DVD

¹⁰ “Molecular Geometry” from Further Readings

¹¹ “Ammonia” 3-D Model from Instructor’s Resource CD/DVD

¹² “Water” 3-D Model from Instructor’s Resource CD/DVD

- All Cl atoms are located at the vertices of a tetrahedron with the C at its center.
- In order to predict molecular shape, we assume that the valence electrons repel each other.
 - Therefore, the molecule adopts the three-dimensional geometry that minimizes this repulsion.
 - We call this model the **Valence-Shell Electron-Pair Repulsion (VSEPR)** model.

FORWARD REFERENCES

- Molecular shapes will affect such physical properties as viscosity (Chapter 11) and boiling points of structural isomers of organic compounds (Chapter 24).
- Molecular shapes and structures of many compounds will be used throughout the textbook, but in particular in Chapters 22 and 24.

9.2 The VSEPR Model^{13,14,15,16,17,18,19,20,21,22}

- A covalent bond forms between two atoms when a pair of electrons occupies the space between the atoms.
 - This is a **bonding pair** of electrons.
 - Such a region is an **electron domain**.
- A **nonbonding pair** or **lone pair** of electrons defines an electron domain located principally on one atom.
 - Example: NH₃ has three bonding pairs and one lone pair.
- VSEPR predicts that the best arrangement of electron domains is the one that minimizes the repulsions among them.
 - The arrangement of electron domains about the central atom of an AB_n molecule is its **electron-domain geometry**.
 - There are five different electron-domain geometries:
 - Linear (two electron domains), trigonal planar (three domains), tetrahedral (four domains), trigonal bipyramidal (five domains) and octahedral (six domains).
- The **molecular geometry** is the arrangement of the atoms in space.
 - To determine the shape of a molecule we distinguish between lone pairs and bonding pairs.
 - We use the electron domain geometry to help us predict the molecular geometry.
 - Draw the Lewis structure.
 - Count the total number of electron domains around the central atom.
 - Arrange the electron domains in one of the above geometries to minimize electron-electron repulsion.
 - Next, determine the three-dimensional structure of the molecule.
 - We ignore lone pairs in the molecular geometry.
 - Describe the molecular geometry in terms of the angular arrangement of the bonded atoms.
 - Multiple bonds are counted as one electron domain.

¹³ “Who Needs Lewis Structures To Get VSEPR Geometries?” from Further Readings

¹⁴ “VSEPR” Animation from Instructor’s Resource CD/DVD

¹⁵ Table 9.1 from Transparency Pack

¹⁶ “Teaching Molecular Geometry with the VSEPR Model” from Further Readings

¹⁷ “Teaching VSEPR: The Plastic Egg Model” from Further Readings

¹⁸ “VSEPR—Basic Molecular Configurations” 3-D Model from Instructor’s Resource CD/DVD

¹⁹ Table 9.2 from Transparency Pack

²⁰ “Ozone” 3-D Model from Instructor’s Resource CD/DVD

²¹ “Boron Trifluoride” 3-D Model from Instructor’s Resource CD/DVD

²² “Trichlorotin(II) Ion” 3-D Model from Instructor’s Resource CD/DVD

Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles^{23,24}

- We refine VSEPR to predict and explain slight distortions from “ideal” geometries.
- Consider three molecules with tetrahedral electron domain geometries:
 - CH₄, NH₃, and H₂O.
 - By experiment, the H–X–H bond angle decreases from C (109.5° in CH₄) to N (107° in NH₃) to O (104.5° in H₂O).
 - A bonding pair of electrons is attracted by two nuclei. They do not repel as much as lone pairs which are primarily attracted by only one nucleus.
 - Electron domains for nonbonding electron pairs thus exert greater repulsive forces on adjacent electron domains.
 - They tend to compress the bond angles.
 - The bond angle decreases as the number of nonbonding pairs increases.
 - Similarly, electrons in multiple bonds repel more than electrons in single bonds. (e.g. in Cl₂CO the O–C–Cl angle is 124.3°, and the Cl–C–Cl bond angle is 111.4°).
- We will encounter 11 basic molecular shapes:
 - Three atoms (AB₂)
 - Linear
 - Bent
 - Four atoms (AB₃)
 - Trigonal planar
 - Trigonal pyramidal
 - T-shaped
 - Five atoms (AB₄)
 - Tetrahedral
 - Square planar
 - Seesaw
 - Six atoms (AB₅)
 - Trigonal bipyramidal
 - Square pyramidal
 - Seven atoms (AB₆)
 - Octahedral

Molecules with Expanded Valence Shells^{25,26,27}

- Atoms that have expanded octets have five electron domains (trigonal bipyramidal) or six electron domains (octahedral) electron-domain geometries.
 - Trigonal bipyramidal structures have a plane containing three electron pairs.
 - The fourth and fifth electron pairs are located above and below this plane.
 - In this structure two trigonal pyramids share a base.
 - For octahedral structures, there is a plane containing four electron pairs.
 - Similarly, the fifth and sixth electron pairs are located above and below this plane.
 - Two square pyramids share a base.
- Consider a trigonal bipyramid.
 - The three electron pairs in the plane are called *equatorial*.

²³ “Multiple Bonds and the VSEPR Model” from Further Readings

²⁴ “Lewis Structures are Models for Predicting Molecular Structure, *Not* Electronic Structure” from Further Readings

²⁵ Table 9.3 from Transparency Pack

²⁶ “Sulfur Tetrafluoride” 3-D Model from Instructor’s Resource CD/DVD

²⁷ “Iodine Pentafluoride” 3-D Model from Instructor’s Resource CD/DVD

- The two electron pairs above and below this plane are called *axial*.
- The axial electron pairs are 180° apart and 90° to the equatorial electrons.
- The equatorial electron pairs are 120° apart.
- To minimize electron–electron repulsion, nonbonding pairs are always placed in equatorial positions and bonding pairs in either axial or equatorial positions.
- Consider an octahedron.
 - The four electron pairs in the plane are at 90° to each other.
 - The two axial electron pairs are 180° apart and at 90° to the electrons in the plane.
 - Because of the symmetry of the system, each position is equivalent.
 - If we have five bonding pairs and one lone pair, it doesn't matter where the lone pair is placed.
 - The molecular geometry is square pyramidal.
 - If two nonbonding pairs are present, the repulsions are minimized by pointing them toward opposite sides of the octahedron.
 - The molecular geometry is square planar.

Shapes of Larger Molecules^{28,29}

- In acetic acid, CH_3COOH , there are three interior atoms: two C and one O.
- We assign the molecular (and electron-domain) geometry about each interior (central) atom separately.
 - The geometry around the first C is tetrahedral.
 - The geometry around the second C is trigonal planar.
 - The geometry around the O is bent (tetrahedral).

FORWARD REFERENCES

- The consequence of water having an sp^3 hybridized oxygen atom and bent molecular shape will be linked to its ability to form 4 hydrogen bonds in the structure of ice in Chapter 11 (section 11.2).
- Octahedral vs. tetrahedral metal complexes will be discussed in Chapter 23 (section 23.6).

9.3 Molecular Shape and Molecular Polarity^{30,31,32,33,34,35,36,37,38,39,40}

- Polar molecules interact with electric fields.
- We previously saw that binary compounds are polar if their centers of negative and positive charge do not coincide.

²⁸ “The Use of Molecular Modeling and VSEPR Theory in the Undergraduate Curriculum to Predict the Three-Dimensional Structure of Molecules” from Further Readings

²⁹ “Acetic Acid” 3-D Model from Instructor’s Resource CD/DVD

³⁰ Figure 9.12 from Transparency Pack

³¹ “Molecular Polarity” Activity from Instructor’s Resource CD/DVD

³² “Tetrahedral Geometry and the Dipole Moment of Molecules” from Further Readings

³³ “Bending a Stream of Water” from Live Demonstrations

³⁴ “Difficulties with the Geometry and Polarity of Molecules: Beyond Misconceptions” from Further Readings

³⁵ “The Ropes: A Molecular Polarity Activity” from Further Readings

³⁶ “Identifying Polar and Nonpolar Molecules” from Further Readings

³⁷ “The Significance of the Bond Angle in Sulfur Dioxide” from Further Readings

³⁸ “Put the Body to Them!” from Further Readings

³⁹ “Chloromethane” 3-D Model from Instructor’s Resource CD/DVD

⁴⁰ “Hydrogen Chloride” 3-D Model from Instructor’s Resource CD/DVD

- If two charges, equal in magnitude and opposite in sign, are separated by a distance d , then a *dipole* is established.
- The dipole moment, μ , is given by:

$$\mu = Qr$$
 - where Q is the magnitude of the charge.
- We can extend this to polyatomic molecules.
 - For each bond in a polyatomic molecule, we can consider the **bond dipole**.
 - The dipole moment due only to the two atoms in the bond is the bond dipole.
 - Because bond dipoles and dipole moments are *vector quantities*, the orientation of these individual dipole moments determines whether the molecule has an overall dipole moment.
 - Examples:
 - In CO_2 each $\delta^+\text{C}-\text{O}\delta^-$ dipole is canceled because the molecule is linear.
 - In H_2O , the $\delta^+\text{H}-\text{O}\delta^-$ dipoles do not cancel because the molecule is bent.
- It is possible for a molecule with polar bonds to be either polar or nonpolar.
 - Example:
 - For diatomic molecules:
 - polar bonds always result in an overall dipole moment.
 - For triatomic molecules:
 - if the molecular geometry is bent, there is an overall dipole moment.
 - if the molecular geometry is linear, and the B atoms are the same, there is no overall dipole moment.
 - if the molecular geometry is linear and the B atoms are different, there is an overall dipole moment.
 - For molecules with four atoms:
 - if the molecular geometry is trigonal pyramidal, there is an overall dipole moment;
 - if the molecular geometry is trigonal planar, and the B atoms are identical, there is no overall dipole moment;
 - if the molecular geometry is trigonal planar and the B atoms are different, there is an overall dipole moment.

FORWARD REFERENCES

- Molecular polarity will affect such physical properties as viscosity, vapor pressure and energy changes associated with phase changes of compounds (Chapter 11).
- Molecular polarity vs. miscibility will be discussed in Chapter 13 (section 13.3).
- Polar functional groups in otherwise nonpolar organic compounds will be further discussed in Chapter 24 (section 24.4).

9.4 Covalent Bonding and Orbital Overlap^{41,42,43}

- Lewis structures and VSEPR theory give us the shape and location of electrons in a molecule.
 - They do not explain why a chemical bond forms.
- How can quantum mechanics be used to account for molecular shape? What are the orbitals that are involved in bonding?
- We use **valence-bond theory**:
 - A covalent bond forms when the orbitals on two atoms *overlap*.
 - The shared region of space between the orbitals is called the *orbital overlap*.
 - There are two electrons (usually one from each atom) of opposite spin in the orbital overlap.

⁴¹ “Demystifying Introductory Chemistry Part 2: Bonding and Molecular Geometry without Orbitals—The Electron-Domain Model” from Further Readings

⁴² “Grade-12 Students’ Misconceptions of Covalent Bonding and Structure” from Further Readings

⁴³ Figure 9.14 from Transparency Pack

- As two nuclei approach each other, their atomic orbitals overlap.
- As the amount of overlap increases, the energy of the interaction decreases.
- At some distance the minimum energy is reached.
 - The minimum energy corresponds to the bonding distance (or bond length).
- As the two atoms get closer, their nuclei begin to repel and the energy increases.
- At the bonding distance, the attractive forces between nuclei and electrons just balance the repulsive forces (nucleus-nucleus, electron-electron).

9.5 Hybrid Orbitals^{44,45}

- We can apply the idea of orbital overlap and valence-bond theory to polyatomic molecules.

sp Hybrid Orbitals⁴⁶

- Consider the BeF₂ molecule.
 - Be has a 1s²2s² electron configuration.
 - There is no unpaired electron available for bonding.
 - We conclude that the atomic orbitals are not adequate to describe orbitals in molecules.
- We know that the F–Be–F bond angle is 180° (VSEPR theory).
- We also know that one electron from Be is shared with each one of the unpaired electrons from F.
- We assume that the Be orbitals in the Be–F bond are 180° apart.
- We could promote an electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding.
 - BUT the geometry is still not explained.
- We can solve the problem by allowing the 2s and one 2p orbital on Be to mix or form two new **hybrid orbitals** (a process called **hybridization**).
 - The two equivalent hybrid orbitals that result from mixing an *s* and a *p* orbital and are called *sp* hybrid orbitals.
 - The two lobes of an *sp* hybrid orbital are 180° apart.
 - According to the valence-bond model, a linear arrangement of electron domains implies *sp* hybridization.
 - Since only one of 2p orbitals of Be has been used in hybridization, there are two unhybridized *p* orbitals remaining on Be.
 - The electrons in the *sp* hybrid orbitals form shared electron bonds with the two fluorine atoms.

*sp*² and *sp*³ Hybrid Orbitals^{47,48,49}

- Important: when we mix *n* atomic orbitals, we must get *n* hybrid orbitals.
- Three *sp*² hybrid orbitals are formed from hybridization of one *s* and two *p* orbitals.
 - Thus, there is one unhybridized *p* orbital remaining.
 - The large lobes of the *sp*² hybrids lie in a trigonal plane.
 - Molecules with trigonal planar electron-pair geometries have *sp*² orbitals on the central atom.
- Four *sp*³ hybrid orbitals are formed from hybridization of one *s* and three *p* orbitals.
 - Therefore, there are four large lobes.
 - Each lobe points towards the vertex of a tetrahedron.
 - The angle between the large lobes is 109.5°.
 - Molecules with tetrahedral electron pair geometries are *sp*³ hybridized.

⁴⁴ “A Colorful Demonstration to Simulate Orbital Hybridization” from Further Readings

⁴⁵ “Hybridization” Animation from Instructor’s Resource CD/DVD

⁴⁶ Figure 9.15 from Transparency Pack

⁴⁷ Figure 9.17 from Transparency Pack

⁴⁸ Figure 9.18 from Transparency Pack

⁴⁹ “*s-p* Hybridization” Activity from Instructor’s Resource CD/DVD

- Since there are only three p orbitals, trigonal bipyramidal and octahedral electron-pair geometries must involve d orbitals.
- Trigonal bipyramidal electron pair geometries require sp^3d hybridization.
- Octahedral electron pair geometries require sp^3d^2 hybridization.
- Note that the electron pair VSEPR geometry corresponds well with the hybridization.
 - Use of d orbitals in making hybrid orbitals corresponds well with the idea of an expanded octet.

Hybrid Orbital Summary⁵⁰

- We need to know the electron-domain geometry before we can assign hybridization.
- To assign hybridization:
 - Draw a Lewis structure.
 - Assign the electron-domain geometry using VSEPR theory.
 - Specify the hybridization required to accommodate the electron pairs based on their geometric arrangement.
 - Name the geometry by the positions of the atoms.

FORWARD REFERENCES

- Hybridization of C atoms in carbon nanotubes and polymers will be mentioned in Chapter 12 (section 12.9).
- sp , sp^2 and sp^3 hybridizations will be utilized throughout Chapter 24.
- Hybrid orbitals will be utilized in the metal-ligand bond formation in Chapter 23 (section 23.6).

9.6 Multiple Bonds^{51,52,53,54,55}

- In the covalent bonds we have seen so far the electron density has been concentrated symmetrically about the *internuclear axis*.
- **Sigma (σ) bonds:** electron density lies on the axis between the nuclei.
 - All single bonds are σ bonds.
- What about overlap in multiple bonds?
 - **Pi (π) bonds:** electron density lies above and below the plane of the nuclei.
 - A double bond consists of one σ bond and one π bond.
 - A triple bond has one σ bond and two π bonds.
- Often, the p orbitals involved in π bonding come from unhybridized orbitals.
- For example: ethylene, C_2H_4 , has a $C=C$ double bond:
 - One σ and one π bond.
 - Both C atoms sp^2 hybridized.
 - Both C atoms with trigonal planar electron-pair and molecular geometries.
- For example: acetylene, C_2H_2 , has a $C\equiv C$ triple bond
 - The electron-domain geometry of each C is linear.
 - Therefore, the C atoms are sp hybridized.
 - The sp hybrid orbitals form the $C-C$ and $C-H$ σ bonds.
 - There are *two* unhybridized p orbitals on each C atom.
 - *Both* unhybridized p orbitals form the *two* π bonds;
 - One π bond is above and below the plane of the nuclei;

⁵⁰ Table 9.4 from Transparency Pack

⁵¹ Figure 9.23 from Transparency Pack

⁵² “Multiple Bonds” Activity from Instructor’s Resource CD/DVD

⁵³ Figure 9.24 from Transparency Pack

⁵⁴ “Ethene (ethylene)” 3-D Model from Instructor’s Resource CD/DVD

⁵⁵ “Ethyne (acetylene)” 3-D Model from Instructor’s Resource CD/DVD

- One π bond is in front and behind the plane of the nuclei.
- When triple bonds form (e.g., N_2), one π bond is always above and below and the other is in front and behind the plane of the nuclei.

Resonance Structures, Delocalization, and π Bonding^{56,57,58,59,60,61,62,63}

- So far all the bonds we have encountered are localized between two nuclei.
- In the case of benzene:
 - There are six localized C–C σ bonds and six localized C–H σ bonds
 - Each C atom is sp^2 hybridized.
 - There is one unhybridized p orbital on each carbon atom, resulting in six unhybridized carbon p orbitals in a ring.
- In benzene the three π bonds are **delocalized** over the entire ring (i.e., the π electrons are shared by all six carbon atoms).
- Experimentally, all C–C bonds are the same length in benzene.
 - Therefore, all C–C bonds are of the same type (recall single bonds are longer than double bonds).

General Conclusions⁶⁴

- Every pair of bonded atoms shares one or more pairs of electrons.
- Two electrons shared between atoms on the same axis as the nuclei are σ bonds.
- σ Bonds are always localized in the region between two bonded atoms.
- If two atoms share more than one pair of electrons, the additional pairs form π bonds.
- When resonance structures are possible, delocalization is also possible.

FORWARD REFERENCES

- Delocalized electrons in metallic solids will be mentioned in Chapter 12 (section 12.3).
- Delocalized π bonds in graphite will be further discussed in Chapter 12 (section 12.7).
- Multiple bonds in polymerization, rubber, and biopolymers will be discussed in Chapter 12 (section 12.8).
- Effectiveness of orbital overlap in the formation of π bonds in 2nd vs. 3rd row elements will be compared in Chapter 22 (section 22.1).
- The role of π bonds in O_2 and other oxygen containing compounds, as well as a delocalized π bond in ozone will be discussed in Chapter 22 (section 22.5).
- Alternating double bonds in chlorophyll will be discussed in Chapter 23 (section 23.3).
- π bonds in alkenes and alkynes will be discussed in Chapter 24 (section 24.3).
- Delocalized π bonds in aromatic compounds will be mentioned in Chapter 24 (section 24.3).

9.7 Molecular Orbitals^{65,66,67,68}

- Some aspects of bonding are not explained by Lewis structures, VSEPR theory and hybridization.

⁵⁶ “The ‘Big Dog-Puppy Dog’ Analogy for Resonance” from Further Readings

⁵⁷ Figure 9.26 from Transparency Pack

⁵⁸ Figure 9.27 from Transparency Pack

⁵⁹ “Resonance Analogy Using Cartoon Characters” from Further Readings

⁶⁰ “Explaining Resonance—A Colorful Approach” from Further Readings

⁶¹ “A Visual Aid for Teaching the Resonance Concept” from Further Readings

⁶² “Delocalization—The Key Concept of Covalent Bonding” from Further Readings

⁶³ “Benzene” 3-D Model from Instructor’s Resource CD/DVD

⁶⁴ “Orbital Bartending” from Further Readings

⁶⁵ “Molecular Orbital Theory” Animation from Instructor’s Resource CD/DVD

⁶⁶ “Molecular Orbital Theory of Bond Order and Valency” from Further Readings

⁶⁷ “The Eye’s Photochemistry: A Quick Snap” from Further Readings

⁶⁸ “The Molecules of Visual Excitation” from Further Readings

- For example:
 - Why does O₂ interact with a magnetic field?
 - Why are some molecules colored?
- For these molecules, we use **molecular orbital theory**.
- Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in **molecular orbitals (MO)**.
- Molecular orbitals:
 - Some characteristics are similar to those of atomic orbitals.
 - Each contains a maximum of two electrons with opposite spins.
 - Each has a definite energy.
 - Electron density distribution can be visualized with contour diagrams.
 - However, unlike atomic orbitals, molecular orbitals are associated with an *entire molecule*.

The Hydrogen Molecule⁶⁹

- When two AOs overlap, two MOs form.
- Therefore, 1s (H) + 1s (H) must result in two MOs for H₂:
 - One has electron density between the nuclei (**bonding MO**);
 - One has little electron density between the nuclei (**antibonding MO**).
- **Sigma (σ) MOs** have electron density in both molecular orbitals centered about the internuclear axis.
- The σ bonding MO is lower in energy than the σ* (antibonding) MO.
- **The energy-level diagram or MO diagram** shows the energies of the orbitals in a molecule.
 - The total number of electrons in all atoms are placed in the MOs starting from lowest energy (σ_{1s}) and ending when all electrons have been accommodated.
 - Note that electrons in MOs have opposite spins.

Bond Order

- Define **bond order** = ½ (bonding electrons – antibonding electrons).
 - Bond order = 1 for single bond.
 - Bond order = 2 for double bond.
 - Bond order = 3 for triple bond.
 - Fractional bond orders are possible.
- For example, consider the molecule H₂.
 - H₂ has two bonding electrons.
 - Bond order for H₂ is:

$$\frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons}) = \frac{1}{2} (2 - 0) = 1.$$
 - Therefore, H₂ has a single bond.
- For example, consider the species He₂.
 - He₂ has two bonding electrons and two antibonding electrons.
 - Bond order for He₂ is:

$$\frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons}) = \frac{1}{2} (2 - 2) = 0.$$
 - Therefore He₂ is *not* a stable molecule.
- MO theory correctly predicts that hydrogen forms a diatomic molecule but that helium does not!

FORWARD REFERENCES

- Molecular orbitals in silicon-containing materials will be mentioned in Chapter 12 (section 12.7).

⁶⁹ Figure 9.32 from Transparency Pack

9.8 Period 2 Diatomic Molecules

- We look at homonuclear diatomic molecules (e.g., Li_2 , Be_2 , B_2 etc.).
- AOs combine according to the following rules:
 - The number of MOs = number of AOs.
 - AOs of similar energy combine (e.g., $1s + 1s$ rather than $1s + 2s$).
 - As overlap increases, the energy of the bonding MO decreases and the energy of the antibonding MO increases.
 - Pauli: each MO has at most two electrons, with spins paired.
 - Hund: for degenerate orbitals, each MO is first occupied singly before spin pairing occurs.

Molecular Orbitals for Li_2 and Be_2 ⁷⁰

- Each $1s$ orbital combines with another $1s$ orbital to give one σ_{1s} and one σ_{1s}^* orbital, both of which are occupied (since Li and Be have $1s^2$ electron configurations).
- Each $2s$ orbital combines with another $2s$ orbital to give one σ_{2s} and one σ_{2s}^* orbital.
- The energies of the $1s$ and $2s$ orbitals are sufficiently different so that there is no cross mixing of orbitals (i.e., we do not get $1s + 2s$).
- Consider the bonding in Li_2 .
 - There are a total of six electrons in Li_2 .
 - 2 electrons in σ_{1s} .
 - 2 electrons in σ_{1s}^* .
 - 2 electrons in σ_{2s} .
 - 0 electrons in σ_{2s}^* .
 - Therefore the bond order is $\frac{1}{2}(4 - 2) = 1$.
 - Since the $1s$ AOs are completely filled, the σ_{1s} and σ_{1s}^* are filled.
 - We generally ignore core electrons in MO diagrams.
 - Core electrons usually don't contribute significantly to bonding in molecule formation.
- Consider bonding in Be_2 .
 - There are a total of eight electrons in Be_2 .
 - 2 electrons in σ_{1s} .
 - 2 electrons in σ_{1s}^* .
 - 2 electrons in σ_{2s} .
 - 2 electrons in σ_{2s}^* .
 - Therefore the bond order is $\frac{1}{2}(4 - 4) = 0$.
 - Be_2 does not exist.

Molecular Orbitals from $2p$ Atomic Orbitals⁷¹

- There are two ways in which two p orbitals can overlap:
 - End on so that the resulting MO has electron density on the axis between nuclei (i.e., σ type orbital).
 - Sideways, so that the resulting MO has electron density above and below the axis between nuclei.
 - These are called **π (π) molecular orbitals**.
- The six p -orbitals (two sets of three) must give rise to six MOs:
 - σ_{2p} , σ_{2p}^* , π_{2p} , π_{2p}^* , π_{2p} and π_{2p}^* .
 - Therefore, there are a maximum of two π bonds which can come from p orbitals.
 - The relative energies of these six orbitals can change.

⁷⁰ Figure 9.35 from Transparency Pack

⁷¹ Figure 9.36 from Transparency Pack

Electron Configurations for B₂ through Ne₂^{72,73,74}

- Features of the energy-level diagrams for these elements:
 - 2s orbitals are lower in energy than 2p orbitals so both σ_{2s} orbitals (σ_{2s} and σ_{2s}^*) are lower in energy than the lowest energy MO derived from the 2p AOs.
 - There is greater overlap between 2p_z orbitals.
 - They point directly towards one another, so the σ_{2p} MO is lower in energy than the π_{2p} orbitals.
 - The σ_{2p}^* MO is higher in energy than the π_{2p}^* orbitals.
 - The π_{2p} and π_{2p}^* orbitals are doubly degenerate.
 - As the atomic number decreases, it becomes more likely that a 2s orbital on one atom can interact with the 2p orbital on the other.
 - As the 2s–2p interaction increases, the σ_{2s} MO lowers and the σ_{2p} MO increases in energy.
 - For B₂, C₂ and N₂ the σ_{2p} orbital is higher in energy than the π_{2p} .
 - For O₂, F₂ and Ne₂ the σ_{2p} orbital is lower in energy than the π_{2p} .
 - Once we know the relative orbital energies, we add the required number of electrons to the MOs, taking into account Pauli's exclusion principle and Hund's rule.
- As bond order increases,
 - bond length decreases.
 - bond energy increases.

Electron Configurations and Molecular Properties⁷⁵

- Two types of magnetic behavior:
 - **paramagnetism** (unpaired electrons in molecule)
 - strong attraction between magnetic field and molecule
 - **diamagnetism** (no unpaired electrons in molecule)
 - weak repulsion between magnetic field and molecule
- Magnetic behavior is detected by determining the mass of a sample in the presence and absence of a magnetic field:
 - A large increase in mass indicates paramagnetism.
 - A small decrease in mass indicates diamagnetism.
- Experimentally, O₂ is paramagnetic, has a short bond length (1.21 Å) and high bond dissociation energy (495 kJ/mol).
 - The Lewis structure for O₂ shows no unpaired electrons.
 - The MO diagram for O₂ shows 2 unpaired electrons in the π_{2p}^* orbital.
 - This suggests a double bond.
 - The MO diagram for O₂ predicts both paramagnetism and the double bond (bond order = 2).

Heteronuclear Diatomic Molecules

- Heteronuclear diatomic molecules contain 2 different elements.
- If both atoms do not differ greatly in electronegativity, the description of their MOs will be similar to those for homonuclear diatomic molecules.

FORWARD REFERENCES

- The HOMO and LUMO gap will be mentioned in Chapter 12 (section 12.7).
- Magnetism in coordination chemistry will be discussed in Chapter 23 (section 23.5).

⁷² Figure 9.41 from Transparency Pack

⁷³ Figure 9.42 from Transparency Pack

⁷⁴ “The Relative Energies of Molecular Orbitals for Second-Row Homonuclear Diatomic Molecules: The Effect of *s-p* Mixing” from Further Readings

⁷⁵ “Oxygen” 3-D Model from Instructor's Resource CD/DVD

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