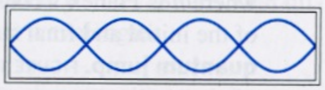
these ideas. An electron confined in a real atom will need to be a much more complex three-dimensional standing wave. But, just like the simple particle in a box, it will have quantized energies. Furthermore, we expect a typical energy difference between adjacent energy levels will be a few electron volts.

Now, this is an intriguing result. We found that visible and ultraviolet photons of light have energies of a few electron volts. We also know that atoms emit *discrete* wavelengths of visible and ultraviolet light, with photon energies of a few electron volts. Now we see that an electron confined in an atomic-size box has energy levels spaced a few electron volts apart. Might there be a connection between these phenomena? We will explore this topic in the next section.

STOP TO THINK 39.3 What is the quantum number of this particle confined in a box?



39.5 Bohr's Model of Atomic Quantization

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Thomson's electron and Rutherford's nucleus made it clear that the atom has a *structure* of some sort. The challenge at the beginning of the 20th century was to deduce, from experimental evidence, the correct structure. The difficulty of this task cannot be exaggerated. The evidence about atoms, such as observations of atomic spectra, was very indirect, and experiments were carried out with only the simplest measuring devices. Using observations as a guide, physicists were attempting to construct a *model* of the atom that could successfully explain the various experiments.

Rutherford's nuclear model was the most successful of various proposals, but Rutherford's model failed to explain why atoms are stable or why their spectra are discrete. 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 Niels Bohr. Bohr, shown as young man in **FIGURE 39.16**, was born, educated, and spent most of his life in Denmark. He later established an institute in Copenhagen that, for many decades, was the leading center for the development of quantum physics. Although few discoveries bear Bohr's name, he was the intellectual driving force behind the development of quantum mechanics and the mentor of many of the young physicists who reshaped physics in the 1920s and 1930s.

FIGURE 39.16 Niels Bohr.

After receiving his doctoral degree in physics in 1911, Bohr went to England to work in Rutherford's laboratory. Rutherford had just, within the previous year, completed his development of the nuclear model of the atom. Rutherford's model certainly contained a kernel of truth, but 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 for the structure of atoms. 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:

1. An atom consists of negative electrons orbiting a very small positive nucleus, as in the Rutherford model.
2. Atoms can exist only in certain **stationary states.** Each stationary state corresponds to a particular set of electron orbits around the nucleus. These states are distinct and can be numbered $n = 1, 2, 3, 4, \ldots$, where n is the *quantum number.*

3. Each stationary state has a discrete, well-defined energy E_n. That is, atomic energies are *quantized.* The stationary states of an atom are numbered in order of increasing energy: $E_1 < E_2 < E_3 < E_4 < \ldots$.
4. The lowest energy state of the atom, with energy E_1, is *stable* and can persist indefinitely. It is called the **ground state** of the atom. Other stationary states with energies $E_2, E_3, E_4, \ldots$ are called **excited states** of the atom.
5. An atom can "jump" from one stationary state to another by emitting or absorbing a photon of frequency

$$f_{\text{photon}} = \frac{\Delta E_{\text{atom}}}{h} \tag{39.17}$$

where h is Planck's constant and $\Delta E_{\text{atom}} = |E_f - E_i|$. E_i and E_f are the energies of the initial and final states. Such a jump is called a **transition** or, sometimes, a **quantum jump.** FIGURE 39.17a is a schematic view of the emission and absorption of photons in an atom with stationary states.

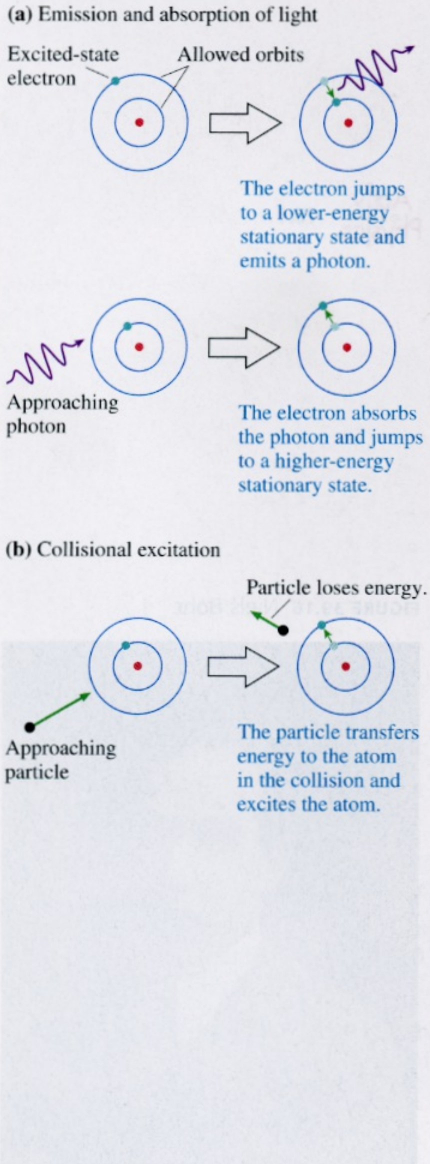


FIGURE 39.17 An atom can change stationary states by emitting or absorbing a photon or by undergoing a collision.

6. An atom can move from a lower energy state to a higher energy state by absorbing energy $\Delta E_{\text{atom}} = E_f - E_i$ in an inelastic collision with an electron or another atom. This process, called **collisional excitation,** is shown in FIGURE 39.17b.
7. Atoms seek the lowest energy state. An atom in an excited state, if left alone, will jump to lower and lower energy states until it reaches the ground state.

Bohr's model builds upon Rutherford's model, but it adds two new ideas that are derived from Einstein's ideas of quanta. The first, expressed in assumption 2, is that only certain electron orbits are "allowed" or can exist. The second, expressed in assumption 5, is that **the atom can jump from one state to another by emitting or absorbing a photon of just the right frequency to conserve energy.**

According to Einstein, a photon of frequency f has energy $E_{\text{photon}} = hf$. 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 $E_{\text{photon}} = \Delta E_{\text{atom}}$. This photon must have exactly the frequency given by Equation 39.17 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.

NOTE ▶ When an atom is excited to a higher energy level by absorbing a photon, the photon vanishes. Thus energy conservation requires $E_{\text{photon}} = \Delta E_{\text{atom}}$. When an atom is excited to a higher energy level in a collision with a particle, such as an electron or another atom, the particle still exists after the collision and still has energy. Thus energy conservation requires the less stringent condition $E_{\text{particle}} \geq \Delta E_{\text{atom}}$. ◀

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

1. **Matter is stable.** An atom in its ground state has 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.** In a gas discharge tube, the current-carrying electrons moving through the tube occasionally collide with the atoms. A collision transfers energy to an atom and can kick it to an excited state. Once the atom is in an excited state, it can emit photons of light—a discrete emission spectrum—as it jumps back 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 $1 \to 2$, $1 \to 3$, . . . in which the atom jumps from $n = 1$ to a higher value of n by absorbing a photon. Transitions such as $2 \to 3$ are *not* observed because there are essentially no atoms in $n = 2$ at any instant of time. On the other hand, atoms that have been excited to the $n = 3$ state by collisions can emit photons corresponding to transitions $3 \to 1$ *and* $3 \to 2$. Thus the wavelength corresponding to $\Delta E_{atom} = E_3 - E_1$ is seen in both emission and absorption, but transitions with $\Delta E_{atom} = E_3 - E_2$ occur in emission only.

5. **Each element in the periodic table has a unique spectrum.** The energies of the stationary states are 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 emit and absorb photons of different wavelengths.

EXAMPLE 39.9 The wavelength of an emitted photon

An atom has stationary states with energies $E_j = 4.00$ eV and $E_k = 6.00$ eV. What is the wavelength of a photon emitted in a quantum jump from state k to state j?

MODEL To conserve energy, the emitted photon must have exactly the energy lost by the atom in the quantum jump.

SOLVE The atom can jump from the higher energy state k to the lower energy state j by emitting a photon. The atom's change in energy is $\Delta E_{atom} = -2.00$ eV, so the photon energy must be $E_{photon} = 2.00$ eV. The photon frequency is

$$f = \frac{E_{photon}}{h} = \frac{2.00 \text{ eV}}{4.14 \times 10^{-15} \text{ eV s}} = 4.83 \times 10^{14} \text{ Hz}$$

The wavelength of this photon is

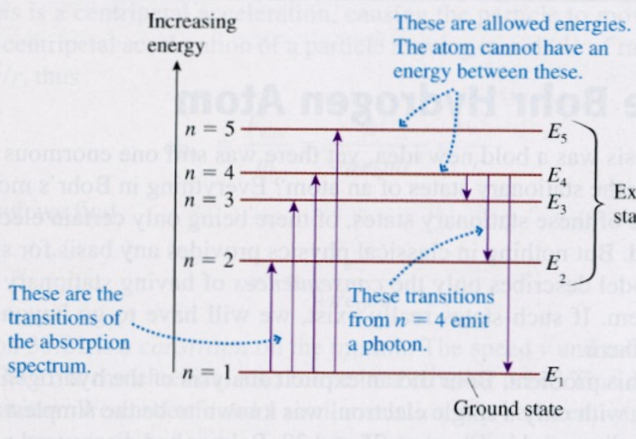
$$\lambda = \frac{c}{f} = 621 \text{ nm}$$

ASSESS 621 nm is a visible-light wavelength.

Energy-Level Diagrams

An **energy-level diagram,** such as the one shown in FIGURE 39.18, is a useful pictorial representation of the stationary-state energies. An energy-level diagram is less a graph than it is a picture. The vertical axis represents energy, but the horizontal axis is not a scale. Think of this as a picture of a ladder in which the energies are the rungs of the ladder. The lowest rung, with energy E_1, is the ground state. Higher rungs are labeled by their quantum numbers, $n = 2, 3, 4, \ldots$

FIGURE 39.18 An energy-level diagram.



Energy-level diagrams are especially useful for showing transitions, or quantum jumps, in which a photon of light is emitted or absorbed. As examples, Figure 39.18 shows upward transitions in which a photon is absorbed by a ground-state atom ($n = 1$) and downward transitions in which a photon is emitted from an $n = 4$ excited state.

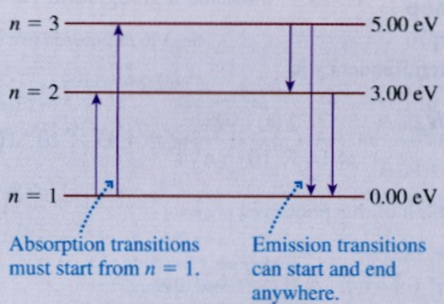
EXAMPLE 39.10 Emission and absorption

An atom has stationary states $E_1 = 0.00$ eV, $E_2 = 3.00$ eV, and $E_3 = 5.00$ eV. What wavelengths are observed in the absorption spectrum and in the emission spectrum of this atom?

MODEL 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. But 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.

VISUALIZE FIGURE 39.19 shows an energy-level diagram for the atom.

FIGURE 39.19 The atom's energy-level diagram.



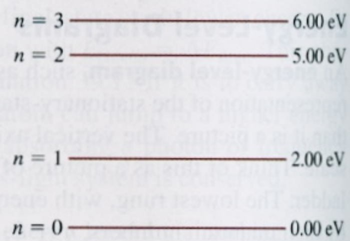
SOLVE This atom will absorb photons on the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions, with $\Delta E_{1\rightarrow2} = 3.00$ eV and $\Delta E_{1\rightarrow3} = 5.00$ eV. From $f = \Delta E_{atom}/h$ and $\lambda = c/f$, we find that the wavelengths in the absorption spectrum are

$$1 \rightarrow 2 \qquad f = 3.00 \text{ eV}/h = 7.25 \times 10^{14} \text{ Hz}$$
$$\lambda = 414 \text{ nm (blue)}$$
$$1 \rightarrow 3 \qquad f = 5.00 \text{ eV}/h = 1.21 \times 10^{15} \text{ Hz}$$
$$\lambda = 248 \text{ nm (ultraviolet)}$$

The emission spectrum will also have the 414 nm and 248 nm wavelengths due to the $2 \rightarrow 1$ and $3 \rightarrow 1$ quantum jumps from excited states 2 and 3 to the ground state. In addition, the emission spectrum will contain the $3 \rightarrow 2$ quantum jump with $\Delta E_{3\rightarrow2} = -2.00$ eV that is *not* seen in absorption because there are too few atoms in the $n = 2$ state to absorb. We found in Example 39.9 that a 2.00 eV transition corresponds to a wavelength of 621 nm. Thus the emission wavelengths are

$$2 \rightarrow 1 \qquad \lambda = 414 \text{ nm (blue)}$$
$$3 \rightarrow 1 \qquad \lambda = 248 \text{ nm (ultraviolet)}$$
$$3 \rightarrow 2 \qquad \lambda = 621 \text{ nm (orange)}$$

STOP TO THINK 39.4 A photon with a wavelength of 414 nm has energy $E_{photon} = 3.00$ eV. Do you expect to see a spectral line with $\lambda = 414$ 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 $\lambda = 414$ nm in the absorption spectrum? If so, what transition or transitions will absorb it?



39.6 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 Chapters 25 and 38, Balmer had discovered a fairly simple formula that characterized 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.