Problems

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•, ••, •••: Problems of increasing difficulty. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **BIO**: Biosciences problems.

DISCUSSION QUESTIONS

Q41.1 Particle A is described by the wave function $\psi(x, y, z)$. Particle B is described by the wave function $\psi(x, y, z)e^{i\phi}$, where ϕ is a real constant. How does the probability of finding particle A within a volume dV around a certain point in space compare with the probability of finding particle B within this same volume?

Q41.2 What are the most significant differences between the Bohr model of the hydrogen atom and the Schrödinger analysis? What are the similarities?

Q41.3 For a body orbiting the sun, such as a planet, comet, or asteroid, is there any restriction on the z-component of its orbital angular momentum such as there is with the z-component of the electron's orbital angular momentum in hydrogen? Explain.

Q41.4 Why is the analysis of the helium atom much more complex than that of the hydrogen atom, either in a Bohr type of model or using the Schrödinger equation?

Q41.5 The Stern–Gerlach experiment is always performed with beams of *neutral* atoms. Wouldn't it be easier to form beams using *ionized* atoms? Why won't this work?

Q41.6 (a) If two electrons in hydrogen atoms have the same principal quantum number, can they have different orbital angular momentum? How? (b) If two electrons in hydrogen atoms have the same orbital angular-momentum quantum number, can they have different principal quantum numbers? How?

Q41.7 In the Stern–Gerlach experiment, why is it essential for the magnetic field to be *inhomogeneous* (that is, nonuniform)?

Q41.8 In the ground state of the helium atom one electron must have "spin down" and the other "spin up." Why?

Q41.9 An electron in a hydrogen atom is in an s level, and the atom is in a magnetic field $\vec{B} = B\hat{k}$. Explain why the "spin up" state $\left(m_s = +\frac{1}{2}\right)$ has a higher energy than the "spin down" state $\left(m_s = -\frac{1}{2}\right)$.

Q41.10 The central-field approximation is more accurate for alkali metals than for transition metals such as iron, nickel, or copper. Why?

Q41.11 Table 41.3 shows that for the ground state of the potassium atom, the outermost electron is in a $4s$ state. What does this tell you about the relative energies of the $3d$ and $4s$ levels for this atom? Explain.

Q41.12 Do gravitational forces play a significant role in atomic structure? Explain.

Q41.13 Why do the transition elements $(Z = 21 \text{ to } 30)$ all have similar chemical properties?

Q41.14 Use Table 41.3 to help determine the ground-state electron configuration of the neutral gallium atom (Ga) as well as the ions Ga^+ and Ga^-. Gallium has an atomic number of 31.

Q41.15 On the basis of the Pauli exclusion principle, the structure of the periodic table of the elements shows that there must be a fourth quantum number in addition to n, l, and m_l. Explain.

Q41.16 A small amount of magnetic-field splitting of spectral lines occurs even when the atoms are not in a magnetic field. What causes this?

Q41.17 The ionization energies of the alkali metals (that is, the lowest energy required to remove one outer electron when the atom is in its ground state) are about 4 or 5 eV, while those of the noble gases are in the range from 11 to 25 eV. Why is there a difference?

Q41.18 The energy required to remove the $3s$ electron from a sodium atom in its ground state is about 5 eV. Would you expect the energy required to remove an additional electron to be about the same, or more, or less? Why?

Q41.19 What is the "central-field approximation" and why is it only an approximation?

Q41.20 The nucleus of a gold atom contains 79 protons. How does the energy required to remove a $1s$ electron completely from a gold atom compare with the energy required to remove the electron from the ground level in a hydrogen atom? In what region of the electromagnetic spectrum would a photon with this energy for each of these two atoms lie?

Q41.21 (a) Can you show that the orbital angular momentum of an electron in any given direction (e.g., along the z-axis) is *always* less than or equal to its total orbital angular momentum? In which cases would the two be equal to each other? (b) Is the result in part (a) true for a classical object, such as a spinning top or planet?

Q41.22 An atom in its ground level absorbs a photon with energy equal to the K absorption edge. Does absorbing this photon ionize this atom? Explain.

Q41.23 Can a hydrogen atom emit x rays? If so, how? If not, why not?

EXERCISES

Section 41.2 Particle in a Three-Dimensional Box

41.1 • For a particle in a three-dimensional box, what is the degeneracy (number of different quantum states with the same energy) of the following energy levels: (a) $3\pi^2\hbar^2/2mL^2$ and (b) $9\pi^2\hbar^2/2mL^2$?

41.2 • **CP** Model a hydrogen atom as an electron in a cubical box with side length L. Set the value of L so that the volume of the box equals the volume of a sphere of radius $a = 5.29 \times 10^{-11}$ m, the Bohr radius. Calculate the energy separation between the ground and first excited levels, and compare the result to this energy separation calculated from the Bohr model.

41.3 • **CP** A photon is emitted when an electron in a three-dimensional box of side length 8.00×10^{-11} m makes a transition from the $n_X = 2, n_Y = 2, n_Z = 1$ state to the $n_X = 1, n_Y = 1, n_Z = 1$ state. What is the wavelength of this photon?

41.4 • For each of the following states of a particle in a three-dimensional box, at what points is the probability distribution function a maximum: (a) $n_X = 1, n_Y = 1, n_Z = 1$ and (b) $n_X = 2, n_Y = 2, n_Z = 1$?

41.5 •• A particle is in the three-dimensional box of Section 41.1. For the state $n_X = 2, n_Y = 2, n_Z = 1$, for what planes (in addition to the walls of the box) is the probability distribution function zero? Compare this number of planes to the corresponding number of planes where $|\psi|^2$ is zero for the lower-energy state $n_X = 2, n_Y = 1, n_Z = 1$ and for the ground state $n_X = 1, n_Y = 1, n_Z = 1$.

41.6 • What is the energy difference between the two lowest energy levels for a proton in a cubical box with side length 1.00×10^{-14} m, the approximate diameter of a nucleus?

Section 41.3 The Hydrogen Atom

41.7 •• Consider an electron in the *N* shell. (a) What is the smallest orbital angular momentum it could have? (b) What is the largest orbital angular momentum it could have? Express your answers in terms of $\hbar$ and in SI units. (c) What is the largest orbital angular momentum this electron could have in any chosen direction? Express your answers in terms of $\hbar$ and in SI units. (d) What is the largest spin angular momentum this electron could have in any chosen direction? Express your answers in terms of $\hbar$ and in SI units. (e) For the electron in part (c), what is the ratio of its spin angular momentum in the z-direction to its orbital angular momentum in the z-direction?

41.8 • An electron is in the hydrogen atom with $n = 5$. (a) Find the possible values of L and L_z for this electron, in units of $\hbar$. (b) For each value of L, find all the possible angles between $\vec{L}$ and the z-axis. (c) What are the maximum and minimum values of the magnitude of the angle between $\vec{L}$ and the z-axis?

41.9 • The orbital angular momentum of an electron has a magnitude of 4.716×10^{-34} kg · m²/s. What is the angular-momentum quantum number l for this electron?

41.10 • Consider states with angular-momentum quantum number $l = 2$. (a) In units of $\hbar$, what is the largest possible value of L_z? (b) In units of $\hbar$, what is the value of L? Which is larger: L or the maximum possible L_z? (c) For each allowed value of L_z, what angle does the vector $\vec{L}$ make with the $+z$-axis? How does the minimum angle for $l = 2$ compare to the minimum angle for $l = 3$ calculated in Example 41.3?

41.11 • Calculate, in units of $\hbar$, the magnitude of the maximum orbital angular momentum for an electron in a hydrogen atom for states with a principal quantum number of 2, 20, and 200. Compare each with the value of $n\hbar$ postulated in the Bohr model. What trend do you see?

41.12 • (a) Make a chart showing all the possible sets of quantum numbers l and m_l for the states of the electron in the hydrogen atom when $n = 5$. How many combinations are there? (b) What are the energies of these states?

41.13 •• (a) How many different $5g$ states does hydrogen have? (b) Which of the states in part (a) has the largest angle between $\vec{L}$ and the z-axis, and what is that angle? (c) Which of the states in part (a) has the smallest angle between $\vec{L}$ and the z-axis, and what is that angle?

41.14 •• **CALC** (a) What is the probability that an electron in the $1s$ state of a hydrogen atom will be found at a distance less than $a/2$ from the nucleus? (b) Use the results of part (a) and of Example 41.4 to calculate the probability that the electron will be found at distances between $a/2$ and a from the nucleus.

41.15 • **CALC** In Example 41.4 fill in the missing details that show that $P = 1 - 5e^{-2}$.

41.16 • Show that $\Phi(\phi) = e^{im_l\phi} = \Phi(\phi + 2\pi)$ (that is, show that $\Phi(\phi)$ is periodic with period 2π) if and only if m_l is restricted to the values $0, \pm1, \pm2, \ldots$. (*Hint:* Euler's formula states that $e^{i\phi} = \cos\phi + i\sin\phi$.)

Section 41.4 The Zeeman Effect

41.17 • A hydrogen atom in a $3p$ state is placed in a uniform external magnetic field $\vec{B}$. Consider the interaction of the magnetic field with the atom's orbital magnetic dipole moment. (a) What field magnitude B is required to split the $3p$ state into multiple levels with an energy difference of 2.71×10^{-5} eV between adjacent levels? (b) How many levels will there be?

41.18 • A hydrogen atom is in a d state. In the absence of an external magnetic field the states with different m_l values have (approximately) the same energy. Consider the interaction of the magnetic field with the atom's orbital magnetic dipole moment. (a) Calculate the splitting (in electron volts) of the m_l levels when the atom is put in a 0.400-T magnetic field that is in the $+z$-direction. (b) Which m_l level will have the lowest energy? (c) Draw an energy-level diagram that shows the d levels with and without the external magnetic field.

41.19 • A hydrogen atom in the $5g$ state is placed in a magnetic field of 0.600 T that is in the z-direction. (a) Into how many levels is this state split by the interaction of the atom's orbital magnetic dipole moment with the magnetic field? (b) What is the energy separation between adjacent levels? (c) What is the energy separation between the level of lowest energy and the level of highest energy?

41.20 •• **CP** A hydrogen atom undergoes a transition from a $2p$ state to the $1s$ ground state. In the absence of a magnetic field, the energy of the photon emitted is 122 nm. The atom is then placed in a strong magnetic field in the z-direction. Ignore spin effects; consider only the interaction of the magnetic field with the atom's orbital magnetic moment. (a) How many different photon wavelengths are observed for the $2p \rightarrow 1s$ transition? What are the m_l values for the initial and final states for the transition that leads to each photon wavelength? (b) One observed wavelength is exactly the same with the magnetic field as without. What are the initial and final m_l values for the transition that produces a photon of this wavelength? (c) One observed wavelength with the field is longer than the wavelength without the field. What are the initial and final m_l values for the transition that produces a photon of this wavelength? (d) Repeat part (c) for the wavelength that is shorter than the wavelength in the absence of the field.

Section 41.5 Electron Spin

41.21 •• **CP Classical Electron Spin.** (a) If you treat an electron as a classical spherical object with a radius of 1.0×10^{-17} m, what angular speed is necessary to produce a spin angular momentum of magnitude $\sqrt{\frac{3}{4}}\hbar$? (b) Use $v = r\omega$ and the result of part (a) to calculate the speed v of a point at the electron's equator. What does your result suggest about the validity of this model?

41.22 •• A hydrogen atom in the $n = 1$, $m_s = -\frac{1}{2}$ state is placed in a magnetic field with a magnitude of 0.480 T in the $+z$-direction. (a) Find the magnetic interaction energy (in electron volts) of the electron with the field. (b) Is there any orbital magnetic dipole moment interaction for this state? Explain. Can there be an orbital magnetic dipole moment interaction for $n \neq 1$?

41.23 • Calculate the energy difference between the $m_s = \frac{1}{2}$ ("spin up") and $m_s = -\frac{1}{2}$ ("spin down") levels of a hydrogen atom in the $1s$ state when it is placed in a 1.45-T magnetic field in the *negative* z-direction. Which level, $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$, has the lower energy?

41.24 • **CP** The hyperfine interaction in a hydrogen atom between the magnetic dipole moment of the proton and the spin magnetic dipole moment of the electron splits the ground level into two levels separated by 5.9×10^{-6} eV. (a) Calculate the wavelength and frequency of the photon emitted when the atom makes a transition between these states, and compare your answer to the value given at the end of Section 41.5. In what part of the electromagnetic spectrum does this lie? Such photons are emitted by cold hydrogen clouds in interstellar space; by detecting these photons, astronomers can learn about the number and density of such clouds. (b) Calculate the effective magnetic field experienced by the electron in these states (see Fig. 41.18). Compare your result to the effective magnetic field due to the spin-orbit coupling calculated in Example 41.7.

41.25 • A hydrogen atom in a particular orbital angular momentum state is found to have j quantum numbers $\frac{7}{2}$ and $\frac{9}{2}$. What is the letter that labels the value of l for the state?

Section 41.6 Many-Electron Atoms and the Exclusion Principle

41.26 • For germanium (Ge, $Z = 32$), make a list of the number of electrons in each subshell ($1s$, $2s$, $2p$, ...). Use the allowed values of the quantum numbers along with the exclusion principle; do *not* refer to Table 41.3.

41.27 • Make a list of the four quantum numbers n, l, m_l, and m_s for each of the 10 electrons in the ground state of the neon atom. Do *not* refer to Table 41.2 or 41.3.

41.28 •• (a) Write out the ground-state electron configuration ($1s^2$, $2s^2$, ...) for the carbon atom. (b) What element of next-larger Z has chemical properties similar to those of carbon? Give the ground-state electron configuration for this element.

41.29 •• (a) Write out the ground-state electron configuration ($1s^2$, $2s^2$, ...) for the beryllium atom. (b) What element of next-larger Z has chemical properties similar to those of beryllium? Give the ground-state electron configuration of this element. (c) Use the procedure of part (b) to predict what element of next-larger Z than in (b) will have chemical properties similar to those of the element you found in part (b), and give its ground-state electron configuration.

41.30 • For magnesium, the first ionization potential is 7.6 eV. The second ionization potential (additional energy required to remove a second electron) is almost twice this, 15 eV, and the third ionization potential is much larger, about 80 eV. How can these numbers be understood?

41.31 • The $5s$ electron in rubidium (Rb) sees an effective charge of $2.771e$. Calculate the ionization energy of this electron.

41.32 • The energies of the $4s$, $4p$, and $4d$ states of potassium are given in Example 41.9. Calculate Z_{eff} for each state. What trend do your results show? How can you explain this trend?

41.33 • (a) The doubly charged ion N^{2+} is formed by removing two electrons from a nitrogen atom. What is the ground-state electron configuration for the N^{2+} ion? (b) Estimate the energy of the least strongly bound level in the L shell of N^{2+}. (c) The doubly charged ion P^{2+} is formed by removing two electrons from a phosphorus atom. What is the ground-state electron configuration for the P^{2+} ion? (d) Estimate the energy of the least strongly bound level in the M shell of P^{2+}.

41.34 • (a) The energy of the $2s$ state of lithium is -5.391 eV. Calculate the value of Z_{eff} for this state. (b) The energy of the $4s$ state of potassium is -4.339 eV. Calculate the value of Z_{eff} for this state. (c) Compare Z_{eff} for the $2s$ state of lithium, the $3s$ state of sodium (see Example 41.8), and the $4s$ state of potassium. What trend do you see? How can you explain this trend?

41.35 • Estimate the energy of the highest-l state for (a) the L shell of Be^+ and (b) the N shell of Ca^+.

Section 41.7 X-Ray Spectra

41.36 • A K_α x ray emitted from a sample has an energy of 7.46 keV. Of which element is the sample made?

41.37 • Calculate the frequency, energy (in keV), and wavelength of the K_α x ray for the elements (a) calcium (Ca, $Z = 20$); (b) cobalt (Co, $Z = 27$); (c) cadmium (Cd, $Z = 48$).

41.38 •• The energies for an electron in the K, L, and M shells of the tungsten atom are $-69{,}500$ eV, $-12{,}000$ eV, and -2200 eV, respectively. Calculate the wavelengths of the K_α and K_β x rays of tungsten.

PROBLEMS

41.39 • In terms of the ground-state energy $E_{1,1,1}$, what is the energy of the highest level occupied by an electron when 10 electrons are placed into a cubical box?

41.40 •• CALC A particle in the three-dimensional box of Section 41.2 is in the ground state, where $n_X = n_Y = n_Z = 1$. (a) Calculate the probability that the particle will be found somewhere between $x = 0$ and $x = L/2$. (b) Calculate the probability that the particle will be found somewhere between $x = L/4$ and $x = L/2$. Compare your results to the result of Example 41.1 for the probability of finding the particle in the region $x = 0$ to $x = L/4$.

41.41 •• CALC A particle is in the three-dimensional box of Section 41.2. (a) Consider the cubical volume defined by $0 \le x \le L/4$, $0 \le y \le L/4$, and $0 \le z \le L/4$. What fraction of the total volume of the box is this cubical volume? (b) If the particle is in the ground state ($n_X = 1, n_Y = 1, n_Z = 1$) calculate the probability that the particle will be found in the cubical volume defined in part (a). (c) Repeat the calculation of part (b) when the particle is in the state $n_X = 2, n_Y = 1, n_Z = 1$.

41.42 •• CALC A particle is described by the normalized wave function $\psi(x, y, z) = Axe^{-\alpha x^2}e^{-\beta y^2}e^{-\gamma z^2}$, where A, α, β, and γ are all real, positive constants. The probability that the particle will be found in the infinitesimal volume $dx\,dy\,dz$ centered at the point (x_0, y_0, z_0) is $|\psi(x_0, y_0, z_0)|^2\,dx\,dy\,dz$. (a) At what value of x_0 is the particle most likely to be found? (b) Are there values of x_0 for which the probability of the particle being found is zero? If so, at what x_0?

41.43 •• CALC A particle is described by the normalized wave function $\psi(x, y, z) = Ae^{-\alpha(x^2+y^2+z^2)}$, where A and α are real, positive constants. (a) Determine the probability of finding the particle at a distance between r and $r + dr$ from the origin. (*Hint:* See Problem 41.42. Consider a spherical shell centered on the origin with inner radius r and thickness dr.) (b) For what value of r does the probability in part (a) have its maximum value? Is this the same value of r for which $|\psi(x, y, z)|^2$ is a maximum? Explain any differences.

41.44 •• CP CALC **A Three-Dimensional Isotropic Harmonic Oscillator.** An isotropic harmonic oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k'(x^2 + y^2 + z^2)$. (*Isotropic* means that the force constant k' is the same in all three coordinate directions.) (a) Show that for this potential, a solution to Eq. (41.5) is given by $\psi = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$. In this expression, $\psi_{n_x}(x)$ is a solution to the one-dimensional harmonic oscillator Schrödinger equation, Eq. (40.44), with energy $E_{n_x} = \left(n_x + \frac{1}{2}\right)\hbar\omega$. The functions $\psi_{n_y}(y)$ and $\psi_{n_z}(z)$ are analogous one-dimensional wave functions for oscillations in the y- and z-directions. Find the energy associated with this ψ. (b) From your results in part (a) what are the ground-level and first-excited-level energies of the three-dimensional isotropic oscillator? (c) Show that there is only one state (one set of quantum numbers n_x, n_y, and n_z) for the ground level but three states for the first excited level.

41.45 •• CP CALC **Three-Dimensional Anisotropic Harmonic Oscillator.** An oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k_1'(x^2 + y^2) + \frac{1}{2}k_2'z^2$, where $k_1' > k_2'$. This oscillator is called *anisotropic* because the force constant is not the same in all three coordinate directions. (a) Find a general expression for the energy levels of the oscillator (see Problem 41.44). (b) From your results in part (a), what are the ground-level and first-excited-level energies of this oscillator? (c) How many states (different sets of quantum numbers n_x, n_y, and n_z) are there for the ground level and for the first excited level? Compare to part (c) of Problem 41.44.

41.46 •• An electron in hydrogen is in the $5f$ state. (a) Find the largest possible value of the z-component of its angular momentum. (b) Show that for the electron in part (a), the corresponding x- and y-components of its angular momentum satisfy the equation $\sqrt{L_x^2 + L_y^2} = \hbar\sqrt{3}$.

41.47 •• (a) Show that the total number of atomic states (including different spin states) in a shell of principal quantum number n is $2n^2$. [*Hint:* The sum of the first N integers $1 + 2 + 3 + \cdots + N$ is equal to $N(N+1)/2$.] (b) Which shell has 50 states?

41.48 •• (a) What is the lowest possible energy (in electron volts) of an electron in hydrogen if its orbital angular momentum is $\sqrt{12}\hbar$? (b) What are the largest and smallest values of the z-component of the orbital angular momentum (in terms of $\hbar$) for the electron in part (a)? (c) What are the largest and smallest values of the spin angular momentum (in terms of $\hbar$) for the electron in part (a)? (d) What are the largest and smallest values of the orbital angular momentum (in terms of $\hbar$) for an electron in the M shell of hydrogen?

41.49 • Consider an electron in hydrogen having total energy -0.5440 eV. (a) What are the possible values of its orbital angular momentum (in terms of $\hbar$)? (b) What wavelength of light would it take to excite this electron to the next higher shell? Is this photon visible to humans?

41.50 • (a) Show all the distinct states for an electron in the N shell of hydrogen. Include all four quantum numbers. (b) For an f electron in the N shell, what is the largest possible orbital angular momentum and the greatest positive value for the component of this angular momentum along any chosen direction (the z-axis)? What is the magnitude of its spin angular momentum? Express these quantities in units of $\hbar$. (c) For an electron in the d state of the N shell, what are the maximum and minimum angles between its angular momentum vector and any chosen direction (the z-axis)? (d) What is the largest value of the orbital angular momentum for an f electron in the M shell?

41.51 • (a) The energy of an electron in the $4s$ state of sodium is -1.947 eV. What is the effective net charge of the nucleus "seen" by this electron? On the average, how many electrons screen the nucleus? (b) For an outer electron in the $4p$ state of potassium, on the average 17.2 inner electrons screen the nucleus. (i) What is the effective net charge of the nucleus "seen" by this outer electron? (ii) What is the energy of this outer electron?

41.52 • **CALC** For a hydrogen atom, the probability $P(r)$ of finding the electron within a spherical shell with inner radius r and outer radius $r + dr$ is given by Eq. (41.25). For a hydrogen atom in the $1s$ ground state, at what value of r does $P(r)$ have its maximum value? How does your result compare to the distance between the electron and the nucleus for the $n = 1$ state in the Bohr model, Eq. (41.26)?

41.53 •• **CALC** Consider a hydrogen atom in the $1s$ state. (a) For what value of r is the potential energy $U(r)$ equal to the total energy E? Express your answer in terms of a. This value of r is called the *classical turning point*, since this is where a Newtonian particle would stop its motion and reverse direction. (b) For r greater than the classical turning point, $U(r) > E$. Classically, the particle cannot be in this region, since the kinetic energy cannot be negative. Calculate the probability of the electron being found in this classically forbidden region.

41.54 • **CP** **Rydberg Atoms.** *Rydberg atoms* are atoms whose outermost electron is in an excited state with a *very* large principal quantum number. Rydberg atoms have been produced in the laboratory and detected in interstellar space. (a) Why do all neutral Rydberg atoms with the same n value have essentially the same ionization energy, independent of the total number of electrons in the atom? (b) What is the ionization energy for a Rydberg atom with a principal quantum number of 350? What is the radius in the Bohr model of the Rydberg electron's orbit? (c) Repeat part (b) for $n = 650$.

41.55 ••• **CALC** The wave function for a hydrogen atom in the $2s$ state is

$$\psi_{2s}(r) = \frac{1}{\sqrt{32\pi a^3}}\left(2 - \frac{r}{a}\right)e^{-r/2a}$$

(a) Verify that this function is normalized. (b) In the Bohr model, the distance between the electron and the nucleus in the $n = 2$ state is exactly $4a$. Calculate the probability that an electron in the $2s$ state will be found at a distance less than $4a$ from the nucleus.

41.56 •• **CALC** The normalized wave function for a hydrogen atom in the $2s$ state is given in Problem 41.55. (a) For a hydrogen atom in the $2s$ state, at what value of r is $P(r)$ maximum? How does your result compare to $4a$, the distance between the electron and the nucleus in the $n = 2$ state of the Bohr model? (b) At what value of r (other than $r = 0$ or $r = \infty$) is $P(r)$ equal to zero, so that the probability of finding the electron at that separation from the nucleus is zero? Compare your result to Fig. 41.9.

41.57 •• (a) For an excited state of hydrogen, show that the smallest angle that the orbital angular momentum vector $\vec{L}$ can have with the z-axis is

$$(\theta_L)_{\min} = \arccos\left(\frac{n-1}{\sqrt{n(n-1)}}\right)$$

(b) What is the corresponding expression for $(\theta_L)_{\max}$, the largest possible angle between $\vec{L}$ and the z-axis?

41.58 •• (a) If the value of L_z is known, we cannot know either L_x or L_y precisely. But we can know the value of the quantity $\sqrt{L_x^2 + L_y^2}$. Write an expression for this quantity in terms of l, m_l, and $\hbar$. (b) What is the meaning of $\sqrt{L_x^2 + L_y^2}$? (c) For a state of nonzero orbital angular momentum, find the maximum and minimum values of $\sqrt{L_x^2 + L_y^2}$. Explain your results.

41.59 •• **CALC** The normalized radial wave function for the $2p$ state of the hydrogen atom is $R_{2p} = \left(1/\sqrt{24a^5}\right)re^{-r/2a}$. After we average over the angular variables, the radial probability function becomes $P(r)\,dr = (R_{2p})^2r^2\,dr$. At what value of r is $P(r)$ for the $2p$ state a maximum? Compare your results to the radius of the $n = 2$ state in the Bohr model.

41.60 •• **CP** **Stern–Gerlach Experiment.** In a Stern–Gerlach experiment, the deflecting force on the atom is $F_z = -\mu_z(dB_z/dz)$, where μ_z is given by Eq. (41.40) and dB_z/dz is the magnetic-field gradient. In a particular experiment the magnetic-field region is 50.0 cm long; assume the magnetic-field gradient is constant in this region. A beam of silver atoms enters the magnetic field with a speed of 525 m/s. What value of dB_z/dz is required to give a separation of 1.0 mm between the two spin components as they exit the field? (*Note:* The magnetic dipole moment of silver is the same as that for hydrogen, since its valence electron is in an $l = 0$ state.)

41.61 • Consider the transition from a $3d$ to a $2p$ state of hydrogen in an external magnetic field. Assume that the effects of electron spin can be ignored (which is not actually the case) so that the magnetic field interacts only with the orbital angular momentum. Identify each allowed transition by the m_l values of the initial and final states. For each of these allowed transitions, determine the shift of the transition energy from the zero-field value and show that there are three different transition energies.

41.62 •• An atom in a $3d$ state emits a photon of wavelength 475.082 nm when it decays to a $2p$ state. (a) What is the energy (in electron volts) of the photon emitted in this transition? (b) Use the selection rules described in Section 41.4 to find the allowed transitions if the atom is now in an external magnetic field of 3.500 T. Ignore the effects of the electron's spin. (c) For the case in part (b), if the energy of the $3d$ state was originally -8.50000 eV with no magnetic field present, what will be the energies of the states into which it splits in the magnetic field? (d) What are the allowed wavelengths of the light emitted during transition in part (b)?

41.63 •• **CALC Spectral Analysis.** While studying the spectrum of a gas cloud in space, an astronomer magnifies a spectral line that results from a transition from a p state to an s state. She finds that the line at 575.050 nm has actually split into three lines, with adjacent lines 0.0462 nm apart, indicating that the gas is in an external magnetic field. (Ignore effects due to electron spin.) What is the strength of the external magnetic field?

41.64 •• A hydrogen atom makes a transition from an $n = 3$ state to an $n = 2$ state (the Balmer H_α line) while in a magnetic field in the $+z$-direction and with magnitude 1.40 T. (a) If the magnetic quantum number is $m_l = 2$ in the initial ($n = 3$) state and $m_l = 1$ in the final ($n = 2$) state, by how much is each energy level shifted from the zero-field value? (b) By how much is the wavelength of the H_α line shifted from the zero-field value? Is the wavelength increased or decreased? Disregard the effect of electron spin. [*Hint:* Use the result of Problem 39.86(c).]

41.65 • **CP** A large number of hydrogen atoms in $1s$ states are placed in an external magnetic field that is in the $+z$-direction. Assume that the atoms are in thermal equilibrium at room temperature, $T = 300$ K. According to the Maxwell–Boltzmann distribution (see Section 39.4), what is the ratio of the number of atoms in the $m_s = \frac{1}{2}$ state to the number in the $m_s = -\frac{1}{2}$ state when the magnetic-field magnitude is (a) 5.00×10^{-5} T (approximately the earth's field); (b) 0.500 T; (c) 5.00 T?

41.66 •• **Effective Magnetic Field.** An electron in a hydrogen atom is in the $2p$ state. In a simple model of the atom, assume that the electron circles the proton in an orbit with radius r equal to the Bohr-model radius for $n = 2$. Assume that the speed v of the orbiting electron can be calculated by setting $L = mvr$ and taking L to have the quantum-mechanical value for a $2p$ state. In the frame of the electron, the proton orbits with radius r and speed v. Model the orbiting proton as a circular current loop, and calculate the magnetic field it produces at the location of the electron.

41.67 •• **Weird Universe.** In another universe, the electron is a spin-$\frac{3}{2}$ rather than a spin-$\frac{1}{2}$ particle, but all other physics are the same as in our universe. In this universe, (a) what are the atomic numbers of the lightest two inert gases? (b) What is the ground-state electron configuration of sodium?

41.68 • For an ion with nuclear charge Z and a single electron, the electric potential energy is $-Ze^2/4\pi\epsilon_0 r$ and the expression for the energies of the states and for the normalized wave functions are obtained from those for hydrogen by replacing e^2 by Ze^2. Consider the N^{6+} ion with seven protons and one electron. (a) What is the ground-state energy in electron volts? (b) What is the ionization energy required to remove the electron from the N^{6+} ion if it is initially in the ground state? (c) What is the distance a [given for hydrogen by Eq. (41.26)] for this ion? (d) What is the wavelength of the photon emitted when the N^{6+} ion makes a transition from the $n = 2$ state to the $n = 1$ ground state?

41.69 •• A hydrogen atom in an $n = 2$, $l = 1$, $m_l = -1$ state emits a photon when it decays to an $n = 1$, $l = 0$, $m_l = 0$ ground state. (a) In the absence of an external magnetic field, what is the wavelength of this photon? (b) If the atom is in a magnetic field in the $+z$-direction and with a magnitude of 2.20 T, what is the shift in the wavelength of the photon from the zero-field value? Does the magnetic field increase or decrease the wavelength? Disregard the effect of electron spin. [*Hint:* Use the result of Problem 39.86(c).]

41.70 •• A lithium atom has three electrons, and the $^2S_{1/2}$ ground-state electron configuration is $1s^2 2s$. The $1s^2 2p$ excited state is split into two closely spaced levels, $^2P_{3/2}$ and $^2P_{1/2}$, by the spin-orbit interaction (see Example 41.7 in Section 41.5). A photon with wavelength 67.09608 μm is emitted in the $^2P_{3/2} \rightarrow {}^2S_{1/2}$ transition, and a photon with wavelength 67.09761 μm is emitted in the $^2P_{1/2} \rightarrow {}^2S_{1/2}$ transition. Calculate the effective magnetic field seen by the electron in the $1s^2 2p$ state of the lithium atom. How does your result compare to that for the $3p$ level of sodium found in Example 41.7?

41.71 • Estimate the minimum and maximum wavelengths of the characteristic x rays emitted by (a) vanadium ($Z = 23$) and (b) rhenium ($Z = 45$). Discuss any approximations that you make.

41.72 •• **CP Electron Spin Resonance.** Electrons in the lower of two spin states in a magnetic field can absorb a photon of the right frequency and move to the higher state. (a) Find the magnetic-field magnitude B required for this transition in a hydrogen atom with $n = 1$ and $l = 0$ to be induced by microwaves with wavelength λ. (b) Calculate the value of B for a wavelength of 3.50 cm.

CHALLENGE PROBLEMS

41.73 ••• Each of $2N$ electrons (mass m) is free to move along the x-axis. The potential-energy function for each electron is $U(x) = \frac{1}{2}k'x^2$, where k' is a positive constant. The electric and magnetic interactions between electrons can be ignored. Use the exclusion principle to show that the minimum energy of the system of $2N$ electrons is $\hbar N^2\sqrt{k'/m}$. (*Hint:* See Section 40.5 and the hint given in Problem 41.47.)

41.74 ••• **CP** Consider a simple model of the helium atom in which two electrons, each with mass m, move around the nucleus (charge $+2e$) in the same circular orbit. Each electron has orbital angular momentum $\hbar$ (that is, the orbit is the smallest-radius Bohr orbit), and the two electrons are always on opposite sides of the nucleus. Ignore the effects of spin. (a) Determine the radius of the orbit and the orbital speed of each electron. [*Hint:* Follow the procedure used in Section 39.3 to derive Eqs. (39.8) and (39.9). Each electron experiences an attractive force from the nucleus and a repulsive force from the other electron.] (b) What is the total kinetic energy of the electrons? (c) What is the potential energy of the system (the nucleus and the two electrons)? (d) In this model, how much energy is required to remove both electrons to infinity? How does this compare to the experimental value of 79.0 eV?

41.75 ••• **CALC** Repeat the calculation of Problem 41.53 for a one-electron ion with nuclear charge Z. (See Problem 41.68.) How does the probability of the electron being found in the classically forbidden region depend on Z?

Answers

Chapter Opening Question ?

Helium is inert because it has a filled K shell, while sodium is very reactive because its third electron is loosely bound in an L shell. See Section 41.6 for more details.

Test Your Understanding Questions

41.1 Answer: (iv) If $U(x, y, z) = 0$ in a certain region of space, we can rewrite the time-independent Schrödinger equation [Eq. (41.5)] for that region as $\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2 = (-2mE/\hbar^2)\psi$. We are told that all of the second derivatives of $\psi(x, y, z)$ are positive in this region, so the left-hand side of this equation is positive. Hence the right-hand side $(-2mE/\hbar^2)\psi$ must also be positive. Since $E > 0$, the quantity $-2mE/\hbar^2$ is negative, and so $\psi(x, y, z)$ must be negative.

41.2 Answer: (iv), (ii), (i) and (iii) (tie) Equation (41.16) shows that the energy levels for a cubical box are proportional to the quantity $n_X{}^2 + n_Y{}^2 + n_Z{}^2$. Hence ranking in order of this quantity is the same as ranking in order of energy. For the four cases we are given, we have (i) $n_X{}^2 + n_Y{}^2 + n_Z{}^2 = 2^2 + 3^2 + 2^2 = 17$; (ii) $n_X{}^2 + n_Y{}^2 + n_Z{}^2 = 4^2 + 1^2 + 1^2 = 18$; (iii) $n_X{}^2 + n_Y{}^2 + n_Z{}^2 = 2^2 + 2^2 + 3^2 = 17$; and (iv) $n_X{}^2 + n_Y{}^2 + n_Z{}^2 = 1^2 + 3^2 + 3^2 = 19$. The states $(n_X, n_Y, n_Z) = (2, 3, 2)$ and $(n_X, n_Y, n_Z) = (2, 2, 3)$ have the same energy (they are degenerate).

41.3 Answer: (ii) and (iii) (tie), (i) An electron in a state with principal quantum number n is most likely to be found at $r = n^2a$. This result is independent of the values of the quantum numbers l and m_l. Hence an electron with $n = 2$ (most likely to be found at $r = 4a$) is more likely to be found near $r = 5a$ than an electron with $n = 1$ (most likely to be found at $r = a$).

41.4 Answer: no All that matters is the component of the electron's orbital magnetic moment along the direction of $\vec{B}$. We called this quantity μ_z in Eq. (41.32) because we *defined* the positive z-axis to be in the direction of $\vec{B}$. In reality, the names of the axes are entirely arbitrary.

41.5 Answer: (iv) For the magnetic moment to be perfectly aligned with the z-direction, the z-component of the spin vector $\vec{S}$ would have to have the same absolute value as $\vec{S}$. However, the possible values of S_z are $\pm\frac{1}{2}\hbar$ [Eq. (41.37)], while the magnitude of the spin vector is $S = \sqrt{\frac{3}{4}}\hbar$ [Eq. (41.38)]. Hence $\vec{S}$ can never be perfectly aligned with any one direction in space.

41.6 Answer: more difficult If there were no exclusion principle, all 11 electrons in the sodium atom would be in the level of lowest energy (the 1s level) and the configuration would be $1s^{11}$. Consequently, it would be more difficult to remove the first electron. (In a real sodium atom the valence electron is in a screened 3s state, which has a comparatively high energy.)

41.7 Answer: (iv) An absorption edge appears if the photon energy is just high enough to remove an electron in a given energy level from the atom. In a sample of high-temperature hydrogen we expect to find atoms whose electron is in the ground level ($n = 1$), the first excited level ($n = 2$), and the second excited level ($n = 3$). From Eq. (41.21) these levels have energies $E_n = (-13.60\text{ eV})/n^2 = -13.60\text{ eV}, -3.40\text{ eV}$, and -1.51 eV (see Fig. 38.9b).

Bridging Problem

Answers: (a) 2.37×10^{-10} m

(b) Values of (n_X, n_Y, n_Z, m_s) for the 22 electrons: $(1, 1, 1, +\frac{1}{2})$, $(1, 1, 1, -\frac{1}{2})$, $(2, 1, 1, +\frac{1}{2})$, $(2, 1, 1, -\frac{1}{2})$, $(1, 2, 1, +\frac{1}{2})$, $(1, 2, 1, -\frac{1}{2})$, $(1, 1, 2, +\frac{1}{2})$, $(1, 1, 2, -\frac{1}{2})$, $(2, 2, 1, +\frac{1}{2})$, $(2, 2, 1, -\frac{1}{2})$, $(2, 1, 2, +\frac{1}{2})$, $(2, 1, 2, -\frac{1}{2})$, $(1, 2, 2, +\frac{1}{2})$, $(1, 2, 2, -\frac{1}{2})$, $(3, 1, 1, +\frac{1}{2})$, $(3, 1, 1, -\frac{1}{2})$, $(1, 3, 1, +\frac{1}{2})$, $(1, 3, 1, -\frac{1}{2})$, $(1, 1, 3, +\frac{1}{2})$, $(1, 1, 3, -\frac{1}{2})$, $(2, 2, 2, +\frac{1}{2})$, $(2, 2, 2, -\frac{1}{2})$

(c) 20.1 eV, 40.2 eV, 60.3 eV, 73.7 eV, and 80.4 eV

(d) 60.3 eV versus 4.52×10^3 eV