30 ATOMIC PHYSICS

Figure 30.1 Individual carbon atoms are visible in this image of a carbon nanotube made by a scanning tunneling electron microscope. (credit: Taner Yildirim, National Institute of Standards and Technology, via Wikimedia Commons)

Learning Objectives

30.1 Discovery of the Atom
30.2 Discovery of the Parts of the Atom: Electrons and Nuclei
30.3 Bohr’s Theory of the Hydrogen Atom
30.4 X Rays: Atomic Origins and Applications
30.5 Applications of Atomic Excitations and De-Excitations
30.6 The Wave Nature of Matter Causes Quantization
30.7 Patterns in Spectra Reveal More Quantization
30.8 Quantum Numbers and Rules
30.9 The Pauli Exclusion Principle

Introduction to Atomic Physics

From childhood on, we learn that atoms are a substructure of all things around us, from the air we breathe to the autumn leaves that blanket a forest trail. Invisible to the eye, the existence and properties of atoms are used to explain many phenomena—a theme found throughout this text. In this chapter, we discuss the discovery of atoms and their own substructures; we then apply quantum mechanics to the description of atoms, and their properties and interactions. Along the way, we will find, much like the scientists who made the original discoveries, that new concepts emerge with applications far beyond the boundaries of atomic physics.

30.1 Discovery of the Atom

How do we know that atoms are really there if we cannot see them with our eyes? A brief account of the progression from the proposal of atoms by the Greeks to the first direct evidence of their existence follows.

People have long speculated about the structure of matter and the existence of atoms. The earliest significant ideas to survive are due to the ancient Greeks in the fifth century BCE, especially those of the philosophers Leucippus and Democritus. (There is some evidence that philosophers in both India and China made similar speculations, at about the same time.) They considered the question of whether a substance can be divided without limit into ever smaller pieces. There are only a few possible answers to this question. One is that infinitesimally small subdivision is possible. Another is what Democritus in particular believed—that there is a smallest unit that cannot be further subdivided. Democritus called this the atom. We now know that atoms themselves can be subdivided, but their identity is destroyed in the process, so the Greeks were correct in a respect. The Greeks also felt that atoms were in constant motion, another correct notion.

The Greeks and others speculated about the properties of atoms, proposing that only a few types existed and that all matter was formed as various combinations of these types. The famous proposal that the basic elements were earth, air, fire, and water was brilliant, but incorrect. The Greeks had identified the most common examples of the four states of matter (solid, gas, plasma, and liquid), rather than the basic elements. More than 2000 years passed before observations could be made with equipment capable of revealing the true nature of atoms.

Over the centuries, discoveries were made regarding the properties of substances and their chemical reactions. Certain systematic features were recognized, but similarities between common and rare elements resulted in efforts to transmute them (lead into gold, in particular) for financial gain. Secrecy was endemic. Alchemists discovered and rediscovered many facts but did not make them broadly available. As the Middle Ages ended, alchemy gradually faded, and the science of chemistry arose. It was no longer possible, nor considered desirable, to keep discoveries secret. Collective knowledge grew, and by the beginning of the 19th century, an important fact was well established—the masses of reactants in specific chemical reactions always have a particular mass ratio. This is very strong indirect evidence that there are basic units (atoms and molecules) that have these same mass ratios. The English chemist John Dalton (1766–1844) did much of this work, with significant contributions by the Italian physicist Amedeo Avogadro (1776–1856). It was Avogadro who developed the idea of a fixed number of atoms and molecules in a mole, and this special number is called Avogadro’s number in his honor. The Austrian physicist Johann Josef Loschmidt was the first to measure the value of the constant in 1865 using the kinetic theory of gases.
Patterns and Systematics

The recognition and appreciation of patterns has enabled us to make many discoveries. The periodic table of elements was proposed as an organized summary of the known elements long before all elements had been discovered, and it led to many other discoveries. We shall see in later chapters that patterns in the properties of subatomic particles led to the proposal of quarks as their underlying structure, an idea that is still bearing fruit.

Knowledge of the properties of elements and compounds grew, culminating in the mid-19th-century development of the periodic table of the elements by Dmitri Mendeleev (1834–1907), the great Russian chemist. Mendeleev proposed an ingenious array that highlighted the periodic nature of the properties of elements. Believing in the systematics of the periodic table, he also predicted the existence of then-unknown elements to complete it. Once these elements were discovered and determined to have properties predicted by Mendeleev, his periodic table became universally accepted.

Also during the 19th century, the kinetic theory of gases was developed. Kinetic theory is based on the existence of atoms and molecules in random thermal motion and provides a microscopic explanation of the gas laws, heat transfer, and thermodynamics (see Introduction to Temperature, Kinetic Theory, and the Gas Laws and Introduction to Laws of Thermodynamics). Kinetic theory works so well that it is another strong indication of the existence of atoms. But it is still indirect evidence—individual atoms and molecules had not been observed. There were heated debates about the validity of kinetic theory until direct evidence of atoms was obtained.

The first truly direct evidence of atoms is credited to Robert Brown, a Scottish botanist. In 1827, he noticed that tiny pollen grains suspended in still water moved about in complex paths. This can be observed with a microscope for any small particles in a fluid. The motion is caused by the random thermal motions of fluid molecules colliding with particles in the fluid, and it is now called Brownian motion. (See Figure 30.2.) Statistical fluctuations in the numbers of molecules striking the sides of a visible particle cause it to move first this way, then that. Although the molecules cannot be directly observed, their effects on the particle can be. By examining Brownian motion, the size of molecules can be calculated. The smaller and more numerous they are, the smaller the fluctuations in the numbers striking different sides.

Figure 30.2 The position of a pollen grain in water, measured every few seconds under a microscope, exhibits Brownian motion. Brownian motion is due to fluctuations in the number of atoms and molecules colliding with a small mass, causing it to move about in complex paths. This is nearly direct evidence for the existence of atoms, providing a satisfactory alternative explanation cannot be found.

It was Albert Einstein who, starting in his epochal year of 1905, published several papers that explained precisely how Brownian motion could be used to measure the size of atoms and molecules. (In 1905 Einstein created special relativity, proposed photons as quanta of EM radiation, and produced a theory of Brownian motion that allowed the size of atoms to be determined. All of this was done in his spare time, since he worked days as a patent examiner. Any one of these very basic works could have been the crowning achievement of an entire career—yet Einstein did even more in later years.) Their sizes were only approximately known to be $10^{-10}$ m, based on a comparison of latent heat of vaporization and surface tension made in about 1805 by Thomas Young of double-slit fame and the famous astronomer and mathematician Simon Laplace.

Using Einstein’s ideas, the French physicist Jean-Baptiste Perrin (1870–1942) carefully observed Brownian motion; not only did he confirm Einstein’s theory; he also produced accurate sizes for atoms and molecules. Since molecular weights and densities of materials were well established, knowing atomic and molecular sizes allowed a precise value for Avogadro’s number to be obtained. (If we know how big an atom is, we know how many fit into a certain volume.) Perrin also used these ideas to explain atomic and molecular agitation effects in sedimentation, and he received the 1926 Nobel Prize for his achievements. Most scientists were already convinced of the existence of atoms, but the accurate observation and analysis of Brownian motion was conclusive—it was the first truly direct evidence.

A huge array of direct and indirect evidence for the existence of atoms now exists. For example, it has become possible to accelerate ions (much as electrons are accelerated in cathode-ray tubes) and to detect them individually as well as measure their masses (see More Applications of Magnetism for a discussion of mass spectrometers). Other devices that observe individual atoms, such as the scanning tunneling electron microscope, will be discussed elsewhere. (See Figure 30.3.) All of our understanding of the properties of matter is based on and consistent with the atom. The atom’s substructures, such as electron shells and the nucleus, are both interesting and important. The nucleus in turn has a substructure, as do the particles of which it is composed. These topics, and the question of whether there is a smallest basic structure to matter, will be explored in later parts of the text.
30.2 Discovery of the Parts of the Atom: Electrons and Nuclei

Just as atoms are a substructure of matter, electrons and nuclei are substructures of the atom. The experiments that were used to discover electrons and nuclei reveal some of the basic properties of atoms and can be readily understood using ideas such as electrostatic and magnetic force, already covered in previous chapters.

Charges and Electromagnetic Forces

In previous discussions, we have noted that positive charge is associated with nuclei and negative charge with electrons. We have also covered many aspects of the electric and magnetic forces that affect charges. We will now explore the discovery of the electron and nucleus as substructures of the atom and examine their contributions to the properties of atoms.

The Electron

Gas discharge tubes, such as that shown in Figure 30.4, consist of an evacuated glass tube containing two metal electrodes and a rarefied gas. When a high voltage is applied to the electrodes, the gas glows. These tubes were the precursors to today’s neon lights. They were first studied seriously by Heinrich Geissler, a German inventor and glassblower, starting in the 1860s. The English scientist William Crookes, among others, continued to study what for some time were called Crookes tubes, wherein electrons are freed from atoms and molecules in the rarefied gas inside the tube and are accelerated from the cathode (negative) to the anode (positive) by the high potential. These “cathode rays” collide with the gas atoms and molecules and excite them, resulting in the emission of electromagnetic (EM) radiation that makes the electrons’ path visible as a ray that spreads and fades as it moves away from the cathode.

Gas discharge tubes today are most commonly called cathode-ray tubes, because the rays originate at the cathode. Crookes showed that the electrons carry momentum (they can make a small paddle wheel rotate). He also found that their normally straight path is bent by a magnet in the direction expected for negative charge. These were the first direct indications of electrons and their charge.

Figure 30.4 A gas discharge tube glows when a high voltage is applied to it. Electrons emitted from the cathode are accelerated toward the anode; they excite atoms and molecules in the gas, which glow in response. Once called Geissler tubes and later Crookes tubes, they are now known as cathode-ray tubes (CRTs) and are found in older TVs, computer screens, and x-ray machines. When a magnetic field is applied, the beam bends in the direction expected for negative charge. (credit: Paul Downey, Flickr)

The English physicist J. J. Thomson (1856–1940) improved and expanded the scope of experiments with gas discharge tubes. (See Figure 30.5 and Figure 30.6.) He verified the negative charge of the cathode rays with both magnetic and electric fields. Additionally, he collected the rays in a metal cup and found an excess of negative charge. Thomson was also able to measure the ratio of the charge of the electron to its mass, $q_e / m_e$ —an important step to finding the actual values of both $q_e$ and $m_e$. Figure 30.7 shows a cathode-ray tube, which produces a narrow beam of electrons
that passes through charging plates connected to a high-voltage power supply. An electric field $E$ is produced between the charging plates, and the cathode-ray tube is placed between the poles of a magnet so that the electric field $E$ is perpendicular to the magnetic field $B$ of the magnet. These fields, being perpendicular to each other, produce opposing forces on the electrons. As discussed for mass spectrometers in More Applications of Magnetism, if the net force due to the fields vanishes, then the velocity of the charged particle is $v = E/B$. In this manner, Thomson determined the velocity of the electrons and then moved the beam up and down by adjusting the electric field.

Figure 30.5 J. J. Thomson (credit: www.firstworldwar.com, via Wikimedia Commons)

Figure 30.6 Diagram of Thomson’s CRT. (credit: Kurzon, Wikimedia Commons)

Figure 30.7 This schematic shows the electron beam in a CRT passing through crossed electric and magnetic fields and causing phosphor to glow when striking the end of the tube.

To see how the amount of deflection is used to calculate $q_e/m_e$, note that the deflection is proportional to the electric force on the electron:

$$F = q_eE.$$  \hspace{1cm} (30.1)

But the vertical deflection is also related to the electron’s mass, since the electron’s acceleration is

$$a = \frac{F}{m_e}.$$  \hspace{1cm} (30.2)

The value of $F$ is not known, since $q_e$ was not yet known. Substituting the expression for electric force into the expression for acceleration yields

$$a = \frac{F}{m_e} = \frac{q_eE}{m_e}.$$  \hspace{1cm} (30.3)
Gathering terms, we have

$$\frac{q_e}{m_e} = \frac{a}{E}. \quad (30.4)$$

The deflection is analyzed to get $a$, and $E$ is determined from the applied voltage and distance between the plates; thus, $\frac{q_e}{m_e}$ can be determined.

With the velocity known, another measurement of $\frac{q_e}{m_e}$ can be obtained by bending the beam of electrons with the magnetic field. Since $F_{mag} = q_e B = m_e a$, we have $\frac{q_e}{m_e} = \frac{a}{vB}$. Consistent results are obtained using magnetic deflection.

What is so important about $\frac{q_e}{m_e}$, the ratio of the electron’s charge to its mass? The value obtained is

$$\frac{q_e}{m_e} = -1.76 \times 10^{11} \text{ C/kg (electron)}. \quad (30.5)$$

This is a huge number, as Thomson realized, and it implies that the electron has a very small mass. It was known from electroplating that about $10^8 \text{ C/kg}$ is needed to plate a material, a factor of about 1000 less than the charge per kilogram of electrons. Thomson went on to do the same experiment for positively charged hydrogen ions (now known to be bare protons) and found a charge per kilogram about 1000 times smaller than that for the electron, implying that the proton is about 1000 times more massive than the electron. Today, we know more precisely that

$$\frac{q_p}{m_p} = 9.58 \times 10^7 \text{ C/kg (proton)}, \quad (30.6)$$

where $q_p$ is the charge of the proton and $m_p$ is its mass. This ratio (to four significant figures) is 1836 times less charge per kilogram than for the electron. Since the charges of electrons and protons are equal in magnitude, this implies $m_p = 1836m_e$.

Thomson performed a variety of experiments using differing gases in discharge tubes and employing other methods, such as the photoelectric effect, for freeing electrons from atoms. He always found the same properties for the electron, proving it to be an independent particle. For his work, the important pieces of which he began to publish in 1897, Thomson was awarded the 1906 Nobel Prize in Physics. In retrospect, it is difficult to appreciate how astonishing it was to find that the atom has a substructure. Thomson himself said, “It was only when I was convinced that the experiment left no escape from it that I published my belief in the existence of bodies smaller than atoms.”

Thomson attempted to measure the charge of individual electrons, but his method could determine its charge only to the order of magnitude expected.

Since Faraday’s experiments with electroplating in the 1830s, it had been known that about 100,000 C per mole was needed to plate singly ionized ions. Dividing this by the number of ions per mole (that is, by Avogadro’s number), which was approximately known, the charge per ion was calculated to be about $1.6 \times 10^{-19} \text{ C}$, close to the actual value.

An American physicist, Robert Millikan (1868–1953) (see Figure 30.8), decided to improve upon Thomson’s experiment for measuring $q_e$ and was eventually forced to try another approach, which is now a classic experiment performed by students. The Millikan oil drop experiment is shown in Figure 30.9.
The Millikan oil drop experiment produced the first accurate direct measurement of the charge on electrons, one of the most fundamental constants in nature. Fine drops of oil become charged when sprayed. Their movement is observed between metal plates with a potential applied to oppose the gravitational force. The balance of gravitational and electric forces allows the calculation of the charge on a drop. The charge is found to be quantized in units of $-1.6 \times 10^{-19}$ C, thus determining directly the charge of the excess and missing electrons on the oil drops.

In the Millikan oil drop experiment, fine drops of oil are sprayed from an atomizer. Some of these are charged by the process and can then be suspended between metal plates by a voltage between the plates. In this situation, the weight of the drop is balanced by the electric force:

$$m_{\text{drop}} g = q_e E$$

The electric field is produced by the applied voltage, hence, $E = V / d$, and $V$ is adjusted to just balance the drop's weight. The drops can be seen as points of reflected light using a microscope, but they are too small to directly measure their size and mass. The mass of the drop is determined by observing how fast it falls when the voltage is turned off. Since air resistance is very significant for these submicroscopic drops, the more massive drops fall faster than the less massive, and sophisticated sedimentation calculations can reveal their mass. Oil is used rather than water, because it does not readily evaporate, and so mass is nearly constant. Once the mass of the drop is known, the charge of the electron is given by rearranging the previous equation:

$$q_e = m_{\text{drop}} g d / V,$$

where $d$ is the separation of the plates and $V$ is the voltage that holds the drop motionless. (The same drop can be observed for several hours to see that it really is motionless.) By 1913 Millikan had measured the charge of the electron $q_e$ to an accuracy of 1%, and he improved this by a factor of 10 within a few years to a value of $-1.60 \times 10^{-19}$ C. He also observed that all charges were multiples of the basic electron charge and that sudden changes could occur in which electrons were added or removed from the drops. For this very fundamental direct measurement of $q_e$ and for his studies of the photoelectric effect, Millikan was awarded the 1923 Nobel Prize in Physics.

With the charge of the electron known and the charge-to-mass ratio known, the electron’s mass can be calculated. It is

$$m = \frac{q_e}{(q_e/m_e)}$$

Substituting known values yields

$$m_e = \frac{-1.60 \times 10^{-19} \text{ C}}{-1.76 \times 10^{11} \text{ C/kg}}$$

or

$$m_e = 9.11 \times 10^{-31} \text{ kg (electron’s mass)},$$

where the round-off errors have been corrected. The mass of the electron has been verified in many subsequent experiments and is now known to an accuracy of better than one part in one million. It is an incredibly small mass and remains the smallest known mass of any particle that has mass. (Some particles, such as photons, are massless and cannot be brought to rest, but travel at the speed of light.) A similar calculation gives the masses of other particles, including the proton. To three digits, the mass of the proton is now known to be

$$m_p = 1.67 \times 10^{-27} \text{ kg (proton’s mass)},$$

which is nearly identical to the mass of a hydrogen atom. What Thomson and Millikan had done was to prove the existence of one substructure of atoms, the electron, and further to show that it had only a tiny fraction of the mass of an atom. The nucleus of an atom contains most of its mass, and the nature of the nucleus was completely unanticipated.

Another important characteristic of quantum mechanics was also beginning to emerge. All electrons are identical to one another. The charge and mass of electrons are not average values; rather, they are unique values that all electrons have. This is true of other fundamental entities at the submicroscopic level. All protons are identical to one another, and so on.
The Nucleus

Here, we examine the first direct evidence of the size and mass of the nucleus. In later chapters, we will examine many other aspects of nuclear physics, but the basic information on nuclear size and mass is so important to understanding the atom that we consider it here.

Nuclear radioactivity was discovered in 1896, and it was soon the subject of intense study by a number of the best scientists in the world. Among them was New Zealander Lord Ernest Rutherford, who made numerous fundamental discoveries and earned the title of “father of nuclear physics.” Born in Nelson, Rutherford did his postgraduate studies at the Cavendish Laboratories in England before taking up a position at McGill University in Canada where he did the work that earned him a Nobel Prize in Chemistry in 1908. In the area of atomic and nuclear physics, there is much overlap between chemistry and physics, with physics providing the fundamental enabling theories. He returned to England in later years and had six future Nobel Prize winners as students. Rutherford used nuclear radiation to directly examine the size and mass of the atomic nucleus. The experiment he devised is shown in Figure 30.10. A radioactive source that emits alpha radiation was placed in a lead container with a hole in one side to produce a beam of alpha particles, which are a type of ionizing radiation ejected by the nuclei of a radioactive source. A thin gold foil was placed in the beam, and the scattering of the alpha particles was observed by the glow they caused when they struck a phosphor screen.

![Figure 30.10](image.png)

Figure 30.10 Rutherford's experiment gave direct evidence for the size and mass of the nucleus by scattering alpha particles from a thin gold foil. Alpha particles with energies of about 5 MeV are emitted from a radioactive source (which is a small metal container in which a specific amount of a radioactive material is sealed), are collimated into a beam, and fall upon the foil. The number of particles that penetrate the foil or scatter to various angles indicates that gold nuclei are very small and contain nearly all of the gold atom’s mass. This is particularly indicated by the alpha particles that scatter to very large angles, much like a soccer ball bouncing off a goalie’s head.

Alpha particles were known to be the doubly charged positive nuclei of helium atoms that had kinetic energies on the order of 5 MeV when emitted in nuclear decay, which is the disintegration of the nucleus of an unstable nuclide by the spontaneous emission of charged particles. These particles interact with matter mostly via the Coulomb force, and the manner in which they scatter from nuclei can reveal nuclear size and mass. This is analogous to observing how a bowling ball is scattered by an object you cannot see directly. Because the alpha particle’s energy is so large compared with the typical energies associated with atoms (MeV versus eV), you would expect the alpha particles to simply crash through a thin foil much like a supersonic bowling ball would crash through a few dozen rows of bowling pins. Thomson had envisioned the atom to be a small sphere in which equal amounts of positive and negative charge were distributed evenly. The incident massive alpha particles would suffer only small deflections in such a model. Instead, Rutherford and his collaborators found that alpha particles occasionally were scattered to large angles, some even back in the direction from which they came! Detailed analysis using conservation of momentum and energy—particularly of the small number that came straight back—implied that gold nuclei are very small compared with the size of a gold atom, contain almost all of the atom’s mass, and are tightly bound. Since the gold nucleus is several times more massive than the alpha particle, a head-on collision would scatter the alpha particle straight back toward the source. In addition, the smaller the nucleus, the fewer alpha particles that would hit one head on.

![Diagram](image.png)

Although the results of the experiment were published by his colleagues in 1909, it took Rutherford two years to convince himself of their meaning. Like Thomson before him, Rutherford was reluctant to accept such radical results. Nature on a small scale is so unlike our classical world that even those at the forefront of discovery are sometimes surprised. Rutherford later wrote: “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. On consideration, I realized that this scattering backwards ... [meant] ... the greatest part of the mass of the atom was concentrated in a tiny nucleus.” In 1911, Rutherford published his analysis together with a proposed model of the atom. The size of the nucleus was determined to be about $10^{-15}$ m, or 100,000 times smaller than the atom. This implies a huge density, on the order of $10^{15}$ g/cm$^3$, vastly unlike any macroscopic matter. Also implied is the existence of previously unknown nuclear forces to counteract the huge repulsive Coulomb forces among the positive charges in the nucleus. Huge forces would also be consistent with the large energies emitted in nuclear radiation.

The small size of the nucleus also implies that the atom is mostly empty inside. In fact, in Rutherford’s experiment, most alphas went straight through the gold foil with very little scattering, since electrons have such small masses and since the atom was mostly empty with nothing for the alpha to hit. There were already hints of this at the time Rutherford performed his experiments, since energetic electrons had been observed to penetrate thin foils more easily than expected. Figure 30.11 shows a schematic of the atoms in a thin foil with circles representing the size of the atoms (about $10^{-10}$ m) and dots representing the nuclei. (The dots are not to scale—if they were, you would need a microscope to see them.) Most alpha particles miss the small nuclei and are only slightly scattered by electrons. Occasionally, (about once in 8000 times in Rutherford’s experiment), an alpha hits a nucleus head-on and is scattered straight backward.
An expanded view of the atoms in the gold foil in Rutherford's experiment. Circles represent the atoms (about $10^{-10}$ m in diameter), while the dots represent the nuclei (about $10^{-15}$ m in diameter). To be visible, the dots are much larger than scale. Most alpha particles crash through but are relatively unaffected because of their high energy and the electron's small mass. Some, however, head straight toward a nucleus and are scattered straight back. A detailed analysis gives the size and mass of the nucleus.

Based on the size and mass of the nucleus revealed by his experiment, as well as the mass of electrons, Rutherford proposed the planetary model of the atom. The planetary model of the atom pictures low-mass electrons orbiting a large-mass nucleus. The sizes of the electron orbits are large compared with the size of the nucleus, with mostly vacuum inside the atom. This picture is analogous to how low-mass planets in our solar system orbit the large-mass Sun at distances large compared with the size of the sun. In the atom, the attractive Coulomb force is analogous to gravitation in the planetary system. (See Figure 30.12.) Note that a model or mental picture is needed to explain experimental results, since the atom is too small to be directly observed with visible light.

Rutherford's planetary model of the atom was crucial to understanding the characteristics of atoms, and their interactions and energies, as we shall see in the next few sections. Also, it was an indication of how different nature is from the familiar classical world on the small, quantum mechanical scale. The discovery of a substructure to all matter in the form of atoms and molecules was now being taken a step further to reveal a substructure of atoms that was simpler than the 92 elements then known. We have continued to search for deeper substructures, such as those inside the nucleus, with some success. In later chapters, we will follow this quest in the discussion of quarks and other elementary particles, and we will look at the direction the search seems now to be heading.

Bohr's Theory of the Hydrogen Atom

The great Danish physicist Niels Bohr (1885–1962) made immediate use of Rutherford's planetary model of the atom. (Figure 30.14). Bohr became convinced of its validity and spent part of 1912 at Rutherford's laboratory. In 1913, after returning to Copenhagen, he began publishing his theory of the simplest atom, hydrogen, based on the planetary model of the atom. For decades, many questions had been asked about atomic characteristics. From their sizes to their spectra, much was known about atoms, but little had been explained in terms of the laws of physics. Bohr's theory explained the atomic spectrum of hydrogen and established new and broadly applicable principles in quantum mechanics.
**Mysteries of Atomic Spectra**

As noted in *Quantization of Energy*, the energies of some small systems are quantized. Atomic and molecular emission and absorption spectra have been known for over a century to be discrete (or quantized). (See *Figure 30.15.*) Maxwell and others had realized that there must be a connection between the spectrum of an atom and its structure, something like the resonant frequencies of musical instruments. But, in spite of years of efforts by many great minds, no one had a workable theory. (It was a running joke that any theory of atomic and molecular spectra could be destroyed by throwing a book of data at it, so complex were the spectra.) Following Einstein’s proposal of photons with quantized energies directly proportional to their wavelengths, it became even more evident that electrons in atoms can exist only in discrete orbits.

![Figure 30.14](credit: Unknown Author, via Wikimedia Commons)

**Figure 30.14** Niels Bohr, Danish physicist, used the planetary model of the atom to explain the atomic spectrum and size of the hydrogen atom. His many contributions to the development of atomic physics and quantum mechanics, his personal influence on many students and colleagues, and his personal integrity, especially in the face of Nazi oppression, earned him a prominent place in history. (credit: Unknown Author, via Wikimedia Commons)

In some cases, it had been possible to devise formulas that described the emission spectra. As you might expect, the simplest atom—hydrogen, with its single electron—has a relatively simple spectrum. The hydrogen spectrum had been observed in the infrared (IR), visible, and ultraviolet (UV), and several series of spectral lines had been observed. (See *Figure 30.16.*) These series are named after early researchers who studied them in particular depth.

The observed *hydrogen-spectrum wavelengths* can be calculated using the following formula:

$$\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

where $\lambda$ is the wavelength of the emitted EM radiation and $R$ is the *Rydberg constant*, determined by the experiment to be

$$R = 1.097 \times 10^7 \text{ m}^{-1}.$$

The constant $n_i$ is a positive integer associated with a specific series. For the Lyman series, $n_i = 1$; for the Balmer series, $n_i = 2$; for the Paschen series, $n_i = 3$; and so on. The Lyman series is entirely in the UV, while part of the Balmer series is visible with the remainder UV. The Paschen series and all the rest are entirely IR. There are apparently an unlimited number of series, although they lie progressively farther into the infrared and become difficult to observe as $n_i$ increases. The constant $n_f$ is a positive integer, but it must be greater than $n_i$. Thus, for the Balmer...
series, \( n_f = 2 \) and \( n_i = 3, 4, 5, 6, \ldots \). Note that \( n_i \) can approach infinity. While the formula in the wavelengths equation was just a recipe designed to fit data and was not based on physical principles, it did imply a deeper meaning. Balmer first devised the formula for his series alone, and it was later found to describe all the other series by using different values of \( n_f \). Bohr was the first to comprehend the deeper meaning. Again, we see the interplay between experiment and theory in physics. Experimentally, the spectra were well established, an equation was found to fit the experimental data, but the theoretical foundation was missing.

![Figure 30.16](image)

**Figure 30.16** A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of \( n_f \) and \( n_i \) are shown for some of the lines.

### Example 30.1 Calculating Wave Interference of a Hydrogen Line

What is the distance between the slits of a grating that produces a first-order maximum for the second Balmer line at an angle of 15º?

**Strategy and Concept**

For an Integrated Concept problem, we must first identify the physical principles involved. In this example, we need to know (a) the wavelength of light as well as (b) conditions for an interference maximum for the pattern from a double slit. Part (a) deals with a topic of the present chapter, while part (b) considers the wave interference material of *Wave Optics*.

**Solution for (a)**

**Hydrogen spectrum wavelength.** The Balmer series requires that \( n_f = 2 \). The first line in the series is taken to be for \( n_i = 3 \), and so the second would have \( n_i = 4 \).

The calculation is a straightforward application of the wavelength equation. Entering the determined values for \( n_f \) and \( n_i \) yields

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = (1.097 \times 10^7 \text{ m}^{-1}) \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 2.057 \times 10^6 \text{ m}^{-1}. 
\]

Inverting to find \( \lambda \) gives

\[
\lambda = \frac{1}{2.057 \times 10^6 \text{ m}^{-1}} = 486 \times 10^{-9} \text{ m} = 486 \text{ nm}. 
\]

**Discussion for (a)**

This is indeed the experimentally observed wavelength, corresponding to the second (blue-green) line in the Balmer series. More impressive is the fact that the same simple recipe predicts all of the hydrogen spectrum lines, including new ones observed in subsequent experiments. What is nature telling us?

**Solution for (b)**

**Double-slit interference (Wave Optics).** To obtain constructive interference for a double slit, the path length difference from two slits must be an integral multiple of the wavelength. This condition was expressed by the equation

\[
d \sin \theta = m \lambda, \quad (30.17)
\]

where \( d \) is the distance between slits and \( \theta \) is the angle from the original direction of the beam. The number \( m \) is the order of the interference; \( m = 1 \) in this example. Solving for \( d \) and entering known values yields

\[
d = \frac{(1)(486 \text{ nm})}{\sin 15^\circ} = 1.88 \times 10^{-6} \text{ m}. \quad (30.18)
\]

**Discussion for (b)**

This number is similar to those used in the interference examples of *Introduction to Quantum Physics* (and is close to the spacing between slits in commonly used diffraction glasses).
Bohr’s Solution for Hydrogen

Bohr was able to derive the formula for the hydrogen spectrum using basic physics, the planetary model of the atom, and some very important new proposals. His first proposal is that only certain orbits are allowed: we say that the orbits of electrons in atoms are quantized. Each orbit has a different energy, and electrons can move to a higher orbit by absorbing energy and drop to a lower orbit by emitting energy. If the orbits are quantized, the amount of energy absorbed or emitted is also quantized, producing discrete spectra. Photon absorption and emission are among the primary methods of transferring energy into and out of atoms. The energies of the photons are quantized, and their energy is explained as being equal to the change in energy of the electron when it moves from one orbit to another. In equation form, this is

\[ \Delta E = hf = E_i - E_f. \]  

(30.19)

Here, \( \Delta E \) is the change in energy between the initial and final orbits, and \( hf \) is the energy of the absorbed or emitted photon. It is quite logical (that is, expected from our everyday experience) that energy is involved in changing orbits. A blast of energy is required for the space shuttle, for example, to climb to a higher orbit. What is not expected is that atomic orbits should be quantized. This is not observed for satellites or planets, which can have any orbit given the proper energy. (See Figure 30.17.)

Figure 30.17 The planetary model of the atom, as modified by Bohr, has the orbits of the electrons quantized. Only certain orbits are allowed, explaining why atomic spectra are discrete (quantized). The energy carried away from an atom by a photon comes from the electron dropping from one allowed orbit to another and is thus quantized. This is likewise true for atomic absorption of photons.

Figure 30.18 shows an energy-level diagram, a convenient way to display energy states. In the present discussion, we take these to be the allowed energy levels of the electron. Energy is plotted vertically with the lowest or ground state at the bottom and with excited states above. Given the energies of the lines in an atomic spectrum, it is possible (although sometimes very difficult) to determine the energy levels of an atom. Energy-level diagrams are used for many systems, including molecules and nuclei. A theory of the atom or any other system must predict its energies based on the physics of the system.

Figure 30.18 An energy-level diagram plots energy vertically and is useful in visualizing the energy states of a system and the transitions between them. This diagram is for the hydrogen-atom electrons, showing a transition between two orbits having energies \( E_4 \) and \( E_2 \).

Bohr was clever enough to find a way to calculate the electron orbital energies in hydrogen. This was an important first step that has been improved upon, but it is well worth repeating here, because it does correctly describe many characteristics of hydrogen. Assuming circular orbits, Bohr proposed that the angular momentum \( L \) of an electron in its orbit is quantized, that is, it has only specific, discrete values. The value for \( L \) is given by the formula
\[ L = m_e v r_n = n \frac{h}{2\pi} (n = 1, 2, 3, \ldots), \]  

(30.20)

where \( L \) is the angular momentum, \( m_e \) is the electron’s mass, \( r_n \) is the radius of the \( n \)th orbit, and \( h \) is Planck’s constant. Note that angular momentum is \( L = I \omega \). For a small object at a radius \( r \), \( I = m r^2 \) and \( \omega = v / r \), so that \( L = \left[ m r^2 \right] \left( \frac{v}{r} \right) = m rv \). Quantization says that this value of \( mrv \) can only be equal to \( \frac{h}{2} \), \( 2 \frac{h}{2} \), \( 3 \frac{h}{2} \), etc. At the time, Bohr himself did not know why angular momentum should be quantized, but using this assumption he was able to calculate the energies in the hydrogen spectrum, something no one else had done at the time.

From Bohr’s assumptions, we will now derive a number of important properties of the hydrogen atom from the classical physics we have covered in the text. We start by noting the centripetal force causing the electron to follow a circular path is supplied by the Coulomb force. To be more general, we note that this analysis is valid for any single-electron atom. So, if a nucleus has \( Z \) protons (\( Z = 1 \) for hydrogen, 2 for helium, etc.) and only one electron, that atom is called a hydrogen-like atom. The spectra of hydrogen-like ions are similar to hydrogen, but shifted to higher energy by the greater attractive force between the electron and nucleus. The magnitude of the centripetal force is \( m_e v^2 / r_n \), while the Coulomb force is \( k(Zq_e q_e) / r_n^2 \). The tacit assumption here is that the nucleus is more massive than the stationary electron, and the electron orbits about it. This is consistent with the planetary model of the atom. Equating these,

\[ \frac{k(Zq_e q_e)^2}{r_n^2} = m_e v^2 \quad \text{(Coulomb = centripetal).} \]  

(30.21)

Angular momentum quantization is stated in an earlier equation. We solve that equation for \( v \), substitute it into the above, and rearrange the expression to obtain the radius of the orbit. This yields:

\[ r_n = \frac{n^2}{Z} a_B, \text{ for allowed orbits}(n = 1, 2, 3, \ldots), \]  

(30.22)

where \( a_B \) is defined to be the Bohr radius, since for the lowest orbit \( (n = 1) \) and for hydrogen \( (Z = 1) \), \( r_1 = a_B \). It is left for this chapter’s Problems and Exercises to show that the Bohr radius is

\[ a_B = \frac{h^2}{4\pi^2 m_e k q_e^2} = 0.529 \times 10^{-10} \text{ m}. \]  

(30.23)

These last two equations can be used to calculate the radii of the allowed (quantized) electron orbits in any hydrogen-like atom. It is impressive that the formula gives the correct size of hydrogen, which is measured experimentally to be very close to the Bohr radius. The earlier equation also tells us that the orbital radius is proportional to \( n^2 \), as illustrated in Figure 30.19.

Figure 30.19 The allowed electron orbits in hydrogen have the radii shown. These radii were first calculated by Bohr and are given by the equation \( r_n = \frac{n^2}{Z} a_B \). The lowest orbit has the experimentally verified diameter of a hydrogen atom.

To get the electron orbital energies, we start by noting that the electron energy is the sum of its kinetic and potential energy:

\[ E_n = KE + PE. \]  

(30.24)

Kinetic energy is the familiar \( KE = \frac{1}{2} m_e v^2 \), assuming the electron is not moving at relativistic speeds. Potential energy for the electron is electrical, or \( PE = q_e V \), where \( V \) is the potential due to the nucleus, which looks like a point charge. The nucleus has a positive charge \( Z q_e \);
thus, \( V = kZq_e / r_n \), recalling an earlier equation for the potential due to a point charge. Since the electron’s charge is negative, we see that
\[
PE = -kZq_e / r_n.
\]
Entering the expressions for \( KE \) and \( PE \), we find
\[
E_n = \frac{1}{2} m_e v^2 - k\frac{Z q_e^2}{r_n}.
\]
\[(30.25)\]
Now we substitute \( r_n \) and \( v \) from earlier equations into the above expression for energy. Algebraic manipulation yields
\[
E_n = -\frac{Z^2}{n^2} E_0 (n = 1, 2, 3, ...)
\]
\[(30.26)\]
for the orbital energies of hydrogen-like atoms. Here, \( E_0 \) is the ground-state energy \((n = 1)\) for hydrogen \((Z = 1)\) and is given by
\[
E_0 = 2\pi^2 q_e^4 m_e k^2 / h^2 = 13.6 \text{ eV}.
\]
\[(30.27)\]
Thus, for hydrogen,
\[
E_n = -\frac{13.6}{n^2} \text{ eV} (n = 1, 2, 3, ...).
\]
\[(30.28)\]
Figure 30.20 shows an energy-level diagram for hydrogen that also illustrates how the various spectral series for hydrogen are related to transitions between energy levels.

![Energy-level diagram for hydrogen showing the Lyman, Balmer, and Paschen series of transitions. The orbital energies are calculated using the above equation, first derived by Bohr.](image)

Electron total energies are negative, since the electron is bound to the nucleus, analogous to being in a hole without enough kinetic energy to escape. As \( n \) approaches infinity, the total energy becomes zero. This corresponds to a free electron with no kinetic energy, since \( r_n \) gets very large for large \( n \), and the electric potential energy thus becomes zero. Thus, 13.6 eV is needed to ionize hydrogen (to go from –13.6 eV to 0, or unbound), an experimentally verified number. Given more energy, the electron becomes unbound with some kinetic energy. For example, giving 15.0 eV to an electron in the ground state of hydrogen strips it from the atom and leaves it with 1.4 eV of kinetic energy.

Finally, let us consider the energy of a photon emitted in a downward transition, given by the equation to be
\[
\Delta E = hf = E_i - E_f.
\]
\[(30.29)\]
Substituting \( E_n = (-13.6 \text{ eV} / n^2) \), we see that
\[ hf = (13.6 \text{ eV}) \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \]  

(30.30)

Dividing both sides of this equation by \( hc \) gives an expression for \( 1/\lambda \):

\[ \frac{hf}{hc} = \frac{f}{c} = \frac{1}{\lambda} = (13.6 \text{ eV}) \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \]  

(30.31)

It can be shown that

\[ \frac{(13.6 \text{ eV})}{hc} = \frac{(13.6 \text{ eV}) \left( 1.602 \times 10^{-19} \text{ J/eV} \right)}{(6.626 \times 10^{-34} \text{ J s}) \left( 2.998 \times 10^8 \text{ m/s} \right)} = 1.097 \times 10^7 \text{ m}^{-1} = R \]  

(30.32)

is the Rydberg constant. Thus, we have used Bohr’s assumptions to derive the formula first proposed by Balmer years earlier as a recipe to fit experimental data.

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \]  

(30.33)

We see that Bohr’s theory of the hydrogen atom answers the question as to why this previously known formula describes the hydrogen spectrum. It is because the energy levels are proportional to \( 1/n^2 \), where \( n \) is a non-negative integer. A downward transition releases energy, and so \( n_f \) must be greater than \( n_i \). The various series are those where the transitions end on a certain level. For the Lyman series, \( n_f = 1 \) — that is, all the transitions end in the ground state (see also Figure 30.20). For the Balmer series, \( n_f = 2 \), or all the transitions end in the first excited state; and so on. What was once a recipe is now based in physics, and something new is emerging—angular momentum is quantized.

**Triumphs and Limits of the Bohr Theory**

Bohr did what no one had been able to do before. Not only did he explain the spectrum of hydrogen, he correctly calculated the size of the atom from basic physics. Some of his ideas are broadly applicable. Electron orbital energies are quantized in all atoms and molecules. Angular momentum is quantized. The electrons do not spiral into the nucleus, as expected classically (accelerated charges radiate, so that the electron orbits classically would decay quickly, and the electrons would sit on the nucleus—matter would collapse). These are major triumphs.

But there are limits to Bohr’s theory. It cannot be applied to multielectron atoms, even one as simple as a two-electron helium atom. Bohr’s model is what we call semiclassical. The orbits are quantized (nonclassical) but are assumed to be simple circular paths (classical). As quantum mechanics was developed, it became clear that there are no well-defined orbits; rather, there are clouds of probability. Bohr’s theory also did not explain that some spectral lines are doublets (split into two) when examined closely. We shall examine many of these aspects of quantum mechanics in more detail, but it should be kept in mind that Bohr did not fail. Rather, he made very important steps along the path to greater knowledge and laid the foundation for all of atomic physics that has since evolved.

**PhET Explorations: Models of the Hydrogen Atom**

How did scientists figure out the structure of atoms without looking at them? Try out different models by shooting light at the atom. Check how the prediction of the model matches the experimental results.

**Figure 30.21 Models of the Hydrogen Atom**

(http://cnx.org/content/m42596/1.5/hydrogen-atom_en.jar)

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**30.4 X Rays: Atomic Origins and Applications**

Each type of atom (or element) has its own characteristic electromagnetic spectrum. X rays lie at the high-frequency end of an atom’s spectrum and are characteristic of the atom as well. In this section, we explore characteristic x rays and some of their important applications.

We have previously discussed x rays as a part of the electromagnetic spectrum in Photon Energies and the Electromagnetic Spectrum. That module illustrated how an x-ray tube (a specialized CRT) produces x rays. Electrons emitted from a hot filament are accelerated with a high voltage, gaining significant kinetic energy and striking the anode.

There are two processes by which x rays are produced in the anode of an x-ray tube. In one process, the deceleration of electrons produces x rays, and these x rays are called bremsstrahlung, or braking radiation. The second process is atomic in nature and produces characteristic x rays, so-called because they are characteristic of the anode material. The x-ray spectrum in Figure 30.22 is typical of what is produced by an x-ray tube, showing a broad curve of bremsstrahlung radiation with characteristic x-ray peaks on it.
The spectrum in Figure 30.22 is collected over a period of time in which many electrons strike the anode, with a variety of possible outcomes for each hit. The broad range of x-ray energies in the bremsstrahlung radiation indicates that an incident electron’s energy is not usually converted entirely into photon energy. The highest-energy x-ray produced is one for which all of the electron’s energy was converted to photon energy. Thus the accelerating voltage and the maximum x-ray energy are related by conservation of energy. Electric potential energy is converted to kinetic energy and then to photon energy, so that $E_{\text{max}} = hf_{\text{max}} = qV$. Units of electron volts are convenient. For example, a 100-kV accelerating voltage produces x-ray photons with a maximum energy of 100 keV.

Some electrons excite atoms in the anode. Part of the energy that they deposit by collision with an atom results in one or more of the atom’s inner electrons being knocked into a higher orbit or the atom being ionized. When the anode’s atoms de-excite, they emit characteristic electromagnetic radiation. The most energetic of these are produced when an inner-shell vacancy is filled—that is, when an $n = 1$ or $n = 2$ shell electron has been excited to a higher level, and another electron falls into the vacant spot. A characteristic x-ray (see Photon Energies and the Electromagnetic Spectrum) is electromagnetic (EM) radiation emitted by an atom when an inner-shell vacancy is filled. Figure 30.23 shows a representative energy-level diagram that illustrates the labeling of characteristic x-rays. X-rays created when an electron falls into an $n = 1$ shell vacancy are called $K_{\alpha}$ when they come from the next higher level; that is, an $n = 2$ to $n = 1$ transition. The labels $K, L, M, \ldots$ come from the older alphabetical labeling of shells starting with $K$ rather than using the principal quantum numbers 1, 2, 3, \ldots. A more energetic $K_{\beta}$ x-ray is produced when an electron falls into an $n = 1$ shell vacancy from the $n = 3$ shell; that is, an $n = 3$ to $n = 1$ transition. Similarly, when an electron falls into the $n = 2$ shell from the $n = 3$ shell, an $L_{\alpha}$ x-ray is created. The energies of these x-rays depend on the energies of electron states in the particular atom and, thus, are characteristic of that element: every element has its own set of x-ray energies. This property can be used to identify elements, for example, to find trace (small) amounts of an element in an environmental or biological sample.

### Example 30.2 Characteristic X-Ray Energy

Calculate the approximate energy of a $K_{\alpha}$ x-ray from a tungsten anode in an x-ray tube.

**Strategy**

How do we calculate energies in a multiple-electron atom? In the case of characteristic x-rays, the following approximate calculation is reasonable. Characteristic x-rays are produced when an inner-shell vacancy is filled. Inner-shell electrons are nearer to the nucleus than others in an atom and thus feel little net effect from the others. This is similar to what happens inside a charged conductor, where its excess charge is distributed over the surface so that it produces no electric field inside. It is reasonable to assume the inner-shell electrons have hydrogen-like
energies, as given by \( E_n = -\frac{Z^2}{n^2}E_0 \) \((n = 1, 2, 3, \ldots)\). As noted, a \( K \alpha \) x-ray is produced by an \( n = 2 \) to \( n = 1 \) transition. Since there are two electrons in a filled \( K \) shell, a vacancy would leave one electron, so that the effective charge would be \( Z - 1 \) rather than \( Z \). For tungsten, \( Z = 74 \), so that the effective charge is 73.

**Solution**

\( E_n = -\frac{Z^2}{n^2}E_0 \) \((n = 1, 2, 3, \ldots)\) gives the orbital energies for hydrogen-like atoms to be \( E_n = -(Z^2 / n^2)E_0 \), where \( E_0 = 13.6 \text{ eV} \). As noted, the effective \( Z \) is 73. Now the \( K \alpha \) x-ray energy is given by

\[
E_{K\alpha} = \Delta E = E_i - E_f = E_2 - E_1,
\]

where

\[
E_1 = -\frac{Z^2}{1^2}E_0 = -\frac{73^2}{1}(13.6 \text{ eV}) = -72.5 \text{ keV}
\]

and

\[
E_2 = -\frac{Z^2}{2^2}E_0 = -\frac{73^2}{4}(13.6 \text{ eV}) = -18.1 \text{ keV}.
\]

Thus,

\[
E_{K\alpha} = -18.1 \text{ keV} - (-72.5 \text{ keV}) = 54.4 \text{ keV}.
\]

**Discussion**

This large photon energy is typical of characteristic x rays from heavy elements. It is large compared with other atomic emissions because it is produced when an inner-shell vacancy is filled, and inner-shell electrons are tightly bound. Characteristic x ray energies become progressively larger for heavier elements because their energy increases approximately as \( Z^2 \). Significant accelerating voltage is needed to create these inner-shell vacancies. In the case of tungsten, at least 72.5 kV is needed, because other shells are filled and you cannot simply bump one electron to a higher filled shell. Tungsten is a common anode material in x-ray tubes; so much of the energy of the impinging electrons is absorbed, raising its temperature, that a high-melting-point material like tungsten is required.

**Medical and Other Diagnostic Uses of X-rays**

All of us can identify diagnostic uses of x-ray photons. Among these are the universal dental and medical x rays that have become an essential part of medical diagnostics. (See Figure 30.25 and Figure 30.26.) X rays are also used to inspect our luggage at airports, as shown in Figure 30.24, and for early detection of cracks in crucial aircraft components. An x ray is not only a noun meaning high-energy photon, it also is an image produced by x rays, and it has been made into a familiar verb—to be x-rayed.

**Figure 30.24** An x-ray image reveals fillings in a person's teeth. (credit: Dmitry G, Wikimedia Commons)

**Figure 30.25** This x-ray image of a person's chest shows many details, including an artificial pacemaker. (credit: Sunzi99, Wikimedia Commons)
The most common x-ray images are simple shadows. Since x-ray photons have high energies, they penetrate materials that are opaque to visible light. The more energy an x-ray photon has, the more material it will penetrate. So an x-ray tube may be operated at 50.0 kV for a chest x-ray, whereas it may need to be operated at 100 kV to examine a broken leg in a cast. The depth of penetration is related to the density of the material as well as to the energy of the photon. The denser the material, the fewer x-ray photons get through and the darker the shadow. Thus x rays excel at detecting breaks in bones and in imaging other physiological structures, such as some tumors, that differ in density from surrounding material. Because of their high photon energy, x rays produce significant ionization in materials and damage cells in biological organisms. Modern uses minimize exposure to the patient and eliminate exposure to others. Biological effects of x rays will be explored in the next chapter along with other types of ionizing radiation such as those produced by nuclei.

As the x-ray energy increases, the Compton effect (see Photon Momentum) becomes more important in the attenuation of the x-rays. Here, the x-ray scatters from an outer electron shell of the atom, giving the ejected electron some kinetic energy while losing energy itself. The probability for attenuation of the x-rays depends upon the number of electrons present (the material's density) as well as the thickness of the material. Chemical composition of the medium, as characterized by its atomic number $Z$, is not important here. Low-energy x-rays provide better contrast (sharper images). However, due to greater attenuation and less scattering, they are more absorbed by thicker materials. Greater contrast can be achieved by injecting a substance with a large atomic number, such as barium or iodine. The structure of the part of the body that contains the substance (e.g., the gastro-intestinal tract or the abdomen) can easily be seen this way.

Breast cancer is the second-leading cause of death among women worldwide. Early detection can be very effective, hence the importance of x-ray diagnostics. A mammogram cannot diagnose a malignant tumor, only give evidence of a lump or region of increased density within the breast. X-ray absorption by different types of soft tissue is very similar, so contrast is difficult; this is especially true for younger women, who typically have denser breasts. For older women who are at greater risk of developing breast cancer, the presence of more fat in the breast gives the lump or tumor more contrast. MRI (Magnetic resonance imaging) has recently been used as a supplement to conventional x-rays to improve detection and eliminate false positives. The subject's radiation dose from x-rays will be treated in a later chapter.

A standard x-ray gives only a two-dimensional view of the object. Dense bones might hide images of soft tissue or organs. If you took another x-ray from the side of the person (the first one being from the front), you would gain additional information. While shadow images are sufficient in many applications, far more sophisticated images can be produced with modern technology. Figure 30.27 shows the use of a computed tomography (CT) scanner, also called computed axial tomography (CAT) scanner. X-rays are passed through a narrow section (called a slice) of the patient's body (or body part) over a range of directions. An array of many detectors on the other side of the patient registers the x-rays. The system is then rotated around the patient and another image is taken, and so on. The x-ray tube and detector array are mechanically attached and so rotate together. Complex computer image processing of the relative absorption of the x-rays along different directions produces a highly-detailed image. Different slices are taken as the patient moves through the scanner on a table. Multiple images of different slices can also be computer analyzed to produce three-dimensional information, sometimes enhancing specific types of tissue, as shown in Figure 30.28. G. Hounsfield (UK) and A. Cormack (US) won the Nobel Prize in Medicine in 1979 for their development of computed tomography.
Figure 30.28 This three-dimensional image of a skull was produced by computed tomography, involving analysis of several x-ray slices of the head. (credit: Emailshankar, Wikimedia Commons)

X-Ray Diffraction and Crystallography

Since x-ray photons are very energetic, they have relatively short wavelengths. For example, the 54.4-keV $K_{\alpha}$ x ray of Example 30.2 has a wavelength $\lambda = \frac{hc}{E} = 0.0228$ nm. Thus, typical x-ray photons act like rays when they encounter macroscopic objects, like teeth, and produce sharp shadows; however, since atoms are on the order of 0.1 nm in size, x rays can be used to detect the location, shape, and size of atoms and molecules. The process is called x-ray diffraction, because it involves the diffraction and interference of x rays to produce patterns that can be analyzed for information about the structures that scattered the x rays. Perhaps the most famous example of x-ray diffraction is the discovery of the double-helix structure of DNA in 1953 by an international team of scientists working at the Cavendish Laboratory—American James Watson, Englishman Francis Crick, and New Zealand–born Maurice Wilkins. Using x-ray diffraction data produced by Rosalind Franklin, they were the first to discern the structure of DNA that is so crucial to life. For this, Watson, Crick, and Wilkins were awarded the 1962 Nobel Prize in Physiology or Medicine. There is much debate and controversy over the issue that Rosalind Franklin was not included in the prize.

Figure 30.29 shows a diffraction pattern produced by the scattering of x rays from a crystal. This process is known as x-ray crystallography because of the information it can yield about crystal structure, and it was the type of data Rosalind Franklin supplied to Watson and Crick for DNA. Not only do x rays confirm the size and shape of atoms, they give information on the atomic arrangements in materials. For example, current research in high-temperature superconductors involves complex materials whose lattice arrangements are crucial to obtaining a superconducting material. These can be studied using x-ray crystallography.

Figure 30.29 X-ray diffraction from the crystal of a protein, hen egg lysozyme, produced this interference pattern. Analysis of the pattern yields information about the structure of the protein. (credit: Del45, Wikimedia Commons)

Historically, the scattering of x rays from crystals was used to prove that x rays are energetic EM waves. This was suspected from the time of the discovery of x rays in 1895, but it was not until 1912 that the German Max von Laue (1879–1960) convinced two of his colleagues to scatter x rays from crystals. If a diffraction pattern is obtained, he reasoned, then the x rays must be waves, and their wavelength could be determined. (The spacing of atoms in various crystals was reasonably well known at the time, based on good values for Avogadro’s number.) The experiments were convincing, and the 1914 Nobel Prize in Physics was given to von Laue for his suggestion leading to the proof that x rays are EM waves. In 1915, the unique father-and-son team of Sir William Henry Bragg and his son Sir William Lawrence Bragg were awarded a joint Nobel Prize for inventing the x-ray spectrometer and the then-new science of x-ray analysis. The elder Bragg had migrated to Australia from England just after graduating in mathematics. He learned physics and chemistry during his career at the University of Adelaide. The younger Bragg was born in Adelaide but went back to the Cavendish Laboratories in England to a career in x-ray and neutron crystallography; he provided support for Watson, Crick, and Wilkins for their work on unraveling the mysteries of DNA and to Max Perutz for his 1962 Nobel Prize-winning work on the structure of hemoglobin. Here again, we witness the enabling nature of physics—establishing instruments and designing experiments as well as solving mysteries in the biomedical sciences.

Certain other uses for x rays will be studied in later chapters. X rays are useful in the treatment of cancer because of the inhibiting effect they have on cell reproduction. X rays observed coming from outer space are useful in determining the nature of their sources, such as neutron stars and possibly black holes. Created in nuclear bomb explosions, x rays can also be used to detect clandestine atmospheric tests of these weapons. X rays can cause excitations of atoms, which then fluoresce (emitting characteristic EM radiation), making x-ray-induced fluorescence a valuable analytical tool in a range of fields from art to archaeology.
30.5 Applications of Atomic Excitations and De-Excitations

Many properties of matter and phenomena in nature are directly related to atomic energy levels and their associated excitations and de-excitations. The color of a rose, the output of a laser, and the transparency of air are but a few examples. (See Figure 30.30.) While it may not appear that glow-in-the-dark pajamas and lasers have much in common, they are in fact different applications of similar atomic de-excitations.

![Figure 30.30](image.png)

Light from a laser is based on a particular type of atomic de-excitation. (credit: Jeff Keyzer)

The color of a material is due to the ability of its atoms to absorb certain wavelengths while reflecting or reemitting others. A simple red material, for example a tomato, absorbs all visible wavelengths except red. This is because the atoms of its hydrocarbon pigment (lycopene) have levels separated by a variety of energies corresponding to all visible photon energies except red. Air is another interesting example. It is transparent to visible light, because there are few energy levels that visible photons can excite in air molecules and atoms. Visible light, thus, cannot be absorbed. Furthermore, visible light is only weakly scattered by air, because visible wavelengths are so much greater than the sizes of the air molecules and atoms. Light must pass through kilometers of air to scatter enough to cause red sunsets and blue skies.

Fluorescence and Phosphorescence

The ability of a material to emit various wavelengths of light is similarly related to its atomic energy levels. Figure 30.31 shows a scorpion illuminated by a UV lamp, sometimes called a black light. Some rocks also glow in black light, the particular colors being a function of the rock’s mineral composition. Black lights are also used to make certain posters glow.

![Figure 30.31](image.png)

Objects glow in the visible spectrum when illuminated by an ultraviolet (black) light. Emissions are characteristic of the mineral involved, since they are related to its energy levels. In the case of scorpions, proteins near the surface of their skin give off the characteristic blue glow. This is a colorful example of fluorescence in which excitation is induced by UV radiation while de-excitation occurs in the form of visible light. (credit: Ken Bosma, Flickr)

In the fluorescence process, an atom is excited to a level several steps above its ground state by the absorption of a relatively high-energy UV photon. This is called **atomic excitation**. Once it is excited, the atom can de-excite in several ways, one of which is to re-emit a photon of the same energy as excited it, a single step back to the ground state. This is called **atomic de-excitation**. All other paths of de-excitation involve smaller steps, in which lower-energy (longer wavelength) photons are emitted. Some of these may be in the visible range, such as for the scorpion in Figure 30.31. **Fluorescence** is defined to be any process in which an atom or molecule, excited by a photon of a given energy, and de-excites by emission of a lower-energy photon.

Fluorescence can be induced by many types of energy input. Fluorescent paint, dyes, and even soap residues in clothes make colors seem brighter in sunlight by converting some UV into visible light. X rays can induce fluorescence, as is done in x-ray fluoroscopy to make brighter visible images. Electric discharges can induce fluorescence, as in so-called neon lights and in gas-discharge tubes that produce atomic and molecular spectra. Common fluorescent lights use an electric discharge in mercury vapor to cause atomic emissions from mercury atoms. The inside of a fluorescent light is coated with a fluorescent material that emits visible light over a broad spectrum of wavelengths. By choosing an appropriate coating, fluorescent lights can be made more like sunlight or like the reddish glow of candlelight, depending on needs. Fluorescent lights are more efficient in converting electrical energy into visible light than incandescent filaments (about four times as efficient), the blackbody radiation of which is primarily in the infrared due to temperature limitations.

This atom is excited to one of its higher levels by absorbing a UV photon. It can de-excite in a single step, re-emitting a photon of the same energy, or in several steps. The process is called fluorescence if the atom de-excites in smaller steps, emitting energy different from that which excited it. Fluorescence can be induced by a variety of energy inputs, such as UV, x-rays, and electrical discharge.

The spectacular Waitomo caves on North Island in New Zealand provide a natural habitat for glow-worms. The glow-worms hang up to 70 silk threads of about 30 or 40 cm each to trap prey that fly towards them in the dark. The fluorescence process is very efficient, with nearly 100% of the energy input turning into light. (In comparison, fluorescent lights are about 20% efficient.)

Fluorescence has many uses in biology and medicine. It is commonly used to label and follow a molecule within a cell. Such tagging allows one to study the structure of DNA and proteins. Fluorescent dyes and antibodies are usually used to tag the molecules, which are then illuminated with UV light and their emission of visible light is observed. Since the fluorescence of each element is characteristic, identification of elements within a sample can be done this way.
Figure 30.32 shows a commonly used fluorescent dye called fluorescein. Below that, Figure 30.33 reveals the diffusion of a fluorescent dye in water by observing it under UV light.

Figure 30.32 Fluorescein, shown here in powder form, is used to dye laboratory samples. (credit: Benjah-bmm27, Wikimedia Commons)

Figure 30.33 Here, fluorescent powder is added to a beaker of water. The mixture gives off a bright glow under ultraviolet light. (credit: Bricksnite, Wikimedia Commons)

Nano-Crystals

Recently, a new class of fluorescent materials has appeared—“nano-crystals.” These are single-crystal molecules less than 100 nm in size. The smallest of these are called “quantum dots.” These semiconductor indicators are very small (2–6 nm) and provide improved brightness. They also have the advantage that all colors can be excited with the same incident wavelength. They are brighter and more stable than organic dyes and have a longer lifetime than conventional phosphors. They have become an excellent tool for long-term studies of cells, including migration and morphology. (Figure 30.34.)

Figure 30.34 Microscopic image of chicken cells using nano-crystals of a fluorescent dye. Cell nuclei exhibit blue fluorescence while neurofilaments exhibit green. (credit: Weerapong Prasongchean, Wikimedia Commons)

Once excited, an atom or molecule will usually spontaneously de-excite quickly. (The electrons raised to higher levels are attracted to lower ones by the positive charge of the nucleus.) Spontaneous de-excitation has a very short mean lifetime of typically about $10^{-8}$ s. However, some levels have significantly longer lifetimes, ranging up to milliseconds to minutes or even hours. These energy levels are inhibited and are slow in de-exciting because their quantum numbers differ greatly from those of available lower levels. Although these level lifetimes are short in human terms, they are many orders of magnitude longer than typical and, thus, are said to be metastable, meaning relatively stable. Phosphorescence is the de-excitation of a metastable state. Glow-in-the-dark materials, such as luminous dials on some watches and clocks and on children’s toys and pajamas, are made of phosphorescent substances. Visible light excites the atoms or molecules to metastable states that decay slowly, releasing the stored excitation energy partially as visible light. In some ceramics, atomic excitation energy can be frozen in after the ceramic has cooled from its firing. It is very slowly released, but the ceramic can be induced to phosphoresce by heating—a process called “thermoluminescence.” Since the release is slow, thermoluminescence can be used to date antiquities. The less light emitted, the older the ceramic. (See Figure 30.35.)
Lasers

Lasers today are commonplace. Lasers are used to read bar codes at stores and in libraries, laser shows are staged for entertainment, laser printers produce high-quality images at relatively low cost, and lasers send prodigious numbers of telephone messages through optical fibers. Among other things, lasers are also employed in surveying, weapons guidance, tumor eradication, retinal welding, and for reading music CDs and computer CD-ROMs.

Why do lasers have so many varied applications? The answer is that lasers produce single-wavelength EM radiation that is also very coherent—that is, the emitted photons are in phase. Laser output can, thus, be more precisely manipulated than incoherent mixed-wavelength EM radiation from other sources. The reason laser output is so pure and coherent is based on how it is produced, which in turn depends on a metastable state in the lasing material. Suppose a material had the energy levels shown in Figure 30.36. When energy is put into a large collection of these atoms, electrons are raised to all possible levels. Most return to the ground state in less than about $10^{-8}$ s, but those in the metastable state linger. This includes those electrons originally excited to the metastable state and those that fell into it from above. It is possible to get a majority of the atoms into the metastable state, a condition called a population inversion.

Figure 30.35 Atoms frozen in an excited state when this Chinese ceramic figure was fired can be stimulated to de-excite and emit EM radiation by heating a sample of the ceramic—a process called thermoluminescence. Since the states slowly de-excite over centuries, the amount of thermoluminescence decreases with age, making it possible to use this effect to date and authenticate antiquities. This figure dates from the 11th century. (credit: Vassil, Wikimedia Commons)

Figure 30.36 (a) Energy-level diagram for an atom showing the first few states, one of which is metastable. (b) Massive energy input excites atoms to a variety of states. (c) Most states decay quickly, leaving electrons only in the metastable and ground state. If a majority of electrons are in the metastable state, a population inversion has been achieved.
Once a population inversion is achieved, a very interesting thing can happen, as shown in Figure 30.37. An electron spontaneously falls from the metastable state, emitting a photon. This photon finds another atom in the metastable state and stimulates it to decay, emitting a second photon of the same wavelength and in phase with the first, and so on. **Stimulated emission** is the emission of electromagnetic radiation in the form of photons of a given frequency, triggered by photons of the same frequency. For example, an excited atom, with an electron in an energy orbit higher than normal, releases a photon of a specific frequency when the electron drops back to a lower energy orbit. If this photon then strikes another electron in the same high-energy orbit in another atom, another photon of the same frequency is released. The emitted photons and the triggering photons are always in phase, have the same polarization, and travel in the same direction. The probability of absorption of a photon is the same as the probability of stimulated emission, and so a majority of atoms must be in the metastable state to produce energy. Einstein (again Einstein, and back in 1917!) was one of the important contributors to the understanding of stimulated emission of radiation. Among other things, Einstein was the first to realize that stimulated emission and absorption are equally probable. The laser acts as a temporary energy storage device that subsequently produces a massive energy output of single-wavelength, in-phase photons.

The name **laser** is an acronym for light amplification by stimulated emission of radiation, the process just described. The process was proposed and developed following the advances in quantum physics. A joint Nobel Prize was awarded in 1964 to American Charles Townes (1915–), and Nikolay Basov (1922–2001) and Aleksandr Prokhorov (1916–2002), from the Soviet Union, for the development of lasers. The Nobel Prize in 1981 went to Arthur Schawlow (1921–1999) for pioneering laser applications. The original devices were called masers, because they produced microwaves. The first working laser was created in 1960 at Hughes Research labs (CA) by T. Maiman. It used a pulsed high-powered flash lamp and a ruby rod to produce red light. Today the name laser is used for all such devices developed to produce a variety of wavelengths, including microwave, infrared, visible, and ultraviolet radiation. Figure 30.38 shows how a laser can be constructed to enhance the stimulated emission of radiation. Energy input can be from a flash tube, electrical discharge, or other sources, in a process sometimes called optical pumping. A large percentage of the original pumping energy is dissipated in other forms, but a population inversion must be achieved. Mirrors can be used to enhance stimulated emission by multiple passes of the radiation back and forth through the lasing material. One of the mirrors is semitransparent to allow some of the light to pass through. The laser output from a laser is a mere 1% of the light passing back and forth in a laser.
Figure 30.38 Typical laser construction has a method of pumping energy into the lasing material to produce a population inversion. (a) Spontaneous emission begins with some photons escaping and others stimulating further emissions. (b) and (c) Mirrors are used to enhance the probability of stimulated emission by passing photons through the material several times.

Lasers are constructed from many types of lasing materials, including gases, liquids, solids, and semiconductors. But all lasers are based on the existence of a metastable state or a phosphorescent material. Some lasers produce continuous output; others are pulsed in bursts as brief as $10^{-14}$ s. Some laser outputs are fantastically powerful—some greater than $10^{12}$ W—but the more common, everyday lasers produce something on the order of $10^{-3}$ W. The helium-neon laser that produces a familiar red light is very common. Figure 30.39 shows the energy levels of helium and neon, a pair of noble gases that work well together. An electrical discharge is passed through a helium-neon gas mixture in which the number of atoms of helium is ten times that of neon. The first excited state of helium is metastable and, thus, stores energy. This energy is easily transferred by collision to neon atoms, because they have an excited state at nearly the same energy as that in helium. That state in neon is also metastable, and this is the one that produces the laser output. (The most likely transition is to the nearby state, producing 1.96 eV photons, which have a wavelength of 633 nm and appear red.) A population inversion can be produced in neon, because there are so many more helium atoms and these put energy into the neon. Helium-neon lasers often have continuous output, because the population inversion can be maintained even while lasing occurs. Probably the most common lasers in use today, including the common laser pointer, are semiconductor or diode lasers, made of silicon. Here, energy is pumped into the material by passing a current in the device to excite the electrons. Special coatings on the ends and fine cleavings of the semiconductor material allow light to bounce back and forth and a tiny fraction to emerge as laser light. Diode lasers can usually run continually and produce outputs in the milliwatt range.

Figure 30.39 Energy levels in helium and neon. In the common helium-neon laser, an electrical discharge pumps energy into the metastable states of both atoms. The gas mixture has about ten times more helium atoms than neon atoms. Excited helium atoms easily de-excite by transferring energy to neon in a collision. A population inversion in neon is achieved, allowing lasing by the neon to occur.

There are many medical applications of lasers. Lasers have the advantage that they can be focused to a small spot. They also have a well-defined wavelength. Many types of lasers are available today that provide wavelengths from the ultraviolet to the infrared. This is important, as one needs to
be able to select a wavelength that will be preferentially absorbed by the material of interest. Objects appear a certain color because they absorb all other visible colors incident upon them. What wavelengths are absorbed depends upon the energy spacing between electron orbitals in that molecule. Unlike the hydrogen atom, biological molecules are complex and have a variety of absorption wavelengths or lines. But these can be determined and used in the selection of a laser with the appropriate wavelength. Water is transparent to the visible spectrum but will absorb light in the UV and IR regions. Blood (hemoglobin) strongly reflects red but absorbs most strongly in the UV.

Laser surgery uses a wavelength that is strongly absorbed by the tissue it is focused upon. One example of a medical application of lasers is shown in Figure 30.40. A detached retina can result in total loss of vision. Burns made by a laser focused to a small spot on the retina form scar tissue that can hold the retina in place, salvaging the patient’s vision. Other light sources cannot be focused as precisely as a laser due to refractive dispersion of different wavelengths. Similarly, laser surgery in the form of cutting or burning away tissue is made more accurate because laser output can be very precisely focused and is preferentially absorbed because of its single wavelength. Depending upon what part or layer of the retina needs repairing, the appropriate type of laser can be selected. For the repair of tears in the retina, a green argon laser is generally used. This light is absorbed well by tissues containing blood, so coagulation or “welding” of the tear can be done.

Figure 30.40 A detached retina is burned by a laser designed to focus on a small spot on the retina, the resulting scar tissue holding it in place. The lens of the eye is used to focus the light, as is the device bringing the laser output to the eye.

In dentistry, the use of lasers is rising. Lasers are most commonly used for surgery on the soft tissue of the mouth. They can be used to remove ulcers, stop bleeding, and reshape gum tissue. Their use in cutting into bones and teeth is not quite so common; here the erbium YAG (yttrium aluminum garnet) laser is used.

The massive combination of lasers shown in Figure 30.41 can be used to induce nuclear fusion, the energy source of the sun and hydrogen bombs. Since lasers can produce very high power in very brief pulses, they can be used to focus an enormous amount of energy on a small glass sphere containing fusion fuel. Not only does the incident energy increase the fuel temperature significantly so that fusion can occur, it also compresses the fuel to great density, enhancing the probability of fusion. The compression or implosion is caused by the momentum of the impinging laser photons.

Figure 30.41 This system of lasers at Lawrence Livermore Laboratory is used to ignite nuclear fusion. A tremendous burst of energy is focused on a small fuel pellet, which is imploded to the high density and temperature needed to make the fusion reaction proceed. (credit: Lawrence Livermore National Laboratory, Lawrence Livermore National Security, LLC, and the Department of Energy)

Music CDs are now so common that vinyl records are quaint antiquities. CDs (and DVDs) store information digitally and have a much larger information-storage capacity than vinyl records. An entire encyclopedia can be stored on a single CD. Figure 30.42 illustrates how the information is stored and read from the CD. Pits made in the CD by a laser can be tiny and very accurately spaced to record digital information. These are read by having an inexpensive solid-state infrared laser beam scatter from pits as the CD spins, revealing their digital pattern and the information encoded upon them.
Figure 30.42 A CD has digital information stored in the form of laser-created pits on its surface. These in turn can be read by detecting the laser light scattered from the pit. Large information capacity is possible because of the precision of the laser. Shorter-wavelength lasers enable greater storage capacity.

Holograms, such as those in Figure 30.43, are true three-dimensional images recorded on film by lasers. Holograms are used for amusement, decoration on novelty items and magazine covers, security on credit cards and driver’s licenses (a laser and other equipment is needed to reproduce them), and for serious three-dimensional information storage. You can see that a hologram is a true three-dimensional image, because objects change relative position in the image when viewed from different angles.

Figure 30.43 Credit cards commonly have holograms for logos, making them difficult to reproduce (credit: Dominic Alves, Flickr)

The name hologram means “entire picture” (from the Greek holo, as in holistic), because the image is three-dimensional. Holography is the process of producing holograms and, although they are recorded on photographic film, the process is quite different from normal photography. Holography uses light interference or wave optics, whereas normal photography uses geometric optics. Figure 30.44 shows one method of producing a hologram. Coherent light from a laser is split by a mirror, with part of the light illuminating the object. The remainder, called the reference beam, shines directly on a piece of film. Light scattered from the object interferes with the reference beam, producing constructive and destructive interference. As a result, the exposed film looks foggy, but close examination reveals a complicated interference pattern stored on it. Where the interference was constructive, the film (a negative actually) is darkened. Holography is sometimes called lensless photography, because it uses the wave characteristics of light as contrasted to normal photography, which uses geometric optics and so requires lenses.

Figure 30.44 Production of a hologram. Single-wavelength coherent light from a laser produces a well-defined interference pattern on a piece of film. The laser beam is split by a partially silvered mirror, with part of the light illuminating the object and the remainder shining directly on the film.

Light falling on a hologram can form a three-dimensional image. The process is complicated in detail, but the basics can be understood as shown in Figure 30.45, in which a laser of the same type that exposed the film is now used to illuminate it. The myriad tiny exposed regions of the film are dark and block the light, while less exposed regions allow light to pass. The film thus acts much like a collection of diffraction gratings with various spacings. Light passing through the hologram is diffracted in various directions, producing both real and virtual images of the object used to expose
the film. The interference pattern is the same as that produced by the object. Moving your eye to various places in the interference pattern gives you different perspectives, just as looking directly at the object would. The image thus looks like the object and is three-dimensional like the object.

Figure 30.45 A transmission hologram is one that produces real and virtual images when a laser of the same type as that which exposed the hologram is passed through it. Diffraction from various parts of the film produces the same interference pattern as the object that was used to expose it.

The hologram illustrated in Figure 30.45 is a transmission hologram. Holograms that are viewed with reflected light, such as the white light holograms on credit cards, are reflection holograms and are more common. White light holograms often appear a little blurry with rainbow edges, because the diffraction patterns of various colors of light are at slightly different locations due to their different wavelengths. Further uses of holography include all types of 3-D information storage, such as of statues in museums and engineering studies of structures and 3-D images of human organs. Invented in the late 1940s by Dennis Gabor (1900–1970), who won the 1971 Nobel Prize in Physics for his work, holography became far more practical with the development of the laser. Since lasers produce coherent single-wavelength light, their interference patterns are more pronounced. The precision is so great that it is even possible to record numerous holograms on a single piece of film by just changing the angle of the film for each successive image. This is how the holograms that move as you walk by them are produced—a kind of lensless movie.

In a similar way, in the medical field, holograms have allowed complete 3-D holographic displays of objects from a stack of images. Storing these images for future use is relatively easy. With the use of an endoscope, high-resolution 3-D holographic images of internal organs and tissues can be made.

30.6 The Wave Nature of Matter Causes Quantization

After visiting some of the applications of different aspects of atomic physics, we now return to the basic theory that was built upon Bohr’s atom. Einstein once said it was important to keep asking the questions we eventually teach children not to ask. Why is angular momentum quantized? You already know the answer. Electrons have wave-like properties, as de Broglie later proposed. They can exist only where they interfere constructively, and only certain orbits meet proper conditions, as we shall see in the next module.

Following Bohr’s initial work on the hydrogen atom, a decade was to pass before de Broglie proposed that matter has wave properties. The wave-like properties of matter were subsequently confirmed by observations of electron interference when scattered from crystals. Electrons can exist only in locations where they interfere constructively. How does this affect electrons in atomic orbits? When an electron is bound to an atom, its wavelength must fit into a small space, something like a standing wave on a string. (See Figure 30.46.) Allowed orbits are those orbits in which an electron constructively interferes with itself. Not all orbits produce constructive interference. Thus only certain orbits are allowed—the orbits are quantized.

Figure 30.46 (a) Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (b) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (c) If the wavelength does not fit into the circumference, the electron interferes destructively; it cannot exist in such an orbit.

For a circular orbit, constructive interference occurs when the electron’s wavelength fits neatly into the circumference, so that wave crests always align with crests and wave troughs align with troughs, as shown in Figure 30.46 (b). More precisely, when an integral multiple of the electron’s wavelength equals the circumference of the orbit, constructive interference is obtained. In equation form, the condition for constructive interference and an allowed electron orbit is

\[ n\lambda_n = 2\pi r_n (n = 1, 2, 3 \ldots) \]

where \( \lambda_n \) is the electron’s wavelength and \( r_n \) is the radius of that circular orbit. The de Broglie wavelength is \( \lambda = h/p = h/mv \), and so here \( \lambda = h/m_e v \). Substituting this into the previous condition for constructive interference produces an interesting result:
\[
\frac{nh}{m_e v} = 2\pi r_n.
\]

Rearranging terms, and noting that \( L = mvr \) for a circular orbit, we obtain the quantization of angular momentum as the condition for allowed orbits:

\[
L = m_e v r_n = n \frac{h}{2\pi} (n = 1, 2, 3 \ldots)
\]

This is what Bohr was forced to hypothesize as the rule for allowed orbits, as stated earlier. We now realize that it is the condition for constructive interference of an electron in a circular orbit. Figure 30.47 illustrates this for \( n = 3 \) and \( n = 4 \).

### Waves and Quantization

The wave nature of matter is responsible for the quantization of energy levels in bound systems. Only those states where matter interferes constructively exist, or are “allowed.” Since there is a lowest orbit where this is possible in an atom, the electron cannot spiral into the nucleus. It cannot exist closer to or inside the nucleus. The wave nature of matter is what prevents matter from collapsing and gives atoms their sizes.

#### Figure 30.47
The third and fourth allowed circular orbits have three and four wavelengths, respectively, in their circumferences.

Because of the wave character of matter, the idea of well-defined orbits gives way to a model in which there is a cloud of probability, consistent with Heisenberg’s uncertainty principle. Figure 30.48 shows how this applies to the ground state of hydrogen. If you try to follow the electron in some well-defined orbit using a probe that has a small enough wavelength to get some details, you will instead knock the electron out of its orbit. Each measurement of the electron’s position will find it to be in a definite location somewhere near the nucleus. Repeated measurements reveal a cloud of probability like that in the figure, with each speck the location determined by a single measurement. There is not a well-defined, circular-orbit type of distribution. Nature again proves to be different on a small scale than on a macroscopic scale.

#### Figure 30.48
The ground state of a hydrogen atom has a probability cloud describing the position of its electron. The probability of finding the electron is proportional to the darkness of the cloud. The electron can be closer or farther than the Bohr radius, but it is very unlikely to be a great distance from the nucleus.

There are many examples in which the wave nature of matter causes quantization in bound systems such as the atom. Whenever a particle is confined or bound to a small space, its allowed wavelengths are those which fit into that space. For example, the particle in a box model describes a particle free to move in a small space surrounded by impenetrable barriers. This is true in blackbody radiators (atoms and molecules) as well as in atomic and molecular spectra. Various atoms and molecules will have different sets of electron orbits, depending on the size and complexity of the system. When a system is large, such as a grain of sand, the tiny particle waves in it can fit in so many ways that it becomes impossible to see that the allowed states are discrete. Thus the correspondence principle is satisfied. As systems become large, they gradually look less grainy, and quantization becomes less evident. Unbound systems (small or not), such as an electron freed from an atom, do not have quantized energies, since their wavelengths are not constrained to fit in a certain volume.
30.7 Patterns in Spectra Reveal More Quantization

High-resolution measurements of atomic and molecular spectra show that the spectral lines are even more complex than they first appear. In this section, we will see that this complexity has yielded important new information about electrons and their orbits in atoms.

In order to explore the substructure of atoms (and knowing that magnetic fields affect moving charges), the Dutch physicist Hendrik Lorentz (1853–1930) suggested that his student Pieter Zeeman (1865–1943) study how spectra might be affected by magnetic fields. What they found became known as the Zeeman effect, which involved spectral lines being split into two or more separate emission lines by an external magnetic field, as shown in Figure 30.50. For their discoveries, Zeeman and Lorentz shared the 1902 Nobel Prize in Physics.

Zeeman splitting is complex. Some lines split into three lines, some into five, and so on. But one general feature is that the amount the split lines are separated is proportional to the applied field strength, indicating an interaction with a moving charge. The splitting means that the quantized energy of an orbit is affected by an external magnetic field, causing the orbit to have several discrete energies instead of one. Even without an external magnetic field, very precise measurements showed that spectral lines are doublets (split into two), apparently by magnetic fields within the atom itself.

Bohr’s theory of circular orbits is useful for visualizing how an electron’s orbit is affected by a magnetic field. The circular orbit forms a current loop, which creates a magnetic field of its own, \( B_{\text{orb}} \), as seen in Figure 30.51. Note that the orbital magnetic field \( B_{\text{orb}} \) and the orbital angular momentum \( L_{\text{orb}} \) are along the same line. The external magnetic field and the orbital magnetic field interact; a torque is exerted to align them. A torque rotating a system through some angle does work so that there is energy associated with this interaction. Thus, orbits at different angles to the external magnetic field have different energies. What is remarkable is that the energies are quantized—the magnetic field splits the spectral lines into several discrete lines that have different energies. This means that only certain angles are allowed between the orbital angular momentum and the external field, as seen in Figure 30.52.
The approximate picture of an electron in a circular orbit illustrates how the current loop produces its own magnetic field, called $B_{orb}$. It also shows how $B_{orb}$ is along the same line as the orbital angular momentum $L_{orb}$.

Only certain angles are allowed between the orbital angular momentum and an external magnetic field. This is implied by the fact that the Zeeman effect splits spectral lines into several discrete lines. Each line is associated with an angle between the external magnetic field and magnetic fields due to electrons and their orbits.

We already know that the magnitude of angular momentum is quantized for electron orbits in atoms. The new insight is that the direction of the orbital angular momentum is also quantized. The fact that the orbital angular momentum can have only certain directions is called space quantization. Like many aspects of quantum mechanics, this quantization of direction is totally unexpected. On the macroscopic scale, orbital angular momentum, such as that of the moon around the earth, can have any magnitude and be in any direction.

Detailed treatment of space quantization began to explain some complexities of atomic spectra, but certain patterns seemed to be caused by something else. As mentioned, spectral lines are actually closely spaced doublets, a characteristic called fine structure, as shown in Figure 30.53. The doublet changes when a magnetic field is applied, implying that whatever causes the doublet interacts with a magnetic field. In 1925, Sem Goudsmit and George Uhlenbeck, two Dutch physicists, successfully argued that electrons have properties analogous to a macroscopic charge spinning on its axis. Electrons, in fact, have an internal or intrinsic angular momentum called intrinsic spin $S$. Since electrons are charged, their intrinsic spin creates an intrinsic magnetic field $B_{int}$, which interacts with their orbital magnetic field $B_{orb}$. Furthermore, electron intrinsic spin is quantized in magnitude and direction, analogous to the situation for orbital angular momentum. The spin of the electron can have only one magnitude, and its direction can be at only one of two angles relative to a magnetic field, as seen in Figure 30.54. We refer to this as spin up or spin down for the electron. Each spin direction has a different energy; hence, spectroscopic lines are split into two. Spectral doublets are now understood as being due to electron spin.
Upon close examination, spectral lines are doublets, even in the absence of an external magnetic field. The electron has an intrinsic magnetic field that interacts with its orbital magnetic field.

The intrinsic magnetic field of an electron is attributed to its spin, \( S \), roughly pictured to be due to its charge spinning on its axis. This is only a crude model, since electrons seem to have no size. The spin and intrinsic magnetic field of the electron can make only one of two angles with another magnetic field, such as that created by the electron’s orbital motion. Space is quantized for spin as well as for orbital angular momentum.

These two new insights—that the direction of angular momentum, whether orbital or spin, is quantized, and that electrons have intrinsic spin—help to explain many of the complexities of atomic and molecular spectra. In magnetic resonance imaging, it is the way that the intrinsic magnetic field of hydrogen and biological atoms interact with an external field that underlies the diagnostic fundamentals.

### 30.8 Quantum Numbers and Rules

Physical characteristics that are quantized—such as energy, charge, and angular momentum—are of such importance that names and symbols are given to them. The values of quantized entities are expressed in terms of quantum numbers, and the rules governing them are of the utmost importance in determining what nature is and does. This section covers some of the more important quantum numbers and rules—all of which apply in chemistry, material science, and far beyond the realm of atomic physics, where they were first discovered. Once again, we see how physics makes discoveries which enable other fields to grow.

The energy states of bound systems are quantized, because the particle wavelength can fit into the bounds of the system in only certain ways. This was elaborated for the hydrogen atom, for which the allowed energies are expressed as \( E_n \propto \frac{1}{n^2} \), where \( n = 1, 2, 3, \ldots \). We define \( n \) to be the principal quantum number that labels the basic states of a system. The lowest-energy state has \( n = 1 \), the first excited state has \( n = 2 \), and so on. Thus the allowed values for the principal quantum number are

\[
 n = 1, 2, 3, \ldots \tag{30.41}
\]

This is more than just a numbering scheme, since the energy of the system, such as the hydrogen atom, can be expressed as some function of \( n \), as can other characteristics (such as the orbital radii of the hydrogen atom).

The fact that the magnitude of angular momentum is quantized was first recognized by Bohr in relation to the hydrogen atom; it is now known to be true in general. With the development of quantum mechanics, it was found that the magnitude of angular momentum \( L \) can have only the values

\[
 L_n = \sqrt{n(n+1)} \hbar \]

where \( \hbar \) is the reduced Planck constant.
where \( l \) is defined to be the **angular momentum quantum number**. The rule for \( l \) in atoms is given in the parentheses. Given \( n \), the value of \( l \) can be any integer from zero up to \( n - 1 \). For example, if \( n = 4 \), then \( l \) can be 0, 1, 2, or 3.

Note that for \( n = 1 \), \( l \) can only be zero. This means that the ground-state angular momentum for hydrogen is actually zero, not \( \hbar / 2\pi \) as Bohr proposed. The picture of circular orbits is not valid, because there would be angular momentum for any circular orbit. A more valid picture is the cloud of probability shown for the ground state of hydrogen in Figure 30.48. The electron actually spends time in and near the nucleus. The reason the electron does not remain in the nucleus is related to Heisenberg’s uncertainty principle—the electron’s energy would have to be much too large to be confined to the small space of the nucleus. Now the first excited state of hydrogen has \( n = 2 \), so that \( l \) can be either 0 or 1, according to the rule in \( L = \sqrt{l(l+1)} \frac{\hbar}{2\pi} \). Similarly, for \( n = 3 \), \( l \) can be 0, 1, or 2. It is often most convenient to state the value of \( l \), a simple integer, rather than calculating the value of \( L \) from \( L = \sqrt{l(l+1)} \frac{\hbar}{2\pi} \). For example, for \( l = 2 \), we see that

\[
L = \sqrt{2(2+1)} \frac{\hbar}{2\pi} = \sqrt{6} \frac{\hbar}{2\pi} = 0.390\hbar = 2.58 \times 10^{-34} \text{ J} \cdot \text{s}.
\]

It is much simpler to state \( l = 2 \).

As recognized in the Zeeman effect, the **direction of angular momentum is quantized**. We now know this is true in all circumstances. It is found that the component of angular momentum along one direction in space, usually called the \( z \)-axis, can have only certain values of \( L_z \). The direction in space must be related to something physical, such as the direction of the magnetic field at that location. This is an aspect of relativity. Direction has no meaning if there is nothing that varies with direction, as does magnetic force. The allowed values of \( L_z \) are

\[
L_z = m_l \frac{\hbar}{2\pi} \quad (m_l = -l, -l+1, ..., -1, 0, 1, ..., l-1, l),
\]

where \( L_z \) is the **\( z \)-component of the angular momentum** and \( m_l \) is the angular momentum projection quantum number. The rule in parentheses for the values of \( m_l \) is that it can range from \(-l\) to \( l\) in steps of one. For example, if \( l = 2 \), then \( m_l \) can have the five values \(-2, -1, 0, 1, \) and 2. Each \( m_l \) corresponds to a different energy in the presence of a magnetic field, so that they are related to the splitting of spectral lines into discrete parts, as discussed in the preceding section. If the \( z \)-component of angular momentum can have only certain values, then the angular momentum can have only certain directions, as illustrated in Figure 30.55.

**Example 30.3 What Are the Allowed Directions?**

Calculate the angles that the angular momentum vector \( \mathbf{L} \) can make with the \( z \)-axis for \( l = 1 \), as illustrated in Figure 30.55.

**Strategy**
Figure 30.55 represents the vectors $\mathbf{L}$ and $\mathbf{L}_z$ as usual, with arrows proportional to their magnitudes and pointing in the correct directions. $\mathbf{L}$ and $\mathbf{L}_z$ form a right triangle, with $\mathbf{L}$ being the hypotenuse and $\mathbf{L}_z$ the adjacent side. This means that the ratio of $\mathbf{L}_z$ to $\mathbf{L}$ is the cosine of the angle of interest. We can find $\mathbf{L}$ and $\mathbf{L}_z$ using $L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$ and $L_z = m \frac{\hbar}{2\pi}$.

Solution

We are given $l = 1$, so that $m_l$ can be $+1$, 0, or $-1$. Thus $\mathbf{L}$ has the value given by $L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$.

$L_z$ can have three values, given by $L_z = m \frac{\hbar}{2\pi}$.

As can be seen in Figure 30.55, $\cos \theta = \frac{L_z}{L}$, and so for $m_l = +1$, we have

$$\cos \theta_1 = \frac{L_z}{L} = \frac{\hbar}{\sqrt{2\pi}} = \frac{1}{\sqrt{2}} = 0.707.$$  

Thus,

$$\theta_1 = \cos^{-1} 0.707 = 45.0^\circ.$$  

Similarly, for $m_l = 0$, we find $\cos \theta_2 = 0$; thus,

$$\theta_2 = \cos^{-1} 0 = 90.0^\circ.$$  

And for $m_l = -1$,

$$\cos \theta_3 = \frac{L_z}{L} = \frac{-\hbar}{\sqrt{2\pi}} = -\frac{1}{\sqrt{2}} = -0.707,$$

so that

$$\theta_3 = \cos^{-1} (-0.707) = 135.0^\circ.$$  

Discussion

The angles are consistent with the figure. Only the angle relative to the $z$-axis is quantized. $\mathbf{L}$ can point in any direction as long as it makes the proper angle with the $z$-axis. Thus the angular momentum vectors lie on cones as illustrated. This behavior is not observed on the large scale.

To see how the correspondence principle holds here, consider that the smallest angle ($\theta_1$ in the example) is for the maximum value of $m_l = 0$, namely $m_l = l$. For that smallest angle,

$$\cos \theta_1 = \frac{L_z}{L} = \frac{l}{\sqrt{l(l+1)}}$$

which approaches 1 as $l$ becomes very large. If $\cos \theta = 1$, then $\theta = 0^\circ$. Furthermore, for large $l$, there are many values of $m_l$, so that all angles become possible as $l$ gets very large.

Intrinsic Spin Angular Momentum Is Quantized in Magnitude and Direction

There are two more quantum numbers of immediate concern. Both were first discovered for electrons in conjunction with fine structure in atomic spectra. It is now well established that electrons and other fundamental particles have intrinsic spin, roughly analogous to a planet spinning on its axis. This spin is a fundamental characteristic of particles, and only one magnitude of intrinsic spin is allowed for a given type of particle. Intrinsic angular momentum is quantized independently of orbital angular momentum. Additionally, the direction of the spin is also quantized. It has been found that the magnitude of the intrinsic (internal) spin angular momentum, $S$, of an electron is given by

$$S = \sqrt{s(s+1)} \frac{\hbar}{2\pi} \quad (s = 1/2 \text{ for electrons}),$$

(30.53)
where $s$ is defined to be the spin quantum number. This is very similar to the quantization of $L$ given in $L = \sqrt{l(l+1)}\frac{\hbar}{2\pi}$, except that the only value allowed for $s$ for electrons is $1/2$.

The direction of intrinsic spin is quantized, just as is the direction of orbital angular momentum. The direction of spin angular momentum along one direction in space, again called the $z$-axis, can have only the values

$$S_z = m_s \frac{\hbar}{2\pi} \left( m_s = -\frac{1}{2}, +\frac{1}{2} \right)$$

for electrons. $S_z$ is the z-component of spin angular momentum and $m_s$ is the spin projection quantum number. For electrons, $s$ can only be $1/2$, and $m_s$ can be either $+1/2$ or $-1/2$. Spin projection $m_s = +1/2$ is referred to as spin up, whereas $m_s = -1/2$ is called spin down. These are illustrated in Figure 30.54.

### Intrinsic Spin

In later chapters, we will see that intrinsic spin is a characteristic of all subatomic particles. For some particles $s$ is half-integral, whereas for others $s$ is integral—there are crucial differences between half-integral spin particles and integral spin particles. Protons and neutrons, like electrons, have $s = 1/2$, whereas photons have $s = 1$, and other particles called pions have $s = 0$, and so on.

To summarize, the state of a system, such as the precise nature of an electron in an atom, is determined by its particular quantum numbers. These are expressed in the form $(n, l, m_l, m_s)$—see Table 30.1 For electrons in atoms, the principal quantum number can have the values $n = 1, 2, 3, ...$. Once $n$ is known, the values of the angular momentum quantum number are limited to $l = 1, 2, 3, ..., n - 1$. For a given value of $l$, the angular momentum projection quantum number can have only the values $m_l = -l, -l + 1, ..., -1, 0, 1, ..., l - 1, l$. Electron spin is independent of $n, l$, and $m_l$, always having $s = 1/2$. The spin projection quantum number can have two values, $m_s = 1/2$ or $-1/2$.

### Table 30.1 Atomic Quantum Numbers

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Allowed values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal quantum number</td>
<td>$n$</td>
<td>1, 2, 3, ...</td>
</tr>
<tr>
<td>Angular momentum</td>
<td>$l$</td>
<td>0, 1, 2, ..., $n-1$</td>
</tr>
<tr>
<td>Angular momentum projection</td>
<td>$m_l$</td>
<td>$-l, -l + 1, ..., -1, 0, 1, ..., l - 1, l$ (or 0, ±1, ±2, ..., ±$l$)</td>
</tr>
<tr>
<td>Spin$^[1]$</td>
<td>$s$</td>
<td>1/2(electrons)</td>
</tr>
<tr>
<td>Spin projection</td>
<td>$m_s$</td>
<td>$-1/2, +1/2$</td>
</tr>
</tbody>
</table>

Figure 30.56 shows several hydrogen states corresponding to different sets of quantum numbers. Note that these clouds of probability are the locations of electrons as determined by making repeated measurements—each measurement finds the electron in a definite location, with a greater chance of finding the electron in some places rather than others. With repeated measurements, the pattern of probability shown in the figure emerges. The clouds of probability do not look like nor do they correspond to classical orbits. The uncertainty principle actually prevents us and nature from knowing how the electron gets from one place to another, and so an orbit really does not exist as such. Nature on a small scale is again much different from that on the large scale.

---

1. The spin quantum number $s$ is usually not stated, since it is always $1/2$ for electrons
Figure 30.56 Probability clouds for the electron in the ground state and several excited states of hydrogen. The nature of these states is determined by their sets of quantum numbers, here given as \((n, \ell, m)\). The ground state is \((0, 0, 0)\); one of the possibilities for the second excited state is \((3, 2, 1)\). The probability of finding the electron is indicated by the shade of color; the darker the coloring the greater the chance of finding the electron.

We will see that the quantum numbers discussed in this section are valid for a broad range of particles and other systems, such as nuclei. Some quantum numbers, such as intrinsic spin, are related to fundamental classifications of subatomic particles, and they obey laws that will give us further insight into the substructure of matter and its interactions.

PhET Explorations: Stern-Gerlach Experiment

The classic Stern-Gerlach Experiment shows that atoms have a property called spin. Spin is a kind of intrinsic angular momentum, which has no classical counterpart. When the z-component of the spin is measured, one always gets one of two values: spin up or spin down.

Figure 30.57 Stern-Gerlach Experiment (http://cnx.org/content/m42614/1.10/stern-gerlach_en.jar)

30.9 The Pauli Exclusion Principle

Multiple-Electron Atoms

All atoms except hydrogen are multiple-electron atoms. The physical and chemical properties of elements are directly related to the number of electrons a neutral atom has. The periodic table of the elements groups elements with similar properties into columns. This systematic organization is related to the number of electrons in a neutral atom, called the \textbf{atomic number}, \(Z\). We shall see in this section that the exclusion principle is key to the underlying explanations, and that it applies far beyond the realm of atomic physics.
In 1925, the Austrian physicist Wolfgang Pauli (see Figure 30.58) proposed the following rule: No two electrons can have the same set of quantum numbers. That is, no two electrons can be in the same state. This statement is known as the Pauli exclusion principle, because it excludes electrons from being in the same state. The Pauli exclusion principle is extremely powerful and very broadly applicable. It applies to any identical particles with half-integral intrinsic spin—that is, having \( s = 1/2, 3/2, \ldots \). Thus no two electrons can have the same set of quantum numbers.

**Pauli Exclusion Principle**

No two electrons can have the same set of quantum numbers. That is, no two electrons can be in the same state.

Figure 30.58 The Austrian physicist Wolfgang Pauli (1900–1958) played a major role in the development of quantum mechanics. He proposed the exclusion principle; hypothesized the existence of an important particle, called the neutrino, before it was directly observed; made fundamental contributions to several areas of theoretical physics; and influenced many students who went on to do important work of their own. (credit: Nobel Foundation, via Wikimedia Commons)

Let us examine how the exclusion principle applies to electrons in atoms. The quantum numbers involved were defined in Quantum Numbers and Rules as \( n, l, m_l, s \), and \( m_s \). Since \( s \) is always \( 1/2 \) for electrons, it is redundant to list \( s \), and so we omit it and specify the state of an electron by a set of four numbers \( (n, l, m_l, m_s) \). For example, the quantum numbers \( (2, 1, 0, -1/2) \) completely specify the state of an electron in an atom.

Since no two electrons can have the same set of quantum numbers, there are limits to how many of them can be in the same energy state. Note that \( n \) determines the energy state in the absence of a magnetic field. So we first choose \( n \), and then we see how many electrons can be in this energy state or energy level. Consider the \( n = 1 \) level, for example. The only value \( l \) can have is 0 (see Table 30.1 for a list of possible values once \( n \) is known), and thus \( m_l \) can only be 0. The spin projection \( m_s \) can be either \( +1/2 \) or \( -1/2 \), and so there can be two electrons in the \( n = 1 \) state. One has quantum numbers \( (1, 0, 0, +1/2) \), and the other has \( (1, 0, 0, -1/2) \).

Figure 30.59 illustrates that there can be one or two electrons having \( n = 1 \), but not three.
Figure 30.59 The Pauli exclusion principle explains why some configurations of electrons are allowed while others are not. Since electrons cannot have the same set of quantum numbers, a maximum of two can be in the $n = 1$ level, and a third electron must reside in the higher-energy $n = 2$ level. If there are two electrons in the $n = 1$ level, their spins must be in opposite directions. (More precisely, their spin projections must differ.)

**Shells and Subshells**

Because of the Pauli exclusion principle, only hydrogen and helium can have all of their electrons in the $n = 1$ state. Lithium (see the periodic table) has three electrons, and so one must be in the $n = 2$ level. This leads to the concept of shells and shell filling. As we progress up in the number of electrons, we go from hydrogen to helium, lithium, beryllium, boron, and so on, and we see that there are limits to the number of electrons for each value of $n$. Higher values of the shell $n$ correspond to higher energies, and they can allow more electrons because of the various combinations of $l$, $m_l$, and $m_s$ that are possible. Each value of the principal quantum number $n$ thus corresponds to an atomic shell into which a limited number of electrons can go. Shells and the number of electrons in them determine the physical and chemical properties of atoms, since it is the outermost electrons that interact most with anything outside the atom.

The probability clouds of electrons with the lowest value of $l$ are closest to the nucleus and, thus, more tightly bound. Thus when shells fill, they start with $l = 0$, progress to $l = 1$, and so on. Each value of $l$ thus corresponds to a subshell.

The table given below lists symbols traditionally used to denote shells and subshells.

<table>
<thead>
<tr>
<th>Shell</th>
<th>Subshell</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$</td>
<td>$l = 0$</td>
<td>$s$</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>$l = 1$</td>
<td>$p$</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>$l = 2$</td>
<td>$d$</td>
</tr>
<tr>
<td>$n = 4$</td>
<td>$l = 3$</td>
<td>$f$</td>
</tr>
<tr>
<td>$n = 5$</td>
<td>$l = 4$</td>
<td>$g$</td>
</tr>
<tr>
<td>$n = 6$</td>
<td>$l = 5$</td>
<td>$h$</td>
</tr>
<tr>
<td>$n = 7$</td>
<td>$l = 6$</td>
<td>$i$</td>
</tr>
</tbody>
</table>

To denote shells and subshells, we write $nl$ with a number for $n$ and a letter for $l$. For example, an electron in the $n = 1$ state must have $l = 0$, and it is denoted as a $1s$ electron. Two electrons in the $n = 1$ state is denoted as $1s^2$. Another example is an electron in the $n = 2$ state with $l = 1$, written as $2p$. The case of three electrons with these quantum numbers is written $2p^3$. This notation, called spectroscopic notation, is generalized as shown in Figure 30.60.

2. It is unusual to deal with subshells having $l$ greater than 6, but when encountered, they continue to be labeled in alphabetical order.
Counting the number of possible combinations of quantum numbers allowed by the exclusion principle, we can determine how many electrons it takes to fill each subshell and shell.

**Example 30.4 How Many Electrons Can Be in This Shell?**

List all the possible sets of quantum numbers for the \( n = 2 \) shell, and determine the number of electrons that can be in the shell and each of its subshells.

**Strategy**

Given \( n = 2 \) for the shell, the rules for quantum numbers limit \( l \) to be 0 or 1. The shell therefore has two subshells, labeled \( 2s \) and \( 2p \). Since the lowest \( l \) subshell fills first, we start with the \( 2s \) subshell possibilities and then proceed with the \( 2p \) subshell.

**Solution**

It is convenient to list the possible quantum numbers in a table, as shown below.

![Figure 30.61](image)

**Discussion**

It is laborious to make a table like this every time we want to know how many electrons can be in a shell or subshell. There exist general rules that are easy to apply, as we shall now see.

The number of electrons that can be in a subshell depends entirely on the value of \( l \). Once \( l \) is known, there are a fixed number of values of \( m_l \), each of which can have two values for \( m_s \). First, since \( m_l \) goes from \(-l\) to \( l \) in steps of 1, there are \( 2l + 1 \) possibilities. This number is multiplied by 2, since each electron can be spin up or spin down. Thus the maximum number of electrons that can be in a subshell is \( 2(2l + 1) \).

For example, the \( 2s \) subshell in Example 30.4 has a maximum of 2 electrons in it, since \( 2(2l + 1) = 2(1 + 1) = 2 \) for this subshell. Similarly, the \( 2p \) subshell has a maximum of 6 electrons, since \( 2(2l + 1) = 2(2 + 1) = 6 \). For a shell, the maximum number is the sum of what can fit in the subshells. Some algebra shows that the maximum number of electrons that can be in a shell is \( 2n^2 \).

For example, for the first shell \( n = 1 \), and so \( 2n^2 = 2 \). We have already seen that only two electrons can be in the \( n = 1 \) shell. Similarly, for the second shell, \( n = 2 \), and so \( 2n^2 = 8 \). As found in Example 30.4, the total number of electrons in the \( n = 2 \) shell is 8.

**Example 30.5 Subshells and Totals for \( n = 3 \)**

How many subshells are in the \( n = 3 \) shell? Identify each subshell, calculate the maximum number of electrons that will fit into each, and verify that the total is \( 2n^2 \).

**Strategy**

Subshells are determined by the value of \( l \); thus, we first determine which values of \( l \) are allowed, and then we apply the equation “maximum number of electrons that can be in a subshell = \( 2(2l + 1) \)” to find the number of electrons in each subshell.

**Solution**

![Figure 30.61](image)
Since \( n = 3 \), we know that \( l \) can be 0, 1, or 2; thus, there are three possible subshells. In standard notation, they are labeled the \( 3s \), \( 3p \), and \( 3d \) subshells. We have already seen that 2 electrons can be in an \( s \) state, and 6 in a \( p \) state, but let us use the equation “maximum number of electrons that can be in a subshell = \( 2(2l + 1) \)” to calculate the maximum number in each:

3\( s \) has \( l = 0 \); thus, \( 2(2\cdot0 + 1) = 2(0 + 1) = 2 \)  
3\( p \) has \( l = 1 \); thus, \( 2(2\cdot1 + 1) = 2(2 + 1) = 6 \)  
3\( d \) has \( l = 2 \); thus, \( 2(2\cdot2 + 1) = 2(4 + 1) = 10 \)

Total = 18  
(in the \( n = 3 \) shell)

The equation “maximum number of electrons that can be in a shell = \( 2n^2 \)” gives the maximum number in the \( n = 3 \) shell to be:

\[
\text{Maximum number of electrons} = 2n^2 = 2(3)^2 = 2(9) = 18.
\]  
(30.56)

Discussion

The total number of electrons in the three possible subshells is thus the same as the formula \( 2n^2 \). In standard (spectroscopic) notation, a filled \( n = 3 \) shell is denoted as \( 3s^2 3p^6 3d^{10} \). Shells do not fill in a simple manner. Before the \( n = 3 \) shell is completely filled, for example, we begin to find electrons in the \( n = 4 \) shell.

Shell Filling and the Periodic Table

Table 30.3 shows electron configurations for the first 20 elements in the periodic table, starting with hydrogen and its single electron and ending with calcium. The Pauli exclusion principle determines the maximum number of electrons allowed in each shell and subshell. But the order in which the shells and subshells are filled is complicated because of the large numbers of interactions between electrons.
Table 30.3 Electron Configurations of Elements Hydrogen Through Calcium

<table>
<thead>
<tr>
<th>Element</th>
<th>Number of electrons (Z)</th>
<th>Ground state configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1s&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>1s&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>1s&lt;sup&gt;2&lt;/sup&gt; 2s&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Be</td>
<td>4</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>N</td>
<td>7</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>F</td>
<td>9</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ne</td>
<td>10</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>2s&lt;sup&gt;2&lt;/sup&gt; 2p&lt;sup&gt;6&lt;/sup&gt; 3s&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>P</td>
<td>15</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cl</td>
<td>17</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>3s&lt;sup&gt;2&lt;/sup&gt; 3p&lt;sup&gt;6&lt;/sup&gt; 4s&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>4s&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Examining the above table, you can see that as the number of electrons in an atom increases from 1 in hydrogen to 2 in helium and so on, the lowest-energy shell gets filled first—that is, the \( n = 1 \) shell fills first, and then the \( n = 2 \) shell begins to fill. Within a shell, the subshells fill starting with the lowest \( l \), or with the \( s \) subshell, then the \( p \), and so on, usually until all subshells are filled. The first exception to this occurs for potassium, where the \( 4s \) subshell begins to fill before any electrons go into the \( 3d \) subshell. The next exception is not shown in Table 30.3; it occurs for rubidium, where the \( 5s \) subshell starts to fill before the \( 4d \) subshell. The reason for these exceptions is that \( l = 0 \) electrons have probability clouds that penetrate closer to the nucleus and, thus, are more tightly bound (lower in energy).

Figure 30.62 shows the periodic table of the elements, through element 118. Of special interest are elements in the main groups, namely, those in the columns numbered 1, 2, 13, 14, 15, 16, 17, and 18.
The number of electrons in the outermost subshell determines the atom's chemical properties, since it is these electrons that are farthest from the nucleus and thus interact most with other atoms. If the outermost subshell can accept or give up an electron easily, then the atom will be highly reactive chemically. Each group in the periodic table is characterized by its outermost electron configuration. Perhaps the most familiar is Group 18 (Group VIII), the noble gases (helium, neon, argon, etc.). These gases are all characterized by a filled outer subshell that is particularly stable. This means that they have large ionization energies and do not readily give up an electron. Furthermore, if they were to accept an extra electron, it would be in a significantly higher level and thus loosely bound. Chemical reactions often involve sharing electrons. Noble gases can be forced into unstable chemical compounds only under high pressure and temperature.

Group 17 (Group VII) contains the halogens, such as fluorine, chlorine, iodine and bromine, each of which has one less electron than a neighboring noble gas. Each halogen has 5 \( p \) electrons (a \( p^5 \) configuration), while the \( p \) subshell can hold 6 electrons. This means the halogens have one vacancy in their outermost subshell. They thus readily accept an extra electron (it becomes tightly bound, closing the shell as in noble gases) and are highly reactive chemically. The halogens are also likely to form singly negative ions, such as \( Cl^- \), fitting an extra electron into the vacancy in the outer subshell. In contrast, alkali metals, such as sodium and potassium, all have a single \( s \) electron in their outermost subshell (an \( s^1 \) configuration) and are members of Group 1 (Group I). These elements easily give up their extra electron and are thus highly reactive chemically. As you might expect, they also tend to form singly positive ions, such as \( Na^+ \), by losing their loosely bound outermost electron. They are metals (conductors), because the loosely bound outer electron can move freely.

Of course, other groups are also of interest. Carbon, silicon, and germanium, for example, have similar chemistries and are in Group 4 (Group IV). Carbon, in particular, is extraordinary in its ability to form many types of bonds and to be part of long chains, such as inorganic molecules. The large group of what are called transitional elements is characterized by the filling of the \( d \) subshells and crossing of energy levels. Heavier groups, such as the lanthanide series, are more complex—their shells do not fill in simple order. But the groups recognized by chemists such as Mendeleev have an explanation in the substructure of atoms.

**Glossary**

- **angular momentum quantum number**: a quantum number associated with the angular momentum of electrons
- **atom**: basic unit of matter, which consists of a central, positively charged nucleus surrounded by negatively charged electrons
- **atomic de-excitation**: process by which an atom transfers from an excited electronic state back to the ground state electronic configuration; often occurs by emission of a photon
- **atomic excitation**: a state in which an atom or ion acquires the necessary energy to promote one or more of its electrons to electronic states higher in energy than their ground state
atomic number: the number of protons in the nucleus of an atom

Bohr radius: the mean radius of the orbit of an electron around the nucleus of a hydrogen atom in its ground state

Brownian motion: the continuous random movement of particles of matter suspended in a liquid or gas

cathode-ray tube: a vacuum tube containing a source of electrons and a screen to view images

double-slit interference: an experiment in which waves or particles from a single source impinge upon two slits so that the resulting interference pattern may be observed

energies of hydrogen-like atoms: Bohr formula for energies of electron states in hydrogen-like atoms: \( E_n = -\frac{Z^2}{n^2}E_0(n = 1, 2, 3, \ldots) \)

energy-level diagram: a diagram used to analyze the energy level of electrons in the orbits of an atom

fine structure: the splitting of spectral lines of the hydrogen spectrum when the spectral lines are examined at very high resolution

fluorescence: any process in which an atom or molecule, excited by a photon of a given energy, de-excites by emission of a lower-energy photon

hologram: means entire picture (from the Greek word holo, as in holistic), because the image produced is three dimensional

holography: the process of producing holograms

hydrogen spectrum wavelengths: the wavelengths of visible light from hydrogen; can be calculated by \( \frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \)

hydrogen-like atom: any atom with only a single electron

intrinsic magnetic field: the magnetic field generated due to the intrinsic spin of electrons

intrinsic spin: the internal or intrinsic angular momentum of electrons

laser: acronym for light amplification by stimulated emission of radiation

magnitude of the intrinsic (internal) spin angular momentum: given by \( S = \sqrt{s(s + 1)} \frac{\hbar}{2\pi} \)

metastable: a state whose lifetime is an order of magnitude longer than the most short-lived states

orbital angular momentum: an angular momentum that corresponds to the quantum analog of classical angular momentum

orbital magnetic field: the magnetic field generated due to the orbital motion of electrons

Pauli exclusion principle: a principle that states that no two electrons can have the same set of quantum numbers; that is, no two electrons can be in the same state

phosphorescence: the de-excitation of a metastable state

planetary model of the atom: the most familiar model or illustration of the structure of the atom

population inversion: the condition in which the majority of atoms in a sample are in a metastable state

quantum numbers: the values of quantized entities, such as energy and angular momentum

Rydberg constant: a physical constant related to the atomic spectra with an established value of \( 1.097 \times 10^7 \text{ m}^{-1} \)

shell: a probability cloud for electrons that has a single principal quantum number

space quantization: the fact that the orbital angular momentum can have only certain directions

spin projection quantum number: quantum number that can be used to calculate the intrinsic electron angular momentum along the \( z \)-axis

spin quantum number: the quantum number that parameterizes the intrinsic angular momentum (or spin angular momentum, or simply spin) of a given particle

stimulated emission: emission by atom or molecule in which an excited state is stimulated to decay, most readily caused by a photon of the same energy that is necessary to excite the state

subshell: the probability cloud for electrons that has a single angular momentum quantum number \( l \)

x rays: a form of electromagnetic radiation

x-ray diffraction: a technique that provides the detailed information about crystallographic structure of natural and manufactured materials
Zeeman effect: the effect of external magnetic fields on spectral lines

z-component of spin angular momentum: component of intrinsic electron spin along the z-axis

z-component of the angular momentum: component of orbital angular momentum of electron along the z-axis

Section Summary

30.1 Discovery of the Atom
- Atoms are the smallest unit of elements; atoms combine to form molecules, the smallest unit of compounds.
- The first direct observation of atoms was in Brownian motion.
- Analysis of Brownian motion gave accurate sizes for atoms (10^{-10} m on average) and a precise value for Avogadro's number.

30.2 Discovery of the Parts of the Atom: Electrons and Nuclei
- Atoms are composed of negatively charged electrons, first proved to exist in cathode-ray-tube experiments, and a positively charged nucleus.
- All electrons are identical and have a charge-to-mass ratio of \( \frac{q_e}{m_e} = -1.76 \times 10^{11} \text{ C/kg} \).
- The positive charge in the nuclei is carried by particles called protons, which have a charge-to-mass ratio of \( \frac{q_p}{m_p} = 9.57 \times 10^7 \text{ C/kg} \).
- Mass of electron, \( m_e = 9.11 \times 10^{-31} \text{ kg} \).
- Mass of proton, \( m_p = 1.67 \times 10^{-27} \text{ kg} \).
- The planetary model of the atom pictures electrons orbiting the nucleus in the same way that planets orbit the sun.

30.3 Bohr’s Theory of the Hydrogen Atom
- The planetary model of the atom pictures electrons orbiting the nucleus in the way that planets orbit the sun. Bohr used the planetary model to develop the first reasonable theory of hydrogen, the simplest atom. Atomic and molecular spectra are quantized, with hydrogen spectrum wavelengths given by the formula

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right),
\]

where \( \lambda \) is the wavelength of the emitted EM radiation and \( R \) is the Rydberg constant, which has the value \( R = 1.097 \times 10^7 \text{ m}^{-1} \).
- The constants \( n_i \) and \( n_f \) are positive integers, and \( n_i \) must be greater than \( n_f \).
- Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by

\[
\Delta E = hf = E_i - E_f,
\]

where \( \Delta E \) is the change in energy between the initial and final orbits and \( hf \) is the energy of an absorbed or emitted photon. It is useful to plot orbital energies on a vertical graph called an energy-level diagram.
- Bohr proposed that the allowed orbits are circular and must have quantized orbital angular momentum given by

\[
L = m_e v_r n = n \frac{\hbar}{2\pi} (n = 1, 2, 3 ...),
\]

where \( L \) is the angular momentum, \( v_r \) is the radius of the \( n \)th orbit, and \( \hbar \) is Planck’s constant. For all one-electron (hydrogen-like) atoms, the radius of an orbit is given by

\[
r_n = \frac{n^2}{Z} a_B \text{ (allowed orbits } n = 1, 2, 3 ...),
\]

where \( Z \) is the atomic number of an element (the number of electrons is has when neutral) and \( a_B \) is defined to be the Bohr radius, which is

\[
a_B = \frac{\hbar^2}{4\pi^2 m_e q_e^2} = 0.529 \times 10^{-10} \text{ m}.
\]
- Furthermore, the energies of hydrogen-like atoms are given by

\[
E_n = -\frac{Z^2}{n^2} E_0 (n = 1, 2, 3 ...),
\]

where \( E_0 \) is the ground-state energy and is given by

\[
E_0 = \frac{2\pi^2 q_e^4 m_e k^2}{\hbar^2} = 13.6 \text{ eV}.
\]

Thus, for hydrogen,
$E_n = -\frac{13.6 \text{ eV}}{n^2}(n_0 = 1, 2, 3 ...)$.

- The Bohr Theory gives accurate values for the energy levels in hydrogen-like atoms, but it has been improved upon in several respects.

### 30.4 X Rays: Atomic Origins and Applications
- X rays are relatively high-frequency EM radiation. They are produced by transitions between inner-shell electron levels, which produce x rays characteristic of the atomic element, or by accelerating electrons.
- X rays have many uses, including medical diagnostics and x-ray diffraction.

### 30.5 Applications of Atomic Excitations and De-Excitations
- An important atomic process is fluorescence, defined to be any process in which an atom or molecule is excited by absorbing a photon of a given energy and de-excited by emitting a photon of a lower energy.
- Some states live much longer than others and are termed metastable.
- Phosphorescence is the de-excitation of a metastable state.
- Lasers produce coherent single-wavelength EM radiation by stimulated emission, in which a metastable state is stimulated to decay.
- Lasing requires a population inversion, in which a majority of the atoms or molecules are in their metastable state.

### 30.6 The Wave Nature of Matter Causes Quantization
- Quantization of orbital energy is caused by the wave nature of matter. Allowed orbits in atoms occur for constructive interference of electrons in the orbit, requiring an integral number of wavelengths to fit in an orbit’s circumference; that is,
  \[ n\lambda = 2\pi r_n (n = 1, 2, 3 ...), \]
  where $\lambda_n$ is the electron’s de Broglie wavelength.
- Owing to the wave nature of electrons and the Heisenberg uncertainty principle, there are no well-defined orbits; rather, there are clouds of probability.
- Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by
  \[ \Delta E = hf = E_f - E_i, \]
  where $\Delta E$ is the change in energy between the initial and final orbits and $hf$ is the energy of an absorbed or emitted photon.
- It is useful to plot orbit energies on a vertical graph called an energy-level diagram.
- The allowed orbits are circular, Bohr proposed, and must have quantized orbital angular momentum given by
  \[ L = m_s \hbar r_n = n\frac{\hbar}{2\pi}(n = 1, 2, 3 ...), \]
  where $L$ is the angular momentum, $r_n$ is the radius of orbit $n$, and $\hbar$ is Planck’s constant.

### 30.7 Patterns in Spectra Reveal More Quantization
- The Zeeman effect—the splitting of lines when a magnetic field is applied—is caused by other quantized entities in atoms.
- Both the magnitude and direction of orbital angular momentum are quantized.
- The same is true for the magnitude and direction of the intrinsic spin of electrons.

### 30.8 Quantum Numbers and Rules
- Quantum numbers are used to express the allowed values of quantized entities. The principal quantum number $n$ labels the basic states of a system and is given by
  \[ n = 1, 2, 3, ... \]
- The magnitude of angular momentum is given by
  \[ L = \sqrt{l(l+1)}\frac{\hbar}{2\pi} \quad (l = 0, 1, 2, ..., n-1), \]
  where $l$ is the angular momentum quantum number. The direction of angular momentum is quantized, in that its component along an axis defined by a magnetic field, called the $z$-axis, is given by
  \[ L_z = m_f \frac{\hbar}{2\pi} \quad (m_f = -l, -l+1, ... -1, 0, 1, ... l-1, l), \]
  where $L_z$ is the $z$-component of the angular momentum and $m_f$ is the angular momentum projection quantum number. Similarly, the electron’s intrinsic spin angular momentum $S$ is given by
  \[ S = \sqrt{s(s+1)}\frac{\hbar}{2\pi} \quad (s = 1/2 \text{ for electrons}), \]
  where $S_z$ is the $z$-component of spin angular momentum and $m_s$ is the spin projection quantum number. Spin projection $m_s=+1/2$ is referred to as spin up, whereas $m_s=-1/2$ is called spin down. Table 30.1 summarizes the atomic quantum numbers and their allowed values.

### 30.9 The Pauli Exclusion Principle
- The state of a system is completely described by a complete set of quantum numbers. This set is written as $\{n, l, m_f, m_s\}$. 

The Pauli exclusion principle says that no two electrons can have the same set of quantum numbers; that is, no two electrons can be in the same state.
This exclusion limits the number of electrons in atomic shells and subshells. Each value of $n$ corresponds to a shell, and each value of $l$ corresponds to a subshell.
The maximum number of electrons that can be in a subshell is $2(2l + 1)$.
The maximum number of electrons that can be in a shell is $2n^2$.

### Conceptual Questions

#### 30.1 Discovery of the Atom

1. Name three different types of evidence for the existence of atoms.
2. Explain why patterns observed in the periodic table of the elements are evidence for the existence of atoms, and why Brownian motion is a more direct type of evidence for their existence.
3. If atoms exist, why can’t we see them with visible light?

#### 30.2 Discovery of the Parts of the Atom: Electrons and Nuclei

4. What two pieces of evidence allowed the first calculation of $m_e$, the mass of the electron?
   (a) The ratios $q_e/m_e$ and $q_p/m_p$.
   (b) The values of $q_e$ and $E_B$.
   (c) The ratio $q_e/m_e$ and $q_e$.
   Justify your response.
5. How do the allowed orbits for electrons in atoms differ from the allowed orbits for planets around the sun? Explain how the correspondence principle applies here.

#### 30.3 Bohr’s Theory of the Hydrogen Atom

6. How do the allowed orbits for electrons in atoms differ from the allowed orbits for planets around the sun? Explain how the correspondence principle applies here.
7. Explain how Bohr’s rule for the quantization of electron orbital angular momentum differs from the actual rule.
8. What is a hydrogen-like atom, and how are the energies and radii of its electron orbits related to those in hydrogen?

#### 30.4 X Rays: Atomic Origins and Applications

9. Explain why characteristic x rays are the most energetic in the EM emission spectrum of a given element.
10. Why does the energy of characteristic x rays become increasingly greater for heavier atoms?
11. Observers at a safe distance from an atmospheric test of a nuclear bomb feel its heat but receive none of its copious x rays. Why is air opaque to x rays but transparent to infrared?
12. Lasers are used to burn and read CDs. Explain why a laser that emits blue light would be capable of burning and reading more information than one that emits infrared.
13. Crystal lattices can be examined with x rays but not UV. Why?
14. CT scanners do not detect details smaller than about 0.5 mm. Is this limitation due to the wavelength of x rays? Explain.

#### 30.5 Applications of Atomic Excitations and De-Excitations

15. How do the allowed orbits for electrons in atoms differ from the allowed orbits for planets around the sun? Explain how the correspondence principle applies here.
16. Atomic and molecular spectra are discrete. What does discrete mean, and how are discrete spectra related to the quantization of energy and electron orbits in atoms and molecules?
17. Hydrogen gas can only absorb EM radiation that has an energy corresponding to a transition in the atom, just as it can only emit these discrete energies. When a spectrum is taken of the solar corona, in which a broad range of EM wavelengths are passed through very hot hydrogen gas, the absorption spectrum shows all the features of the emission spectrum. But when such EM radiation passes through room-temperature hydrogen gas, only the Lyman series is absorbed. Explain the difference.
18. Lasers are used to burn and read CDs. Explain why a laser that emits blue light would be capable of burning and reading more information than one that emits infrared.
19. The coating on the inside of fluorescent light tubes absorbs ultraviolet light and subsequently emits visible light. An inventor claims that he is able to do the reverse process. Is the inventor’s claim possible?
20. What is the difference between fluorescence and phosphorescence?
21. How can you tell that a hologram is a true three-dimensional image and that those in 3-D movies are not?

#### 30.6 The Wave Nature of Matter Causes Quantization

22. How is the de Broglie wavelength of electrons related to the quantization of their orbits in atoms and molecules?
30.7 Patterns in Spectra Reveal More Quantization

23. What is the Zeeman effect, and what type of quantization was discovered because of this effect?

30.8 Quantum Numbers and Rules

24. Define the quantum numbers \( n \), \( l \), \( m_l \), \( s \), and \( m_s \).

25. For a given value of \( n \), what are the allowed values of \( l \)?

26. For a given value of \( l \), what are the allowed values of \( m_l \)? What are the allowed values of \( m_l \) for a given value of \( n \)? Give an example in each case.

27. List all the possible values of \( s \) and \( m_s \) for an electron. Are there particles for which these values are different? The same?

30.9 The Pauli Exclusion Principle

28. Identify the shell, subshell, and number of electrons for the following: (a) \( 2p^3 \). (b) \( 4d^9 \). (c) \( 3s^1 \). (d) \( 5g^{16} \).

29. Which of the following are not allowed? State which rule is violated for any that are not allowed. (a) \( 1p^3 \) (b) \( 2p^8 \) (c) \( 3g^{11} \) (d) \( 4f^2 \)
30.1 Discovery of the Atom

30. Using the given charge-to-mass ratios for electrons and protons, and knowing the magnitudes of their charges are equal, what is the ratio of the proton’s mass to the electron’s? (Note that since the charge-to-mass ratios are given to only three-digit accuracy, your answer may differ from the accepted ratio in the fourth digit.)

31. (a) Calculate the mass of a proton using the charge-to-mass ratio given for it in this chapter and its known charge. (b) How does your result compare with the proton mass given in this chapter?

32. If someone wanted to build a scale model of the atom with a nucleus 1.00 m in diameter, how far away would the nearest electron need to be?

30.2 Discovery of the Parts of the Atom: Electrons and Nuclei

33. Rutherford found the size of the nucleus to be about $10^{-15}$ m. This implied a huge density. What would this density be for gold?

34. In Millikan’s oil-drop experiment, one looks at a small oil drop held motionless between two plates. Take the voltage between the plates to be 2033 V, and the plate separation to be 2.00 cm. The oil drop (of density 0.81 g/cm$^3$) has a diameter of $4.0 \times 10^{-6}$ m. Find the charge on the drop, in terms of electron units.

35. (a) An aspiring physicist wants to build a scale model of a hydrogen atom for her science fair project. If the atom is 1.00 m in diameter, how big should she try to make the nucleus? (b) How easy will this be to do?

30.3 Bohr’s Theory of the Hydrogen Atom

36. By calculating its wavelength, show that the first line in the Lyman series is UV radiation.

37. Find the wavelength of the third line in the Lyman series, and identify the type of EM radiation.

38. Look up the values of the quantities in $a_B = \frac{\hbar^2}{4\pi^2 m_e k q_e^2}$, and verify that the Bohr radius $a_B$ is $0.529 \times 10^{-10}$ m.

39. Verify that the ground state energy $E_0$ is 13.6 eV by using $E_0 = \frac{2\pi^2 q_e^2 m_e k^2}{\hbar^2}$.

40. If a hydrogen atom has its electron in the $n = 4$ state, how much energy in eV is needed to ionize it?

41. A hydrogen atom in an excited state can be ionized with less energy than when it is in its ground state. What is $n$ for a hydrogen atom if 0.850 eV of energy can ionize it?

42. Find the radius of a hydrogen atom in the $n = 2$ state according to Bohr’s theory.

43. Show that $(13.6 \text{ eV})/\hbar c = 1.097 \times 10^7$ m = $R$ (Rydberg’s constant), as discussed in the text.

44. What is the smallest-wavelength line in the Balmer series? Is it in the visible part of the spectrum?

45. Show that the entire Paschen series is in the infrared part of the spectrum. To do this, you only need to calculate the shortest wavelength in the series.

46. Do the Balmer and Lyman series overlap? To answer this, calculate the shortest-wavelength Balmer line and the longest-wavelength Lyman line.

47. (a) Which line in the Balmer series is the first one in the UV part of the spectrum? (b) How many Balmer series lines are in the visible part of the spectrum? (c) How many are in the UV?

48. A wavelength of 4.653 μm is observed in a hydrogen spectrum for a transition that ends in the $n_f = 5$ level. What was $n_i$ for the initial level of the electron?

49. A singly ionized helium ion has only one electron and is denoted He$^+$. What is the ion’s radius in the ground state compared to the Bohr radius of hydrogen atom?

50. A beryllium ion with a single electron (denoted Be$^{3+}$) is in an excited state with radius the same as that of the ground state of hydrogen. (a) What is $n$ for the Be$^{3+}$ ion? (b) How much energy in eV is needed to ionize the ion from this excited state?

51. Atoms can be ionized by thermal collisions, such as at the high temperatures found in the solar corona. One such ion is C$^{+5}$, a carbon atom with only a single electron.

52. Verify Equations $r_n = \frac{n^2 \hbar^2}{Ze^2}$ and $a_B = \frac{\hbar^2}{4\pi^2 m_e k q_e^2}$ using the approach stated in the text. That is, equate the Coulomb and centripetal forces and then insert an expression for velocity from the condition for angular momentum quantization.

53. The wavelength of the four Balmer series lines for hydrogen are found to be 410.3, 434.2, 486.3, and 665.5 nm. What average percentage difference is found between these wavelength numbers and those predicted by $\frac{1}{\lambda} = R\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$? It is amazing how well a simple formula (disconnected originally from theory) could duplicate this phenomenon.

30.4 X Rays: Atomic Origins and Applications

54. (a) What is the shortest-wavelength x-ray radiation that can be generated in an x-ray tube with an applied voltage of 50.0 kV? (b) Calculate the photon energy in eV. (c) Explain the relationship of the photon energy to the applied voltage.

55. A color television tube also generates some x rays when its electron beam strikes the screen. What is the shortest wavelength of these x rays, if a 30.0-kV potential is used to accelerate the electrons? (Note that TVs have shielding to prevent these x rays from exposing viewers.)

56. An x-ray tube has an applied voltage of 100 kV. (a) What is the most energetic x-ray photon it can produce? Express your answer in electron volts and joules. (b) Find the wavelength of such an X-ray.

57. The maximum characteristic x-ray photon energy comes from the capture of a free electron into a $K$ shell vacancy. What is this photon energy in keV for tungsten, assuming the free electron has no initial kinetic energy?

58. What are the approximate energies of the $K_\alpha$ and $K_\beta$ x rays for copper?
30.5 Applications of Atomic Excitations and De-Excitations

59. Figure 30.39 shows the energy-level diagram for neon. (a) Verify that the energy of the photon emitted when neon goes from its metastable state to the one immediately below is equal to 1.96 eV. (b) Show that the wavelength of this radiation is 633 nm. (c) What wavelength is emitted when the neon makes a direct transition to its ground state?

60. A helium-neon laser is pumped by electric discharge. What wavelength electromagnetic radiation would be needed to pump it? See Figure 30.39 for energy-level information.

61. Ruby lasers have chromium atoms doped in an aluminum oxide crystal. The energy level diagram for chromium in a ruby is shown in Figure 30.64. What wavelength is emitted by a ruby laser?

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>0.0 eV</td>
</tr>
<tr>
<td>First</td>
<td>2.3 eV</td>
</tr>
<tr>
<td>Second</td>
<td>1.79 eV</td>
</tr>
<tr>
<td>Metastable</td>
<td></td>
</tr>
</tbody>
</table>

Figure 30.64 Chromium atoms in an aluminum oxide crystal have these energy levels, one of which is metastable. This is the basis of a ruby laser. Visible light can pump the atom into an excited state above the metastable state to achieve a population inversion.

62. (a) What energy photons can pump chromium atoms in a ruby laser from the ground state to its second and third excited states? (b) What are the wavelengths of these photons? Verify that they are in the visible part of the spectrum.

63. Some of the most powerful lasers are based on the energy levels of neodymium in solids, such as glass, as shown in Figure 30.65. (a) What average wavelength light can pump the neodymium into the levels above its metastable state? (b) Verify that the 1.17 eV transition produces 1.06 µm radiation.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>0.0 eV</td>
</tr>
<tr>
<td>First</td>
<td>2.1 eV</td>
</tr>
<tr>
<td>Metastable</td>
<td>1.67 eV</td>
</tr>
<tr>
<td>Second</td>
<td>1.17 eV (1.06 µm)</td>
</tr>
</tbody>
</table>

Figure 30.65 Neodymium atoms in glass have these energy levels, one of which is metastable. The group of levels above the metastable state is convenient for achieving a population inversion, since photons of many different energies can be absorbed by atoms in the ground state.

30.8 Quantum Numbers and Rules

64. If an atom has an electron in the \( n = 5 \) state with \( m_l = 3 \), what are the possible values of \( l \)?

65. An atom has an electron with \( m_l = 2 \). What is the smallest value of \( n \) for this electron?

66. What are the possible values of \( m_f \) for an electron in the \( n = 4 \) state?

67. What, if any, constraints does a value of \( m_f = 1 \) place on the other quantum numbers for an electron in an atom?

68. (a) Calculate the magnitude of the angular momentum for an \( l = 1 \) electron. (b) Compare your answer to the value Bohr proposed for the \( n = 1 \) state.

69. (a) What is the magnitude of the angular momentum for an \( l = 1 \) electron? (b) Calculate the magnitude of the electron’s spin angular momentum. (c) What is the ratio of these angular momenta?

70. Repeat Exercise 30.69 for \( l = 3 \).

71. (a) How many angles can \( L \) make with the \( z \)-axis for an \( l = 2 \) electron? (b) Calculate the value of the smallest angle.

72. What angles can the spin \( S \) of an electron make with the \( z \)-axis?

30.9 The Pauli Exclusion Principle

73. (a) How many electrons can be in the \( n = 4 \) shell?

(b) What are its subshells, and how many electrons can be in each?

74. (a) What is the minimum value of \( l \) for a subshell that has 11 electrons in it?

(b) If this subshell is in the \( n = 5 \) shell, what is the spectroscopic notation for this atom?

75. (a) If one subshell of an atom has 9 electrons in it, what is the minimum value of \( l \)? (b) What is the spectroscopic notation for this atom, if this subshell is part of the \( n = 3 \) shell?

76. (a) List all possible sets of quantum numbers \( (n, l, m_l, m_s) \) for the \( n = 3 \) shell, and determine the number of electrons that can be in the shell and each of its subshells.

(b) Show that the number of electrons in the shell equals \( 2n^2 \) and that the number in each subshell is \( 2l(l+1) \).

77. Which of the following spectroscopic notations are not allowed? (a) \( 5s^1 \) (b) \( 1d^1 \) (c) \( 4s^3 \) (d) \( 3p^7 \) (e) \( 5g^{15} \). State which rule is violated for each that is not allowed.

78. Which of the following spectroscopic notations are allowed (that is, which violate none of the rules regarding values of quantum numbers)?

(a) \( 1s^1 \) (b) \( 1d^1 \) (c) \( 4s^2 \) (d) \( 3p^7 \) (e) \( 6h^{20} \)

79. (a) Using the Pauli exclusion principle and the rules relating the allowed values of the quantum numbers \( (n, l, m_l, m_s) \), prove that the maximum number of electrons in a subshell is \( 2n^2 \).

(b) In a similar manner, prove that the maximum number of electrons in a shell is \( 2n^2 \).

80. Integrated Concepts

Estimate the density of a nucleus by calculating the density of a proton, taking it to be a sphere 1.2 fm in diameter. Compare your result with the value estimated in this chapter.

81. Integrated Concepts

The electric and magnetic forces on an electron in the CRT in Figure 30.7 are supposed to be in opposite directions. Verify this by determining the direction of each force for the situation shown. Explain how you obtain the directions (that is, identify the rules used).

82. (a) What is the distance between the slits of a diffraction grating that produces a first-order maximum for the first Balmer line at an angle of 20.0º?
(b) At what angle will the fourth line of the Balmer series appear in first order?
(c) At what angle will the second-order maximum be for the first line?

83. Integrated Concepts
A galaxy moving away from the earth has a speed of 0.0100c. What wavelength do we observe for an \( n_1 = 7 \) to \( n_f = 2 \) transition for hydrogen in that galaxy?

84. Integrated Concepts
Calculate the velocity of a star moving relative to the earth if you observe a wavelength of 9.10 nm for ionized hydrogen capturing an electron directly into the lowest orbital (that is, \( n_1 = \infty \rightarrow n_f = 1 \), or a Lyman series transition).

85. Integrated Concepts
In a Millikan oil-drop experiment using a setup like that in Figure 30.9, a 500-V potential difference is applied to plates separated by 2.50 cm. (a) What is the mass of an oil drop having two extra electrons that is suspended motionless by the field between the plates? (b) What is the diameter of the drop, assuming it is a sphere with the density of olive oil?

86. Integrated Concepts
What double-slit separation would produce a first-order maximum at 3.00° for 25.0-keV x rays? The small answer indicates that the wave character of x rays is best determined by having them interact with very small objects such as atoms and molecules.

87. Integrated Concepts
In a laboratory experiment designed to duplicate Thomson’s determination of \( q_e/m_e \), a beam of electrons having a velocity of 6.00x10^7 m/s enters a 5.00x10^-3 T magnetic field. The beam moves perpendicular to the field in a path having a 6.80-cm radius of curvature. Determine \( q_e/m_e \) from these observations, and compare the result with the known value.

88. Integrated Concepts
Find the value of \( I \), the orbital angular momentum quantum number, for the moon around the earth. The extremely large value obtained implies that it is impossible to tell the difference between adjacent quantized orbits for macroscopic objects.

89. Integrated Concepts
Particles called muons exist in cosmic rays and can be created in particle accelerators. Muons are very similar to electrons, having the same charge and spin, but they have a mass 207 times greater. When muons are captured by an atom, they orbit just like an electron but with a smaller radius, since the mass in \( d_B = \frac{h^2}{4\pi^2 m_e k q_e} = 0.529x10^{-10} \) m is 207 \( m_e \).

(a) Calculate the radius of the \( n = 1 \) orbit for a muon in a uranium ion ( \( Z = 92 \)).

(b) Compare this with the 7.5-fm radius of a uranium nucleus. Note that since the muon orbits inside the electron, it falls into a hydrogen-like orbit. Since your answer is less than the radius of the nucleus, you can see that the photons emitted as the muon falls into its lowest orbit can give information about the nucleus.

90. Integrated Concepts
Calculate the minimum amount of energy in joules needed to create a population inversion in a helium-neon laser containing 1.00x10^-4 moles of neon.

91. Integrated Concepts
A carbon dioxide laser used in surgery emits infrared radiation with a wavelength of 10.6 \( \mu \mbox{m} \). In 1.00 ms, this laser raised the temperature of 1.00 cm^3 of flesh to 100°C and evaporated it.

(a) How many photons were required? You may assume flesh has the same heat of vaporization as water. (b) What was the minimum power output during the flash?

92. Integrated Concepts
Suppose an MRI scanner uses 100-MHz radio waves.

(a) Calculate the photon energy.
(b) How does this compare to typical molecular binding energies?

93. Integrated Concepts
(a) An excimer laser used for vision correction emits 193-nm UV. Calculate the photon energy in eV.
(b) These photons are used to evaporate corneal tissue, which is very similar to water in its properties. Calculate the amount of energy needed per molecule of water to make the phase change from liquid to gas. That is, divide the heat of vaporization in kJ/kg by the number of water molecules in a kilogram.

(c) Convert this to eV and compare to the photon energy. Discuss the implications.

94. Integrated Concepts
A neighboring galaxy rotates on its axis so that stars on one side move toward us as fast as 200 km/s, while those on the other side move away as fast as 200 km/s. This causes the EM radiation we receive to be Doppler shifted by velocities over the entire range of ±200 km/s. What range of wavelengths will we observe for the 656.0-nm line in the Balmer series of hydrogen emitted by stars in this galaxy? (This is called line broadening.)

95. Integrated Concepts
A pulsar is a rapidly spinning remnant of a supernova. It rotates on its axis, sweeping hydrogen along with it so that hydrogen on one side moves toward us as fast as 50.0 km/s, while that on the other side moves away as fast as 50.0 km/s. This means that the EM radiation we receive will be Doppler shifted over a range of ±50.0 km/s. What range of wavelengths will we observe for the 91.20-nm line in the Lyman series of hydrogen? (Such line broadening is observed and actually provides part of the evidence for rapid rotation.)

96. Integrated Concepts
Prove that the velocity of charged particles moving along a straight path through perpendicular electric and magnetic fields is \( v = E/B \). Thus crossed electric and magnetic fields can be used as a velocity selector independent of the charge and mass of the particle involved.

97. Unreasonable Results
(a) What voltage must be applied to an X-ray tube to obtain 0.0100-fm-wavelength X-rays for use in exploring the details of nuclei? (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

98. Unreasonable Results
A student in a physics laboratory observes a hydrogen spectrum with a diffraction grating for the purpose of measuring the wavelengths of the emitted radiation. In the spectrum, she observes a yellow line and finds its wavelength to be 589 nm. (a) Assuming this is part of the Balmer series, determine \( n_f \), the principal quantum number of the initial state.

(b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

99. Construct Your Own Problem
The solar corona is so hot that most atoms in it are ionized. Consider a hydrogen-like atom in the corona that has only a single electron. Construct a problem in which you calculate selected spectral energies and wavelengths of the Lyman, Balmer, or other series of this atom that could be used to identify its presence in a very hot gas. You will need to
choose the atomic number of the atom, identify the element, and choose which spectral lines to consider.

100. Construct Your Own Problem

Consider the Doppler-shifted hydrogen spectrum received from a rapidly receding galaxy. Construct a problem in which you calculate the energies of selected spectral lines in the Balmer series and examine whether they can be described with a formula like that in the equation

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \]

but with a different constant \( R \).