

With the success of Balmer's formula, it was natural to ask what happens if the 2^2 in Equation 25.1 is changed to 1^2 or 3^2 or m^2 . It was easy to calculate that all spectral lines in the series with 1^2 , if they existed, would have fairly extreme ultraviolet wavelengths, while all those in the series with 3^2 would be in the infrared. Spectroscopists accepted the challenge and went to work developing the techniques for infrared and ultraviolet spectroscopy.

The $m = 1$ series was discovered by Theodore Lyman and is called the Lyman series. The $m = 3$ series, found by Louis Paschen, is called the Paschen series. They confirmed, beyond doubt, that Balmer's formula could be generalized to

$$\lambda = \frac{91.18 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} \quad \begin{cases} m = 1 & \text{Lyman series} \\ m = 2 & \text{Balmer series} \\ m = 3 & \text{Paschen series} \\ \vdots & \end{cases} \quad (25.2)$$

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

As spectroscopists acquired ever more data, it became increasingly clear that Equation 25.2 could predict *every* line in the hydrogen spectrum, from the extreme ultraviolet to the far infrared.

Surely Balmer's success was not a mere coincidence. There must be some underlying meaning to his formula. But what? Balmer did not present a *theory*. He simply said, "Here's a formula that accurately calculates the wavelengths in the hydrogen spectrum." In effect, Balmer's formula was a challenge. Any successful theory of atoms must be able to *derive* Equation 25.2 from the basic laws and principles of the theory. It was 30 years before a theory was proposed that could meet this challenge.

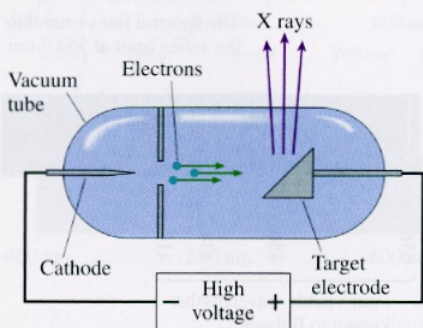
It is particularly striking that Equation 25.2 depends on two *integers*. Hydrogen atoms simply do not emit wavelengths for $m = 1.6$ or for $n = 3.4$. This must tell us *something* important about the structure of the hydrogen atom. Newtonian mechanics does not deal in such "discrete" quantities. Masses, forces, velocities, and energies can take on any value at all; they are not restricted to having only some values but not others.

However, we have seen one exception to this: standing waves. Standing waves exist for only certain frequencies and wavelengths that are described by an *integer* called the mode number. Could there, somehow, be a connection between standing waves and the structure of atoms? To answer this question, we must probe yet deeper into the nature of light and matter.

25.2 X-Ray Diffraction

In 1895, the German physicist Wilhelm Röntgen made a remarkable discovery. The late 19th century was a period in which the technology of vacuum tubes was being perfected, and Röntgen was studying how electrons (called *cathode rays* at the time) traveled through a vacuum. He sealed an electron-producing cathode and a metal target electrode into a vacuum tube, such as shown in **FIGURE 25.4**. A high voltage pulled electrons from the cathode and accelerated them to very high speeds before they struck the target. Röntgen and others had done similar experiments previously, but one day he happened by chance to have left a sealed envelope containing film near the vacuum tube. He was later surprised to discover that the film had been exposed even though it had never been removed from the envelope. This serendipitous discovery was the beginning of the study of x rays.

FIGURE 25.4 Röntgen's x-ray tube.



Röntgen quickly found that the vacuum tube was the source of whatever was exposing the film. But he had no idea what was coming from the tube, so he called them **x rays**, using the algebraic symbol x as meaning “unknown.” X rays were unlike anything, particle or wave, ever discovered. Röntgen was not successful at reflecting the rays or at focusing them with a lens. He showed that they travel in straight lines, like particles, but they also pass right through most solid materials, something no known particle could do.

By the early 1900s, scientists suspected that x rays were an electromagnetic wave with a wavelength much shorter than that of visible light. At about the same time, scientists were first discovering that the size of an atom is ≈ 0.1 nm, and it was suggested that solids might consist of atoms arranged in crystalline lattices. In 1912, the German scientist Max von Laue noted that *if* x rays are waves with very short wavelengths, and *if* solids are atomic crystals with the atoms spaced about 0.1 nm apart, then x rays passing through a crystal ought to undergo diffraction from the “three-dimensional grating” of the crystal.

X-ray diffraction by crystals was soon confirmed experimentally. Measurements showed that x rays are indeed electromagnetic waves, not fundamentally different from visible light, with wavelengths in the range 0.01 nm to 10 nm.

FIGURE 25.5a shows a simple cubic lattice of atoms. The crystal structure of most materials is more complex than this, but a cubic lattice will help you understand the ideas of x-ray diffraction. We’ll often draw just one *plane* of atoms, as in FIGURE 25.5b, so you’ll have to visualize the three-dimensional structure of the crystal.

Suppose that a beam of x rays is incident at angle θ on the plane of atoms shown in FIGURE 25.6a. (Imagine the plane extending out of the page.) Most of the x rays are transmitted through the plane, because we know that x rays penetrate solids, but a small fraction of the wave may be reflected. The reflected wave obeys the law of reflection—the angle of reflection equals the angle of incidence—and the figure has been drawn accordingly.

A solid is not one plane of atoms but many parallel planes. As x rays pass through a solid, a small fraction of the wave reflects from each of the parallel planes of atoms shown in Figure 25.5b. The *net* reflection from the solid is the *superposition* of the waves reflected by each atomic plane. For most angles of incidence, the phases of the reflected waves are all different and their superposition is very near zero. In other words, as Röntgen observed, solids don’t reflect x rays. However, there are a few specific angles of incidence for which the reflected waves all happen to be in phase. For these angles of incidence, the reflected waves interfere constructively to produce a strong reflection. This strong x-ray reflection at a few specific angles of incidence is called **x-ray diffraction**.

You can see from FIGURE 25.6b that the wave reflecting from any particular plane travels an extra distance $\Delta r = 2d\cos\theta$ before combining with the reflection from the plane immediately above it, where d is the spacing between the atomic planes. If $\Delta r = m\lambda$, these two waves will be in phase when they recombine. But the same geometry applies to all the planes of atoms. If the reflections from two neighboring planes are in phase, then *all* the reflections from *all* the planes are in phase and will interfere constructively to produce a strong reflection.

Consequently, x rays will strongly reflect from the crystal when the angle of incidence θ_m satisfies

$$\Delta r = 2d\cos\theta_m = m\lambda \quad m = 1, 2, 3, \dots \quad (25.3)$$

Equation 25.3 is called the **Bragg condition**, named for physicist W. L. Bragg, who developed this technique for producing x-ray diffraction.

NOTE ▶ Our reasoning is very similar to the reasoning we used in Chapter 21 to understand constructive and destructive interference in thin films. ◀

FIGURE 25.5 Atoms arranged in a cubic lattice.

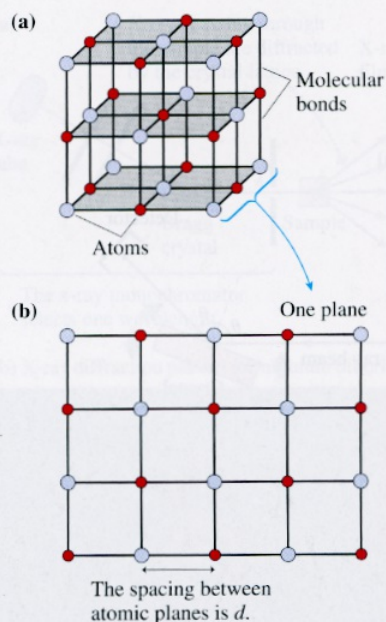
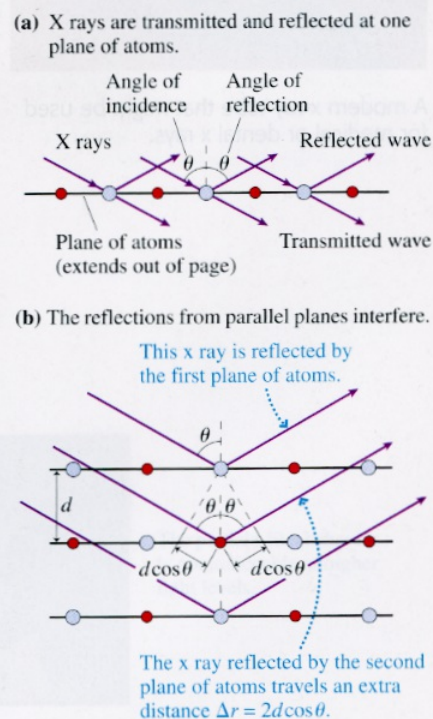
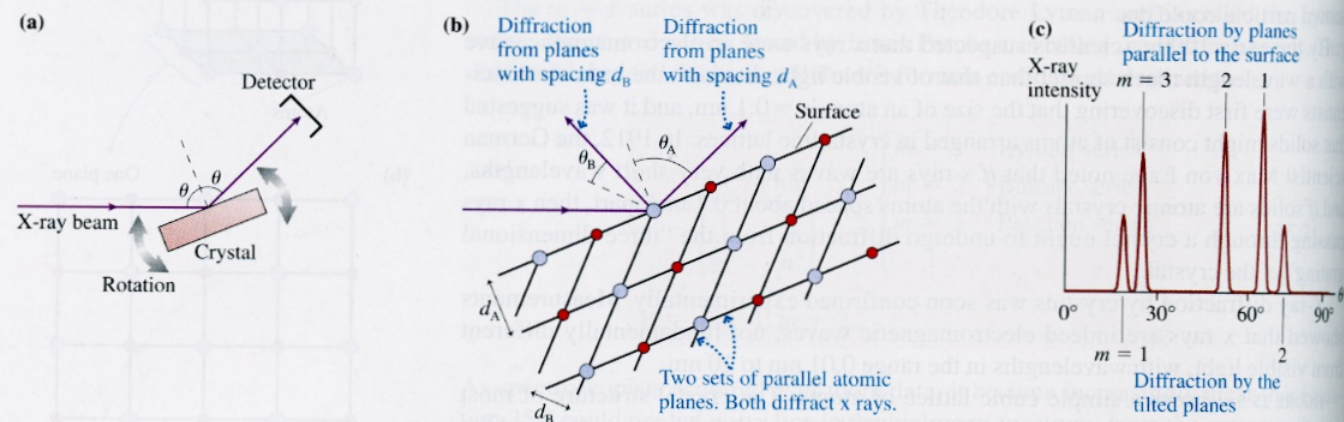


FIGURE 25.6 The x-ray reflections from parallel atomic planes interfere constructively to cause strong reflections for certain angles of incidence.



X-ray diffraction is measured by rotating a crystal through a range of angles, as shown in **FIGURE 25.7a**. A graph of the reflected x-ray intensity versus angle θ is called the *x-ray diffraction spectrum*, and it contains valuable information about the structure of the crystal.

FIGURE 25.7 Producing and measuring an x-ray diffraction spectrum.



One complicating factor is that a crystal can be “sliced” into more than one set of parallel planes of atoms. **FIGURE 25.7b** shows a set of atomic planes with spacing d_A and another set of planes with spacing $d_B = d_A/\sqrt{2}$. The planes parallel to the surface cause diffraction if θ_A satisfies the Bragg condition for spacing d_A . Independently, the planes tilted at 45° cause diffraction if θ_B satisfies the Bragg condition for spacing d_B .

FIGURE 25.7c shows a simulated x-ray diffraction spectrum for a cubic lattice with atomic spacing $d_1 = 0.20$ nm and x-ray wavelength $\lambda = 0.12$ nm. These are typical values. Real x-ray diffraction spectra are usually more complicated than this spectrum, but such spectra contain information with which scientists can deduce the crystalline structure of the solid.

Notice that the experimentally measured angle θ , which is measured from the surface of the crystal, is angle θ_A for the planes parallel to the surface. The experimental angle is *not* the same as angle θ_B , so it takes a little geometry to match the measured angles to the angles at which the tilted planes cause diffraction. The details will be left for a homework problem.

EXAMPLE 25.1 Analyzing x-ray diffraction

X rays with a wavelength of 0.105 nm are diffracted by a crystal. Diffraction maxima are observed at angles 31.6° and 55.4° and at no angles between these two. What is the spacing between the atomic planes causing this diffraction?

MODEL The angles must satisfy the Bragg condition. We don’t know the values of m , but they are two consecutive values. Notice that θ_m decreases as m increases, so 31.6° corresponds to the larger value of m .

SOLVE d and λ are the same for both diffractions, so we can use the Bragg condition to find

$$\frac{m+1}{m} = \frac{\cos 31.6^\circ}{\cos 55.4^\circ} = 1.50 = \frac{3}{2}$$

Thus 55.4° is the second-order diffraction and 31.6° is the third-order diffraction. With this information we can use the Bragg condition again to find

$$d = \frac{2\lambda}{2\cos\theta_2} = \frac{0.105 \text{ nm}}{\cos 55.4^\circ} = 0.185 \text{ nm}$$

ASSESS This is a reasonable value for the spacing in a crystal.



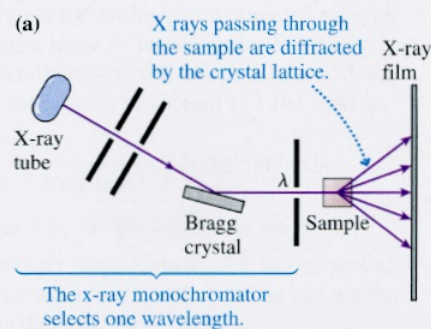
A modern x-ray tube that might be used for medical or dental x rays.

Although the Bragg procedure is straightforward, practical x-ray diffraction looks at the diffraction of x rays that are *transmitted* through a crystal. **FIGURE 25.8a** shows a typical experiment. An x-ray tube generates several x-ray wavelengths, so Bragg diffraction is first used to select just one of these wavelengths by rotating a crystal to an angle meeting the Bragg condition. This part of the apparatus is called an *x-ray monochromator*, a device that selects one (mono) wavelength.

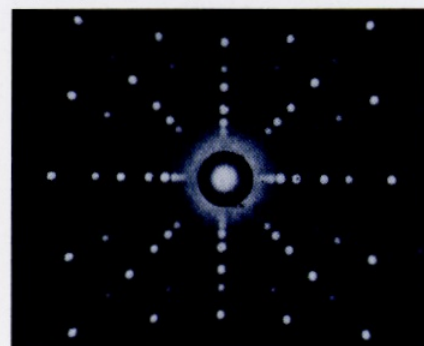
The known wavelength then passes through the sample and is diffracted by the three-dimensional grating of the crystal lattice. An x-ray film behind the sample records the locations of constructive interference. Because the grating is three-dimensional, the diffraction pattern consists of bright points rather than lines or fringes. **FIGURE 25.8b** shows a typical diffraction pattern. You can see that it is quite complicated. Nonetheless, crystallographers have developed many powerful analysis tools for deciphering such patterns. These techniques are computationally very intense, but modern supercomputers have made such analyses routine.

Today, x-ray diffraction is an essential tool for studying the atomic and molecular structure of solids. The most important properties of solids—their strength, chemical properties, ability to be cut or welded, optical properties, and so on—are consequences of their crystal structure. Modern engineering could not exist without the knowledge of materials gained through x-ray diffraction. Similarly, x-ray diffraction was used to deduce the double-helix structure of DNA, and it continues to elucidate the structures of biological molecules such as proteins. The techniques of x-ray diffraction are likely to become even more important in the future as physicists develop new superconducting materials, molecular biologists produce “designer drugs,” and engineers design atomic-size nanostructures.

FIGURE 25.8 Using x-ray diffraction to study the atomic structure of a sample.



(b) X-ray diffraction pattern for niobium diboride



STOP TO THINK 25.1 The first-order diffraction of monochromatic x rays from crystal A occurs at an angle of 20° . The first-order diffraction of the same x rays from crystal B occurs at 30° . Which crystal has the larger atomic spacing?

25.3 Photons

FIGURE 25.9 shows three photographs made with a camera in which the film has been replaced by a special high-sensitivity detector. A correct exposure, at the right, shows a perfectly normal photograph of a woman. But with very faint illumination (left), the picture is *not* just a dim version of the properly exposed photo. Instead, it is a collection of dots. A few points on the detector have registered the presence of light, but most have not. As the illumination increases, the density of these dots increases until the dots form a full picture.

FIGURE 25.9 Photographs made with increasing levels of light intensity.



The photo at very low light levels shows individual points, as if particles are arriving at the detector.

The particle-like behavior is not noticeable at higher light levels.

Increasing light intensity