

Chapter 3 Molecular Shape and Structure

The VSEPR Model (Sections 3.1–3.3)

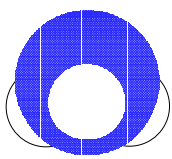
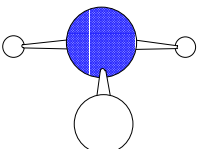
Key Concepts

molecular formula, structural formula, space-filling model, ball-and-stick model, bond angle, valence-shell electron-pair repulsion (VSEPR) model, bonding pairs, lone pairs, central atom, electron arrangement about central atom, multiple *versus* single bonds, polar bond, nonpolar bond, polar molecule, nonpolar molecule; molecular shapes: linear, angular (bent), trigonal planar, trigonal pyramidal, tetrahedral, square pyramidal, trigonal bipyramidal, octahedral, T-shaped, seesaw, square pyramidal, square planar

Representation of Molecules

- **Molecular formula** → Number and types of atoms present in the molecule or ion
- **Structural formula** → Atoms represented by chemical symbols, linked by lines
- **Lewis structure** → Atoms represented by chemical symbols, valence electrons shown as lines (*bonds*) or dots (*lone pairs*)
- **Space-filling model** → Shaded or colored shapes (atoms) that fit into one another
- **Ball-and-stick model** → Shaded or colored balls (atoms) linked by sticks (bonds)

Examples for Ammonia

Type	Example	Advantage(s)	Disadvantage(s)
Molecular formula	NH ₃	Shows chemical composition	No structural information
Structural formula	$\begin{array}{c} \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	Shows chemical connectivity (which atoms are bonded together)	Little three-dimensional structural information
Lewis structure	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$	Shows chemical connectivity and all valence electrons involved in bonding, reactivity	Little three-dimensional structural information
Space-filling model		Three-dimensional contour of molecule clearly visible	Bonds difficult to see, particularly for interior atoms
Ball-and-stick model		Atoms, connectivity, and general shape visible	Poor representation of actual bonds and atoms

3.1 The Basic VSEPR (Valence-Shell Electron-Pair Repulsion) Model

Example 3.1a Use the VSEPR model to predict the *shape* of (1) fluoromethane, CH_3F ; (2) the phosphate anion, PO_4^{3-} ; (3) sulfur hexafluoride, SF_6 ; and (4) tetrafluoroethene (tetrafluoroethylene), C_2F_4 . All are molecules with no lone pairs ($m = 0$).

Solution For each molecule, follow the general procedure outlined above.

Answer (1) The Lewis structure of CH_3F (C is the central atom) is $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\ddot{\text{F}}: \\ | \\ \text{H} \end{array}$

The molecule has 14 valence electrons. There are four bonding electron pairs around carbon. The shape is *tetrahedral*. The bond angles will *not* be exactly 109.5° because the terminal atoms are *not* all identical. The molecule CH_3F is an AX_4 species. The lone pairs on the fluorine atom are not considered because it is a *terminal* atom.

(2) One Lewis structure of PO_4^{3-} is $\left[\begin{array}{c} \ddot{\text{O}} \\ || \\ \ddot{\text{O}}-\text{P}-\ddot{\text{O}}: \\ | \\ \ddot{\text{O}}: \end{array} \right]^{3-}$

The molecule has 32 valence electrons. Because the multiple bond is counted as one electron pair (a *single* unit of high electron density), there are then four bonding electron pairs around phosphorus. The shape is again *tetrahedral*. The terminal atoms are identical. The bond angles are *exactly* 109.5° . The anion PO_4^{3-} is an AX_4 species. The Lewis structure is an example of octet expansion on the central P atom. An equally acceptable Lewis structure with four single bonds between P and O gives the same answer.

(3) The Lewis structure of SF_6 is $\begin{array}{c} \ddot{\text{F}}:\ddot{\text{F}}:\ddot{\text{F}}: \\ \diagdown \quad | \quad \diagup \\ \text{S} \\ \diagup \quad | \quad \diagdown \\ \ddot{\text{F}}:\ddot{\text{F}}:\ddot{\text{F}}: \end{array}$

The molecule has 48 valence electrons. There are six bonding electron pairs around sulfur. The shape is *octahedral*. The terminal atoms are identical. The bond angles are exactly 90° and 180° . The molecule SF_6 is an AX_6 species. The Lewis structure is an example of octet expansion on the central S atom.

(4) The Lewis structure of C_2F_4 (each C is a central atom) is $\begin{array}{c} \ddot{\text{F}}:\ddot{\text{F}}: \\ | \quad | \\ \ddot{\text{F}}:-\text{C}=\text{C}-\ddot{\text{F}}: \\ | \quad | \\ \ddot{\text{F}}:\ddot{\text{F}}: \end{array}$

The molecule has 36 valence electrons. Because the multiple bond is counted as one electron pair, there are three bonding electron pairs around each carbon atom. The shape is *trigonal planar* on each end of the molecule. The molecule C_2F_4 is an AX_3AX_3 species. As before, the lone pairs on the fluorine atoms are not considered because they are on *terminal* atoms.

Note: According to the VSEPR method, one might expect a *twisted* structure that minimizes electron repulsion for molecule (4). Experiments show, however, that this and similar molecules containing double bonds are planar overall. Its inability to predict planarity in this instance is a failing of the VSEPR method.

Example 3.1b Name the type of species according to the VSEPR formula (AX_nE_m) and predict the shapes of the following molecules (1) carbon disulfide, CS_2 , and (2) ethane, C_2H_6 . Both are molecules with no lone pairs ($m = 0$).

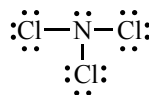
Answer (1) AX_2 , linear; (2) AX_4AX_4 , tetrahedral at each C atom

3.2 Molecules with Lone Pairs on the Central Atom

Example 3.2a Use the VSEPR model to predict the shape of (1) trichloroamine, NCl_3 ; (2) xenon tetrafluoride, XeF_4 ; (3) xenon difluoride, XeF_2 ; and (4) sulfur tetrafluoride, SF_4 . All are molecules with lone pairs ($m \neq 0$).

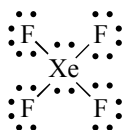
Solution Follow the general procedure used in Section 3.2 for each molecule, but consider the modifications indicated above.

Answer (1) The Lewis structure of NCl_3 (N is the central atom) is



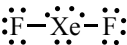
The molecule has 26 valence electrons. There are four electron pairs around nitrogen (three bonding pairs and one lone pair). The electron arrangement is *tetrahedral*. The shape is *trigonal pyramidal*. The lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair value. Therefore, the bond angles [$\angle \text{Cl-N-Cl}$] will be smaller than 109.5° . The molecule NCl_3 is an AX_3E species. The lone pairs on the chlorine atoms are not considered because they are on *terminal* atoms.

(2) The Lewis structure of XeF_4 is



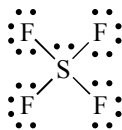
The molecule has 36 valence electrons. There are six electron pairs around xenon (four bonding pairs and two lone pairs). The electron arrangement is *octahedral*. The shape is *square planar* because the lone pairs prefer opposite corners of the octahedron. The bond angles will be 90° and 180° in the plane of the molecule. The molecule XeF_4 is an AX_4E_2 species. The lone pairs on the fluorine atoms are not considered because they are on *terminal* atoms.

(3) The Lewis structure of XeF_2 is



The molecule has 22 valence electrons. There are five electron pairs around xenon (two bonding pairs and three lone pairs). The electron arrangement is *trigonal bipyramidal*. The shape is *linear* because the lone pairs prefer the *equatorial* positions. The bond angle will be 180° . The molecule XeF_2 is an AX_2E_3 species. The lone pairs on the fluorine atoms are not considered because they are on *terminal* atoms.

(4) The Lewis structure of SF_4 is



The molecule has 34 valence electrons. There are five electron pairs around sulfur (four bonding pairs and one lone pair). The electron arrangement is *trigonal bipyramidal*. The shape is *seesaw* because the lone pair prefers one of the *equatorial* positions. The bond angles will be less than 120° in the equatorial plane and less than 90° between the axial and equatorial positions (greater repulsions between bonding and lone pair electrons than between bonding electron pairs). The molecule SF_4 is an AX_4E species. The lone pairs on the fluorine atoms are not considered because they are on *terminal* atoms.

Example 3.2b Name the type of species according to the VSEPR formula (AX_nE_m) and predict the shapes of the following molecules: (1) sulfur dioxide, SO_2 ; (2) the triiodide anion, I_3^- ; (3) iodine pentafluoride, IF_5 ; (4) methyl alcohol, CH_3OH . All are molecules with lone pairs ($m \neq 0$).

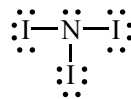
Answer (1) AX_2E , angular; (2) AX_2E_3 , linear; (3) AX_5E , square pyramidal; (4) AX_4 , tetrahedral at C, AX_2E_2 , angular at the O atom.

3.3 Polar Molecules (Review Section 2.13)

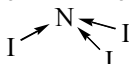
Example 3.3a Identify which, if any, of the following molecules are polar:
 (1) nitrogen triiodide, NI_3 ; (2) xenon difluoride, XeF_2 ; (3) carbon tetrachloride, CCl_4 .
 All three molecules have polar bonds.

Solution Determine the shape of the molecule by using VSEPR theory. Decide whether the symmetry of the molecule leads to a nonzero dipole moment.

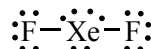
Answer (1) The Lewis structure of NI_3 (N is the central atom) is



The molecule has 26 valence electrons. The electron arrangement is *tetrahedral*. The shape is *trigonal pyramidal*. The molecule NI_3 is an AX_3E species. The bond dipoles do *not* cancel and the molecule is *polar*.



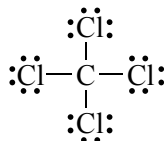
(2) The Lewis structure of XeF_2 is



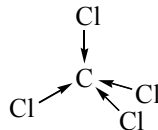
The molecule has 22 valence electrons. The electron arrangement is *trigonal bipyramidal*. The shape is *linear* because the lone pairs prefer the equatorial positions. The molecule XeF_2 is an AX_2E_3 species. The bond angle will be 180° , and the bond dipoles cancel. The molecule is *nonpolar*.



(3) The Lewis structure of CCl_4 is



The molecule has 32 valence electrons. The electron arrangement and shape are both *tetrahedral*. The molecule CCl_4 is an AX_4 species. The bond angles of 109.5° point to four of the eight corners of a cube in such a way that the bond dipoles cancel. The molecule is *nonpolar*.



Note: For *identical* terminal atoms, all VSEPR formulas with $m = 0$ yield *nonpolar* molecules. Assuming that the *bonds* are all *polar*, the formulas with $m \neq 0$ all yield *polar* molecules, except for AX_2E_3 and AX_4E_2 , which are *nonpolar*.

Example 3.3b Identify which, if any, of the following molecules are polar:
 (1) water, H_2O ; (2) methane, CH_4 ; (3) iodine trichloride, ICl_3 .

Answer (1) AX_2E_2 , angular, *polar*; (2) AX_4 , tetrahedral, *nonpolar*;
 (3) AX_3E_2 , T-shaped, *polar*.

Note: The C–H *bond* is essentially *nonpolar*. Molecules containing only C and H that have nonsymmetrical arrangements of atoms are essentially *nonpolar*.

Valence-Bond (VB) Theory (Sections 3.4–3.8)

Key Concepts

valence-bond theory, localized electron model, σ -bond, π -bond, nodal surface, overlap of atomic orbitals, single bond, double bond, triple bond, promotion, hybridization of atomic orbitals, hybrid atomic orbitals, hybridization schemes and relation to geometry, sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , hydrocarbons, alkanes, alkenes, alkynes, properties of double bonds

3.4 Sigma (σ) and Pi (π) Bonds

Example 3.4a Use the valence-bond theory to describe the bonding in (1) H_2 ; (2) HCl ; (3) O_2 .

- Answer**
- (1) In H_2 , each H atom has one unpaired electron in a $1s$ -orbital. Two H atoms with *opposite* spins are brought together to form H_2 . The two $1s$ -orbitals overlap to form *one* σ -bond (paired electrons).
 - (2) In HCl , the H atom has one unpaired electron in a $1s$ -orbital; the Cl atom has one unpaired electron in a $3p$ -orbital. The two orbitals overlap end-to-end to form *one* σ -bond (paired electrons).
 - (3) In O_2 , the O atom ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) has two unpaired electrons. The half-occupied $2p_z$ -orbitals overlap end-to-end with each other to form *one* σ -bond. The half-occupied $2p_y$ -orbitals overlap side-by-side to form *one* π -bond. Thus, O_2 has a *double bond* consisting of *one* σ -bond and *one* π -bond (an electron pair in each bond). The two electrons in a bonding pair have opposite spins.

Note: The z -axis is customarily chosen to be the bond axis.

Note: The *molecular orbital theory* has an improved description of the bonding in the O_2 molecule, which is a *biradical* (see Sections 2.10 and 3.11).

Example 3.4b Use the valence-bond theory to describe the bonding in (1) CO ; (2) NO^- ; (3) Li_2 (gas-phase, high temperature molecule).

- Answer**
- (1) triple bond: *one* σ -bond and *two* π -bonds [isoelectronic with N_2]
 - (2) double bond: *one* σ -bond and *one* π -bond [isoelectronic with O_2]
 - (3) single bond: *one* σ -bond [two $2s$ -orbitals overlapping]

3.5 Hybridization of Orbitals

Example 3.5a Use the valence-bond theory and hybridization to describe the bonding in BF_3 .

Solution The ground-state electron configuration of B is $[He]2s^2 2p_x^1$. The molecule BF_3 has a *trigonal-planar* shape with three equal B–F single bonds (using the VSEPR technique). To account for this with the VB theory, *promote* one $2s$ -electron on B to a vacant $2p$ -orbital $\{2s^2 2p_x^1 \rightarrow 2s^1 2p_x^1 2p_y^1\}$. *Mix* or *hybridize* the resulting half-filled valence orbitals (one $2s$ - and two $2p$ -orbitals) to get *three* sp^2 hybrid orbitals, each with one unpaired electron. Now overlap *one* hybrid orbital with one $2p$ -orbital of F (end-to-end). Overlap a *second* hybrid orbital of B with a $2p$ -orbital of another F. Repeat with the *third* hybrid orbital and the last F atom. One obtains three σ -bonds $[B(sp^2)-F(2p)]$.

Example 3.5b Use the valence-bond theory and hybridization to describe the bonding in CH_4 .

Answer There are four σ -bonds $[\text{C}(sp^3)\text{--H}(1s)]$. See Section 3.5 in the text.

Note: Valence atomic orbitals that are empty *or* that are needed to make π -bonds are *not* hybridized, unless they are needed to produce coordinate covalent σ -bonds (as in BF_4^-).

Example 3.5c Use the VB theory to predict the hybridization, shape, and bond angle(s) in (1) trichloroamine, NCl_3 ; (2) xenon tetrafluoride, XeF_4 ; (3) xenon difluoride, XeF_2 ; (4) sulfur tetrafluoride, SF_4 . See the Lewis structures in Example 3.2a.

Solution Follow the general hybridization scheme for each molecule.

- Answer**
- (1) According to its Lewis structure, NCl_3 has one lone pair and *three* σ -bonds to the central N atom. *Four* valence atomic orbitals on N must be hybridized to form four sp^3 hybrid orbitals. Three of the hybrid orbitals overlap end-to-end with three $3p$ -orbitals on Cl to form three σ -bonds. The remaining hybrid orbital on N contains the lone-pair electrons. The electron arrangement is *tetrahedral*. The shape is *trigonal pyramidal*. The lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair value. Therefore, the bond angles will be smaller than 109.5° . The same adjustments to the bond angle(s) are used as in the VSEPR model.
 - (2) According to its Lewis structure, XeF_4 has two lone pairs and four σ -bonds to the central Xe atom. Six valence atomic orbitals on Xe must be hybridized to form six sp^3d^2 hybrid orbitals. *Four* of the hybrid orbitals overlap end-to-end with four $2p$ -orbitals on F to form four σ -bonds. The remaining two hybrid orbitals on Xe contain the two lone pairs. The electron arrangement is *octahedral*. The shape is *square planar* because the lone pairs prefer opposite corners of the octahedron. The bond angles will be 90° and 180° in the plane of the molecule.
 - (3) According to its Lewis structure, XeF_2 has three lone pairs and two σ -bonds to the central Xe atom. Five valence atomic orbitals on Xe must be hybridized to form five sp^3d hybrid orbitals. Two of the hybrid orbitals overlap end-to-end with two $2p$ -orbitals on F to form two σ -bonds. The remaining three hybrid orbitals on Xe contain the three lone pairs. The electron arrangement is *trigonal bipyramidal*. The shape is *linear* because the lone pairs prefer the equatorial positions. The bond angle will be 180° .
 - (4) According to its Lewis structure, SF_4 has one lone pair and four σ -bonds to the central S atom. Five valence atomic orbitals on S must be hybridized to form five sp^3d hybrid orbitals. Four of the hybrid orbitals overlap end-to-end with four $2p$ -orbitals on F to form four σ -bonds. The last hybrid orbital contains the lone pair. The electron arrangement is *trigonal bipyramidal*. The shape is *seesaw*, because the lone pair prefers one of the equatorial positions. The bond angles will be less than 120° in the equatorial plane and less than 90° between the axial and equatorial positions (greater repulsions between bonding and lone pair electrons than between bonding electron pairs).

Example 3.5d Use the VB theory to predict the hybridization, shape, and bond angle(s) in (1) sulfur dioxide, SO_2 ; (2) the triiodide anion, I_3^- ; (3) iodine pentafluoride, IF_5 ; (4) methyl alcohol, CH_3OH . See Example 3.2b.

Answer (1) **S**: sp^2 (three), angular, $<120^\circ$; (2) **I**: sp^3d (five), linear, 180° ; (3) **I**: sp^3d^2 (six), square pyramidal, $<90^\circ$ and $<180^\circ$; (4) **C**: sp^3 (four), tetrahedral, $\sim 109.5^\circ$ and **O**: sp^3 (four), angular, $<109.5^\circ$.

3.6 Hybridization in More Complex Molecules

Example 3.6a Use the VB theory to describe the geometry and bonding in acetaldehyde, CH_3CHO , a molecule with *two* central atoms.

Solution The Lewis structure shows *two* central C atoms: one with a *tetrahedral* electron arrangement (sp^3 hybridization, methyl carbon atom) and one with a *trigonal-planar* electron arrangement (sp^2 hybridization, aldehyde carbon atom). The Lewis structure and three-dimensional representation are



The C–C σ -bond forms from the overlap of an sp^3 hybrid orbital on the methyl C atom with an sp^2 hybrid orbital on the aldehyde C atom: σ -bond $[\text{C}(sp^3)\text{--C}(sp^2)]$.

The C=O σ -bond forms from the overlap of an sp^2 hybrid on the aldehyde C atom with one $2p$ -orbital on the oxygen atom: σ -bond $[\text{C}(sp^2)\text{--O}(2p)]$.

Each of three C–H single bonds forms from the overlap of an sp^3 hybrid on the methyl C atom with an H $1s$ -orbital: three σ -bonds $[\text{C}(sp^3)\text{--H}(1s)]$.

One C–H single bond forms from the overlap of an sp^2 hybrid orbital on the aldehyde C atom with an H $1s$ -orbital: one σ -bond $[\text{C}(sp^2)\text{--H}(1s)]$.

The C=O π -bond is formed by the side-by-side overlap of a $2p$ -orbital on C with a $2p$ -orbital on O (unhybridized orbitals): one π -bond $[\text{C}(2p)\text{--O}(2p)]$.

The shape of acetaldehyde is *tetrahedral* at the methyl C atom and *trigonal planar* at the aldehyde C-atom. Bonding consists of a C–C single (σ) bond, four C–H single (σ) bonds and a C=O double bond (σ plus π) formed from the atomic and hybrid orbitals given above.

The bond angles are three $\angle \text{H--C--H} \sim 109.5^\circ$, three $\angle \text{H--C--C} \sim 109.5^\circ$, one $\angle \text{C--C=O} \sim 120^\circ$, one $\angle \text{O=C--H} \sim 120^\circ$, and one $\angle \text{C--C--H} \sim 120^\circ$.

Note: In acetaldehyde, the methyl group is relatively free to rotate with respect to the aldehyde group about the C–C σ -bond.

Example 3.6b Describe the geometry, hybridization, and bonding in methylacetylene, HCCCH_3 , a molecule with *three* central atoms.

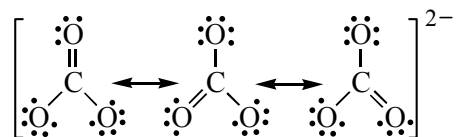
Answer The *shape* at C atoms: *linear*, *linear*, *tetrahedral*. *Hybridization* at C atoms: sp , sp , sp^3 . *Bonding*: four C–H σ -bonds, one $\text{C}\equiv\text{C}$ triple bond (one σ plus two π), one C–C σ -bond. *Bond angles*: one $\angle \text{H--C}\equiv\text{C} = 180^\circ$, one $\angle \text{C}\equiv\text{C--C} = 180^\circ$, three $\angle \text{C--C--H} \sim 109.5^\circ$, three $\angle \text{H--C--H} \sim 109.5^\circ$.

3.8 Characteristics of Double Bonds

Example 3.8a Describe the structure of the carbonate anion, CO_3^{2-} , in terms of hybrid orbitals, bond angles, and σ - and π -bonds.

Solution The Lewis structure given below implies a trigonal-planar geometry with sp^2 hybridization at C and $120^\circ \angle \text{O--C--O}$ bond angles. The nonhybridized C $2p$ -orbital can overlap with O $2p$ -orbitals to form a π -bond in each of three ways corresponding to

the resonance structures below. Therefore, each carbon-oxygen bond can be viewed as one σ -bond and one-third of a π -bond.



Example 3.8b Describe the structure of the nitrite anion, NO_2^- , in terms of hybrid orbitals, bond angles, and σ - and π -bonds.

Answer There is sp^2 hybridization at N and somewhat less than a $120^\circ \angle \text{O}-\text{N}-\text{O}$ bond angle. The nonhybridized N $2p$ -orbital can overlap with O $2p$ -orbitals to form a π -bond in each of two ways. Each nitrogen-oxygen bond can be viewed as one σ -bond and one-half of a π -bond.

Molecular Orbital (MO) Theory (Sections 3.9–3.13)

Key Concepts

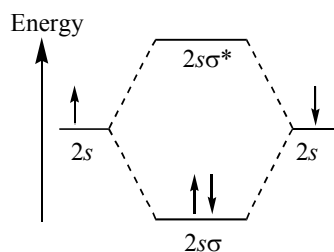
electron-deficient compound, paramagnetism, diamagnetism, molecular orbital (MO), linear combination of atomic orbitals (LCAO), bonding orbital, antibonding orbital, nonbonding orbital, molecular orbital energy-level diagram (correlation diagram), σ -orbital, π -orbital, homonuclear diatomic molecule, bond order, heteronuclear diatomic molecule, delocalized electrons, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), electronic conductor, metallic conductor, semiconductor, superconductor, insulator, band theory, conduction band, valence band, band gap, doping, n-type semiconductor, p-type semiconductor, p-n junctions

3.10 Molecular Orbitals (MOs)

Example 3.10a Show schematically the overlap of two $2s$ AOs on adjacent Li atoms to form a $2s\sigma$ -bonding orbital (constructive interference) and a $2s\sigma^*$ -antibonding orbital (destructive interference). Draw an energy-level diagram to show that the bonding MO is lower in energy than the atomic $2s$ -orbitals and the antibonding MO is higher in energy by about the same amount. Consider the Li_2 molecule. Show the locations of the two valence electrons in both the *separated* atomic orbitals and the molecular orbitals in the energy-level diagram.

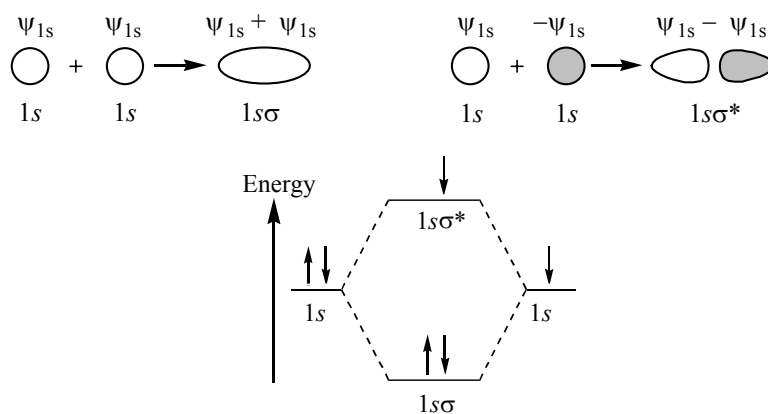
Solution





Example 3.10b Show schematically the overlap of two $1s$ AOs on adjacent H atoms to form a $1s\sigma$ -bonding orbital (constructive interference) and a $1s\sigma^*$ -antibonding orbital (destructive interference). Draw an energy-level diagram to show that the bonding MO is lower in energy than the atomic $1s$ -orbitals and the antibonding MO is higher in energy by about the same amount. Consider the H_2^- molecular anion. Show the locations of the three valence electrons in both the *separated* atomic orbitals and the molecular orbitals in the energy-level diagram.

Solution



3.11 The Electron Configurations of Diatomic Molecules

Example 3.11a Determine the bond order in Li_2 . See Example 3.10a for the correlation diagram.

Solution There are two electrons in the $2s\sigma$ -bonding MO, so $N = 2$. There are no electrons in the $2s\sigma^*$ -antibonding MO, so $N^* = 0$. The bond order is $\frac{1}{2}(2 - 0) = 1$.
This picture is similar to the VB theory with a single σ -bond between the Li atoms.

Example 3.11b Determine the bond order in H_2^- . See Example 3.10b for the correlation diagram.

Solution There are two electrons in the $1s\sigma$ -bonding MO, so $N = 2$. There is one unpaired electron in the $1s\sigma^*$ -antibonding MO, so $N^* = 1$. The bond order is $\frac{1}{2}(2 - 1) = 1/2$.
The MO theory predicts a net bond that is *half* a single bond value.

Note: The ultimate stability of molecular anions requires a more detailed treatment. The H_2^- anion is actually unstable in the gas phase, as is Li_2^- . The ion H_2^- is bound with respect to its dissociation to a neutral hydrogen atom and an atomic hydrogen anion. The ion is not stable, however, with respect to the neutral hydrogen molecule, which is formed after the extra electron detaches [$\text{H}_2^- \rightarrow \text{H}_2 + \text{e}^-$]. The consequence of this behavior is that the electron affinity E_{ea} of H_2 is less than zero. The homonuclear diatomic molecules in Period 2 with *positive* values of E_{ea} (stable molecular anions) are C_2 , O_2 , and F_2 .

Example 3.11c Determine the ground-state, valence-shell electron MO configuration, number of unpaired electrons and bond order for (1) Li_2^+ and (2) C_2 .

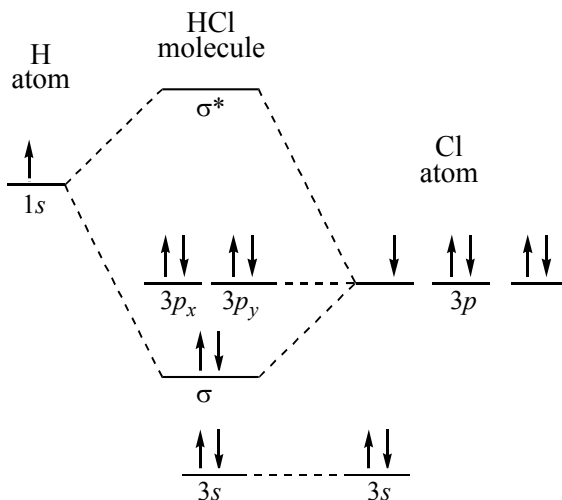
- Solution**
- (1) The molecular ion Li_2^+ has *one* valence electron, which should be placed in the $2s\sigma$, which is a bonding MO. The valence electron configuration is $(2s\sigma)^1$, which represents one unpaired electron. $N = 1$ and $N^* = 0$. Bond order $= \frac{1}{2}(1 - 0) = 1/2$.
The molecular ion is stable in the gas phase.
- (2) The molecule C_2 has *eight* valence electrons, which should be placed in the $2s\sigma$, $2s\sigma^*$, and two *degenerate* $2p\pi$ MOs. The valence electron configuration is $(2s\sigma)^2 (2s\sigma^*)^2 (2p\pi)^4$, which represents all paired electrons. $N = 6$ and $N^* = 2$. Bond order $= \frac{1}{2}(6 - 2) = 2$.
The MO theory predicts an *unusual* double bond: *two* π -bonds and *no* σ -bond. The molecule is very stable and is found in flames and interstellar space.

Example 3.11d Determine the ground-state, valence-shell electron MO configuration, number of unpaired electrons and bond order for (1) O_2^+ and (2) Be_2 .

- Solution**
- (1) The molecular ion O_2^+ has *eleven* valence electrons, which should be placed in the $2s\sigma$, $2s\sigma^*$, $2p\sigma$, two *degenerate* $2p\pi$, and one of the *degenerate* $2p\pi^*$ MOs. The valence electron configuration is $(2s\sigma)^2 (2s\sigma^*)^2 (2p\sigma)^2 (2p\pi)^4 (2p\pi^*)^1$, which represents one unpaired electron. $N = 8$ and $N^* = 3$. Bond order $= \frac{1}{2}(8 - 3) = 5/2$.
The MO theory predicts unusual bonding: *one* σ -bond and *one* and *one-half* π -bonds. The bond order is greater than in O_2 [$\text{BO} = 2$], which has *two* unpaired electrons and is *paramagnetic*. The molecular ion is stable in the gas phase.
- (2) The molecule Be_2 has *four* valence electrons, which are placed in the $2s\sigma$ and $2s\sigma^*$ MOs. The valence electron configuration is $(2s\sigma)^2 (2s\sigma^*)^2$, which represents full pairing of electrons. $N = 2$ and $N^* = 2$. Bond order $= \frac{1}{2}(2 - 2) = 0$.
The MO theory predicts *no* chemical bond.

3.12 Bonding in Heteronuclear Diatomic Molecules

Example 3.12 Using a MO energy-level diagram, describe the bonding in HCl and give the electron configuration of its *valence* electrons.



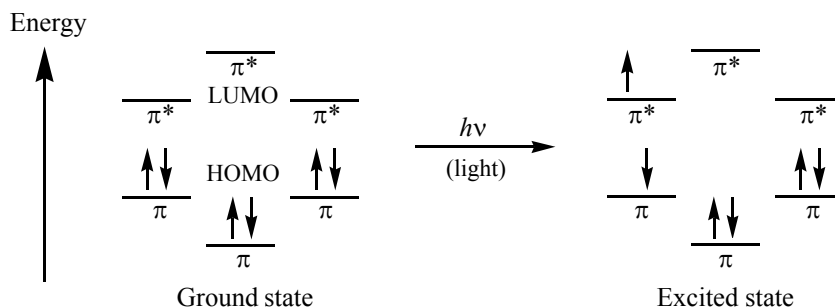
Solution

The valence orbitals are H [$1s$ -orbital], Cl [$3s$ - and three $3p$ -orbitals]. The more electronegative atom is Cl, so we expect the $3s$ - and $3p$ -orbitals of Cl to be lower in energy than the $1s$ -orbital of H. The polar covalent bond of H–Cl is formed from the overlap of the H $1s$ -orbital and the Cl $3p_z$ -orbital. (The z -axis is customarily chosen to be the bond axis.) The correlation diagram shows the resulting σ -bonding orbital and σ^* -antibonding orbital. The electronic configuration is $(\text{Cl } 3s)^2 \sigma^2 (\text{Cl } 3p_x)^2 (\text{Cl } 3p_y)^2$.

Note: The Cl $3s$ -orbital is a *nonbonding* σ MO, and the Cl $3p_x$ - and Cl $3p_y$ -orbitals are *nonbonding* π MOs.

3.13 Orbitals in Polyatomic Molecules

Example 3.13a Consider the *delocalized* π -electron system in benzene. The ultraviolet absorption spectrum of benzene is interpreted as the excitation of an electron from the *highest occupied molecular orbital* (**HOMO**) to the *lowest unoccupied molecular orbital* (**LUMO**). In benzene, the HOMO is a *bonding* π MO and the LUMO is an *antibonding* π^* MO. The bond order of the π -system changes from 3 to 2. The schematic energies and electron occupancies of the π and π^* MOs are



Example 3.13b Consider the HCl molecule described in Example 3.12. As in the case of benzene, the ultraviolet absorption spectrum is interpreted as the excitation of an electron from a HOMO to a LUMO. In the case of HCl, the HOMO is a *nonbonding* π MO (Cl $3p_x$ or Cl $3p_y$) and the LUMO is an *antibonding* σ^* MO. The bond order of the molecule changes from 1 to 0.5.