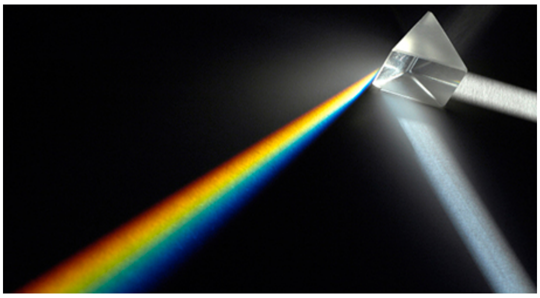
Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*



Unit Overview

Using light as a probe, scientists found innovative ways to make inferences about the inner structure of the atom. In this unit, we will follow the gradual change from considering the atom as a single indivisible particle to a later understanding of the atom composed of its constituent subatomic parts, including the electron, the first subatomic particle to be discovered, the proton, and the neutron. This new picture of matter lead to the development of the quantum model of the atom, as well as ways to identify traces of chemical elements, whether on Earth, in the Sun, or in a distant galaxy.

by Louisa Morrison

Sections

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Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 1: Introduction

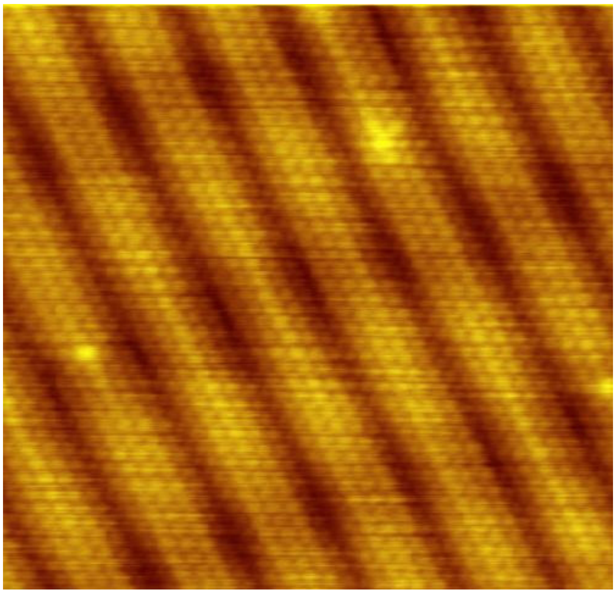


Figure 3-1. Image of a Gold Surface Taken with a Scanning Tunneling Microscope (STM)

Image of gold [Au (100)] surface created by using a scanning tunneling microscope (STM). The individual atoms are visible. Techniques such as STM allow scientists to learn about the inner structure of atoms and their components.

Atoms are tiny: A million of them fit across a human hair. At this minuscule size, they are not visible to the human eye; the closest we can get to "seeing" individual atoms is with the scanning electron microscope, which can create images of matter at the atomic scale—outlining the shapes of individual atoms. Atomic scientists have found innovative ways of using observable phenomena to make inferences about the inner structure of the atom over the years. Gerd Binnig (born 1947) and Heinrich Rohrer (1933–2013), the Nobel Prize-winning inventors of the scanning tunneling microscope, allowed the atom to be visualized. (Figure 3-1) In this unit, we will follow the gradual change from considering the atom as a single indivisible particle to a later understanding of the atom composed of its constituent subatomic parts. This revolution in understanding the atom, which began in the late 19th century and continued through the first decades of the 20th century, is key to today's science and technology: electricity and electronics, nuclear power, atomic clocks, and many other inventions.

Before the late 19th century, chemists had no methods for probing the inner structure of the atom, so they assumed that the atom was indivisible—just as described by John Dalton early in the century. Gradually, scientists developed new techniques to probe the atom, and they used these phenomena to make inferences about the inner structure of the atom and its components. What we call "**subatomic**

particles"—electrons, protons, and neutrons—were discovered in breakthrough investigations starting in the 1870s. The astonishing detail made visible by the scanning tunneling microscope is just one of the results of a long series of experiments that have culminated in the modern model of the atom, which continues to evolve today.

Glossary

Subatomic particles

The particles into which an atom can be split.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 2: The Electron

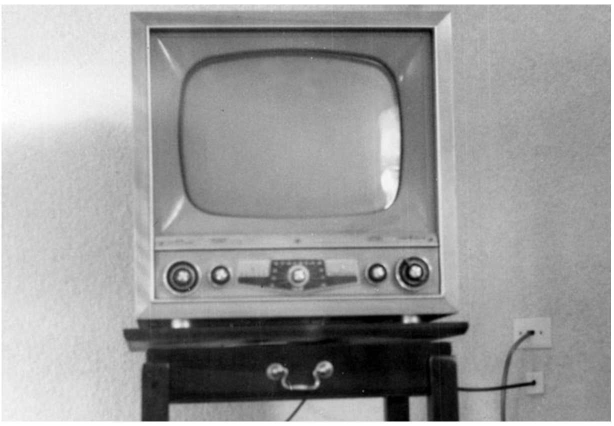


Figure 3-2. Cathode Ray Tube Television, ca. 1953

Cathode ray tubes found their greatest use in television sets and computer monitors. Inside the CRT, a tightly focused beam of electrons, steered by electromagnets, hits a detector on the inside face of the tube, which glows and creates the image as the beam is scanned quickly across and up and down over the detector. In color televisions, three separate beams light up red, green, and blue detectors. Today, cathode ray tubes are being replaced by sleeker flat screen technology.

The first indication that the atom could be divided into smaller parts stemmed from experiments with an early precursor to neon signs and televisions—**cathode ray tube** (CRT). (Figure 3-2) Sir Joseph John (J.J.) Thomson (1856–1940), a British-born physicist, sought to understand the glowing beam created within a CRT, and his experimentation resulted in the discovery of the electron.

In the late 1800s, scientists experimented by running high-voltage electricity through sealed glass tubes, which had been outfitted with two metal electrodes that pass through the glass casing and are separated by a distance of a few centimeters. When most of the air has been pumped out, and the electricity is applied, electrons are ejected from the negative electrode inside the tube and accelerate as they approach the positive electrode. When the high-speed electrons hit a detector screen placed inside the tube, they create a glow, making their path visible. The beam was called a "cathode ray" because its direction of travel was from the negative connector (the cathode) to the positive one; scientists called this apparatus a "cathode ray tube." When objects were placed in the path of the beam, they cast a shadow, providing evidence that some form of matter was passing through the tubes. (Figure 3-3)

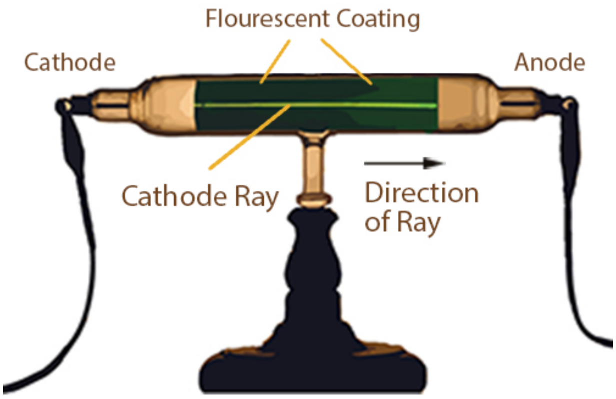


Figure 3-3. Cathode Ray Tube

When high-voltage electricity is applied across the electrodes at either end of the tube, electrons are knocked off gas molecules inside the evacuated tube and travel toward the positive anode. Inside the tube, this stream of electrons hits a specially coated screen and is visible as a bright line. Early cathode ray tubes were perfected by the British physicist, William Crookes and further developed by J.J. Thomson.

Thomson named these particles "corpuscles." (Later, the scientific community decided to use a previously coined term: "electron.") Thomson inferred that his electrons are a part of every atom. He tried making the electrodes out of different metals, and they always produced the same results: a glowing beam. Then, he tried deflecting the beam and discovered that the beam curved in response to both magnets and electric fields. This supported the idea that the particles in the beam were negatively charged.

As a physicist, Thomson assumed that electrons emit light only when they are in motion. Since matter does not always glow, he devised a model of matter, which he called the "Plum Pudding Model," in which the electrons are evenly distributed and held in place by a positive pudding-like "goo." (Figure 3-4)

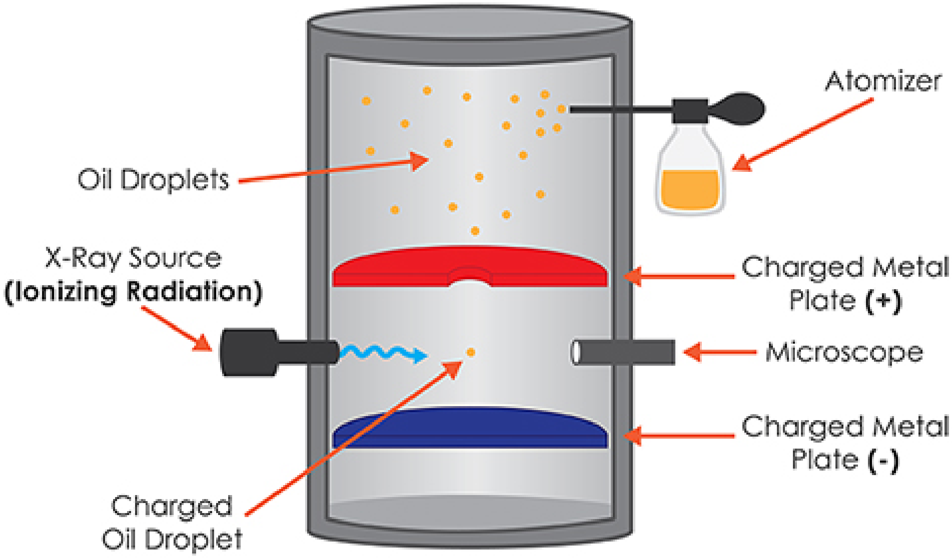
Figure 3-4. Plum Pudding Model of the Atom

The brown pudding is the positively charged substance that keeps the raisins, or electrons, in place. The positive forces push on all sides of the electrons, keeping them stationary.

Thomson's discovery of the electron was an enormous accomplishment because, for the first time, the atom was determined not to be the smallest indivisible particle of matter, but rather the atom itself had smaller, or subatomic, components. Thomson was not able to determine the mass or charge of the particle independently. However, using the deflection of the beam by an electric field, Thomson *was* able to measure the electron's mass-to-charge ratio.

Robert Millikan's Oil Drop Experiment

The technique for measuring the mass of an electron using tiny drops of oil was first perfected by the American physicist, Robert Millikan, and his student, Harvey Fletcher, in 1909. Inside an experimental chamber, a perfume atomizer created a fine spray of oil whose droplets could be watched with a light microscope. An X-ray source ionized the air in the chamber and created free electrons, which in turn, attached themselves to the oil droplets. As the individual drops fell by gravity through a small opening into a space between two charged plates, their behavior was observed closely.



Simplified scheme of Millikan's oil drop experiment. © Science Media Group.

By observing the droplets behavior without the electric field, the size and mass of the oil droplet could be determined. Once in between the two plates, they saw two opposing forces at work: gravity pushing the oil droplet down and the electric field pushing the oil droplet up. When the electric field was on, they adjusted to different values until the droplet stopped moving and the forces equaled each other.

Over the course of many, many trials of the experiment, Millikan and his graduate students found that the charge on the oil droplets was always approximately a multiple of 1.6 x 10-19 coulombs, the standard unit of electric charge. Once Millikan determined the charge, he was able to use Thomson's measurement of the mass-to-charge ratio to calculate the mass of an electron.

Millikan was not the first to think of studying charged droplets in an electric field, but he was the only one to think of studying oil drops rather than water drops. Other scientists ran similar experiments, but found that water would evaporate before the procedure finished. Millikan and his students worked painstakingly from 1908 to 1917 on the problem of the exact charge of the electron. He was awarded the Nobel Prize in Physics in 1923, even though there has been some controversy over his data. We now know that he selected certain trials to use in his published paper, so his data appeared more accurate and precise than it really was.

By 1897, Thomson could conclude that the cathode rays were composed of particles more than 1,000 times smaller than the lightest atom, hydrogen. Another scientist, Robert Millikan, taking advantage of Thomson's calculated mass-to-charge, used the deflection of tiny drops of oil in another experiment to determine exact values of the mass and charge of an electron.

Glossary

Cathode ray tube

An evacuated tube with two electrodes inside it. High voltage electricity is applied to the negative electrode, creating a stream of electrons that travel to the positive electrode.

Electrons

Negatively charged subatomic particles.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 3: The Nucleus

In 1911, two years after the measurement of the mass and charge of the electron, Ernest Rutherford (1871–1937), a New Zealand native and protégé of Thomson, began experiments to explore the atom and the reigning plum pudding model by bombarding a thin gold foil with fast-moving particles. The results of the famous gold foil experiment provided new evidence that would lead to new discoveries and the need for a new model for the atom.

Rutherford's research, conducted at the Cavendish Laboratory at the University of Cambridge, focused on radioactive elements, such as radium, thorium, and uranium, and the particles emitted by them. Radioactive elements are unstable, and when they undergo radioactive **decay**, they change into other elements. (For more on radioactive decay, see Unit 12.) In the process, they emit one or more types of particles. For example, the decay of some heavy elements, such as radium, emits **alpha particles**. In alpha decay, the particles are ejected at high speed and can travel a few centimeters in air but can easily be stopped by a sheet of paper.

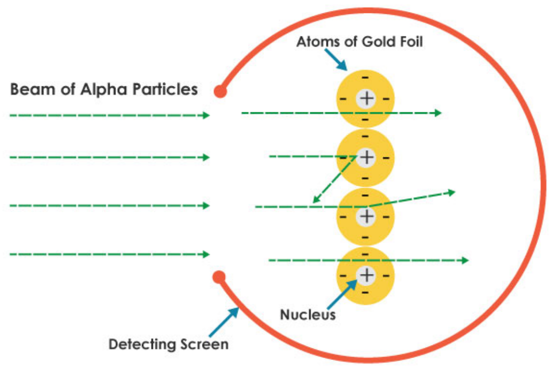


Figure 3-5. Rutherford's Gold Foil Experiment

Rutherford expected the alpha particles to pass through the Plum Pudding Model of the atom undisturbed, but he observed that a small portion of the particles were deflected, indicating a small, concentrated positive charge.

Rutherford and his students, Hans Geiger and Ernest Marsden, used a source of alpha particles to bombard a target of an extremely thin piece of gold, which was surrounded by a detector that would indicate when it was struck by the alpha particles. Even though the foil had a thickness of 20,000 atoms, according to the plum pudding model, the alpha particles should pass right through the foil without any deflection. Rutherford explained this by hypothesizing that the diffuse positive charge of the "goo" would not have been strong enough to repel the alpha particles. When they ran the experiment, most of the particles did travel directly from their source in a line straight through the gold foil. However, to their astonishment, for about 1 out of 8,000 particles, Rutherford and his team discovered that the alpha particles were deflected from their straight path by over 90 degrees. From this observation, they proposed a new theory that the atom must be mostly open space with a heavy and dense region of positive charge in the middle. It had to be positive because it repelled the positively charged alpha particles. Forever putting to rest the plum pudding model, Rutherford is reported to have said about their discovery, "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

In effect, by sending this beam of fast-moving, relatively heavy positive particles through the foil, and finding that a certain number were strongly deflected, Rutherford had probed inside the atom and found a deep, dense core that had previously been undetected. In 1912, Rutherford named this small, dense area of positive charge the "**nucleus**." His new model of the atom placed most of the atom’s mass and all its positive charge in this tiny, dense nucleus, which is surrounded by much smaller, negatively charged particles (the electrons) occupying mostly empty space. Rutherford did not know what was in the nucleus exactly, just that it had to be small, densely heavy, and positive. Later experiments would define the nucleus more precisely.

Glossary

Alpha particle
A product of nuclear decay that is two protons and two neutrons, which form a particle with a structure identical to that of a helium nucleus with a charge of +2.

Decay
Occurs when the nucleus of an unstable atom disintegrates, emitting radiation (such as alpha particles, beta particles, or positrons) causing the atom to lose energy and become a different isotope.

Nucleus
The core of the atom, which consists of protons and neutrons. The diameter of the nucleus is extremely small relative to the diameter of the entire atom, which includes its electron cloud. The number of protons in the nucleus determines which element the atom is.

CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 4: Inside the Nucleus—Protons and Neutrons

Rutherford's gold foil experiment showed that the atom has a dense area of positive charge at the center, but it would take further investigations to discover exactly what was inside the nucleus. Unlike the previous discoveries of the electron and the nucleus, these new particles were theorized first, then gradually confirmed through a series of experiments.

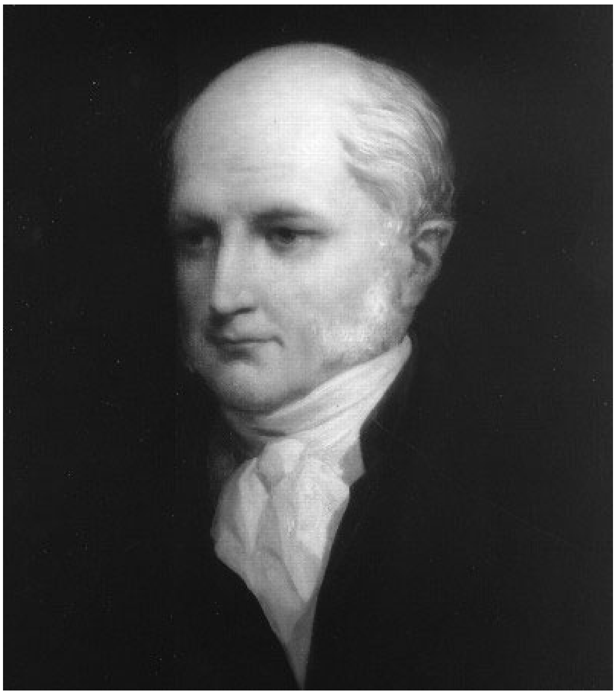


Figure 3-6. English Chemist William Prout

William Prout was born in Gloucestershire, England, and practiced medicine in London. At the same time, he found time to conduct experiments in chemistry and compared the densities of different elements in their gaseous form at the same temperature and pressure. He discovered that the density of most of the elements he tested were multiples of the density of hydrogen, from which he inferred that the atomic weights of the heavier elements must also be multiples of the atomic weights of hydrogen as well. He is remembered today mainly for what is called Prout's hypothesis.

Near the beginning of the 19th century, the English chemist William Prout (1785–1850) pointed out that the atomic masses of all the elements seemed to be multiples of a particular fundamental particle, which he called the "protyle." The protyle, which has the same mass as hydrogen, was declared to be the building block of all elements. While more accurate measurements of atomic mass seemed to cast doubt on this hypothesis, Prout's theory was an influence on Rutherford, who, in 1917, set up a series of experiments to see if he could separate atoms into smaller components. Rutherford's chosen technique was to knock particles out of different gases by bombarding them with alpha particles.

Rutherford initially set up a source of alpha particles to target a chamber filled with hydrogen. He and his team observed that the collisions produced a new particle that traveled much farther than the original alpha particles—leading to the conclusion that it had a smaller mass than the alpha particle. These same particles resulted when they filled the chamber with other light elements such as nitrogen, fluorine, and phosphorous. Since the new particle, which was found to have a positive charge as well, had an identical signature on their detectors as a hydrogen nucleus, they hypothesized that this particle must be the same as a hydrogen atom's nucleus. Since this particle was knocked out of the nuclei of all of the elements on which they tried this experiment, Rutherford and his colleagues concluded that every atom must contain these positive particles in the nucleus.

In 1919, Rutherford officially announced this discovery—a new subatomic particle with a mass 1,800 times greater than an electron's and a positive charge that was the same size but opposite sign to the electron's charge. He named it the **proton**, a nod perhaps to Prout's protyle. The proton, one of which is found in the hydrogen atom, is found in multiple numbers in all the other elements. We recognize the proton today as one of the building blocks of the atomic nucleus and the basis of the positive charge found in the nucleus of all atoms.

Between Rutherford's discoveries of the nucleus and the proton, scientists began to notice clear patterns in how big the positive charge was on the nucleus. Antonius van den Broek (1870–1926) was an amateur physicist who was the first to notice this. He said each element had a different charge on its nucleus, and then in later experiments by Henry Moseley (1887–1915), it was confirmed. Moseley called this unique number *Z*, the atomic number for an element. With Rutherford's discovery of the proton, it became clear that this atomic number was the number of protons in the nucleus. (Moseley will be covered in more depth in Unit 4.)

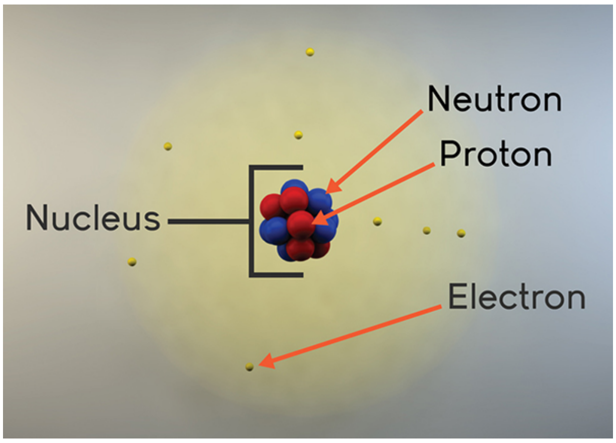


Figure 3-7. The Atom That Chadwick Proposed with the Neutron

Following his work in Rutherford's lab at Cambridge, British physicist James Chadwick won the 1935 Nobel Prize in Physics for his 1932 discovery of the neutron.

The **neutron** was the last major subatomic particle to be discovered. Experiments showed that, except for hydrogen, there were fewer protons in the nucleus than in the atomic mass. This means that, assuming a proton has a mass of one, each element, if it had only protons in the nucleus, would have a mass that matched its atomic number. Helium, for example, has two protons, but an atomic mass of four. Rutherford, in fact, predicted the existence of the neutron fairly soon after discovering the proton, but he postulated that it was simply a proton and an electron paired up inside the nucleus whose net electrical charge added up to zero.

In the decades after World War I, scientists continued to experiment with different types of radiation. In 1931, Walther Bothe (1891–1957) and his student, Herbert Becker, in Germany discovered that when alpha particles bombarded light elements, such as beryllium, lithium, or boron, an unusually penetrating radiation was produced. James Chadwick (1891–1974), a former student of Ernest Rutherford, investigated this new type of radiation and determined that it consisted of a beam of neutral particles, which have a high penetrating power because they are not repelled by the nucleus as are alpha particles. These three particles—electrons, protons, and neutrons—together serve as the subatomic building blocks of the atom.

Discovery of the Neutron Made the Atomic Bomb Possible

After Chadwick discovered the neutron, beams of neutrons were targeted at uranium atoms, which triggered the uranium atoms to split. This, in turn, released more neutrons. One of the early hurdles for the scientists in developing an atomic bomb was to successfully create a chain reaction, whereby the products of the first reaction then cause subsequent reactions. In World War II, Chadwick led the British collaboration with the Manhattan Project, the Americans' secret atomic bomb development program.

To summarize: The electron is light and negatively charged, and exists in a region outside the nucleus. Most of the mass of an atom consists of the protons and neutrons—each one of which is approximately 1,800 times more massive than an electron. This places most of the mass, and all the positive charge, inside the nucleus. In a neutral atom, the numbers of protons and electrons is equal, so the total charge balances out. Finally, within the nucleus, the number of neutrons can be anywhere from zero to almost double the number of protons, though there are almost always more neutrons than protons in the nucleus. As we shall see in the next unit, for many elements, the number of neutrons can vary, even for one specific number of protons. These variants of the different elements are called "**inertia**."

The discovery of the neutron was an important milestone in the long investigations leading to the modern concept of the atom, but it was by no means enough on its own to complete the story. For that, we have to look again at the electron and its interactions with light to bring into focus the rest of the picture: the quantum view of the atom.

Glossary

Inertia
The measure of an object's reluctance to accelerate under an applied force.

Neutron
A subatomic particle with no net electric charge that combines with protons to form the nucleus of the atom. The number of neutrons in an atom determines the isotope of the element.

Proton
A positively charged subatomic particle that combines with neutrons to form the nucleus of the atom. The number of protons in the nucleus uniquely determines which specific element that atom is.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 5: The Electromagnetic Spectrum

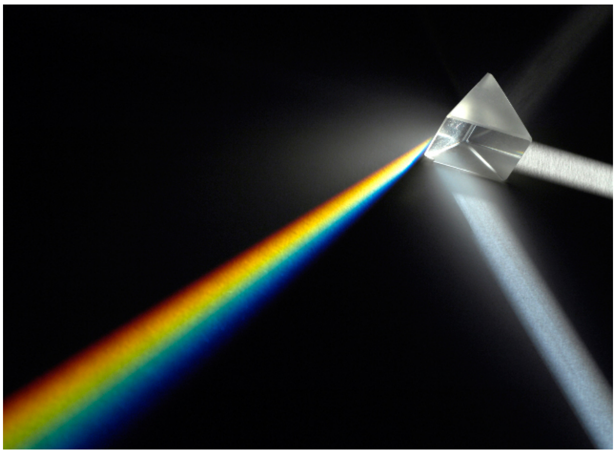


Figure 3-8. A Prism Makes Visible the Rainbow of Colors Present in White Light

A triangular glass prism, similar to the one used by Sir Isaac Newton, can be used to divide white light into its constituent colors.

In 1666, Sir Isaac Newton (1642–1727) used a prism to split sunlight into its many colors, and introduced the term "spectrum." This was the first step toward using light as a tool for exploring the inner workings of the atom.

Matter is capable of absorbing or emitting light, and chemists can detect and use this light to understand what is happening on the atomic level. The study of matter by means of the light that it gives off or absorbs is called "**spectroscopy**." The field of spectroscopy began in 1814 with the invention of the spectroscope, a device for seeing and measuring the brightness of types of light. The spectroscope was invented by German optician Joseph von Fraunhofer (1787–1826). (His work is described in more detail in the sidebar.)

Figure 3-9. Joseph von Fraunhofer in His Laboratory

A spectroscope has an optical system that isolates a source of electromagnetic radiation and then splits that source into its component frequencies, allowing the relative brightness of each to be compared and recorded. Most spectroscopes are calibrated to known light sources; modern-day spectroscopes are essential tools in chemical analysis, in astronomy, and in industry.

However, the Sun produces other wavelengths of light, which are invisible to the human eye, and unsurprisingly these forms of light were discovered much later than visible light. In order to categorize light, we need to understand that light is the more common name for "**electromagnetic radiation**." Also, all electromagnetic radiation can be described as being a wave, and thus has interesting properties that come from that. There are three main properties of electromagnetic radiation that can vary: energy (E), frequency (v), and wavelength (λ). Wavelength and frequency are **inversely proportional**; long wavelengths correspond to high frequencies and vice versa. Energy is directly proportional to frequency; the higher the frequency, the larger the energy. Gamma rays are high-energy waves that are emitted during certain types of nuclear reactions, whereas radio waves have long wavelengths and are completely safe to humans.

In addition to gamma rays and radio waves, two other forms of light exist: **infrared** (which has a longer wavelength than visible light) and **ultraviolet** (which has a shorter wavelength than visible light). In fact, the electromagnetic spectrum is a continuum that includes radio waves at the long wavelength end, through microwaves, infrared, visible light, ultraviolet, X-rays, and, finally, to gamma rays at the shortest wavelength end. Nonetheless, one characteristic of all types of radiation is that they have the same speed in a vacuum, approximately 3×10^8 meters per second, which is equivalent to about 700 million miles per hour.

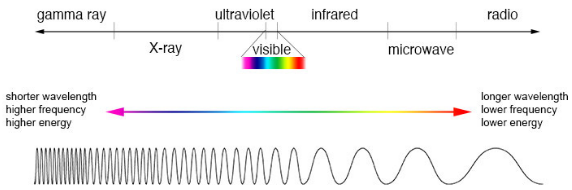


Figure 3-10. Electromagnetic Spectrum

A diagram of the electromagnetic spectrum showing the regions of the spectrum in order by increasing energy (decreasing wavelength). Notice that as the wavelengths get shorter, the frequency of the waves (how often the waves pass) increases .

While we often refer to radio signals by their frequencies, it's more customary to refer to visible light by its wavelength. Knowing the **speed of light**, and the wavelength of the light under consideration, allows the calculation of its frequency. Visible light occupies the part of the electromagnetic spectrum from 400 to 800 nanometers (nm), where a nanometer is one-billionth of a meter. The longest visible wavelengths—800 nm—are red, and the shortest—400 nm—are violet; wavelengths shorter than 400 nm are ultraviolet; those longer than 800 nm are infrared.

Microwaves

One of the portions of the electromagnetic spectrum contains microwaves. Microwave ovens are a popular method of cooking food quickly. First, the microwaves are absorbed by water molecules that cause them to vibrate. These vibrating water molecules bump into the food molecules. This kinetic energy of motion is converted into thermal energy, and the temperature increases.

Microwave. © Wikimedia Commons, CC License 3.0. Author: Mk2010, 15 October 2011.

The added heat cooks and warms up the food. This also means that food must have a reasonable amount of moisture in it for a microwave to be able to heat it up. Microwaves are able to pass through many materials, such as ceramic or plastic, but are reflected by metal. Microwave ovens have benefits over conventional ovens, for example, cooking less dense materials evenly and quickly. In a conventional oven, the heat has to be conducted inward from the outside.

The shorter the wavelength, the more energetic is the emitted energy. For example, a mixture of hydrogen and oxygen gas will not explode when exposed to visible light, but shining ultraviolet light on a container of oxygen and hydrogen will trigger the reaction. Likewise, exposing one's skin to bright light by itself will not cause skin damage, but exposure to ultraviolet light can cause tanning, sunburn, and in some cases skin cancer.

Glossary

Electromagnetic radiation

Radiation that is emitted and moves in a wave-like shape. It is synonymous with the word "light."

Infrared

A form of electromagnetic radiation that falls between the visible light and microwave areas of the electromagnetic spectrum. Infrared light is further divided into "far," "mid," and "near" regions. Far infrared light is thermal, and we experience it as heat. Near infrared waves are used in fiber optic telecommunications.

Inversely proportional

Two variables are inversely proportional to each other if as the value of one variable increases, the value of another variable decreases at the same rate.

Spectroscopy

The study of light being absorbed or emitted by matter.

Speed of light

The speed of light in vacuum is 299,799,458 meters per second, and is the maximum speed any energy or matter can travel.

Ultraviolet

A form of electromagnetic radiation that falls between X-rays and visible light. Ultraviolet radiation from the sun is filtered through the Earth's atmosphere, mitigating its harmful effects on human health, yet the small fraction that penetrates the atmosphere can cause skin damage and cancer.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 6: Light from Elements

Fireworks, which date back more than 1,000 years, are enjoyed by people worldwide to celebrate a new year, an anniversary, or a victory. The Chinese, who invented fireworks in the 7th century CE, knew that the many colors produced by fireworks come from different chemical compounds. It would not be until the second half of the 19th century that scientists would have the tools to understand the elements present in these compounds and have the skills to observe the light that they produced. This combination led scientists to learn more about the structure of the atom for each element in terms of the behavior of its electrons, which are actually responsible for the light the elements are creating.

Figure 3-11. Fireworks Display

Fireworks manufacturers use a range of compounds to take advantage of the striking colors created by the different elements. For example, strontium compounds are used to create the bright red colors in fireworks. Other colors can be created by more common elements so that sodium compounds create the yellow fireworks, and copper compounds make the blue-green ones. These colors are visible evidence of the behavior of electrons in atoms as energy is added into an atom, but this connection took almost two centuries of investigation to uncover.

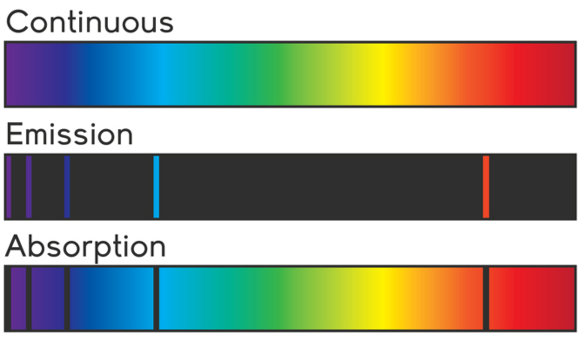


Figure 3-12. Three Different Types of Spectra

In a continuous spectrum, instead of one or more bright lines, there is a broad range of colors. This is the kind of spectrum produced by a hot, glowing object, such as an incandescent light bulb or a coil on a stove. In a line spectrum or emission spectrum, signature bright lines at certain colors are produced by the different elements. This is the kind of spectrum produced by a flame test or gas discharge tube. In an absorption line spectrum, the light from a continuous source travels through a gas or other transparent material, and the atoms and molecules of that material absorb light at specific wavelengths, producing a dark line, but the remainder of the continuous spectrum passes through. Note that for the same element, the emitted wavelengths of light should match perfectly with the dark spaces, or absorbed wavelengths.

In the 1800s, scientists used increasingly sophisticated spectroscopes to closely examine the pattern of light given off by many different processes. The way this light spectrum looked could be categorized in one of three ways shown in Figure 3-12. In the middle of the 19th century, two German scientists, Gustav Kirchhoff (1824–1887) and Robert Bunsen (1811–1899), collaborated at the University of Heidelberg to study spectroscopy. Kirchhoff and Bunsen realized that when they placed very pure samples of specific elements in a flame, they always saw the same colors and emission spectra through their spectroscope. They categorized the spectra of several elements (sodium, lithium, and potassium) and, expanding their tests further, saw unique, deep blue lines in a sample of mineral water from Dürkheim. After concentrating the dissolved salts from 44 metric tons of this water, they had enough to identify a previously unknown element: cesium. Later, they went on to discover the element rubidium using the same method. In effect, each element has its own "spectral signature," one that is constant, no matter how the light is generated. As discussed in the next section, this is an important clue to the electronic structure of the atom.

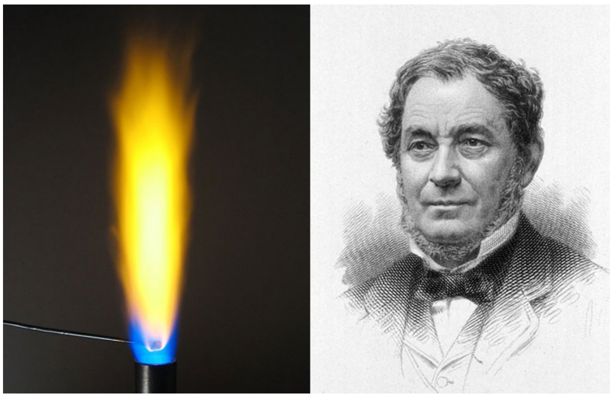


Figure 3-13. Robert Bunsen and the Bunsen Burner

Left panel: A Bunsen burner is used to create a bright yellow flame by heating a small quantity of table salt. Right panel: Robert Bunsen (1811–1899) was a German chemist whose name is familiar to legions of chemists and chemistry students through his most famous invention, the Bunsen burner, which allowed a hot, clean-burning flame to be created safely in the laboratory. A pioneer in the field of spectroscopy, his tool enabled the identification of several new elements.

In 1868, there was a full solar eclipse that offered a special opportunity to use spectroscopy to analyze the elements present in solar prominences, the large, red flames erupting from the Sun's surface. Observers noted that the prominences were mostly made of hydrogen, but there was a yellow band of light that did not match up with the spectrum of hydrogen or any other element scientists had seen on Earth. Assuming that there was a yet undiscovered element present on the Sun, they named this element "helium" after Helios, the Sun god of the ancient Greeks. It would be another 27 years before helium was identified on Earth.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 7: The Spectral Lines of Hydrogen

Hydrogen, which consists of one proton and one electron, is the simplest atom. Conveniently, it also has the simplest emission spectrum of any element. In the late 1800s and early 1900s, the spectrum of hydrogen was closely studied to try to find a mathematical relationship between the wavelengths of the emission lines in order to make a better model of the atom. Early workers in spectroscopy looked at the visible emission of hydrogen and noticed that there is always one purple line, two blue lines, and one red line.

Figure 3-14. Spectral Lines of Hydrogen

The fact that hydrogen atoms emit or absorb radiation at a limited number of frequencies implies that these atoms can only absorb radiation with certain energies. This suggests that there are only a limited number of energy levels within the hydrogen atom. These energy levels are countable. The energy levels of the hydrogen atom are quantized.

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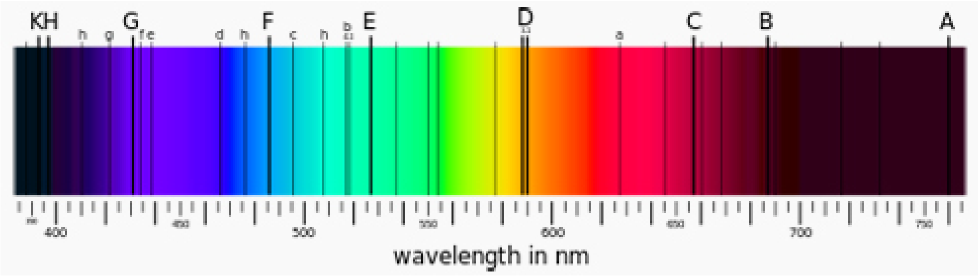
The Swedish physicist, Anders Jonas Ångström (1814–1874), carefully measured these lines, and created a catalog of their locations. In 1885, the Swiss mathematician, Johann Balmer (1825–1898), developed an equation that predicts where the four lines would fall in the visible spectrum by their wavelengths, but he was unable to explain why hydrogen always produces the same distinctive pattern.

When elements are heated or subjected to a high voltage in a gas discharge tube, their emission line spectra can extend into the infrared or ultraviolet as well. Theodore Lyman (1874–1954), an American scientist, studied the hydrogen emission spectra in the ultraviolet range. He discovered the same pattern of lines in the ultraviolet that had been found by Balmer and Ångström in the visible range. Friedrich Paschen (1865–1947), a German physicist, studied the emission of hydrogen in the infrared range, and he also found the pattern. Each of these scientists (Lyman, Balmer, Paschen) has given his name to a series of lines in the hydrogen spectrum.

Fraunhofer Lines

By comparing spectra from different sources, astronomers and chemists saw dark lines representing the light that elements absorbed as the light passed from the star to the Earth. These lines serve as the signatures of the same specific elements in the stars and on Earth.

Joseph von Fraunhofer (1787–1826) used a spectroscope and discovered the thin, dark lines in the spectrum of light created by the Sun and other stars. The absorption spectrum that he observed shows the lines that now bear his name. Fraunhofer lines are clearly visible in this modern version of the solar spectrum derived from observations in the Kitt Peak Solar Atlas. These lines indicate the presence of sodium, iron, oxygen, and many other elements that are also present on Earth.



Fraunhofer Lines. © Wikimedia Commons, Public Domain.

Fraunhofer was the first to examine the spectra of different stars, and noticed that the spectra of bright stars differed from the spectrum produced by the Sun. Since then, the field of astrophysics has applied the laboratory techniques first developed by Fraunhofer, Kirchhoff, and Bunsen more broadly to the study of the universe. By photographing star fields through a prism, Edward Pickering (1846–1919), Annie Jump Cannon (1863–1941), and Williamina Fleming (1857–1911) at the Harvard College Observatory were able to study the lines in the spectra of stars. Based on the different features of the spectra emitted by stars of different sizes and ages, Cannon spent more than 20 years of her life classifying more than 250,000 stars into about 10 categories. She was the first woman to receive a doctorate in science from Oxford University; her classification system, the "Henry Draper Catalog," has been in place since 1922.

In 1888, the Swedish physicist Johannes Rydberg (1854–1919) presented an equation that unified the series of lines described by Balmer, Ångström, and the others by placing integers (n = 1, 2, 3, etc.) into the equation for the lines. Each series corresponded to a different n. However, Rydberg, like the others, did not have a physical explanation for the pattern that he had documented.

Other elements also produced predictable patterns, but were different from hydrogen. For example, helium produces multiple blue and purple lines, one green, one yellow, and one red; unfortunately, no simple equation, like the Rydberg equation, could model what was going on in helium, the second most simple element in the universe. The reasons behind the hydrogen emission spectra remained a mystery for more than 30 years until Niels Bohr (1885–1962), a Danish physicist, solved the puzzle of the emission spectra by developing a new model of the atom. But before we examine that, let us turn to another line of evidence that was perplexing physicists at the turn of the century: the photoelectric effect.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 8: Photoelectric Effect

At the end of the 19th century, a variety of physical processes couldn't be explained using the science and physics that had been used since the time of Isaac Newton. This includes nearly all of the ways that light and matter interact already discussed in this unit, such as the emission spectra of the atoms. It also includes two others that are discussed in this section: the photoelectric effect and blackbody radiation.

The **photoelectric effect** is the name given to the process when light shines on an object made out of an element, and then electrons are emitted from that object, usually in the form of electricity. In a classic photoelectric cell, there is a surface coated with a material such as cesium. When light strikes the surface, some of the electrons are ejected from the atoms and travel through to an electrode, where they are collected. The photoelectric effect is one of the principles exploited in many modern broad-ranging technologies—from the digital imaging devices in cameras and smartphones to motion sensors.

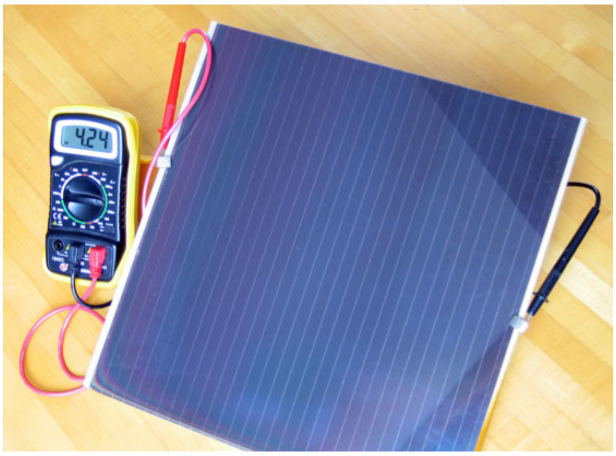


Figure 3-15. Photovoltaic Cell

A demonstration of the conversion of light energy to electric energy in photovoltaic cells by a process similar to the photoelectric effect. When light falls on the silicon material in the cell, electrons are ejected from the silicon atoms, which flow to the metal electrode, causing a measurable current in the meter.

In the late 19th century, the photoelectric effect proved a dilemma for scientists. They had observed that when blue or ultraviolet light strikes the photosensitive surface, a current is created, and the brighter the light, the larger the current. But if red light is used, no matter how bright the light, there is no current. However, as shorter and shorter wavelengths of light are used to strike the surface, at one point, a threshold is reached (in the case of cesium, in the yellow part of the visible spectrum) where the current starts to be detected. Why?

The seed to the solution was planted by Max Planck (1858–1947), a German theoretical physicist whose specialty of study was the field of thermodynamics, a topic that is taken up in more detail in Unit 9. In 1894, when he was a professor at the University of Berlin, he was commissioned by the local electric companies to try to find a way to make more efficient light bulbs. Others had studied the radiation coming off of hot objects, and had found, as any blacksmith knows, that the hotter the object, the shorter the average wavelength of light coming off the object.

Until Planck, no one had been able to come up with a theoretical description to quantify this phenomenon, called "**blackbody radiation**" which is the term for the characteristic continuous spectrum of light that comes from objects at any given temperature. By 1905, it was clear that the existing science, based on classical mechanics predicted an ideal blackbody would radiate infinite power. This clearly doesn't happen; if it did, every time a person turned on a heating coil on a stove, she would get an instantaneous sunburn. Plank found a solution to this anomaly in classical physics, named the "ultraviolet catastrophe." He proposed that if light is emitted not continuously, but in discrete packets of energy called "**photons**," he could explain blackbody radiation. In particular, Planck calculated that the energy of electromagnetic radiation is emitted in packets that are multiples of a very tiny discrete packet of energy, 6.63×10^{-34} J•s, which is now known as Planck's constant (*h*).

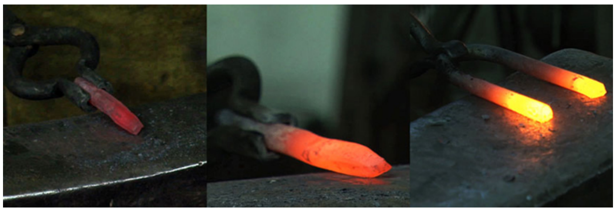


Figure 3-16. Blacksmith Working Iron at Different Temperatures

Three photographs of iron from a blacksmith shop show how the radiation coming off hot objects varies by temperature. On the left, an object is glowing mainly in the infrared (which we can't see) and in the long wavelengths of red light. In the center, we see a hotter object that is glowing orange. Finally, on the right is an object which is much hotter, and it glows bright yellow. Eventually, if the metal were heated to a high enough temperature, it would look like and be called white hot because it would be giving off a full continuous spectrum of light covering the whole visible range. Like the coil on a stove, these pieces of metal are examples blackbodies. Blackbody radiation is the continuous spectrum of energy that is produced by objects that are related to their temperature.

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A common analogy compares quantized energy with the rungs of a ladder. In order to climb the ladder, one must put in enough energy to raise one's foot above the rung. Putting in too little energy will result in no net climb; intermediate levels are not allowed—one can only go up or down in increments of one or more whole rungs. Planck's theory of quantized energy was first presented in 1900 in Berlin at a conference. Planck himself was unsure of the validity of his calculations, but he was proven correct and his work was instrumental for Albert Einstein's (1879–1955) future work on a phenomenon on the photoelectric effect. Planck received the Nobel Prize in 1918.

This discovery—that amounts of energy are quantized, or can only occur in set intervals—revolutionized chemistry and physics, launched the field of quantum mechanics, transformed the classical view of the atom, and led directly to the modern model of the atom which we still use today. Whether or not Planck's discovery led to more efficient light bulbs, his theory of the quantum nature of energy has had huge implications.

Quantum mechanics provides the solution to the problem of the photoelectric effect. In 1905, Albert Einstein connected the dots when he published a paper that linked the quantum energy packets proposed by Planck with the photoelectric effect—in particular, the observation that only light of a certain minimal energy level could eject electrons. If light itself were discrete packets of energy (photons), then Einstein could explain mathematically what was happening. In the end, the take-home message of Einstein's work is this: These photons needed to have enough energy (a low enough wavelength) to create the photoelectric current. The number of photons that strike the surface does not matter if the photons don't have enough energy.

Glossary

Blackbody radiation

A type of electromagnetic radiation that is emitted by a black body (a nonreflective and opaque object at uniform and constant temperature), such as the light emitted by a glowing hot stove coil.

Photoelectric effect

The name given to what happens when light shines on the surface of an element, and then electrons are emitted from it, usually in the form of electricity.

Photon

An elementary particle (a particle lacking substituent parts) and the quantum (smallest unit) of electromagnetic radiation (light).

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 9: The Quantum Model

A Danish physicist, Niels Bohr (1885–1962) came up with the first model for the atom that explained the spectroscopic data that had been collected for the hydrogen atom. This was also the first model that used this idea of quantization, that energies come in these discrete packets of specific sizes. A former student of Ernest Rutherford, he applied the quantum approach to come up with a new structure of the atom. In 1913, Bohr postulated that the electrons orbit the nucleus at specific distances from the nucleus, and each orbit had a different energy associated with it. Each one of these energy levels corresponded to one of Rydberg's integers, with the lowest, n = 1, corresponding to the ground state, or lowest energy level.

When an atom absorbs energy, the electron jumps to a higher energy level. Then, it releases the energy in the form of a photon when it spontaneously falls back down to a lower energy level. One of Bohr's key insights was that an atom cannot absorb or give off energy at just any level. Instead, the energy is absorbed or emitted in discrete amounts, or quanta, as predicted by Max Planck. Bohr proposed that the lines in the emission spectrum of hydrogen correspond to specific changes in the energy of its sole electron. With only one electron, the hydrogen atom's electron had a very limited number of energy levels to jump between, and only four of those energies fell in the visible spectrum, which were those four colored lines in the Balmer series. Because these atoms can absorb light and jump up to higher levels or they can get excited to higher levels and fall back down and emit light, both emission and absorption spectra can be explained for hydrogen with the Bohr model of the atom.

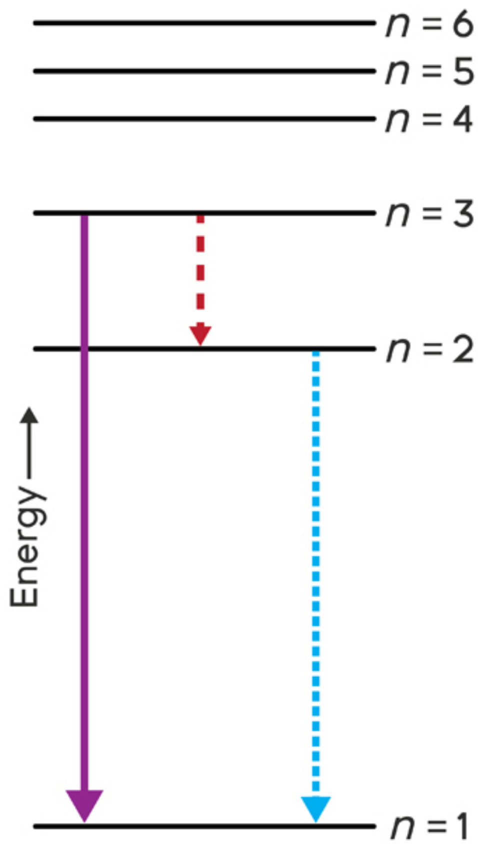

Figure 3-17. Energy Levels of a Hydrogen Atom

Bohr proposed that the different emission lines correspond to the transition of an electron from one energy level to another. In this schematic picture of the hydrogen atom, the different energy levels are labeled on the right. The transition from n = 3 to n = 2, a relatively small difference, gives rise to a particular red light (red arrow). The transition from n = 2 to n = 1, is a longer difference, therefore the photon given off has a higher energy (blue-green arrow). The biggest transition is from n = 3 to n = 1; this photon might be in the ultraviolet (purple arrow).

While Bohr's theory was a crucial step toward the development of quantum mechanics, unfortunately it worked very well for hydrogen with its one electron, but it didn't extend well to elements that had more than one electron.

Nonetheless, his theory held until 1926, when Austrian physicist Erwin Schrödinger (1887–1961) put forward a new mathematical framework to describe the energy levels of the hydrogen electron, the **Schrödinger equation**. The Schrödinger equation takes the mathematics that models waves, such as a ripple on a pond or the sound of a vibrating string, and applies them to describe the **wavefunction** of a particle, like the electron in an atom. This means that electrons behave as both particles and waves, according to quantum mechanics. This concept of the **wave-particle duality** states that all forms of electromagnetic energy, as well as atoms and subatomic particles, have both characteristics simultaneously: those of a wave and those of a particle. It was Louis de Broglie (1892–1987), a French prince and mathematician, who found a mathematical relationship between moving particles and their wavelike properties.

Werner Heisenberg and Niels Bohr

The year 1927 marked the publication of the Heisenberg uncertainty principle, in which the German theoretical physicist, Werner Heisenberg (1901–1976), proposed that there is a limit to the precision to which certain pairs of quantities, for example, the location and the momentum (or energy) of a particle, can be known simultaneously. This meant that the energies of the electrons, which are fixed, preclude knowing their precise locations in the atom. They also preclude having the electron spiral in toward the nucleus.

During World War II, Heisenberg and other German theoretical physicists were attacked for practicing "Jewish science," presumably because of Bohr and Einstein's role in furthering the field. Heisenberg's attempts to maintain his own national identity and the preeminence of German science made him enemies on all sides. Heisenberg and Bohr had a very close relationship that was ended by their differing alliances during World War II. Bohr, a Jewish man, lived in Copenhagen, Denmark. Heisenberg was a proud German, but was not particularly attached to the Nazi party. Bohr and Heisenberg worked on opposing efforts to develop the atomic bomb. Heisenberg spoke at a conference in German-occupied Copenhagen in September 1941. Bohr and Heisenberg met alone; the details of this meeting were kept secret for decades and inspired lots of speculation. The two men were never close friends again, and the scientific community at large shunned Heisenberg. (For more information and a dramatic interpretation of the meeting, consult the Tony Award-winning play *Copenhagen*.)

The **quantum model of the atom** is very complex; the equations of the wavefunctions are very complicated, but we can summarize the important things that come out of this final model of the atom. Rather than modeling the electron as a planet orbiting around a nucleus (or sun), these wavefunctions actually show regions of space where the electron is likely to be found. We still call these regions of space "orbitals," but it means we do not actually know where the electron is, just where we are likely to find it. These orbitals also come in a variety of shapes and sizes, and that information can also be pulled out of the Schrödinger equation and its wavefunction solutions. This means that at any point in time, the nucleus is surrounded by what we call a "cloud of electrons." In the next unit, we will talk more about these orbitals and the implications they have for the electrons held within them.

Taken together, all these discoveries, and more, form the basis of the quantum model of the atom, which is the current framework by which we understand the interactions of atoms and their electrons. This model can be used to explain the properties of the elements and how they combine to make chemical compounds simply by understanding how their electrons behave. These topics will be revisited in Unit 4 and other units in the course. However, we can summarize the model as follows:

- Atoms are composed of two separate parts: a small, dense, positively charged nucleus and a much larger, diffuse, and negatively charged cloud of electrons.
- Electrons in an atom must be in specifically allowed energy levels, which are called "orbitals." These are not specific places, but a region of space around the nucleus where the electron is likely to be found.
- As an atom absorbs or emits energy, an electron must move from one energy level to another. Most times, the form of energy involved in electronic transitions is light. Only certain specific energies of light can be absorbed or emitted by an atom of a specific element.

Glossary

Quantum model of the atom
A model of the atom that describes the electrons in the atom as having only very specific values of energy and locations in space.

Schrödinger equation
A differential equation that, when solved for an atom, gives many possible solutions, corresponding to different possible wave functions for that atom. This equation is important in quantum mechanics because it demonstrates that an atomic orbital can be described as a probability distribution map of the position of an electron (rather than a rigidly defined orbital, in which the location of an electron can be known).

Wave particle duality
In quantum mechanics, when fast moving particles of matter or photons of energy blur the lines between the wave-like nature of light and the particle-like nature of an object.

Wavefunction
In the solutions to the Schrödinger equation, electrons can be associated with mathematical functions, called "wavefunctions," that relate to their energy and probable locations in space.

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 10: Conclusion

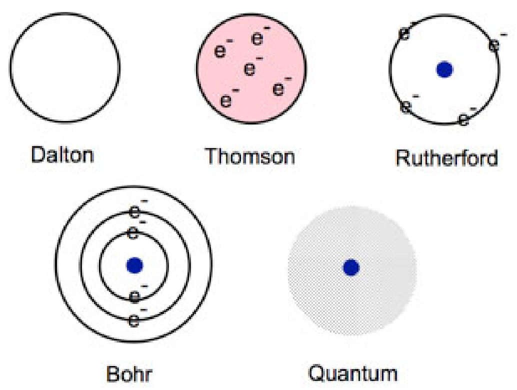

Figure 3-18. The Progression of the Models of the Atom

A progression of the models of the atom over time from Dalton to quantum with the major characteristics labeled.

To summarize, the quantum model of the atom is a culmination of many experiments by many diligent physicists, chemists, and mathematicians. The atom has a nucleus, which is a dense area of positive charge, surrounded by mostly empty space with electrons. The dense nucleus is made of protons and neutrons, and the electrons are in orbitals, which represent probable locations based on energy. The orbitals are also known as the electron clouds. Electrons changing energy levels is what produces unique colors and distinct emission spectra.

Above is a summary diagram of scientists' vision of the atom over time. The atom and its subatomic particles were steadily unveiled as researchers realized how to manipulate spectroscopic techniques.

CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 3: *Atoms and Light—Exploring Atomic and Electronic Structure*

Section 11: Further Reading

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