

2.3: Atomic Spectroscopy and the Bohr Model

The discovery of the particle nature of light began to break down the division that existed in nineteenth-century physics between electromagnetic radiation, which was thought of as a wave phenomenon, and the small particles (protons, neutrons, and electrons) that compose atoms, which were thought to follow Newton's laws of motion. Just as the photoelectric effect suggested the particle nature of light, certain observations about atoms began to suggest a wave nature for particles. The most important of these observations came from *atomic spectroscopy*, the study of the electromagnetic radiation absorbed and emitted by atoms.

Atomic Spectra

When an atom absorbs energy—in the form of heat, light, or electricity—it often re-emits that energy as light. For example, a neon sign is composed of one or more glass tubes filled with neon gas. When an electric current is passed through the tube, the neon atoms absorb some of the electrical energy and re-emit it as the familiar red light of a neon sign. If the atoms in the tube are different (that is, not neon), they emit light of a different color. In other words, atoms of each element emit light of a characteristic color. Mercury atoms, for example, emit light that appears blue, helium atoms emit light that appears violet, and hydrogen atoms emit light that appears reddish (Figure 2.10).

Figure 2.10 Mercury, Helium, and Hydrogen

Each element emits a characteristic color.



The red light from a neon sign is emitted by neon atoms that have absorbed electrical energy, which they re-emit as visible radiation.

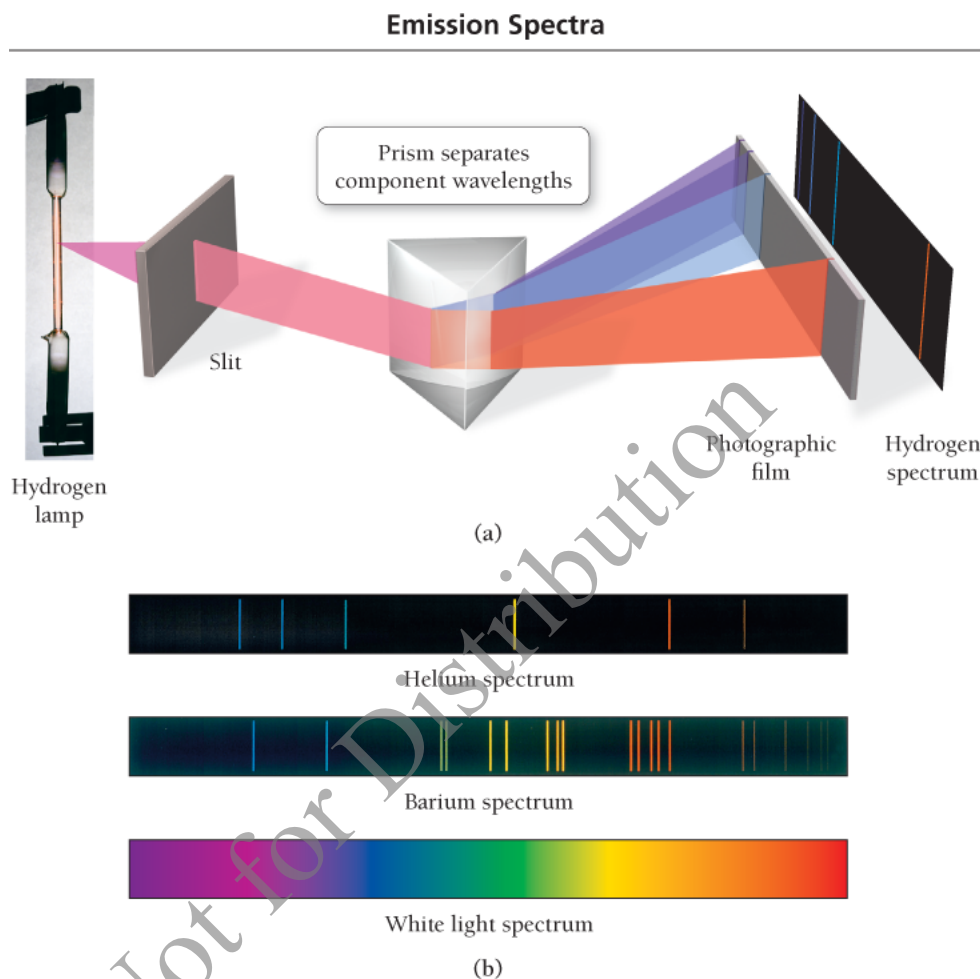
Remember that the color of visible light is determined by its wavelength.

Closer inspection of the light emitted by various atoms reveals that it contains several distinct wavelengths. We

can separate the light emitted by a single element in a glass tube into its constituent wavelengths by passing it through a prism (just like we separate the white light from a light bulb), as shown in [Figure 2.11a](#). The result is a series of bright lines called an **emission spectrum**. The emission spectrum of a particular element is always the same—it consists of the same bright lines at the same characteristic wavelengths—and we can use it to identify the element. For example, light arriving from a distant star contains the emission spectra of the elements that compose the star. Analysis of the light allows us to identify the elements present in the star.

Figure 2.11 Emission Spectra

(a) The light emitted from a hydrogen, helium, or barium lamp consists of specific wavelengths, which can be separated by passing the light through a prism. (b) The resulting bright lines constitute an emission spectrum characteristic of the element that produced it.



Notice the differences between the white light spectrum and the emission spectra of hydrogen, helium, and barium in [Figure 2.11b](#). The white light spectrum is *continuous*, meaning that there are no sudden interruptions in the intensity of the light as a function of wavelength—the spectrum consists of light of all wavelengths. The emission spectra of hydrogen, helium, and barium, however, are not continuous—they consist of bright lines at specific wavelengths, with complete darkness in between. That is, only certain discrete wavelengths of light are present. Classical physics could not explain why these spectra consisted of discrete lines. In fact, according to classical physics, an atom composed of an electron orbiting a nucleus should emit a continuous white light spectrum. Even more problematic, the electron should lose energy as it emits the light and spiral into the nucleus. According to classical physics, an atom should not even be stable.

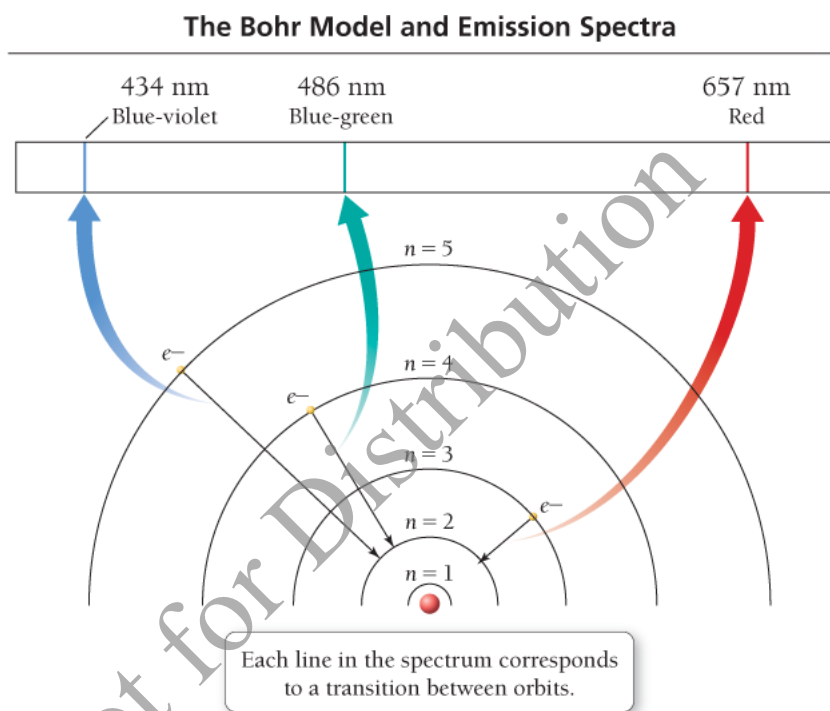
Johannes Rydberg, a Swedish mathematician, analyzed many atomic spectra and developed an equation that predicts the wavelengths of the hydrogen emission spectrum. Although these predictions are accurate, Rydberg's equation gives little insight into *why* atomic spectra are discrete, *why* atoms are stable, or *why* his equation works.

The Rydberg equation is $1/\lambda = R(1/m^2 - 1/n^2)$, where R is the Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$), and m and n are integers.

The Bohr Model

The Danish physicist Niels Bohr (1885–1962) attempted to develop a model for the atom that explained atomic spectra. In his model, electrons travel around the nucleus in circular orbits (analogous to those of the planets around the sun). However, in contrast to planetary orbits—which can theoretically exist at any distance from the sun—Bohr’s orbits exist only at specific, fixed distances from the nucleus. The energy of each Bohr orbit is also fixed, or quantized. Bohr called these orbits *stationary states* and suggested that, although they obey the laws of classical mechanics, they also possess “a peculiar, mechanically unexplainable, stability.” We now know that the stationary states were really manifestations of the wave nature of the electron, which we will expand upon shortly. Bohr further proposed that, in contradiction to classical electromagnetic theory, no radiation is emitted by an electron orbiting the nucleus in a stationary state. It is only when an electron jumps, or makes a *transition*, from one stationary state to another that radiation is emitted or absorbed (Figure 2.12).

Figure 2.12 The Bohr Model and Emission Spectra for the Hydrogen Atom



The transitions between stationary states in a hydrogen atom are quite unlike any transitions that we might be familiar with in the macroscopic world. The electron is *never* observed *between states*; it is observed only in one state or another. The emission spectrum of an atom consists of discrete lines because the stationary states exist only at specific, fixed energies. The energy of the photon emitted when an electron makes a transition from one stationary state to another is the energy difference between the two stationary states. Transitions between stationary states that are closer together, therefore, produce light of lower energy (longer wavelength) than transitions between stationary states that are farther apart.

In spite of its initial success in explaining the line spectrum of hydrogen, the Bohr model left many unanswered questions. It did, however, serve as an intermediate model between a classical view of the electron and a fully quantum-mechanical view, and therefore has great historical and conceptual importance. Nonetheless, it was ultimately replaced by a more complete quantum-mechanical theory that fully incorporated the wave nature of the electron. We examine this theory in Section 2.4.

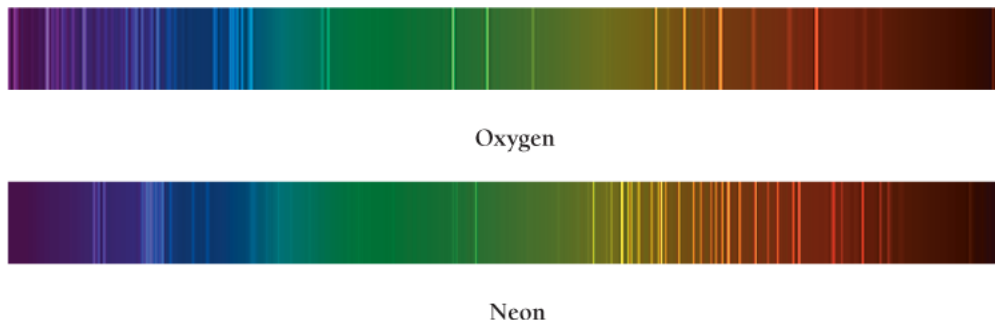
Atomic Spectroscopy and the Identification of

Elements

When you check out of the grocery store, a laser scanner reads the barcode on the items that you buy. Each item has a unique code that identifies it and its price. Similarly, each element in the periodic table has a spectrum unlike that of any other element. [Figure 2.13](#) shows the emission spectra of oxygen and neon. (In [Figure 2.11](#), we saw the emission spectra of hydrogen, helium, and barium.) Each spectrum is unique and, as such, can be used to identify the substance.

Figure 2.13 Emission Spectra of Oxygen and Neon

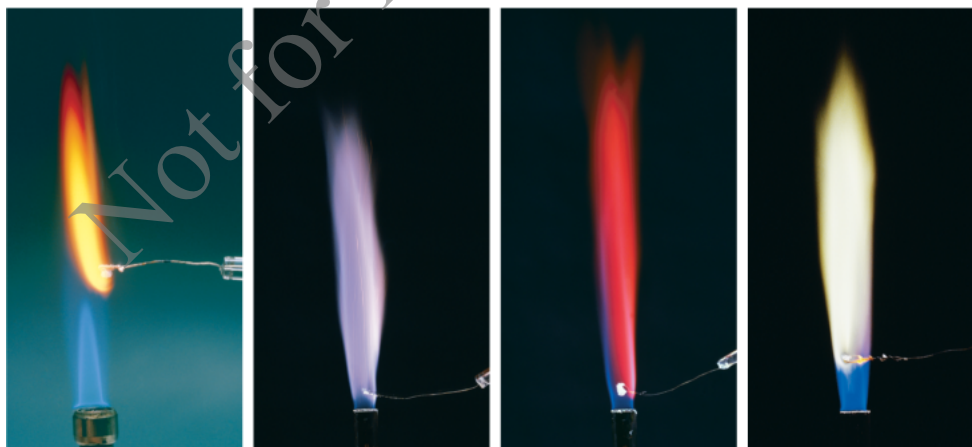
The emission spectrum of each element is unique, and we can use it to identify the element.



The presence of intense lines in the spectra of a number of metals is the basis for *flame tests*, simple tests used to identify elements in ionic compounds in the absence of a precise analysis of a compound's spectrum. For example, the emission spectrum of sodium features two closely spaced, bright yellow lines. When a crystal of a sodium salt (or a drop of a solution containing a sodium salt) is put into a flame, the flame glows bright yellow ([Figure 2.14](#)). As [Figure 2.14](#) shows, other metals exhibit similarly characteristic colors in flame tests. Each color represents an especially bright spectral emission line (or a combination of two or more such lines). Similar emissions form the basis of the colors seen in fireworks.

Figure 2.14 Flame Tests for Sodium, Potassium, Lithium, and Barium

We can identify elements by the characteristic color of the light they produce when heated. The colors derive from especially bright lines in their emission spectra.



Although the *emission* of light from elements is easier to detect, the *absorption* of light by elements is even more commonly used for purposes of identification. Whereas an emission spectrum consists of bright lines on a dark background, an **absorption spectrum** consists of dark lines on a bright background ([Figure 2.15](#)). An absorption spectrum is measured by passing white light through a sample and observing what wavelengths are *missing* due to absorption by the sample. Notice that, in the spectra of mercury in [Figure 2.15](#), the absorption lines are at the same wavelengths as the emission lines. This is because the processes that produce them are mirror images. In emission, an electron makes a transition from a higher-energy level to a lower-energy one. In absorption, the transition is between the same two energy levels, but from the lower level to the higher one.

Figure 2.15 Emission and Absorption Spectrum of Mercury

Elements absorb light of the same wavelengths that they radiate when heated. When these wavelengths are subtracted from a beam of white light, the result is a pattern of dark lines corresponding to an absorption spectrum.



Fireworks typically contain the salts of such metals as sodium, calcium, strontium, barium, and copper. Emissions from these elements produce the brilliant colors of pyrotechnic displays.

Absorption spectrometers, found in most chemistry laboratories, typically plot the intensity of absorption as a function of wavelength. Such plots are useful both for identifying substances (qualitative analysis) and for determining the concentration of substances (quantitative analysis). Quantitative analysis is possible because the amount of light absorbed by a sample depends on the concentration of the absorbing substance within the sample. For example, the concentration of Ca^{2+} in a hard water sample can be determined by measuring the quantity of light absorbed by the calcium ion at its characteristic wavelength.

Not for Distribution