林盈廷

高雄醫學大學
生命科學院
生物科技學系 助理教授

第一教學大樓 N1038 室
校內分機: 2792
ytlin@kmu.edu.tw

Reference Books

- Physical Chemistry for the Life Sciences
  (Engel, Drobny and Reid)
- Biophysical Chemistry
  (James P. Allen)

Lecture

Quantum Chemistry and Spectroscopy (I)

把物質切到最小，我們知道：

它表面上是粒子，實際上是波動。

Tiny Particle Wave equation

- Wind wave
- Airy wave theory
- Wave equation
- Acoustic wave equation
- Vibrations of a circular drum
- Standing wave
- Electromagnetic wave equation
- **Schrödinger equation**

Schröedinger equation

CORBIS-Bettmann

Figure 10.4 Erwin Schrödinger (1887–1961). Schrödinger proposed an expression of quantum mechanics that was different from but equivalent to Heisenberg's. His expression is useful because it expresses the behavior of electrons in terms of something we understand—waves. The Schrödinger equation is the central equation of quantum mechanics.

Schröedinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi$$

Total energy

Potential energy

Kinetic energy

$$\hbar=\frac{h}{2\pi}=1.054\times10^{-34}\ Js$$

Chapter 13, Physical Chemistry for the Life Sciences (Engel, Drobny and Reid)

Quantum Chemistry 的七個法則

➔用來形成 Schröedinger equation

（也就是可用來描述電子的波動方程式）

Quantum Mechanics 的七個法則

Table 10.2 The postulates of quantum mechanics

Postulate I. The state of a system of particles is given by a wavefunction Ψ, which is a function of the coordinates of the particles and the time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable. (Discussed in section **10.2**)

Postulate II. For every physical observable or variable O, there exists a corresponding Hermitian operator $\hat{O}$. Operators are constructed by writing their classical expressions in terms of position and (linear) momentum, then replacing "x times" (that is, $x\,\cdot$) for each x variable and $-i\hbar(\partial/\partial x)$ for each p_x variable in the expression. Similar substitutions must be made for y and z coordinates and momenta. (Section **10.3**)

Postulate III. The only values of observables that can be obtained in a single measurement are the eigenvalues of the eigenvalue equation constructed from the corresponding operator and the wavefunction Ψ:

$$\hat{O}\Psi = K \cdot \Psi$$

where K is a constant. (Section **10.3**)

Postulate IV. Wavefunctions must satisfy the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

(Section **10.14**) (If it is assumed that Ψ is separable into functions of time and position, we find that this expression can be rewritten to get the time-independent Schrödinger equation, $\hat{H}\Psi = E\Psi$.) (section **10.7**)

Postulate V. The average value of an observable, $\langle O\rangle$, is given by the expression

$$\langle O\rangle = \int_{\substack{\text{all}\\\text{space}}} \Psi^*\hat{O}\Psi\, d\tau$$

for normalized wavefunctions. (Section **10.9**)

Postulate VI. The set of eigenfunctions for any quantum mechanical operator is a complete mathematical set of functions.

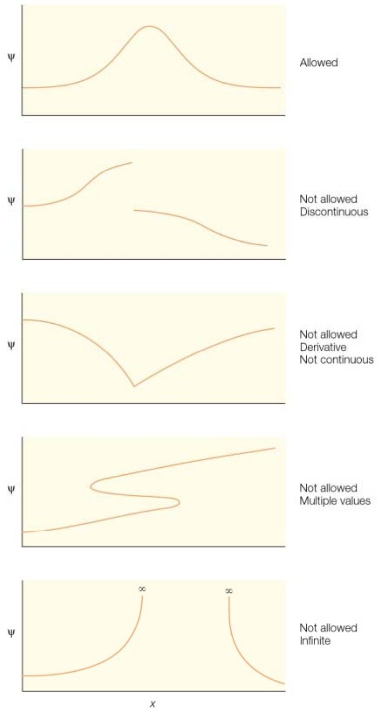
Postulate VII. If, for a given system, the wavefunction Ψ is a linear combination of nondegenerate wavefunctions Ψ_n which have eigenvalues a_n:

$$\Psi = \sum_n c_n\Psi_n \quad \text{and} \quad \hat{A}\Psi_n = a_n\Psi_n$$

then the probability that a_n will be the value of the corresponding measurement is $|c_n|^2$. The construction of Ψ as the combination of all possible Ψ_n's is called the *superposition principle.*

Quantum Mechanics 法則 1

Postulate I. The state of a system of particles is given by a wavefunction Ψ, which is a function of the coordinates of the particles and the time. Ψ contains all information that can be determined about the state of the system. Ψ must be single-valued, continuous, and bounded, and $|\Psi|^2$ must be integrable. (Discussed in section **10.2**)



$$\Psi(x, y, z)$$

Quantum Mechanics 法則 2

Postulate II. For every physical observable or variable O, there exists a corresponding Hermitian operator $\hat{O}$. Operators are constructed by writing their classical expressions in terms of position and (linear) momentum, then replacing "x times" (that is, $x\cdot$) for each x variable and $-i\hbar(\partial/\partial x)$ for each p_x variable in the expression. Similar substitutions must be made for y and z coordinates and momenta. (Section **10.3**)

$$p_x \qquad \hat{O} = -i\hbar\left(\frac{\partial}{\partial x}\right)$$

Table 10.1 Operators for various observables and their classical counterparts[a]

Observable	Operator	Classical counterpart
Position	$\hat{x} = x \cdot$	x
	And so forth for coordinates other than x	
Momentum (linear)	$\widehat{p_x} = -i\hbar\frac{\partial}{\partial x}$	$p_x = mv_x$
	And so forth for coordinates other than x	
Momentum (angular)	$\widehat{L_x} = -i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right)$	$L_x = yp_z - zp_y$
Kinetic energy, 1-D[b]	$\hat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	$K = \frac{1}{2}mv_x^2 = \frac{p_x^2}{2m}$
Kinetic energy, 3-D[b]	$\hat{K} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$	$K = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ $= \frac{p_x^2 + p_y^2 + p_z^2}{2m}$
Potential energy:		
Harmonic oscillator	$\hat{V} = \frac{1}{2}kx^2 \cdot$	$V = \frac{1}{2}kx^2$
Coulombic	$\hat{V} = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \cdot$	$V = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r}$
Total energy	$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$	$H = \frac{p^2}{2m} + V$

[a]Operators expressed in x, y, and/or z are Cartesian operators; operators expressed in r, θ, and/or ϕ are spherical polar operators.

[b]The kinetic energy operator is also symbolized by $\hat{T}$.

ation

Quantum Mechanics 法則 3

Postulate III. The only values of observables that can be obtained in a single measurement are the eigenvalues of the eigenvalue equation constructed from the corresponding operator and the wavefunction Ψ:

$$\hat{O}\Psi = K \cdot \Psi$$

where K is a constant. (Section 10.3)

observables

Quantum Mechanics 法則 4

Postulate IV. Wavefunctions must satisfy the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

time dependent

Quantum Mechanics 法則 5

Postulate V. The average value of an observable, $\langle O \rangle$, is given by the expression

$$\langle O \rangle = \int_{\substack{\text{all} \\ \text{space}}} \Psi^* \hat{O} \Psi \, d\tau$$

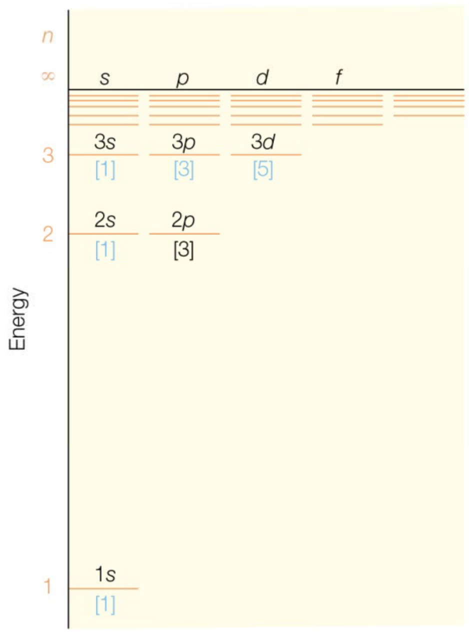
for normalized wavefunctions. (Section **10.9**)

average observables

Quantum Mechanics 法則 6

Postulate VI. The set of eigenfunctions for any quantum mechanical operator is a complete mathematical set of functions.

$$\int_{-\infty}^{\infty} \psi_i^*(x)\psi_j(x)dx = \begin{cases} 0, i \neq j \\ 1, i = j \end{cases} \qquad (13.21)$$



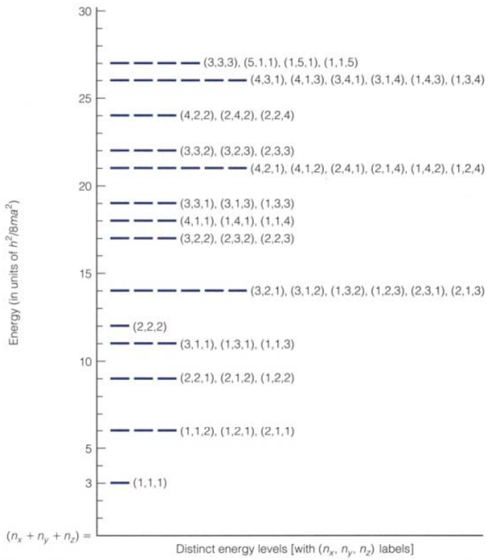


Figure 10.13 The energy levels of the 3-D particle-in-a-(cubical)-box. In this system, different wavefunctions can have the same energy. This is an example of degeneracy.

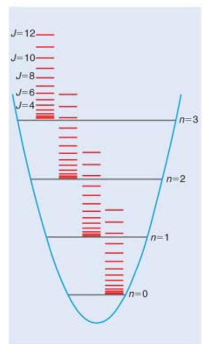


Figure: 18-08

Quantum Mechanics 法則 7

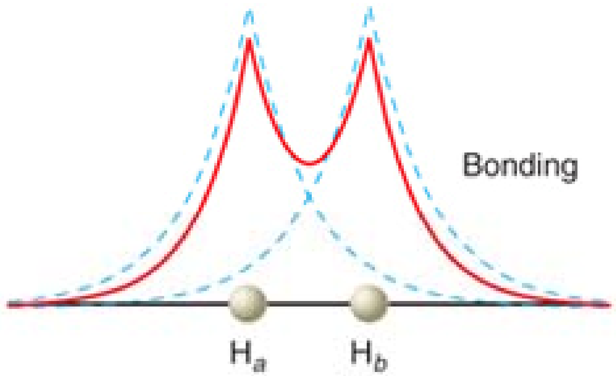
Postulate VII. If, for a given system, the wavefunction Ψ is a linear combination of nondegenerate wavefunctions Ψ_n which have eigenvalues a_n:

$$\Psi = \sum_n c_n \Psi_n \quad \text{and} \quad \hat{A}\Psi_n = a_n \Psi_n$$

then the probability that a_n will be the value of the corresponding measurement is $|c_n|^2$. The construction of Ψ as the combination of all possible Ψ_n's is called the *superposition principle.*

波

可以相加減



Different Systems

(Chapter 14 ~ Chapter 18)

- 不同的系統，
  有不同的 Schröedinger equation 的解

Schröedinger equation 的解，是 Orthogonal。

$$\int_{-\infty}^{\infty} \psi_i^*(x)\psi_j(x)dx = \begin{cases} 0, i \neq j \\ 1, i = j \end{cases} \qquad (13.21)$$

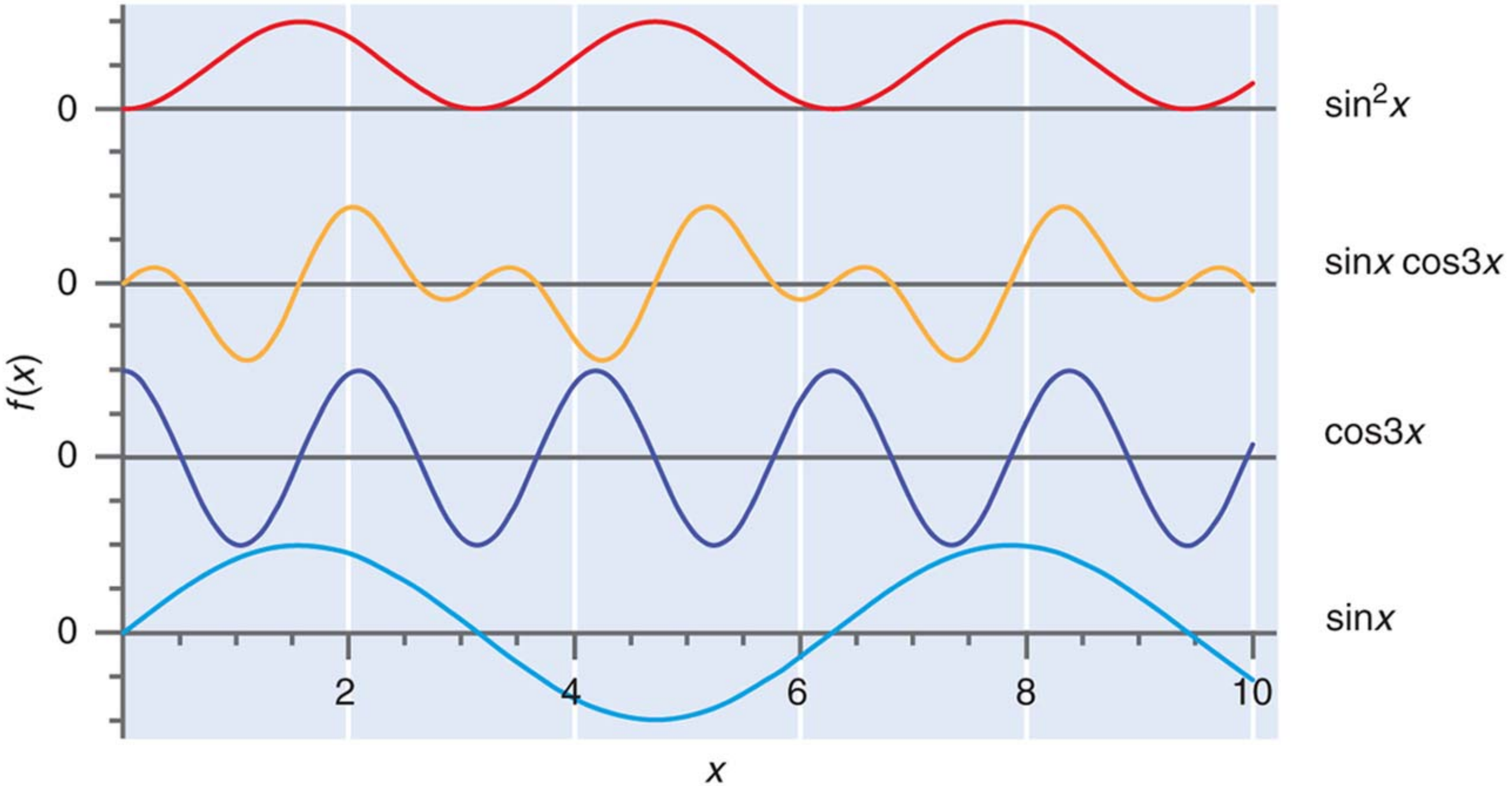
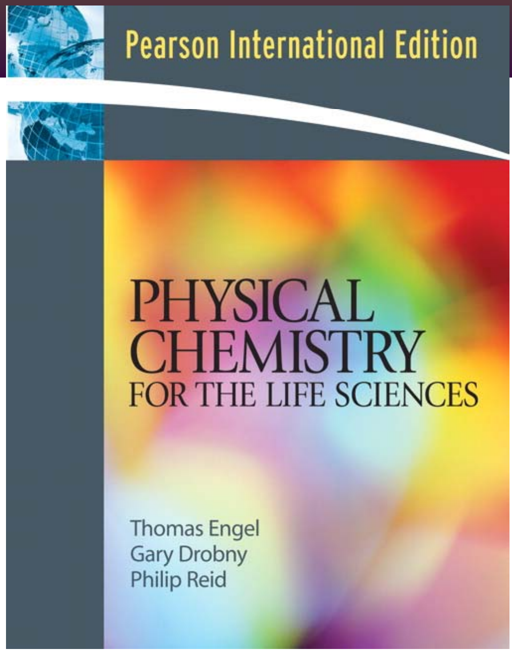


Figure: 13-02EP

Physical Chemistry

For the Life Sciences

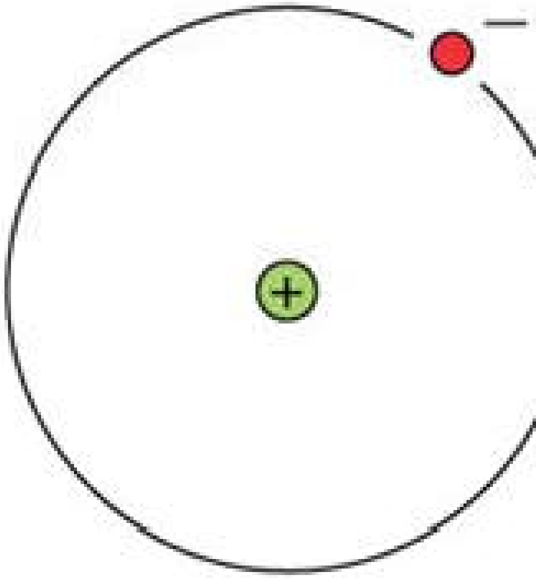


CHAPTER 15

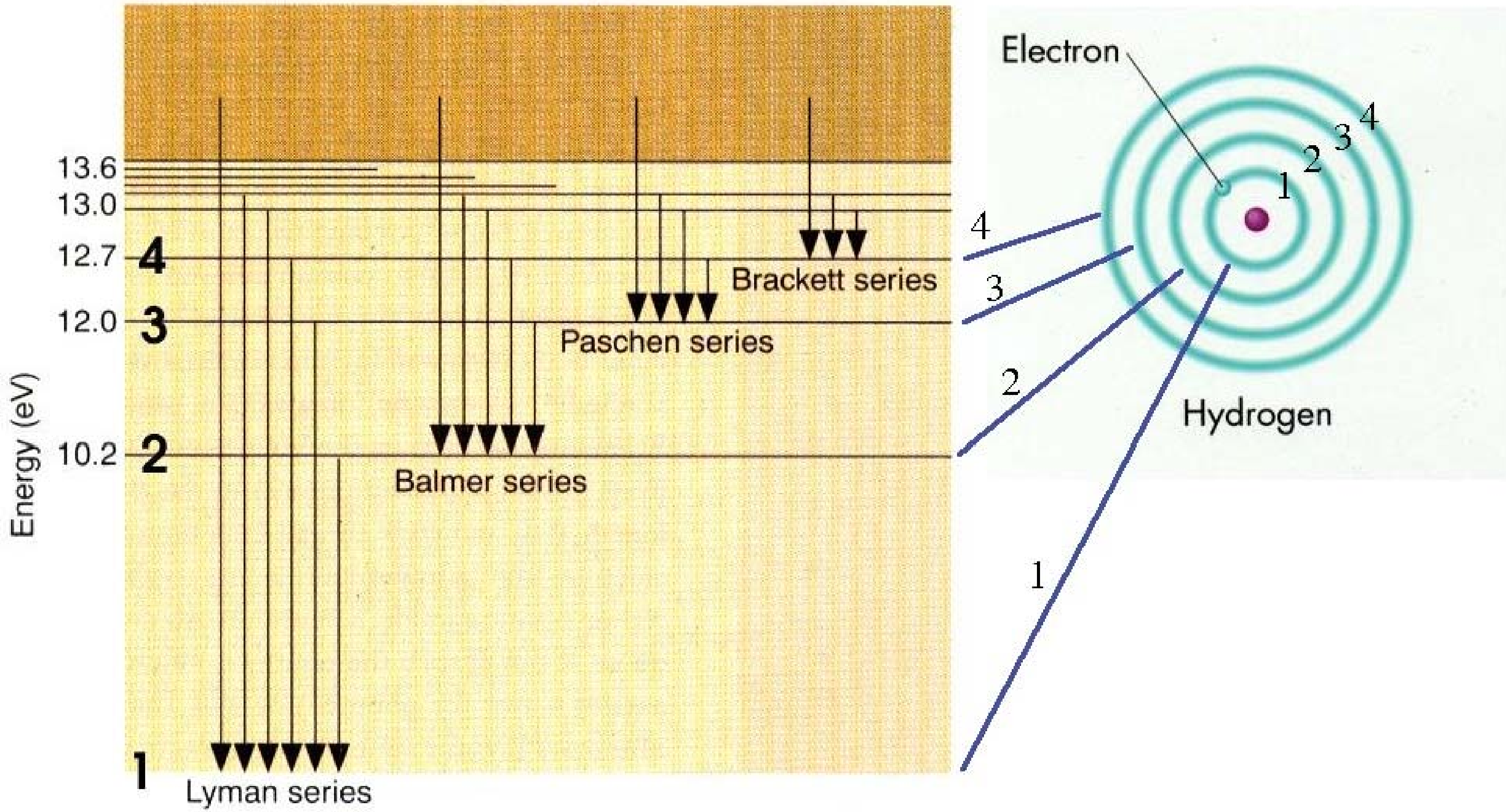
The Hydrogen Atom and Many-Electron Atoms

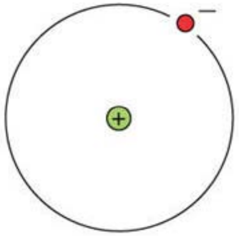
Y.T.Lin's Presentation

Hydrogen Atom



Energy levels of the H atom





Schröedinger equation for hydrogen atom

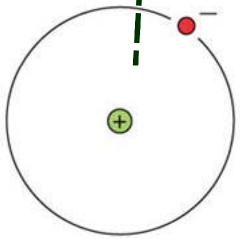
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi$$

E

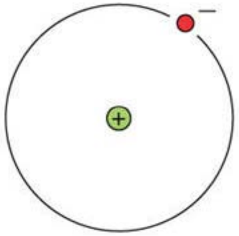
ψ

TABLE 2.1 Selected Properties of the Three Basic Subatomic Particles

Name	Charge	Mass (amu)	Mass (grams)
Electron (e)	−1	5.4×10^{-4}	9.1095×10^{-28}
Proton (p)	+1	1.00	1.6725×10^{-24}
Neutron (n)	0	1.00	1.6750×10^{-24}



Chapter 13, Physical Chemistry for the Life Sciences (Engel, Drobny and Reid)



Schröedinger equation for hydrogen atom

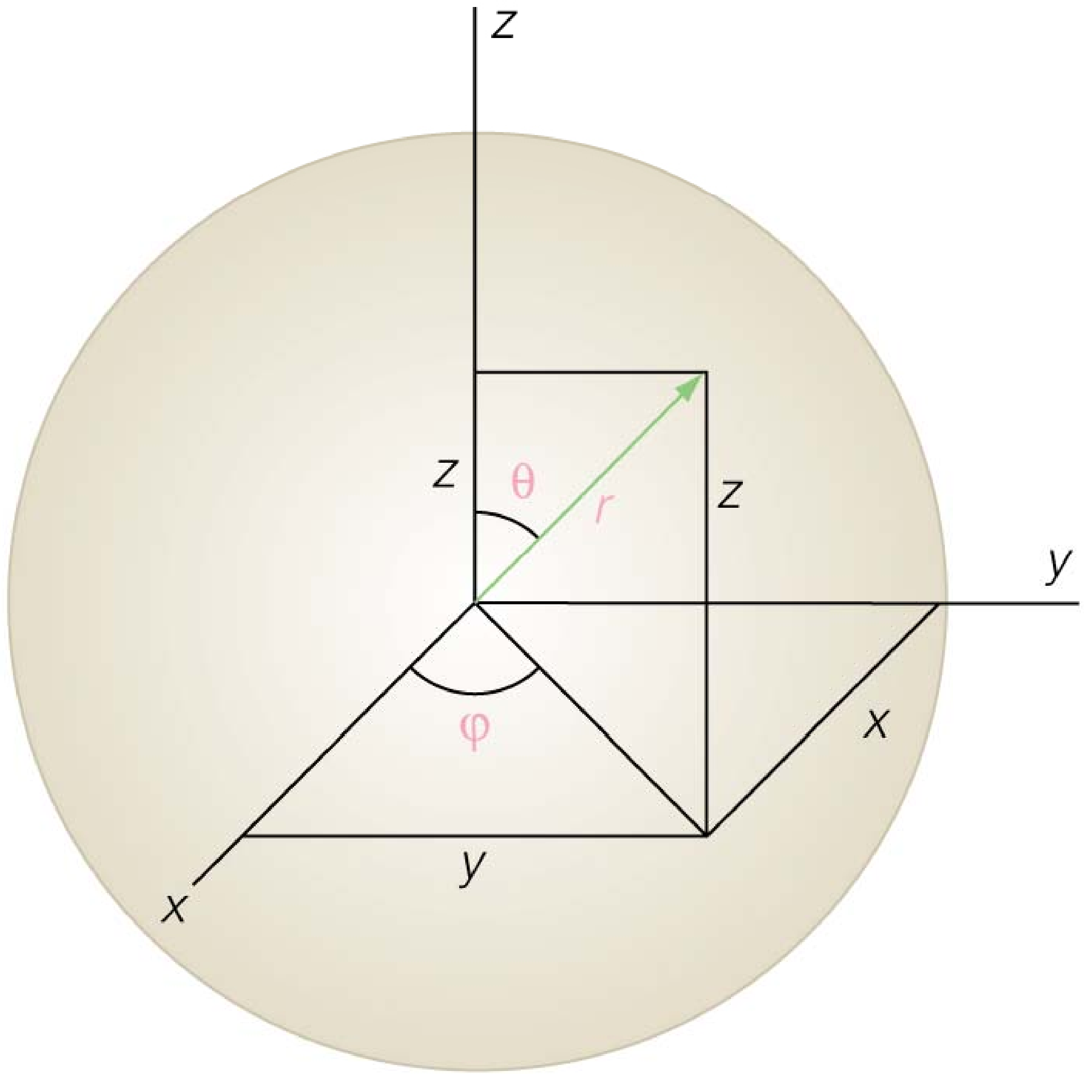
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi$$

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial y^2}-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial z^2}+V\psi=E\psi$$

$$\Psi(x, y, z)$$

↓

$$\Psi(r, \theta, \phi)$$



$$\Psi(x, y, z)$$

$$\downarrow$$

$$\Psi(r, \theta, \phi)$$

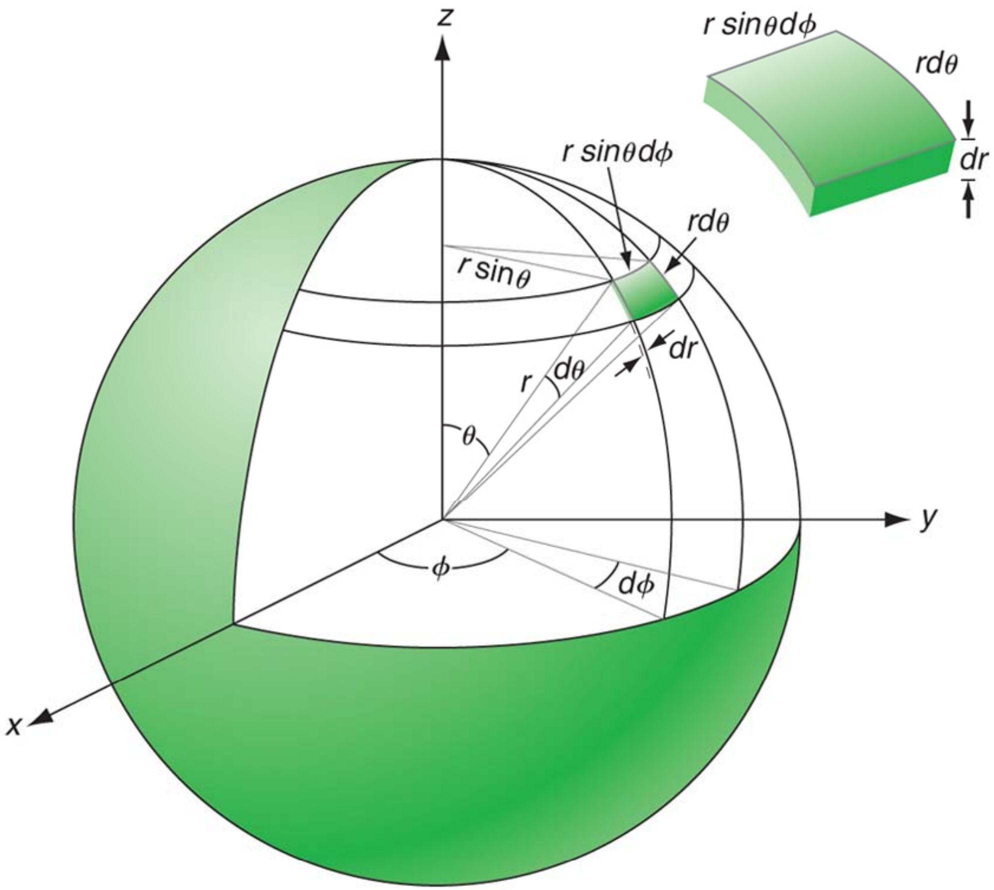
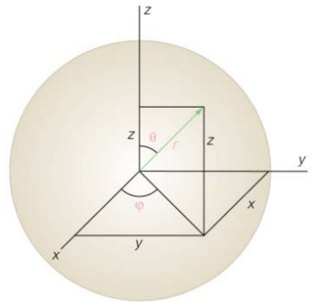


Figure: 13-07

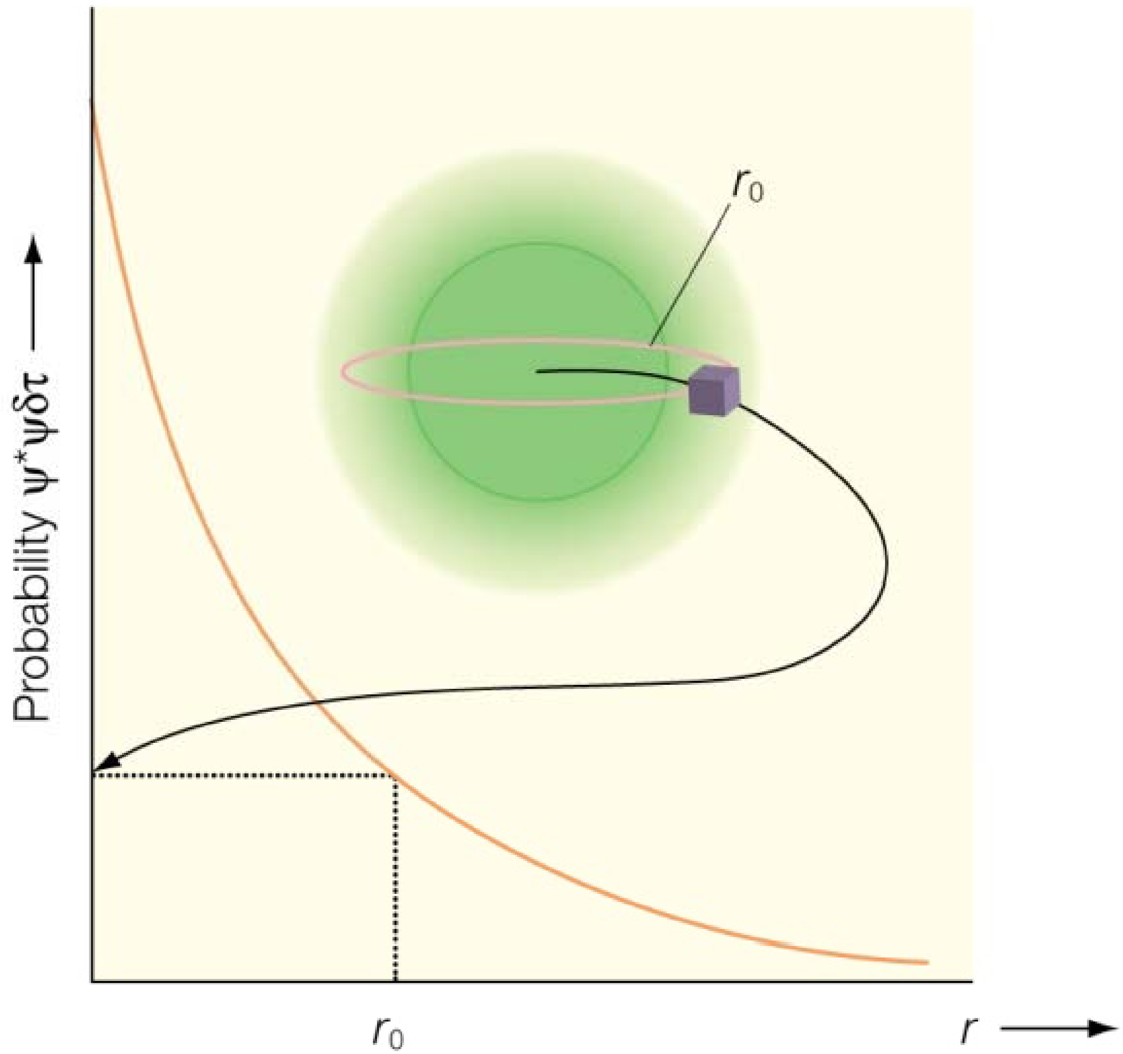
$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial y^2}-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial z^2}+V\psi=E\psi$$



$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}+\frac{\partial^2\Psi}{\partial\phi^2}\right]-\frac{e^2}{4\pi\varepsilon_0 r}\Psi=E\Psi$$

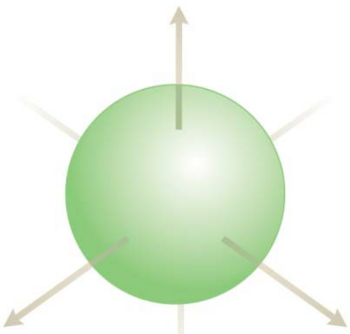
(15.2)

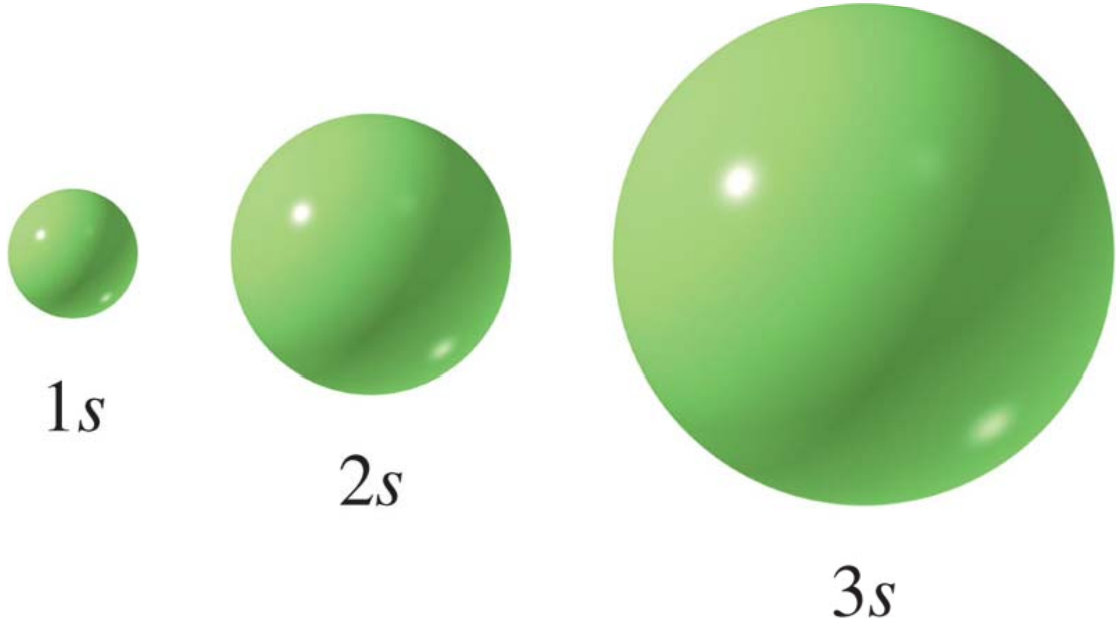
Orbital Shapes



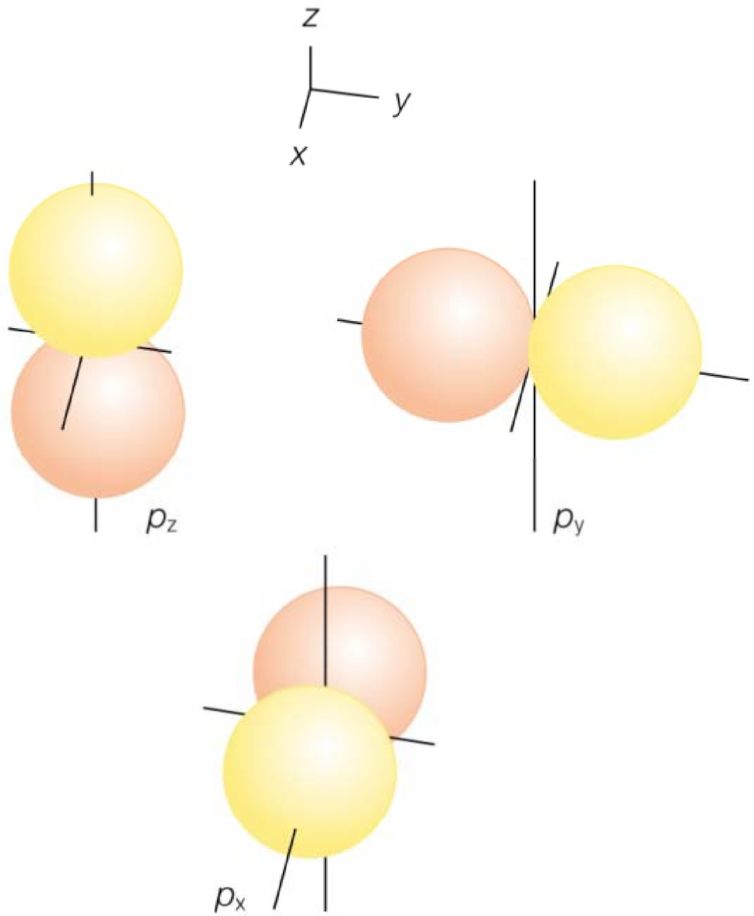
Orbital Shapes

- *s* is spherically symmetrical



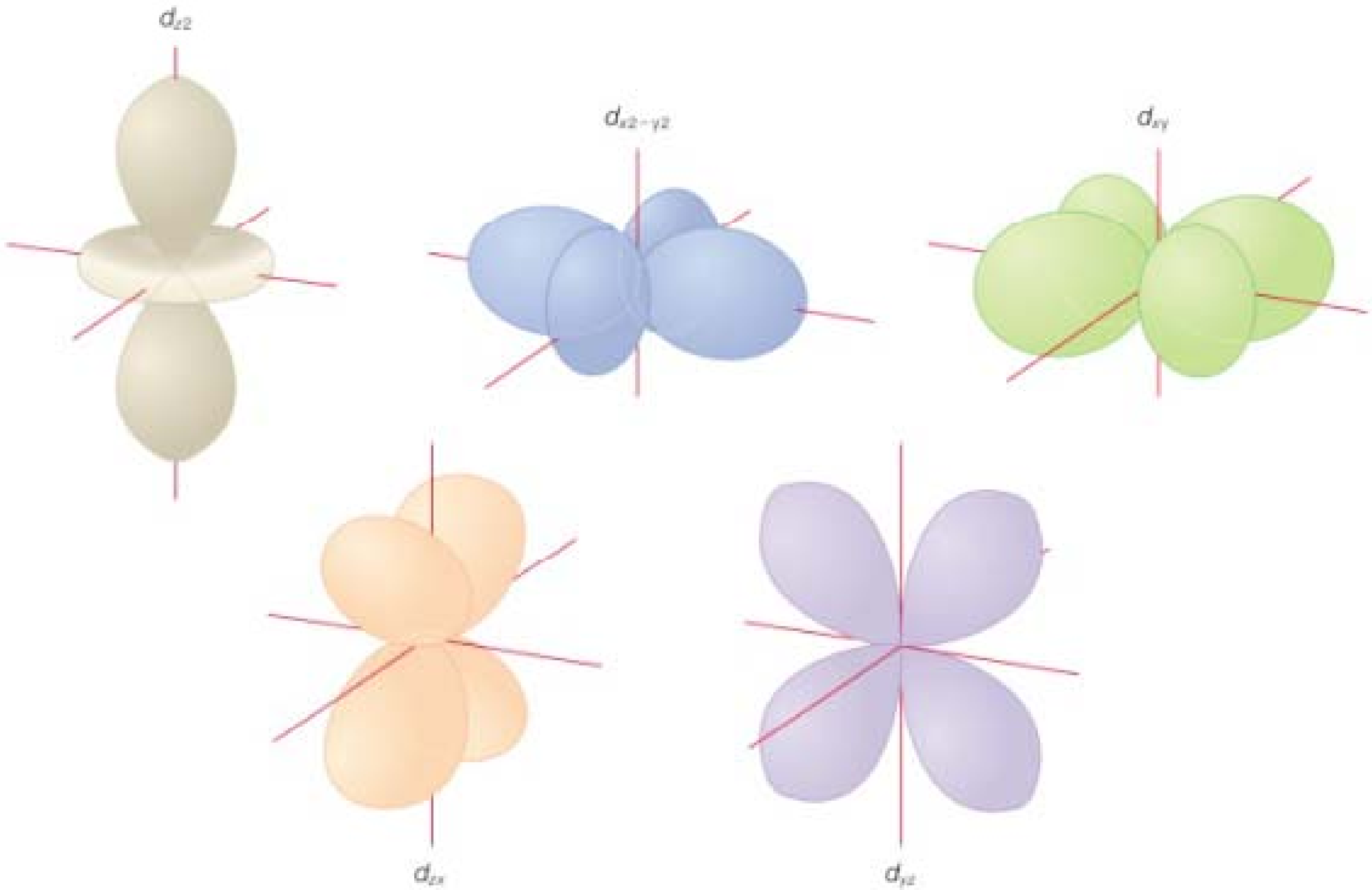


Orbital Shapes



- Each *p* has a shape much like a dumbbell, differing in the direction extending into space

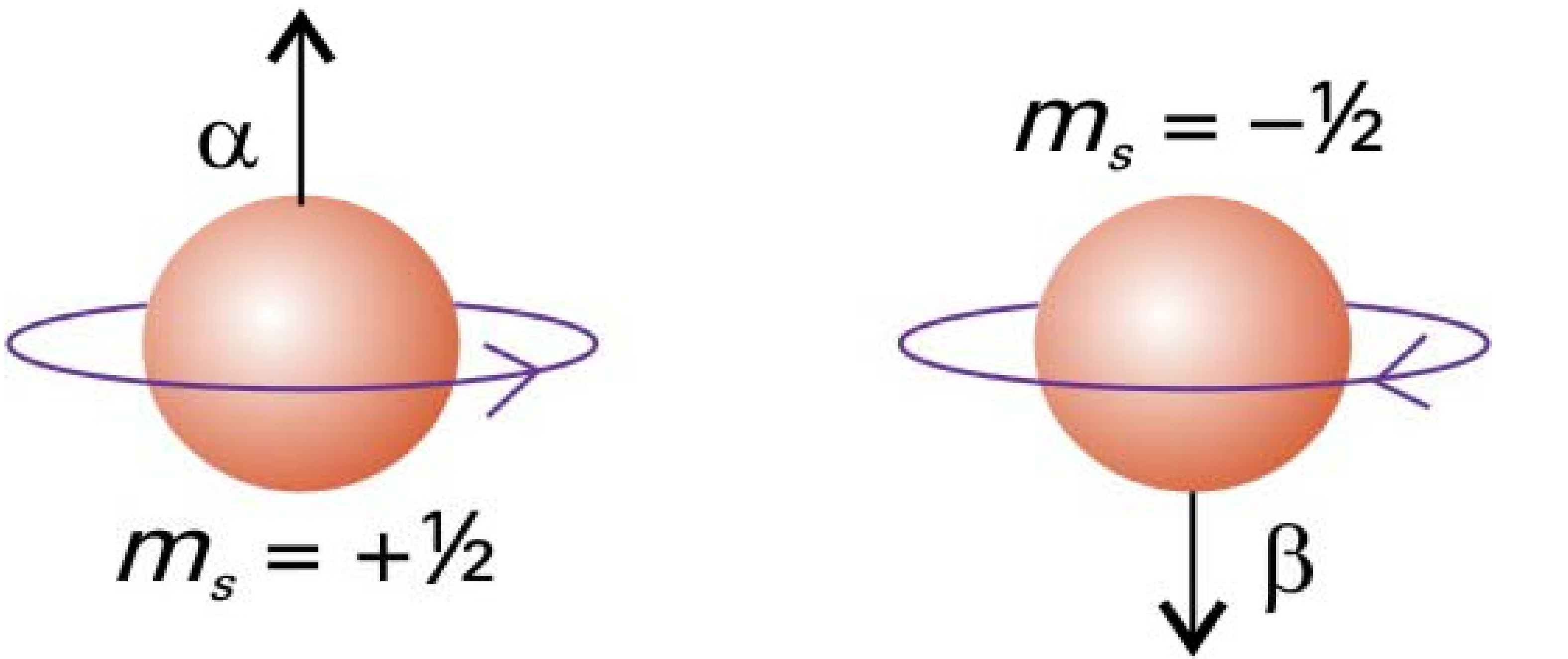
Orbital Shapes



Subshell	Number of orbitals
s	1
p	3
d	5
f	7

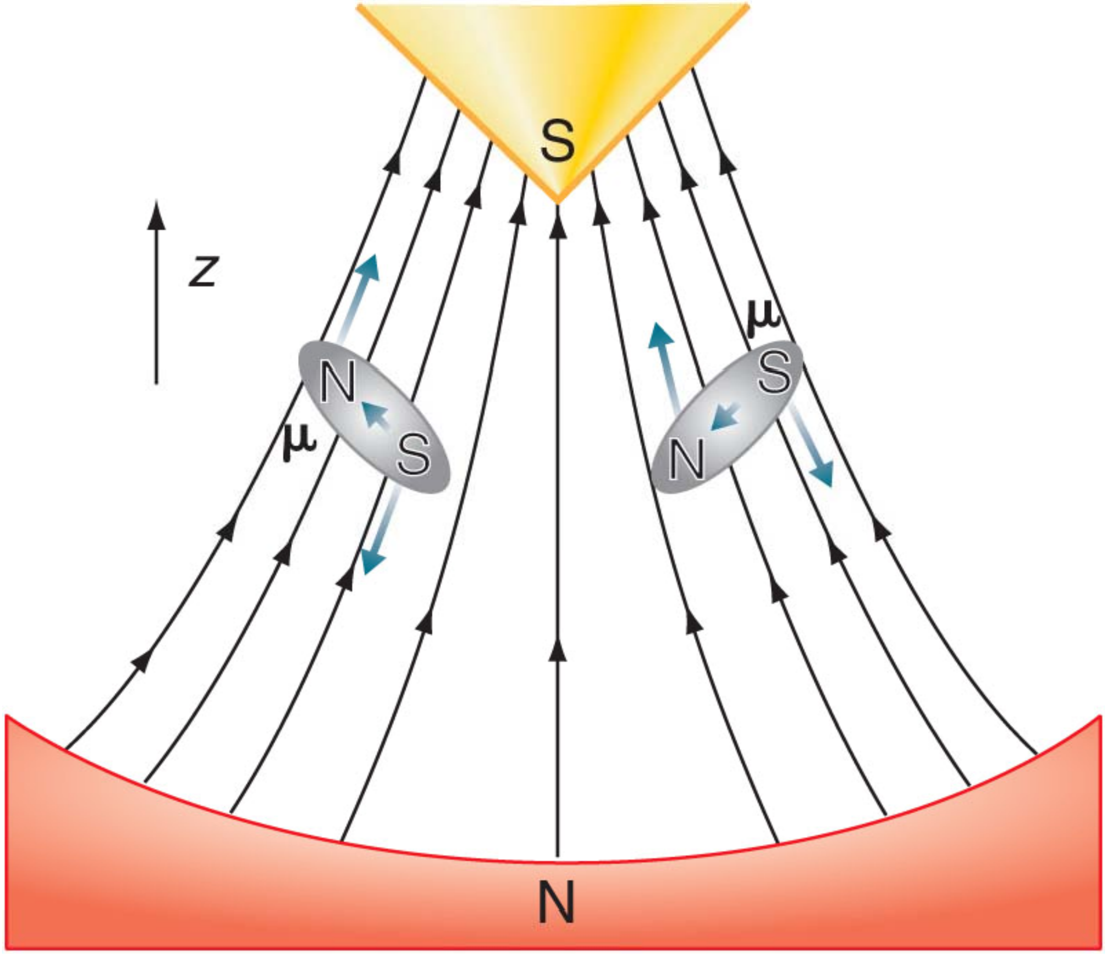
- How many electrons can be in the 4d subshell?

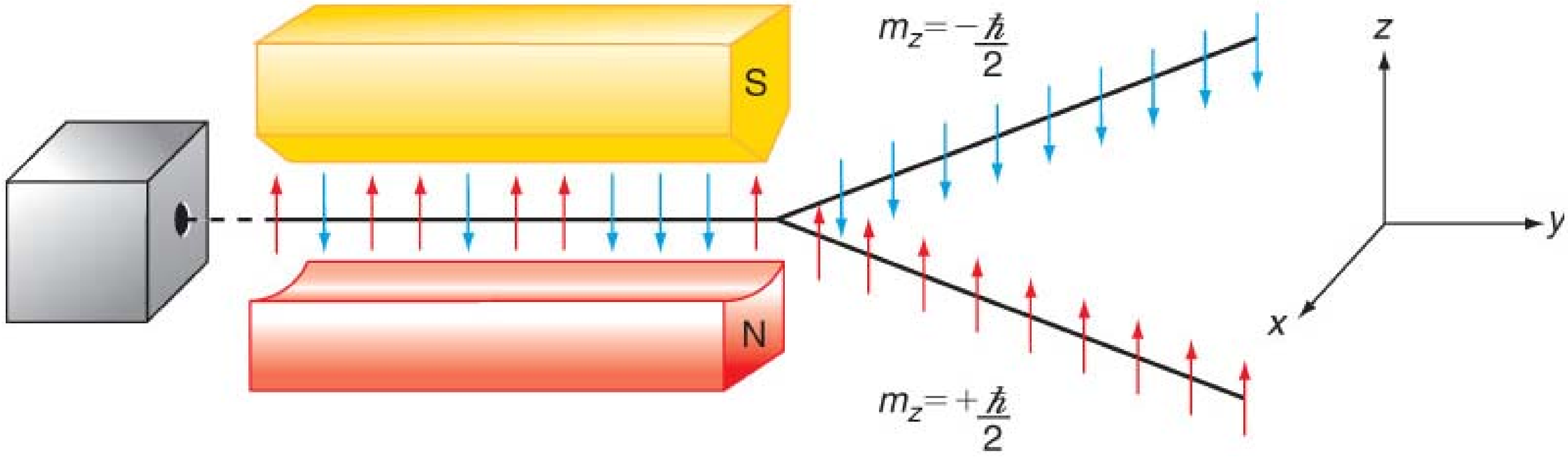
Electron Spin

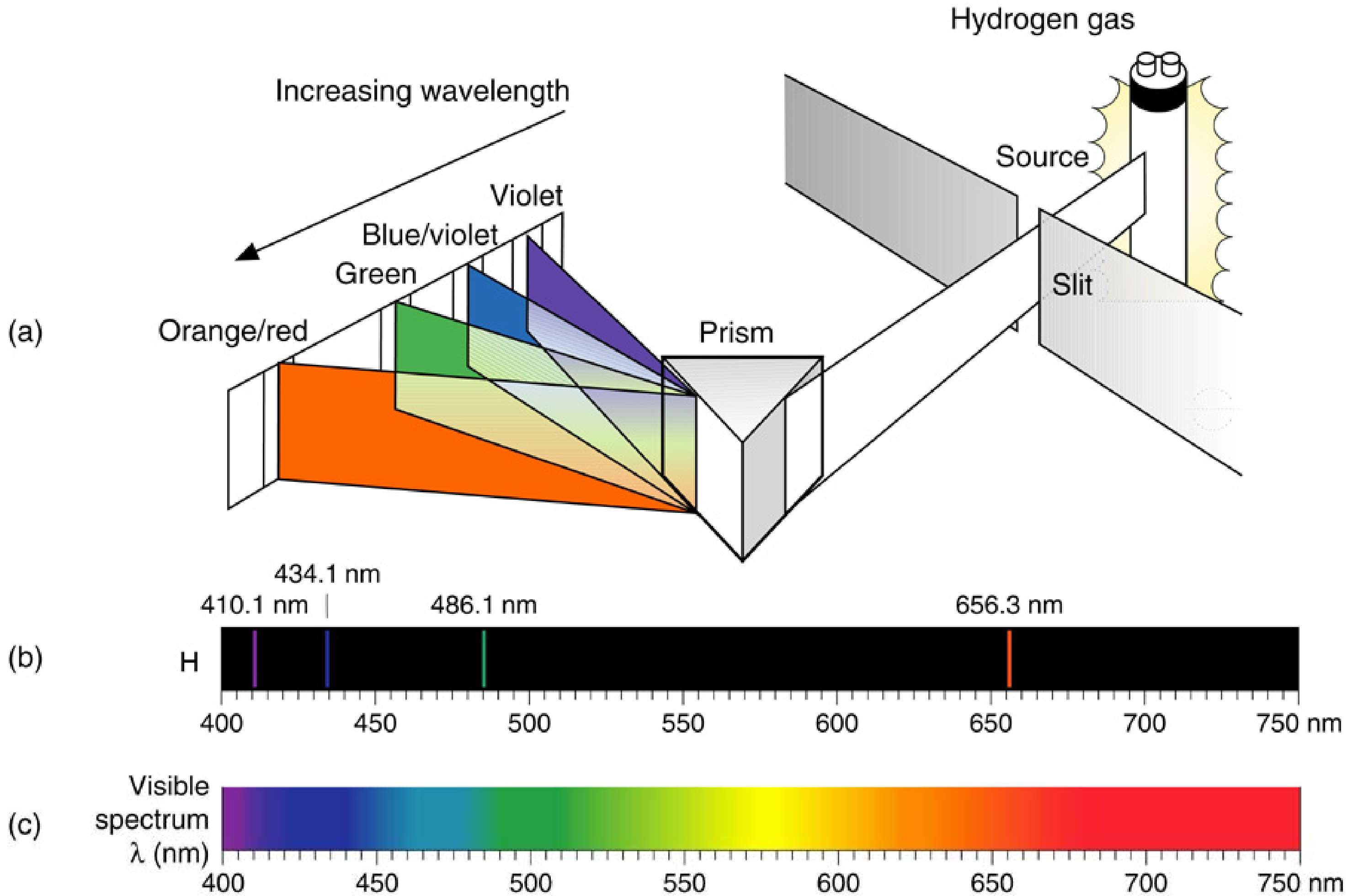


α electron

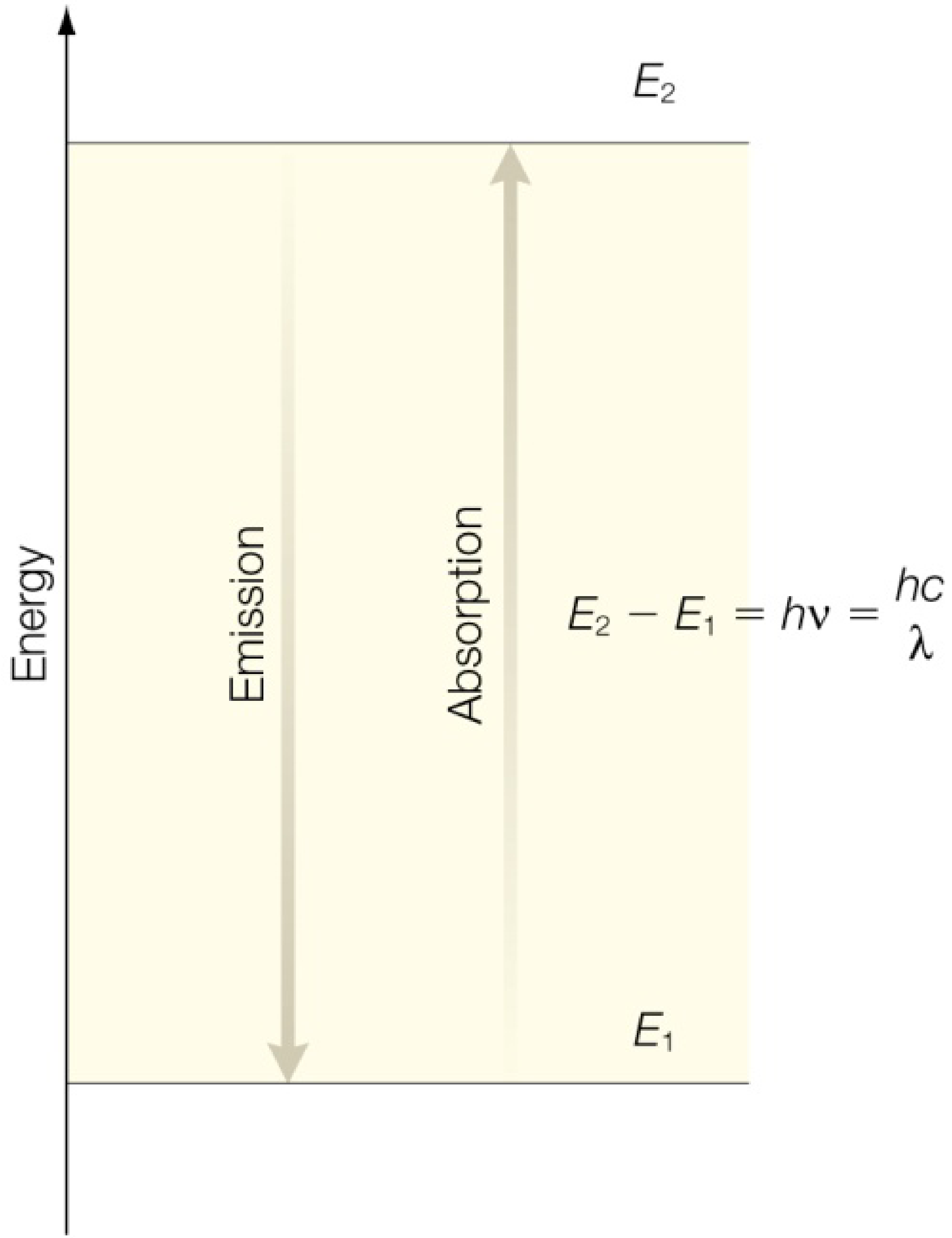
β electron


S
z
μ
N
S
μ
S
N
N


S
N
$m_z = -\frac{\hbar}{2}$
$m_z = +\frac{\hbar}{2}$
z
y
x



The emission spectrum of hydrogen lead to the modern understanding of the electronic structure of the atom



E_2
Energy
Emission
Absorption
$E_2 - E_1 = h\nu = \frac{hc}{\lambda}$
E_1

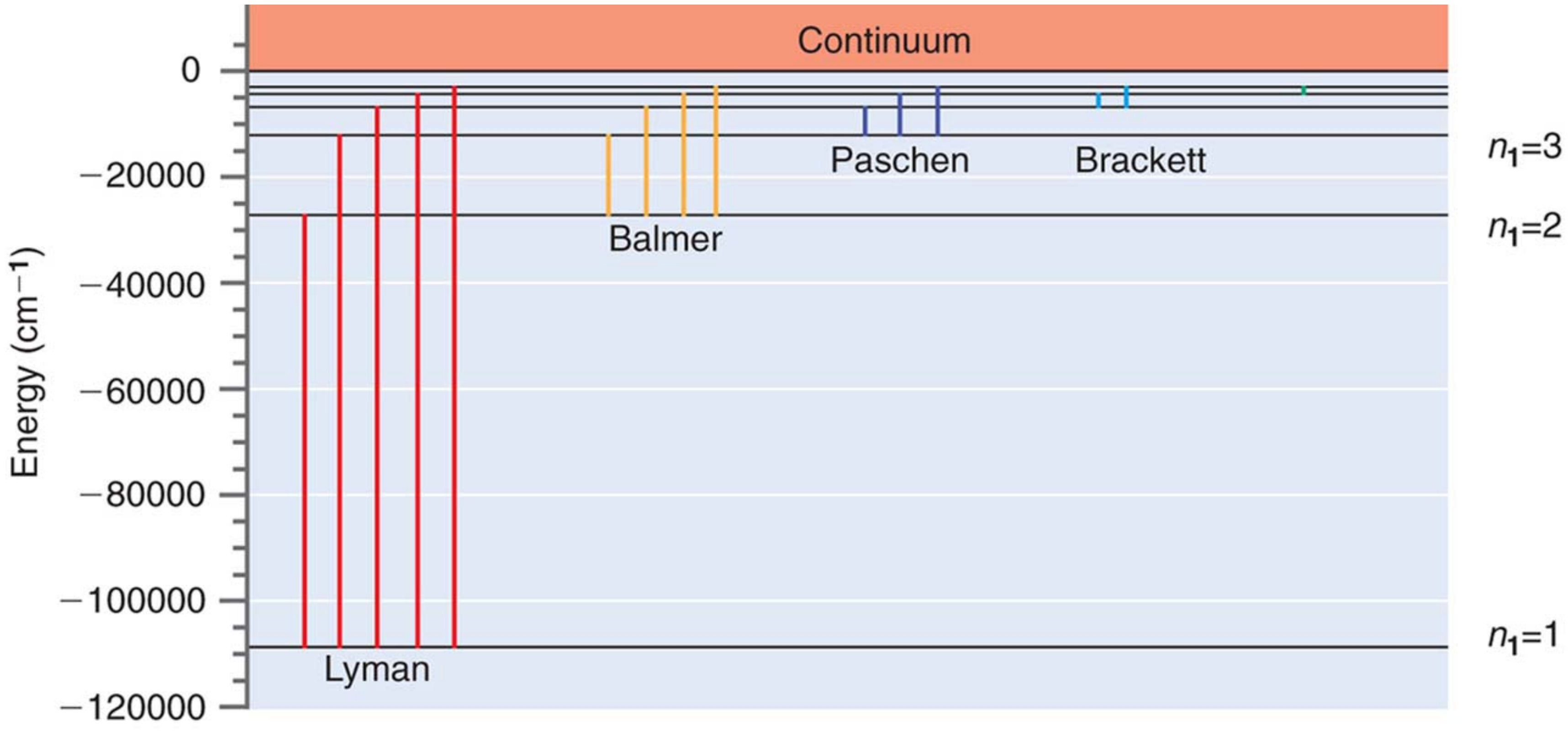


FIGURE 15.2

Energy-level diagram for the hydrogen atom showing the allowed transitions for $n < 6$. Because for $E > 0$, the energy levels are continuous, the absorption spectrum will be continuous above an energy that depends on the initial n value. The different sets of transitions are named after the scientists who first investigated them.

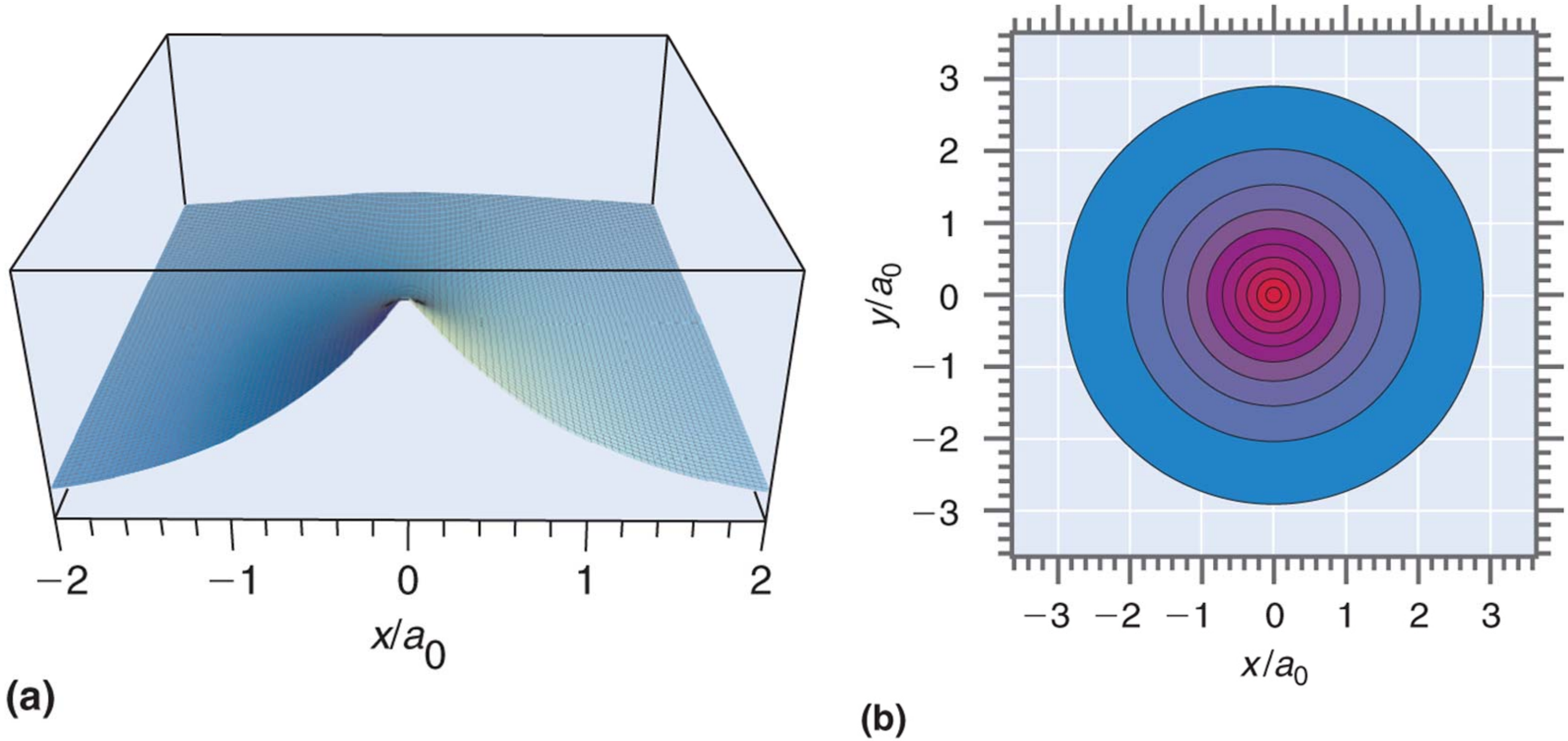


FIGURE 15.3

(a) 3-D perspective and (b) contour plot of $\psi_{100}(r)$. Red and blue contours correspond to the most positive and least positive values, respectively, of the wave function.

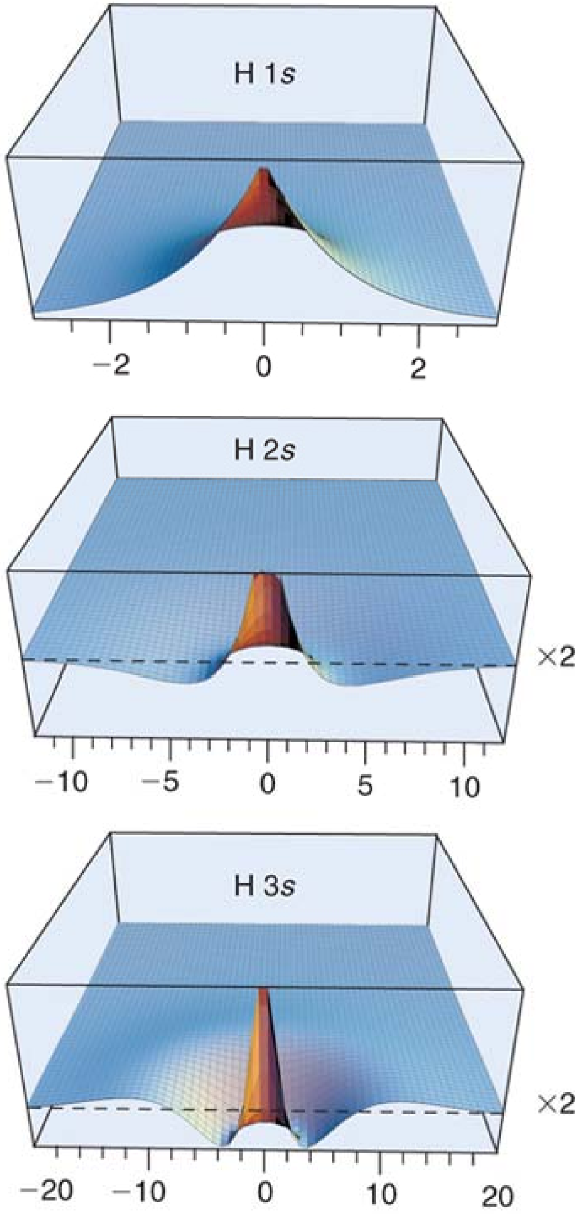


FIGURE 15.4

Three-dimensional perspective plots of the 1*s*, 2*s*, and 3*s* orbitals. The dashed lines indicate the zero of amplitude for the wave functions. The "×2" refers to the fact that the amplitude of the wave function has been multiplied by 2 to make the subsidiary maxima apparent.

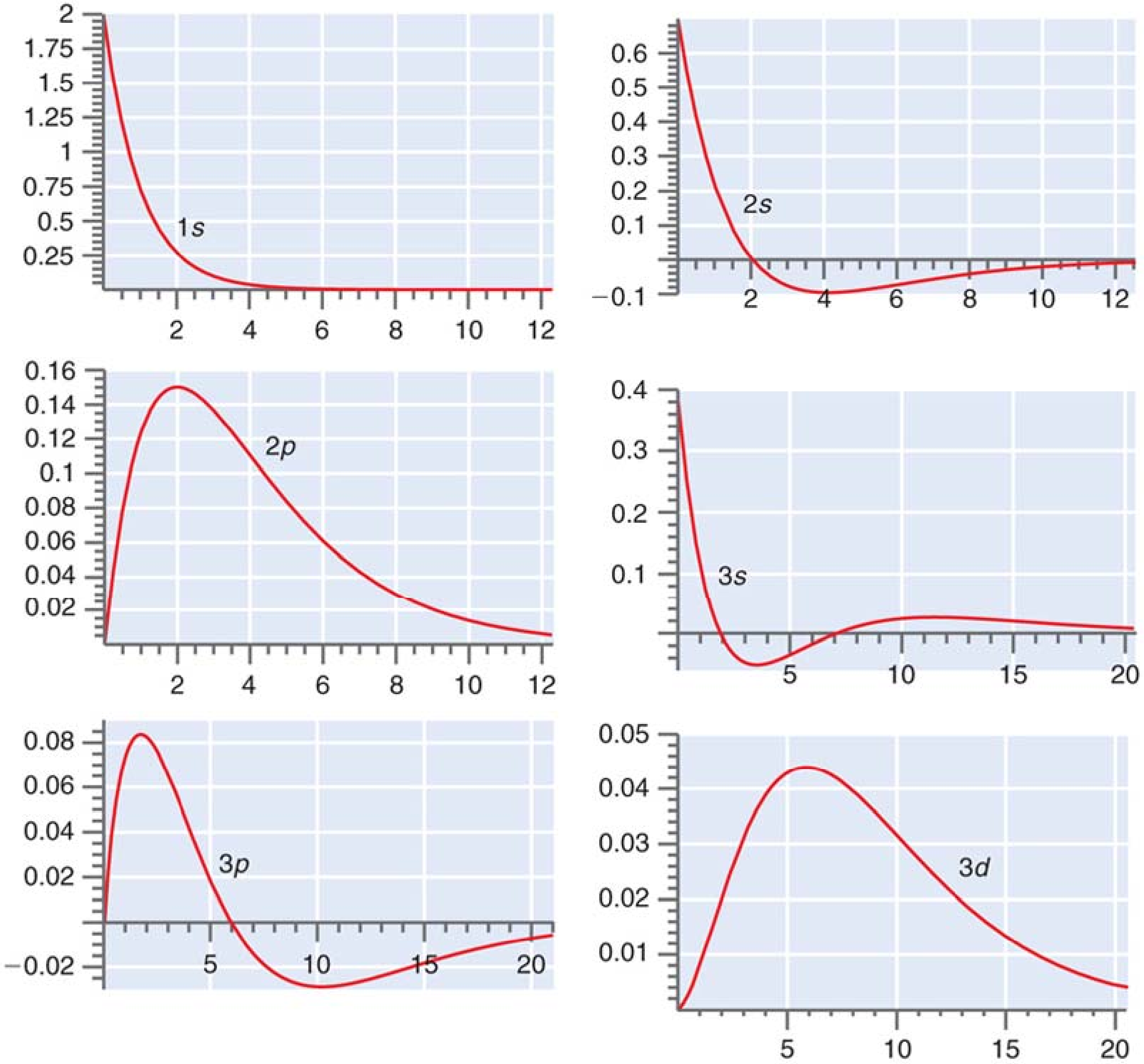


FIGURE 15.5

Plot of $a_0^{3/2}R(r)$ versus r/a_0 for the first few H atomic orbitals.

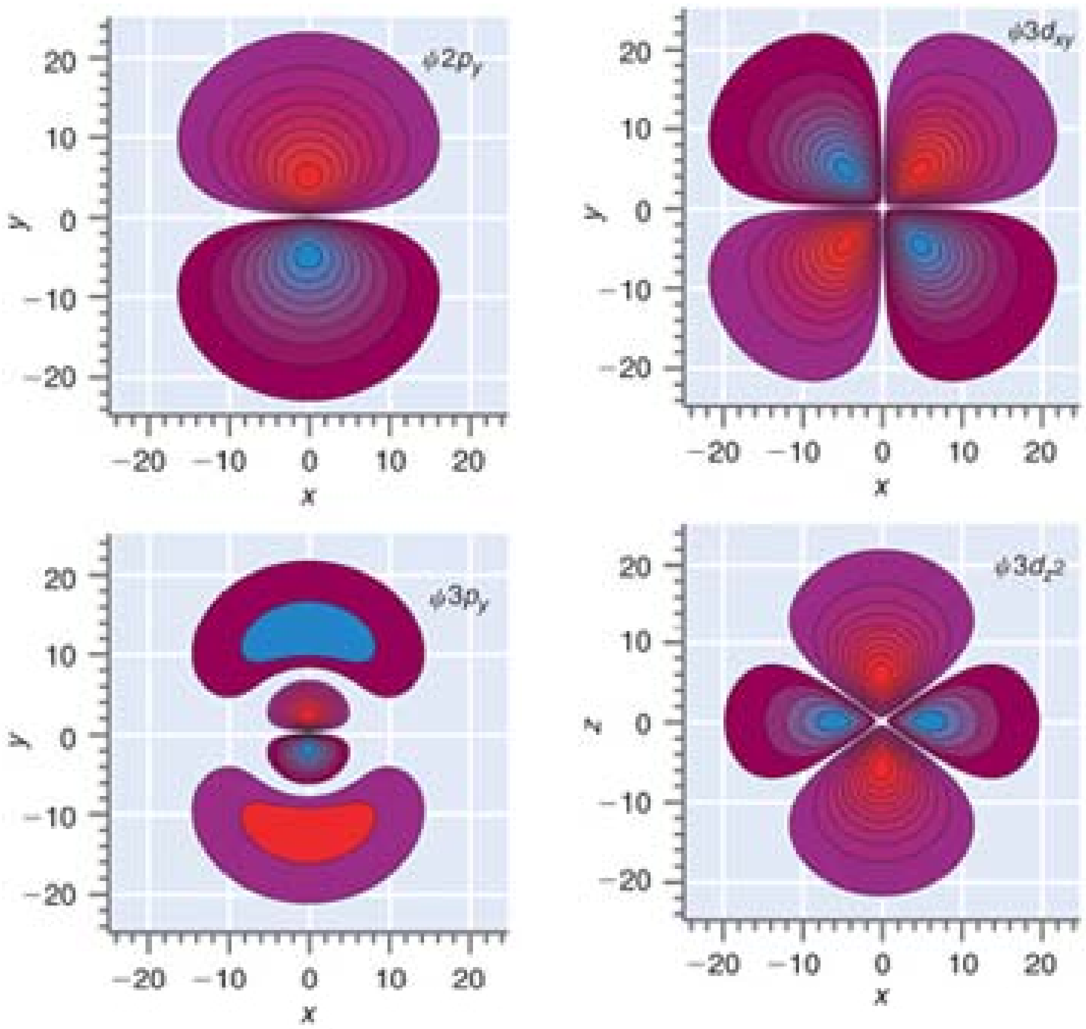


FIGURE 15.6

Contour plot for the orbitals indicated. The colors red and blue indicate the most positive and least positive values, respectively, of the wave function amplitude. Distances are in units of a_0.

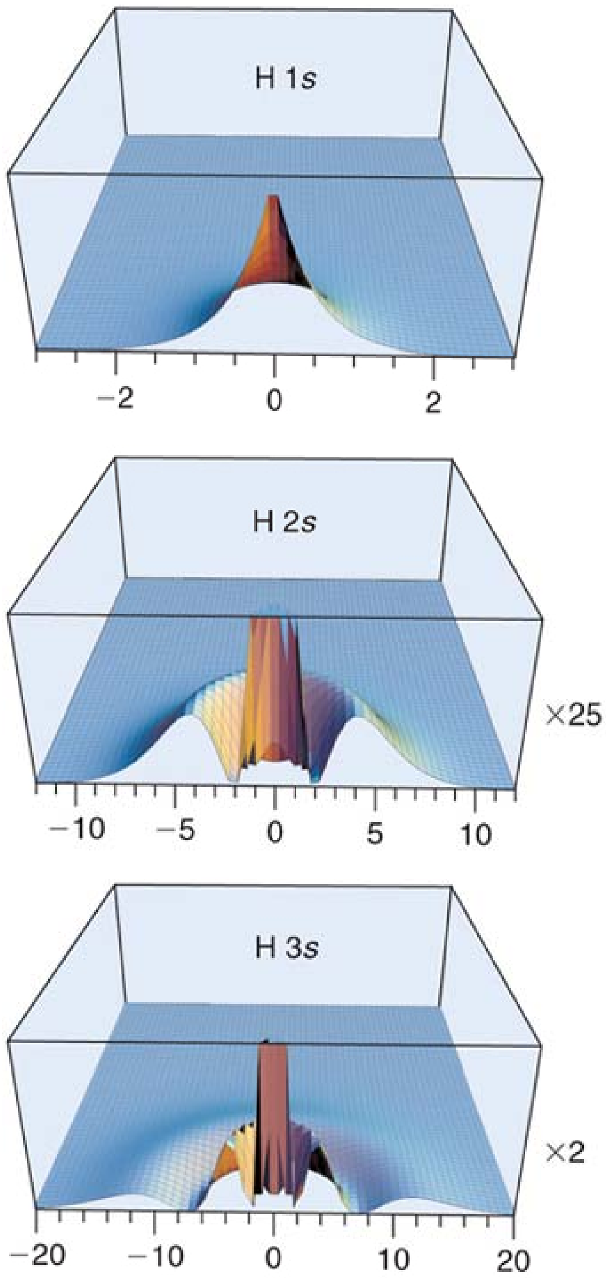


FIGURE 15.7

3-D perspective plots of the square of the wave functions for the orbitals indicated. The numbers on the axes are in units of a_0.

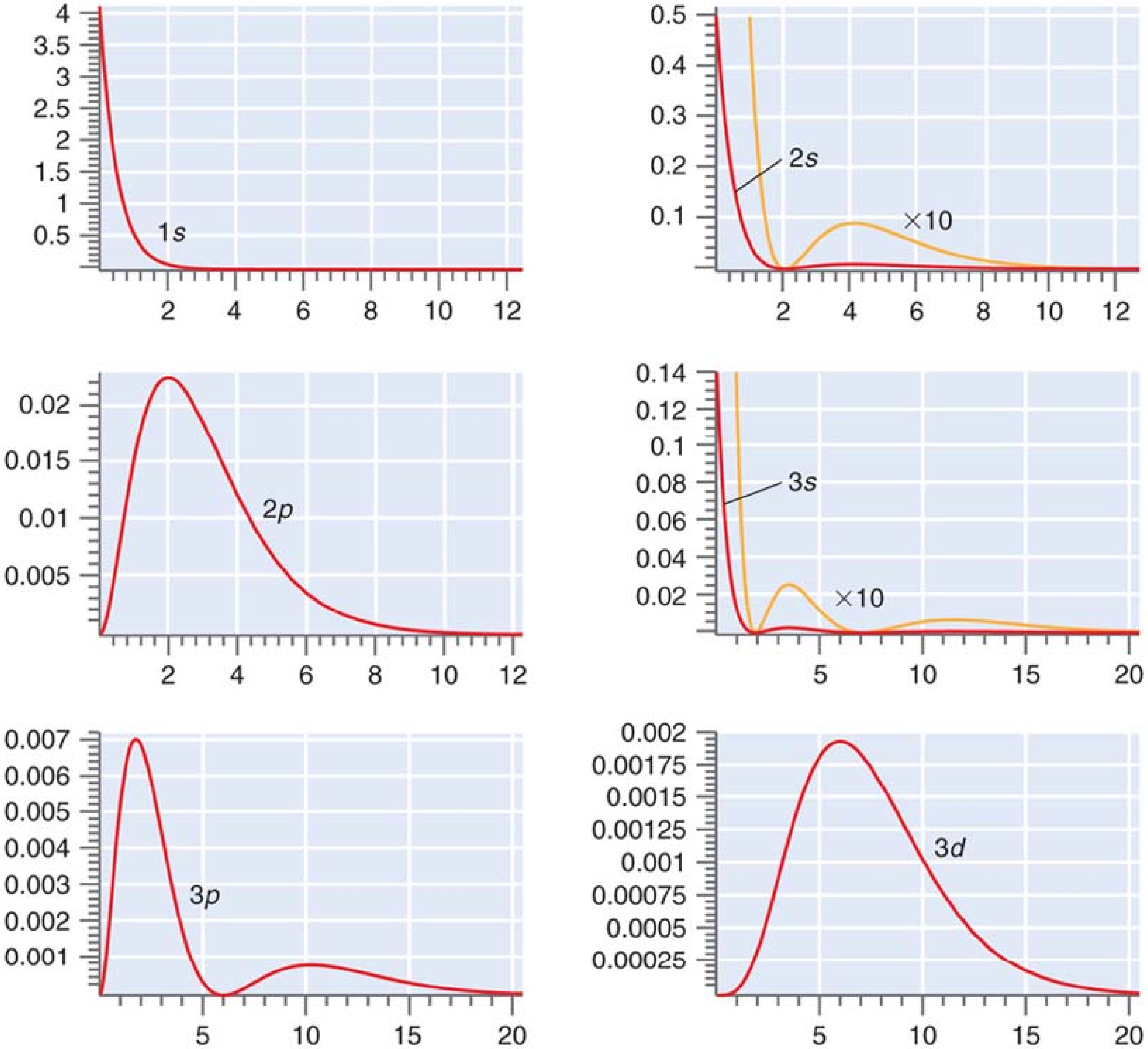


FIGURE 15.8

Plot of $a_0^3R^2(r)$ versus r/a_0 for the first few H atomic orbitals. The numbers on the horizontal axis are in units of a_0.

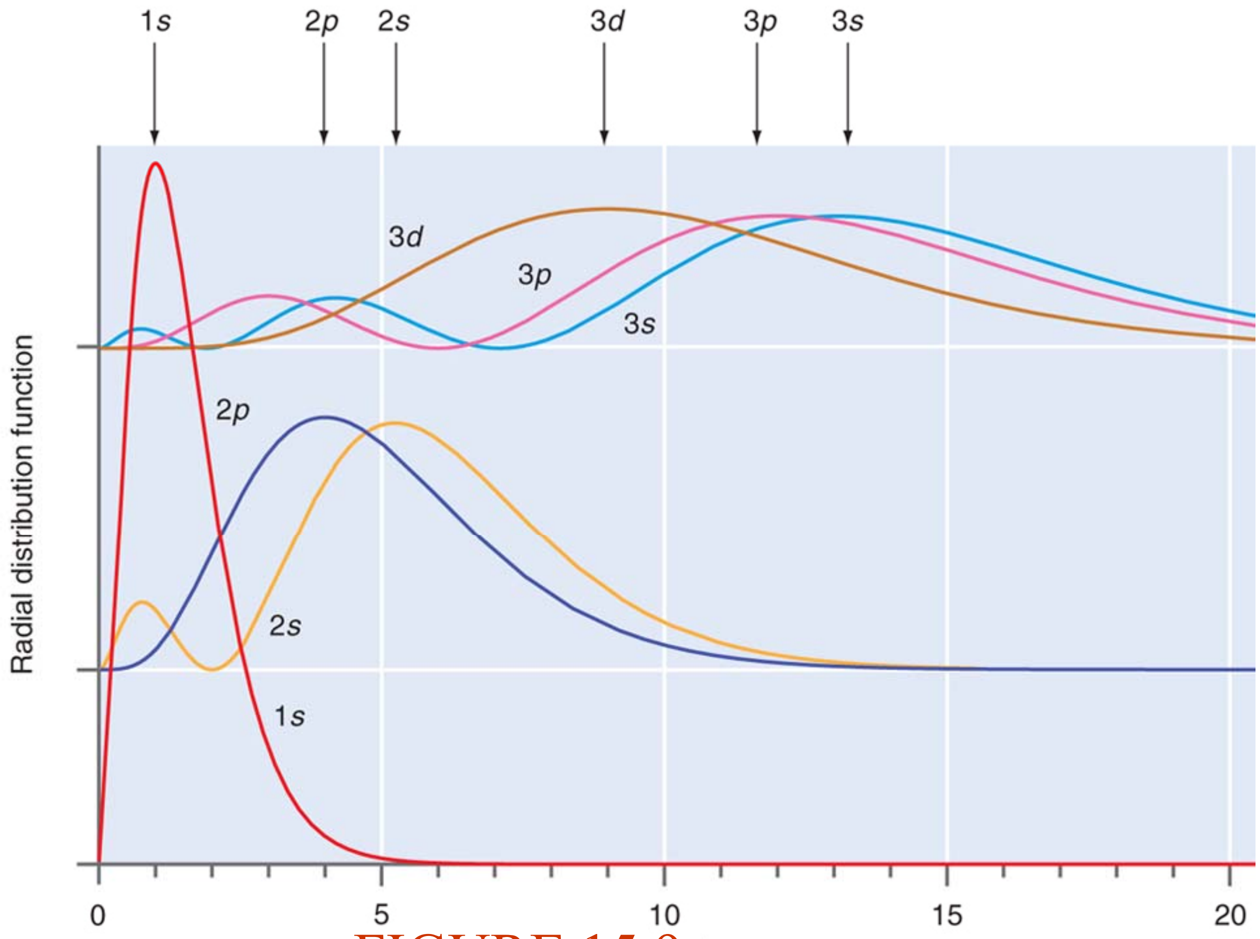


FIGURE 15.9

Plot of $r^2 a_0^3 R^2(r)$ versus r/a_0 for the first few H atomic orbital. The curves for $n = 2$ and $n = 3$ have been displaced vertically as indicated. The position of the principal maxima for each orbital is indicated by an arrow.

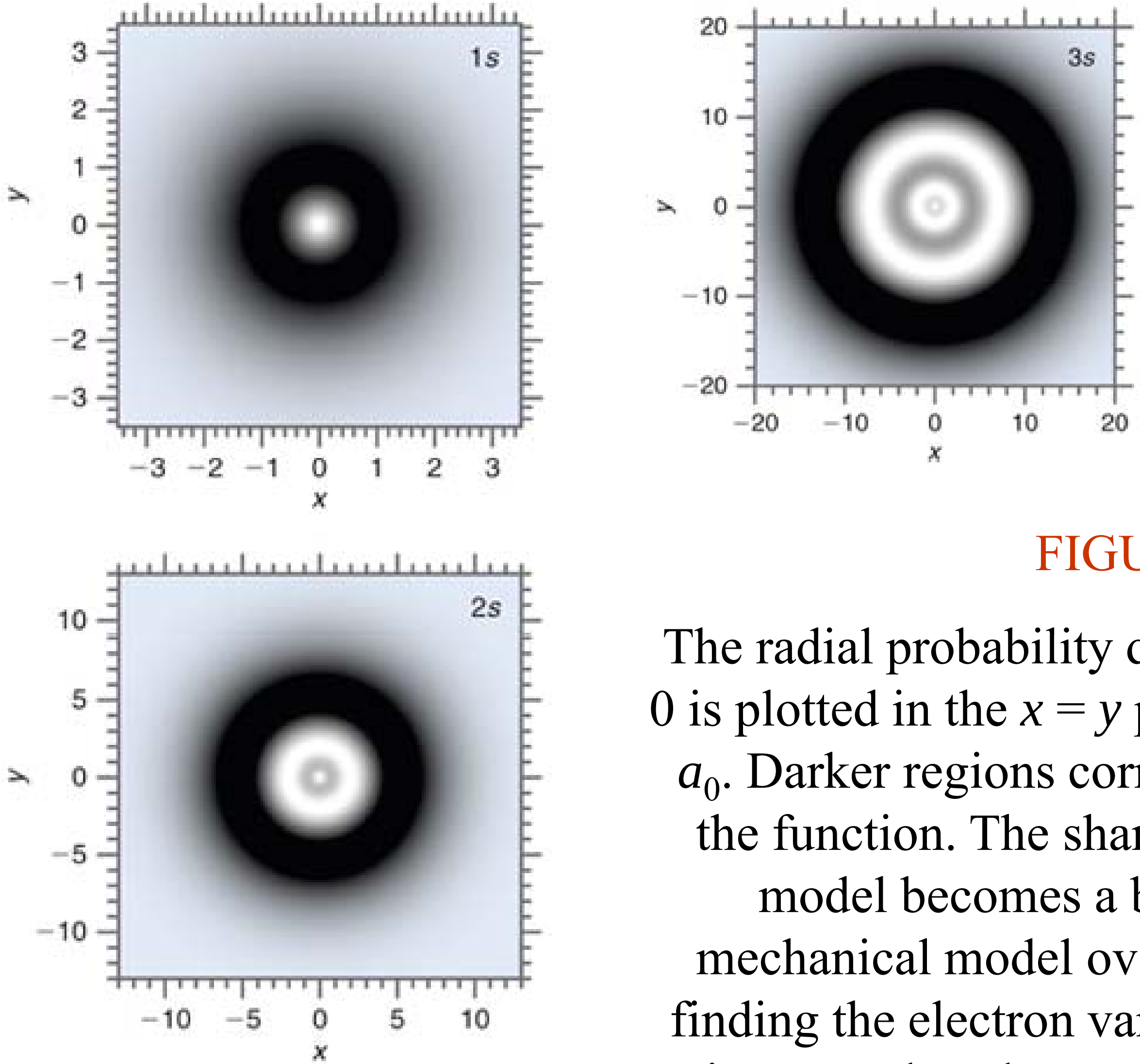
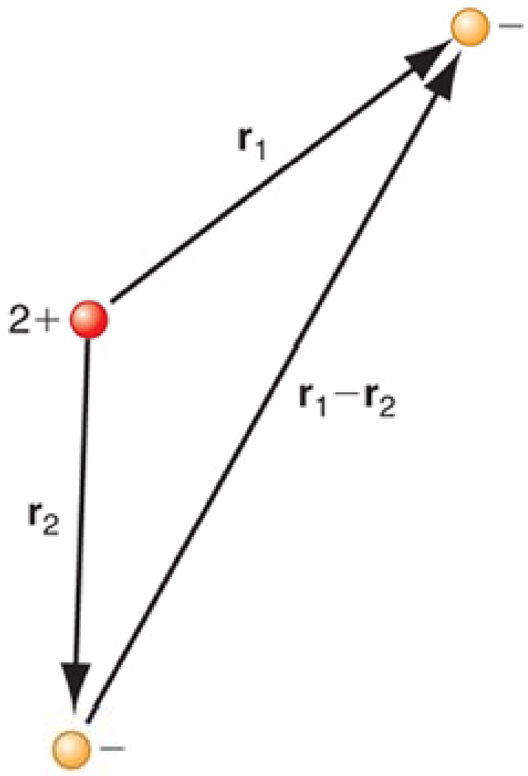


FIGURE 15.11

The radial probability distribution evaluated for $z = 0$ is plotted in the $x = y$ plane with lengths in units of a_0. Darker regions correspond to greater values of the function. The sharp circle in a classical shell model becomes a broad ring in a quantum mechanical model over which the probability of finding the electron varies. Less intense subsidiary rings are also observed for the 2*s* and 3*s* orbitals.

P. 370

Helium Atom



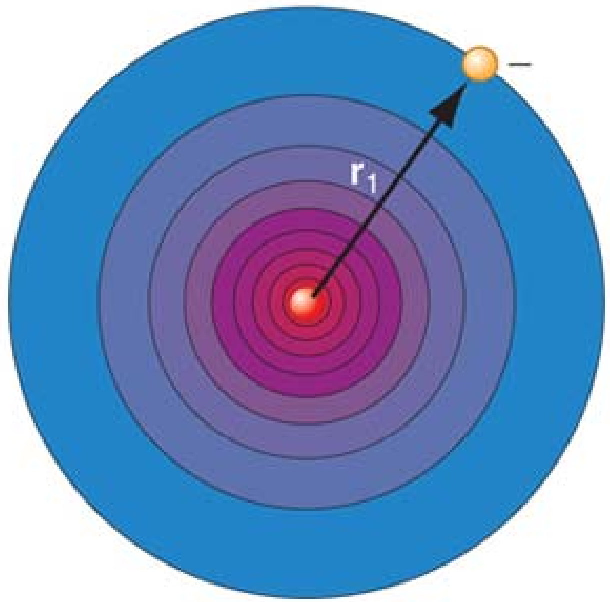


FIGURE 15.12

The top image shows the proton and two electrons that need to be considered for correlated electron motion. The bottom image shows that if the position of electron 2 is averaged over its orbit, electron 1 see a spherically symmetric charge distribution due to the helium nucleus and electron 2.

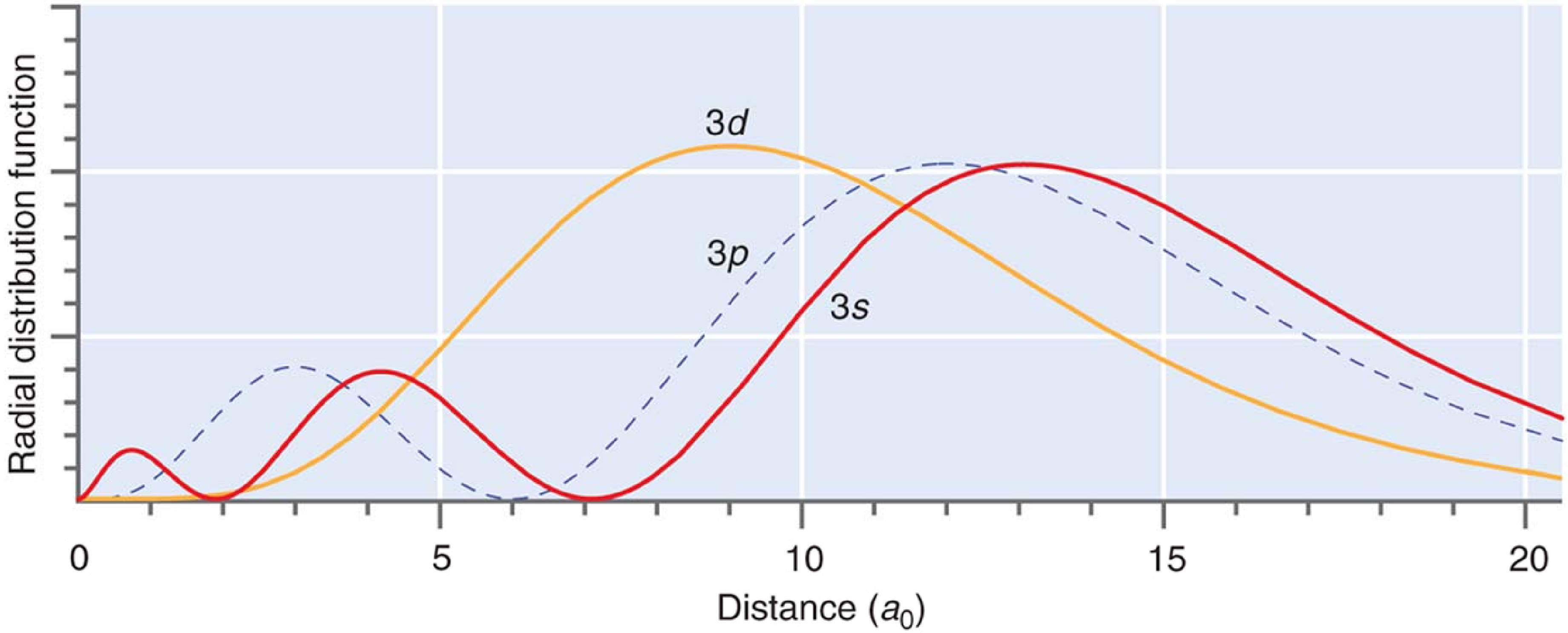
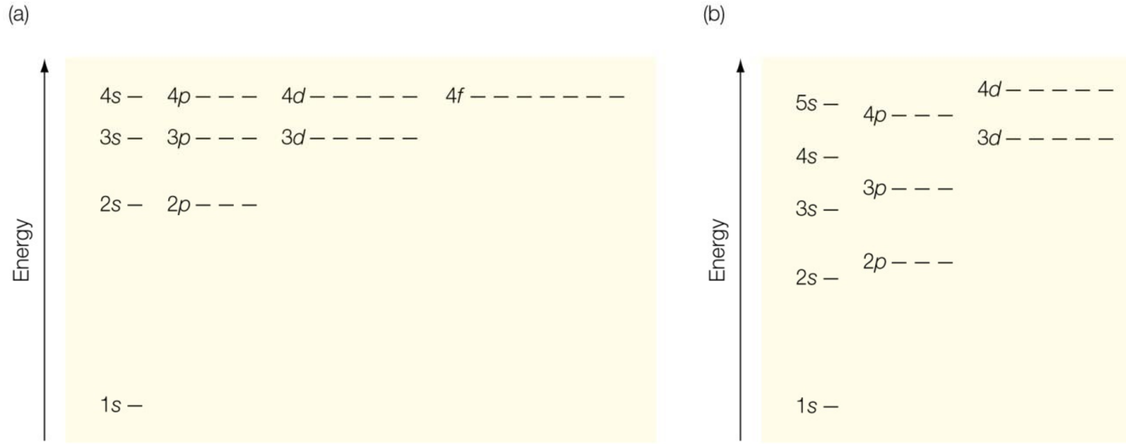


FIGURE 15.15

Radial probability distributions for the 3*s*, 3*p*, and 3*d* orbitals of the H atom as a function of distance in units of a_0.



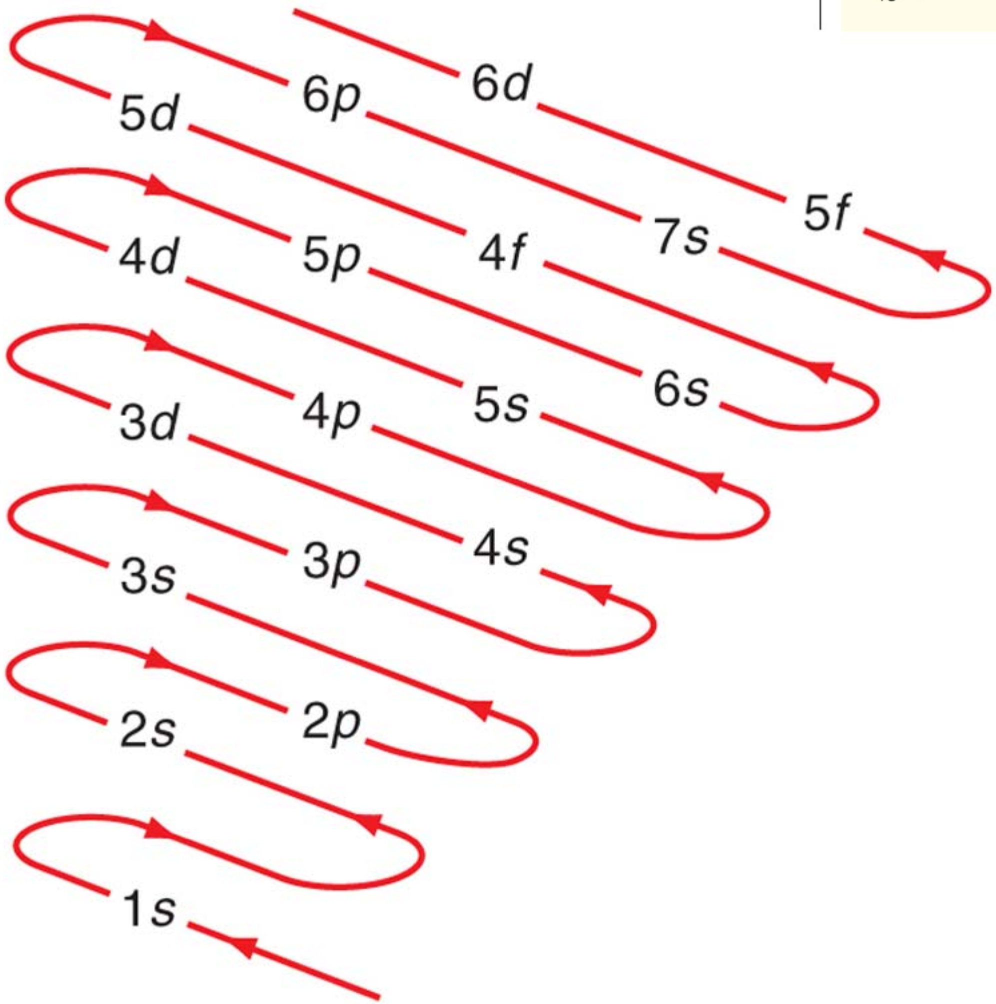


FIGURE 15.16

The order in which orbitals in many-electron atoms are filled for most atoms is described by the red line.

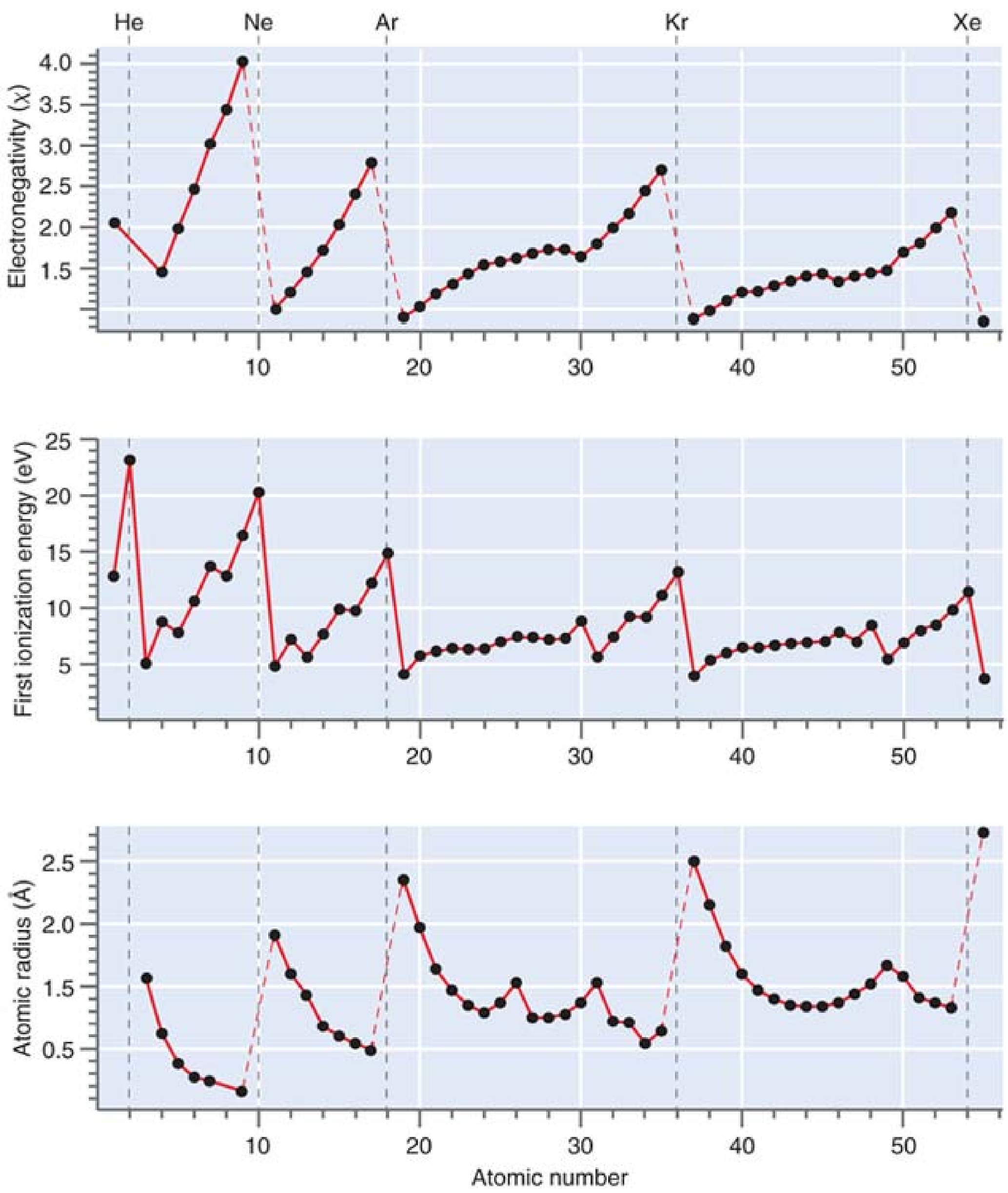
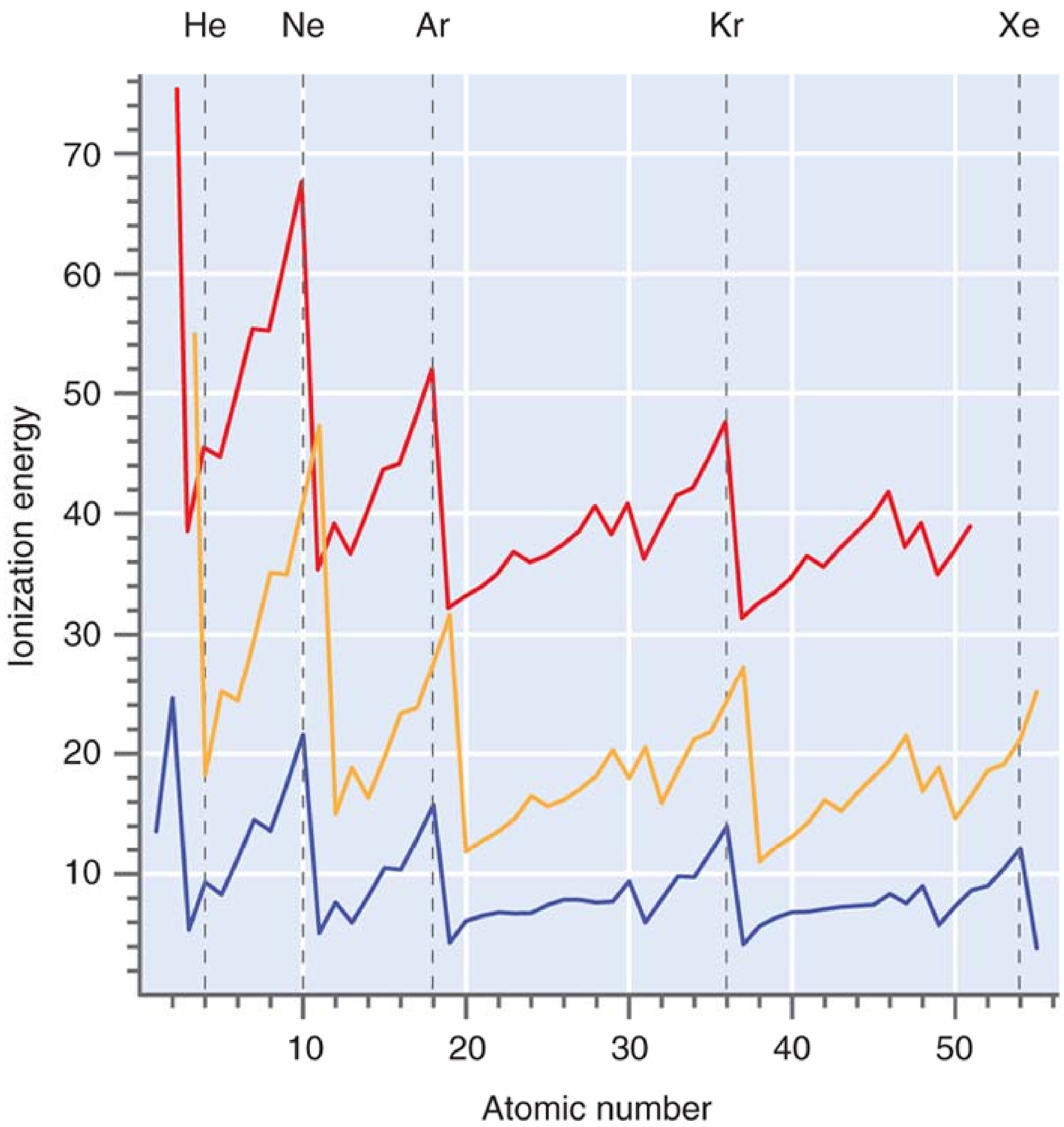


FIGURE 15.17

The covalent atomic radius, first ionization energy, and electronegativity are plotted as a function of the atomic number for the first 55 elements. Dashed vertical lines mark the completion of each period.



Problems P15.30

- Metals (main-group)
- Metals (transition)
- Metals (inner transition)
- Metalloids
- Nonmetals

REPRESENTATIVE ELEMENTS | TRANSITION ELEMENTS | REPRESENTATIVE ELEMENTS

Period	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	(9)	(10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** 1.008																	2 He 4.003
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (263)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (267)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 (285)		114 (289)		116 (292)		

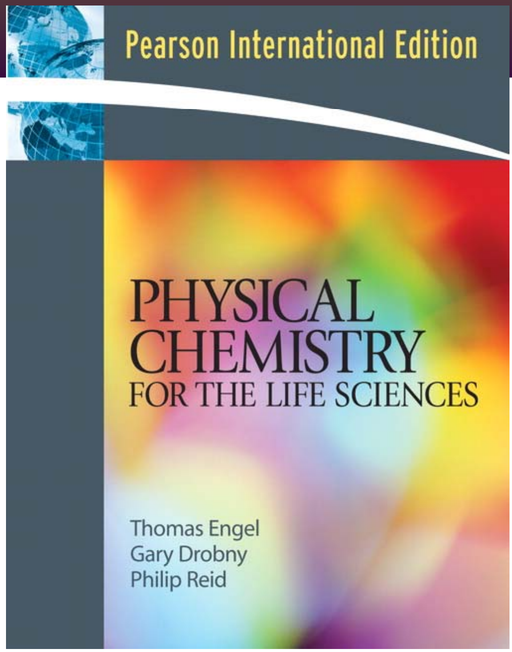
INNER TRANSITION ELEMENTS

6	Lanthanides	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
7	Actinides	90 **Th** 232.0	91 **Pa** (231)	92 **U** 238.0	93 **Np** (237)	94 **Pu** (242)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

H_2^+

Physical Chemistry

For the Life Sciences



CHAPTER 16

Chemical Bonding in Diatomic Molecules

Y.T.Lin's Presentation

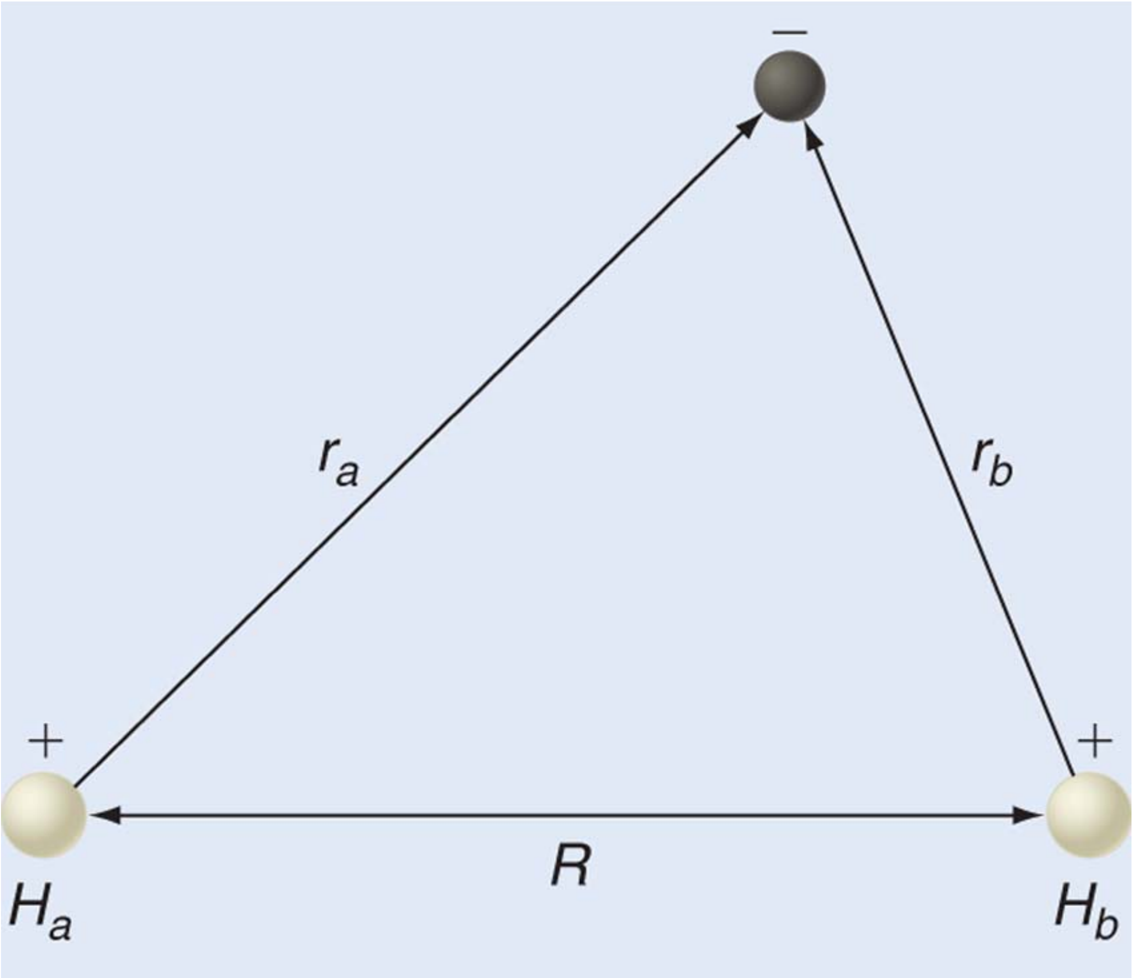


FIGURE 16.1

The two protons and the electron are shown at one instant in time. The quantities R, r_a, and r_b represent the distances between the charged particles.

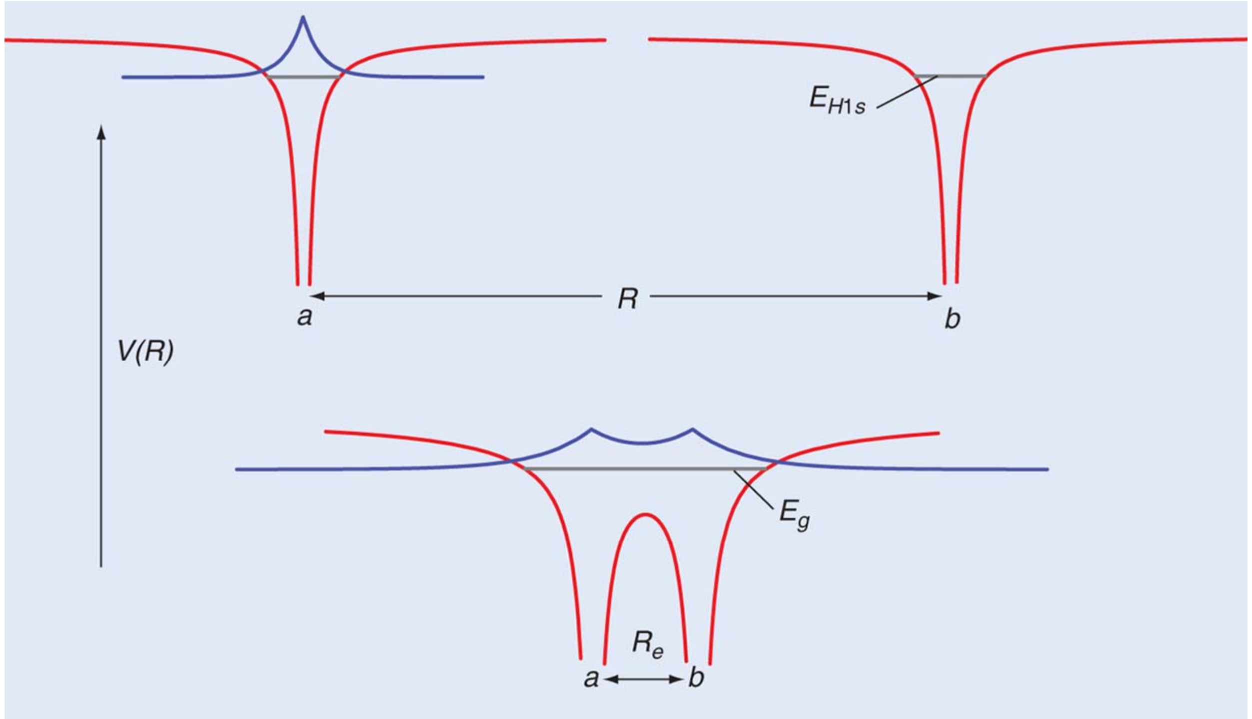


FIGURE 16.2

The potential energy of the H_2^+ molecule is shown for two different values of R (red curves). At large distances, the electron will be localized in a 1*s* orbital either on nucleus *a* or *b*. However, at the equilibrium bond length R_e, the two Coulomb potentials overlap, allowing the electron to be delocalized over the whole molecule. The blue curve represents the amplitude of the atomic (top panel) and molecular (bottom panel) wave functions, and the solid horizontal lines represent the corresponding energy eigenvalues.

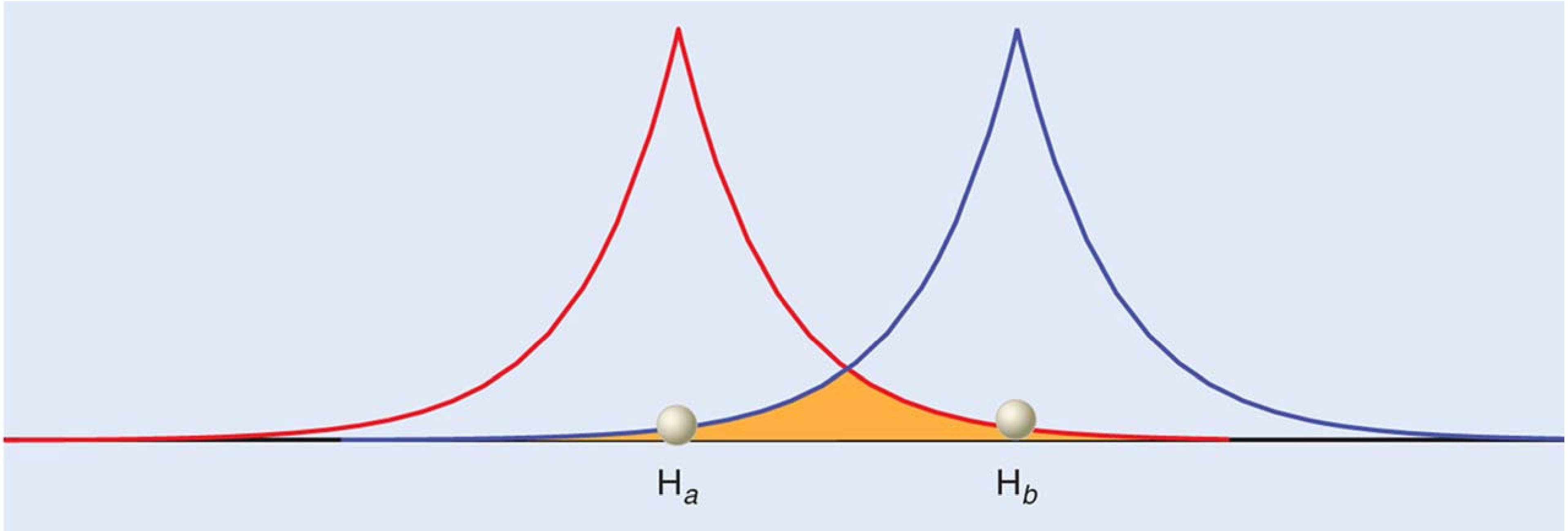


FIGURE 16.3

The amplitude of two H 1*s* atomic orbitals is shown along an axis connecting the atoms. The overlap is appreciable only for regions in which the amplitude of both Aos is significantly different from zero. Such a region is shown in yellow.

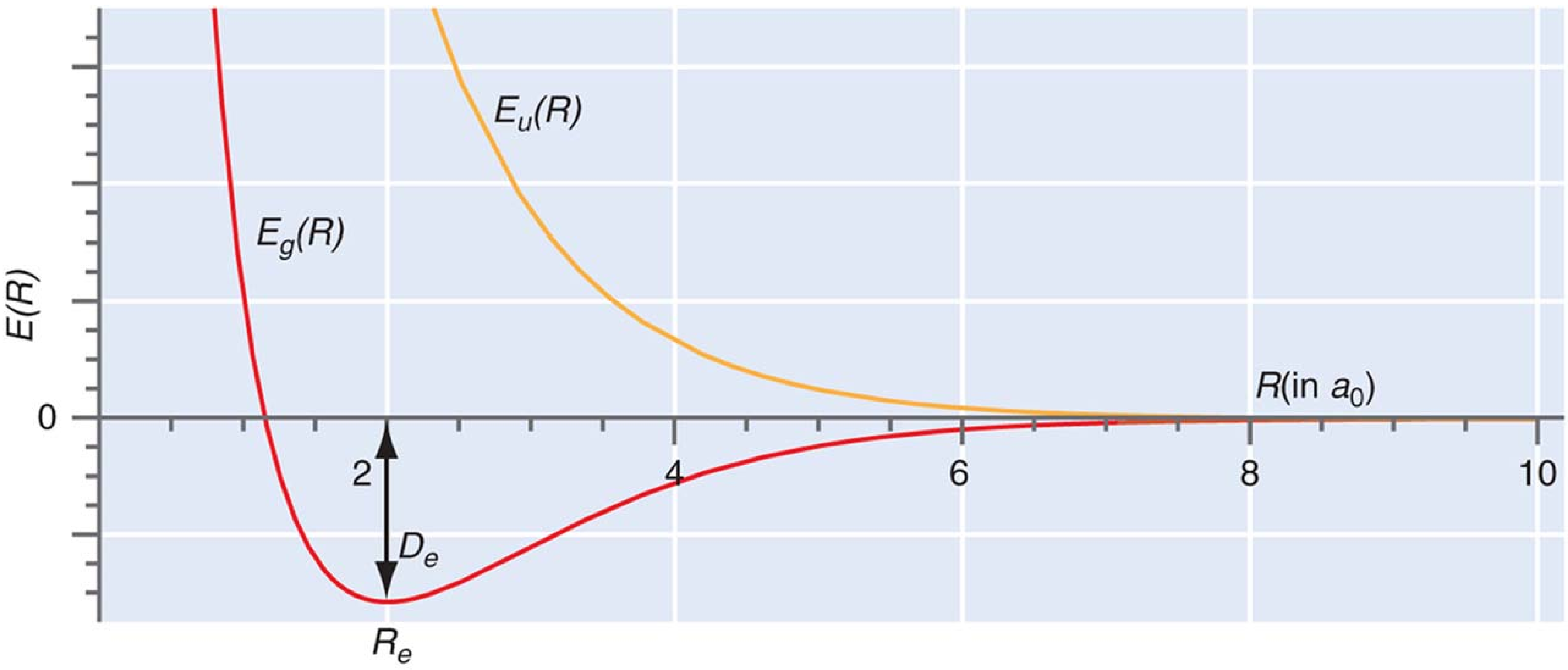


FIGURE 16.4

Schematic energy functions $E(R)$ are shown for the g and u states in the approximate solution discussed. The zero of energy corresponds to widely separated H and H^+ species.

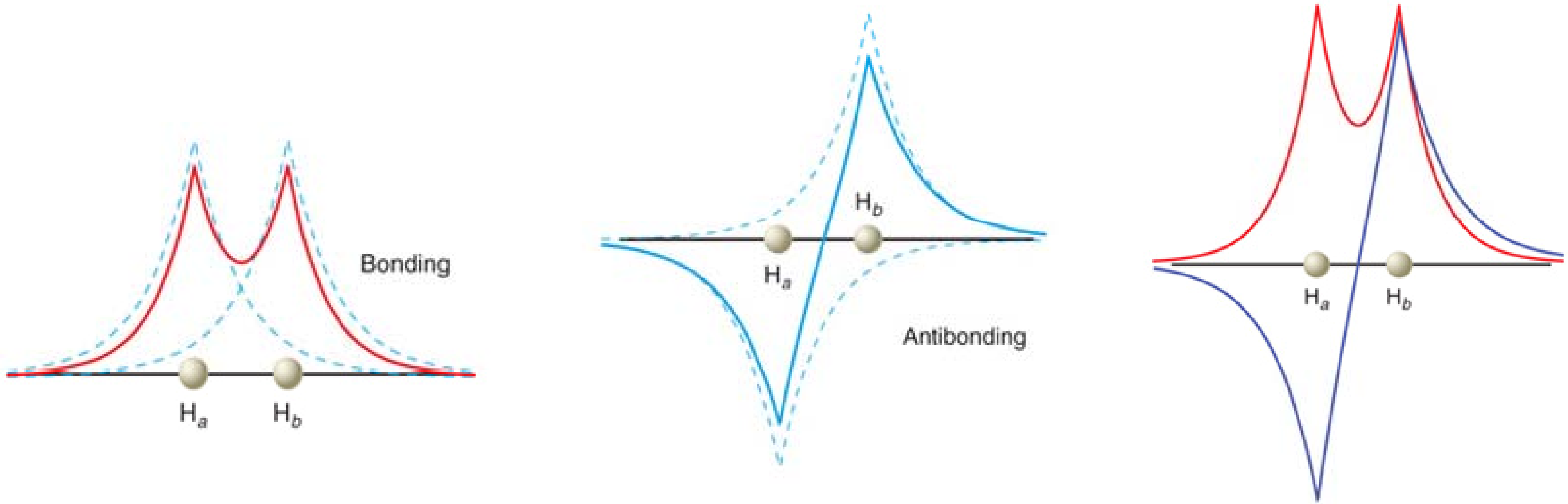


FIGURE 16.5

Molecular wave functions ψ_g and ψ_u (solid lines), evaluated along the internuclear axis, are shown in the top two panels. The unmodified (ζ = 1) H 1*s* orbitals from which they were generated are shown as dashed lines. The bottom panel shows a direct comparison of ψ_g and ψ_u .

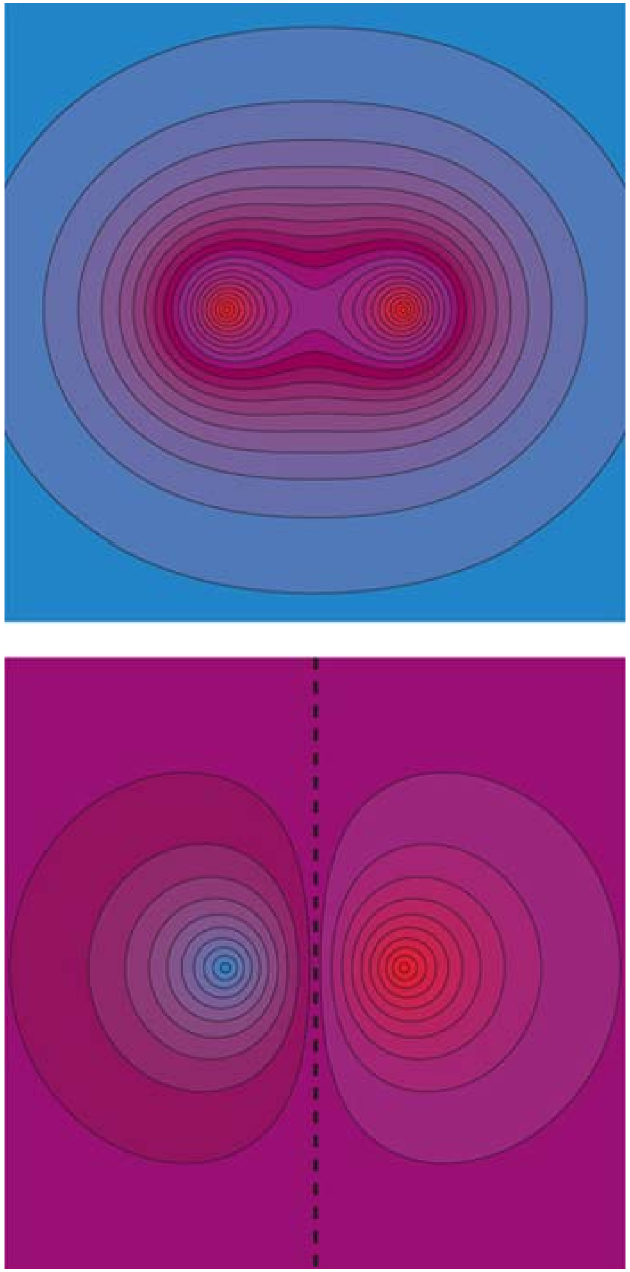


FIGURE 16.6

Contour plots of ψ_g (left) and ψ_u (right). The minimum amplitude is shown as blue, and the maximum amplitude is shown as red for each plot. The dashed line indicates the position of the nodal plane in ψ_u .

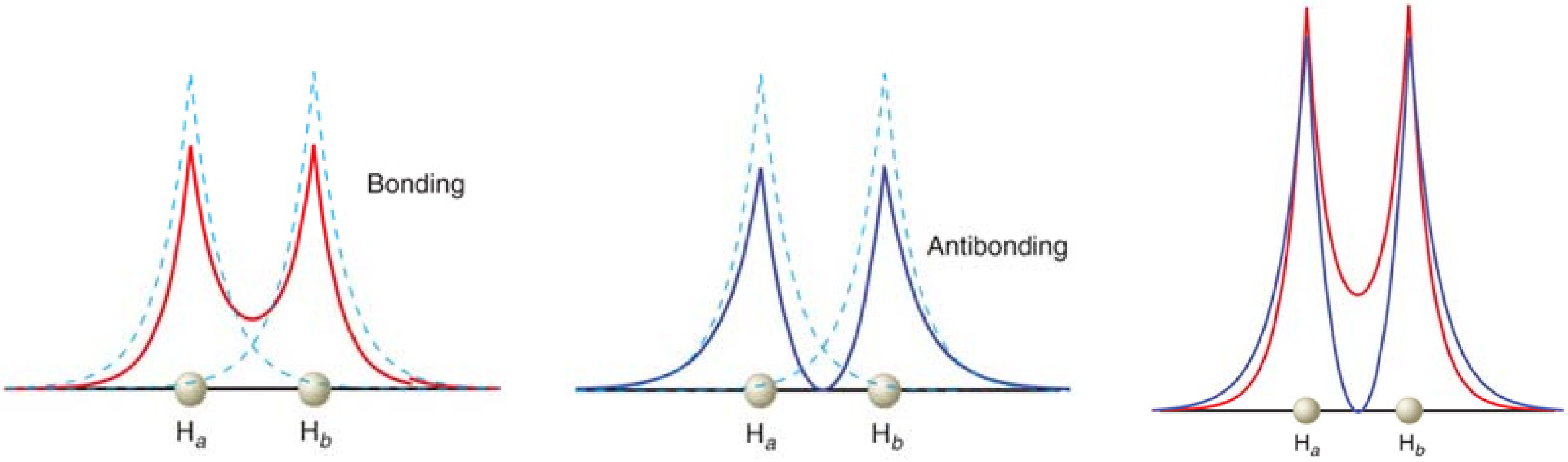
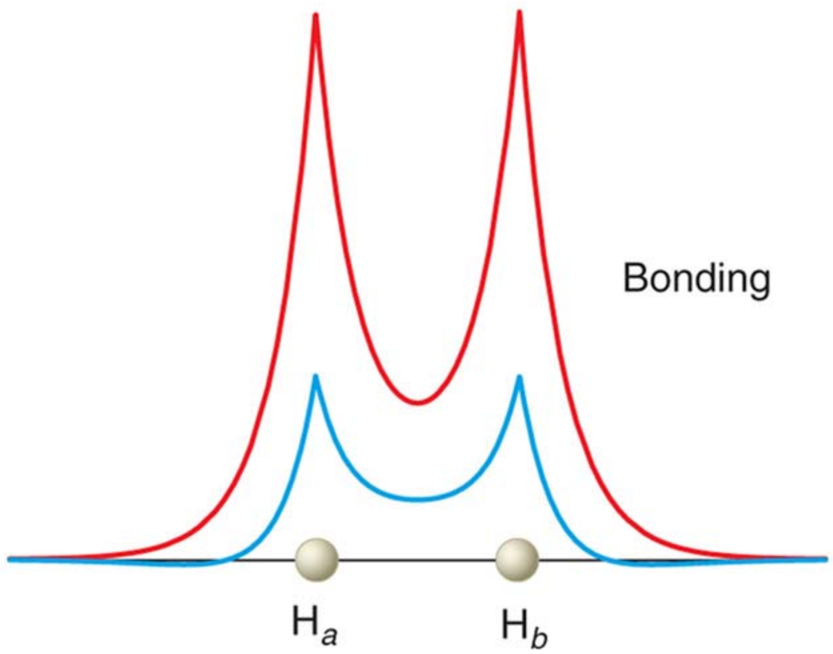
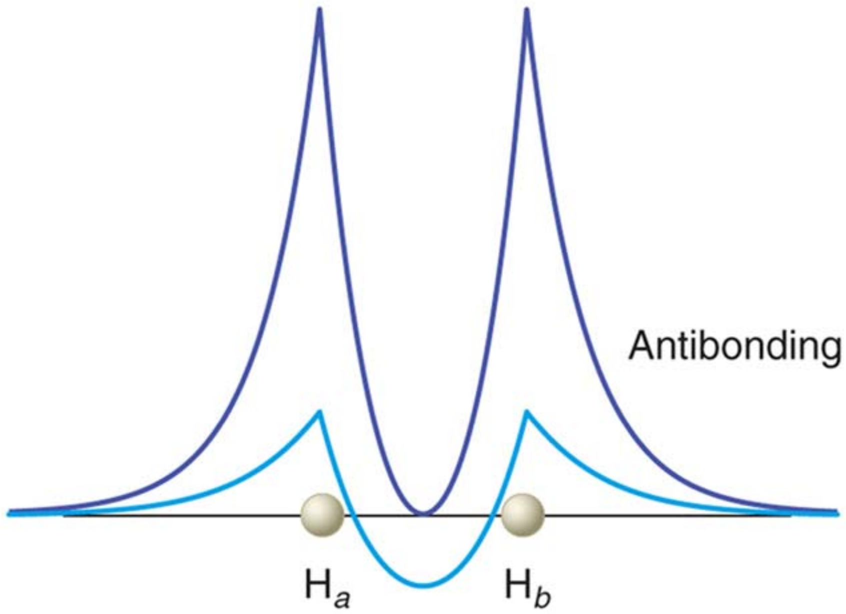


FIGURE 16.7

The upper two panels show the probability densities ψ_g^2 and ψ_u^2 along the internuclear axis for the bonding and antibonding wave functions. The dashed lines show ½ $\psi_{H1S_a}^2$ and ½ $\psi_{H1S_b}^2$, which are the probability densities for unmodified ($\zeta = 1$) H 1*s* orbitals on each nucleus. The lowest panel shows a direct comparison of ψ_g^2 and ψ_u^2. Both molecular wave functions are correctly normalized in three dimensions.





$$\Delta\psi_u^2 = \psi_u^2 - 1/2(\psi_{H1S_a})^2 - 1/2(\psi_{H1S_b})^2$$

$$\Delta\psi_g^2 = \psi_g^2 - 1/2(\psi_{H1S_a})^2 - 1/2(\psi_{H1S_b})^2$$

ψ_g^2 FIGURE 16.8 ψ_u^2

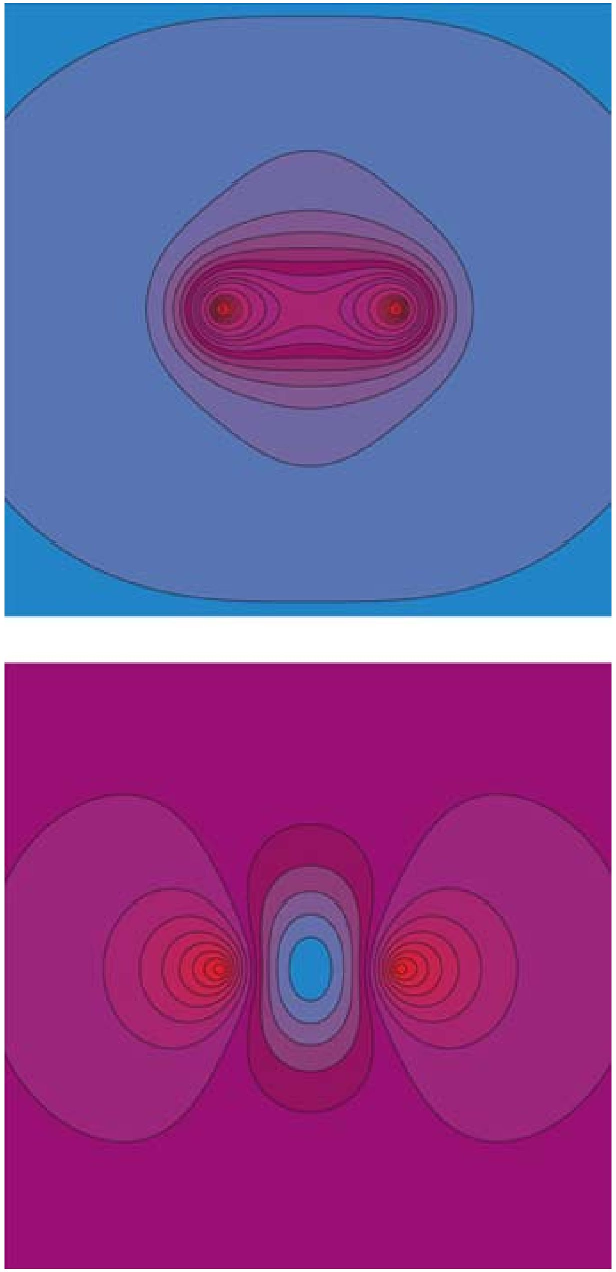
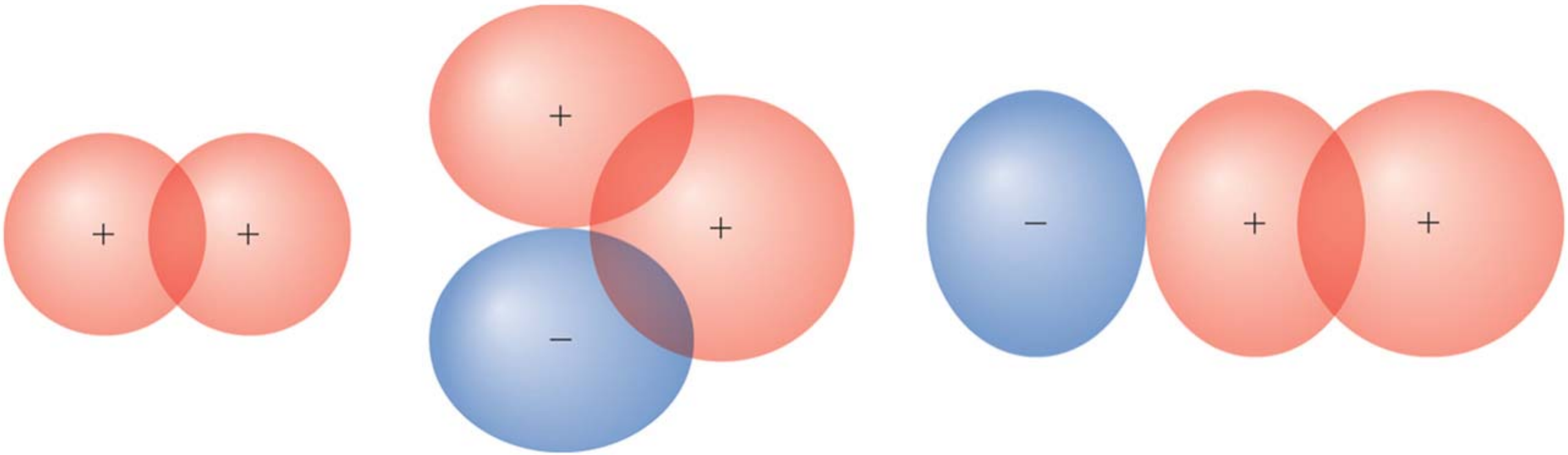


FIGURE 16.9

Contour plots of $\Delta\psi_g^2$ (top) and $\Delta\psi_u^2$ (bottom). The red areas in the top image correspond to positive values for $\Delta\psi_g^2$, and the gray area corresponds to negative values for $\Delta\psi_g^2$. The blue area in the bottom image corresponds to negative values for $\Delta\psi_u^2$, and the red areas just outside of the bonding region correspond to positive values for $\Delta\psi_u^2$. The color in the corners of each contour plot corresponds to $\Delta\psi^2 = 0$.



FUGURE 16.10

The overlap between two 1*s* orbitals (σ + σ), a 1*s* and a 2p_x or 2p_y (σ + π), and a 1*s* and a 2p_z (σ + σ) are depicted from left to right. Note that two shaded areas in the middle panel have opposite signs, so the net overlap of these two atomic orbitals of different symmetry is zero.

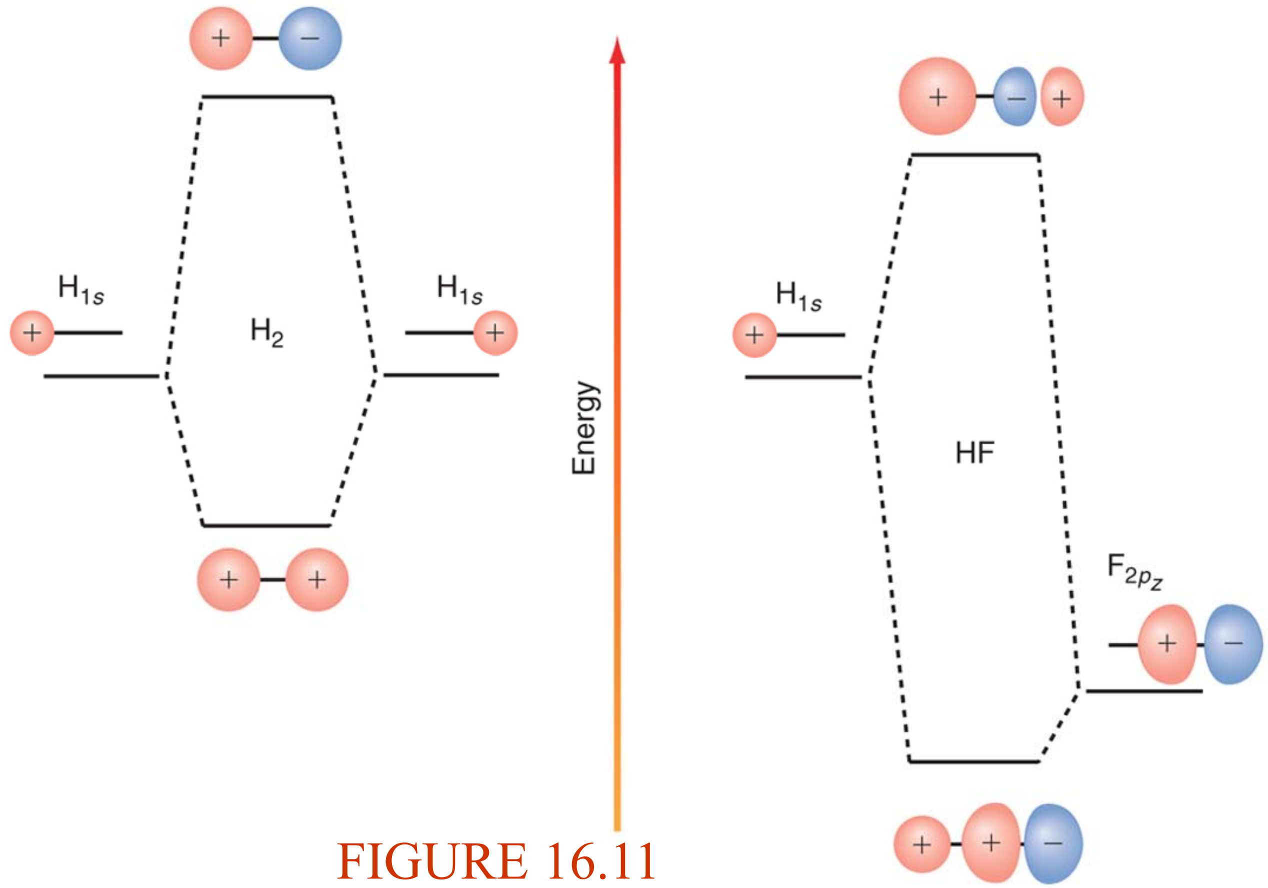


FIGURE 16.11

Molecular orbital energy diagram for a qualitative description of bonding in H_2 and HF. The atomic orbitals are shown to the left and right, and the molecular orbitals are shown in the middle. Dashed lines connect the MO with the Aos from which it was constructed. Shaded circles have a diameter proportional to the coefficients c_{ij}. Red and blue shading signifies positive and negative signs of the AO coefficients, respectively.

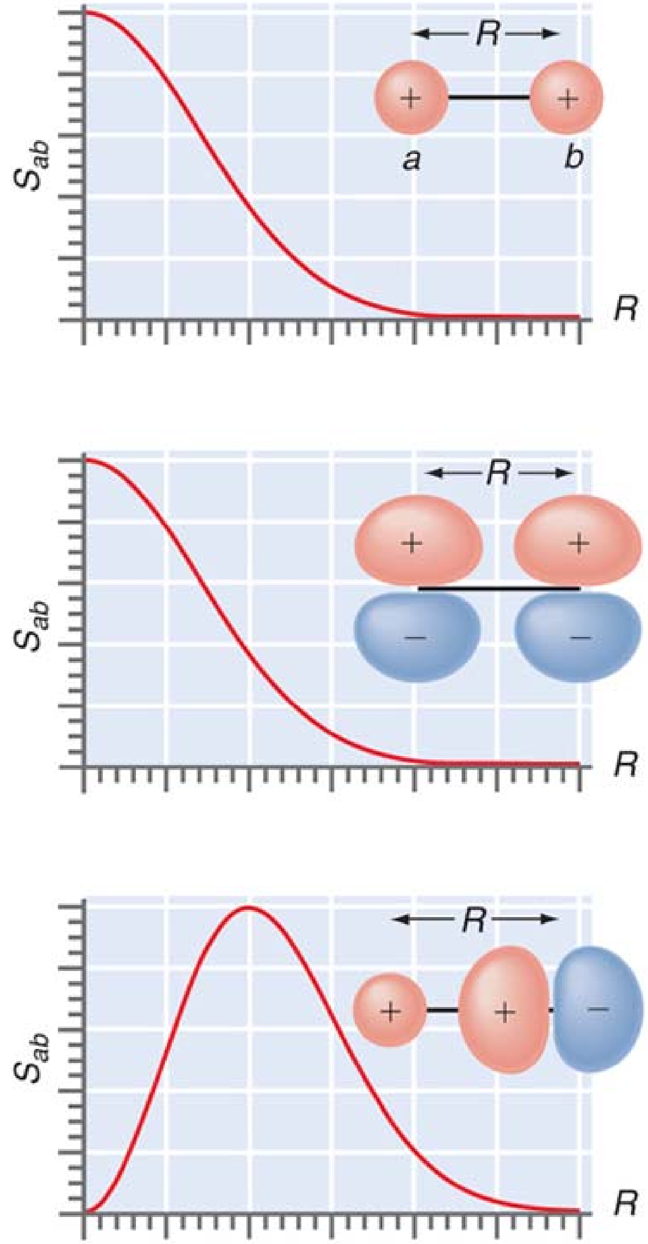


FIGURE 16.12

Variation of overlap with internuclear distance for *s* and *p* orbitals.

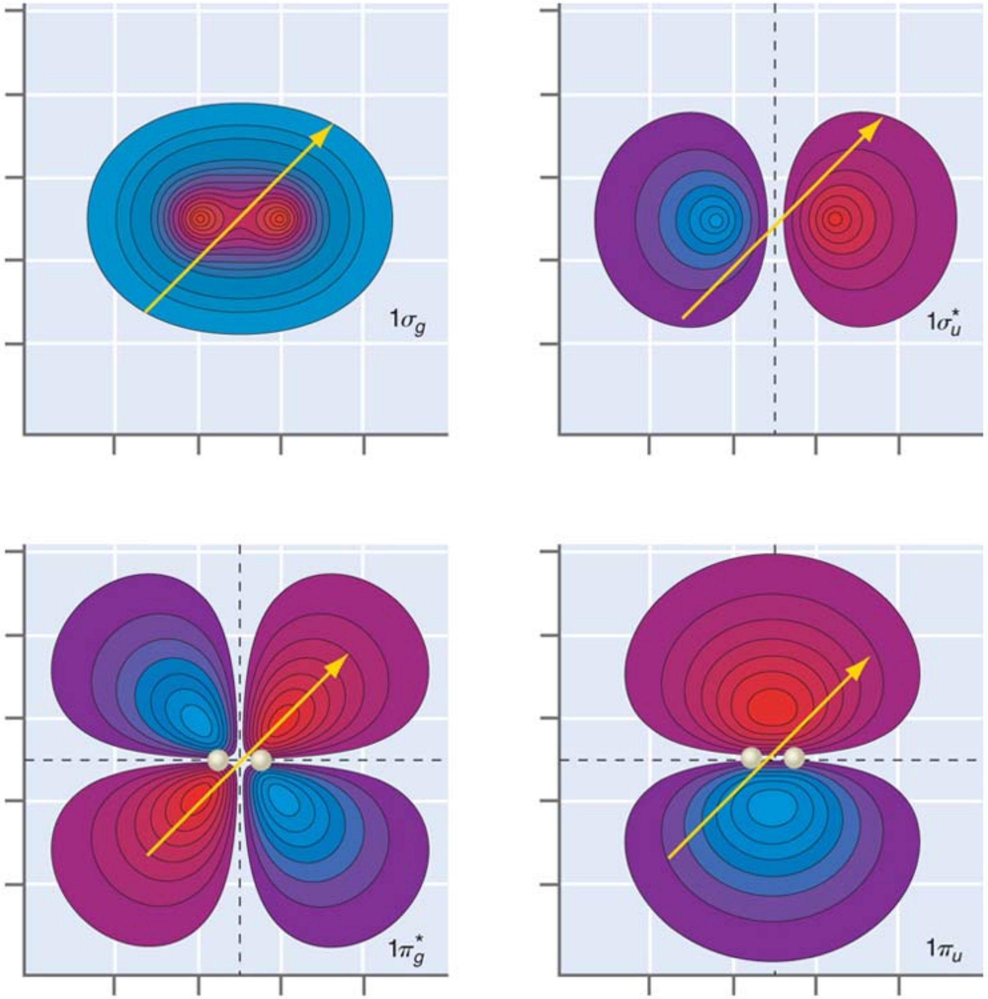


FIGURE 16.13

Contour plots of several bonding and antibonding orbitals of H_2^+. Red and blue contours correspond to the most positive and least positive amplitudes, respectively. The yellow arrows show the transformation $(x, y, z) \rightarrow (-x, -y, -z)$ for each orbital. If the amplitude of the wave function changes sign under this transformation, it has u symmetry. If it is unchanged, it has g symmetry.

TABLE 16.1 Molecular Orbitals Used to Describe Chemical Bonding in Homonuclear Diatomic Molecules

MO Designation	Alternate	Character	Atomic Orbitals
$1\sigma_g$	$\sigma_g(1s)$	Bonding	$1s$
$1\sigma_u^*$	$\sigma_u^*(1s)$	Antibonding	$1s$
$2\sigma_g$	$\sigma_g(2s)$	Bonding	$2s\ (2p_z)$
$2\sigma_u^*$	$\sigma_u^*(2s)$	Antibonding	$2s\ (2p_z)$
$3\sigma_g$	$\sigma_g(2p_z)$	Bonding	$2p_z\ (2s)$
$3\sigma_u^*$	$\sigma_u^*(2p_z)$	Antibonding	$2p_z\ (2s)$
$1\pi_u$	$\pi_u(2p_x, 2p_y)$	Bonding	$2p_x, 2p_y$
$1\pi_g^*$	$\pi_g^*(2p_x, 2p_y)$	Antibonding	$2p_x, 2p_y$

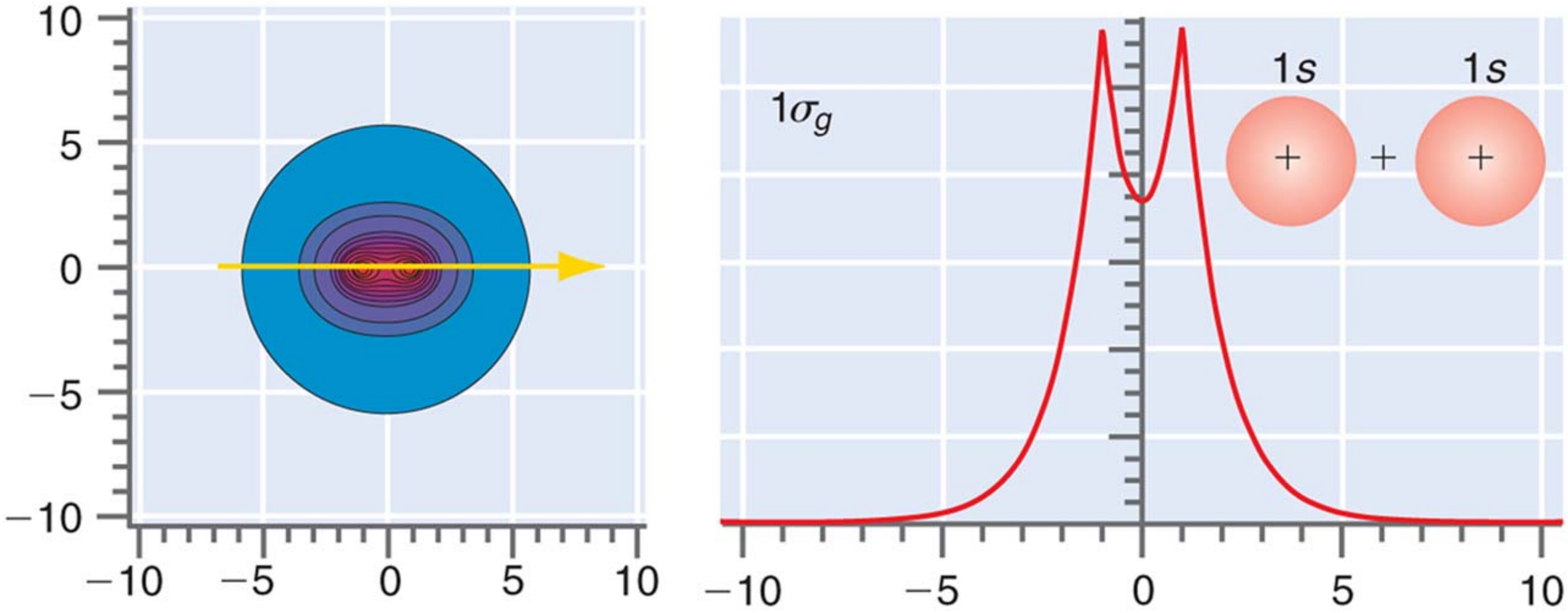


FIGURE 16.14

MOs based on the ground and excited states for H_2^+ generated from 1*s*, 2*s*, and 2*p* atomic orbitals. Contour plots are shown on the left and line scans along the path indicated by the yellow arrow are shown on the right. Red and blue contours correspond to the most positive and least positive amplitudes, respectively. Dashed lines and curves indicate nodal surfaces. Length are in units of a_0, and $R_e = 2.00\ a_0$.

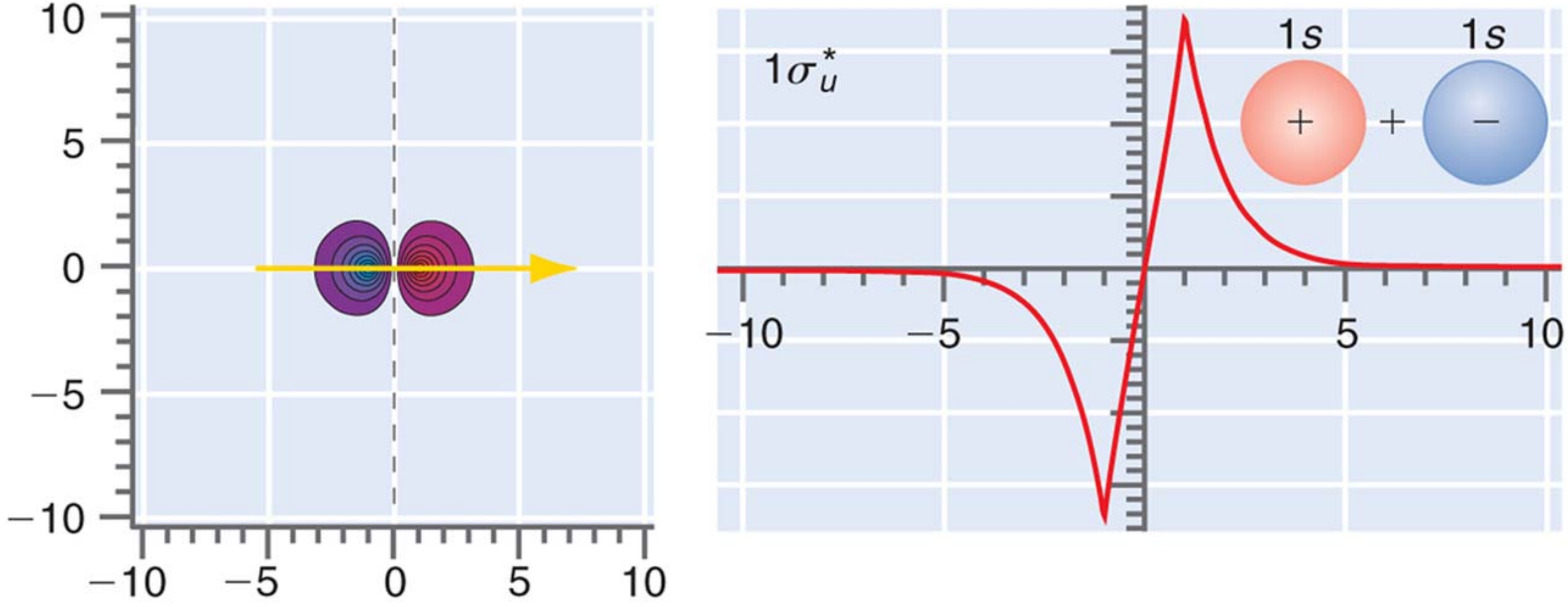


FIGURE 16.14

(continued)

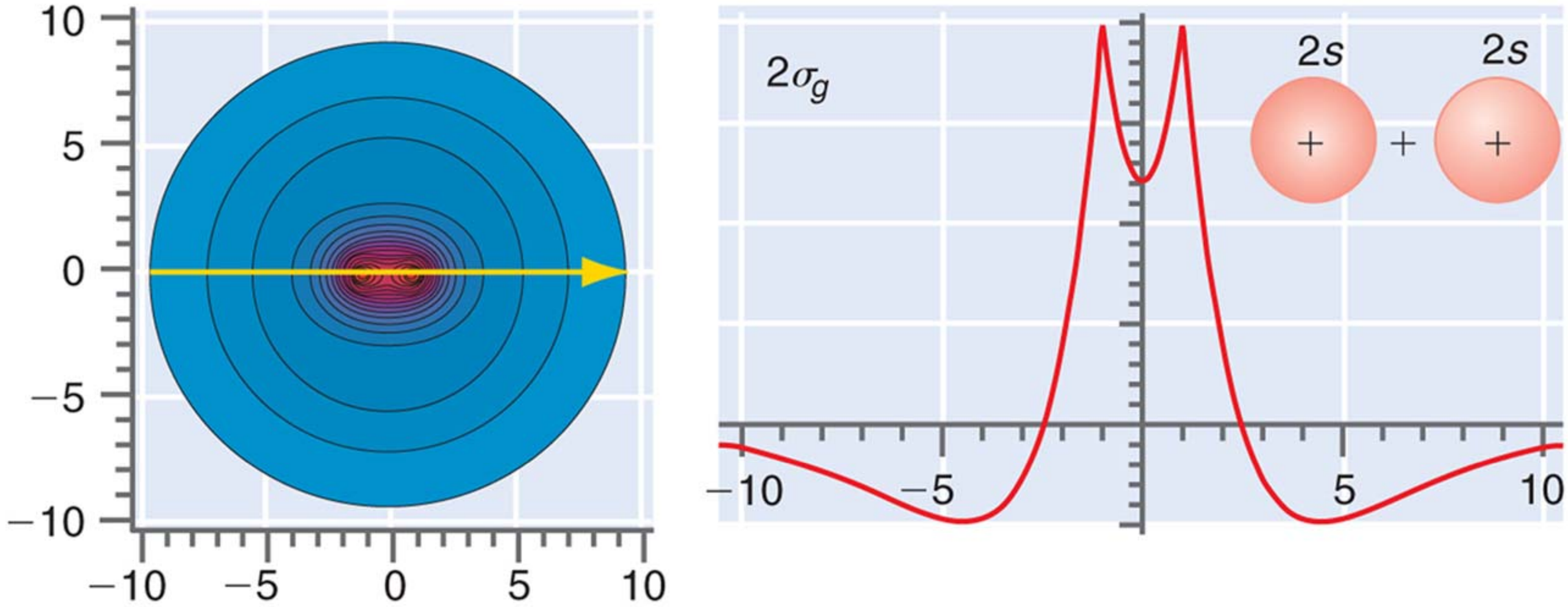


FIGURE 16.14

(continued)

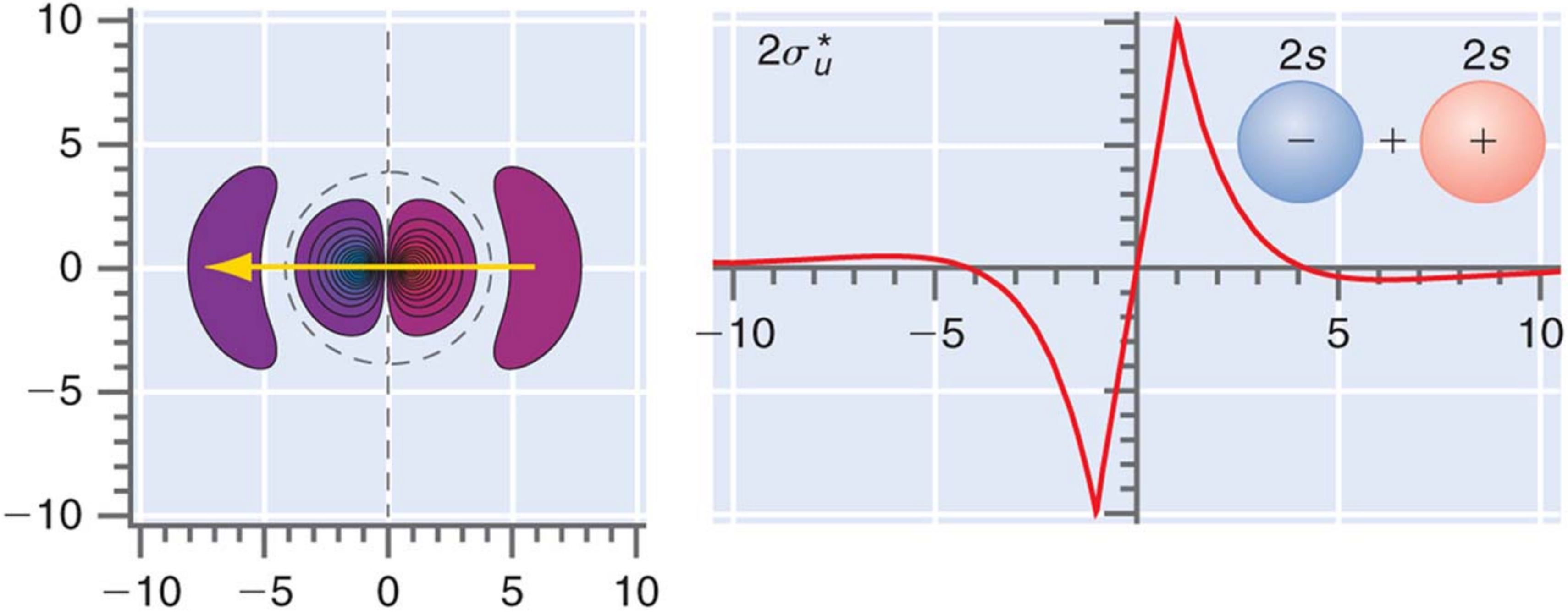


FIGURE 16.14

(continued)

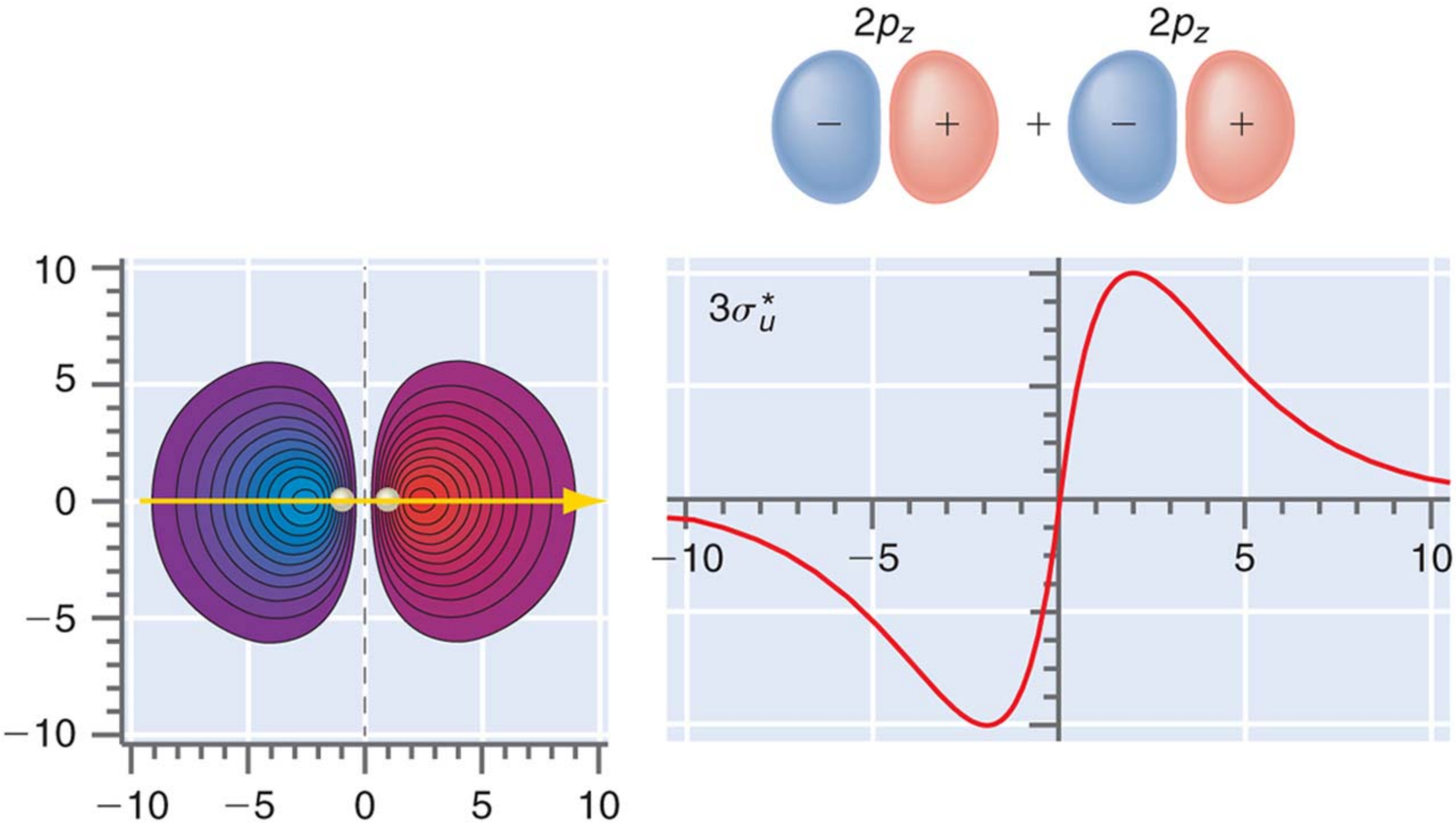


FIGURE 16.14

(continued)

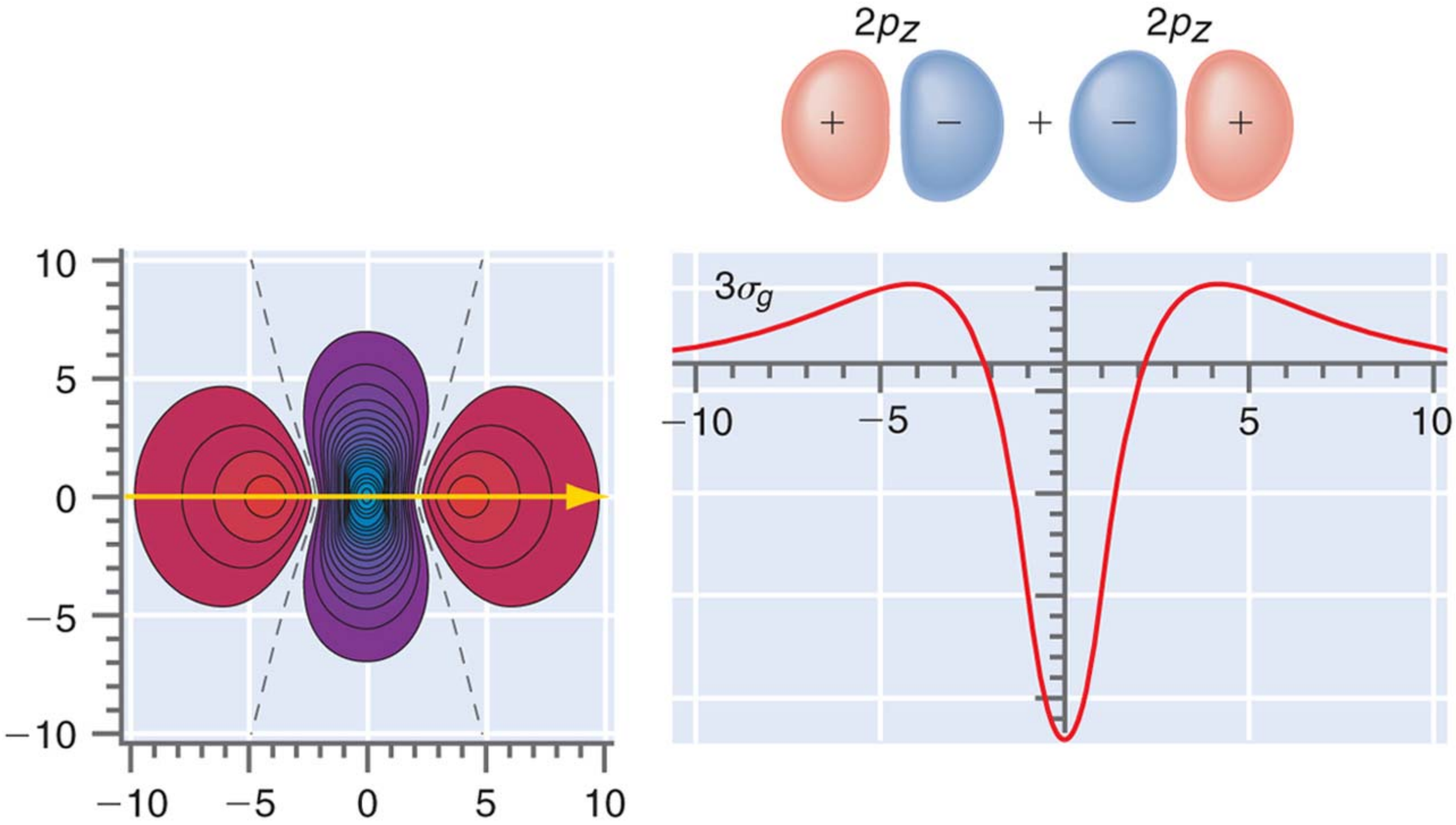


FIGURE 16.14

(continued)

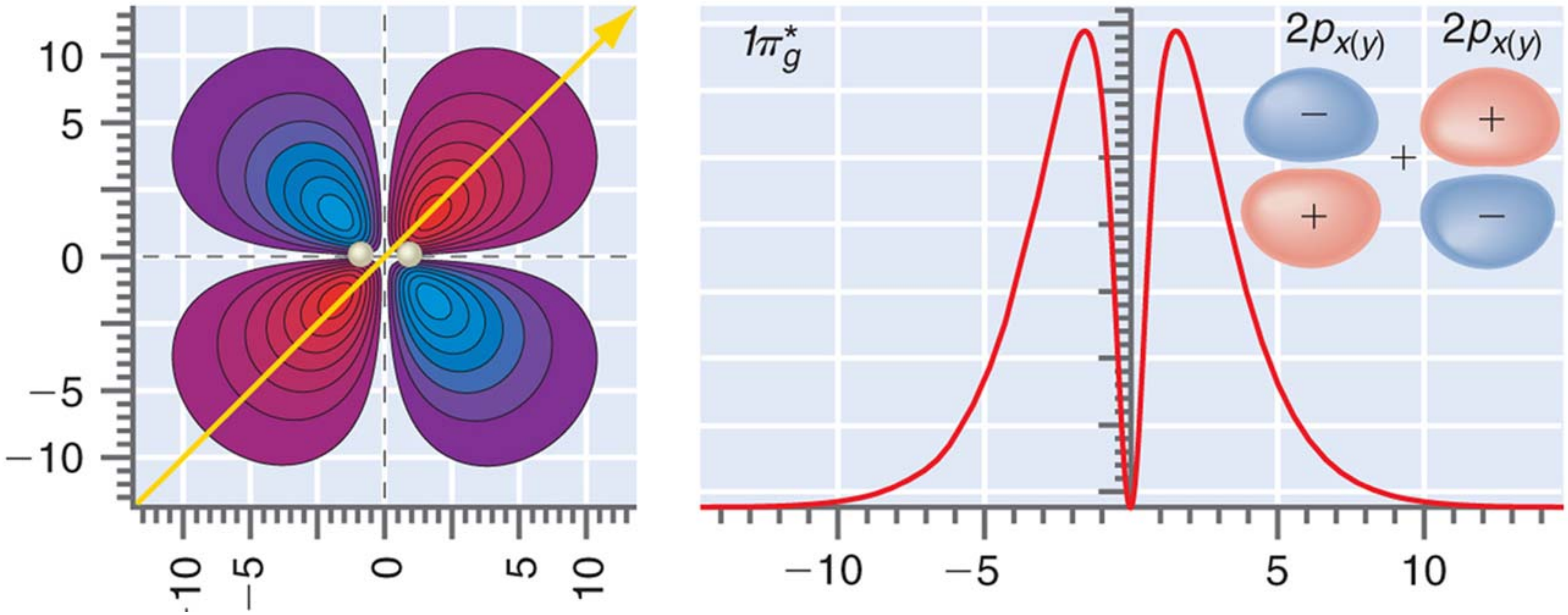


FIGURE 16.14

(continued)

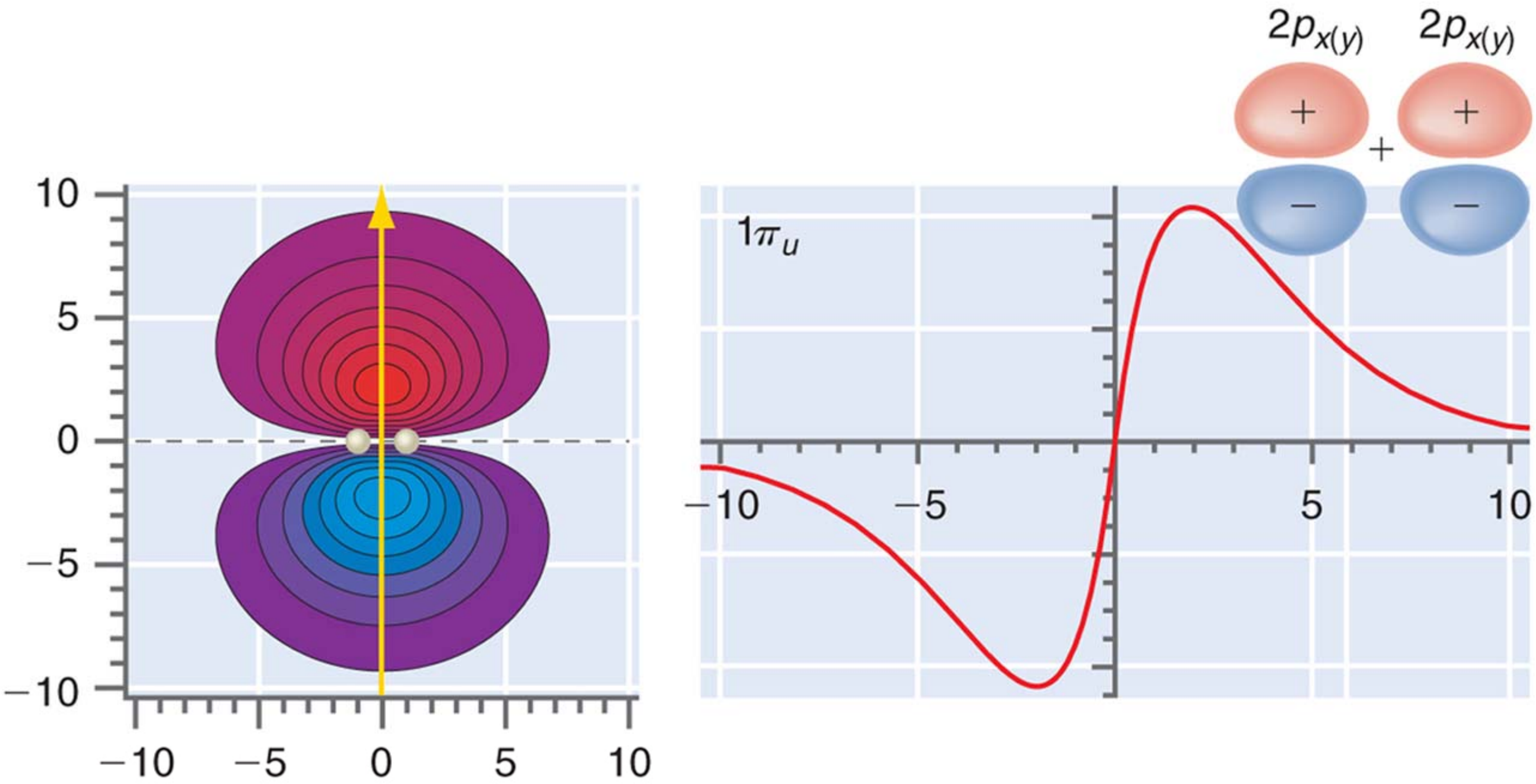


FIGURE 16.14

(continued)

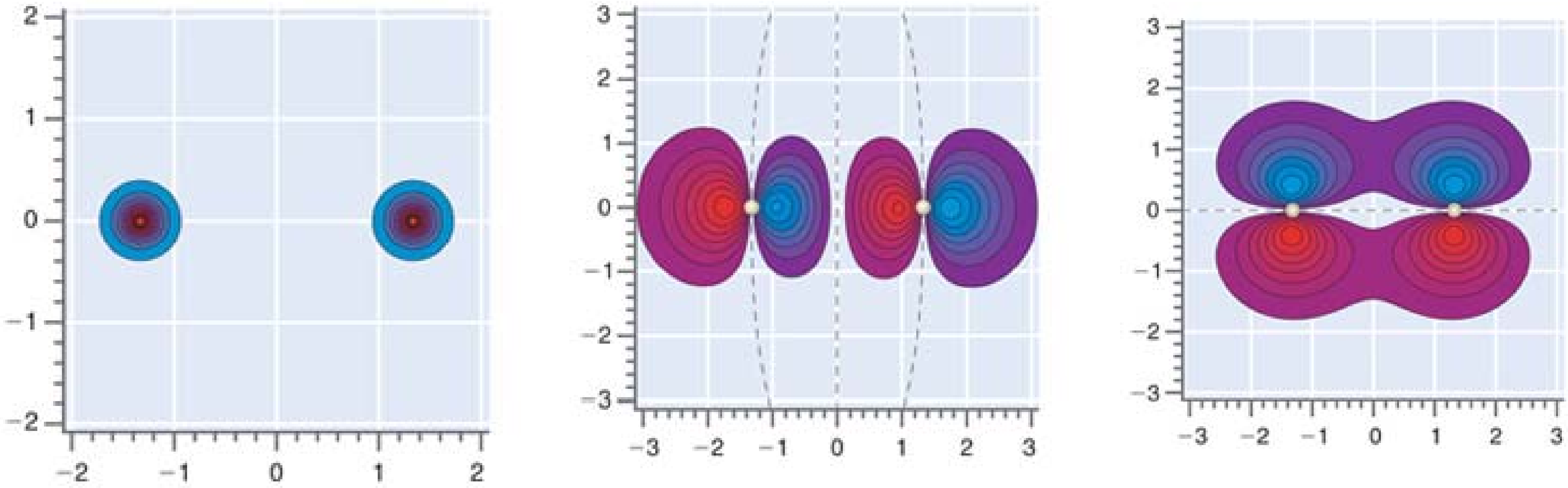


FIGURE 16.15

Contour plots for $1\sigma_g$ (top), $3\sigma_u^*$ (center), and $1\pi_u$ (bottom) H_2^+ MOs with ζ values appropriate to F_2. Red and blue contours correspond to the most positive and least positive amplitudes, respectively. Dashed lines indicate nodal surfaces. Light circles indicate position of nuclei. Length are in units of a_0, and $R_e = 2.66\ a_0$.

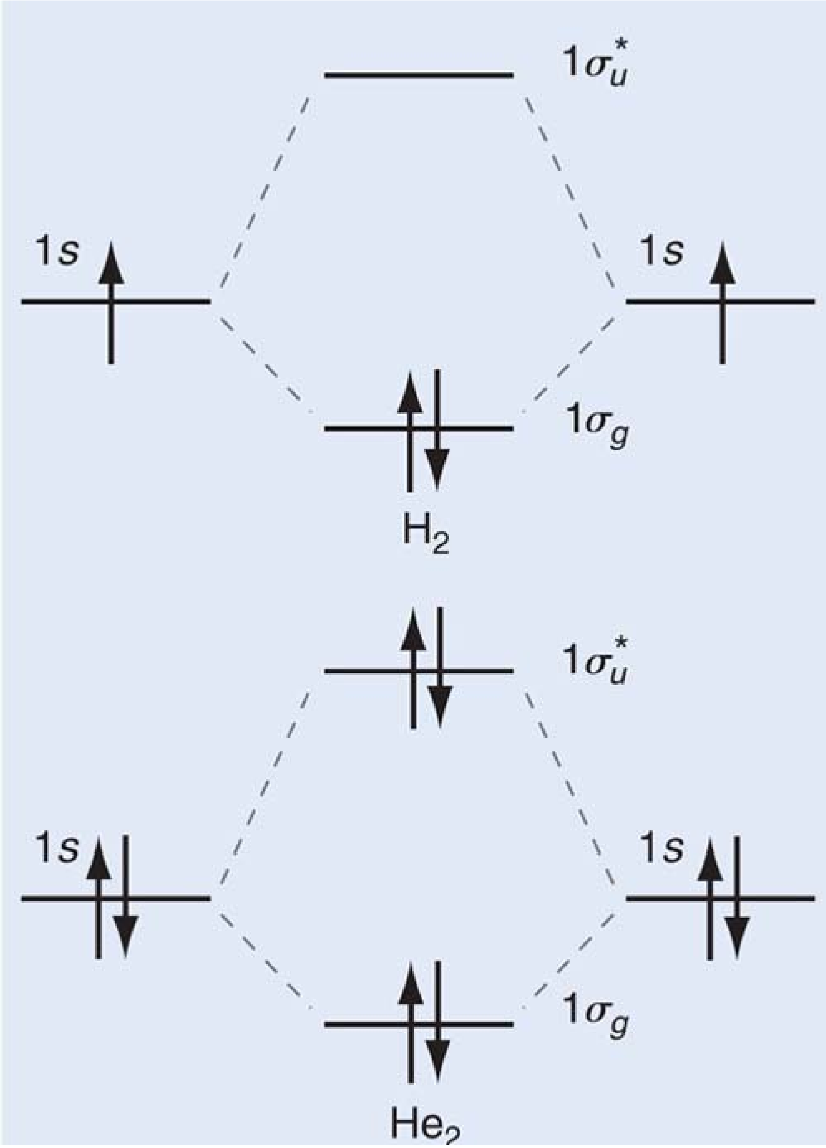


FIGURE 16.16

Atomic and molecular orbital energies and occupation for H_2 and He_2. Upward- and downward-pointing arrows indicate α and β spins. The energy splitting between the MO levels is not to scale.

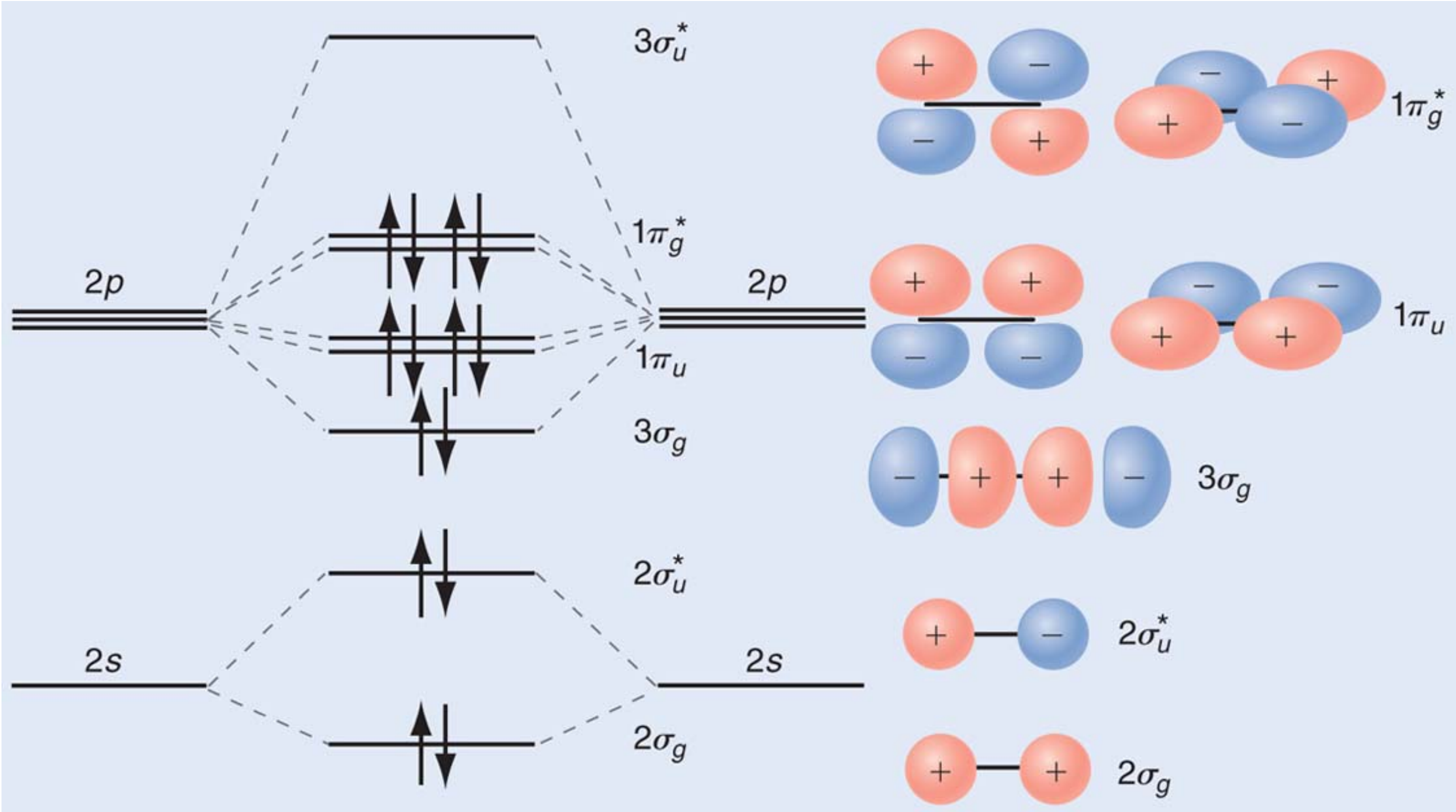


FIGURE 16.17

Schematic MO energy diagram for the valence electrons in F_2. The degenerate *p* and π orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown as solid lines. Minor contributions due to *s*-*p* mixing have been neglected. The MOs are schematically depicted to the right of the figure. The $1\sigma_g$ and $1\sigma_u^*$ MOs are not shown.

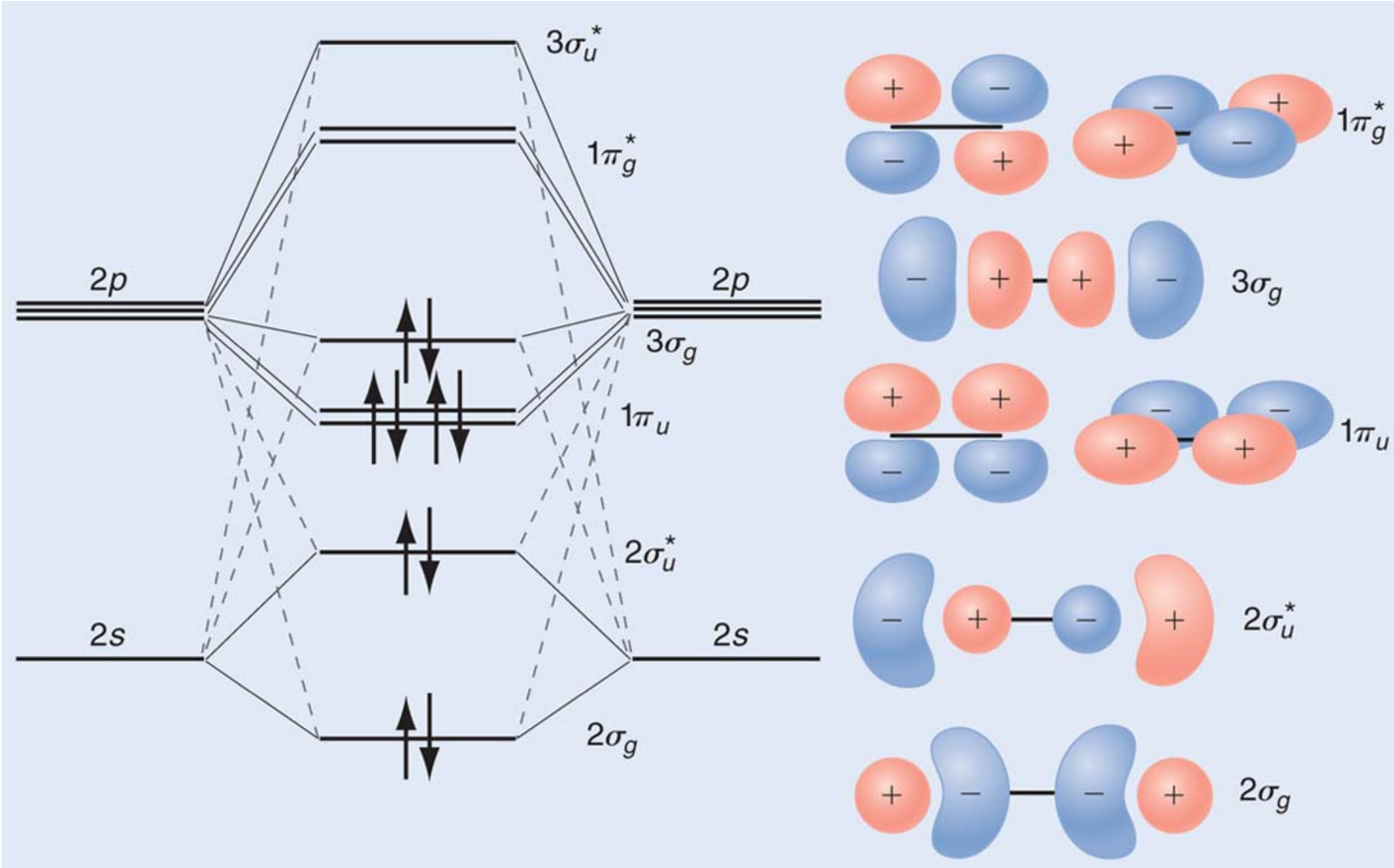


FIGURE 16.18

Schematic MO energy diagram for the valence electrons in N_2. The degenerate *p* and π orbitals are shown slightly offset in energy. The dominant AO contributions to the MOs are shown as solid lines. Lesser contributions arising from *s*-*p* mixing are shown as dashed lines. The MOs are schematically depicted to the right of the figure. The $1\sigma_g$ and $1\sigma_u^*$ MOs are not shown.

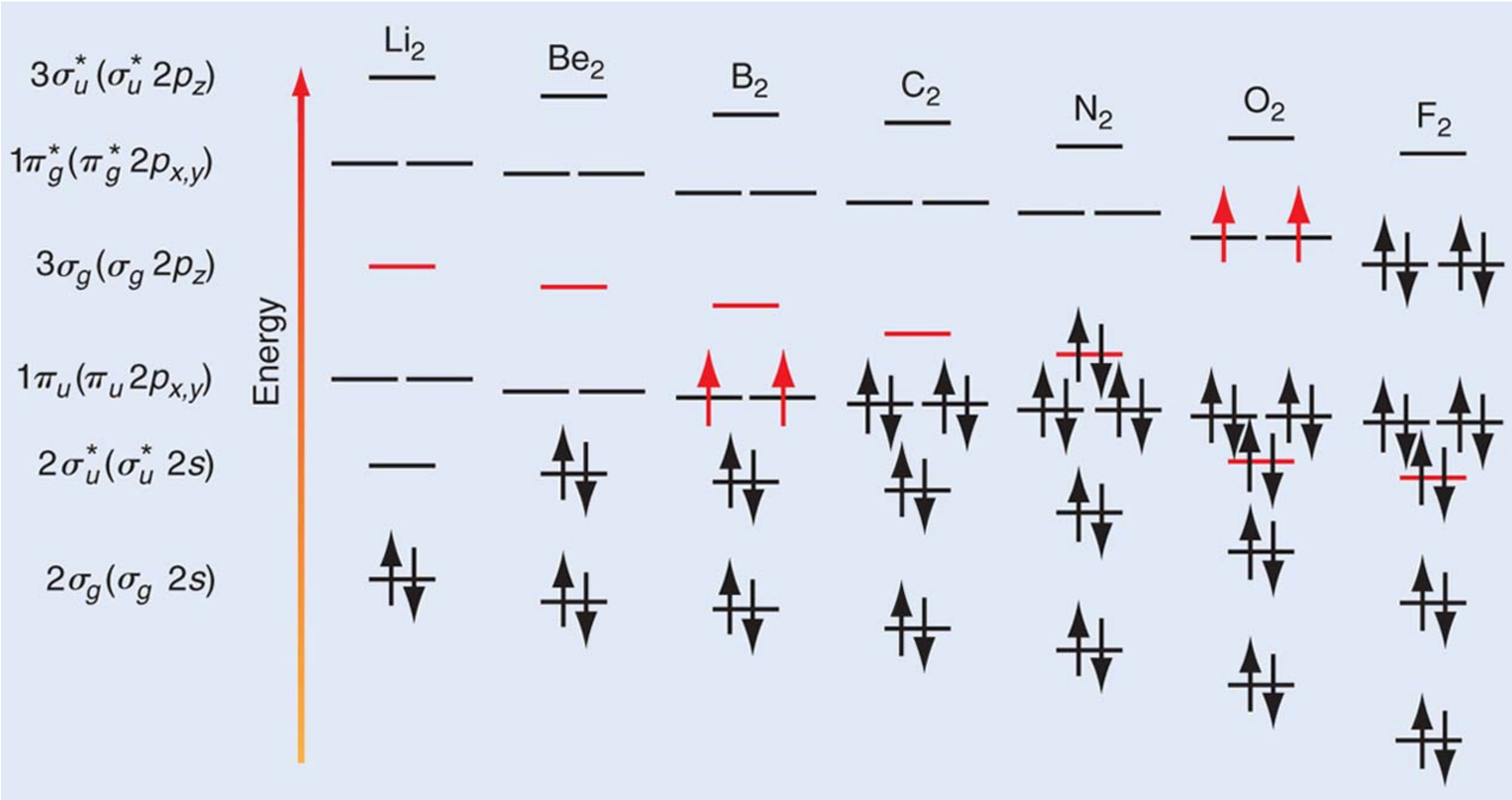


FIGURE 16.19

Relative molecular orbital energy levels for the second row diatomic (not to scale). Both notations are given for the molecular orbitals. The $1\sigma_g$ (σ_g 1s) and $1\sigma_u^*(\sigma_u^* 1s)$ orbitals lie at much lower values of energy and are not shown. (not to scale.)

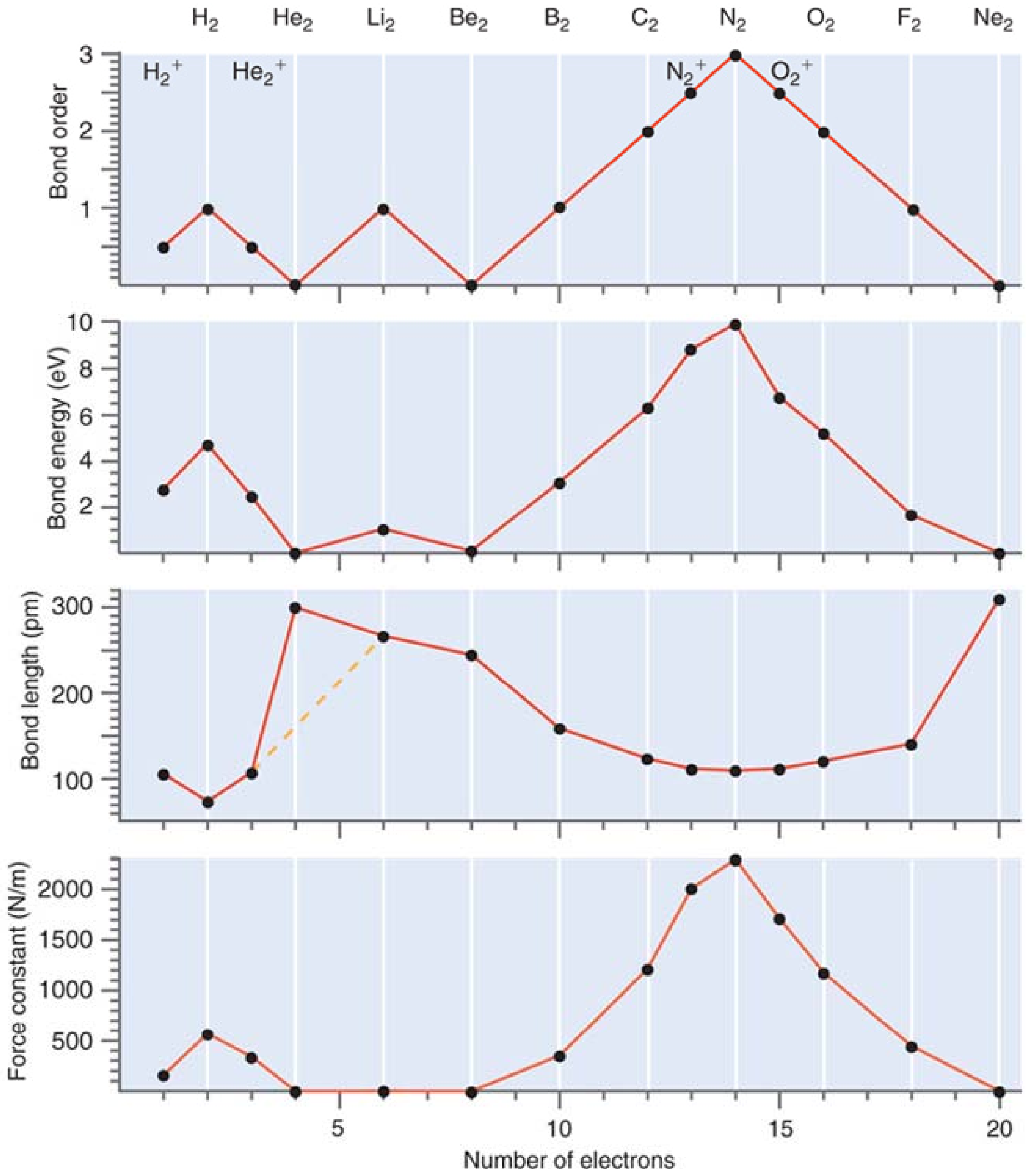


FIGURE 16.20

Bond energy, bond length, and vibrational force constant of the first 10 diatomic molecules as a function of the number of electrons in the molecule. The upper panel shows the calculated bond order for these molecules. The dashed line indicates the dependence of the bond length on the number of electrons if the He_2 data point is omitted.

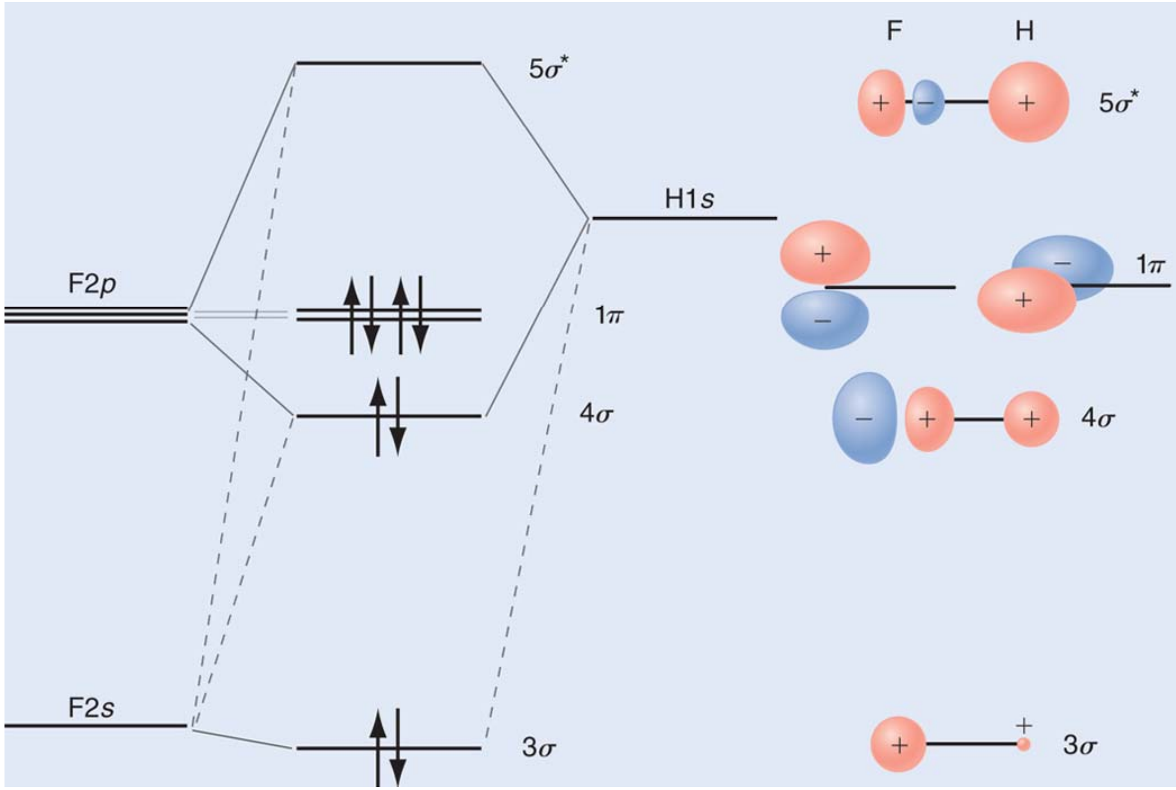


FIGURE 16.21

Schematic energy diagram showing the relationship between the atomic and molecular orbital energy levels for the valence electrons in HF. The degenerate *p* and π orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown as solid lines. Lesser contributions are shown as dashed lines. The MOs are depicted to the right of the figure.

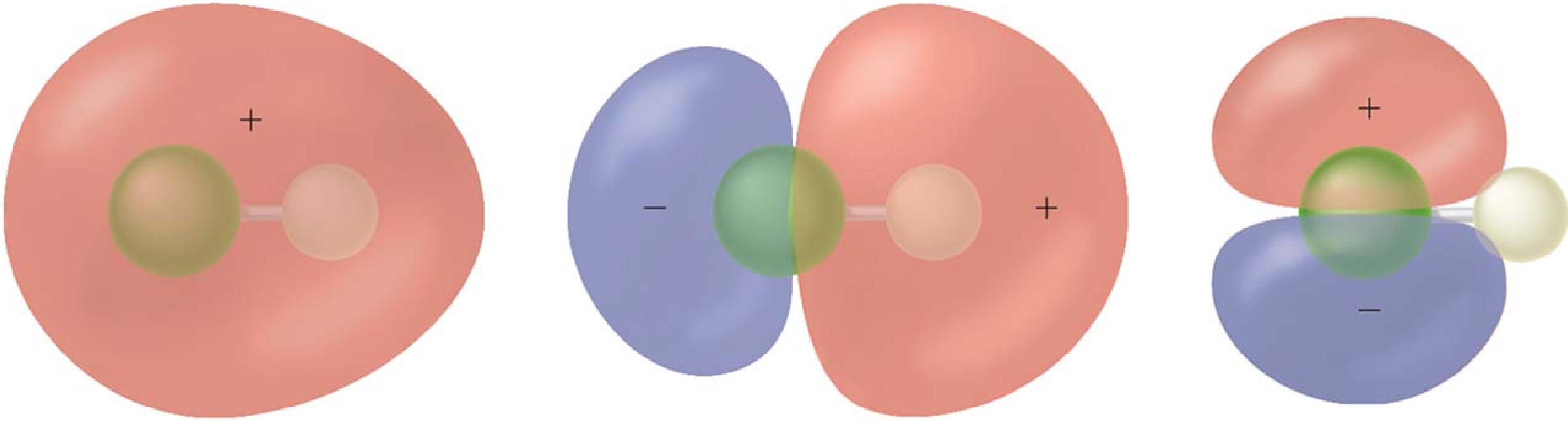


FIGURE 16.22

The 3σ, 4σ, and 1π MOs for HF are shown from left to right.

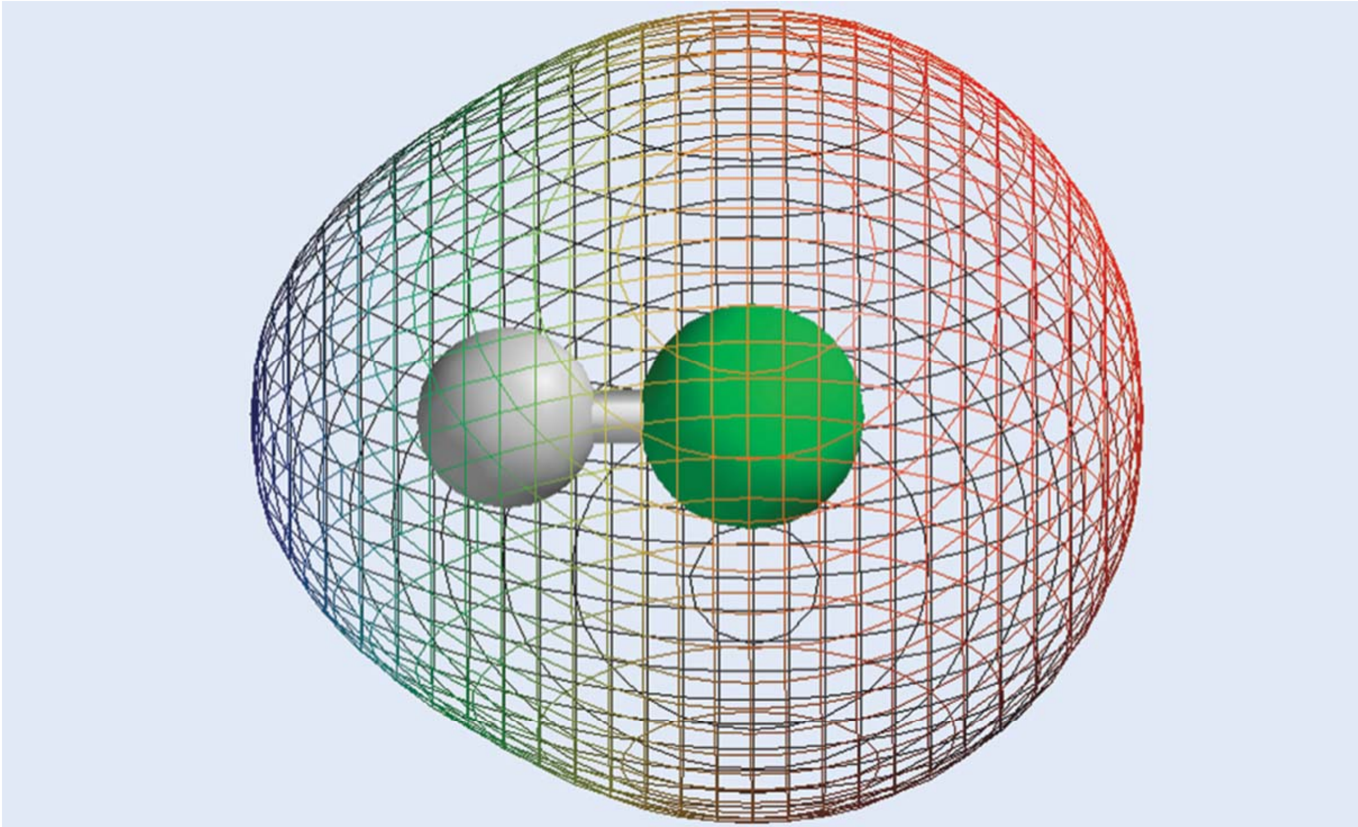
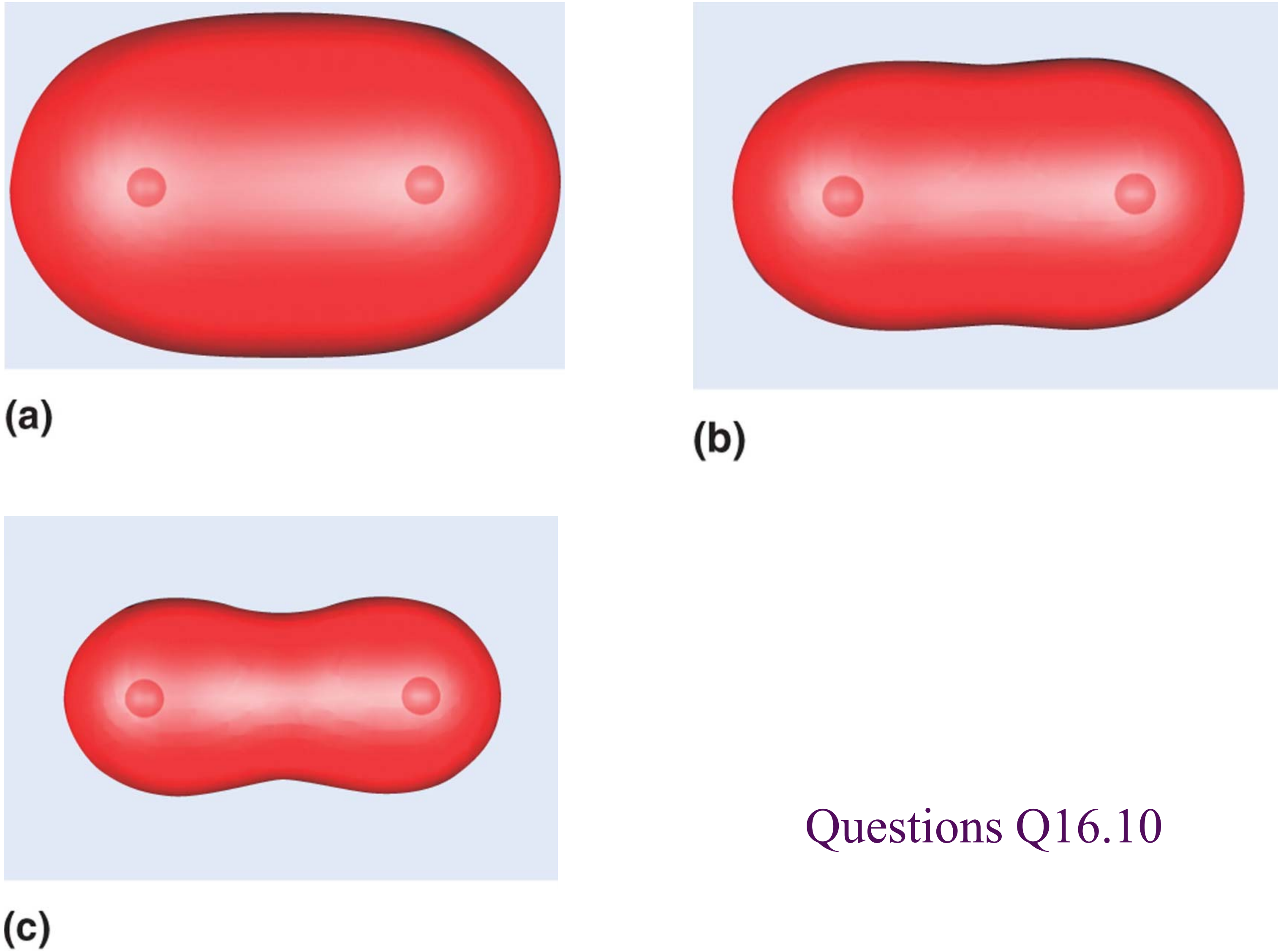
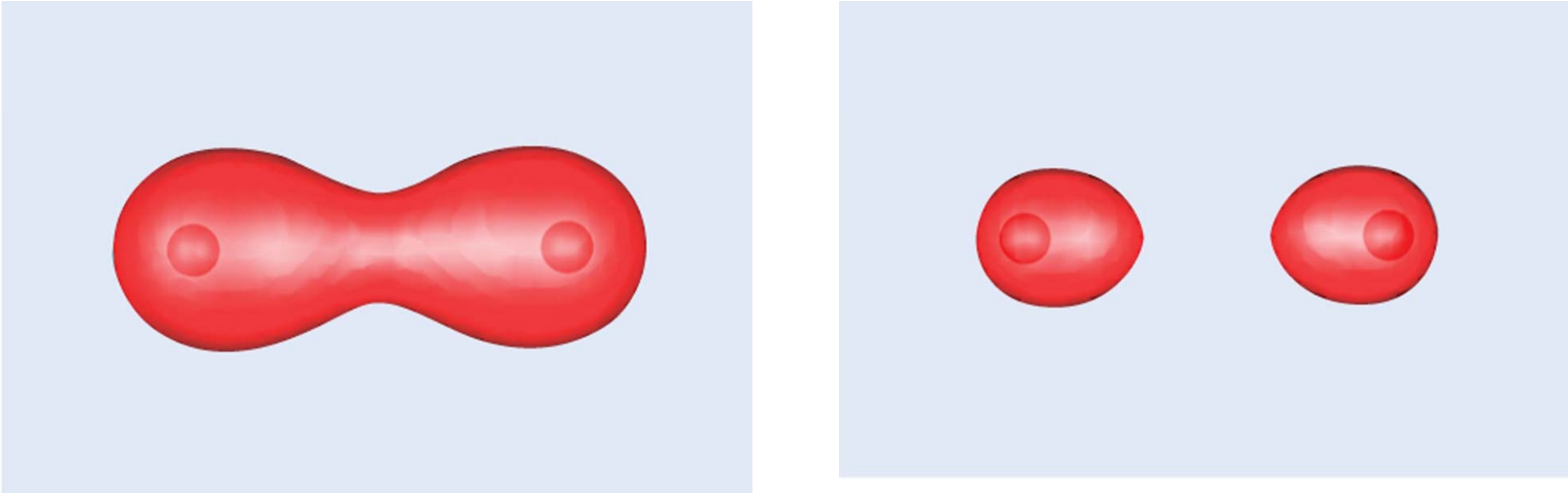


FIGURE 16.23

The grid shows a surface of constant electron density for the HF molecule. The fluorine atom is shown in green. The color shading on the grid indicates the value of the molecular electrostatic potential. Red and blue correspond to negative and positive values, respectively.

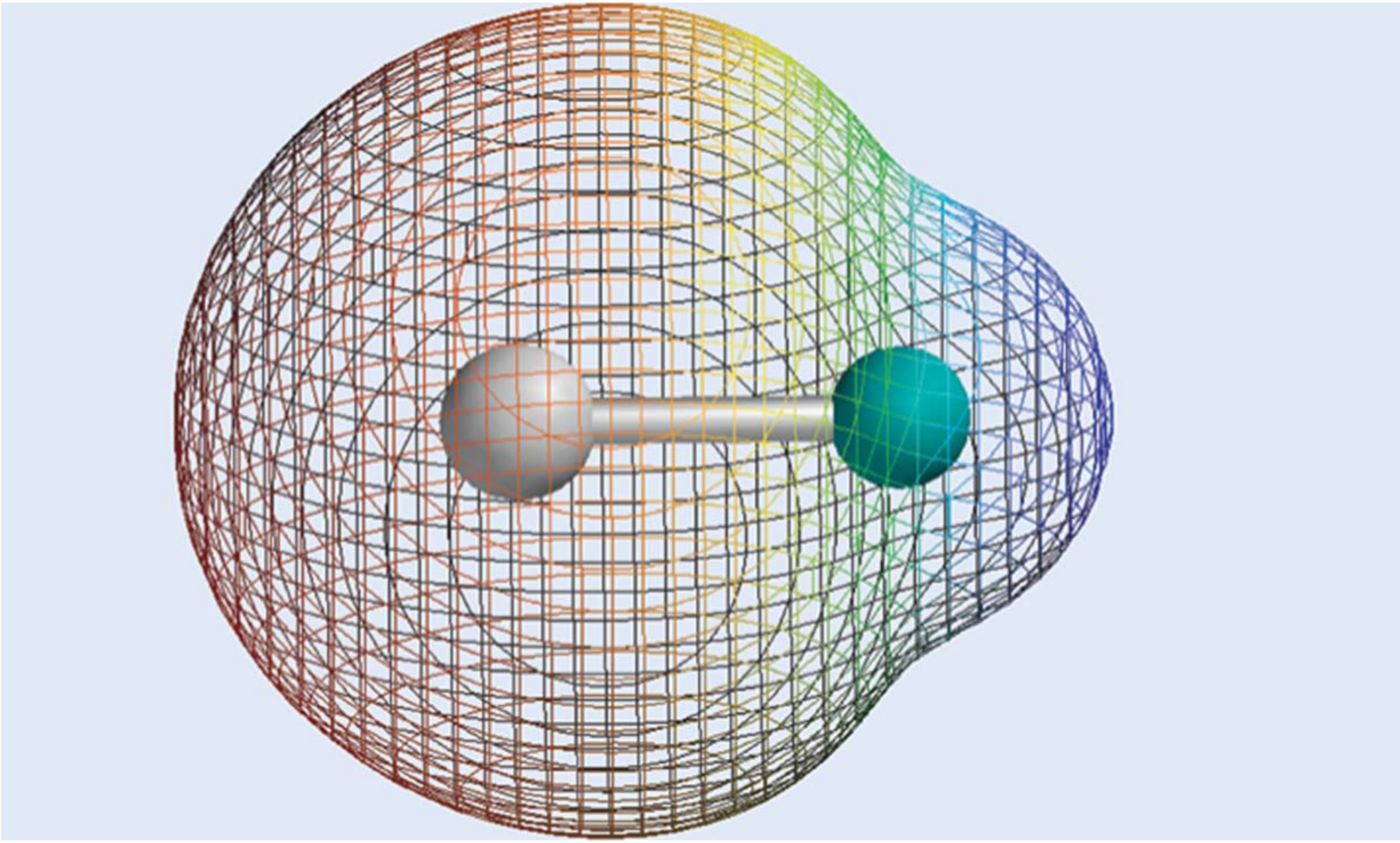


Questions Q16.10

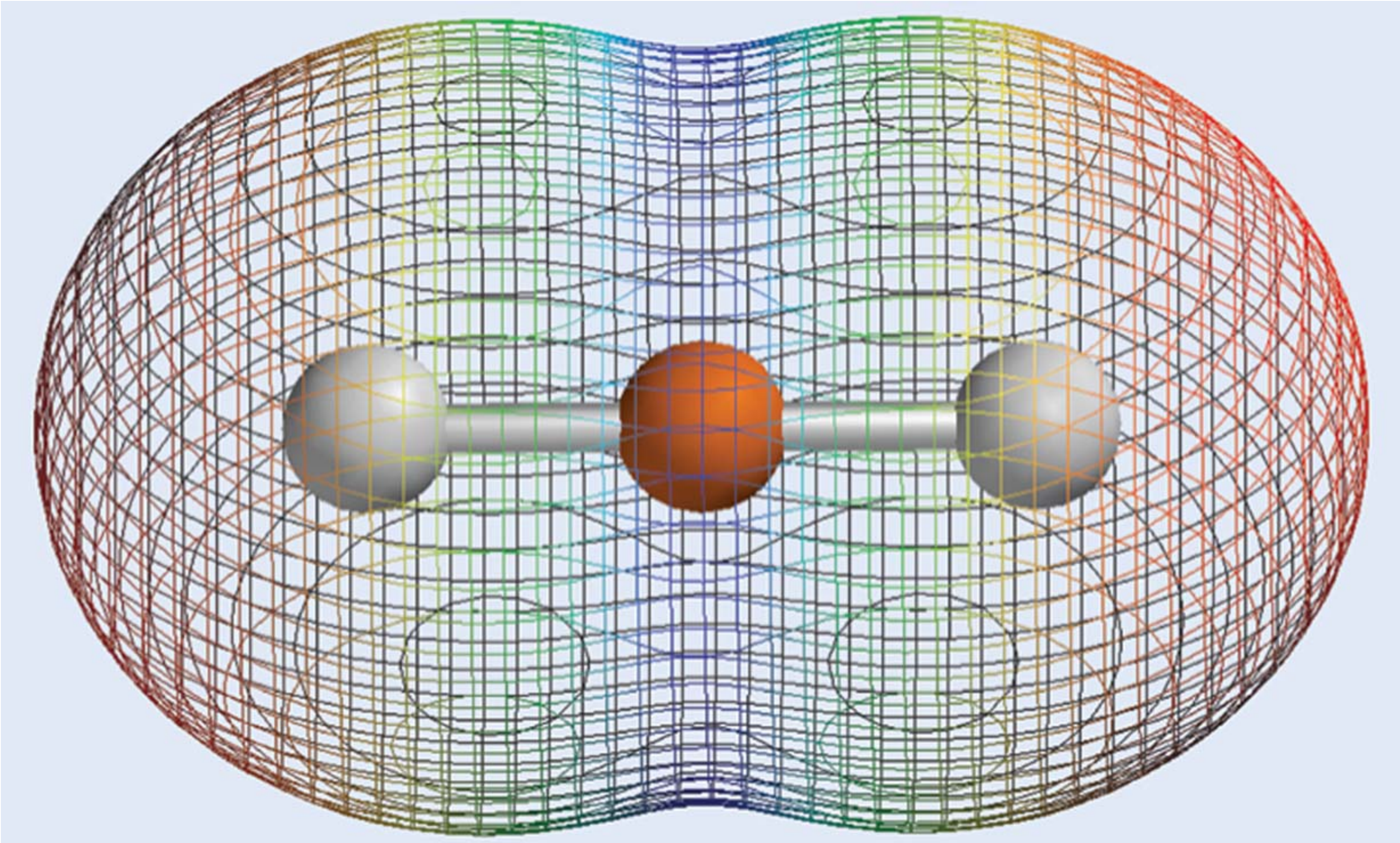


(d) (e)

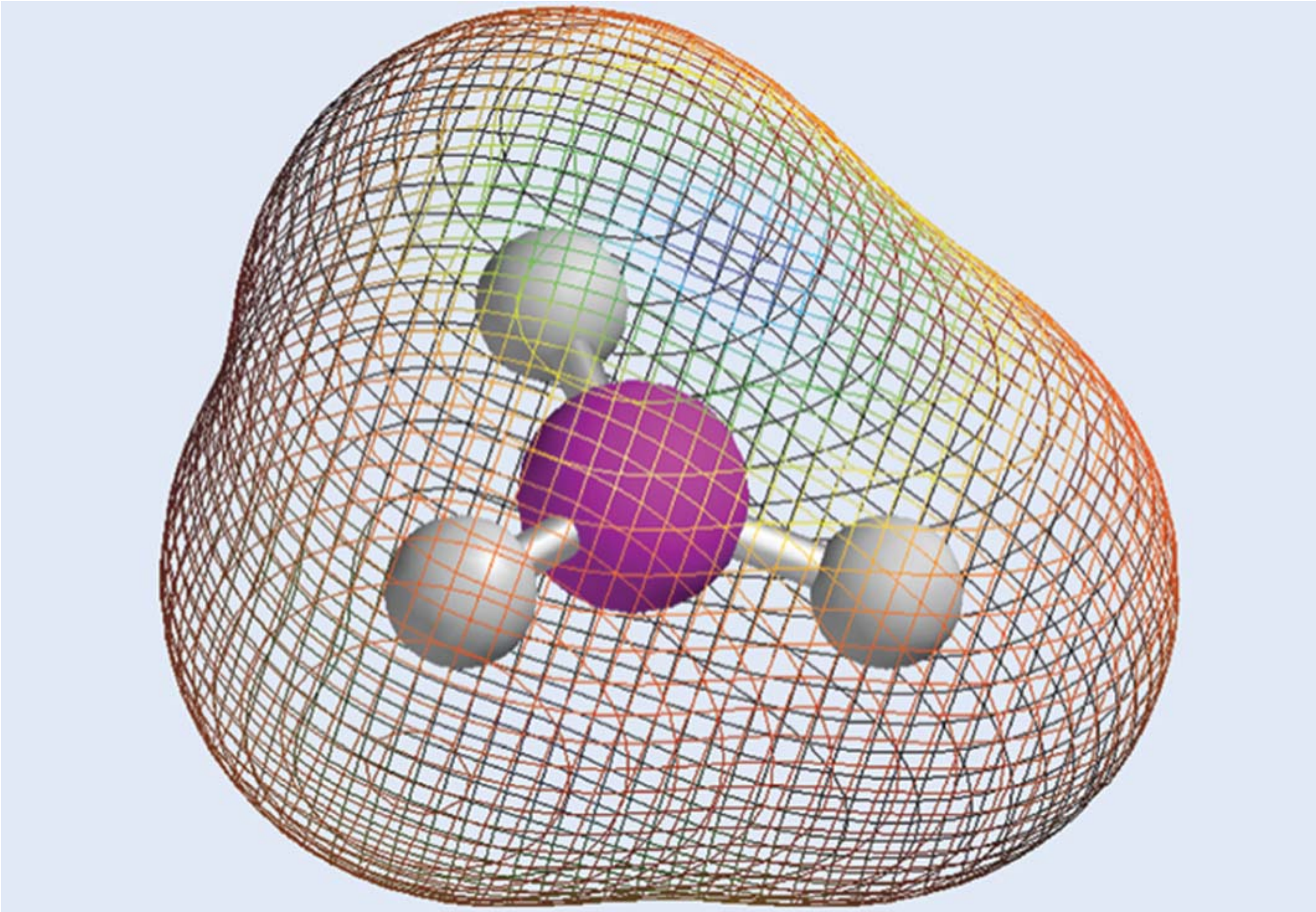
Questions Q16.10 (continued)



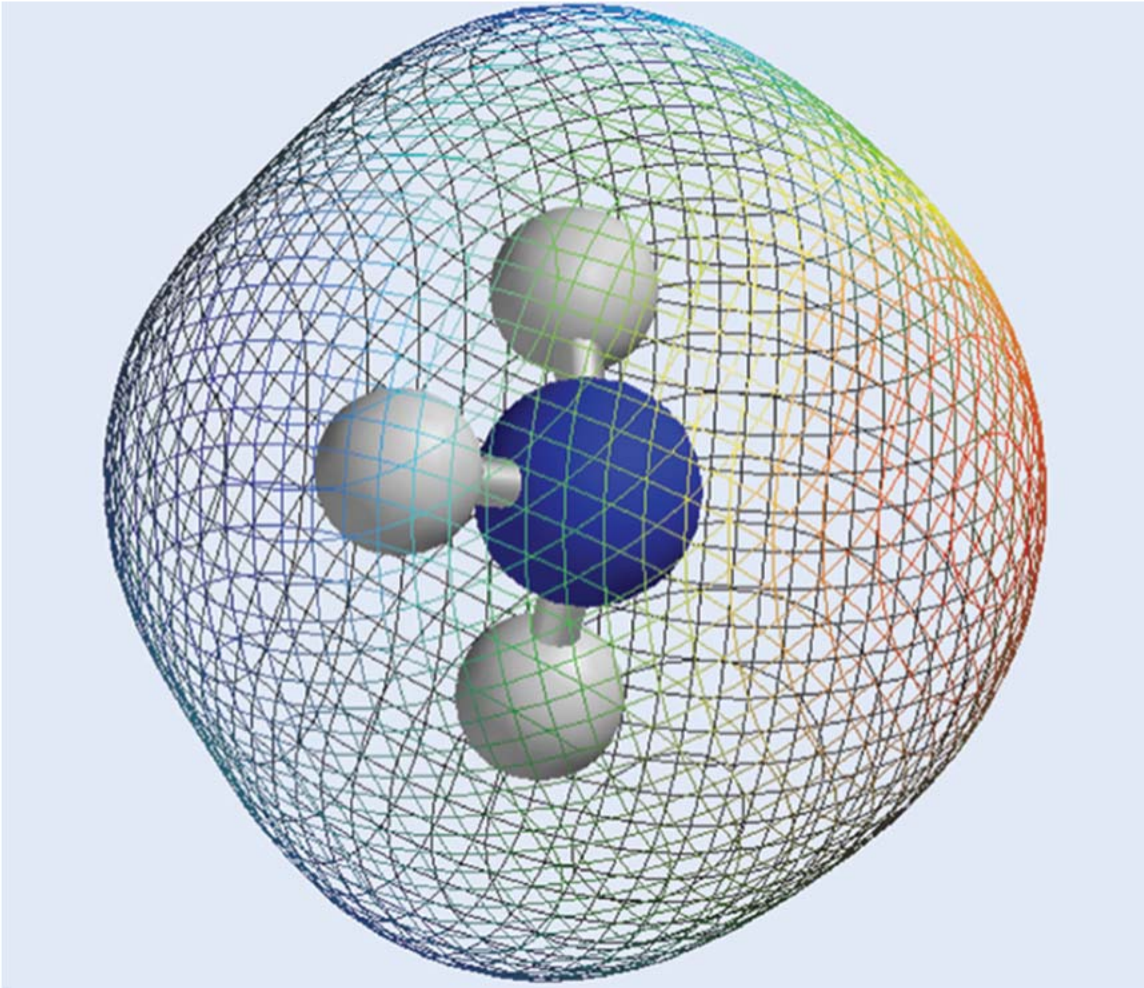
Questions Q16.20



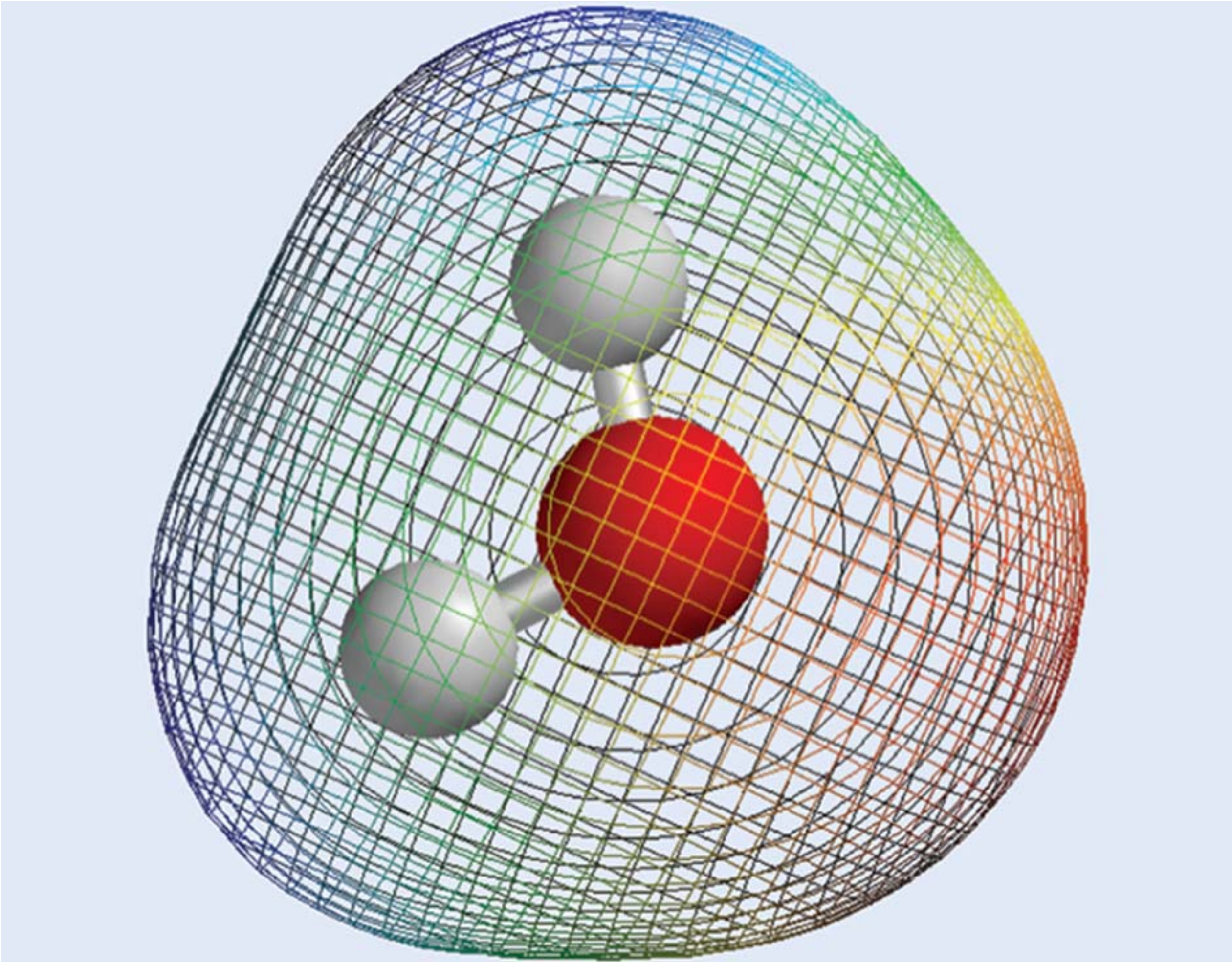
Questions Q16.21



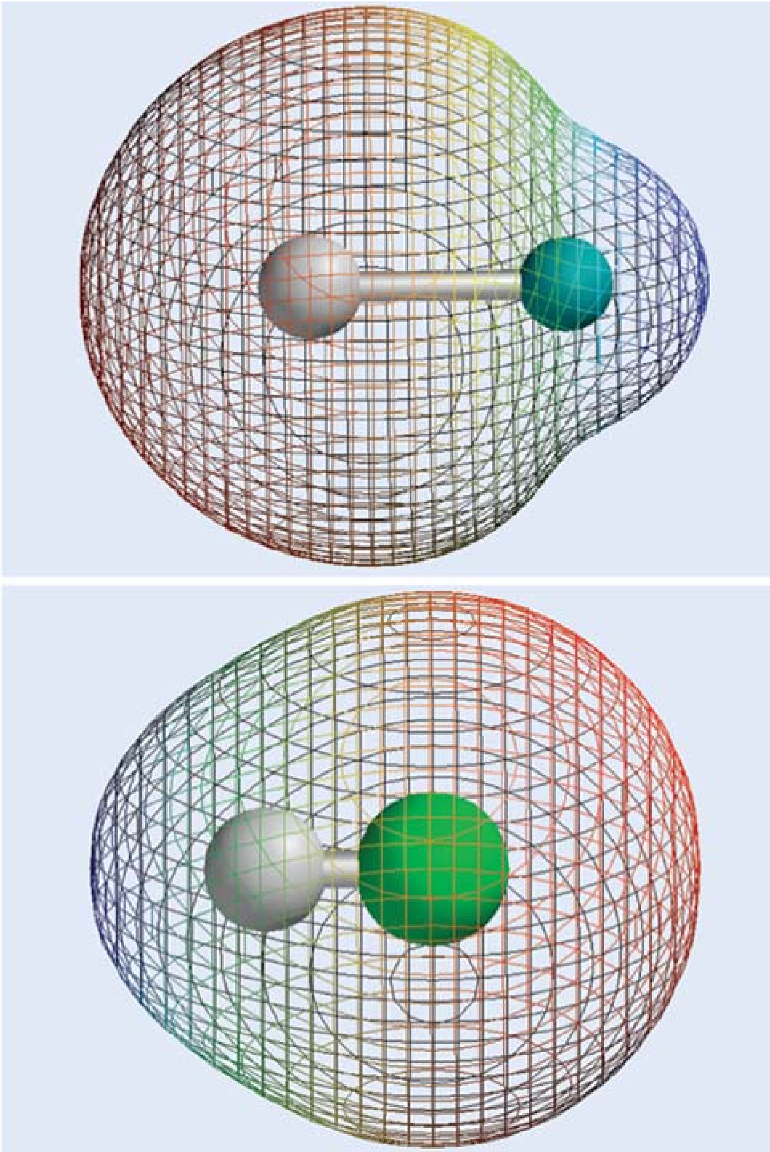
Questions Q16.22



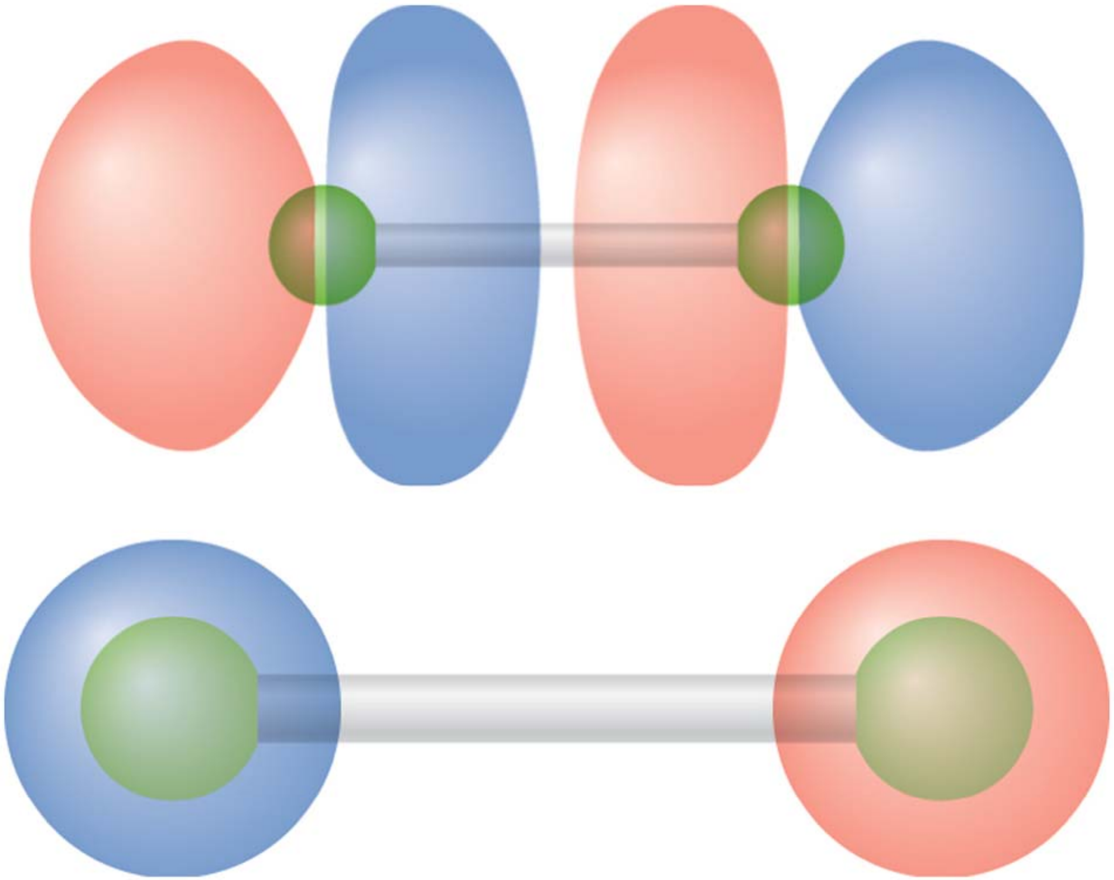
Questions Q16.23



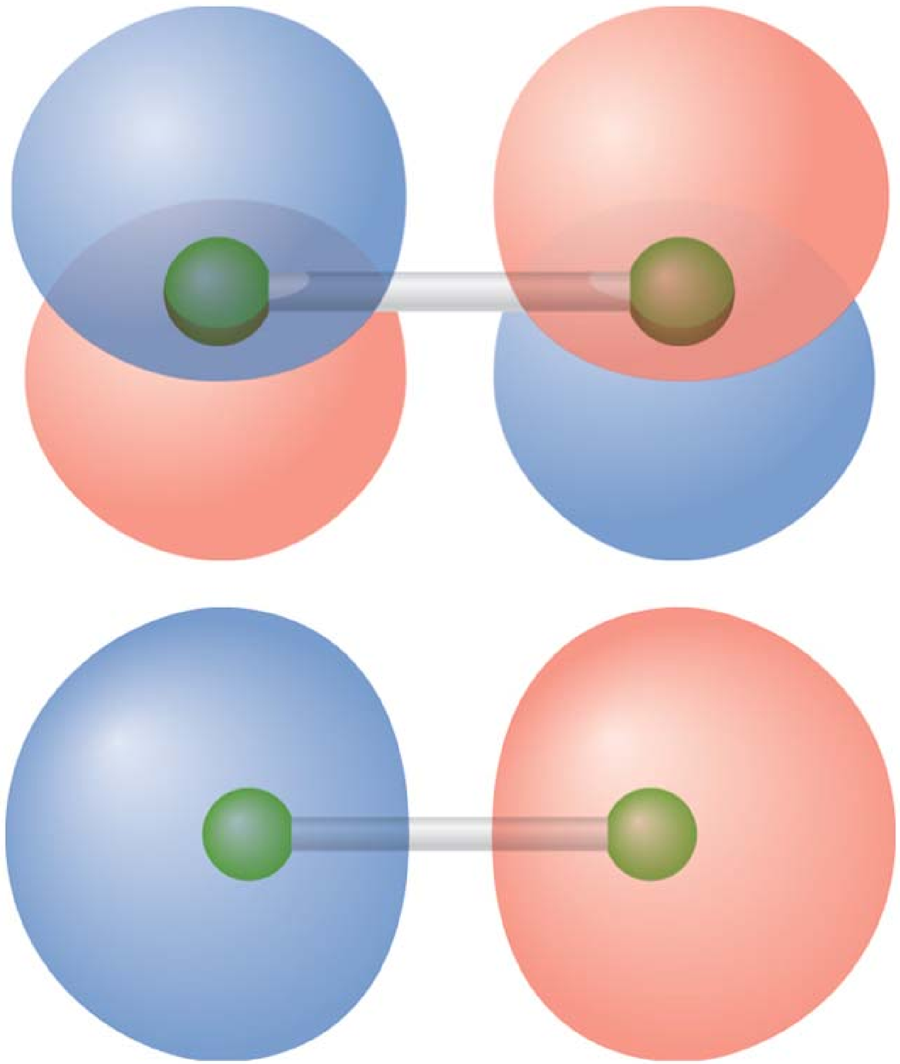
Questions Q16.24



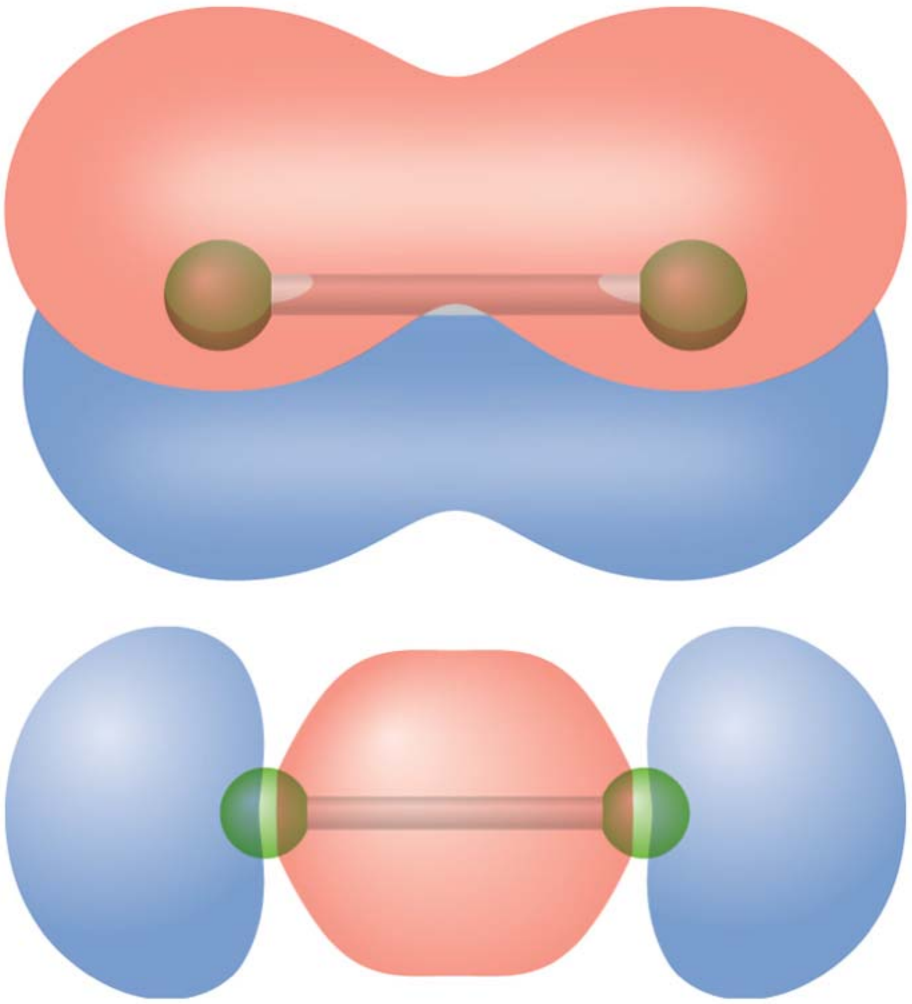
Questions Q16.25



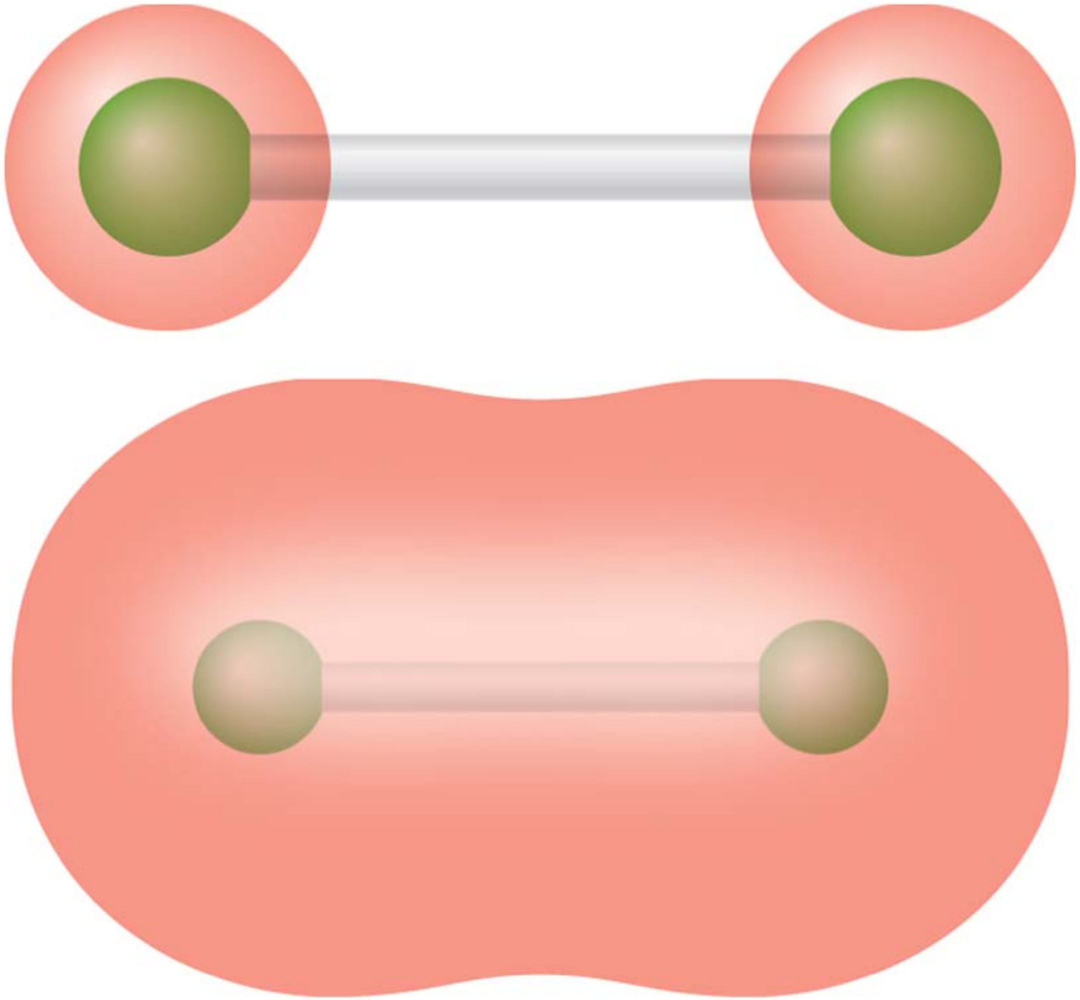
Questions Q16.26



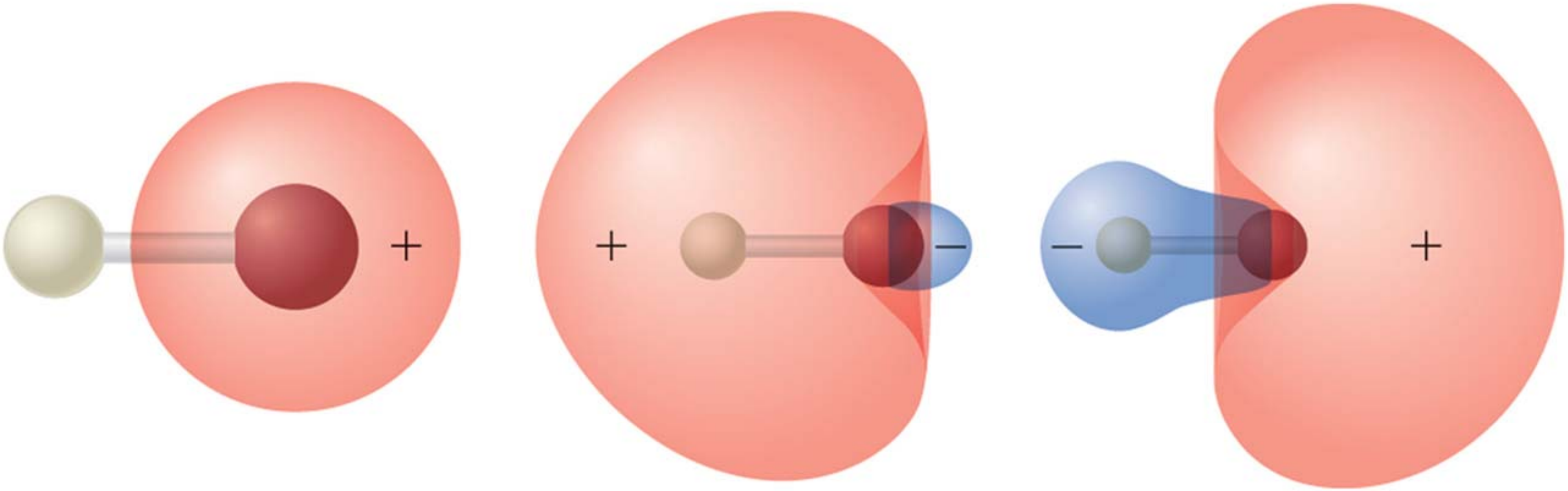
Questions Q16.27



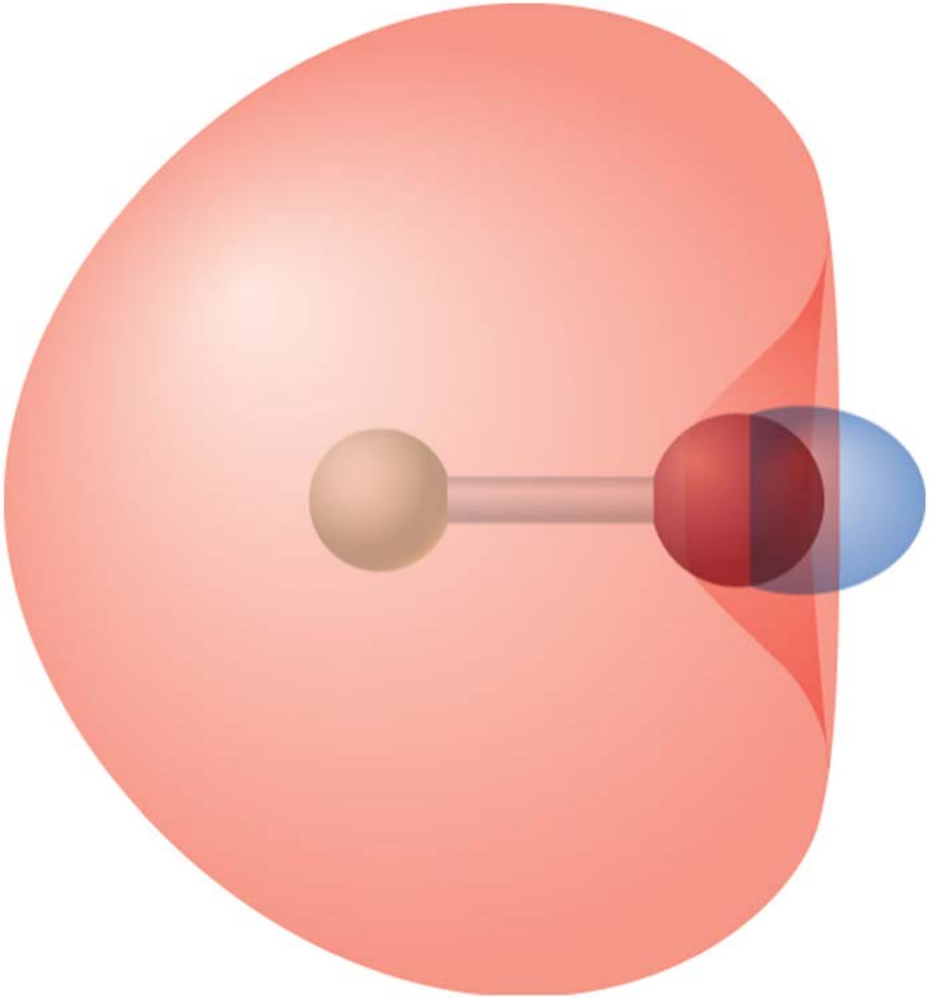
Questions Q16.28



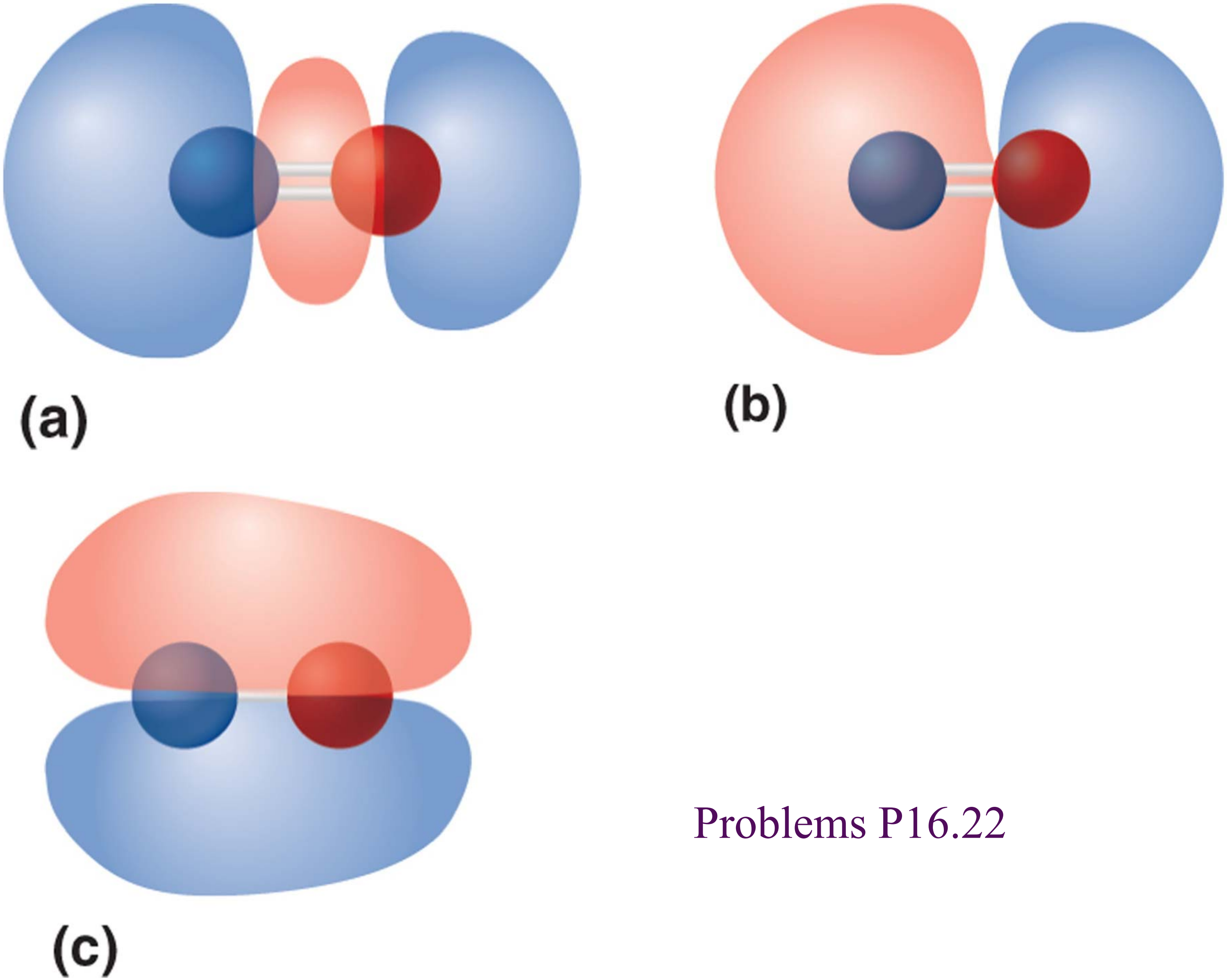
Questions Q16.29



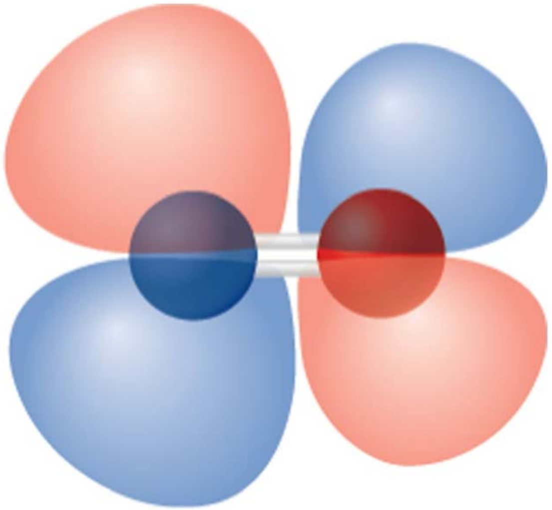
Problems P16.18



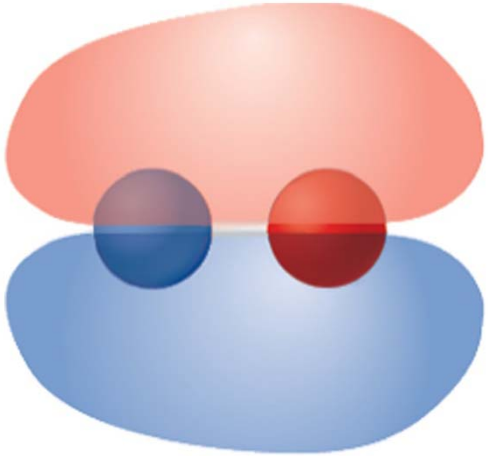
Problems P16.20



Problems P16.22



(d)



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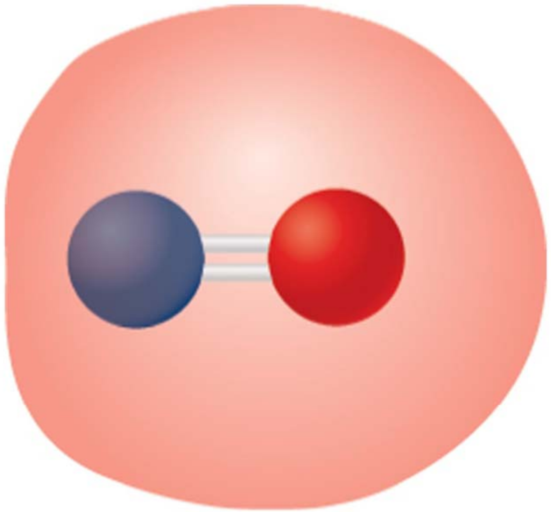
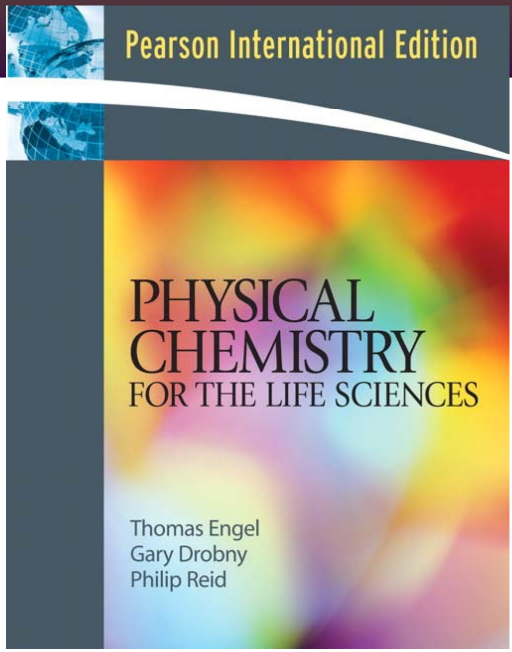


(f)

Problems P16.22 (continued)

Physical Chemistry

For the Life Sciences



CHAPTER 17

Molecular Structure and Energy Levels for Polyatomic Molecules

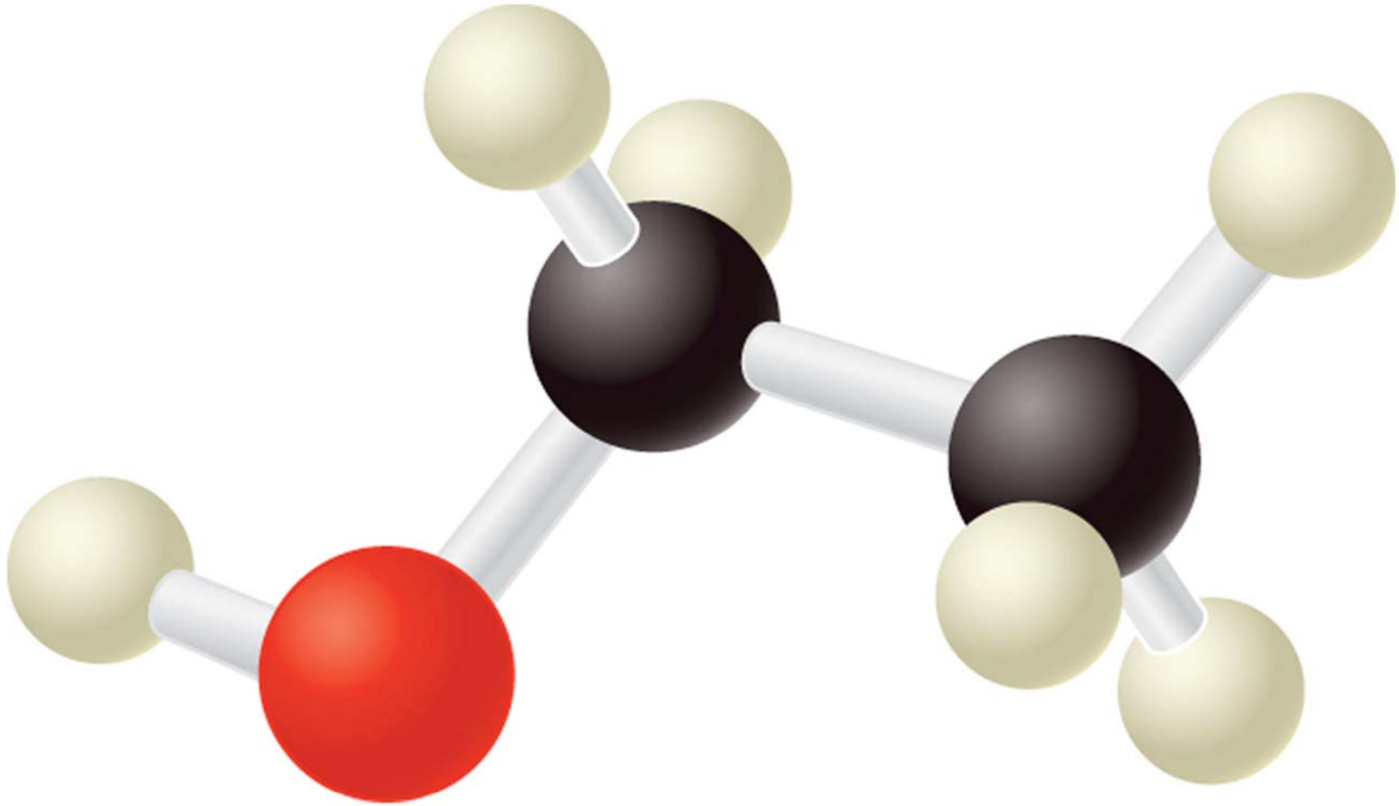
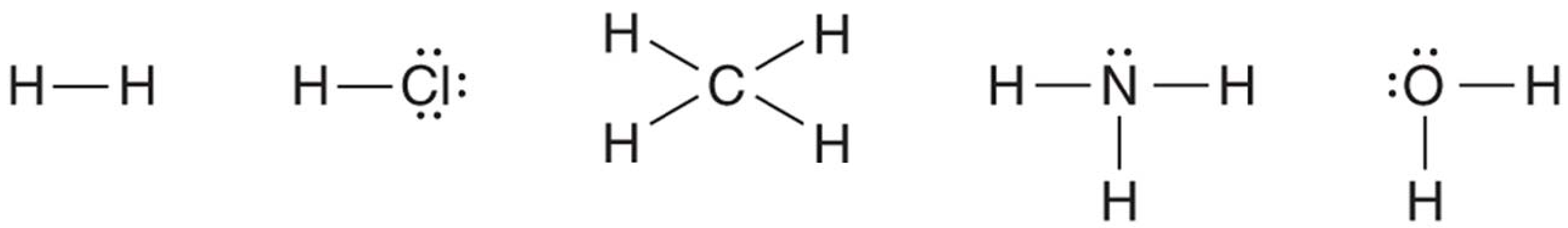


FIGURE 17.1

Ethanol depicted in the form of a ball-and-stick model.

Lewis Structure



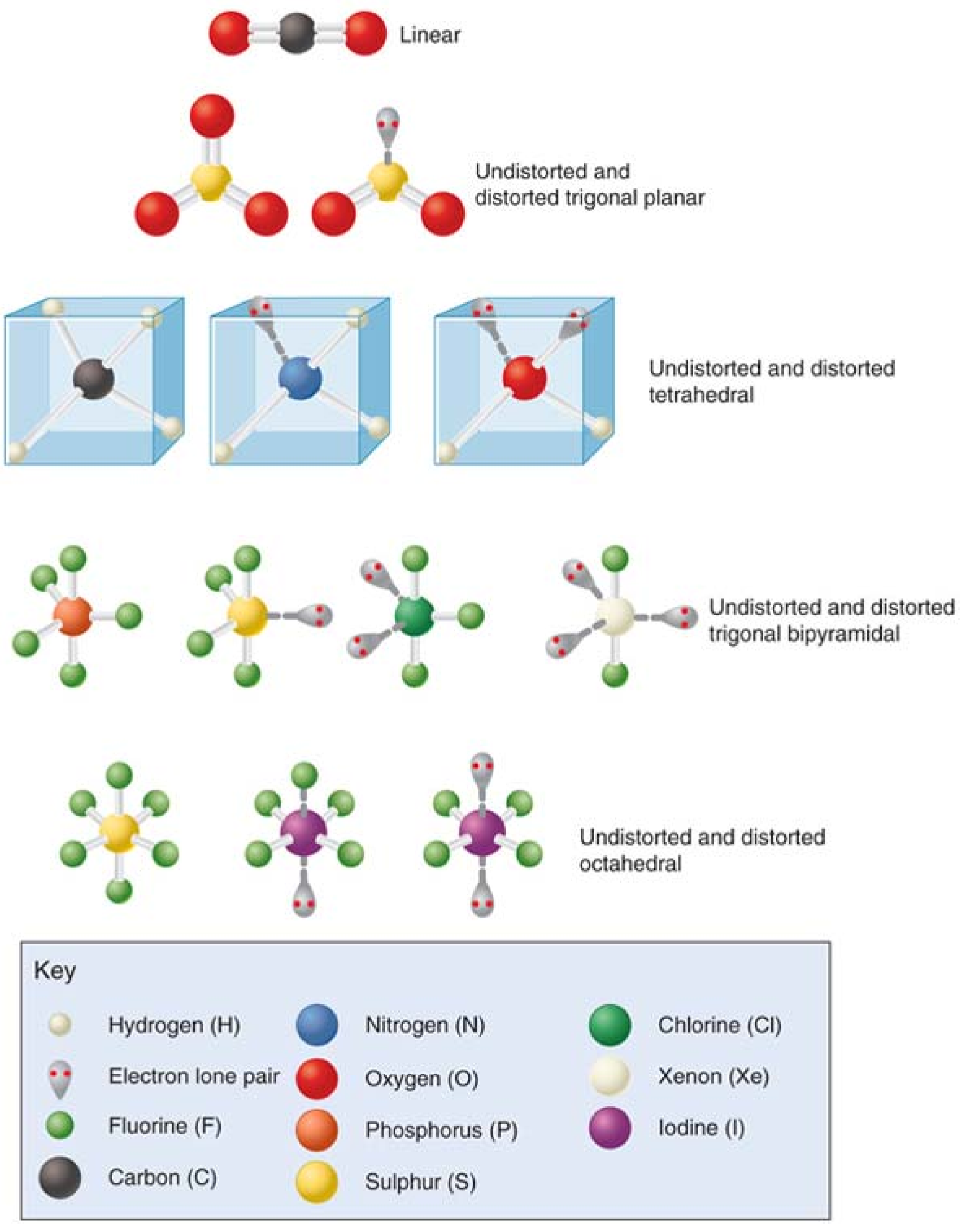


FIGURE 17.2

Examples of correctly predicted molecular shapes using the VSEPR model.

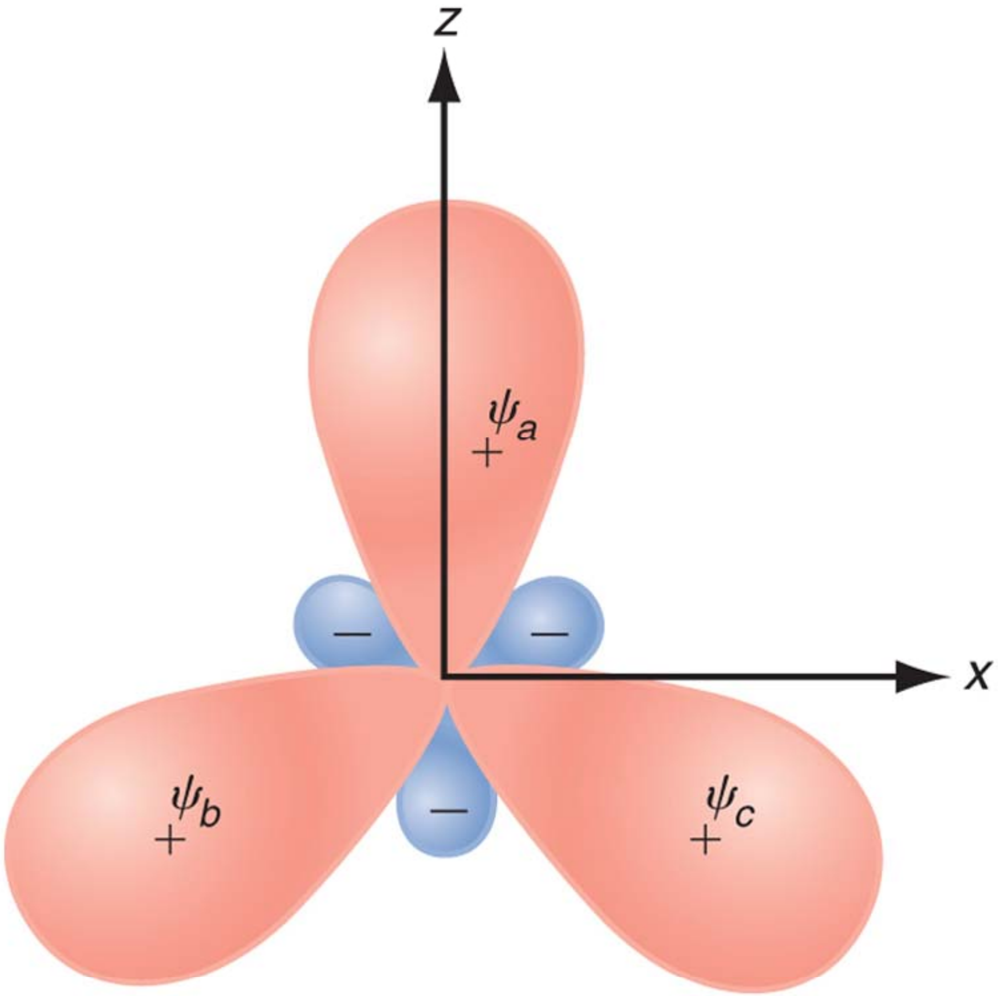
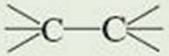
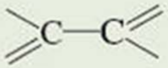


FIGURE 17.3

Geometry of the sp^2-hybrid orbitals used in Equation (17.1). In this and in most of the figures in this chapter, we use a “slimmed down” picture of hybrid orbitals to separate individual orbitals. A more correct form for *s*-*p* hybrid oritals is shown in Figure 17.5.

TABLE 17.1 C—C Bond Type

Carbon—Carbon Bond Types	σ Bond Hybridization	*s*-to-*p* Ratio	Angle between Equivalent σ Bonds (°)	Carbon—Carbon Single Bond Length (pm)
	sp^3	1:3	109.4	154
	sp^2	1:2	120	146
	sp	1:1	180	138

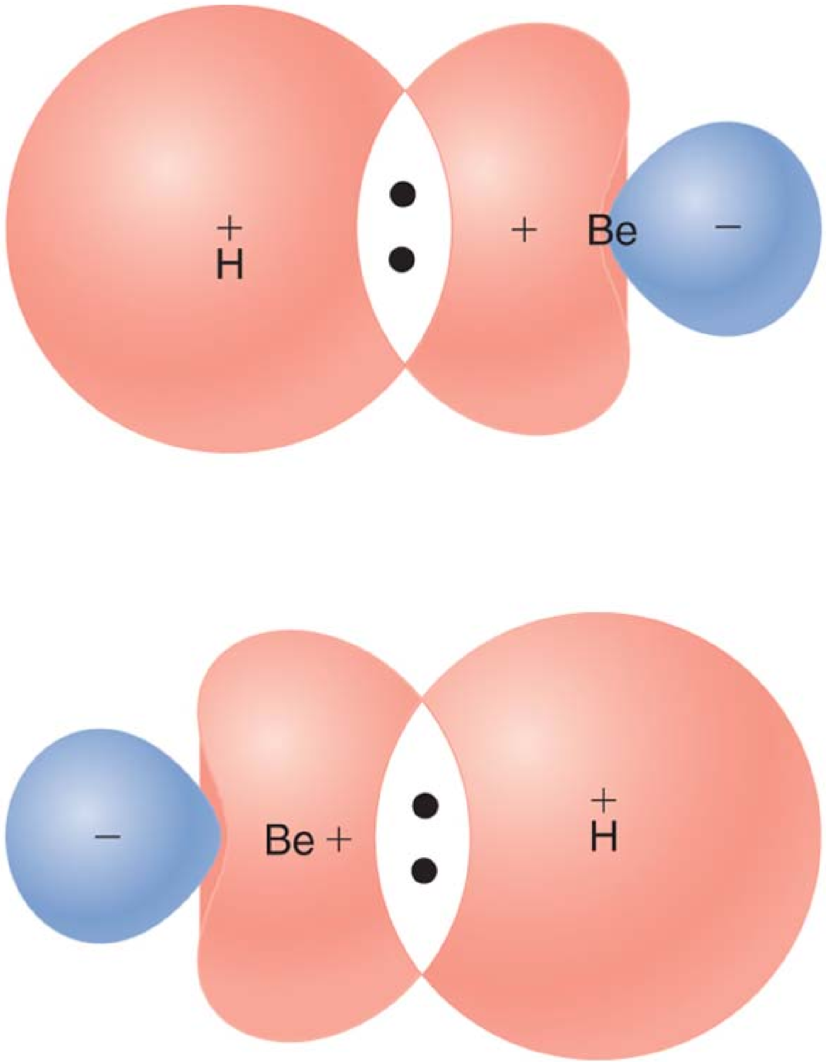


FIGURE 17.4

Bonding in BeH_2 using two *sp*-hybrid orbitals on Be. The two Be-H hybrid bonding orbitals are shown separately.

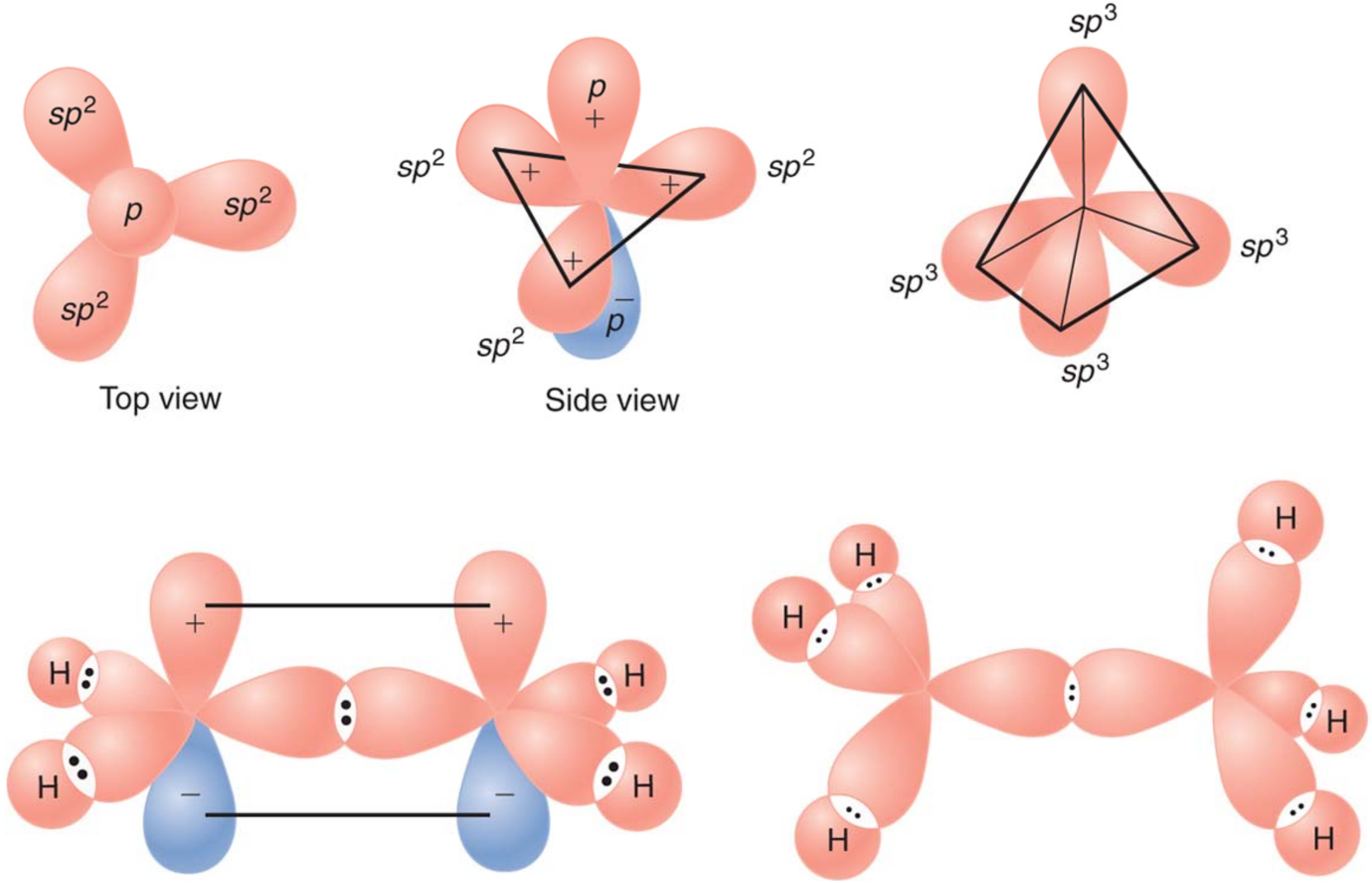


FIGURE 17.5

The top panel shows the arrangement of the hybrid orbitals for sp^2 and sp^3 carbon. The bottom panel shows a schematic depiction of bonding in ethene (left) and ethane (right) using hybrid bonding orbitals.

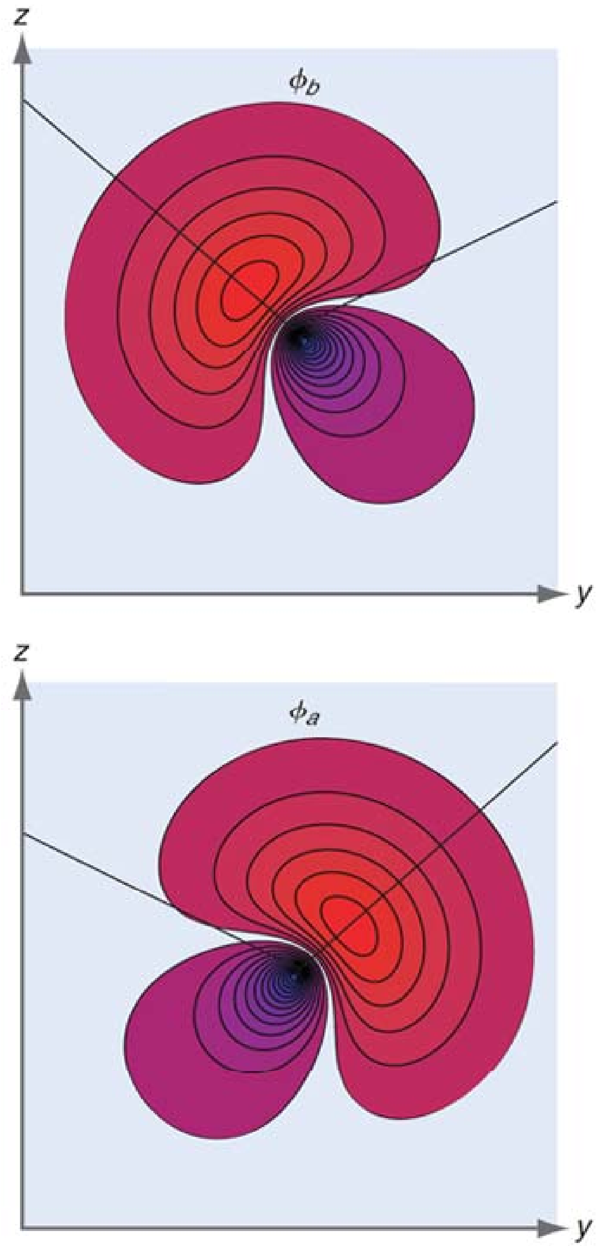


FIGURE 17.6

Directed hybrid bonding orbitals for H_2O. The black lines show the desired bond angle and orbital orientation. Red and blue contours correspond to the most positive and least positive values of the amplitude.

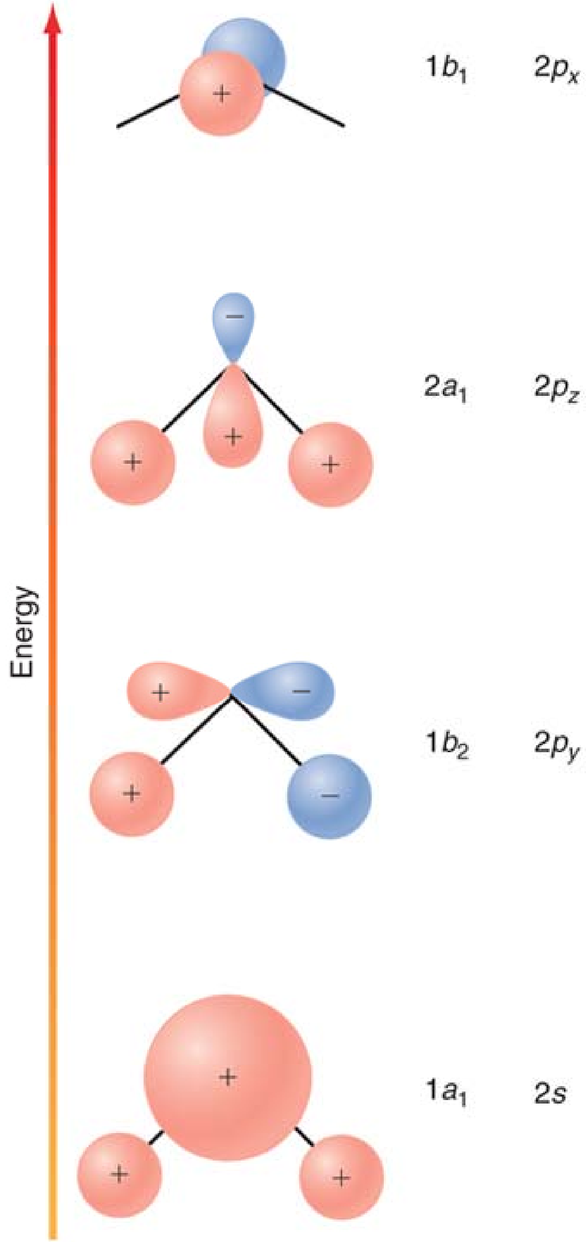


FIGURE 17.7

The valence MOs occupied in the ground state of water are shown in order of increasing orbital energy. The MOs are depicted in terms of the AOs from which they are constructed. The second column gives the MOs symmetry, and the third column lists the dominant AO orbital on the oxygen atom.

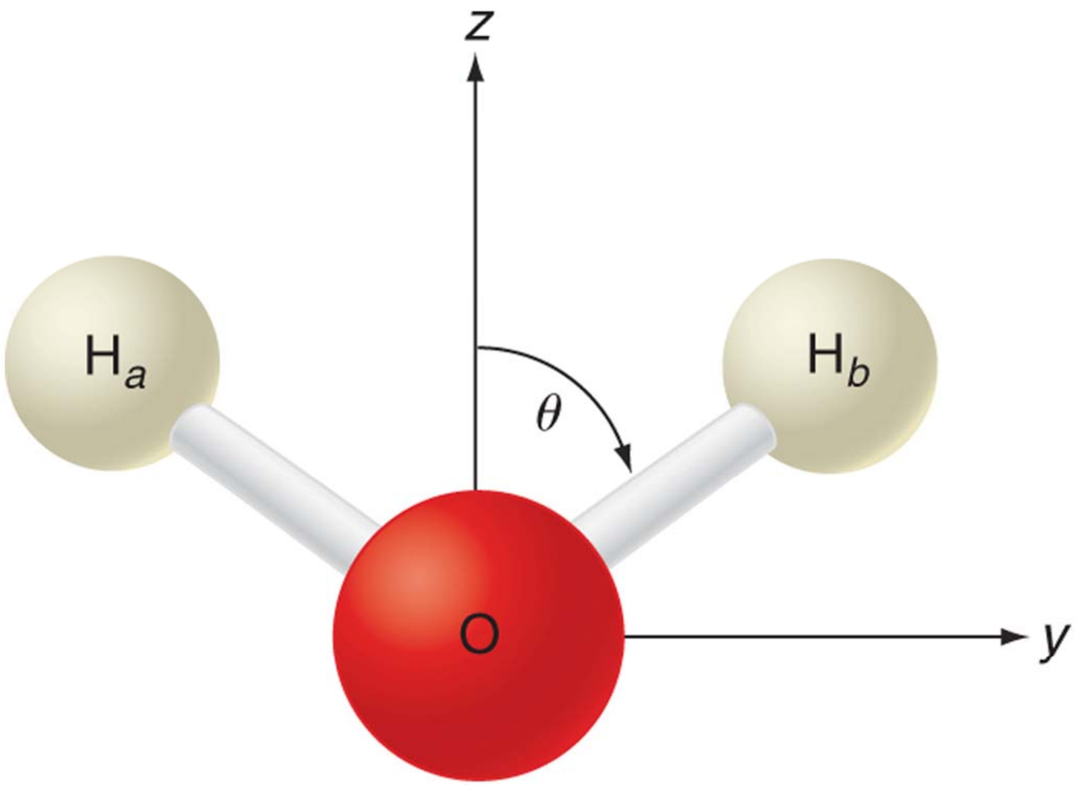


FIGURE 17.8

Coordinate system used to generate the hybrid orbitals on the oxygen atom that are suitable to describe the structure of H_2O.

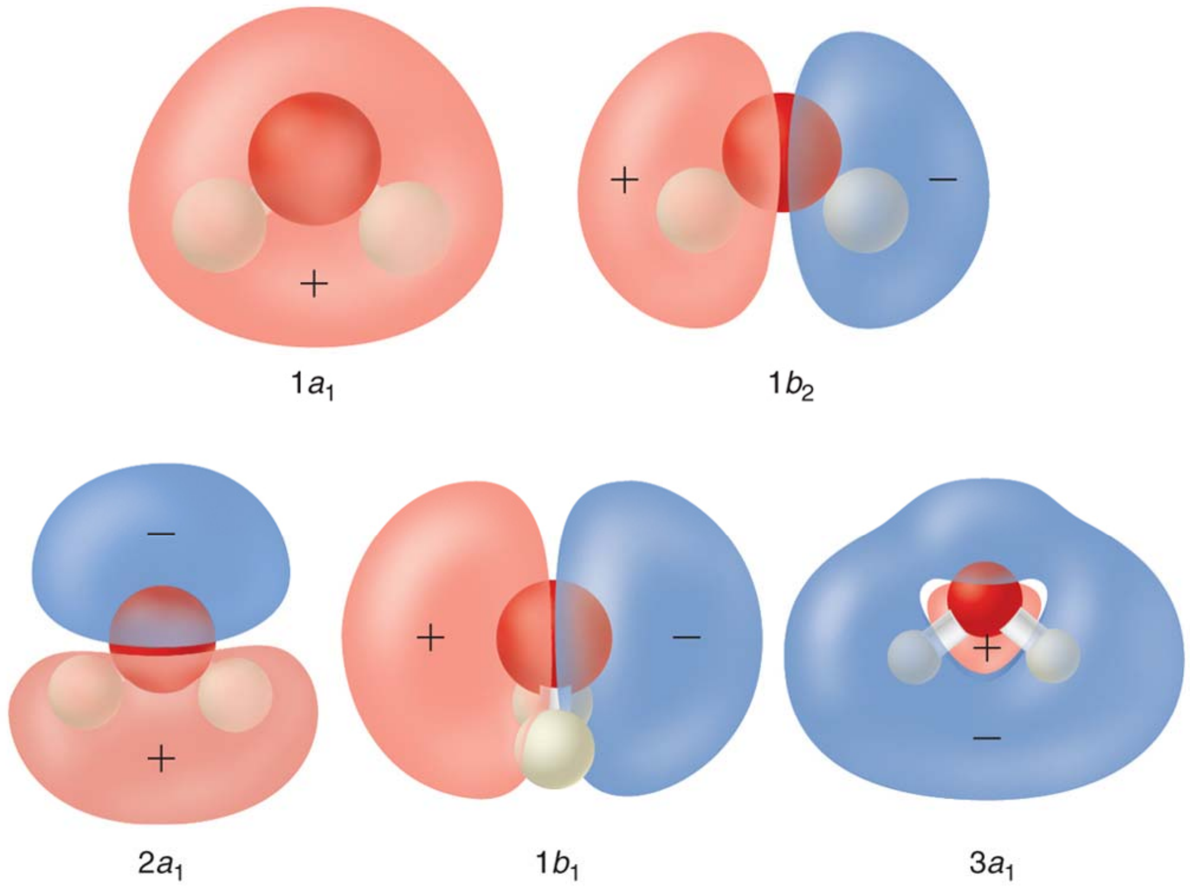


FIGURE 17.9

The first five valence MOs for H_2O are depicted. The $1b_1$ and $3a_1$ MOs are the HOMO and LUMO, respectively. Note that the $1b_1$ MO is the AO corresponding to the nonbonding $2p_x$ electrons on oxygen.

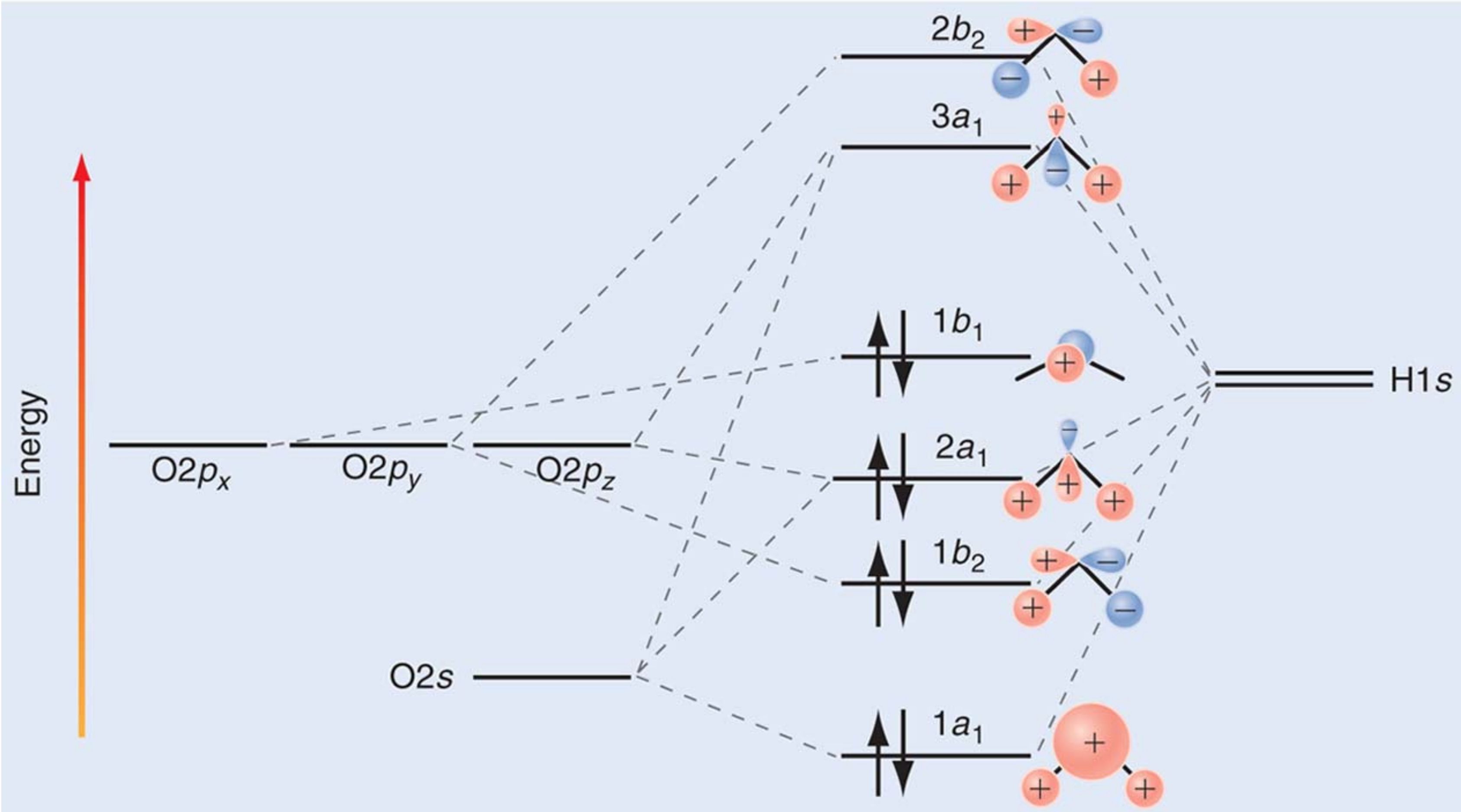


FIGURE 17.10

Molecular orbital energy-level diagram for H_2O at its equilibrium geometry. To avoid clutter, minor AO contributions to the MOs and the $1a_1$ MO generated from the O1s AO are not shown.

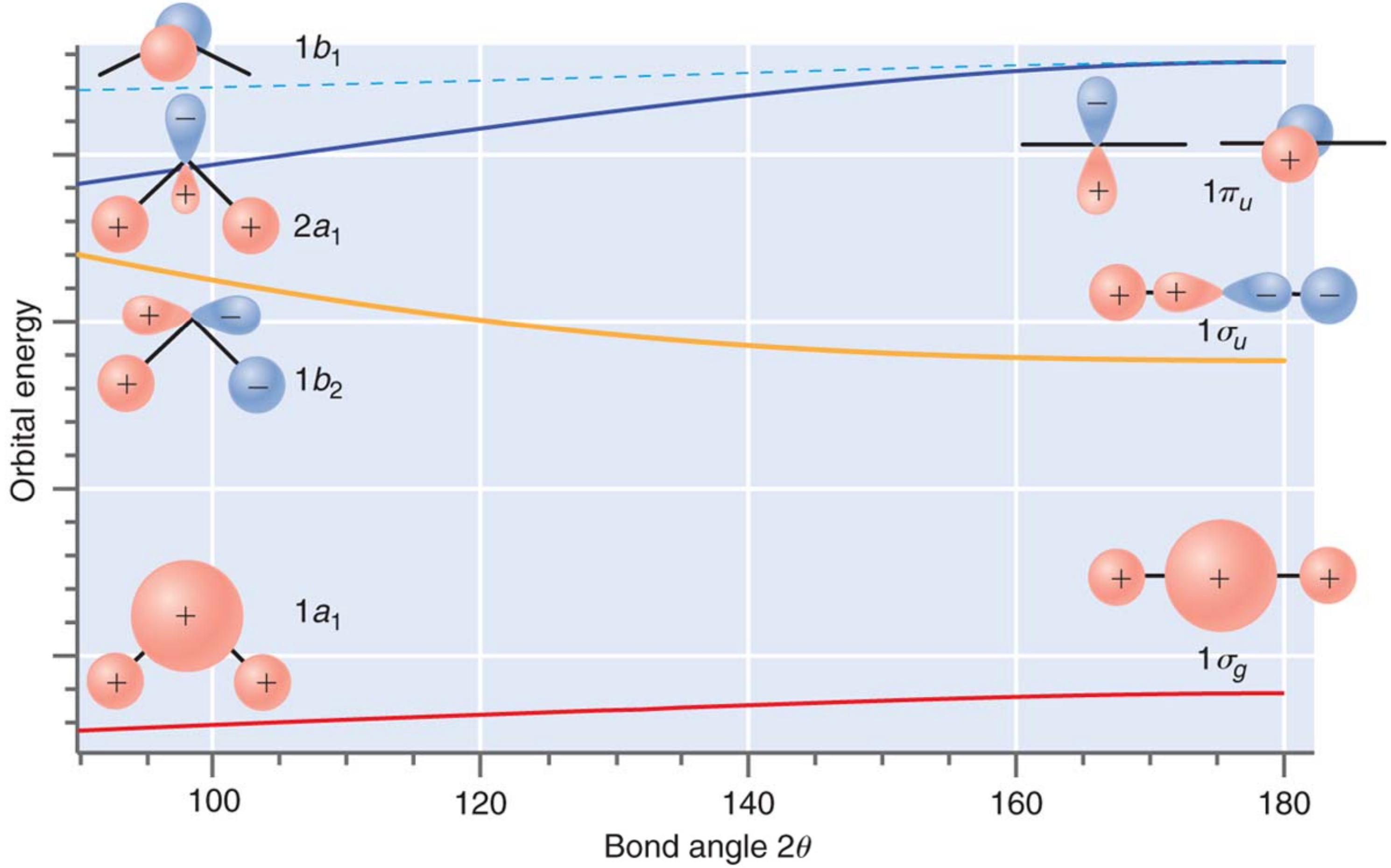


FIGURE 17.11

Schematic variation of the MO energies for water with bond angle. The symbols used on the left to describe the MOs are based on symmetry considerations and are valid for $2\theta < 180^\circ$.

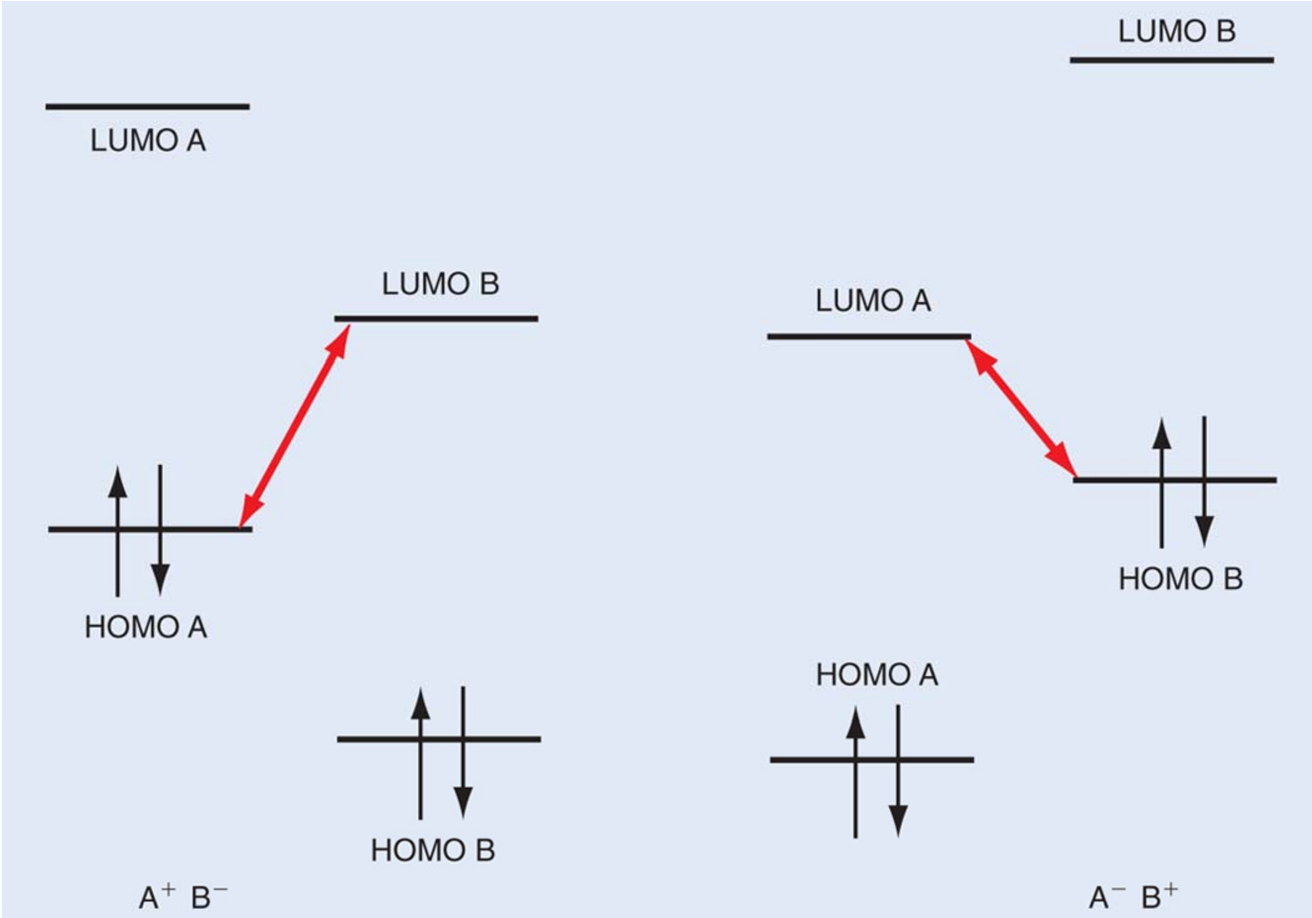


FIGURE 17.12

Interaction between two species A and B. The difference in energies between the HOMO and LUMO orbitals on A and B will determine the direction of charge transfer.

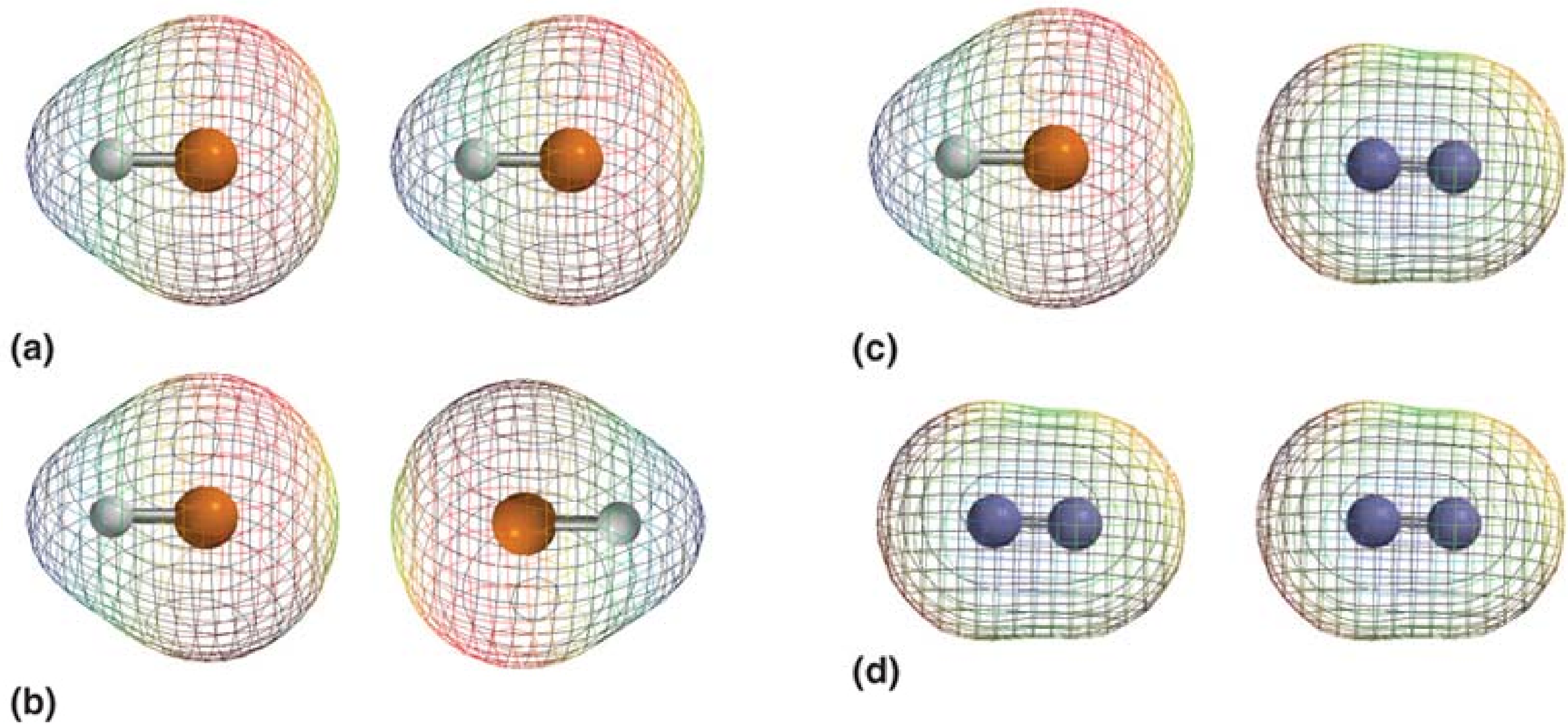


FIGURE 17.13

(a) Two dipolar HCl molecules with this relative orientation attract one another. (b) Two dipolar HCl molecules with this relative orientation repel one another. (c) The dipolar HCl molecule indices a dipole moment in N_2. (d) Two N_2 molecules experience a net attractive interaction through the time fluctuating dipole moments on each molecule.

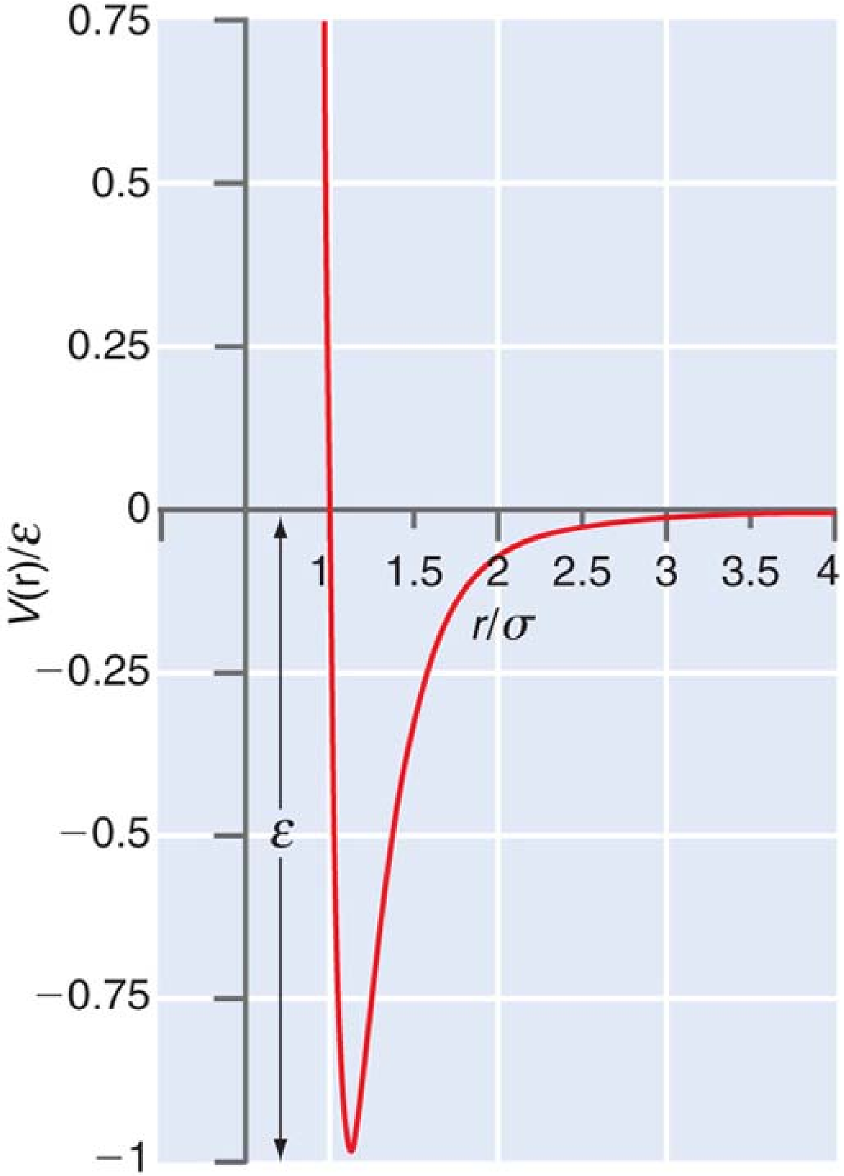


FIGURE 17.14

The Lennard-Jones potential of Equation (17.5) is plotted against the reduced length r/σ.

TABLE 17.2 Values for the Lennard-Jones Parameters ε and σ

Atom/ Molecule	$10^{21}\varepsilon$(J)	Normal Boiling Temperature (K)	σ(pm)
He	0.141	4.2	256
N_2	1.31	77.4	370
CO	1.38	81.7	358
CH_4	2.05	90.8	378
C_3H_8	3.34	231	564

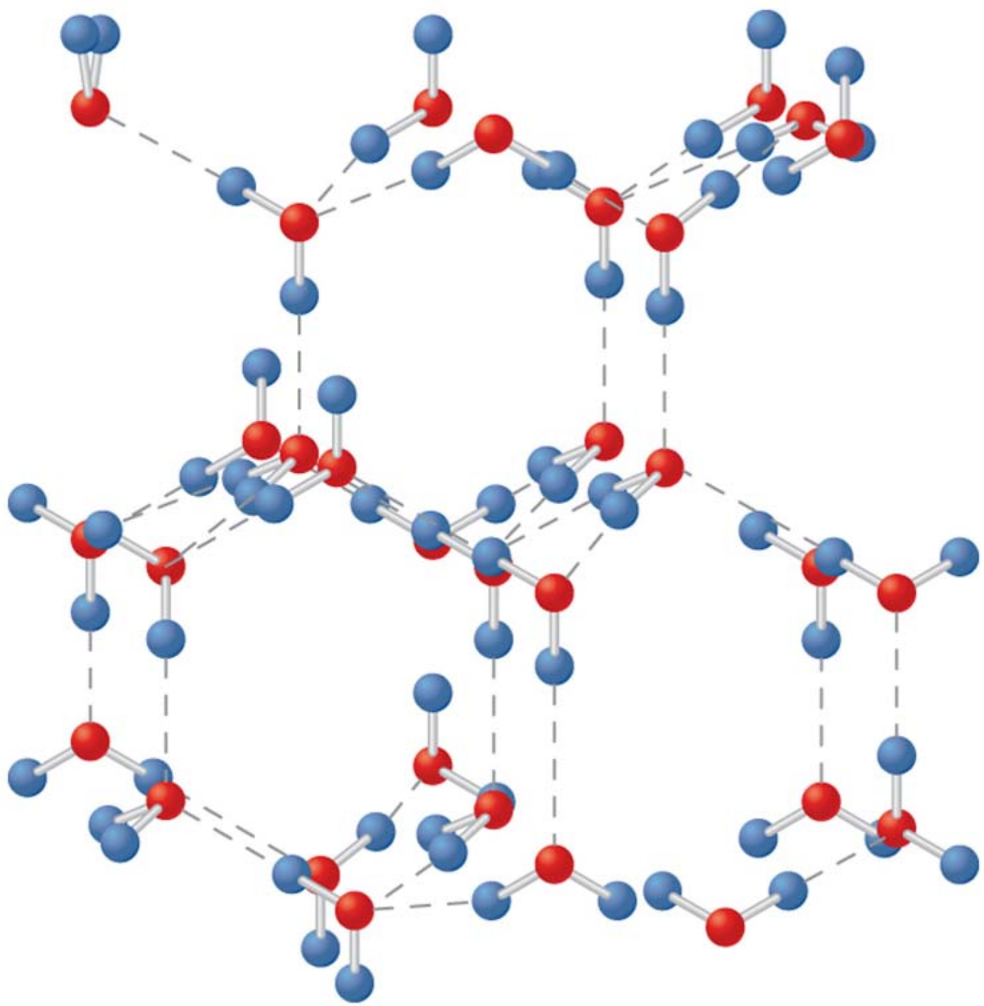


FIGURE 17.15

The crystal structure of hexagonal ice, which is the most stable solid phase at 1 bar, is shown. Note that hydrogen bonds connect each of the atoms in the water molecule to its neighbors.

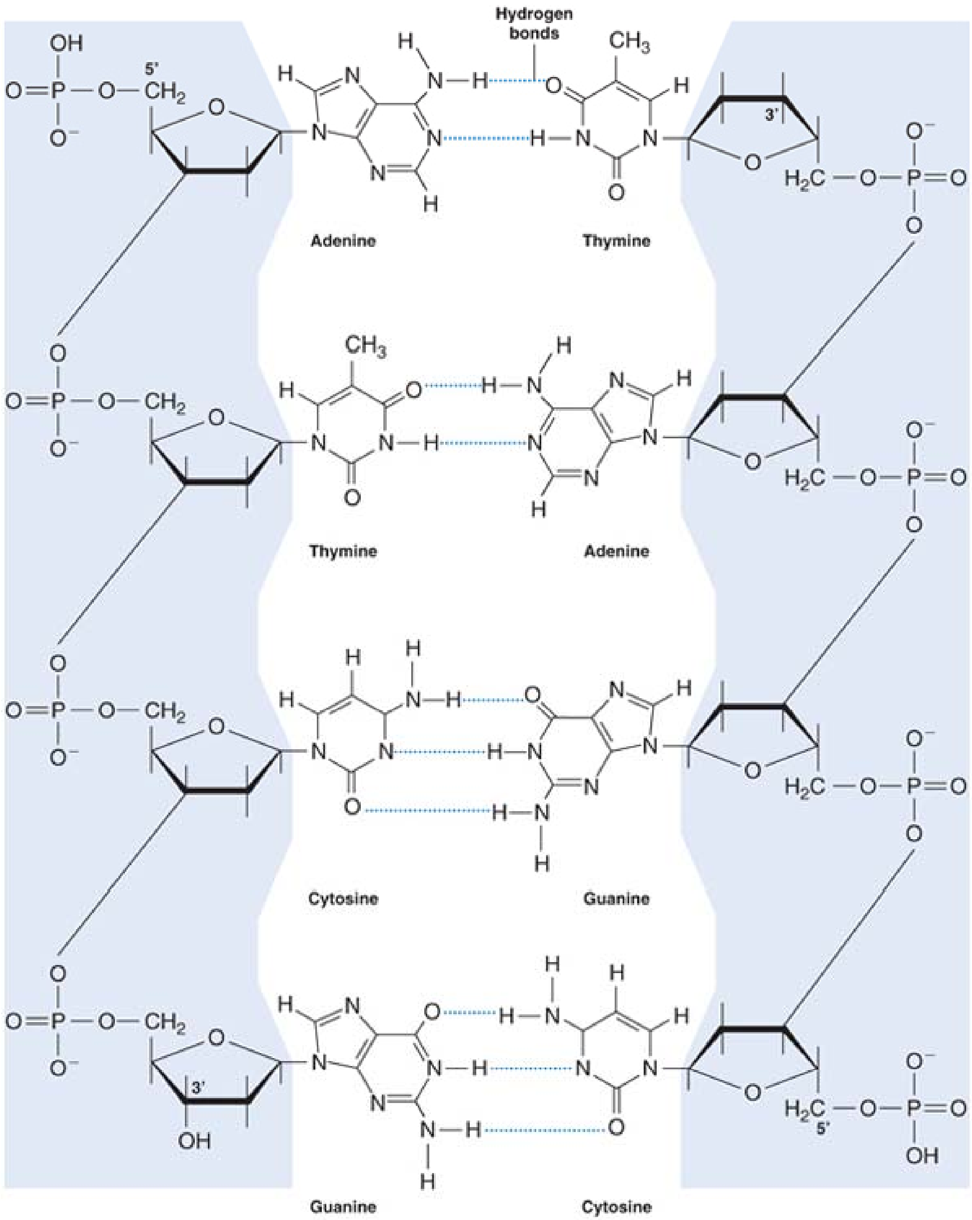
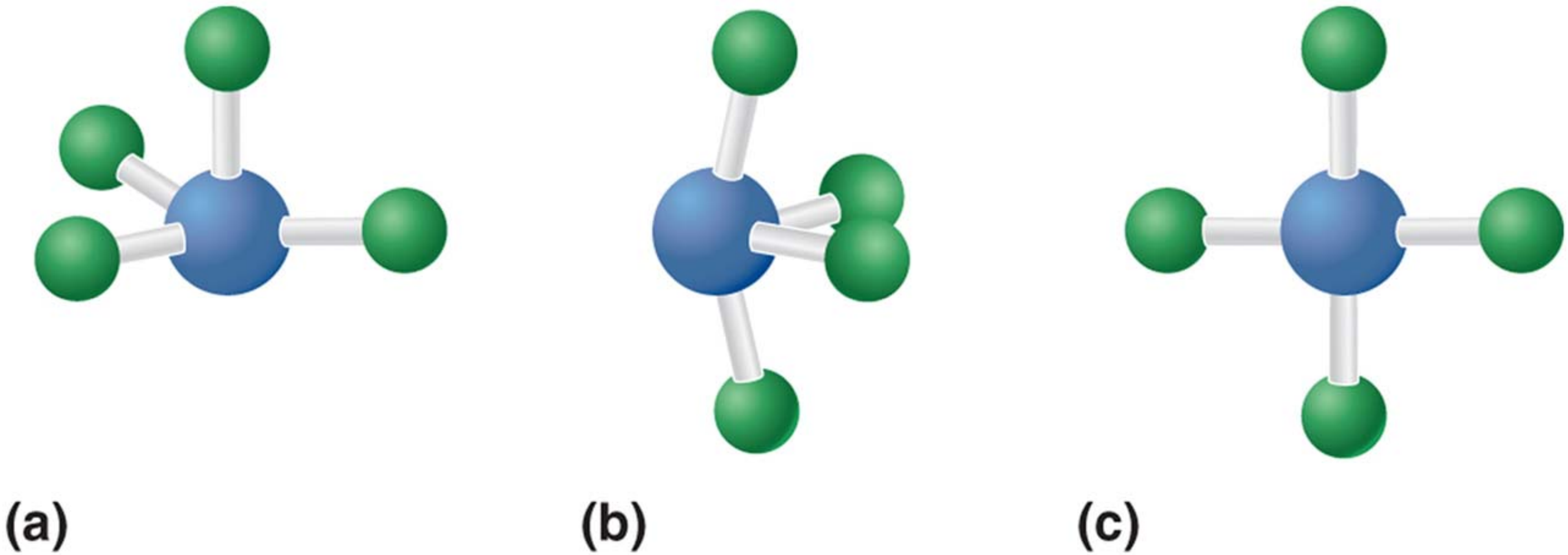


FIGURE 17.16

Hydrogen bonding between thymine and adenine and between guanine and cytosine are the dominant interactions that stabilize the double helix structure of DNA.



Problems P17.2

End of Lecture

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