Atoms, electrons andthe periodic table

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1 A new view of the world

"Anyone who is not shocked by quantum theory has not understood it."
Niels Bohr, as quoted by John Gribbin in "In search of Schrödinger's Cat."

What we call "classical" physics is based on our experience of what we perceive as the "real world". Even without knowing the details of Newton's laws of motion that describe the behavior of macroscopic bodies, we have all developed an intuitive understanding of this behavior; it is a part of everyone's personal view of the world. By analogy, we tend to view atoms and molecules in much the same way, that is, simply as miniature versions of the macroscopic objects we know from everyday life.

Equally familiar to us is radiant energy: light, thermal radiation, and radio waves are all forms of electromagnetic radiation that can be described in terms of simple wave motions whose nature and behavior have been thoroughly understood since James Clerk Maxwell developed his detailed theory of electromagnetism in the middle part of the nineteenth century.

Toward the end of that century, however, certain phenomena began to be noticed that seemed to be inconsistent with this dichotomy of particles and waves. This prompted further questions and further experiments which led eventually to the realization that classical physics while it appears to be "the truth", is by no means the whole truth. In particular, it cannot accurately describe the behavior of objects that are extremely small or fast-moving.

Chemistry began as an entirely empirical, experimental science, dealing with the classification and properties of substances and with their transformations in chemical reactions. As this large body of facts developed into a science (one of whose functions is always to explain and correlate known facts and to predict new ones), it has become necessary to focus increasingly on the nature and behavior of individual atoms and of their own constituent parts, especially the electrons. Because of their small mass, the behavior of electrons in atoms and molecules cannot be adequately explained by classical physics, and without a thorough understanding of the behavior of electrons, it is impossible to achieve a real understanding of the chemical and physical properties of matter. The purpose of this introductory unit is to summarize the major ideas of quantum theory that will be needed to treat atomic and molecular structure later on in the course.

Quantum theory can be presented simply as a set of assumptions which are developed through mathematical treatment. This is in fact the best route to take if one is to use quantum mechanics as a working tool. More than this, however, quantum theory brings with it a set of concepts that have far-reaching philosophical implications and which should be a part of the intellectual equipment of anyone who claims to

have a general education in the sciences. A major objective of this chapter will be to introduce you to "the quantum way of thinking" and to show how this led to a profound break with the past, and a shift in our way of viewing the world that has no parallel in Western intellectual history.

Particles and waves

By the end of the nineteenth century, the enormous success of the recently developed kinetic molecular theory of gases had dispelled most doubts about the atomic nature of matter; the material world was seen to consist of particles that had distinct masses and sizes, and which moved in trajectories just as definite as those of billiard balls.

Light. The development of our ideas about light and radiation was not quite as direct. In the 17th century, heat was regarded as a substance called *caloric* whose invisible atoms could flow from one object to another, thus explaining thermal conduction. This view of heat as a material fluid seemed to be confirmed by the observation that heat can pass through a vacuum, a phenomenon that we now call *radiant heat*. Isaac Newton, whose experiments with a prism in 1672 led to his famous textbook *"Optiks"*, noted that light seemed to react with green plants to produce growth, and must therefore be a "substance" having atoms of its own. By 1800, the corpuscular (particle) theory of light was generally accepted.

And yet there were questions. Count Rumford's observation that the drill bits employed in boring cannons produced more frictional heat when they were worn and dull led to the overthrow of the caloric theory [1] In 1812, Christiaan Huygens showed how a number of optical effects could be explained if light had a wavelike nature, and this led Fresnel to develop an elaborate wave theory of light. By 1818 the question of "particle or wave" had become so confused that the French Academy held a great debate intended to settle the matter once for all. The mathematician Poisson pointed out that Fresnel's wave theory had a ridiculous consequence: the shadow cast by a circular disk should have a bright spot of light at its center, where waves arriving in phase would reinforce each other. Fresnel performed the experiment and was entirely vindicated: if the light source is sufficiently point-like (an extended source such as the sun or an ordinary lamp will not work), this diffraction effect is indeed observed.

Heat. By this time it was known that radiant heat and "cold" could be focussed and transmitted by mirrors, and in 1800 William Herschel discovered that radiant heat could be sensed in the dark region just beyond the red light refracted by a prism. Light and radiant heat, which had formerly been considered separate, were now recognized as

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1. The caloric theory assumed that small particles are able to contain more heat than large ones, so that when a metal is sawn or drilled, some of its heat is released as the filings are produced. A dull drill produces few filings, and according to this theory, should produce little heat, but Rumford was able to show that the amount of heat produced is in fact independent of the state of the drill, and depends only on the amount of mechanical work done in turning it.

one, although the question of precisely what was doing the "waving" was something of an embarrassment.

The quantum revolution

By 1890, physicists were congratulating themselves on having tidied up the world into the two realms of particulate matter and of wavelike radiant energy, which by then had been shown by James Clerk Maxwell to be forms of electromagnetic energy.

No sooner had all this been accomplished, than the cracks began to appear; these quickly widened into chasms, and within twenty years the entire foundations of classical physics had disintegrated; it would not be until the 1920's that anyone with a serious interest in the nature of the microscopic world would find a steady place to stand.

Cathode rays. The atom was the first to go. It had been known for some time that when a high voltage is applied to two separated pieces of metal in an evacuated tube, "cathode rays" pass between them. These rays could be detected by their ability to cause certain materials to give off light, or fluoresce, and were believed to be another form of electromagnetic radiation. Then, in the 1890s, J.J. Thompson and Jean Perrin showed that cathode rays are composed of particles having a measurable mass (less than 1/1000 of that of the hydrogen atom), they carry a fixed negative electric charge, and that they come from atoms. This last conclusion went so strongly against the prevailing view of atoms as the ultimate, un-cuttable stuff of the world that Thompson only reluctantly accepted it, and having done so, quickly became the object of widespread ridicule.

Radioactivity. But worse was soon to come; not only were atoms shown not to be the smallest units of matter, but the work of the Curies established that atoms are not even immutable; atoms of high atomic weight such as uranium and radium give off penetrating beams of radiation and in the process change into other elements, disintegrating through a series of stages until they turn into lead. Among the various kinds of radiation that accompany radioactive disintegration are the very same cathode rays that had been produced artificially by Thompson, and which we now know as electrons.

Radiation is quantized

The wave theory of radiation was also running into difficulties. Any object at a temperature above absolute zero gives off radiant energy; if the object is moderately worm, we sense this as radiant heat. As the temperature is raised, a larger proportion of shorter-wavelength radiation is given off, so that at sufficiently high temperatures the object becomes luminous. The origin of this radiation was thought to lie in the thermally-induced oscillations of the atoms within the object, and on this basis the mathematical physicist James Rayleigh had worked out a formula that related the wavelengths given off to the temperature. Unfortunately, this formula did not work; it predicted that most

of the radiation given off at any temperature would be of very short wavelength, which would place it in the ultraviolet region of the spectrum. What was most disconcerting is that no one could say *why* Rayleigh's formula did not work, based as it was on sound classical physics; this puzzle became known as the "scandal of the ultraviolet".

Quanta. In 1899 the German physicist Max Planck pointed out that one simple change in Rayleigh's argument would produce a formula that accurately describes the radiation spectrum of a perfect radiator, which is known as a "black body". Rayleigh assumed that such an object would absorb and emit amounts of radiation in amounts of any magnitude, ranging from minute to very large. This is just what one would expect on the basis of the similar theory of mechanical physics which had long been well established. Planck's change for which he could offer no physical justification other than that it works, was to discard this assumption, and to require that the absorption or emission of radiation occur only in discrete chunks, or *quanta*.

Max Planck had unlocked the door that would lead to the resurrection of the corpuscular theory of radiation. Only a few years later, Albert Einstein would kick the door open and walk through.

The photoelectric effect.

By1900 it was known that a beam of light, falling on a piece of metal, could cause electrons to be ejected from its surface. Evidently the energy associated with the light overcomes the binding energy of the electron in the metal; any energy the light supplies in excess of this binding energy appears as kinetic energy of the emitted electron. What seemed peculiar, however, was that the energy of the ejected electrons did not depend on the intensity of the light as classical physics would predict. Instead, the energy of the photoelectrons (as they are called) varies with the color, or wavelength of the light; the higher the frequency (the shorter the wavelength), the greater the energy of the ejected electrons.

In 1905, Albert Einstein, then an unknown clerk in the Swiss Patent Office[1], published a remarkable paper in which he showed that if light were regarded as a collection of individual particles, a number of phenomena, including the photoelectric effect, could be explained. Each particle of light, which we now know as a **photon** , has associated with it a distinct energy that is proportional to the frequency   of the light, and which corresponds to Planck's energy quanta. The energy of the photon is given by

$$e = h \quad = \frac{hc}{\quad} \tag{1}$$

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1. The 1905 volume of *Annalen der Physik* is now an expensive collector's item, for in that year Einstein published three major papers, any one of which would have guaranteed him his place in posterity. The first, on the photoelectric effect, eventually won him the Nobel Prize. The second paper, on Brownian motion, amounted to the first direct confirmation of the atomic theory of matter. The third paper, his most famous, *"On the electrodynamics of moving bodies"*, set forth the special theory of relativity.

in which *h* is Planck's constant, 6.63E-34 J-s and *c* is the velocity of light, 3.00E8 m s^{-1}. The photoelectric effect is only seen if the photon energy *e* exceeds the binding energy of the electron in the metal; it is clear from the above equation that as the wavelength increases, *e* decreases, and eventually no electrons will be released.

Einstein had in effect revived the corpuscular theory of light, although it would not be until about 1915 that sufficient experimental evidence would be at hand to convince most of the scientific world, but not all of it: Max Planck, whose work had led directly to the revival of the particle theory of light, remained one of the strongest doubters.

Matter and energy united

The concept of energy was slow to develop in science, partly because it was not adequately differentiated from the related quantities of force and motion. It was generally agreed that some agent of motion and change must exist; Descartes suggested, for example, that God, when creating the world, had filled it with "vortices" whose motions never ceased, but which could be transferred to other objects and thus give them motion. Gradually the concepts of *vis viva* and *vis mortua* developed; these later became kinetic and potential energy. Later on, the cannon-boring experiments of James Joule led to the connections between heat and work. Finally, the invention of the steam engine forced the birth of the science of thermodynamics, whose founding law was that a quantity known as *energy* can be transferred from one object to another through the processes of heat and work, but that the energy itself is strictly conserved.

Relativity. If Einstein's first 1905 paper put him on the scientific map, the third one made him a scientific celebrity[1].

In effect, Einstein merely asked a simple question about Faraday's law of electromagnetic induction, which says that a moving electric charge (such as is produced by an electric current flowing in a conductor) will create a magnetic field. Similarly, a moving magnetic field will induce an electric current. In either case, something has to be moving. Why, Einstein asked, does this motion have to be relative to that of the room in which the experiment is performed— that is, relative to the Earth? A stationary charge creates no field, but we know that there is really no such thing as a stationary charge, since the Earth itself is in motion; what, then, do motion and velocity ultimately relate to?

The answer, Einstein suggested, is that the only constant and unchanging velocity in the universe is that of light. This being so, the beam emitted by the headlight of a moving vehicle, for example, can travel no faster than the light coming from a stationary one. This in turn suggested (through the Lorentz transformation (we are leaving out a few

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1. The appearance of his general theory of relativity in 1919 would finally make Einstein into a reluctant public celebrity and scientific superstar. This theory explained gravity as a consequence of the curvature of space-time.

steps here!) that mass, as well as velocity (and thus also, time) are relative in that they depend entirely on the motion of the observer. Two observers, moving at different velocities relative to each other, will report different masses for the same object, and will age at different rates. Further, the faster an object moves with respect to an observer, the greater is its mass, and the harder it becomes to accelerate it to a still greater velocity. As the velocity of an object approaches the speed of light, its mass approaches infinity, making it impossible for an object to move as fast as light.

Mass–energy. Where does this additional mass come from? Simply from the kinetic energy of the object; this equivalence of mass and energy, expressed by the famous relation $e = mc^2$, is the most well known consequence of special relativity. The reason that photons alone can travel at the velocity of light is that these particles possess zero rest mass to start with. You can think of ordinary matter as "congealed energy", trapped by its possession of rest mass, whereas light is energy that has been liberated of its mass.

Basic quantum concepts

Wave motion. We use the term "wave" to refer to a quantity which changes in a repeating or periodic manner with time. Such quantities are widespread in nature; think of the motions of the ocean surface, the pressure variations in an organ pipe, or the vibrations of a plucked guitar string. What is interesting about all such repeating phenomena is that they can be described by the same mathematical equations.

Wave motion arises when a disturbance of some kind is propagated through a medium; pressure variations through air, transverse motions through a guitar string, or variations in the intensities of the local electric and magnetic fields in space; which constitutes *electromagnetic radiation*. For each medium, there is a characteristic velocity at which the disturbance travels.

There are three measurable properties of wave motion: *amplitude*, *wavelength*, and *frequency*, the number of vibrations per second. The relation between the wavelength and frequency of a wave is determined by the propagation velocity

$$= \tag{2}$$

In other words, the distance travelled by the wave in one second (the velocity) must contain the length   exactly *n* times.

Energy units and magnitudes. It is useful to develop some feeling for the various magnitudes of energy that we must deal with. The basic SI unit of energy is the Joule; the appearance of this unit in Planck's constant *h* allows us to express the energy equivalent of light in joules. For example, light of wavelength 500 nm, which appears blue-green to the human eye, would have a frequency of

$$= \frac{c}{\lambda} = \frac{3 \times 10^{8} \text{m s}^{-1}}{5 \times 10^{-7} \text{m}} = 6 \times 10^{14} \text{s}^{-1} \tag{3}$$

The quantum of energy carried by a single photon of this frequency is

$$= h = (6.63 \times 10^{-34} \text{J s}) \times (6 \times 10^{14} \text{s}^{-1}) = 4.0 \times 10^{19} \text{J} \tag{4}$$
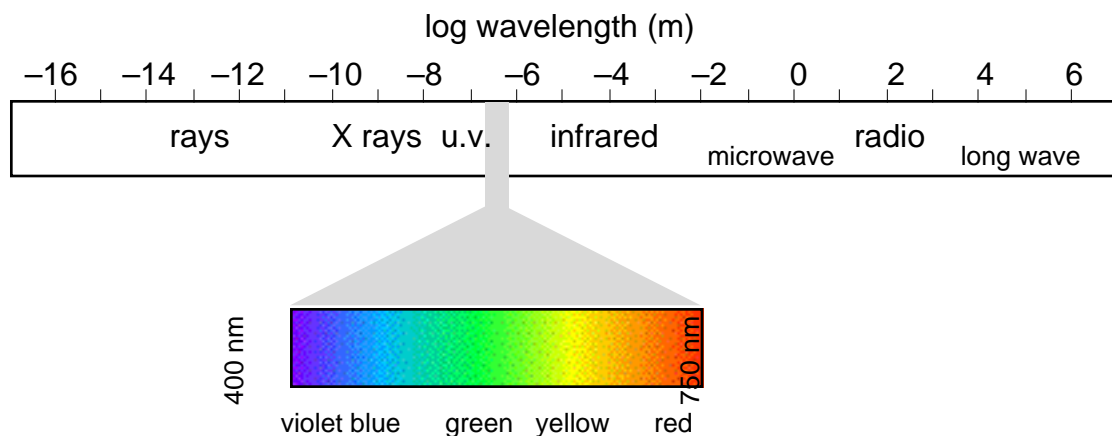
Another energy unit that is commonly employed in atomic physics is the electron volt; this is the kinetic energy that an electron acquires upon being accelerated across a 1-volt potential difference. The relationship 1 eV = 1.6022E–19 J gives an energy of 2.5 eV for the photons of blue-green light.

> Two small flashlight batteries will produce about 2.5 volts, and thus could, in principle, give an electron about the same amount of kinetic energy that blue-green light can supply. Because the energy produced by a battery derives from a chemical reaction, this quantity of energy is representative of the magnitude of the energy changes that accompany chemical reactions.

In more familiar terms, one mole of 500-nm photons would have an energy equivalent of Avogadro's number times 4E-19 J, or 240 kJ per mole. This is comparable to the amount of energy required to break some chemical bonds. Many substances are able to undergo chemical reactions following light-induced disruption of their internal bonding; such molecules are said to be photochemically active.

The electromagnetic spectrum.

We have seen that light can be regarded both as a massless particle, the photon, and as a periodic electromagnetic disturbance having wavelike properties. The complete range of wavelengths with electromagnetic energy can be propagated is much wider than the range of visible light, which extends from about 400 nm (blue) to 750 nm (red). Wavelengths somewhat longer than those of red light are perceived as heat, or thermal radiation; most of the warmth we receive from the Sun is in this form. Still longer wavelengths, ranging from millimeters to meters, correspond to radio waves. Heat (infrared) and radio photons have energies too low to disrupt chemical bonds, but they can interact with molecules in ways that provide a valuable means of indentifying particular structural features. The more energetic photons in the ultraviolet region from 400 nm down to about 100 nm can induce photochemical reactions in many substances. The range from 100 nm to 10 nm corresponds to X-rays. At still shorter walengths are gamma rays, the most energetic electromagnetic radiation of all.

log wavelength (m)

−16   −14   −12   −10   −8   −6   −4   −2   0   2   4   6

rays   X rays u.v.   infrared   radio

microwave   long wave

400 nm

750 nm

violet blue   green yellow   red

Continuous spectra.

Any body whose temperature is above absolute zero emits radiation covering a broad range of wavelengths. At very low temperatures the predominant wavelengths are in the radio microwave region. As the temperature increases, the wavelengths decrease; at room temperature, most of the emission is in the infrared. At still higher temperatures, objects begin to emit in the visible region, at first in the red, and then moving toward the blue as the temperature is raised.

These *thermal emission* spectra are described as *continuous spectra*, since all wavelengths within the broad emission range are present. When sunlight is refracted by rain droplets into a rainbow or by a prism onto a viewing screen, a continuous spectrum is seen.
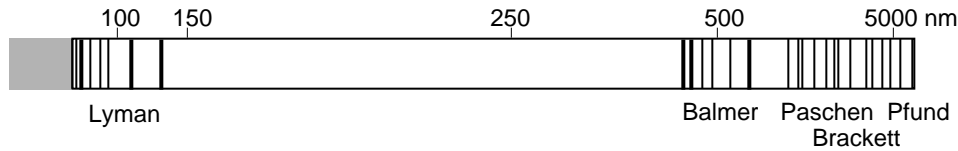
Line spectra.

Whenever a substance absorbs a photon, the energy carried by the photon is transferred to the absorbing atom or molecule, raising it to an excited state. The number of such states and their energies depend on the particular substance and the nature of the change that leads to the excitation, which is commonly a change in mechanical motion (such as vibration) or a change in the orbital arrangement of electrons. If a substance does not possess an excited state that corresponds to the energy of the light, then no light will be absorbed.

For example, the fact that plant leaves are green tells us that the chlorophyll molecules within them can absorb red light and blue light, but not green light, which is simply reflected back toward the source. If one plots the amount of energy absorbed as a function of wavelength, the resulting plot is called the *absorption spectrum* of the substance.

Atoms have much simpler spectra than molecules, and they can not only absorb light, but they are also able to emit it in a process known as *fluorescence*. The wavelengths absorbed or emitted by atoms generally correspond to very specific, sharply defined wavelengths. These wavelengths appear as bright lines on a photographic record of the spectrum, and are therefore known as *line spectra*. True line spectra are produced only by isolated atoms; in molecules the spectra tend to

be spread out into broader wavelength ranges. More importantly, these discrete spectra are entirely different from the continuous spectra emitted by objects at a high temperature, which we described above. By mapping the absorption or emission lines of a given atom and expressing these wavelengths to energies, it is possible to draw up a list of the permissible energy states for that element.

Atomic line spectra of hydrogen and other simple atoms were first studied in the late 1800's, but it was not until after Einstein's relation between energy and wavelength had become known around 1915 that these spectra could be meaningfully interpreted so that they could serve as useful clues to the structure of the atom.

Atomic line emission spectra are produced by passing the substance through electric arcs or discharges where large amounts of energy are available to raise the atoms to high-energy states; as the atoms fall back to their ground states, the excess energy is released as fluorescence at wavelengths corresponding to the allowed emission lines. Each kind of atom has its own characteristic line spectrum that can serve to identify it, very much like a fingerprint. One common use of atomic emission spectra is to determine what elements are present in the crankcase oil of an engine. Because different parts of the engine are composed of different alloys, this can help show what parts of the engine are undergoing excessive wear.

Particles and waves

If light has a particle nature, why should particles not possess wavelike characteristics? In 1923 a young French physicist, Louis de Broglie, published an argument showing that matter should indeed have a wavelike nature. The *de Broglie wavelength* of a body is inversely proportional to its momentum *mv*:

$$= \frac{h}{mv} \tag{5}$$

If you explore the magnitude of the quantities in this equation, it will be apparent that the wavelengths of all but the lightest bodies are insignificantly small fractions of their dimensions, so that the objects of our everyday world all have definite boundaries. Even individual atoms are sufficiently massive that their wave character is not observable in most kinds of experiments.

Electrons, however, are another matter; the electron was in fact the first particle whose wavelike character was seen experimentally, fol-

lowing de Broglie's prediction. Its small mass (9.1E-31 kg) made it an obvious candidate, and velocities of around 100 km/s are easily obtained, yielding a value of   in the above equation that well exceeds what we think of as the "radius" of the electron. At such velocities the electron behaves as if it is "spread out" to atomic dimensions; a beam of these electrons can be diffracted by the ordered rows of atoms in a crystal in much the same way as visible light is diffracted by the closely-spaced groves of a CD record. Electron diffraction has become an important tool for investigating the structures of molecules and of solid surfaces. A more familiar exploitation of the wavelike properties of electrons is seen in the electron microscope, whose utility depends on the fact that the wavelength of the electrons is much less than that of visible light, thus allowing the electron beam to reveal detail on a correspondingly smaller scale.

The uncertainty principle

In 1927, the German physicist Werner Heisenberg pointed out that the wave nature of matter leads to a profound and far-reaching conclusion: no method of observation, however perfectly it is carried out, can reveal both the exact *location* and momentum (and thus the *velocity*) of a particle. Suppose that you wish to measure the exact location of a particle that is at rest (zero momentum). To accomplish this, you must "see" the molecule by illuminating it with light or other radiation. But the light acts like a beam of photons, each of which possesses the momentum $h/$. When a photon collides with the particle, it transfers some of its momentum to the particle, thus altering both its position and momentum. This is the origin of the widely known concept that the very process of observation will change the value of the quantity being observed.

The Heisenberg principle can be expressed mathematically by the inequality

$$ x \times \ p \ \ \frac{h}{2} \tag{6} $$

in which the 's represent the uncertainties with which the location and momentum are known. Notice how the form of this expression predicts that if the location of an object is known exactly ($x = 0$), then the uncertainty in the momentum must be infinite, meaning that nothing at all about the velocity can be known. Similarly, if the velocity were specified exactly, then the location would be entirely uncertain and the particle could be anywhere.

One interesting consequence of this principle is that even at a temperature of absolute zero, the molecules in a crystal must still possess a small amount of *zero point* vibrational motion, sufficient to limit the precision to which we can measure their locations in the crystal lattice.

An equivalent formulation of the uncertainty principle relates the uncertainties associated with a measurement of the energy of a system to the time t taken to make the measurement:

A common consequence of this relation is that the spectral lines emitted by atoms from energy states that have very short lifetimes tend to be spread out in wavelength (large x), and therefore appear somewhat fuzzy in a spectrum. This is in fact a common method of measuring the lifetimes of excited atomic states.

2 Structure of the atom

Our goal in this unit is to help you understand how the arrangement of the periodic table of the elements must follow as a necessary consequence of the fundamental laws of the quantum behavior of matter. The modern theory of the atom makes full use of the wave-particle duality of matter. In order to develop and present this theory in a comprehensive way, we would require a number of mathematical tools that lie beyond the scope of this course. We will therefore present the theory in a semi-qualitative manner, emphasizing its results and their applications, rather than its derivation.

Models of the atom

The planetary model

The demonstration by Thompson that all atoms contain units of negative electric charge led to the first model of the atom which envisaged the electrons being spread out uniformly throughout the spherical volume of the atom. Ernest Rutherford, a New Zealander who started out as Thompson's student at Cambridge, distrusted this "raisin pudding" model (as he called it) and soon put it to rest; Rutherford's famous alpha-ray bombardment experiment showed that nearly all the mass of the atom is concentrated in an extremely small (and thus extremely dense) body called the nucleus. This led him to suggest the planetary model of the atom, in which the electrons revolve in orbits around the nuclear "sun". Even though this model has long since been discredited, it seems to have found a permanent place in popular depictions of the atom, and certain aspects of it remain useful in describing and classifying atomic structure and behavior. The planetary model of the atom assumed that the electrostatic attraction between the central nucleus and the electron is exactly balanced by the centrifugal force created by the revolution of the electron in its orbit. If this balance were not present, the electron would either fall into the nucleus, or it would be flung out of the atom.

The difficulty with this picture is that it is inconsistent with a well established fact of classical electrodynamics which says that whenever an electric charge undergoes a change in velocity or direction (which must happen if the electron circles around the nucleus), it must continually radiate energy. If electrons actually followed such a trajectory, all atoms would act is miniature broadcasting stations. Moreover, the radiated energy would come from the kinetic energy of the orbiting electron; as this energy gets radiated away, there is less centrifugal force to oppose the attractive force due to the nucleus. The electron would quickly fall into the nucleus, following a trajectory that became known as the "death spiral of the electron". According to classical physics, no atom based on this model could exist for more than a brief fraction of a second.

Bohr's model.   Niels Bohr[1] was a brilliant Danish physicist who came to dominate the world of atomic and nuclear physics during the first half of the twentieth century. Bohr suggested that the planetary model could be saved if one new assumption were made: certain "special states of motion" of the electron, corresponding to different orbital radii, would not result in radiation, and could therefore persist indefinitely without the electron falling into the nucleus.

Specifically, Bohr postulated that the angular momentum of the electron, mvr (the mass and angular velocity of the electron and in an orbit of radius r) is restricted to values that are integral multiples of $h/2p$. The radius of one of these allowed Bohr orbits is given by

$$r = \frac{nh}{2 \ mv}$$ **(7)**

n which h is Planck's constant, m is the mass of the electron, v is the orbital velocity, and n is an integer that can have the values 1, 2, 3, etc.

The most revolutionary aspect of this assumption was its use of the variable integer n; this was the first application of the concept of the quantum number to matter. The larger the value of n, the larger the radius of the electron orbit, and the greater the potential energy of the electron.

> As the electron moves to orbits of increasing radius, it does so in opposition to the restoring force due to the positive nucleus, and its potential energy is thereby raised. This is entirely analogous to the increase in potential energy that occurs when any mechanical system moves against a restoring force— as, for example, when a rubber band is stretched or a weight is lifted.

Thus what Bohr was saying, in effect, is that the atom can exist only in certain discrete energy states: the energy of the atom is *quantized*.

Bohr noted that this quantization nicely explained the observed emission spectrum of the hydrogen atom. The electron is normally in its smallest allowed orbit, corresponding to $n = 1$; upon excitation in an electrical discharge or by ultraviolet light, the atom absorbs energy and the electron gets promoted to higher quantum levels. These higher excited states of the atom are unstable, so after a very short time (around 10^{-9} sec) the electron falls into lower orbits and finally into the innermost one, which corresponds to the atom's ground state. The energy lost on each jump is given off as a photon, and the frequency of this light provides a direct experimental measurement of the difference in the energies of the two states, according to the Planck-Einstein relationship $e = h$.

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1. For a fascinating and highly recommended biography, see Ruth Moore: "Niels Bohr: the man, his science, and the world they changed". Knopf, 1966.

Vibrations, standing waves and bound states

Bohr's theory worked; it completely explained the observed spectrum of the hydrogen atom, and this triumph would later win him a Nobel prize. The main weakness of the theory, as Bohr himself was the first to admit, is that it could offer no good explanation of how these special orbits immunized the electron from radiating its energy away. The only justification for the proposal, other than that it seems to work, comes from its analogy to certain aspects of the behavior of vibrating mechanical systems.

displacement
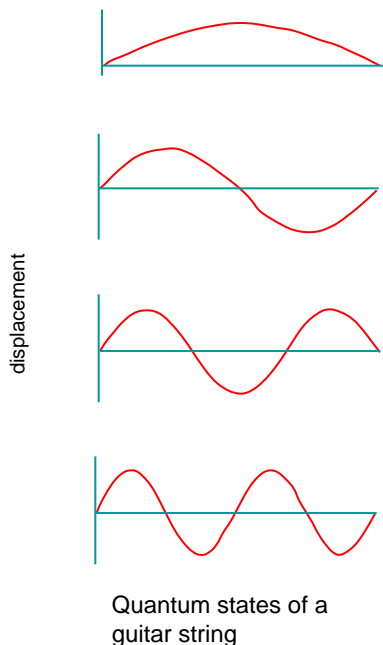
Consider a guitar string. In order to produce a tone when plucked, it must be fixed at each end (that is, it must be a bound system) and it must be under some tension. Only under these conditions will a transverse disturbance be countered by a restoring force (the string's tension) so as to set up a sustained vibration. Having the string tied down at both ends places a very important *boundary condition* on the motion: the only allowed modes of vibration are those whose wavelengths produce zero displacements at the bound ends of the string. In its lowest-energy mode of vibration there is a single wave whose point of maximum displacement is placed at the center of the string. In musical terms, this corresponds to the *fundamental* note to which the string is tuned; in terms of the theory of vibrations, it corresponds to a "quantum number" of 1. Higher modes, known musically as *overtones*, contain 2, 3, 4 and more points of maximum displacement ("nodes") spaced evenly along the string, corresponding to higher quantum numbers and higher energies. A similar kind of quantization occurs in other musical instruments; in each case the vibrations, whether of a stretched string, a column of air, or of a stretched membrane, are restricted to certain simple, fixed patterns known as *standing waves*.

Quantum states of a
guitar string

The analogy with the atom can be seen by imagining a guitar string that has been closed into a circle. The circle is the electron orbit, and the boundary condition is that the waves must not interfere with themselves along the circle. This condition can only be met if the circumference of an orbit can exactly accommodate an integral number of wavelengths. Thus only certain discrete orbital radii and energies are allowed.

Unbound states.   If a guitar string is plucked so harshly that it breaks, the restoring force and boundary conditions that restricted its motions to a few discrete harmonically related frequencies are suddenly absent; with no constraint on its movement, the string's mechanical energy is dissipated in a random way without musical effect.

In the same way, if an atom absorbs so much energy that the electron is no longer bound to the nucleus, then the energy states of the atom are no longer quantized; instead of the line spectrum associated with discrete energy jumps, the spectrum degenerates into a continuum in which all possible electron energies are allowed. The energy at which the *ionization continuum* of an atom begins is easily observed spectroscopically, and serves as a simple method of experimentally measuring the energy with which the electron is bound to the atom.

Modern theory of the atom

About ten years after Bohr had developed his theory, de Broglie showed that the electron should have wavelike properties of its own, thus making the analogy with the mechanical theory of standing waves somewhat less artificial. One serious difficulty with the Bohr model still remained, however: it was unable to explain the spectrum of any atom more complicated than hydrogen. A refinement suggested by Sommerfeld assumed that some of the orbits are elliptical instead of circular, and invoked a second quantum number, l, that indicated the degree of ellipticity. This concept proved useful, and it also began to offer some correlation with the placement of the elements in the periodic table.

The Schrödinger equation

By 1926, de Broglie's theory of the wave nature of the electron had been experimentally confirmed, and the stage was set for its extension to all matter in general. At about the same time, three apparently very different theories that attempted to treat matter in general terms were developed. These were Schrödinger's wave mechanics, Heisenberg's matrix mechanics, and a more abstract theory of P.A.M. Dirac. These eventually were seen to be mathematically equivalent, and all continue to be useful.

Of these alternative treatments, the one developed by Schrödinger is the most easily visualized. Schrödinger started with the simple requirement that the total energy of the electron is the sum of its kinetic and potential energies:

$$\frac{mv^2}{2} + \frac{-e^2}{r} = E \tag{8}$$

The second term represents the potential energy of an electron (whose charge is denoted by *e*) at a distance *r* from a proton (the nucleus of the hydrogen atom). In quantum mechanics it is generally easier to deal with equations that use momentum ($p = mv$) rather than velocity, so the next step is to make this substitution:

$$\frac{p^2}{2m} - \frac{e^2}{r} = E \tag{9}$$

This is still an entirely classical relation, as valid for the waves on a guitar string as for those of the electron in a hydrogen atom. The third step is the big one: in order to take into account the wavelike character of the hydrogen atom, a mathematical expression that describes the position and momentum of the electron at all points in space is applied to both sides of the equation. The function, denoted by (*psi*), "modulates" the equation of motion of the electron so as to reflect the fact that the electron manifests itself more in some locations that at others. This yields the celebrated *Schrödinger equation*

$$\frac{p^2}{2m} - \frac{e^2}{r} \quad = E \tag{10}$$

Physical significance of the wave function

How can such a simple-looking expression contain within it the quantum-mechanical description of an electron in an atom— and thus, by extension, of all matter? The catch, as you may well suspect, lies in discovering the correct form of psi, which is known as the wave function. As this names suggests, the value of   is a function of location in space relative to that of the proton which is the source of the binding force acting on the electron. As in any system composed of standing waves, certain boundary conditions must be applied, and these are also contained in ; the major ones are that the value of   must approach zero as the distance from the nucleus approaches infinity, and that the function be continuous.

When the functional form of   has been worked out, the Schrödinger equation is said to have been solved for a particular atomic system. The details of how this is done are beyond the scope of this course, but the consequences of doing so are extremely important to us. Once the form of   is known, the allowed energies *E* of an atom can be predicted from Eq. (10). Soon after Schrödinger's proposal, his equation was solved for several atoms, and in each case the predicted energy levels agreed exactly with the observed spectra.

There is another very useful kind of information contained in . Recalling that its value depends on the location in space with respect to the nucleus of the atom, the square of this function, ^{2}, evaluated at any given point, represents the *probability* of finding the electron at that particular point. The significance of this cannot be overemphasized; although the electron remains a particle having a definite charge and mass, and question of "where" it is located is no longer meaningful. Any single experimental observation will reveal a definite location for the electron, but this will in itself have little significance; only a large number of such observations (similar to a series of multiple exposures of a photographic film) will yield meaningful results which will show that the electron can "be" anywhere with at least some degree of probability. This does not mean that the electron is "moving around" to all of these places, but that the concept of location has limited meaning for a particle as small as the electron. If we count only those locations in space at which the probability of the electron manifesting itself exceeds some arbitrary value, we find that the ^{2} function defines a definite three-dimensional region which we call an *orbital*.

Why doesn't the electron fall into the nucleus

We can now return to the question which Bohr was unable to answer in 1912. Even the subsequent discovery of the wavelike nature of the electron and the analogy with standing waves in mechanical systems did not really answer the question; the electron is still a particle having a negative charge and is attracted to the nucleus.

The answer comes from the Heisenberg uncertainty principle, which says that a quantum particle such as the electron cannot simultaneously have sharply-defined values of location and of momentum (and thus kinetic energy). To understand the implications of this restriction, suppose that we place the electron in a small box. The walls of the box define the precision x to which the location is known; the smaller the box, the more exactly will we know the location of the electron. But as the box gets smaller, the uncertainty in the electron's kinetic energy will increase. As a consequence of this uncertainty, the electron will at times possess so much kinetic energy (the "confinement energy") that it may be able to penetrate the wall and escape the confines of the box[1].
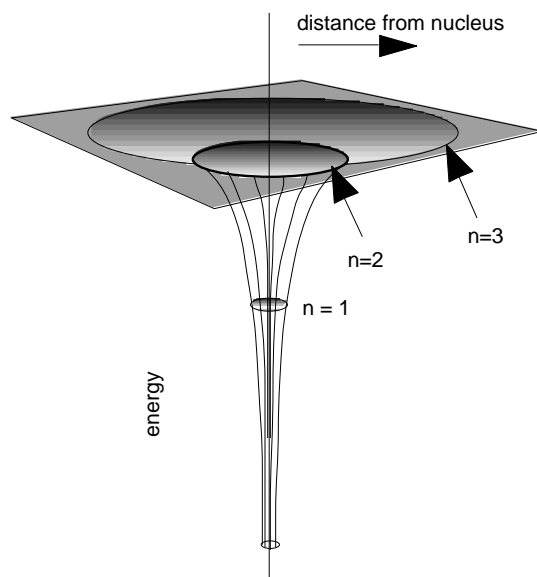
The region near the nucleus can be thought of as an extremely small funnel-shaped box, the walls of which correspond to the electrostatic attraction that must be overcome if an electron confined within this region is to escape. As an electron is drawn toward the nucleus by electrostatic attraction, the volume to which it is confined diminishes rapidly. Because its location is now more precisely known, its kinetic energy must become more uncertain; the electron's kinetic energy rises more rapidly than its potential energy falls, so that it gets ejected back into its minimum allowed orbital corresponding to $n = 1$.

We can also dispose of the question of why the orbiting electron does not radiate its kinetic energy away as it revolves around the nucleus. The Schrödinger equation completely discards any concept of a definite path or trajectory of a particle; what was formerly known as an "orbit" is now an "orbital", defined as the locations in space at which the probability of finding the electrons exceeds some arbitrary value. It should be noted that this wavelike character of the electron coexists with its possession of a momentum, and thus of an effective velocity, even though its motion does not imply the existence of a definite path or trajectory that we associate with a more massive particle.

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1. This process is known as *tunneling*; the *tunnel effect* is exploited in various kinds of semiconductor devices, and it is the mechanism whereby electrons jump between an electrode and a solution in batteries and other electrochemical devices.

3 Electrons in atoms

The modern view of atomic structure dismisses entirely the old but comfortable planetary view of electrons circling around the nucleus in fixed orbits. As so often happens in science, however, the old out-moded theory contains some elements of truth that are retained in the new theory. In particular, the old Bohr orbits still remain, albeit as spherical shells rather than as two-dimensional circles, but their physical significance is different: instead of defining the "paths" of the electrons, they merely indicate the locations in the space around the nucleus at which the probability of finding the electron has its maximum value. The electron retains its particle-like mass and momentum, but because the mass is so small, its wavelike properties predominate. The latter give rise to patterns of standing waves that define the possible states of the electron in the atom.

The simplest atom

The single electron of the hydrogen atom is bound to the nucleus by the opposite electric charges of the two particles. The energy required to remove the electrons from one mole of hydrogen atoms has been determined experimentally to be 1312 kJ; this quantity is known as the *ionization energy* of the hydrogen atom. If an electron is just removed from the atom without being given any kinetic energy of its own, its energy would be raised from its initial value of –1312 kJ to zero. In other words, the potential energy of an electron that is bound to an atom is always negative.

The line emission spectrum is the major source of information about an atom; each spectral line represents an energy difference between two possible *electronic states* of the atom. By analyzing these differences, one can map out these states, assigning an energy to each. The lowest, and only stable state of the atom will be the so-called *ground state*, which for hydrogen is at –1312 kJ. Other allowed states will have higher energies, all corresponding to larger average distances between the electron and the nucleus. There is no limit to the possible number of allowed states, but because the energy differences between successively higher states diminish, these differences approach zero at the zero-energy ionization limit. Beyond this (that is, in the range of positive energy values) the electron is unbound and may have any energy without restriction; this corresponds, as we pointed out earlier, to the continuum part of the spectrum.

The figure below shows some of the more well known series of line spectra of hydrogen. The series ending at the second allowed energy level was discovered by Balmer, a German high school teacher, in 1895. These lines fall into the visible range of wavelengths. The lines of the Lyman series are in the ultraviolet, while most of the other series are in the infrared part of the spectrum.
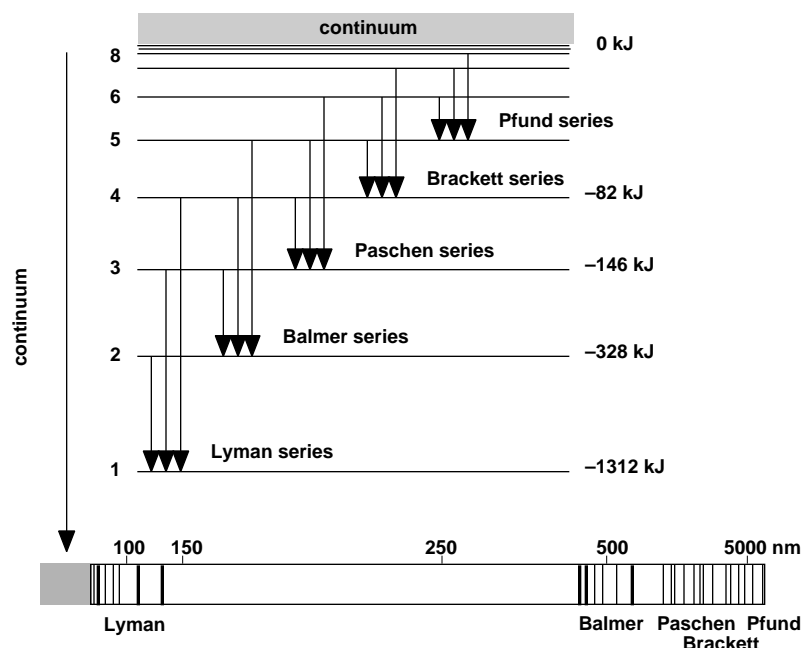
Figure 4   Major spectral series of the hydrogen.atom.
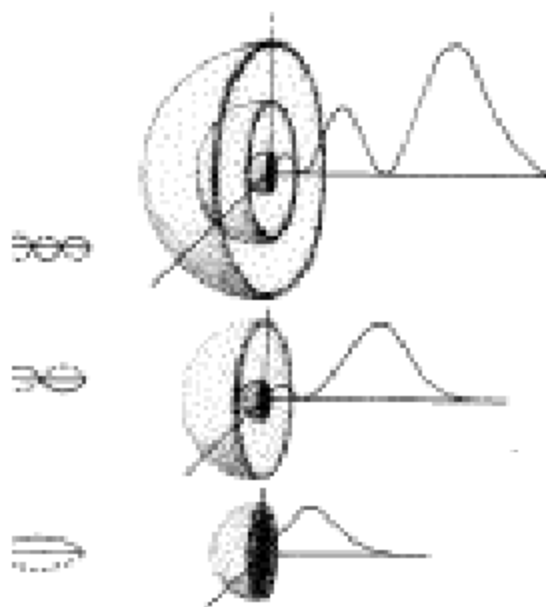
Principal quantum number.

The energy states depicted above correspond to the old Bohr orbits, with the lowest, $n = 1$, being the ground state. Notice how the states crowd together at high energies. The highest numbered state on the diagram is 8, but there are an infinite number of higher ones that gradually merge into the continuum region[1].

According to modern quantum theory, the various allowed states of existence of the electron in an atom correspond to different standing wave patterns. Fig. 1 on page 20 depicts some of these patterns in relation to those that occur on a vibrating guitar string. The main difference is that the electron waves occupy all three dimensions of space, whereas the guitar strings vibrate in only two dimensions. Aside from this, the similarities are striking. Each wave pattern is identified by an integer number *n*, which in the case of the atom is known as the *principal quantum number*. The value of *n* tells how many peaks of amplitude (antinodes) exist in that particular standing wave pattern; the more peaks there are, the higher the energy of the state.

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1. States having *n* values as large as 1000 have been observed experimentally; these are sometimes known as *superexcited* states. Their energies are still less than zero, however.

Figure 1

Radial nodes and antinodes in the first three *s* orbitals of hydrogen.

Physical significance of   *n*

The potential energy of the electron is given by the formula

$$E = \frac{-4\pi^2 e^4 m}{h^2 n^2}$$

in which *e* is the charge of the electron, *n* is its mass, *h* is Planck's constant, and *n* is the principal quantum number. The negative sign ensures that the potential energy is always negative. Notice that this energy in inversely proportional to the square of *n*, so that the energy rises toward zero as n becomes very large, but that it can never exceed zero.

This formula was actually part of Bohr's original theory, and is still applicable to the hydrogen atom, although not to atoms containing two or more electrons. In the Bohr model, each value of n corresponded to an orbit of a different radius. The larger the radius, the higher the potential energy of the electron; the inverse square relationship between electrostatic potential energy and distance is reflected in the inverse square relation between the energy and *n* in the above formula.

Although the concept of a definite trajectory or orbit of the electron is no longer tenable, the same orbital radii that relate to the different values of n in Bohr's theory now have a new significance: they give the average distance of the electron from the nucleus. As you can see from the figure, the averaging process must encompass several probability peaks in the case of higher values of *n*. The spatial distribution of these probability maxima defines the particular *orbital*. We sometimes refer to an orbital as an "electron cloud", but this term should not be

taken to imply that the electron itself is somehow smeared out in space; it is only the probability of finding it at any given location that varies, but any experiment that does locate it will see the entire electron.

This physical interpretation of the principal quantum number as an index of the average distance of the electron from the nucleus turns out to be extremely useful from a chemical standpoint, because it relates directly to the tendency for an atom to lose or gain electrons in chemical reactions.

The angular momentum quantum number

$l = 0$

The electron wave functions that are derived from Schrödinger's theory are characterized by several quantum numbers. The first one, n, describes the nodal behavior of the probability distribution of the electron, and correlates with its potential energy and average distance from the nucleus as we have just described.

The wave theory developed by Schrödinger predicts that for any value of n, the electron can exist in different states, all having the same potential energy. These additional states are distinguished by other quantum numbers. The first of these is the quantum number *l*, known as the angular momentum quantum number.

$l = 1$

The value of *l* determines the *shape* of the orbital[1]. When *l* = 0, the orbital is spherical in shape. If *l* = 1, the orbital is elongated into something resembling a figure 8 shape, and higher values of *l* correspond to still more complicated shapes.
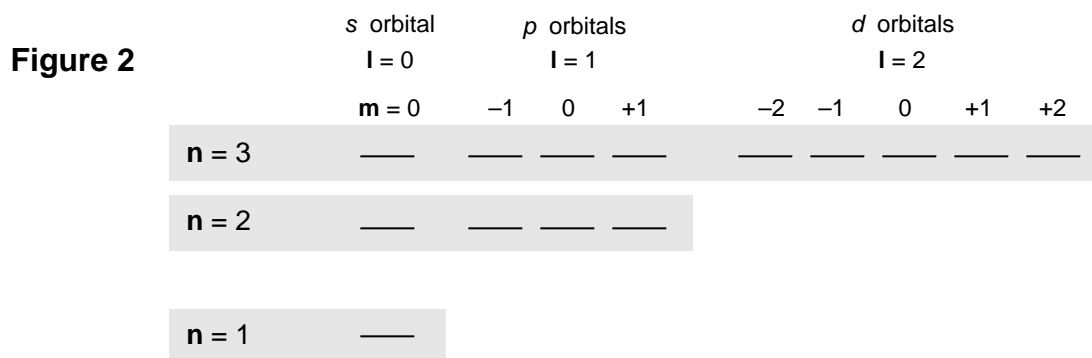
$l = 2$

The possible values that *l* can take are strictly limited by the value of the principal quantum number; *l* can be no greater than $n - 1$. This means that for $n = 1$, *l* can only have the single value zero which corresponds to a spherical orbital possessing no angular momentum. For historical reasons, the orbitals corresponding to different values of *l* are designated by letters, starting with *s* for *l* = 0, *p* or *l* = 1, *d* for *l* = 2, and *f* for *l* = 3. Thus an electron that occupies an orbital whose quan-

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1. More precisely, *l* determines the number of *angular nodes*, that is, the number of regions of zero probability encountered in a 360° rotation around the center.

tum numbers are $n = 1$ is said to be in an s orbital. A $3d$ orbital is one with $n = 3$ and $l = 2$.

Figure 2

	s orbital l = 0	*p* orbitals l = 1			*d* orbitals l = 2				
	m = 0	−1	0	+1	−2	−1	0	+1	+2
n = 3	——	——	——	——	——	——	——	——	——
n = 2	——	——	——	——					
n = 1	——								

Even though the different values of l correspond to different orbital shapes, the average distance of the electron from the nucleus is the same for all, as long as the value of n is the same. In the hydrogen atom this means that the energy of the electron, which depends only on its average distance from the nucleus, is independent of l.

Figure 3

	n = 1	n = 2	n = 3
l = 0			
l = 1			
l = 2			
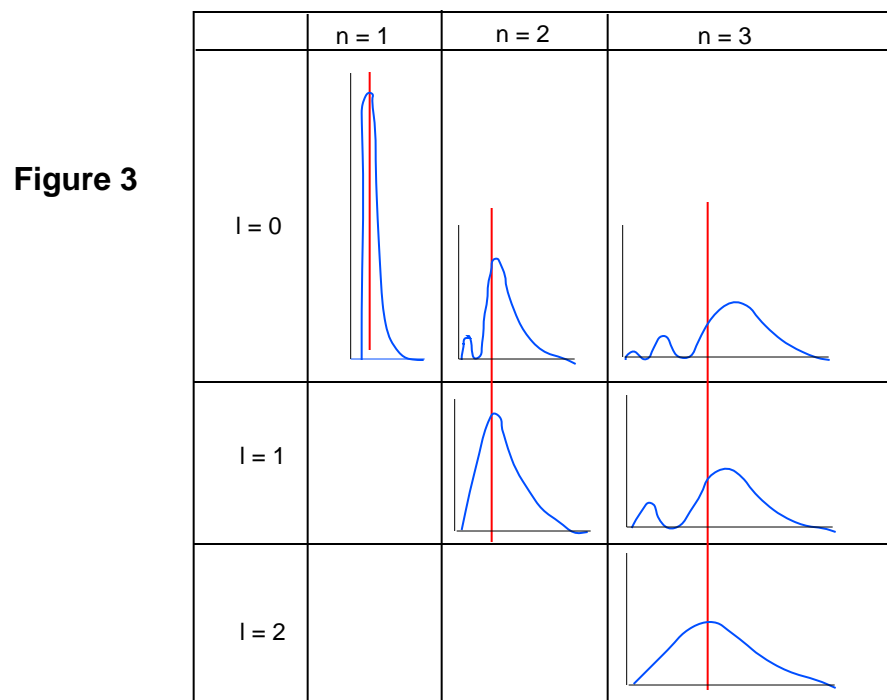
The figure shows several graphs in which the electron probability is plotted as a function of distance from the nucleus. Notice how the average probability is the same for every l-value for a given value of n.

The magnetic quantum number

An s-orbital, corresponding to $l = 0$, is spherical in shape and therefore has no special directional properties. The probability cloud of a p orbital is aligned principally along an axis extending along any of the

three directions of space, and an additional quantum number is required to specify the particular orientation.

The quantum number *n* can assume $2l + 1$ values for each value of *l*, from $-l$ through 0 to $+l$. When $l = 0$ the only possible value of *m* will also be zero, and for the p orbital in which $l = 1$, *m* can be –1, 0, and +1. Higher values of *l* correspond to more complicated orbital shapes, and these give rise to more possible orientations of these shapes in space, and thus to more values of *m*.

The chart in Fig. 3 shows all the orbitals that are possible for the first three values of the principal quantum number of the hydrogen atom. Notice again that the energy of the electron depends only on *n*[1].

"Direction in space" has no meaning in the absence of any force field that serves to establish a reference direction. For an isolated atom there is no such external field, and for this reason there is no distinction between the orbitals having different values of *m*.

If the atom is placed in an external magnetic or electrostatic field, a coordinate system is established, and the orbitals having different values of *m* will split into slightly different energy levels. This effect was first seen in the case of a magnetic field, and this is the origin of the term *magnetic* quantum number. A better name would simply be "orientational quantum number", since a magnetic field is only one special way of establishing a directionality in space.

The electrostatic field created when other atoms or ions come close to an atom can cause the energies of orbitals having different direction properties to split up into different energy levels; this is the origin of the colors seen in many inorganic salts of transition elements, such as the blue color of copper sulfate.

Quantum numbers and the periodic table

Electron-electron repulsion

We have seen that it takes 1312 kJ of energy to remove the electron from a mole of hydrogen atoms. What might we expect this value to be for helium? Helium contains two electrons, but its nucleus contains two protons; each electron "sees" both protons, so we might expect that the electrons of helium would be bound twice as strongly as the electron of hydrogen. The ionization energy of helium should therefore be twice 1312 kJ/mol, or 2612 kJ/mol. However, if one looks at the spectrum of helium[2], the continuum is seen to begin at a wavelength

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1. This is almost, but not entirely true. Because there is a finite but small probability that the electron will come close to the nucleus, there is an interaction between the magnetic moment of the nucleus and the electron that gives rise to a very small energy difference. This turns out to be very good evidence for the validity of Schrödinger's treatment of the hydrogen atom.

2. Recall that helium was discovered by means of its spectrum; a yellow line whose wavelength did not match that of any known element was observed in the solar spectrum in 1868.

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corresponding to an ionization energy of 3272 kJ/mol, or about 90% of the predicted value.

Why are the electrons in helium bound less tightly than the +2 nuclear charge would lead us to expect? The answer is that there is another effect to consider: the repulsion between the two electrons; the resulting electron-electron repulsion subtracts from the force holding the electron to the nucleus, reducing the local binding of each.

Hydrogen–like atoms

This is a small but very important class of species that includes hydrogen itself together one-electron ions such as He^+, Li^{2+}, etc. All have simple spectra whose major features were adequately explained by Bohr's model. The ionization energies of these species increase rapidly as the nuclear charge increases, because the increasing attraction pulls the electron closer to the nucleus, thus producing an even greater attractive force[1].

All other atoms and ions contain two or more electrons. These have more complex spectra, and their ionization energies are strongly affected by electron-electron repulsion. More importantly, the ionization energies of multi-electron atoms reveal that the different electrons are non-equivalent; some are bound more tightly than others.

Figure 4

This diagram shows the relative energies of the 1*s*, 2*s*, and 2*p* orbitals in the atoms of H, He, and Li. The energies of the 1*s* orbitals fall rapidly as *Z* increases. The fall in energies of the 2*s* orbitals is smaller owing to electron-electron repulsion. The 2*p* orbitals have a node at the nucleus and are less affected by *Z* but are more affected by electron repulsion, so they remain higher than the 2*s* orbitals.

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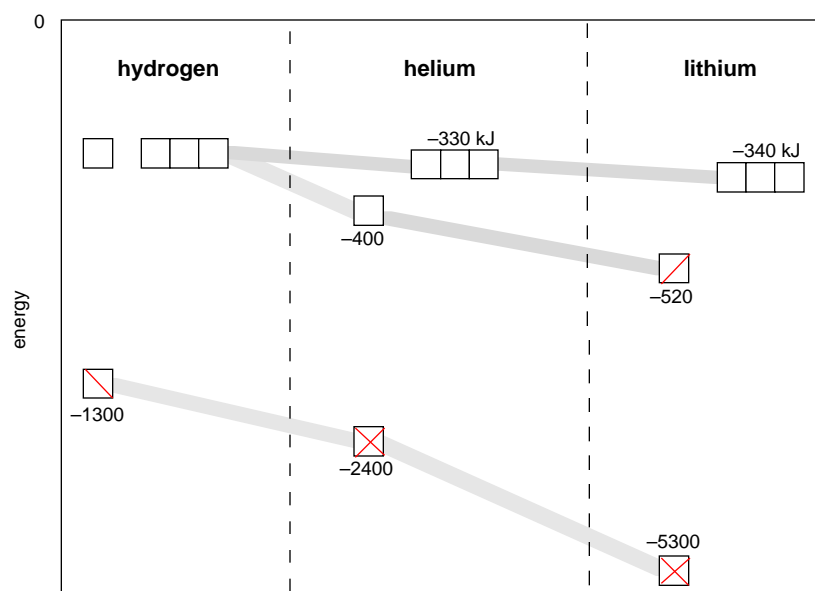
1. The force of electrostatic attraction is $q_1 q_2 / r$, where q_1 and q_2 are the charges of the interacting particles (nucleus and electron) and r is the distance between them.

Quantum theory of multi-electron atoms

In the discussion of the hydrogen atom, we saw that an electron orbital is characterized by three quantum numbers, *n*, *l*, and *m*. For hydrogen and other one-electron species, the energy of the orbital depends only on the principal quantum number *n*. In all other atoms, however, electron-electron repulsion acts to split up the energies of orbitals having different shapes (different values of *l*).

Electron spin and the exclusion principle

Certain fundamental particles have associated with them a magnetic moment that can align itself in either of two directions with respect to some external magnetic field. The electron is one such particle, and the direction of its magnetic moment is called its *spin*. The mechanical analogy implied by this term is easy to visualize, but should not be taken literally. Physical rotation of an electron is meaningless; electron spin is a relativistic effect having no classical counterpart.

A basic principle of modern physics states that for particles that possess spin, no two of them can be in identical quantum states within the same system. The quantum state of a particle is defined by the values of its quantum numbers, so what this means is that no two electrons in the same atom can have the same set of quantum numbers. This is known as the *Pauli exclusion principle*, named after the German physicist Wolfgang Pauli.

A given orbital is characterized by a fixed set of the quantum numbers *n*, *l,* and *m*. The electron spin itself constitutes a fourth quantum number *s*, which can take the two values +1 and −1. Thus a given orbital can contain two electrons having opposite spins; two such electrons are often referred to as an *electron pair*.

Electron configurations of the elements

The Exclusion Principle limits the number of electrons that can occupy any atomic orbital to two. There are $2l + 1$ orbitals of any one type; electrons occupying orbitals of the same type (that is, having a given pair of values of *n* and *l*), will have identical energies. As the principal quantum number *n* increases, so does the maximum allowed value of *l*, and thus the numbers of orbitals of a given type, and the number of electrons that can occupy a given energy level. Fig. 5 on page 26 shows this quite clearly; only two electrons in any atom can have $n = 1$, in which they occupy the 1s orbital. For $n = 4$, there are four different orbital types, accommodating a maximum of 32 electrons in *s*, *p*, *d*, and *f* orbitals.

The electron configuration of an atom specifies the distribution of electrons among the various orbitals. The *Aufbau* (German for "building-up") principle is a simple method of working out atomic electron configurations in which we imagine that electrons are fed in to an atom as

the charge of its nucleus is increased. The rules for applying the Aufbau principle are the following:

• Electrons occupy the lowest-energy available orbitals; lower-energy orbitals are filled before the higher ones.

• No more than two electrons can occupy any orbital.

• For the lighter elements, electrons will fill orbitals of the same type only one electron at a time, so that their spins are all unpaired. They will begin to pair up only after all the orbitals are half-filled. This principle, which is a consequence of the electrostatic repulsion between electrons, is known as *Hund's rule*.

Inspection of a table of electron configurations of the elements reveals a few apparent non-uniformities in the filling of the orbitals. These always occur in the transition series (*d-* or *f-* block), and are a consequence of the very small energy differences between some of the orbitals. A good example is copper, which "should" have the outer-shell configuration $3d^9 4s^2$. The actual configuration of the Cu atom appears to be $3d^{10} 4s^1$. Although the 4*s* orbital is normally slightly below the 3*d* orbital energy, the two are so close that interactions between the two when one is empty and the other is not can lead to a reversal. Detailed calculations in which the shapes and densities of the charge distributions are considered predict that the relative energies of many orbitals can reverse in this way.

Periodic table.   In general, the higher the value of the principal quantum number, the higher the potential energy of the orbital. Owing to the differences in the energies of orbitals having different values of *l*, a *d*-orbital will be at a higher energy than the *s* orbital of the next-higher value of *n*. As the figure below shows, this leads to a grouping of orbitals according to energy. Each group begins with an *s* orbital as its lowest-energy member, and ends with a *p* orbital having the same value of *n* as its highest-energy member. In between, however, are the *d-* and *f* orbitals corresponding to lower values of *n*.
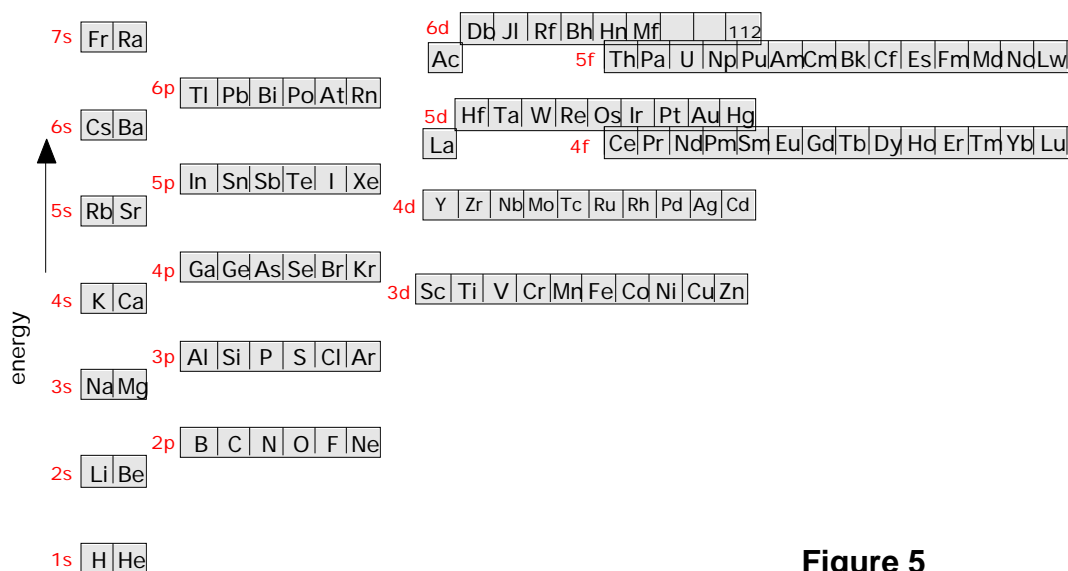

Figure 5

The above diagram illustrates the link between the electron configurations of the elements and the layout of the periodic table. Each row commences with two *s*-block elements whose highest occupied orbitals have $l = 0$ and continues through the *p* block. At the end of the rows corresponding to $n > 1$ is an element having a p^6 configuration, a so-called *noble gas* element. These elements are part of the *p* block of the periodic table in which the highest occupied orbitals have $l = 1$. At l values of 2 and 3, *d*- and *f*-block element sequences are added.

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Figure 6

"Long form" of the periodic table showing blocks and column numbering. Each block is named according to orbital type that is being filled in elements of successively larger *Z*.

There are many different ways of constructing periodic tables, some of which border on the bizarre. The one shown above is known as the "long form", and is similar in most respects to those found in textbooks.

There has recently been a change in the designation of the groups (columns). In the past, two different systems of Roman numerals and letters were used,   North Americans added the letter *B* to the *d*-block groups (as shown above), while the rest of the world used *A*. In 1985, a new international system was adopted in which the columns were simply labeled 1-18; this is the system we use here. Although this system has met sufficient resistance in North America to slow its incorporation into textbooks, it seems likely that the "one to eighteen" system will gradually take over as older professors (the main hold-outs!) retire.

For $n = 1$ there is no *p* block, and the *s* block is split so that helium is placed in the same group as the other inert gases, which it resembles chemically. For $n = 2$ there is a *p* block but no *d* block; in the usual "long form" of the periodic table it is customary to leave a gap between these two blocks in order to accommodate the d blocks that occur at $n = 3$ and above. At $n = 4$ we introduce an f block, but in order to hold the table to reasonable dimensions the f blocks are placed below the main body of the table.

7 Periodic properties of the elements

The first periodic tables published by Mendeleev and others in the 19th Century were based entirely on the observed properties of the elements that were known at the time. These include physical properties such as melting point, density, metallic nature, etc., and chemical properties, especially *valence* (combining power). In this section we will examine some of the more important physical and chemical properties that vary periodically with atomic number.

The shell model of the atom

The properties of an atom depend ultimately on the number of electrons in the various orbitals, and on the nuclear charge which determines the compactness of the orbitals. In order to relate the properties of the elements to their locations in the periodic table, it is often convenient to make use of a simplified view of the atom in which the nucleus is surrounded by one or more concentric spherical shells, each having a radius corresponding to the average distance between the nucleus and the electrons in the orbital comprising that shell. The shell model (as with any scientific model) is less a description of the world than a simplified way of looking at it that helps us to understand and correlate diverse phenomena.

Figure 8

Shell model of the atom showing the valence electrons of the representative elements.
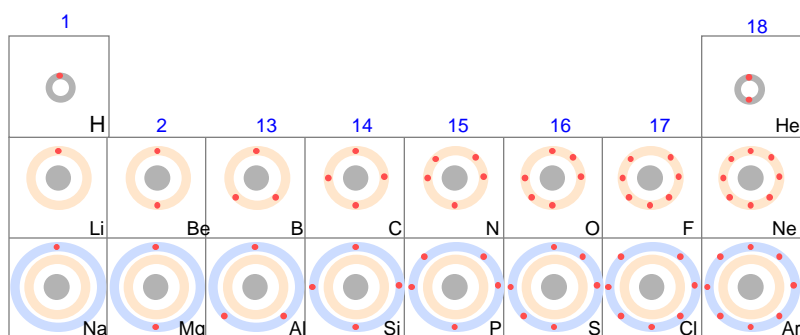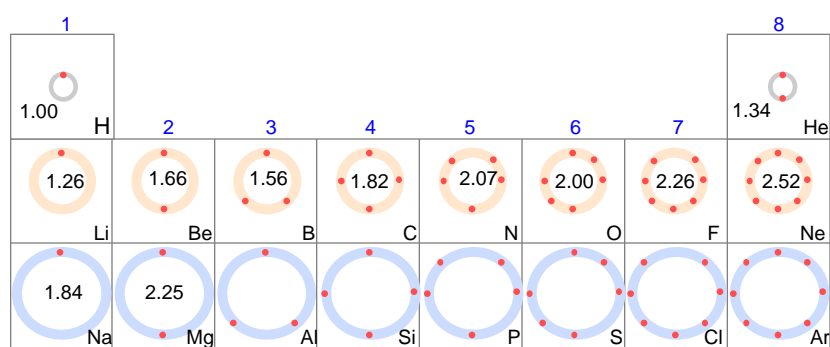
Effective nuclear charge

Those electrons in the outmost or *valence* shell are especially important because they are the ones that can engage in the sharing and exchange that is responsible for chemical reactions; how tightly they are bound to the atom determines much of the *chemistry* of the element. The degree of binding is the result of two opposing forces: the attraction between the electron and the nucleus, and the repulsions between the electron in question and all the other electrons in the atom. All that matters is the net force, the difference between the nuclear attraction and the totality of the electron-electron repulsions.

We can simplify the shell model even further by imagining that the valence shell electrons are the *only* electrons in the atom, and that the nuclear charge has whatever value would be required to bind these electrons as tightly as is observed experimentally. Because the number of electrons in this model is less than *Z*, the required nuclear charge will also be smaller. and is known as the *effective nuclear charge*.

Effective nuclear charge is essentially the positive charge that a valence electron "sees". Part of the difference between *Z* and $Z_{effective}$ is due to any other electrons in the valence shell, but this is usually only a minor contributor because these electrons tend to act as if they are spread out in a diffuse spherical shell of larger radius. The main actors here are the electrons in the much more compact inner shells which surround the nucleus and exert what is often called a *shielding* effect on the valence electrons.

Figure 9

Effective nuclear charge of the first twelve elements.

The formula for calculating effective nuclear charge is not very complicated, but we will skip a discussion of it here. An even simpler although rather crude procedure is to just subtract the number of inner-shell electrons from the nuclear charge; the result is a form of effective nuclear charge which is called the *core charge* of the atom.

Sizes of atoms and ions

2r
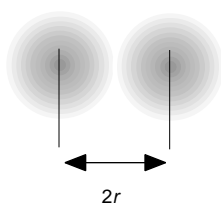
The concept of "size" is somewhat ambiguous when applied to the scale of atoms and molecules. The reason for this is apparent when you recall that an atom has no definite boundary; there is a finite (but very small) probability of finding the electron of a hydrogen atom, for example, 1 cm, or even 1 km from the nucleus. It is not possible to specify a definite value for the radius of an isolated atom or molecule. Instead, we must content ourselves with observing (most commonly by X-ray diffraction experiments) the distances between adjacent atoms in molecules or solids.

A rough idea of the size of a metallic atom can be obtained simply by measuring the density of a sample of the metal. This tells us the number of atoms per unit volume of the solid. The atoms are assumed to be spheres of radius *r* in contact with each other, each of which sits in a cubic box of edge length 2*r*. The volume of each box is just the total volume of the solid divided by the number of

atoms in that mass of the solid; the atomic radius is the cube root of *r*

Defining atomic radii

The radius of an atom or ion cannot be measured directly; in most cases it can only be *inferred* from measurements of the distance between adjacent nuclei in a crystalline solid. Because such solids fall into several different classes, several kinds of atomic radius are defined:

covalent

van der Waals

1. **Metallic radius** is half the distance between nuclei in a metallic crystal.
2. **Covalent radius** is half the distance between like atoms that are bonded together in a molecule.
3. **van der Waals radius** is the effective radius of adjacent atoms which are not chemically bonded in a solid, but are presumably in "contact". An example would be the distance between the iodine atoms of adjacent I_2 molecules in crystalline iodine.
4. **Ionic radius** is the effective radius of ions in solids such as NaCl. It is easy enough to measure the distance between adjacent rows of Na^+ and Cl^- ions in such a crystal, but there is no unambiguous way to decide what parts of this distance are attributable to each ion. The best one can do is make estimates based on studies of several different ionic solids (LiI, KI, NaI, for example) that contain one ion in common. Many such estimates have been made, and they turn out to be remarkably consistent.

LiI   KI
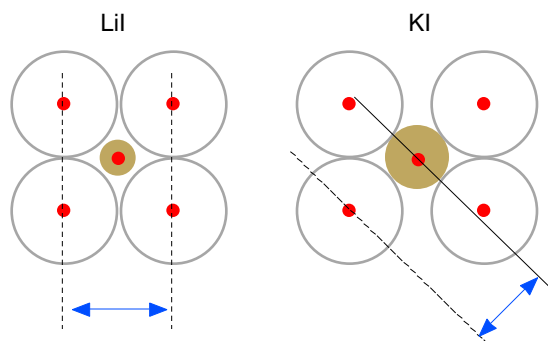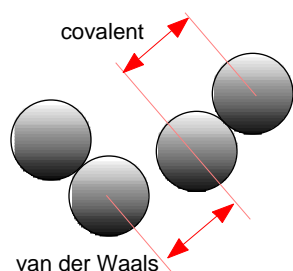
The lithium ion is sufficiently small that the iodide ions are in contact, so I-I distances are twice the ionic radius of I^-. This is not true for KI, but here, adjacent potassium and iodide ions are in contact, allowing estimation of the K^+ ionic radius.

Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapor phase (covalent radius), and of course it forms ionic solids as mentioned above.

Distances on the atomic scale have traditionally been expressed in Ångstrom units (1 Å = 10^{-8} cm), but nowadays the picometer is preferred; 1 pm = 10^{-12} m = 10^{-10} cm = 100 Å. The radii of atoms and ions are typically in the range 70-400 pm.

Periodic trends in atomic radii.

We would expect the size of an atom to depend mainly on the principal quantum number of the highest occupied orbital; in other words, on the "number of occupied electron shells". Since each row in the periodic table corresponds to an increment in *n*, atomic radius increases as we move down a column.

The other important factor is the nuclear charge; the higher the atomic number, the more strongly will the electrons be drawn toward the nucleus, and the smaller the atom. This effect is responsible for the contraction we observe as we move across the periodic table from left to right.

Covalent radii - pm
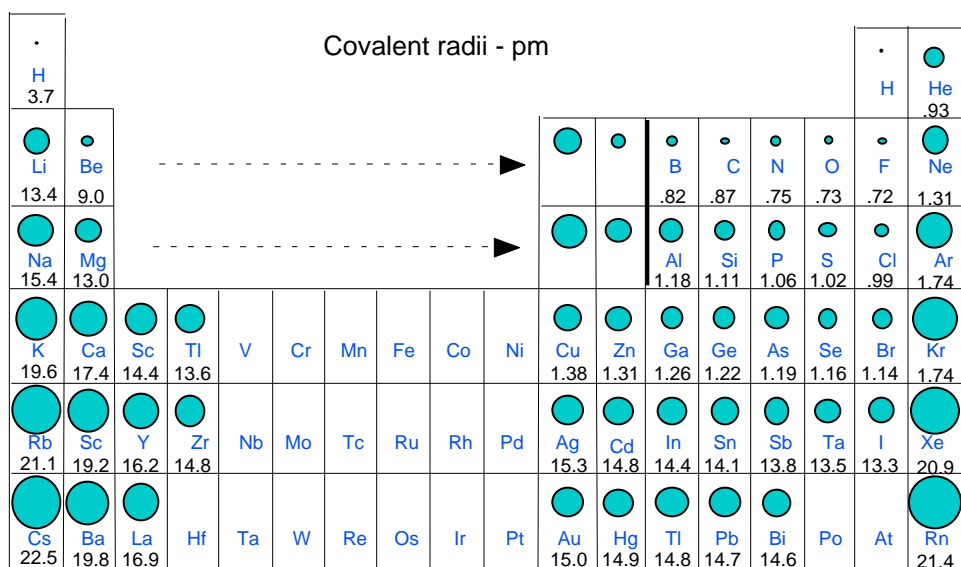
The figure shows a periodic table in which the sizes of the atoms are represented graphically. The apparent discontinuities in this diagram reflect the difficulty of comparing the radii of atoms of metallic and nonmetallic bonding types. Radii of the noble gas elements are estimate from those of nearby elements.

Ionic radii .

A **positive ion** is always smaller than the neutral atom, owing to the diminished electron-electron repulsion. If a second electron is lost, the ion gets even smaller; for example, the ionic radius of Fe^{2+} is 76 pm, while that of Fe^{3+} is 65 pm. If formation of the ion involves complete emptying of the outer shell, then the decrease in radius is especially great.

atom	Li	Na	K	Rb	Cs
atomic radius, pm	122	157	202	216	235
ionic radius	60	95	133	148	169
percent decrease	51	40	34	31	28

The hydrogen ion H^+ is in a class by itself; having no electron cloud at all, its radius is that of the bare proton, or about 0.1 pm— a contraction of 99.999%! Because the unit positive charge is concentrated into such a small volume of space, the *charge density* of the hydrogen ion is extremely high; it interacts very strongly with other matter, including water molecules, and it exists in solution as the *hydronium ion* H_3O^+.

Negative ions are always larger than the parent ion; the addition of one or more electrons to an existing shell increases electron-electron repulsion which results in a general expansion of the atom. An **isoelectronic series** is a sequence of species all having the same number of electrons (and thus the same amount of electron-electron repulsion) but differing in nuclear charge. The effect of increasing nuclear charge on the radius is clearly seen.

Figure 10

Relative radii of members of an isoelectronic series.

| O^{2-} | F^- | Ne | Na^+ | Mg^{2+} |
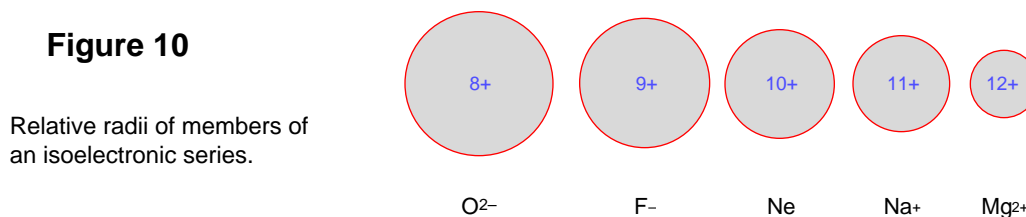
Periodic trends in ion formation

Chemical reactions are based largely on the interactions between the most loosely bound electrons in atoms, so it is not surprising that the tendency of an atom to gain or lose electrons is one of its fundamental chemical properties.
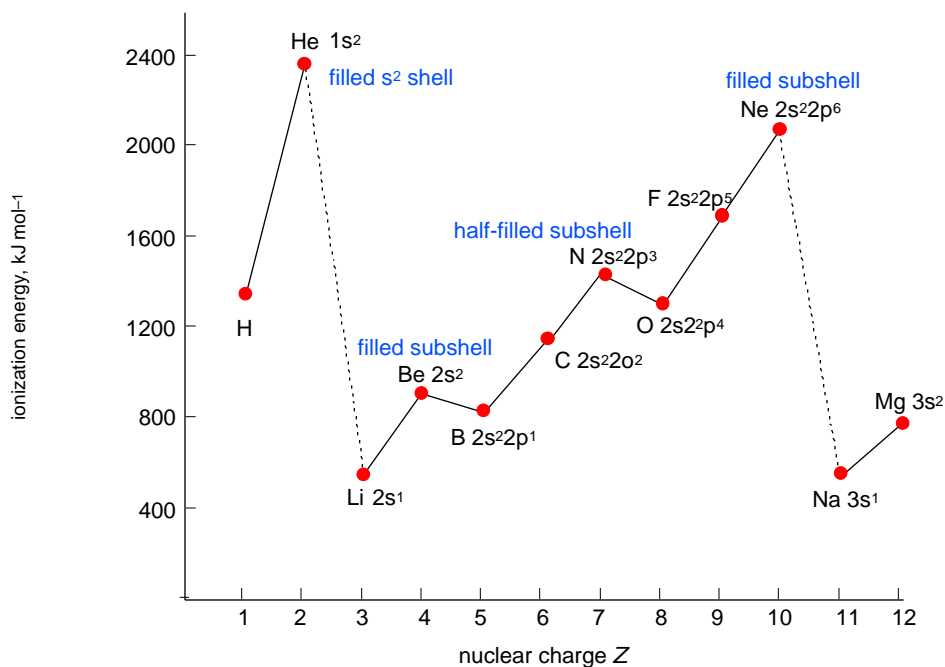
Ionization energy

This term always refers to the formation of *positive* ions. In order to remove an electron from an atom, work must be done to overcome the electrostatic attraction between the electron and the nucleus; this work is called the *ionization energy* of the atom and corresponds to the reaction

$$M(g) \longrightarrow M^+(g) + e^-$$

An atom has as many ionization energies as it has electrons. Electrons are always removed from the highest-energy occupied orbital. Successive ionization energies of an atom increase rapidly due both to reduced electron-electron repulsion and the additional positive charge that binds the remaining electrons even more tightly. An examination of the successive ionization energies of the first ten elements provides experimental confirmation that the binding of the two innermost electrons (1s orbital) is significantly different from that of the $n = 2$ electrons.

Careful inspection of the successive ionization energies of the atoms in a given row of the periodic table reveals some interesting irregularities that can be related to the slightly lower energies (greater stabili-

ties) of electrons in half-filled and completely-filled (spin-unpaired) subshells. One such series is shown in the Figure below.

Ionization energies increase as we move across the periodic table, owing to the increase in the nuclear charge Z. They decrease as we move down the table because in each period the electron is being removed from a shell one step farther from the nucleus than in the atom immediately above it. This results in the familiar zig-zag lines when the first ionization energies are plotted as a function of Z.

Electron affinity

Formation of a negative ion occurs when an electron from some external source enters the atom and become incorporated into the lowest-energy orbital that possesses a vacancy. Because the entering electron is attracted to the positive nucleus, the formation of negative ions is usually exothermic. The energy given off is the *electron affinity* of the atom. For some atoms, the electron affinity appears to be slightly negative; that is, energy is absorbed when the electron combines with the atom. In general, electron affinities tend to be much smaller than ionization energies, suggesting that they are controlled by opposing factors having similar magnitudes. These two factors are, as before, the nuclear charge and electron-electron repulsion. But the latter, only a minor actor in positive ion formation, is now much more significant. One reason for this is that the electrons contained in the inner shells of the atom exert a collective negative charge that partially cancels the charge of the nucleus, thus exerting a so-called *shielding* effect which diminishes the tendency for negative ions to form.

Because of these opposing effects, the periodic trends in electron affinities are not as clear as are those of ionization energies. This is particularly evident in the first few rows of the periodic table, in which small effects tend to be magnified anyway because an added electron produces a large percentage increase in the number of electrons in the atom.

H 73																	He −21
Li 60	Be −19											B 27	C 122	N −7	O 141	F 328	Ne −29
Na 53	Mg −19											Al 43	Si 134	P 72	S 200	Cl 349	Ar −35
K 48	Ca −10	Sc 18	Ti 8	V 51	Cr 64	Mn	Fe 16	Co 64	Ni 112	Cu 118	Zn −47	Ga 29	Ge 116	As 78	Se 195	Br 325	Kr −39
Cs 47	Sr	Y 30	Zr 41	Nb 86	Mo 72	Tc 53	Ru 101	Rh 110	Pd 54	Ag 126	Cd −32	In 29	Sn 116	Sb 103	Te 190	I 295	Xe −41
Rb 45	Ba	La	Hf 31	Ta 79	W 14	Re 106	Os 101	Ir 205	Pt 223	Au −61	Hg	Tl 20	Pb 35	Bi 91	Po 183	At 270	Rn −41
Fr 44	Ra	Ac	Db	Jl	Rf	Bh	Hn	Mt									

Figure 11

Electron affinities. Numbers are kJ released per mole of mononegative ions formed; negative values correspond

In general, we can say that electron affinities become more exothermic as we move from left to right across a period (owing to increased nuclear charge and smaller atom size). There are some interesting irregularities, however:

- In the Group 2 elements, the filled 2s orbital apparently shields the nucleus so effectively that the electron affinities are slightly endothermic.
- The Group 15 elements have rather low values, due possibly to the need to place the added electron in a half-filled p orbital; why the electron affinity of nitrogen should be endothermic is not clear.

The vertical trend is for electron affinity to become less exothermic in successive periods owing to better shielding of the nucleus by more inner shells and the greater size of the atom, but here also there are some apparent anomalies.

Chemical trends

A study of the trends in ionization energies and electron affinities can provide much insight into the balance of forces acting on electrons in an atom, but these values are properties of *isolated atoms*, and provide only indirect information about the chemical behavior of an element.

Atoms join together into molecules and other aggregates as a result of interaction between their electron clouds. In the simplest terms, this can be reduced to the sharing or transfer of electrons between the highest-energy occupied orbital of one atom and the lowest-energy vacant orbital. When two identical atoms join together, as in H_2 or I_2, the electrons must necessarily be shared equally between the two

atoms. In all other cases, we can expect that one atom will attract the shared electrons a bit more strongly, so that the sharing will be unequal. In an extreme case, this leads to the so-called "ionic" bond that is found in ionic solids such as NaCl.

Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more e*lectronegative.* Elements with low electronegativities (the metallic elements) are said to be *electropositive.*

It is important to understand that electronegativities are properties of atoms that are chemically bound to each other; there is no way of measuring the electronegativity of an isolated atom. Moreover, the same atom can exhibit different electronegativities in different chemical environments, so the "electronegativity of an element" is only a general guide to its chemical behavior rather than an exact specification of its behavior in a particular compound. Nevertheless, electronegativity is eminently useful in summarizing the chemical behavior of an element. You will make considerable use of electronegativity when you study chemical bonding and the chemistry of the individual elements.
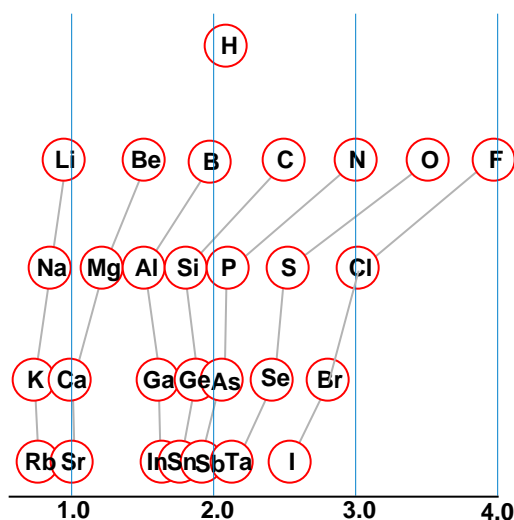
Because there is no single definition of electronegativity, any numerical scale for measuring it must of necessity be somewhat arbitrary. Most such scales are themselves based on atomic properties that are directly measurable and which relate in one way or the other to electron-attracting propensity. The most widely used of these scales was devised by Linus Pauling and is related to ionization energy and electron affinity. The Pauling scale runs from 0 to 4; the highest electron affinity, 4.0, is assigned to fluorine, while cesium has the lowest value of 0.7. Values less than about 2.2 are usually associated with electropositive, or metallic character. In the representation of the scale shown in figure, the elements are arranged in rows corresponding to their locations in the periodic table. The correlation is obvious; electronegativity is associated with the higher rows and the rightmost columns.

Polarizability and polarizing power

The symmetrical pictures of atomic electron clouds that you have seen apply only to isolated atoms and ions. In the presence of an external electrostatic field, these electron clouds will be deformed, with the electron density being concentrated toward a positive charge and away from a negative charge. *Polarizability* is a measure of the ease with which an external electric field is able to distort the charge cloud of an

atom or molecule (thus polarizability is not exclusively an atomic property). The external field can come from a nearby ion, or even from the polar end of a molecule that is electrically neutral but does not have its electron cloud distributed evenly.

In general, large species and especially large negative ions are more polarizable than smaller species. The less polarizable an ion is, the greater is its *polarizing power*; ions with a high *charge density*, or charge per unit volume. exhibit the greatest polarizing power. Thus a small ion such as Li^+ is more polarizing than K^+, for example, H^+ is the most polarizing ion of all owing to its minute volume as a bare proton.

Polarizability and polarizing power are correlated with many aspects of chemical behavior, and they provide an important link between this behavior and the position of the element in the periodic table.

Polarizability is also important for understanding some of the physical properties of substances. In uncharged species such as the noble gas atoms and neutral molecules, random momentary unbalances in charge distribution act to polarize adjacent atoms or molecules, creating a net attractive force that increases with the polarizability of the molecule. This is the origin of the universal weak attraction that is responsible for holding molecules together in the liquid and solid states in the absence of any more direct attractive forces.