

Exercises

Review Questions

1. Why do we use other bonding theories in addition to the Lewis model?
2. What is a chemical bond according to valence bond theory?
3. In valence bond theory, what determines the geometry of a molecule?
4. In valence bond theory, the interaction energy between the electrons and nucleus of one atom with the electrons and nucleus of another atom is usually negative (stabilizing) when _____.
5. What is hybridization? Why is hybridization necessary in valence bond theory?
6. How does hybridization of the atomic orbitals in the central atom of a molecule help lower the overall energy of the molecule?
7. How is the *number* of hybrid orbitals related to the number of standard atomic orbitals that are hybridized?
8. Sketch each hybrid orbital.
 - a. sp
 - b. sp^2
 - c. sp^3
 - d. sp^3d
 - e. sp^3d^2
9. In the Lewis model, the two bonds in a double bond look identical. However, valence bond theory shows that they are not. Describe a double bond according to valence bond theory. Explain why rotation is restricted about a double bond but not about a single bond.
10. Name the hybridization scheme that corresponds to each electron geometry.
 - a. linear
 - b. trigonal planar
 - c. tetrahedral
 - d. trigonal bipyramidal
 - e. octahedral
11. What is a chemical bond according to molecular orbital theory?
12. Explain the difference between hybrid atomic orbitals in valence bond theory and LCAO molecular orbitals in molecular orbital theory.
13. What is a bonding molecular orbital?
14. What is an antibonding molecular orbital?
15. What is the role of wave interference in determining whether a molecular orbital is bonding or antibonding?
16. In molecular orbital theory, what is bond order? Why is it important?
17. How is the number of molecular orbitals approximated by a linear combination of atomic orbitals related to the number of atomic orbitals used in the approximation?
18. Sketch each molecular orbital.
 - a. σ_{2s}
 - b. σ_{2s}^*
 - c. σ_{2p}
 - d. σ_{2p}^*
 - e. π_{2p}
 - f. π_{2p}^*
19. Draw an energy diagram for the molecular orbitals of period 2 diatomic molecules. Show the difference in ordering for B_2 , C_2 , and N_2 compared to O_2 , F_2 , and Ne_2 .
20. Why does the energy ordering of the molecular orbitals of the second-period diatomic molecules change in going from N_2 to O_2 ?
21. Explain the difference between a paramagnetic species and a diamagnetic one.

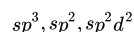
22. When applying molecular orbital theory to heteronuclear diatomic molecules, the atomic orbitals used may be of different energies. If two atomic orbitals of different energies make two molecular orbitals, how are the energies of the molecular orbitals related to the energies of the atomic orbitals? How is the shape of the resultant molecular orbitals related to the shapes of the atomic orbitals?
23. In molecular orbital theory, what is a nonbonding orbital?
24. Write a short paragraph describing chemical bonding according to the Lewis model, valence bond theory, and molecular orbital theory. Indicate how the theories differ in their description of a chemical bond and indicate the strengths and weaknesses of each theory. Which theory is correct?

Problems by Topic

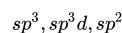
Note: Answers to all odd-numbered Problems can be found in [Appendix III](#). Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but somewhat more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

Valence Bond Theory

25. The valence electron configurations of several atoms are shown below. How many bonds can each atom make without hybridization?
- Be $2s^2$
 - P $3s^2 3p^3$
 - F $2s^2 2p^5$
26. The valence electron configurations of several atoms are shown below. How many bonds can each atom make without hybridization?
- B $2s^2 2p^1$
 - N $2s^2 2p^3$
 - O $2s^2 2p^4$
27. Draw orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in PH_3 . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of 93.3° ?
28. Draw orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in SF_2 . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of 98.2° ?
29. Draw orbital diagrams (boxes with arrows in them) to represent the electron configuration of carbon before and after sp^3 hybridization.
30. Draw orbital diagrams (boxes with arrows in them) to represent the electron configurations of carbon before and after sp hybridization.
31. Which hybridization scheme allows the formation of at least one π bond?



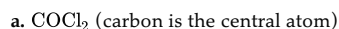
32. Which hybridization scheme allows the central atom to form more than four bonds?



33. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in [Examples 6.1](#) and [6.2](#).
- CCl_4
 - NH_3
 - OF_2
 - CO_2
34. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in [Examples 6.1](#) and [6.2](#).
- CH_2Br_2



35. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 6.1 and 6.2.

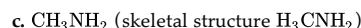
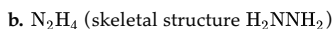
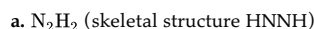


36. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 6.1 and 6.2.



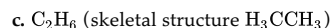
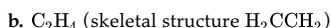
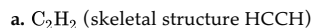
37. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom.

Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 6.1 and 6.2.

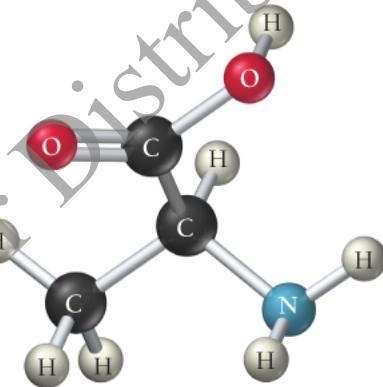


38. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom.

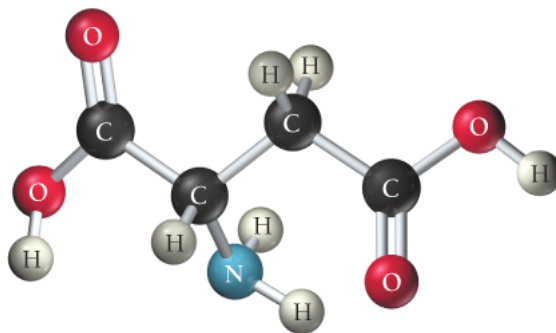
Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 6.1 and 6.2.



39. Consider the structure of the amino acid alanine. Indicate the hybridization about each interior atom.



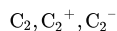
40. Consider the structure of the amino acid aspartic acid. Indicate the hybridization about each interior atom.



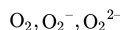
Molecular Orbital Theory

41. Sketch the bonding molecular orbital that results from the linear combination of two 1s orbitals. Indicate the

- region where interference occurs and state the kind of interference (constructive or destructive).
42. Sketch the antibonding molecular orbital that results from the linear combination of two $1s$ orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).
43. Draw an MO energy diagram and predict the bond order of Be_2^+ and Be_2^- . Do you expect these molecules to exist in the gas phase?
44. Draw an MO energy diagram and predict the bond order of Li_2^+ and Li_2^- . Do you expect these molecules to exist in the gas phase?
45. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the $2p_x$ atomic orbitals in a homonuclear diatomic molecule. (The $2p_x$ orbitals are those whose lobes are oriented along the bonding axis.)
46. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the $2p_z$ atomic orbitals in a homonuclear diatomic molecule. (The $2p_z$ orbitals are those whose lobes are oriented perpendicular to the bonding axis.) How do these molecular orbitals differ from those obtained from linear combinations of the $2p_y$ atomic orbitals? (The $2p_y$ orbitals are also oriented perpendicular not only to the bonding axis, but also to the $2p_z$ orbitals.)
47. Using the molecular orbital energy ordering for second-period homonuclear diatomic molecules in which the π_{2p} orbitals lie at *lower* energy than the σ_{2p} , draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?
- 4
 - 6
 - 8
 - 9
48. Using the molecular orbital energy ordering for second-period homonuclear diatomic molecules in which the π_{2p} orbitals lie at *higher* energy than the σ_{2p} , draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?
- 10
 - 12
 - 13
 - 14
49. Apply molecular orbital theory to predict if each molecule or ion exists in a relatively stable form.
- H_2^{2-}
 - Ne_2
 - He_2^{2+}
 - F_2^{2-}
50. Apply molecular orbital theory to predict if each molecule or ion exists in a relatively stable form.
- C_2^{2+}
 - Li_2
 - Be_2^{2+}
 - Li_2^{2-}
51. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?



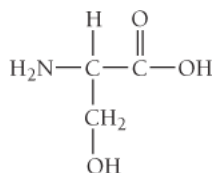
52. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?



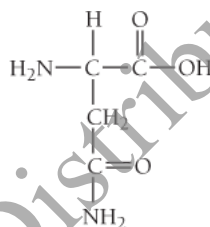
53. Draw an MO energy diagram for CO. (Use the energy ordering of O_2 .) Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.
54. Draw an MO energy diagram for HCl. Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

Cumulative Problems

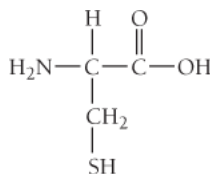
55. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.
- COF_2 (carbon is the central atom)
 - S_2Cl_2 (ClSSCl)
 - SF_4
56. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.
- IF_5
 - CH_2CHCH_3
 - CH_3SH
57. Amino acids are biological compounds that link together to form proteins, the workhorse molecules in living organisms. The skeletal structures of several simple amino acids are shown here. For each skeletal structure, determine the hybridization about each interior atom.
- serine



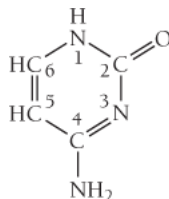
- asparagine



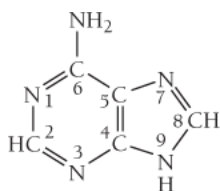
- licysteine



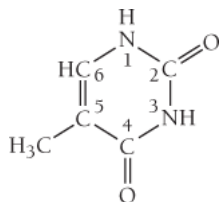
58. The genetic code is based on four different bases with the structures shown here. Determine the hybridization in each interior atom in these four bases.
- cytosine
 - adenine
 - thymine
 - guanine
-



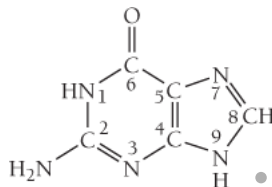
b.



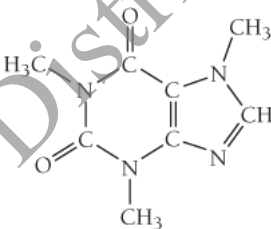
c.



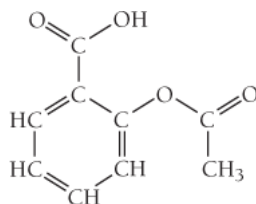
d.



59. The structure of caffeine, present in coffee and many soft drinks, is shown here. How many pi bonds are present in caffeine? How many sigma bonds? Insert the lone pairs in the molecule. Which kinds of orbitals do the lone pairs occupy?



60. The structure of acetylsalicylic acid (aspirin) is shown here. How many pi bonds are present in acetylsalicylic acid? How many sigma bonds? Which parts of the molecule are free to rotate? Which parts are rigid?

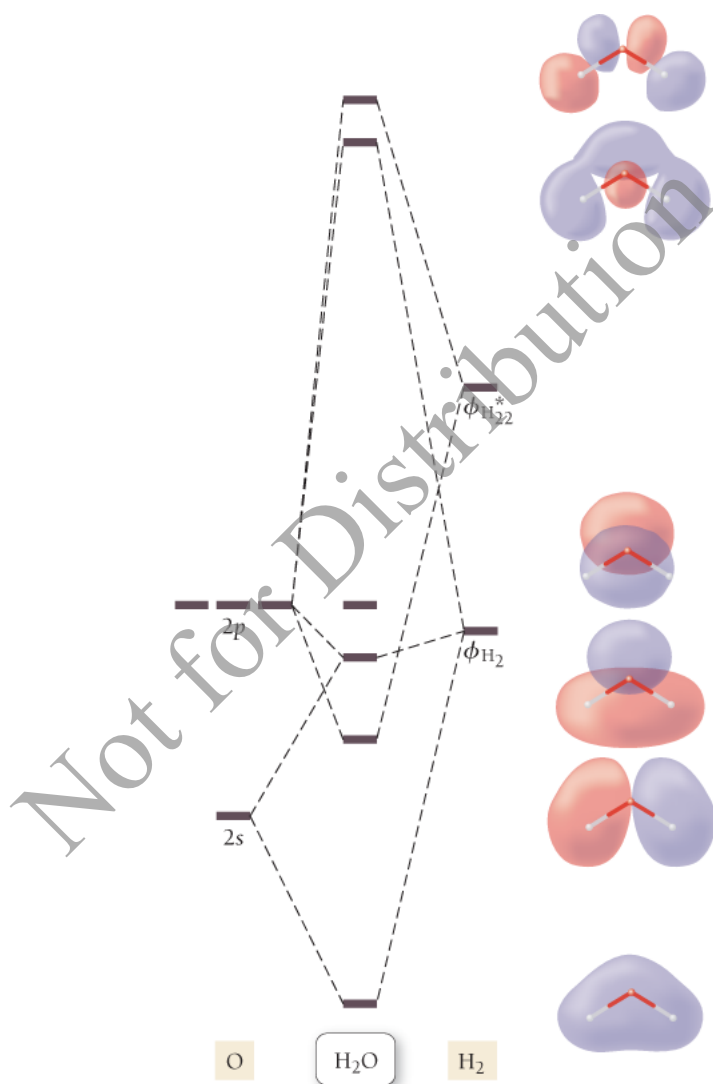


61. Draw a molecular orbital energy diagram for ClF. (Assume that the σ_p orbitals are lower in energy than the π orbitals.) What is the bond order in ClF?
62. Draw Lewis structures and MO diagrams for CN^+ , CN , and CN^- . According to the Lewis model, which species is most stable? According to MO theory, which species is most stable? Do the two theories agree?
63. Bromine can form compounds or ions with any number of fluorine atoms from one to five. Write the formulas of all five of these species, assign a hybridization, and describe their electron and molecular geometry.
64. The compound C_3H_4 has two double bonds. Describe its bonding and geometry, using a valence bond approach.
65. How many hybrid orbitals do we use to describe each molecule?

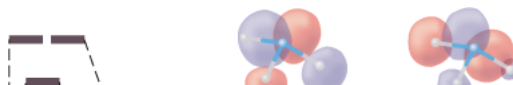
- a. N_2O_5
 - b. $\text{C}_2\text{H}_5\text{NO}$ (4 C–H bonds and one O–H bond)
 - c. BrCN (no formal charges)
66. Indicate which orbitals overlap to form the σ bonds in each compound.
- a. BeBr_2
 - b. HgCl_2
 - c. ICN

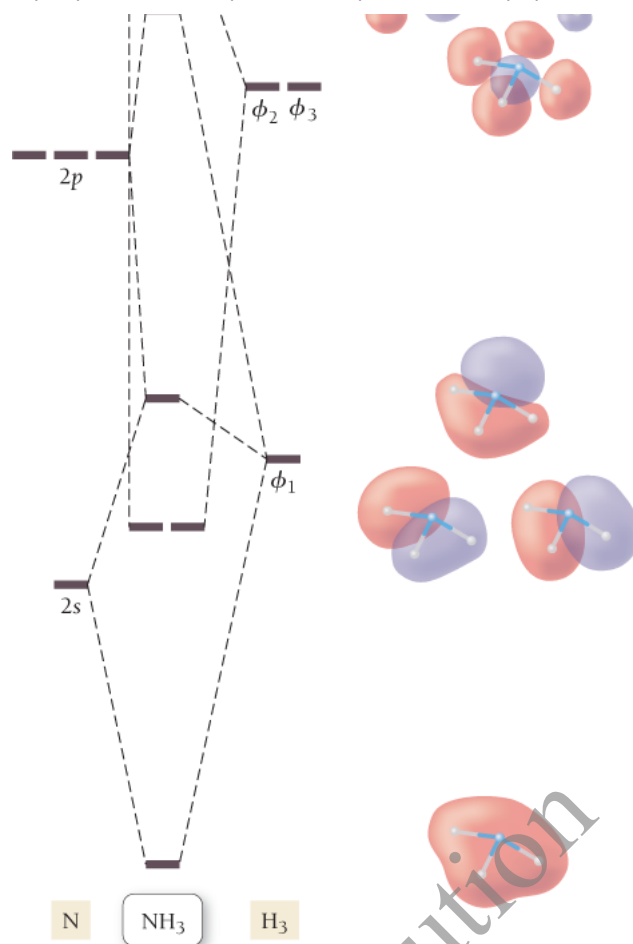
Challenge Problems

67. In VSEPR theory, which uses the Lewis model to determine molecular geometry, the trend of decreasing bond angle in CH_4 , NH_3 , and H_2O is accounted for by the greater repulsion of lone pair electrons compared to bonding pair electrons. How is this trend accounted for in valence bond theory?
68. The results of a molecular orbital calculation for H_2O are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is H_2O stable? Explain.

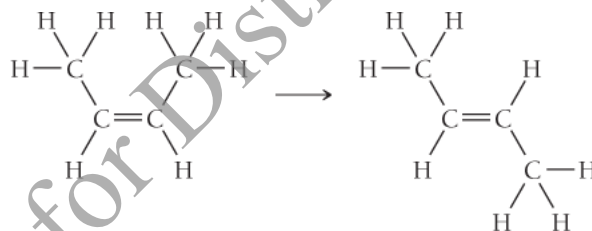


69. The results of a molecular orbital calculation for NH_3 are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is NH_3 stable? Explain.





70. *cis*-2-Butene isomerizes (changes its structure) to *trans*-2-butene via the reaction:



- If isomerization requires breaking the pi bond, what minimum energy is required for isomerization in J/mol? In J/molecule?
 - If the energy for isomerization comes from light, what minimum frequency of light is required? In what portion of the electromagnetic spectrum does this frequency lie?
71. The ion CH_5^+ can form under very special high-energy conditions in the vapor phase in a mass spectrometer. Propose a hybridization for the carbon atom and predict the geometry.
72. Neither the VSEPR model nor the hybridization model is able to account for the experimental observation that the F—Ba—F bond angle in gaseous BaF_2 is 108° rather than the predicted 180° . Suggest some possible explanations for this observation.

Conceptual Problems

73. How does each of the three major bonding theories (the Lewis model, valence bond theory, and molecular orbital theory) define a single chemical bond? A double bond? A triple bond? How are these definitions similar? How are they different?
74. The most stable forms of the nonmetals in groups 4A, 5A, and 6A of the first period are molecules with multiple bonds. Beginning with the second period, the most stable forms of the nonmetals of these groups are

molecules without multiple bonds. Propose an explanation for this observation based on valence bond theory.

75. Consider the bond energies of three iodine halides:

• Bond	• Bond Energy
• Br—Cl	• 218 kJ/mol
• Br—Br	• 193 kJ/mol
• I—Br	• 175 kJ/mol

How might you use valence bond theory to help explain this trend?

Questions for Group Work

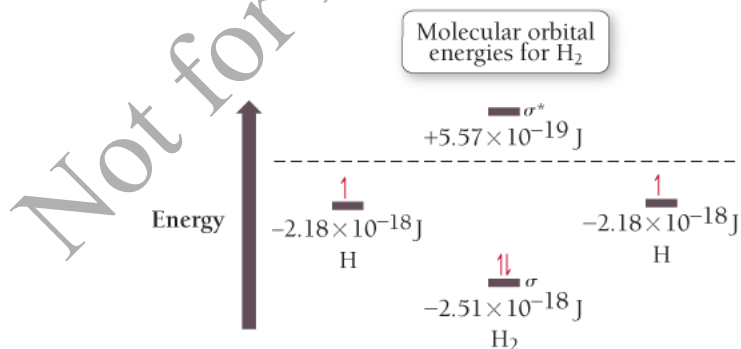
Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

76. How many atomic orbitals form a set of sp^3 hybrid orbitals? A set of sp^2 hybrid orbitals? A set of sp hybrid orbitals? What is the relationship between these numbers and the number of electron groups around the central atom?
77. Have each group member pick one of these hybridization schemes (sp , sp^2 , and sp^3) and describe it to the other group members. In the description, include a drawing of the orbitals in the hybridization scheme and indicate how to determine if that hybridization scheme is the correct one for a particular atom in a molecule.
78. Divide your group into two subgroups. Have one subgroup use molecular orbital theory to explain bonding in N_2^+ and the other in N_2^- . Then have the entire group describe how the bond strengths in these ions are different from those of the bonds in neutral N_2 .

Data Interpretation and Analysis

79. A molecular orbital calculation for H_2 results in the molecular orbital diagram shown here. The energy listed next to each orbital in the diagram corresponds to the energy of an electron in that orbital according to the calculation. Study the diagram and answer the questions that follow.



- What is the ionization energy of H in kJ/mol?
- Based on the calculation, what is the ionization energy of H_2 in kJ/mol?
- Based on the calculation, what is the bond energy for H_2 in kJ/mol? (*Hint: The bond energy is the difference between the energies of the two electrons when they are in H atoms and the energies of the two electrons when they are in H_2 .*)
- Look up the bond energy for H_2 in [Table 5.3](#). How does the calculated bond energy compare to the experimentally measured bond energy? Calculate the percent difference between the calculated bond energy and the experimentally measured bond energy.

Answers to Conceptual Connections

ANSWERS TO CONCEPTUAL CONNECTIONS

Cc 6.1 (a) In the Lewis model, a covalent chemical bond is the sharing of electrons (represented by dots). (b) In valence bond theory, a covalent chemical bond is the overlap of half-filled atomic orbitals. (c) The answers are different because the Lewis model and valence bond theory are different models for chemical bonding. They both make useful and often similar predictions, but the assumptions of each model are different, and so are their respective descriptions of a chemical bond.

Cc 6.2 According to valence bond theory, a double bond is actually composed of two different kinds of bonds, one σ and one π . The orbital overlap in the π bond is side to side between two p orbitals and consequently different from the end-to-end overlap in a σ bond. Because the bonds are different types, the bond energy of the double bond is not just the bond energy of the single bond doubled.

Cc 6.3 (a) Because carbon has two electron groups in CO_2 (the two double bonds), the geometry is linear and the hybridization is sp .

Cc 6.4 In molecular orbital theory, atoms join together (or bond) when the electrons in the atoms can lower their energy by occupying the molecular orbitals of the resultant molecule. Unlike the Lewis model or valence bond theory, the chemical "bonds" in MO theory are not localized between atoms but spread throughout the entire molecule.

Not for Distribution

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