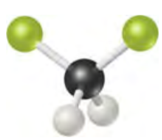
Molecular Shape and Orbitals
Problem Set

9.1 A certain AB_4 molecule has a "seesaw" shape:

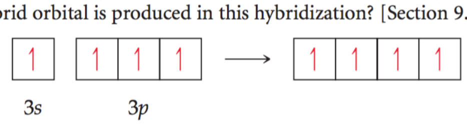
From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

9.2 **(a)** If these three balloons are all the same size, what angle is formed between the red one and the green one? **(b)** If additional air is added to the blue balloon so that it gets larger, what happens to the angle between the red and green balloons? **(c)** What aspect of the VSEPR model is illustrated by part (b)? [Section 9.2]

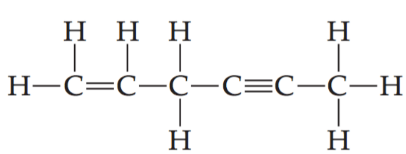
9.4 The molecule shown here is *difluoromethane* (CH_2F_2), which is used as a refrigerant called R-32. **(a)** Based on the structure, how many electron domains surround the C atom in this molecule? **(b)** Would the molecule have a nonzero dipole moment? **(c)** If the molecule is polar, in what direction will the overall dipole moment vector point in the molecule? [Sections 9.2 and 9.3]



9.7 The orbital diagram that follows presents the final step in the formation of hybrid orbitals by a silicon atom. What type of hybrid orbital is produced in this hybridization? [Section 9.5]

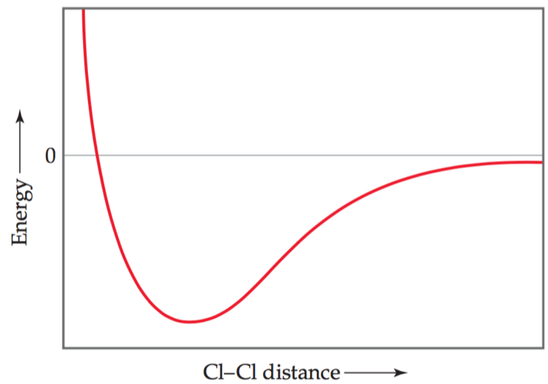


9.8 In the hydrocarbon

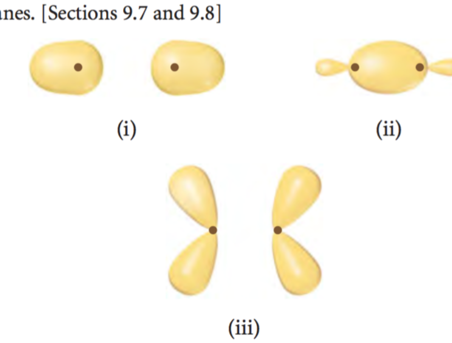


(a) What is the hybridization at each carbon atom in the molecule? **(b)** How many σ bonds are there in the molecule? **(c)** How many π bonds? (d) Identify all the 120° bond angles in the molecule. [Section 9.6]

9.5 The following plot shows the potential energy of two Cl atoms as a function of the distance between them. **(a)** To what does an energy of zero correspond in this diagram? **(b)** According to the valence-bond model, why does the energy decrease as the Cl atoms move from a large separation to a smaller one? **(c)** What is the significance of the Cl—Cl distance at the minimum point in the plot? **(d)** Why does the energy rise at Cl—Cl distances less than that at the minimum point in the plot? **(e)** How can you estimate the bond strength of the Cl—Cl bond from the plot? [Section 9.4]



9.9 For each of these contour representations of molecular orbitals, identify **(a)** the atomic orbitals (*s* or *p*) used to construct the MO **(b)** the type of MO (σ or π), **(c)** whether the MO is bonding or antibonding, and **(d)** the locations of nodal planes. [Sections 9.7 and 9.8]



9.14 Describe the bond angles to be found in each of the following molecular structures: **(a)** planar trigonal, **(b)** tetrahedral, **(c)** octahedral, **(d)** linear.

9.16 What property of the electron causes electron domains to have an effect on molecular shapes?

9.17 **(a)** How does one determine the number of electron domains in a molecule or ion? **(b)** What is the difference between a *bonding electron domain* and a *nonbonding electron domain*?

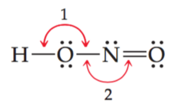
9.18 Would you expect the nonbonding electron-pair domain in NH_3 to be greater or less in size than for the corresponding one in PH_3? Explain.

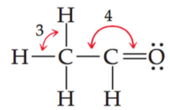
9.19 In which of these molecules or ions does the presence of nonbonding electron pairs produce an effect on molecular shape, assuming they are all in the gaseous state? **(a)** SiH_4, **(b)** PF_3, **(c)** HBr, **(d)** HCN, **(e)** SO_2.

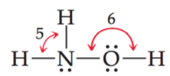
9.23 What is the difference between the electron-domain geometry and the molecular geometry of a molecule? Use the water molecule as an example in your discussion. Why do we need to make this distinction?

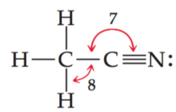
9.27 Give the electron-domain and molecular geometries for the following molecules and ions: **(a)** HCN, **(b)** SO_3^{2-}, **(c)** SF_4, **(d)** PF_6^-, **(e)** NH_3Cl^+, **(f)** N_3^-.

9.32 Give approximate values for the indicated bond angles in the following molecules:

(a) 

(b) 

(c) 

(d) 

9.34 The three species NH_2^-, NH_3, and NH_4^+ have H—N—H bond angles of 105°, 107°, and 109°, respectively. Explain this variation in bond angles.

9.37 What is the distinction between a bond dipole and a molecular dipole moment?

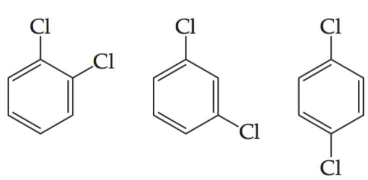
9.39 **(a)** Does SCl_2 have a dipole moment? If so, in which direction does the net dipole point? **(b)** Does $BeCl_2$ have a dipole moment? If so, in which direction does the net dipole point?

9.40 **(a)** The PH_3 molecule is polar. Does this offer experimental proof that the molecule cannot be planar? Explain. **(b)** It turns out that ozone, O_3, has a small dipole moment. How is this possible, given that all the atoms are the same?

9.42 **(a)** What conditions must be met if a molecule with polar bonds is nonpolar? **(b)** What geometries will signify nonpolar molecules for AB_2, AB_3, and AB_4 geometries?

9.43 Predict whether each of the following molecules is polar or nonpolar: **(a)** IF, **(b)** CS_2, **(c)** SO_3, **(d)** PCl_3, **(e)** SF_6, **(f)** IF_5.

9.46 Dichlorobenzene, $C_6H_4Cl_2$, exists in three forms (isomers) called *ortho*, *meta*, and *para*:



ortho *meta* *para*

Which of these has a nonzero dipole moment? Explain.

9.49 Consider the bonding in an MgH_2 molecule. **(a)** Draw a Lewis structure for the molecule, and predict its molecular geometry. **(b)** What hybridization scheme is used in MgH_2? **(c)** Sketch one of the two-electron bonds between an Mg hybrid orbital and an H 1*s* atomic orbital.

9.50 How would you expect the extent of overlap of the bonding atomic orbitals to vary in the series IF, ICl, IBr, and I_2? Explain your answer.

9.51 Fill in the blank spaces in the following chart. If the molecule column is blank, find an example that fulfills the conditions of the rest of the row.

Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2			
		sp^3	Yes
		sp^3	No
	Trigonal planar		No
SF_4			
	Octahedral		No
		sp^2	Yes
	Trigonal bipyramidal		No
XeF_2			

9.52 Why are there no sp^4 or sp^5 hybrid orbitals?

9.60 **(a)** If the valence atomic orbitals of an atom are *sp* hybridized, how many unhybridized *p* orbitals remain in the valence shell? How many π bonds can the atom form? **(b)** Imagine that you could hold two atoms that are bonded together, twist them, and not change the bond length. Would it be easier to twist (rotate) around a single σ bond or around a double (σ plus π) bond, or would they be the same? Explain.

9.62 The nitrogen atoms in N_2 participate in multiple bonding, whereas those in hydrazine, N_2H_4, do not. **(a)** Draw Lewis structures for both molecules. **(b)** What is the hybridization of the nitrogen atoms in each molecule? **(c)** Which molecule has the stronger N—N bond?

9.67 **(a)** What is the difference between a localized π bond and a delocalized one? **(b)** How can you determine whether a molecule or ion will exhibit delocalized π bonding? **(c)** Is the π bond in NO_2^- localized or delocalized?

9.59 **(a)** Draw a picture showing how two *p* orbitals on two different atoms can be combined to make a sigma bond. **(b)** Sketch a π bond that is constructed from *p* orbitals. **(c)** Which is generally stronger, a σ bond or a π bond? Explain. **(d)** Can two *s* orbitals combine to form a π bond? Explain.

9.68 **(a)** Write a single Lewis structure for SO_3, and determine the hybridization at the S atom. **(b)** Are there other equivalent Lewis structures for the molecule? **(c)** Would you expect SO_3 to exhibit delocalized π bonding? Explain.

9.70 What hybridization do you expect for the atom indicated in red in each of the following species?
(a) $CH_3CO_2^-$; **(b)** PH_4^+; **(c)** AlF_3; **(d)** $H_2C{=}CH{-}CH_2^+$

9.71 **(a)** What is the difference between hybrid orbitals and molecular orbitals? **(b)** How many electrons can be placed into each MO of a molecule? **(c)** Can antibonding molecular orbitals have electrons in them?

9.77 **(a)** What are the relationships among bond order, bond length, and bond energy? **(b)** According to molecular orbital theory, would either Be_2 or Be_2^+ be expected to exist? Explain.

9.79 (**a**) What does the term *diamagnetism* mean? (**b**) How does a diamagnetic substance respond to a magnetic field? (**c**) Which of the following ions would you expect to be diamagnetic: N_2^{2-}, O_2^{2-}, Be_2^{2+}, C_2^{-} ?

9.80 (**a**) What does the term *paramagnetism* mean? (**b**) How can one determine experimentally whether a substance is paramagnetic? (**c**) Which of the following ions would you expect to be paramagnetic: O_2^{+}, N_2^{2-}, Li_2^{+}, O_2^{2-} ? For those ions that are paramagnetic, determine the number of unpaired electrons.

9.81 Using Figures 9.35 and 9.43 as guides, draw the molecular orbital electron configuration for (**a**) B_2^{+}, (**b**) Li_2^{+}, (**c**) N_2^{+}, (**d**) Ne_2^{2+}. In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.