PROBLEMS

8.1 Particle in a Three-Dimensional Box

1. A particle of mass m moves in a three-dimensional box with edge lengths L_1, L_2, and L_3. Find the energies of the six lowest states if $L_1 = L$, $L_2 = 2L$, and $L_3 = 2L$. Which of these energies are degenerate?
2. An electron moves in a cube whose sides have a length of 0.2 nm. Find values for the energy of (a) the ground state and (b) the first excited state of the electron.
3. A particle of mass m moves in a three-dimensional box with sides L. If the particle is in the third excited level, corresponding to $n^2 = 11$, find (a) the energy of the particle, (b) the combinations of n_1, n_2, and n_3 that would give this energy, and (c) the wavefunctions for these different states.
4. A particle of mass m moves in a two-dimensional box of sides L. (a) Write expressions for the wavefunctions and energies as a function of the quantum numbers n_1 and n_2 (assuming the box is in the xy plane). (b) Find the energies of the ground state and first excited state. Is either of these states degenerate? Explain.
5. Assume that the nucleus of an atom can be regarded as a three-dimensional box of width 2×10^{-14} m. If a proton moves as a particle in this box, find (a) the ground-state energy of the proton in MeV and (b) the energies of the first and second excited states. (c) What are the degeneracies of these states?
6. Obtain the stationary states for a *free* particle in three dimensions by separating the variables in Schrödinger's equation. Do this by substituting the separable form $\Psi(\mathbf{r}, t) = \psi_1(x)\psi_2(y)\psi_3(z)\phi(t)$ into the time-dependent Schrödinger equation and dividing each term by $\Psi(\mathbf{r}, t)$. Isolate all terms depending only on x from those depending only on y, and so on, and argue that four separate equations must result, one for each of the unknown functions ψ_1, ψ_2, ψ_3, and ϕ. Solve the resulting equations. What dynamical quantities are sharp for the states you have found?
7. For a particle confined to a cubic box of dimension L, show that the normalizing factor is $A = (2/L)^{3/2}$, the *same* value for *all* the stationary states. How is this result changed if the box has edge lengths L_1, L_2, and L_3, all of which are different?
8. Consider a particle of mass m confined to a three-dimensional cube of length L so small that the particle motion is *relativistic*. Obtain an expression for the allowed particle energies in this case. Compute the ground-state energy for an electron if $L = 10$ fm (10^{-5} nm), a typical nuclear dimension.

8.2 Central Forces and Angular Momentum

9. If an electron has an orbital angular momentum of 4.714×10^{-34} J·s, what is the orbital quantum number for this state of the electron?
10. Consider an electron for which $n = 4$, $\ell = 3$, and $m_\ell = 3$. Calculate the numerical value of (a) the orbital angular momentum and (b) the z component of the orbital angular momentum.
11. The orbital angular momentum of the Earth in its motion about the Sun is 4.83×10^{31} kg·m^2/s. Assuming it is quantized according to Equation 8.16, find (a) the value of ℓ corresponding to this angular momentum and (b) the fractional change in $|\mathbf{L}|$ as ℓ changes from ℓ to $\ell + 1$.

8.5 Atomic Hydrogen and Hydrogen-like Ions

12. The normalized ground-state wavefunction for the electron in the hydrogen atom is

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

where r is the radial coordinate of the electron and a_0 is the Bohr radius. (a) Sketch the wavefunction versus r. (b) Show that the probability of finding the electron between r and $r + dr$ is given by $|\psi(r)|^2 4\pi r^2\, dr$. (c) Sketch the probability versus r and from your sketch find the radius at which the electron is most likely to be found. (d) Show that the wavefunction as given is normalized. (e) Find the probability of locating the electron between $r_1 = a_0/2$ and $r_2 = 3a_0/2$.
13. (a) Determine the quantum numbers ℓ and m_ℓ for the He^+ ion in the state corresponding to $n = 3$. (b) What is the energy of this state?
14. (a) Determine the quantum numbers ℓ and m_ℓ for the Li^{2+} ion in the states for which $n = 1$ and $n = 2$. (b) What are the energies of these states?
15. In obtaining the results for hydrogen-like atoms in Section 8.5, the atomic nucleus was assumed to be immobile due to its much larger mass compared with that of the electron. If this assumption is relaxed, the results remain valid if the electron mass m is replaced everywhere by the *reduced mass* μ of the electron–nucleus combination:

$$\mu = \frac{mM}{m + M}$$

Here M is the nuclear mass. (a) Making this replacement in Equation 8.38, show that a more general expression for the allowed energies of a one-electron atom with atomic number Z is

$$E_n = -\frac{\mu k^2 e^4}{2\hbar^2}\left\{\frac{Z^2}{n^2}\right\}$$

(b) The wavelength for the $n = 3$ to $n = 2$ transition of the hydrogen atom is 656.3 nm (visible red light). What is the wavelength of this same transition in singly ionized helium? In positronium? (*Note:* Positronium is an "atom" consisting of a bound positron–electron pair. A positron is a positively charged electron.)

16. Calculate the possible values of the z component of angular momentum for an electron in a d subshell.
17. Calculate the angular momentum for an electron in (a) the $4d$ state and (b) the $6f$ state of hydrogen.
18. A hydrogen atom is in the $6g$ state. (a) What is the principal quantum number? (b) What is the energy of the atom? (c) What are the values for the orbital quantum number and the magnitude of the electron's orbital angular momentum? (d) What are the possible values for the magnetic quantum number? For each value, find the corresponding z component of the electron's orbital angular momentum and the angle that the orbital angular momentum vector makes with the z-axis.
19. Prove that the nth energy level of an atom has degeneracy equal to n^2.
20. For fixed electron energy, the orbital quantum number ℓ is limited to $n - 1$. We can obtain this result from a semiclassical argument using the fact that the largest angular momentum describes circular orbits, where all the kinetic energy is in orbital form. For hydrogen-like atoms, $U(r) = -Zke^2/r$, and the energy in circular orbits becomes

$$E = \frac{|\mathbf{L}|^2}{2mr^2} - \frac{Zke^2}{r}$$

Quantize this relation using the rules of Equations 8.16 and 8.38, together with the Bohr result for the allowed values of r, to show that the largest integer value of ℓ consistent with the total energy is $\ell_{\text{max}} = n - 1$.

21. Suppose that a hydrogen atom is in the $2s$ state. Taking $r = a_0$, calculate values for (a) $\psi_{2s}(a_0)$, (b) $|\psi_{2s}(a_0)|^2$, and (c) $P_{2s}(a_0)$.
22. The radial part of the wavefunction for the hydrogen atom in the $2p$ state is given by

$$R_{2p}(r) = Are^{-r/2a_0}$$

where A is a constant and a_0 is the Bohr radius. Using this expression, calculate the average value of r for an electron in this state.

23. A dimensionless number that often appears in atomic physics is the *fine-structure constant* α, given by

$$\alpha = \frac{ke^2}{\hbar c}$$

where k is the Coulomb constant. (a) Obtain a numerical value for $1/\alpha$. (b) In scattering experiments, the "size" of the electron is the *classical electron radius,* $r_0 = ke^2/m_ec^2$. In terms of α, what is the ratio of the Compton wavelength, $\lambda = h/m_ec$, to the classical electron radius? (c) In terms of α, what is the ratio of the Bohr radius, a_0, to the Compton wavelength? (d) In terms of α, what is the ratio of the *Rydberg wavelength,* $1/R$, to the Bohr radius?

24. Calculate the average potential and kinetic energies for the electron in the ground state of hydrogen.
25. Compare the most probable distances of the electron from the proton in the hydrogen $2s$ and $2p$ states with the radius of the second Bohr orbit in hydrogen, $4a_0$.
26. Compute the probability that a $2s$ electron of hydrogen will be found inside the Bohr radius for this state, $4a_0$. Compare this with the probability of finding a $2p$ electron in the same region.
27. Use the Java applet available at our companion Web site (http://info.brookscole.com/mp3e → QMTools Simulations → Problem 8.27) to display the radial waveforms for the $n = 3$ level of atomic hydrogen. Locate the most probable distance from the nucleus for an electron in the $3s$ state. Do the same for an electron in the $3p$ and $3d$ states. What does the simple Bohr theory predict for this case?
28. *Angular Variation of Hydrogen Wavefunctions.* Use the Java applet of the preceding problem to display the electron clouds for the $n = 4$ states of atomic hydrogen. Observe the distinctly different symmetries of the s, p, d, and f orbitals in the case $m_\ell = 0$. Which of these orbitals is most extended, that is, in which orbital is the electron likely to be found furthest away from the nucleus? Explore the effect of the magnetic quantum number m_ℓ on the overall appearance and properties of the $n = 4$ orbitals. Can you identify any trends?
29. As shown in Example 8.9, the average distance of the electron from the proton in the hydrogen ground state is 1.5 bohrs. For this case, calculate Δr, the uncertainty in distance about the average value, and compare it with the average itself. Comment on the significance of your result.
30. Calculate the uncertainty product $\Delta r \Delta p$ for the $1s$ electron of a hydrogen-like atom with atomic number Z. (*Hint:* Use $\langle p \rangle = 0$ by symmetry and deduce $\langle p^2 \rangle$ from the average kinetic energy, calculated as in Problem 24.)

ADDITIONAL PROBLEMS

31. An electron outside a dielectric is attracted to the surface by a force $F = -A/x^2$, where x is the perpendicular distance from the electron to the surface and A is a constant. Electrons are prevented from crossing the surface, since there are no quantum states in the dielectric for them to occupy. Assume that the surface is infinite in extent, so that the problem is effectively one-dimensional. Write the Schrödinger equation for an electron outside the surface $x > 0$. What is the appropriate boundary condition at $x = 0$? Obtain a formula for the allowed energy

levels in this case. (*Hint:* Compare the equation for $\psi(x)$ with that satisfied by the effective one-dimensional wavefunction $g(r) = rR(r)$ for hydrogen-like atoms.)

32. *The Spherical Well.* The three-dimensional analog of the square well in one dimension, the spherical well is commonly used to model the potential energy of nucleons (protons, neutrons) in an atomic nucleus. It is defined by a potential $U(r)$ that is zero everywhere inside a sphere and takes a large (possibly infinite) positive value outside this sphere. Use the Java applet available at our companion Web site (http://info.brookscole.com/mp3e → QMTools Simulations → Problem 8.32) to find the ground-state energy for a proton bound to a spherical well of radius 9.00 fm and height 30.0 MeV. Is the ground state an *s* state? Explain. Also report the most probable distance from the center of the well for this nucleon.

33. Use the Java applet of Problem 32 to find the first three excited-state energy levels for the spherical well described there. What orbital quantum numbers ℓ describe these states? Determine the degeneracy of each excited level and display the probability clouds for the degenerate wavefunctions.

34. Example 8.9 found the most probable value and the average value for the distance of the electron from the proton in the ground state of a hydrogen atom. For comparison, find the *median* value as follows. (a) Derive an expression for the probability, as a function of r, that the electron in the ground state of hydrogen will be found outside a sphere of radius r centered on the nucleus. (b) Find the value of r for which the probability of finding the electron outside a sphere of radius r is equal to the probability of finding the electron inside this sphere. (You will need to solve a transcendental equation numerically.)