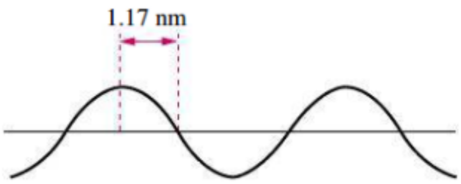
PRACTICE EXAMPLE B: By using a two-photon process (that is, two sequential excitations), a chemist is able to excite the electron in a hydrogen atom to the 5*d* level. Not all excitations are possible; they are governed by selection rules (see Are You Wondering 8-6). Use the selection rules to identify the possible intermediate levels (more than one are possible) involved, and calculate the frequencies of the two photons involved in each process. Identify the transitions allowed when a sample of hydrogen atoms excited to the 5*d* level exhibits an emission spectrum. When a sample of gaseous sodium atoms is similarly excited to the 5*d* level, what would be the difference in the emission spectrum observed?

Exercises

Electromagnetic Radiation

1. A hypothetical electromagnetic wave is pictured here. What is the wavelength of this radiation?



2. For the electromagnetic wave described in Exercise 1, what are **(a)** the frequency, in hertz, and **(b)** the energy, in joules per photon?
3. The magnesium spectrum has a line at 266.8 nm. Which of these statements about this radiation is (are) correct? Explain.
(a) It has a higher frequency than radiation with wavelength 402 nm.
(b) It is visible to the eye.
(c) It has a greater speed in a vacuum than does red light of wavelength 652 nm.
(d) Its wavelength is longer than that of X-rays.
4. The most intense line in the cerium spectrum is at 418.7 nm.
(a) Determine the frequency of the radiation producing this line.
(b) In what part of the electromagnetic spectrum does this line occur?
(c) Is it visible to the eye? If so, what color is it? If not, is this line at higher or lower energy than visible light?
5. *Without doing detailed calculations*, determine which of the following wavelengths represents light of the highest frequency: **(a)** 6.7×10^{-4} cm; **(b)** 1.23 mm; **(c)** 80 nm; **(d)** 6.72 μm.
6. *Without doing detailed calculations*, arrange the following electromagnetic radiation sources in order of increasing frequency: **(a)** a red traffic light; **(b)** a 91.9 MHz radio transmitter; **(c)** light with a frequency of $3.0 \times 10^{14}\ s^{-1}$; **(d)** light with a wavelength of 49 nm.
7. How long does it take light from the sun, 93 million miles away, to reach Earth?
8. In astronomy, distances are measured in *light-years*, the distance that light travels in one year. What is the distance of one light-year expressed in kilometers?

Photons and the Photoelectric Effect

9. Determine
(a) the energy, in joules per photon, of radiation of frequency $7.39 \times 10^{15}\ s^{-1}$;
(b) the energy, in kilojoules per mole, of radiation of frequency $1.97 \times 10^{14}\ s^{-1}$.
10. Determine
(a) the frequency, in hertz, of radiation having an energy of 8.62×10^{-21} J/photon;
(b) the wavelength, in nanometers, of radiation with 360 kJ/mol of energy.
11. A certain radiation has a wavelength of 574 nm. What is the energy, in joules, of **(a)** one photon; **(b)** a mole of photons of this radiation?
12. What is the wavelength, in nanometers, of light with an energy content of 2112 kJ/mol? In what portion of the electromagnetic spectrum is this light?
13. *Without doing detailed calculations*, indicate which of the following electromagnetic radiations has the greatest energy per photon and which has the least: **(a)** 662 nm; **(b)** 2.1×10^{-5} cm; **(c)** 3.58 μm; **(d)** 4.1×10^{-6} m.
14. *Without doing detailed calculations*, arrange the following forms of electromagnetic radiation in *increasing* order of energy per mole of photons: **(a)** radiation with $\nu = 3.0 \times 10^{15}\ s^{-1}$; **(b)** an infrared heat lamp; **(c)** radiation having $\lambda = 7000$ Å; **(d)** dental X-rays.
15. In what region of the electromagnetic spectrum would you expect to find radiation having an energy per photon 100 times that associated with 988 nm radiation?
16. High-pressure sodium vapor lamps are used in street lighting. The two brightest lines in the sodium spectrum are at 589.00 and 589.59 nm. What is the difference in energy per photon of the radiations corresponding to these two lines?

17. The lowest-frequency light that will produce the photoelectric effect is called the *threshold frequency*. **(a)** The threshold frequency for indium is $9.96 \times 10^{14}\,s^{-1}$. What is the energy, in joules, of a photon of this radiation? **(b)** Will indium display the photoelectric effect with UV light? With infrared light? Explain.

18. The minimum energy required to cause the photoelectric effect in potassium metal is 3.69×10^{-19} J. Will photoelectrons be produced when visible light shines on the surface of potassium? If 520 nm radiation is shone on potassium, what is the velocity of the ejected electrons?

Atomic Spectra

19. Use the Balmer equation (8.4) to determine
(a) the frequency, in s^{-1}, of the radiation corresponding to $n = 5$;
(b) the wavelength, in nanometers, of the line in the Balmer series corresponding to $n = 7$;
(c) the value of n corresponding to the Balmer series line at 380 nm.

20. How would the Balmer equation (8.4) have to be modified to predict lines in the infrared spectrum of hydrogen? [*Hint:* Compare equations (8.4) and (8.6).]

21. What is ΔE for the transition of an electron from $n = 6$ to $n = 3$ in a hydrogen atom? What is the frequency of the spectral line produced?

22. What is ΔE for the transition of an electron from $n = 5$ to $n = 2$ in a hydrogen atom? What is the frequency of the spectral line produced?

23. To what value of n in equation (8.4) does the line in the Balmer series at 389 nm correspond?

24. The Lyman series of the hydrogen spectrum can be represented by the equation

$$\nu = 3.2881 \times 10^{15}\,s^{-1}\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad (\text{where } n = 2, 3, \ldots)$$

(a) Calculate the maximum and minimum wavelength lines, in nanometers, in this series.
(b) What value of n corresponds to a spectral line at 95.0 nm?
(c) Is there a line at 108.5 nm? Explain.

25. Calculate the wavelengths, in nanometers, of the first four lines of the Balmer series of the hydrogen spectrum, starting with the *longest* wavelength component.

26. A line is detected in the hydrogen spectrum at 1880 nm. Is this line in the Balmer series? Explain.

Energy Levels and Spectrum of the Hydrogen Atom

27. Calculate the energy, in joules, of a hydrogen atom when the electron is in the sixth energy level.

28. Calculate the increase in energy, in joules, when an electron in the hydrogen atom is excited from the first to the third energy level.

29. What are the **(a)** frequency, in s^{-1}, and **(b)** wavelength, in nanometers, of the light emitted when the electron in a hydrogen atom drops from the energy level $n = 7$ to $n = 4$? **(c)** In what portion of the electromagnetic spectrum is this light?

30. *Without doing detailed calculations*, indicate which of the following electron transitions requires the greatest amount of energy to be *absorbed* by a hydrogen atom: from **(a)** $n = 1$ to $n = 2$; **(b)** $n = 2$ to $n = 4$; **(c)** $n = 3$ to $n = 9$; **(d)** $n = 10$ to $n = 1$.

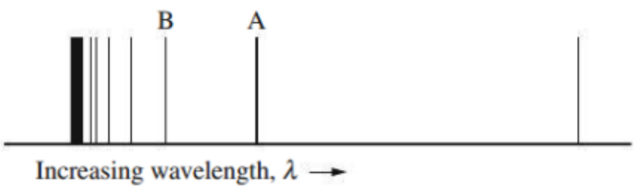
31. For a hydrogen atom, determine
(a) the energy level corresponding to $n = 8$;
(b) whether there is an energy level at -2.500×10^{-19} J;
(c) the ionization energy, if the electron is initially in the $n = 6$ level.

32. *Without doing detailed calculations*, indicate which of the following electron transitions in the hydrogen atom results in the emission of light of the longest wavelength. **(a)** $n = 4$ to $n = 3$; **(b)** $n = 1$ to $n = 2$; **(c)** $n = 1$ to $n = 6$; **(d)** $n = 3$ to $n = 2$.

33. What electron transition in a hydrogen atom, starting from $n = 7$, will produce light of wavelength 410 nm?

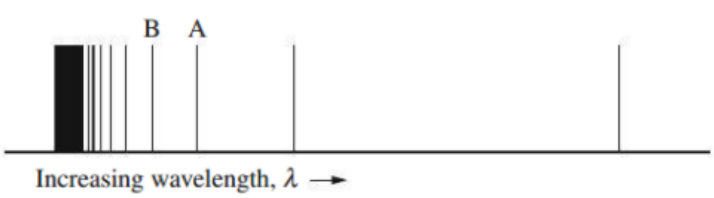
34. What electron transition in a hydrogen atom, ending in $n = 3$, will produce light of wavelength 1090 nm?

35. The emission spectrum below for a one-electron (hydrogen-like) species in the gas phase shows all the lines, before they merge together, resulting from transitions to the ground state from higher energy states. Line A has a wavelength of 103 nm.



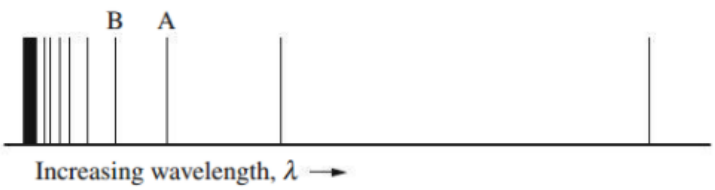
(a) What are the upper and lower principal quantum numbers corresponding to the lines labeled A and B?
(b) Identify the one-electron species that exhibits the spectrum.

36. The emission spectrum below for a one-electron (hydrogen-like) species in the gas phase shows all the lines, before they merge together, resulting from transitions to the first excited state from higher energy states. Line A has a wavelength of 434 nm.



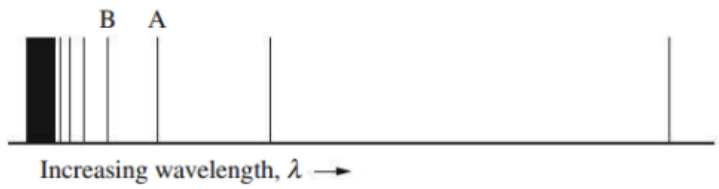
(a) What are the upper and lower principal quantum numbers corresponding to the lines labeled A and B?
(b) Identify the one-electron species that exhibits the spectrum.

37. The emission spectrum below for a one-electron (hydrogen-like) species in the gas phase shows all the lines, before they merge together, resulting from transitions to the first excited state from higher energy states. Line A has a wavelength of 27.1 nm.



(a) What are the upper and lower principal quantum numbers corresponding to the lines labeled A and B?
(b) Identify the one-electron species that exhibits the spectrum.

38. The emission spectrum below for a one-electron (hydrogen-like) species in the gas phase shows all the lines, before they merge together, resulting from transitions to the ground state from higher energy states. Line A has a wavelength of 10.8 nm.



(a) What are the upper and lower principal quantum numbers corresponding to the lines labeled A and B?
(b) Identify the one-electron species that exhibits the spectrum.

Wave–Particle Duality

39. Which must possess a greater velocity to produce matter waves of the same wavelength (such as 1 nm), protons or electrons? Explain your reasoning.
40. What must be the velocity, in meters per second, of a beam of electrons if they are to display a de Broglie wavelength of 850 nm?
41. Calculate the de Broglie wavelength, in nanometers, associated with a 145 g baseball traveling at a speed of 168 km/h. How does this wavelength compare with typical nuclear or atomic dimensions?
42. What is the wavelength, in nanometers, associated with a 9.7 g bullet with a muzzle velocity of 887 m s^{-1}, that is, considering the bullet to be a matter wave? Comment on the feasibility of an experimental measurement of this wavelength.

The Heisenberg Uncertainty Principle

43. The uncertainty relation $\Delta x \Delta p \geq h/(4\pi)$, expression (8.11), is valid for motion in any direction. For circular motion, the relation may be expressed as $\Delta r \Delta p \geq h/(4\pi)$, where Δr is the uncertainty in radial position and Δp is the uncertainty in the momentum along the *radial* direction. Describe how Bohr's model of the hydrogen atom violates the uncertainty relation expressed in the form $\Delta r \Delta p \geq h/(4\pi)$.
44. Although Einstein made some early contributions to quantum theory, he was never able to accept the Heisenberg uncertainty principle. He stated, "God does not play dice with the Universe." What do you suppose Einstein meant by this remark? In reply to Einstein's remark, Niels Bohr is supposed to have said, "Albert, stop telling God what to do." What do you suppose Bohr meant by this remark?
45. A proton is accelerated to one-tenth the velocity of light, and this velocity can be measured with a precision of 1%. What is the uncertainty in the position of this proton?
46. Show that the uncertainty principle is not significant when applied to large objects such as automobiles. Assume that m is precisely known; assign a reasonable value to either the uncertainty in position or the uncertainty in velocity, and estimate a value of the other.
47. What must be the velocity of electrons if their associated wavelength is to equal the Bohr radius, a_0?
48. What must be the velocity of electrons if their associated wavelength is to equal the *longest* wavelength line in the Lyman series? [*Hint:* Refer to Figure 8-13.]

Wave Mechanics

49. A standing wave in a string 42 cm long has a total of six nodes (including those at the ends). What is the wavelength, in centimeters, of this standing wave?
50. What is the length of a string that has a standing wave with four nodes (including those at the ends) and $\lambda = 17$ cm?
51. Calculate the wavelength of the electromagnetic radiation required to excite an electron from the ground state to the level with $n = 4$ in a one-dimensional box 5.0×10^1 pm long.
52. An electron in a one-dimensional box requires a wavelength of 618 nm to excite an electron from the $n = 2$ level to the $n = 4$ level. Calculate the length of the box.

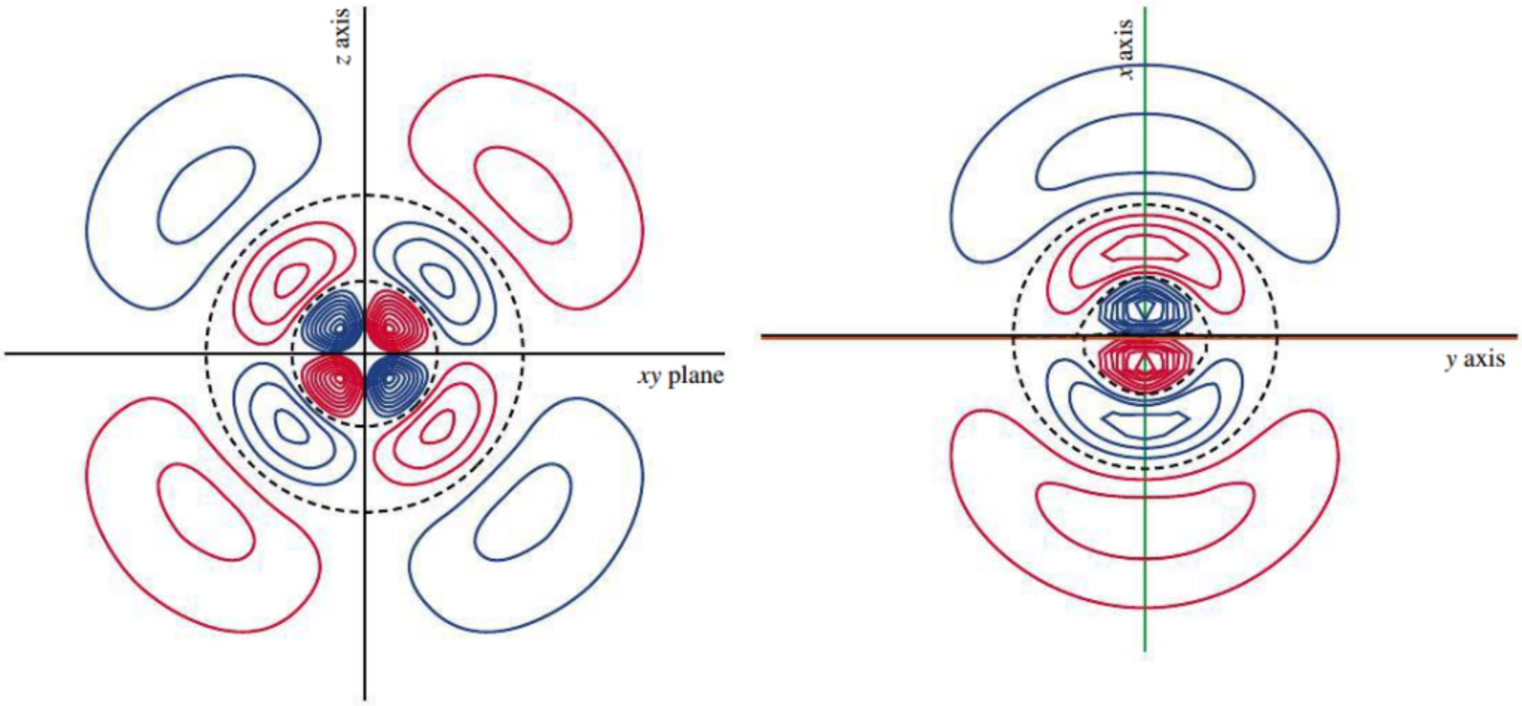
53. An electron in a 20.0 nm box is excited from the ground state into a higher energy state by absorbing a photon of wavelength 8.60×10^{-5} m. Determine the final energy state.
54. Calculate the wavelength of the electromagnetic radiation required to excite a proton from the ground state to the level with $n = 4$ in a one-dimensional box 5.0×10^1 pm long.
55. Describe some of the differences between the orbits of the Bohr atom and the orbitals of the wave mechanical atom. Are there any similarities?
56. The greatest probability of finding the electron in a small-volume element of the 1*s* orbital of the hydrogen atom is at the nucleus. Yet the most probable distance of the electron from the nucleus is 53 pm. How can you reconcile these two statements?

Quantum Numbers and Electron Orbitals

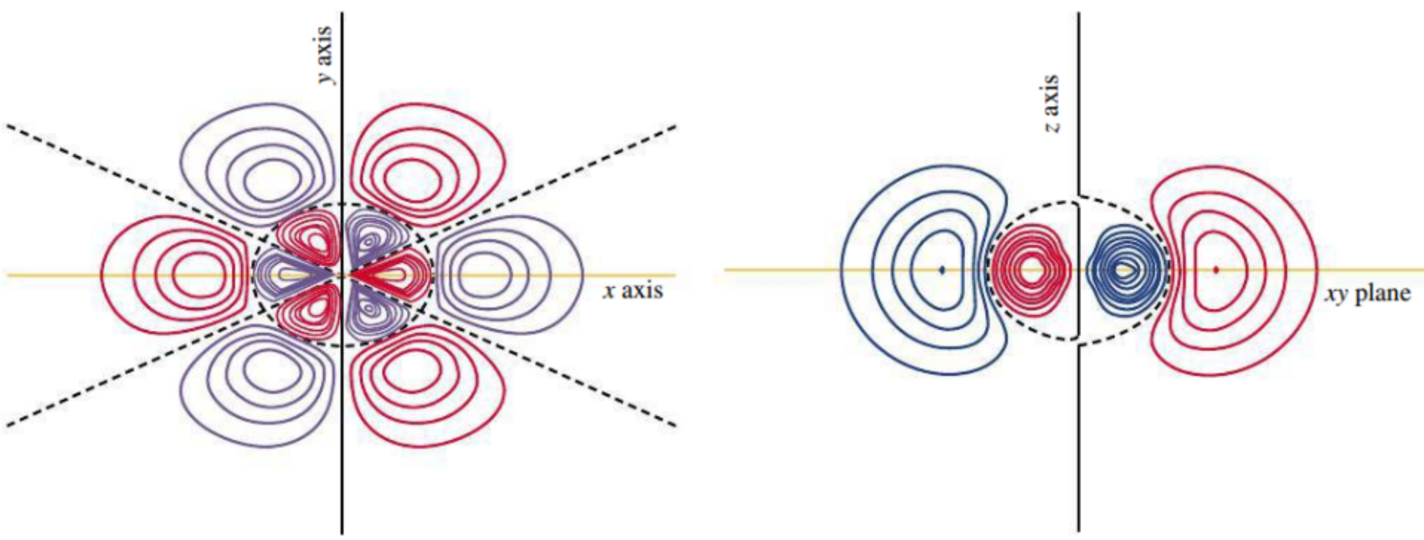
57. Select the correct answer and explain your reasoning. An electron having $n = 3$ and $m_\ell = 0$ **(a)** must have $m_s = +\frac{1}{2}$; **(b)** must have $\ell = 1$; **(c)** may have $\ell = 0, 1,$ or 2; **(d)** must have $\ell = 2$.
58. Write an acceptable value for each of the missing quantum numbers.
    (a) $n = 3, \ell = ?, m_\ell = 2, m_s = +\frac{1}{2}$
    (b) $n = ?, \ell = 2, m_\ell = 1, m_s = -\frac{1}{2}$
    (c) $n = 4, \ell = 2, m_\ell = 0, m_s = ?$
    (d) $n = ?, \ell = 0, m_\ell = ?, m_s = ?$
59. What type of orbital (i.e., 3*s*, 4*p*, ...) is designated by these quantum numbers?
    (a) $n = 5, \ell = 1, m_\ell = 0$
    (b) $n = 4, \ell = 2, m_\ell = -2$
    (c) $n = 2, \ell = 0, m_\ell = 0$
60. Which of the following statements is (are) correct for an electron with $n = 4$ and $m_\ell = 2$? Explain.
    (a) The electron is in the fourth principal shell.
    (b) The electron may be in a *d* orbital.
    (c) The electron may be in a *p* orbital.
    (d) The electron must have $m_s = +\frac{1}{2}$.
61. Concerning the electrons in the shells, subshells, and orbitals of an atom, how many can have
    (a) $n = 4, \ell = 2, m_\ell = 1$, and $m_s = +\frac{1}{2}$?
    (b) $n = 4, \ell = 2$, and $m_\ell = 1$?
    (c) $n = 4$ and $\ell = 2$?
    (d) $n = 4$?
    (e) $n = 4, \ell = 2$, and $m_s = +\frac{1}{2}$?
62. Concerning the concept of subshells and orbitals,
    (a) How many subshells are found in the $n = 3$ level?
    (b) What are the names of the subshells in the $n = 3$ level?
    (c) How many orbitals have the values $n = 4$ and $\ell = 3$?
    (d) How many orbitals have the values $n = 3, \ell = 2$, and $m_\ell = -2$?
    (e) What is the total number of orbitals in the $n = 4$ level?

The Shapes of Orbitals and Radial Probabilities

63. Calculate the finite value of r, in terms of a_0, at which the node occurs in the wave function of the 2*s* orbital of a hydrogen atom.
64. Calculate the finite value of r, in terms of a_0, at which the node occurs in the wave function of the 2*s* orbital of a Li^{2+} ion.
65. Show that the probability of finding a $2p_y$ electron in the *xz* plane is zero.
66. Show that the probability of finding a $3d_{xz}$ electron in the *xy* plane is zero.
67. Prepare a two-dimensional plot of $Y(\theta, \phi)$ for the p_y orbital in the *xy* plane.
68. Prepare a two-dimensional plot of $Y^2(\theta, \phi)$ for the p_y orbital in the *xy* plane.
69. Using a graphical method, show that in a hydrogen atom the radius at which there is a maximum probability of finding an electron is a_0 (53 pm).
70. Use a graphical method or some other means to show that in a Li^{2+} ion, the radius at which there is a maximum probability of finding an electron is $\frac{a_0}{3}$ (18 pm).
71. Identify the orbital that has **(a)** one radial node and one angular node; **(b)** no radial nodes and two angular nodes; **(c)** two radial nodes and three angular nodes.
72. Identify the orbital that has **(a)** two radial nodes and one angular node; **(b)** five radial nodes and zero angular nodes; **(c)** one radial node and four angular nodes.
73. A contour map for an atomic orbital of hydrogen is shown at the top of page 370 for the *xy* and *xz* planes. Identify the orbital.



74. A contour map for an atomic orbital of hydrogen is shown below for the *xy* and *xz* planes. Identify the type $(s, p, d, f, g \ldots)$ of orbital.

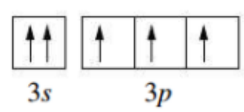


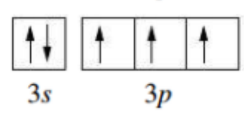
Electron Configurations

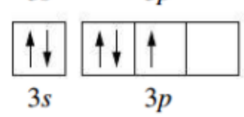
75. On the basis of the periodic table and rules for electron configurations, indicate the number of **(a)** 2*p* electrons in N; **(b)** 4*s* electrons in Rb; **(c)** 4*d* electrons in As; **(d)** 4*f* electrons in Au; **(e)** unpaired electrons in Pb; **(f)** elements in group 14 of the periodic table; **(g)** elements in the sixth period of the periodic table.

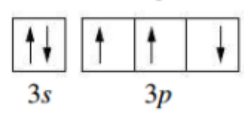
76. Based on the relationship between electron configurations and the periodic table, give the number of **(a)** outer-shell electrons in an atom of Sb; **(b)** electrons in the fourth principal electronic shell of Pt; **(c)** elements whose atoms have six outer-shell electrons; **(d)** unpaired electrons in an atom of Te; **(e)** transition elements in the sixth period.

77. Which of the following is the correct orbital diagram for the ground-state electron configuration of phosphorus? Explain what is wrong with each of the others.

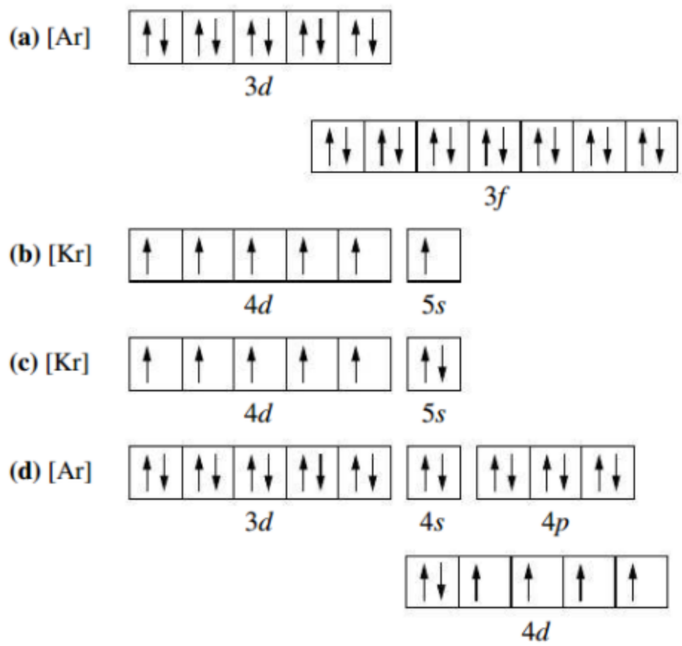
(a) [Ne] 

(b) [Ne] 

(c) [Ne] 

(d) [Ne] 

78. Which of the following is the correct orbital diagram for the ground-state electron configuration of molybdenum? Explain what is wrong with each of the others.

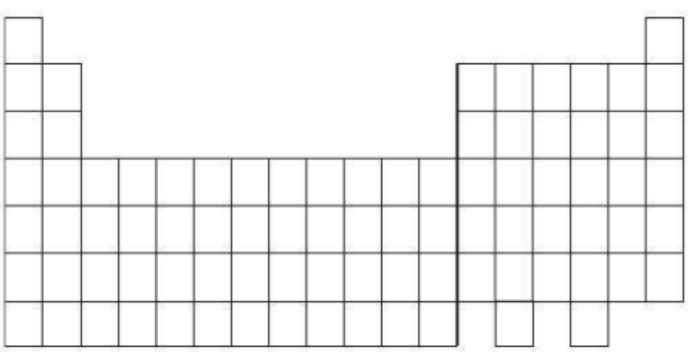


79. Use the basic rules for electron configurations to indicate the number of **(a)** unpaired electrons in an atom of P; **(b)** 3*d* electrons in an atom of Br; **(c)** 4*p* electrons in an atom of Ge; **(d)** 6*s* electrons in an atom of Ba; **(e)** 4*f* electrons in an atom of Au.

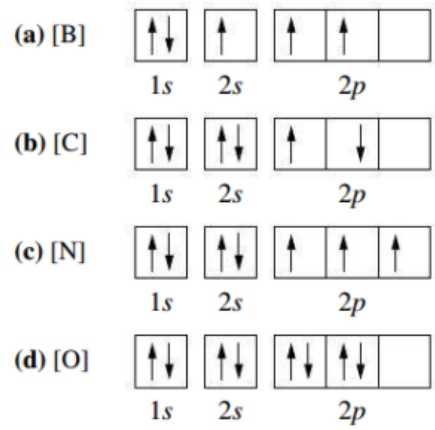
80. Use orbital diagrams to show the distribution of electrons among the orbitals in **(a)** the 4*p* subshell of Br; **(b)** the 3*d* subshell of Co^{2+}, given that the two electrons lost are 4*s*; **(c)** the 5*d* subshell of Pb.

81. The recently discovered element 114, Flerovium, should most closely resemble Pb.
(a) Write the electron configuration of Pb.
(b) Propose a plausible electron configuration for element 114.

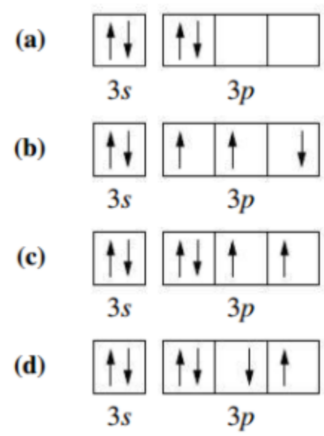
82. Without referring to any tables or listings in the text, mark an appropriate location in the blank periodic table provided for each of the following: **(a)** the fifth-period noble gas; **(b)** a sixth-period element whose atoms have three unpaired *p* electrons; **(c)** a *d*-block element having one 4*s* electron; **(d)** a *p*-block element that is a metal.



83. Which of the following electron configurations corresponds to the ground state and which to an excited state?



84. To what neutral atom do the following valence-shell configurations correspond? Indicate whether the configuration corresponds to the ground state or an excited state.



85. What is the expected ground-state electron configuration for each of the following elements? **(a)** mercury; **(b)** calcium; **(c)** polonium; **(d)** tin; **(e)** tantalum; **(f)** iodine.

86. What is the expected ground-state electron configuration for each of the following elements? **(a)** tellurium; **(b)** cesium; **(c)** selenium; **(d)** platinum; **(e)** osmium; **(f)** chromium.

87. The following electron configurations correspond to the ground states of certain elements. Name each element. **(a)** $[Rn]6d^27s^2$; **(b)** $[He]2s^22p^2$; **(c)** $[Ar]3d^34s^2$; **(d)** $[Kr]4d^{10}5s^25p^4$; **(e)** $[Xe]4f^26s^26p^1$.

88. The following electron configurations correspond to the ground states of certain elements. Name each element. **(a)** $[Ar]3d^{10}4s^24p^3$; **(b)** $[Ne]3s^23p^4$; **(c)** $[Ar]3d^14s^2$; **(d)** $[Kr]4d^65s^2$; **(e)** $[Xe]4f^{12}6s^2$.

Integrative and Advanced Exercises

89. Derive the Balmer and Rydberg equations from equation (8.6).

90. Electromagnetic radiation can be transmitted through a vacuum or empty space. Can heat be similarly transferred? Explain.

91. The *work function* is the energy that must be supplied to cause the release of an electron from a photoelectric material. The corresponding photon frequency is the threshold frequency. The higher the energy of the incident light, the more kinetic energy the electrons have in moving away from the surface. The work function for mercury is equivalent to 435 kJ/mol photons.
(a) Can the photoelectric effect be obtained with mercury by using visible light? Explain.
(b) What is the kinetic energy, in joules, of the ejected electrons when light of 215 nm strikes a mercury surface?
(c) What is the velocity, in meters per second, of the ejected electrons in part (b)?

92. Infrared lamps are used in cafeterias to keep food warm. How many photons per second are produced by an infrared lamp that consumes energy at the rate of 95 W and is 14% efficient in converting this energy to infrared radiation? Assume that the radiation has a wavelength of 1525 nm.

93. In 5.0 s, a 75 watt light source emits 9.91×10^{20} photons of a monochromatic (single wavelength) radiation. What is the color of the emitted light?

94. Determine the de Broglie wavelength of the electron ionized from a He^+ ion in its ground state using light of wavelength 208 nm.

95. The Pfund series of the hydrogen spectrum has as its *longest* wavelength component a line at 7400 nm. Describe the electron transitions that produce this series. That is, give a quantum number that is common to this series.

96. Between which two levels of the hydrogen atom must an electron fall to produce light of wavelength 1876 nm?

97. Use appropriate relationships from the chapter to determine the wavelength of the line in the emission spectrum of He^+ produced by an electron transition from $n = 5$ to $n = 2$.

98. Draw an energy-level diagram that represents all the possible lines in the emission spectrum of hydrogen atoms produced by electron transitions, in one or more steps, from $n = 5$ to $n = 1$.

99. An atom in which just one of the outer-shell electrons is excited to a very high quantum level n is called a "high Rydberg" atom. In some ways, all these atoms resemble a hydrogen atom with its electron in a high n level. Explain why you might expect this to be the case.

100. If all other rules governing electron configurations were valid, what would be the electron configuration of cesium if **(a)** there were *three* possibilities for electron spin; **(b)** the quantum number ℓ could have the value n?

101. Ozone, O_3, absorbs ultraviolet radiation and dissociates into O_2 molecules and O atoms: $O_3 + h\nu \longrightarrow O_2 + O$. A 1.00 L sample of air at 22 °C and 748 mmHg contains 0.25 ppm of O_3. How much energy, in joules, must be absorbed if all the O_3 molecules in the sample of air are to dissociate? Assume that each photon absorbed causes one O_3 molecule to dissociate, and that the wavelength of the radiation is 254 nm.

102. Radio signals from *Voyager 1* in the 1970s were broadcast at a frequency of 8.4 GHz. On Earth, this radiation was received by an antenna able to detect signals as weak as 4×10^{-21} W. How many photons per second does this detection limit represent?

103. Certain metal compounds impart colors to flames—sodium compounds, yellow; lithium, red; barium, green—and flame tests can be used to detect these elements. **(a)** At a flame temperature of 800 °C, can collisions between gaseous atoms with average kinetic energies supply the energies required for the emission of visible light? **(b)** If not, how do you account for the excitation energy?

104. The angular momentum of an electron in the Bohr hydrogen atom is mur, where m is the mass of the electron, u, its velocity, and r, the radius of the Bohr orbit. The angular momentum can have only the values $nh/2\pi$, where n is an integer (the number of the Bohr orbit). Show that the *circumferences* of the various Bohr orbits are integral multiples of the de Broglie wavelengths of the electron treated as a matter wave.

105. A molecule of chlorine can be dissociated into atoms by absorbing a photon of sufficiently high energy. Any excess energy is translated into kinetic energy as the atoms recoil from one another. If a molecule of chlorine at rest absorbs a photon of 300 nm wavelength, what will be the velocity of the two recoiling atoms? Assume that the excess energy is equally divided between the two atoms. The bond energy of Cl_2 is 242.6 kJ mol^{-1}.

106. Refer to the Integrative Example. Determine whether or not $n = 138$ is a bound state. If it is, what sort of state is it? What is the radius of the orbit and how many revolutions per second does the electron make about the nucleus?

107. Using the relationships given in Table 8.2, find the finite values of r, in terms of a_0, of the nodes for a 3s orbital.

108. Use a graphical method or some other means to determine the radius at which the probability of finding a 2s orbital is maximum.

109. Using the relationships in Table 8.2, prepare a sketch of the 95% probability surface of a $4p_x$ orbital.

110. Given that the volume of a sphere is $V = (4/3)\pi r^3$, show that the volume, dV, of a thin spherical shell of radius r and thickness dr is $4\pi r^2 dr$. [Hint: This exercise can be done easily and elegantly by using calculus. It can also be done without using calculus by expressing the volume of a thin spherical shell as a volume difference, $(4/3)\pi(r + dr)^3 - (4/3)\pi r^3$, and simplifying the expression. To obtain the correct result by using the latter approach, you must remember that dr represents a very small distance.]

111. In the ground state of a hydrogen atom, what is the probability of finding an electron anywhere in a sphere of radius **(a)** a_0, or **(b)** $2a_0$? [*Hint:* This exercise requires calculus.]

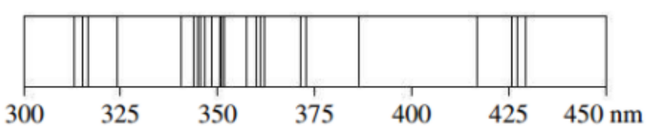
112. When atoms in excited states collide with unexcited atoms they can transfer their excitation energy to those atoms. The most efficient energy transfer occurs when the excitation energy matches the energy of an excited state in the unexcited atom. Assuming that we have a collection of excited hydrogen atoms in the $2s^1$ excited state, are there any transitions of He^+ that could be most efficiently excited by the hydrogen atoms?

Feature Problems

Principal Spectral Lines of Some Period 4 Transition Elements (nm)

V	306.64	309.31	318.40	318.54	327.11	437.92	438.47	439.00
Cr	357.87	359.35	360.53	361.56	425.44	427.48	428.97	520.45
Mn	257.61	259.37	279.48	279.83	403.08	403.31	403.45	
Fe	344.06	358.12	372.00	373.49	385.99			
Ni	341.48	344.63	345.85	346.17	349.30	351.51	352.45	361.94

113. We have noted that an emission spectrum is a kind of "atomic fingerprint." The various steels are alloys of iron and carbon, usually containing one or more other metals. Based on the principal lines of their atomic spectra, which of the metals in the table above are likely to be present in a steel sample whose hypothetical emission spectrum is pictured? Is it likely that still other metals are present in the sample? Explain.



▲ **Hypothetical emission spectrum**
In a real spectrum, the photographic images of the spectral lines would differ in depth and thickness depending on the strengths of the emissions producing them. Some of the spectral lines would not be seen because of their faintness.

114. Balmer seems to have deduced his formula for the visible spectrum of hydrogen just by manipulating numbers. A more common scientific procedure is to graph experimental data and then find a mathematical equation to describe the graph. Show that equation (8.4) describes a straight line. Indicate which variables must be plotted, and determine the numerical values of the slope and intercept of this line. Use data from Figure 8-12 to confirm that the four lines in the visible spectrum of hydrogen fall on the straight-line graph.

115. The Rydberg–Ritz combination principle is an empirical relationship proposed by Walter Ritz in 1908 to explain the relationship among spectral lines of the hydrogen atom. The principle states that the spectral lines of the hydrogen atom include frequencies that are either the sum or the difference of the frequencies of two other lines. This principle is obvious to us, because we now know that spectra arise from transitions between energy levels, and the energy of a transition is proportional to the frequency.

The frequencies of the first ten lines of an emission spectrum of hydrogen are given in the table at the bottom of this page. In this problem, use ideas from this chapter to identify the transitions involved, and apply the Rydberg–Ritz combination principle to calculate the frequencies of other lines in the spectrum of hydrogen.

(a) Use Balmer's original equation, $\lambda = Bm^2/(m^2 - n^2)$, with $B = 346.6$ nm, to develop an expression for the frequency $\nu_{m,n}$ of a line involving a transition from level m to level n, where $m > n$.

(b) Use the expression you derived in (a) to calculate the expected ratio of the frequencies of the first two lines in each of the Lyman, Balmer, and Paschen series: $\nu_{2,1}/\nu_{3,1}$ (for the Lyman series); $\nu_{3,2}/\nu_{3,1}$ (for the Balmer series); and $\nu_{4,3}/\nu_{5,3}$ (for the Paschen series). Compare your calculated ratios to the observed ratio $2.465263/2.921793 = 0.843750$ to identify the series as the Lyman, Balmer, or Paschen series. For each line in the series, specify the transition (quantum numbers) involved. Use a diagram, such as that given in Figure 8-13, to summarize your results.

(c) Without performing any calculations, and starting from the Rydberg formula, equation (8.4), show that $\nu_{2,1} + \nu_{3,2} = \nu_{3,1}$, and thus, $\nu_{3,1} - \nu_{2,1} = \nu_{3,2}$. This is an illustration of the Rydberg–Ritz combination principle: the frequency of a spectral line is equal to the sum or difference of frequencies of other lines.

(d) Use the Rydberg–Ritz combination principle to determine, if possible, the frequencies for the other two series named in (b). [*Hint*: The diagram you drew in part (b) might help you identify the appropriate combinations of frequencies.]

(e) Identify the transition associated with a line of frequency $2.422405 \times 10^{13}\ s^{-1}$, one line in a series of lines discovered in 1953 by C. J. Humphreys.

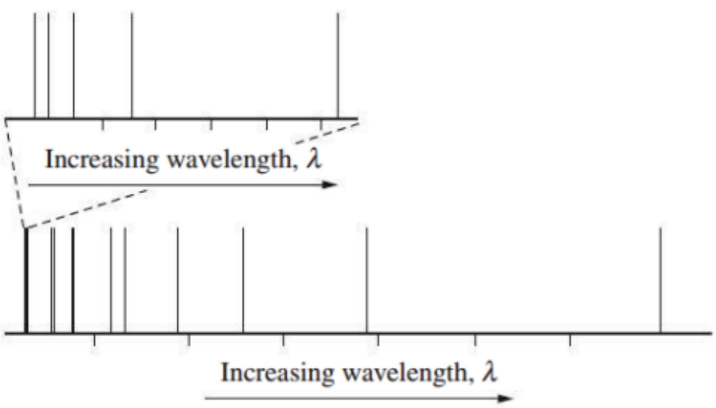
Frequencies ($\times 10^{15}\ s^{-1}$) of the First Ten Lines in an Emission Spectrum of Hydrogen

2.465263	2.921793	3.081578	3.155536	3.195711	3.219935	3.235657	3.246436	3.254147	3.259851

116. Emission and absorption spectra of the hydrogen atom exhibit line spectra characteristic of quantized systems. In an absorption experiment, a sample of hydrogen atoms is irradiated with light with wavelengths ranging from 100 to 1000 nm. In an emission spectrum experiment, the hydrogen atoms are excited through an energy source that provides a range of energies from 1230 to 1240 kJ mol^{-1} to the atoms. Assume that the absorption spectrum is obtained at room temperature, when all atoms are in the ground state.
(a) Calculate the position of the lines in the absorption spectrum.
(b) Calculate the position of the lines in the emission spectrum.
(c) Compare the line spectra observed in the two experiments. In particular, will the number of lines observed be the same?

117. Diffraction of radiation takes place when the distance between the scattering centers is comparable to the wavelength of the radiation.
(a) What velocity must helium atoms possess to be diffracted by a film of silver atoms in which the spacing is 100 pm?
(b) Electrons accelerated through a certain potential are diffracted by a thin film of gold. Would you expect a beam of protons accelerated through the same potential to be diffracted when it strikes the film of gold? If not, what would you expect to see instead?

118. The emission spectrum below is for hydrogen atoms in the gas phase. The spectrum is of the first few emission lines from principal quantum number 6 down to all possible lower levels.



As discussed in Are You Wondering 8-6, not all possible de-excitations are possible; the transitions are governed by *selection rules*. Using the selection rules from Are You Wondering 8-6, identify the transitions, in terms of the types of orbital (s, p, d, f), involved, that are observed in the spectrum shown above.

In the presence of a magnetic field, the lines split into more lines according to the magnetic quantum number. Using the selection rule for m_ℓ, identify the line(s) in the spectrum that split(s) into the greatest number of lines.

119. (This exercise requires calculus.) In this exercise, use ideas from this chapter to develop the solution to the particle-in-a-box problem. We begin by writing the Schrödinger equation for a particle of mass m moving in one dimension:

$$-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

The equation above is the one-dimensional version of equation (8.15). For a particle in a box, there are no forces acting on the particle (except at the boundaries of the box), and so the potential energy, V, of the particle is constant. Without loss of generality, we can assume that the value of V is zero in the box.
(a) Show that, for a particle in a box, the equation above can be written in the form $d^2\psi/dx^2 = -a^2\psi^2$, where $a^2 = 8\pi^2 mE/h^2$.
(b) Show that $\psi = A\sin(ax)$ is a solution to the equation $d^2\psi/dx^2 = -a^2\psi^2$, by differentiating ψ twice with respect to x.
(c) Following the same approach you used in (b), show that $\psi = A\cos(ax)$ is also a solution to the equation $d^2\psi/dx^2 = -a^2\psi^2$.
(d) For a particle in a box, the probability density, ψ^2, must be zero at $x = 0$. To ensure that this is so, we must have $\psi = 0$ at $x = 0$. This requirement is called a *boundary condition*. Use this boundary condition to establish that the wave function for a particle in the box must be of the form $\psi = A\sin(ax)$, not $\psi = A\cos(ax)$.
(e) Using the result from (d), show that the boundary condition $\psi = 0$ at $x = L$ requires that $aL = n\pi$ so that the wave function may be written as $\psi = A\sin(n\pi x/L)$. [*Hint*: $\sin z = 0$ when z is an integer multiple of π.]
(f) Using the result $aL = n\pi$ from (e) and the fact that $a^2 = 8\pi^2 mE/h^2$, as established in (a), show that $E = n^2h^2/(8mL^2)$.
(g) We know for sure (the probability is 1) that the particle must be somewhere between $x = 0$ and $x = L$. Mathematically, we express this condition as $\int_0^L \psi^2 dx = 1$. It is called a *normalization condition*. Using the result $\psi = A\sin(n\pi x/L)$ from (e), show that the normalization condition requires that $A = \sqrt{2/L}$. [*Hint*: The integral $\int_0^L \sin^2(n\pi x/L)dx$ has the value $L/2$.]

Working through this problem will walk you through the basic procedure for solving a quantum mechanical problem: Writing down the Schrödinger equation for the system of interest (part a); establishing the general form of the solutions (parts b and c); and using appropriate boundary conditions and a normalization condition to determine not only the specific form of ψ but also the allowed values for E (parts d–g).

120. In 1913, Danish physicist Neils Bohr proposed a theory for the hydrogen atom in which the electron is imagined to be moving around a stationary nucleus in one of many possible circular orbits, each of which has a fixed energy and radius. By using classical physics and imposing a quantization condition, Bohr derived equations for the energies and radii of these orbits. Derive Bohr's equations by using the following steps. Note: Steps (a), (b), and (d) are based on fundamental ideas from classical physics. Step (c) introduces a new idea, a quantization condition, that causes the energies and radii of the orbits to take on certain well-defined values.
(a) Write down an expression for the total energy, E, of the electron (mass m_e) moving in a circular orbit of radius r with speed u. [*Hint*: See Appendix B, specifically equations (B.12) and (B.14).]
(b) Use the condition that the force of attraction between the electron and proton has the same magnitude as the centrifugal force, $m_e u^2/r$, to show that the total energy of the electron is $E = -e^2/(8\pi\epsilon_0 r)$. [*Hint*: See equation (B.13) in Appendix B.]
(c) Use the information from (b), along with the quantization condition that the orbital angular momentum, $\ell = mur$, of the electron in the nth orbit ($n = 1, 2, 3$, etc.) is $n \times h/(2\pi)$ to show that the energy and radius of the nth orbit are, respectively, $E_n = -R_\infty/n^2$ and $r_n = a_0 \times n^2$, with $R_\infty = m_e e^4/(8\epsilon_0^2 h^2) = 2.17987 \times 10^{-18}$ J and $a_0 = h^2\epsilon_0/(\pi m_e e^2)$. $= 5.29177 \times 10^{-11}$ m. [*Hint*: Use the conditions given in (b) and (c) to eliminate both u and r from the expression given in (b) for E.]
(d) Convert $R_\infty = 2.17987 \times 10^{-18}$ J to $R_H = 2.17869 \times 10^{-18}$ J by replacing m_e in the expression for R_∞ with the so-called reduced mass $\mu = m_e m_p/(m_e + m_p)$, where $m_p = 1.67262 \times 10^{-27}$ kg is the mass of the proton. The conversion of R_∞ to R_H corrects for the fact that, because the proton is not infinitely massive compared to the electron, the nucleus is not actually stationary.

Self-Assessment Exercises

121. In your own words, define the following terms or symbols: **(a)** λ; **(b)** ν; **(c)** h; **(d)** ψ; **(e)** principal quantum number, n.

122. Briefly describe each of the following ideas or phenomena: **(a)** atomic (line) spectrum; **(b)** photoelectric effect; **(c)** matter wave; **(d)** Heisenberg uncertainty principle; **(e)** electron spin; **(f)** Pauli exclusion principle; **(g)** Hund's rule; **(h)** orbital diagram; **(i)** electron charge density; **(j)** radial electron density.

123. Explain the important distinctions between each pair of terms: **(a)** frequency and wavelength; **(b)** ultraviolet and infrared light; **(c)** continuous and discontinuous spectra; **(d)** traveling and standing waves; **(e)** quantum number and orbital; **(f)** *spdf* notation and orbital diagram; **(g)** *s* block and *p* block; **(h)** main group and transition element; **(i)** the ground state and excited state of a hydrogen atom.

124. Describe two ways in which the orbitals of multielectron atoms resemble hydrogen orbitals and two ways in which they differ from hydrogen orbitals.

125. Explain the phrase *effective nuclear charge*. How is this related to the shielding effect?

126. With the help of sketches, explain the difference between a p_x, p_y, and p_z orbital.

127. With the help of sketches, explain the difference between a $2p_z$ and $3p_z$ orbital.

128. If traveling at equal speeds, which of the following matter waves has the longest wavelength? Explain. **(a)** electron; **(b)** proton; **(c)** neutron; **(d)** α particle (He^{2+}).

129. For electromagnetic radiation transmitted through a vacuum, state whether each of the following properties is directly proportional to, inversely proportional to, or independent of the frequency: **(a)** velocity; **(b)** wavelength; **(c)** energy per mole. Explain.

130. Construct a concept map representing the ideas of quantum mechanics.

131. Construct a concept map representing the atomic orbitals of hydrogen and their properties.

132. Construct a concept map for the configurations of multielectron atoms.