

**General References**


**Problems**

8.1 The ions $H^+_2$ and $H_2^+$ have been observed in gas discharges.  
   a. $H_2^+$ has been reported to have a bond distance of 106 pm and a bond dissociation enthalpy of 255 kJmol$^{-1}$. Comparable values for the neutral molecule are 74.2 pm and 436 kJmol$^{-1}$. Are these values for $H_2^+$ in agreement with the molecular orbital picture of this ion? Explain.  
   b. Assuming $H_2^+$ to be triangular (the probable geometry), describe the molecular orbitals of this ion and determine the expected H—H bond order.

8.2 The species $He_2^+$ and $HeH^+$ have been observed spectroscopically. Prepare molecular orbital diagrams for these two ions. What would you predict for the bond order of each?

8.3 The chemical species $IF_2^-$ and $XeF_4$ are known. Is the isoelectronic ion $CsF_4^+$ plausible? If it could be made, predict and sketch its most likely shape. Comment on whether such an ion might or might not be possible.

8.4 The equilibrium constant for the formation of the cryptand $[Sr\{cryptand(2.2.1)\}]^{2+}$ is larger than the equilibrium constants for the analogous calcium and barium cryptands. Suggest an explanation. (See E. Kauffmann, J-M. Lehn, J-P. Sauvage, Helv. Chim. Acta, 1976, 59, 1099.)

8.5 Gas phase $BeF_2$ is monomeric and linear. Prepare a molecular orbital description of the bonding in $BeF_2$.

8.6 In the gas phase, $BeCl_2$ forms a dimer of the following structure:

\[
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl}
\end{array}
\]

Describe the bonding of the chlorine bridges in this dimer in molecular orbital terms.

8.7 $BF$ can be obtained by reaction of $BF_3$ with boron at 1850 °C and low pressure; $BF$ is highly reactive but can be preserved at liquid nitrogen temperature (77 K). Prepare a molecular orbital diagram of $BF$. How would the molecular orbitals of $BF$ differ from CO, with which $BF$ is isoelectronic?

8.8 N-heterocyclic carbenes, such as the example shown here, have become increasingly important in both main group and transition-metal chemistry. For example, the first report of a stable neutral molecule having a boron–boron double bond used this N-heterocyclic carbene to bond to each of the borons in a product of the reaction of $RBBBr_3$ with the powerful reducing agent $KC_8$ (potassium graphite) in diethylether solvent. (See Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, III, P. v. R. Schleyer, G. H. Robinson, J. Am. Chem. Soc., 2007, 129, 12412.)

   a. What was the structure of this first molecule with a B = B bond? What evidence was cited for a double bond?
   b. If $RSiCl_4$ was used in place of $RBBBr_3$, an equally notable silicon compound was formed. What was this compound, and what parallels were noted with the reaction in Part a? (See Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, Science, 2008, 321, 1069.)

![Diagram of R, an N-heterocyclic carbene](image-url)
8.20 8.20 Al₂(CH₃)₆ is isostructural with diborane, B₂H₆. On the basis of the orbitals involved, describe the Al—C—Al bonding for the bridging methyl groups in Al₂(CH₃)₆.

8.10 Referring to the description of bonding in diborane in Figure 8.1.2:
  a. Show that the representation \( \Gamma(p) \) reduces to \( A_g + B_{1u} \).
  b. Show that the representation \( \Gamma(p) \) reduces to \( B_{2g} + B_{3u} \).
  c. Show that the representation \( \Gamma(1s) \) reduces to \( A_g + B_{3u} \).
  d. Using the \( D_2h \) character table, verify that the angles for the group orbitals match their respective symmetry designations \( (A_g, B_{1g}, B_{1u}, B_{3u}) \).

8.11 The compound C(PPh₃)₂ is bent at carbon; the P—C—P angle in one form of this compound has been reported as 130.1°. Account for the nonlinearity at carbon.

8.12 The C—C distances in carbides of formula MC₃ are in the range 119 to 124 pm if M is a Group 2 (IIIA) metal or other metal commonly forming a 2+ ion, but in the approximate range 128 to 130 pm for Group 3 (IIIB) metals, including the lanthanides. Why is the C—C distance greater for the carbides of the Group 3 metals?

8.13 The half-life of \(^{14}C\) is 5730 years. A sample taken for radiocarbon dating was found to contain 56 percent of its original \(^{14}C\). What was the age of the sample? (Radioactive decay of \(^{14}C\) follows first-order kinetics.)

8.14 Prepare a model of buckminsterfullerene, C₆₀. By referring to the character table, verify that this molecule has \( Iₗ \) symmetry.

8.15 Determine the point groups of the following:
  a. The unit cell of diamond
  b. C₂₀
  c. C₇₀
  d. The nanoribbons shown in Figure 8.18

8.16 What is graphene? How has it been synthesized, and what might be some of its potential uses? (See D. C. Elias, et al., Science, 2009, 323, 610.)

8.17 Prepare a sheet showing an extended graphene structure, approximately 12 by 15 fused carbon rings or larger. Use this sheet to show how the graphene structure could be rolled up to form (a) a zigzag nanotube, (b) an armchair nanotube, and (c) a chiral nanotube. Is more than one chiral structure possible? (See M. S. Dresselhaus, G. Dresselhaus, and R. Saito, Carbon, 1995, 33, 883.)

8.18 To what extent has using carbon nanotubes for delivery of the anticancer agent cisplatin shown promise in the killing of cancer cells? (See J. F. Rusling, J. S. Gutkind, A. A. Bhirde, et al., ACS Nano, 2009, 3, 307.) The reader is encouraged to search the recent literature to find more up to date references in this ongoing area of research.


8.20 Explain the increasing stability of the 2+ oxidation state for the Group 14 (IVA) elements with increasing atomic number.

8.21 1,2-Diiododisilane has been observed in both \textit{anti} and \textit{gauche} conformations. (See K. Hassler, W. Koell, K. Schenzel, J. Mol. Struct., 1995, 348, 353.) For the \textit{anti} conformation, shown here,

\[
\text{I} - \text{Si} = \text{Si} - \text{I}
\]

a. What is the point group?

b. Predict the number of infrared-active silicon–hydrogen stretching vibrations.

8.22 The reaction \( P_i(g) \leftrightarrow 2 P(g) \) has \( \Delta H = 217 \text{ kJ mol}^{-1} \). If the bond energy of a single phosphorus–phosphorus bond is 200 \text{ kJ mol}^{-1}, calculate the bond energy of the \( \text{P} = \text{P} \) bond. Compare the value you obtain with the bond energy in \( N_2(946 \text{ kJ mol}^{-1}) \), and suggest an explanation for the difference in bond energies in \( P_2 \) and \( N_2 \).

8.23 The azide ion, \( \text{N}_3^- \), is linear with equal N—N bond distances.

a. Describe the pi molecular orbitals of azide.

b. Describe in HOMO-LUMO terms the reaction between azide and \( \text{H}^+ \) to form hydrazoic acid, \( \text{HN}_3 \).

8.24 In aqueous solution, hydrazine is a weaker base than ammonia. Why? (\( pK_b \) values at 25 °C: \( \text{NH}_3, 4.74; \text{N}_2\text{H}_4, 6.07 \))

8.25 The bond angles for the hydrides of the Group 15 (VA) elements are as follows: \( \text{NH}_3, 107.8°; \text{PH}_3, 93.6°; \text{AsH}_3, 91.8°; \) and \( \text{SbH}_3, 91.3° \). Account for this trend.

8.26 Gas-phase measurements show that the nitric acid molecule is planar. Account for the planarity of this molecule.

8.27 With the exception of \( \text{NO}_2^- \), all the molecules and ions in Table 8.10 are planar. Assign their point groups.


a. Which isomer has the lower electronic ground state at 298 K (and by how much) on the basis of the computational work?

b. Describe the proposed isomerization mechanisms. Which has a lower activation barrier (and by how much)?

c. Using SbF₅ as the Lewis acid, draw a Lewis structure of the species proposed to lower the isomerization barrier for \( \text{trans-N}_2\text{F}_2 \). Which mechanism is presumed to be operative in this case? Describe the expected geometric changes in the \( \text{trans-N}_2\text{F}_2\text{SbF}_5 \) adduct, and how these facilitate the isomerization.

8.29 Use the Latimer diagrams for phosphorus in Appendix B.7 to construct Frost diagrams for acidic and basic conditions. Provide balanced reduction half-reactions for all adjacent couples in these Latimer diagrams.
8.30 What type of interaction holds the \( O_2 \) units together in the \( O_3 \) structure? How does this interaction stabilize the larger molecule? (Hint: consider the molecular orbitals of \( O_2 \). See R. Steudel, M. W. Wong, *Angew. Chem., Int. Ed.*, 2007, 46, 1768.)

8.31 The sulfur–sulfur distance in \( S_2 \), the major component of sulfur vapor above \(~720^\circ\) C, is 189 pm, significantly shorter than the sulfur–sulfur distance of 206 pm in \( S_8 \). Suggest an explanation for the shorter distance in \( S_2 \). (See C. L. Liao, C. Y. Ng, *J. Chem. Phys.*, 1986, 84, 778.)

8.32 Because of its high reactivity with most chemical reagents, \( F_2 \) is ordinarily synthesized electrochemically. However, the chemical synthesis of \( F_2 \) has been recorded via the reaction

\[
2 \text{K}_2\text{MnF}_6 + 4 \text{SbF}_5 \rightarrow 4 \text{KSbF}_6 + 2 \text{MnF}_3 + \text{F}_2
\]


8.33 a. Chlorine forms a variety of oxides, among them \( \text{Cl}_2\text{O} \) and \( \text{Cl}_2\text{O}_2 \). \( \text{Cl}_2\text{O} \) has a central oxygen; \( \text{Cl}_2\text{O}_2 \) also has a central oxygen atom, bridging two \( \text{ClO}_2 \) groups. Of these two compounds, which would you predict to have the smaller \( \text{Cl}--\text{O}--\text{Cl} \) angle? Explain briefly.

b. The dichromate ion, \( \text{Cr}_2\text{O}_7^{2-} \), has the same structure as \( \text{Cl}_2\text{O}_7 \), with oxygen now bridging two \( \text{CrO}_3 \) groups. Which of these two oxygen-bridged species do you expect to have the smaller outer–atom–O–outer atom angle? Explain briefly.

8.34 The triiodide ion \( \text{I}_3^- \) is linear, but \( \text{I}_3^+ \) is bent. Explain.

8.35 Although \( \text{B}_2\text{H}_6 \) has \( D_{2h} \) symmetry, \( \text{I}_3\text{Cl}_6 \) is planar. Account for the difference in the structures of these two molecules.

8.36 \( \text{BrF}_3 \) undergoes autodissociation according to the equilibrium

\[
2 \text{BrF}_3 \leftrightarrow \text{BrF}_2^+ + \text{BrF}_4^-
\]

Ionic fluorides such as \( \text{KF} \) behave as bases in \( \text{BrF}_3 \), whereas some covalent fluorides such as \( \text{SbF}_3 \) behave as acids. On the basis of the solvent system concept, write balanced chemical equations for these acid–base reactions of fluorides with \( \text{BrF}_3 \).

8.37 The diatomic cations \( \text{Br}_2^+ \) and \( \text{I}_2^+ \) are both known.

a. On the basis of the molecular orbital model, what would you predict for the bond orders of these ions? Would you predict these cations to have longer or shorter bonds than the corresponding neutral diatomic molecules?

b. \( \text{Br}_2^+ \) is red, and \( \text{I}_2^+ \) is bright blue. What electronic transition is most likely responsible for absorption in these ions? Which ion has the more closely spaced HOMO and LUMO?

c. \( \text{I}_2 \) is violet, and \( \text{I}_2^+ \) is blue. On the basis of frontier orbitals (identify them), account for the difference in their colors.

8.38 \( \text{I}_2^- \) exists in equilibrium with its dimer \( \text{I}_2^{2+} \) in solution. \( \text{I}_2^- \) is paramagnetic and the dimer is diamagnetic. Crystal structures of compounds containing \( \text{I}_2^{2+} \) have shown this ion to be planar and rectangular, with two short \( I--I \) distances (258 pm) and two longer distances (326 pm).

a. Using molecular orbitals, propose an explanation for the interaction between two \( \text{I}_2^+ \) units to form \( \text{I}_2^{2+} \).

b. Which form is favored at high temperature, \( \text{I}_2^- \) or \( \text{I}_2^{2+} \)? Why?

8.39 How many possible isomers are there of the ion \( \text{IO}_2\text{F}_2^{2-} \)? Sketch these, and indicate the point group for each. The observed ion has IR-active iodine–oxygen stretches at 802 and 834 cm\(^{-1}\). What does this indicate about the most likely structure? (See J. P. Mack, J. A. Boatz, M. Gerken, *Inorg. Chem.*, 2008, 47, 3243.)

8.40 What is a superhalogen? Does it contain a halogen? By searching the literature, find the earliest reference to this term and the rationale for the name "superhalogen." Also provide examples of modern chemical applications of superhalogens.

8.41 Bartlett’s original reaction of xenon with \( \text{PtF}_6 \) apparently yielded products other than the expected \( \text{Xe}^+\text{PtF}_6^- \). However, when xenon and \( \text{PtF}_6 \) are reacted in the presence of a large excess of sulfur hexafluoride, \( \text{Xe}^+\text{PtF}_6^- \) is apparently formed. Suggest the function of \( \text{SF}_6 \) in this reaction. (See: K. Seppelt, D. Lentz, *Progr. Inorg. Chem.*, 1982, 29, 170.)

8.42 On the basis of VSEPR, predict the structures of \( \text{XeOF}_3 \), \( \text{XeOF}_4 \), \( \text{XeO}_2\text{F}_2 \), and \( \text{XeO}_2\text{F}_4 \). Assign the point group of each.

8.43 The sigma bonding in the linear molecule \( \text{XeF}_2 \) may be described as a three-center, four-electron bond. If the \( z \) axis is assigned as the internuclear axis, use the \( p_z \) orbitals on each of the atoms to prepare a molecular orbital description of the sigma bonding in \( \text{XeF}_2 \).

8.44 The \( \text{OTeF}_6 \) group can stabilize compounds of xenon in formal oxidation states IV and VI. On the basis of VSEPR, predict the structures of \( \text{Xe}(\text{OTeF}_6)_4 \) and \( \text{O}==\text{Xe}(\text{OTeF}_6)_4 \).

8.45 Write a balanced equation for the oxidation of \( \text{Mn}^{2+} \) to \( \text{MnO}_4^- \) by the perxenate ion in acidic solution; assume that neutral \( \text{Xe} \) is formed.

8.46 The ion \( \text{XeF}_5^- \) is a rare example of pentagonal planar geometry. On the basis of the symmetry of this ion, predict the number of IR-active \( \text{Xe}--\text{F} \) stretching bands.

8.47 \( \text{XeOF}_4 \) has one of the more interesting structures among noble gas compounds. On the basis of its symmetry,

a. Obtain a representation based on all the motions of the atoms in \( \text{XeOF}_4 \).

b. Reduce this representation to its component irreducible representations.

c. Classify these representations, indicating which are for translational, rotational, and vibrational motion.

8.48 The ion \( \text{XeF}_2^{2-} \) has not been reported. Would you expect this ion to be bent or linear? Suggest why it remains elusive.

8.49 Photolysis of a solid mixture of \( \text{H}_2\text{O} \), \( \text{N}_2\text{O} \), and \( \text{Xe} \) at 9 K, followed by annealing, gave a product identified as \( \text{H}_2\text{XeO}(\text{H}) \) (L. Khriachtchev, K. Isokoski, A. Cohen, M. Räsänen, R. B. Gerber, *J. Am. Chem. Soc.*, 2008, 130, 6114). Supporting evidence included infrared data, with a band at 1379.7 cm\(^{-1}\), assigned to \( \text{Xe}==\text{H} \) stretching. When the experiment was repeated using deuterated water
containing both D₂O and H₂O, bands at 1432.7 cm⁻¹, 1034.7 cm⁻¹, and 1003.3 cm⁻¹, were observed, together with the band at 1379.7 cm⁻¹. Account for the infrared data from the experiment conducted using deuterated water.

8.50 Use the Latimer diagram for xenon in basic solution in Appendix B.7 to:

a. Construct balanced half-reactions for the HXeO₃⁻/HXeO₄⁻ and HXeO₄⁻/Xe redox couples.
b. Use these half-reactions to show that the disproportionation of HXeO₄⁻ in basic solution is spontaneous by calculating $E^\circ$ and $\Delta G^\circ$ for the reaction.

8.51 Although atmospheric ozone depletion is a widely known phenomenon, the estimate that as much as 90% of the xenon originally in Earth’s atmosphere is now absent is largely unknown. The synthesis and study of XeO₂ (D. S. Brock, G. J. Schrobilgen, J. Am. Chem. Soc., 2011, 133, 6265) supports the hypothesis that the reaction of SiO₂ from the Earth’s core with Xe may be responsible for the depletion of this noble gas.

a. Describe how the synthesis of XeO₂ is carried out, including the reactants, conditions, temperature sensitivity, and hazards associated with the synthesis.
b. Explain why monomeric XeO₂ would likely be soluble in water.
c. Raman spectroscopic studies were vital to characterize XeO₂. What experimental observation suggested that XeO₂ only contains Xe—O bonding? What experimental observation suggested that XeO₂ did not contain any hydrogen atoms?

8.52 Liquid NSF₃ reacts with [XeF][AsF₆] to form [F₅SNXeF][AsF₆], 1. On mild warming in the solid state, compound 1 rearranges to [F₅SNXe][AsF₂], 2. Reaction of compound 2 with HF yields [F₅SNH₂][AsF₃], 3, [F₅SNH(Xe)][AsF₆], 4, and XeF₂. (See G. L. Smith, H. P. A. Mercier, G. J. Schrobilgen, Inorg. Chem., 2007, 46, 1369; Inorg. Chem., 2008, 47, 4173; and J. Am. Chem. Soc., 2009, 131, 4173.)

a. What is the bond order in [XeF]⁺?
b. Of compounds 1 through 4, which has the longest S—N distance? The shortest?
c. Which of the compounds 1 through 4 is most likely to have linear bonding around the nitrogen atom? 
d. By the VSEPR approach, is the bonding around Xe expected to be linear or bent in compound 1? 
e. In compounds 2 and 3, are the NXe and NH₂ groups likely to occupy axial or equatorial sites on sulfur? 
f. In compounds 2 and 3, which bonds are more likely to be longer, the S—Fₐxial bonds or S—Fₑquatorial bonds?

8.53 Determine the point groups:

a. O₈ (Figure 8.34)
b. S₈ (Figure 8.35)
c. A chiral nanotube
d. The section of β-graphyne shown in Figure 8.23
e. XeF₃O⁺

The following problems require the use of molecular modeling software.

8.54 It has been proposed that salts containing the cation [FBeNg]⁺, where Ng = He, Ne, or Ar, may be stable. Use molecular modeling software to calculate and display the molecular orbitals of [FBeNe]⁺. Which molecular orbitals would be the primary ones engaged in bonding in this ion? (See M. Aschi, F. Grandinetti, Angew. Chem., Int. Ed., 2000, 39, 1690.)

8.55 The dixenon cation Xe₂⁺ has been characterized structurally. Using molecular modeling software, calculate and observe the energies and shapes of the molecular orbitals of this ion. Classify each of the seven highest-energy occupied orbitals as $\sigma$, $\pi$, or $\delta$, and as bonding or antibonding. The bond in this compound was reported as the longest main group–main group bond observed to date. Account for this very long bond. (See T. Drews, K. Seppelt, Angew. Chem., Int. Ed., 1997, 36, 273.)

8.56 To further investigate the bonding in the O₈ structure, construct an O₈ unit, and calculate and display its molecular orbitals. Which orbitals are involved in holding the O₂ units together? In each of these orbitals, identify the atomic orbitals that are primarily involved. (See Figure 8.34; additional structural details can be found in L. F. Lundegaard, G. Weck, M. I. McMahon, S. I. Desgreniers, P. Loubeyre, Science, 2006, 443, 201 and R. Steudel, M. W. Wong, Angew. Chem., Int. Ed., 2007, 46, 1768.)