Atoms: Their Structure, Properties, and Component Particles

The atom is the smallest unit into which matter can be divided without the release of electrically charged particles. It also is the smallest unit of matter that has the characteristic properties of a chemical element. As such, the atom is the basic building block of chemistry.

Most of the atom is empty space. The rest consists of a positively charged nucleus of protons and neutrons surrounded by a cloud of negatively charged electrons. The nucleus is small and dense compared to the electrons, which are the lightest charged particles in nature. Electrons are attracted to any positive charge by their electric force; in an atom, electric forces bind the electrons to the nucleus.

It is easier to describe an atom mathematically than conceptually, and so physicists have developed several models to explain its various characteristics. In some respects, the electrons in an atom behave like particles orbiting the nucleus. In others, the electrons behave like waves frozen in position around the nucleus. Such wave patterns, called orbitals, describe the distribution of individual electrons. The behaviour of an atom is strongly influenced by these orbital properties, and its chemical properties are determined by orbital groupings known as shells.

This article opens with a broad overview of the fundamental properties of the atom and its constituent particles and forces. A more mathematical and technical discussion of its structure and nucleus is provided in subsequent sections. Included too is a historical survey of the most influential concepts about the atom that have been formulated through the centuries. For additional information pertaining to nuclear structure and elementary particles, see subatomic particles. For coverage of other related topics in the Macropedia and Micropedia, see the Pro-pedia, sections 111, 112, 121, 122, 124, 125, and 128.

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**Constituent particles and forces**

Most matter consists of an agglomeration of molecules, which can be separated relatively easily. Molecules, in turn, are composed of atoms joined by chemical bonds that are more difficult to break. Each individual atom consists of smaller particles—namely, electrons and nuclei. These particles are electrically charged, and the electric forces on the charge are responsible for holding the atom together. Atoms of a given element differ from those of other elements in the number of their electrons. Also, atoms form molecules by lending and sharing electrons. Some elements, such as alkali metals, have an electron that is loosely bound to the nucleus and thus easily removed in chemical reactions; other elements, such as the noble (or inert) gases, have very tightly bound electrons as most of its is its as.

It is composed of protons, which have a positive charge, and neutrons, which have no charge. These constituent protons and neutrons collectively are called nucleons. Protons, neutrons, and the electrons surrounding them are long-lived particles present in all ordinary, naturally occurring atoms. Other subatomic particles may be found in association with these three types of particles. They can be created only with the addition of enormous amounts of energy, however, and are very short-lived.

All atoms are roughly the same size, whether they have three or 90 electrons. Approximately 50,000,000,000 of about 10^24 atoms are aligned in a row would measure one centimetre (0.4 inch). A convenient unit of length for measuring atomic sizes is the angstrom (Å), defined as 10^-10 metre. The radius of an atom measures 1–2 Å.

Compared to the overall size of the atom, the nucleus is even more minute. It is in the same proportion to the atom as a marble is to a football field. In volume, the nucleus takes up only 10^-14 of the space in the atom—i.e., one part in 100,000,000,000,000. A convenient unit of length for measuring nuclear sizes is the femtometre (fm), which equals 10^-13 metre. The diameter of a nucleus depends on the number of particles it contains and ranges from about 4 fm for a light nucleus such as carbon to 15 fm for a heavy nucleus such as lead. In spite of the small size of the nucleus, virtually all the mass of the atom is concentrated there. The protons are massive, positively charged particles, whereas the neutrons have no charge and are nearly as massive as the protons. The fact that nuclei can have anywhere from one to about 250 nucleons with their wide variation in mass. The lightest nucleus, that of hydrogen, is 1.836 times more massive than an electron, while heavy nuclei are nearly 500,000 times more massive.

**Size of the nucleus**

Although electrons exhibit complicated behaviour within an atom, they are characterized completely by a few parameters that define their charge, mass, an internal motion called spin, and magnetic moment. All electrons have identical properties. As the lightest charged particles in existence, they are absolutely stable because they cannot decay into smaller units. Their charge and mass, which are important determinants of atomic properties, are listed in Table 1. The spin of the electron provides it with a directional orientation. The electron has a magnetic moment along its spin axis. (Magnetic moment is a property of a particle, which, like a compass needle, causes its axis to align in a magnetic field.) Electrons are subject not only to the electromagnetic force but also to the force of gravity and the so-called weak interaction, the force primarily manifested in the radioactive decay of nuclei.

**Electrons**

The most important characteristic of an atom is its atomic number, which is defined as the number of units of positive charge in the nucleus. A neutral atom has an equal number of protons and electrons, so that the positive and negative charges exactly balance. The atomic number determines the chemical properties of an atom, including the kinds of molecules that can be formed and their binding energies. Hence, the atomic number determines an atom's characteristics as an element. (An element is composed of atoms with the same atomic number.) Elements found in nature range from atomic number 1, hydrogen, to atomic number 92, uranium. In addition, artificial elements with atomic numbers beyond 100 have been produced.

**Hadrons and quarks**

**Leptons**

**Properties of Atoms**

**Atomic number.** The single most important characteristic of an atom is its atomic number, which is defined as the number of units of positive charge in the nucleus. A neutral atom has an equal number of protons and electrons, so that the positive and negative charges exactly balance. The atomic number determines the chemical properties of an atom, including the kinds of molecules that can be formed and their binding energies. Hence, the atomic number determines an atom's characteristics as an element. (An element is composed of atoms with the same atomic number.) Elements found in nature range from atomic number 1, hydrogen, to atomic number 92, uranium. In addition, artificial elements with atomic numbers beyond 100 have been produced.

**Atomic mass number.** The total number of nucleons (both protons and neutrons) in an atom is the atomic mass number, or mass number. Atoms with the same atomic number but different atomic masses are called...
Isotopes. Isotopes have identical chemical properties, yet they can have very different nuclear properties (see below Isotopes). The nuclear properties of an atom include possible radioactivity (the propensity to become radioactive in nuclear reactions), magnetic properties, and weight. The element potassium, for example, has two natural isotopes, $^{39}$K and $^{41}$K. They form exactly the same compounds, but $^{40}$K is radioactive and decays into another element. In scientific notation, the isotope of potassium with 19 protons, 20 neutrons, and a total of 39 nucleons can be written either as $^{40}$K or as $^{40}$Pr.

Because isotopes have the same number of protons, all of the isotopes of a given element occupy the same place in the periodic table of elements. Most elements have stable isotopes. For example, hydrogen has three isotopes, each with one proton. The nucleus of ordinary hydrogen is an isotope called hydrogen, but the isotope deuterium has a neutron bound to the proton. Both of these isotopes are stable. The third hydrogen isotope, tritium, has two neutrons and is radioactive. Radioactive isotopes can be made for many elements; the more the number of neutrons deviates from the optimum number for that atomic mass, the shorter the life of the radioactive isotope.

Atomic weight. The term atomic weight, or atomic mass, refers to the mass of a fixed number of atoms of an element. The standard scientific unit for dealing with atoms in macroscopic quantities is the mole (mol), which is defined arbitrarily as the amount of substance with as many atoms or other units as there are in 12 grams of the carbon isotope $^{12}$C. The number of atoms in a mole is called Avogadro’s number, the value of which is approximately $6 \times 10^{23}$. The atomic mass of an element is expressed in daltons, or more commonly atomic mass units (amu’s), is the number of grams in one mole of the element. The amu is convenient because atomic masses and atomic weights are equal to atomic mass numbers and therefore are close to integer values.

Historically, the law for chemical combination according to molar weights was the primary evidence for the existence of atoms and molecules. For example, two grams of hydrogen combine with 16 grams of oxygen to form water. This represents two moles of hydrogen of atomic weight 1 combining with one mole of oxygen of atomic weight 16. Elements consisting of a mixture of several isotopes may not have an atomic mass close to an integer, because the mass will be the weighted average of the different isotopes. An example is chlorine, which has two common isotopes, $^{35}$Cl and $^{37}$Cl, and a weighted average mass of 35.5 amu.

Electric charge. The normal atom is electrically neutral, meaning that it carries a net electric charge of zero. Some atoms, however, have lost or gained electrons in chemical reactions or in collisions with other particles. Atoms with a net charge, either from the gain or loss of electrons, are called ions. An ion with a net positive charge becomes a positive ion; if it gains an electron, it becomes a negative ion.

The charge on any particle is a whole multiple of the electron’s charge, either positive or negative. The quarks are an exception to this rule. They have charges of $+\frac{1}{3}e$ and $-\frac{1}{3}e$. However, they exist only in groups, and each group as a whole has an integral multiple of the electron’s charge. The amount of charge in this fundamental unit is equal to $1.6 \times 10^{-19}$ coulomb. This means that in a current of one ampere—roughly what a 100-watt light bulb uses in the ordinary 110-volt household circuit—about 6 $\times 10^{18}$ electrons pass through the wire every second.

Electron shells. The behavior of electron clouds of atoms is quite subtle and is governed by the laws of quantum mechanics. According to these laws, electrons occupy various regions of the atom in frozen wave patterns called orbitals. The orbitals are most easily visualized as clouds surrounding the nucleus. The shape and size of the orbital, and the energy of the electron, are calculated by differential equations. The orbitals vary in shape from smooth and spherical for the electrons most tightly bound to the nucleus to rather diffuse and lumpy for the least bound electrons. The hydrogen atom has a single electron in a spherical cloud. The electron could go into other orbitals, but it would require additional energy in the atom to do so. The quantum theory provides that the energy of an atom can only change in definite amounts called quanta. The different possible states an atom can be in, with each of its own definite energy, are called energy levels. The light emitted from a specific frequency associated with the energy quanta. Energy at the atomic level is often expressed in electron volts (eV). There are $2.26 \times 10^{15}$ eV in one kilowatt-hour. To remove an electron from an atom requires several electron volts, depending on the atom. Visible light has a quantum energy of about 2 eV. Each electron in a multielectron atom has its own orbit, according to a law of quantum mechanics known as the Pauli principle (also called the Pauli exclusion principle or exclusion principle). Thus, in atoms with many electrons, many different kinds of orbitals are occupied. A group of orbitals with the same or nearly the same energy is called a shell. The pattern of filled and unfilled shells in each element is different; this variety gives the elements their distinctive characteristics.

Chemical behavior. The chemical behavior of atoms depends on the shells of the more loosely bound electrons. The Pauli principle is responsible for chemical valence, the principle of chemistry according to which atoms of one element bond to a definite number of atoms of another element according to simple counting rules. If these shells are completely filled, the electrons are tightly bound and the atom does not readily share or lend its electrons to form chemical bonds. If there is only one electron in the last shell, it is weakly bound and the atom can be easily ionized. Examples of these situations are helium, which has a filled shell and is an inert gas, and lithium, which has one more electron in the next shell and is a highly reactive metal.

One kind of chemical bond is the ionic bond, in which a loosely bound electron from one atom transfers to another to form a closer shell in another atom. The two ions are held together by their electrical forces. Another kind of bond is the covalent bond. In this situation, the electron clouds of one atom are distorted by the presence of another atom. In the new cloud pattern, the outer electrons are more concentrated in the region between the two atoms. Thus, the atoms share their electrons. This allows atoms of the same element to form chemical bonds, which could not happen with ionic bonds. Chemical-bond energies typically measure several electron volts.

Nuclear properties. Like atoms, nuclei have a shell structure with the protons and neutrons in orbitals. Nuclei can exist in states of different energy, but ordinary stable nuclei are always in the lowest bound state. The scale of these energies is 1,000,000 times as large as atomic or chemical energies.

Nuclei can undergo transformations that affect their binding energies. If a transformation leads to more tightly bound nuclei, the excess energy will be released in some form. If one mole of atoms undergoes a nuclear transformation and releases 1,000,000 electron volts (1 MeV) of energy per nucleus, the total energy will be $10^{14}$ joules.

Some transformations can take place spontaneously, and such a process is called radioactive decay. In one form of radioactivity, a neutron in the nucleus is converted to a proton or vice versa. If the same process occurs, the nucleus is disintegrated into two lower mass numbers. One example of these is, 1,000,000 times as large as atomic or chemical energies. nuclear transformations also take place in nuclear reactions, which are the processes that occur when a nucleus is struck by some external particle. In a fusion reaction, two light nuclei come together and merge into a single heavier nucleus. Another important reaction is fission, the division of a nucleus into two roughly equal parts. Fission can be induced in the heaviest elements by reactions with free
neutrons. Both fusion and fission can release energy by reforming the nuclei so that their atomic masses are closer to the middle range where nuclei have maximum binding energy (see below Nuclear fission and Nuclear fusion).

Development of atomic theory

The concept of the atom that Western scientists accepted in broad outline from the 1600s until about 1900 originated with Greek philosophers in the 5th century BC. Their speculation about a hard, indivisible fundamental particle called the atom was replaced by a more sophisticated theory supported by experiment and mathematical deduction. It was 2,000 years before modern physicists realized that the atom is indeed divisible and that it is not hard, solid, or impenetrable.

THE ATOMIC PHILOSOPHY OF THE EARLY GREEKS

Leucippus of Miletus (5th century BC) is thought to have originated the atomic philosophy. His famous disciple, Democritus of Abdera, developed and named the building blocks of matter atoms, meaning literally "indivisible," about 430 BC. Democritus believed that atoms were uniformly hard, impenetrable, and indecomposable and that they moved in infinite numbers through empty space until stopped. Differences in atomic shape and size determined the various properties of matter. In Democritus' philosophy, atoms existed not only for matter but also for such qualities as perception and the human soul. For example, fearlessness was caused by needle-shaped atoms, while the color white was composed of smooth-surfaced atoms. The atoms of the soul were considered to be particularly fine. Democritus developed his atomic philosophy as a middle ground between two opposing Greek theories about reality and the illusion of change. He argued that matter was subdivided into indivisible and impenetrable particles that created the appearance of change when they joined and separated from others.

The philosopher Epicurus of Samos (341–270 BC) used Democritus' ideas to try to quiet the fears of superstitious Greeks. According to Epicurus' materialistic philosophy, the entire universe was composed exclusively of atoms and void, and so even the gods were subject to natural laws. Most of what is known about the atomic philosophy of the early Greeks comes from Aristotle's attacks on it and from a long poem, De rerum natura ("On the Nature of Things"), which the Latin poet and philosopher Titus Lucretius Carus (c. 95–55 BC) wrote to popularize its ideas. The Greek atomist theory was historically and philosophically, but it has no scientific value. It was not based on observations of nature, measurements, tests, or experiments. Instead, the Greeks used mathematics and reason almost exclusively when they wrote about physics. Like the later theologians of the Middle Ages, they wanted an all-encompassing theory to explain the universe, not merely a detailed experimental view of a tiny portion of it. Science constituted only one aspect of their broad philosophical system. Thus, Plato and Aristotle attacked Democritus' atomic theory on philosophical grounds rather than on scientific ones. Plato valued abstract ideas more than the physical world and rejected the notion that attributes such as goodness and beauty were "mechanical manifestations of material atoms." Where Democritus believed that matter could not move through space without a vacuum and that light was the rapid movement of particles through a void, Aristotle rejected the existence of vacuums because he could not conceive of the physical universe being empty. Aristotle's imagination was not as rich as Democritus', since his conception prevailed in medieval Christian Europe; its science was based on revelation and reason, and the Roman Catholic theologians rejected Democritus as materialistic and atheistic.

THE EMERGENCE OF EXPERIMENTAL SCIENCE

De rerum natura, which was rediscovered in the 15th century, helped fuel the 17th-century debate between orthodox Aristotelian views and the new experimental science. The poem was printed in 1649 and popularized by Pierre Gassendi, a French priest who tried to separate Epicurus' atomism from its materialistic background by arguing that God created atoms.

Soon after Galileo Galilei expressed his belief that vacuums can exist (1638), scientists began studying the properties of air and partial vacuums to test the relative merits of Aristotelian orthodoxy and the atomic theory. The experimental evidence about air was only gradually separated from this philosophical controversy.

The Anglo-Irish chemist Robert Boyle began his systematic study of air in 1658 after he learned that Otto von Guericke, a German physicist and engineer, had invented an improved air pump four years earlier. In 1662 Boyle published the first physical law expressed in the form of an equation that describes the functional dependence of two variable quantities. This formulation became known as Boyle's law. From the beginning, Boyle wanted to analyze the elasticity of air quantitatively, not just qualitatively, and to separate the particular experimental problem about air's "spring" from the surrounding philosophical issues. Pouring mercury into the open end of a closed J-shaped tube, Boyle forced the air in the short side of the tube to contract under the pressure of the mercury on top. By doubling the height of the mercury column, he roughly doubled the pressure and halved the volume of air. By tripling the pressure, he cut the volume of air to a third, and so on.

This behaviour can be formulated mathematically in the relation $PV = k$, where $P$ and $V$ are the pressure and volume under one set of conditions and $P'$ and $V'$ represent them under different conditions. Boyle's law says that pressure and volume are inversely related for a given quantity of gas. Although it is only approximately true for real gases, Boyle's law is an extremely useful idealization that played an important role in the development of atomic theory.

Soon after his air-pressure experiments, Boyle wrote that all matter is composed of solid particles arranged into molecules to give material its different properties. He explained that all things are "made of one Catholic Matter common to them all, and . . . differ but in the shape, size, motion or rest, and texture of the small parts they consist of."

In France Boyle's law is called Mariotte's law after the physicist Edme Mariotte, who discovered the empirical relationship independently in 1676. Mariotte realized that the law holds true only under constant temperature; otherwise, the volume of gas expands when heated or contracts when cooled.

Forty years later, Isaac Newton expressed a typical 18th-century view of the atom that was similar to that of Democritus, Boyle, and Gassendi. In the last query in his book Opticks (1704), Newton stated:

All these things being considered, it seems probable to me that God in the beginning form'd Matter in solid, massy, hard, impenetrable, moveable Particles, of such Sizes and Figures, and with such other Properties, and in such Proportion to Space, as most conduced to the End for which he form'd them; and that these primitive Particles being Solids, are incomparably harder than any porous Bodies compounded of them; even so very hard, as never to wear or break in pieces; no ordinary Power being able to divide what God himself made one in the first Creation.

By the end of the 18th century chemists were just beginning to learn how chemicals combine. In 1794 Joseph-Louis Proust of France published his law of definite proportions (also known as Proust's law). He stated that the components of chemical compounds always combine in the same proportions by weight. For example, Proust found that no matter where he got his samples of the compound copper carbonate, they were composed by weight of five parts copper, four parts oxygen, and one part carbon.

THE BEGINNINGS OF MODERN ATOMIC THEORY

Experimental foundation of atomic chemistry. The British chemist and physicist John Dalton extended Proust's work and converted the atomic philosophy of the Greeks into a scientific theory between 1803 and 1808. His book New System of Chemical Philosophy (part I, 1808; part II, 1810) was the first application of atomic Law of definite proportions
Dalton's application of atomic theory to chemistry. It provided a physical picture of how elements combine to form compounds and a phenomenological reason for believing that atoms exist. His work, together with that of Joseph-Louis Gay-Lussac of France and Amedeo Avogadro of Italy, provided the experimental foundation of atomic chemistry.

On the basis of the law of definite proportions, Dalton deduced the law of multiple proportions, which stated that when two elements form more than one compound by combining in more than one proportion by weight, the weights of one element in one of the compounds is in simple, integer ratios to its weights in the other compounds. For example, Dalton knew that oxygen and carbon can combine to form two different compounds and that carbon dioxide (CO₂) contains twice as much oxygen by weight as carbon monoxide (CO). In this case, the ratio of oxygen to carbon in the compounds is 2:1. Gay-Lussac, the other is the simple integer ratio 1:2. Although Dalton called his theory "modern" to differentiate it from Democritus' philosophy, he retained the Greek term atom to honor the ancients.

Dalton had begun his atomic studies by wondering why oxygen and nitrogen gases do not separate when the heaviest on the bottom and the lightest on the top. He decided that atoms are not infinite in variety as had been supposed and that they are limited to one of a kind for each element. Proposing that all the atoms of a given element have the same fixed mass, he concluded that these elements react in definite proportions to form compounds because their constituent atoms reate in definite proportion to produce compounds. He then tried to figure out the masses for well-known compounds. To do so, Dalton made a faulty but understandable assumption that the simplest hypothesis about atomic combinations was true. He maintained that the molecules of an element were single atoms. Thus, if two elements formed only one compound, he believed that one atom of each element combined with one atom of another element. For example, describing the formation of water, he said that one atom of hydrogen and one of oxygen would combine to form H₂O instead of H₂O. Dalton's mistaken belief that atoms react together by attractive forces was accepted and formed the basis of most 19th-century chemistry. As long as scientists worked with masses as ratios, a consistent chemistry could be developed because they did not need to know whether the atoms were separate or joined together as molecules.

Gay-Lussac soon took the relationship between chemical masses implied by Dalton's atomic theory and expanded it to volumetric relationships of gases. In 1809 he published two observations about gases that have come to be known as Gay-Lussac's law of combining gases. The first part of the law says that, when gases combine chemically, they combine in volumes proportional to their volumes at the same pressure and temperature. Gay-Lussac illustrated this part of his law with three oxides of nitrogen. The compound NO has equal parts of nitrogen and oxygen by volume. Similarly, in the compound N₂O, the two parts by volume of nitrogen combine with one part of oxygen. He found corresponding volumes of nitrogen and oxygen to be equal. Thus, Gay-Lussac's law states that the ratios of the chemical constituents within a compound, unlike Dalton's law of multiple proportions, which relates only one constituent of a compound with the same constituent in other compounds.

The second part of Gay-Lussac's law states that if gases combine to form gases, the volumes of the products are also in simple numerical ratios to the volume of the original gases. This part of the law was illustrated by the combination of carbon monoxide and oxygen to form carbon dioxide. Gay-Lussac noted that the volume of the carbon dioxide is equal to the volume of carbon monoxide plus twice the volume of oxygen. He did not realize, however, that the reason that only half as much oxygen is needed is because the oxygen molecule splits in two to give a single atom to each molecule of carbon monoxide. In his "Mémoire sur la combinaison des substances gazeuses, les unes avec les autres" (1809; "Memoir on the Combination of Gaseous Substances with Each Other"), Gay-Lussac wrote:

Thus it appears evident to me that gases always combine in the simplest proportions when they act on one another; and we have seen in reality in all the preceding examples that the ratio of combination is 1 to 1, 1 to 2 or 1 to 3, ... Gases combine in whatever proportions they may combine, always give rise to compounds whose elements by volume are multiples of each other. Not only, however, do gases combine in very simple proportions, as we have just seen, but the apparent contraction of volume which they experience on combination has also a simple relation to the volume of the gases, or at least to one of them.

Gay-Lussac's work raised the question of whether atoms differ from molecules and, if so, how many atoms and molecules are in a volume of gas. Amedeo Avogadro, building on Dalton's efforts, solved the puzzle, but his work unfortunately was ignored for 50 years.

In 1811 Avogadro proposed two hypotheses: (1) the atoms of elemental gases may be joined together in molecules rather than existing as separate atoms, as Dalton believed. (2) Equal volumes of gases contain equal numbers of molecules. These hypotheses explained why only half a volume of oxygen was necessary to combine with a volume of carbon monoxide to form carbon dioxide. Each oxygen molecule has two atoms, and each atom of oxygen joins one molecule of carbon monoxide.

Until the early 1860s, however, the allegiance of chemists to another concept espoused by the eminent Swedish chemist Jöns Jacob Berzelius blocked acceptance of Avogadro's ideas. (Berzelius was influential among chemists because he had determined the atomic weights of many elements extremely accurately.) Berzelius contended incorrectly that all atoms of a similar element repel each other because they have the same electric charge. He thought that only atoms with opposite charges could combine to form molecules.

Because early chemists did not know how many atoms were in a molecule, their chemical notation systems were in a state of chaos by the mid-19th century. Berzelius and his followers, for example, used the general formula MO for the chief metallic oxides, while others assigned the formula used today, M₂O₃. A single formula stood for different substances, depending on the chemist: H₂O was water or hydrogen peroxide; C₂H₆ was marsh gas or ethylene. Proponents of the system used today based their chemical notation on an empirical law formulated in 1819 by the French scientists Pierre-Louis Dulong and Alexis-Thérèse Petit concerning the specific heat of elements. According to the so-called Dulong-Petit law, the specific heat of all elements is the same on a per atom basis. This law, however, was found to have many exceptions and was not fully understood until the development of quantum theory in the 20th century.

To resolve such problems of chemical notation, the Sicilian chemist Stanisław Mendeleyev wrote "Principles of the Periodic System of the Elements" in 1863 and expanded them at the First International Chemical Congress, which met in Karlsruhe, Ger., in 1860. A noted German chemistry professor wrote later that, when he heard Avogadro's theory at the congress, "It was as though scales fell from my eyes, doubt vanished, and was replaced by a feeling of peaceful certainty." Within a few years, Avogadro's hypotheses were widely accepted in the world of chemistry.

Atomic weights and the periodic table. As more and more elements were discovered during the 19th century, scientists began to wonder how the physical properties of the elements were related to their atomic weights. During the 1860s several schemes were suggested. The Russian chemist Dmitry Ivanovich Mendeleyev based his system on the atomic weights of the elements as determined by Avogadro's theory of diatomic molecules. In his paper of 1869 introducing the periodic table, he credited Cannizzaro for using "unshakable and indubitable" methods to determine atomic weights. "The elements, if arranged according to their atomic weights, show a distinct periodicity of their properties. . . . Elements exhibiting similarities in their chemical behavior have atomic weights which are approximately equal (as in the case of Pt, Ir, Os) or they possess atomic weights which increase in a uniform manner (as in the case of Kr, Rubidium, Cs)." Skipping
hydrogen because it is anomalous, Mendeleev arranged the 63 elements known to exist at the time into six groups according to valence. Valence, which is the combining power of an element, determines the proportions of the elements in a compound. For example, H₂O combines oxygen with a valence of 2 and hydrogen with a valence of 1. Recognizing that chemical qualities change gradually as atomic weight increases, Mendeleev predicted a new element wherever there was a gap in atomic weights between adjacent elements. His system was thus a research tool and not merely a system of classification. Mendeleev’s periodic table raised an important question, however, for future atomic theory to answer: Where does the pattern of atomic weights come from?

**Kinetic theory of gases.** Whereas Avogadro’s theory of diatomic gases was ignored for 50 years, the kinetic theory of gases was rejected for more than a century. The kinetic theory relates the independent motion of molecules to the mechanical and thermal properties of gases—namely, their pressure, volume, temperature, viscosity, and heat conductivity. Three men—Daniel Bernoulli in 1738, John Herapath in 1820, and John James Waterston in 1845—independently developed the theory. The kinetic theory of gases, like the theory of diatomic molecules, was a simple physical idea that chemists ignored in favour of an elaborate explanation of the properties of gases. Bernoulli, a Swiss mathematician and scientist, worked out the first quantitative mathematical treatment of the kinetic theory in 1738, picturing gases as consisting of an enormous number of particles in very fast, chaotic motion (see Figure 1). He derived Boyle’s law by assuming that gas pressure is caused by the direct impact of particles on the walls of their container. He understood the difference between heat and temperature, realizing that heat makes gas particles move faster and that temperature merely measures the propensity of heat to flow from one body to another. In spite of its accuracy, Bernoulli’s theory remained virtually unknown during the 18th century and early 19th century for several reasons. First, chemistry was more popular than physics among scientists of the day, and Bernoulli’s theory involved mathematics. Second, Newton’s reputation insured the success of his more comprehensible theory that gas atoms repel one another. Finally, Joseph Black, another noted British scientist, developed the caloric theory of heat, which proposed that heat was an invisible substance permeating matter. At the time, the fact that heat could be transmitted by light seemed a persuasive argument that heat and motion had nothing to do with each other.

Herapath, an amateur ignored by his contemporaries, published his version of the kinetic theory in 1821. He also derived an empirical relation akin to Boyle’s law but did not understand correctly the role of heat and temperature in determining the pressure of a gas.

Waterston’s efforts met with a similar fate. A civil engineer and amateur physicist, he could not even get his work published by the scientific community, which had become increasingly professional throughout the 19th century. Nevertheless, Waterston made the first statement of the law of equipartition of energy, according to which all kinds of particles have equal amounts of thermal energy. He derived practically all the consequences of the fact that pressure exerted by a gas is related to the number of molecules per cubic centimetre, their mass, and their mean squared velocity. He derived the basic equation of kinetic theory, which reads \( P = N M V^2 \). Here \( P \) is the pressure of a volume of gas, \( N \) is the number of molecules per unit volume, \( M \) is the mass of the molecule, and \( V^2 \) is the average velocity squared of the molecules. Recognizing that the kinetic energy of a molecule is proportional to \( MV^2 \) and that the heat energy of a gas is proportional to the temperature, Waterston expressed the law as \( \frac{P V}{T} = \text{constant} \).

During the late 1850s, a decade after Waterston had formulated his law, the scientific community was finally ready to accept a kinetic theory of gases. The studies of heat undertaken by the British physicist James Prescott Joule during the 1840s had shown that heat is a form of energy. This work, together with the law of the conservation of energy that he helped to establish, had persuaded scientists to discard the caloric theory by the mid-1850s. The caloric theory had required that a substance contain a definite amount of caloric (i.e., a hypothetical weightless fluid) to be turned into heat; however, experiments showed that any amount of heat can be generated in a substance by putting enough energy into it. Thus, there was no point to hypothesizing such a special fluid as caloric.

At first, after the collapse of the caloric theory, physicists had nothing with which to replace it. Joule, however, discovered Herapath’s kinetic theory and used it to calculate the velocity of hydrogen molecules in 1851. Then Rudolf Clausius developed the kinetic theory mathematically in 1857, and the scientific world took note. Clausius and two other physicists, James Clerk Maxwell and Ludwig Eduard Boltzmann (who developed the kinetic theory of gases in the 1860s), introduced sophisticated mathematics into physics for the first time since Newton. In his 1860 paper "Illustrations of the Dynamical Theory of Gases," Maxwell used probability to produce his famous distribution curve for the velocities of gas molecules. Employing Newtonian laws of mechanics, he also provided a mathematical basis for Avogadro’s theory. Maxwell, Clausius, and Boltzmann assumed that gas particles were in constant motion, that they were tiny compared to their space, and that their interactions were very brief. They then related the motion of the particles to pressure, volume, and temperature. Interestingly, none of the three committed himself on the nature of the particles.

**Studies of the Properties of Atoms**

**Size of atoms.** The first modern estimates of the size of atoms and the numbers of atoms in a given volume were made by the German chemist Joseph Loschmidt in 1865. Loschmidt used the results of kinetic theory and some rough estimates to do his calculation. The size of the atoms and the distance between them in the gaseous state are related both to the contraction of gas upon liquefaction and to the mean free path traveled by molecules in a gas. The mean free path, in turn, can be found from the thermal conductivity and diffusion rates in the gas. Loschmidt calculated the size of the atom and the spacing between atoms by finding a solution common to these relationships. His result for Avogadro’s number is remarkably close to the present accepted value of \( 6.022 \times 10^{23} \). The precise definition of Avogadro’s number is the number of atoms in 12 grams of the carbon isotope \(^{12}\text{C} \). Loschmidt’s result for the diameter of an atom was approximately \( 10^{-10} \) centimetres.

Much later, in 1908, the French physicist Jean Perrin used Brownian motion to determine Avogadro’s number.
Brownian motion, first observed in 1827 by the Scottish botanist Robert Brown, is the continuous movement of tiny particles suspended in water. Their movement is caused by the thermal motion of water molecules bumping into the particles. Perrin's argument for determining Avogadro's number makes an analogy between particles in the liquid and molecules in the atmosphere. The thinning of air at high altitudes depends on the balance between the gravitational force pulling the molecules down and their thermal motion forcing them up. The relationship between the weight of the particles and the height of the atmosphere would be the same for Brownian particles suspended in water. Perrin counted particles of gum mastic at different heights in his water sample and inferred the mass of atoms from the rate of decrease. He then divided the result into the molar weight of atoms to determine Avogadro's number. After Perrin, few scientists could dispute the existence of atoms.

Electric properties of atoms. While atomic theory was set back by the failure of scientists to accept simple physical ideas like the diatomic and the kinetic theory of gases, it was also delayed by the preoccupation of physicists with mechanics for almost 200 years, from Newton to the 20th century. Nevertheless, several 19th-century investigators, working in the relatively ignored field of electricity, magnetism, and optics, provided important clues about the interior of the atom. The studies in electrodynamics made by the British physicist Michael Faraday and those of J.J. Thomson indicated for the first time that something existed apart from palpable matter, and data obtained by Gustav Robert Kirchhoff of Germany about elemental spectral lines raised questions that would only be answered in the 20th century by quantum mechanics. Until Faraday's electrolysis experiments, scientists had had no conception of the nature of the forces binding atoms together in a molecule. Faraday concluded that electrical forces existed inside the molecule after he had produced an electric current and a chemical reaction in a solution with the electrodes of a voltaic cell. No matter what solution or electrode material he used, a fixed quantity of current sent through an electrolyte always caused a specific amount of material to form on an electrode of the electrolytic cell. Faraday concluded that each ion of a given compound has exactly the same charge. Later, he discovered that the ionic charges are integral multiples of a single unit of charge, never fractions.

On the practical level, Faraday did for charge what Dalton had done for the chemical combination of atomic masses. That is to say, Faraday demonstrated that it takes a definite amount of charge to convert an ion of an element into an atom of the element and that the amount of charge depends on the element used. The unit of charge that releases a gram atomic weight of a simple ion was named the Faraday in his honour. For example, one faraday of charge passing through water releases one gram of hydrogen and eight grams of oxygen. In this manner, Faraday gave scientists a rather precise value for the ratios of the masses of atoms to the electric charges of ions. The ratios of the mass of the hydrogen atom to the charge of the electron was found to be $1.035 \times 10^{-4}$ kilogram per coulomb. Faraday did not know the size of his electrolytic unit of charge in units such as coulombs any more than Dalton knew the magnitude of his unit of atomic weight in grams. Nevertheless, scientists could determine the ratio of these units easily.

More significantly, Faraday's work was the first to imply the electrical nature of matter and the existence of subatomic particles and a fundamental unit of charge. Faraday wrote: "The atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual affinity." Faraday did not, however, conclude that atoms cause electricity.

Light and spectral lines. In 1865 Maxwell unified the laws of electricity and magnetism in his publication "A Dynamical Theory of the Electromagnetic Field." In this paper, he concluded that light is an electromagnetic wave. His theory was confirmed by the German physicist Heinrich Hertz, who produced radio waves with sparks in 1887. With light understood as an electromagnetic wave, Maxwell's theory could be applied to the emission of light from atoms. The theory failed, however, to describe spectral lines and the fact that atoms do not lose all their energy when they radiate light. The problem was not with Maxwell's theory of light itself but rather with its description of the oscillating electron currents generating light. Only quantum mechanics could explain this behaviour (see below The laws of quantum mechanics).

By far the richest clues about the structure of the atom came from spectral lines. Mounting a particularly fine prism on a telescope, the German physicist and optician Joseph von Fraunhofer had discovered between 1814 and 1824 hundreds of dark lines in the spectrum of the Sun. He labeled the most prominent of these lines with the letters A through G. Together, they are now called Fraunhofer lines. A generation later, Kirchhoff heated different elements to incandescence in order to study the different coloured vapours emitted. Observing the vapours through a spectroscope, he discovered that each element has a unique and characteristic pattern of spectral lines. Each element produces the same set of identifying lines, even when it is combined chemically with other elements. In 1859 Kirchhoff and the German chemist Robert Wilhelm Bunsen discovered two new elements—cesium and rubidium—by first observing their spectral lines.

Johann Jakob Balmer, a Swiss secondary-school teacher with a penchant for numerology, studied hydrogen's spectral lines and found a constant relationship between the wavelengths of the element's four visible lines (see Figure 2). In 1885 he published a generalized mathematical formula for all of the lines of hydrogen. The Swedish physicist Johannes Rydberg extended Balmer's work in 1890 and found a general rule applicable to many elements. Soon more series were discovered elsewhere in the spectrum of hydrogen and in the spectra of other elements as well. Stated in terms of the frequency of the light rather than its wavelength, the formula may be expressed:

$$v = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right).$$

Here, n and m are integers and $R$ is a constant. In the Balmer lines, $m$ is equal to 2 and n takes on the values 3, 4, 5, and 6.

Adapted from W. Finkenruth, Structure of Matter (1964): Springer-Verlag, Heidelberg.

Figure 2: Spectrum of atomic hydrogen, showing the series of Balmer lines.

Discovery of electrons. During the 1880s and '90s, scientists searched cathode rays for the carrier of the electrical properties in matter. Their work culminated in J.J. Thomson's discovery of the electron in 1897. The existence of the electron showed that the 2,000-year-old conception of the atom as a homogeneous particle was wrong and that in fact the atom has a complex structure.

Cathode-ray studies began in 1854 when Heinrich Geissler, a glassblower and technical assistant to the German physicist Julius Plücker, improved the vacuum tube. Plücker discovered cathode rays in 1858 by sealing two electrodes inside the tube, evacuating the air, and forcing electric current between the electrodes. He found a green glow on the wall of his glass tube and attributed it to rays emanating from the cathode. In 1869, with better vacuums, Plücker's pupil Johann W. Hittorf saw a shadow cast by an object placed in front of the cathode. The shadow proved that the cathode rays originated from the cathode. The British physicist and chemist Sir William Crookes investigated cathode rays in 1879 and found that they were bent by a magnetic field; the direction of deflection Crookes's study of cathode rays
suggested that they were negatively charged particles. As the luminescence did not depend on what gas had been in the vacuum or what metal the electrodes were made of, he concluded that the rays were properties of the electric current itself. As a result of Crooke's work, cathode rays were widely studied, and the tubes came to be called Crookes tubes. Although Crookes believed that the particles were electrified charged particles, his work did not settle the issue of whether cathode rays were particles or radiation similar to light. By the late 1800s the controversy over the nature of cathode rays had divided the physics community into two camps. Most French and British physicists, influenced by Crookes, thought that cathode rays were electrically charged particles because they were affected by magnets. Most German physicists, on the other hand, believed that the rays were waves because they traveled in straight lines and were unaffected by gravity. A crucial test of the nature of the cathode rays was how they would be affected by electric fields. Heinrich Hertz, the aforementioned German physicist, reported that the cathode rays were not deflected when they passed between two oppositely charged plates in an 1892 experiment. The English physicist Thomson thought Hertz's vacuum might have been faulty and that residual gas might have reduced the effect of the electric field on the cathode rays.

Thomson repeated Hertz's experiment with a better vacuum in 1897. He directed the cathode rays between two parallel aluminum plates to the end of a tube, where they were observed as luminescence on the glass. When the top aluminum plate was negative, the rays moved down; when the upper plate was positive, the rays moved up. The deflection was proportional to the difference in potential between the plates. With both magnetic and electric deflections observed, it was clear that cathode rays were electrically charged particles. Thomson's discovery established the particulate nature of electricity. Accordingly, he called his particles electrons.

From the magnitude of the electrical and magnetic deflections, Thomson could calculate the ratio of mass to charge of the electrons. This ratio was known for atoms from electrochemical studies. Measuring and comparing it to the number for an atom, he discovered that the mass of the electron was very small, merely \( \frac{1}{1836} \) that of a hydrogen ion. When scientists realized that an electron was virtually 1,000 times lighter than the smallest atom, they understood how cathode rays and how electric current could flow through copper wires. In deriving the mass-to-charge ratio, Thomson had calculated the electron's velocity. It was \( \frac{1}{10} \) the speed of light, thus amounting to roughly 30,000 kilometers per second (18,000 miles per second). Thomson emphasized that the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state; a state in which all matter, that is, matter derived from different sources such as hydrogen, oxygen, etc., is of one and the same kind; this matter being the substance from which all the chemical elements are built up. Thus, the electron was the smallest atomic particle identified, the smallest and the fastest bit of matter known at the time.

In 1910 and 1911 the American physicist Robert Andrews Millikan greatly improved a method employed by Thomson for measuring the electron charge directly. Millikan produced microscopic oil droplets and observed them falling in the space between two electrically charged plates. Some of the droplets became charged and could be suspended by a delicate adjustment of the electric field. Millikan knew the weight of the droplets from their rate of fall when the electric field was turned off. From the balance of the gravitational and electrical forces, he could determine the charge on the droplets. He could calibrate the charges only in integral multiples of a quantity that in contemporary units is \( 1.602 \times 10^{-19} \) coulomb. Millikan's electron charge experiment was the first to detect and measure the effect of an individual subatomic particle. Besides confirming the particulate nature of electricity, his experiment also supported previous determinations of Avogadro's number. Avogadro's number times the unit of charge gives Faraday's constant, the amount of charge required to electrolyze one mole of a chemical ion.

Identification of positive ions. In addition to electrons, positively charged particles also emanate from the anode in an energized Crookes tube. The German physicist Wilhelm Wien analyzed these positive rays in 1898 and found that the particles have a mass-to-charge ratio more than 1,000 times larger than that of the electron. Because the ratio of the particles is also comparable to the mass-to-charge-ratio of the residual atoms in the discharge tube, scientists suspected that the rays were actually ions from the gases in the tube.

In 1913 Thomson refined Wien's apparatus to separate different ions and measure their mass-to-charge ratio on photographic plates. He sorted out the many ions in various charge states produced in a discharge tube. When he conducted his atomic mass experiments with neon gas, he found that a beam of neon atoms subjected to electric and magnetic forces split into two parabolas instead of one on a photographic plate. Chemists had assumed the atomic weight of neon was 20.2, but the traces on Thomson's photographic plate suggested atomic weights of 20.0 and 22.0, with the former parabola being the latter. He concluded that neon consisted of two stable isotopes: primarily neon-20, with a small percentage of neon-22. Eventually, a third isotope, neon-21, was discovered in very small quantities. It is now known that 1,000 neon atoms will contain 909 of neon-20, 88 of neon-22, and 3 of neon-21. Dalton's assumption that all atoms of a substance have an identical mass and that the atomic weight of an element is its mass was thus disproved. Today, the atomic weight of an element is recognized as the weighted average of the masses of its isotopes.

Francis William Aston, an English physicist, improved Thomson's technique when he developed the mass spectrometer in 1919. This device spread out the beam of positive ions into a "mass spectrum" of lines similar to the way light is separated into a spectrum. Aston analyzed about 50 elements over the next six years and discovered that most have isotopes.

Discovery of radioactivity. Like Thomson's discovery of the electron, the discovery of radioactivity in uranium by the French physicist Henri Bequerel in 1896 forced scientists to radically change their ideas about atomic structure. Radioactivity demonstrated that the atom was neither indivisible nor immutable. Instead of serving merely as an inert matrix for electrons, the atom could change form and emit an enormous amount of energy. Furthermore, radioactivity itself became an important tool for revealing the interior of the atom.

The German physicist Wilhelm Conrad Röntgen had discovered X rays in 1895, and Becquerel thought they might be related to fluorescence and phosphorescence, processes in which substances absorb and emit energy as light. In the course of his investigations, Becquerel stored some photographic plates and uranium salts in a desk drawer. Expecting to find the plates only lightly fogged, he developed them and was surprised to find sharp images of the salts. He then began experiments that showed that uranium salts emit a penetrating radiation independent of external influences. Becquerel also demonstrated that the radiation could discharge electrified bodies. In this case, discharge means the removal of electric charge, and it is now understood that the radiation ionizing molecules of air allows the air to conduct an electric current. Early studies of radioactivity relied on measuring ionization power or on observing the effects of radiation on photographic plates.

In 1898 the French physicists Pierre and Marie Curie discovered the strongly radioactive elements polonium and radium, which occur naturally in uranium minerals. Marie determined the term radioactivity for the spontaneous emission of ionizing, penetrating rays by certain atoms (see below).

Experiments conducted by the British physicist Ernest Rutherford in 1899 showed that radioactive substances emit more than one kind of ray. It was determined that part of the radiation is 100 times more penetrating than the rest and can pass through aluminum foil \( \frac{1}{10} \) of a
millimetre thick. Rutherford named the less penetrating emanations alpha rays and the more powerful ones beta rays, after the first two letters of the Greek alphabet. Investigators who, in 1899, found that beta rays were deflected by a magnetic field concluded that they are negatively charged particles similar to cathode rays. In 1903 Rutherford found that alpha rays were deflected slightly in the opposite direction, showing that they are massive, positively charged particles. Much later, Rutherford proved that alpha rays are nuclei of helium atoms by collecting the rays in an evacuated tube and detecting the buildup of helium gas over several days. A third kind of radiation was identified by the French chemist Paul Villard in 1900. Designated as the gamma ray, it is not deflected by magnets and is much more penetrating than alpha particles. Gamma rays are electromagnetic radiation, like light or X rays, but with much shorter wavelengths. Because of these shorter wavelengths, gamma rays have higher frequencies and are even more penetrating than X rays. In 1902, while studying the radioactivity of thorium, Rutherford and the English chemist Frederick Soddy discovered that radioactivity was associated with changes inside the atom that transformed thorium into a different element. They found that thorium continually generates a chemically different substance that is intensely radioactive. The radioactivity eventually makes the new element disappear. Watching the process, Rutherford and Soddy formulated the exponential decay law, which states that a fixed fraction of the original element will decay in a unit of time. For example, half of the thorium product decays in four days, half the remaining sample in the next four days, and so on.

Until the 20th century, physicists had studied such subjects as mechanics, heat, and electromagnetism that they could understand by applying common sense or by extrapolating from everyday experiences. The discovery of the electron and radioactivity, however, showed that classical Newtonian mechanics could not explain phenomena at atomic and subatomic levels. As the primacy of classical mechanics crumbled during the early 20th century, quantum mechanics was born. Since then, experiments and theories have led physicists into a world that is often extremely abstract and seemingly contradictory.

MODELS OF ATOMIC STRUCTURE

Thomson’s discovery of the negatively charged electron had raised theoretical problems for physicists as early as 1897, because atoms as a whole are electrically neutral. Where was the neutralizing positive charge and what held it in place? Between 1903 and 1907 Thomson tried to solve the mystery by adapting an atomic model that had been proposed by Lord Kelvin in 1900. According to this theoretical system, often referred to as the “plum pudding” model, the atom is a sphere of uniformly distributed positive charge about one angstrom in diameter. Electrons are embedded in a regular pattern like raisins in a plum pudding to neutralize the positive charge. The advantage of the Thomson model was that it was inherently stable: if electrons were displaced, the attraction to the unit returned to their original positions. In another contemporary model, the atom resembled the solar system or the planet Saturn, with rings of electrons surrounding a concentrated positive charge. The Japanese physicist Hantaro Nagaoka, in particular, developed the “Saturnian” system in 1904. The atom, as postulated in this model, was inherently unstable because, by radiating continuously, the electron would gradually lose energy and spiral into the nucleus. No electron could thus remain in any particular orbit indefinitely.

Rutherford’s nuclear model. Rutherford overturned Thomson’s plum pudding model in 1911 with his well-known gold foil experiment in which he demonstrated that the atom has a tiny, massive nucleus. Five years earlier Rutherford had noticed that alpha particles, beamed through a hole onto a photographic plate, would make a sharp-edged picture, while alpha particles beamed through a sheet of mica only 20 micrometres (or about 0.002 centimetre) thick would make an impression with blurry edges. For some parti-

clones, the blurring corresponded to a two-degree deflection. Remembering those results, Rutherford had his postdoctoral fellow, Hans Geiger, and an undergraduate student, Ernest Marsden, repeat the experiment. The young scientists beamed alpha particles through gold foil and detected them as flashes of light or scintillations on a screen. The gold foil was only 0.00004 centimetre thick. Most of the alpha particles went straight through the foil, but some were deflected by the foil and hit a spot on a screen placed off to one side. Geiger and Marsden found that about one in 20,000 alpha particles had been deflected 45° or more. Rutherford asked why so many alpha particles passed through the gold foil while a few were deflected so greatly. “It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper, and it came back to hit you,” Rutherford said later. “One conclusion that can be drawn is that there must be a form of electrostatic radiation, like light or X rays, but with much shorter wavelength. Because of these shorter wavelengths, gamma rays have higher frequencies and are even more penetrating than X rays. In 1902, while studying the radioactivity of thorium, Rutherford and the English chemist Frederick Soddy discovered that radioactivity was associated with changes inside the atom that transformed thorium into a different element. They found that thorium continually generates a chemically different substance that is intensely radioactive. The radioactivity eventually makes the new element disappear. Watching the process, Rutherford and Soddy formulated the exponential decay law, which states that a fixed fraction of the original element will decay in a unit of time. For example, half of the thorium product decays in four days, half the remaining sample in the next four days, and so on.

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that, in some cases, the order by atomic weights was incorrect. For example, cobalt has a larger atomic mass than nickel, but Moseley found that it has atomic number 27, while nickel has 28. When Mendeleev constructed the periodic table, he based his system on the atomic masses of the elements and had to put cobalt and nickel out of order to make the chemical properties fit better. In a few places where Moseley found more than one integer between elements, he predicted correctly that a new element would be discovered. Because there is just one element for each atomic number, scientists could be confident for the first time of the completeness of the periodic table; no unexpected new elements would be discovered.

**Bohr's shell model.** In 1913 Bohr proposed his quantized shell model of the atom to explain how electrons can have stable orbits around the nucleus. The motion of the electrons in the Rutherford model was unstable because, according to classical mechanics and electromagnetic theory, any charged particle moving on a curved path emits electromagnetic radiation; thus, the electrons would lose energy and spiral into the nucleus. To remedy the stability problem, Bohr modified the Rutherford model by requiring that the electrons move in orbits of fixed size and energy. The energy of an electron depends on the size of the orbit and is lower for smaller orbits. Radiation can occur only when the electron jumps from one orbit to another. The atom will be completely stable in the state with the smallest orbit, since there is no orbit of lower energy into which the electron can jump.

Bohr's starting point was to realize that classical mechanics by itself could never explain the atom's stability. A stable atom has a certain size so that any equation describing it must contain some fundamental constant or combination of constants with a dimension of length. The classical fundamental constants—namely, the charges and the masses of the electron and the nucleus—cannot be combined to make a length. Bohr noticed, however, that the quantum constant formulated by the German physicist Max Planck (see below) has dimensions which, when combined with the mass and charge of the electron, produce a measure of length. Numerically, the measure is close to the known size of atoms. This encouraged Bohr to use Planck's constant in searching for a theory of the atom.

Planck had introduced his constant in 1900 in a formula explaining the light radiation emitted from heated bodies. According to classical theory, comparable amounts of light energy should be produced at all frequencies. This is not only contrary to observation but also implies the absurd result that the total energy radiated by a heated body should be infinite. Planck postulated that energy can only be emitted or absorbed in discrete amounts, which he called quanta (the Latin word for "how much"). The energy quantum is related to the frequency of the light by a new constant, Planck's constant, h. When a body is heated, its radiant energy in a particular frequency range is, according to classical theory, proportional to the temperature of the body. With Planck's hypothesis, however, the radiation can occur only in quantum amounts of energy. If the radiant energy is less than the quantum of energy, the amount of light in that frequency range will be reduced. Planck's formula correctly describes radiation from heated bodies. Planck's constant has the dimensions of action, which may be expressed as units of energy multiplied by time, units of momentum multiplied by length, or units of angular momentum. For example, Planck's constant can be written as $h = 6.6 \times 10^{-34}$ joule seconds or $6.6 \times 10^{-34}$ kilogram-metre/second-metres.

Using Planck's constant, Bohr obtained an accurate formula for the energy levels of the hydrogen atom (see Figure 3). He postulated that the angular momentum of the electron is quantized—in other words, it can have only discrete values. He assumed that otherwise electrons obey the laws of classical mechanics by traveling around the nucleus in circular orbits. Because of the quantization, the electronic orbits have fixed sizes and energies. The orbits are labeled by an integer, the quantum number $n$.

With his model, Bohr explained how electrons could jump from one orbit to another only by emitting or absorbing energy in fixed quanta. For example, if an electron jumps one orbit closer to the nucleus, it must emit energy equal to the difference of the energies of the two orbits. Conversely, when the electron jumps to a larger orbit, it must absorb a quantum of light equal in energy to the difference in orbits.

Bohr's model accounts for the stability of atoms because the electron cannot lose more energy than it has in the smallest orbit, the one with $n = 1$. The model also explains the Balmer formula for the spectral lines of hydrogen. The frequency of the light is related to its energy by Einstein's formula $E = hv$. The light energy is calculated from the difference in energies between the two orbits. The Balmer formula can be expressed as the difference of two terms, each term giving the energy of an orbit. Bohr's model not only explains the form of the Balmer formula but also accurately gives the value of the constant of proportionality $R$.

The usefulness of Bohr's theory extends beyond the hydrogen atom. Bohr himself noted that the formula also applies to the singly ionized helium atom, which, like hydrogen, has a single electron. The nucleus of the helium atom has twice the charge of the hydrogen nucleus, however. In Bohr's formula the charge of the electron is raised to the fourth power. Two of those powers stem from the charge on the nucleus; the other two come from the charge on the electron itself. Bohr modified his formula for the hydrogen atom to fit the helium atom by doubling the charge on the nucleus. Moseley applied Bohr's formula with an arbitrary atomic charge $Z$ to explain the K- and L-series X-ray spectra of heavier atoms. The German physicists James Franck and Gustav Hertz confirmed the existence of quantum states in atoms in experiments reported in 1914. They made atoms absorb energy by bombarding them with electrons. The atoms would only absorb discrete amounts of energy from the electron beam. When the energy of an electron was below the threshold for producing an excited state, the atom would not absorb any energy.

Bohr's theory had major drawbacks, however. Except for the spectra of X rays in the K and L series, it could not explain properties of atoms having more than one electron. The binding energy of the helium atom, which has two electrons, was not understood until the development of quantum mechanics. Several features of the spectrum were inexplicable even in the hydrogen atom. High-resolution spectroscopy shows that the individual spectral lines...
of hydrogen are divided into several closely spaced, fine lines. In a magnetic field the lines split even further. The German physicist Arnold Sommerfeld modified Bohr's theory by quantizing the shapes and orientations of orbits to introduce additional energy levels corresponding to the fine spectral lines. The quantization of the orientation of the angular momentum vector was confirmed in an experiment in 1922 by other German physicists, Otto Stern and Walter Gerlach. They passed a beam of silver atoms through a nonhomogeneous magnetic field, one that is stronger on one side than on the other. The field deflected the atoms according to their magnetic moments. (The magnetic moment of an object such as an atom or a compass needle is the measure of its interaction with a magnetic field. The moment points in some direction and is associated in classical physics with orbital currents and the angular momentum of charges.) In their experiment, Stern and Gerlach found only two deflections, not the continuous distribution of deflections that would have been seen if the magnetic moment had been oriented in any direction. Thus, it was determined that the magnetic moment and the angular momentum of an atom can have only two orientations. The discrete orientations of the orbits explain some of the magnetic field effects—namely, the so-called nuclear effect, which is the splitting of a spectral line into three sublines. These sublines correspond to quantum jumps in which the angular momentum along the magnetic field is increased by one unit, decreased by one unit, or left unchanged.

An additional quantum number was needed to complete the description of electrons in an atom. In 1925 Samuel A. Goudsmit and George E. Uhlenbeck, two graduate students in physics at the University of Leiden, in The Netherlands, added a quantum number to account for the fact that some spectral lines are divided into more sublines than can be explained with the original quantum numbers. Goudsmit and Uhlenbeck postulated that an electron has an internal spinning motion and that the corresponding angular momentum is one-half of the orbital angular momentum quantum. An electron has a magnetic moment, and its energy depends on whether the spin is aligned with or against the magnetic field. Independently, the Austrian-born physicist Wolfgang Pauli also suggested adding a two-valued quantum number for electrons, but for different reasons. He needed this additional quantum number to formulate his exclusion principle, which serves as the atomic basis of the periodic table and the chemical behaviour of the elements. According to the exclusion principle, one electron at most can occupy an orbital, taking into account all the quantum numbers available if the angular momentum and its orientation are considered appropriate.

In spite of these modifications, Bohr's model seemed to be a dead end by the early 1920s. It did not explain most fine spectral lines or the anomalous Zeeman effect, which is a complicated type of spectral line splitting that sometimes involves up to 15 sublines. (Its name notwithstanding the anomalous Zeeman effect is more the aforementioned normal Zeeman effect.) Efforts to generalize the model to multielectron atoms had proved futile, and physicists despaired of ever explaining them.

The laws of quantum mechanics. Within a few short years scientists developed a consistent theory of the atom that explained its fundamental structure and its interactions. Crucial to the development of the theory was new evidence indicating that light and matter have both wave and particle characteristics at the atomic and subatomic levels. Theoreticians had objected to the fact that Bohr had used an ad hoc hybrid of classical Newtonian dynamics for the atom and some quantum postulates for limiting the motion. The new theory ignored the fact that electrons are particles and treated them as waves. By 1926, physicists had developed the laws of quantum mechanics, also called wave mechanics, to explain atomic and subatomic phenomena.
his energy calculation was quite accurate. With Hylleraas’ explanation of the two-electron atom, physicists realized that the Schrödinger equation could be a powerful mathematical tool for describing nature on the atomic level, even if exact solutions could not be obtained.

The antiparticles. The English physicist P.A.M. Dirac introduced a new equation for the electron in 1928. The Schrödinger equation does not satisfy the principles of relativity, and so it can be used to describe only those phenomena in which the particles move much more slowly than the velocity of light. In order to satisfy the principles of relativity, Dirac had to postulate not one but four distinct wave functions for the electron. Two of these correspond to the two spin orientations. The remaining components allowed additional states of the electron that had not yet been observed. Dirac interpreted them as antiparticles with a charge opposite to that of the electron. The discovery was made by the American physicist Carl David Anderson who proved the existence of antiparticles and was a triumph for Dirac’s theory. After his discovery, subatomic particles could no longer be considered immutable. Given enough energy, electrons and positrons can be created from a few particles in a vacuum tube. They also can decay into some other form of energy. The history of subatomic physics from this point has been much the story of finding new kinds of particles that can be created in vacuums.

ADVANCES IN NUCLEAR AND SUBATOMIC PHYSICS

The 1920s witnessed further advances in nuclear physics with Rutherford’s discovery of induced radioactivity. Bombardment of light nuclei by alpha particles produced new radioactive nuclei. In 1928 the Russian-born American physicist George Gamow explained the lifetimes in alpha radioactivity using the Schrödinger equation.

Discovered of neutrons. The constitution of the nucleus was poorly understood at the time because the only known particles were the electron and the proton. It had been established that nuclei are typically about twice as heavy as can be accounted for by protons alone and thus have to contain more than just such particles. A consistent theory was impossible until the English physicist James Chadwick discovered the neutron in 1932. He found that alpha particles reacted with beryllium nuclei, ejecting neutral particles with nearly the same mass as protons. Almost all nuclear phenomena can be understood in terms of a nucleus composed of neutrons and protons. Surprisingly, the protons and neutrons in the nucleus behave to a large extent as though they were in independent wave functions, just like the electrons in an atom. Each neutron or proton is described by a wave pattern with peaks and nodes and angular momentum quantum numbers. The theory of the nucleus based on these independent wave functions is called liquid-drop model. It was developed in 1935 by the American physicist Hans Jensen of West Germany, and it developed in succeeding decades into a comprehensive theory of the nucleus.

The interactions of neutrons with nuclei had been studied during the mid-1930s by the Italian-born American physicist Enrico Fermi and others who presumed the neutron was a particle composed of nucleons, which, unlike protons or alpha particles, are not repelled from the nucleus by a positive charge. When a neutron is captured, the new nucleus has one higher unit of atomic mass. If a nearby isotope of that atomic mass is more stable, the new nucleus will be radioactive, convert the neutron to a proton, and assume the more stable form. Nuclear fission was discovered by the German chemists Otto Hahn and Fritz Strassmann in 1938. In fission, a uranium nucleus captures a neutron and gains enough energy to trigger the inherent instability of the nucleus, which splits into two lighter nuclei of roughly equal size. The fission process releases more neutrons, which can be used to produce further fissions (see below Nuclear fission). The first nuclear reactor, a device designed to permit controlled fission chain reactions, was constructed at the University of Chicago under Fermi’s direction, and the first self-sustaining chain reaction was achieved in this reactor in 1942. In 1945 American scientists produced the first atomic bomb, which used uncontrolled fission reactions in either uranium or the artificial element plutonium.

Quantum field theory. Dirac not only proposed the relativistic equation for the electron but also initiated the relativistic treatment of interactions between particles, known as quantum field theory. An important aspect of quantum field theory is that interactions can extend only over a given distance if there is a particle to carry the force. The electromagnetic force, which operates over a long distance, is carried by a particle called the photon, the light quantum. In 1934 the Japanese physicist Yukawa Hideki proposed that there should be a particle that carries the nuclear force as well. Because the force is short-range, the particle should be massive. Massive particles were indeed found in cosmic rays, but these did not have the correct interaction properties. They were later dubbed muons. Evidence for Yukawa’s particle, known as the pion, was found in cosmic rays in 1947 by the British physicist Cecil Frank Powell. The existence of the pion was confirmed when the particle was created in a particle accelerator in 1948.

Since then, the number of subatomic particles discovered has grown enormously. Most of them have been created and studied by means of accelerators that produce high-energy collisions between particles. The new particles, formed by the collision process, live only a short time before decaying into more stable particles. Particularly noteworthy among the many particles discovered since 1960 are those responsible for the interaction in beta radioactivity. In quantum field theory, beta radioactivity is a manifestation of an interaction called the weak force. The particles that transmit this force are known as W and Z particles. These messenger particles, or bosons, were discovered in 1983 during experiments at the European Organization for Nuclear Research (CERN).

Hadrons and quarks. Many of the newly discovered particles did not at first seem to have any specific role in subatomic physics. Particles of a class known as hadrons, which includes protons and neutrons, interact strongly with one another. They show patterns analogous to the patterns of energy levels in atoms. Just as the existence of energy levels in hydrogen is explained by the presence of the electron, the different hadrons are considered to be energy levels of a more fundamental particle inside them. The specific patterns of the hadrons have been explained by postulating a new fundamental constituent, the quark. Three quarks are thought to combine to form a proton, a neutron, or any of the massive hadrons known as baryons. A quark combines with an antiquark to form mesons such as the pion.

Quarks have never been observed, and physicists do not expect to find one. Presumably the forces between quarks are so strong that they cannot be separated from other quarks in a hadron. There are several indirect confirmations of the existence of quarks. In 1974 Physicists developed a quantum field theory known as quantum chromodynamics (QCD) during the mid-1970s to accommodate quarks and their peculiar properties. This theory explains qualitatively the confinement of quarks to hadrons. Physicists believe that the theory should explain all aspects of hadrons, but mathematical complications unfortunately prevent rigorous calculations.

Atomic structure and interactions

Electrons

As noted above, the electron was the first subatomic particle discovered. Its interactions determine atomic structure, the chemical behaviour of atoms in molecules, and the properties of large aggregates of atoms such as bulk solids. There are four kinds of forces in nature, and the electron is subject to three of them—gravity, electromagnetism, and weak interaction. Only the electromagnetic
force is significant in determining the properties of atoms and their chemistry. Within the framework of the equations used to describe the motion of the electron, the only two numerical properties that need to be specified are the electron's mass and its charge. These are given in Table I along with other basic atomic constants.

The first four levels of complexity in the equations used to describe the properties of electrons. At the simplest level, classical equations such as Newton's equation are applied. The motion of the electron beam in a television tube is adequately described by classical physics.

The equations of classical physics, however, become invalid when one attempts to describe the motion with distances smaller than the de Broglie wavelength of the electron (see MECHANICS: Quantum mechanics). Atomic properties fall into this small-distance regime, and quantum equations must be used. The simplest quantum equation is the above-mentioned Schrödinger equation, which is obtained when the de Broglie wavelength of the electron is small compared to the speed of light. The electron is described by a function that obeys a wave equation. The function may be visualized as a cloud; where the function is large, the cloud is dense and the electron's presence is strongly felt. Atomic and chemical structure is well described by the Schrödinger wave function. In two dimensions, the wave functions are complex functions of the coordinates of the electron. The first property is spin, which is an internal rotational motion of the electron. The magnitude of an electron's spin is fixed, but its orientation in space can vary. Spin appears in the Schrödinger equation as an attribute of the electron. There are, in fact, two separate wave functions associated with the probability that spin will be pointed in a particular direction or in the opposite direction. Other spin orientations are obtained by suitably combining the two functions to make intermediate directions. The other non-classical property involved is the Pauli exclusion principle, which states in its general form that the wave function of identical particles must be reversed when the coordinates of the particles are interchanged. As a consequence of the Pauli principle, two electrons cannot have the same wave function. This principle is extremely important in determining the structure of atoms, molecules, and bulk matter.

The third level of complexity in the description of the electron is Dirac's equation (see above), which is a quantum equation postulated to satisfy the requirements of Einstein's relativity. Any particle governed by the Dirac equation is called a fermion; the electron is the most familiar example. The mathematics of the Dirac equation require that its particles have two spin orientations and obey the so-called Pauli exclusion principle. A Schrödinger equation for two electrons moving in an average electric field must then be solved. Each electron has its own wave function, which is called an orbital.

A technical difficulty with this method is that the electric field is not known ahead of time because it depends on the charge distribution of the ions. In turn, the charge distribution can be determined only from the wave functions, which require prior knowledge of the field. The density is overcome by solving the Schrödinger equation in successive approximations. First, one makes a guess for the field, finds the wave functions, and then uses the derived charge distribution to make a better approximation for the field. This iterative process is continued until the final charge and electric field distribution agree with the input to the Schrödinger equation. The Hartree method (sometimes called the Hartree–Fock method to give credit to V. Fock, a Soviet physicist who generalized Hartree's scheme) is widely used to describe electrons in atoms, molecules, and solids.

The hydrogen atom. Bohr's model of the hydrogen atom is rudimentary but nevertheless remarkably accurate in its predicted energy levels. The derivation of the energy formula is as follows. Bohr begins with the classical equation relating the velocity of a charged particle in a circular orbit, $v$, to the radius of the orbit $r$ and the electric force constants. The equation, obtained by balancing the centrifugal force and the electric force, is

$$ \frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}. $$
Next, Bohr postulates that angular momentum is quantized in integer multiples of the reduced Planck's constant, \( h \). The angular momentum is then given by the formula

\[ m \nu r = nh, \]

where \( m \) is the mass of the electron, and \( n \) is an integer, which can have values 1, 2, 3, and so on. The two equations are combined to solve for the unknown quantities \( \nu \) and \( r \). The resulting orbits have discrete radii, depending on \( n \). The energies of the electrons in these orbits are given by Bohr's formula,

\[ E_n = \frac{m_e e^4}{(4\pi \epsilon_0)^2 \hbar^2} \frac{1}{n^2}. \]

When the Schrödinger equation is solved for the hydrogen atom, one finds that the possible energies of the electron are the same as those in Bohr's model (see Figure 4). The wave functions associated with these energies are, however, quite different from the circular orbits hypothesized by Bohr. The lowest orbital is a spherically symmetric function. It falls off with distance from the nucleus \( r \) according to

\[ \exp\left(-r/a_0\right). \]

Here, \( a_0 \) is a length constant, which happens to coincide with the radius of the smallest Bohr orbit. Known as the Bohr radius, it is given by the formula

\[ a_0 = \frac{4\pi \hbar^2}{m_e e^2}. \]

The numerical value of \( a_0 \) is 0.53 angstrom; the meaning and values of the other quantities in this equation are given in Table 1. Since the wave function depends only on distance and not on angle, the electron cloud surrounding the nucleus has a spherical shape. Its radius is roughly one angstrom. The electron probability is highest at the nucleus and in its immediate vicinity. The probability falls off smoothly with distance from the nucleus, vanishing completely only at infinite distance. The wave function falls to inconsequentially small values at moderate distances, however. For example, the probability for the particle to be farther than 10\( a_0 \) from the nucleus is only 1 in 30,000.

![Figure 4: Energy levels of the hydrogen atom, according to Bohr's model and quantum mechanics using the Schrödinger equation and the Dirac equation.](image)

Higher states of the hydrogen atom have more complex patterns in the wave function. All of the bound states of the hydrogen atom may be described by wave functions having the form

\[ (\text{polynomial in } x, y, \text{ and } z) \exp\left(-r/n \ a_0\right), \]

where \( n \) is a positive integer called the principal quantum number. The energy of the state is given by Bohr's formula with the same integer value of \( n \). Several different states may have the same energy, in which case they are said to be degenerate. Shells are sets of degenerate states. The number of distinct orbitals in a shell is its degeneracy or its multiplicity. For example, there are four orbitals with \( n = 2 \) at the energy \( E_2 \) in the Bohr formula, forming a shell. One of the orbitals in this shell, like the ground state, has a spherically symmetric wave function. Spherically symmetric orbitals are called s states; the nomenclature for orbitals of different symmetry is provided in Table 2. The excited s state differs from the ground state in that it is smaller at the centre, and it goes through zero at some intermediate distance from the nucleus. The excited s state has another peak beyond this point, and the overall probability extends farther out than in the ground state.

<table>
<thead>
<tr>
<th>Quantum number</th>
<th>Degeneracy</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>p</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>d</td>
</tr>
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<td>3</td>
<td>7</td>
<td>f</td>
</tr>
</tbody>
</table>

States are distinguished from each other by numerical labels called quantum numbers. The principal quantum number \( n \) has already been mentioned. Three additional quantum numbers are associated with the electron wave functions of the hydrogen atom. Two of these depend on the polynomial function of \( x, y, \) and \( z \) in the wave function. Conventionally, these two quantum numbers are labeled \( l \), representing orbital angular momentum, and \( m \), representing the orientation of the angular momentum with respect to some axis. The states of different \( l \) are often designated by letters, as given in Table 2. There are several general rules for determining the values of \( l \) and \( m \) allowed in a wave function. The orbital angular momentum takes on integer values starting from \( l = 0 \). Spherically symmetric wave functions have \( l = 0 \). Positive values of \( l \) apply to states whose wave function varies with angle. The more lobes there are in the angular pattern of the wave function, the higher is the value of \( l \). The \( m \) quantum number, also called the magnetic quantum number, is restricted to a range of integers depending on \( l \). The \( m \) quantum number ranges from \(-l\) to \(+l\) in integer steps to \(+l\). Distinct states exist for all values of \( m \) in this range. Thus, wave functions with a given orbital angular momentum \( l \) always have a degeneracy equal to \( 2l + 1 \). The quantum number \( l \) and the associated degeneracy \( 2l + 1 \) of the \( m \) states is a general feature of

![Figure 5: Electron densities in wave functions of the Schrödinger equation.](image)

(A) The lowest s orbital, recognizable by its spherical symmetry and the absence of any nodes. (B,C,D) The three p orbitals.
wave functions obtained in physical systems with a force directed toward a centre. For example, the ground state of the hydrogen atom is spherically symmetric with $l = 0$ and only one distinct orientation. The $p$-wave states in the $n = 2$ shell have orbital angular momentum $l = 1$. By the rules of the orientational degeneracy, there are three distinct $p$-wave states, labeled $m = -1$, 0, and +1. In higher shells one finds $l = 2$ states, which have two angular nodal surfaces and a degeneracy of 5.

The relationship between the principal quantum number $n$ and the orbital angular momentum $l$ has not been discussed up to this point. For each value of $n$, states of the hydrogen atom exist with $l$ ranging from 0 to $n - 1$. The fact that all $l$ states for a given $n$ are degenerate is a special circumstance of the Schrödinger equation for the hydrogen atom. Each of the $l$s has a multiplet of $m$ states, described in the previous paragraph.

The Schrödinger equation and Bohr's formula are quite accurate, but small states is very small, so that transitions in the hydrogen spectrum, and the actual multiplicity of states is twice that predicted by the Schrödinger equation. These flaws can be corrected by introducing the electron spin, with either the Schrödinger equation or the more precise Dirac equation. The electron spin behaves exactly like angular momentum, but with a value $1/2$. These are two $m$ states, with values $-1/2$ and $+1/2$, which provide the needed doubling in the multiplicity of states. The interaction of the spin changes the energies of the states, so they are no longer independent of $l$. The coupling of the spin to the orbital angular momentum is treated by defining a new angular momentum quantum number $j$. For a given $l$, $j$ can have the value $l + 1/2$ or $l - 1/2$, depending on whether the orientations of the spin and orbital angular momentum are parallel or antiparallel. However, in an $l = 0$ state such as the ground state, only $j = 1/2$ is allowed. This method of combining spin and orbital angular momentum is known as spin-orbit coupling. In the Dirac equation, the $n = 2$ state is split by combining in equal amounts the spin orbit coupling, with the $j = 1/2$ states slightly lower than the $j = 1/2$ state. The predicted splitting agrees very well with the observed fine structure in the spectrum.

Further refinements to the theory of the hydrogen atom have been made with quantum field theory. The theory predicts a very small energy difference between the two multiplets with $j = 1/2$. This tiny splitting has been observed, and its magnitude agrees with theory.

One final ingredient completes the description of the hydrogen atom — the interaction of its electron with the magnetic moment of its nucleus. The proton nucleus of ordinary hydrogen has a spin of $1/2$ and a magnetic moment. The energies of the atom depend on the relative orientation of the electron and the proton’s spin. This can be characterized by a new quantum number, the total spin $F$. It can have a value 0 or 1, depending on whether the two spins are parallel or antiparallel. The energy difference between these two states is in the microwave region of the electromagnetic spectrum. The frequency of the radiation is $1.4 \times 10^{14}$ hertz, which is a well-known feature of the radiation from interstellar hydrogen gas observed in radio astronomy.

**Multielectron atoms.** The properties of multielectron atoms are governed to a large extent by simple principles that determine the electron wave function. Electrons are placed in orbitals similar to the wave functions of hydrogen, starting with the lowest energy $n = 1$ orbital. The Pauli principle requires that each electron go into a different orbital. (It should be remembered that the two spin orientations in a wave function count as different orbitals.) With this procedure, each element acquires a unique structure of electron orbitals that gives it its characteristic atomic and chemical properties. A simple example is the helium atom. Helium has two electrons, both of which go into the $n = 1$ orbitals according to the spin degeneracy rule. All $n = 1$ electrons are tightly bound, and so the helium atom is not readily ionized; neither does it form chemical bonds by sharing its electrons with other atoms. The next element, lithium, has three electrons; only two can go in the $n = 1$ orbitals, so the third must be placed in an $n = 2$ orbital. This shell is much higher in energy; thus, the last electron is loosely bound. The ionization energy, which is the energy required to remove an electron from an atom, shows clearly the effects of the electron shells. Figure 6, displaying the ionization energies of the elements, shows that helium is the highest of any element. There is a big jump from helium to lithium, which needs only 5 eV of energy to ionize.

![Figure 6: Ionization energies of the elements.](image)

The shell behaviour of complex atoms is derived from the approximate solution of the Schrödinger equation, since exact solutions to the multielectron equation do not exist. The Hartree method (see above), treating each electron with its own wave function, gives an adequate approximation for most purposes. In Hartree's theoretical scheme, the Pauli principle is imposed by requiring all wave functions of the electrons to be distinct. An important part of the Hartree theory is the behaviour of the self-consistent field governing the electron cloud. A small electron cloud is defined as the distance from the nucleus, the Hartree field is virtually the same as the field of the nucleus. The contribution from the electrons is small because they are spread out in all directions. At large distances the nucleus appears to be surrounded by a cloud of electrons screening its positive charge with their negative charges. The last electron, if it is far away, "sees" a field resembling that of a single positive charge. The electron wave functions in this potential are qualitatively very similar to the hydrogen wave functions, retaining strong shell effects. The range of the wave functions and their energies, however, depend on both the atomic number and the presence of electrons in other shells. The $n = 1$ electrons are closest to the nucleus and are exposed to nearly its full electric field. The highest shell electrons are farthest away on average and feel a field similar to that of a hydrogen atom.

The size of atoms does not vary much from element to element, growing only slightly from light to heavy elements. This is due to a compensation between two opposing tendencies. The outer electrons of heavy atoms are in higher shells, the probability distributions of which are farther from the nucleus. On the other hand, the size of each shell is dependent on nuclear charge; the higher charge in heavier nuclei pulls a given shell in closer.

**Atomic spectroscopy and lasers.** The energy levels of atoms are studied by measuring the wavelengths of light emitted by the atoms in excited states. Atoms become excited when they absorb energy. In a gas, excited atoms are produced with heat or electric currents. The light emitted is analyzed in a spectrograph, which disperses the light in different directions according to its wavelength or frequency. Transitions from higher to lower energy levels appear as bright lines in the spectrum (Figure 7). This technique is known as emission spectroscopy. If white light is passed through a gas of the element being studied, light will be absorbed for those frequencies that allow a transition of the atom from the ground state to an excited state. The absorption creates a dark line in the spectrum of the white light. This is called absorption spectroscopy. The characteristics of the lines can be measured with great accuracy using spectographs together with other optical.
Figure 7: Energy levels of the neon atom. The orbitals occupied by the six outer electrons are indicated on the levels. The transition responsible for the red light from common lasers (wavelength of 6330 Å) is shown by the arrow.

The frequency shift from atomic motion, known as the Doppler effect, limits the resolution to about 1 part in 10,000. However, with intense light at a fixed frequency available from lasers, one can preferentially excite atoms moving at some particular velocity. Modern instrumentation makes it possible to observe structure in the lines to 1 part in 10,000,000. This accuracy allows the effects of nuclear spin, size, and shape to be measured directly with atomic lines.

The principle of the laser is based on the transitions between energy levels in an atom, or molecule. Normally, more atoms are in lower states than in upper states. Energy would be absorbed from a beam of radiation because most of the transitions would go from a lower level to an upper one. If the number of atoms in the upper and lower states is equal, there will be the same number of transitions in both directions. Therefore, the intensity of the atom's light beam would not change going through the medium. Conditions for the laser are obtained if more atoms are in the upper state than in the lower state; this is called a population inversion. As a result, a laser has more transitions going downward than upward, and a beam going through the medium is amplified. Passing the amplified beam back and forth between mirrors produces the very high intensity laser light.

Characterestic X rays. The inner shells of an atom are responsible for the characteristic X rays of an element. These are X rays of definite wavelengths emitted when atoms are bombarded with energetic electrons or other forms of radiation. The radiation knocks an inner electron out of its orbital, leaving a vacancy. An electron from a higher shell then jumps into the empty orbital, emitting a photon in the process. Because of the strong binding of inner shells in heavy atoms, such photons are produced with energies ranging from 100 to 100,000 eV in the X-ray region of the electromagnetic spectrum. The approximate energies of these transitions are given by the Bohr formula with a modified value of the nuclear charge. More accurate values for the energies can be calculated on the basis of the Hartree theory.

The ionization energy of atoms depends on the energy of the electron orbitals in the highest occupied shells. The variation of these energies with atomic number displays a periodic behaviour, as seen in Figure 6. Particularly noticeable is the increase in ionization energy as the p shells of the atom are filled. This is precisely what one expects to find: as the charge of the nucleus increases, the binding energy of the orbitals in a given shell increases. When a shell is filled, the next electron must go into a higher, less bound shell, producing a break in the ionization-energy plot. The fact that the behaviour is periodic shows that the inner cores of atoms act on the outer electrons in much the same way for different atomic numbers. The nuclear charge is screened by the inner electrons so that the outer electrons are effectively governed by the field from a lower atomic number.

The electron affinity of atoms exhibits a similar periodicity. Electron affinity is the binding energy of the extra electron when an atom forms a negative ion. Such atoms as helium that have all their electrons in tightly bound filled shells do not attract additional electrons strongly enough to bind them. On the other hand, such atoms as fluorine that have a single vacancy in a tightly bound shell readily attract and capture an extra electron into that orbital. The systematics of the electron affinities are shown in Figure 8. Obviously, the behaviour of the loosely bound electrons and shell effects are crucial to the understanding of the chemical properties of elements. The basic period of eight in the periodic table is associated with the filling of the s and p orbitals of a given n shell (see Figure 9).

For each spin orientation, there are one s orbital and three p orbitals, for a total degeneracy of eight. In the hydrogen atom, the s and p shells are degenerate, and in complex atoms they remain close in energy. Higher angular momentum shells, however, have considerably less binding than their s and p partners in the same n shell. As a result, they are filled out of sequence in the periodic table. For example, the 3d shell is filled after the 4s shell.

Figure 8: Electron affinities of the elements. The shell of the most bound vacancy is indicated by its spectroscopic designation.
extension corresponds to the fact that in $s$ and $p$ orbitals the electron probability is significant to larger distances. Most of chemistry has to do with these outer electrons. The $l = 3$ shell ($f$ shell) is well shielded by other electrons, and the elements that differ only in the number of $f$-shell electrons have very similar chemical properties.

Atomic bond types occur when atoms are connected by chemical bonds. The forces between atoms are complex and varied. In close proximity, all atoms repel each other. At intermediate distances, the forces of chemical binding are prominent. Finally, at large distances, all atoms are attracted to each other by a much weaker force. These forces are all explained by the quantum theory of electrons in atoms. In the presence of other atoms, the electrons become rearranged. If the new arrangement has less energy, it is the preferred state of the atoms, and there is an attractive force to reach this state. Conversely, if the rearrangement increases the energy, the resulting force between the atoms is repulsive. The rearrangement of electrons may take place in different ways, and different names are given for the resulting chemical bonds (see below).

The universal repulsion between atoms at short distances is responsible for atoms taking up a definite amount of space and for the incompressibility of solid materials. This repulsion has two causes. First, as the atoms are pushed into each other, the shielding provided by the electron cloud around each nucleus is less effective and the electric force between the two nuclei repels them. A second repulsive influence arises from the Pauli principle. Not only is it forbidden to have two electrons with the same wave function but the wave functions must be different enough to construct an antisymmetric total wave function. When two atoms are close together, the electrons in the overlapping region spend part of their time in their original orbitals and part of their time in orbitals of higher energy in order to satisfy the Pauli principle.

In chemical bonds, the rearrangement of electrons leaves atoms in a state of lower energy, stabilizing them at fixed distances from each other in definite geometric configurations. The amount of energy associated with chemical bonds ranges from 1 to 10 eV. A number of different kinds of bonds are recognized in chemistry. If the rearrangement causes a net shift of the electron's probability from one orbital to another, it is called covalent. An extreme example of this would be an ionic bond, in which an electron has moved from an orbital in one atom to that in the other. This electron transfer gives one atom a net positive charge and the other a net negative charge. The two resulting ions are then held together by the electric force of attraction between unlike charges. An example of ionic bonding occurs in alkali halide crystals such as sodium chloride (common table salt). The alkali metals are easily ionized, and the halogens have a strong affinity for additional electrons, as seen in Figures 6 and 8. The original concept of chemical binding was based on the sharing of opposite charges.

Strong chemical bonding of the homopolar, or covalent, type also occurs. In this case there is no net transfer of electrons from one atom to another. The rearrangement of the electron distribution is more subtle. In a covalent bond between two atoms, the electron density shifts from the outer surfaces of the atoms to the region between the two atomic centers. In general this does not happen, because the Pauli principle affects the wave functions by spreading the electrons apart. The Pauli principle, however, may be satisfied for a pair of electrons by giving them opposite spin orientations, in which case the spatial wave functions are combined to bring the two electrons closer together. A covalent bond can be formed between two atoms if there is an unpaired electron on each atom in the bonded state. The electrons will have their spins opposite and aligned. An atom can form a number of covalent bonds equal to the number of its unpaired electrons, which in turn determines its chemical activity. For example, the nitrogen atom has five electrons distributed over four orbitals in the $n = 2$ $s$ and $p$ shells. Two electrons must occupy the same orbital as a pair, but the remaining three electrons can go unpaired in separate orbitals, giving nitrogen a valence of 3.

The geometry of chemical bonding, with definite angles between the bonds in triatomic and more complicated molecules, depends on the geometry of orbitals with lobes extending at various angles. If atoms bonded with pure $p$ orbitals, the bonds would extend out at 90° angles from each other like the wave functions depicted in Figure 5. Hybridization produces wave functions with different geometries. In the carbon atom, for example, the hybridization yields four bonds directed toward the corners of a tetrahedron.

The ionic and covalent bonds are two extremes in a range of bonding behavior. The bonding wave functions do not need to be localized on two neighboring atoms. In so-called delocalized bonding the electron wave functions extend over several atoms. All of these properties can be predicted quite well using the Hartree-Fock theory. The positions of the atomic centers are first roughly estimated. The Schrödinger equation is then solved for each electron, with the requirement that the total forces from all the atoms be consistent with the total charge density from the electrons and nuclei. After the wave functions of all the electrons are found, the energy of the molecule can be calculated. This is repeated for other positions of the atomic centers until the best is found. The resulting arrangement of atomic centers and electron wave functions provides the configuration of the stable molecule. Depending on the behavior of the Hartree-Fock wave functions, one can find various kinds of chemical bonds. The Hartree-Fock theory is quite reliable in predicting the geometry of molecules and the character of the bonds, but it is less successful in predicting accurate bond energies.

Some forces between atoms at larger distances are too weak to form chemical bonds. These forces have two origins. One long-range force is associated with the electric field of fields that extend outside of any molecule with heteropolar electron distributions. An example is the water molecule, which has a net shift of electron charges from the hydrogen atoms to those of oxygen. The electric field attracts both positively and negatively charged ions, depending on the orientation of the water molecule. This explains why liquid water is such a good solvent for polar and ionic bonded molecules. Another long-range force, called the van der Waals force, is a weak attraction between all atoms. It provides the cohesive force in nonpolar liquids such as liquid air or gasoline. These liquids have a low boiling point because the bond energies of the van der Waals force are very low (only a few tenths of an electron volt). The force arises from a surface effect in quantum mechanics—namely, the existence of fluctuating electric fields outside an atom even though the electron wave function surrounds the nucleus and neutralizes its charge. The fluctuating fields are associated with the possible positions of the electron if it is frozen at some particular spot in its orbital.

Observing atoms. Individual atoms are far too small to be seen in any light microscope. The inherent limitation on such a microscope is the wavelength of light, which determines the minimum size of an image. In comparison, the distance between atoms in a solid is less than 1,000ths of the wavelength of light. Therefore, the minimum size of any image would contain too many atoms for the eye to differentiate. There are, however, several direct methods for observing individual atoms and their arrangement in molecules and solids. In a transmission
electron microscope, electrons are transmitted through the material to be studied. Images are formed because the electrons are absorbed differently by different atoms. With this technique, one can just barely see the individual atoms of the heaviest elements when they are separated by several atomic lengths (see Figure 10). Another technique involves the use of a field-ion microscope. In this case, a wire with a very fine tip is placed in a near-vacuum and given a positive electric charge. Individual atoms on the surface of the tip ionize residual gas molecules. The ions are then accelerated by the charge in straight lines away from the tip. They form spots on photographic plates at different positions corresponding to the location of atoms on the tip (see Figure 11). A third imaging technique is called scanning tunneling electron microscopy. Here, a wire with an extremely fine point is positioned within 10⁻⁹ metres of the surface to be studied. Electrons jump from the surface to the wire through individual atoms on the surface. The probe wire is moved back and forth over the surface in a raster pattern, and variations in the electron current indicate the positions of the atoms.

The positions of atoms in solids and molecules are commonly determined by wave diffraction. Diffraction refers to the highly directional patterns formed by waves when they travel through regularly ordered mediums. Diffraction techniques use a crystal or a large number of atoms in a regular arrangement. The pattern of the waves reflected from the crystal depends on the relative positions of the atoms in the crystal. The information contained in the wave pattern is far from complete, however, so there may be ambiguities in reconstructing the atomic arrangement. The most common technique of this kind is X-ray diffraction. X-rays are similar to visible light, but they have much shorter wavelengths. Radiation of this type that can be used for diffraction has a wavelength of 10⁻¹⁰ metre or smaller, which is even smaller than atoms. As the X-ray waves are most affected by the electrons in atoms, this technique locates atoms primarily by their electron cloud. Another diffraction technique uses neutrons from a nuclear reactor. Neutrons, like all particles, have wave properties and can be diffracted from a crystal. Neutrons of a particular wavelength are beamed on a crystal, and diffraction sends them off in various directions. The geometric arrangement of the atoms being studied is inferred from the diffraction pattern. Neutron waves interact most strongly with atomic nuclei, and so this technique complements X-ray diffraction by mapping the nuclear centres of atoms.

**Bulk matter.** The behaviour of bulk matter depends on the relative magnitude of the binding forces between atoms or molecules and the thermal energy of motion. The thermal energy of motion at room temperature is about 0.025 eV. If the binding energy is less than about 10 times the thermal energy, the substance will be in a gaseous state under normal conditions. This typically applies to small molecules such as air molecules that interact only by the weak van der Waals force. With larger ratios of binding energies to thermal energies, the substance condenses into a liquid or a solid. Solids are classified into several types, depending on the kind of bonding between their atoms. Four main types of ordered solids are ionic crystals, molecular crystals, covalent crystals, and metals. Ionic crystals are held together entirely by the electrostatic forces between ions. Common table salt is an example. A molecular crystal is composed of distinct molecules held together by weaker forces such as the van der Waals force. In covalent crystals the chemical bonds extend from atom to atom over the entire crystal. Diamond, a form of carbon, is an example of a covalently bonded solid; as in simple organic compounds, each carbon atom has four bonds pointed to the corners of a tetrahedron. In metals the concept of chemical valence breaks down. The atoms are closely packed together, and the number of neighbours for a given atom is determined more by the geometry of touching spheres than by the number of valence electrons.

The Hartree theory provides a common framework for describing the varying properties of these different kinds of solids. The electron orbitals are allowed to spread out over the entire solid. Effectively, one deals with an infinite number of electrons and orbitals, which can be handled with mathematical techniques developed by the Swiss-born U.S. physicist Felix Bloch and others. The orbitals display shell-like features even in a very large system. There are groups of orbitals with energies close together. Known as bands, they are separated by gaps in energy.

The characteristics of any such solid depend very much on the extent to which the orbitals are filled in the highest band. This filling level is called the Fermi energy. If...
the orbitals are completely filled up to the band gap, the states of the electrons are essentially fixed and the material will be an insulator. On the other hand, if the band is only partially filled, electrons can jump from one state to another with only an infinitesimal change in energy. In this case, the electrons can move about, and the material is a conductor. The sharp distinction between insulators and conductors becomes blurred in materials called semiconductors, which have small energy gaps. In silicon, for instance, the energy gap is only 1.4 eV, and it is possible to make silicon conduct by exciting electrons to the higher band. In some materials there is no energy gap between the occupied and empty orbitals, but the number of orbitals at the Fermi energy is so small that conductivity is poor. Graphite, another form of carbon, has a band structure of this type.

**THE NUCLEUS**

Nucleons. The protons and neutrons that make up the atomic nucleus are the lightest members of the baryon family of subatomic particles. The proton has a mass of $1.673 \times 10^{-27}$ kilogram, which is 1,836 times larger than the mass of the electron. The neutron has approximately the same mass as the proton—$1.675 \times 10^{-27}$ kilogram. Subatomic masses are commonly expressed in units of rest energy, which is related to mass by Einstein’s formula $E = mc^2$. The proton’s rest energy is 938.3 MeV and that of the neutron is 939.6 MeV. All baryons except the proton are unstable and can decay into lighter baryons. The neutron, having more rest energy than the proton, can decay into a proton with the emission of an electron and an anti-neutrino. Its lifetime outside the nucleus is 10 minutes. In the nucleus the binding energy is larger than the difference in rest energies between the neutron and the proton. The binding forces stabilize the nucleus against the decay of its neutrons.

Other properties of nucleons are their charge, spin, and magnetic moment. The change on a proton is equal and opposite to the electron’s charge. The neutron is uncharged. Like electrons and other elementary fermions, nucleons have a spin quantum number of $\frac{1}{2}$ and are described by a wave function that is doubled in multiplicity by two spin orientations. Nucleons and electrons also have a magnetic moment associated with their spin. However, the numerical value of a nucleon’s magnetic moment, unlike an electron’s, is quite different from that predicted by the Dirac equation; in fact, the proton’s moment is 2.8 times the value predicted. Furthermore, the neutron has a somewhat smaller moment opposite to that of the proton, though according to the Dirac equation it should have none at all.

While electrons are point particles, nucleons have a finite extension. The distribution of the positive charge in a proton can be measured in electron scattering experiments. The charge is distributed in a smooth cloud extending to a distance of about $1 \times 10^{-15}$ metre, or 1 femtometre, from the centre. The neutron is neutral overall, but electron scattering measurements show that it also has an internal structure with a slight positive charge in the core surrounded by a shell of negative charge.

**Internuclear forces.** The most important characteristic that distinguishes nucleons from electrons and other leptons is that it has to do with the forces acting on them. Nucleons are subject to the three forces of nature affecting leptons: gravitation, electromagnetism, and the weak force. However, nucleons also exert a very powerful force on each other—namely, the nuclear, or strong, force. This force has an extremely short range so that its effects are not felt outside an atom. Indeed, even within an atom, the strong force is insignificant just a few femtions (one fermi $= 10^{-15}$ metre) from the surface of the nucleus. By contrast, the effects of the electromagnetic and gravitational forces can be felt all at distances.

The character of the strong force is rather complicated and only partially understood. At very small distances between nucleons, less than one femtometre, the force is repulsive and tends to keep the nucleons apart. At intermediate distances, about one to two femtometres, the force is strongly attractive and can bind the nucleons by energy amounting to many millions of electron volts. Beyond a few femtometres, the strong force becomes inconstant in comparison to the electromagnetic force. A graph of the behaviour of the strong force is shown in Figure 12.

The effects of the strong force are seen in the interactions of free nucleons and the binding energy of nuclei. Nucleon interactions can be studied by bombarding hydrogen with a beam of protons or neutrons. The beam particles passing within a certain distance of a proton from the hydrogen target will be deflected by the strong force. The strength of the interaction between beam and target nucleons is characterized by a quantity called the cross section, which has units of area. It is the apparent area of the target particle that intercepts the beam particle and results in an interaction or a deflection. The cross section of high-energy nucleons scattering or otherwise interacting with each other is about four square femtometres. If the particles are thought of as spheres that interact when they come into contact, the radius of the individual nucleon sphere would be about 0.7 femtometre. At low energies the cross sections become larger, partly because there is more time for the forces to act with slower moving particles. Quantum wave effects also become more important at low energy; they allow the influence of the force to be felt at larger distances and help increase the cross section.

Most of the existing detailed knowledge about nuclear forces comes from matching observed cross sections, including their dependence on energy and scattering angle, with quantum mechanical calculations based on models of the strong force. Yukawa’s meson exchange picture (see above) explains the major features of the strong force beyond one femtometre. In quantum field theory, two particles may exert a force on each other at a distance only by exchanging a third particle. The particles exchanged in the strong force are mesons. The pion, the lightest of the mesons, is responsible for the longest range portion of the strong force. When the pion is exchanged, it can transfer a charge from one nucleon to another. In this process, called an exchange interaction, a proton is converted to a neutron and a neutron becomes a proton. At shorter distances, heavier mesons become important, and several pions may be exchanged at the same time. The main
attraction between nucleons in bound nuclei is caused by the exchange of multiple pions and higher mesons. The exchange of mesons also can change the internal structure of the nucleon, transforming it into some other baryon. Even when there is not enough energy to produce the excited baryon, its effects are felt in the strong force.

The strong force also depends on the spin orientation of the nucleons. This dependence adds to the complexity of the force. For example, the force between protons and neutrons is most attractive when the spins are pointing in the same direction. On the other hand, the Pauli principle does not allow two protons with parallel spins to be located close to each other, and the interaction with the opposite spin alignment is weaker. Part of the spin dependence is known as the tensor force. This force reorients the spin and exerts a torque on the nucleons. The tensor force helps explain a property of the deuteron, which is a neutron and proton bound together. Under the influence of ordinary forces, the wave function would be spherically symmetric. Due to the tensor force, however, the deuteron is elongated in shape. The elongation is measured as its quadrupole moment. Another significant part of the spin-dependent force is the spin-orbit force. This force acts when the nucleons are moving around each other and have orbital angular momentum. It tends to align the orbital angular momentum with the spin orientation.

An important consequence of the strong force is the binding of nuclei. The simplest example is the deuteron, with a binding energy of 2.2 MeV. The binding energy is the sum of an interaction energy and a kinetic energy of the particles. By itself, the interaction energy is much more than 2 MeV, but a large kinetic energy nearly cancels it. In heavier nuclei the interaction energy is higher because there are more neighbouring nucleons; consequently, the binding is greater. Protons also are attracted to each other by the strong force, but their interaction is not sufficient to bind them together. Thus, there is no isotope of helium consisting only of two protons.

Shape and size of nuclei. Most nuclei are spherical, and their size is determined by the number of nucleons present. The density of nucleons is roughly constant in the interior of a nucleus, and so the volume of the sphere is proportional to the atomic mass number. In this respect, the nucleus resembles a liquid drop, the volume of which is proportional to the amount of matter it contains. The density of nucleons in the interior of a nucleus is about 3 X 10^17 kilograms per cubic metre; each nucleon takes up about six cubic femtometres of volume. The radii of nucleons in nature range from two to eight femtometres.

The constant interior density of nuclei, called the saturation property, is quite different from the distribution of electrons in atoms. The density of electrons varies considerably with their distance from the centre of the atom; electrons are highly concentrated in the inner shells and more dispersed in the outer ones. The saturation of nuclear matter, on the other hand, arises from a delicate balance between the attractive and repulsive components of the nuclear force. Aspects of the interaction contributing to the saturation are: (1) the short-range repulsion that prevents the nucleons from occupying the same volume; (2) the change in exchange that is less effective at high density; (3) the tensor force; and (4) the interactions that make internal excitations of the nucleons.

The most precise information on nuclear sizes comes from: electron-scattering measurements. Because of their quantum-wave properties, electrons scattering from nuclei exhibit preferential scattering at specific angles. Detailed pictures of the size and shape of the nucleus can be inferred from these diffusion patterns. Figure 13 shows an example of inferred charge density on a slice through the centre of a nucleus of lead-208. The charge is roughly uniform inside a sphere and has a diffuse edge on the surface. The density falls from its inner value to zero over a distance of roughly two femtometres. One does not see the individual particles in the nucleus because their wave functions are diffuse clouds. There are, however, perceptible variations in density in the interior. These oscillations show that the wave functions of the nucleons inside a nucleus have a shell behaviour just like the electrons in atoms. The peaks occur at positions where the proton wave functions are maximal, and the valleys occur where the wave functions pass through zero.

Mass and binding energy. The mass of a nucleus is typically about 1 percent less than the total mass of the nucleons composing it. This mass deficiency is related to the binding energy of nuclei by Einstein's formula \( E = mc^2 \). The binding energy determines which nuclei are stable and how much energy is released in a nuclear reaction. The picture of the nucleus as a charged liquid drop describes the overall trends of the binding energies. Each particle in the interior of a classical liquid is bound by the same amount. Very roughly, nuclear binding energies behave accordingly, with a typical binding energy of 8 MeV per nucleon. In detail, the trend of nuclear binding energies may be seen in Figure 14, which graphs the binding energy per nucleon as a function of the atomic mass number. The graph shows the near constancy of the binding energy from nuclei as light as helium-4 up to very heavy nuclei. By contrast, the binding energy of atoms varies greatly with atomic number because their inner shells are so tightly bound.

Particles at the surface of a liquid have fewer neighbours to interact with, so there is surface tension and a deficiency of energy from the surface. In the same way, lighter nuclei have a relatively large surface-to-volume ratio and are not as strongly bound. This may be seen in Figure 14 in the behaviour of the curve for smaller atomic mass numbers.

Repulsion between the charges of protons reduces the binding energy of a nucleus. The negative contribution from this repulsion is called the Coulomb energy. The effect is largest for the highest atomic numbers, which are the most highly charged nuclei. The surface energy favouring large nuclei and the Coulomb energy favouring low atomic numbers oppose each other; consequently, the optimum mass number for a nucleus is in the middle...
region, around mass 60 and the iron nucleus. Nuclear energy can be released by any process that transforms nuclei to others closer to the middle masses. Thus, nuclear energy can be released by fusing light nuclei or by splitting heavy nuclei in the fission process. Energy production in stars results primarily from the fusion of hydrogen to make helium. Hotter stars can fuse heavier elements, but all nuclear energy is exhausted when iron is attained as a fusion product. Terrestrial elements are believed to have been formed by this process of stellar nucleosynthesis. Elements heavier than iron may have been formed by very transient processes in supernova explosions. (For a more detailed discussion of stellar nucleosynthesis, see STARS AND STAR CLUSTERS.)

Nuclear binding energy also depends on the relative numbers of neutrons and protons in a nucleus. In light nuclei the most binding is obtained with an equal number of neutrons and protons, which optimizes the neutron-proton attraction. In heavier nuclei the Coulomb repulsion between protons gives more binding to nuclei with an excess of neutrons. The most stable heavy nuclei have 50 or more neutrons than protons.

Nuclear spin and magnetic moment. Nuclei, like atoms or other particles, may have an internal angular momentum called spin. Because of the characteristics of the forces involved, the spin of a nucleus is zero if the nucleus has an even number of neutrons and protons. Nuclei with an odd number of nucleons always have a half-integer spin. In many cases the odd number of nucleons is determined from the nuclear shell model (see below). A nucleus with a spin also has a magnetic moment aligned along the spin axis. The magnetic moment of a nucleus is very weak compared to that of an electron, but it can still produce an observable effect in atomic properties. The magnetic field from a nucleus disturbs the degeneracy of atomic levels and causes the atomic spectral lines to split. This splitting is called hyperfine structure, as distinguished from the fine-structure splitting caused by the magnetic moment of electrons.

An important application of nuclear magnetism is a method of analysis called magnetic resonance. In this technique, a material is placed in a strong magnetic field that tends to align the nuclear spins. Partially aligned spins will precess about the magnetic field direction, the way a gyroscopic precesses when it is subjected to an outside torque. With the application of an extra time-varying magnetic field, the nuclei can be induced to precess in phase with each other. The resulting precessional motion of the spins causes the magnetization of the material to vary at a definite frequency, which is detected as a radiofrequency signal from the material. Magnetic resonance has several practical applications. Based on the fact that the precession rate is proportional to the field, it can be used to measure magnetic fields precisely. Notable is its use in a medical diagnostic procedure known as magnetic resonance imaging (MRI; see RADIATION: Imaging techniques). The nucleus most commonly employed in magnetic resonance is the proton in the hydrogen atom. Because the hydrogen nucleus has the largest magnetic moment for its spin, it provides the strongest resonance signals. Other nuclei used include those of phosphorus and fluorine.

Energy levels. Nuclei have energy levels just as atoms do. A typical excitation energy of a nuclear level is 1 MeV, which is 1,000,000 times larger than atomic energy levels. As in atomic transitions, a quantum of light may be emitted when the nucleus changes states. These quanta are the gamma rays that are often by-products of radioactivity.

Each energy level is characterized by its own values of spin, magnetic moment, and quadrupole moment. In addition, the quantum numbers of isotopic spin and parity are useful for describing nuclear levels. The isotopic spin quantum number characterizes the symmetry of the wave function when neutrons are interchanged with protons. Levels can exist in different nuclei with wave functions that are identical except for the interchange of neutrons and protons. Except for the Coulomb energy, these sets of wave functions have the same energies; the sets are called isospin multiplets (Figure 15). The parity quantum num-

Figure 15: The energy levels of three nuclei with A = 6, relative to the ground state of 1H. After subtraction of the calculated electrostatic energy, the isospin T = 1 levels exist in all three nuclei.

ber can take on only two values, even or odd, depending on whether the wave function reverses sign when the coordinates of the particles are reversed. The parity and spin quantum numbers are useful in understanding the rates of transitions between energy levels; selection rules govern changes in spin and parity for the favoured transitions.

To excite nuclei out of their ground states, energy must be provided from some external source. A common way to do this is with nuclear reactions. A nucleus is bombarded with energetic particles of one sort or another. The particles interact, giving up part of their energy to induce an excited state of the nucleus. Under special circumstances it is possible to excite a nucleus with the gamma ray produced by another nucleus. In a nuclear process known as the Mössbauer effect, the nucleus of some isotope absorbs a gamma ray that has been emitted by another nucleus of the same isotope. Because the transitions take place between the same two levels, the gamma ray has exactly the right energy to be absorbed. The effect is difficult to produce because part of the transition energy normally goes to nuclear recoil during emission and absorption and is unavailable to the gamma ray.

Among the energy levels to which a nucleus can be excited, a few correspond to simple modes of motion for the nucleons. Deformed nuclei (see below) can be given energy in the form of rotational motion. Nuclei also can vibrate, and corresponding vibrational states may be found among the energy levels. Giant dipole resonance is an example of a nuclear vibration exhibited by all nuclei. In this mode of motion neutrons and protons in the nucleus oscillate back and forth, with the neutrons moving against the protons, as shown in Figure 16. Because there is a large oscillating electric field associated with this motion, gamma rays are absorbed and emitted readily. Another kind of vibration is called the quadrupole vibration. In this mode the nucleus oscillates in shape, changing between

Mössbauer effect


Figure 16: Nuclear vibratory motion in the giant dipole resonance. Protons and neutrons, indicated by circles and solid dots, move in opposite directions.
prolate and oblate spheroids. This mode is easily excited by the inelastic scattering of particles from the nucleus. Its properties are deduced from the diffraction pattern observed in the scattering. In yet another kind of vibration, called the breathing mode, the nucleus expands and contracts. The frequency of this breathing mode depends on the compressibility of the nuclear medium and is used to establish its value.

Nuclear shell model. A comprehensive explanation of many nuclear properties is provided by a theory known as the shell model. It is based on the Hartree approximation to the Schrödinger equation. As noted earlier, this approximation assumes that all the particles have independent wave functions governed by a common force field. Of course, the forces in the nucleus are different from those in the atom as a whole. In the nuclear Hartree theory the forces are too strong to include directly, varying violently from repulsive to attractive. Instead, true interaction is replaced by smoother forces that are adjusted to reproduce the saturation property of nuclei.

The resulting force field pulls the nucleons in when they come to the surface, but it cancels out when nucleons are in the interior. The nucleons behave as though they were in a potential well with a flat bottom. The nuclear shells are the sets of wave functions that go with this flat-bottomed potential well. Some of the properties of these shells are similar to those of atomic shells, but there are also important differences. Provided the well is spherically symmetric, the shells have an angular momentum quantum number, as do the atomic shells. The lowest shell is the s shell, which can hold a neutron and proton of each spin orientation. Thus, the two protons and two neutrons of helium-4 fill the s shell and give this light nucleus its unusual stability. The energy levels of higher shells are shown in Figure 17. Differences from the atomic levels in hydrogen are readily apparent. First, there is no degeneracy between the s and p shells, so that the atomic periodicity of 8 does not occur in nuclear physics. Second, the spin-orbit force makes shells that have nucleon spin parallel to orbital angular momentum lower in energy than the shell with antiparallel spin. For example, in the p shell, there are two sub-shells, the \( p_0 \) and the \( p_1 \). The \( p_0 \) with orbital angular momentum 1 parallel to spin angular momentum 1/2, is lower in energy than the \( p_1 \), which has an antiparallel spin and orbital angular momentum. Combining orbital and spin angular momentum in this way is called \( j \) coupling. The number of protons or neutrons that can go in a j shell is its multiplicity equal to \( 2j + 1 \). From this filling rule and the shell ordering in Figure 17, one can determine the shell structure of a nucleus for any given proton and neutron numbers.

An important consequence of the \( j \) coupling is the energy gap between shells that occurs at proton or neutron numbers 28, 50, 82, and 126. These so-called magic numbers are the nuclear equivalent of the atomic numbers of the noble (or inert) gases 2, 10, 18, 36, 54, 86. Nuclei with magic numbers of protons and neutrons are unusually stable and have especially large gaps between their ground and excited states.

The ground state of nuclei with an odd number of neutrons or protons has a spin that is often given by a simple rule—namely, that the angular momentum of all the nucleons except the last is zero. The last nucleon has the angular momentum of its shell, which gives the spin of the nucleus. For example, the nucleus of lithium-7 consists of three protons and four neutrons. According to the rule, the spin of lithium-7 is determined by the shell of the third proton. This is the \( p_0 \) shell, and indeed the spin of the nucleus is \( 3/2 \). Another property that can be inferred from the shell model is the parity of the nucleus. It can be determined from the shell model simply by combining the parities of the individual shell wave functions for nucleons.

Nuclear excited states are described in the shell model either by changing the orbitals that nucleons occupy in a shell or by moving nucleons from a lower shell to a higher one. Wave functions constructed in this way accurately describe the excited-state properties of light nuclei and nuclei near magic numbers. Outside of these limited regions of nuclei, the shell model allows an enormous number of states. The numerical complexity of dealing with so many states, however, prevents precise calculations from being carried out. A simplified treatment of the wave function explaining many properties of nuclear vibrations is based on a generalization of the Hartree method to allow the potential field to vary in time. The nucleons move in the time-varying field, and the frequency of motion can be calculated by requiring the solutions to the Schrödinger equation to be consistent with the field in which they move.

Deformed nuclei. Not all nuclei are spherical in shape. In certain regions of the periodic table, many nuclei are spheroidal. Typically, these nuclei have a prolate distortion, meaning that they have an elongated shape like a lemon. For example, the nuclei near mass number 160 are prolate spheroids, with the longer axis about 30 percent larger than the other two axes. The existence of these deformations was first detected in atomic spectra: the quadrupole moment distorts the electric field around the nucleus, producing characteristic features in the hyperfine structure of the atomic spectrum. The energy levels of these nuclei also exhibit characteristic features. Any nucleus capable of rotation and governed by the laws of quantum mechanics has energy levels with spacings that increase uniformly with higher angular momentum. Deformed nuclei exhibit this type of spectrum (see Figure 18).

Deformations can be explained by the Hartree theory of the nuclear wave function. The orbitals describing the individual nucleons are rarely spherically symmetric; many are, in fact, quite elongated. When a shell is filled, the various asymmetries in the different orbitals balance out so that the entire shell has a spherical mass distribution. If a shell is only partly filled, the overall shape deviates more or less from spherical symmetry, depending on which particular orbitals are occupied. In the case of an atom, the repulsion of the electrons tends to make the overall shape spherical: when one electron is in an orbital elongated in a certain direction, the energy is minimized if the other electrons are in orbitals elongated in other directions. The
overall density ends up being close to spherical, even when the individual orbitals are not. In a nucleus there is a net attraction between nucleons so that, if a proton's orbital is elongated in some particular direction, the neutron would tend to be in a similarly directed orbital. Many nucleons can come together and deform the entire nucleus. When the Hartree equations are solved for nuclei with partially filled shells, the resulting potential well is elongated and the nucleons occupy states elongated in the same direction.

Nuclear reactions. Nuclear reactions mediated by the strong force can occur when a nucleus is bombarded by some hadronic projectile, such as a proton, a pion, or another nucleus. For a reaction to occur, the projectile must come within a few femtometres of the nucleus, preventing positively charged particles from producing reactions at low energy. Since the nucleus is positively charged, a similarly charged projectile will not be able to come within range unless it has enough energy to overcome the force of the electric repulsion. For example, alpha particles will not come close enough to interact with an iron nucleus unless their energy exceeds about 10 MeV. For low highly charged nuclei, the numbers are smaller; a proton of 1 MeV can interact with a lithium nucleus. The first artificial nuclear reactions were induced by using a voltage source of 1,000,000 volts to accelerate protons to an energy of 1 MeV and bombard a lithium target. At high bombarding energies the electrostatic force is less important, and the cross section for producing a reaction is approximately equal to the area of a circle with the radius of the nucleus.

Neutrons can induce reactions at very low energies, even thermal energies, because they are not repelled by the positive charge of the nucleus. The cross section for reactions with thermal neutrons can be extremely large because the wave function of the neutron is spread out at low energy. Radioactive nuclei are commonly produced by bombarding nuclei with neutrons in nuclear reactors.

Reactions induced by hadronic projectiles may be divided into two main categories: direct reactions and more complex reactions. In direct reactions the projectile retains most of its energy and momentum. A small amount of energy is transferred to the target, producing transitions to particular excited states. These direct reactions occur when the projectile passes near the target nucleus without penetrating it. The angular distribution of scattered projectile particles shows diffraction behaviour depending on

the properties of the energy level excited. An example of a direct reaction is the following:

\[ p + ^{40}\text{Ca} \rightarrow d + ^{40}\text{Ca}. \]

Here, a proton, \( p \), passes by the calcium-40 nucleus, picking up a neutron to form a deuterium, \( d \). The deuterium comes off in approximately the same direction as the motion of the incident proton but with diffractional variations in intensity at different angles. From the diffraction pattern, the orbital angular momentum of the neutron in the target may be inferred. Measurements such as these were important in establishing the validity of the shell model.

If the projectile goes into the target nucleus, it is likely to be absorbed completely, sharing its energy with the other nucleons in the nucleus. The resulting highly excited nucleus, called a compound nucleus, can decay in many different ways. The main constraints in determining the possible reactions are that the total number of neutrons and protons, the total charge, and the total energy must remain the same. These are the conservation laws for baryon number, charge, and energy. In principle, it is possible to change a neutron into a proton or vice versa in a hadronic reaction, but the probability is so small that this cannot be observed in the laboratory.

An example of a reaction following this complex path is

\[ a + ^{14}\text{N} \rightarrow ^{1}\text{O} + p, \]

This reaction was observed by Rutherford, who used alpha particles from a radioactive source. This provided enough energy to allow the alpha particle, \( a \), to touch and fuse with the nitrogen-14 nucleus. There is a high probability that the resulting compound nucleus will decay by emitting a proton, but it can decay by other modes as well. The following example is a reaction that takes place when a hydrogen-containing medium is bombarded with low-energy neutrons, \( n \):

\[ n + ^{1}\text{H} \rightarrow ^{1}\text{H} + \gamma \]

In this case, the energy released is equal to the binding energy of hydrogen-2, which is given off in the gamma ray, \( \gamma \). Many different kinds of reactions are possible in collisions induced by accelerated particles. Accelerators can give the projectiles enough energy to disrupt the nucleus completely and create new particles in the process. For example, a cyclotron can boost carbon nuclei to an energy of 500 MeV, enough to dissociate all the nucleons in a target nucleus of oxygen. In practice, such a reaction would involve many different processes, and the end result would be the fusion and dissociation of the nuclei into fragments of various sizes (see Figure 19). The annihilation of a pion in a nucleus is another example of a hadronic reaction. In this process, the rest energy of the pion would be released, dissociating the nucleus and giving kinetic energy to nucleons or other fragments.

Nuclear reactions also can be induced by leptons such as electrons and neutrinos. The probability for an electron-induced reaction is smaller than for a hadronic reaction because of the difference in forces. The main process is inelastic scattering, in which the nucleus is excited to a higher energy level. If the inelastic scattering transfers a large amount of energy to the nucleus (e.g., 20 MeV or larger), the nucleus becomes disrupted and ejects particles.

The weak interaction also causes reactions, but these are very difficult to observe. One part of the weak interaction changes a neutron into a proton or vice versa and brings about a corresponding conversion between an electron and a neutrino. The direction of the change is such as to conserve the total charge. An example of a neutrino-induced reaction is the reaction by which neutrinos were detected from a supernova in 1987. In this case, the neutrinos—or more precisely antineutrinos, \( \bar{\nu} \)—from the cosmic object interacted with protons of hydrogen atoms in a large tank of water. Positrons, \( e^+ \), were created according to the reaction...
\[ \bar{\nu} + p \rightarrow n + e^+ \]

The positrons were detected by the light they emitted as they traveled through the water. (G.F.B./S.MeG.)