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General References

There are many books describing bonding and molecular orbitals, with levels ranging from those even more descriptive and qualitative than the treatment in this chapter to those designed for the theoretician interested in the latest methods. A classic that starts at the level of this chapter and includes many more details is R. McWeeny's revision of *Coulson's Valence*, 3rd ed., Oxford University Press, Oxford, 1979. A different approach that uses the concept of generator orbitals is that of J. G. Verkade in *A Pictorial Approach to Molecular Bonding and Vibrations*, 2nd ed., Springer-Verlag, New York, 1997. The group theory approach in this chapter is similar to that of F. A. Cotton in *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, New York, 1990. A more recent book that extends the description is Y. Jean and F. Volatron, *An Introduction to Molecular Orbitals*, translated and edited by J. K. Burdett, Oxford University Press, Oxford, 1993. J. K. Burdett's *Molecular Shapes*, John Wiley & Sons, New York, 1980, and B. M. Gimarc's, *Molecular Structure and Bonding*, Academic Press, New York, 1979, are both good introductions to the qualitative molecular orbital description of bonding.

This is the first chapter that includes problems involving molecular modeling software. Discussion of such software is beyond the scope of this text. E. G. Lewars, *Computational Chemistry*, 2nd ed., Springer, New York, 2011 provides a readable introduction to the theory and applications of molecular modeling. In addition, examples of uses of molecular modeling in chemistry curricula are discussed in L. E. Johnson, T. Engel, *J. Chem. Educ.*, **2011**, *88*, 569 and references cited therein.

Problems

5.1 Expand the list of orbitals considered in Figures 5.2 and 5.3 by using all three *p* orbitals of atom A and all five *d* orbitals of atom B. Which of these have the necessary match of symmetry for bonding and antibonding orbitals? These combinations are rarely seen in simple molecules but can be important in transition metal complexes.

5.2 On the basis of molecular orbitals, predict the shortest bond, and provide a brief explanation.
 a. Li_2^+ Li_2
 b. F_2^+ F_2
 c. He_2^+ HHe^+ H_2^+

5.3 On the basis of molecular orbitals, predict the weakest bond, and provide a brief explanation.
 a. P_2 S_2 Cl_2
 b. S_2^+ S_2 S_2^-
 c. NO^- NO NO^+

5.4 Compare the bonding in O_2^{2-}, O_2^-, and O_2. Include Lewis structures, molecular orbital structures, bond lengths, and bond strengths in your discussion.

5.5 Although the peroxide ion, O_2^{2-}, and the acetylide ion, C_2^{2-}, have long been known, the diazenide ion N_2^{2-} has only been prepared much more recently. By comparison with the other diatomic species, predict the bond order,

bond distance, and number of unpaired electrons for N_2^{2-}.
(See G. Auffermann, Y. Prots, R. Kniep, *Angew. Chem.,
Int. Ed.*, **2001**, *40*, 547.)
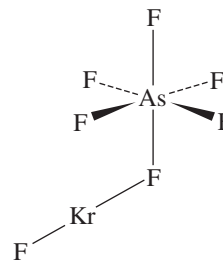
5.6 High-resolution photoelectron spectroscopy has provided
information on the energy levels and bond distance in the
ion Ar_2^+. Prepare a molecular orbital energy-level diagram
for this ion. How would you expect the bond distance in
Ar_2^+ to compare with 198.8 pm, the bond distance in Cl_2?
(See A. Wüst, F. Merkt, *J. Chem. Phys.*, **2004**, *120*, 638.)

5.7 **a.** Prepare a molecular orbital energy-level diagram for
NO, showing clearly how the atomic orbitals interact
to form MOs.
   b. How does your diagram illustrate the difference in elec-
tronegativity between N and O?
   c. Predict the bond order and the number of unpaired
electrons.
   d. NO^+ and NO^- are also known. Compare the bond
orders of these ions with the bond order of NO. Which
of the three would you predict to have the shortest
bond? Why?

5.8 **a.** Prepare a molecular orbital energy-level diagram for
the cyanide ion. Use sketches to show clearly how the
atomic orbitals interact to form MOs.
   b. What is the bond order for cyanide, and how many
unpaired electrons does cyanide have?
   c. Which molecular orbital of CN^- would you predict to
interact most strongly with a hydrogen $1s$ orbital to form
an H—C bond in the reaction $CN^- + H^+ \rightarrow HCN$?
Explain.

5.9 NF is a known molecule!
   a. Construct a molecular orbital energy-level diagram for
NF, being sure to include sketches that show how the
valence orbitals of N and F interact to form molecular
orbitals.
   b. What is the most likely bond order for NF?
   c. What are the point groups of the molecular orbitals of
this molecule?
   (See D. J. Grant, T-H. Wang, M. Vasiliu, D. A. Dixon,
K. O. Christe, *Inorg. Chem.* **2011**, *50*, 1914 for refer-
ences and theoretical calculations of numerous small
molecules and ions having formula N_xF_y.)

5.10 The hypofluorite ion, OF^-, can be observed only with
difficulty.
   a. Prepare a molecular orbital energy level diagram for
this ion.
   b. What is the bond order, and how many unpaired
electrons are in this ion?
   c. What is the most likely position for adding H^+ to the
OF^- ion? Explain your choice.

5.11 Reaction of KrF_2 with AsF_5 at temperatures between -78
and $-53\,°C$ yields $[KrF][AsF_6]$, a compound in which
KrF^+ interacts strongly with AsF_6^- through a fluorine
bridge, as shown. Would you predict the Kr—F bond to
be shorter in KrF^+ or in KrF_2? Provide a brief explanation.
(See J. F. Lehmann, D. A. Dixon, G. J. Schrobilgen, *Inorg.
Chem.*, **2001**, *40*, 3002.)

5.12 Although KrF^+ and XeF^+ have been studied, $KrBr^+$ has
not yet been prepared. For $KrBr^+$:
   a. Propose a molecular orbital diagram, showing the inter-
actions of the valence shell s and p orbitals to form
molecular orbitals.
   b. Toward which atom would the HOMO be polarized?
Why?
   c. Predict the bond order.
   d. Which is more electronegative, Kr or Br? Explain your
reasoning.

5.13 Prepare a molecular orbital energy level diagram for SH^-,
including sketches of the orbital shapes and the number of
electrons in each of the orbitals. If a program for calculat-
ing molecular orbitals is available, use it to confirm your
predictions or to explain why they differ.

5.14 Methylene, CH_2, plays an important role in many reac-
tions. One possible structure of methylene is linear.
   a. Construct a molecular orbital energy-level diagram for
this species. Include sketches of the group orbitals, and
indicate how they interact with the appropriate orbitals
of carbon.
   b. Would you expect linear methylene to be diamagnetic
or paramagnetic?

5.15 Beryllium hydride, BeH_2, is linear in the gas phase.
   a. Construct a molecular orbital energy level diagram for
BeH_2. Include sketches of the group orbitals, and indicate
how they interact with the appropriate orbitals of Be.
   b. If you have worked Problem 5.14, compare the results
of these two problems.

5.16 In the gas phase, BeF_2 forms linear monomeric molecules.
Prepare a molecular orbital energy-level diagram for BeF_2,
showing clearly which atomic orbitals are involved in
bonding and which are nonbonding.

5.17 For the compound XeF_2 do the following:
   a. Sketch the valence shell group orbitals for the fluorine
atoms (with the z axes collinear with the molecular axis).
   b. For each of the group orbitals, determine which out-
ermost s, p, and d orbitals of xenon are of suitable
symmetry for interaction and bonding.

5.18 TaH_5 has been predicted to have C_{4v} symmetry, with a
calculated axial H—Ta—H angle of approximately 117.5°.
Using the six-step approach described in Section 5.4.2,
describe the bonding in TaH_5 on the basis of matching
group orbitals and central atom orbitals according to their
symmetry. (See C. A. Bayse, M. B. Hall, *J. Am. Chem.
Soc.*, **1999**, *121*, 1348.)

5.19 Describe the bonding in ozone, O_3, on the basis of matching group orbitals and central-atom orbitals according to their symmetry. Include both σ and π interactions, and try to put the resulting orbitals in approximate order of energy.

5.20 Describe the bonding in SO_3 by using group theory to find the molecular orbitals. Include both σ and π interactions, and try to put the resulting orbitals in approximate order of energy. (The actual results are more complex because of mixing of orbitals, but a simple description can be found by the methods given in this chapter.)

5.21 The ion H_3^+ has been observed, but its structure has been the subject of some controversy. Prepare a molecular orbital energy level diagram for H_3^+, assuming a cyclic structure. (The same problem for a linear structure is given in Exercise 5.4 in Section 5.4.2.)

5.22 Use molecular orbital arguments to explain the structures of SCN^-, OCN^-, and CNO^-, and compare the results with the electron-dot pictures of Chapter 3.

5.23 Thiocyanate and cyanate ions both bond to H^+ through the nitrogen atoms (HNCS and HNCO), whereas SCN^- forms bonds with metal ions through either nitrogen or sulfur, depending on the rest of the molecule. What does this suggest about the relative importance of S and N orbitals in the MOs of SCN^-? (Hint: See the discussion of CO_2 bonding in Section 5.4.2.)

5.24 The thiocyanate ion, SCN^-, can form bonds to metals through either S or N (see Problem 5.23). What is the likelihood of cyanide, CN^-, forming bonds to metals through N as well as C?

5.25 The isomeric ions NSO^- (thiazate) and SNO^- (thionitrite) ions have been reported. (S. P. So, *Inorg. Chem.*, **1989**, *28*, 2888).
  a. On the basis of the resonance structures of these ions, predict which would be more stable.
  b. Sketch the approximate shapes of the π and $\pi*$ orbitals of these ions.
  c. Predict which ion would have the shorter N—S bond and which would have the higher energy N—S stretching vibration? (Stronger bonds have higher energy vibrations.)

5.26 Apply the projection operator method to derive the group orbital SALCs for H_2O given in Section 5.4.3. Confirm using the squares of the coefficients that the group orbital wave function equations are normalized and that each $1s$ orbital contributes equally to the two group orbitals.

5.27 Apply the projection operator method to derive the group orbital SALCs for BF_3 on the basis of the irreducible representations given in Figure 5.31 for sets of $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively. Employ a set of three identical orbitals where all have the same bias (i.e., the group orbitals with A_1', A_2', and A_2'' symmetry in Figure 5.31) as a starting point. For each determination, provide a table like that in Section 5.4.4 to tabulate wave function coefficients, their squares, and how these values simultaneously satisfy the normalization requirement and

confirm that each atomic orbital contributes equally to each set of group orbitals.

5.28 A set of four group orbitals derived from four $3s$ atomic orbitals is necessary to examine the bonding in $[PtCl_4]^-$, a square planar complex. Deduce the wave function equations for these four SALCs using the $3s$ labeling scheme specified, starting with the irreducible representations for these group orbitals. Using sketches of the deduced orbitals, symmetry characteristics of the representations, and a coefficient table like that in Section 5.4.4, deduce the SALCs not derived initially from the character table analysis. Provide normalized equations and a sketch for each group orbital.
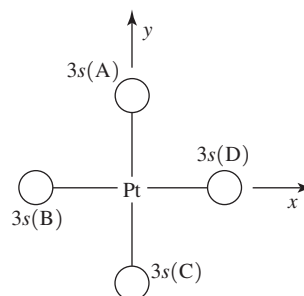
5.29 The projection operator method has applications beyond the deduction of group orbital SALCs. Deduce the wave function equations for the six π molecular orbitals of benzene, using the labels specified for each $2p_z$ orbital. First, derive initial SALCs using *each* representation of the D_{6h} point group; some combinations will afford zero. Using sketches of the deduced orbitals, symmetry characteristics of the representations, and a coefficient table like that in Section 5.4.4, deduce the SALCs not derived initially from the character table analysis. Provide normalized equations and a sketch for each π molecular orbital.
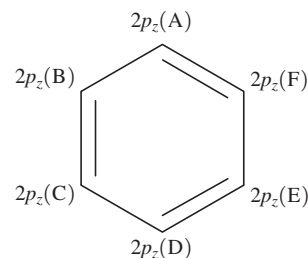
5.30 Although the Cl_2^+ ion has not been isolated, it has been detected in the gas phase by UV spectroscopy. An attempt to prepare this ion by reaction of Cl_2 with IrF_6 yielded not Cl_2^+, but the rectangular ion Cl_4^+. (See S. Seidel, K. Seppelt, *Angew. Chem., Int. Ed.*, **2000**, *39*, 3923.)
  a. Compare the bond distance and bond energy of Cl_2^+ with Cl_2.

b. Account for the bonding in Cl_4^+. This ion contains two short Cl—Cl bonds and two much longer ones. Would you expect the shorter Cl—Cl distances in Cl_4^+ to be longer or shorter than the Cl—Cl distance in Cl_2? Explain.

5.31 BF_3 is often described as a molecule in which boron is electron deficient, with an electron count of six. However, resonance structures can be drawn in which boron has an octet, with delocalized π electrons.

a. Draw these structures.

b. Find the molecular orbital in Figure 5.32 that shows this delocalization and explain your choice.

c. BF_3 is *the* classic Lewis acid, accepting a pair of electrons from molecules with lone pairs. Find the orbital in Figure 5.32 that is this acceptor; explain your choice, including why it looks like a good electron acceptor.

d. What is the relationship between the orbitals identified in Parts b and c?

5.32 SF_4 has C_{2v} symmetry. Predict the possible hybridization schemes for the sulfur atom in SF_4.

5.33 Consider a square pyramidal AB_5 molecule. Using the C_{4v} character table, determine the possible hybridization schemes for central atom A. Which of these would you expect to be most likely?

5.34 In coordination chemistry, many square-planar species are known (for example, $[PtCl_4]^{2-}$). For a square planar molecule, use the appropriate character table to determine the types of hybridization possible for a metal surrounded in a square-planar fashion by four ligands; consider hybrids used in σ bonding only.

5.35 For the molecule PCl_5:

a. Using the character table for the point group of PCl_5, determine the possible type(s) of hybrid orbitals that can be used by P in forming σ bonds to the five Cl atoms.

b. What type(s) of hybrids can be used in bonding to the axial chlorine atoms? To the equatorial chlorine atoms?

c. Considering your answer to part b, explain the experimental observation that the axial P—Cl bonds (219 pm) are longer than the equatorial bonds (204 pm).

The following problems require the use of molecular modeling software.

5.36 a. Identify the point group of the $1a_2''$, $2a_2''$, $1a_2'$, and $1e''$ molecular orbitals in Figure 5.32.

b. Use molecular modeling software to calculate and view the molecular orbitals of BF_3.

c. Do any of the molecular orbitals show interactions between B and F?

d. Print out the contributions of the atomic orbitals to the $3a_1'$, $4a_1'$, $1a_2''$, $1a_2'$, and $2a_2''$ molecular orbitals, confirming (if you can) the atomic orbital combinations shown in Figure 5.32.

5.37 The ions and molecules NO^+, CN^-, CO, and N_2 and N_2 form an isoelectronic series. The changing nuclear charges will also change the molecular energy levels of the orbitals formed from the $2p$ atomic orbitals $(1\pi, 3\sigma,$ and $1\pi^*)$. Use molecular modeling software for the following:

a. Calculate and display the shapes of these three molecular orbitals for each species (CO and N_2 are included in this chapter).

b. Compare the shapes of each of the orbitals for each of the species (for example, the shapes of the 1π orbitals for each). What trends do you observe?

c. Compare the energies of each of the orbitals. For which do you see evidence of mixing?

5.38 Molecular modeling software is typically capable of calculations on molecules that are hypothetical, even seemingly bizarre, in their structures. Beginning with N_2, calculate and display molecular orbitals of the isoelectronic CO, BF, and BeNe (which is truly hypothetical!). Compare the shapes of the matching molecular orbital in this series What trends do you observe?

5.39 Calculate and display the orbitals for the linear molecule BeH_2. Describe how they illustrate the interaction of the outer group orbitals with the orbitals on the central atom. Compare your results with the answer to Problem 5.15.

5.40 Calculate and display the orbitals for the linear molecule BeF_2. Compare the orbitals and their interactions with those of BeH_2 from Problem 5.39. In particular, indicate the outer group orbitals that do not interact with orbitals on the central atom.

5.41 The azide ion, N_3^-, is another linear triatomic species. Calculate and display the orbitals for this ion, and compare the three highest energy occupied orbitals with those of BeF_2. How do the outer atom group orbitals differ in their interactions with the central atom orbitals? How do the orbitals compare with the CO_2 orbitals discussed in Section 5.4.2?

5.42 Calculate and display the molecular orbitals of the ozone molecule, O_3. Which orbitals show π interactions? Compare your results with your answer to Problem 5.19.

5.43 a. Calculate and display the molecular orbitals for linear and cyclic H_3^+.

b. Which species is more likely to exist (i.e., which is more stable)?

5.44 Diborane, B_2H_6, has the structure shown.

a. Using the point group of the molecule, create a representation using the $1s$ orbitals on the hydrogens as a basis. Reduce this representation, and sketch group orbitals matching each of the irreducible representations. (Suggestion: Treat the bridging and terminal hydrogens separately.)

b. Calculate and display the molecular orbitals. Compare the software-generated images with the group orbital sketches from part a, and explain how hydrogen can form "bridges" between two B atoms. (This type of bonding is discussed in Chapter 8.)