# Chapter 10 Theories of Covalent Bonding

**END–OF–CHAPTER PROBLEMS**

10.1 Plan: Table 10.1 describes the types of hybrid orbitals that correspond to the various electron-group arrangements. The number of hybrid orbitals formed by a central atom is equal to the number of electron groups arranged around that central atom.

Solution:

1. trigonal planar: three electron groups - three hybrid orbitals: ***sp*2**

b) octahedral: six electron groups - six hybrid orbitals: ***sp*3*d*2**

c) linear: two electron groups - two hybrid orbitals: ***sp***

d) tetrahedral: four electron groups - four hybrid orbitals: ***sp*3**

e) trigonal bipyramidal: five electron groups - five hybrid orbitals: ***sp*3*d***

10.3 Carbon and silicon have the same number of valence electrons, but the outer level of electrons is *n* = 2 for carbon and *n* = 3 for silicon. Thus, silicon has3*d* orbitals in addition to 3*s* and3*p* orbitals available for bonding in its outer level, to form up to six hybrid orbitals, whereas carbon has only2*s* and2*p* orbitals available in its outer level to form up to four hybrid orbitals.

10.5 Plan: The *number* of hybrid orbitals is the same as the number of atomic orbitals before hybridization. The *type* depends on the orbitals mixed. The name of the type of hybrid orbital comes from the number and type of atomic orbitals mixed. The number of each type of atomic orbital appears as a superscript in the name of the hybrid orbital.

Solution:

a) There are six unhybridized orbitals, and therefore **six** hybrid orbitals result. The type is ***sp*3*d*2** since one *s*,

three *p*, and two *d* atomic orbitals were mixed.

b) **Four *sp*3** hybrid orbitals form from three *p* and one *s* atomic orbitals.

10.7 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central nitrogen atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

a) The three electron groups (one double bond, one lone pair, and one unpaired electron) around

nitrogen require three hybrid orbitals. The hybridization is ***sp*2**.



b) The nitrogen has three electron groups (one single bond, one double bond, and one unpaired

electron), requiring three hybrid orbitals so the hybridization is ***sp*2**.



c) The nitrogen has three electron groups (one single bond, one double bond, and one lone pair) so the hybridization is ***sp*2**.



10.9 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central chlorine atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

a) The Cl has four electron groups (one lone pair, one lone electron, and two double bonds) and therefore four hybrid orbitals are required; the hybridization is ***sp*3**. Note that in ClO2, the *π* bond is formed by the overlap of *d* orbitals from chlorine with *p* orbitals from oxygen.



b) The Cl has four electron groups (one lone pair and three bonds) and therefore four hybrid orbitals are required; the hybridization is ***sp*3**.



c) The Cl has four electron groups (four bonds) and therefore four hybrid orbitals are required;

the hybridization is ***sp*3**.



10.11 Plan: Draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Once the type of hybridization is known, the types of atomic orbitals that will mix to form those hybrid orbitals are also known.

Solution:

a) Silicon has four electron groups (four bonds) requiring four hybrid orbitals; four *sp*3 hybrid orbitals are made from **one *s* and three *p* atomic orbitals**.



b) Carbon has two electron groups (two double bonds) requiring two hybrid orbitals; two *sp* hybrid orbitals are made from **one *s* and one *p* orbital**.



c) Sulfur is surrounded by five electron groups (four bonding pairs and one lone pair), requiring five hybrid orbitals; five *sp*3*d* hybrid orbitals are formed from **one *s* orbital, three *p* orbitals, and one *d* orbital**.



d) Nitrogen is surrounded by four electron groups (three bonding pairs and one lone pair) requiring four hybrid orbitals; four *sp*3 hybrid orbitals are formed from **one *s* orbital and three *p* orbitals**.



10.13 Plan: To determine hybridization, draw the Lewis structure of the reactants and products and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Recall that *sp* hydrid orbitals are oriented in a linear geometry, *sp*2 in a trigonal planar geometry, *sp*3 in a tetrahedral geometry, *sp*3*d* in a trigonal bipyramidal geometry, and *sp*3*d*2 in an octahedral geometry.

Solution:

a) The P in PH3 has four electron groups (one lone pair and three bonds) and therefore four hybrid

orbitals are required; the hybridization is *sp*3. The P in the product also has four electron groups

(four bonds) and again four hybrid orbitals are required. The hybridization of P remains *sp*3. There is no change in hybridization. Illustration **B** best shows the hybridization of P during the reaction as ***sp*3 *→ sp*3***.*

b) The B in BH3 has three electron groups (three bonds) and therefore three hybrid orbitals are

required; the hybridization is *sp*2. The B in the product has four electron groups (four bonds) and four hybrid orbitals are required. The hybridization of B is now *sp*3. The hybridization of B changes from ***sp*2 to *sp*3**; this is best shown by illustration **A**.



10.15 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Write the electron configuration of the central atom and mix the appropriate atomic orbitals to form the hybrid orbitals.

Solution:

a) Germanium is the central atom in GeCl4. Its electron configuration is [Ar]4*s*23*d*104*p*2. Ge has four electron groups (four bonds), requiring four hybrid orbitals. Hybridization is *sp*3 around Ge. One of the 4*s* electrons is moved to a 4*p* orbital and the four orbitals are hybridized.





Isolated Ge atom Hybridized Ge atom

b) Boron is the central atom in BCl3. Its electron configuration is [He]2*s*22*p*1. B has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is *sp*2 around B. One of the 2*s* electrons is moved to an empty 2*p* orbital and the three atomic orbitals are hybridized. One of the 2*p* atomic orbitals is not involved in the hybridization.





Isolated B atom Hybridized B atom

c) Carbon is the central atom in CH3+. Its electron configuration is [He]2*s*22*p*2. C has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is *sp*2 around C.

One of the 2*s* electrons is moved to an empty 2*p* orbital; three orbitals are hybridized and one electron is removed to form the +1 ion.



 Isolated C atom Hybridized C atom

10.17 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. Write the electron configuration of the central atom and mix the appropriate atomic orbitals to form the hybrid orbitals.

Solution:

a) In SeCl2, Se is the central atom and has four electron groups (two single bonds and two lone pairs), requiring four hybrid orbitals so Se is *sp*3 hybridized. The electron configuration of Se is [Ar]4*s*23*d*104*p*4. The 4*s* and 4*p* atomic orbitals are hybridized. Two *sp*3 hybrid orbitals are filled with lone electron pairs and two *sp*3 orbitals bond with the chlorine atoms.





b) In H3O+, O is the central atom and has four electron groups (three single bonds and one lone pair), requiring four hybrid orbitals. O is *sp*3 hybridized. The electron configuration of O is [He]2*s*22*p*4. The 2*s* and 2*p* orbitals are hybridized. One *sp*3 hybrid orbital is filled with a lone electron pair and three *sp*3 orbitals bond with the hydrogen atoms.





c) I is the central atom in IF4– with six electron groups (four single bonds and two lone pairs) surrounding it. Six hybrid orbitals are required and I has *sp*3*d*2 hybrid orbitals. The *sp*3*d*2 hybrid orbitals are composed of one *s* orbital, three *p* orbitals, and two *d* orbitals. Two *sp*3*d*2 orbitals are filled with a lone pair and four *sp*3*d*2 orbitals bond with the fluorine atoms.





10.20 Plan: A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two bonds. A  bond is the result of orbitals overlapping side to side.

Solution:

a) **False**, a double bond is one σ and one  bond.

b) **False**, a triple bond consists of one σ and two  bonds.

c) **True**

d) **True**

e) **False**, a  bond consists of one pair of electrons; it occurs after a σ bond has been previously formed.

f) **False**, end-to-end overlap results in a bond with electron density along the bond axis.

10.21 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

Solution:

a) Nitrogen is the central atom in NO3–. Nitrogen has three surrounding electron groups (two single bonds and one double bond), so it is ***sp*2** hybridized. Nitrogen forms **three  bonds** (one each for the N–O bonds) and **one  bond** (part of the N=O double bond).



b) Carbon is the central atom in CS2. Carbon has two surrounding electron groups (two double bonds), so it is ***sp*** hybridized. Carbon forms **two  bonds** (one each for the C–S bonds) and **two  bonds** (part of the two C=S double bonds).



c) Carbon is the central atom in CH2O. Carbon has three surrounding electron groups (two single bonds and one double bond), so it is ***sp*2** hybridized. Carbon forms **three  bonds** (one each for the two C–H bonds and one C–O bond) and **one  bond** (part of the C=O double bond).



10.23 Plan: To determine hybridization, draw the Lewis structure and count the number of electron groups around the central nitrogen atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

Solution:

a) In FNO, three electron groups (one lone pair, one single bond, and one double bond) surround the central N atom. Hybridization is ***sp*2** around nitrogen. One  bond exists between F and N, and one  and one  bond exist between N and O. Nitrogen participates in a total of **2 σ and 1 π bonds**.



b) In C2F4, each carbon has three electron groups (two single bonds and one double bond) with ***sp*2** hybridization. The bonds between C and F are  bonds. The C–C bond consists of one  and one  bond. Each carbon participates in a total of **three σ and one π bonds**.



c) In (CN)2, each carbon has two electron groups (one single bond and one triple bond) and is ***sp*** hybridized with a  bond between the two carbon atoms and a  and two  bonds comprising each C–N triple bond. Each carbon participates in a total of **two σ and two π bonds**.



10.25 Plan: A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

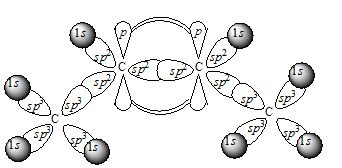
Solution:

The double bond in 2-butene restricts rotation of the molecule, so that *cis* and *trans* structures result. The two structures are shown below:



*cis* *trans*

The carbon atoms participating in the double bond each have three surrounding groups, so they are *sp*2 hybridized. The =C–H  bonds result from the head-on overlap of a C *sp*2 orbital and an H *s* orbital. The C–CH3 bonds are also  bonds, resulting from the head-on overlap of an *sp*2 orbital and an *sp*3 orbital. The C=C bond contains 1 σ bond (head on overlap of two *sp*2 orbitals) and 1  bond (sideways overlap of unhybridized *p* orbitals). Finally, C–H bonds in the methyl (–CH3) groups are  bonds resulting from the overlap of the *sp*3 orbital of C with the *s* orbital of H.



10.26 Four molecular orbitals form from the four *p* atomic orbitals. In forming molecular orbitals, the total number of molecular orbitals must equal the number of atomic orbitals. Two of the four molecular orbitals formed are bonding orbitals and two are antibonding.

10.28 a) Bonding MOs have lower energy than antibonding MOs. The bonding MO’s lower energy, even lower than its constituent atomic orbitals, accounts for the stability of a molecule in relation to its individual atoms. However, the sum of energy of the MOs must equal the sum of energy of the AOs.

b) The node is the region of an orbital where the probability of finding the electron is zero, so the nodal plane is the plane that bisects the node perpendicular to the bond axis. There is no node along the bond axis (probability is positive between the two nuclei) for the bonding MO. The antibonding MO does have a nodal plane.

c) The bonding MO has higher electron density between nuclei than the antibonding MO.

10.30 Plan: Like atomic orbitals, any one MO holds a maximum of two electrons. Two atomic orbitals combine to form two molecular orbitals, a bonding and an antibonding MO.

Solution:

a) **Two** electrons are required to fill a σ-bonding molecular orbital. Each molecular orbital requires two electrons.

b) **Two** electrons are required to fill a π-antibonding molecular orbital. There are two π-antibonding orbitals, each holding a maximum of two electrons.

c) **Four** electrons are required to fill the two σ molecular orbitals (two electrons to fill the σ-bonding and two to fill the σ-antibonding) formed from two 1*s* atomic orbitals.

10.32 Plan: Recall that a bonding MO has a region of high electron density between the nuclei while an antibonding MO has a node, or region of zero electron density between the nuclei. MOs formed from *s* orbitals, or from *p* orbitals overlapping end to end, are called and MOs formed by the side-to-side overlap of *p* orbitals are called . A superscript star (\*) is used to designate an antibonding MO. To write the electron configuration of F2+, determine the number of valence electrons and write the sequence of MO energy levels, following the sequence order given in the text.

Solution:

a) A is the **\*2*p*** molecular orbital (two *p* orbitals overlapping side to side with a node between them); B is the **2*p*** molecular orbital (two *p* orbitals overlapping end to end with no node); C is the **2*p*** molecular orbital (two *p* orbitals overlapping side to side with no node); D is the **\*2*p*** molecular orbital (two *p* orbitals overlapping end to end with a node).

b) F2+ has thirteen valence electrons: [2 x F(7e–) – 1 (from + charge)]. The MO electron configuration is (σ2*s*)2(\*2*s*)2(2*p*)2(2*p*)2(2*p*)2(\*2*p*)2(\*2*p*)1. The **\*2*p*** molecular orbital, A, **2*p*** molecular orbital, B, and **2*p*** molecular orbital, C, are all occupied by at least one electron. The **\*2*p*** molecular orbital is unoccupied.

c) A **\*2*p*** molecular orbital, A, has only one electron.

10.34 Plan: To write the electron configuration of Be2+, determine the number of electrons and write the sequence of MO energy levels, following the sequence order given in the text. Bond order = ½[(no. of electrons in bonding MO) – (no. of electrons in antibonding MO)]. Recall that a diamagnetic substance has no unpaired electrons.

Solution:

a) Be2+ has a total of seven electrons [2 x Be(4e–) – 1 (from + charge)]. The molecular orbital configuration is (σ1*s*)2(\*1*s*)2(σ2*s*)2(\*2*s*)1 and bond order = ½(4 – 3) = 1/2. With a bond order of 1/2 the Be2+ ion will be **stable**.

b) No, the ion has one unpaired electron in the \*2*s*MO, so it is **paramagnetic**, not diamagnetic.

c) Valence electrons would be those in the molecular orbitals at the *n* = 2 level, so the valence electron configuration is **(σ2*s*)2(\*2*s*)1**.

10.36 Plan: Write the electron configuration of each species by determining the number of electrons and writing the sequence of MO energy levels, following the sequence order given in the text. Calculate the bond order: bond order = ½[(no. of electrons in bonding MO) – (no. of electrons in antibonding MO)]. Bond energy increases as bond order increases; bond length decreases as bond order increases.

Solution:

C2– Total electrons = 6 + 6 + 1 = 13

MO configuration: (σ1*s*)2(\*1*s*)2(σ2*s*)2(\*2*s*)2(π2*p*)4(σ2*p*)1

Bond order = 1/2(9 – 4) = 2.5

C2 Total electrons = 6 + 6 = 12

MO configuration: (σ1*s*)2(\*1*s*)2(σ2*s*)2(\*2*s*)2(π2*p*)4

Bond order = 1/2(8 – 4) = 2

C2+ Total electrons = 6 + 6 – 1 = 11

MO configuration: (σ1*s*)2(\*1*s*)2(σ2*s*)2(\*2*s*)2(π2*p*)3

Bond order = 1/2(7 – 4) = 1.5

a) Bond energy increases as bond order increases: **C2+ < C2 < C2–**

b) Bond length decreases as bond energy increases, so the order of increasing bond length will be opposite that of increasing bond energy. Increasing bond length: **C2– < C2 < C2+**

10.40 Plan: To determine hybridization, count the number of electron groups around each of the C, O, and N atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

Solution:

a) Each of the six C atoms in the ring has three electron groups (two single bonds and a double bond) and has ***sp*2** hybridization; all of the other C atoms have four electron groups (four single bonds) and have ***sp*3** hybridization; all of the O atoms have four electron groups (two single bonds and two lone pairs) and have ***sp*3** hybridization; the N atom has four electron groups (three single bonds and a lone pair) and has ***sp*3** hybridization.

b) Each of the single bonds is a  bond; each of the double bonds has one  bond for a total of **26  bonds**.

c) The ring has three double bonds each of which is composed of one  bond and one  bond; so there are three  bonds each with two electrons for a total of **six electrons.**

10.42 Plan: To determine hybridization, count the number of electron groups around each C and N atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

Solution:

a) Every single bond is a  bond. There is one  bond in each double bond as well. There are **17 ** bonds in isoniazid. Every atom-to-atom connection contains a  bond.

b) All carbon atoms have three surrounding electron groups (two single and one double bond), so their hybridization is ***sp*2**. The ring N also has three surrounding electron groups (one single bond, one double bond, and one lone pair), so its hybridization is also ***sp*2**. The other two N atoms have four surrounding electron groups (three single bonds and one lone pair) and are ***sp*3** hybridized.

10.44 Plan: To determine the hybridization in each species, count the number of electron groups around the underlined atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

a) B changes from ***sp*2 → *sp*3**. Boron in BF3 has three electron groups with *sp*2 hybridization. In BF4–, four electron groups surround B with *sp*3 hybridization.



b) P changes from ***sp*3 → *sp*3*d***. Phosphorus in PCl3 is surrounded by four electron groups (three bonds to Cl and one lone pair) for *sp*3 hybridization. In PCl5, phosphorus is surrounded by five electron groups for *sp*3*d* hybridization.



c) C changes from ***sp* → *sp*2**. Two electron groups surround C in C2H2 and three electron groups surround C in C2H4.



d) Si changes from ***sp*3 → *sp*3*d*2**. Four electron groups surround Si in SiF4 and six electron groups surround Si in SiF62–.



e) **No change**, S in SO2 is surrounded by three electron groups (one single bond, one double

bond, and one lone pair) and in SO3 is surrounded by three electron groups (two single bonds and one double bond); both have *sp*2 hybridization.



10.46 Plan: To determine the molecular shape and hybridization, count the number of electron groups around the P, N, and C atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

P (3 single bonds and 1 double bond) AX4 **tetrahedral** ***sp*3**

N (3 single bonds and 1 lone pair) AX3E **trigonal pyramidal** ***sp*3**

C1 and C2 (4 single bonds) AX4 **tetrahedral** ***sp*3**

C3 (2 single bonds and 1 double bond) AX3 **trigonal planar** ***sp*2**

10.51 Plan: To determine the hybridization, count the number of electron groups around the atoms. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group.

Solution:

a) **B and D** show hybrid orbitals that are present in the molecule. B shows *sp*3hybrid orbitals, used by atoms that have four groups of electrons. In the molecule, the C atom in the CH3 group, the S atom, and the O atom all have four groups of electrons and would have *sp*3 hybrid orbitals. D shows *sp*2 hybrid orbitals, used by atoms that have three groups of electrons. In the molecule, the C bonded to the nitrogen atom, the C atoms involved in the C=C bond, and the nitrogen atom all have three groups of electrons and would have *sp*2 hybrid orbitals.

b) The C atoms in the C≡C bond have only two electron groups and would have ***sp* hybrid orbitals**. These orbitals are not shown in the picture.

c) There are **two sets of *sp*** hybrid orbitals, **four sets of *sp*2** hybrid orbitals, and **three sets of *sp*3**hybrid orbitals in the molecule.

10.52 Plan: Draw a resonance structure that places the double bond between the C and N atoms.

Solution:

The resonance gives the C–N bond some double bond character, which hinders rotation about the C–N bond. The C–N single bond is a σ bond; the resonance interaction exchanges a C–O π bond for a C–N π bond.



10.55 Plan: To determine hybridization, count the number of electron groups around each C and O atom. Hybridize that number of orbitals. Single, double, and triple bonds all count as one electron group. An unshared pair (lone pair) of electrons or one unshared electron also counts as one electron group. A single bond is a  bond which is the result of two orbitals overlapping end to end; a double bond consists of one  bond and one  bond; and a triple bond consists of one  bond and two  bonds.

Solution:

a) The six carbon atoms in the ring each have three surrounding electron groups (two single bonds

and one double bond) with *sp*2 hybrid orbitals. The two carbon atoms participating in the C=O bond are also *sp*2 hybridized. The single carbon in the –CH3 group has four electron groups (four single bonds) and is *sp*3 hybridized. The two central oxygen atoms, one in a C–O–H configuration and the other in a C–O–C configuration, each have four surrounding electron groups (two single bonds and two lone pairs) and are *sp*3 hybridized. The O atoms in the two C=O bonds have three electron groups (one double bond and two lone pairs) and are *sp*2 hybridized.

Summary: C in –CH3: ***sp*3**, all other C atoms (8 total): ***sp*2**, O in C=O (2 total): ***sp*2**, O in the C–O bonds (2 total): ***sp*3**.

b) The **two** C=O bonds are localized; the double bonds on the ring are delocalized as in benzene.

c) Each carbon with three surrounding groups has *sp*2 hybridization and trigonal planar shape; therefore, **eight** carbon atoms have this shape. Only **one** carbon in the CH3 group has four surrounding groups with *sp*3 hybridization and tetrahedral shape.

10.56 Plan: In the *cis* arrangement, the two H atoms are on the same side of the double bond; in the *trans* arrangement, the two H atoms are on different sides of the double bond.

Solution:

a) **Four** different isomeric fatty acids: *trans*-*cis*, *cis*-*cis*, *cis*-*trans*, *trans*-*trans*.

b) With three double bonds, there are 2n = 23 = **8 isomers** possible.

*cis-cis-cis trans-trans-trans*

*cis-trans-cis trans-cis-trans*

*cis-cis-trans trans-cis-cis*

*cis-trans-trans trans-trans-cis*