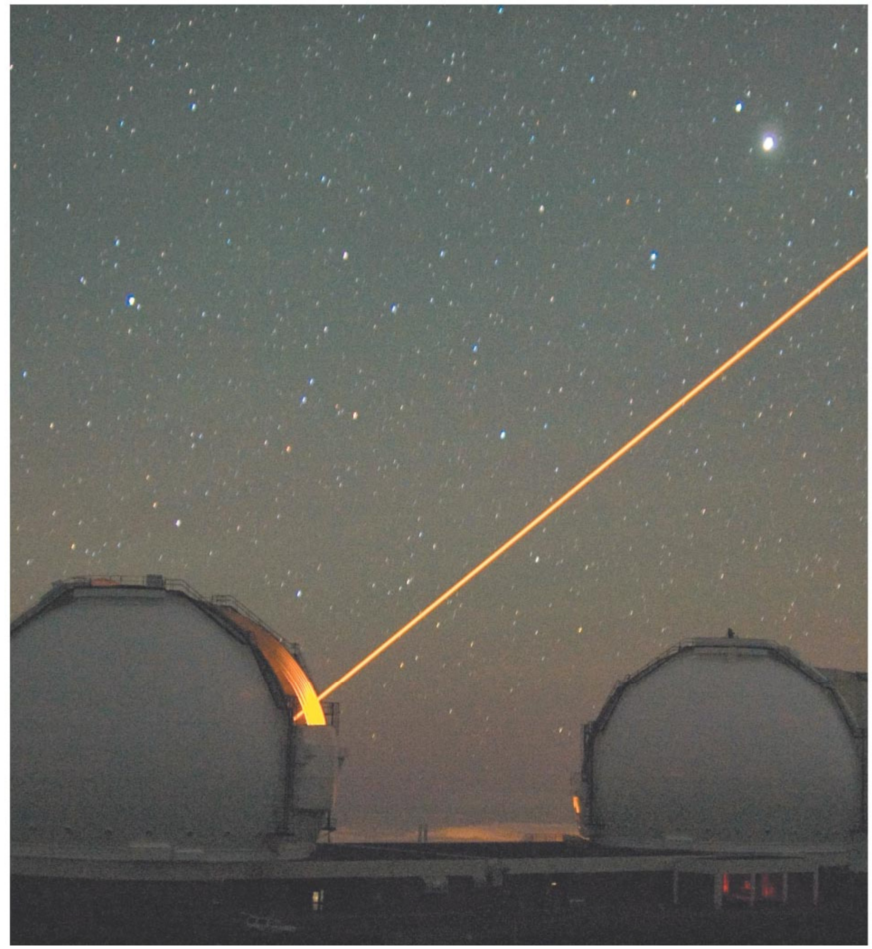
Chapter 42. Atomic Physics

Quantum mechanics provides us with an understanding of atomic structure and atomic properties. Lasers are one of the most important applications of the quantum-mechanical properties of atoms and light.



Chapter Goal: To understand the structure and properties of atoms.

Chapter 42. Atomic Physics

Topics:

- The Hydrogen Atom: Angular Momentum and Energy
- The Hydrogen Atom: Wave Functions and Probabilities
- The Electron's Spin
- Multielectron Atoms
- The Periodic Table of the Elements
- Excited States and Spectra
- Lifetimes of Excited States
- Stimulated Emission and Lasers

Hydrogen atom – solving Schrodinger's Equation

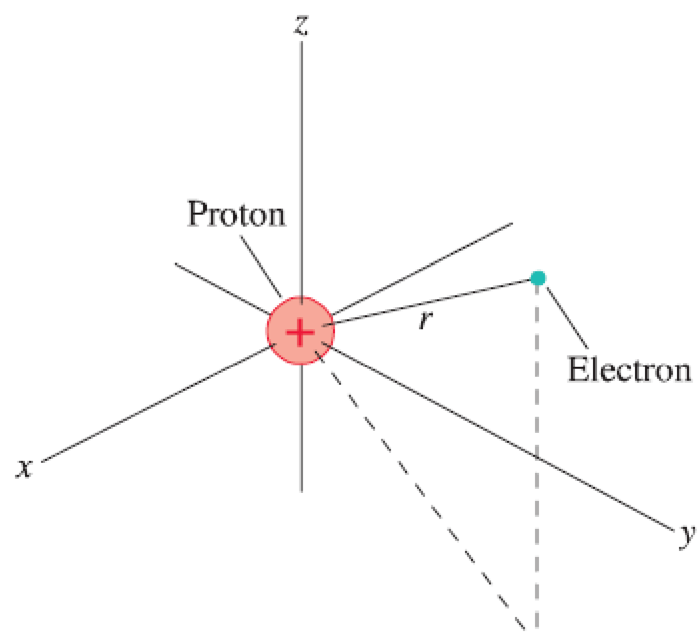
1. Specify a potential-energy function.
2. Solve the Schrödinger equation to find the wave functions, allowed energy levels, and other quantum properties.

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

Solve Schrodinger equation in 3-D:
Spherical coordinates;
boundary conditions on radial, periodic boundary conditions on theta and phi

Leads to quantization of energy, restrictions on total angular momentum and z-component of angular momentum

FIGURE 42.1 The electron in a hydrogen atom is distance r from the proton.



The normalized position wavefunctions, given in spherical coordinates are:

$$\psi_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^{\ell} L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_{\ell}^{m}(\vartheta,\varphi)$$

where:

$$\rho = \frac{2r}{na_0}$$

a_0 is the Bohr radius.

$L_{n-\ell-1}^{2\ell+1}(\rho)$ are the generalized Laguerre polynomials of degree $n-\ell-1$.

$Y_{\ell}^{m}(\vartheta,\varphi)$ is a spherical harmonic function of degree ℓ and order m.

The quantum numbers can take the following values:

$$n = 1, 2, 3, \dots$$
$$\ell = n-1, n-2, \dots, 1, 0$$
$$m = -\ell, \dots, \ell.$$

Stationary States of Hydrogen

Solutions to the Schrödinger equation for the hydrogen atom potential energy exist only if three conditions are satisfied:

1. The atom's energy must be one of the values

$$E_n = -\frac{1}{n^2}\left(\frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_B}\right) = -\frac{13.60 \text{ eV}}{n^2} \qquad n = 1, 2, 3, \ldots$$

where a_B is the Bohr radius. The integer n is called the **principal quantum number.** These energies are the same as those in the Bohr hydrogen atom.

Stationary States of Hydrogen

2. The angular momentum *L* of the electron's orbit must be one of the values

$$L = \sqrt{l(l+1)}\hbar \qquad l = 0, 1, 2, 3, \ldots, n-1$$

The integer *l* is called the **orbital quantum number.**

3. The *z*-component of the angular momentum must be one of the

$$L_z = m\hbar \qquad m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$

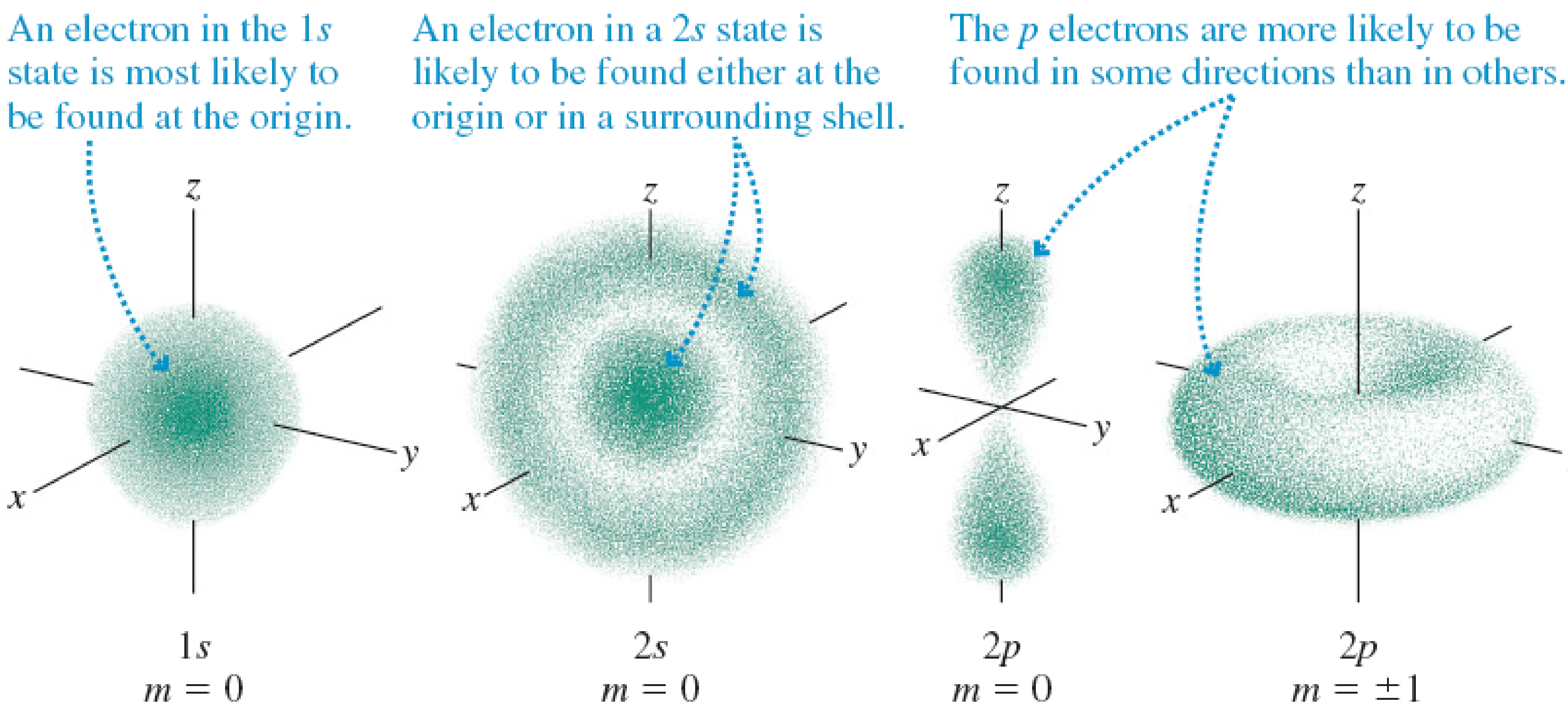
The integer *m* is called the **magnetic quantum number.**

Each stationary state of the hydrogen atom is identified by a triplet of quantum numbers (*n*, *l*, *m*).

TABLE 42.1 Symbols used to represent quantum number *l*

l	Symbol
0	*s*
1	*p*
2	*d*
3	*f*

FIGURE 42.5 The probability densities of the electron in the $1s$, $2s$, and $2p$ states of hydrogen.



The Hydrogen Atom: Wave Functions and Probabilities

The probability of finding an electron within a shell of radius *r* and thickness *δr* around a proton is

$$\text{Prob}(\text{in } \delta r \text{ at } r) = |R_{nl}(r)|^2 \delta V = 4\pi r^2 |R_{nl}(r)|^2 \delta r = P_r(r)\,\delta r$$

$$P_r(r) = 4\pi r^2 |R_{nl}(r)|^2$$

where the first three radial wave functions of the electron in a neutral hydrogen atom are

$$R_{1s}(r) = \frac{1}{\sqrt{\pi a_B^3}} e^{-r/a_B}$$

$$R_{2s}(r) = \frac{1}{\sqrt{8\pi a_B^3}} \left(1 - \frac{r}{2a_B}\right) e^{-r/2a_B}$$

$$R_{2p}(r) = \frac{1}{\sqrt{24\pi a_B^3}} \left(\frac{r}{2a_B}\right) e^{-r/2a_B}$$

FIGURE 42.6 The 1*s* and 2*s* radial wave functions of hydrogen.

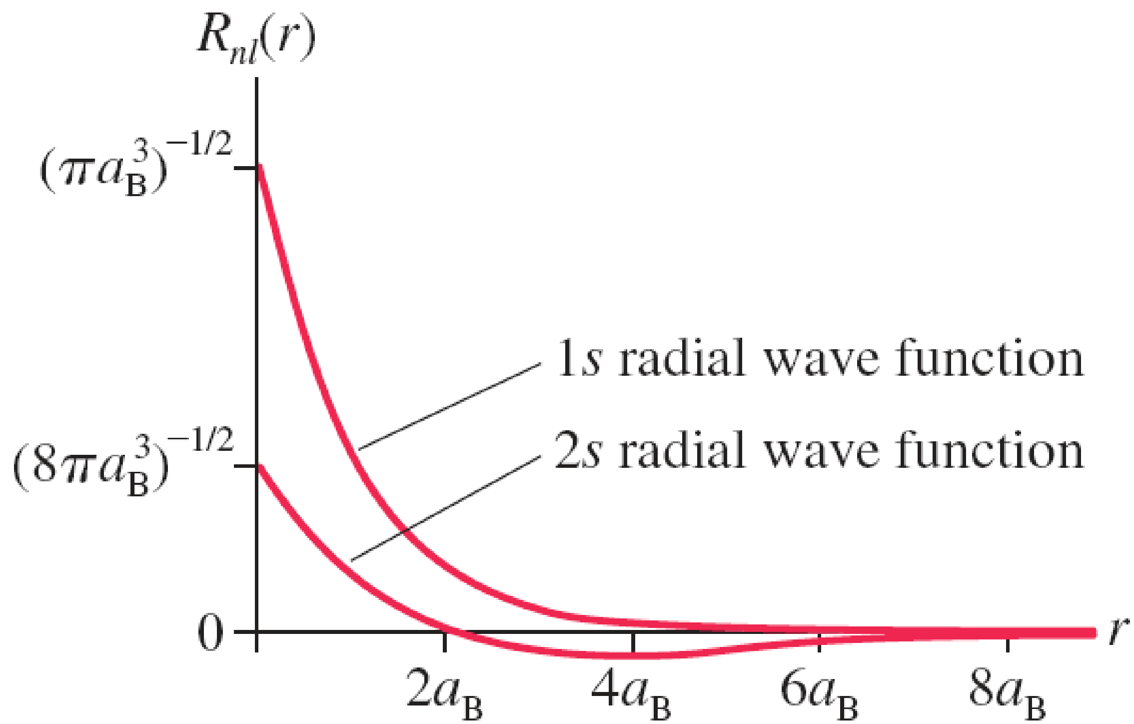


FIGURE 42.8 The radial probability densities for $n = 1$, 2, and 3.

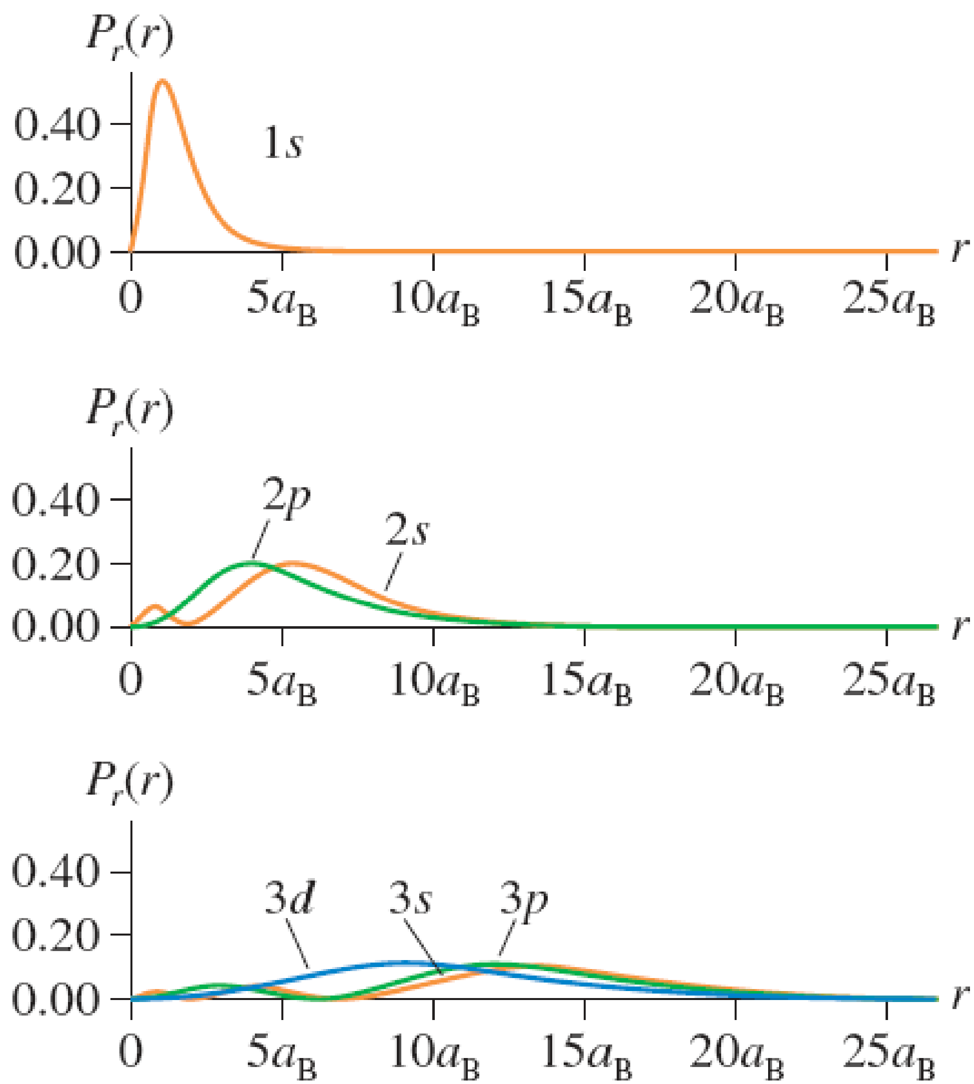


FIGURE 42.2 The angular momentum of an elliptical orbit.

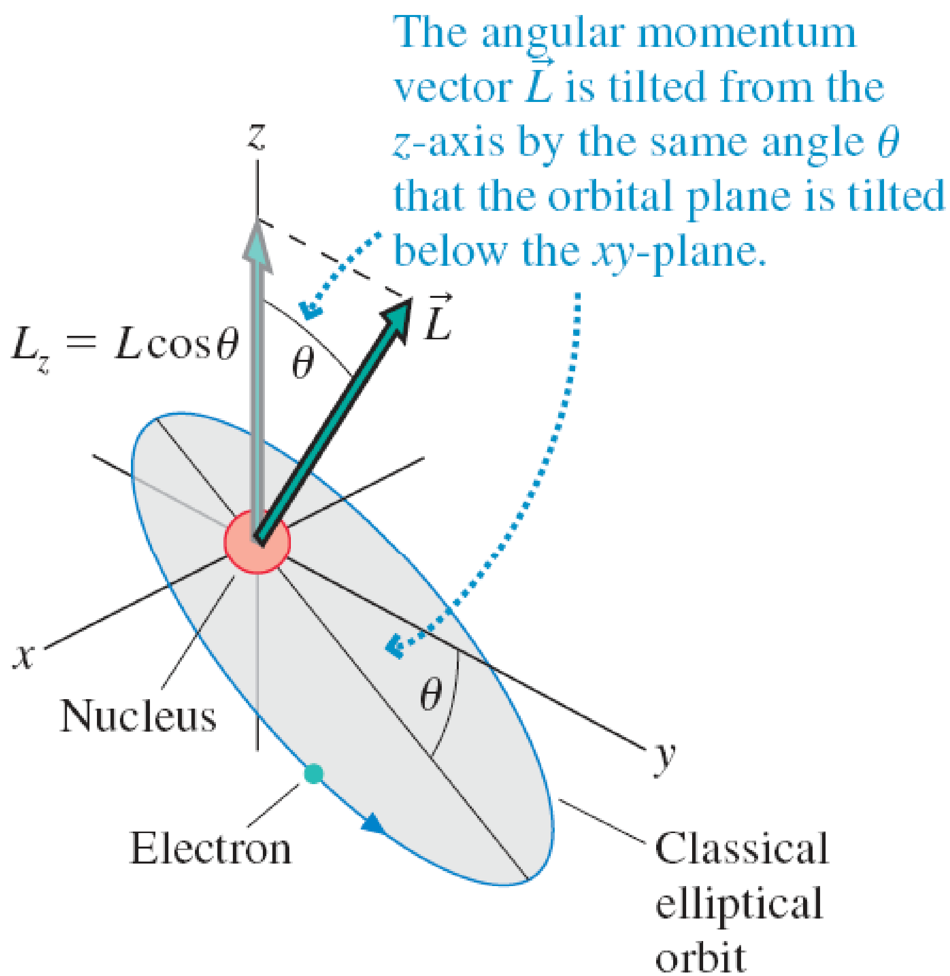
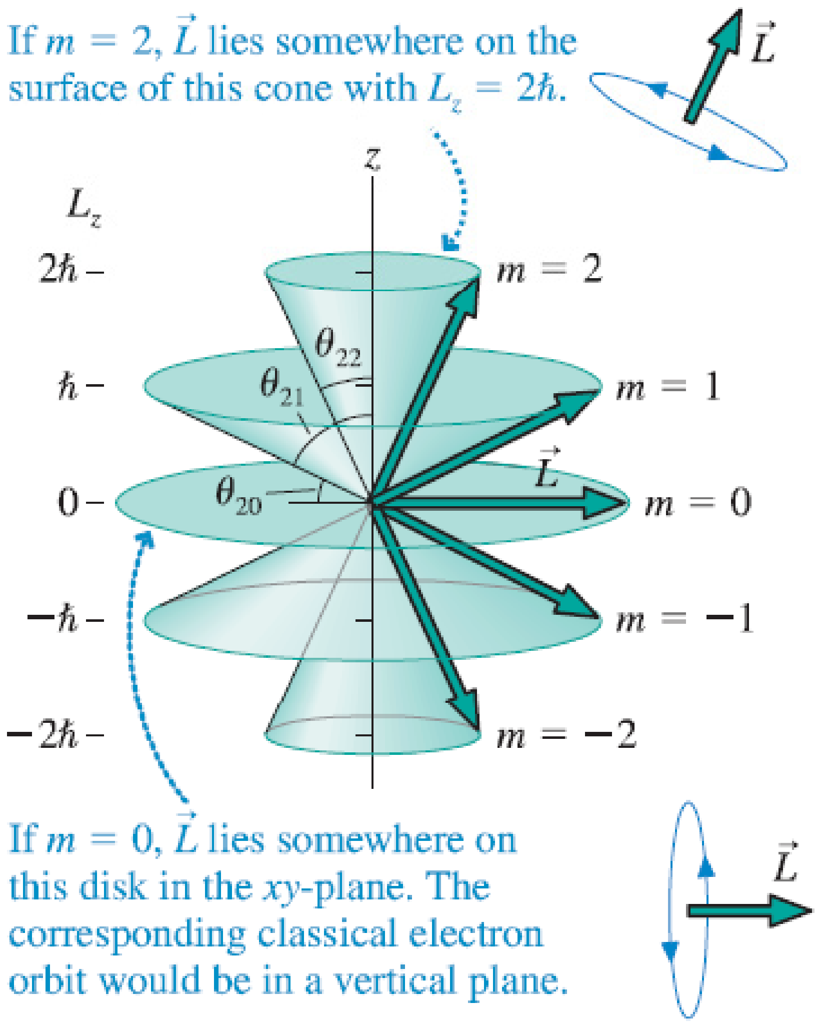
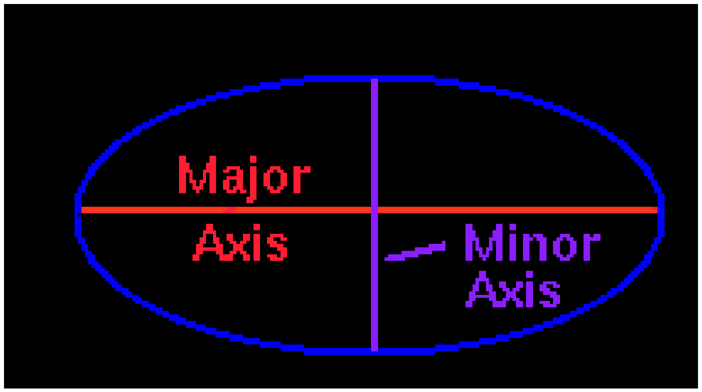


FIGURE 42.3 The five possible orientations of the angular momentum vector for $l = 2$. The angular momentum vectors all have length $L = \sqrt{6}\hbar = 2.45\hbar$.



States with smaller l correspond to elliptical orbits.



Small body orbiting a central body

In astrodynamics the **orbital period** T (in seconds) of a small body orbiting a central body in a circular or elliptical orbit is:

$$T = 2\pi\sqrt{a^3/\mu}$$

where:

- a is length of orbit's semi-major axis,
- $\mu = GM$ is the standard gravitational parameter,
- G is the gravitational constant,
- M the mass of the central body.

Note that for all ellipses with a given semi-major axis, the orbita

FIGURE 42.9 More circular orbits have larger angular momenta.

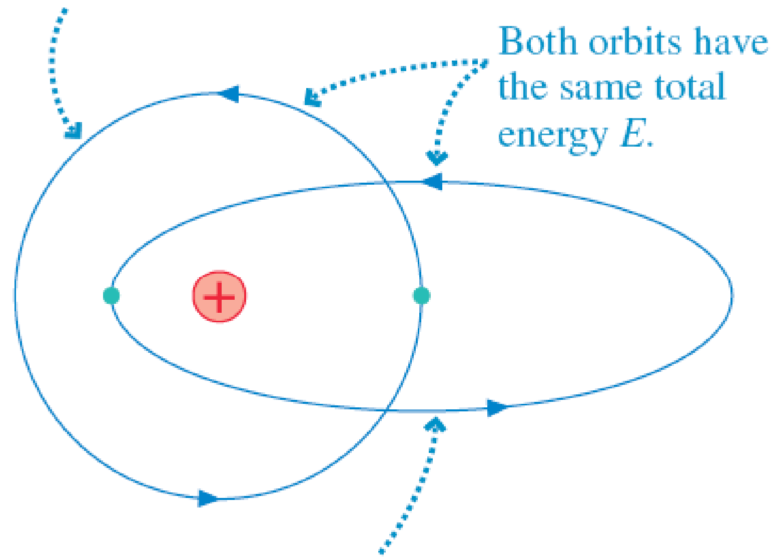


FIGURE 42.4 Energy-level diagram for the hydrogen atom.

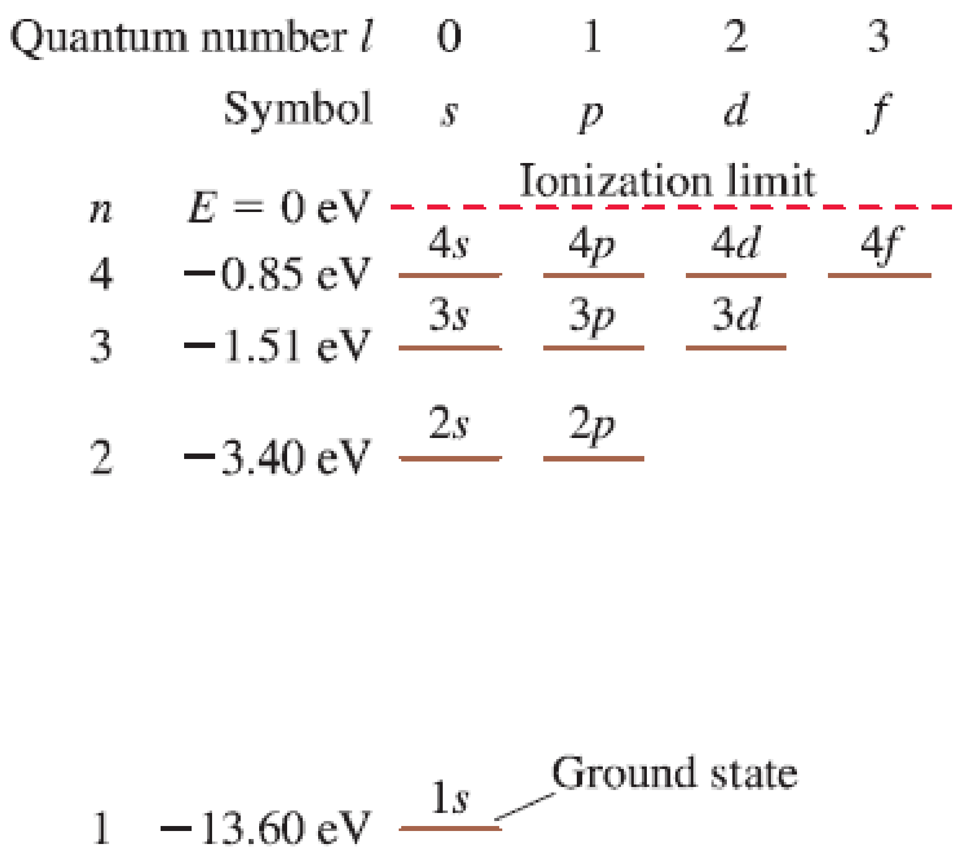


FIGURE 42.11 The Stern-Gerlach experiment.

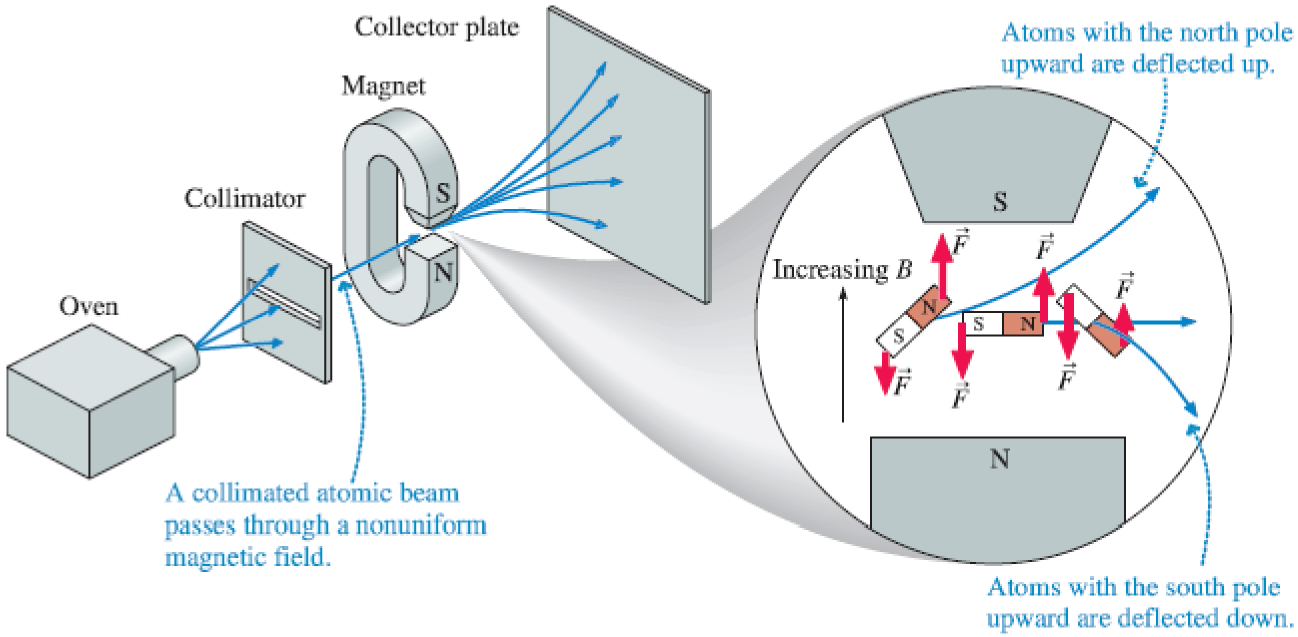


FIGURE 42.10 An orbiting electron generates a magnetic moment.

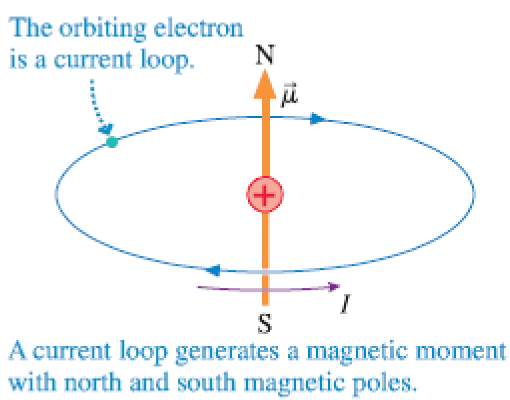
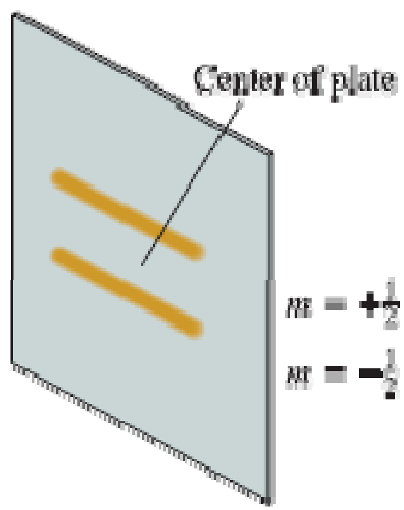
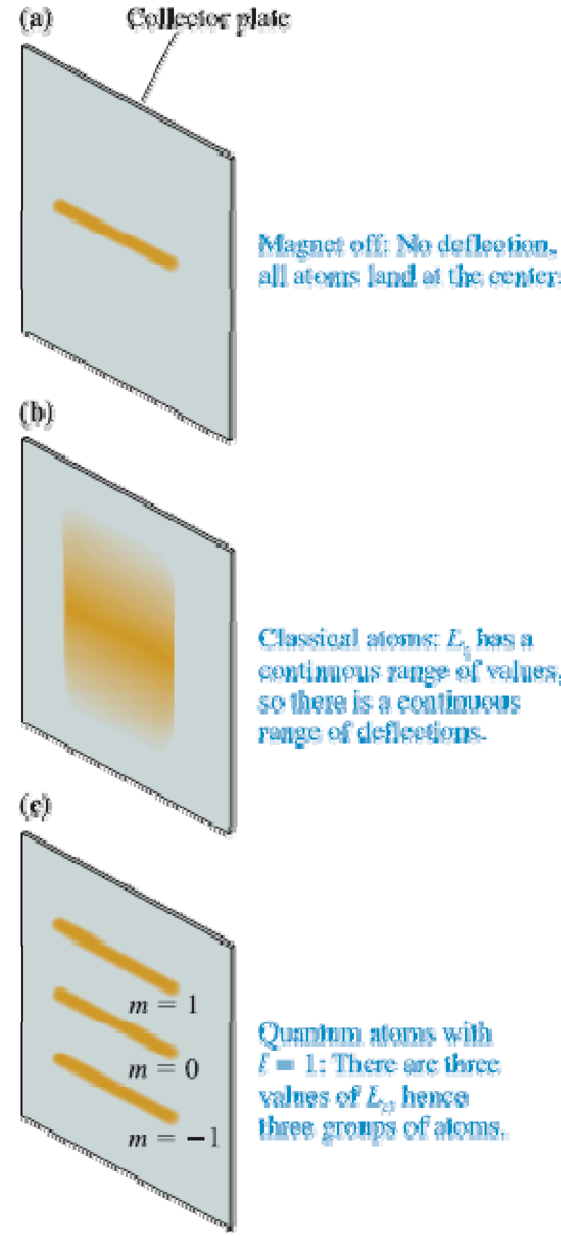


FIGURE 42.13 The outcome of the Stern-Gerlach experiment for hydrogen atoms.





The Electron's Spin

If the electron has an inherent magnetic moment, it must have an inherent angular momentum. This angular momentum is called the electron's **spin,** which is designated vector-***S***.

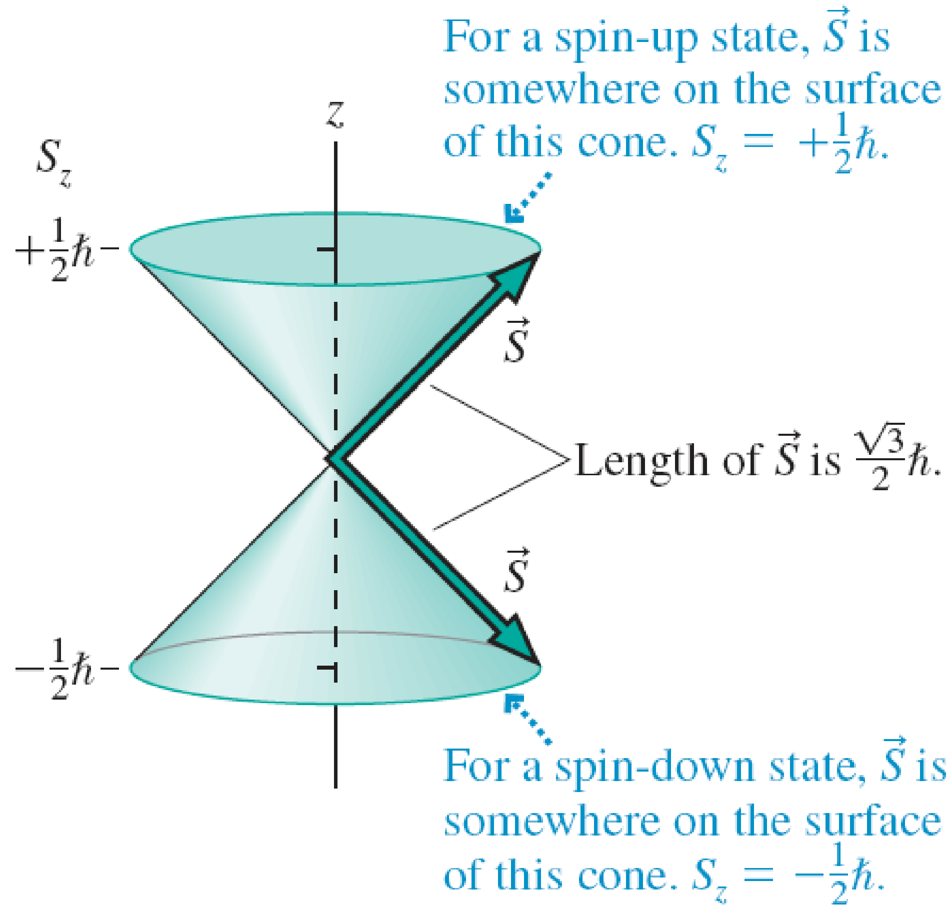
The *z*-component of this spin angular momentum is

$$S_z = m_s \hbar \quad \text{where } m_s = +\tfrac{1}{2} \quad \text{or} \quad -\tfrac{1}{2}$$

The quantity m_s is called the **spin quantum number.**

The *z*-component of the spin angular momentum vector is determined by the electron's orientation. The $m_s = +\frac{1}{2}$ state, with $S_z = +\frac{1}{2}$ *h*-bar, is called the **spin-up** state and the $m_s = -\frac{1}{2}$ state is called the **spin-down** state.

FIGURE 42.14 The spin angular momentum has two possible orientations.



Multielectron Atoms

- When analyzing a multielectron atom, each electron is treated independently of the other electrons.
- This approach is called the **independent particle approximation,** or IPA.
- This approximation allows the Schrödinger equation for the atom to be broken into *Z* separate equations, one for each electron.
- A major consequence of the IPA is that **each electron can be described by a wave function having the same four quantum numbers n, l, m, and m_s used to describe the single electron of hydrogen.**
- A major difference, however, is that the energy of an electron in a multielectron atom depends on both *n and l.*

FIGURE 42.15 An energy-level diagram for electrons in a multielectron atom.

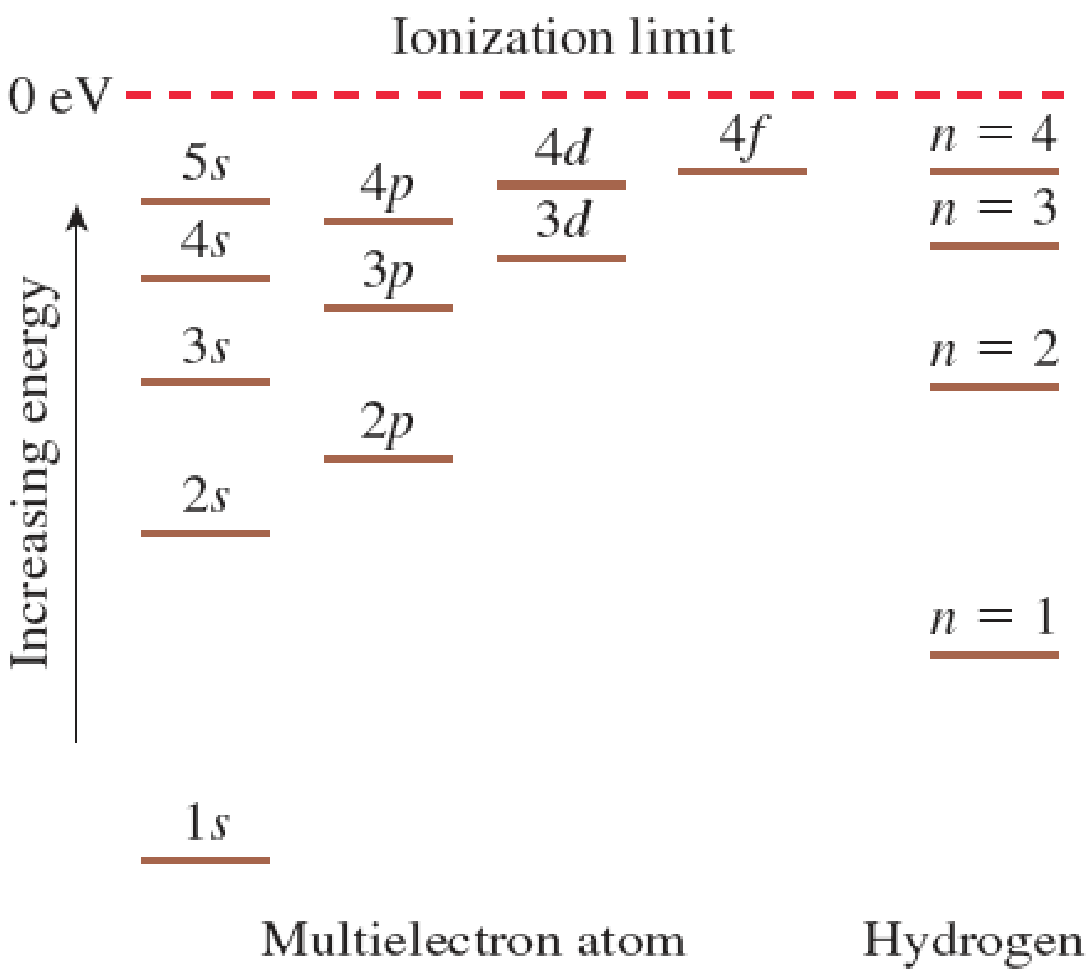


FIGURE 42.16 High-l and low-l orbitals in a multielectron atom.

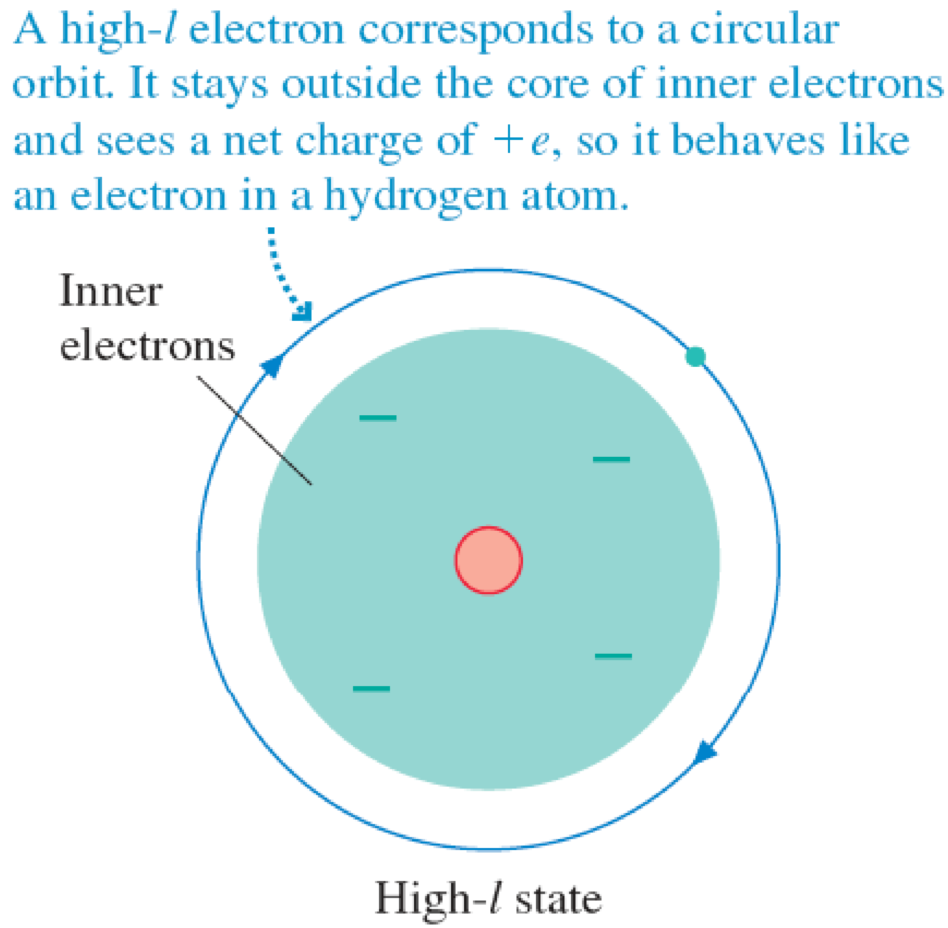
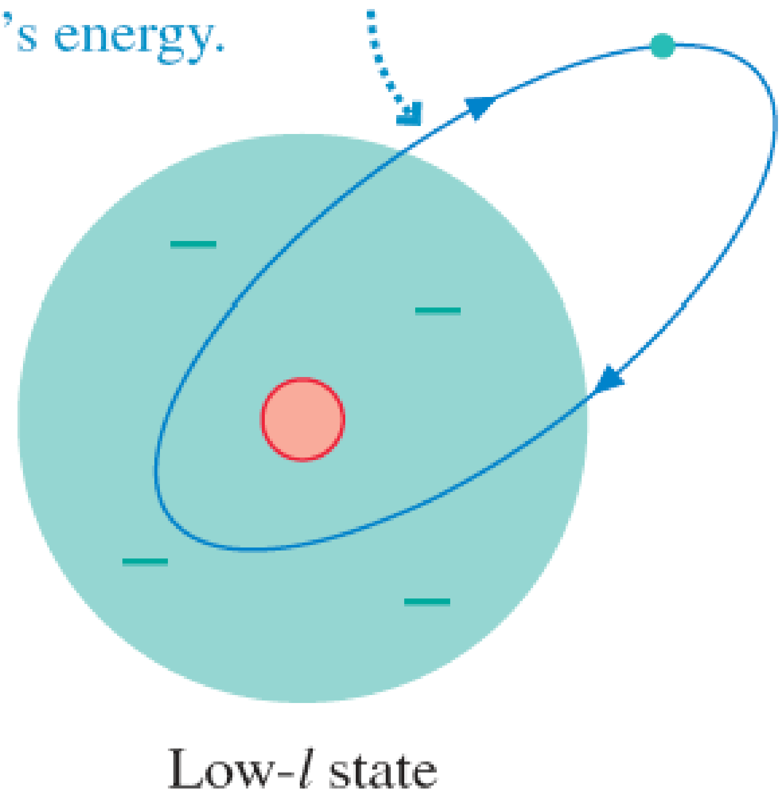


FIGURE 42.16 High-l and low-l orbitals in a multielectron atom.



The Pauli Exclusion Principle

In 1925, Pauli hypothesized that no two electrons in a quantum system can be in the same quantum state.

In other words, **no two electrons can have exactly the same set of quantum numbers** *n*, *l*, *n* and m_s.

If one electron is present in a state, it *excludes* all others.

This statement, which is called the **Pauli exclusion principle,** turns out to be an extremely profound statement about the nature of matter.

FIGURE 42.22 Filling the $2p$ subshell with the elements boron through neon.

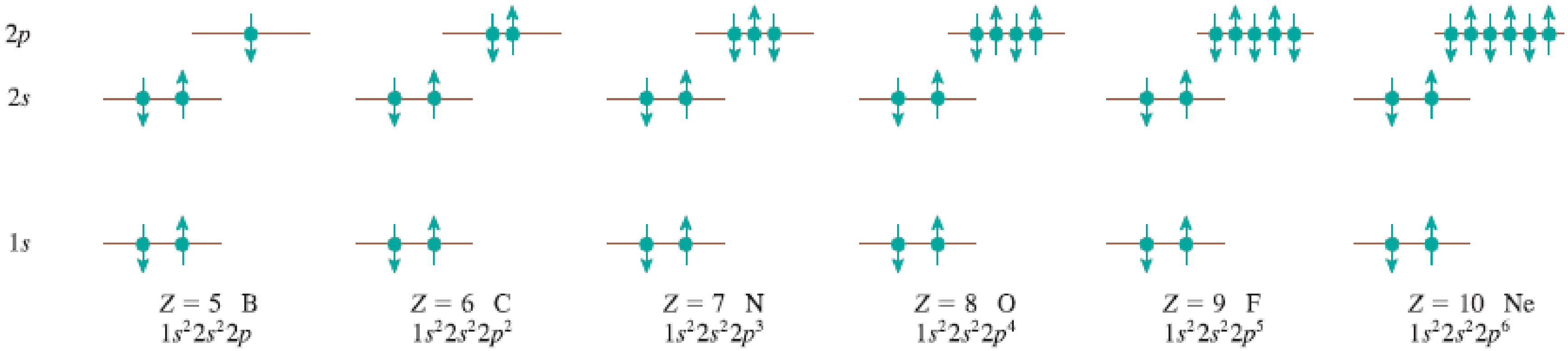


FIGURE 42.15 An energy-level diagram for electrons in a multielectron atom.

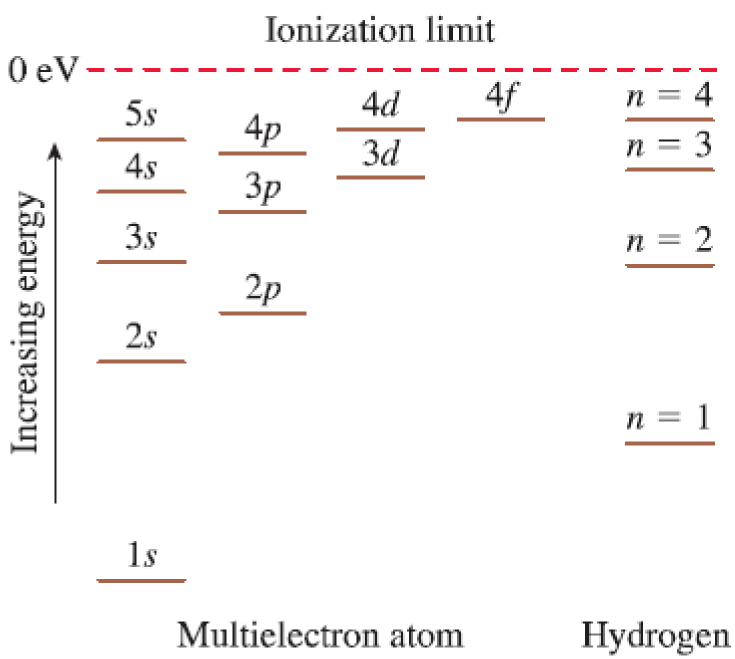


FIGURE 42.20 The modern periodic table of the elements, showing the atomic number Z of each.

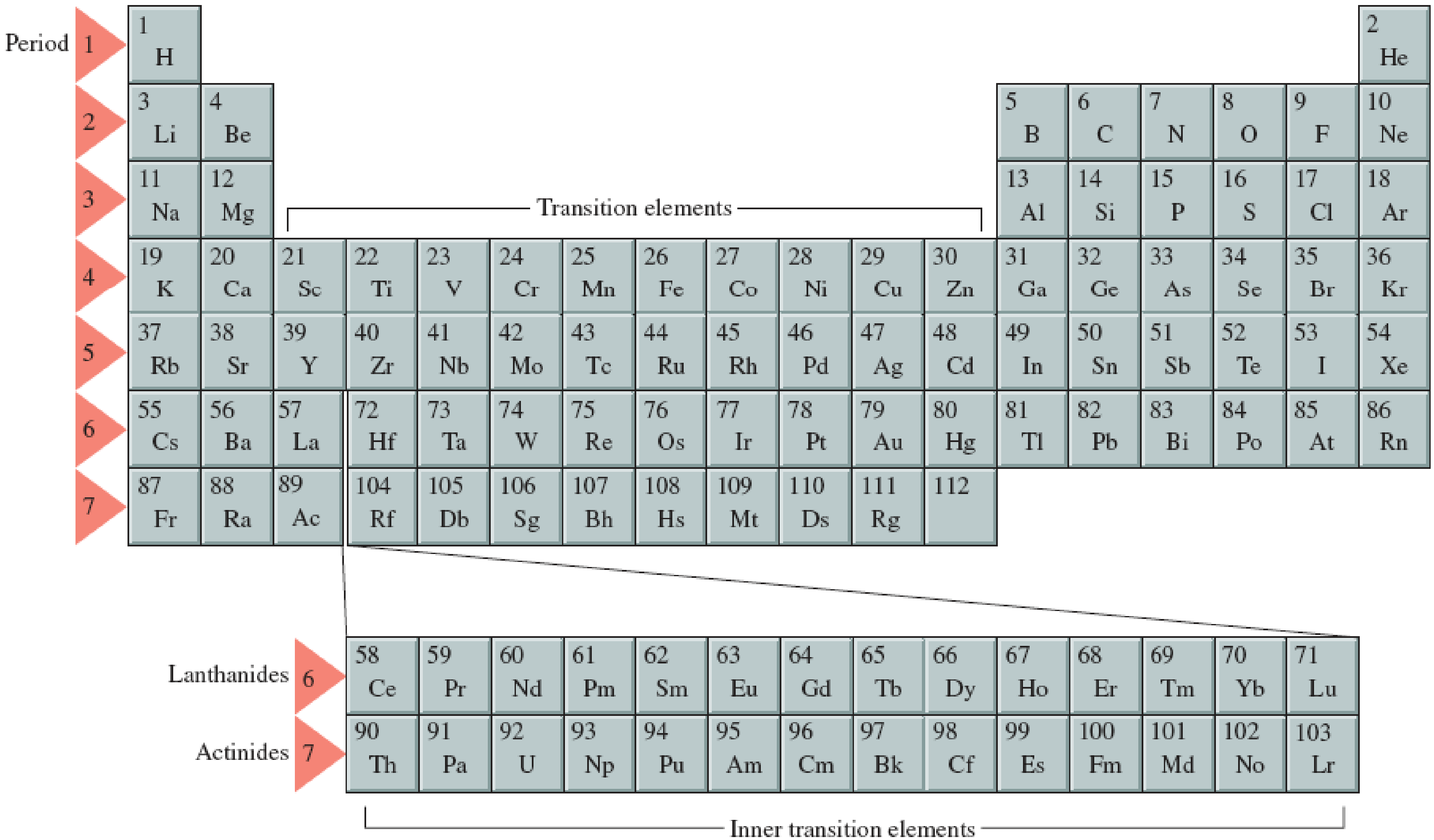
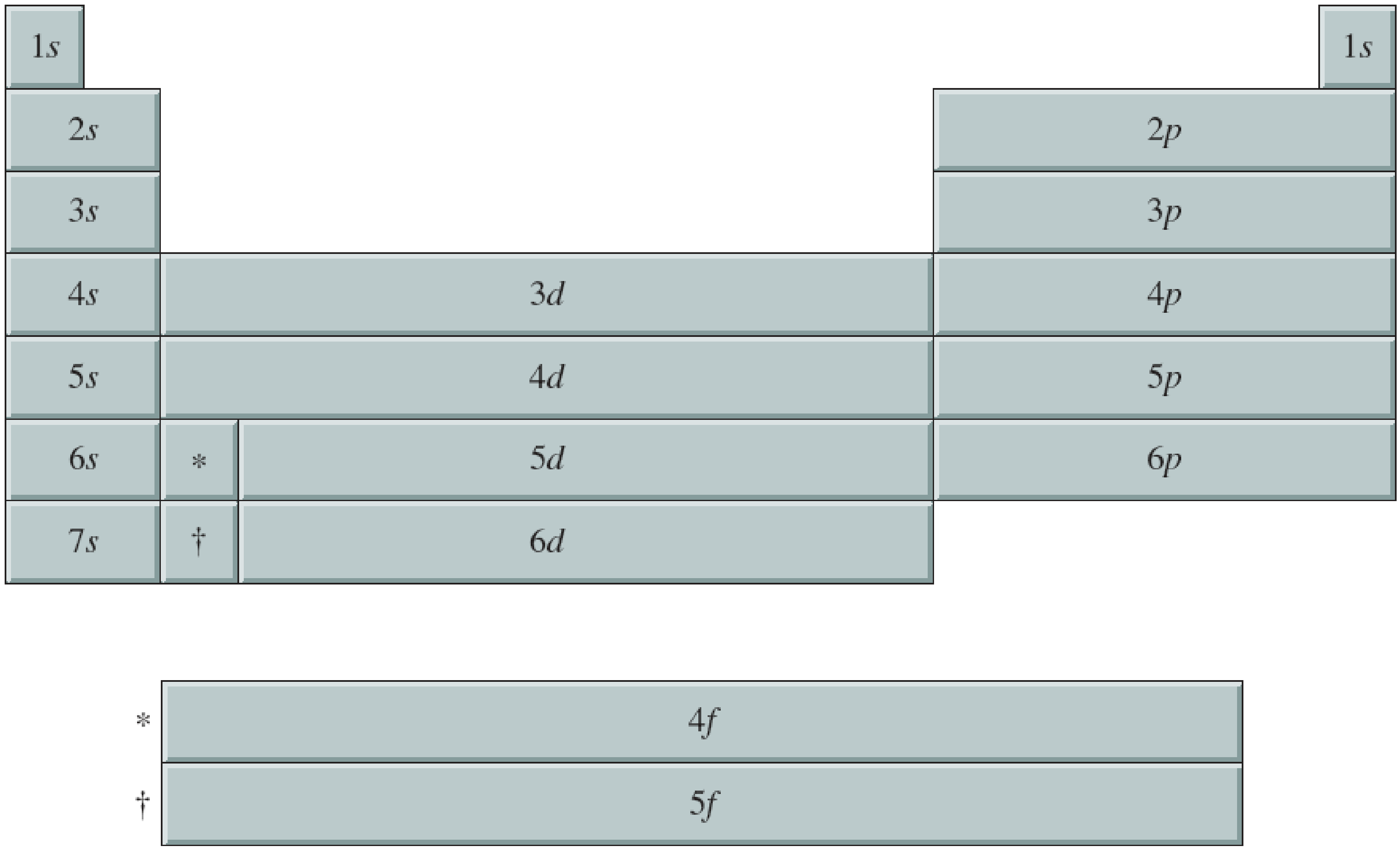


FIGURE 42.23 Summary of the order in which subshells are filled in the periodic table.



Excited States and Spectra

An atom can jump from one stationary state, of energy E_1, to a higher-energy state E_2 by absorbing a photon of frequency

$$f = \frac{\Delta E_{\text{atom}}}{h} = \frac{E_2 - E_1}{h}$$

In terms of the wavelength:

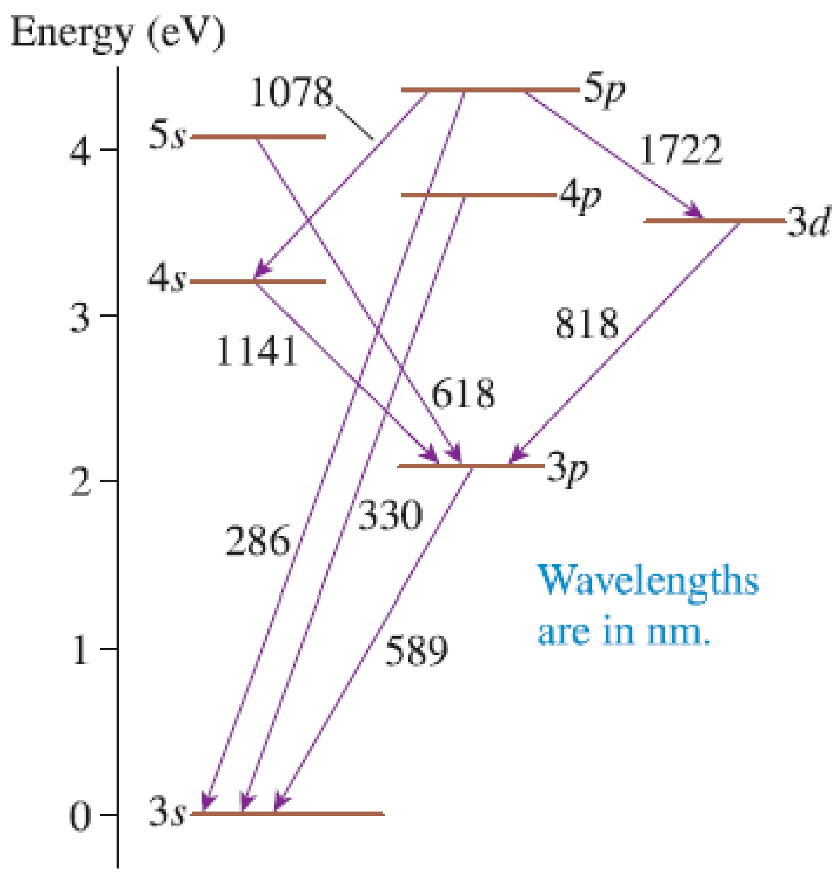
$$\lambda = \frac{c}{f} = \frac{hc}{\Delta E_{\text{atom}}} = \frac{1240\ \text{eV nm}}{\Delta E\,(\text{in eV})}$$

Note that a transition from a state in which the valence electron has orbital quantum number l_1 to another with orbital quantum number l_2 is allowed only if

$$\Delta l = |l_2 - l_1| = 1 \quad \text{(selection rule for emission and absorption)}$$

FIGURE 42.28 The emission spectrum of sodium.

(a)



Lifetimes of Excited States

Consider an experiment in which N_0 excited atoms are created at time $t = 0$. The number of excited atoms remaining at time t is described by the exponential function

$$N_{\text{exc}} = N_0 e^{-t/\tau}$$

where

$$\tau = \frac{1}{r} = \text{the } \textit{lifetime} \text{ of the excited state}$$

FIGURE 42.32 Three types of radiative transitions.

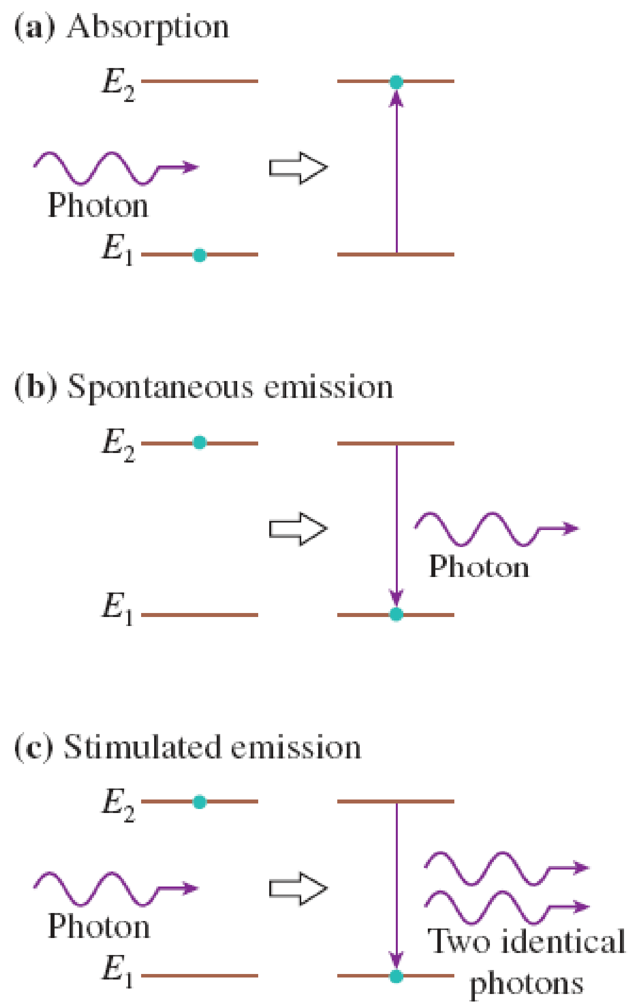


FIGURE 42.34 Stimulated emission creates a chain reaction of photon production in a population of excited atoms.

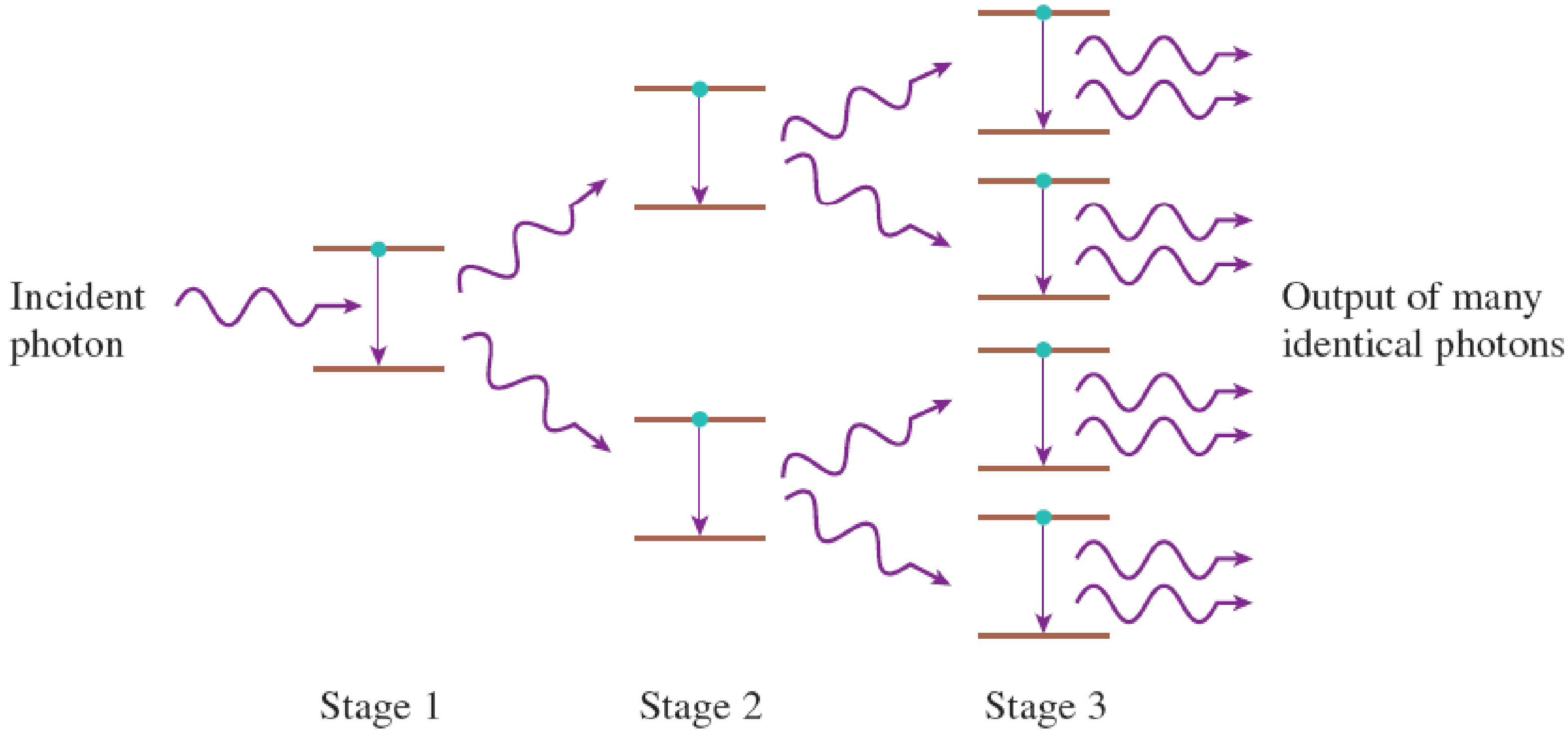


FIGURE 42.35 Lasing takes place in an optical cavity.