

internuclear axis and are called  $\pi$  orbitals.

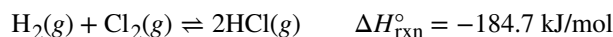
We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

## Exercises

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### 8.1 Valence Bond Theory

1. Explain how  $\sigma$  and  $\pi$  bonds are similar and how they are different.
2. Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.
  - (a) Use the bond energy found in **Table 8.1** to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)
  - (b) Use the enthalpy of reaction and the bond energies for  $H_2$  and  $Cl_2$  to solve for the energy of one mole of HCl bonds.



3. Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.
4. Use valence bond theory to explain the bonding in  $F_2$ , HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.
5. Use valence bond theory to explain the bonding in  $O_2$ . Sketch the overlap of the atomic orbitals involved in the bonds in  $O_2$ .
6. How many  $\sigma$  and  $\pi$  bonds are present in the molecule HCN?
7. A friend tells you  $N_2$  has three  $\pi$  bonds due to overlap of the three  $p$ -orbitals on each N atom. Do you agree?
8. Draw the Lewis structures for  $CO_2$  and CO, and predict the number of  $\sigma$  and  $\pi$  bonds for each molecule.

- (a)  $CO_2$
- (b) CO

### 8.2 Hybrid Atomic Orbitals

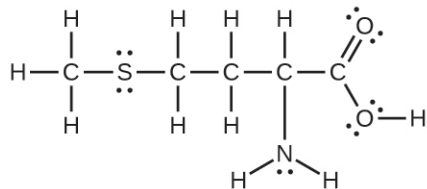
9. Why is the concept of hybridization required in valence bond theory?
10. Give the shape that describes each hybrid orbital set:
  - (a)  $sp^2$
  - (b)  $sp^3d$
  - (c)  $sp$
  - (d)  $sp^3d^2$
11. Explain why a carbon atom cannot form five bonds using  $sp^3d$  hybrid orbitals.

12. What is the hybridization of the central atom in each of the following?

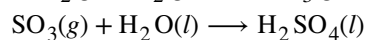
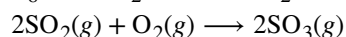
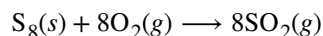
- (a)  $\text{BeH}_2$
- (b)  $\text{SF}_6$
- (c)  $\text{PO}_4^{3-}$
- (d)  $\text{PCl}_5$

13. A molecule with the formula  $\text{AB}_3$  could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

14. Methionine,  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ , is an amino acid found in proteins. The Lewis structure of this compound is shown below. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?



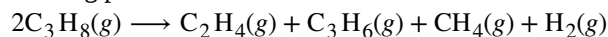
15. Sulfuric acid is manufactured by a series of reactions represented by the following equations:



Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

- (a) circular  $\text{S}_8$  molecule
- (b)  $\text{SO}_2$  molecule
- (c)  $\text{SO}_3$  molecule
- (d)  $\text{H}_2\text{SO}_4$  molecule (the hydrogen atoms are bonded to oxygen atoms)

16. Two important industrial chemicals, ethene,  $\text{C}_2\text{H}_4$ , and propene,  $\text{C}_3\text{H}_6$ , are produced by the steam (or thermal) cracking process:



For each of the four carbon compounds, do the following:

- (a) Draw a Lewis structure.
- (b) Predict the geometry about the carbon atom.
- (c) Determine the hybridization of each type of carbon atom.

17. For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass.

- (a) What is the formula of the compound?
- (b) Write a Lewis structure for the compound.
- (c) Predict the shape of the molecules of the compound.
- (d) What hybridization is consistent with the shape you predicted?

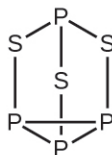
18. Consider nitrous acid,  $\text{HNO}_2$  (HONO).

(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the  $\text{HNO}_2$  molecule?

(c) What is the hybridization on the internal oxygen and nitrogen atoms in  $\text{HNO}_2$ ?

19. Strike-anywhere matches contain a layer of  $\text{KClO}_3$  and a layer of  $\text{P}_4\text{S}_3$ . The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match.  $\text{KClO}_3$  contains the  $\text{ClO}_3^-$  ion.  $\text{P}_4\text{S}_3$  is an unusual molecule with the skeletal structure.



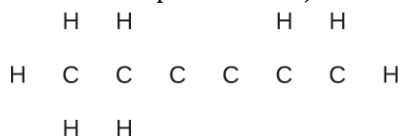
(a) Write Lewis structures for  $\text{P}_4\text{S}_3$  and the  $\text{ClO}_3^-$  ion.

(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in  $\text{P}_4\text{S}_3$  and the  $\text{ClO}_3^-$  ion.

20. Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



21. Write Lewis structures for  $\text{NF}_3$  and  $\text{PF}_5$ . On the basis of hybrid orbitals, explain the fact that  $\text{NF}_3$ ,  $\text{PF}_3$ , and  $\text{PF}_5$  are stable molecules, but  $\text{NF}_5$  does not exist.

22. In addition to  $\text{NF}_3$ , two other fluoro derivatives of nitrogen are known:  $\text{N}_2\text{F}_4$  and  $\text{N}_2\text{F}_2$ . What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

### 8.3 Multiple Bonds

23. The bond energy of a C–C single bond averages  $347 \text{ kJ mol}^{-1}$ ; that of a  $\text{C} \equiv \text{C}$  triple bond averages  $839 \text{ kJ mol}^{-1}$ . Explain why the triple bond is not three times as strong as a single bond.

24. For the carbonate ion,  $\text{CO}_3^{2-}$ , draw all of the resonance structures. Identify which orbitals overlap to create each bond.

25. A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile,  $\text{H}_3\text{CCN}$ . It is present in paint strippers.

(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form  $\sigma$  bonds.

(c) Describe the atomic orbitals that form the  $\pi$  bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

26. For the molecule allene,  $\text{H}_2\text{C} = \text{C} = \text{CH}_2$ , give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

27. Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

- (a) ClNO (N is the central atom)
- (b) CS<sub>2</sub>
- (c) Cl<sub>2</sub>CO (C is the central atom)
- (d) Cl<sub>2</sub>SO (S is the central atom)
- (e) SO<sub>2</sub>F<sub>2</sub> (S is the central atom)
- (f) XeO<sub>2</sub>F<sub>2</sub> (Xe is the central atom)
- (g) ClO<sub>2</sub>F<sub>2</sub><sup>+</sup> (Cl is the central atom)

28. Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

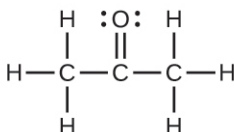
- (a) H<sub>3</sub>PO<sub>4</sub>, phosphoric acid, used in cola soft drinks
- (b) NH<sub>4</sub>NO<sub>3</sub>, ammonium nitrate, a fertilizer and explosive
- (c) S<sub>2</sub>Cl<sub>2</sub>, disulfur dichloride, used in vulcanizing rubber
- (d) K<sub>4</sub>[O<sub>3</sub>POPO<sub>3</sub>], potassium pyrophosphate, an ingredient in some toothpastes

29. For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

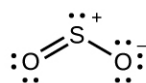
- (a) ozone (O<sub>3</sub>) central O hybridization
- (b) carbon dioxide (CO<sub>2</sub>) central C hybridization
- (c) nitrogen dioxide (NO<sub>2</sub>) central N hybridization
- (d) phosphate ion (PO<sub>4</sub><sup>3-</sup>) central P hybridization

30. For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

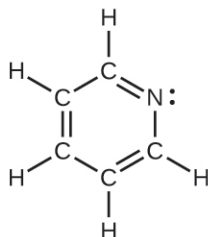
- (a) Hybridization of each carbon



- (b) Hybridization of sulfur



- (c) All atoms



31. Draw the orbital diagram for carbon in CO<sub>2</sub> showing how many carbon atom electrons are in each orbital.

### 8.4 Molecular Orbital Theory

32. Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two s orbitals and from two p orbitals.

33. How are the following similar, and how do they differ?

- (a)  $\sigma$  molecular orbitals and  $\pi$  molecular orbitals
- (b)  $\psi$  for an atomic orbital and  $\psi$  for a molecular orbital
- (c) bonding orbitals and antibonding orbitals

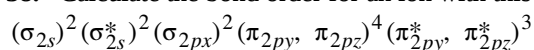
34. If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

35. Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

36. Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

37. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

38. Calculate the bond order for an ion with this configuration:



39. Explain why an electron in the bonding molecular orbital in the  $H_2$  molecule has a lower energy than an electron in the 1s atomic orbital of either of the separated hydrogen atoms.

40. Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

- (a)  $Na_2^{2+}$
- (b)  $Mg_2^{2+}$
- (c)  $Al_2^{2+}$
- (d)  $Si_2^{2+}$
- (e)  $P_2^{2+}$
- (f)  $S_2^{2+}$
- (g)  $F_2^{2+}$
- (h)  $Ar_2^{2+}$

41. Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

- (a)  $H_2$ ,  $H_2^+$ ,  $H_2^-$
- (b)  $O_2$ ,  $O_2^{2+}$ ,  $O_2^{2-}$
- (c)  $Li_2$ ,  $Be_2^+$ ,  $Be_2$
- (d)  $F_2$ ,  $F_2^+$ ,  $F_2^-$
- (e)  $N_2$ ,  $N_2^+$ ,  $N_2^-$

42. For the first ionization energy for an  $N_2$  molecule, what molecular orbital is the electron removed from?

43. Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

- (a) H and  $H_2$
- (b) N and  $N_2$
- (c) O and  $O_2$
- (d) C and  $C_2$
- (e) B and  $B_2$

44. Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

45. A friend tells you that the  $2s$  orbital for fluorine starts off at a much lower energy than the  $2s$  orbital for lithium, so the resulting  $\sigma_{2s}$  molecular orbital in  $F_2$  is more stable than in  $Li_2$ . Do you agree?

46. True or false: Boron contains  $2s^2 2p^1$  valence electrons, so only one  $p$  orbital is needed to form molecular orbitals.

47. What charge would be needed on  $F_2$  to generate an ion with a bond order of 2?

48. Predict whether the MO diagram for  $S_2$  would show  $s$ - $p$  mixing or not.

49. Explain why  $N_2^{2+}$  is diamagnetic, while  $O_2^{4+}$ , which has the same number of valence electrons, is paramagnetic.

50. Using the MO diagrams, predict the bond order for the stronger bond in each pair:

- (a)  $B_2$  or  $B_2^+$
- (b)  $F_2$  or  $F_2^+$
- (c)  $O_2$  or  $O_2^{2+}$
- (d)  $C_2^+$  or  $C_2^-$