Unit 32

Hand-out

27–2 Planck's Quantum Hypothesis; Blackbody Radiation

Blackbody Radiation

One of the observations that was unexplained at the end of the nineteenth century was the spectrum of light emitted by hot objects. We saw in Section 14–8 that all objects emit radiation whose total intensity is proportional to the fourth power of the Kelvin (absolute) temperature (T^4). At normal temperatures $(\approx 300\,\mathrm{K})$, we are not aware of this electromagnetic radiation because of its low intensity. At higher temperatures, there is sufficient infrared radiation that we can feel heat if we are close to the object. At still higher temperatures (on the order of 1000 K), objects actually glow, such as a red-hot electric stove burner or the element in a toaster. At temperatures above 2000 K, objects glow with a yellow or whitish color, such as white-hot iron and the filament of a lightbulb. The light emitted is of a continuous range of wavelengths or frequencies, and the spectrum is a plot of intensity vs. wavelength or frequency. As the temperature increases, the electromagnetic radiation emitted by objects not only increases in total intensity but is strongest at higher and higher frequencies.

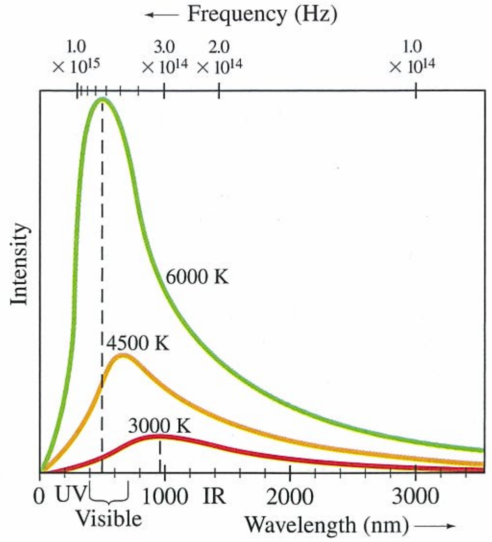


FIGURE 27–4 Measured spectra of wavelengths and frequencies emitted by a blackbody at two different temperatures.

The spectrum of light emitted by a hot dense object is shown in Fig. 27–4 for an idealized **blackbody**. A blackbody is a body that would absorb all the radiation falling on it (and so would appear black under reflection when illuminated from outside). The radiation such a blackbody would emit when hot and luminous, called **blackbody radiation** (though not necessarily black in color), is the easiest to deal with, and the radiation approximates that from many real objects. The 6000-K curve in Fig. 27–4, corresponding to the temperature of the surface of the Sun, peaks in the visible part of the spectrum. For lower temperatures, the total radiation drops considerably and the peak occurs at longer wavelengths (or lower frequencies). Hence the blue end of the visible spectrum (and the UV) is relatively weaker at lower temperatures. (This is why objects glow with a red color at around 1000 K.) It is found experimentally that the wavelength at the peak of the spectrum, λ_P, is related to the Kelvin temperature T by

Blackbody radiation

$$\lambda_P T = 2.90 \times 10^{-3}\,\mathrm{m\cdot K}. \qquad \textbf{(27–2)}$$

This is known as **Wien's law**.

EXAMPLE 27–1 **The Sun's surface temperature.** Estimate the temperature of the surface of our Sun, given that the Sun emits light whose peak intensity occurs in the visible spectrum at around 500 nm.

APPROACH We assume the Sun acts as a blackbody, and use $\lambda_P = 500\,\mathrm{nm}$ in Wien's law (Eq. 27–2).

SOLUTION Wien's law gives

$$T = \frac{2.90 \times 10^{-3}\,\mathrm{m\cdot K}}{\lambda_P} = \frac{2.90 \times 10^{-3}\,\mathrm{m\cdot K}}{500 \times 10^{-9}\,\mathrm{m}} \approx 6000\,\mathrm{K}.$$

EXAMPLE 27–2 **Star color.** Suppose a star has a surface temperature of 32,500 K. What color would this star appear?

APPROACH We assume the star emits radiation as a blackbody, and solve for λ_P in Wien's law, Eq. 27–2.

SOLUTION From Wien's law we have

$$\lambda_P = \frac{2.90 \times 10^{-3}\,\mathrm{m\cdot K}}{T} = \frac{2.90 \times 10^{-3}\,\mathrm{m\cdot K}}{3.25 \times 10^{4}\,\mathrm{K}} = 89.2\,\mathrm{nm}.$$

The peak is in the UV range of the spectrum, and will be way to the left in Fig. 27–4. In the visible region, the curve will be descending, so the shortest visible wavelengths will be strongest. Hence the star will appear bluish (or blue-white).

NOTE This example helps us to understand why stars have different colors (reddish for the coolest stars, orangish, yellow, white, bluish for "hotter" stars.)

EXERCISE A What is the color of an object at 4000 K?

Planck's Quantum Hypothesis

In the year 1900, Max Planck (1858–1947) proposed a theory that was able to reproduce the graphs of Fig. 27–4. His theory, still accepted today, made a new and radical assumption: that the energy of the oscillations of atoms within molecules cannot have just any value; instead each has energy which is a multiple of a minimum value related to the frequency of oscillation by

$$E = hf.$$

Here h is a new constant, now called **Planck's constant**, whose value was estimated by Planck by fitting his formula for the blackbody radiation curve to experiment. The value accepted today is

$$h = 6.626 \times 10^{-34}\,\mathrm{J \cdot s}.$$

Planck's assumption suggests that the energy of any molecular vibration could be only some whole number multiple of hf:

Planck's quantum hypothesis

$$E = nhf, \qquad n = 1, 2, 3, \cdots, \tag{27–3}$$

where n is called a **quantum number** ("quantum" means "discrete amount" as opposed to "continuous"). This idea is often called **Planck's quantum hypothesis**, although little attention was brought to this point at the time. In fact, it appears that Planck considered it more as a mathematical device to get the "right answer" rather than as a discovery comparable to those of Newton. Planck himself continued to seek a classical explanation for the introduction of h. The recognition that this was an important and radical innovation did not come until later, after about 1905 when others, particularly Einstein, entered the field.

The quantum hypothesis, Eq. 27–3, states that the energy of an oscillator can be $E = hf$, or $2hf$, or $3hf$, and so on, but there cannot be vibrations with energies between these values. That is, energy would not be a continuous quantity as had been believed for centuries; rather it is **quantized**—it exists only in discrete amounts. The smallest amount of energy possible (hf) is called the **quantum of energy**. Recall from Chapter 11 that the energy of an oscillation is proportional to the amplitude squared. Thus another way of expressing the quantum hypothesis is that not just any amplitude of vibration is possible. The possible values for the amplitude are related to the frequency f.

A simple analogy may help. A stringed instrument such as a violin or guitar can be played over a continuous range of frequencies by moving your finger along the string. A flute or piano, on the other hand, is "quantized" in the sense that only certain frequencies (notes) can be played. Or compare a ramp, on which a box can be placed at any height, to a flight of stairs on which the box can have only certain discrete amounts of potential energy, as shown in Fig. 27–5.

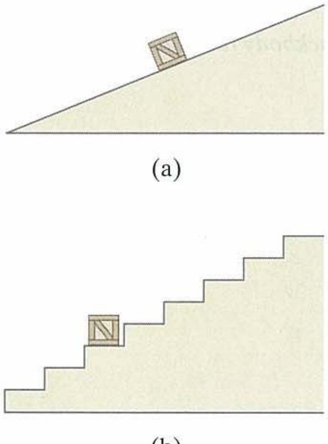


FIGURE 27–5 Ramp versus stair analogy. (a) On a ramp, a box can have continuous values of potential energy. (b) But on stairs, the box can have only discrete (quantized) values of energy.

27–3 Photon Theory of Light and the Photoelectric Effect

In 1905, the same year that he introduced the special theory of relativity, Einstein made a bold extension of the quantum idea by proposing a new theory of light. Planck's work had suggested that the vibrational energy of molecules in a radiating object is quantized with energy $E = nhf$, where n is an integer and f is the frequency of molecular vibration. Einstein argued that when light is emitted by a molecular oscillator, the molecule's vibrational energy of nhf must decrease by an amount hf (or by $2hf$, etc.) to another integer times hf, such as $(n-1)hf$. Then to conserve energy, the light ought to be emitted in packets, or *quanta*, each with an energy

Photon energy

$$E = hf, \tag{27–4}$$

where f is here the frequency of the emitted light.

Again h is Planck's constant. Since all light ultimately comes from a radiating source, this suggests that perhaps *light is transmitted as tiny particles*, or **photons**, as they are now called, in addition to the waves predicted by Maxwell's electromagnetic theory. The photon theory of light was also a radical departure from classical ideas. Einstein proposed a test of the quantum theory of light: quantitative measurements on the photoelectric effect.

Photons

When light shines on a metal surface, electrons are found to be emitted from the surface. This effect is called the **photoelectric effect** and it occurs in many materials, but is most easily observed with metals. It can be observed using the apparatus shown in Fig. 27–6. A metal plate P and a smaller electrode C are placed inside an evacuated glass tube, called a **photocell**. The two electrodes are connected to an ammeter and a source of emf, as shown. When the photocell is in the dark, the ammeter reads zero. But when light of sufficiently high frequency illuminates the plate, the ammeter indicates a current flowing in the circuit. We explain completion of the circuit by imagining that electrons, ejected by the impinging radiation, flow across the tube from the plate to the "collector" C as indicated in Fig. 27–6.

Photoelectric effect

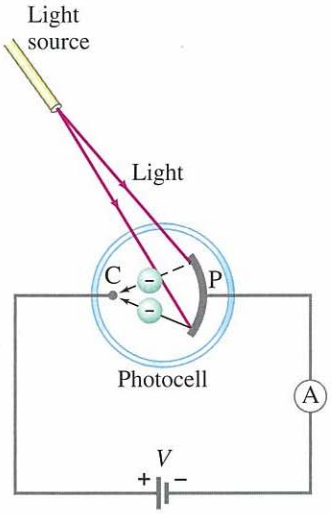


FIGURE 27–6 The photoelectric effect.

That electrons should be emitted when light shines on a metal is consistent with the electromagnetic (EM) wave theory of light: the electric field of an EM wave could exert a force on electrons in the metal and eject some of them. Einstein pointed out, however, that the wave theory and the photon theory of light give very different predictions on the details of the photoelectric effect. For example, one thing that can be measured with the apparatus of Fig. 27–6 is the maximum kinetic energy ($\mathrm{KE}_{\max}$) of the emitted electrons. This can be done by using a variable voltage source and reversing the terminals so that electrode C is negative and P is positive. The electrons emitted from P will be repelled by the negative electrode, but if this reverse voltage is small enough, the fastest electrons will still reach C and there will be a current in the circuit. If the reversed voltage is increased, a point is reached where the current reaches zero—no electrons have sufficient kinetic energy to reach C. This is called the *stopping potential*, or *stopping voltage*, V_0, and from its measurement, $\mathrm{KE}_{\max}$ can be determined using conservation of energy (loss of KE = gain in PE):

$$\mathrm{KE}_{\max} = eV_0 .$$

Now let us examine the details of the photoelectric effect from the point of view of the wave theory versus Einstein's particle theory.

First the wave theory, assuming monochromatic light. The two important properties of a light wave are its intensity and its frequency (or wavelength). When these two quantities are varied, the wave theory makes the following predictions:

Wave theory predictions

1. If the light intensity is increased, the number of electrons ejected and their maximum kinetic energy should be increased because the higher intensity means a greater electric field amplitude, and the greater electric field should eject electrons with higher speed.
2. The frequency of the light should not affect the kinetic energy of the ejected electrons. Only the intensity should affect $\mathrm{KE}_{\max}$.

One photon collides with one electron, ejecting it

The photon theory makes completely different predictions. First we note that in a monochromatic beam, all photons have the same energy $(= hf)$. Increasing the intensity of the light beam means increasing the number of photons in the beam, but does not affect the energy of each photon as long as the frequency is not changed. According to Einstein's theory, an electron is ejected from the metal by a collision with a single photon. In the process, all the photon energy is transferred to the electron and the photon ceases to exist. Since electrons are held in the metal by attractive forces, some minimum energy W_0 is required just to get an electron out through the surface. W_0 is called the **work function**, and is a few electron volts $(1\,\mathrm{eV} = 1.6 \times 10^{-19}\,\mathrm{J})$ for most metals. If the frequency f of the incoming light is so low that hf is less than W_0, then the photons will not have enough energy to eject any electrons at all. If $hf > W_0$, then electrons will be ejected and energy will be conserved in the process. That is, the input energy (of the photon), hf, will equal the outgoing kinetic energy KE of the electron plus the energy required to get it out of the metal, W:

$$hf = \mathrm{KE} + W. \qquad \textbf{(27–5a)}$$

The least tightly held electrons will be emitted with the most kinetic energy $(\mathrm{KE}_{\max})$, in which case W in this equation becomes the work function W_0, and KE becomes $\mathrm{KE}_{\max}$:

$$hf = \mathrm{KE}_{\max} + W_0. \qquad \text{[least bound electrons]} \quad \textbf{(27–5b)}$$

Many electrons will require more energy than the bare minimum (W_0) to get out of the metal, and thus the kinetic energy of such electrons will be less than the maximum.

From these considerations, the photon theory makes the following predictions:

Photon theory predictions

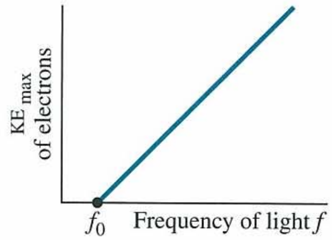
1. An increase in intensity of the light beam means more photons are incident, so more electrons will be ejected; but since the energy of each photon is not changed, the maximum kinetic energy of electrons is not changed by an increase in intensity.
2. If the frequency of the light is increased, the maximum kinetic energy of the electrons increases linearly, according to Eq. 27–5b. That is,

$$\mathrm{KE}_{\max} = hf - W_0.$$

This relationship is plotted in Fig. 27–7.

3. If the frequency f is less than the "cutoff" frequency f_0, where $hf_0 = W_0$, no electrons will be ejected, no matter how great the intensity of the light.

FIGURE 27–7 Photoelectric effect: the maximum kinetic energy of ejected electrons increases linearly with the frequency of incident light. No electrons are emitted if $f < f_0$.



These predictions of the photon theory are clearly very different from the predictions of the wave theory. In 1913–1914, careful experiments were carried out by R. A. Millikan. The results were fully in agreement with Einstein's photon theory.

One other aspect of the photoelectric effect also confirmed the photon theory. If extremely low light intensity is used, the wave theory predicts a time delay before electron emission so that an electron can absorb enough energy to exceed the work function. The photon theory predicts no such delay—it only takes one photon (if its frequency is high enough) to eject an electron—and experiments showed no delay. This too confirmed Einstein's photon theory.

EXAMPLE 27–3 **Photon energy.** Calculate the energy of a photon of blue light, $\lambda = 450\,\text{nm}$ in air (or vacuum).

APPROACH The photon has energy $E = hf$ (Eq. 27–4) where $f = c/\lambda$ (Eq. 22–4).

SOLUTION Since $f = c/\lambda$, we have

$$E = hf = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}\,\text{J}\cdot\text{s})(3.0 \times 10^{8}\,\text{m/s})}{(4.5 \times 10^{-7}\,\text{m})} = 4.4 \times 10^{-19}\,\text{J},$$

or $(4.4 \times 10^{-19}\,\text{J})/(1.60 \times 10^{-19}\,\text{J/eV}) = 2.8\,\text{eV}$. (See definition of eV in Section 17–4, $1\,\text{eV} = 1.60 \times 10^{-19}\,\text{J}$.)

EXERCISE B A beam contains infrared light of a single wavelength, 1000 nm, and monochromatic UV at 100 nm, both of the same intensity. Are there more 100-nm photons or more 1000-nm photons?

EXAMPLE 27–4 **Photoelectron speed and energy.** What is the kinetic energy and the speed of an electron ejected from a sodium surface whose work function is $W_0 = 2.28\,\text{eV}$ when illuminated by light of wavelength (*a*) 410 nm, (*b*) 550 nm?

APPROACH We first find the energy of the photons ($E = hf = hc/\lambda$). If it is greater than W_0, then electrons will ejected with varying amounts of KE, with a maximum of $\text{KE}_{\text{max}} = hf - W_0$.

SOLUTION (*a*) For $\lambda = 410\,\text{nm}$,

$$hf = \frac{hc}{\lambda} = 4.85 \times 10^{-19}\,\text{J} \qquad \text{or} \qquad 3.03\,\text{eV}.$$

The maximum kinetic energy an electron can have is given by Eq. 27–5b, $\text{KE}_{\text{max}} = 3.03\,\text{eV} - 2.28\,\text{eV} = 0.75\,\text{eV}$, or $(0.75\,\text{eV})(1.60 \times 10^{-19}\,\text{J/eV}) = 1.2 \times 10^{-19}\,\text{J}$. Since $\text{KE} = \frac{1}{2}mv^2$ where $m = 9.1 \times 10^{-31}\,\text{kg}$,

$$v_{\text{max}} = \sqrt{\frac{2\text{KE}}{m}} = 5.1 \times 10^{5}\,\text{m/s}.$$

Most ejected electrons will have less KE and less speed than these maximum values.

(*b*) For $\lambda = 550\,\text{nm}$, $hf = hc/\lambda = 3.61 \times 10^{-19}\,\text{J} = 2.26\,\text{eV}$. Since this photon energy is less than the work function, no electrons are ejected.

NOTE In (*a*) we used the nonrelativistic equation for kinetic energy. If v had turned out to be more than about $0.1c$, our calculation would have been inaccurate by more than a percent or so, and we would probably prefer to redo it using the relativistic form (Eq. 26–6).

EXERCISE C Determine the lowest frequency and the longest wavelength needed to emit electrons from sodium.

It is easy to show (see Problem 28) just by converting units that the energy of a photon in electron volts, when given the wavelength λ in nm, is

$$E\,(\text{eV}) = \frac{1.240 \times 10^{3}\,\text{eV}\cdot\text{nm}}{\lambda\,(\text{nm})}. \qquad \text{[photon energy in eV]}$$

27–11 Atomic Spectra: Key to the Structure of the Atom

Earlier in this Chapter we saw that heated solids (as well as liquids and dense gases) emit light with a continuous spectrum of wavelengths. This radiation is assumed to be due to oscillations of atoms and molecules, which are largely governed by the interaction of each atom or molecule with its neighbors.

Rarefied gases can also be excited to emit light. This is done by intense heating, or more commonly by applying a high voltage to a "discharge tube" containing the gas at low pressure, Fig. 27–20. The radiation from excited gases had been observed early in the nineteenth century, and it was found that the spectrum was not continuous, but *discrete*. Since excited gases emit light of only certain wavelengths, when this light is analyzed through the slit of a spectroscope or spectrometer, a **line spectrum** is seen rather than a continuous spectrum. The line spectra emitted by a number of elements in the visible region are shown here in Fig. 27–21, and also in Chapter 24, Fig. 24–28. The **emission spectrum** is characteristic of the material and can serve as a type of "fingerprint" for identification of the gas.

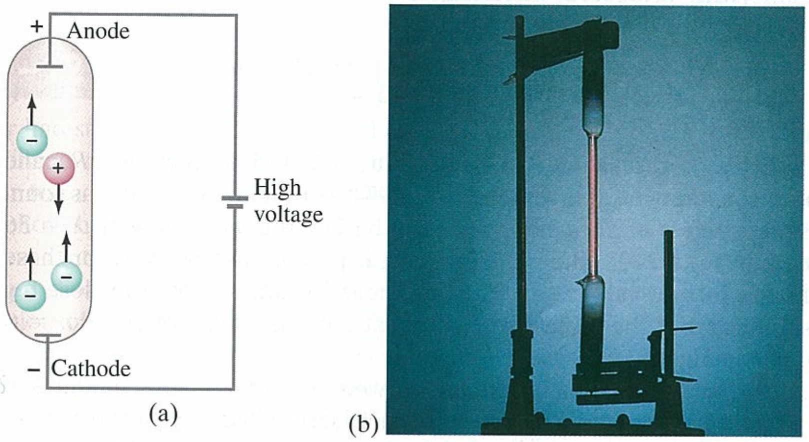
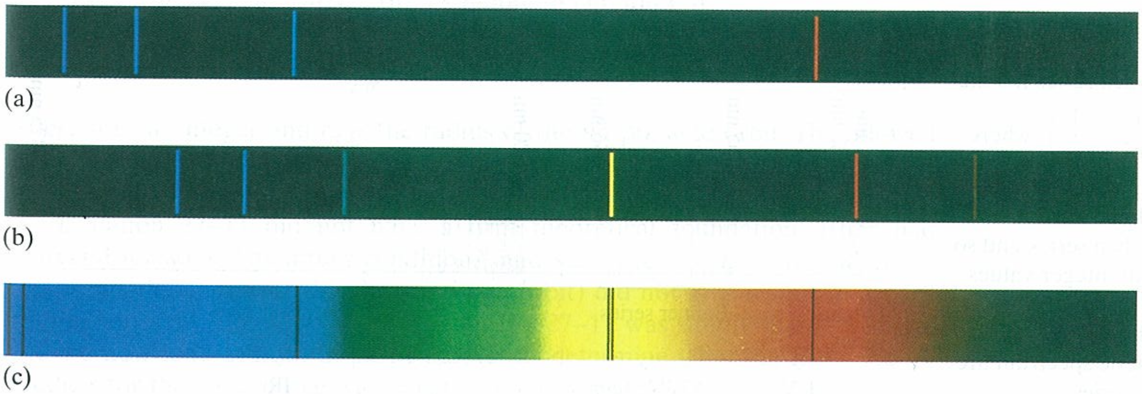


FIGURE 27–20 Gas-discharge tube: (a) diagram; (b) photo of an actual discharge tube for hydrogen.

We also saw (Chapter 24) that if a continuous spectrum passes through a rarefied gas, dark lines are observed in the emerging spectrum, at wavelengths corresponding to lines normally emitted by the gas. This is called an **absorption spectrum** (Fig. 27–21c), and it became clear that gases can absorb light at the same frequencies at which they emit. Using film sensitive to ultraviolet and to infrared light, it was found that gases emit and absorb discrete frequencies in these regions as well as in the visible.

FIGURE 27–21 Emission spectra of the gases (a) atomic hydrogen, (b) helium, and (c) the *solar absorption* spectrum.



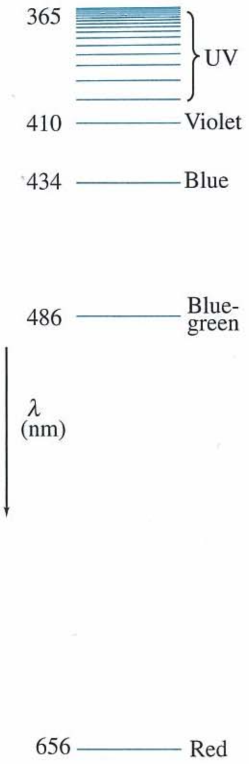


FIGURE 27–22 Balmer series of lines for hydrogen.

In low density gases, the atoms are far apart on the average and hence the light emitted or absorbed is assumed to be by *individual atoms* rather than through interactions between atoms, as in a solid, liquid, or dense gas. Thus the line spectra serve as a key to the structure of the atom: any theory of atomic structure must be able to explain why atoms emit light only of discrete wavelengths, and it should be able to predict what these wavelengths are.

Hydrogen is the simplest atom—it has only one electron orbiting its nucleus. It also has the simplest spectrum. The spectrum of most atoms shows little apparent regularity. But the spacing between lines in the hydrogen spectrum decreases in a regular way, Fig. 27–22. Indeed, in 1885, J. J. Balmer (1825–1898) showed that the four lines in the visible portion of the hydrogen spectrum (with measured wavelengths 656 nm, 486 nm, 434 nm, and 410 nm) have wavelengths that fit the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, \cdots. \qquad \textbf{(27–9)}$$

Here n takes on the values 3, 4, 5, 6 for the four visible lines, and R, called the **Rydberg constant**, has the value $R = 1.0974 \times 10^7\,\mathrm{m^{-1}}$. Later it was found that this **Balmer series** of lines extended into the UV region, ending at $\lambda = 365\,\mathrm{nm}$, as shown in Fig. 27–22. Balmer's formula, Eq. 27–9, also worked for these lines with higher integer values of n. The lines near 365 nm became too close together to distinguish, but the limit of the series at 365 nm corresponds to $n = \infty$ (so $1/n^2 = 0$ in Eq. 27–9).

Later experiments on hydrogen showed that there were similar series of lines in the UV and IR regions, and each series had a pattern just like the Balmer series, but at different wavelengths, Fig. 27–23. Each of these series was found to fit a formula with the same form as Eq. 27–9 but with the $1/2^2$ replaced by $1/1^2, 1/3^2, 1/4^2$, and so on. For example, the so-called **Lyman series** contains lines with wavelengths from 91 nm to 122 nm (in the UV region) and fits the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \qquad n = 2, 3, \cdots.$$

And the wavelengths of the **Paschen series** (in the IR region) fit

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \qquad n = 4, 5, \cdots.$$

The Rutherford model was unable to explain why atoms emit line spectra. It had other difficulties as well. According to the Rutherford model, electrons orbit the nucleus, and since their paths are curved the electrons are accelerating. Hence they should give off light like any other accelerating electric charge (Chapter 22). Since light carries off energy and energy is conserved, the electron's own energy must decrease to compensate. Hence electrons would be

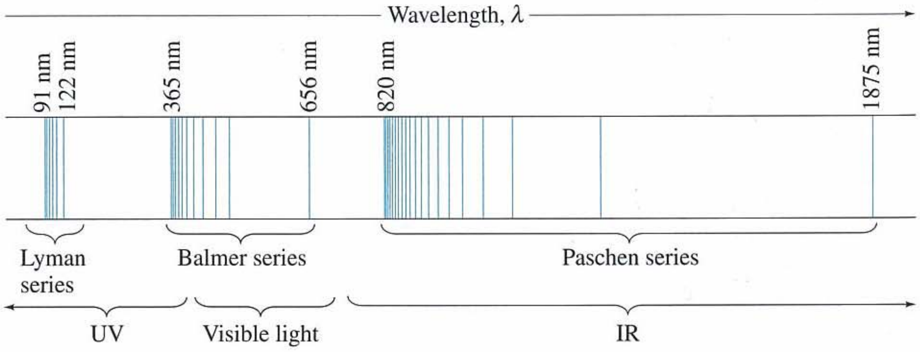


FIGURE 27–23 Line spectrum of atomic hydrogen. Each series fits the formula $\frac{1}{\lambda} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$ where $n' = 1$ for the Lyman series, $n' = 2$ for the Balmer series, $n' = 3$ for the Paschen series, and so on; n can take on all integer values from $n = n' + 1$ up to infinity. The only lines in the visible region of the electromagnetic spectrum are part of the Balmer series.

expected to spiral into the nucleus. As they spiraled inward, their frequency would increase in a short time and so too would the frequency of the light emitted. Thus the two main difficulties of the Rutherford model are these: (1) it predicts that light of a continuous range of frequencies will be emitted, whereas experiment shows line spectra; (2) it predicts that atoms are unstable—electrons would quickly spiral into the nucleus—but we know that atoms in general are stable, because there is stable matter all around us.

Clearly Rutherford's model was not sufficient. Some sort of modification was needed, and Niels Bohr provided it in a model that included the quantum hypothesis. Although the Bohr model has been superceded, it did provide a crucial stepping stone to our present understanding. And some aspects of the Bohr model are still useful today, so we examine it in detail in the next Section.

27–12 The Bohr Model

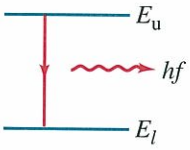
Bohr had studied in Rutherford's laboratory for several months in 1912 and was convinced that Rutherford's planetary model of the atom had validity. But in order to make it work, he felt that the newly developing quantum theory would somehow have to be incorporated in it. The work of Planck and Einstein had shown that in heated solids, the energy of oscillating electric charges must change discontinuously—from one discrete energy state to another, with the emission of a quantum of light. Perhaps, Bohr argued, the electrons in an atom also cannot lose energy continuously, but must do so in quantum "jumps." In working out his model during the next year, Bohr postulated that electrons move about the nucleus in circular orbits, but that only certain orbits are allowed. He further postulated that an electron in each orbit would have a definite energy and would move in the orbit *without radiating energy* (even though this violated classical ideas since accelerating electric charges are supposed to emit EM waves; see Chapter 22). He thus called the possible orbits **stationary states**. Light is emitted, he hypothesized, only when an electron jumps from a higher (upper) stationary state to another of lower energy. When such a jump occurs, a single photon of light is emitted whose energy, by energy conservation, is given by

Stationary state

$$hf = E_{\mathrm{u}} - E_l, \qquad \textbf{(27–10)}$$

where E_{u} refers to the energy of the upper state and E_l the energy of the lower state. See Fig. 27–24.

FIGURE 27–24 An atom emits a photon (energy $= hf$) when its energy changes from E_{u} to a lower energy E_l.



Bohr set out to determine what energies these orbits would have, since the spectrum of light emitted could then be predicted from Eq. 27–10. In the Balmer formula he had the key he was looking for. Bohr quickly found that his theory would be in accord with the Balmer formula if he assumed that the electron's angular momentum L is quantized and equal to an integer n times $h/2\pi$. As we saw in Chapter 8 angular momentum is given by $L = I\omega$, where I is the moment of inertia and ω is the angular velocity. For a single particle of mass m moving in a circle of radius r with speed v, $I = mr^2$ and $\omega = v/r$; hence, $L = I\omega = (mr^2)(v/r) = mvr$. Bohr's **quantum condition** is

$$L = mvr_n = n\frac{h}{2\pi}, \qquad n = 1, 2, 3, \cdots, \qquad \textbf{(27–11)}$$

Angular momentum quantized

where n is an integer and r_n is the radius of the n^{th} possible orbit. The allowed orbits are numbered $1, 2, 3, \cdots$, according to the value of n, which is called the **principal quantum number** of the orbit.

Quantum number, n

Equation 27–11 did not have a firm theoretical foundation. Bohr had searched for some "quantum condition," and such tries as $E = hf$ (where E represents the energy of the electron in an orbit) did not give results in accord with experiment. Bohr's reason for using Eq. 27–11 was simply that it worked; and we now look at how. In particular, let us determine what the Bohr theory predicts for the measurable wavelengths of emitted light.

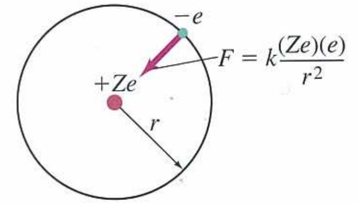


FIGURE 27–25 Electric force (Coulomb's law) keeps the negative electron in orbit around the positively charged nucleus.

An electron in a circular orbit of radius r (Fig. 27–25) would have a centripetal acceleration v^2/r produced by the electrical force of attraction between the negative electron and the positive nucleus. This force is given by Coulomb's law,

$$F = k\frac{(Ze)(e)}{r^2},$$

where $k = 1/4\pi\epsilon_0 = 9.00 \times 10^9\,\mathrm{N\cdot m^2/C^2}$. The charge on the electron is $q_1 = -e$, and that on the nucleus is $q_2 = +Ze$, where Z is the number of positive charges[†] (i.e., protons). For the hydrogen atom, $Z = +1$.

In Newton's second law, $F = ma$, we substitute Coulomb's law for F and $a = v^2/r_n$ for a particular allowed orbit of radius r_n, and obtain

$$F = ma$$
$$k\frac{Ze^2}{r_n^2} = \frac{mv^2}{r_n}.$$

We solve this for r_n,

$$r_n = \frac{kZe^2}{mv^2},$$

and then substitute for v from Eq. 27–11 (which says $v = nh/2\pi mr_n$):

$$r_n = \frac{kZe^2 4\pi^2 mr_n^2}{n^2h^2}.$$

We solve for r_n (it appears on both sides, so we cancel one of them) and find

$$r_n = \frac{n^2h^2}{4\pi^2mkZe^2} = \frac{n^2}{Z}r_1 \tag{27–12}$$

where

$$r_1 = \frac{h^2}{4\pi^2mke^2}.$$

Equation 27–12 gives the radii of each possible orbit. The smallest orbit is for $n = 1$, and for hydrogen ($Z = 1$) has the value

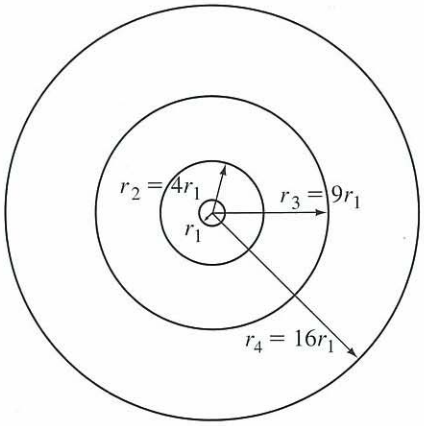
Bohr radius

$$r_1 = \frac{(1)^2(6.626 \times 10^{-34}\,\mathrm{J\cdot s})^2}{4(3.14)^2(9.11 \times 10^{-31}\,\mathrm{kg})(9.00 \times 10^9\,\mathrm{N\cdot m^2/C^2})(1.602 \times 10^{-19}\,\mathrm{C})^2}$$
$$r_1 = 0.529 \times 10^{-10}\,\mathrm{m}. \tag{27–13}$$

The radius of the smallest orbit in hydrogen, r_1, is sometimes called the **Bohr radius**. From Eq. 27–12, we see that the radii of the larger orbits[‡] increase as n^2, so

$$r_2 = 4r_1 = 2.12 \times 10^{-10}\,\mathrm{m},$$
$$r_3 = 9r_1 = 4.76 \times 10^{-10}\,\mathrm{m},$$
$$\vdots$$
$$r_n = n^2r_1, \qquad n = 1, 2, 3, \cdots.$$

FIGURE 27–26 Possible orbits in the Bohr model of hydrogen; $r_1 = 0.529 \times 10^{-10}$ m.



The first four orbits are shown in Fig. 27–26. Notice that, according to Bohr's model, an electron can exist only in the orbits given by Eq. 27–12. There are no allowable orbits in between.

For an atom with $Z \neq 1$, we can write the orbital radii, r_n, using Eq. 27–12:

$$r_n = \frac{n^2}{Z}(0.529 \times 10^{-10}\,\mathrm{m}), \qquad n = 1, 2, 3, \cdots. \tag{27–14}$$

In each of its possible orbits, the electron in a Bohr model atom would have

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[†] We include Z in our derivation so that we can treat other single-electron ("hydrogenlike") atoms such as the ions $\mathrm{He^+}$ ($Z = 2$) and $\mathrm{Li^{2+}}$ ($Z = 3$). Helium in the neutral state has two electrons; if one electron is missing, the remaining $\mathrm{He^+}$ ion consists of one electron revolving around a nucleus of charge $+2e$. Similarly, doubly ionized lithium, $\mathrm{Li^{2+}}$, also has a single electron, and in this case $Z = 3$.

[‡] Be careful not to believe that these well-defined orbits actually exist. Today electrons are better thought of as forming "clouds," as discussed in Chapter 28.

a definite energy, as the following calculation shows. The total energy equals the sum of the kinetic and potential energies. The potential energy of the electron is given by $\text{PE} = qV = -eV$, where V is the potential due to a point charge $+Ze$ as given by Eq. 17–5: $V = kQ/r = kZe/r$. So

$$\text{PE} = -eV = -k\frac{Ze^2}{r}.$$

The total energy E_n for an electron in the n^{th} orbit of radius r_n is the sum of the kinetic and potential energies:

$$E_n = \frac{1}{2}mv^2 - \frac{kZe^2}{r_n}.$$

When we substitute v from Eq. 27–11 and r_n from Eq. 27–12 into this equation, we obtain

$$E_n = -\frac{2\pi^2 Z^2 e^4 m k^2}{h^2}\frac{1}{n^2} \qquad n = 1, 2, 3, \cdots. \qquad \textbf{(27–15a)}$$

Energy levels

If we evaluate the constant term in Eq. 27–15a and convert it to electron volts, as is customary in atomic physics, we obtain

$$E_n = -(13.6\,\text{eV})\frac{Z^2}{n^2}, \qquad n = 1, 2, 3, \cdots. \qquad \textbf{(27–15b)}$$

The lowest energy level $(n = 1)$ for hydrogen $(Z = 1)$ is

$$E_1 = -13.6\,\text{eV}.$$

Ground state of hydrogen

Since n^2 appears in the denominator of Eq. 27–15b, the energies of the larger orbits in hydrogen $(Z = 1)$ are given by

$$E_n = \frac{-13.6\,\text{eV}}{n^2}.$$

For example,

$$E_2 = \frac{-13.6\,\text{eV}}{4} = -3.40\,\text{eV},$$

$$E_3 = \frac{-13.6\,\text{eV}}{9} = -1.51\,\text{eV}.$$

Excited states (first two)

We see that not only are the orbit radii quantized, but from Eqs. 27–15, so is the energy. The quantum number n that labels the orbit radii also labels the energy levels. The lowest **energy level** or **energy state** has energy E_1, and is called the **ground state**. The higher states, E_2, E_3, and so on, are called **excited states**.

Notice that although the energy for the larger orbits has a smaller numerical value, all the energies are less than zero. Thus, $-3.4\,\text{eV}$ is a greater energy than $-13.6\,\text{eV}$. Hence the orbit closest to the nucleus (r_1) has the lowest total energy. The reason the energies have negative values has to do with the way we defined the zero for potential energy. For two point charges, $\text{PE} = kq_1q_2/r$ corresponds to zero PE when the two charges are infinitely far apart as discussed in Section 17–5. Thus, an electron that can just barely be free from the atom by reaching $r = \infty$ (or, at least, far from the nucleus) with zero KE will have $E = \text{KE} + \text{PE} = 0 + 0 = 0$, corresponding to $n = \infty$ in Eqs. 27–15. If an electron is free and has some kinetic energy, then $E > 0$. To remove an electron that is part of an atom requires an energy input (otherwise atoms would not be stable). Since $E \geq 0$ for a free electron, then it makes sense that an electron bound to an atom must have $E < 0$. That is, energy must be added to bring the electron's total energy up, from a negative value to at least zero in order to free it.

The minimum energy required to remove an electron from the ground state of an atom is called the **binding energy** or **ionization energy**. The ionization energy for hydrogen has been measured to be 13.6 eV, and this corresponds precisely to removing an electron from the lowest state, $E_1 = -13.6\,\text{eV}$, up to $E = 0$ where it can be free.

Binding energy (ionization energy)

It is useful to show the various possible energy values as horizontal lines on an energy-level diagram. This is shown for hydrogen in Fig. 27–27.[†] The electron in a hydrogen atom can be in any one of these levels according to Bohr theory. But it could never be in between, say at $-9.0\,\text{eV}$. At room temperature, nearly all H atoms will be in the ground state ($n = 1$). At higher temperatures, or during an electric discharge when there are many collisions between free electrons and atoms, many atoms can be in excited states ($n > 1$). Once in an excited state, an atom's electron can jump down to a lower state, and give off a photon in the process. This is, according to the Bohr model, the origin of the emission spectra of excited gases.

Line spectra emission explained

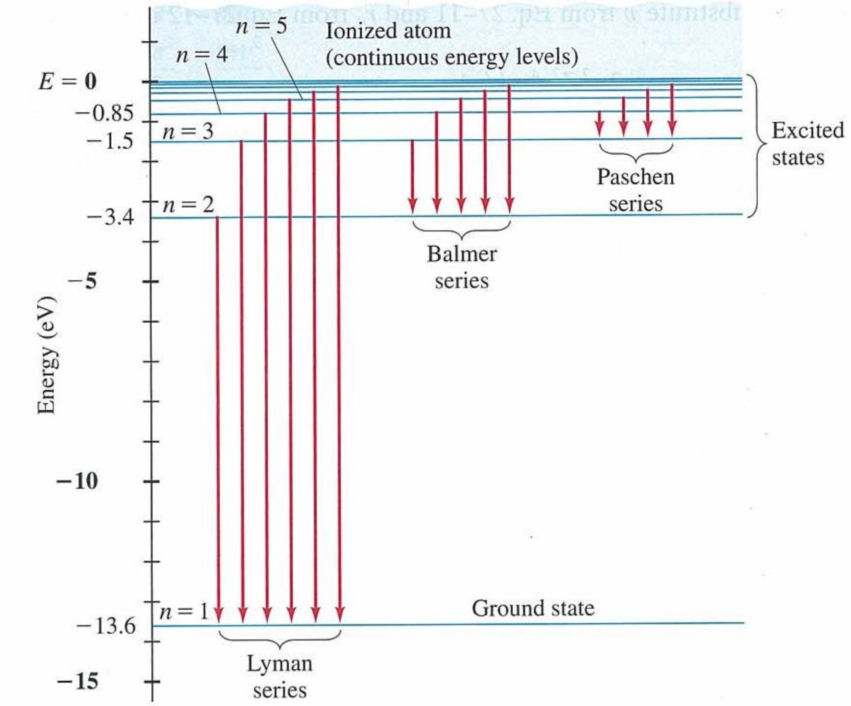

FIGURE 27–27 Energy-level diagram for the hydrogen atom, showing origin of spectral lines for the Lyman, Balmer, and Paschen series (Fig. 27–23). Each vertical arrow represents an atomic transition that gives rise to the photons of one spectral line (a single wavelength or frequency).

The vertical arrows in Fig. 27–27 represent the transitions or jumps that correspond to the various observed spectral lines. For example, an electron jumping from the level $n = 3$ to $n = 2$ would give rise to the 656-nm line in the Balmer series, and the jump from $n = 4$ to $n = 2$ would give rise to the 486-nm line (see Fig. 27–22). We can predict wavelengths of the spectral lines emitted by combining Eq. 27–10 with Eq. 27–15. Since $hf = hc/\lambda$, we have from Eq. 27–10

$$\frac{1}{\lambda} = \frac{hf}{hc} = \frac{1}{hc}\left(E_n - E_{n'}\right),$$

where n refers to the upper state and n' to the lower state. Then using Eq. 27–15,

$$\frac{1}{\lambda} = \frac{2\pi^2 Z^2 e^4 m k^2}{h^3 c}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \tag{27–16}$$

This theoretical formula has the same form as the experimental Balmer formula, Eq. 27–9, with $n' = 2$. Thus we see that the Balmer series of lines corresponds to transitions or "jumps" that bring the electron down to the second energy level. Similarly, $n' = 1$ corresponds to the Lyman series and $n' = 3$ to the Paschen series (see Fig. 27–27).

[†] Note that above $E = 0$, an electron is free and can have any energy (E is not quantized). Thus there is a continuum of energy states above $E = 0$, as indicated in the energy-level diagram of Fig. 27–27.

When the constant in Eq. 27–16 is evaluated with $Z = 1$, it is found to have the measured value of the Rydberg constant, $R = 1.0974 \times 10^7\,\mathrm{m}^{-1}$ in Eq. 27–9, in accord with experiment (see Problem 53).

Absorption lines explained

The great success of Bohr's model is that it gives an explanation for why atoms emit line spectra, and accurately predicts the wavelengths of emitted light for hydrogen. The Bohr model also explains absorption spectra: photons of just the right wavelength can knock an electron from one energy level to a higher one. To conserve energy, only photons that have just the right energy will be absorbed. This explains why a continuous spectrum of light entering a gas will emerge with dark (absorption) lines at frequencies that correspond to emission lines (Fig. 27–21c).

The Bohr theory also ensures the stability of atoms. It establishes stability by decree: the ground state is the lowest state for an electron and there is no lower energy level to which it can go and emit more energy. Finally, as we saw above, the Bohr theory accurately predicts the ionization energy of 13.6 eV for hydrogen. However, the Bohr model was not so successful for other atoms, and has been superseded as we shall discuss in the next Chapter. We discuss the Bohr model because it *was* an important start and because we still use the concept of stationary states, the ground state, and transitions between states. Also, the terminology used in the Bohr model is still used by chemists and spectroscopists.

EXAMPLE 27–12 **Wavelength of a Lyman line.** Use Fig. 27–27 to determine the wavelength of the first Lyman line, the transition from $n = 2$ to $n = 1$. In what region of the electromagnetic spectrum does this lie?

APPROACH We use Eq. 27–10, $hf = E_\mathrm{u} - E_l$, with the energies obtained from Fig. 27–27 to find the energy and the wavelength of the transition. The region of the electromagnetic spectrum is found using the EM spectrum in Fig. 22–8.

SOLUTION In this case, $hf = E_2 - E_1 = \{-3.4\,\mathrm{eV} - (-13.6\,\mathrm{eV})\} = 10.2\,\mathrm{eV} = (10.2\,\mathrm{eV})(1.60 \times 10^{-19}\,\mathrm{J/eV}) = 1.63 \times 10^{-18}\,\mathrm{J}$. Since $\lambda = c/f$, we have

$$\lambda = \frac{c}{f} = \frac{hc}{E_2 - E_1} = \frac{(6.63 \times 10^{-34}\,\mathrm{J\cdot s})(3.00 \times 10^8\,\mathrm{m/s})}{1.63 \times 10^{-18}\,\mathrm{J}} = 1.22 \times 10^{-7}\,\mathrm{m},$$

or 122 nm, which is in the UV region of the EM spectrum, Fig. 22–8. See also Fig. 27–23.

NOTE An alternate approach would be to use Eq. 27–16 to find λ, and it gives the same result.

EXAMPLE 27–13 **Wavelength of a Balmer line.** Determine the wavelength of light emitted when a hydrogen atom makes a transition from the $n = 6$ to the $n = 2$ energy level according to the Bohr model.

APPROACH We can use Eq. 27–16 or its equivalent, Eq. 27–9, with $R = 1.097 \times 10^7\,\mathrm{m}^{-1}$.

SOLUTION We find

$$\frac{1}{\lambda} = (1.097 \times 10^7\,\mathrm{m}^{-1})\left(\frac{1}{4} - \frac{1}{36}\right) = 2.44 \times 10^6\,\mathrm{m}^{-1}.$$

So $\lambda = 1/(2.44 \times 10^6\,\mathrm{m}^{-1}) = 4.10 \times 10^{-7}\,\mathrm{m}$ or 410 nm. This is the fourth line in the Balmer series, Fig. 27–22, and is violet in color.