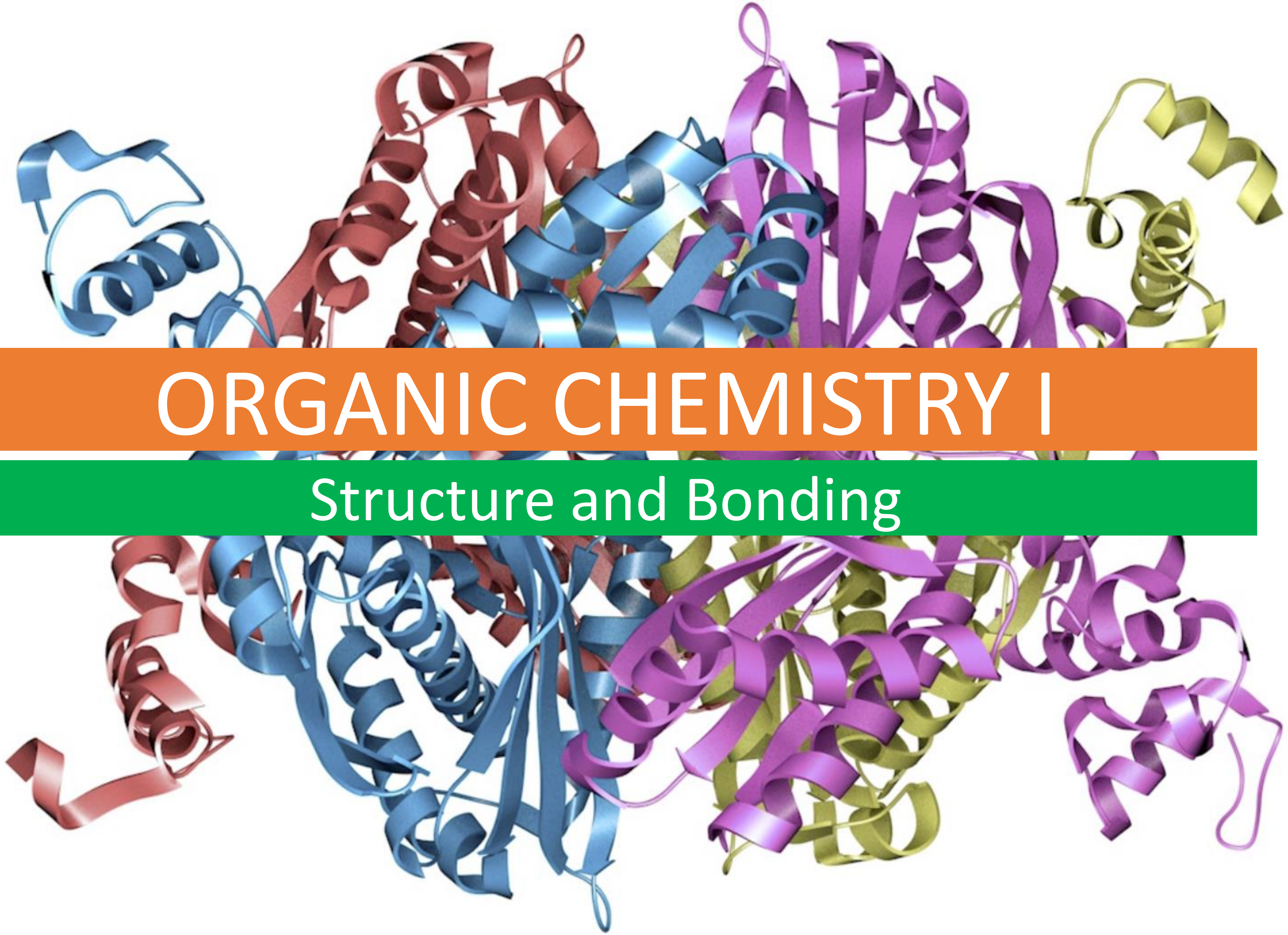
ORGANIC CHEMISTRY I

Structure and Bonding

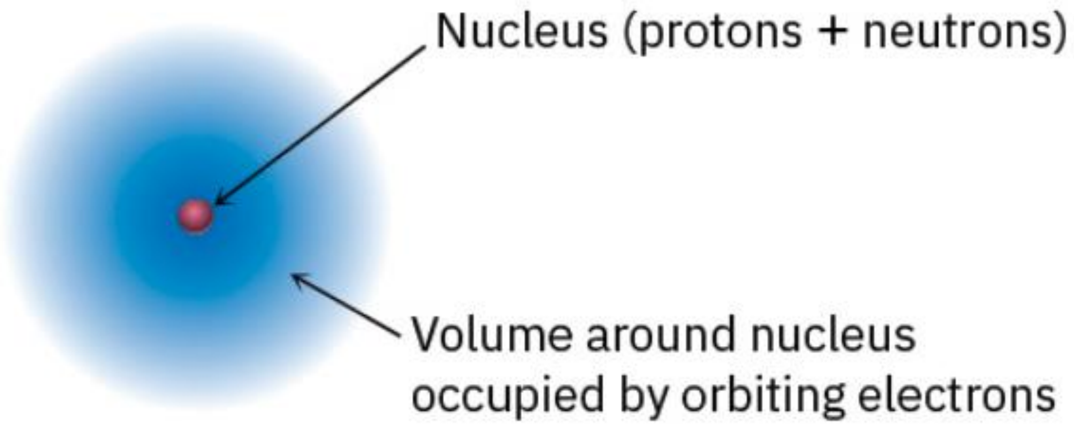


CHAPTER CONTENTS

1.1 Atomic Structure: **The Nucleus**

Structure of an atom

- Positively charged *nucleus* (very dense, protons and neutrons) and small (10^{-15} m)
  Negatively charged electrons are in a cloud (10^{-10} m) around nucleus
- Diameter is about 2×10^{-10} m (200 *picometers* (pm)) [the unit *angstrom* (Å) is 10^{-10} m = 100 pm]



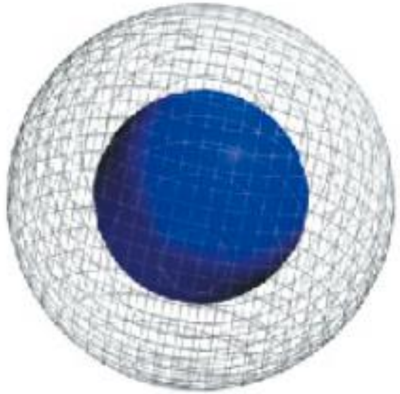


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FIGURE 1.3 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the blue solid surface than at the gray mesh surface.

Atomic Number and Atomic Mass

- The *atomic number* (*Z*) is the number of protons in the atom's nucleus
- The *mass number* (*A*) is the number of protons plus neutrons
- All the atoms of a given element have the same atomic number
- **Isotopes** are atoms of the same element that have different numbers of neutrons and therefore different mass numbers
- The **atomic mass** (*atomic weight*) of an element is the weighted average mass in atomic mass units (amu) of an element’s naturally occurring isotopes

1.2 Atomic Structure: **Orbitals**

An ***s*** orbital is **spherical**, a ***p*** orbital is **dumbbell-shaped,** and four of the five ***d*** orbitals are *cloverleaf-shaped*. Different **lobes** of *p* orbitals are often drawn for convenience as teardrops, but their actual shape is more like that of a doorknob, as indicated.

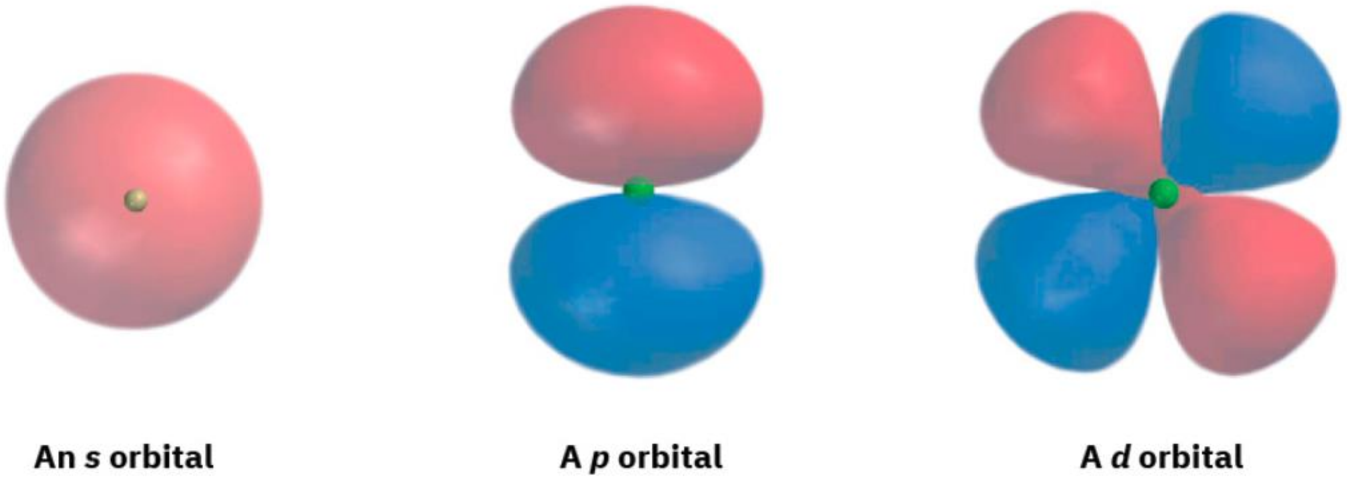


FIGURE 1.4 Representations of *s*, *p*, and *d* orbitals.

Orbitals and Shells

- Orbitals are grouped in **shells** of increasing size and energy
- Different shells contain different numbers and kinds of orbitals
- Each orbital can be occupied by two electrons
- First shell contains one *s* orbital, denoted 1*s*, holds only two electrons
- Second shell contains one *s* orbital (2*s*) and three *p* orbitals (2*p*), eight electrons
- Third shell contains an *s* orbital (3*s*), three *p* orbitals (3*p*), and five *d* orbitals (3*d*), 18 electrons

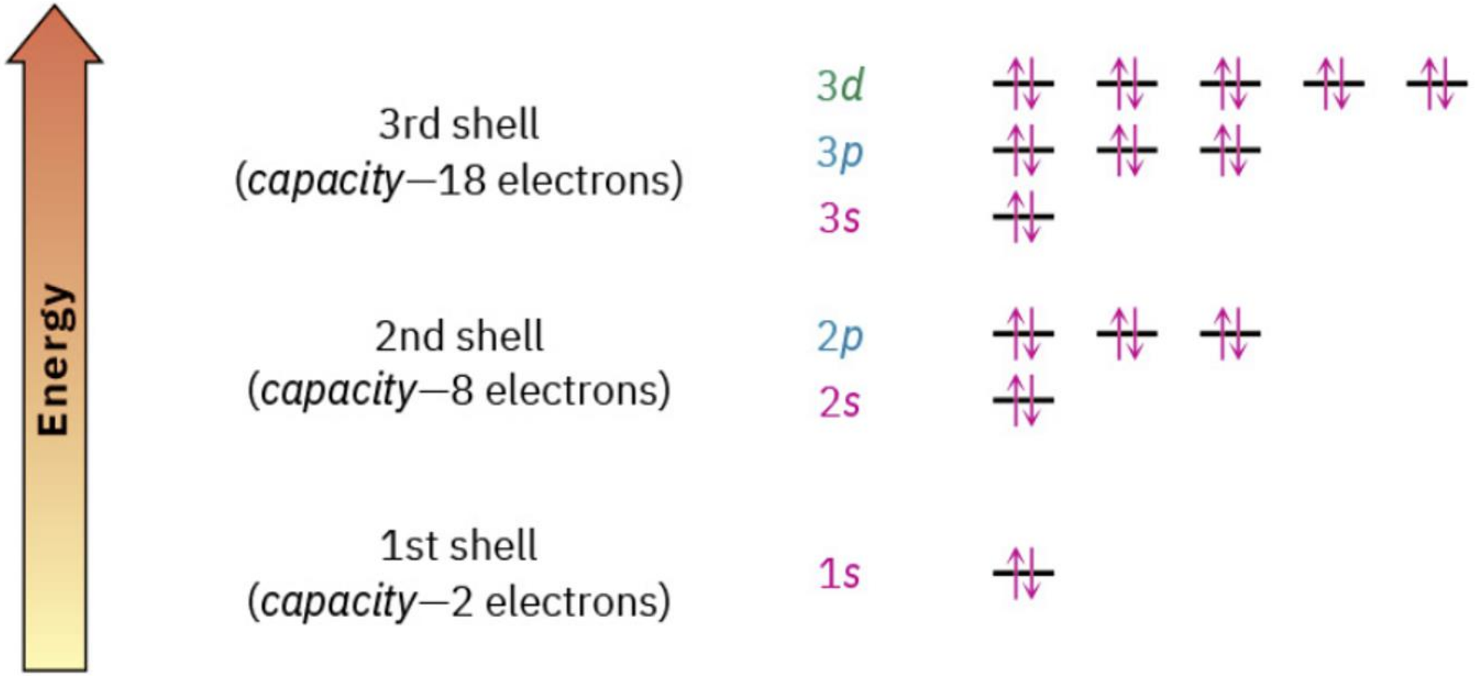


FIGURE 1.5 Energy levels of electrons in an atom.

p-Orbitals

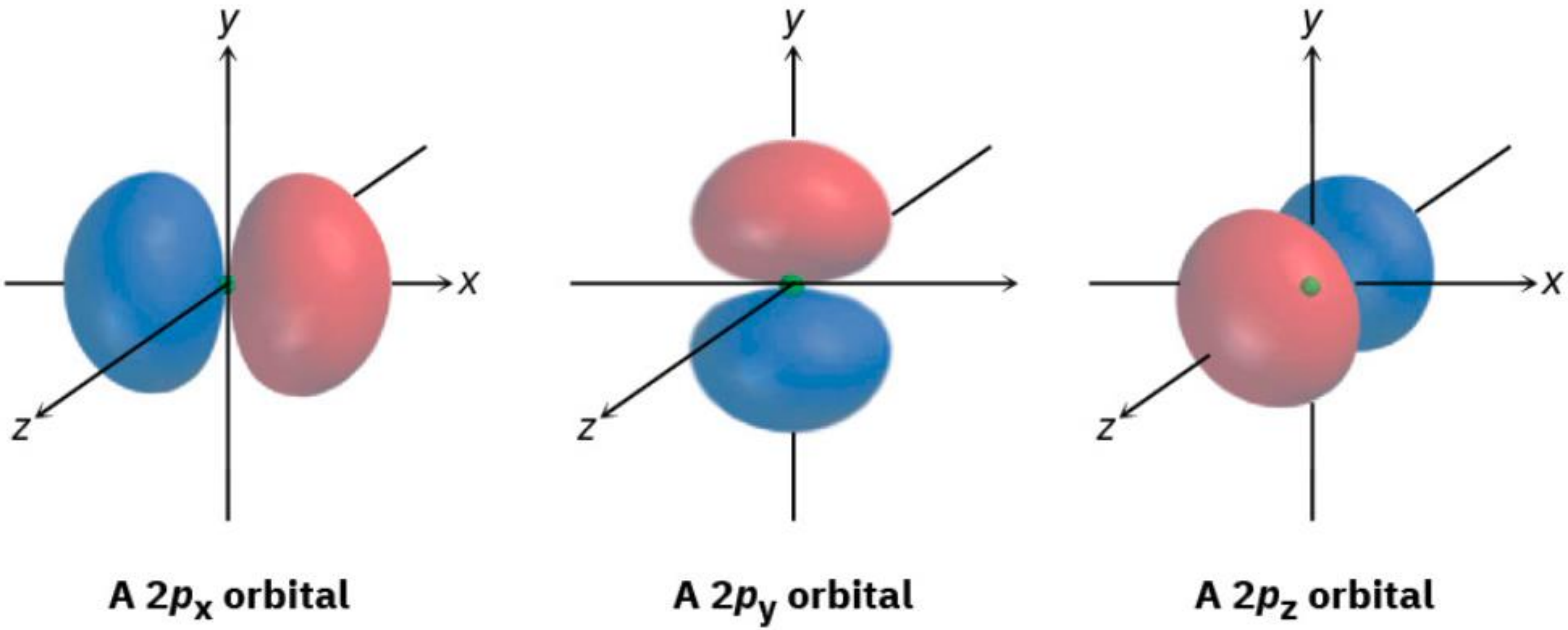


FIGURE 1.6 Shapes of the 2p orbitals. Each of the three mutually perpendicular, dumbbell-shaped orbitals has two lobes separated by a node. The two lobes have different algebraic signs in the corresponding wave function, as indicated by the different colors.

1.3 Atomic Structure: Electron Configurations

The lowest-energy arrangement, or **ground-state electron configuration**, of an atom is a list of the orbitals occupied by its electrons. We can predict this arrangement by following three rules.

RULE 1

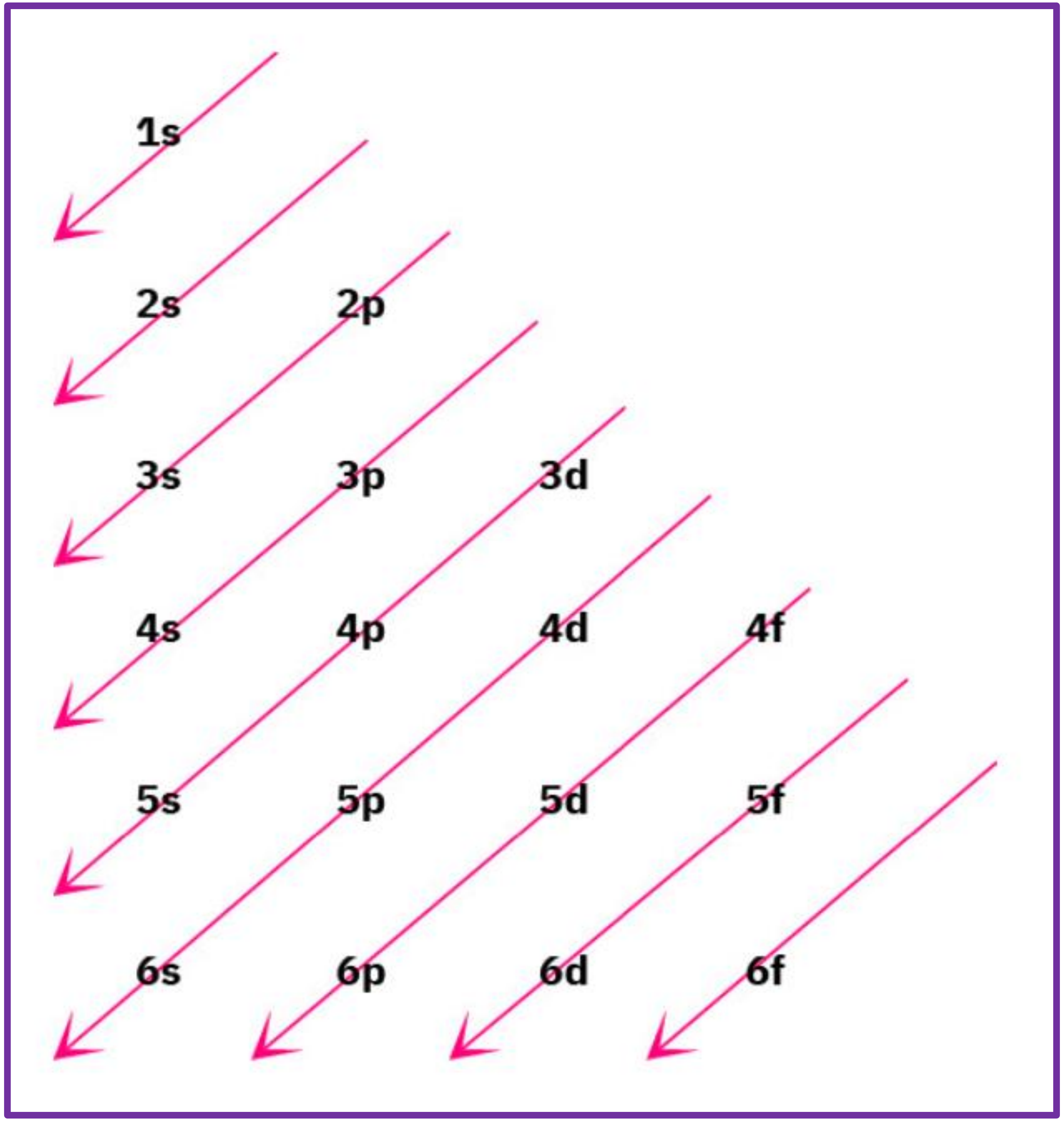
The lowest-energy orbitals fill up first, 1*s* → 2*s* → 2*p* → 3*s* → 3*p* → 3*d* → 4*s* → 3*d* according to the following graphic, a statement called the **Aufbau principle**. Note that the 4s orbital lies between the 3p and 3d orbitals in energy.

RULE 2

Electrons act in some ways as if they were spinning around an axis, somewhat as the earth spins. This spin can have two orientations, denoted as up (↑) and down (↓). Only two electrons can occupy an orbital, and they must have opposite spins, a statement called the **Pauli exclusion principle**.

RULE 3

If two or more empty orbitals of equal energy are available, one electron occupies each with spins parallel until all orbitals are half-full, a statement called **Hund’s rule**.


1s
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
5f
6s
6p
6d
6f

Some examples of how these rules apply are shown in **TABLE 1.1**.

TABLE 1.1 Ground-State Electron Configurations of Some Elements

Element	Atomic number	Configuration
Hydrogen	1	1*s* ↑
Carbon	6	2*p* ↑ ↑ — 2*s* ↑↓ 1*s* ↑↓
Phosphorus	15	3*p* ↑ ↑ ↑ 3*s* ↑↓ 2*p* ↑↓ ↑↓ ↑↓ 2*s* ↑↓ 1*s* ↑↓

PROBLEM 1-1

what is the ground-state:

(a) Oxygen (b) Nitrogen (c) Sulfur

PROBLEM 1-2

How many electrons does each of the following biological trace elements have in its outermost electron shell?

(a) Magnesium (b) Cobalt (c) Selenium

1.4 Development of Chemical Bonding Theory

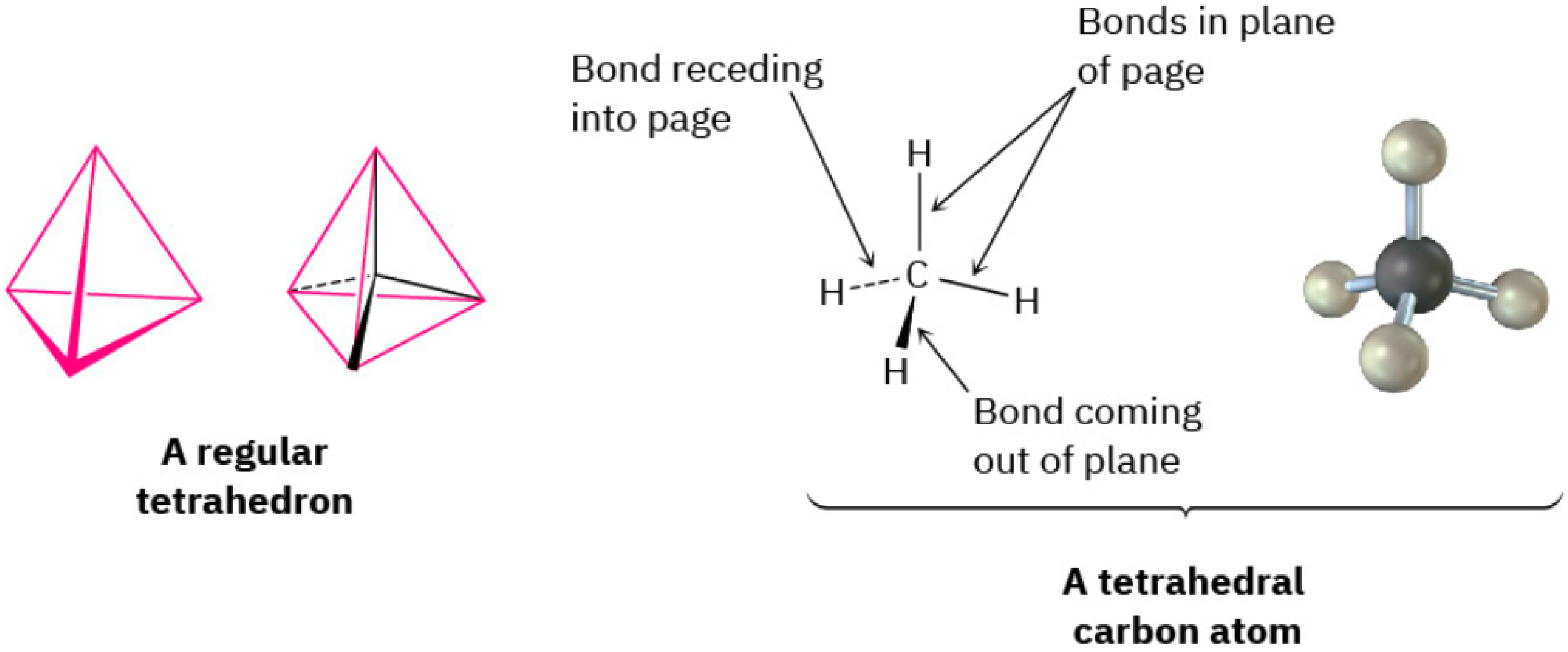
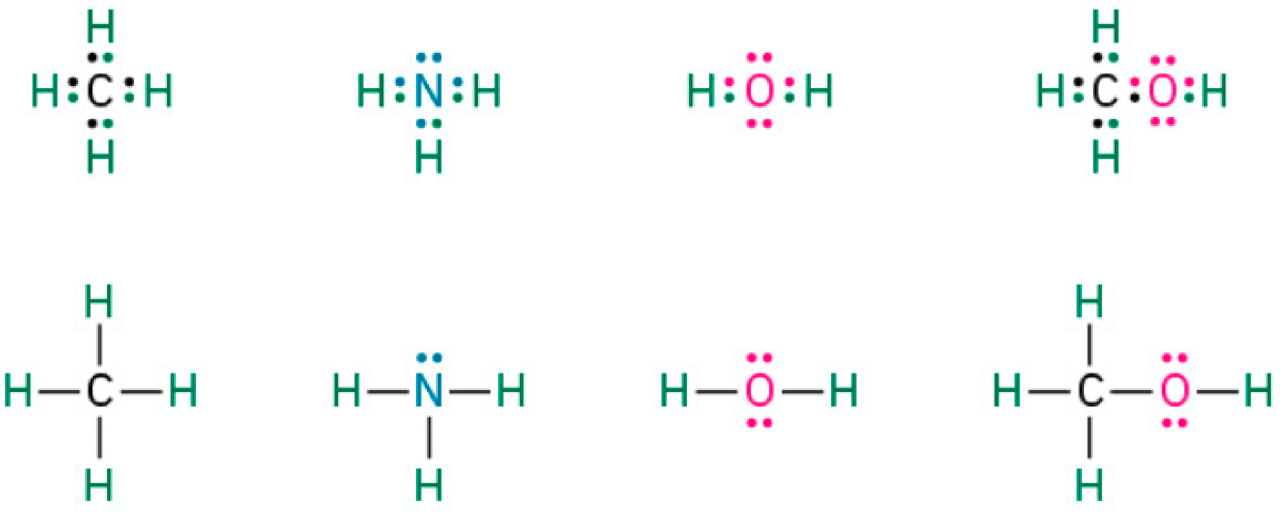


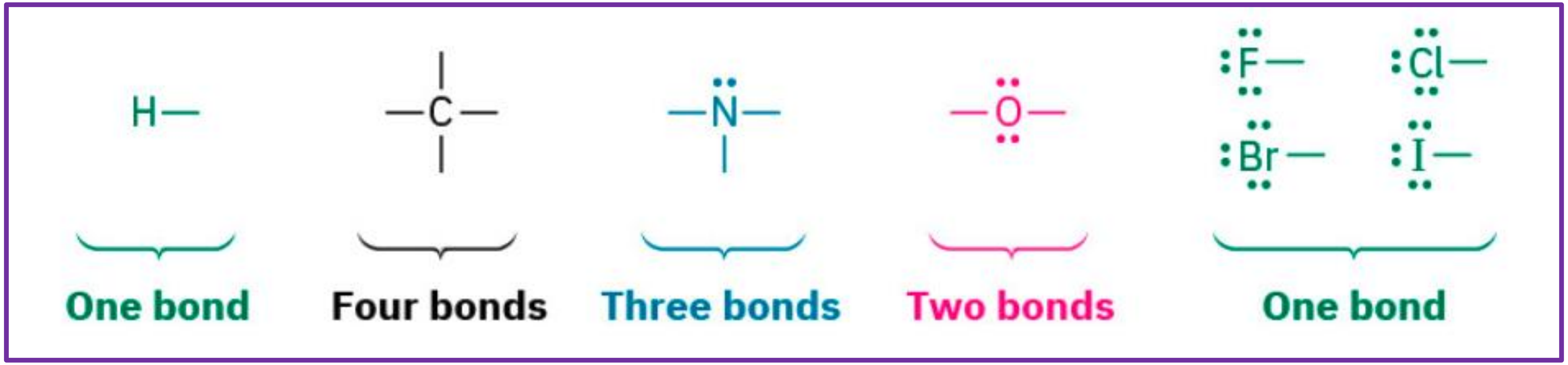
FIGURE 1.7 A representation of van't Hoff's tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page toward the viewer, and the dashed line represents a bond going back behind the plane of the page away from the viewer.

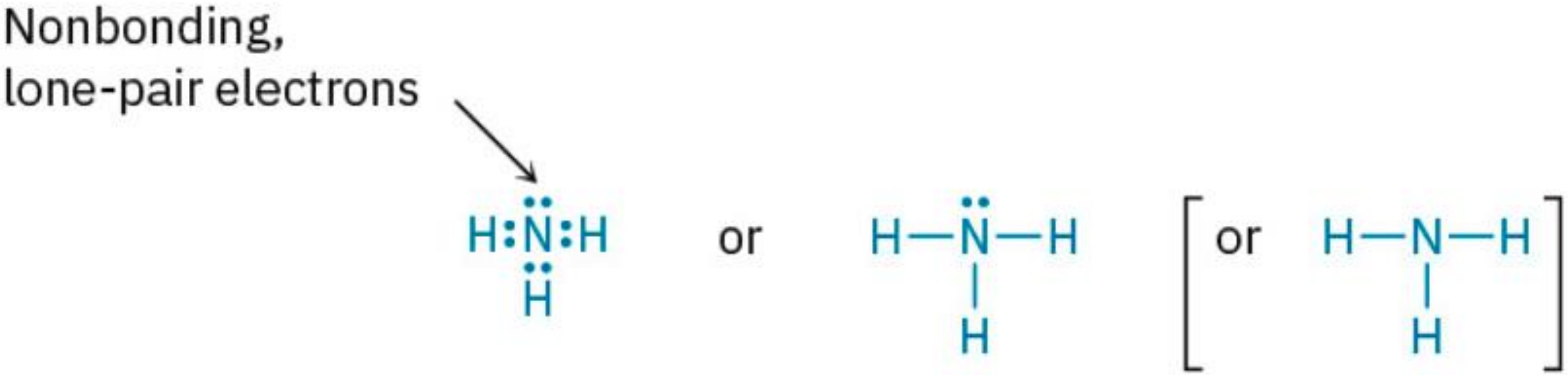


Electron-dot structures (Lewis structures)

Line-bond structures (Kekulé structures)

Methane (CH_4) | **Ammonia (NH_3)** | **Water (H_2O)** | **Methanol (CH_3OH)**


One bond
Four bonds
Three bonds
Two bonds
One bond


Nonbonding,
lone-pair electrons
or
or

Ammonia

WORKED EXAMPLE 1.1

Predicting the Number of Bonds Formed by Atoms in Molecules

How many hydrogen atoms does phosphorus bond to in forming phosphine, $PH_?$?

Strategy

Identify the periodic group of phosphorus, and find from that how many electrons (bonds) are needed to make an octet.

Solution

Phosphorus is in group 5A of the periodic table and has five valence electrons. It thus needs to share three more electrons to make an octet and therefore bonds to three hydrogen atoms, giving PH_3.

WORKED EXAMPLE 1.2

Drawing Electron-Dot and Line-Bond Structures

Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl.

WORKED EXAMPLE 1.2

Drawing Electron-Dot and Line-Bond Structures

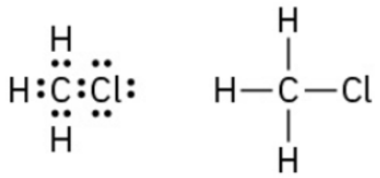
Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl.

Strategy

Remember that a covalent bond—that is, a pair of shared electrons—is represented as a line between atoms.

Solution

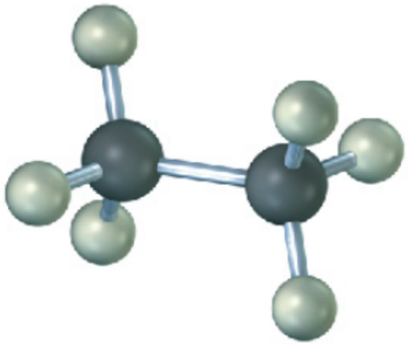
Hydrogen has one valence electron, carbon has four valence electrons, and chlorine has seven valence electrons. Thus, chloromethane is represented as



Chloromethane

PROBLEM 1-3 Draw a molecule of chloroform, $CHCl_3$, using solid, wedged, and dashed lines to show its tetrahedral geometry.

PROBLEM 1-4 Convert the following representation of ethane, C_2H_6, into a conventional drawing that uses solid, wedged, and dashed lines to indicate tetrahedral geometry around each carbon (black = C, gray = H).



Ethane

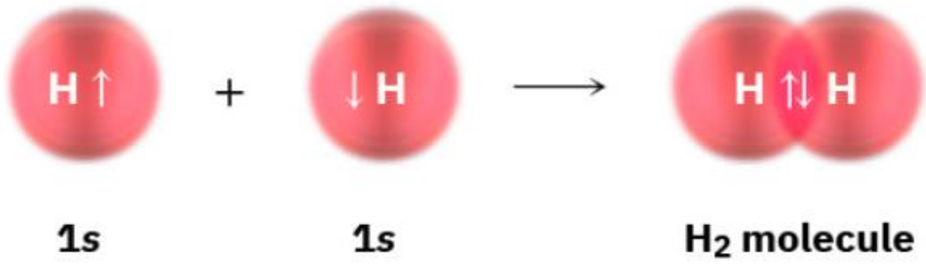
PROBLEM 1-5 What are likely formulas for the following substances?
(a) $CCl_?$ **(b)** $AlH_?$ **(c)** $CH_?Cl_2$ **(d)** SiF **(e)** $CH_3NH_?$

PROBLEM 1-6 Write line-bond structures for the following substances, showing all nonbonding electrons:
(a) $CHCl_3$, chloroform **(b)** H_2S, hydrogen sulfide **(c)** CH_3NH_2, methylamine

(d) CH_3Li, methyllithium

PROBLEM 1-7 Why can't an organic molecule have the formula C_2H_7?

1.5 Describing Chemical Bonds: Valence Bond Theory



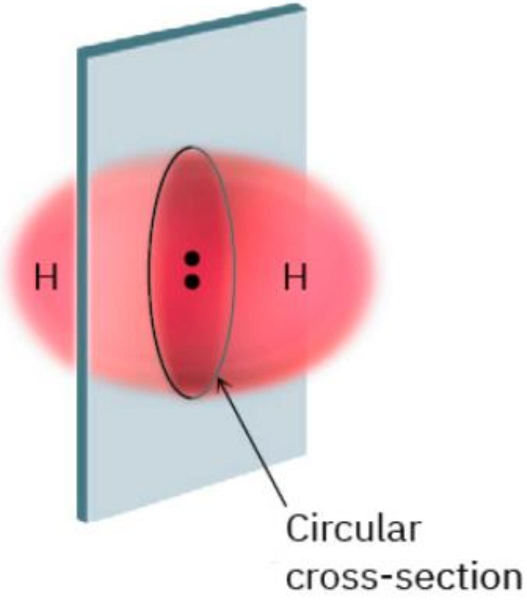
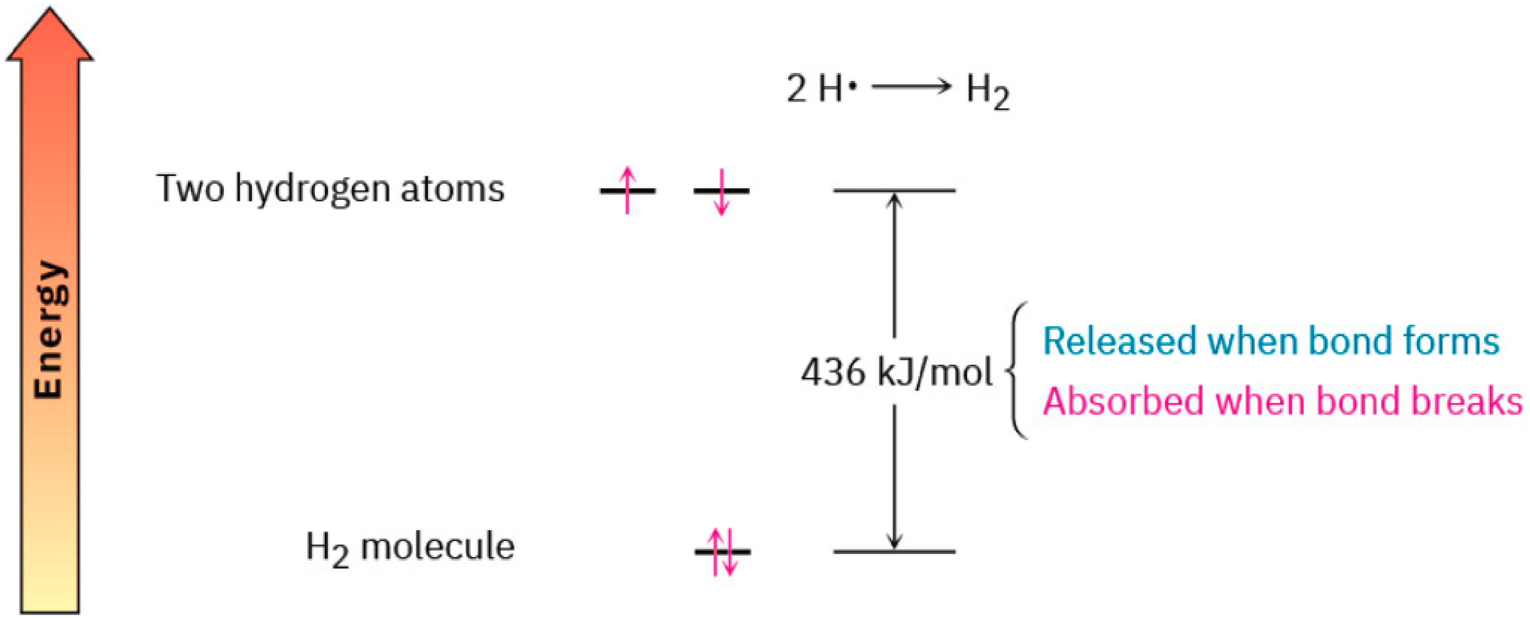


FIGURE 1.8 The cylindrical symmetry of the H–H σ bond in an H_2 molecule. The intersection of a plane cutting through the σ bond is a circle.

FIGURE 1.9 Relative energy levels of two H atoms and the H_2 molecule. The H_2 molecule has 436 kJ/mol (104 kcal/mol) less energy than the two separate H atoms, so 436 kJ/mol of energy is released when the H–H bond forms. Conversely, 436 kJ/mol is absorbed when the H–H bond breaks.



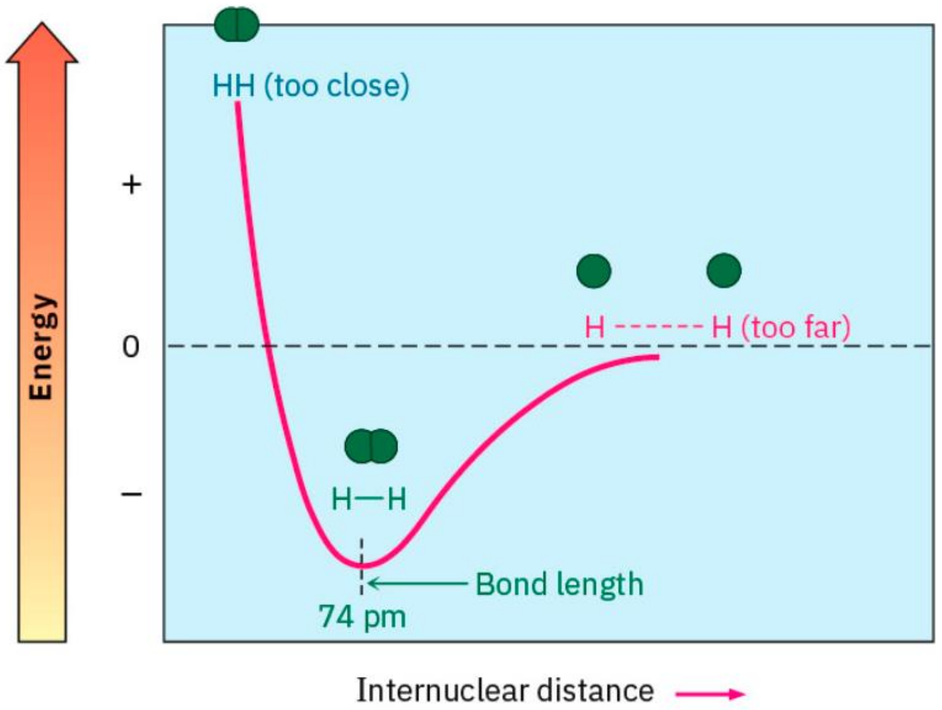


FIGURE 1.10 A plot of energy versus internuclear distance for two hydrogen atoms. The distance between nuclei at the minimum energy point is the bond length.

1.6 sp^3 Hybrid Orbitals and the Structure of Methane

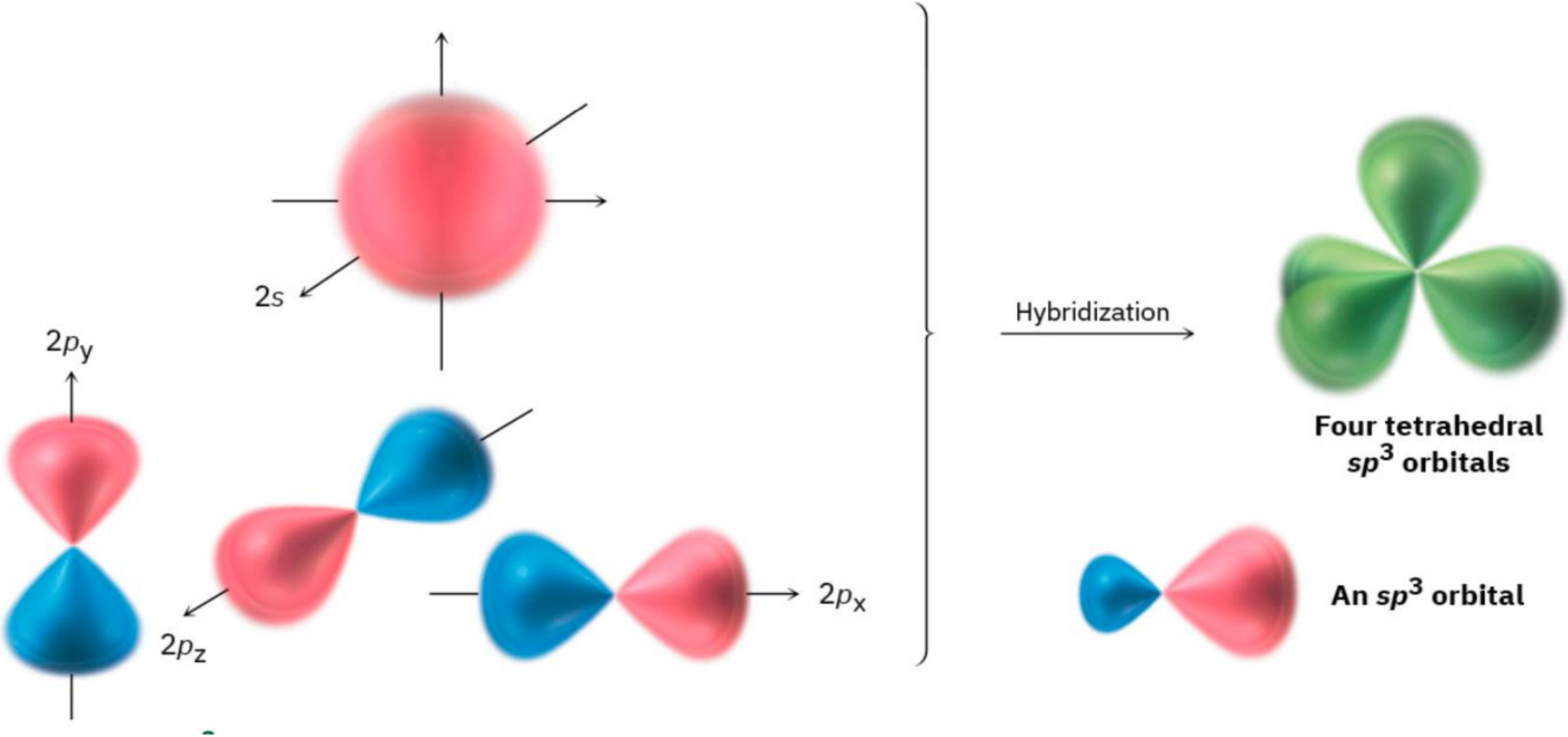


FIGURE 1.11 Four sp^3 hybrid orbitals, oriented toward the corners of a regular tetrahedron, are formed by the combination of an s orbital and three p orbitals (red/blue). The sp^3 hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds to other atoms.

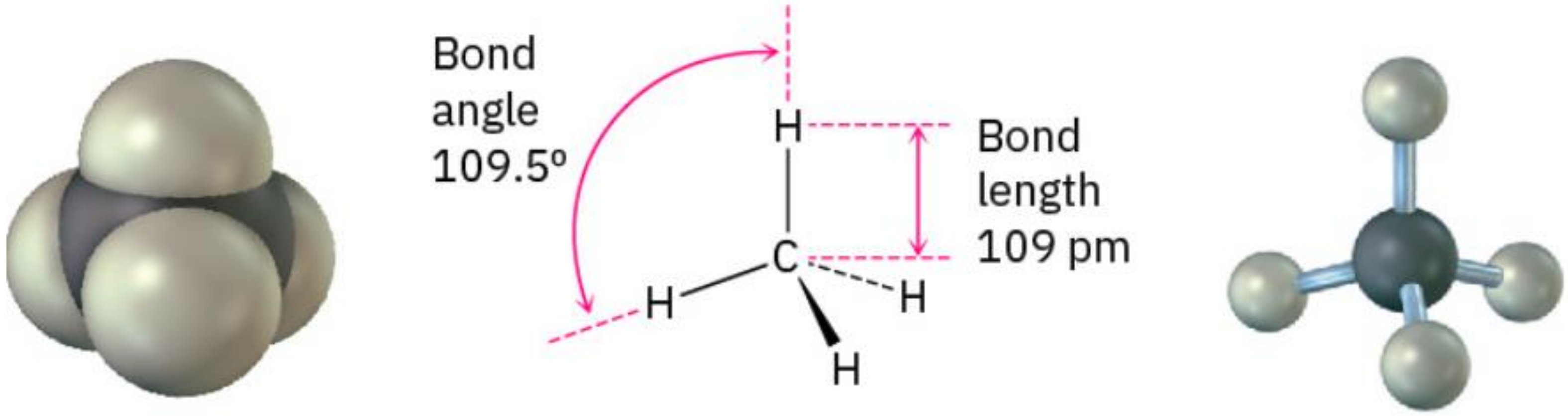


FIGURE 1.12 The structure of methane, showing its 109.5° bond angles.

1.7 sp^3 Hybrid Orbitals and the Structure of Ethane

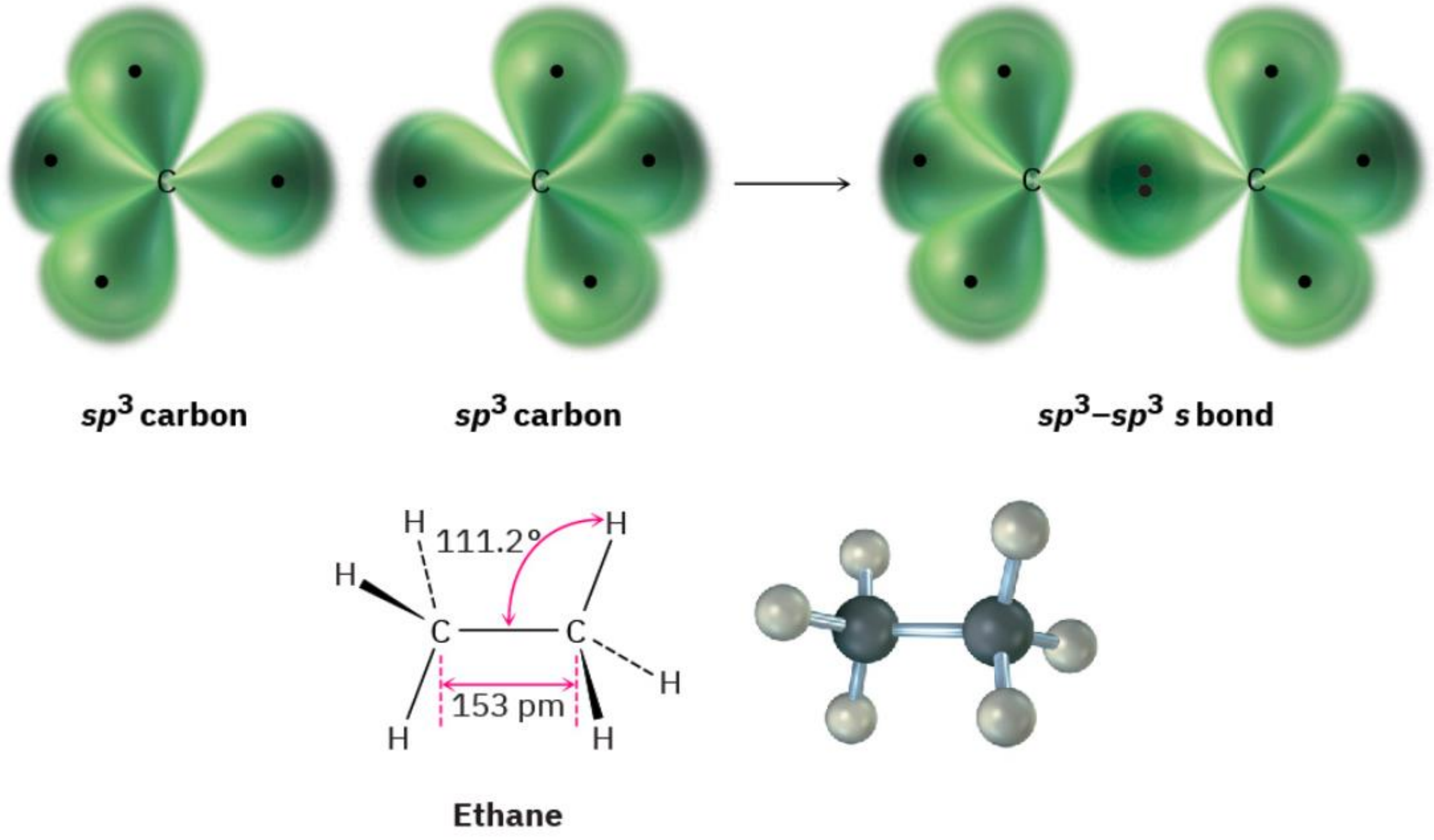


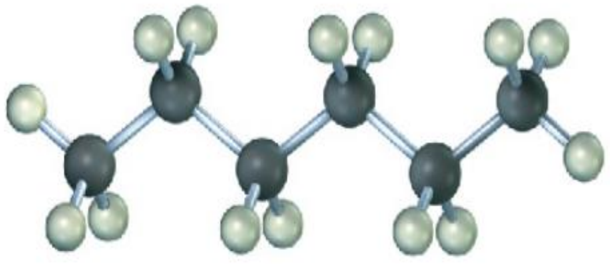
FIGURE 1.13 The structure of ethane. The carbon–carbon bond is formed by σ overlap of two sp^3 hybrid orbitals. For clarity, the smaller

PROBLEM 1-8

Draw a line-bond structure for propane, CH3CH2CH3. Predict the value of each bond angle, and indicate the overall shape of the molecule.

PROBLEM 1.9

Convert the following molecular model of hexane, a component of gasoline, into a line-bond structure (black = C, gray = H).



Hexane

1.8 sp^2 Hybrid Orbitals and the Structure of Ethylene

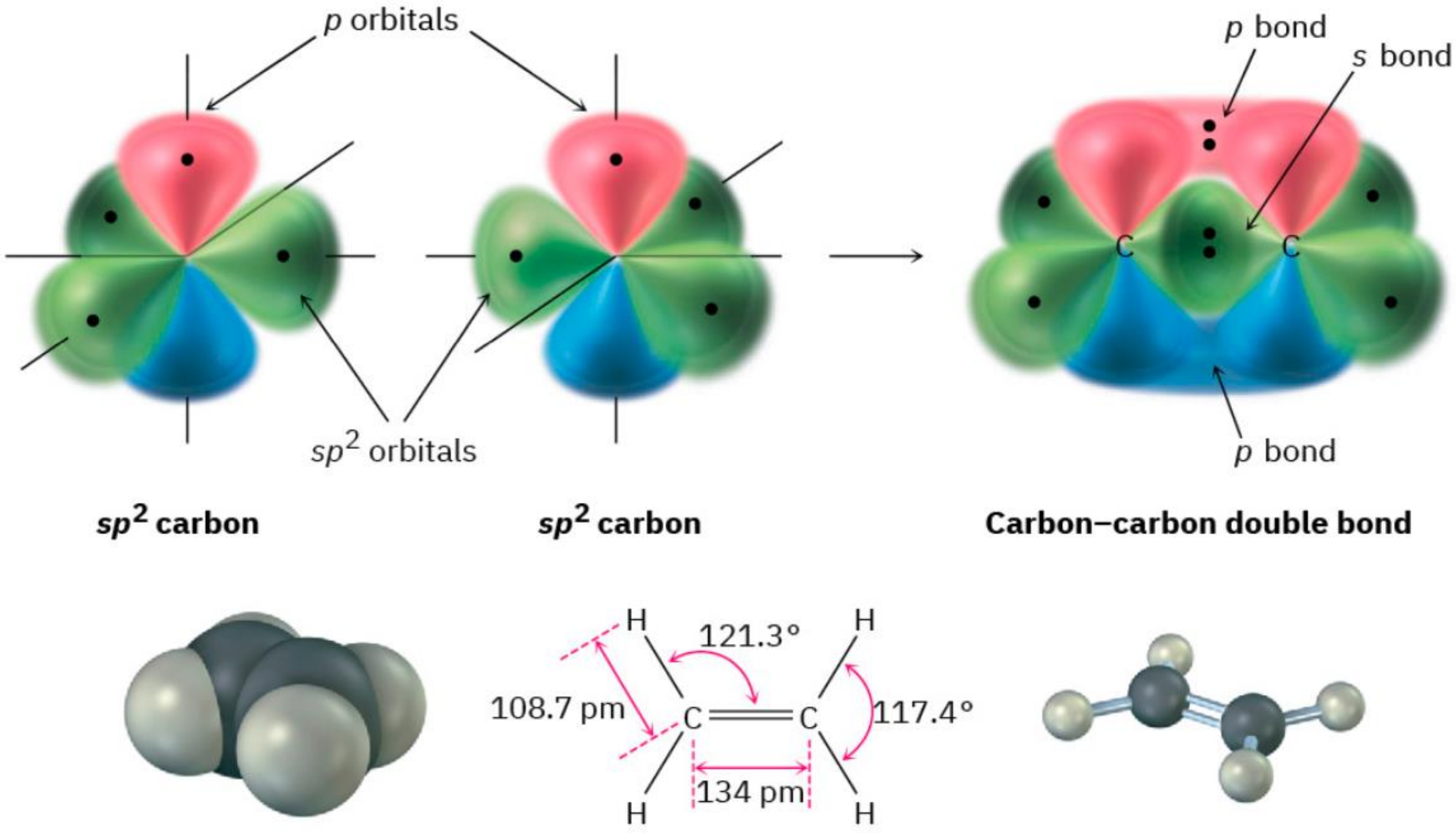


FIGURE 1.15 The structure of ethylene. One part of the double bond in ethylene results from σ (head-on) overlap of sp_2 hybrid orbitals, and the other part results from π (sideways) overlap of unhybridized p orbitals (red/blue). The π bond has regions of electron density above and below a line drawn between nuclei.

WORKED EXAMPLE 1.3

Drawing Electron-Dot and Line-Bond Structures

Commonly used in biology as a tissue preservative, formaldehyde, CH_2O, contains a carbon–*oxygen* double bond. Draw electron-dot and line-bond structures of formaldehyde, and indicate the hybridization of the carbon orbitals.

Strategy

We know that hydrogen forms one covalent bond, carbon forms four, and oxygen forms two. Trial and error, combined with intuition, is needed to fit the atoms together.

Solution

There is only one way that two hydrogens, one carbon, and one oxygen can combine:

Electron-dot structure **Line-bond structure**

Like the carbon atoms in ethylene, the carbon atom in formaldehyde is in a double bond and its orbitals are therefore sp^2-hybridized.

PROBLEM 1-10

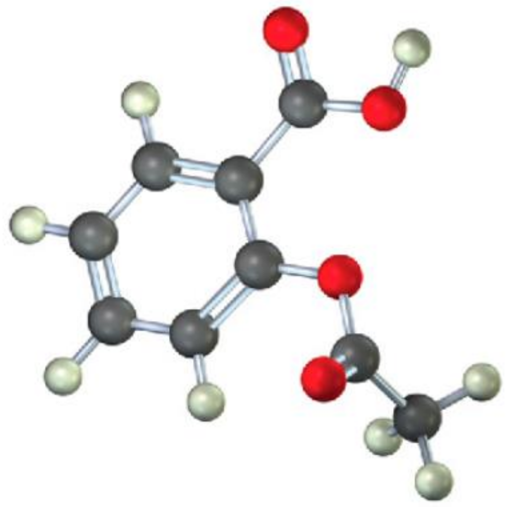
Draw a line-bond structure for propene, $CH_3CH{=}CH_2$. Indicate the hybridization of the orbitals on each carbon, and predict the value of each bond angle.

PROBLEM 1-11

Draw a line-bond structure for 1,3-butadiene, $H_2C{=}CH{-}CH{=}CH_2$. Indicate the hybridization of the orbitals on each carbon, and predict the value of each bond angle.

PROBLEM 1-12

A molecular model of aspirin (acetylsalicylic acid) is shown. Identify the hybridization of the orbitals on each carbon atom in aspirin,and tell which atoms have lonepairs of electrons (black= C, red = O, gray = H).



Aspirin
(acetylsalicylic acid)

1.9 *sp* Hybrid Orbitals and the Structure of Acetylene

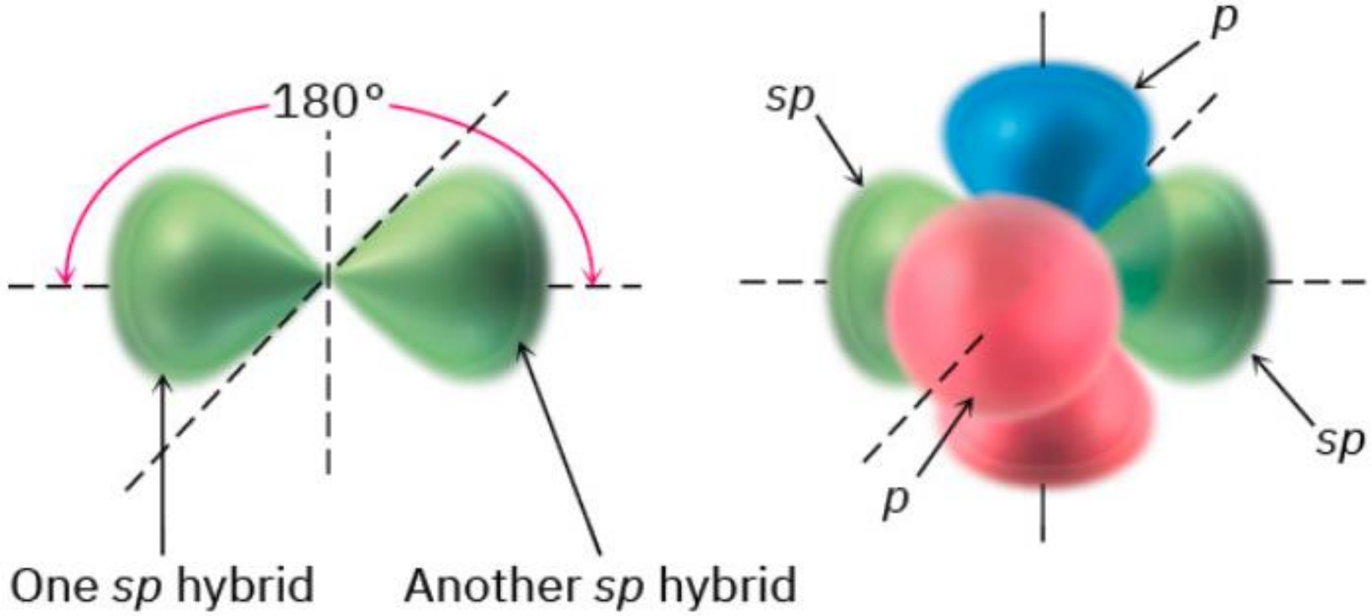


FIGURE 1.16 *sp* Hybridization. The two *sp* hybrid orbitals are oriented 180° away from each other, perpendicular to the two remaining *p* orbitals (red/blue).

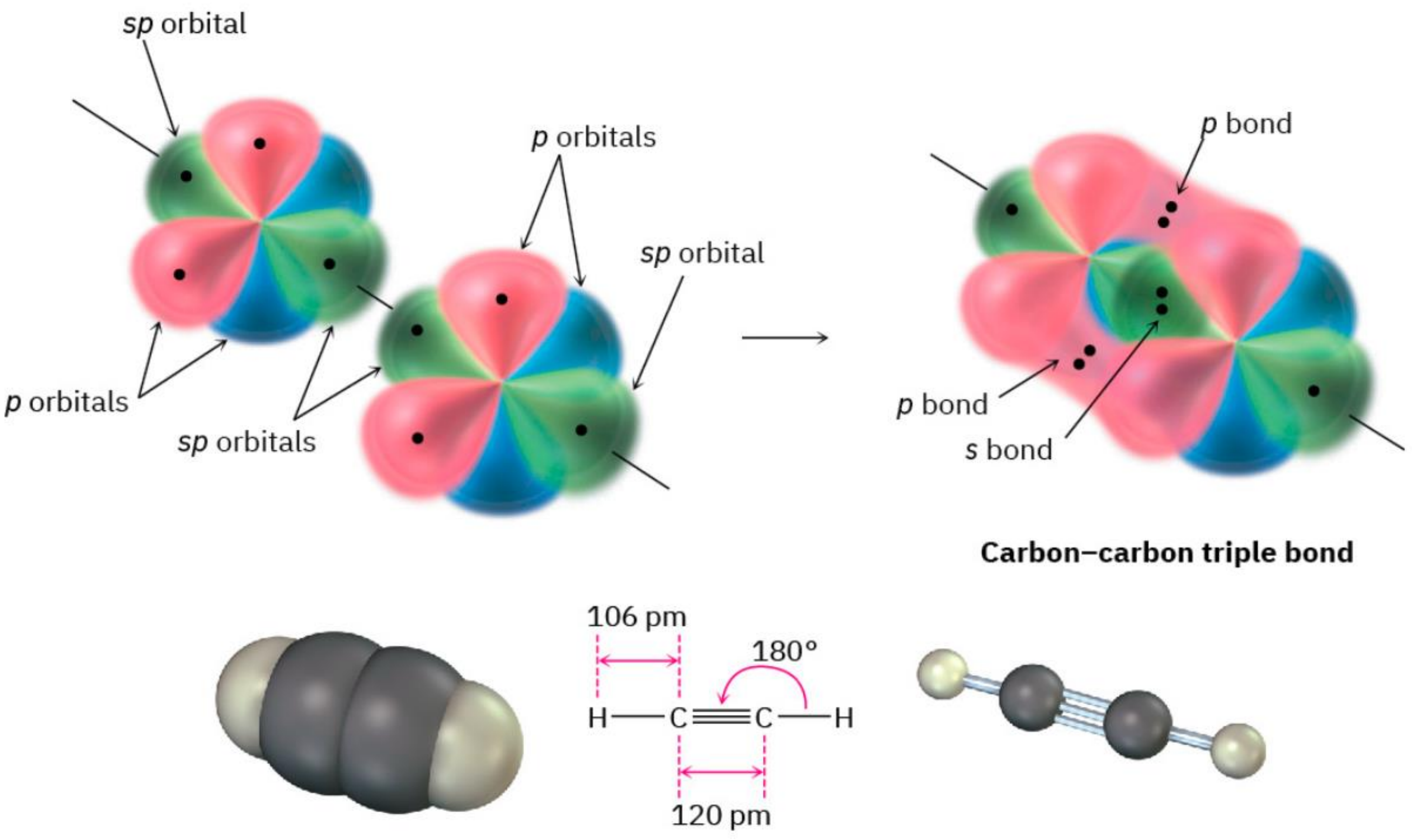


FIGURE 1.17 The structure of acetylene. The two carbon atoms are joined by one sp–sp σ bond and two p–p π bonds.

TABLE 1.2 Comparison of C–C and C–H Bonds in Methane, Ethane, Ethylene, and Acetylene

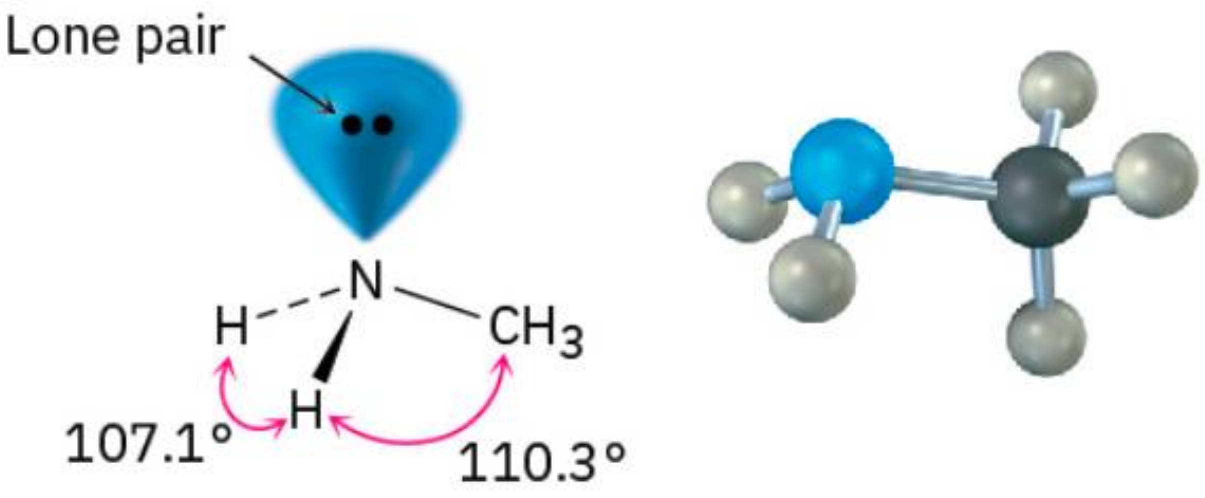
Molecule	Bond	Bond strength (kJ/mol)	Bond strength (kcal/mol)	Bond length (pm)
Methane, CH_4	(sp^3) C–H	439	105	109
Ethane, CH_3CH_3	(sp^3) C–C (sp^3)	377	90	153
	(sp^3) C–H	421	101	109
Ethylene, $H_2C{=}CH_2$	(sp^2) C=C (sp^2)	728	174	134
	(sp^2) C–H	464	111	109
Acetylene, $HC{\equiv}CH$	(sp) C≡C (sp)	965	231	120
	(sp) C–H	558	133	106

PROBLEM 1-13

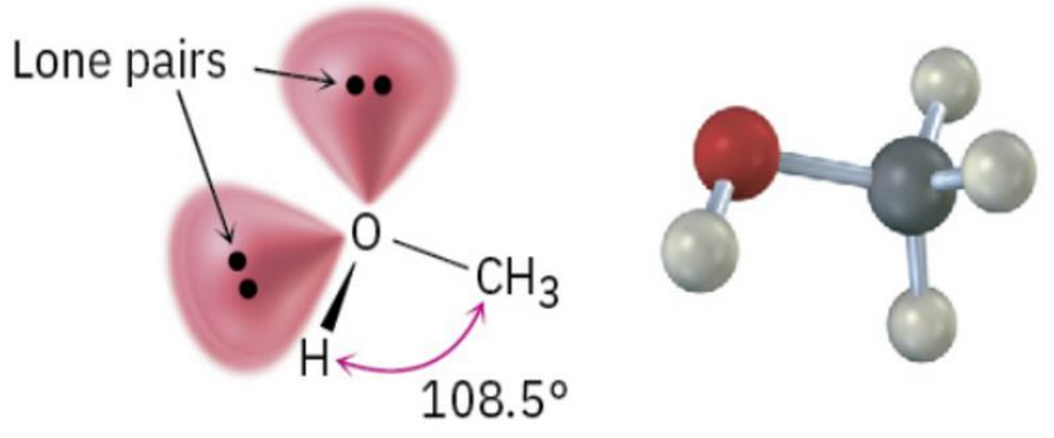
Draw a line-bond structure for propyne, $CH_3C{\equiv}CH$. Indicate the hybridization of the orbitals on each carbon, and predict a value for each bond angle.

1.10 Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

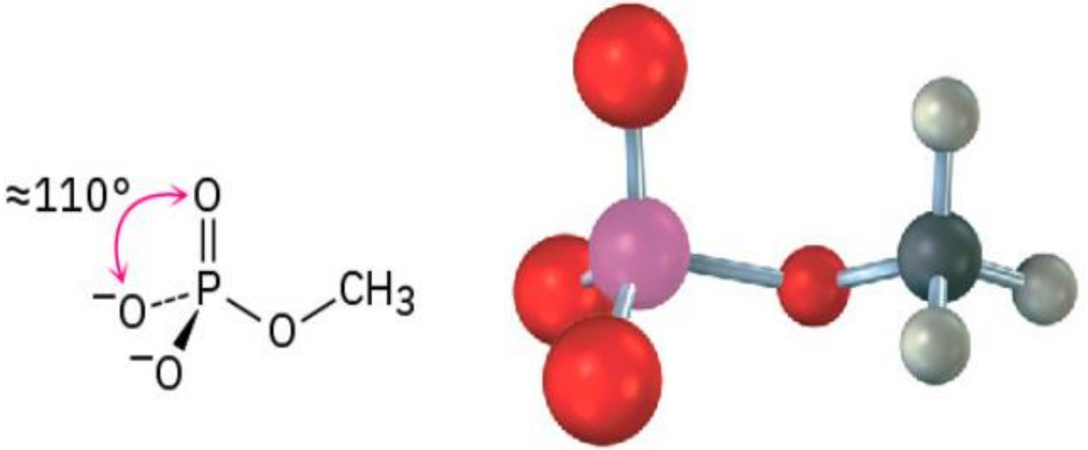
The valence-bond concept of orbital hybridization described in the previous four sections is not limited to carbon. Covalent bonds formed by other elements can also be described using hybrid orbitals.



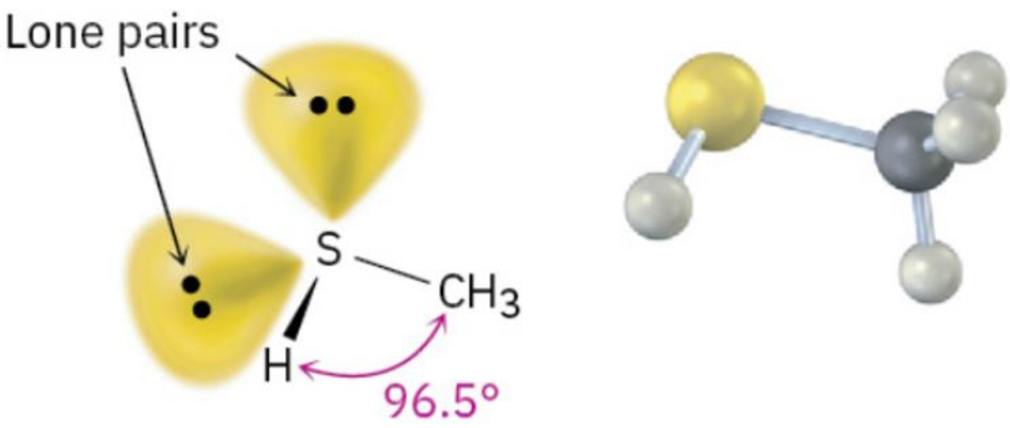
Methylamine



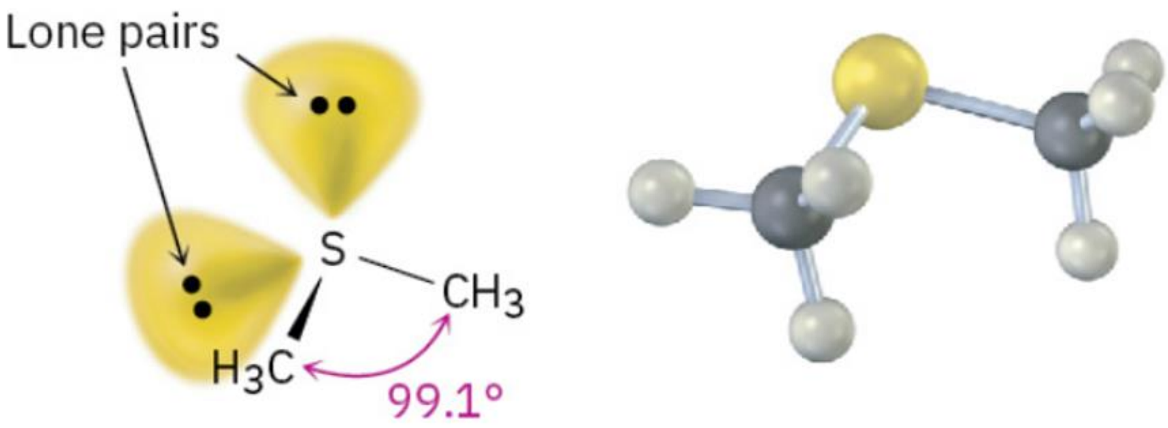
Methanol
(methyl alcohol)



Methyl phosphate
(an organophosphate)



Methanethiol



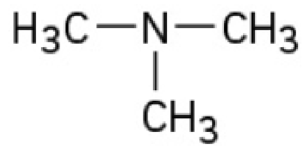
Dimethyl sulfide

PROBLEM 1-14

Identify all non bonding lone pairs of electrons in the following molecules,and tell what geometry you expect for each of the indicated atoms.

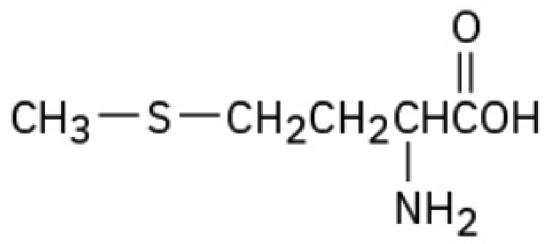
(a) The oxygen atom in dimethyl ether, CH_3–O–CH_3

(b) The nitrogen atom in trimethylamine,



(c) The phosphorus atom in phosphine, PH_3

(d) The sulfur atom in the amino acid methionine,



1.11 Describing Chemical Bonds: Molecular Orbital Theory

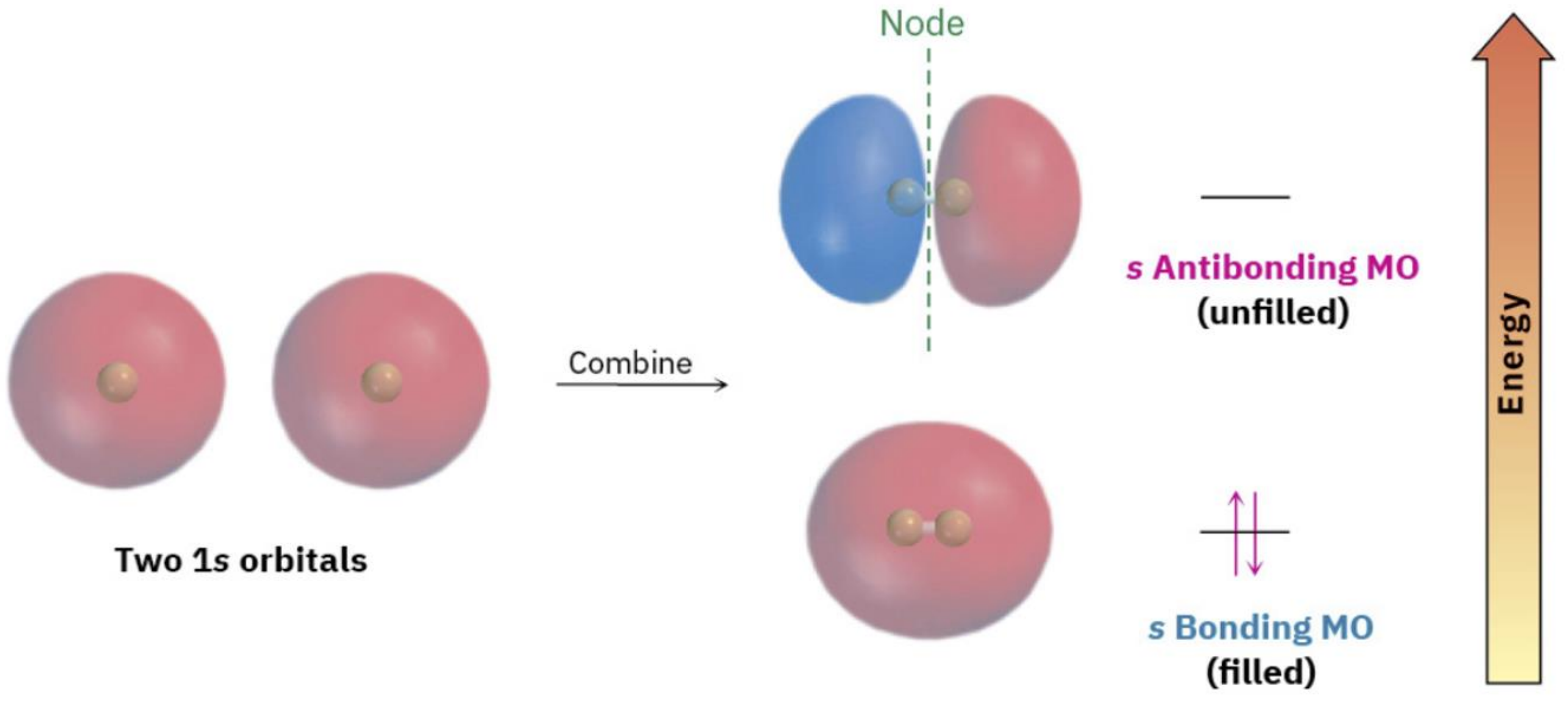
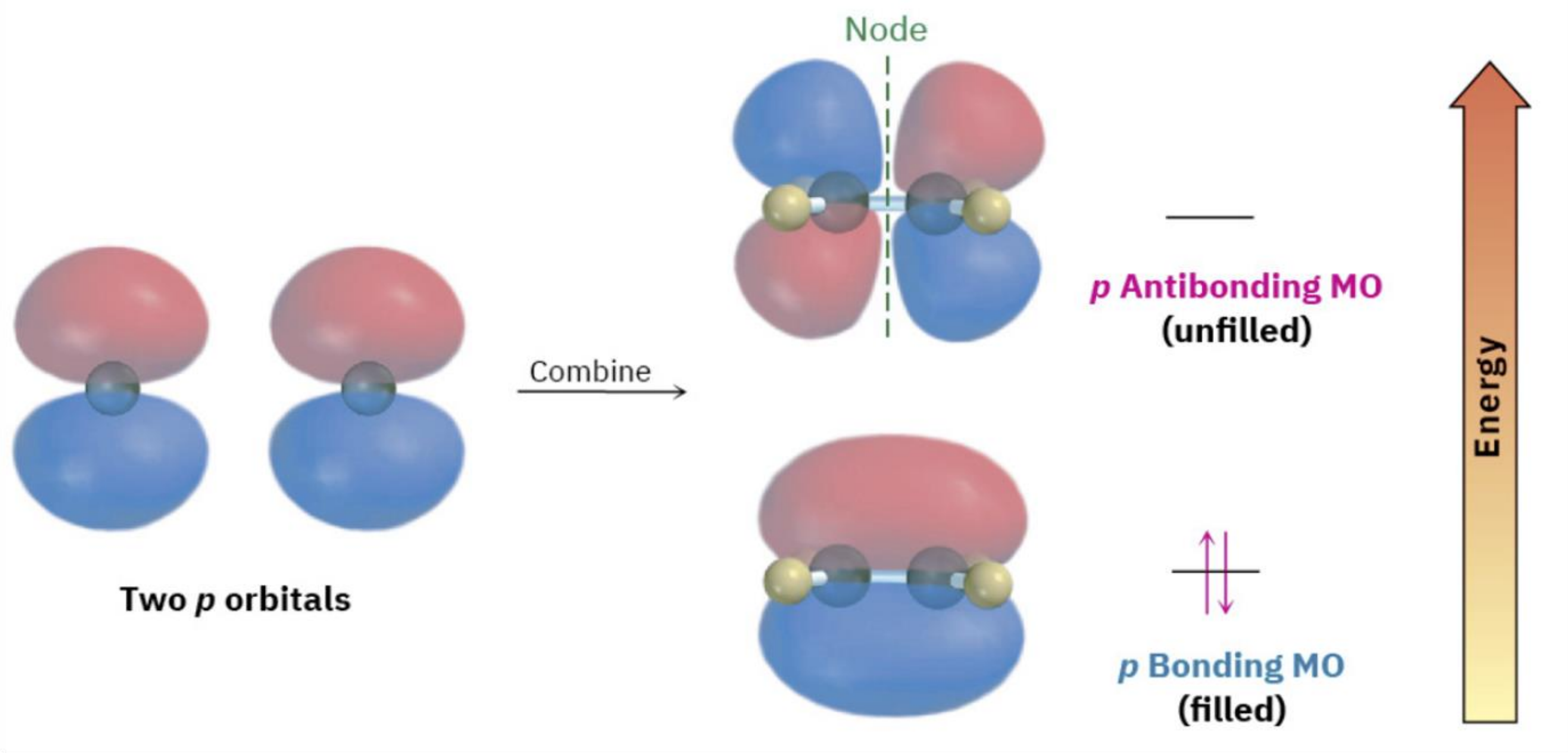
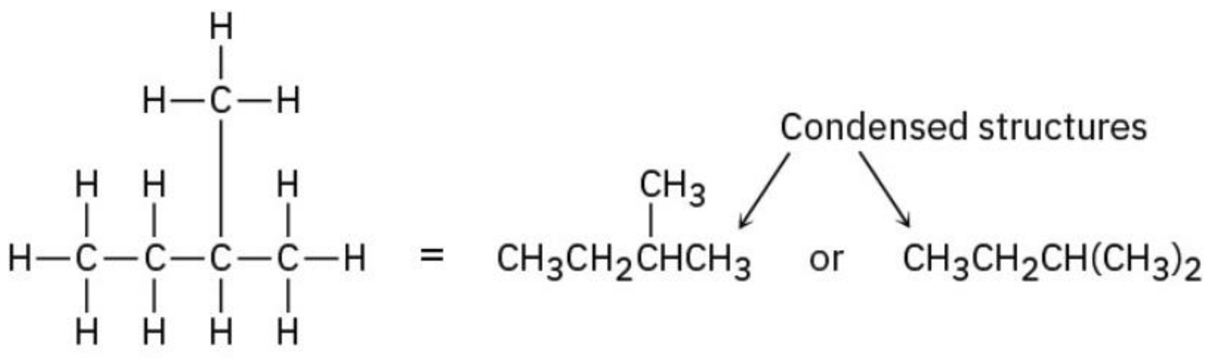


FIGURE 1.18 Molecular orbitals of H_2. Combination of two hydrogen 1*s* atomic orbitals leads to two H_2 molecular orbitals. The lower-energy, bonding MO is filled, and the higher-energy, antibonding MO is unfilled.


Node
Combine
p Antibonding MO
(unfilled)
Two p orbitals
p Bonding MO
(filled)
Energy

1.12 Drawing Chemical Structures



2-Methylbutane

Even simpler than condensed structures are **skeletal structures** such as those shown in **TABLE 1.3**. The rules for drawing skeletal structures are straightforward.

RULE 1

Carbon atoms aren’t usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.

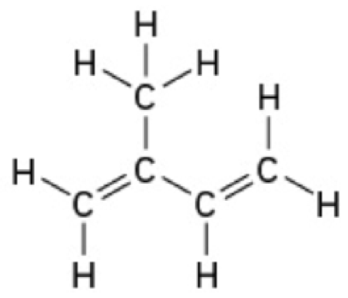
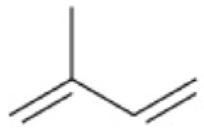
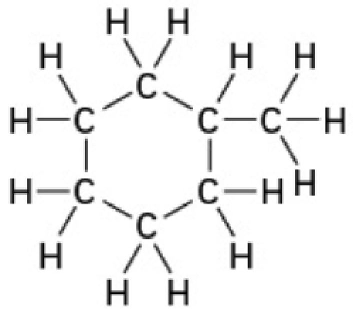
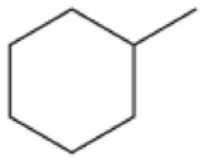
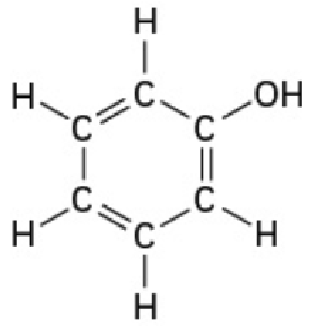
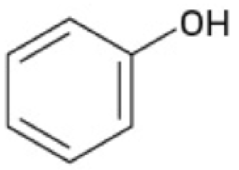
RULE 2

Hydrogen atoms bonded to carbon aren’t shown. Because carbon always has a valence of 4, we mentally supply the correct number of hydrogen atoms for each carbon.

RULE 3

Atoms other than carbon and hydrogen are shown.

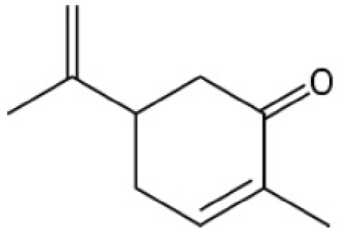
TABLE 1.3 Line-bond and Skeletal Structures for Some Compounds

Compound	Line-bond structure	Skeletal structure
Isoprene, C_5H_8		
Methylcyclohexane, C_7H_{14}		
Phenol, C_6H_6O		

WORKED EXAMPLE 1.4

Interpreting a Line-Bond Structure

Carvone, a substance responsible for the odor of spearmint, has the following structure. Tell how many hydrogens are bonded to each carbon, and give the molecular formula of carvone.

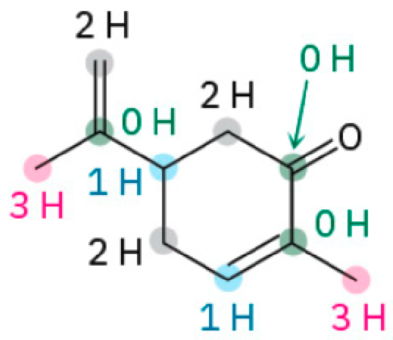


Carvone

Strategy

The end of a line represents a carbon atom with 3 hydrogens, CH_3; a two-way intersection is a carbon atom with 2 hydrogens, CH_2; a three-way intersection is a carbon atom with 1 hydrogen, CH; and a four-way intersection is a carbon atom with no attached hydrogens.

Solution

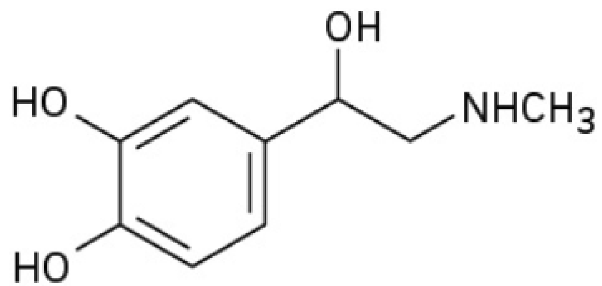


Carvone ($C_{10}H_{14}O$)

PROBLEM 1-15

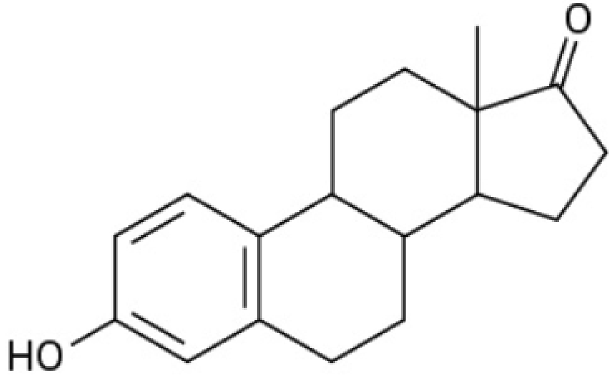
How many hydrogens are bonded to each carbon in the following compounds, and what is the molecular formula of each substance?

(a)



Adrenaline

(b)



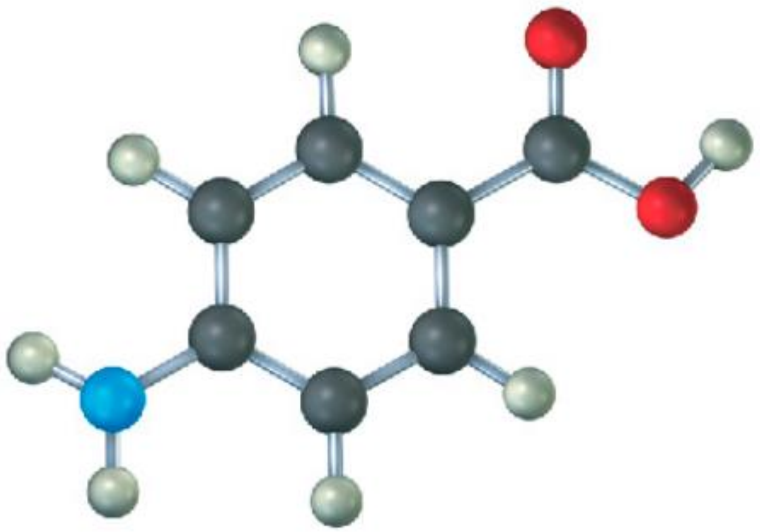
Estrone (a hormone)

PROBLEM1-16

Propose skeletal structures for compounds that satisfy the following molecular formulas:There is more than one possibility in each case.

(a) C_5H_{12} (b) C_2H_7N (c) C_3H_6O (d) C_4H_9Cl

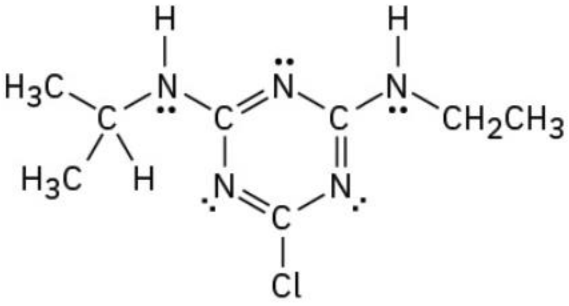
PROBLEM 1-17 The following molecular model is a representation of para-amino benzoic acid (PABA), the active ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal structure (black = C, red = O, blue = N, gray = H).



para-**Aminobenzoic acid**
(PABA)

CHEMISTRY MATTERS

Organic Foods: Risk versus Benefit



Atrazine

FIGURE 1.20 How dangerous is the pesticide being sprayed on this crop? (credit: “NRCSAR83001(265) by USDA Natural Resources Conservation Service/Wikimedia Commons, Public Domain)