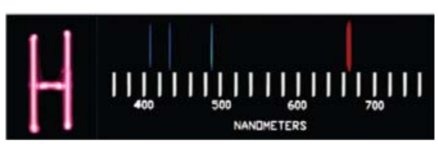
SUMMARY

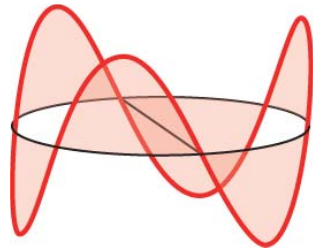
LO1 Visible light is one form of **electromagnetic radiation**. Like the other forms, it has wave properties described by characteristic **wavelengths (λ)** and **frequencies (ν)**, and it travels through a vacuum at the speed of light, $c = 2.998 \times 10^8$ m/s. (Section 3.1 (Chapter03-01.xhtml))

LO2 According to quantum theory there are discrete energy levels in atoms, which means they absorb or emit discrete amounts of energy called **photons**. Planck used these energy **quanta** to explain the radiation emitted by incandescent objects, and Einstein used them to explain the **photoelectric effect**. The radiant energy required to dislodge a photoelectron from a metal surface is called the **work function (Φ)** of the metal. (Section 3.3 (Chapter03-03.xhtml))

LO3 Free atoms in flames and in gas-discharge tubes produce **atomic emission spectra** consisting of narrow bright lines at characteristic wavelengths. When continuous radiation passes through atomic gases, absorption produces the dark lines of **atomic absorption spectra**. The bright lines of an element's emission spectrum and the dark lines of its absorption spectrum are at the same wavelengths. Balmer derived an equation that accounted for the bright lines in the visible emission spectrum of hydrogen and that predicted the existence of bright lines in the UV and IR regions of hydrogen's emission spectrum. Bohr proposed that the lines predicted by Balmer were related to energy levels occupied by electrons inside the hydrogen atom. A **ground-state** atom or ion has all its electrons in the lowest possible energy levels. Other arrangements are called **excited states**. **Electron transitions** from higher to lower energy levels in an atom cause the atom to emit particular frequencies of radiation; absorption of radiation of the same frequencies accompanies electron transitions from the same lower to higher energy levels. (Sections 3.2 (Chapter03-02.xhtml) and 3.4 (Chapter03-04.xhtml))

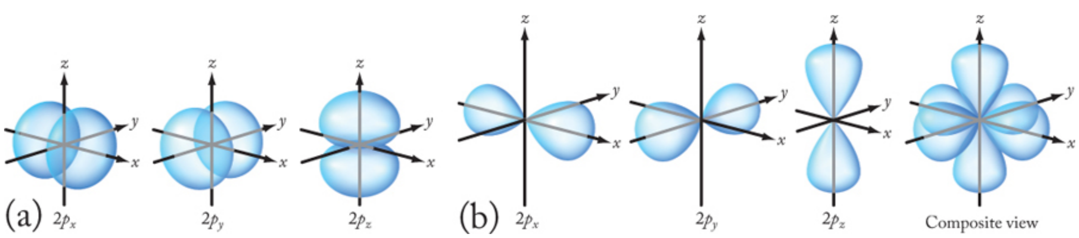


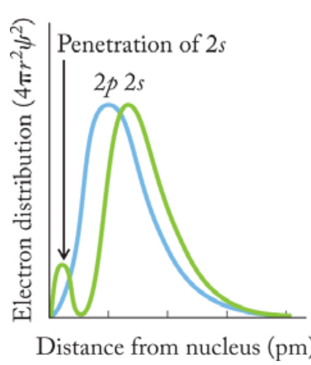
LO4 De Broglie proposed that electrons in atoms as well as all other moving particles have wave properties and can be treated as **matter waves**. He explained the stability of the electron orbits in the Bohr hydrogen atom in terms of **standing waves**: the circumferences of the allowed orbits



had to be whole-number multiples of the hydrogen electron's characteristic wavelength. The **Heisenberg uncertainty principle** states that both the position and momentum of an electron cannot be precisely known at the same time. (Section 3.5 (Chapter03-05.xhtml))

LO5 The solutions to **Schrödinger's wave equation** are mathematical expressions called **wave functions** **(ψ)** where ψ^2 defines the regions within an atom, called **orbitals**, where electron densities are high. Each orbital has a unique set of three **quantum numbers**: **principal quantum number** n, which defines orbital size and energy level; **angular momentum quantum number** ℓ, which defines orbital shape; and **magnetic quantum number** m_ℓ, which defines orbital orientation in space. Two electrons in the same orbital have opposite **spin quantum numbers** m_s: $+\frac{1}{2}$ and $-\frac{1}{2}$. The **Pauli exclusion principle** states that no two electrons in an atom can have the same four values of n, ℓ, m_ℓ, and m_s. Orbitals have characteristic three-dimensional sizes, shapes, and orientations that are depicted by boundary–surface representations. All *s* orbitals are spheres that increase in size with increasing values of n. Each of the three *p* orbitals in any $n \geq 2$ shell has two lobes aligned along the x-, y-, or z-axis. The five *d* orbitals in $n \geq 3$ shells come in two forms: four are shaped like a four-leaf clover, and the fifth has two lobes oriented along the z-axis and a torus surrounding the middle of the two lobes. (Sections 3.6 (Chapter03-06.xhtml) and 3.7 (Chapter03-07.xhtml))





LO6 According to the **aufbau principle**, electrons fill the lowest-energy atomic orbitals of a ground-state atom first. **Effective nuclear charge (Z_{eff})** is the net nuclear charge felt by outer-shell electrons when they are shielded from the full nuclear charge by inner-shell electrons. Greater Z_{eff} means lower energy. An **electron configuration** is a set of numbers and letters expressing the number of electrons in each occupied orbital in an atom. The electrons in the outermost occupied shell of an

atom are **valence electrons**. They are lost, gained, or shared in chemical reactions. All the orbitals of a given *p*, *d*, or *f* subshell are said to be degenerate, which means they all have the same energy. **Hund's rule** states that in any set of degenerate orbitals, each orbital must contain one electron before any orbital in the set can accept a second electron. We use **orbital diagrams** to show in detail how electrons are distributed among orbitals, which are represented by boxes. Atoms of group 1 and group 2 elements tend to lose electrons and form 1+ and 2+ cations, respectively. In so doing they become **isoelectronic** with the noble gas in the preceding period. Atoms in groups 16 and 17 tend to gain electrons to form 2− and 1− anions, respectively, thereby becoming isoelectronic with the noble gas at the end of their period. When transition metals form ions, the electrons are removed from the shell of highest *n* until the charge on the ion is achieved. (Sections 3.8 (Chapter03-08.xhtml) and 3.9 (Chapter03-09.xhtml))

LO7 The sizes of atoms increase with increasing atomic number in a group of elements because valence-shell electrons with higher *n* values are, on average, farther from the nucleus. However, the sizes of atoms decrease with increasing atomic number across a row of elements because the valence electrons experience higher effective nuclear charges. Anions are larger than their parent atoms due to additional electron–electron repulsion, but cations are smaller than their parent atoms—sometimes much smaller when all the electrons in the valence shell are lost. (Section 3.10 (Chapter03-10.xhtml))

LO8 **Ionization energy (IE)** is the amount of energy needed to remove 1 mole of electrons from 1 mole of atoms or ions in the gas phase. IE values generally increase with increasing effective nuclear charge across a row and decrease with increasing atomic number down a group in the periodic table. The energy differences between the different shells and subshells of atoms are reflected in the values of successive ionization energies (IE_1, IE_2, IE_3, ...). **Electron affinity (EA)** is the energy change that occurs when 1 mole of electrons combines with 1 mole of atoms or ions in the gas phase. The EA values of many main group elements are negative, indicating that energy is released when they acquire electrons. (Sections 3.11 (Chapter03-11.xhtml) and 3.12 (Chapter03-12.xhtml))

PARTICULATE **PREVIEW WRAP-UP**

1. Model (a) shows electrons moving around the nucleus of atom, in

keeping with the Rutherford model.

2. Concentric circles suggest electrons orbit the nucleus at different distances from it.
3. Model (a) suggests that electrons orbit the nuclei of atoms in concentric circular orbits; model (b) shows a more probabilistic picture of electron distribution, with regions of high electron densities at different distances from the nucleus.

PROBLEM-SOLVING SUMMARY

Type of Problem	Concepts and Equations		Sample Exercises
Calculating frequency from wavelength	$\nu = \frac{c}{\lambda}$	(3.2)	**3.1 (Chapter03-01.xhtml#ATOMS3-1)**
Calculating the energy of a photon	$E = \frac{hc}{\lambda}$	(3.4)	**3.2 (Chapter03-03.xhtml#ATOMS3-2)**
Using the work function	$\Phi = h\nu_0 = h\nu - KE_{electron}$	(3.5, 3.6)	**3.3 (Chapter03-03.xhtml#ATOMS3-3)**
Calculating the wavelength of a line in the hydrogen spectrum	$\lambda(\text{nm}) = \left(\frac{364.56\, m^2}{m^2 - n^2}\right)$	(3.7)	**3.4 (Chapter03-04.xhtml#ATOMS3-4)**
	$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^{\ 2}} - \frac{1}{n_2^{\ 2}}\right)$	(3.8)	
Calculating the energy of a transition in a hydrogen atom	$\Delta E = -2.178 \times 10^{-18}\ \text{J}\left(\frac{1}{n_{final}^{\ 2}} - \frac{1}{n_{initial}^{\ 2}}\right)$	(3.11)	**3.5 (Chapter03-04.xhtml#ATOMS3-5)**
Calculating the wavelength of a particle in motion	$\lambda = \frac{h}{mu}$	(3.12)	**3.6 (Chapter03-05.xhtml#ATOMS3-6)**
Calculating Heisenberg uncertainties	$\Delta x \cdot m\Delta u \geq \frac{h}{4\pi}$	(3.14)	**3.7 (Chapter03-05.xhtml#ATOMS3-7)**

Type of Problem	Concepts and Equations	Sample Exercises
Identifying the subshells and orbitals in an energy level and valid quantum number sets	n is the shell number; ℓ defines both the subshell and the type of orbital; an orbital has a unique combination of allowed n, ℓ, and m_ℓ values; ℓ is any integer from 0 to $(n - 1)$; m_ℓ is any integer from $-\ell$ to $+\ell$, including zero; m_s equals $+\frac{1}{2}$ or $-\frac{1}{2}$.	**3.8 (Chapter03-06.xhtml#ATOMS3-8), 3.9 (Chapter03-06.xhtml#ATOMS3-9)**
Writing electron configurations of atoms and ions	Orbitals fill up in the following sequence: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^{10}$, $6p^6$, $7s^2$, $5f^{14}$, $6d^{10}$, $7p^6$, where superscripts represent the maximum numbers of electrons. Orbitals in electron configurations are arranged based on increasing value of n. In forming transition metal ions, electrons in orbitals with the highest n value are removed first; there is enhanced stability in half-filled and filled d subshells.	**3.10 (Chapter03-08.xhtml#ATOMS3-10)–3.12 (Chapter03-09.xhtml#ATOMS3-12)**
Ordering atoms and ions by size	In general, sizes decrease left to right across a row and increase down a column of the periodic table; cations are smaller and anions are larger than their parent atoms.	**3.13 (Chapter03-10.xhtml#ATOMS3-13)**
Recognizing trends in ionization energies	First ionization energies increase across a row and decrease down a column.	**3.14 (Chapter03-11.xhtml#ATOMS3-14)**

VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

3.1. Which of the elements highlighted in Figure P3.1 consists of atoms with

a. a single *s* electron in their outermost shells? (More than one answer is possible.)

b. filled sets of *s* and *p* orbitals in their outermost shells?

c. filled sets of *d* orbitals?

d. half-filled sets of *d* orbitals?

e. two *s* electrons in their outermost shells?

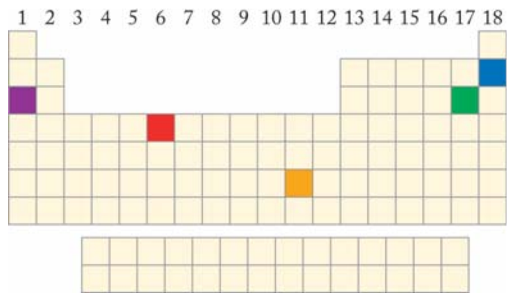


FIGURE P3.1

3.2. Which of the highlighted elements in Figure P3.1 has the greatest number of unpaired electrons per ground-state atom?

3.3. Which of the highlighted elements in Figure P3.1 form common monatomic ions that are (a) larger than their parent atoms and (b) smaller than their parent atoms?

3.4. Which of the highlighted elements in Figure P3.4 forms monatomic ions by

a. losing an *s* electron?

b. losing two *s* electrons?

c. losing two *s* electrons and a *d* electron?

d. adding an electron to a *p* orbital?

e. adding electrons to two *p* orbitals?

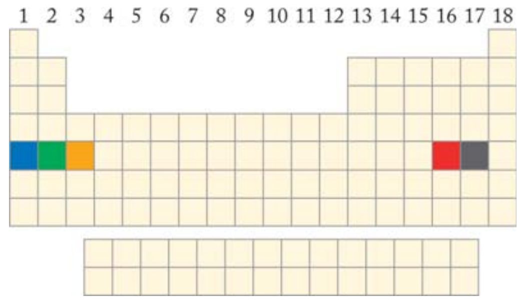


FIGURE P3.4

3.5. Which of the highlighted elements in Figure P3.4 form(s) common monatomic ions that are smaller than their parent atoms?

3.6. Rank the highlighted elements in Figure P3.4 based on (a) increasing size of their atoms and (b) increasing first ionization energy.

3.7. Suppose three beams of radiation are focused on a negatively charged metallic surface. The beam represented by the A waves in Figure P3.7 causes photoelectrons to be emitted from the surface. Which of the following statements accurately describes the abilities of the beams represented by waves B and C to also produce photoelectrons from this surface?

a. Neither the B nor the C wave can produce photoelectrons.

b. Both the B and C waves should produce photoelectrons if the sources of the waves are bright enough.

c. The B wave may or may not produce photoelectrons, but the C wave surely will.

d. The C wave may or may not produce photoelectrons, but the B wave surely will.

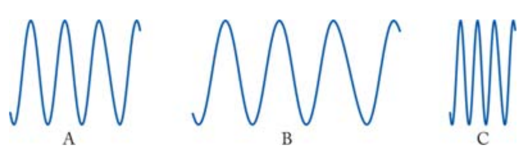


FIGURE P3.7

3.8. A group 2 element (M) and a group 17 element (X) have nearly the same atomic radius, as shown by the relative sizes of the blue and red spheres representing their atoms in Figure P3.8. Are the two elements in the same row of the periodic table? If not, which one is in the higher row?

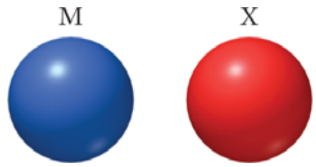


FIGURE P3.8

3.9. Which of the pairs of spheres in Figure P3.9 best depicts the relative sizes of the cation and anion formed by atoms of the elements M and X from Figure P3.8?

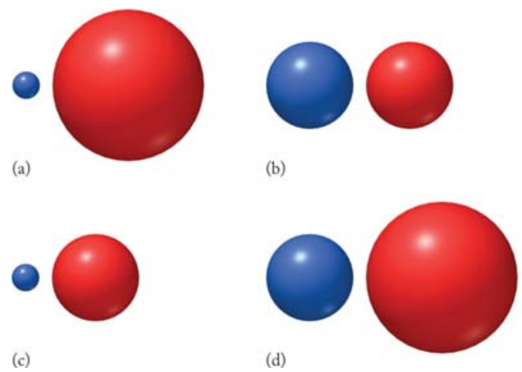


FIGURE P3.9

3.10. The arrows A, B, and C in Figure P3.10 show three transitions among the n = 3, 4, and 5 energy levels in a single-electron ion.

a. Assuming the transitions are accompanied by the loss or gain of electromagnetic energy, do the arrows depict absorption or emission of radiation?

b. The spectral lines of the transitions are, in order of increasing wavelength, 80, 117, and 253 nm. Which wavelength goes with which arrow?

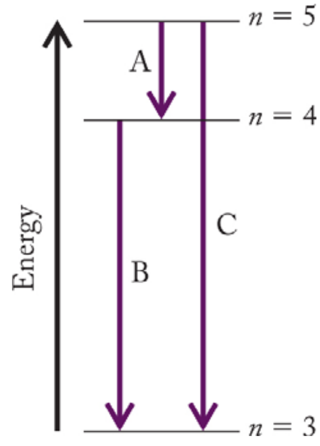


FIGURE P3.10

3.11. **Quantum Dot Televisions** Some flat panel displays and TV sets use quantum dots (nanocrystals of cadmium selenide and cadmium sulfide) to generate colors. The colors of the quantum dots in Figure P3.11 are determined by particle size and composition.

a. In which of the containers do the quantum dots emit photons with the greatest energies?

b. In which of the containers do the quantum dots emit photons with the longest wavelengths?

c. In which of the container are the quantum dots larger than in any of the others. (Hint: see Figure 3.14.)

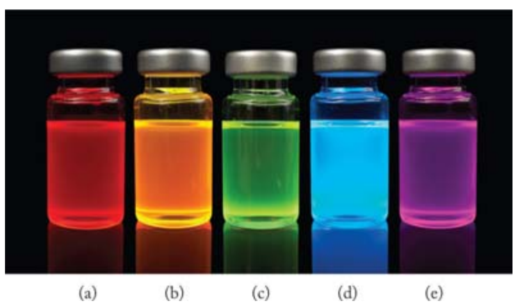


FIGURE P3.11

3.12. Use representations [A] through [I] in Figure P3.12 to answer questions a–f.

a. Between [A] and [I], which valence-shell *s* electron experiences the stronger attraction to its nucleus?

b. Which representations depict the loss of an electron and which depict the gain of an electron?

c. Which representation depicts quantized processes?

d. Which representations depict the probabilistic nature of quantum mechanics?

e. What processes are represented in [C], [D], [F], and [G]?

f. Which representation is consistent with zero probability of an electron being in the nucleus of an atom?

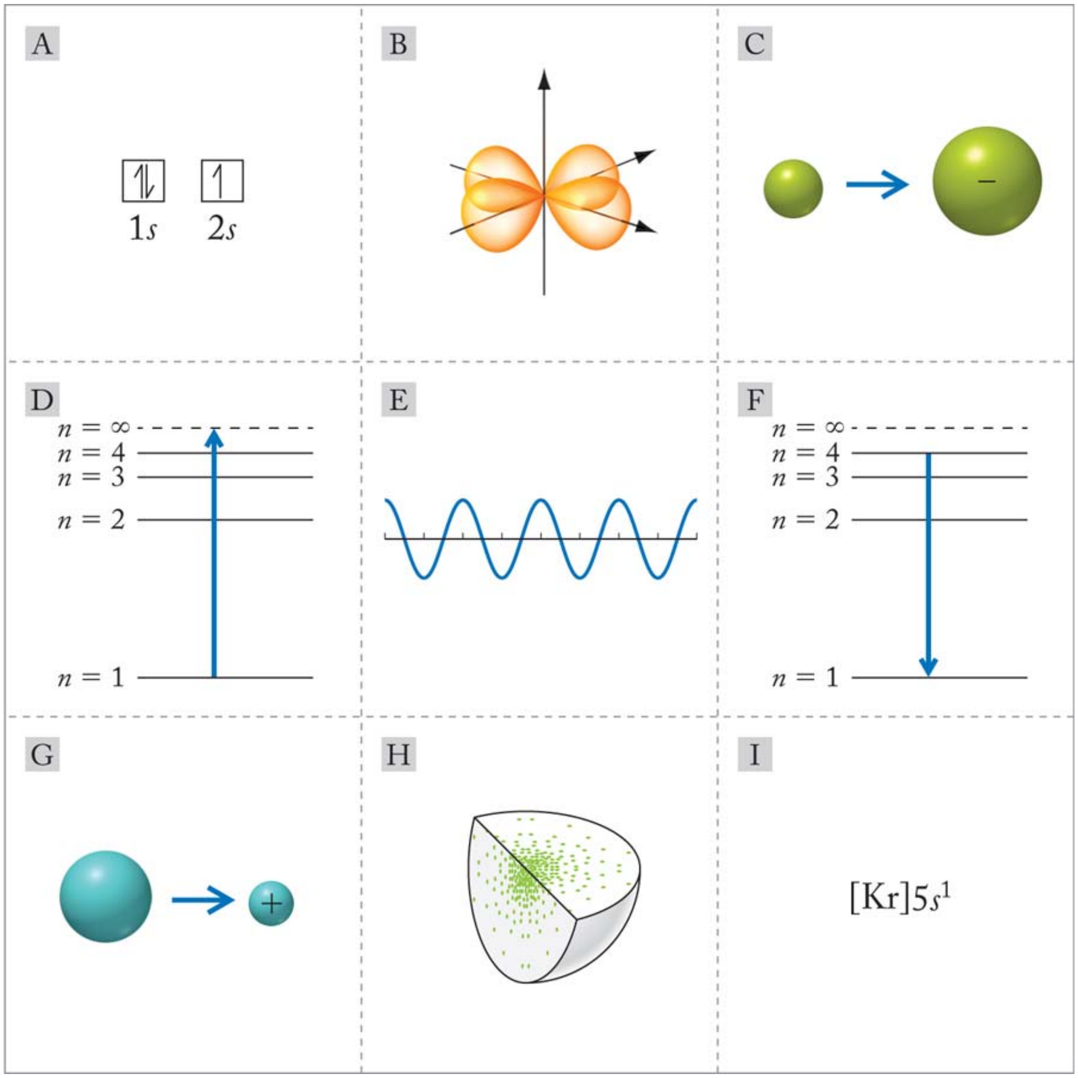


FIGURE P3.12

QUESTIONS AND PROBLEMS

Waves of Light

Concept Review

3.13. Why are the various forms of radiant energy called *electromagnetic* radiation?

3.14. Explain with a sketch why the frequencies of long-wavelength waves of electromagnetic radiation are lower than those of short-wavelength waves.

3.15. **Dental X-Rays** When X-ray images are taken of your teeth and gums in the dentist's office, your body is covered with a lead shield. Explain the need for this precaution.

3.16. **UV Radiation and Skin Cancer** Ultraviolet radiation causes skin damage that may lead to cancer, but exposure to infrared radiation does not seem to cause skin cancer. Why?

3.17. **Lava** As hot molten lava cools, it begins to solidify and no longer glows in the dark. Does this mean it no longer emits any kind of electromagnetic radiation? If not, what kind of radiation is it likely to emit once it is no longer "red" hot?

*3.18. If light consists of waves, why don't objects look "wavy" to us?

Problems

3.19. **Mercury Vapor Lamps** Lights containing mercury vapor (Figure P3.19) are used in sports arenas, factories, and streetlights. The wavelength of a bright line in the visible emission spectrum of mercury vapor is 546.1 nm. What is the frequency of this radiation? Does emission at this wavelength contribute to the greenish glow observed in a mercury vapor lamp?

FIGURE P3.19

3.20. **Submarine Communications** The Russian and American navies developed extremely low-frequency communications networks to send messages to submerged submarines. The frequency of the carrier wave of the Russian network was 82 Hz, while the Americans used 76 Hz.

a. What was the ratio of the wavelengths of the Russian network to the American network?

b. To calculate the actual underwater wavelength of the transmissions in either network, what additional information would you need?

3.21. **Broadcast Frequencies** FM radio stations broadcast in a band of frequencies between 88 and 108 megahertz (MHz). Calculate the wavelengths corresponding to the broadcast frequencies of the following radio stations:

a. KRNU (Lincoln, NE), 90.3 MHz

b. WBRU (Providence, RI), 95.5 MHz

c. WYLD (New Orleans, LA), 98.5 MHz

d. WAAF (Boston, MA), 107.3 MHz

3.22. **Remote Keyless Systems** The doors of most automobiles can be unlocked by pushing a button on a key chain (Figure P3.22). These devices operate on frequencies in the MHz range. Calculate the wavelength of (a) the 315 MHz radiation emitted by remote keyless systems in North American cars and (b) the 434 MHz radiation used to unlock the doors of European and Asian cars. Where do these frequencies lie in the electromagnetic spectrum?

FIGURE P3.22

3.23. In 1895 German physicist Wilhelm Röntgen discovered X-rays. He also discovered that X-rays emitted by different metals have different wavelengths. Which X-rays have the higher frequency, those emitted by (a) Cu (λ = 0.154 nm) or (b) iron (λ = 194 pm)?

3.24. **Garage Door Openers** The remote control units for garage door openers transmit electromagnetic radiation. Before 2005 they operated on a frequency of 390 MHz, but since 2005, the operating wavelength has been 952 mm. Which radiation has the lower frequency, the pre-2005 or the post-2005 devices?

3.25. **Speed of Light** How long does it take light to reach Earth from the sun when the distance between them is 149.6 million kilometers?

3.26. **Exploration of the Solar System** The *Voyager 1* spacecraft was launched in 1977 to explore the outer solar system and interstellar space. By December 2012, it was 1.85×10^{10} km from Earth and still sending and receiving data. How long did it take a signal from Earth to reach *Voyager 1* over this distance?

Atomic Spectra

Concept Review

3.27. Describe the similarities and differences in the atomic emission and absorption spectra of an element.

3.28. Are the Fraunhofer lines the result of atomic emission or atomic absorption?

3.29. How did the study of the atomic emission spectra of the elements lead to the identification of the origins of the Fraunhofer lines in sunlight?

*3.30. How would the appearance of the Fraunhofer lines in the solar spectrum be changed if sunlight were passed through a flame containing high-temperature sodium atoms?

Particles of Light: Quantum Theory

Concept Review

3.31. What is a quantum?

3.32. What is a photon?

3.33. If a piece of tungsten metal were heated to 1000 K, would it emit light in the dark? If so, what color?

3.34. **Incandescent Lightbulbs** A variable power supply is connected to an incandescent lightbulb. At the lowest power setting, the bulb feels warm to the touch but produces no light. At medium power, the lightbulb filament emits a red glow. At the highest power, the lightbulb emits white light. Explain this emission pattern.

Problems

3.35. **Tanning Booths** Prolonged exposure to ultraviolet radiation in tanning booths significantly increases the risk of skin cancer. What is the energy of a photon of UV light with a wavelength of 3.00×10^{-7} m?

3.36. **Remote Control** Most remote controllers for AV equipment emit radiation with the wavelength profile shown in Figure P3.36. What type of radiation is shown and what is the energy of a photon at the peak wavelength?

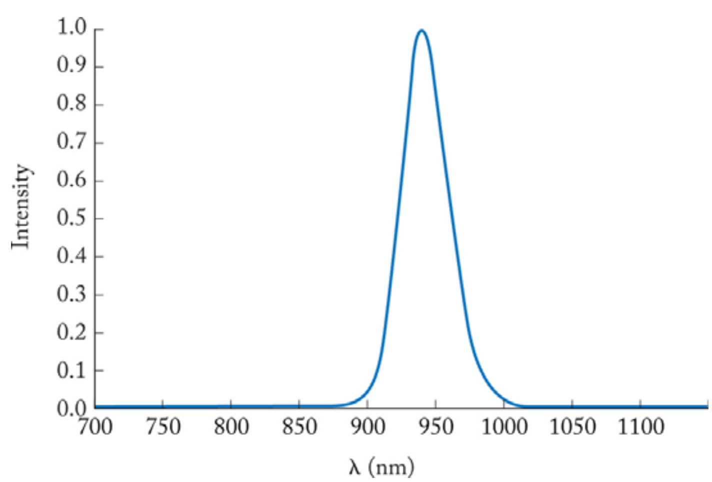


FIGURE P3.36

3.37. Which of the following have quantized values? Explain your selections.

a. The elevation of the treads of a moving escalator

b. The elevations at which the doors of an elevator open

c. The speed of an automobile

3.38. Which of the following have quantized values? Explain your selections.

a. The pitch of a note played on a slide trombone

b. The pitch of a note played on a flute

c. The wavelengths of light produced by the heating elements in a toaster

d. The wind speed at the top of Mt. Everest

3.39. When a piece of gold foil is irradiated with UV radiation (λ = 132 nm), electrons are ejected with a kinetic energy of 7.34×10^{-19} J. What is the work function of gold?

3.40. The first ionization energy of a gas-phase atom of a particular element is 6.24×10^{-19} J. What is the maximum wavelength of electromagnetic radiation that could ionize this atom?

3.41. **Solar Power** Photovoltaic cells convert solar energy into electricity. Could germanium ($\Phi = 7.21 \times 10^{-19}$ J) be used to convert visible sunlight to electricity? Assume that most of the electromagnetic energy from the sun in the visible region is at wavelengths shorter than 600 nm.

3.42. With reference to Problem 3.41, could tin ($\Phi = 6.20 \times 10^{-19}$ J) be used to construct solar cells?

***3.43.** Pieces of potassium ($\Phi = 3.68 \times 10^{-19}$ J) and sodium ($\Phi = 4.41 \times 10^{-19}$ J) metal are exposed to radiation with a wavelength of 300 nm. Which metal emits electrons with the greater velocity? What is the velocity of the electrons?

3.44. Titanium ($\Phi = 6.94 \times 10^{-19}$ J) and silicon ($\Phi = 7.24 \times 10^{-19}$ J) surfaces are irradiated with UV radiation with a wavelength of 250 nm. Which surface emits electrons with the longer wavelength? What is the wavelength of the electrons emitted by the titanium surface?

3.45. **Red Lasers** The power of a red laser (λ = 630 nm) is 1.00 watt (abbreviated W, where 1 W = 1 J/s). How many photons per second does the laser emit?

*3.46. **Starlight** The energy density of starlight in interstellar space is 10^{-15} J/m^3. If the average wavelength of starlight is 500 nm, what is the corresponding density of photons per cubic meter of space?

The Hydrogen Spectrum and the Bohr Model

Concept Review

3.47. Why is the Balmer equation considered a special case of the Rydberg equation?

3.48. How does the value of n of an orbit in the Bohr model of hydrogen relate to the energy of an electron in that orbit?

3.49. Does the electromagnetic energy emitted by an excited-state H atom depend on the individual values of n_1 and n_2 or only on the difference between them $(n_1 - n_2)$?

3.50. Explain the difference between a ground-state H atom and an excited-state H atom.

3.51. Without calculating any wavelength values, predict which of the following four electron transitions in the hydrogen atom is associated with radiation having the shortest wavelength.

a. $n = 1 \rightarrow n = 2$

b. $n = 2 \rightarrow n = 3$

c. $n = 3 \rightarrow n = 4$

d. $n = 4 \rightarrow n = 5$

3.52. Without calculating any frequency values, rank the following transitions in the hydrogen atom in order of increasing frequency of the electromagnetic radiation that could produce them.

a. $n = 4 \rightarrow n = 6$

b. $n = 6 \rightarrow n = 8$

c. $n = 9 \rightarrow n = 11$

d. $n = 11 \rightarrow n = 13$

3.53. Electron transitions from $n = 2$ to $n = 3$, 4, 5, or 6 in hydrogen atoms are responsible for some of the Fraunhofer lines in the sun's spectrum. Are there any Fraunhofer lines due to transitions that start from the ground-state hydrogen atoms?

3.54. In the visible portion of the atomic emission spectrum of hydrogen, are there any bright lines due to electron transitions to the ground state?

3.55. Balmer observed a hydrogen emission line for the transition from $n = 6$ to $n = 2$, but not for the transition from $n = 7$ to $n = 2$. Why?

*3.56. In what ways should the emission spectra of H and He^+ be alike, and in what ways should they be different?

Problems

3.57. What is the wavelength of the photons emitted by hydrogen atoms when they undergo $n = 4 \rightarrow n = 3$ transitions? In which region of the electromagnetic spectrum does this radiation occur?

3.58. What is the frequency of the photons emitted by hydrogen atoms when they undergo $n = 5 \rightarrow n = 3$ transitions? In which region of the electromagnetic spectrum does this radiation occur?

***3.59.** The energies of photons emitted by one-electron atoms and ions fit the equation

$$E = (2.18 \times 10^{-18}\ \text{J})Z^2\left(\frac{1}{n_1^{\ 2}} - \frac{1}{n_2^{\ 2}}\right)$$

where Z is the atomic number, n_1 and n_2 are positive integers, and $n_2 > n_1$. Is the emission associated with the $n = 2 \rightarrow n = 1$ transition in a one-electron ion ever in the visible region? Why or why not?

*3.60. Can transitions from higher energy states to the $n = 2$ state in He^+ ever produce visible light? If so, for what values of n_2? Refer to the equation in Problem 3.59.

***3.61.** By absorbing different wavelengths of light, an electron in a hydrogen atom undergoes a transition from $n = 2$ to $n = 3$ and then from $n = 3$ to $n = 4$.

a. Are the wavelengths for the two transitions additive—that is, does $\lambda_{2\rightarrow4} = \lambda_{2\rightarrow3} + \lambda_{3\rightarrow4}$?

b. Are the energies of the two transitions additive—that is, does $E_{2\rightarrow4} = E_{2\rightarrow3} + E_{3\rightarrow4}$?

*3.62. The hydrogen atomic emission spectrum includes a UV line with a wavelength of 92.3 nm.

a. Is this line associated with a transition between different excited states or between an excited state and the ground state?

b. What is the energy of the longest-wavelength photon that a ground-state hydrogen atom can absorb?

Electrons as Waves

Concept Review

3.63. Identify the symbols in the de Broglie relation, $\lambda = h/mu$, and explain how the relation links the properties of a particle to those of a wave.

3.64. Why do matter waves *not* add significantly to the challenge of hitting a baseball thrown at 99 mph (44 m/s)?

3.65. Would the density or shape of an object have an effect on its de Broglie wavelength?

3.66. How does de Broglie's hypothesis that electrons behave like waves explain the stability of the electron orbits in a hydrogen atom?

3.67. Two objects are moving at the same speed. Which (if any) of the following statements about them are true?

a. The de Broglie wavelength of the heavier object is longer than that of the lighter one.

b. If one object has twice as much mass as the other, then its wavelength is one-half the wavelength of the other.

c. Doubling the speed of one of the objects will have the same effect on its wavelength as doubling its mass.

3.68. Which (if any) of the following statements about the frequency of a particle is true?

a. Heavy, fast-moving objects have lower frequencies than those of lighter, faster-moving objects.

b. Only very light particles can have high frequencies.

c. Doubling the mass of an object and halving its speed result in no change in its frequency.

Problems

3.69. Calculate the wavelengths of the following objects:

a. A muon (a subatomic particle with a mass of 1.884×10^{-28} kg) traveling at 325 m/s

b. Electrons ($m_e = 9.10938 \times 10^{-31}$ kg) moving at 4.05×10^{6} m/s in an electron microscope

c. An 82 kg sprinter running at 9.9 m/s

d. Earth (mass = 6.0×10^{24} kg) moving through space at 3.0×10^{4} m/s

3.70. How rapidly would each of the following particles be moving if they all had the same wavelength as a photon of red light (λ = 750 nm)?

a. An electron of mass 9.10938×10^{-28} g

b. A proton of mass 1.67262×10^{-24} g

c. A neutron of mass 1.67493×10^{-24} g

d. An α particle of mass 6.64×10^{-24} g

3.71. **Particles in a Cyclotron** The first cyclotron was built in 1930 at the University of California, Berkeley, and was used to accelerate molecular ions of hydrogen, H_2^+, to a velocity of 4×10^{6} m/s. (Modern cyclotrons can accelerate particles to nearly the speed of light.) If the relative uncertainty in the velocity of the H_2^+ ion was 3%, what was the uncertainty of its position?

3.72. **Radiation Therapy** An effective treatment for some cancerous tumors involves irradiation with “fast” neutrons. The neutrons from one treatment source have an average velocity of 3.1×10^{7} m/s. If the velocities of individual neutrons are known to within 2% of that value, what is the uncertainty in the position of one of them?

Quantum Numbers and the Sizes and Shapes of Atomic Orbitals

Concept Review

3.73. How does the concept of an orbit in the Bohr model of the hydrogen atom differ from the concept of an orbital in quantum theory?

3.74. What properties of an orbital are defined by each of the three quantum numbers n, ℓ, and m_ℓ?

3.75. How many quantum numbers are needed to identify an orbital?

3.76. How many quantum numbers are needed to identify an electron in an atom?

Problems

3.77. How many orbitals are there in an atom with each of the following principal quantum numbers? (a) 1; (b) 2; (c) 3; (d) 4; (e) 5

3.78. How many orbitals are there in an atom with the following combinations of quantum numbers?

a. $n = 3, \ell = 2$

b. $n = 3, \ell = 1$

c. $n = 4, \ell = 2, m_\ell = 2$

3.79. What are the possible values of quantum number ℓ when $n = 4$?

3.80. What are the possible values of m_ℓ when $\ell = 2$?

3.81. Which subshell corresponds to each of the following sets of quantum numbers?

a. $n = 6, \ell = 0$

b. $n = 3, \ell = 2$

c. $n = 2, \ell = 1$

d. $n = 5, \ell = 4$

3.82. Which subshell corresponds to each of the following sets of quantum numbers?

a. $n = 7, \ell = 1$

b. $n = 4, \ell = 2$

c. $n = 3, \ell = 0$

d. $n = 6, \ell = 5$

3.83. How many electrons could occupy orbitals with the following quantum numbers?

a. $n = 2, \ell = 0$

b. $n = 3, \ell = 1, m_\ell = 0$

c. $n = 4, \ell = 2$

d. $n = 1, \ell = 0, m_\ell = 0$

3.84. How many electrons could occupy orbitals with the following quantum numbers?

a. $n = 3$, $\ell = 2$

b. $n = 5$, $\ell = 4$

c. $n = 3$, $\ell = 0$

d. $n = 4$, $\ell = 1$, $m_\ell = 1$

3.85. Which of the following combinations of quantum numbers are allowed?

a. $n = 1$, $\ell = 1$, $m_\ell = 0$, $m_s = +\frac{1}{2}$

b. $n = 3$, $\ell = 0$, $m_\ell = 0$, $m_s = -\frac{1}{2}$

c. $n = 1$, $\ell = 0$, $m_\ell = 1$, $m_s = -\frac{1}{2}$

d. $n = 2$, $\ell = 1$, $m_\ell = 2$, $m_s = +\frac{1}{2}$

3.86. Which of the following combinations of quantum numbers are allowed?

a. $n = 3$, $\ell = 2$, $m_\ell = 0$, $m_s = -\frac{1}{2}$

b. $n = 5$, $\ell = 4$, $m_\ell = 4$, $m_s = +\frac{1}{2}$

c. $n = 3$, $\ell = 0$, $m_\ell = 1$, $m_s = +\frac{1}{2}$

d. $n = 4$, $\ell = 4$, $m_\ell = 1$, $m_s = -\frac{1}{2}$

The Periodic Table and Filling Orbitals; Electron Configurations of Ions

Concept Review

3.87. What is meant when two or more orbitals are said to be degenerate?

3.88. Explain how the electron configurations of the group 2 elements are linked to their location in the periodic table.

3.89. How do we know from examining the periodic table that the 4*s* orbital is filled before the 3*d* orbitals?

3.90. Why do so many transition metals form ions with a 2+ charge?

Problems

3.91. Identify the subshells with the following combinations of quantum numbers and arrange them in order of increasing energy in a multielectron atom:

a. $n = 3$, $\ell = 2$

b. $n = 7$, $\ell = 3$

c. $n = 3$, $\ell = 0$

d. $n = 4$, $\ell = 1$

3.92. Identify the subshells with the following combinations of quantum numbers and arrange them in order of increasing energy in an atom of gold:

a. $n = 2, \ell = 1$

b. $n = 5, \ell = 0$

c. $n = 3, \ell = 2$

d. $n = 4, \ell = 3$

3.93. What are the electron configurations of Li^+, Ca, F^-, Mg^{2+}, and Al^{3+}?

3.94. Which species in Problem 3.93 are isoelectronic with Ne?

3.95. What are the condensed electron configurations of K, K^+, Ba, Ti^{4+}, and Ni?

3.96. In what way are the electron configurations of C, Si, and Ge similar?

3.97. Which of the following orbital diagrams in Figure P3.97 best describes the ground-state electron configuration of Mn? Which one is the orbital diagram for Mn^{2+}?

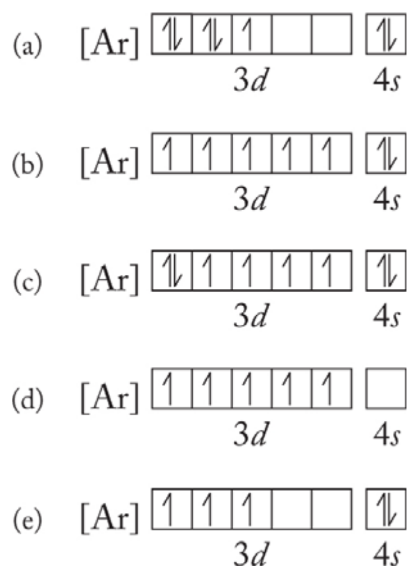


FIGURE P3.97

3.98. Which of the following orbital diagrams in Figure P3.98 best describes the ground-state electron configuration of Pb, Pb^{2+}, and Pb^{4+}?

FIGURE P3.98

3.99. How many unpaired electrons are there in the following ground-state atoms and ions? (a) N; (b) O; (c) P^{3-}; (d) Na^{+}

3.100. How many unpaired electrons are there in the following ground-state atoms and ions? (a) Mn; (b) Ag^{+}; (c) Cu^{3+}; (d) Ti^{2+}

3.101. Identify the element whose condensed electron configuration is $[Ar]3d^24s^2$. How many unpaired electrons are there in the ground state of this atom?

3.102. Identify the element whose condensed electron configuration is $[Ne]3s^23p^3$. How many unpaired electrons are there in the ground state of this atom?

3.103. Which monatomic ion has a charge of 1– and the condensed electron configuration $[Ne]3s^23p^6$? How many unpaired electrons are there in the ground state of this ion?

3.104. Which monatomic ion has a charge of 1+ and the electron configuration $[Kr]4d^{10}5s^2$? How many unpaired electrons are there in the ground state of this ion?

3.105. Which of the following electron configurations represent an excited state?

a. $[He]2s^12p^5$
b. $[Kr]4d^{10}5s^25p^1$
c. $[Ar]3d^{10}4s^24p^5$
d. $[Ne]3s^23p^24s^1$

3.106. Which of the following condensed electron configurations represent an excited state? Could any represent *ground-state* electron configurations of 2+ ions?

a. $[Ar]4s^24p^1$

b. $[Ar]3d^{10}$

c. $[Kr]4d^{10}5s^1$

d. $[Ar]3s^23p^63d^1$

3.107. In which subshell are the highest-energy electrons in a ground-state atom of the isotope ^{131}I? Are the electron configurations of ^{131}I and ^{127}I the same?

*3.108. No known element contains electrons in an $\ell = 4$ subshell in the ground state. If such an element were synthesized, what is the minimum atomic number it would have to have?

The Sizes of Atoms and Ions

Concept Review

3.109. Sodium atoms are much larger than chlorine atoms, but sodium ions are much smaller than chloride ions. Why?

3.110. Why does atomic size tend to decrease with increasing atomic number across a row of the periodic table?

Problems

3.111. Using only the periodic table as a guide, arrange each set of particles by size, largest to smallest:

a. Al, P, Cl, Ar

b. C, Si, Ge, Sn

c. Li^+, Li, Na, K

d. F, Ne, Cl, Cl^-

3.112. Using only the periodic table, arrange each set of particles by size, largest to smallest:

a. Li, B, N, Ne

b. Mg, K, Ca, Sr

c. Rb^+, Sr^{2+}, Cs, Fr

d. S^{2-}, Cl^-, Ar, K^+

Ionization Energies

Concept Review

3.113. How do ionization energies change with increasing atomic number (a) down a group of elements in the periodic table and (b) from left to right across a row?

3.114. Explain the differences in ionization energy between (a) He and Li; (b) Li and Be; (c) Be and B; (d) N and O.

3.115. How does the wavelength of light required to ionize a gas-phase atom change with increasing atomic number down a group in the periodic table?

3.116. Why is the first ionization energy of Al less than that of Mg *and* less than that of Si?

Problems

3.117. Without referring to Figure 3.37, arrange the following groups of elements in order of increasing first ionization energy.

a. F, Cl, Br, I

b. Li, Be, Na, Mg

c. N, O, F, Ne

3.118. Without referring to Figure 3.37, arrange the following groups of elements in order of increasing first ionization energy.

a. Mg, Ca, Sr, Ba

b. He, Ne, Ar, Kr

c. P, S, Cl, Ar

Electron Affinities

Concept Review

3.119. An electron affinity (EA) value that is negative indicates that the free atoms of an element are higher in energy than the 1− anions they form by acquiring electrons. Does this mean that all of the elements with negative EA values exist in nature as anions? Give some examples to support your answer.

3.120. The electron affinities of the group 17 elements are all negative values, but the EA values of the group 18 noble gases are all positive. Explain this difference.

3.121. The electron affinities of the group 17 elements increase with increasing atomic number. Suggest a reason for this trend.

3.122. Ionization energies generally increase with increasing atomic number across the second row of the periodic table, but electron affinities generally decrease. Explain the opposing trends.

Additional Problems

***3.123.** **Colors of Fireworks** Barium compounds are a source of the green colors in many fireworks displays.

a. What is the ground-state electron configuration for Ba?

b. The lowest-energy excited state of Ba has the electron configuration [Xe]$5d^1 6s^1$. What are the possible quantum numbers n, ℓ, and m_ℓ of a $5d$ electron?

c. The excited state in part b is 1.79×10^{-19} J above the ground state. Could emission from this excited state account for the green color in fireworks?

d. Another Ba excited state has the electron configuration [Xe]$6s^1 6p^1$. Its energy is 3.59×10^{-19} J above the ground state. Could transitions from this state to the ground state account for the green color in fireworks?

*3.124. When an atom absorbs an X-ray of sufficient energy, one of its $2s$ electrons may be ejected, creating a hole that can be spontaneously filled when an electron in a higher-energy orbital—$2p$, for example—falls into it. A photon of electromagnetic radiation with an energy that matches the energy lost in the $2p \rightarrow 2s$ transition is emitted. Predict how the wavelengths of $2p \rightarrow 2s$ photons would differ between (a) different elements in the fourth row of the periodic table and (b) different elements in the same column (for example, between the noble gases from Ne to Rn).

***3.125.** Two helium ions (He^+) in the $n = 3$ excited state emit photons of radiation as they return to the ground state. One ion does so in a single transition from $n = 3$ to $n = 1$. The other does so in two steps: $n = 3$ to $n = 2$ and then $n = 2$ to $n = 1$. Which of the following statements about the two pathways is true?

a. The sum of the energies lost in the two-step process is the same as the energy lost in the single transition from $n = 3$ to $n = 1$.

b. The sum of the wavelengths of the two photons emitted in the two-step process is equal to the wavelength of the single photon emitted in the transition from $n = 3$ to $n = 1$.

c. The sum of the frequencies of the two photons emitted in the two-step process is equal to the frequency of the single photon emitted in the transition from $n = 3$ to $n = 1$.

d. The wavelength of the photon emitted by the He^+ ion in the $n = 3$ to $n = 1$ transition is shorter than the wavelength of a photon emitted by a H atom in an $n = 3$ to $n = 1$ transition.

3.126. Use your knowledge of electron configurations to explain the following observations:

a. Silver tends to form ions with a charge of 1+, but the elements to the left and right of silver in the periodic table tend to form ions with 2+ charges.

b. The heavier group 13 elements (Ga, In, and Tl) tend to form ions with charges of 1+ or 3+ but not 2+.

c. The heavier elements of group 14 (Sn and Pb) and group 4 (Ti, Zr, and Hf) tend to form ions with charges of 2+ or 4+.

3.127. Should the same trend in the first ionization energies for elements with atomic numbers Z = 31 through Z = 36 be observed for the second ionization energies of the same elements? Explain why or why not.

3.128. **Chemistry of Photo-Gray Glasses** "Photo-gray" lenses for eyeglasses darken in bright sunshine because the lenses contain tiny, transparent AgCl crystals. Exposure to light removes electrons from Cl^- ions, forming a chlorine atom in an excited state (indicated here by the asterisk):

$$Cl^- \xrightarrow{h\nu} Cl^* + e^-$$

The electrons are transferred to Ag^+ ions, forming silver metal:

$$Ag^+ + e^- \rightarrow Ag$$

Silver metal is reflective, producing the photo-gray color. How might substitution of AgBr for AgCl affect the light sensitivity of photo-gray lenses? In answering this question, consider whether more energy or less is needed to remove an electron from a Br^- ion than from a Cl^- ion.

3.129. Tin (in group 14) forms both Sn^{2+} and Sn^{4+} ions, but magnesium (in group 2) forms only Mg^{2+} ions.

a. Write condensed ground-state electron configurations for the ions Sn^{2+}, Sn^{4+}, and Mg^{2+}.

b. Which neutral atoms have ground-state electron configurations identical to Sn^{2+} and Mg^{2+}?

c. Which 2+ ion is isoelectronic with Sn^{4+}?

3.130. **Fog Lamp Technology** Sodium fog lamps and street lamps contain gas-phase Na atoms and Na^+ ions. Sodium atoms emit yellow-orange light at 589 nm. Do Na^+ ions emit the same yellow-orange light? Explain why or why not.

3.131. Effective nuclear charge (Z_{eff}) is related to atomic number (Z) by a factor called the shielding parameter (σ) according to the equation $Z_{eff} = Z - \sigma$.

a. Calculate Z_{eff} for the outermost s electrons of Ne and Ar, given that σ = 4.24 for Ne and σ = 11.24 for Ar.

b. Explain why the shielding parameter is much greater for Ar than for Ne.

3.132. **Millikan's Experiment** In his oil-drop experiment, Millikan used X-rays to ionize N_2 gas. Electrons lost by N_2 were absorbed by oil droplets. If the wavelength of the X-ray was 154 pm, could he also have filled his device with argon gas, which has an ionization energy of 1521 kJ/mol?

***3.133.** How can an electron get from one lobe of a p orbital to the other without going through the point of zero electron density between them?

3.134. Einstein did not fully accept the uncertainty principle, remarking that "He [God] does not play dice." What do you think Einstein meant? Niels Bohr allegedly responded by saying, "Albert, stop telling God what to do." What do you think Bohr meant?

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