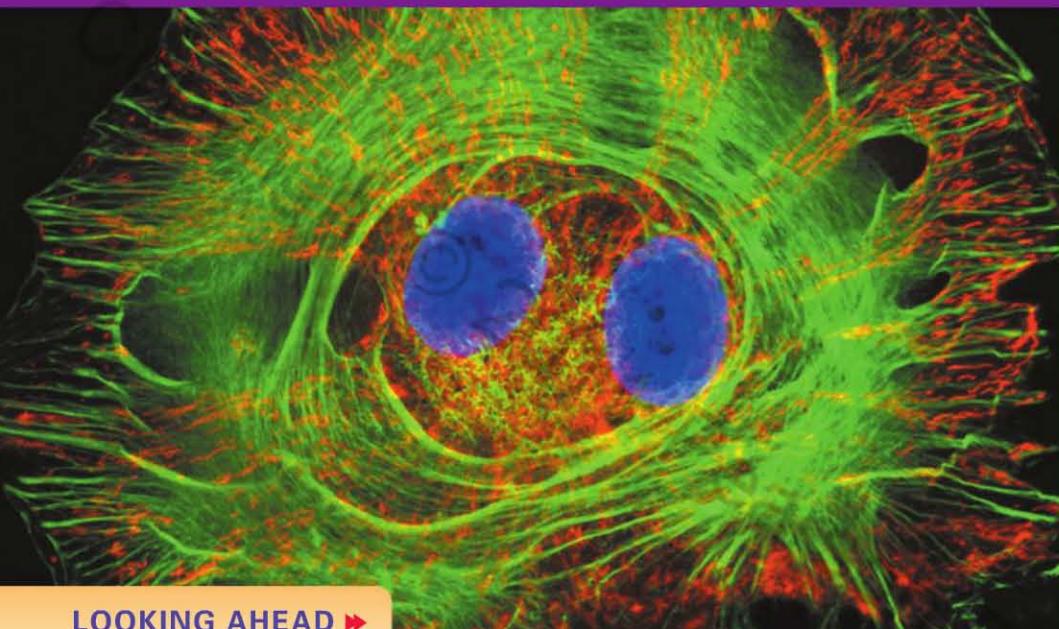


29 Atoms and Molecules



LOOKING AHEAD ➤

The goal of Chapter 29 is to use quantum physics to understand the properties of atoms, molecules, and their spectra.

Spectroscopy

You'll learn how each element can be identified by its distinct spectrum.



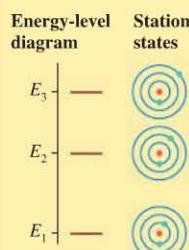
The discrete bright lines given off by these eight different elements (plus water) are important clues into the nature of the atom.

Looking Back ◀◀

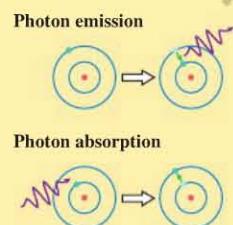
- 17.3 The diffraction grating
- 25.8 Thermal radiation

Bohr's Atomic Model

Niels Bohr proposed a model of the atom in which quantization plays a central role.



Atoms can exist in only certain *stationary states*, each with its own discrete quantized energy.



As atoms "jump" from one energy level to another, they absorb and emit light as photons with discrete energies.

Looking Back ◀◀

- 28.5–28.6 Quantization and energy levels

Lasers

When atoms give off light, they can **stimulate** other atoms to emit light of exactly the same wavelength and phase. This leads to a powerful amplification of the light beam—the **laser**.



The intense beams of light at this laser light show result from the stimulated emission of photons by atoms.

Molecules

The absorption and emission of light by molecules are also described by quantum mechanics.



This false-color map uses the fluorescence of chlorophyll to show the distribution of algae near the coast of Florida.

Quantum-Mechanical Descriptions of the Atom

To understand the structure of atoms we need to use the principles of quantum mechanics. You'll learn that electrons have spin and that no two electrons can be in the same state.



The familiar structure of the periodic table of the elements comes directly from the quantum-mechanical description of atoms.

29.1 Spectroscopy

The interference and diffraction of light were well understood by the end of the 19th century, and the knowledge was used to design practical tools for measuring wavelengths with great accuracy. The primary instrument for measuring the wavelengths of light is a **spectrometer**, such as the one shown in **FIGURE 29.1**. The heart of a spectrometer is a diffraction grating that causes different wavelengths of light to diffract at different angles.

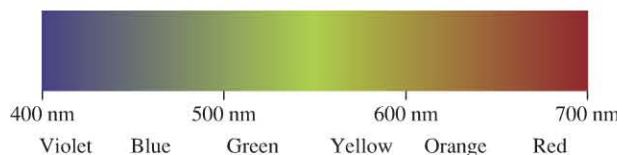
Each wavelength is focused to a different position on the photographic plate or, more likely today, a CCD detector like the one in your digital camera. The distinctive pattern of wavelengths emitted by a source of light and recorded on the detector is called the **spectrum** of the light. Spectroscopists discovered very early that there are two types of spectra: continuous spectra and discrete spectra.

- As you learned in Section 25.8, hot, self-luminous objects, such as the sun or an incandescent lightbulb, emit a **continuous spectrum** in which a rainbow is formed by light being emitted at every possible wavelength.
- In contrast, the light emitted by a gas discharge tube (such as those used to make neon signs) contains only certain discrete, individual wavelengths. Such a spectrum is called a **discrete spectrum**.

FIGURE 29.2 shows examples of spectra as they would appear on the photographic plate of a spectrometer. Each bright line in a discrete spectrum, called a **spectral line**, represents *one* specific wavelength present in the light emitted by the source. A discrete spectrum is sometimes called a *line spectrum* because of its appearance on the plate. You can see that a neon light has its familiar reddish-orange color because nearly all of the wavelengths emitted by neon atoms fall within the wavelength range 600–700 nm that we perceive as orange and red.

FIGURE 29.2 Examples of spectra in the visible wavelength range 400–700 nm. (a) is a continuous spectrum, while (b)–(d) are discrete spectra.

(a) Incandescent lightbulb



(b) Hydrogen



(c) Mercury



(d) Neon



Discrete Spectra of the Elements

If a high voltage is applied to two electrodes sealed in a glass tube filled with a low-pressure gas, the gas begins to glow and emits light with a color that is unique to that gas. *Gas discharge tubes* were developed in the late 19th century, and scientists soon realized that the light was being emitted by the atoms in the gas. These *atomic spectra* were a new way to study the properties of the elements.

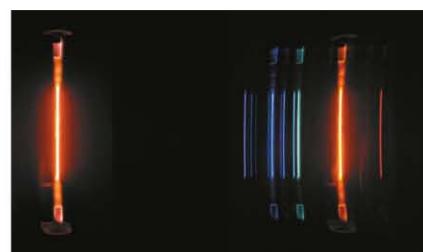
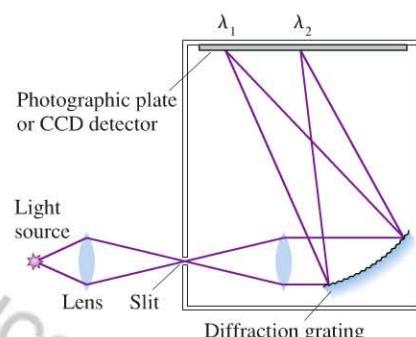
Two important conclusions had been established by the end of the 19th century:

1. The light emitted by atoms in a gas discharge tube has a discrete spectrum. Figure 29.2b–d showed some examples.
2. Every element in the periodic table has its own unique spectrum.



Some modern spectrometers are small enough to hold in your hand. (The rainbow has been added to show the paths that different colors take.)

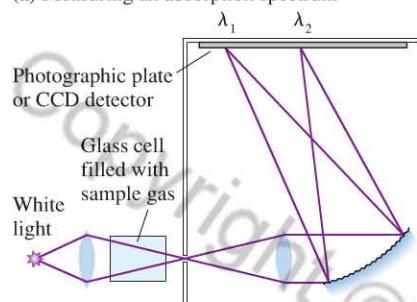
FIGURE 29.1 A diffraction spectrometer.



When the hydrogen discharge tube at the left is viewed through a diffraction grating, its unique discrete spectrum at the right is observed.

FIGURE 29.3 Measuring an absorption spectrum.

(a) Measuring an absorption spectrum



(b) Absorption and emission spectra of sodium

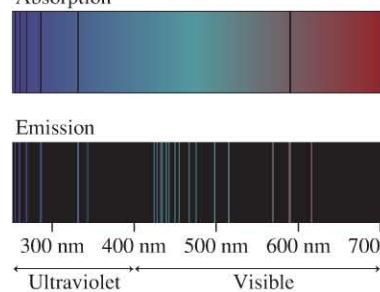
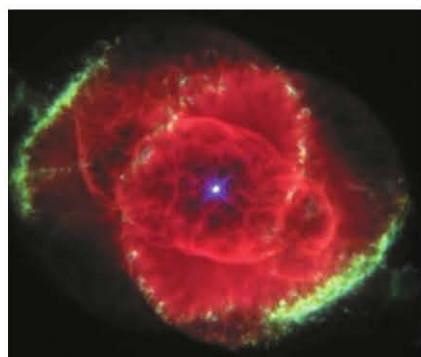


TABLE 29.1 Wavelengths of visible lines in the hydrogen spectrum

| |
|--------|
| 656 nm |
| 486 nm |
| 434 nm |
| 410 nm |



Astronomical colors The red color of this nebula is due to the emission of light from hydrogen atoms. The atoms are excited by intense ultraviolet light from the star in the center. They then emit red light, with $\lambda = 656$ nm, as predicted by the Balmer formula with $m = 2$ and $n = 3$. Spectroscopy of glowing gases from astronomical objects is an invaluable tool for astronomers, because it allows the gases present in objects many light years distant to be identified from earth.

The fact that each element emits a unique spectrum means that atomic spectra can be used as “fingerprints” to identify elements. Consequently, atomic spectroscopy is the basis of many contemporary technologies for analyzing the composition of unknown materials, monitoring air pollutants, and studying the atmospheres of the earth and other planets.

Gases can also *absorb* light. In an absorption experiment, as shown in **FIGURE 29.3a**, a white-light source emits a continuous spectrum that, in the absence of a gas, exposes the film completely and uniformly. When a sample of gas is placed in the light’s path, any wavelengths absorbed by the gas are missing and the film is dark at that wavelength.

Gases not only emit discrete wavelengths, but also absorb discrete wavelengths. But there is an important difference between the emission spectrum and the absorption spectrum of a gas: **Every wavelength that is absorbed by the gas is also emitted, but not every emitted wavelength is absorbed.** The wavelengths in the absorption spectrum appear as a subset of the wavelengths in the emission spectrum. As an example, **FIGURE 29.3b** shows both the emission and the absorption spectra of sodium atoms. All of the absorption wavelengths are prominent in the emission spectrum, but there are many emission lines for which no absorption occurs.

What causes atoms to emit or absorb light? Why a discrete spectrum? Why are some wavelengths emitted but not absorbed? Why is each element different? Nineteenth-century physicists struggled with these questions but could not answer them. Ultimately, classical physics was simply incapable of providing an understanding of atoms.

The only encouraging sign came from an unlikely source. While the spectra of other atoms have dozens or even hundreds of wavelengths, the visible spectrum of hydrogen, between 400 nm and 700 nm, consists of a mere four spectral lines (see Figure 29.2b and Table 29.1). If any spectrum could be understood, it should be that of the first element in the periodic table. The breakthrough came in 1885, not by an established and recognized scientist but by a Swiss school teacher, Johann Balmer. Balmer showed that the wavelengths in the hydrogen spectrum could be represented by the simple formula

$$\lambda = \frac{91.1 \text{ nm}}{\left(\frac{1}{2^2} - \frac{1}{n^2}\right)} \quad n = 3, 4, 5, \dots \quad (29.1)$$

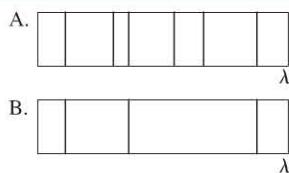
Later experimental evidence, as ultraviolet and infrared spectroscopy developed, showed that Balmer’s result could be generalized to

$$\lambda = \frac{91.1 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} \quad \begin{cases} m \text{ can be } 1, 2, 3, \dots \\ \text{If } m = 1, n \text{ can be } 2, 3, 4, \dots \\ \text{If } m = 2, n \text{ can be } 3, 4, 5, \dots \\ \text{If } m = 3, n \text{ can be } 4, 5, 6, \dots \\ \text{and so on.} \end{cases} \quad (29.2)$$

We now refer to Equation 29.2 as the **Balmer formula**, although Balmer himself suggested only the original version in which $m = 2$. Other than at the very highest levels of resolution, where new details appear that need not concern us in this text, the Balmer formula accurately describes *every* wavelength in the emission spectrum of hydrogen.

The Balmer formula is what we call *empirical knowledge*. It is an accurate mathematical representation found through experimental evidence, but it does not rest on any physical principles or physical laws. Balmer’s formula was useful, but no one was able to *derive* Balmer’s formula from Newtonian mechanics or the theory of electromagnetism. Yet the formula was so simple that it must, everyone agreed, have a simple explanation. It would take 30 years to find it.

STOP TO THINK 29.1 The black lines show the emission or absorption lines observed in two spectra of the same element. Which one is an emission spectrum and which is an absorption spectrum?



29.2 Atoms

It was the ancient Greeks who first had the idea of atoms as indivisible units of matter, but experimental evidence for atoms didn't appear until Dalton, Avogadro, and others began to formulate the laws of chemistry in the early 19th century. The existence of atoms with diameters of approximately 10^{-10} m was widely accepted by 1890, but it was still unknown if atoms were indivisible little spheres or if they had some kind of internal structure.

The 1897 discovery of the electron by J. J. Thomson had two important implications:

- Atoms are not indivisible; they are built of smaller pieces. The electron was the first *subatomic* particle to be discovered.
- The constituents of the atom are *charged particles*. Hence it seems plausible that the atom must be held together by electric forces.

Within a few years, measurements of the electron's charge

$$e = 1.60 \times 10^{-19} \text{ C}$$

and mass

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$

revealed that the electron is much less massive than even the smallest atom.

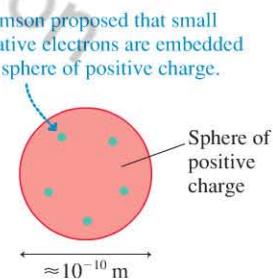
Because the electrons are very small and light compared to the whole atom, it seemed reasonable to think that the positively charged part (protons were not yet known) had most of the mass and would take up most of the space. Thomson suggested that the atom consists of a spherical "cloud" of positive charge, roughly 10^{-10} m in diameter, in which the smaller negative electrons are embedded. The positive charge exactly balances the negative, so the atom as a whole has no net charge. This model of the atom has been called the "plum-pudding model" or the "raisin-cake model" for reasons that should be clear from the picture of FIGURE 29.4. However, Thomson's model of the atom did not stand the tests of time.

Almost simultaneously with Thomson's discovery of the electron, and just one year after Röntgen's discovery of x rays, the French physicist Antoine Henri Becquerel announced his discovery that some new form of "rays" were emitted by crystals of uranium. These rays, like x rays, could expose film and pass through objects, but they were emitted continuously from the uranium without having to "do" anything to it. This was the discovery of **radioactivity**, a topic we'll study in Chapter 30.

One of Thomson's former students, Ernest Rutherford, began a study of these new rays and quickly discovered that a uranium crystal actually emits two *different* rays. The first, which he called **alpha rays**, were easily absorbed by a piece of paper. The second, **beta rays**, could penetrate through at least 0.1 inch of metal and through much greater thicknesses of soft materials. The beta rays turned out to be high-speed electrons emitted by the uranium crystal. Rutherford soon showed that alpha rays are *positively charged* particles, and by 1906 he established that alpha rays (or alpha particles, as we now call them) consist of doubly ionized helium atoms (bare helium nuclei with mass $m = 6.64 \times 10^{-27}$ kg) emitted at high speed ($\approx 3 \times 10^7$ m/s) from the sample.

It had been a shock to discover that atoms are not indivisible—they have an inner structure. Now, with the discovery of radioactivity, it appeared that some atoms were not even stable but could spit out various kinds of charged particles!

FIGURE 29.4 Thomson's raisin-cake model of the atom.



EXAMPLE 29.1 The speed of an alpha particle

Alpha particles are usually characterized by their kinetic energy in MeV. What is the speed of an 8.3 MeV alpha particle?

SOLVE Recall that 1 eV is the energy acquired by an electron accelerating through a 1 V potential difference, with the conversion $1.00 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$. First, we convert the energy to joules:

$$K = 8.3 \times 10^6 \text{ eV} \times \frac{1.60 \times 10^{-19} \text{ J}}{1.00 \text{ eV}} = 1.3 \times 10^{-12} \text{ J}$$

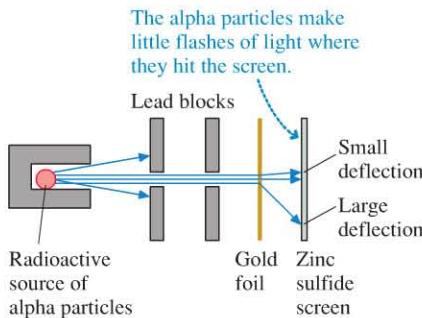
Now, using the alpha-particle mass $m = 6.64 \times 10^{-27} \text{ kg}$ given above, we can find the speed:

$$K = \frac{1}{2}mv^2 = 1.3 \times 10^{-12} \text{ J}$$

$$v = \sqrt{\frac{2K}{m}} = 2.0 \times 10^7 \text{ m/s}$$

ASSESS This is quite fast, about 7% of the speed of light.

FIGURE 29.5 Rutherford's experiment to shoot high-speed alpha particles through a thin gold foil.



I remember two or three days later Geiger coming to me in great excitement and saying, "We have been able to get some of the alpha particles coming backward." It was quite the most incredible event that has ever happened to me in my life. It was almost as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. . . . It was then that I had the idea of an atom with a minute massive center, carrying a charge.

Ernest Rutherford

The First Nuclear Physics Experiment

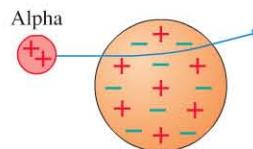
Rutherford soon realized that he could use these high-speed alpha particles as projectiles to probe inside other atoms. In 1909, Rutherford and his students Hans Geiger and Ernest Marsden set up the experiment shown in **FIGURE 29.5** to shoot alpha particles through very thin metal foils. The alpha particle is charged, and it experiences electric forces from the positive and negative charges of the atoms as it passes through the foil. According to Thomson's raisin-cake model of the atom, the forces exerted on the alpha particle by the positive atomic charges should roughly cancel the forces from the negative electrons, causing the alpha particles to experience only slight deflections. Indeed, this was the experimenters' initial observation.

At Rutherford's suggestion, Geiger and Marsden set up the apparatus to see if any alpha particles were deflected at *large* angles. It took only a few days to find the answer. Not only were alpha particles deflected at large angles, but a very few were reflected almost straight backward toward the source!

How can we understand this result? **FIGURE 29.6a** shows that an alpha particle passing through a Thomson atom would experience only a small deflection. But if an atom has a small positive core, such as the one in **FIGURE 29.6b**, a few of the alpha particles can come very close to the core. Because the electric force varies with the inverse square of the distance, the very large force of this very close approach can cause a large-angle scattering or even a backward deflection of the alpha particle. This is what Geiger and Marsden were observing.

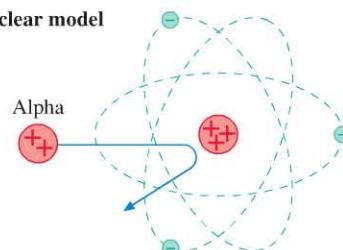
FIGURE 29.6 Alpha particles interact differently with a concentrated positive nucleus than they would with the spread-out charges in Thomson's model.

Thomson model



The alpha particle is only slightly deflected by a Thomson atom because forces from the spread-out positive and negative charges nearly cancel.

Nuclear model



If the atom has a concentrated positive nucleus, some alpha particles will be able to come very close to the nucleus and thus feel a very strong repulsive force.

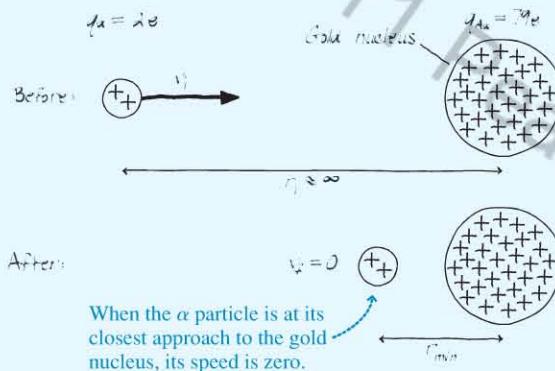
The discovery of large-angle scattering of alpha particles quickly led Rutherford to envision an atom in which negative electrons orbit an unbelievably small, massive, positive **nucleus**, rather like a miniature solar system. This is the **nuclear model of the atom**. Further experiments showed that the diameter of the atomic nucleus is $\approx 1 \times 10^{-14} \text{ m} = 10 \text{ fm}$ ($1 \text{ fm} = 1 \text{ femtometer} = 10^{-15} \text{ m}$), a mere 0.01% the diameter of the atom itself. Thus nearly all of the atom is merely empty space—the void!

EXAMPLE 29.2 Going for the gold!

An 8.3 MeV alpha particle is shot directly toward the nucleus of a gold atom (atomic number 79). What is the distance of closest approach of the alpha particle to the nucleus?

PREPARE Energy is conserved in electric interactions. Assume that the gold nucleus, which is much more massive than the alpha particle, does not move. Also recall that the electric field and potential of a sphere of charge can be found by treating the total charge as a point charge. **FIGURE 29.7** is a before-and-after visual overview; the “before” situation is when the alpha is very far from the gold nucleus, and the “after” situation is when the alpha is at its distance of closest approach to the nucleus. The motion is in and out along a straight line.

FIGURE 29.7 A before-and-after visual overview of an alpha particle colliding with a nucleus.



SOLVE Electric potential energy decreases rapidly with increasing separation, so initially, when the alpha particle is very far away, the system has only the initial kinetic energy of the alpha particle. At the moment of closest approach the alpha particle has just come to rest and so the system has only potential energy. The conservation of energy statement $K_f + U_f = K_i + U_i$

$$0 + \frac{1}{4\pi\epsilon_0} \frac{q_\alpha q_{Au}}{r_{min}} = \frac{1}{2}mv_i^2 + 0$$

where q_α is the alpha-particle charge and we've treated the gold nucleus as a point charge q_{Au} . The solution for r_{min} is

$$r_{min} = \frac{1}{4\pi\epsilon_0} \frac{2q_\alpha q_{Au}}{mv_i^2}$$

The mass of the alpha particle is $m = 6.64 \times 10^{-27}$ kg and its charge is $q_\alpha = 2e = 3.20 \times 10^{-19}$ C. Gold has atomic number 79, so $q_{Au} = 79e = 1.26 \times 10^{-17}$ C. In Example 29.1 we found that an 8.3 MeV alpha particle has speed $v = 2.0 \times 10^7$ m/s. With this information, we can calculate

$$r_{min} = 2.7 \times 10^{-14} \text{ m}$$

This is only about 1/10,000 the size of the atom itself!

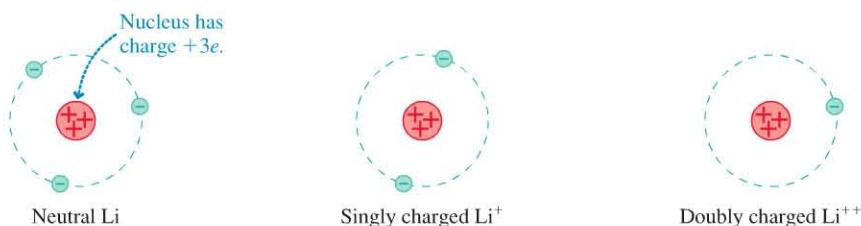
ASSESS We ignored the gold atom's electrons in this example. In fact, they make almost no contribution to the alpha particle's trajectory. The alpha particle is exceedingly massive compared to the electrons, and the electrons are spread out over a distance very large compared to the size of the nucleus. Hence the alpha particle easily pushes them aside without any noticeable change in its velocity.

Using the Nuclear Model

The nuclear model of the atom makes it easy to picture atoms and understand such processes as ionization. For example, the **atomic number** of an element, its position in the periodic table of the elements, is the number of orbiting electrons (of a neutral atom) and the number of units of positive charge in the nucleus. The atomic number is represented by Z . Hydrogen, with $Z = 1$, has one electron orbiting a nucleus with charge $+1e$. Helium, with $Z = 2$, has two orbiting electrons and a nucleus with charge $+2e$. Because the orbiting electrons are very light, an x-ray photon or a rapidly moving particle, such as another electron, can knock one of the electrons away, creating a positive **ion**. Removing one electron makes a singly charged ion, with $q_{ion} = +e$. Removing two electrons creates a doubly charged ion, with $q_{ion} = +2e$. This is shown for lithium ($Z = 3$) in **FIGURE 29.8**.

Experiments soon led to the recognition that the positive charge of the nucleus is associated with a positive subatomic particle called the **proton**. The proton's charge is $+e$, equal in magnitude but opposite in sign to the electron's charge. Further, because nearly all the atomic mass is associated with the nucleus, the proton is about

FIGURE 29.8 Different ionization stages of the lithium atom ($Z = 3$).



1800 times more massive than the electron: $m_p = 1.67 \times 10^{-27}$ kg. Atoms with atomic number Z have Z protons in the nucleus, giving the nucleus charge $+Ze$.

This nuclear model of the atom allows us to understand why, during chemical reactions and when an object is charged by rubbing, electrons are easily transferred but protons are not. The protons are tightly bound in the nucleus, shielded by all the electrons, but outer electrons are easily stripped away. Rutherford's nuclear model has explanatory power that was lacking in Thomson's model.

But there was a problem. Helium, with atomic number 2, has twice as many electrons and protons as hydrogen. Lithium, $Z = 3$, has three electrons and protons. If a nucleus contains Z protons to balance the Z orbiting electrons, and if nearly all the atomic mass is contained in the nucleus, then helium should be twice as massive as hydrogen and lithium three times as massive. But it was known from chemistry measurements that helium is *four times* as massive as hydrogen and lithium is *seven times* as massive.

This difficulty was not resolved until the discovery, in 1932, of a third subatomic particle. This particle has essentially the same mass as a proton but *no* electric charge. It is called the **neutron**. Neutrons reside in the nucleus, with the protons, where they contribute to the mass of the atom but not to its charge. As you'll see in Chapter 30, neutrons help provide the "glue" that holds the nucleus together.

We now know that a nucleus contains Z protons plus N neutrons, as shown in FIGURE 29.9, giving the atom a **mass number** $A = Z + N$. The mass number, which is a dimensionless integer, is *not* the same thing as the atomic mass m . But because the proton and neutron masses are both ≈ 1 u, where

$$1 \text{ u} = 1 \text{ atomic mass unit} = 1.66 \times 10^{-27} \text{ kg}$$

the mass number A is *approximately* the mass in atomic mass units. For example, helium, with two protons and two neutrons ($A = 4$), has atomic mass $m = 6.646 \times 10^{-27}$ kg = 4.003 u ≈ 4 u.

There are a *range* of neutron numbers that happily form a nucleus with Z protons, creating a series of nuclei with the same Z -value (i.e., they are all the same chemical element) but different masses. Such a series of nuclei are called **isotopes**. The notation used to label isotopes is A_Z , where the mass number A is given as a *leading* superscript. The proton number Z is not specified by an actual number but, equivalently, by the chemical symbol for that element. The most common isotope of neon has $Z = 10$ protons and $N = 10$ neutrons. Thus it has mass number $A = 20$ and is labeled ${}^{20}\text{Ne}$. The neon isotope ${}^{22}\text{Ne}$ has $Z = 10$ protons (that's what makes it neon) and $N = 12$ neutrons. Helium has the two isotopes shown in FIGURE 29.10. The rare ${}^3\text{He}$ is only 0.0001% abundant, but it can be isolated and has important uses in scientific research.

FIGURE 29.9 The nucleus of an atom contains protons and neutrons.

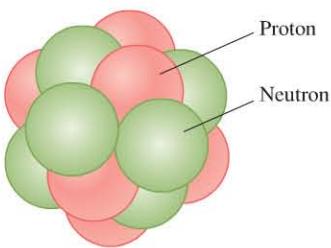
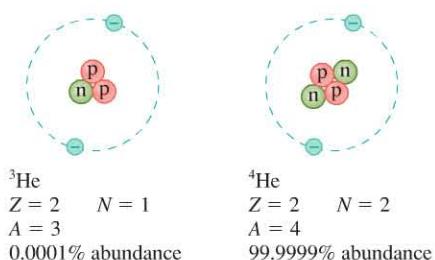


FIGURE 29.10 The two isotopes of helium. ${}^3\text{He}$ is only 0.0001% abundant.



STOP TO THINK 29.2 Carbon is the sixth element in the periodic table. How many protons and how many neutrons are there in a nucleus of the isotope ${}^{14}\text{C}$?

29.3 Bohr's Model of Atomic Quantization

Rutherford's nuclear model was an important step toward understanding atoms, but it had two serious shortcomings. First, electrons orbiting the nucleus in a Rutherford atom are oscillating charged particles. According to Maxwell's theory of electricity and magnetism, these orbiting electrons should act as small antennas and radiate electromagnetic waves. That sounds encouraging, because we know that atoms can emit light, but it was easy to show that a Rutherford atom would radiate a *continuous* rainbow-like spectrum. Thus one failure of Rutherford's model was an inability to predict the discrete nature of emission and absorption spectra.

In addition, atoms would continuously lose energy as they radiated electromagnetic waves. As FIGURE 29.11 shows, this would cause the electrons to spiral into the nucleus! Calculations showed that a Rutherford atom can last no more than about a

microsecond. In other words, classical Newtonian mechanics and electromagnetism predict that an atom with electrons orbiting a nucleus would be highly unstable and would immediately self-destruct. This clearly does not happen.

The experimental efforts of the late 19th and early 20th centuries had been impressive, and there could be no doubt about the existence of electrons, about the small positive nucleus, and about the unique discrete spectrum emitted by each atom. But the theoretical framework for understanding such observations had lagged behind. As the new century dawned, physicists could not explain the structure of atoms, could not explain the stability of matter, could not explain discrete spectra or why an element's absorption spectrum differs from its emission spectrum, and could not explain the origin of x rays or radioactivity.

A missing piece of the puzzle, although not recognized as such for a few years, was Einstein's 1905 introduction of light quanta. If light comes in discrete packets of energy, which we now call photons, and if atoms emit and absorb light, what does that imply about the structure of the atoms? This was the question posed by the Danish physicist Niels Bohr.

Bohr wanted to understand how a solar-system-like atom could be stable and not radiate away all its energy. He soon recognized that Einstein's light quanta had profound implications about the structure of atoms, and in 1913 Bohr proposed a radically new model of the atom in which he added quantization to Rutherford's nuclear atom. The basic assumptions of the **Bohr model of the atom** are as follows:

Understanding Bohr's model

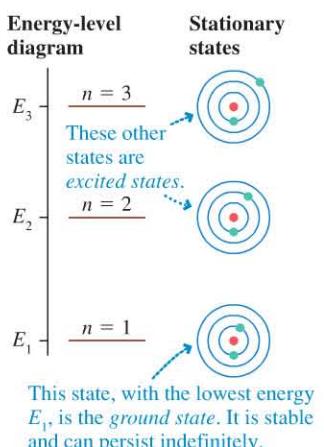
Electrons can exist in only certain allowed orbits.



An electron cannot exist here, where there is no allowed orbit.

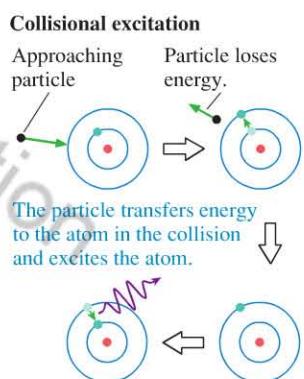
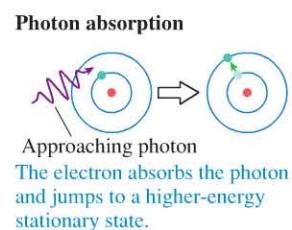
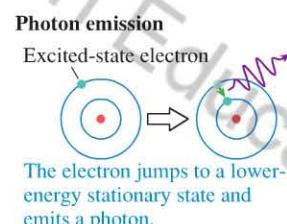
This is one stationary state.
This is another stationary state.

1. The electrons in an atom can exist in only certain *allowed orbits*. A particular arrangement of electrons in these orbits is called a **stationary state**.



This state, with the lowest energy E_1 , is the **ground state**. It is stable and can persist indefinitely.

2. Each stationary state has a discrete, well-defined energy E_n , as the energy-level diagram shows. That is, atomic energies are *quantized*. The stationary states are labeled by the *quantum number* n in order of increasing energy:
 $E_1 < E_2 < E_3 < \dots$



An atom in an excited state jumps to lower states, emitting a photon at each jump.

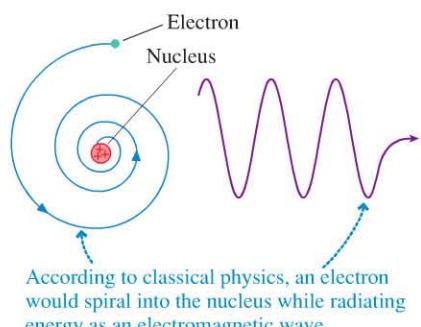
3. An atom can undergo a *transition* or *quantum jump* from one stationary state to another by emitting or absorbing a photon whose energy is exactly equal to the energy difference between the two stationary states.
4. Atoms can also move from a lower-energy state to a higher-energy state by absorbing energy in a collision with an electron or other atom in a process called **collisional excitation**.

The excited atoms soon jump down to lower states, eventually ending in the stable ground state.

Assumption 3 of Bohr's model merges Einstein's idea of light quanta with the law of conservation of energy. Thus an atom can jump from one stationary state to another by emitting or absorbing a photon of just the right frequency to conserve energy. If an atom jumps from an initial state with energy E_i to a final state with lower energy E_f , energy will be conserved if the atom emits a photon with $E_{\text{photon}} = \Delta E_{\text{atom}} = |E_f - E_i|$. Because $E_{\text{photon}} = hf$, this photon must have frequency

$$f_{\text{photon}} = \frac{\Delta E_{\text{atom}}}{h} \quad (29.3)$$

FIGURE 29.11 The fate of a Rutherford atom.



if it is to carry away exactly the right amount of energy. Similarly, an atom can jump to a higher-energy state, for which additional energy is needed, by absorbing a photon of frequency $f_{\text{photon}} = \Delta E_{\text{atom}}/h$. The total energy of the atom-plus-light system is conserved.

The Bohr model also introduces *collisions* as another important mechanism by which a quantum system can gain energy. For example, a fluorescent lightbulb contains mercury vapor at a very low pressure. When you turn on the light, electrons flow back and forth inside the tube. As they do, they occasionally collide with the mercury atoms. These are inelastic collisions in which some of the electron's energy is transferred to the mercury atom, kicking the atom up to a higher energy level. The atom then jumps back to a lower energy level, emitting an ultraviolet photon. The ultraviolet light causes the white paint on the inside surface of the tube to *fluoresce*, a process we'll study later in the chapter.

The implications of Bohr's model are profound. In particular:

- 1. Matter is stable.** Once an atom is in its ground state, there are no states of any lower energy to which it can jump. It can remain in the ground state forever.
- 2. Atoms emit and absorb a *discrete spectrum*.** Only those photons whose frequencies match the energy *intervals* between the stationary states can be emitted or absorbed. Photons of other frequencies cannot be emitted or absorbed without violating energy conservation.
- 3. Emission spectra can be produced by collisions.** Energy from collisions can kick an atom up to an excited state. It then emits photons in a discrete emission spectrum as it jumps down to lower-energy states.
- 4. Absorption wavelengths are a subset of the wavelengths in the emission spectrum.** Recall that all the lines seen in an absorption spectrum are also seen in emission, but many emission lines are *not* seen in absorption. According to Bohr's model, **most atoms, most of the time, are in their lowest energy state**, the $n = 1$ ground state. Thus the absorption spectrum consists of *only* those transitions such as $1 \rightarrow 2$, $1 \rightarrow 3, \dots$ in which the atom jumps from $n = 1$ to a higher value of n by absorbing a photon. Transitions such as $2 \rightarrow 3$ are not observed because there are essentially no atoms in $n = 2$ at any instant of time to do the absorbing. On the other hand, atoms that have been excited to the $n = 3$ state by collisions can emit photons corresponding to transitions $3 \rightarrow 1$ and $3 \rightarrow 2$. Thus the wavelength corresponding to $\Delta E_{\text{atom}} = E_3 - E_1$ is seen in both emission and absorption, but photons with $\Delta E_{\text{atom}} = E_3 - E_2$ occur in emission only.
- 5. Each element in the periodic table has a unique spectrum.** The energies of the stationary states are just the energies of the orbiting electrons. The atom has no other form of energy. Different elements, with different numbers of electrons, have different stable orbits and thus different stationary states. States with different energies will emit and absorb photons of different wavelengths.

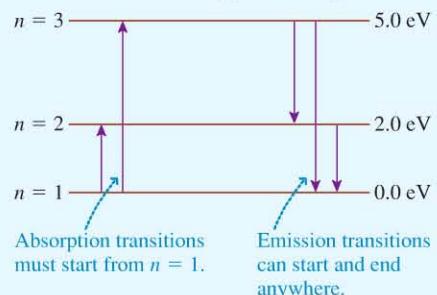
EXAMPLE 29.3

Wavelengths in emission and absorption spectra

An atom has stationary states $E_1 = 0.0 \text{ eV}$, $E_2 = 2.0 \text{ eV}$, and $E_3 = 5.0 \text{ eV}$. What wavelengths are observed in the absorption spectrum and in the emission spectrum of this atom?

PREPARE FIGURE 29.12 shows an energy-level diagram for the atom. Photons are emitted when an atom undergoes a quantum jump from a higher energy level to a lower energy level. Photons are absorbed in a quantum jump from a lower energy level to a higher energy level. However, most of the atoms are in the $n = 1$ ground state, so the only quantum jumps seen in the absorption spectrum start from the $n = 1$ state.

FIGURE 29.12 The atom's energy-level diagram.



SOLVE This atom absorbs photons on the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions, with $\Delta E_{1 \rightarrow 2} = 2.0 \text{ eV}$ and $\Delta E_{1 \rightarrow 3} = 5.0 \text{ eV}$. From $f_{\text{photon}} = \Delta E_{\text{atom}}/h$ and $\lambda = c/f$, we find that the wavelengths in the absorption spectrum are

$$\begin{aligned} 1 \rightarrow 3 & \quad f_{\text{photon}} = 5.0 \text{ eV}/h = 1.2 \times 10^{15} \text{ Hz} \\ & \quad \lambda = 250 \text{ nm (ultraviolet)} \\ 1 \rightarrow 2 & \quad f_{\text{photon}} = 2.0 \text{ eV}/h = 4.8 \times 10^{14} \text{ Hz} \\ & \quad \lambda = 620 \text{ nm (orange)} \end{aligned}$$

The emission spectrum also has the 620 nm and 250 nm wavelengths due to the $2 \rightarrow 1$ and $3 \rightarrow 1$ quantum jumps. In addition, the emission spectrum contains the $3 \rightarrow 2$ quantum jump with $\Delta E_{3 \rightarrow 2} = 3.0 \text{ eV}$ that is *not* seen in absorption because there are too few atoms in the $n = 2$ state to absorb. A similar calculation finds $f_{\text{photon}} = 7.3 \times 10^{14} \text{ Hz}$ and $\lambda = c/f = 410 \text{ nm}$. Thus the emission wavelengths are

$$\begin{aligned} 2 \rightarrow 1 & \quad \lambda = 620 \text{ nm (orange)} \\ 3 \rightarrow 2 & \quad \lambda = 410 \text{ nm (blue)} \\ 3 \rightarrow 1 & \quad \lambda = 250 \text{ nm (ultraviolet)} \end{aligned}$$

STOP TO THINK 29.3 A photon with a wavelength of 410 nm has energy $E_{\text{photon}} = 3.0 \text{ eV}$. Do you expect to see a spectral line with $\lambda = 410 \text{ nm}$ in the emission spectrum of the atom represented by this energy-level diagram? If so, what transition or transitions will emit it? Do you expect to see a spectral line with $\lambda = 410 \text{ nm}$ in the absorption spectrum? If so, what transition or transitions will absorb it?

| | |
|---------|--------|
| $n = 4$ | 6.0 eV |
| $n = 3$ | 5.0 eV |
| $n = 2$ | 2.0 eV |
| $n = 1$ | 0.0 eV |

29.4 The Bohr Hydrogen Atom

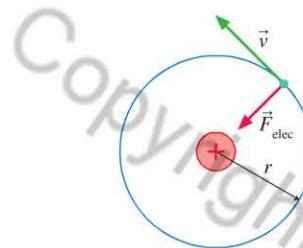
Bohr's hypothesis was a bold new idea, yet there was still one enormous stumbling block: What *are* the stationary states of an atom? Everything in Bohr's model hinges on the existence of these stationary states, of there being only certain electron orbits that are allowed. But nothing in classical physics provides any basis for such orbits. And Bohr's model describes only the *consequences* of having stationary states, not how to find them. If such states really exist, we will have to go beyond classical physics to find them.

To address this problem, Bohr did an explicit analysis of the hydrogen atom. The hydrogen atom, with only a single electron, was known to be the simplest atom. Furthermore, as we discussed in Section 29.1, Balmer had discovered a fairly simple formula that characterizes the wavelengths in the hydrogen emission spectrum. Anyone with a successful model of an atom was going to have to *derive* Balmer's formula for the hydrogen atom.

Bohr's paper followed a rather circuitous line of reasoning. That is not surprising, because he had little to go on at the time. But our goal is a clear explanation of the ideas, not a historical study of Bohr's methods, so we are going to follow a different analysis using de Broglie's matter waves. De Broglie did not propose matter waves until 1924, 11 years after Bohr, but with the clarity of hindsight we can see that treating the electron as a wave provides a more straightforward analysis of the hydrogen atom. Although our route will be different from Bohr's, we will arrive at the same point, and, in addition, we will be in a much better position to understand the work that came after Bohr.

NOTE ▶ Bohr's analysis of the hydrogen atom is sometimes called the *Bohr atom*. It's important not to confuse this analysis, which applies only to hydrogen, with the more general postulates of the *Bohr model of the atom*. Those postulates, which we looked at in the previous section, apply to any atom. To make the distinction clear, we'll call Bohr's analysis of hydrogen the *Bohr hydrogen atom*. ◀

FIGURE 29.13 A Rutherford hydrogen atom. The size of the nucleus is greatly exaggerated.



The Stationary States of the Hydrogen Atom

FIGURE 29.13 shows a Rutherford hydrogen atom, with a single electron orbiting a proton. We will assume a circular orbit of radius r and speed v . We will also assume the proton remains stationary while the electron revolves around it, a reasonable assumption because the proton is roughly 1800 times as massive as the electron. With these assumptions, the atom's energy is the kinetic energy of the electron plus the potential energy of the electron-proton interaction. This is

$$E = K + U = \frac{1}{2}mv^2 + \frac{1}{4\pi\epsilon_0}\frac{q_{\text{elec}}q_{\text{proton}}}{r} = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (29.4)$$

where we used $q_{\text{elec}} = -e$ and $q_{\text{proton}} = +e$.

NOTE ▶ m is the mass of the electron, *not* the mass of the entire atom. ◀

Now the electron, as we are coming to understand it, has both particle-like and wave-like properties. First, let us treat the electron as a charged particle. The proton exerts a Coulomb electric force on the electron:

$$\vec{F}_{\text{elec}} = \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}, \text{toward center} \right) \quad (29.5)$$

This force gives the electron an acceleration $\vec{a}_{\text{elec}} = \vec{F}_{\text{elec}}/m$ that also points to the center. This is a centripetal acceleration, causing the particle to move in its circular orbit. The centripetal acceleration of a particle moving in a circle of radius r at speed v is v^2/r , so that

$$a_{\text{elec}} = \frac{F_{\text{elec}}}{m} = \frac{e^2}{4\pi\epsilon_0 mr^2} = \frac{v^2}{r}$$

Rearranging, we find

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} \quad (29.6)$$

Equation 29.6 is a *constraint* on the motion. The speed v and radius r must obey Equation 29.6 if the electron is to move in a circular orbit. This constraint is not unique to atoms; we earlier found a similar relationship between v and r for orbiting satellites.

Now let's treat the electron as a de Broglie wave. In Section 28.5 we found that a particle confined to a one-dimensional box sets up a standing wave as it reflects back and forth. A standing wave, you will recall, consists of two traveling waves moving in opposite directions. When the round-trip distance in the box is equal to an integer number of wavelengths ($2L = n\lambda$), the two oppositely traveling waves interfere constructively to set up the standing wave.

Suppose that, instead of traveling back and forth along a line, our wave-like particle travels around the circumference of a circle. The particle will set up a standing wave, just like the particle in the box, if there are waves traveling in both directions and if the round-trip distance is an integer number of wavelengths. This is the idea we want to carry over from the particle in a box. As an example, **FIGURE 29.14** shows a standing wave around a circle with $n = 10$ wavelengths.

The mathematical condition for a circular standing wave is found by replacing the round-trip distance $2L$ in a box with the round-trip distance $2\pi r$ on a circle. Thus a circular standing wave will occur when

$$2\pi r = n\lambda \quad n = 1, 2, 3, \dots \quad (29.7)$$

But the de Broglie wavelength for a particle *has* to be $\lambda = h/p = h/mv$. Thus the standing-wave condition for a de Broglie wave is

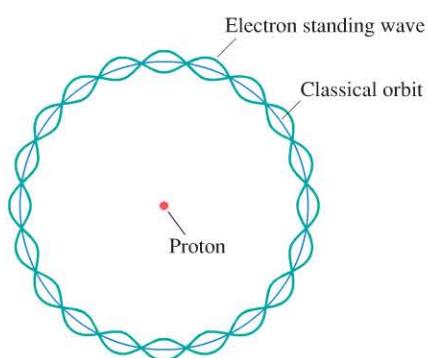
$$2\pi r = n \frac{h}{mv}$$

This condition is true only if the electron's speed is

$$v = \frac{nh}{2\pi mr} \quad n = 1, 2, 3, \dots \quad (29.8)$$

In other words, the electron cannot have just any speed, only the discrete values given by Equation 29.8.

FIGURE 29.14 An $n = 10$ electron standing wave around the orbit's circumference.



The quantity $h/2\pi$ occurs so often in quantum physics that it is customary to give it a special name. We define the quantity \hbar , pronounced “h bar,” as

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} \text{ J} \cdot \text{s} = 6.58 \times 10^{-16} \text{ eV} \cdot \text{s}$$

With this definition, we can write Equation 29.8 as

$$v = \frac{n\hbar}{mr} \quad n = 1, 2, 3, \dots \quad (29.9)$$

This, like Equation 29.6, is another relationship between v and r . This is the constraint that arises from treating the electron as a wave.

Now if the electron can act as both a particle *and* a wave, then both the Equation 29.6 *and* Equation 29.9 constraints have to be obeyed. That is, v^2 as given by the Equation 29.6 particle constraint has to equal v^2 of the Equation 29.9 wave constraint. Equating these gives

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} = \frac{n^2\hbar^2}{m^2 r^2}$$

We can solve this equation to find that the radius r is

$$r_n = n^2 \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad n = 1, 2, 3, \dots \quad (29.10)$$

where we have added a subscript n to the radius r to indicate that it depends on the integer n .

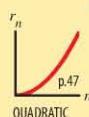
The right-hand side of Equation 29.10, except for the n^2 , is just a collection of constants. Let’s group them all together and define the **Bohr radius** a_B to be

$$a_B = \text{Bohr radius} = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} = 0.0529 \text{ nm}$$

With this definition, Equation 29.10 for the radius of the electron’s orbit becomes

$$r_n = n^2 a_B \quad n = 1, 2, 3, \dots \quad (29.11)$$

Allowed radii of the Bohr hydrogen atom



The first few allowed values of r are

$$r_n = \begin{cases} 0.053 \text{ nm} & n = 1 \\ 0.212 \text{ nm} & n = 2 \\ 0.476 \text{ nm} & n = 3 \\ \vdots & \vdots \end{cases}$$

We have discovered stationary states! That is, a **hydrogen atom can exist only if the radius of the electron’s orbit is one of the values given by Equation 29.11**. Intermediate values of the radius, such as $r = 0.100 \text{ nm}$, cannot exist because the electron cannot set up a standing wave around the circumference. The possible orbits are *quantized*, and integer n is the quantum number.

Hydrogen Atom Energy Levels

Now we can make progress quickly. Knowing the possible radii, we can return to Equation 29.9 and find the possible electron speeds:

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{\hbar}{ma_B} = \frac{v_1}{n} \quad n = 1, 2, 3, \dots \quad (29.12)$$

where $v_1 = \hbar/m a_B = 2.19 \times 10^6 \text{ m/s}$ is the electron’s speed in the $n = 1$ orbit. The speed decreases as n increases.

Finally, we can determine the energies of the stationary states by using Equations 29.11 and 29.12 for r and v in Equation 29.4 for the energy. The algebra is rather messy, but the result simplifies to

$$E_n = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\epsilon_0 r_n} = -\frac{1}{n^2} \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} \right) \quad (29.13)$$

Let's define

$$E_1 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} = 13.60 \text{ eV}$$

We can then write the energy levels of the stationary states of the hydrogen atom as

$$E_n = -\frac{E_1}{n^2} = -\frac{13.60 \text{ eV}}{n^2} \quad n = 1, 2, 3, \dots \quad (29.14)$$

Allowed energies of the Bohr hydrogen atom

This has been a lot of math, so we need to see where we are and what we have learned. Table 29.2 shows values of r_n , v_n , and E_n for quantum numbers $n = 1$ to 4. We do indeed seem to have discovered stationary states of the hydrogen atom. Each state, characterized by its quantum number n , has a unique radius, speed, and energy. These are displayed graphically in FIGURE 29.15, in which the orbits are drawn to scale. Notice how the atom's diameter increases very rapidly as n increases. At the same time, the electron's speed decreases.

FIGURE 29.15 The first four stationary states, or allowed orbits, of the Bohr hydrogen atom drawn to scale.

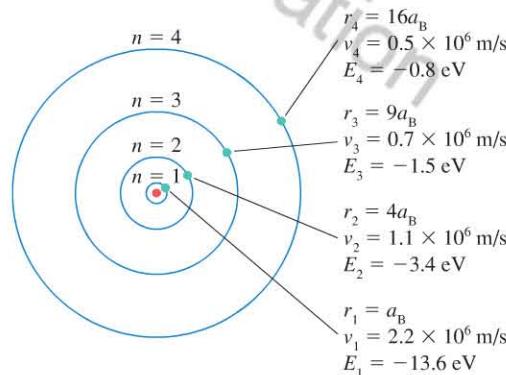


TABLE 29.2 Radii, speeds, and energies for the first four states of the Bohr hydrogen atom

| <i>n</i> | <i>r_n</i> (nm) | <i>v_n</i> (m/s) | <i>E_n</i> (eV) |
|-----------------|----------------------------------|-----------------------------------|----------------------------------|
| 1 | 0.053 | 2.19×10^6 | -13.60 |
| 2 | 0.212 | 1.09×10^6 | -3.40 |
| 3 | 0.476 | 0.73×10^6 | -1.51 |
| 4 | 0.847 | 0.55×10^6 | -0.85 |

EXAMPLE 29.4 Possible electron speeds in a hydrogen atom

Can an electron in a hydrogen atom have a speed of $3.60 \times 10^5 \text{ m/s}$? If so, what are its energy and the radius of its orbit? What about a speed of $3.65 \times 10^5 \text{ m/s}$?

PREPARE To be in a stationary state, the electron must have speed $v_n = v_i/n$, with $n = v_i/v$ an integer. Only if v_i/v is an integer is v an allowed electron speed.

SOLVE A speed of $3.60 \times 10^5 \text{ m/s}$ would require quantum number

$$n = \frac{v_i}{v} = \frac{2.19 \times 10^6 \text{ m/s}}{3.60 \times 10^5 \text{ m/s}} = 6.08$$

This is not an integer, so the electron can *not* have this speed. But if $v = 3.65 \times 10^5 \text{ m/s}$, then

$$n = \frac{2.19 \times 10^6 \text{ m/s}}{3.65 \times 10^5 \text{ m/s}} = 6$$

This is the speed of an electron in the $n = 6$ excited state. An electron in this state has energy

$$E_6 = -\frac{13.60 \text{ eV}}{6^2} = -0.378 \text{ eV}$$

and the radius of its orbit is

$$r_6 = 6^2 a_B = 6^2 (0.0529 \text{ nm}) = 1.90 \text{ nm}$$

It is important to understand why the energies of the stationary states are negative. An electron and a proton bound into an atom have *less* energy than they do when they're separated. We know this because we would have to do work (i.e., *add* energy) to pull the electron and proton apart.

When the electron and proton are completely separated ($r \rightarrow \infty$) and at rest ($v = 0$), their potential energy $U = q_1 q_2 / 4\pi\epsilon_0 r$ and kinetic energy $K = mv^2/2$ are zero. As the electron moves closer to the proton to form a hydrogen atom, its potential energy *decreases*, becoming negative, while the kinetic energy of the orbiting electron increases. Equation 29.13, however, shows that the potential energy decreases faster than the kinetic energy increases, leading to an overall negative energy for the atom. In general, negative energies are characteristic of *bound systems*.

Quantization of Angular Momentum

The angular momentum of a particle in circular motion, whether it is a planet or an electron, is

$$L = mvr$$

You will recall that angular momentum is conserved in orbital motion because a force directed toward a central point exerts no torque on the particle. Bohr used conservation of energy explicitly in his analysis of the hydrogen atom, but what role does conservation of angular momentum play?

The condition that a de Broglie wave for the electron set up a standing wave around the circumference was given, in Equation 29.7, as

$$2\pi r = n\lambda = n \frac{h}{mv}$$

We can rewrite this equation as

$$mvr = n \frac{h}{2\pi} = n\hbar \quad (29.15)$$

But mvr is the angular momentum L for a particle in a circular orbit. It appears that the angular momentum of an orbiting electron cannot have just any value. Instead, it must satisfy

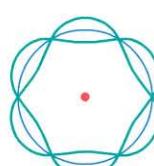
$$L = n\hbar \quad n = 1, 2, 3, \dots \quad (29.16)$$

**Quantization of angular momentum
for the Bohr hydrogen atom**

Thus angular momentum is also quantized! The atom's angular momentum must be an integer multiple of Planck's constant \hbar .

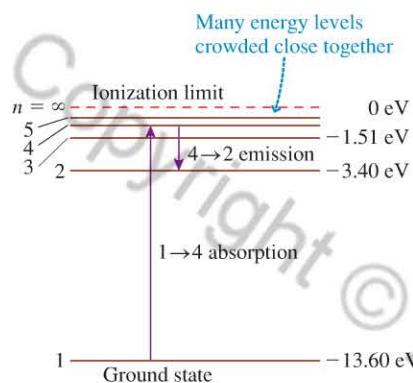
The quantization of angular momentum is a direct consequence of the wave-like nature of the electron. We will find that the quantization of angular momentum plays a major role in the behavior of more complex atoms, leading to the idea of electron shells that you likely have studied in chemistry.

STOP TO THINK 29.4 What is the quantum number of this hydrogen atom?



The Hydrogen Spectrum

FIGURE 29.16 The energy-level diagram of the hydrogen atom.



The most important experimental evidence that we have about the hydrogen atom is its spectrum, so the primary test of the Bohr hydrogen atom is whether it correctly predicts the spectrum. **FIGURE 29.16** is an energy-level diagram for the hydrogen atom. As we noted in Chapter 28, the energies are like the rungs of a ladder. The lowest rung is the ground state, with $E_1 = -13.60 \text{ eV}$. The top rung, with $E = 0 \text{ eV}$, corresponds to a hydrogen ion in the limit $n \rightarrow \infty$. This top rung is called the **ionization limit**. In principle there are an infinite number of rungs, but only the lowest few are shown. The energy levels with higher values of n are all crowded together just below the ionization limit at $n = \infty$.

The figure shows a $1 \rightarrow 4$ transition in which a photon is absorbed and a $4 \rightarrow 2$ transition in which a photon is emitted. For two quantum states m and n , where $n > m$ and E_n is the higher-energy state, an atom can *emit* a photon in an $n \rightarrow m$ transition or *absorb* a photon in an $m \rightarrow n$ transition.

According to the fifth assumption of Bohr's model of atomic quantization, the frequency of the photon emitted in an $n \rightarrow m$ transition is

$$f_{\text{photon}} = \frac{\Delta E_{\text{atom}}}{h} = \frac{E_n - E_m}{h} \quad (29.17)$$

We can use Equation 29.14 for the energies E_n and E_m to predict that the emitted photon has frequency

$$f_{\text{photon}} = \frac{1}{h} \left(\frac{-13.60 \text{ eV}}{n^2} - \frac{-13.60 \text{ eV}}{m^2} \right) = \frac{13.60 \text{ eV}}{h} \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

The frequency is a positive number because $m < n$ and thus $1/m^2 > 1/n^2$.

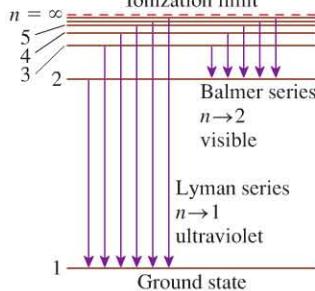
We are more interested in wavelength than frequency, because wavelengths are the quantity measured by experiment. The wavelength of the photon emitted in an $n \rightarrow m$ quantum jump is

$$\lambda_{n \rightarrow m} = \frac{c}{f_{\text{photon}}} = \frac{\lambda_0}{\left(\frac{1}{m^2} - \frac{1}{n^2} \right)} \quad \begin{array}{l} m = 1, 2, 3, \dots \\ n = m + 1, m + 2, \dots \end{array} \quad (29.18)$$

with $\lambda_0 = 91.1 \text{ nm}$. This should look familiar. It is the Balmer formula, Equation 29.2.

It works! Unlike previous atomic models, the **Bohr hydrogen atom correctly predicts the discrete spectrum of the hydrogen atom**. **FIGURE 29.17** shows two series of transitions that give rise to wavelengths in the spectrum. The *Balmer series*, consisting of transitions ending on the $m = 2$ state, gives visible wavelengths, and this is the series that Balmer initially analyzed. The *Lyman series*, ending on the $m = 1$ ground state, is in the ultraviolet region of the spectrum and was not measured until later. These series, as well as others in the infrared, are observed in a discharge tube where collisions with electrons excite the atoms upward from the ground state to state n . They then decay downward by emitting photons. Only the Lyman series is observed in the absorption spectrum because, as noted previously, essentially all the atoms in a quiescent gas are in the ground state.

FIGURE 29.17 Transitions producing the Lyman series and the Balmer series of lines in the hydrogen spectrum.



EXAMPLE 29.5

Wavelengths in galactic hydrogen absorption

Whenever astronomers look at distant galaxies, they find that the light has been strongly absorbed at the wavelength of the $1 \rightarrow 2$ transition in the Lyman series of hydrogen. This absorption tells us that interstellar space is filled with vast clouds of hydrogen left over from the Big Bang. What is the wavelength of the $1 \rightarrow 2$ absorption in hydrogen?

SOLVE Equation 29.18 predicts the *absorption* spectrum of hydrogen if we let $m = 1$. The absorption seen by astronomers is from the ground state of hydrogen ($m = 1$) to its first excited state ($n = 2$). The wavelength is

$$\lambda_{1 \rightarrow 2} = \frac{91.1 \text{ nm}}{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)} = 122 \text{ nm}$$

ASSESS This wavelength is far into the ultraviolet. Ground-based astronomy cannot observe this region of the spectrum because the wavelengths are strongly absorbed by the atmosphere, but with space-based telescopes, first widely used in the 1970s, astronomers see 122 nm absorption in nearly every direction they look.

29.5 The Quantum-Mechanical Hydrogen Atom

Bohr's analysis of the hydrogen atom seemed to be a resounding success. By introducing stationary states, together with Einstein's ideas about light quanta, Bohr was able to provide the first solid understanding of discrete spectra and, in particular, to predict the Balmer formula for the wavelengths in the hydrogen spectrum. And the Bohr hydrogen atom, unlike Rutherford's model, was stable. There was clearly some validity to the idea of stationary states.

But Bohr was completely unsuccessful at explaining the spectra of any other atom. His method did not work even for helium, the second element in the periodic table with a mere two electrons. Although Bohr was clearly on the right track, his inability to extend the Bohr hydrogen atom to more complex atoms made it equally clear that the complete and correct theory remained to be discovered. Bohr's theory was what we now call "semiclassical," a hybrid of classical Newtonian mechanics with the new ideas of quanta. Still missing was a complete theory of motion and dynamics in a quantized universe—a *quantum* mechanics.

In 1925, Erwin Schrödinger introduced this general theory of quantum mechanics, a theory capable of calculating the allowed energy levels (i.e., the stationary states) of any system. The calculations are mathematically difficult, even for a system as simple as the hydrogen atom, and we will present results without proof.

The Bohr hydrogen atom was characterized by a single quantum number n . In contrast, Schrödinger's quantum-mechanical analysis of the hydrogen atom found that it must be described by *four* quantum numbers.

1. Schrödinger found that the *energy* of the hydrogen atom is given by the same expression found by Bohr, or

$$E_n = -\frac{13.60 \text{ eV}}{n^2} \quad n = 1, 2, 3, \dots \quad (29.19)$$

The integer n is called the **principal quantum number**.

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

$$L = \sqrt{l(l+1)} \hbar \quad l = 0, 1, 2, 3, \dots, n-1 \quad (29.20)$$

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

3. The plane of the electron's orbit can be tilted, but only at certain discrete angles. Each allowed angle is characterized by a quantum number m , which must be one of the values

$$m = -l, -l+1, \dots, 0, \dots, l-1, l \quad (29.21)$$

The integer m is called the **magnetic quantum number** because it becomes important when the atom is placed in a magnetic field.

4. The electron's *spin*—discussed below—can point only up or down. These two orientations are described by the **spin quantum number** m_s , which must be one of the values

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2} \quad (29.22)$$

In other words, each stationary state of the hydrogen atom is identified by a quartet of quantum numbers (n, l, m, m_s), and each quantum number is associated with a physical property of the atom.

NOTE ► The energy of the stationary state depends on only the principal quantum number n , not on l, m , or m_s . ◀

EXAMPLE 29.6 Listing quantum numbers

List all possible states of a hydrogen atom that have energy $E = -3.40 \text{ eV}$.

SOLVE Energy depends on only the principal quantum number n . From Equation 29.19, states with $E = -3.40 \text{ eV}$ have

$$n = \sqrt{\frac{-13.60 \text{ eV}}{-3.40 \text{ eV}}} = 2$$

An atom with principal quantum number $n = 2$ could have either $l = 0$ or $l = 1$, but $l \geq 2$ is ruled out. If $l = 0$, the only possible value for the magnetic quantum number m is $m = 0$. If $l = 1$, then

the atom could have $m = -1, m = 0$, or $m = +1$. For each of these, the spin quantum number could be $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$. Thus the possible sets of quantum numbers are

| n | l | m | m_s | n | l | m | m_s |
|-----|-----|-----|----------------|-----|-----|-----|----------------|
| 2 | 0 | 0 | $+\frac{1}{2}$ | 2 | 0 | 0 | $-\frac{1}{2}$ |
| 2 | 1 | 1 | $+\frac{1}{2}$ | 2 | 1 | 1 | $-\frac{1}{2}$ |
| 2 | 1 | 0 | $+\frac{1}{2}$ | 2 | 1 | 0 | $-\frac{1}{2}$ |
| 2 | 1 | -1 | $+\frac{1}{2}$ | 2 | 1 | -1 | $-\frac{1}{2}$ |

These eight states all have the same energy.

TABLE 29.3 Symbols used to represent quantum number l

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

Hydrogen turns out to be unique. For all other elements, the allowed energies depend on both n and l (but not m or m_s). Consequently, it is useful to label the stationary states by their values of n and l . The lowercase letters shown in Table 29.3 are customarily used to represent the various values of quantum number l . These symbols come from spectroscopic notation used in prequantum-mechanics days, when some spectral lines were classified as sharp, others as principal, and so on.

Using these symbols, we call the ground state of the hydrogen atom, with $n = 1$ and $l = 0$, the $1s$ state. The $3d$ state has $n = 3, l = 2$. In Example 29.6, we found two $2s$ states (with $l = 0$) and six $2p$ states (with $l = 1$), all with the same energy.

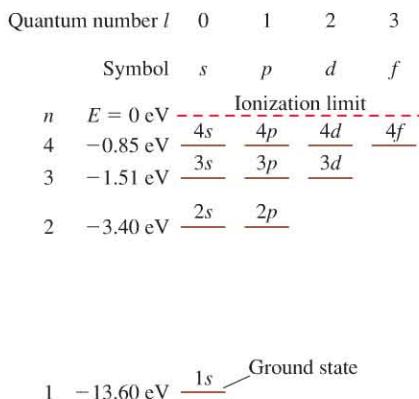
Energy and Angular Momentum Are Quantized

The energy of the hydrogen atom is quantized. The allowed energies of hydrogen, given by Equation 29.19, depend on only the principal quantum number n , but for other atoms the energies will depend on both n and l . In anticipation of using both quantum numbers, FIGURE 29.18 is an energy-level diagram for the hydrogen atom in which the rows are labeled by n and the columns by l . The left column contains all of the $l = 0$ s states, the next column is the $l = 1$ p states, and so on.

Because the quantum condition of Equation 29.20 requires $n > l$, the s states begin with $n = 1$, the p states begin with $n = 2$, and the d states with $n = 3$. That is, the lowest-energy d state is $3d$ because states with $n = 1$ or $n = 2$ cannot have $l = 2$. For hydrogen, where the energy levels do not depend on l , the energy-level diagram shows that the $3s$, $3p$, and $3d$ states have equal energy. Figure 29.18 shows only the first few energy levels for each value of l , but there really are an infinite number of levels, as $n \rightarrow \infty$, crowding together beneath $E = 0$. The dotted line at $E = 0$ is the atom's *ionization limit*, the energy of a hydrogen atom in which the electron has been moved infinitely far away to form an H^+ ion.

You should compare this energy-level diagram to Figure 29.16 for the Bohr atom. Because the energy levels of the quantum-mechanical hydrogen atom are exactly the

FIGURE 29.18 The energy-level diagram for the hydrogen atom.



same as for the Bohr atom, the quantum-mechanical solution also correctly predicts the discrete spectrum of hydrogen.

Classically, the angular momentum L of an orbiting electron can have any value. Not so in quantum mechanics. Equation 29.20 tells us that **the electron's orbital angular momentum is quantized**. The magnitude of the orbital angular momentum must be one of the discrete values

$$L = \sqrt{l(l+1)}\hbar = 0, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar, \dots$$

where l is an integer. The Bohr atom also predicted quantized angular momentum, but the precise values of that prediction turned out to be in error. The quantum-mechanical prediction for L is more complex, but it agrees with experimental observations.

A particularly interesting prediction is that the ground state of hydrogen, with $l = 0$, has *no* angular momentum. A classical particle cannot orbit unless it has angular momentum, but apparently a quantum particle does not have this requirement.

STOP TO THINK 29.5 What are the quantum numbers n and l for a hydrogen atom with $E = -(13.60/9)$ eV and $L = \sqrt{2}\hbar$?

The Electron Spin

You learned in Chapter 24 that a current loop creates a *magnetic dipole moment*, acting like a bar magnet with a north and south pole. In the 1920s, physicists studying the magnetic properties of atoms discovered that the electron has a magnetic dipole moment. The electron has a mass, which allows it to experience gravitational forces, and an electric charge, which allows it to experience electric forces, so perhaps it's not surprising that the electron comes with a magnetic dipole moment, allowing it to experience magnetic forces.

It was first thought that the electron was a very tiny ball of negative charge spinning on its axis. This would give the electron both a magnetic dipole moment and *spin angular momentum*. However, a spinning ball of charge would violate the laws of relativity and other physical laws. As far as we know today, the electron is truly a point particle that happens to have an intrinsic magnetic dipole moment and angular momentum *as if* it were spinning. This inherent angular momentum is called the *electron spin*, but it is a convenient figure of speech, not a factual statement. **The electron has a spin, but it is not a spinning electron.**

The two possible spin quantum numbers $m_s = \pm \frac{1}{2}$ mean that the electron's intrinsic magnetic dipole points in the $+z$ -direction or the $-z$ -direction. These two orientations are called *spin up* and *spin down*. It is convenient to picture a little vector that can be drawn \uparrow for a spin-up state and \downarrow for a spin-down state. We will use this notation in the next section.

29.6 Multielectron Atoms

The quantum-mechanical solution for the hydrogen atom matches the experimental evidence, but so did the Bohr hydrogen atom. One of the first big successes of Schrödinger's quantum mechanics was an ability to calculate the stationary states and energy levels of *multielectron atoms*, atoms in which Z electrons orbit a nucleus with Z protons. A major difference between multielectron atoms and the simple one-electron hydrogen is that the energy of an electron in a multielectron atom depends on both quantum numbers n and l . Whereas the $2s$ and $2p$ states in hydrogen have the same energy, their energies are different in a multielectron atom. The difference arises from the electron-electron interactions that do not exist in a single-electron hydrogen atom.

FIGURE 29.19 An energy-level diagram for electrons in a multielectron atom.

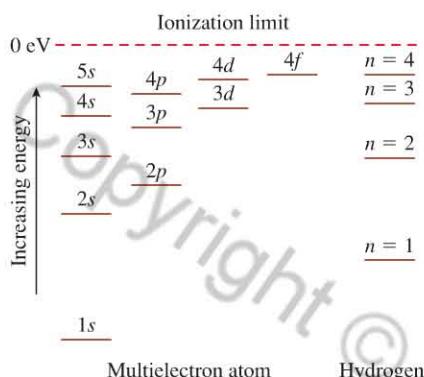


FIGURE 29.20 The ground state and first excited state of helium.

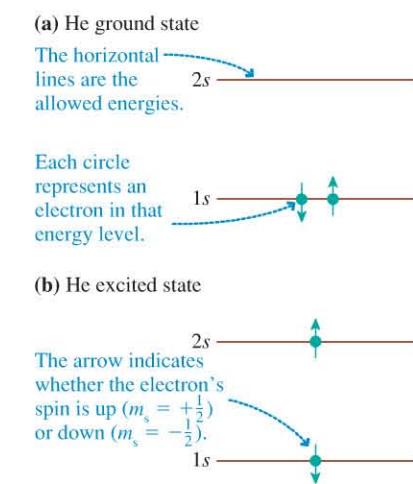


FIGURE 29.21 The ground state and first excited state of lithium.

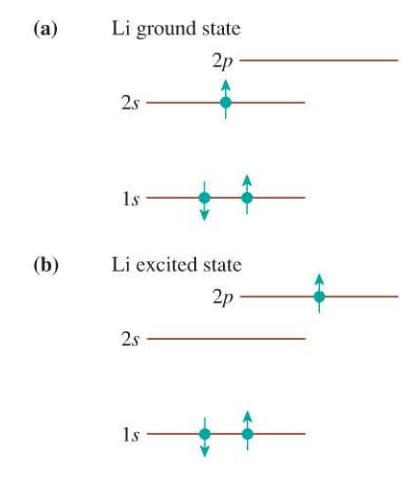


FIGURE 29.19 shows an energy-level diagram for the electrons in a multielectron atom. (Compare this to the hydrogen energy-level diagram in Figure 29.18.) For comparison, the hydrogen-atom energies are shown on the right edge of the figure. Two features of this diagram are of particular interest:

- For each n , the energy increases as l increases until the maximum- l state has an energy very nearly that of the same n in hydrogen. States with small values of l are significantly lower in energy than the corresponding state in hydrogen.
- As the energy increases, states with different n begin to alternate in energy. For example, the $3s$ and $3p$ states have lower energy than a $4s$ state, but the energy of an electron in a $3d$ state is slightly higher. This will have important implications for the structure of the periodic table of the elements.

The Pauli Exclusion Principle

By definition, the ground state of a quantum system is the state of lowest energy. What is the ground state of an atom having Z electrons and Z protons? Because the $1s$ state is the lowest energy state, it seems that the ground state should be one in which all Z electrons are in the $1s$ state. However, this idea is not consistent with the experimental evidence.

In 1925, the Austrian physicist Wolfgang Pauli hypothesized that no two electrons in a quantum system can be in the same quantum state. That is, **no two electrons can have exactly the same set of quantum numbers (n, l, m, m_s)**. If one electron is present in a state, it *excludes* all others. This statement is called the **Pauli exclusion principle**. It turns out to be an extremely profound statement about the nature of matter.

The exclusion principle is not applicable to hydrogen, where there is only a single electron, but in helium, with $Z = 2$ electrons, we must make sure that the two electrons are in different quantum states. This is not difficult. For a $1s$ state, with $l = 0$, the only possible value of the magnetic quantum number is $m = 0$. But there are *two* possible values of m_s —namely, $-\frac{1}{2}$ and $+\frac{1}{2}$. If a first electron is in the spin-down $1s$ state $(1, 0, 0, -\frac{1}{2})$, a second $1s$ electron can still be added to the atom as long as it is in the spin-up state $(1, 0, 0, +\frac{1}{2})$. This is shown schematically in **FIGURE 29.20a**, where the dots represent electrons on the rungs of the “energy ladder” and the arrows represent spin down or spin up.

The Pauli exclusion principle does not prevent both electrons of helium from being in the $1s$ state as long as they have opposite values of m_s , so we predict this to be the ground state. A list of an atom’s occupied energy levels is called its **electron configuration**. The electron configuration of the helium ground state is written $1s^2$, where the superscript 2 indicates two electrons in the $1s$ energy level. An excited state of the helium atom might be the electron configuration $1s2s$. This state is shown in **FIGURE 29.20b**. Here, because the two electrons have different values of n , there is no restriction on their values of m_s .

The states $(1, 0, 0, -\frac{1}{2})$ and $(1, 0, 0, +\frac{1}{2})$ are the only two states with $n = 1$. The ground state of helium has one electron in each of these states, so all the possible $n = 1$ states are filled. Consequently, the electron configuration $1s^2$ is called a **closed shell**.

The next element, lithium, has $Z = 3$ electrons. The first two electrons can go into $1s$ states, with opposite values of m_s , but what about the third electron? The $1s^2$ shell is closed, and there are no additional quantum states having $n = 1$. The only option for the third electron is the next energy state, $n = 2$. The $2s$ and $2p$ states had equal energies in the hydrogen atom, but they do *not* in a multielectron atom. As Figure 29.19 showed, a lower- l state has lower energy than a higher- l state with the same n . The $2s$ state of lithium is lower in energy than $2p$, so lithium’s third ground-state electron will be $2s$. This requires $l = 0$ and $m = 0$ for the third electron, but the value of m_s is not relevant because there is only a single electron in $2s$. **FIGURE 29.21a** shows the electron configuration with the $2s$ electron being spin up, but it could equally well be spin down. The electron configuration for the lithium ground state is written $1s^22s$. This indicates two $1s$ electrons and a single $2s$ electron. One possible excited state of lithium is shown in **FIGURE 29.21b**.

The Periodic Table of the Elements

The 19th century was a time when chemists were discovering new elements and studying their chemical properties. The century opened with the atomic model still not completely validated, and with no one having any idea how many elements there might be. But chemistry developed quickly, and by mid-century it was clear that there were dozens of elements, but not hundreds.

The Russian chemist Dmitri Mendeléev was the first to propose, in 1867, a *periodic* arrangement of the elements based on the regular recurrence of chemical properties. He did so by explicitly pointing out “gaps” where, according to his hypothesis, undiscovered elements should exist. He could then predict the expected properties of the missing elements. The subsequent discovery of these elements verified Mendeléev’s organizational scheme, which came to be known as the *periodic table of the elements*.

One of the great triumphs of the quantum-mechanical theory of multielectron atoms is that it explains the structure of the periodic table. We can understand this structure by looking at the energy-level diagram of FIGURE 29.22, which is an expanded version of the energy-level diagram of Figure 29.19. Just as for helium and lithium, atoms with larger values of Z are constructed by placing Z electrons into the lowest-energy levels that are consistent with the Pauli exclusion principle.

The s states of helium and lithium can each hold two electrons—one spin up and the other spin down—but the higher-angular-momentum states that will become filled for higher- Z atoms can hold more than two electrons. For each value l of the orbital quantum number, there are $2l + 1$ possible values of the magnetic quantum number m_l and, for each of these, two possible values of the spin quantum number m_s . Consequently, each energy level in Figure 29.22 is actually $2(2l + 1)$ different states that, taken together, are called a *subshell*. Table 29.4 lists the number of states in each subshell. Each state in a subshell is represented in Figure 29.22 by a colored dot. The dots’ colors correspond to the periodic table in FIGURE 29.23, which is color coded to show which subshells are being filled as Z increases.

We can now use Figure 29.22 to construct the periodic table in Figure 29.23. We’ve already seen that lithium has two electrons in the $1s$ state and one electron in

FIGURE 29.22 An energy-level diagram showing how many electrons can occupy each subshell.

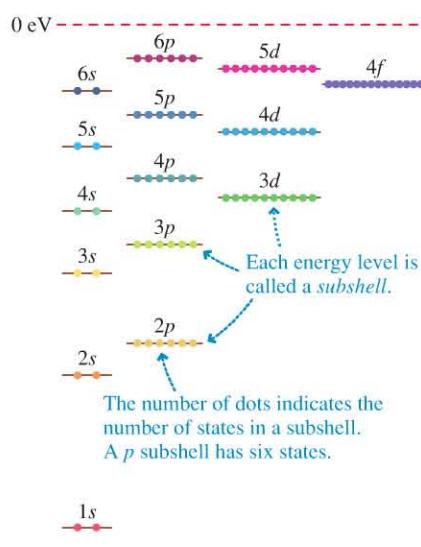
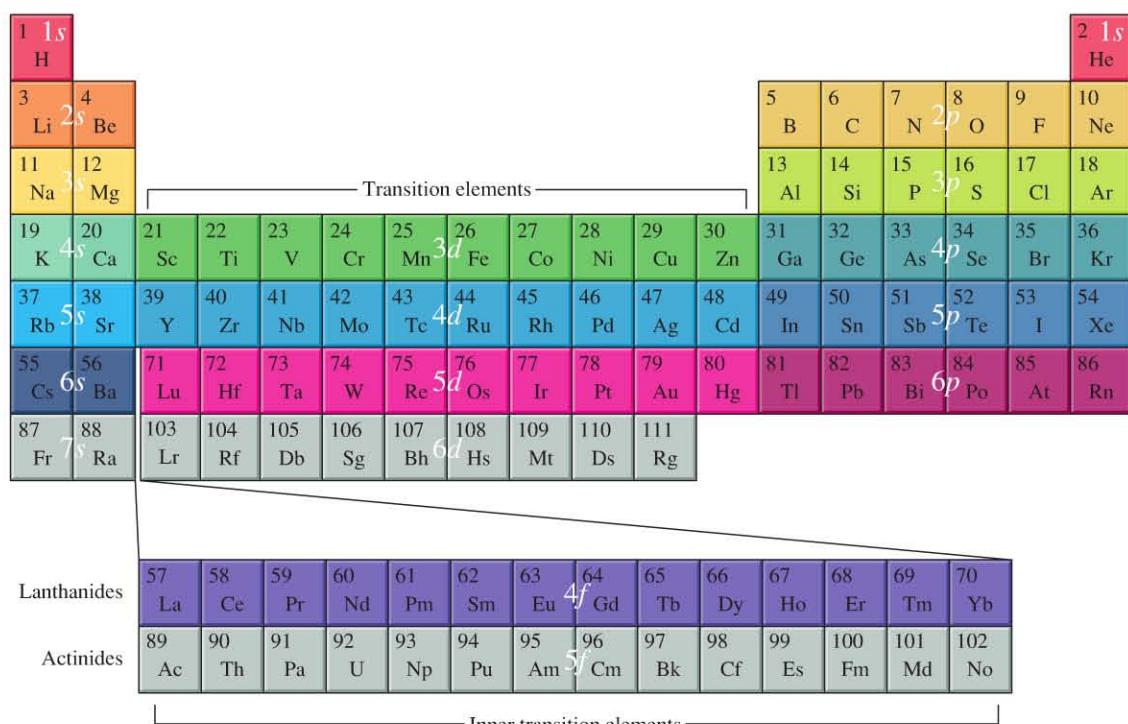


TABLE 29.4 Number of states in each subshell of an atom

| Subshell | l | Number of states |
|----------|-----|------------------|
| s | 0 | 2 |
| p | 1 | 6 |
| d | 2 | 10 |
| f | 3 | 14 |

FIGURE 29.23 The periodic table of the elements. The elements are color coded to the states in the energy-level diagram of Figure 29.22.



the $2s$ state. Four-electron beryllium ($Z = 4$) comes next. We see that there is still an empty state in the $2s$ subshell for this fourth electron to occupy, so beryllium closes the $2s$ subshell and has electron configuration $1s^22s^2$.

As Z increases further, the next six electrons can each occupy states in the $2p$ subshell. These are the elements boron (B) through neon (Ne), completing the second row of the periodic table. Neon, which completes the $2p$ subshell, has ground-state configuration $1s^22s^22p^6$.

The $3s$ subshell is the next to be filled, leading to the elements sodium and magnesium. Filling the $3p$ subshell gives aluminum through argon, completing the third row of the table.

Starting the fourth row of the periodic table are the two $4s$ states of potassium and calcium. Here the table begins to get more complicated. Following the pattern of rows two and three, you might expect the $4p$ subshell to start filling at this point. But, looking carefully at Figure 29.22, you will see that the $3d$ subshell has a slightly lower energy than the $4p$ subshell. Because the ground state of an atom is the *lowest energy state* consistent with the Pauli exclusion principle, the next element—scandium—finds it more favorable to add a $3d$ electron. The ten *transition elements* from scandium (Sc) through zinc (Zn) then fill the 10 states of the $3d$ subshell.

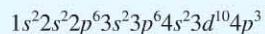
The same pattern applies to the fifth row, where the $5s$, $4d$, and $5p$ subshells fill in succession. In the sixth row, however, after the initial $6s$ states are filled, the $4f$ subshell has the lowest energy, so it begins to fill *before* the $5d$ states. The elements corresponding to the $4f$ subshell, lanthanum through ytterbium, are known as the lanthanides, and they are traditionally drawn as a row separated from the rest of the table. The seventh row follows this same pattern.

Thus the entire periodic table can be built up using our knowledge of the energy-level diagram of a multielectron atom along with the Pauli exclusion principle.

EXAMPLE 29.7 The ground state of arsenic

Predict the ground-state electron configuration of arsenic.

SOLVE The periodic table shows that arsenic (As) has $Z = 33$, so we must identify the states of 33 electrons. Arsenic is in the fourth row, following the first group of transition elements. Argon ($Z = 18$) filled the $3p$ subshell, then calcium ($Z = 20$) filled the $4s$ subshell. The next 10 elements, through zinc ($Z = 30$), filled the $3d$ subshell. The $4p$ subshell starts filling with gallium ($Z = 31$), and arsenic is the third element in this group, so it will have three $4p$ electrons. Thus the ground-state configuration of arsenic is



STOP TO THINK 29.6 Is the electron configuration $1s^22s^22p^43s$ a ground-state configuration or an excited-state configuration?

- A. Ground-state.
- B. Excited-state.
- C. It's not possible to tell without knowing which element it is.

29.7 Excited States and Spectra

The periodic table organizes information about the *ground states* of the elements. These states are chemically most important because most atoms spend most of the time in their ground states. All the chemical ideas of valence, bonding, reactivity, and so on are consequences of these ground-state atomic structures. But the periodic table does not tell us anything about the excited states of atoms. It is the excited states that hold the key to understanding atomic spectra, and that is the topic to which we turn next.

Sodium ($Z = 11$) is a multielectron atom that we will use to illustrate excited states. The ground-state electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$. The first 10 electrons completely fill the $1s$, $2s$, and $2p$ subshells, creating a *neon core* whose electrons are tightly bound together. The $3s$ electron, however, is a *valence electron* that can be easily excited to higher energy levels.

The excited states of sodium are produced by raising the valence electron to a higher energy level. The electrons in the neon core are unchanged. FIGURE 29.24 is an energy-level diagram showing the ground state and some of the excited states of sodium. The $1s$, $2s$, and $2p$ states of the neon core are not shown on the diagram. These states are filled and unchanging, so only the states available to the valence electron are shown. Notice that the zero of energy has been shifted to the ground state. As we have discovered before, the zero of energy can be located where it is most convenient. With this choice, the excited-state energies tell us how far each state is above the ground state. The ionization limit now occurs at the value of the atom's ionization energy, which is 5.14 eV for sodium.

Excitation by Absorption

Left to itself, an atom will be in its lowest-energy ground state. How does an atom get into an excited state? The process of getting it there is called **excitation**, and there are two basic mechanisms: absorption and collision. We'll begin by looking at excitation by absorption.

One of the postulates of the basic Bohr model is that 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 $f_{\text{photon}} = \Delta E_{\text{atom}}/\hbar$. This process is shown in FIGURE 29.25. Because we are interested in spectra, it is more useful to write this in terms of the wavelength:

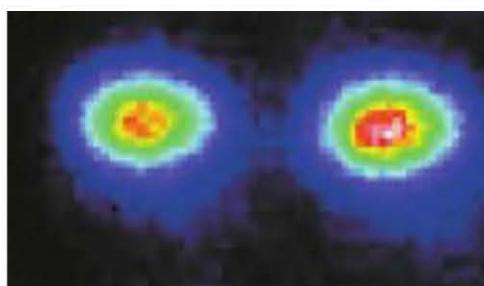
$$\lambda = \frac{c}{f_{\text{photon}}} = \frac{hc}{\Delta E_{\text{atom}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{\Delta E_{\text{atom}}} \quad (29.23)$$

The final expression, which uses the value $hc = 1240 \text{ eV} \cdot \text{nm}$, gives the wavelength in nanometers if ΔE_{atom} is in electron volts.

Not every quantum jump allowed by Equation 29.33 can actually occur in an atom. A quantum-mechanical analysis of how the electrons in an atom interact with a light wave shows that transitions must also satisfy the following **selection rule**: Transitions (either absorption or emission) from a state with orbital quantum number l can occur to only another state whose orbital quantum number differs from the original state by ± 1 , or

$$\Delta l = l_2 - l_1 = \pm 1 \quad (29.24)$$

Selection rule for emission and absorption



The dots of light are being emitted by two beryllium ions held in a device called an ion trap. Each ion, which is excited by an invisible ultraviolet laser, emits about 10^6 visible-light photons per second.

FIGURE 29.24 The $3s$ ground state of the sodium atom and some of the excited states.

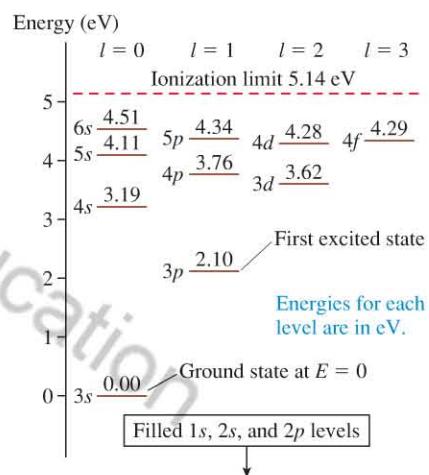
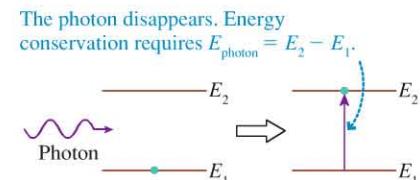


FIGURE 29.25 Excitation by photon absorption.



EXAMPLE 29.8 Analyzing absorption in sodium

What are the two longest wavelengths in the absorption spectrum of sodium? What are the transitions?

SOLVE As Figure 29.24 shows, the sodium ground state is $3s$. Starting from an s state, the selection rule permits quantum jumps only to p states. The lowest excited state is the $3p$ state and $3s \rightarrow 3p$ is an allowed transition ($\Delta l = 1$), so this will be the longest wavelength. You can see from the data in

Figure 29.24 that $\Delta E_{\text{atom}} = 2.10 \text{ eV} - 0.00 \text{ eV} = 2.10 \text{ eV}$ for this transition.

The corresponding wavelength is

$$\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{2.10 \text{ eV}} = 590 \text{ nm}$$

(Because of rounding, the above calculation gives $\lambda = 590 \text{ nm}$. The experimental value is actually 589 nm.)

Continued

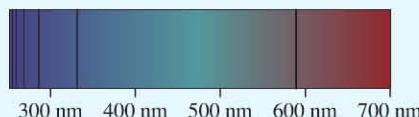
The next excited state is $4s$, but a $3s \rightarrow 4s$ transition is not allowed by the selection rule. The next allowed transition is $3s \rightarrow 4p$, with $\Delta E_{\text{atom}} = 3.76 \text{ eV}$. The wavelength of this transition is

$$\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{3.76 \text{ eV}} = 330 \text{ nm}$$

ASSESS If you look at the sodium spectrum shown in FIGURE 29.26 (which is the same as that shown earlier in Figure 29.3), you will

see that 589 nm and 330 nm are, indeed, the two longest wavelengths in the absorption spectrum.

FIGURE 29.26 The absorption spectrum of sodium.



Collisional Excitation

An electron traveling with a speed of $1.0 \times 10^6 \text{ m/s}$ has a kinetic energy of 2.85 eV. If this electron collides with a ground-state sodium atom, a portion of its energy can be used to excite the atom to a higher-energy state, such as its $3p$ state. This process is called **collisional excitation** of the atom.

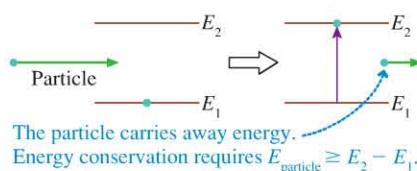
Collisional excitation differs from excitation by absorption in one very fundamental way. In absorption, the photon disappears. Consequently, *all* of the photon's energy must be transferred to the atom. Conservation of energy then requires $E_{\text{photon}} = \Delta E_{\text{atom}}$. In contrast, the electron is still present after collisional excitation and can still have some kinetic energy. That is, the electron does *not* have to transfer its entire energy to the atom. If the electron has an incident kinetic energy of 2.85 eV, it could transfer 2.10 eV to the sodium atom, thereby exciting it to the $3p$ state, and still depart the collision with a speed of $5.1 \times 10^5 \text{ m/s}$ and 0.75 eV of kinetic energy.

To excite the atom, the incident energy of the electron (or any other matter particle) merely has to *exceed* ΔE_{atom} ; that is $E_{\text{particle}} \geq \Delta E_{\text{atom}}$. There's a threshold energy for exciting the atom, but no upper limit. It is all a matter of energy conservation. FIGURE 29.27 shows the idea graphically.

Collisional excitation by electrons is the predominant method of excitation in electrical discharges such as fluorescent lights, street lights, and neon signs. A gas is sealed in a tube at reduced pressure ($\approx 1 \text{ mm Hg}$), then a fairly high voltage ($\approx 1000 \text{ V}$) between electrodes at the ends of the tube causes the gas to ionize, creating a current in which both ions and electrons are charge carriers. The electrons accelerate in the electric field, gaining several eV of kinetic energy, then transfer some of this energy to the gas atoms upon collision. The process does not work at atmospheric pressure because the average distance between collisions is too short for the electrons to gain enough kinetic energy to excite the atoms.

NOTE ► In contrast to photon absorption, there are no selection rules for collisional excitation. Any state can be excited if the colliding particle has sufficient energy. ◀

FIGURE 29.27 Excitation by electron collision.



CONCEPTUAL EXAMPLE 29.9

Possible excitation of hydrogen?

Can an electron with a kinetic energy of 11.4 eV cause a hydrogen atom to emit the prominent red spectral line ($\lambda = 656 \text{ nm}$, $E_{\text{photon}} = 1.89 \text{ eV}$) in the Balmer series?

REASON The electron must have sufficient energy to excite the upper state of the transition. The electron's energy of 11.4 eV is significantly greater than the 1.89 eV energy of a photon with wavelength 656 nm, but don't confuse the energy of the photon with the energy of the excitation. The red spectral line in the Balmer series is emitted in an $n = 3 \rightarrow 2$ quantum jump with $\Delta E_{\text{atom}} = 1.89 \text{ eV}$, but to cause this emission, the electron must excite an atom from its *ground state*, with $n = 1$, up to

the $n = 3$ level. From Figure 29.16, the necessary excitation energy is

$$\begin{aligned}\Delta E_{\text{atom}} &= E_3 - E_1 = (-1.51 \text{ eV}) - (-13.60 \text{ eV}) \\ &= 12.09 \text{ eV}\end{aligned}$$

The electron does *not* have sufficient energy to excite the atom to the state from which the emission would occur.

ASSESS As our discussion of absorption spectra showed, almost all excitations of atoms begin from the ground state. Quantum jumps down in energy, however, can begin and end at any two states allowed by selection rules.

Emission Spectra

The absorption of light is an important process, but it is the emission of light that really gets our attention. The overwhelming bulk of sensory information that we perceive comes to us in the form of light. With the small exception of cosmic rays, all of our knowledge about the cosmos comes to us in the form of light and other electromagnetic waves emitted in various processes. And emission spectra are more than just scientific curiosities. Many of today's artificial light sources, from fluorescent lights to lasers, are applications of emission spectra.

Understanding emission hinges upon the three ideas shown in **FIGURE 29.28**. Once we have determined the energy levels of an atom, from quantum mechanics, we can immediately predict its emission spectrum. We might also ask *how long* an atom remains in an excited state before undergoing a quantum jump to a lower-energy state and emitting a photon. Just as the uncertainty principle prevents us from knowing exactly where an electron is, we also can't determine exactly how long any particular atom spends in the excited state. However, we can determine, both theoretically and experimentally, the *average* time, and the average time an atom spends in the excited state before emitting a photon is called the **lifetime** of that state. A typical excited-state lifetime is just a few nanoseconds.

As an example, **FIGURE 29.29a** shows some of the transitions and wavelengths observed in the emission spectrum of sodium. This diagram makes the point that each wavelength represents a quantum jump between two well-defined energy levels. Notice that the selection rule $\Delta l = \pm 1$ is obeyed in the sodium spectrum. The $5p$ levels can undergo quantum jumps to $3s$, $4s$, or $3d$ but *not* to $3p$ or $4p$.

FIGURE 29.29b shows the emission spectrum of sodium as it would be recorded in a spectrometer. (Many of the lines seen in this spectrum start from higher excited states that are not seen in the rather limited energy-level diagram of Figure 29.29a.) By comparing the spectrum to the energy-level diagram, you can recognize that the spectral lines at 589 nm, 330 nm, 286 nm, and 268 nm form a *series* of lines due to all the possible $np \rightarrow 3s$ transitions. They are the dominant features in the sodium spectrum.

The most obvious visual feature of sodium emission is its bright yellow color, produced by the 589 nm photons emitted in the $3p \rightarrow 3s$ transition. (The lifetime of the $3p$ state happens to be 17 ns.) This is the basis of the *flame test* used in chemistry to test for sodium: A sample is held in a Bunsen burner, and a bright yellow glow indicates the presence of sodium. The 589 nm emission is also prominent in the pinkish-yellow glow of the common sodium-vapor street lights. These operate by creating an electrical discharge in sodium vapor. Most sodium-vapor lights use high-pressure lamps to increase their light output. The high pressure, however, causes the formation of Na_2 molecules, and these molecules emit the pinkish portion of the light.



▲ Seeing the light Some cities close to astronomical observatories use low-pressure sodium lights, and these emit the distinctively yellow 589 nm light of sodium. The glow of city lights is a severe problem for astronomers, but the very specific 589 nm emission from sodium is easily removed with a *sodium filter*; an interference filter that lets all colors pass except the 589 nm yellow sodium light. The photos show the sky near a sodium streetlight without (left) and with (right) a sodium filter. The constellation of Orion, nearly obscured in the left photo, is clearly visible in the right photo.

FIGURE 29.28 Generation of an emission spectrum.

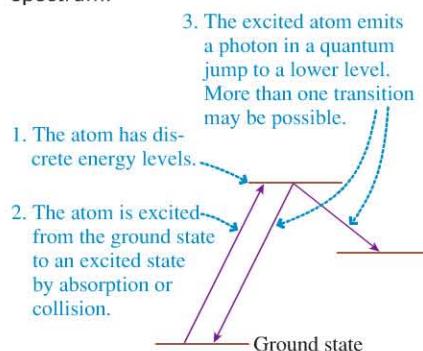


FIGURE 29.29 The emission spectrum of sodium.

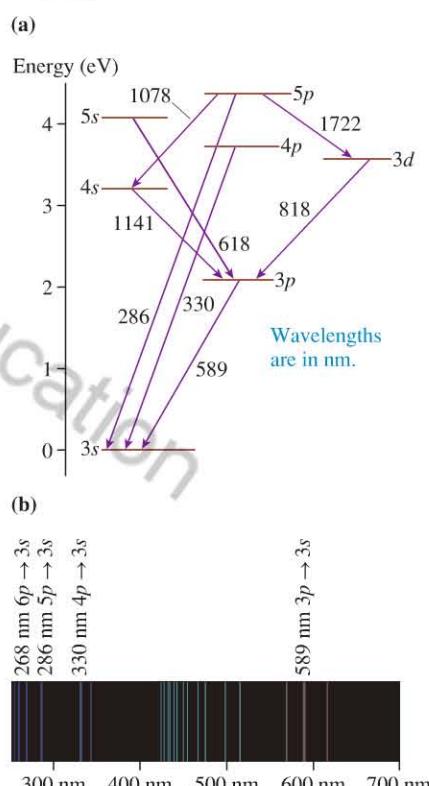
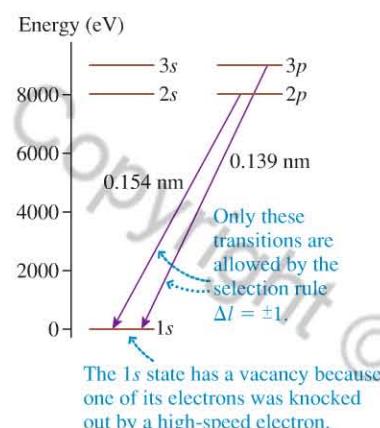


FIGURE 29.30 The generation of x rays from copper atoms.



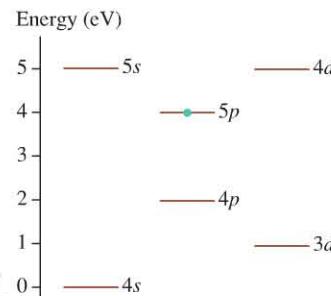
X Rays

Chapter 28 noted that x rays are produced by causing very-high-speed electrons, accelerated with potential differences of many thousands of volts, to crash into metal targets. Rather than exciting the atom's valence electrons, such as happens in a gas discharge tube, these high-speed projectiles are capable of knocking inner-shell electrons out of the target atoms, producing an *inner-shell vacancy*. As **FIGURE 29.30** shows for copper atoms, this vacancy is filled when an electron from a higher shell undergoes a quantum jump into the vacancy, emitting a photon in the process.

In heavy elements, such as copper or iron, the energy difference between the inner and outer shells is very large—typically 10 keV. Consequently, the photon has energy $E_{\text{photon}} \approx 10 \text{ keV}$ and wavelength $\lambda \approx 0.1 \text{ nm}$. These high-energy photons are the x rays discovered by Röntgen. X-ray photons are about 10,000 times more energetic than visible-light photons, and the wavelengths are about 10,000 times smaller. Even so, the underlying physics is the same: A photon is emitted when an electron in an atom undergoes a quantum jump.

STOP TO THINK 29.7 In this hypothetical atom, what is the photon energy E_{photon} of the longest-wavelength photons emitted by atoms in the $5p$ state?

- A. 1.0 eV
- B. 2.0 eV
- C. 3.0 eV
- D. 4.0 eV



29.8 Molecules

Quantum mechanics applies to molecules just as it does to atoms, but molecules are more complex because they have internal modes of storing energy. In particular, molecules can *rotate* about their center of mass, and the atoms can *vibrate* back and forth as if the molecular bonds holding them together were little springs. For the most part, we'll overlook this internal motion and focus our attention on the electrons and the electron energy levels.

A quantum-mechanical analysis of molecules finds the following general results:

- The energy is quantized. Electrons can exist in only certain allowed energy levels.
- The number of energy levels is so extraordinarily high, and the energy levels are jammed so close together, that for all practical purposes the energy levels group into *bands* of allowed energy.
- In thermal equilibrium, nearly all molecules are in the very lowest energy levels.

FIGURE 29.31 shows a generic molecular energy-level diagram for a medium-size molecule. Whereas an atom has a well-defined ground state, a molecule has a broad band of lower energy levels. Similarly, a single excited state, such as the $2s$ state of the hydrogen atom, has been replaced by a band of excited energy levels. Despite the vast number of allowed energy levels, nearly all molecules spend nearly all their time in the very lowest energy levels.

FIGURE 29.31 The molecular energy-level diagram for a medium-size molecule.

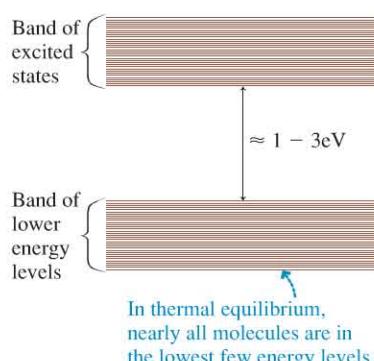
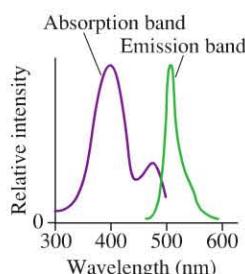
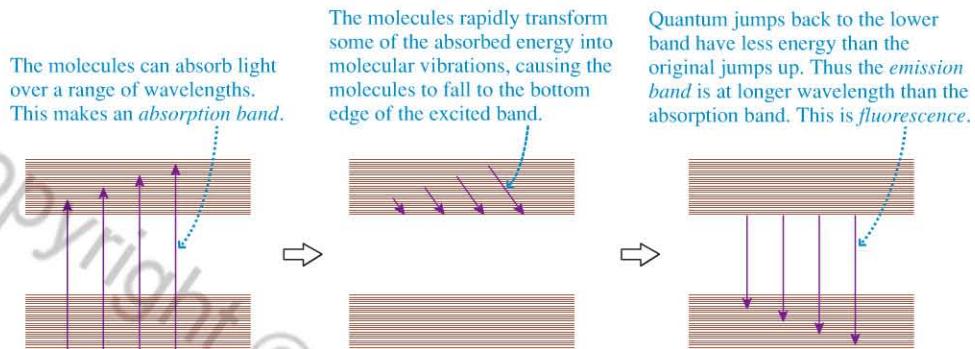


FIGURE 29.32 uses the energy-level diagram to explain two important phenomena of molecular spectroscopy: absorption and fluorescence. Whereas the absorption spectrum of an atom consists of discrete spectral lines, a molecule has a continuous *absorption band*. The absorption of light at a higher frequency (shorter wavelength) followed by the emission of light at a lower frequency (longer wavelength) is called **fluorescence**. Fluorescence occurs in molecules, but not atoms, because molecules can transform some of the absorbed energy into the vibrational energy of the atoms and thus increase the thermal energy of the molecules.

FIGURE 29.32 Molecular absorption and fluorescence.

Fluorescence has many important applications. In biology, fluorescent dyes are used to stain tissue samples for microscopy. In the brilliantly colored photo that opened this chapter, the cells were stained with three different dyes, one of which (blue) was preferentially absorbed in the nucleus and another (green) by actin. The red dye was absorbed by other cell structures. When illuminated with ultraviolet light, which we can't see, each dye fluoresces with its own characteristic color.

► Whiter than white Laundry detergents often contain fluorescent dyes that absorb invisible ultraviolet light and then fluoresce in a broad band of visible wavelengths; that is, they give off white light. Sunlight contains lots of UV, so outdoors your white clothes not only reflect the white visible sunlight, but fluoresce even more white light—"whiter than white." In the photo, you can see how brightly the girl's shirt glows when illuminated with UV light (and, evidently, hair and teeth fluoresce this way as well).

Many biological molecules are fluorescent. A good example is chlorophyll, the green pigment in plants that allows photosynthesis to happen. When illuminated by blue or ultraviolet light, chlorophyll fluoresces an unexpected dark red color. This property of chlorophyll is used by marine biologists to measure the concentration of phytoplankton—microscopic plants—in seawater.

Quite recently, scientists isolated a fluorescent protein from a species of jellyfish. This protein fluoresces green when illuminated with ultraviolet light, so it's been dubbed GFP, for *green fluorescent protein*. GFP has become an important tool in genetics because it can be used to identify when particular genes are being expressed in living cells. This is done by fusing the jellyfish GFP gene to the gene being studied. When the gene is active, the cell manufactures GFP in addition to the usual protein coded by the gene. If the cells are observed under ultraviolet light, a bright green glow from the GFP indicates that the gene is turned on. The cells are dark where the gene is not active. **FIGURE 29.33** shows an example.

The color of GFP may remind you of *bioluminescence*—the summer flashes of fireflies or the green glow of various deep-sea fish—and, indeed, there is a connection. Bioluminescence is actually a form of *chemiluminescence*, the production of light in chemical reactions. Some chemical reactions create reactant molecules in an excited state. These molecules then emit light as they jump to lower energy levels, just as if they had first absorbed shorter-wavelength light. The emitted light has exactly the same spectrum as fluorescence, but the method by which the molecules are excited is different. Light sticks, which come in many colors, are an example of chemiluminescence.

Bioluminescence is just chemiluminescence in a biological organism. Some biochemical reaction—often a catalyzed reaction in an organism—produces a molecule in an excited state, and light is emitted as the molecule jumps to a lower state. In fireflies, the reaction involves an enzyme with the intriguing name *luciferase*. In the jellyfish *Aequoria victoria*, the source of GFP, bioluminescent reactions actually create blue light. However, the blue light is absorbed by the green fluorescent protein—just as predicted by the absorption curve in Figure 29.32—and re-emitted as green fluorescence, giving the jellyfish an eerie green glow when seen in the dark ocean.

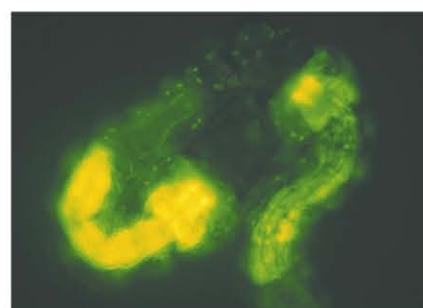
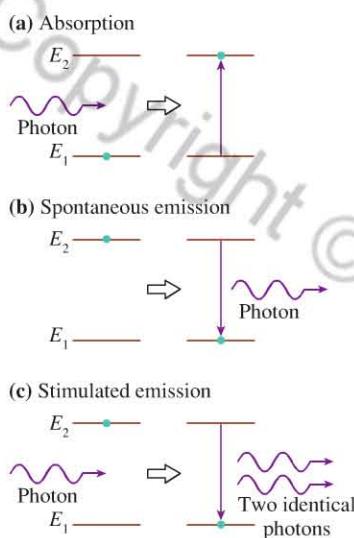
**FIGURE 29.33** Green fluorescent protein shows the locations in mosquito larvae at which a particular gene is being expressed.

FIGURE 29.34 Three types of radiative transitions.

29.9 Stimulated Emission and Lasers

We have seen that an atom can jump from a lower-energy level E_1 to a higher-energy level E_2 by absorbing a photon. **FIGURE 29.34a** illustrates the basic absorption process, with a photon of frequency $f = \Delta E_{\text{atom}}/h$ disappearing as the atom jumps from level 1 to level 2. Once in level 2, as shown in **FIGURE 29.34b**, the atom can emit a photon of the same frequency as it jumps back to level 1. Because this transition occurs spontaneously, without the introduction of outside energy, it is called **spontaneous emission**.

In 1917, four years after Bohr's proposal of stationary states in atoms but still prior to de Broglie and Schrödinger, Einstein was puzzled by how quantized atoms reach thermodynamic equilibrium in the presence of electromagnetic radiation. Einstein found that the processes of absorption and spontaneous emission were not sufficient to allow a collection of atoms to reach thermodynamic equilibrium. To resolve this difficulty, Einstein proposed a third mechanism for the interaction of atoms with light.

The left half of **FIGURE 29.34c** shows a photon with frequency $f = \Delta E_{\text{atom}}/h$ approaching an *excited* atom. If a photon can induce the $1 \rightarrow 2$ transition of absorption, then Einstein proposed that it should also be able to induce a $2 \rightarrow 1$ transition. In a sense, this transition is a *reverse absorption*. But to undergo a reverse absorption, the atom must *emit* a photon of frequency $f = \Delta E_{\text{atom}}/h$. The end result, as seen in the right half of Figure 29.34c, is an atom in level 1 plus *two* photons! Because the first photon induced the atom to emit the second photon, this process is called **stimulated emission**.

Stimulated emission occurs only if the first photon's frequency exactly matches the $E_2 - E_1$ energy difference of the atom. This is precisely the same condition that absorption has to satisfy. More interesting, the emitted photon is *identical* to the incident photon. This means that as the two photons leave the atom they have exactly the same frequency and wavelength, are traveling in exactly the same direction, and are exactly in phase with each other. In other words, **stimulated emission produces a second photon that is an exact clone of the first**.

Stimulated emission is of no importance in most practical situations. Atoms typically spend only a few nanoseconds in an excited state before undergoing spontaneous emission, so the atom would need to be in an extremely intense light wave for stimulated emission to occur prior to spontaneous emission. Ordinary light sources are not nearly intense enough for stimulated emission to be more than a minor effect; hence it was many years before Einstein's prediction was confirmed. No one had doubted Einstein, because he had clearly demonstrated that stimulated emission was necessary to make the energy equations balance, but it seemed no more important than would pennies to a millionaire balancing her checkbook. At least, that is, until 1960, when a revolutionary invention made explicit use of stimulated emission: the laser.

Lasers

The word **laser** is an acronym for the phrase light amplification by the stimulated emission of radiation. The first laser, a ruby laser, was demonstrated in 1960, and several other kinds of lasers appeared within a few months. Today, lasers do everything from being the light source in fiber-optic communications to measuring the distance to the moon, and from playing your CD to performing delicate eye surgery.

But what is a laser? Basically it is a device that produces a beam of highly *coherent* and essentially monochromatic (single-color) light as a result of stimulated emission. **Coherent** light is light in which all the electromagnetic waves have the same phase, direction, and amplitude. It is the coherence of a laser beam that allows it to be very tightly focused or to be rapidly modulated for communications.



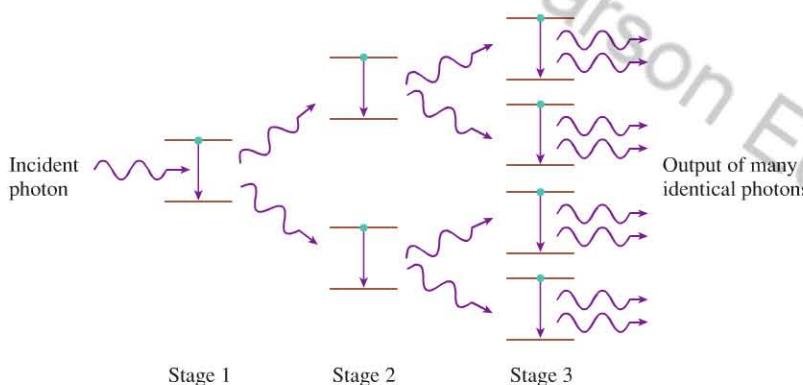
A spectacular laser light show depends on three key properties of coherent laser light: It can be very intense, its color is extremely pure, and the laser beam is narrow with little divergence.

Let's take a brief look at how a laser works. FIGURE 29.35 represents a system of atoms that have a lower energy level E_1 and a higher energy level E_2 . Suppose that there are N_1 atoms in level 1 and N_2 atoms in level 2. Left to themselves, all the atoms would soon end up in level 1 because of the spontaneous emission $2 \rightarrow 1$. To prevent this, we can imagine that some type of excitation mechanism, perhaps an electrical discharge, continuously produces new excited atoms in level 2.

Let a photon of frequency $f = (E_2 - E_1)/h$ be incident on this group of atoms. Because it has the correct frequency, it could be absorbed by one of the atoms in level 1. Another possibility is that it could cause stimulated emission from one of the level 2 atoms. Ordinarily $N_2 \ll N_1$, so absorption events far outnumber stimulated emission events. Even if a few photons were generated by stimulated emission, they would quickly be absorbed by the vastly larger group of atoms in level 1.

But what if we could somehow arrange to place *every* atom in level 2, making $N_1 = 0$? Then the incident photon, upon encountering its first atom, will cause stimulated emission. Where there was initially one photon of frequency f , now there are two. These will strike two additional excited-state atoms, again causing stimulated emission. Then there will be four photons. As FIGURE 29.36 shows, there will be a *chain reaction* of stimulated emission until all N_2 atoms emit a photon of frequency f .

FIGURE 29.36 Stimulated emission creates a chain reaction of photon production in a population of excited atoms.



In stimulated emission, each emitted photon is *identical* to the incident photon. The chain reaction of Figure 29.36 will lead not just to N_2 photons of frequency f , but to N_2 *identical* photons, all traveling together in the same direction with the same phase. If N_2 is a large number, as would be the case in any practical device, the one initial photon will have been *amplified* into a gigantic, coherent pulse of light!

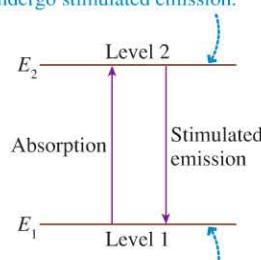
Although the chain reaction of Figure 29.36 illustrates the idea most clearly, it is not necessary for every atom to be in level 2 for amplification to occur. All that is needed is to have $N_2 > N_1$ so that stimulated emission exceeds absorption. Such a situation is called a **population inversion**. The stimulated emission is sustained by placing the *lasing medium*—the sample of atoms that emits the light—in an **optical cavity** consisting of two facing mirrors. As FIGURE 29.37 shows, the photons interact repeatedly with the atoms in the medium as they bounce back and forth. This repeated interaction is necessary for the light intensity to build up to a high level. If one of the mirrors is partially transmitting, some of the light emerges as the *laser beam*.

Lasers in Medicine

The invention of lasers was followed almost immediately by medical applications. Even a small-power laser beam can produce a significant amount of very localized *heating* if focused with a lens. More powerful lasers can easily *cut* through tissue by literally vaporizing it, replacing a stainless steel scalpel with a beam of light. Not only can laser surgery be very precise but it generally has less blood loss than conventional surgery because the heat of the laser seals the blood vessels and capillaries.

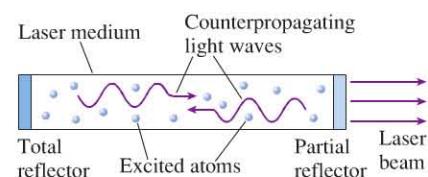
FIGURE 29.35 Energy levels 1 and 2, with populations N_1 and N_2 .

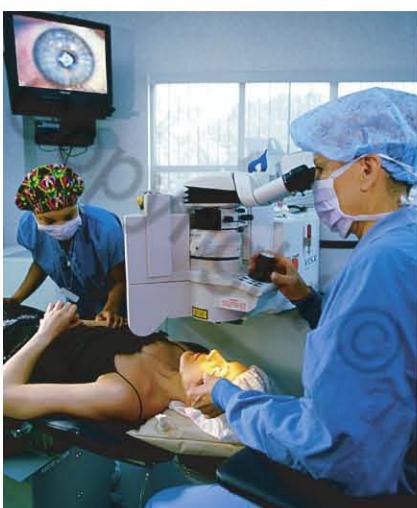
N_2 atoms in level 2. Photons of energy $E_{\text{photon}} = E_2 - E_1$ can cause these atoms to undergo stimulated emission.



N_1 atoms in level 1. These atoms can absorb photons of energy $E_{\text{photon}} = E_2 - E_1$.

FIGURE 29.37 Lasing takes place in an optical cavity.





One common medical use of lasers is to remove plaque from artery walls, thus reducing the risk of stroke or heart attack. In this procedure, an optical fiber is threaded through arteries to reach the site. A powerful laser beam is then fired through the fiber to carefully vaporize the plaque. Laser beams traveling through optical fibers are also used to kill cancer cells in *photodynamic therapy*. In this case, light-sensitive chemicals are injected into the bloodstream and are preferentially taken up by cancer cells. The optical fiber is positioned next to the tumor and illuminates it with just the right wavelength to activate the light-sensitive chemicals and kill the cells. These procedures are minimally invasive, and they can reach areas of the body not readily accessible by conventional surgery.

◀ Laser vision **BIO** Laser-based LASIK surgery can correct for vision defects, such as near- or farsightedness, that result from an incorrect refractive power of the eye. You learned in Chapter 19 that the majority of your eye's focusing power occurs at the surface of the cornea. In LASIK, a special knife first cuts a small, thin flap in the cornea, and this flap is folded out of the way. A computer-controlled ultraviolet laser very carefully vaporizes the underlying corneal tissue to give it the desired shape; then the flap is folded back into place. The procedure takes only a few minutes and requires only a few numbing drops in the eye.

INTEGRATED EXAMPLE 29.10

You learned in Chapters 22 and 25 how an ordinary incandescent bulb works: Current passes through a filament, heating it until it glows white hot. But such bulbs are very inefficient, giving off only a few watts of visible light for every 100 W of electric power supplied to the bulb. Most of the power is, instead, converted into thermal energy.

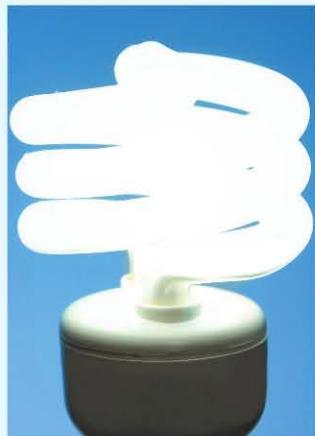
For many years, offices and commercial buildings have used a very different type of lighting, the *fluorescent lamp*.

Recently, compact fluorescent bulbs that can screw into ordinary lamp sockets have begun to make significant inroads into residential use. These bulbs are about four times more efficient than incandescent bulbs at transforming electric energy to visible light.

Inside the glass tube of a fluorescent bulb is a very small amount of mercury, which is in the form of a vapor when the bulb is on. Producing visible light occurs by a three-step process. First, a voltage of about 100 V is applied between electrodes at each end of the tube. This imparts kinetic energy to free electrons in the vapor, causing them to slam into mercury atoms and excite them by collisional excitation. Second, the excited atoms then jump to lower-energy states, emitting UV photons. Finally, the UV photons strike a *phosphor* that coats the inside of the tube, causing it to fluoresce with visible light. This is the light you see.

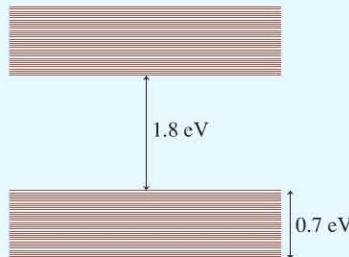
- A mercury atom, after being collisionally excited by an electron, emits a photon with a wavelength of 185 nm in a quantum jump back to the ground state. If the electron starts from rest, what minimum distance must it travel to gain enough kinetic energy to cause this excitation? The 60-cm-long tube has 120 V applied between its ends.

Compact fluorescent lighting



- After being collisionally excited, atoms sometimes emit two photons by jumping first from a high energy level to an intermediate level, giving off one photon, and then from this intermediate level to the ground state, giving off a second photon. An atom is excited to a state that is 7.79 eV above the ground state. It emits a 254-nm-wavelength photon and then a second photon. What is the wavelength of the second photon?
- The energy-level diagram of the molecules in the phosphor is shown in FIGURE 29.38. After excitation by UV photons, what range of wavelengths can the phosphor emit by fluorescence?

FIGURE 29.38 Energy-level diagram of the phosphor molecules.



PREPARE An electron collisionally excites the mercury atom from its ground state to an excited state, increasing the atom's energy by ΔE_{atom} . Then the atom decays back to the ground state, giving off a 185-nm-wavelength photon. In order for collisional excitation to work, the kinetic energy of the incident electron must equal or exceed ΔE_{atom} ; that is, it must equal or exceed the energy of a 185-nm-wavelength photon. The free electrons gain kinetic energy by accelerating through the potential difference inside the tube. We can use conservation of energy to find the distance an electron must travel to gain ΔE_{atom} , the minimum kinetic energy needed to cause an excitation.

In part b, the excited energy of the atom, 7.79 eV, is converted into photon energies. If we can find the energy of the first

254-nm-wavelength photon, the remaining energy must be that of the second photon, from which we can find its wavelength.

An inspection of Figure 29.32 shows that quantum jumps during fluorescence all begin at the bottom of the band of excited states and can end anywhere in the lower energy band. This range of energies will give us the range of wavelengths of the emitted photons.

SOLVE a. The minimum kinetic energy of the electron equals the energy of the 185-nm-wavelength photon that is subsequently emitted. This energy is

$$K_{\min} = \Delta E_{\min} = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{185 \text{ nm}} = 6.7 \text{ eV}$$

where we have used the value of hc from Equation 29.23.

Recall that 1 eV is the kinetic energy gained by an electron as it accelerates through a 1 V potential difference. Here, the electron must gain a kinetic energy of 6.7 eV, so it must accelerate through a potential difference of 6.7 V. The fluorescent tube has a total potential drop of 120 V in 60 cm, or 2.0 V/cm. Thus to accelerate through a 6.7 V potential difference, the electron must travel a distance

$$\Delta x = \frac{6.7 \text{ V}}{2.0 \text{ V/cm}} = 3.4 \text{ cm}$$

b. The first emitted photon has energy

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{254 \text{ nm}} = 4.88 \text{ eV}$$

The energy remaining to the second photon is then $7.79 \text{ eV} - 4.88 \text{ eV} = 2.91 \text{ eV}$; the wavelength of this photon is

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{2.91 \text{ eV}} = 426 \text{ nm}$$

c. The energy of the photon emitted during a quantum jump from the bottom of the upper energy band to the top of the lower energy band is 1.8 eV, corresponding to a wavelength of

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{1.8 \text{ eV}} = 690 \text{ nm}$$

The photon energy for a jump to the bottom of the lower energy band is $1.8 \text{ eV} + 0.7 \text{ eV} = 2.5 \text{ eV}$, with a wavelength of

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{2.5 \text{ eV}} = 500 \text{ nm}$$

Thus this phosphor, after absorbing UV photons, emits visible light with a wavelength range of 500–690 nm.

ASSESS For part a, it seems reasonable that the electron travels only a small fraction of the tube length before gaining enough energy to collisionally excite an atom. The bulb would be very inefficient if electrons had to travel the full length before colliding with a mercury atom. The photon wavelengths in parts b and c also seem reasonable. In particular, the range of wavelengths emitted by the phosphor is a little more than half the visible spectrum, from green through red but missing blue and violet. Compact fluorescent tubes have three different phosphors, each with a somewhat different range of emission wavelengths, to give the full spectrum of white light. Slightly altering the balance between these phosphors distinguishes a “warm white” bulb from a “cool white” bulb.

SUMMARY

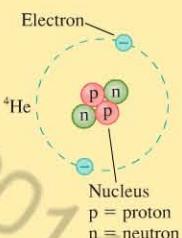
The goal of Chapter 29 has been to use quantum physics to understand the properties of atoms, molecules, and their spectra.

IMPORTANT CONCEPTS

The Structure of an Atom

An atom consists of a very small, positively charged nucleus, surrounded by orbiting electrons.

- The number of protons is the atom's **atomic number** Z .
- The **atomic mass number** A is the number of protons + the number of neutrons.



The Hydrogen Atom

In **Bohr's model of the hydrogen atom** the stationary states are found by requiring an integer number of de Broglie wavelengths to fit around the circumference of the electron's orbit: $2\pi r = n\lambda$. The integer n is the **principal quantum number**.

This leads to energy quantization with

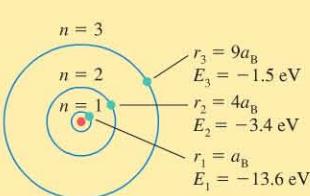
$$E_n = -\frac{13.60 \text{ eV}}{n^2}$$

and orbit radii $r_n = n^2 a_B$, where $a_B = 0.053 \text{ nm}$ is the **Bohr radius**.

The wavelengths of light in the hydrogen atom spectrum are given by the **Balmer formula**:

$$\lambda_{n \rightarrow m} = \frac{91.1 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} \quad m = 1, 2, 3, \dots$$

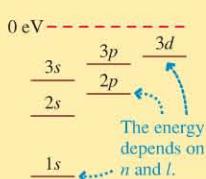
$$n = m + 1, m + 2, \dots$$



Multielectron atoms

Each electron is described by the same quantum numbers (n, l, m, m_s) used for the hydrogen atom, but the energy now depends on l as well as n .

The **Pauli exclusion principle** states that no more than one electron can occupy each quantum state.



APPLICATIONS

Atomic emission spectra are generated by excitation followed by a photon-emitting quantum jump.

- Excitation** occurs by absorption of a photon or by collision.
- A quantum jump can occur only if $\Delta l = \pm 1$.
- Quantized energies give rise to a discrete spectrum.



The Bohr Atom

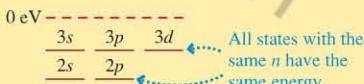
In Bohr's model,

- The atom can exist in only certain **stationary states**. These states correspond to different electron orbits. Each state is numbered by **quantum number** $n = 1, 2, 3, \dots$
- Each state has a discrete, well-defined energy E_n .
- The atom can change its energy by undergoing a **quantum jump** between two states by emitting or absorbing a photon of energy $E_{\text{photon}} = \Delta E_{\text{atom}} = |E_f - E_i|$.

Beyond the Bohr model, quantum mechanics adds several quantized parameters, each with its own quantum number:

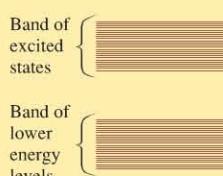
- The **orbital angular momentum**, quantum number l :
$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, 3, \dots, n-1$$
- The **angle of the electrons orbit**, quantum number m :
$$m = -l, -l+1, \dots, 0, \dots, l-1, l$$
- The **direction of the electron spin**, quantum number m_s :
$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

The energy of a hydrogen atom depends only on n :



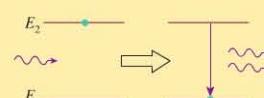
Molecules

In molecules, the states are spaced very closely into **bands** of states. Because electrons can be excited to and from many states, the spectra of molecules are broad, not discrete.



Lasers

A photon with energy $E_{\text{photon}} = E_2 - E_1$ can induce **stimulated emission** of a second photon identical to the first. These photons can then induce more atoms to emit photons. If more atoms are in state 2 than in state 1, this process can rapidly build up an intense beam of identical photons. This is the principle behind the laser.





For homework assigned on MasteringPhysics, go to
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Problems labeled INT integrate significant material from earlier chapters; BIO are of biological or medical interest.

Problem difficulty is labeled as I (straightforward) to III (challenging).

QUESTIONS

Conceptual Questions

- A neon discharge emits a bright reddish-orange spectrum. But a glass tube filled with neon is completely transparent. Why doesn't the neon in the tube absorb orange and red wavelengths?
- The two spectra shown in Figure Q29.2 belong to the same element, a fictional Element X. Explain why they are different.

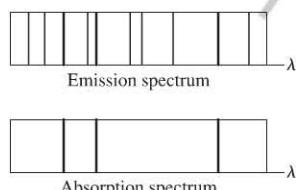


FIGURE Q29.2

- Is a spectral line with wavelength 656.5 nm seen in the absorption spectrum of hydrogen atoms? Why or why not?
- J. J. Thomson studied the ionization of atoms in collisions with electrons. He accelerated electrons through a potential difference, shot them into a gas of atoms, then used a mass spectrometer to detect any ions produced in the collisions. By using different gases, he found that he could produce singly ionized atoms of all the elements that he tried. When he used higher accelerating voltages, he was able to produce doubly ionized atoms of all elements *except* hydrogen.
 - Why did Thomson have to use higher accelerating voltages to detect doubly ionized atoms than to detect singly ionized atoms?
 - What conclusion or conclusions about hydrogen atoms can you draw from these observations? Be specific as to how your conclusions are related to the observations.
- Bohr did not include the gravitational force in his analysis of the hydrogen atom. Is this one of the reasons that his model of the hydrogen atom had only limited success? Explain.
- If an electron is in a *stationary state* of an atom, is the electron at rest? If not, what does the term mean?
- The $n = 3$ state of hydrogen has $E_3 = -1.51 \text{ eV}$.
 - Why is the energy negative?
 - What is the physical significance of the specific number 1.51 eV ?
- For a hydrogen atom, list all possible states (n, l, m, m_s) that have $E = -1.51 \text{ eV}$.
- What are the n and l values of the following states of a hydrogen atom: (a) $4d$, (b) $5f$, (c) $6s$?
- How would you label the hydrogen-atom states with the following (n, l, m) quantum numbers: (a) $(4, 3, 0)$, (b) $(3, 2, 1)$, (c) $(3, 2, -1)$?
- Consider the two hydrogen-atom states $5d$ and $4f$. Which has the higher energy? Explain.

- Does each diagram in Figure Q29.12 represent a possible electron configuration of a neutral element? If so, (i) identify the element and (ii) determine if this is the ground state or an excited state. If not, why not?

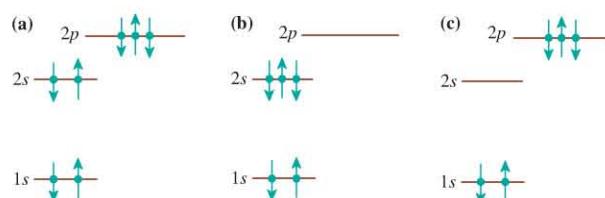


FIGURE Q29.12

- Do the following electron configurations represent a possible state of an element? If so, (i) identify the element and (ii) determine if this is the ground state or an excited state. If not, why not?
 - $1s^2 2s^2 2p^6 3s^2$
 - $1s^2 2s^2 2p^7 3s$
 - $1s^2 2s^2 2p^4 3s^2 3p^2$
- Why is the section of the periodic table labeled as "transition elements" exactly 10 elements wide in all rows?
- An electron is in an f state. Can it undergo a quantum jump to an s state? A p state? A d state? Explain.
- Figure Q29.16 shows the energy-level diagram of Element X.

$E \text{ (eV)}$

$n = 3$
 $n = 2$
 $n = 1$

 - What is the ionization energy of Element X?
 - An atom in the ground state absorbs a photon, then emits a photon with a wavelength of 1240 nm. What conclusion can you draw about the energy of the photon that was absorbed?
 - An atom in the ground state has a collision with an electron, then emits a photon with a wavelength of 1240 nm. What conclusion can you draw about the initial kinetic energy of the electron?
- Which states of a hydrogen atom can be excited by a collision with an electron with kinetic energy $K = 12.5 \text{ eV}$? Explain.
- After the collision the atom is not in its ground state. What happens to the electron? (i) It bounces off with $K > 12.5 \text{ eV}$, (ii) It bounces off with $K = 12.5 \text{ eV}$, (iii) It bounces off with $K < 12.5 \text{ eV}$, (iv) It is absorbed by the atom. Explain your choice.
- After the collision, the atom emits a photon. List all the possible $n \rightarrow m$ transitions that might occur as a result of this collision.
- What is an atom's ionization energy? In other words, if you know the ionization energy of an atom, what is it that you know about the atom?

FIGURE Q29.16

19. Figure Q29.19 shows the energy levels of a hypothetical atom.

- What *minimum* kinetic energy (in eV) must an electron have to collisionally excite this atom and cause the emission of a 620 nm photon? Explain.
- Can an electron with $K = 6$ eV cause the emission of 620 nm light? If so, what is the final kinetic energy of the electron? If not, why not?
- Can a 6 eV photon cause the emission of 620 nm light from this atom? Why or why not?
- Can a 7 eV photon cause the emission of 620 nm light from this atom? Why or why not?

20. Seven possible transitions are identified on the energy-level diagram in Figure Q29.20. For each, is this an allowed transition? If allowed, is it an emission or an absorption transition, and is the photon infrared, visible, or ultraviolet? If not allowed, why not?

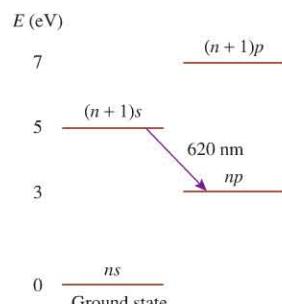


FIGURE Q29.19

22. A glass tube contains 2×10^{11} atoms, some of which are in the ground state and some of which are excited. Figure Q29.22 shows the populations for the atoms' three energy levels. Is it possible for these atoms to be a laser? If so, on which transition would laser action occur? If not, why not?

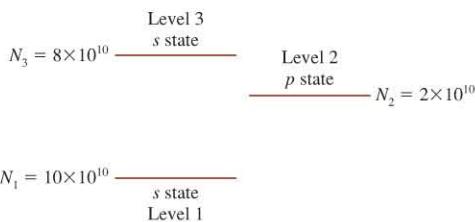


FIGURE Q29.22

Multiple-Choice Questions

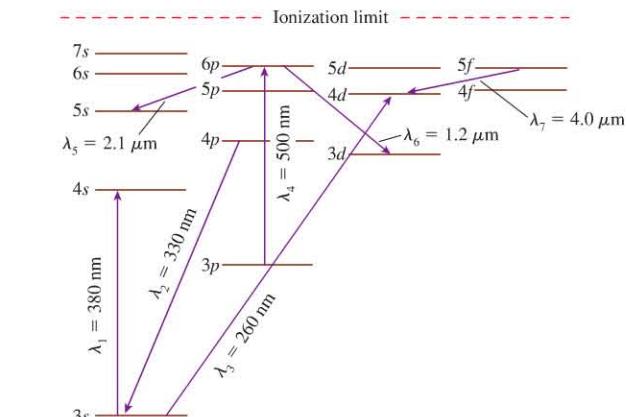


FIGURE Q29.20

21. A 2.0 eV photon is incident on an atom in the p state, as shown in the energy-level diagram in Figure Q29.21. Does the atom undergo an absorption transition, a stimulated emission transition, or neither? Explain.

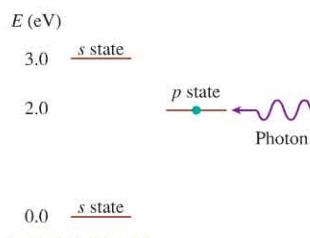


FIGURE Q29.21

23. I An electron collides with an atom in its ground state. The atom then emits a photon of energy E_{photon} . In this process the change ΔE_{elec} in the electron's energy is
- Greater than E_{photon} .
 - Greater than or equal to E_{photon} .
 - Equal to E_{photon} .
 - Less than or equal to E_{photon} .
 - Less than E_{photon} .
24. II How many states are in the $l = 4$ subshell?
- 8
 - 9
 - 16
 - 18
 - 22
25. I What is the ground-state electron configuration of calcium ($Z = 20$)?
- $1s^2 2s^2 2p^6 3s^2 3p^8$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 4p^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4p^2$
26. I An atom emits a photon with a wavelength of 275 nm. By how much does the atom's energy change?
- 0.72 eV
 - 1.06 eV
 - 2.29 eV
 - 3.06 eV
 - 4.51 eV
27. II The energy of a hydrogen atom is -3.40 eV. What is the electron's kinetic energy?
- 1.70 eV
 - 2.62 eV
 - 3.40 eV
 - 5.73 eV
 - 6.80 eV
28. I The angular momentum of an electron in a Bohr hydrogen atom is 3.18×10^{-34} kg · m²/s. What is the atom's energy?
- 13.60 eV
 - 6.73 eV
 - 3.40 eV
 - 1.51 eV
 - 0.47 eV
29. I A "soft x-ray" photon with an energy of 41.8 eV is absorbed by a hydrogen atom in its ground state, knocking the atom's electron out. What is the speed of the electron as it leaves the atom?
- 1.84×10^5 m/s
 - 3.08×10^5 m/s
 - 8.16×10^5 m/s
 - 3.15×10^6 m/s
 - 3.83×10^6 m/s

VIEW ALL SOLUTIONS

PROBLEMS

Section 29.1 Spectroscopy

1. I Figure 29.2b and Table 29.1 showed the wavelengths of the first four lines in the visible spectrum of hydrogen.
- Determine the Balmer formula n and m values for these wavelengths.
 - Predict the wavelength of the fifth line in the spectrum.

2. I The wavelengths in the hydrogen spectrum with $m = 1$ form a series of spectral lines called the Lyman series. Calculate the wavelengths of the first four members of the series.
3. I The Paschen series is analogous to the Balmer series, but with $m = 3$. Calculate the wavelengths of the first three members in the Paschen series. What part(s) of the electromagnetic spectrum are these in?

VIEW ALL SOLUTIONS

Section 29.2 Atoms

4. | How many electrons, protons, and neutrons are contained in the following atoms or ions: (a) ${}^6\text{Li}$, (b) ${}^{13}\text{C}^+$, and (c) ${}^{18}\text{O}^{++}$?
5. | How many electrons, protons, and neutrons are contained in the following atoms or ions: (a) ${}^9\text{Be}^+$, (b) ${}^{12}\text{C}$, and (c) ${}^{15}\text{N}^{++}$?
6. | Write the symbol for an atom or ion with:
 - a. four electrons, four protons, and five neutrons.
 - b. six electrons, seven protons, and eight neutrons.
7. | Write the symbol for an atom or ion with:
 - a. three electrons, three protons, and five neutrons.
 - b. five electrons, six protons, and eight neutrons.

Section 29.3 Bohr's Model of Atomic Quantization

8. | Figure P29.8 is an energy-level diagram for a simple atom. What wavelengths appear in the atom's (a) emission spectrum and (b) absorption spectrum?

FIGURE P29.8
9. | An electron with 2.0 eV of kinetic energy collides with the atom whose energy-level diagram is shown in Figure P29.8.
 - a. Is the electron able to kick the atom to an excited state? Why or why not?
 - b. If your answer to part a was yes, what is the electron's kinetic energy after the collision?
10. | The allowed energies of a simple atom are 0.0 eV, 4.0 eV, and 6.0 eV.
 - a. Draw the atom's energy-level diagram. Label each level with the energy and the principal quantum number.
 - b. What wavelengths appear in the atom's emission spectrum?
 - c. What wavelengths appear in the atom's absorption spectrum?
11. || The allowed energies of a simple atom are 0.0 eV, 4.0 eV, and 6.0 eV. An electron traveling at a speed of 1.6×10^6 m/s collisionally excites the atom. What are the minimum and maximum speeds the electron could have after the collision?

Section 29.4 The Bohr Hydrogen Atom

12. || A researcher observes hydrogen emitting photons of energy 1.89 eV. What are the quantum numbers of the two states involved in the transition that emits these photons?
13. | A hydrogen atom is in the $n = 3$ state. In the Bohr model, how many electron wavelengths fit around this orbit?
14. || A hydrogen atom is in its $n = 1$ state. In the Bohr model, what is the ratio of its kinetic energy to its potential energy?
15. | Show, by actual calculation, that the Bohr radius is 0.0529 nm and that the ground-state energy of hydrogen is -13.60 eV.
16. | a. What quantum number of the hydrogen atom comes closest to giving a 500-nm-diameter electron orbit?
b. What are the electron's speed and energy in this state?
17. | a. Calculate the de Broglie wavelength of the electron in the $n = 1, 2$, and 3 states of the hydrogen atom. Use the information in Table 29.2.
b. Show numerically that the circumference of the orbit for each of these stationary states is exactly equal to n de Broglie wavelengths.
c. Sketch the de Broglie standing wave for the $n = 3$ orbit.
18. | Show, by calculation, that the first three states of the hydrogen atom have angular momenta $\hbar, 2\hbar$, and $3\hbar$, respectively.

19. | Determine all possible wavelengths of photons that can be emitted from the $n = 4$ state of a hydrogen atom.

Section 29.5 The Quantum-Mechanical Hydrogen Atom

20. | List the quantum numbers of (a) all possible $3p$ states and (b) all possible $3d$ states.
21. || When all quantum numbers are considered, how many different quantum states are there for a hydrogen atom with $n = 1$? With $n = 2$? With $n = 3$? List the quantum numbers of each state.
22. | What is the angular momentum of a hydrogen atom in (a) a $4p$ state and (b) a $5f$ state? Give your answers as a multiple of \hbar .
23. | A hydrogen atom has orbital angular momentum 3.65×10^{-34} J · s.
 - a. What letter (s, p, d , or f) describes the electron?
 - b. What is the atom's minimum possible energy? Explain.
24. || A hydrogen atom is in the $5p$ state. Determine (a) its energy, (b) its angular momentum, (c) its quantum number l , and (d) the possible values of its magnetic quantum number m .
25. || The angular momentum of a hydrogen atom is 4.70×10^{-34} J · s. What is the minimum energy, in eV, that this atom could have?

Section 29.6 Multielectron Atoms

26. | Predict the ground-state electron configurations of Mg, Sr, and Ba.
27. || Predict the ground-state electron configurations of Si, Ge, and Pb.
28. | Identify the element for each of these electron configurations. Then determine whether this configuration is the ground state or an excited state.
 - a. $1s^2 2s^2 2p^5$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p$
29. || a. With what element is the $3s$ subshell first completely filled?
b. With what element is the $4d$ subshell first half-filled?
30. | Identify the element for each of these electron configurations. Then determine whether this configuration is the ground state or an excited state.
 - a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^7$
31. | Explain what is wrong with these electron configurations:
 - a. $1s^2 2s^2 2p^8 3s^2 3p^4$
 - b. $1s^2 2s^3 2p^4$
32. || Which has higher energy: an electron in the $4f$ state or an electron in the $7s$ state? Explain.

Section 29.7 Excited States and Spectra

33. | An electron with a speed of 5.00×10^6 m/s collides with an atom. The collision excites the atom from its ground state (0 eV) to a state with an energy of 3.80 eV. What is the speed of the electron after the collision?
34. | Hydrogen gas absorbs light of wavelength 103 nm. Afterward, what wavelengths are seen in the emission spectrum?
35. || What is the minimum wavelength of light that can excite the $4s$ state of sodium?
36. || An electron with a kinetic energy of 3.90 eV collides with a sodium atom. What possible wavelengths of light are subsequently emitted?

37. I a. Is a $4p \rightarrow 4s$ transition allowed in sodium? If so, what is its wavelength? If not, why not?
 b. Is a $3d \rightarrow 4s$ transition allowed in sodium? If so, what is its wavelength? If not, why not?

Section 29.8 Molecules

38. II Figure P29.38 shows a molecular energy-level diagram. What are the longest and shortest wavelengths in (a) the molecule's absorption spectrum and (b) the molecule's fluorescence spectrum?

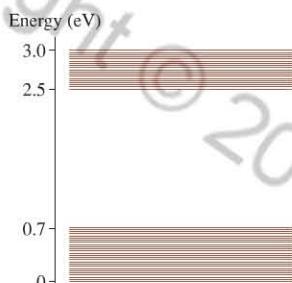


FIGURE P29.38

39. I The molecule whose energy-level diagram is shown in Figure P29.38 is illuminated by 2.7 eV photons. What is the longest wavelength of light that the molecule can emit?

Section 29.9 Stimulated Emission and Lasers

40. I A 1000 W carbon dioxide laser emits an infrared laser beam with a wavelength of $10.6 \mu\text{m}$. How many photons are emitted per second?
 41. II A 1.00 mW helium neon-laser emits a visible laser beam with a wavelength of 633 nm. How many photons are emitted per second?
 42. II In LASIK surgery, a laser is used to reshape the cornea of the eye to improve vision. The laser produces extremely short pulses of light, each containing 1.0 mJ of energy.
 a. In each pulse there are 9.7×10^{14} photons. What is the wavelength of the laser?
 b. Each pulse lasts only 20 ns. What is the average power delivered to the eye during a pulse?
 43. II A ruby laser emits an intense pulse of light that lasts a mere 10 ns. The light has a wavelength of 690 nm, and each pulse has an energy of 500 mJ.
 a. How many photons are emitted in each pulse?
 b. What is the rate of photon emission, in photons per second, during the 10 ns that the laser is "on"?

General Problems

44. III A 2.55 eV photon is emitted from a hydrogen atom. What are the Balmer formula n and m values corresponding to this emission?
 45. I Two of the wavelengths emitted by a hydrogen atom are 102.6 nm and 1876 nm.
 a. What are the Balmer formula n and m values for each of these wavelengths?
 b. For each of these wavelengths, is the light infrared, visible, or ultraviolet?

46. III In Example 29.2 it was assumed that the initially stationary gold nucleus would remain motionless during a head-on collision with an 8.3 MeV alpha particle. What is the actual recoil speed of the gold nucleus after that elastic collision? Assume that the mass of a gold nucleus is exactly 50 times the mass of an alpha particle.

Hint: Review the discussion of perfectly elastic collisions in Chapter 10.

47. I Consider the gold isotope ^{197}Au .
 a. How many electrons, protons, and neutrons are in a neutral ^{197}Au atom?
 b. The gold nucleus has a diameter of 14.0 fm. What is the density of matter in a gold nucleus?
 c. The density of lead is $11,400 \text{ kg/m}^3$. How many times the density of lead is your answer to part b?
 48. II Consider the lead isotope ^{207}Pb .
 a. How many electrons, protons, and neutrons are in a neutral ^{207}Pb atom?
 b. The lead nucleus has a diameter of 14.2 fm. What are the electric potential and the electric field strength at the surface of a lead nucleus?

49. III The diameter of an atom is $1.2 \times 10^{-10} \text{ m}$ and the diameter of its nucleus is $1.0 \times 10^{-14} \text{ m}$. What percent of the atom's volume is occupied by mass and what percent is empty space?

50. I The charge-to-mass ratio of a nucleus, in units of e/u , is $q/m = Z/A$. For example, a hydrogen nucleus has $q/m = 1/1 = 1$.
 a. Make a graph of charge-to-mass ratio versus proton number Z for nuclei with $Z = 5, 10, 15, 20, \dots, 90$. For A , use the average atomic mass shown on the periodic table of elements in Appendix B. Show each of these 18 nuclei as a dot, but don't connect the dots together as a curve.
 b. Describe any trend that you notice in your graph.
 c. What's happening in the nuclei that is responsible for this trend?

51. I If the nucleus is a few fm in diameter, the distance between the centers of two protons must be $\approx 2 \text{ fm}$.
 a. Calculate the repulsive electric force between two protons that are 2.0 fm apart.
 b. Calculate the attractive gravitational force between two protons that are 2.0 fm apart. Could gravity be the force that holds the nucleus together?

52. I In a head-on collision, the closest approach of a 6.24 MeV alpha particle to the center of a nucleus is 6.00 fm. The nucleus is in an atom of what element? Assume that the nucleus is heavy enough to remain stationary during the collision.

53. III An 20 MeV alpha particle is fired toward a ^{238}U nucleus. It follows the path shown in Figure P29.53. What is the alpha particle's speed when it is closest to the nucleus, 20 fm from its center? Assume that the nucleus doesn't move.

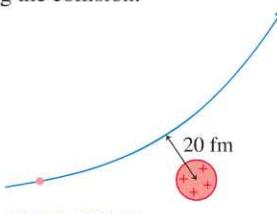


FIGURE P29.53

54. II The oxygen nucleus ^{16}O has a radius of 3.0 fm.
 a. With what speed must a proton be fired toward an oxygen nucleus to have a turning point 1.0 fm from the surface? Assume that the nucleus is heavy enough to remain stationary during the collision.
 b. What is the proton's kinetic energy in MeV?

55. || The absorption spectrum of an atom consists of the wavelengths 200 nm, 300 nm, and 500 nm.

- Draw the atom's energy-level diagram.
- What wavelengths are seen in the atom's emission spectrum?

56. || The first three energy levels of the fictitious element X are shown in Figure P29.56.

- What wavelengths are observed in the absorption spectrum of element X?

Give your answers in nm.

- State whether each of your wavelengths in part a corresponds to ultraviolet, visible, or infrared light.

- An electron with a speed of 1.4×10^6 m/s collides with an atom of element X. Shortly afterward, the atom emits a 1240 nm photon. What was the electron's speed after the collision? Assume that, because the atom is so much more massive than the electron, the recoil of the atom is negligible.

Hint: The energy of the photon is *not* the energy transferred to the atom in the collision.

57. || A simple atom has four lines in its absorption spectrum. Ignoring any selection rules, how many lines will it have in its emission spectrum?

58. || A simple atom has only two absorption lines, at 250 nm and 600 nm. What is the wavelength of the one line in the emission spectrum that does not appear in the absorption spectrum?

59. | What is the wavelength of the series limit (i.e., the shortest possible wavelength) of the Lyman series in hydrogen?

60. || What is the energy of a Bohr hydrogen atom with a 5.18 nm diameter?

61. | A hydrogen atom in the ground state absorbs a 12.75 eV photon. Immediately after the absorption, the atom undergoes a quantum jump to the next-lowest energy level. What is the wavelength of the photon emitted in this quantum jump?

62. | **INT** a. Calculate the orbital radius and the speed of an electron in both the $n = 99$ and the $n = 100$ states of hydrogen.

- Determine the orbital frequency of the electron in each of these states.
- Calculate the frequency of a photon emitted in a $100 \rightarrow 99$ transition.
- Compare the photon frequency of part c to the *average* of your two orbital frequencies from part b. By what percent do they differ?

63. || Two hydrogen atoms collide head-on. The collision brings **INT** both atoms to a halt. Immediately after the collision, both atoms emit a 121.6 nm photon. What was the speed of each atom just before the collision?

64. || A beam of electrons is incident on a gas of hydrogen atoms.

- INT** a. What minimum speed must the electrons have to cause the emission of 656 nm light from the $3 \rightarrow 2$ transition of hydrogen?

- Through what potential difference must the electrons be accelerated to have this speed?

65. || A hydrogen atom in its fourth excited state emits a photon with a wavelength of 1282 nm. What is the atom's maximum possible orbital angular momentum after the emission? Give your answer as a multiple of \hbar .

66. || A particular emission line in the hydrogen spectrum has a wavelength of 656.5 nm. What are all possible transitions (e.g., $6d \rightarrow 2s$) that could give rise to this emission?

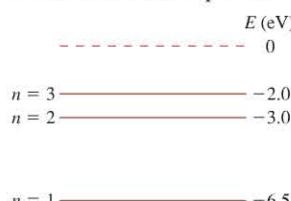


FIGURE P29.56

67. | a. What downward transitions are possible for a sodium atom in the $6s$ state? (See Figure 29.24.)

- What are the wavelengths of the photons emitted in each of these transitions?

68. || The $5d \rightarrow 3p$ transition in the emission spectrum of sodium (see Figure 29.24) has a wavelength of 499 nm. What is the energy of the $5d$ state?

69. || A sodium atom (see Figure 29.24) emits a photon with wavelength 818 nm shortly after being struck by an electron. What minimum speed did the electron have before the collision?

70. || Figure P29.70 shows a few energy levels of the mercury atom. One valence electron is always in the $6s$ state; the other electron changes states.

- Make a table showing all the allowed transitions in the emission spectrum. For each transition, indicate the photon wavelength, in nm.
- What minimum speed must an electron have to excite the 492-nm-wavelength blue emission line in the Hg spectrum?

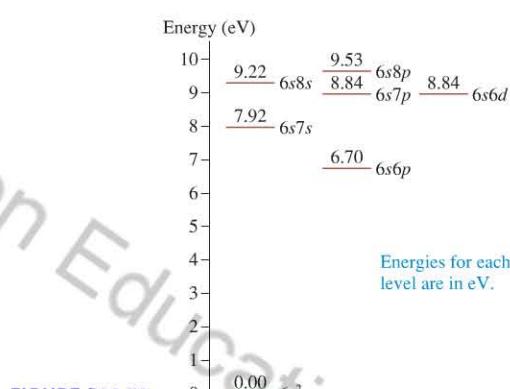


FIGURE P29.70

71. | Figure P29.71 shows the first few energy levels of the lithium atom. Make a table showing all the allowed transitions in the emission spectrum. For each transition, indicate

- The wavelength, in nm.
- Whether the transition is in the infrared, the visible, or the ultraviolet spectral region.

- c. Whether or not the transition would be observed in the lithium absorption spectrum.

72. | **INT** A laser emits 1.00×10^{19} photons per second from an excited state with energy $E_2 = 1.17$ eV. The lower energy level is $E_1 = 0$ eV.

- What is the wavelength of this laser?
- What is the power output of this laser?

73. | Fluorescence microscopy, discussed in Section 29.8, is an important tool in modern cell biology. A variation on this technique depends on a phenomenon known as two-photon excitation. If two photons are absorbed simultaneously (i.e., within about 10^{-16} s), their energies can add. A molecule that is normally excited by a 350 nm photon can be excited by two photons each having half as much energy. For this process to be useful, photons must illuminate the sample at the very high rate of at least 10^{29} photons/m² · s. This is achieved by focusing a

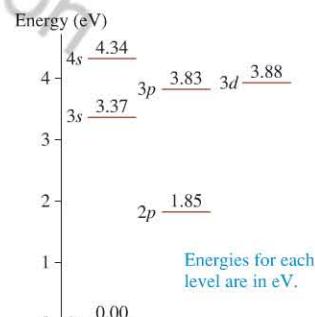


FIGURE P29.71

laser beam to a small spot and by concentrating the power of the laser into very short (10^{-13} s) pulses that are fired 10^8 times each second. Suppose a biologist wants to use two-photon excitation to excite a molecular species that would be excited by 500 nm light in normal one-photon fluorescence microscopy. What minimum intensity (W/m^2) must the laser beam have during each pulse?

Passage Problems

Light-Emitting Diodes

Light-emitting diodes, known by the acronym LED, produce the familiar green and red indicator lights used in a wide variety of consumer electronics. LEDs are semiconductor devices in which the electrons can exist only in certain energy levels. Much like molecules, the energy levels are packed together close enough to form what appears to be a continuous band of possible energies. Energy supplied to an LED in a circuit excites electrons from a *valence band* into a *conduction band*. An electron can emit a photon by undergoing a quantum jump from a state in the conduction band into an empty state in the valence band, as shown in Figure P29.74.

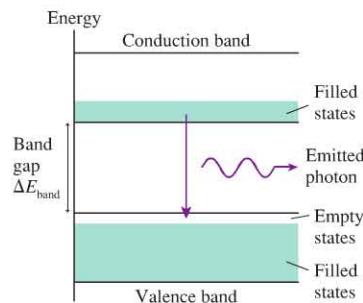


FIGURE P29.74 Energy-level diagram of an LED.

The size of the band gap ΔE_{band} determines the possible energies—and thus the wavelengths—of the emitted photons. Most LEDs emit a narrow range of wavelengths and thus have a distinct color. This makes them well-suited for traffic lights and other applications where a certain color is desired, but it makes them less desirable for general illumination. One way to make a “white” LED is to combine a blue LED with a substance that fluoresces yellow when illuminated with the blue light. The combination of the two colors makes light that appears reasonably white.

74. | An LED emits green light. Increasing the size of the band gap could change the color of the emitted light to
 - A. Red
 - B. Orange
 - C. Yellow
 - D. Blue
75. | Suppose the LED band gap is 2.5 eV, which corresponds to a wavelength of 500 nm. Consider the possible electron transitions in Figure P29.74. 500 nm is the
 - A. Maximum wavelength of the LED.
 - B. Average wavelength of the LED.
 - C. Minimum wavelength of the LED.
76. | The same kind of semiconducting material used to make an LED can also be used to convert absorbed light into electrical energy, essentially operating as an LED in reverse. In this case, the absorption of a photon causes an electron transition from a filled state in the valence band to an unfilled state in the conduction band. If $\Delta E_{\text{band}} = 1.4 \text{ eV}$, what is the minimum wavelength of electromagnetic radiation that could lead to electric energy output?
 - A. 140 nm
 - B. 890 nm
 - C. 1400 nm
 - D. 8900 nm
77. | The efficiency of a light source is the percentage of its energy input that gets radiated as visible light. If some of the blue light in an LED is used to cause a fluorescent material to glow,
 - A. The overall efficiency of the LED is increased.
 - B. The overall efficiency of the LED does not change.
 - C. The overall efficiency of the LED decreases.

STOP TO THINK ANSWERS

Stop to Think 29.1: A is emission, B is absorption. All wavelengths in the absorption spectrum are seen in the emission spectrum, but not all wavelengths in the emission spectrum are seen in the absorption spectrum.

Stop to Think 29.2: 6 protons and 8 neutrons. The number of protons is the atomic number, which is 6. That leaves $14 - 6 = 8$ neutrons.

Stop to Think 29.3: In emission from the $n = 3$ to $n = 2$ transition, but not in absorption. The photon energy has to match the energy difference between two energy levels. Absorption is from the ground state, at $E_1 = 0 \text{ eV}$. There's no energy level at 3 eV to which the atom could jump.

Stop to Think 29.4: $n = 3$. Each antinode is half a wavelength, so this standing wave has three full wavelengths in one circumference.

Stop to Think 29.5: $n = 3, l = 1$, or a $3p$ state.

Stop to Think 29.6: B. The atom would have less energy if the $3s$ electron were in a $2p$ state.

Stop to Think 29.7: C. Emission is a quantum jump to a lower-energy state. The $5p \rightarrow 4p$ transition is not allowed because $\Delta l = 0$ violates the selection rule. The lowest-energy allowed transition is $5p \rightarrow 3d$, with $E_{\text{photon}} = \Delta E_{\text{atom}} = 3.0 \text{ eV}$.