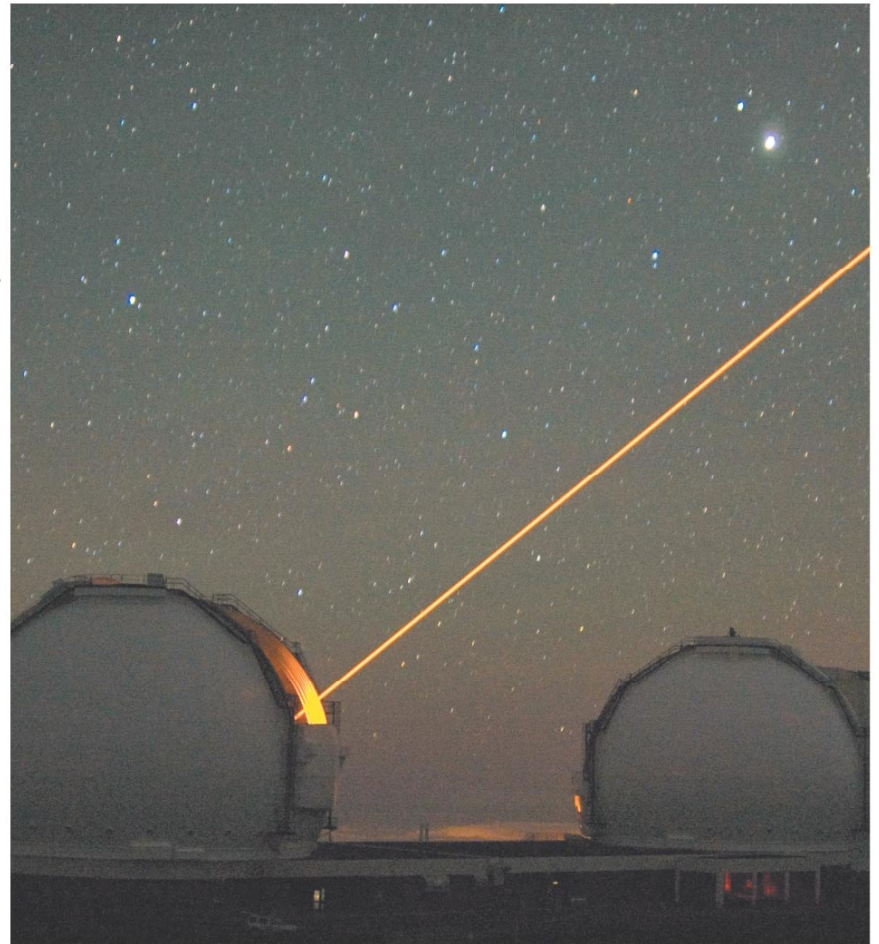


Chapter 42. Atomic Physics

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

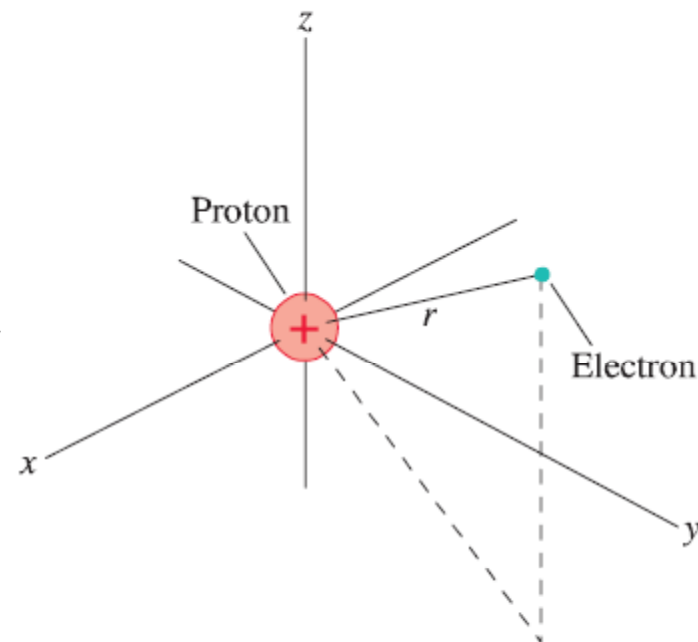
1. Specify a potential-energy function.
2. Solve the Schrödinger equation to find the wave functions, allowed energy levels, and other quantum properties.

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

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

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

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

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

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

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

$$L_z = m\hbar \quad m = -l, -l+1, \dots, 0, \dots, l-1, l$$

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

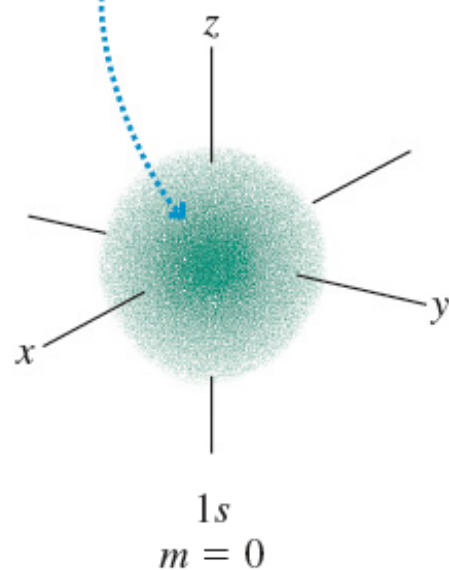
Each stationary state of the hydrogen atom is identified by a triplet of quantum numbers (n, l, m) .

TABLE 42.1 Symbols used to represent quantum number l

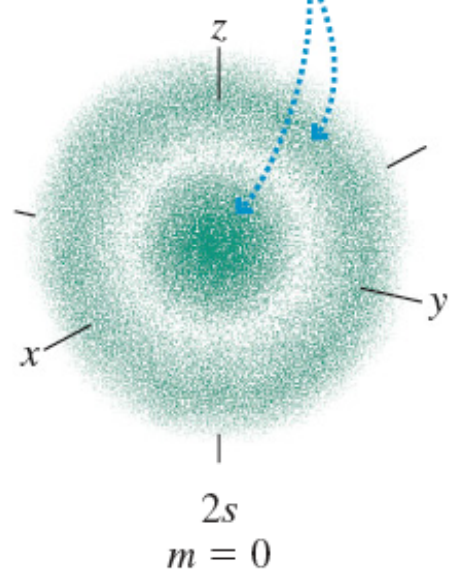
| l | Symbol |
|-----|--------|
| 0 | s |
| 1 | p |
| 2 | d |
| 3 | f |

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

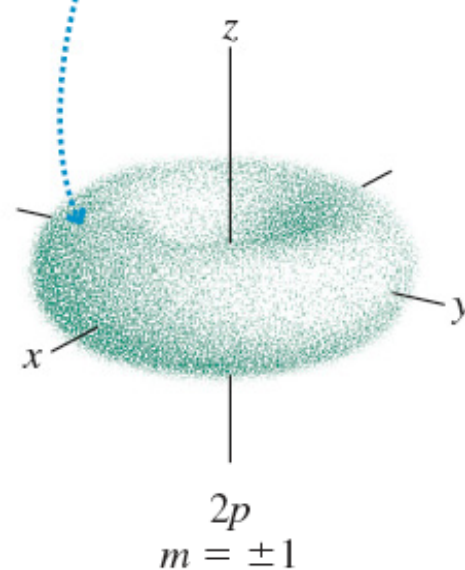
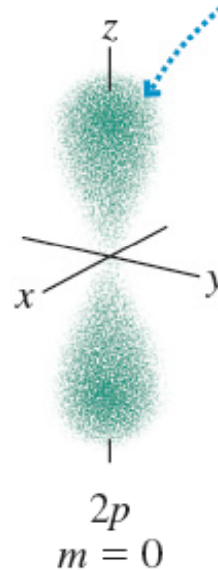
An electron in the $1s$ state is most likely to be found at the origin.



An electron in a $2s$ state is likely to be found either at the origin or in a surrounding shell.



The p electrons are more likely to be found in some directions than in others.



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 1s and 2s radial wave functions of hydrogen.

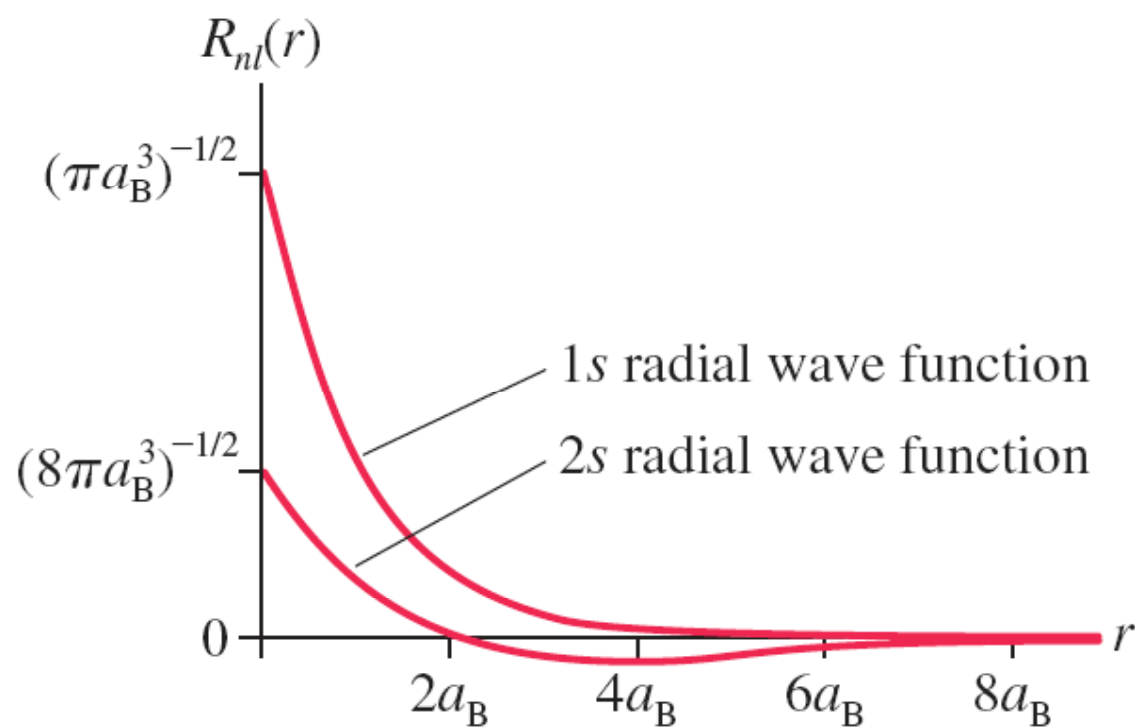


FIGURE 42.8 The radial probability densities for $n = 1, 2$, and 3.

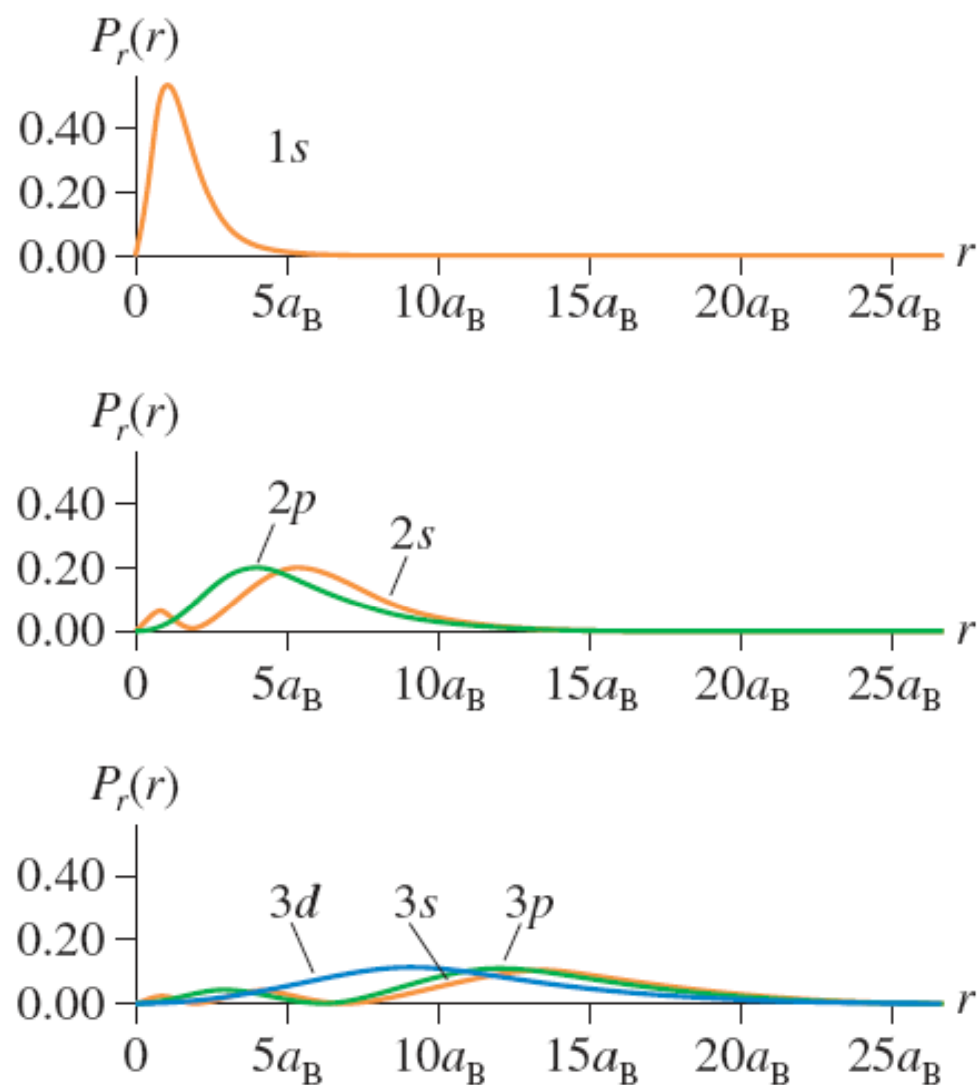


FIGURE 42.2 The angular momentum of an elliptical orbit.

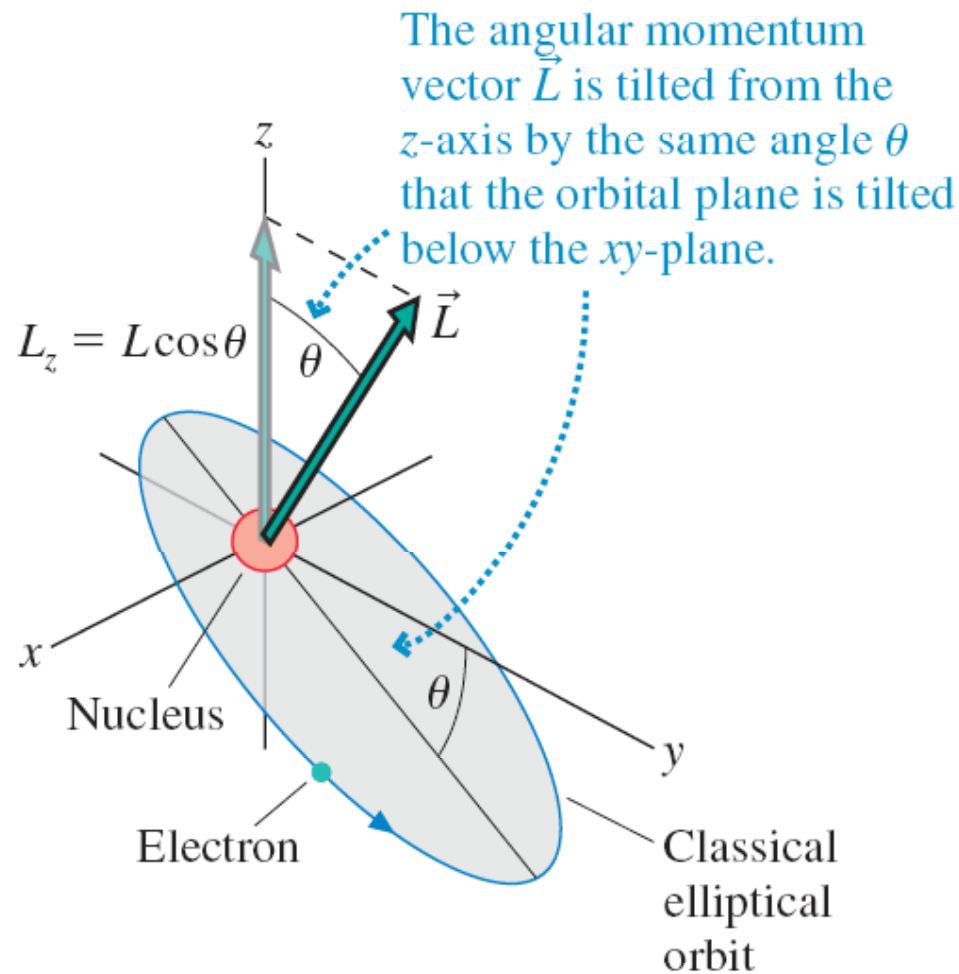
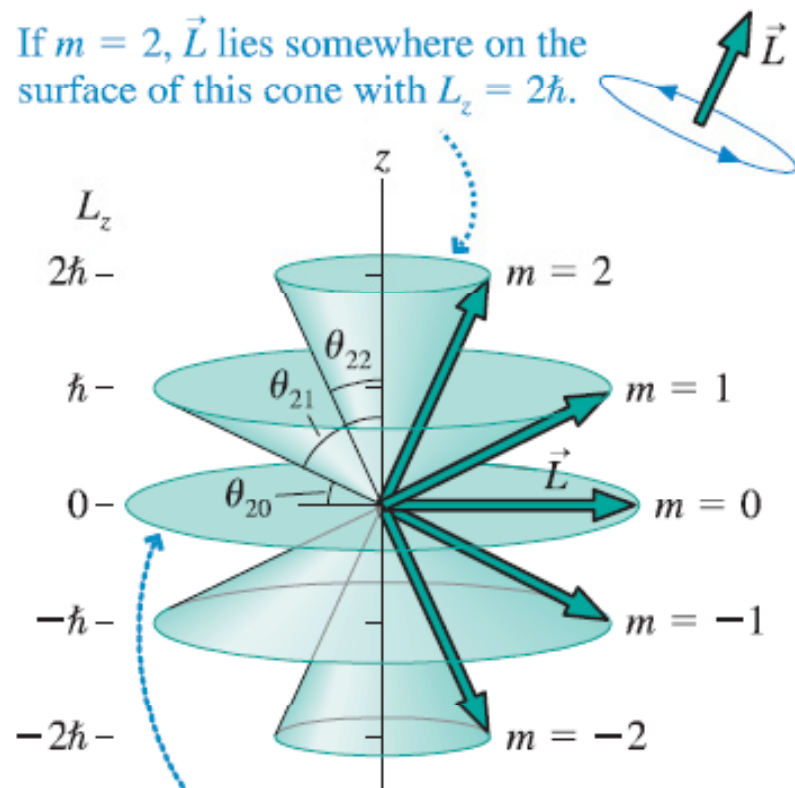
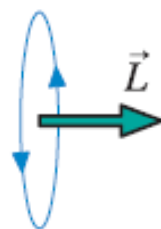


FIGURE 42.3 The five possible orientations of the angular momentum vector for $l = 2$. The angular momentum vectors all have length $L = \sqrt{6}\hbar = 2.45\hbar$.

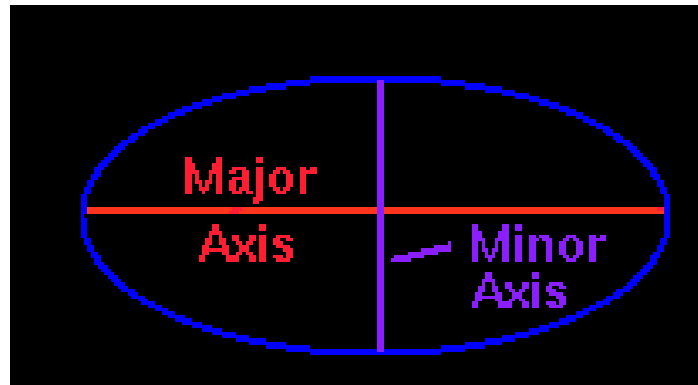
If $m = 2$, \vec{L} lies somewhere on the surface of this cone with $L_z = 2\hbar$.



If $m = 0$, \vec{L} lies somewhere on this disk in the xy -plane. The corresponding classical electron orbit would be in a vertical plane.



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:

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

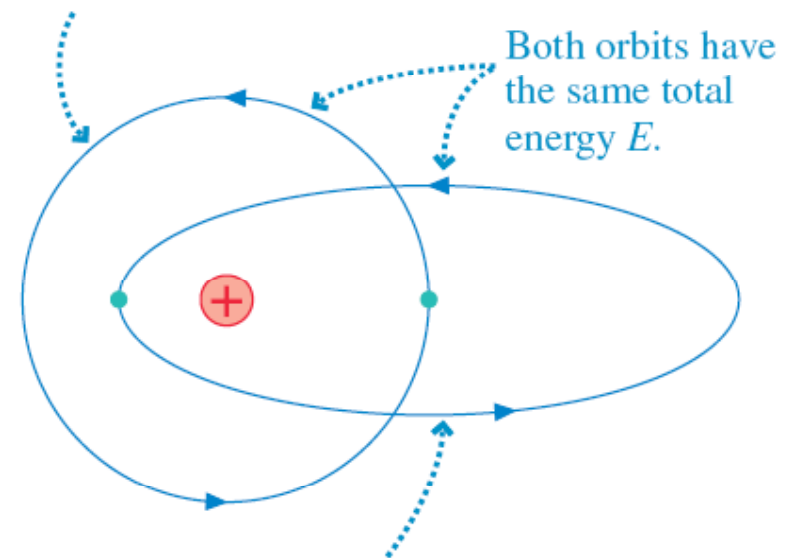
where:

- 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.

The circular orbit has the largest angular momentum. The electron stays at a constant distance from the nucleus.



The elliptical orbit has a smaller angular momentum. Compared to the circular orbit, the electron gets both closer to and farther from the nucleus.

FIGURE 42.4 Energy-level diagram for the hydrogen atom.

| Quantum number l | 0 | 1 | 2 | 3 |
|--------------------|---------------------|-----|-----|-----|
| Symbol | s | p | d | f |
| n | Ionization limit | | | |
| | $E = 0 \text{ eV}$ | | | |
| 4 | -0.85 eV | | | |
| 3 | -1.51 eV | | | |
| 2 | -3.40 eV | | | |
| 1 | -13.60 eV | | | |

Ground state

FIGURE 42.11 The Stern-Gerlach experiment.

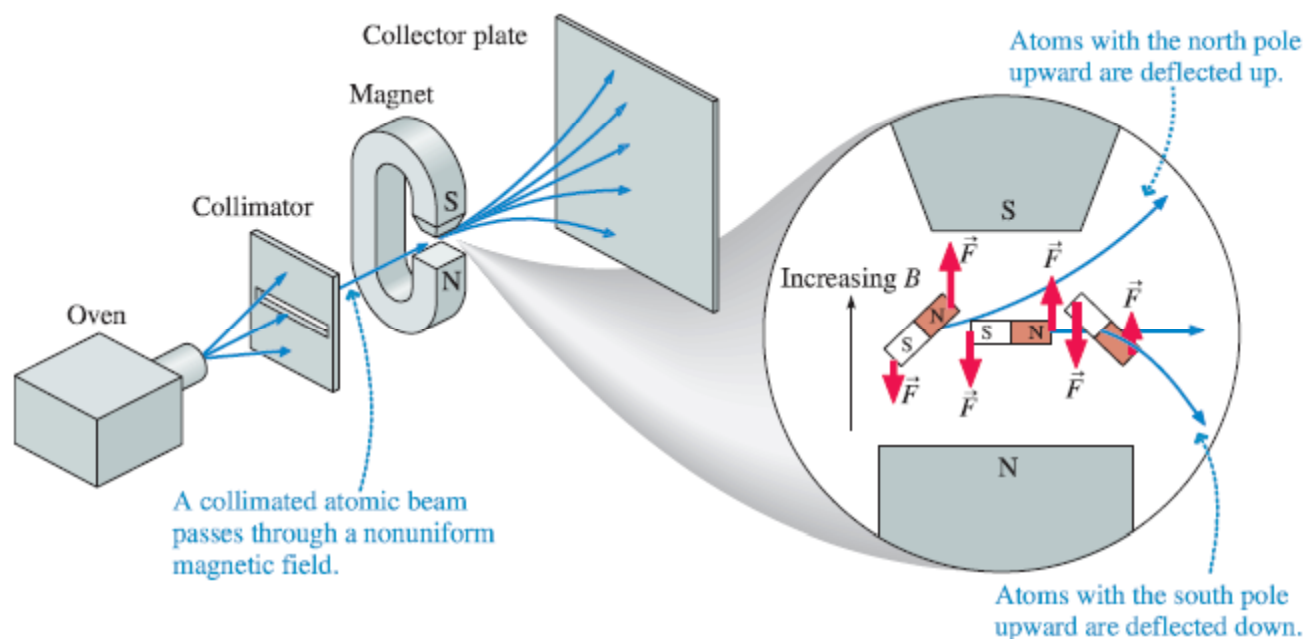


FIGURE 42.10 An orbiting electron generates a magnetic moment.

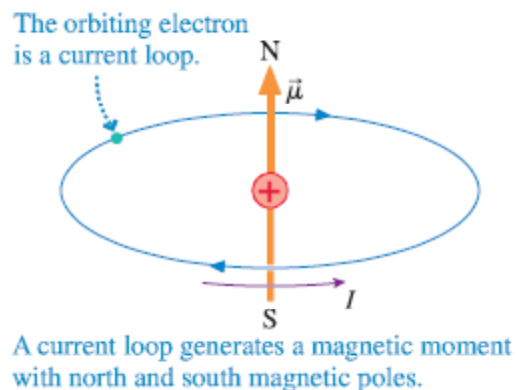
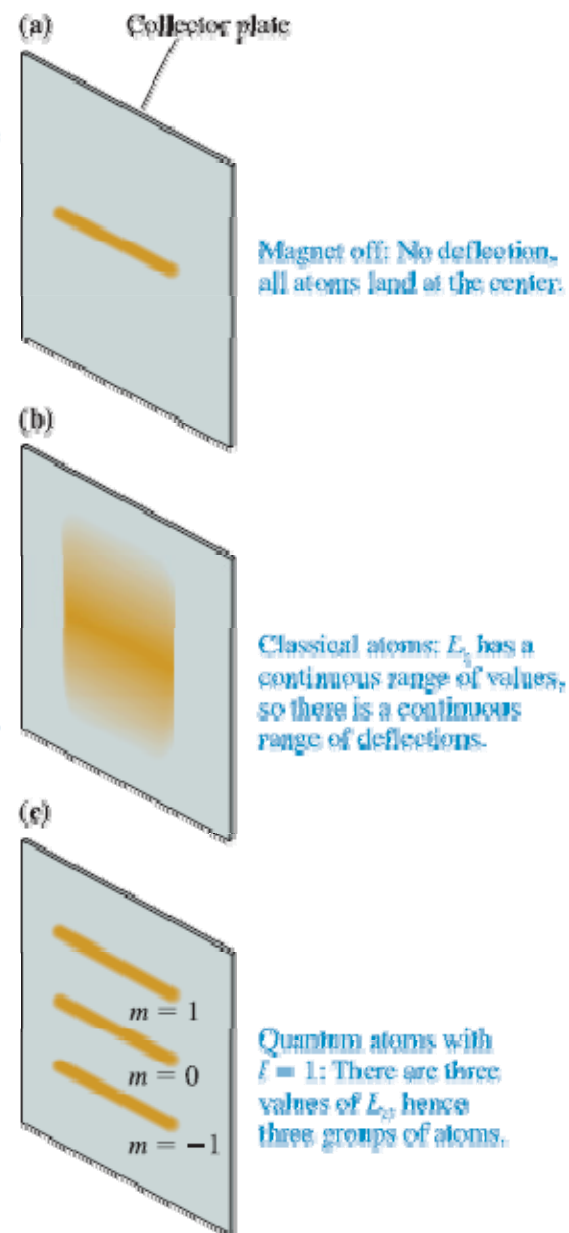
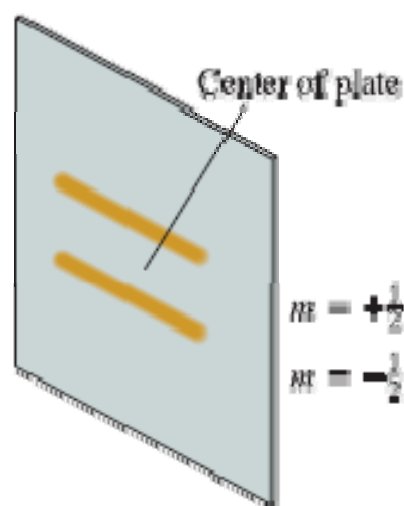


FIGURE 42.13 The outcome of the Stern-Gerlach experiment for hydrogen atoms.



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**.

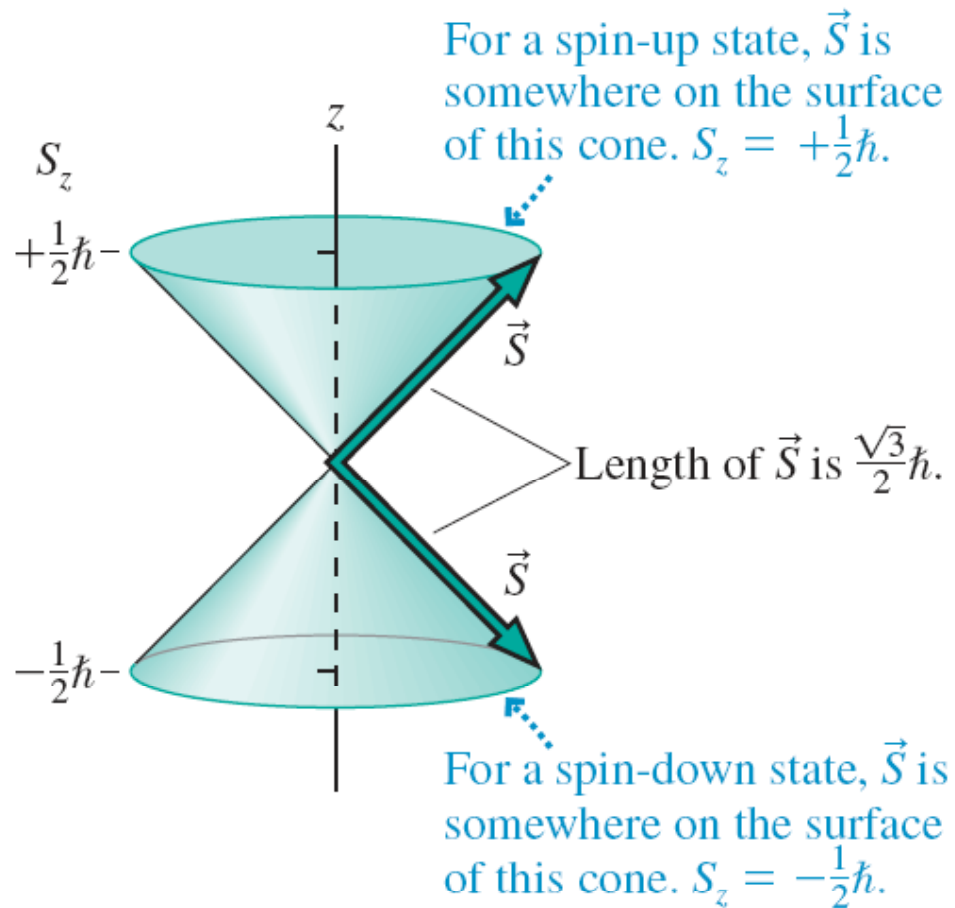
The z-component of this spin angular momentum is

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

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 $S_z = +\frac{1}{2} \hbar$, 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.

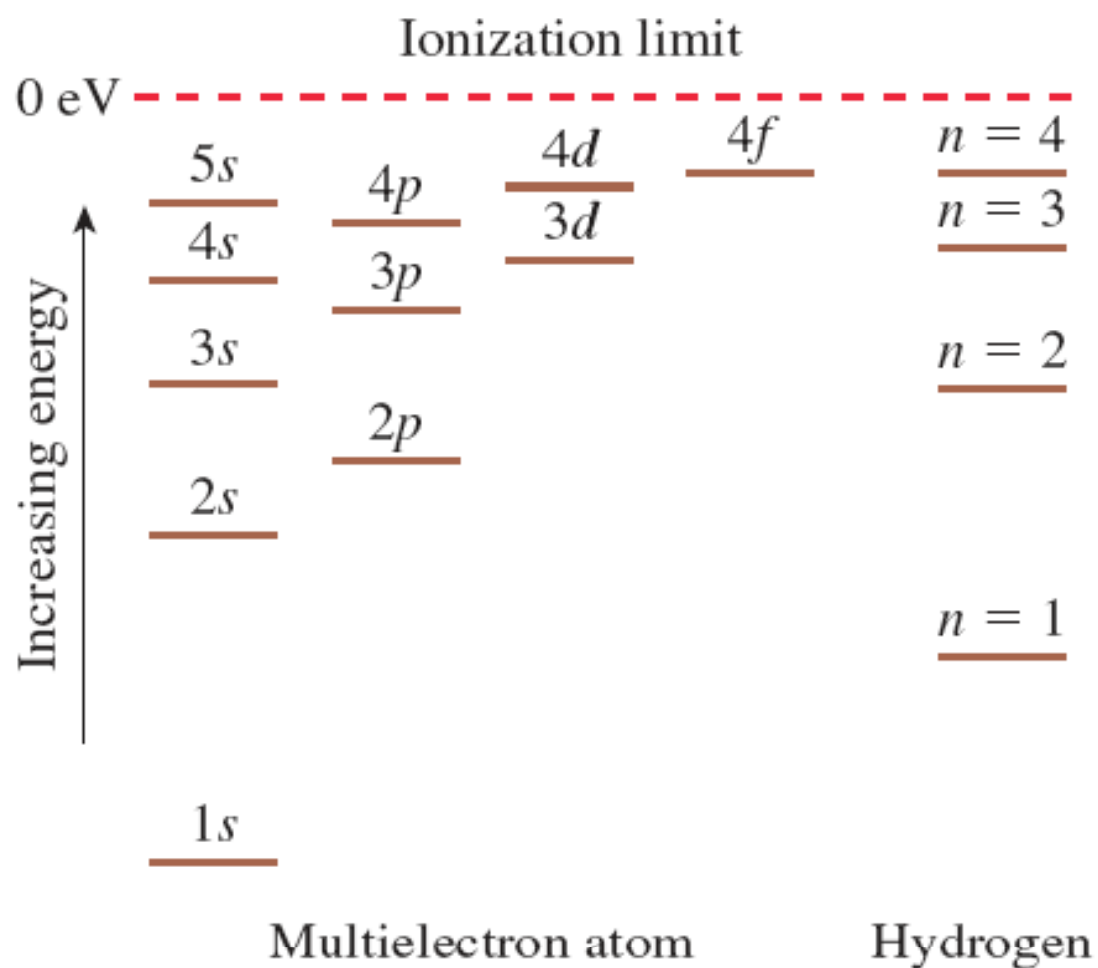


FIGURE 42.16 High- l and low- l orbitals in a multielectron atom.

A high- l electron corresponds to a circular orbit. It stays outside the core of inner electrons and sees a net charge of $+e$, so it behaves like an electron in a hydrogen atom.

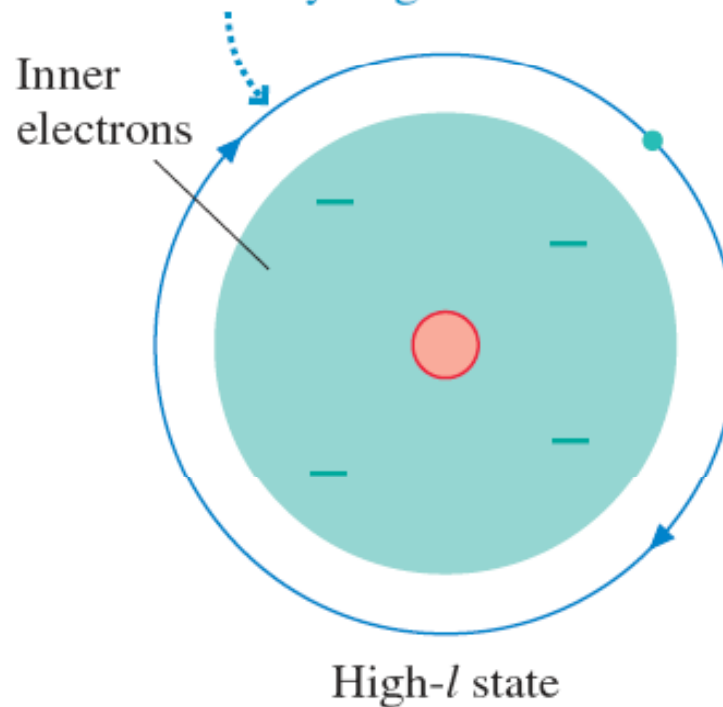
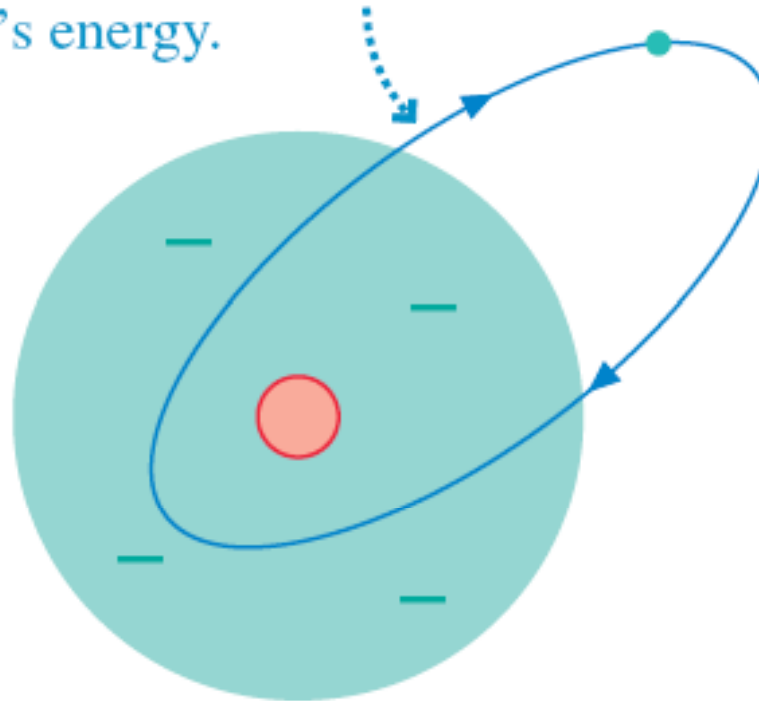


FIGURE 42.16 High- l and low- l orbitals in a multielectron atom.

A low- l electron corresponds to an elliptical orbit. It penetrates into the core and interacts strongly with the nucleus. The electron-nucleus force is attractive, so this interaction lowers the electron's energy.



Low- l state

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 2*p* subshell with the elements boron through neon.

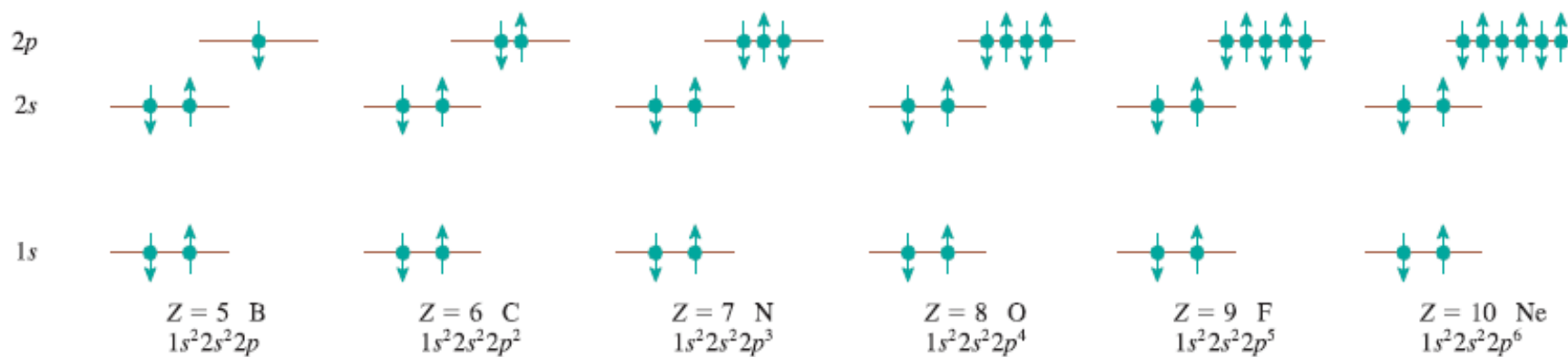


FIGURE 42.15 An energy-level diagram for electrons in a multielectron atom.

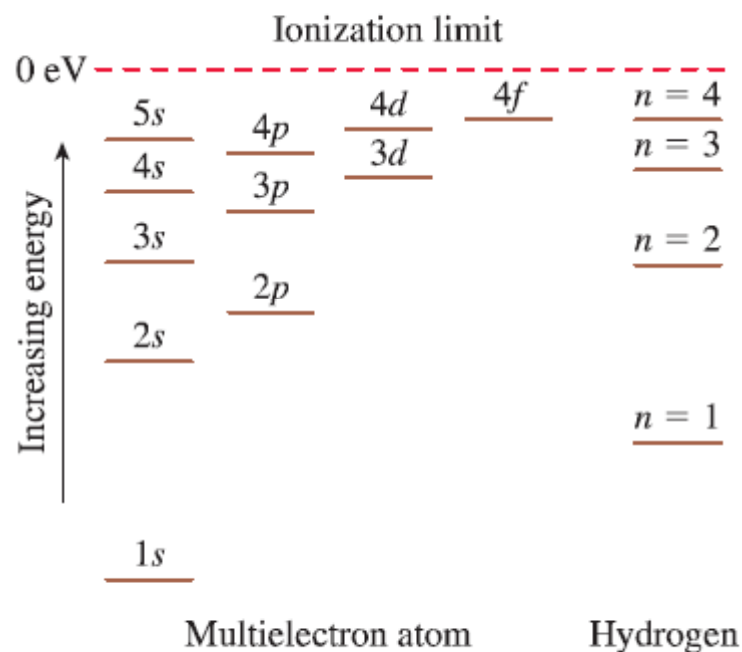


FIGURE 42.20 The modern periodic table of the elements, showing the atomic number Z of each.

| | | | | | | | | | | | | | | | | | | | |
|-------------|----|----|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|----|--|
| Period 1 | 1 | | | | | | | | | | | | | | | | | 2 | |
| | H | | | | | | | | | | | | | | | | | He | |
| 2 | 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 | |
| | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | |
| 3 | 11 | 12 | Transition elements | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | |
| | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| 4 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | |
| | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| 5 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | |
| | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| 6 | 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | |
| | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| 7 | 87 | 88 | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | | | | | | | |
| | Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | | | | | | | | |
| Lanthanides | | | 6 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | | |
| | | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | |
| Actinides | | | 7 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 | | |
| | | | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | |
| | | | Inner transition elements | | | | | | | | | | | | | | | | |

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

| | | | |
|----|----|----|----|
| 1s | | | 1s |
| 2s | | | 2p |
| 3s | | | 3p |
| 4s | 3d | | 4p |
| 5s | 4d | | 5p |
| 6s | * | 5d | 6p |
| 7s | † | 6d | |

| | |
|---|------|
| * | $4f$ |
| † | $5f$ |

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:

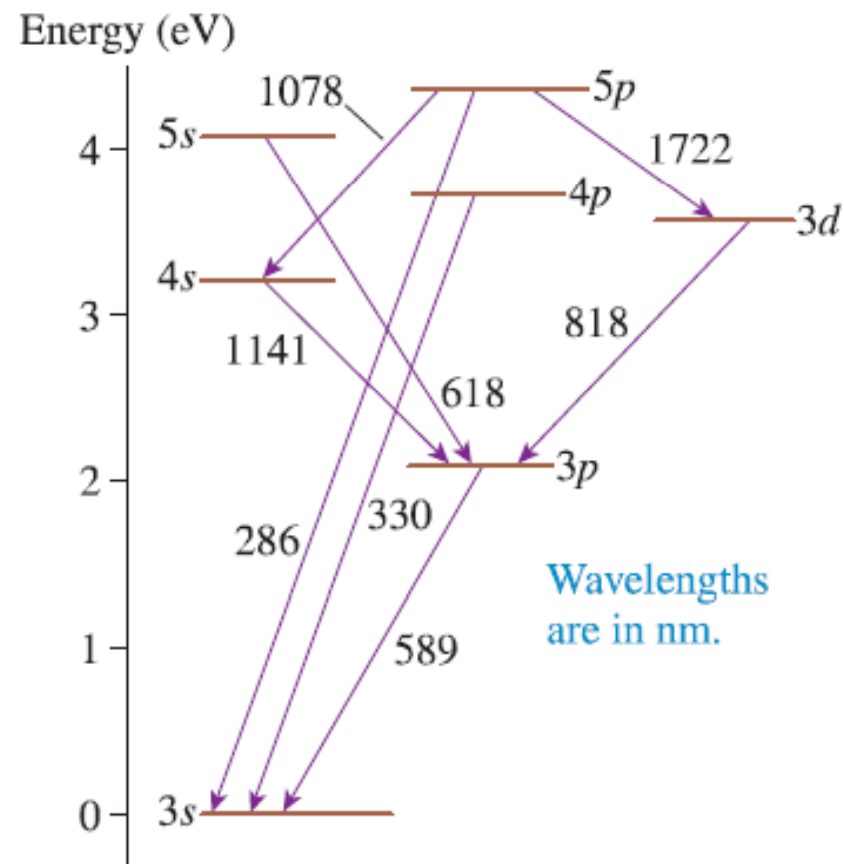
$$\lambda = \frac{c}{f} = \frac{hc}{\Delta E_{\text{atom}}} = \frac{1240 \text{ eV nm}}{\Delta E (\text{in eV})}$$

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

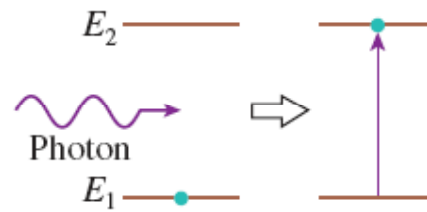
$$N_{\text{exc}} = N_0 e^{-t/\tau}$$

where

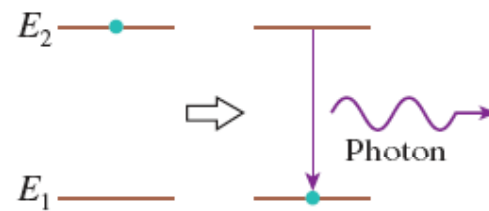
$$\tau = \frac{1}{r} = \text{the } \textit{lifetime} \text{ of the excited state}$$

FIGURE 42.32 Three types of radiative transitions.

(a) Absorption



(b) Spontaneous emission



(c) Stimulated emission

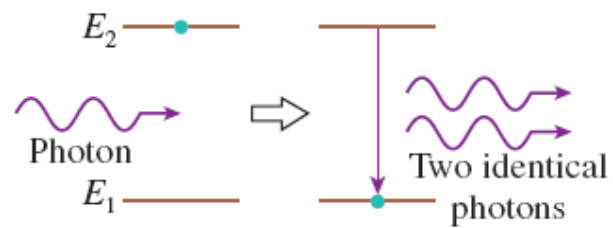


FIGURE 42.34 Stimulated emission creates a chain reaction of photon production in a population of excited atoms.

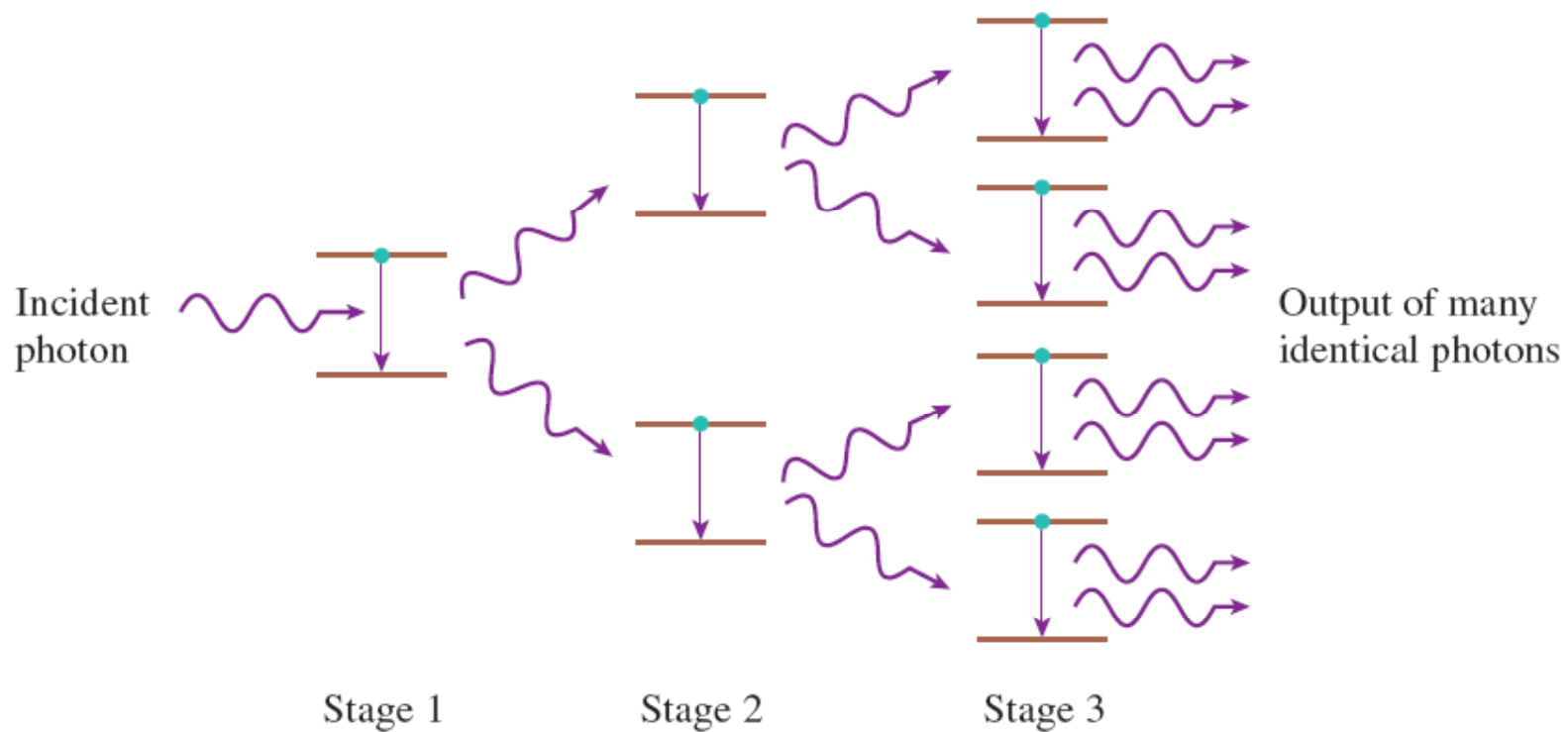


FIGURE 42.35 Lasing takes place in an optical cavity.

