

# Chapter 3 – Orbital Interactions 1

## YOUR TURN 3.1

In Figure 3-2a, draw a circle around the dots so that the nucleus is at the center and the circle encompasses 90% of the dots.

Answers to Your Turns are in the back of the book.

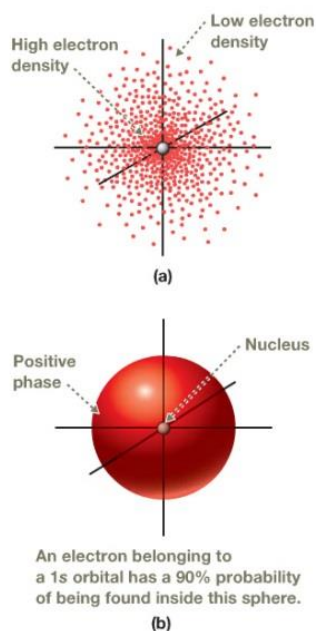


FIGURE 3-2 Representations of the 1s orbital

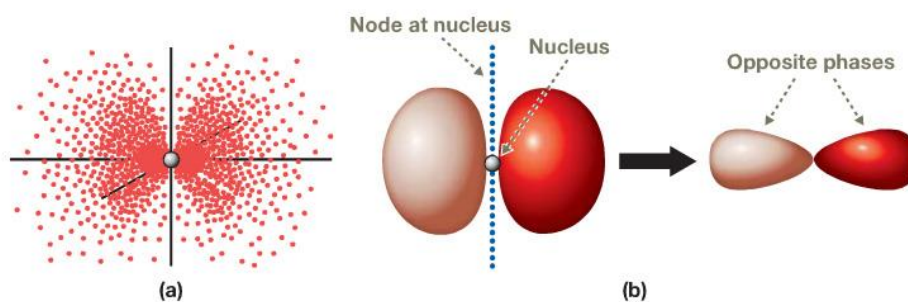


FIGURE 3-3 Representations of a 2p orbital (a) Electron density distribution of a 2p orbital. (b) A solid surface depicting a 2p orbital, indicating two lobes of opposite phase, separated by a nodal plane (left). A simplification of the 2p orbital (right).

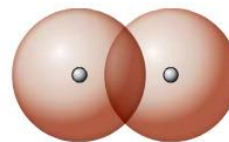
Redraw Figure 3-5 with both initial waves generated on the left side of the rope to represent negative phases.

## 3.3 YOUR TURN

## YOUR TURN 3.4

Redraw Figure 3-5, but this time generate the top wave on the left side of the rope (negative phase) and generate the bottom wave on the right side of the rope (positive phase).

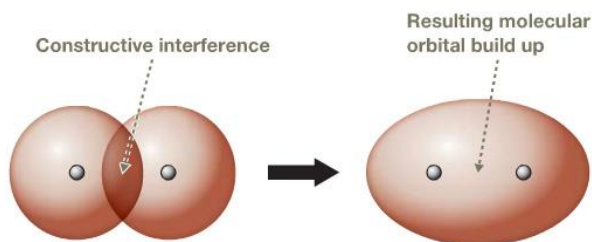
**SOLVED problem 3.1** At the right is a representation of two 1s orbitals overlapping, each with a phase that is opposite the ones in Figure 3-7a. **(a)** Draw the MO that will result from this orbital interaction. **(b)** Is the resulting MO unique compared to the one shown at the right of Figure 3-7a?



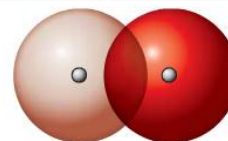
**Think** In the region in which the orbitals overlap, are the phases the same or opposite? Will that lead to constructive interference or destructive interference?

**Solve** Both orbitals are unshaded, indicating that they have the same relative phase. Therefore, constructive interference will take place, and the resulting MO is one that has been built up in the overlap region.

The resulting MO is all a single phase (in this case, unshaded) and has precisely the same shape as the MO shown in Figure 3-7a. Because phase is not a measurable quantity, the two MOs are indistinguishable and thus are not unique.



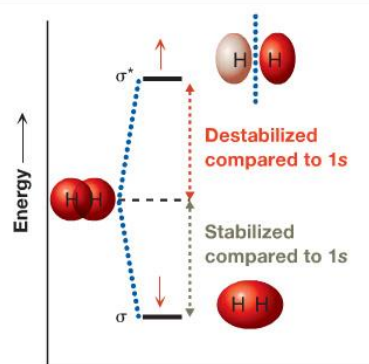
**problem 3.2** To the right is a representation of two 1s orbitals overlapping, each with a phase that is opposite the ones in Figure 3-7b. **(a)** Draw the MO that will result from this orbital interaction. **(b)** Is the resulting MO unique compared to the one shown at the right of Figure 3-7b?



**SOLVED problem 3.3** In Chapter 15, we will learn that light can promote an electron to a higher energy MO. Suppose that light is used to promote one of the two electrons in the  $H_2$  molecule from the  $\sigma$  MO to the  $\sigma^*$  MO, as shown at the right. Is this state more stable, less stable, or about the same as the two separated hydrogen atoms?

**Think** Is an electron in the  $\sigma$  MO stabilized or destabilized compared to an electron in the 1s AO? Is an electron in the  $\sigma^*$  MO stabilized or destabilized relative to an electron in the 1s AO?

**Solve** Compared to electrons in the 1s AO, one electron is stabilized in the  $\sigma$  MO, whereas the other is destabilized by about the same amount in the  $\sigma^*$  MO. When the energies of the electrons are added up, there is essentially no difference between the energy of the  $H_2$  molecule in the state described compared to the isolated atoms.



In the  $H_2$  molecule described in Solved Problem 3.3, what is the HOMO?

**3.5 YOUR TURN**

**problem 3.4** Suppose one electron is removed from an  $\text{H}_2$  molecule, leaving  $\text{H}_2^+$ . Draw the energy diagram similar to Figure 3-8 for this species. Is  $\text{H}_2^+$  more stable, less stable, or about the same as the isolated H atom and  $\text{H}^+$  ion?

In Figure 3-10a, circle and label the area of constructive interference and the area of destructive interference.

3.6 YOUR TURN

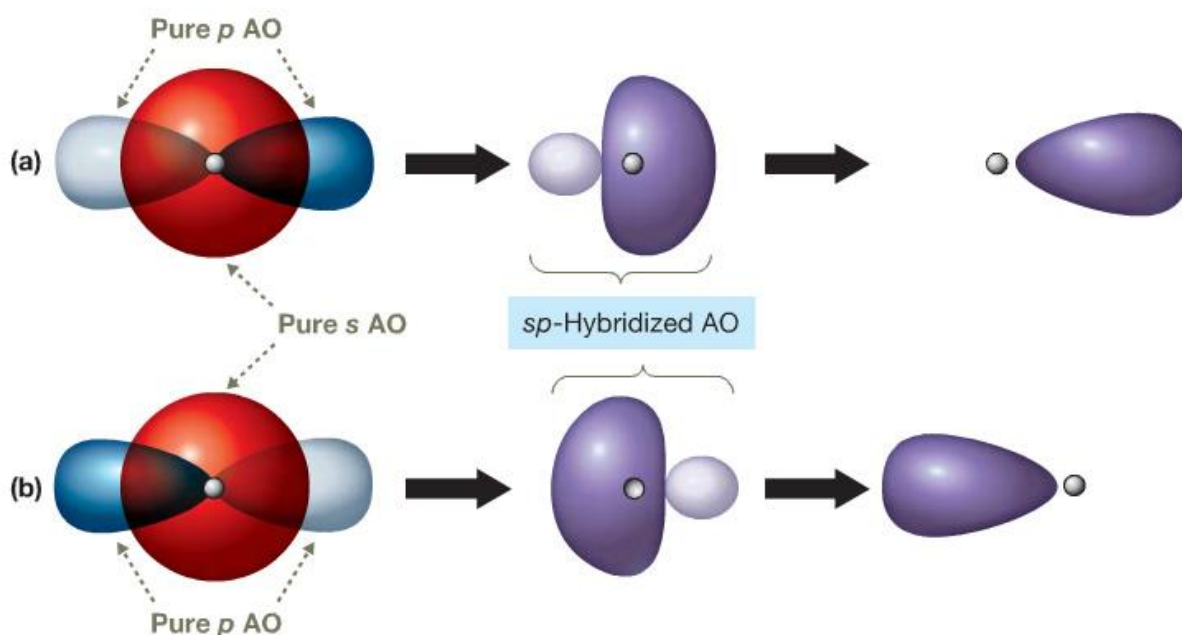
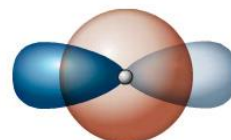


FIGURE 3-10 Generation of two  $sp$ -hybridized orbitals from pure AOs

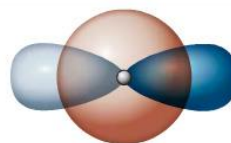
In Figure 3-10b, circle and label the area of constructive interference and the area of destructive interference.

3.7 YOUR TURN

**problem 3.5** Derive the hybridized orbital that would result from the interaction illustrated at the right, in which the phases of the  $s$  and  $p_x$  orbitals are opposite those in Figure 3-10a. Is the resulting orbital different from the ones in Figure 3-10? Explain.



**problem 3.6** Derive the hybridized orbital that would result from the interaction illustrated at the right, in which the phases of the  $s$  and  $p_x$  orbitals are opposite those in Figure 3-10b. Is the resulting orbital different from the ones in Figure 3-10? Explain.

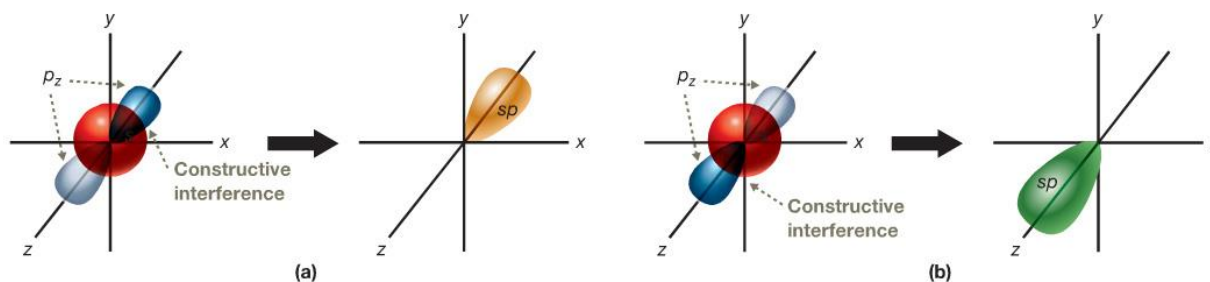
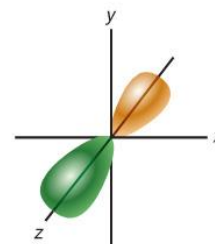


**SOLVED problem 3.7** Consider the pair of  $sp$ -hybridized orbitals at the right.

(a) Draw the orbital interaction that would be necessary to generate the orange  $sp$ -hybridized orbital from pure AOs. (b) Do the same for the green  $sp$ -hybridized orbital.

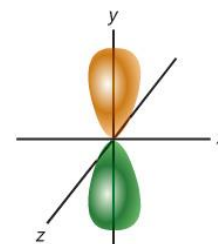
**Think** Along which axis are these  $sp$ -hybridized orbitals aligned? What orbitals must therefore interact? What is the phase of the large lobe of each hybridized orbital?

**Solve** Like any pair of  $sp$ -hybridized orbitals, the ones in the diagram must result from the interaction between an  $s$  and a  $p$  orbital. Because the  $sp$ -hybridized orbitals are aligned along the  $z$  axis, it must be the  $p_z$  orbital that has been used for hybridization, leaving the  $p_x$  and  $p_y$  orbitals unhybridized. The large lobe is shaded in both hybridized orbitals, so the  $s$  and  $p_z$  orbitals must both be shaded where the overlap occurs. The respective interactions are as follows:



**problem 3.8** Consider the pair of  $sp$ -hybridized orbitals at the right.

(a) Draw the orbital interaction that would generate the orange  $sp$ -hybridized orbital from pure AOs. (b) Do the same for the green  $sp$ -hybridized orbital.



In Figure 3-12c, label each orbital as either  $sp^2$ ,  $p_x$ ,  $p_y$ , or  $p_z$ .

### 3.8 YOUR TURN

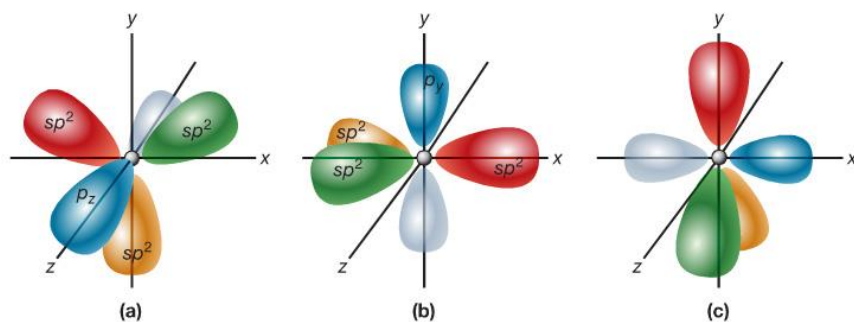
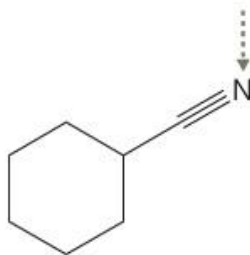
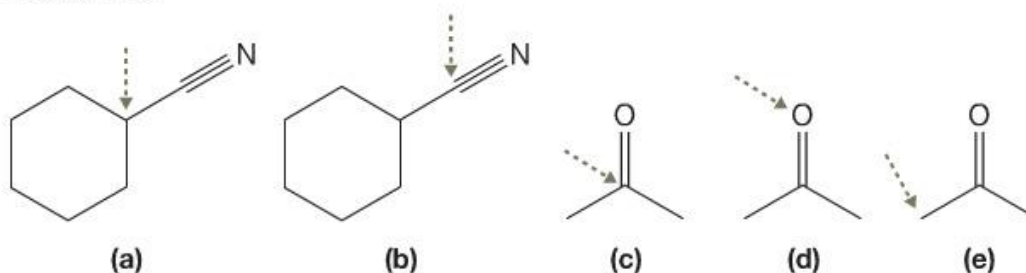


FIGURE 3-12 Three different but equivalent depictions of an  $sp^2$ -hybridized atom (a) The four valence AOs of an  $sp^2$ -hybridized atom in which the  $p_x$  and  $p_y$  orbitals were used for hybridization. The three  $sp^2$ -hybridized AOs occupy the  $xy$  plane, perpendicular to the unhybridized  $p_z$  AO. (b) An  $sp^2$ -hybridized atom in which the  $p_x$  and  $p_z$  orbitals were used for hybridization, leaving the  $p_y$  orbital unhybridized. (c) An  $sp^2$ -hybridized atom in which the  $p_y$  and  $p_z$  orbitals were used for hybridization, leaving the  $p_x$  orbital unhybridized.

**SOLVED problem 3.9** What is the hybridization of the N atom in the following molecule?



**problem 3.10** What is the hybridization of the atom indicated in each of the following molecules?



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**problem 3.11** (a) Draw the structure of a molecule with the formula  $C_5H_8$  that has two  $sp$ -hybridized atoms. (b) Draw the structure of another molecule with that formula that has four  $sp^2$ -hybridized atoms.

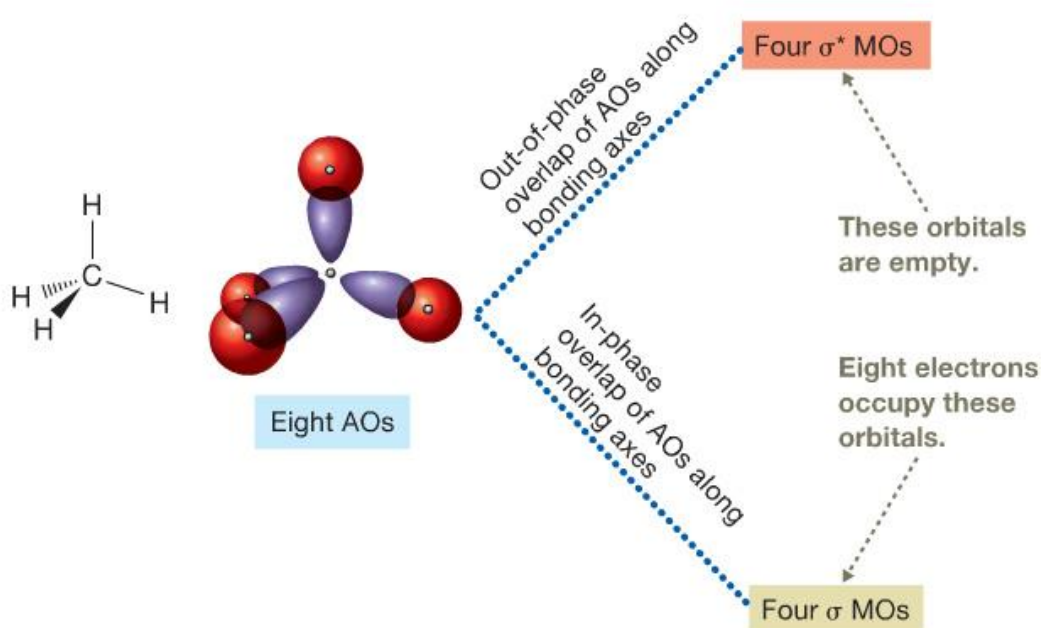
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**SOLVED problem 3.12** (a) Draw an orbital picture of methane ( $CH_4$ ), similar to that in Figure 3-14, indicating the important overlap of AOs. (b) Draw an energy diagram for this molecule, similar to that in Figure 3-15.

**Think** What is the hybridization of C? What valence shell orbitals does it contribute? What orbitals do the H atoms contribute? How many total orbitals should be produced from AO mixing?

**Solve** The C atom is  $sp^3$  hybridized, so it contributes four  $sp^3$ -hybridized orbitals in the valence shell. Each H atom contributes a  $1s$  orbital. The overlap of AOs appears on the left in the following diagram:



The energies of the MOs appear on the right. The eight AOs that overlap do so along the bonding axes, generating four  $\sigma$  and four  $\sigma^*$  MOs. Eight valence electrons completely fill the  $\sigma$  MOs, leaving the  $\sigma^*$  MOs empty.

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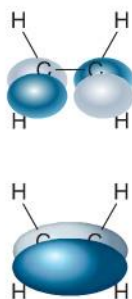
**problem 3.13** (a) Draw an orbital picture of the ammonium ion ( $\text{NH}_4^+$ ), similar to that in Figure 3-14, indicating the important overlap of AOs. (b) Draw an energy diagram for this species, similar to that in Figure 3-15.

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**problem 3.14** (a) Draw an orbital picture of the methylammonium ion ( $\text{CH}_3\text{NH}_3^+$ ), similar to that in Figure 3-14, indicating the important overlap of AOs. (b) Draw an energy diagram for this species, similar to that in Figure 3-15.

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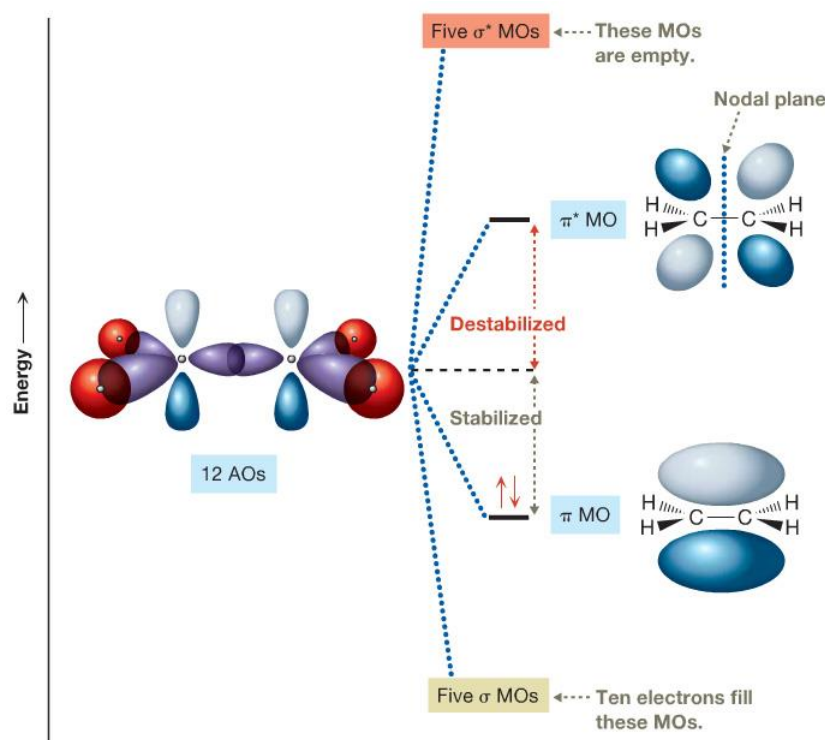
Ethene is shown twice below, with the molecular plane perpendicular to that in Figure 3-19. Identify the  $\pi$  and  $\pi^*$  MOs, and in the  $\pi^*$  MO, draw the nodal plane that is perpendicular to the bonding axis.



**3.9 YOUR TURN**

**YOUR TURN 3.10**

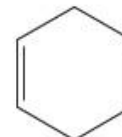
Label the HOMO and LUMO in Figure 3-19.



**FIGURE 3-19** Energy diagram for the formation of ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) from its constituent atoms. The AOs are shown on the left and the resulting MOs are shown on the right. The energies of the five  $\sigma$  MOs are lower than that of the  $\pi$  MO, whereas the energies of the five  $\sigma^*$  MOs are higher than that of the  $\pi^*$  MO.

**SOLVED problem 3.15** How many  $\pi$  bonds are there in a molecule of cyclohexa-1,4-diene? How many  $\sigma$  bonds?

**Think** How many double bonds are there? What is each double bond composed of? How many single bonds are there? What is each single bond composed of?



**Cyclohexa-1,4-diene**

**Solve** There are two  $\text{C}=\text{C}$  double bonds in cyclohexa-1,4-diene. Each is composed of one  $\pi$  bond and one  $\sigma$  bond, for a total of two  $\pi$  bonds and two  $\sigma$  bonds. Additionally, there are 12 single bonds: four  $\text{C}-\text{C}$  single bonds and eight  $\text{C}-\text{H}$  single bonds. Each  $\text{C}-\text{C}$  and  $\text{C}-\text{H}$  single bond is a  $\sigma$  bond, giving a total of 14  $\sigma$  bonds.

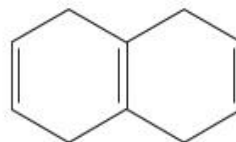
**problem 3.16** How many  $\pi$  bonds and how many  $\sigma$  bonds are in each of the following species?



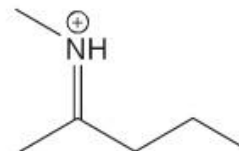
(a)



(b)



(c)

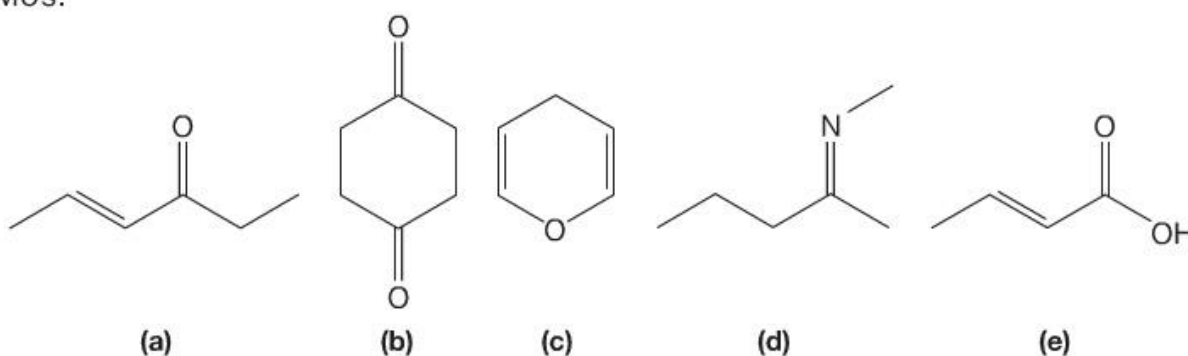


(d)



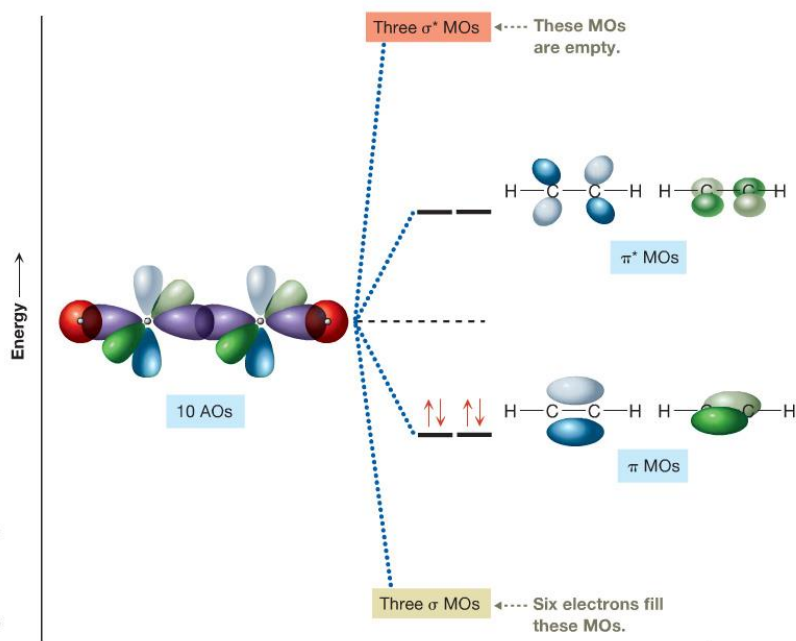
**problem 3.17** Draw an orbital picture of  $\text{H}_2\text{C}=\text{NH}$ , similar to that in Figure 3-22. How many nonbonding MOs do you expect?

**problem 3.18** For each of the following compounds, determine the number of  $\sigma$  bonds, the number of  $\pi$  bonds, and the number of electrons occupying nonbonding MOs.



**YOUR TURN 3.11**

Label the HOMO and the LUMO in Figure 3-25.



**FIGURE 3-25** Energy diagram depicting the formation of MOs in ethyne,  $\text{HC}\equiv\text{CH}$ . The AOs are on the left and the MOs are on the right. Six electrons occupy three  $\sigma$  MOs, and four electrons occupy two  $\pi$  MOs, thus accounting for all 10 valence electrons in ethyne.

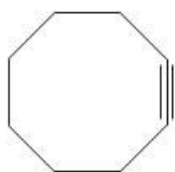
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**problem 3.19** Draw the orbital picture of  $\text{H}-\text{C}\equiv\text{N}$ , which should be similar to Figure 3-24.

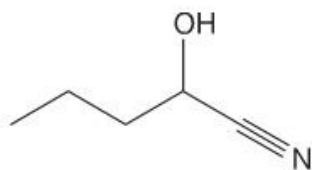
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**problem 3.20** For each of the following species, determine the number of  $\sigma$  bonds, the number of  $\pi$  bonds, and the number of electrons occupying nonbonding orbitals.



(a)



(b)



(c)

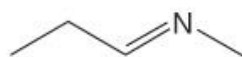


(d)

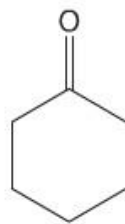
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**problem 3.21** In each of the following molecules, circle all of the atoms that are required to be in the same plane. (Because these are line structures, some atoms may need to be added back in.)



(a)



(b)



(c)

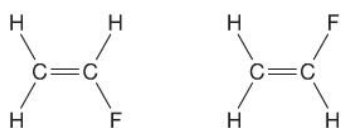
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**problem 3.22** List all of the intermolecular interactions present in *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene. Using this information, explain the difference in their boiling points.

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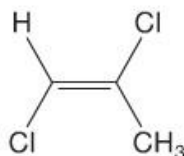
Using a molecular modeling kit, construct the following two molecules and try to line one up with the other. Are they the same or different? (Try all orientations of the two molecules.)



3.12 YOUR TURN

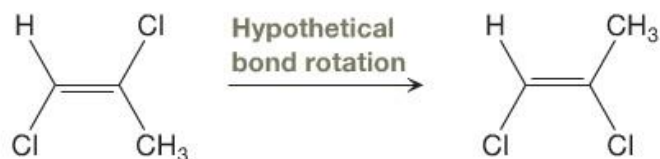
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**SOLVED problem 3.23** Does the following molecule have two distinct configurations about the double bond?



**Think** Does a hypothetical rotation of  $180^\circ$  about the double bond give rise to a different molecule? How can you tell?

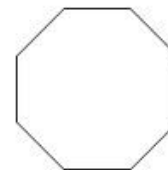
**Solve** One way to answer this question is to compare molecules before and after the hypothetical rotation.



These molecules are different because the one on the left has the Cl atoms on opposite sides of the double bond, whereas the one on the right has the Cl atoms on the same side. A second way to answer this question is simply to look at the substituents (i.e., the atoms or groups) bonded to each atom joined by the double bond. Neither of them is singly bonded to two identical substituents, so two unique configurations about the double bond must exist.

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**problem 3.24** Does cyclooctene have two distinct configurations about its C=C double bond?



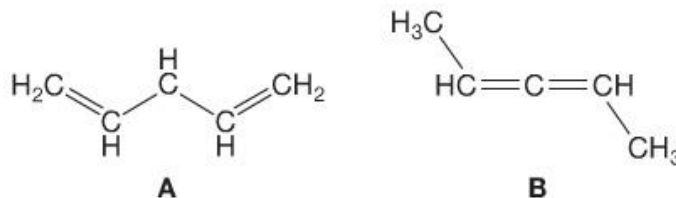
Cyclooctene

**problem 3.25** Draw the form of  $\alpha$ -linolenic acid in which all three double bonds are trans. How many unique structures can be made by changing the cis/trans configurations about the double bonds in  $\alpha$ -linolenic acid?

(a) Using a molecular modeling kit, construct a molecule of  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$ . Is the entire molecule planar? (b) Next, construct a molecule of  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{CH}_2$ . Is that molecule entirely planar?

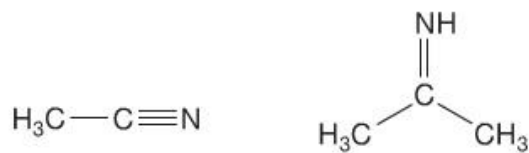
3.13 YOUR TURN

**SOLVED problem 3.26** In which of the following molecules do you think the C=C distances are longer? In which molecule are the C=C bonds stronger?



**Think** What is the hybridization of each atom involved in the C=C bonds? How does that affect bond length and bond strength?

**problem 3.27** In which molecule is the C—C bond shorter? In which molecule is it stronger? Explain.



**3.28** For each of the following species, determine (a) the electron geometry and (b) the hybridization for all nonhydrogen atoms.

- (i)  $\text{CH}_3\text{NH}_2$       (ii)  $\text{CH}_3\text{N}=\text{O}$       (iii)  $\text{CH}_2\text{Cl}_2$       (iv)  $\text{BrCN}$

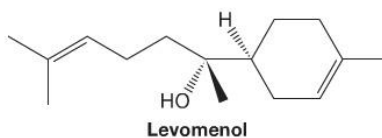
	i	ii	iii	iv
electron geometry				
hybridization				

**3.29** For each of the following species, determine (a) the electron geometry and (b) the hybridization for all nonhydrogen atoms.

- (i)  $\text{C}_2\text{H}_5^+$       (ii)  $\text{C}_2\text{H}_5^-$       (iii)  $\text{CH}_2=\text{OH}^+$       (iv)  $\text{CH}_6\text{N}^+$   
 (v)  $\text{CH}_5\text{O}^+$       (vi)  $\text{C}_3\text{H}_3^-$  (all hydrogens are on the same carbon)

	i	ii	iii	iv	v	vi
electron geometry						
hybridization						

**3.30** Levomenol, a naturally occurring sesquiterpene alcohol, has a sweet-smelling aroma and has been used as a component in fragrances. It also is known to have antimicrobial and anti-inflammatory properties. Determine the electron geometry, hybridization, and molecular geometry for each non-hydrogen atom in levomenol.



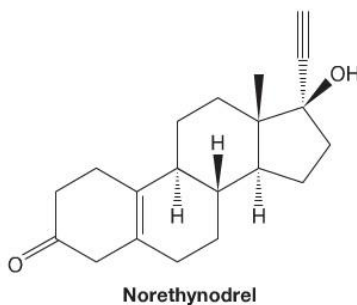
**3.31** Determine the total number of  $\sigma$  bonds and the total number of  $\pi$  bonds in levomenol (Problem 3.30).

**3.32** Bombykol is a pheromone produced by silkworm moths.



Is the configuration around each  $C=C$  double bond cis or trans?

**3.33** Norethynodrel was the synthetic hormone used in Enovid, the first oral contraceptive. (a) Determine the hybridization of each nonhydrogen atom. (b) How many total  $\sigma$  bonds and  $\pi$  bonds does norethynodrel have?



**3.34** Suppose a linear molecule were constructed from three atoms, all of which are found in the second row of the periodic table. How many valence shell AOs would these three atoms contribute toward the production of MOs? How many MOs would be produced by the mixing of these valence shell AOs? (*Hint*: The answer is independent of which orbitals overlap.)

**3.35** For the molecule described in Problem 3.34, suppose that two orbitals from the first atom were to mix with two orbitals from the second atom and that two other orbitals from the second atom were to mix with two orbitals from the third atom. In the resulting molecule, how many bonding MOs would there be in total? How many antibonding MOs? How many nonbonding MOs?

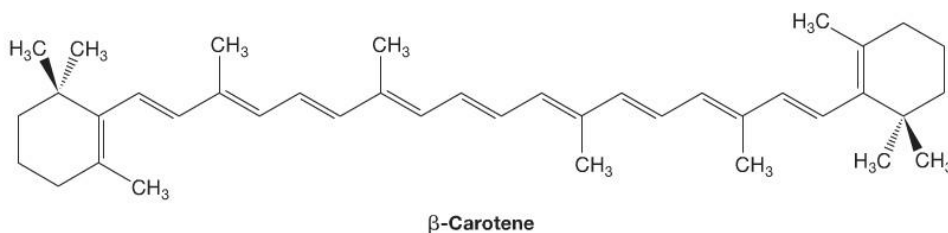
**3.36** For which of the following molecules are there two unique configurations about the double bond? Explain.

- (a)  $(\text{CH}_3)_2\text{C}=\text{CHCl}$       (b)  $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3$   
 (c)  $\text{ClHC}=\text{CHBr}$       (d)  $\text{HC}\equiv\text{CCH}=\text{CHCl}$

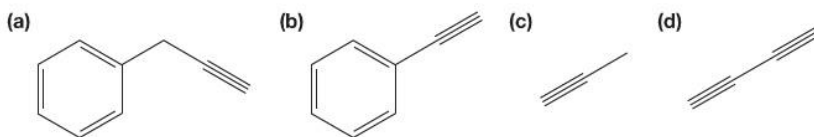
**3.37** How many total electrons reside in MOs of  $\pi$  symmetry in the following cation?



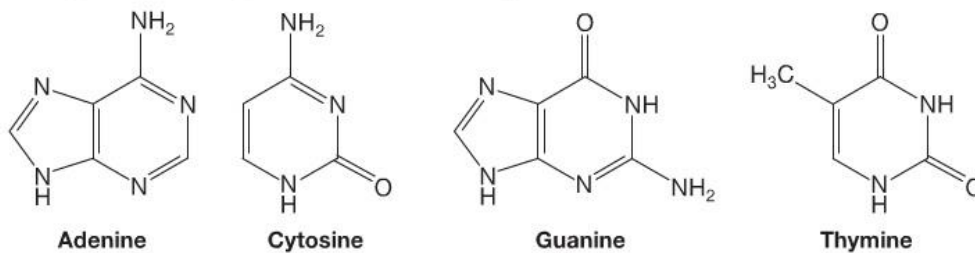
**3.38**  $\beta$ -Carotene is the compound responsible for the orange color of carrots and is the precursor to vitamin A. Judging from the following Lewis structure, how many  $\pi$  bonds does  $\beta$ -carotene have?



**3.39** Which of the following molecules has a  $\sigma$  bond obtained from the overlap between an  $sp$ -hybridized orbital and an  $sp^2$ -hybridized orbital?



**3.40** Adenine, cytosine, guanine, and thymine are the four nitrogenous bases found in DNA.



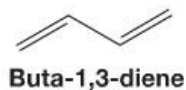
For each molecule, identify all of the nonhydrogen atoms that are required to be in the same plane.

**3.41** (a) Draw the orbital picture for  $\text{:C}\equiv\text{O:}$ , showing the explicit overlap of the contributing AOs. (b) How many MOs of  $\pi$  symmetry are there in total? (c) Draw the orbital energy diagram for CO and identify the HOMO and LUMO.

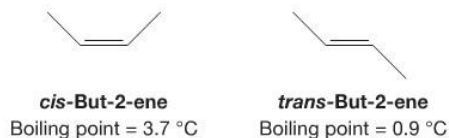
**3.42** (a) Draw the molecular orbital picture for propa-1,2-diene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ . (*Hint*: The three-dimensional geometry is shown in the chapter.) (b) Draw the MO energy diagram for propa-1,2-diene. What is the HOMO? What is the LUMO?

**3.43** Draw the MO picture for buta-1,2,3-triene,  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$ . (*Hint*: See Your Turn 3.13.)

**3.44** Do all of the atoms in buta-1,3-diene have to reside in the same plane? Why or why not?



**3.45** The boiling point of *cis*-but-2-ene is  $3.7\text{ }^\circ\text{C}$ , whereas that of *trans*-but-2-ene is  $0.9\text{ }^\circ\text{C}$ . Explain. (*Hint*: Identify which intermolecular interaction is responsible for the difference in boiling points.)





**3.46** Draw the AO contribution picture of  $\text{CH}_3\text{CH}_2^+$  and the MO energy diagram. What is the HOMO? What is the LUMO?

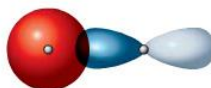
**3.47** Suppose that an electron were added to  $\text{CH}_3\text{CH}_2^+$ , the species in Problem 3.46, yielding uncharged  $\text{CH}_3\text{CH}_2$ . What is the HOMO? What is the LUMO?

**3.48** One of the orbital interactions we did not consider in this chapter is that between an s AO from one atom and a p AO from another atom in the following fashion:



These orbitals will not interact with this orientation. Explain why.

**3.49** The bond in H—Cl can be explained by the overlap between an s orbital from hydrogen and a p orbital from chlorine, as shown in the following diagram:



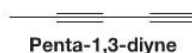
**(a)** Draw the bonding and antibonding MOs that would result from such an interaction. **(b)** What is the symmetry of each of these MOs?

**3.50** The bond in  $\text{Cl}_2$  can be explained by the end-on overlap between two  $p$  AOs, as shown in the following diagram:



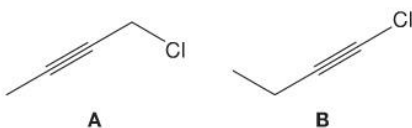
(a) Draw the bonding and antibonding MOs that would result from such an interaction. (b) What is the symmetry of each of these MOs?

**3.51** There are two C—C single bonds in penta-1,3-diyne.



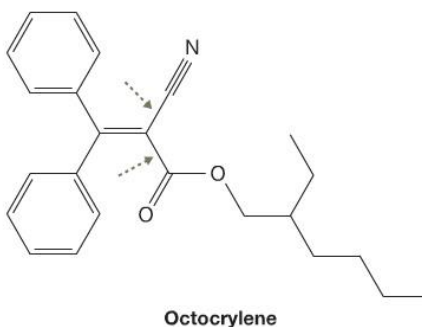
(a) Which of those bonds would you expect to be stronger? (b) Which of those bonds would you expect to be shorter? (c) The molecule is moderately polar, with a dipole moment of 1.37 D. In which direction would you expect the dipole moment to point? Explain.

**3.52** Consider the following two molecules:



(a) In which molecule would you expect the C—Cl bond to be stronger? (b) In which molecule would you expect the C—Cl bond to be shorter? (c) In which molecule would you expect there to be the greater concentration of negative charge on the Cl atom? Explain.

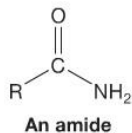
**3.53** Octocrylene is an ingredient found in topical sunscreens. It is a water-resistant molecule that helps protect skin against harmful UVA and UVB radiation.



(a) What is the hybridization of each nonhydrogen atom? (b) Circle all atoms bonded to the acyclic C=C double bond that are required to be in the same plane. (c) Are there two unique configurations possible about the acyclic C=C double bond? Explain. (d) Which of the two C—C single bonds indicated by arrows would you expect to be shorter? Explain.

**3.54** In the chapter, we mentioned that ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) does not undergo free rotation about the C=C double bond because the  $\pi$  bond must be broken to achieve the configuration in which the two  $\text{CH}_2$  groups are perpendicular to each other (Fig. 3-28b). (a) Draw the MO energy diagram for this “twisted ethene” molecule and identify the HOMO and LUMO. (b) By comparing the diagram for this molecule to that in Figure 3-19, explain why the molecule is more stable when it is all planar.

**3.55** An amide is typically drawn with a single bond connecting the carbonyl C atom to the N atom.



If this representation were accurate, we would expect the N atom to be pyramidal, and we would also expect C—N to undergo free rotation. In actuality, however, the N atom is rather planar, and the rotation is quite hindered—properties that give rise to important secondary structures of proteins, such as  $\alpha$  helices and  $\beta$  sheets (Chapter 26). Explain these properties of the amide.