

Atoms and the periodic table

Introduction to the quantum theory of the atom, atomic structure and the periodic table

A Chem1 Virtual Textbook *chapter*

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About this document:

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This document covers its topic at a level appropriate for first-year college chemistry.

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Among the many sources the author drew upon, special mention should be made of Pimentel and Spratley's *Understanding Chemistry*, S. Brush's *Introduction to Concepts and Theories in Physical Science*, P. Atkin's *Quanta*, P. Davies' *The Forces of Nature*, and the inspired writing of Toulmin and Goodfield in *The Architecture of Matter*.

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1 • Quanta: a new view of the world

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 extension, 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.

1.1 The limits of classical physics

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.

In the 1890s, 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. Owing to their extremely small masses, electrons behave as quantum particles which do not obey the rules of classical physics.

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.

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.

The caloric theory of heat assumed that small particles are able to contain more heat than large ones, so that when a material 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.

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

1.2 The quantum revolution

“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*.

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-cutttable stuff of the world that Thompson only reluctantly accepted it, and having done so, quickly became the object of widespread ridicule.

Radioactivity

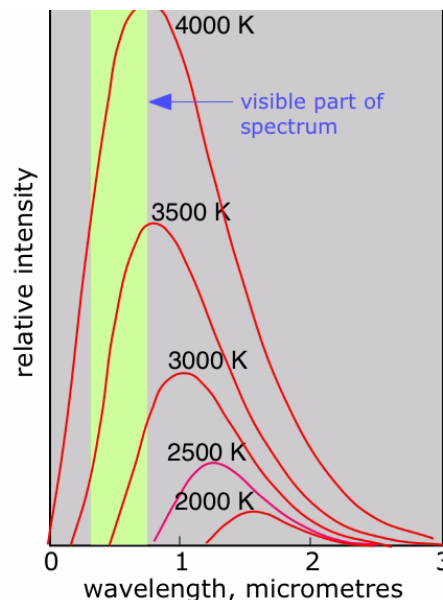
But worse was soon to come; not only were atoms shown not to be the smallest units of matter, but the work of the CURIES established that atoms are not even immutable; atoms of high atomic weight such as uranium and radium give off penetrating beams of radiation and in the process change into other elements, 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.

1.3 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 warm, 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".

Fig. 1: Thermal emission of radiation

These plots show something you already know: when piece of metal or some other material becomes very hot, it begins to glow. Actually, all bodies warmer than absolute zero emit thermal radiation, but at ordinary temperatures the wavelengths are in the far-infrared range, well out of the visible region. At about 3000 K the wavelengths become short enough to reveal themselves to the eye: the body becomes “red hot”. At higher temperatures the radiation extends through more of the visible spectrum and the emission becomes yellow and then white. Notice that at all temperatures shown here, the bulk of the radiation is still in the infrared region; this is the reason that incandescent (tungsten filament) lamps are so inefficient; most of the energy goes into the production of heat.



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

By 1900 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.

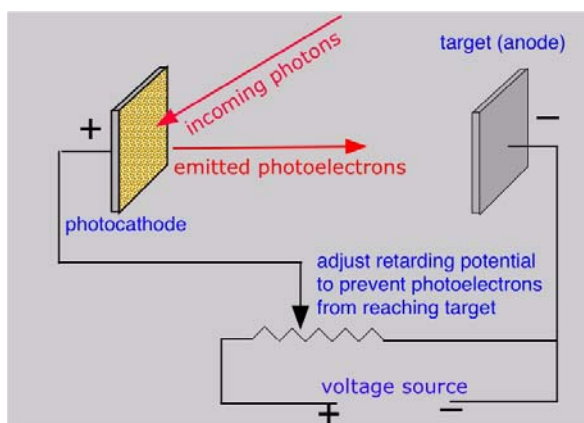


Fig. 2: The photoelectric experiment

In order to be knocked out of the metal, an electron must be given a minimum amount of energy (the ionization energy.) Any energy in excess of this will show up as kinetic energy of the photoelectrons. The purpose of the retarding potential is to counteract this kinetic energy so that we can determine what photon wavelength (energy) corresponds to just the ionization energy.

In 1905, ALBERT EINSTEIN, then an unknown clerk in the Swiss Patent Office, 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

$$e = h\nu = \frac{hc}{\lambda} \quad (1)$$

in which h is Planck's constant, 6.63×10^{-34} J-s, ν (Greek *nu*) is the frequency, λ (*lambda*) is the wavelength, and c is the velocity of light, 3.00×10^8 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.

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.¹

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

1.4 Matter and energy united

Energy

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 Benjamin Thompson (Count Rumford) 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.

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 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.

The speed of light is really the *only* speed in the universe. If you are sitting still, you are moving through time at the speed of light. If you are flying in an airplane, your motions along the three cartesian dimensions subtracts from that along the fourth (time) coordinate, with the result that time, for you, passes more slowly.

Relativity comes into chemistry in two rather indirect ways: it is responsible for the magnetic moment (“spin”) of the electron, and in high-atomic weight atoms in which the electrons have especially high effective velocities, their greater [relativistic] masses cause them

to be bound more tightly to the nucleus— accounting, among other things, for the color of gold, and for the unusual physical and chemical properties of mercury.

Mass-energy

Where does the additional mass of a moving body 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.

Check your understanding of this chapter

- What was the **caloric theory of heat**, and how did Rumford’s experiments in boring cannon barrels lead to its overthrow?
- Define **thermal radiation** and the “*scandal of the ultraviolet*” and the role Max Planck played in introducing the quantum concept.
- What is the **photoelectric effect**? Describe the crucial insight that led Einstein to the concept of the **photon**.

2 • Light, particles and waves

What we call “classical” physics is based on our experience of what we perceive as the “real world” in which objects have definite masses, sizes, locations and velocities. Once we get down to the atomic level, this simple view begins to break down. It becomes totally useless when we move down to the subatomic level and consider the lightest of all chemically-significant particles, the electron. The chemical properties of a particular kind of atom depend on the arrangement and behavior of the electrons which make up almost the entire volume of the atom. The electronic structure of an atom can only be determined indirectly by observing the manner in which atoms absorb and emit light. Light, as you already know, has wavelike properties, so we need to know something about waves in order to interpret these observations. But because the electrons are themselves quantum particles and therefore have wave-like properties of their own, we will find that an understanding of the behavior of electrons in atoms can only be gained through the language of waves.

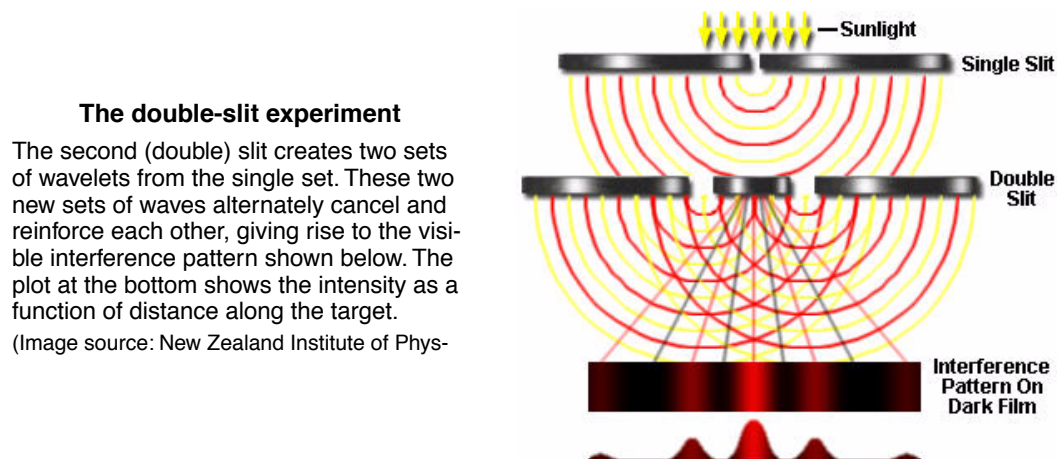
2.1 The language of light

Atoms are far too small to see directly, even with the most powerful optical microscopes. But atoms do interact with and under some circumstances emit light in ways that reveal their internal structures in amazingly fine detail. It is through the “language of light” that we

communicate with the world of the atom. This section will introduce you to the rudiments of this language.

Wave, particle, or what?

In the early 19th century, the English scientist THOMAS YOUNG carried out the famous double-slit experiment which demonstrated that a beam of light, when split into two beams and then recombined, will show interference effects that can only be explained by assuming that light is a wavelike disturbance.



By 1820, AUGUSTIN FRESNEL had put this theory on a sound mathematical basis, but the exact nature of the waves remained unclear until the 1860's when James Clerk Maxwell developed his electromagnetic theory.

But Einstein's 1905 explanation of the photoelectric effect showed that light also exhibits a particle-like nature. The photon is the smallest possible packet (quantum) of light; it has zero mass but a definite energy.

When light-wave interference experiments are conducted with extremely low intensities of light, the wave theory breaks down; instead of recording a smooth succession of interference patterns as shown above, an extremely sensitive detector sees individual pulses—that is, individual photons.

Suppose we conduct the double-slit interference experiment using a beam of light so weak that only one photon at a time passes through the apparatus (it is experimentally possible to count single photons, so this is a practical experiment.) Each photon passes through the first slit, and then through one or the other of the second set of slits, eventually striking the photographic film where it creates a tiny dot. If we develop the film after a sufficient number of photons have passed through, we find the very same interference pattern we obtained with higher-intensity light whose behavior was could be explained by wave interference.

There is something strange here. Each photon, acting as a particle, must pass through one or the other of the pair of slits, so we would expect to get only two groups of spots on the film, each opposite one of the two slits. Instead, it appears that the each particle, on passing through one slit, “knows” about the other, and adjusts its final trajectory so as to build up a wavelike interference pattern.

It gets even stranger: suppose that we set up a detector to determine which slit a photon is heading for, and then block off the other slit with a shutter. We find that the photon sails straight through the open slit and onto the film without trying to create any kind of an interference pattern. Apparently, any attempt to observe the photon as a discrete particle causes it to behave like one.

One well-known physicist (LANDÉ) suggested that perhaps we should coin a new word, *wavicle*, to reflect this duality.

Later on, virtually the same experiment was repeated with electrons, thus showing that particles can have wavelike properties (as the French physicist LOUIS DE BROGLIE predicted in 1923), just as what were conventionally thought to be electromagnetic waves possess particle-like properties.

Is it a particle or is it a wave? For large bodies (most atoms, baseballs, cars) there is no question: the wave properties are insignificant, and the laws of classical mechanics can adequately describe their behaviors. But for particles as tiny as electrons (quantum particles), the situation is quite different:

The physicist Landé once suggested that perhaps we should coin a new word, *wavicle*, to reflect this duality!

instead of moving along well defined paths, a quantum particle seems to have an infinity of paths which thread their way through space, seeking out and collecting information about all possible routes, and then adjusting its behavior so that its final trajectory, when combined with that of others, produces the same overall effect that we would see from a train of waves of wavelength = h/mv .

Taking this idea of quantum indeterminacy to its most extreme, the physicist ERWIN SCHRÖDINGER proposed a “thought experiment” in which the radioactive decay of an atom would initiate a chain of events that would lead to the death of a cat placed in a closed box. The atom has a 50% chance of decaying in an hour, meaning that its wave representation will contain both possibilities until an observation is made. The question, then, is will the cat be simultaneously in an alive-and-dead state until the box is opened? If so, this raises all kinds of interesting questions about the nature of being.

The saga of “Schrödinger’s cat” has inspired a huge amount of commentary and speculation, as well as books, poetry, songs, T-shirts, etc.

What you need to know about waves

We use the term “wave” to refer to a quantity which changes with time. Waves in which the changes occur in a repeating or periodic manner are of special importance and 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 periodic disturbance of some kind is propagated through a medium; pressure variations through air, transverse motions along 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 simple wave motion: *amplitude*, *wavelength*, and *frequency*, the number of vibrations per second. The relation between the wavelength λ (Greek *lambda*) and frequency of a wave ν (Greek *nu*) is determined by the propagation velocity v :

$$v = v\lambda \quad (2)$$

Problem Example 1

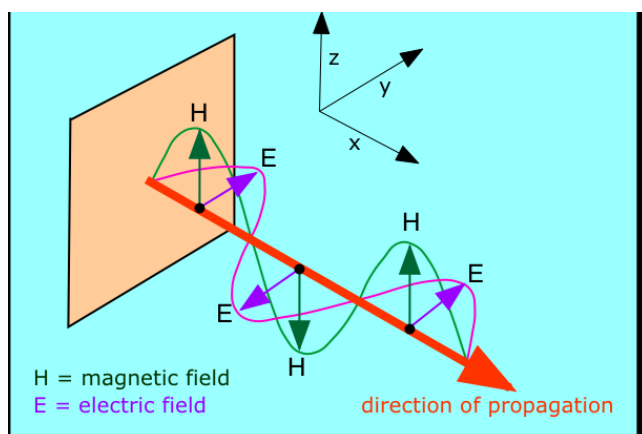
What is the wavelength of the musical note A - 440 hz when it is propagated through air in which the velocity of sound is 343 m s⁻¹?

Solution:

$$\lambda = v / \nu = (343 \text{ m s}^{-1}) / (440 \text{ s}^{-1}) = 0.80 \text{ m}$$

Light and electromagnetic radiation

MICHAEL FARADAY's discovery that electric currents could give rise to magnetic fields and vice versa raised the question of how these effects are transmitted through space. Around 1870, the Scottish physicist JAMES CLERK MAXWELL (1831-1879) showed that this electromagnetic radiation can be described as a train of perpendicular oscillating electric and magnetic fields.



What is “waving” in electromagnetic radiation?

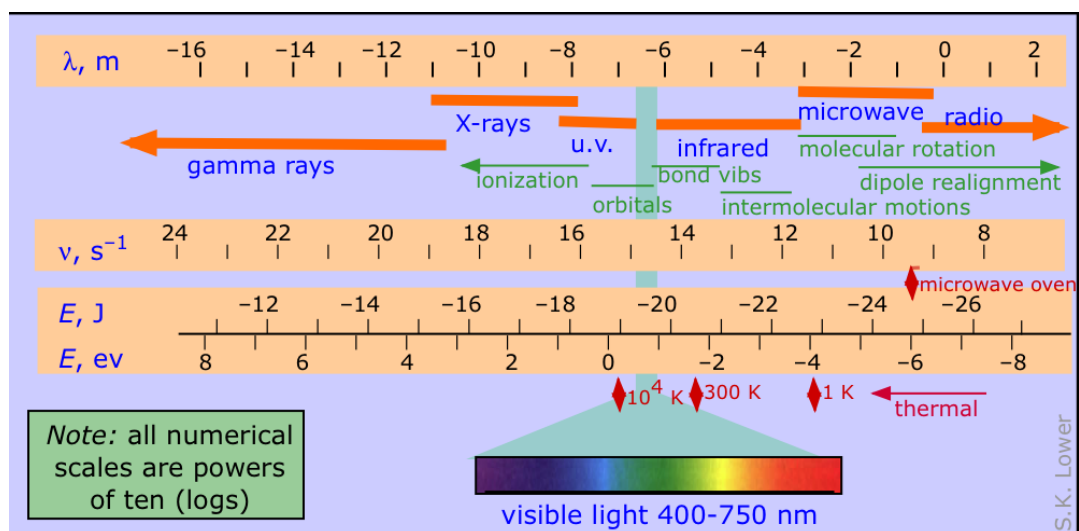
According to Maxwell, it is the strengths of the electric and magnetic fields as they travel through space. The two fields are oriented at right angles to each other and to the direction of travel.

As the electric field changes, it induces a magnetic field, which then induces a new electric field, etc., allowing the wave to propagate itself through space.

Maxwell was able to calculate the speed at which electromagnetic disturbances are propagated, and found that this speed is the same as that of light. He therefore proposed that light is itself a form of electromagnetic radiation whose wavelength range forms only a very small part of the entire electromagnetic spectrum. Maxwell's work served to unify what were once thought to be entirely separate realms of wave motion.

The electromagnetic spectrum

The electromagnetic spectrum is conventionally divided into various parts as depicted in the diagram below, in which the four logarithmic scales correlate the wavelength of electromagnetic radiation with its frequency in hertz (units of s⁻¹) and the energy per photon, expressed both in joules and electron-volts.



The electromagnetic spectrum

The other items shown on the diagram, from the top down, are:

the names used to denote the various wavelength ranges of radiation (you should know their names and the order in which they appear)

the principal effects of the radiation on atoms and molecules

Electromagnetic radiation and chemistry. It's worth noting that radiation in the ultraviolet range can have direct chemical effects by ionizing atoms and disrupting chemical bonds. Longer-wavelength radiation can interact with atoms and molecules in ways that provide a valuable means of indentifying them and revealing particular structural features.

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

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

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

$$e = h\nu = (6.63 \times 10^{-34} \text{ J s}) \times (6 \times 10^{14} \text{ s}^{-1}) = 40 \times 10^{19} \text{ J}$$

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 $1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$ 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 $4 \times 10^{-19} \text{ J}$, 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.

2.2 Spectra: interaction of light and matter

A *spectrum* is basically just a plot showing the intensity of radiation as a function of its frequency or wavelength. Prisms and diffraction gratings are widely employed to observe the spectra of light sources.



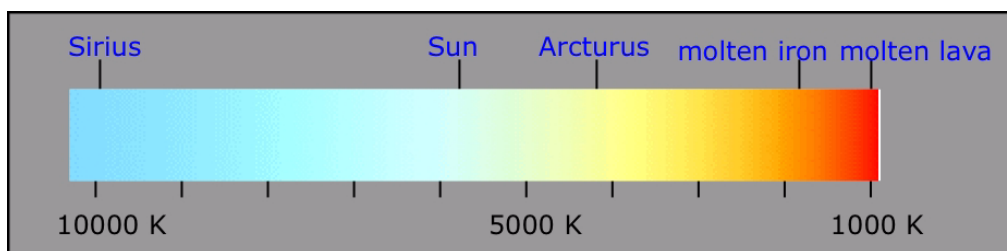
Continuous spectra

A 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.

(You might wish to review the thermal emission plot in Fig. 1.)

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.

The source of thermal emission most familiar to us is the Sun. When sunlight is refracted by rain droplets into a rainbow or by a prism onto a viewing screen, we see the visible part of the spectrum.



Red hot, white hot, blue hot... your rough guide to temperatures of hot objects.

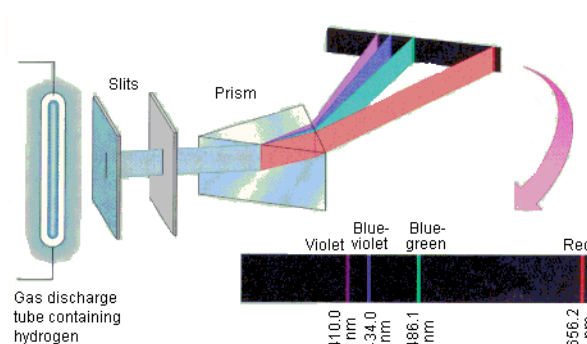
Line spectra

Heat a piece of iron up to near its melting point and it will emit a broad continuous spectrum that the eye perceives as orange-yellow. But if you zap the iron with an electric spark, some of the iron atoms will vaporize and have one or more of their electrons temporarily knocked out of them. As they cool down the electrons will re-combine with the iron ions, losing energy as they move in toward the nucleus and giving up this excess energy as light. The spectrum of this light is anything but continuous; it consists of a series of discrete wavelengths which we call *lines*.

Fig. 3: Observing a line spectrum

A spectrum is most accurately expressed as a plot of intensity as a function of wavelength. Historically, the first spectra were obtained by passing the radiation from a source through a series of narrow slits to obtain a thin beam which was dispersed by a prism so that the different wavelengths are spread out onto a photographic film or viewing screen. The “lines” in line spectra are really images of the slit nearest the prism. Modern spectrophotometers more often employ diffraction gratings rather than prisms, and use electronic sensors connected to a computer.

[Purdue U. image source]



Each chemical element has its own characteristic line spectrum which serves very much like a “fingerprint” capable of identifying a particular element in a complex mixture. Shown below is what you would see if you could look at several different atomic line spectra directly.

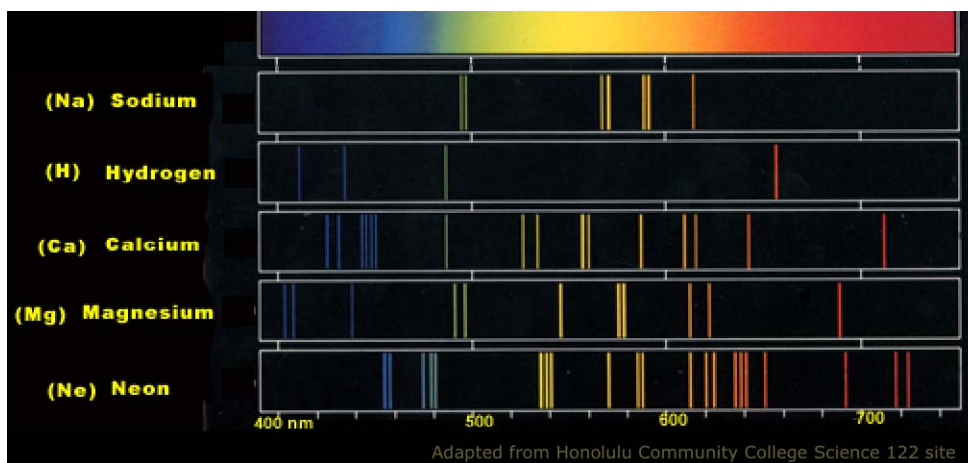


Fig. 4:

What do these spectra tell us about the nature of chemical atoms? We will explore this question in some detail in the next chapter.

Atomic line spectra are extremely useful for identifying small quantities of different elements in a mixture.

- Companies that own large fleets of trucks and buses regularly submit their crankcase engine oil samples to spectrographic analysis. If they find high levels of certain elements (such as vanadium) that occur only in certain alloys, this can signal that certain parts of the engine are undergoing severe wear. This allows the mechanical staff to take corrective action before engine failure occurs.
- A more prosaic application of atomic spectra is determination of the elements present in stars.

If you live in a city, you probably see atomic line light sources every night! “Neon” signs are the most colorful and spectacular, but high-intensity street lighting is the most widespread source. A look at the emission spectrum of sodium (previous page) explains the intense yellow color of these lamps. The spectrum of mercury (not shown) similarly has its strongest lines in the blue-green region.

2.3 Particles and waves

There is one more fundamental concept you need to know before we can get into the details of atoms and their spectra. 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 :

$$\lambda = \frac{h}{mv}$$

If you explore the magnitude of the quantities in this equation (recall that h is around 10^{-33} J s), 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, following de Broglie’s prediction. Its small mass ($9.1\text{E-}31$ kg) made it an obvious candidate, and velocities of around 100 km/s are easily obtained, yielding a value of λ 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 grooves of a CD recording.

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.

2.4 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/λ in which λ is the wavelength of the light. 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

$$\delta x \times \delta y \geq \frac{h}{2\pi} \quad (3)$$

in which the δ 's (deltas) 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 ($\delta x = 0$), 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 δt taken to make the measurement:

The “uncertainty” referred to here goes much deeper than merely limiting our ability to observe the quantity $\delta x \delta p$ to a greater precision than $h/2\pi$. It means, rather, that this product has no exact value, nor, by extension, do position and momentum on a microscopic scale. A more appropriate term would be *indeterminacy*, which is closer to Heisenberg's original word *Ungenauigkeit*.

The revolutionary nature Heisenberg's uncertainty principle soon extended far beyond the arcane world of physics; its consequences quickly entered the realm of ideas and has inspired numerous creative works in the arts—few of which really have much to do with the Principle! A possible exception is Michael Frayn's widely acclaimed play *Copenhagen* that has brought a sense of Heisenberg's thinking to a wide segment of the public.

Check your understanding of this chapter

- Cite two pieces of experimental evidence that demonstrate, respectively, the wave- and particle-like nature of light.
- Define the terms *amplitude*, *wavelength*, and *frequency* as they apply to wave phenomena.
- Give a qualitative description of **electromagnetic radiation** in terms of electrostatic and magnetic fields. Be able to name the principal regions of the **electromagnetic spectrum** (X-rays, infrared region, etc.) and specify their sequence in terms of either wavelength or energy per photon.
- Describe the difference between **line spectra** and **continuous spectra** in terms of both their appearance and their origins.
- What is meant by the **de Broglie wavelength** of a particle? How will the particle's mass and velocity affect the wavelength?
- State the consequences of the **Heisenberg uncertainty principle** in your own words.

3 • The Bohr Model of the Atom

Our goal in this chapter 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.

3.1 Models of the atom

Models are widely employed in science to help understand things that cannot be viewed directly. The idea is to imagine a simplified system or process that might be expected to exhibit the basic properties or behavior of the real thing, and then to test this model against more complicated examples and modify it as necessary. Although one is always on shaky philosophical ground in trying to equate a model with reality, there comes a point when the difference between them becomes insignificant for most practical purposes.

The planetary model

The demonstration by THOMPSON in 1867 that all atoms contain units of negative electric charge led to the first science-based 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 "plum pudding" model (as he called it) and soon put it to rest; Rutherford's famous alpha-ray bombardment experiment (carried out, in 1909, by his students Hans Geiger and Ernest Marsden) 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".

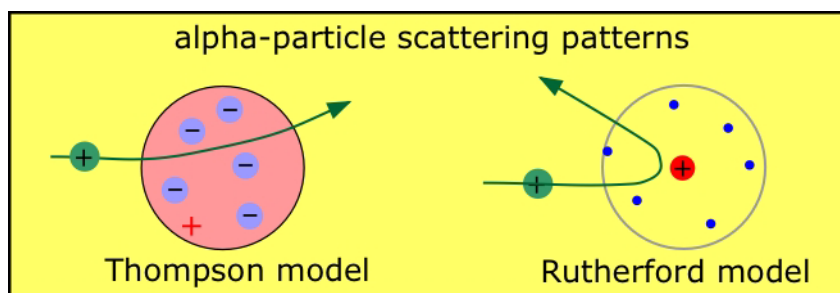


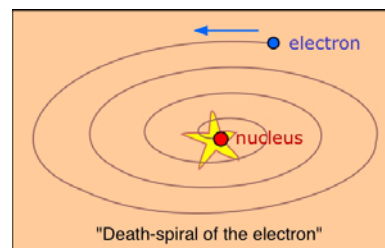
Fig. 5: Thomson and Rutherford models of the atom

The alpha-particle (He^{2+}) is strongly deflected by a central nucleus at which all the atom's positive charge is concentrated.

Even though the planetary 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 (that is, acceleration, 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 as 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

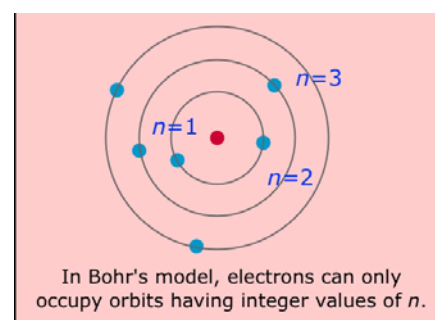
NIELS BOHR was a brilliant Danish physicist who came to dominate the world of atomic and nuclear physics during the first half of the twentieth century. Bohr suggested that the planetary model could be saved if one new assumption were made: certain “special states of motion” of the electron, corresponding 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 $h/2\pi$. The radius of one of these allowed Bohr orbits is given by

$$r = \frac{nh}{\pi 2mv}$$

in which h is Planck's constant, m is the mass of the electron, v is the orbital velocity, and n can have only the integer 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 $e = hv$.

3.2 Vibrations, standing waves and bound states

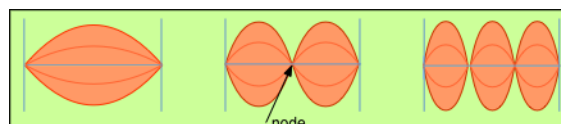
Bohr's theory worked; it completely explained the observed spectrum of the hydrogen atom, and this triumph would later win him a Nobel prize. The main weakness of the theory, as Bohr himself was the first to admit, is that it could offer no good explanation of *why* these special orbits immunized the 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.

Spectrum of a guitar string

In order to produce a tone when plucked, a guitar string must be fixed at each end (that is, it must be a *bound system*) and 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; if the string breaks or becomes unattached at one end, it produces no sound.

Fig. 6: Standing waves in a bound system

The three modes shown are the fundamental, first overtone (octave on the musical scale),



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 as *overtone*s (or, in music, as *octaves*) contain 2, 3, 4 and more points of maximum displacement (*antinodes*) spaced evenly along the string, separated by points of zero displacement (*nodes*). These correspond to successively higher quantum numbers and higher energies.

The vibrational states of the string are quantized in the sense that an integral number of antinodes must be present. Note again that this condition is imposed by the boundary condition that the ends of the string, being fixed in place, must be nodes. Because the locations of the nodes and antinodes do not change as the string vibrates, the vibrational patterns are known as *standing waves*.

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.

Standing waves live in places other than atoms and musical instruments: every time you turn on your **microwave oven**, a complex set of standing waves fills the interior. What is “waving” here is the alternating electrostatic field as a function of location; the wave patterns are determined by the dimensions of the heated space and by the objects placed within it. But the part of a pizza that happens to be located at a node would not get very hot, so all microwave ovens provide a mechanical means of rotating either the food (on a circular platform) or the microwave beam (by means of a rotating deflector) so that all parts will pass through high-amplitude parts of the waves.

Standing waves in the hydrogen atom

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, as depicted in the two diagrams below.

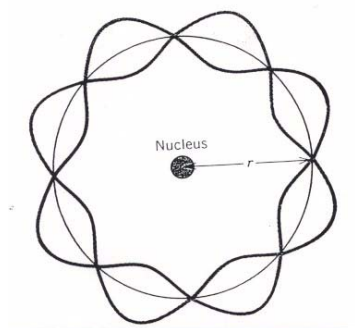
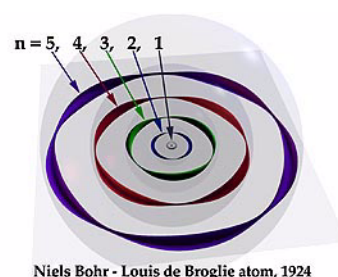


Fig. 7: Circular standing waves

Left: standing waves on a closed circular string are constrained to those having an integral number of peaks and nodes. *Right:* a representation of standing waves of the electron in a hydrogen atom (Kenneth Snelson).



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.

3.3 Spectrum of the hydrogen atom

Hydrogen, the simplest atom, also has the simplest line spectrum (line spectra were briefly introduced on Figure.) The hydrogen spectrum was the first to be observed (by ÅNDERS ANGSTROM in the 1860's). JOHANN BALMER, a German high school teacher, discovered a simple mathematical formula that related the wavelengths of the various lines that are observable in the visible and near-uv parts of the spectrum. This set of lines is now known as the *Balmer Series*.

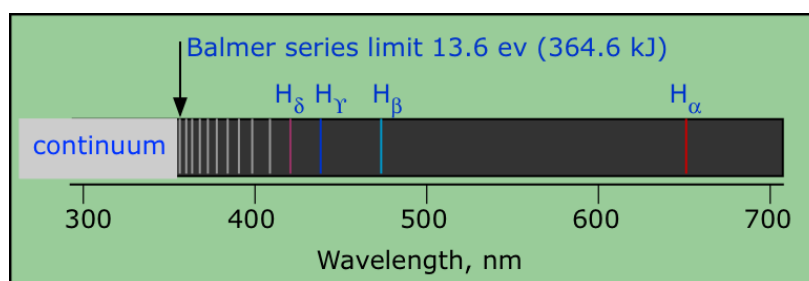
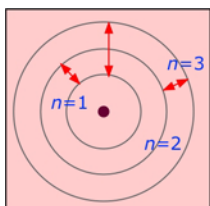


Fig. 8: The Balmer series and ionization limit of hydrogen

The four lines in the visible spectrum (designated by α through δ) were the first observed by Balmer. Notice how the lines crowd together as they approach the ionization limit in the near-ultraviolet part of the spectrum. Once the electron has left the atom, it is in an unbound state and its energy is no longer quantized. When such electrons return to the atom, they emit light corresponding to whatever kinetic energies they happen to possess, producing the continuum radiation.

Other sets of lines in the hydrogen spectrum are the *Lyman* series (in the ultraviolet) and the *Paschen*, *Brackett*, *Pfund* and *Humphrey* series in the infrared.

How the Bohr model explains the hydrogen line spectrum



Each spectral line represents an energy difference between two possible states of the atom. Each of these states corresponds to the electron in the hydrogen atom being in an “orbit” whose radius increases with the quantum number n . The lowest allowed value of n is 1; because the electron is as close to the nucleus as it can get, the energy of the system has its minimum (most negative) value. This is the “normal” (most stable) state of the hydrogen atom, and is called the *ground state*.

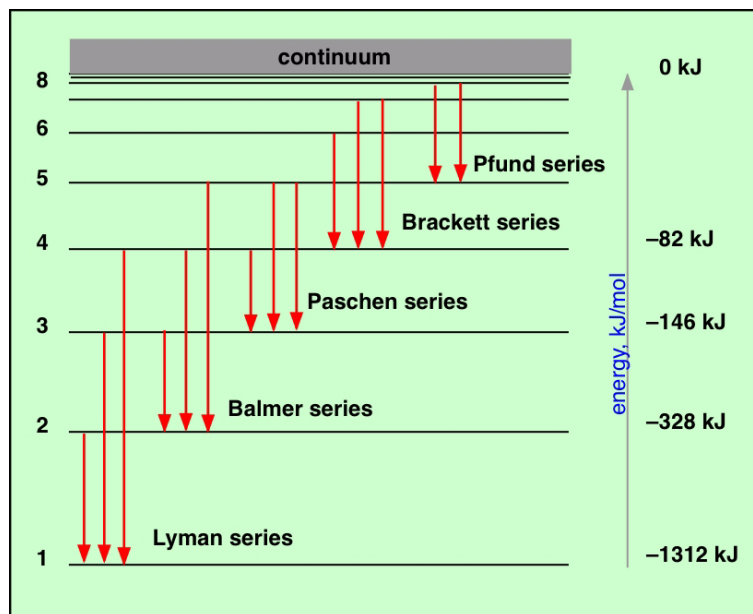
If a hydrogen atom absorbs radiation whose energy corresponds to the difference between that of $n=1$ and some higher value of n , the atom is said to be in an excited state. Excited states are unstable and quickly decay to the ground state, but not always in a single step. For example, if the electron is initially promoted to the $n=3$ state, it can decay either to the ground state or to the $n=2$ state, which then decays to $n=1$. Thus this single $n=1 \rightarrow 3$ excitation can result in the three emission lines depicted in the diagram above, corresponding to $n=3 \rightarrow 1$, $n=3 \rightarrow 2$, and $n=2 \rightarrow 1$.

If, instead, enough energy is supplied to the atom to completely remove the electron, we end up with a hydrogen ion and an electron. When these two particles recombine ($\text{H}^+ + e^- \rightarrow \text{H}$), the electron can initially find itself in a state corresponding to any value of n , leading to the emission of many lines.

Fig. 9: The hydrogen spectral series

The lines of the hydrogen spectrum can be organized into different series according to the value of n at which the emission terminates (or at which absorption originates.) The first few series are named after their discoverers. The most well-known (and first-observed) of these is the Balmer series, which lies mostly in the visible region of the spectrum. The Lyman lines are in the ultraviolet, while the other series lie in the infrared. The lines in each series crowd together as they converge toward the series limit which corresponds to ionization of the atom and is observed as the beginning of the continuum emission. Note that the *ionization energy* of hydrogen (from its ground state) is 1312 kJ mol^{-1} .

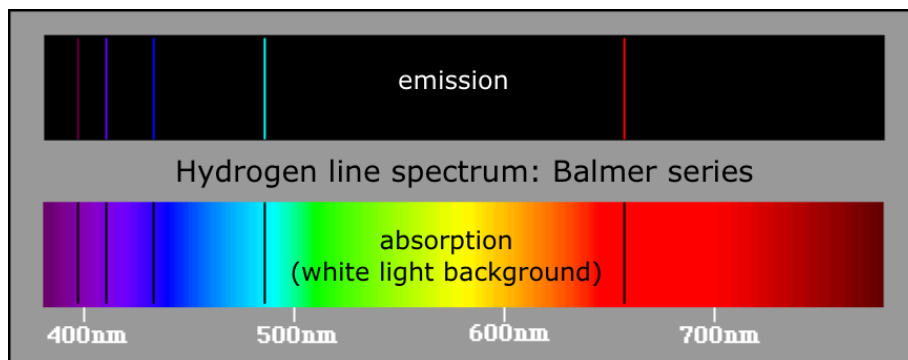
In order to provide a compact display of the above diagram, the vertical energy scale has been distorted and only the longest-wavelength transitions for each



Although an infinite number of n -values are possible, the number of observable lines is limited by our ability to resolve them as they converge into the continuum; this number is around a thousand.

Emission and absorption spectra

The line *emission spectra* we have been discussing are produced when electrons which had previously been excited to values of n greater than 1 fall back to the $n=1$ ground state, either directly, or by way of intermediate- n states. But if light from a continuous source (a hot body such as a star) passes through an atmosphere of hydrogen (such as the star's outer atmosphere), those wavelengths that correspond to the allowed transitions are absorbed, and appear as dark lines superimposed on the continuous spectrum.

**Fig. 10: Emission and absorption spectra of hydrogen**

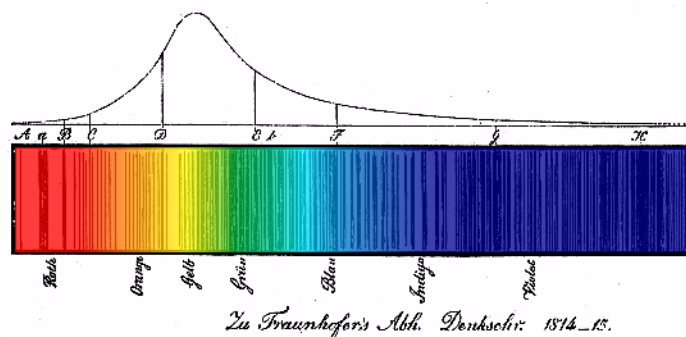
For clarity, only the Balmer series is shown here.

[Adapted from the *Online Journey through Astronomy* Web site.]

These dark absorption lines were first observed by WILLIAM WOLLASTON in his study of the solar spectrum. In 1814, JOSEPH VON FRAUNHOFER (1787-1826) re-discovered them and made accurate measurements of 814 lines, including the four most prominent of the Balmer lines. Somewhat later, KIRCHHOFF and BUNSEN showed that these are atomic line spectra that correspond to the emission spectra that these two workers had observed in the laboratory. Kirchoff and Bunsen found two sets of lines that did not correspond to any known element, which led to their discovery of cesium and rubidium.

Fig. 11: The solar Fraunhofer spectrum

The solar Fraunhofer spectrum contains thousands of lines that show the presence of 67 elements in the cooler layers of the solar atmosphere. The continuous background is thermal emission from the solar "surface".



Check your understanding of this chapter

- Describe the Thompson, Rutherford, and early planetary models of the atom, and explain why the latter is not consistent with classical physics.
- State the major concepts that distinguished Bohr's model of the atom from the earlier planetary model.
- Give an example of a mechanical standing wave; state the meaning and importance of its boundary conditions.
- Sketch out a diagram showing how the concept of a standing wave applies to the description of the electron in a hydrogen atom.
- What is an atomic line emission spectrum? What is the significance of the continuum region of an emission spectrum? Sketch out a drawing showing the essentials of such a spectrum, including the ionization limit and the continuum.
- Describe the way in which Bohr's quantum numbers explain the observed spectrum of a typical atom.
- Explain the relation between the absorption and emission spectrum of an atom.

4 • The quantum atom

The picture of the atom that NIELS BOHR developed in 1913 served as the starting point for modern atomic theory, but it was not long before Bohr himself recognized that the advances in quantum theory that occurred through the 1920's required an even more revolutionary change in the way we view the electron as it exists in the atom. This chapter will attempt to show you this view—or at least the portion of it that can be appreciated without the aid of more than a small amount of mathematics.

4.1 From orbits to orbitals

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:

$$E = \frac{mv^2}{2} + \frac{-e^2}{r} \quad (4)$$

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:

$$E = \frac{p^2}{2m} - \frac{e^2}{r} \quad (5)$$

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 Ψ (*psi*), “modulates” the equation of motion of

the electron so as to reflect the fact that the electron manifests itself with greater probability in some locations than at others. This yields the celebrated *Schrödinger equation*

$$\left(\frac{mv^2}{2} - \frac{e^2}{r}\right)\Psi = E\Psi \quad (6)$$

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 Ψ , which is known as the *wave function*. As this name suggests, the value of Ψ 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 Ψ ; the major ones are that the value of Ψ must approach zero as the distance from the nucleus approaches infinity, and that the function be continuous.

When the functional form of Ψ 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 Ψ is known, the allowed energies E of an atom can be predicted from the above equation. 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 Ψ . Recalling that its value depends on the location in space with respect to the nucleus of the atom, the square of this function Ψ^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 the 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 (in accord with the uncertainty principle) 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 Ψ 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 δx 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.

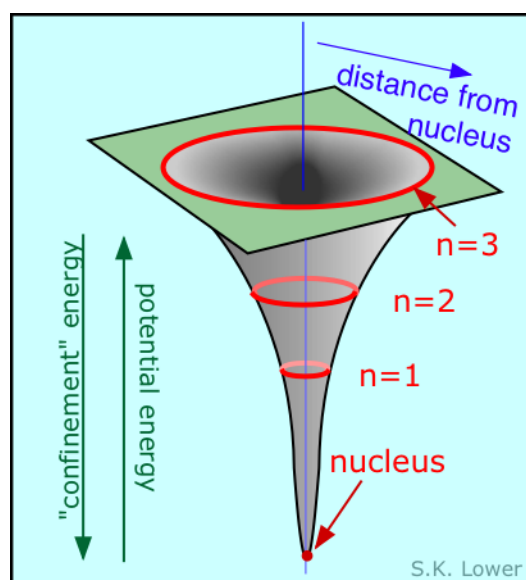
This process is known as *tunneling*; the *tunnel effect* is exploited in various kinds of semiconductor devices, and it is the mechanism whereby electrons jump between dissolved ions and the electrode in batteries and other electrochemical devices.

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 $n=1$.

The electron well

The red circles show the average distance of the electron from the nucleus for the allowed quantum levels (standing wave patterns) of $n=1$ through $n=3$. As n decreases, the potential energy of the system becomes more negative and the electron becomes more confined in space. According to the uncertainty principle, this increases the momentum of the electron, and hence its kinetic energy. The latter acts as a kind of “confinement energy” that restores the electron to one of the allowed levels.

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.



Orbitals

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 outmoded 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 higher values. The electron

retains its particle-like mass and momentum, but because the mass is so small, its wavelike properties dominate. The latter give rise to patterns of standing waves that define the possible states of the electron in the atom.

4.2 The quantum numbers

Modern quantum theory tells us that the various allowed states of existence of the electron in the hydrogen atom correspond to different standing wave patterns. In the preceding lesson we showed examples of standing waves that occur on a vibrating guitar string. The wave patterns of electrons in an atom are different in two important ways:

- Instead of indicating displacement of a point on a vibrating string, the electron waves represent the probability that an electron will manifest itself (appear to be located) at any particular point in space. (Note carefully that this is *not* the same as saying that “the electron is smeared out in space”; at any given instant in time, it is either at a given point or it is not.)
- The electron waves occupy all three dimensions of space, whereas 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.

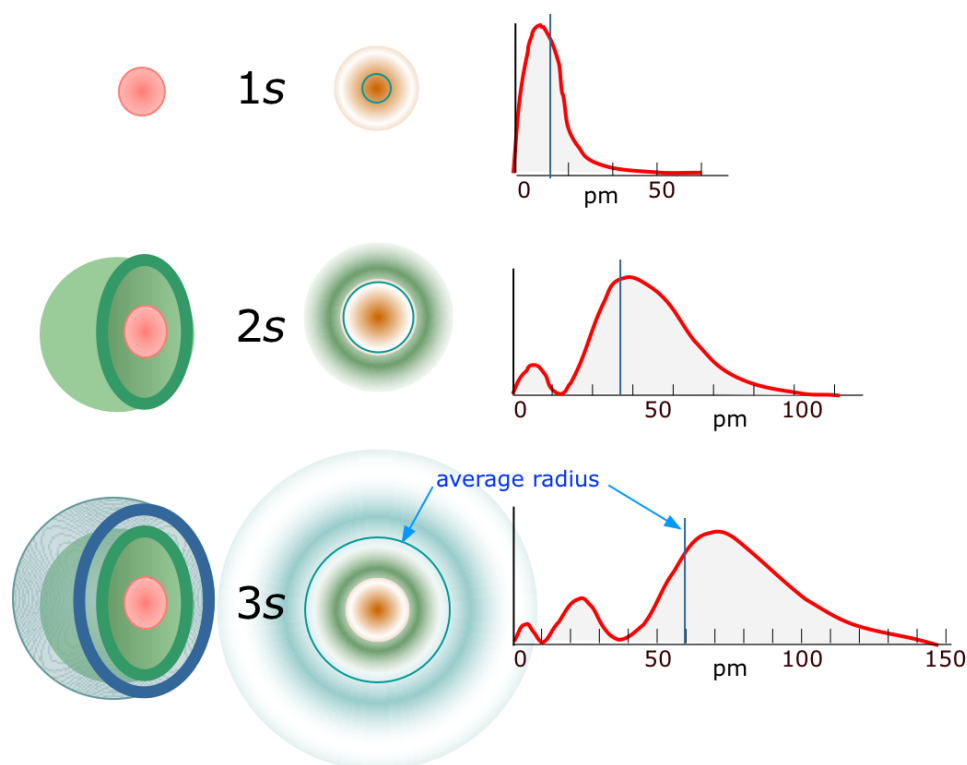


Fig. 12: Shapes and radial distributions of s orbitals

The three simplest orbitals of the hydrogen atom are depicted above in pseudo-3D, in cross-section, and as plots of probability (of finding the electron) as a function of distance from the nucleus. The average radius of the electron probability is shown by the blue circles or plots

in the two columns on the right. These radii correspond exactly to those predicted by the Bohr model.

Physical significance of n

The potential energy of the electron is given by the formula

$$E = \frac{-4\pi^2 e^4 m}{h^2 n^2} \quad (7)$$

in which e is the charge of the electron, m 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 is inversely proportional to the square of n , so that the energy rises toward zero as n becomes very large, but 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 orbital 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.

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 of an atom to lose or gain electrons in chemical reactions.

The angular momentum quantum number

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 theory also predicts that orbitals having the same value of n can differ in shape and in their orientation in space. The quantum number l , known as the *angular momentum quantum number*, determines the shape of the orbital. (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.)

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—but note that the number of peaks in the radial probability distributions (right) decreases with increasing l . 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. For historical reasons, the orbitals corresponding to different values of l are designated by letters, starting with s for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$.

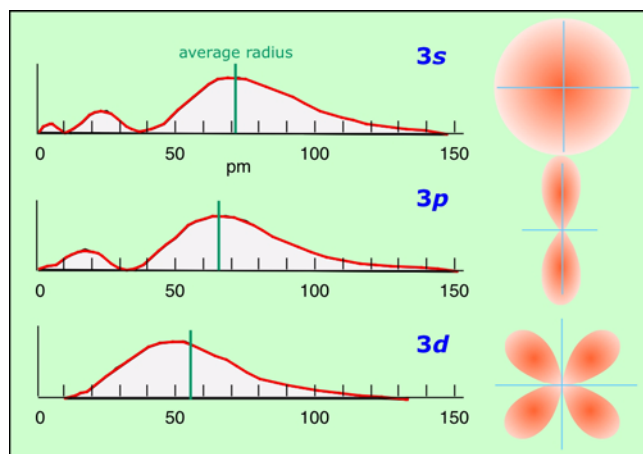


Fig. 13: Radial probability distributions of atomic orbitals with different l values

The shapes and radial distributions of the orbitals corresponding to the three allowed values of l for the $n = 3$ level of hydrogen are shown above. Notice that the average orbital radius r decreases somewhat at higher values of l . The function relationship is given by

$$r = (5.29 \text{ pm}) \frac{n^2}{z} \left[\frac{3}{2} - \frac{l(l-1)}{2n^2} \right]$$

in which z is the nuclear charge of the atom, which of course is unity for hydrogen.

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. The additional quantum number m is required to specify the particular direction along which the orbital is aligned.

“Direction in space” has no meaning in the absence of a 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*. In chemistry, however, electrostatic fields are much more important for defining directions at the atomic level because it is through such fields that nearby atoms in a molecule interact with each other. 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.

The quantum number m 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 ($l = 1$), m can

be -1 , 0 , and $+1$. Higher values of l introduce more complicated orbital shapes which give rise to more possible orientations in space, and thus to more values of m .

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 an 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 the term spin is easy to visualize, but should not be taken literally. Physical rotation of an electron is meaningless. However, the coordinates of the electron's wave function can be rotated mathematically; when this is done, it is found that a rotation of 720° is required to restore the function to its initial value— rather weird, considering that a 360° rotation will leave any extended body unchanged! Electron spin is basically a relativistic effect in which the electron's momentum distorts local space and time. It has no classical counterpart and thus cannot be visualized other than through mathematics.

A basic principle of modern physics states that for particles such as electrons that possess half-integral values of 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 (1900-1958, Nobel Prize 1945).

The exclusion principle was discovered empirically and was placed on a firm theoretical foundation by Pauli in 1925. A complete explanation requires some familiarity with quantum mechanics, so all we will say here is that if two electrons possess the same quantum numbers n , l , m and s (defined below), the wave function that describes the state of existence of the two electrons together collapses to zero, which means that this is an “impossible” situation.

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, which “cancel out” to produce zero magnetic moment. Two such electrons in a single orbital are often referred to as an *electron pair*.

If it were not for the exclusion principle, the atoms of all elements would behave in the same way, and there would be no need for a science of Chemistry!

As we have seen, the lowest-energy standing wave pattern the electron can assume in an atom corresponds to $n=1$, which describes the state of the single electron in hydrogen, and of the two electrons in helium. Since the quantum numbers m and l are zero for $n=1$, the pair of electrons in the helium orbital have the values $(n, l, m, s) = (1, 0, 0, +1)$ and $(1, 0, 0, -1)$ — that is, they differ only in spin. These two sets of quantum numbers are the only ones that are possible for a $n=1$ orbital. The additional elec-

trons in atoms beyond helium must go into higher-energy ($n>1$) orbitals. Electron wave patterns corresponding to these greater values of n are concentrated farther from the nucleus, with the result that these electrons are less tightly bound to the atom and are more accessible to interaction with the electrons of neighboring atoms, thus influencing their chemical behavior. If it were not for the Pauli principle, all the electrons of every element would be in the lowest-energy $n=1$ state, and the differences in the chemical behavior the different ele-

ments would be minimal. Chemistry would certainly be a simpler subject, but it would not be very interesting!

Check your understanding of this chapter

- State the fundamental distinction between **Bohr's original model** of the atom and the modern orbital model.
- Explain the role of the **uncertainty principle** in preventing the electron from falling into the nucleus.
- State the physical meaning of the **principal quantum number** of an electron orbital, and make a rough sketch of the shape of the probability-*vs.*-distance curve for any value of n .
- Sketch out the **shapes** of an s , p , or a typical d orbital.
- Describe the significance of the **magnetic quantum number** as it applies to a p orbital.
- State the **Pauli exclusion principle**.

5 • Electron configurations of the elements

In the previous section you learned that an electron standing-wave pattern characterized by the quantum numbers (n, l, m) is called an *orbital*. According to the *Pauli exclusion principle*, no two electrons in the same atom can have the same set of quantum numbers (n, l, m, s) . This limits the number of electrons in a given orbital to two ($s = \pm 1$), and it requires that atom containing more than two electrons must place them in standing wave patterns corresponding to higher principal quantum numbers n , which means that these electrons will be farther from the nucleus and less tightly bound by it.

In this chapter, we will see how the Pauli restrictions on the allowable quantum numbers of electrons in an atom affect the electronic configuration of the different elements, and, by influencing their chemical behavior, governs the structure of the periodic table.

5.1 One-electron atoms

Let us begin with atoms that contain only a single electron. Hydrogen is of course the only electrically neutral species of this kind, but by removing electrons from heavier elements we can obtain one-electron ions such as He^+ and Li^{2+} , etc. Each has a ground state configuration of $1s^1$, meaning that its single electron exhibits a standing wave pattern governed by the quantum numbers $n=1$, $m=0$ and $l=0$, with the spin quantum number s undefined because there is no other electron to compare it with. All have simple emission spectra whose major features were adequately explained by Bohr's model.

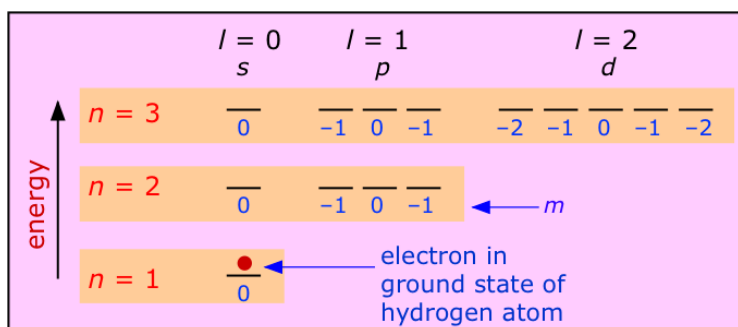


Fig. 14: Relative orbital energies in a one-electron atom

The most important feature of a single-electron atom is that the energy of the electron depends only on the principal quantum number n . As the above diagram shows, the quantum numbers l and m have no effect on the energy; we say that all orbitals having a given value of n are *degenerate*. Thus the emission spectrum produced by exciting the electron to the $n=2$ level consists of a single line, not four lines. The wavelength of this emission line for the atoms H , He^+ and Li^{2+} will diminish with atomic number because the greater nuclear charge will lower the energies of the various n levels. For the same reason, the energies required to remove an electron from these species increases rapidly as the nuclear charge increases, because the increasing attraction pulls the electron closer to the nucleus, thus producing an even greater attractive force.

5.2 Electron-electron repulsion

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, the continuum is seen to begin at a wavelength corresponding to an ionization energy of 2372 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.

Electron-electron repulsion is a major factor in both the spectra and chemical behavior of the elements heavier than hydrogen. In particular, it acts to “break the degeneracy” (split the energies) of orbitals having the same value of n but different l .

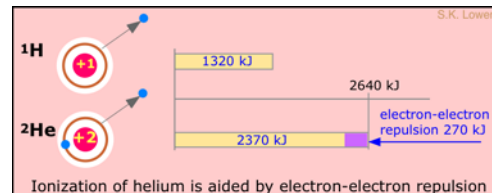
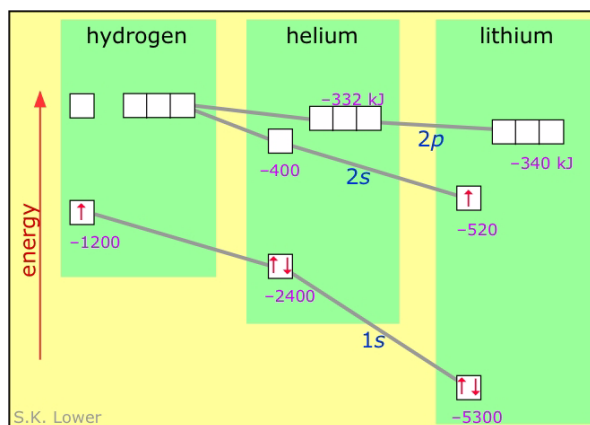


Fig. 15: Orbital energies in the first three elements

The numbers on this diagram show the energies of some orbitals in the atoms of H, He, and Li, relative to the 2s-2p orbitals of H. The energies of the 1s orbitals fall rapidly as Z increases. The fall in energies of the 2s orbitals is smaller owing to electron-electron repulsion. The 2p 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 2s orbitals.



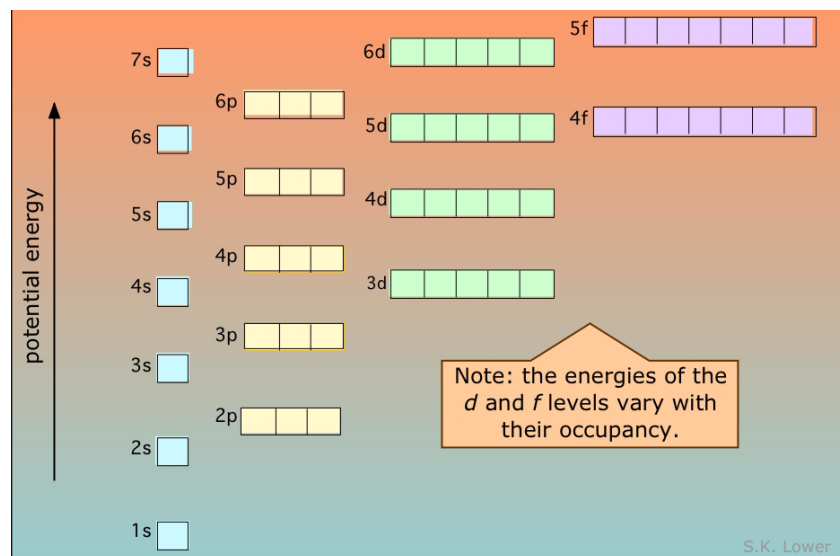


Fig. 16: Atomic orbital energy levels

This diagram shows how the energies of the *s*- and *p*-orbitals of different principal quantum numbers get split as the result of electron-electron repulsion. Notice the contrast with the similar diagram for one-electron atoms near the top of this page. The fact that electrons preferentially fill the lowest-energy empty orbitals is the basis of the rules for determining the electron configuration of the elements and of the structure of the periodic table.

5.3 The Aufbau rules

The German word *Aufbau* means “building up”, and this term has traditionally been used to describe the manner in which electrons are assigned to orbitals as we carry out the imaginary task of constructing the atoms of elements having successively larger atomic numbers. In doing so, we are effectively “building up” the periodic table of the elements, as we shall shortly see.

The preceding diagram illustrates the main idea here. Each orbital is represented as a little box that can hold up to two electrons having opposite spins, which we designated by upward- or downward-pointing arrows. Electrons fill the lowest-energy boxes first, so that additional electrons are forced into wave-patterns corresponding to higher (less negative) energies. Thus in the above diagram, the “third” electron of lithium goes into the higher-energy $2s$ orbital, giving this element an electron configuration which we write $1s^2 2s^1$.

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.
- For the first 18 elements, up to the point where the $3s$ and $3p$ levels are completely filled, this scheme is entirely straightforward and leads to electronic configurations which you are expected to be able to work out for each of these elements.

Problem Example 2

What is the electron configuration of the atom of phosphorus, atomic number 15?

Solution: The number of electrons filling the lowest-energy orbitals are:

1s: 2 electrons, 2s: 2 electrons; 2p: 6 electrons, 3s: 2 electrons. This adds up to 12 electrons. The remaining three electrons go into the 3p orbital, so the complete electron configuration of P is $1s^2 2s^2 2p^6 3s^2 3p^3$.

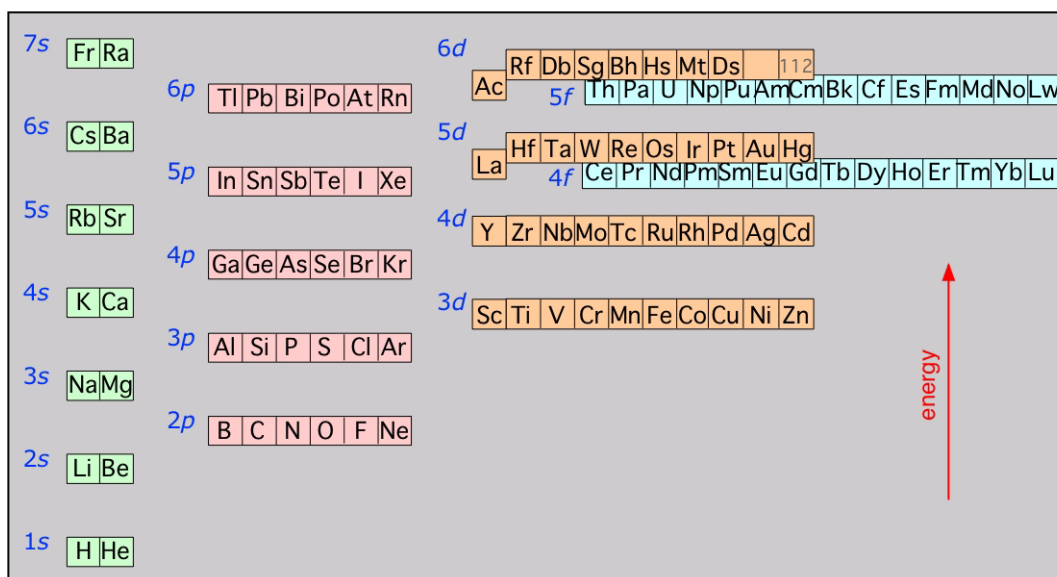


Fig. 17: Energies of highest occupied orbitals of the elements

This diagram illustrates the Aufbau rules as they are applied to all the elements. Note especially how the energies of the nd orbitals fall between the $(n-1)s$ and $(n-1)p$ orbitals so, for example the $3d$ orbitals begin to fill after the $4s$ orbital is filled, but before electrons populate the $4p$ orbitals. A similar relation exists with d - and f -orbitals.

It is very important that you understand this diagram and how it follows from the Pauli exclusion principle. You should be able to reproduce it from memory up to the $6s$ level, because it forms the fundamental basis of the periodic table of the elements.

Some complications involving d - and f -orbitals

Inspection of a table of electron configurations of the elements reveals a few apparent non-uniformities in the filling of the orbitals, as is illustrated below for the elements of the so-called first transition series in which the $3d$ orbitals are being populated. These anomalies are a consequence of the very small energy differences between some of the orbitals, and of the reduced electron-electron repulsion when electrons remain unpaired (*Hund's rule*), as is evident in chromium, which contains six unpaired electrons.

The other anomaly here 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 $4s$ orbital is normally slightly below the $3d$ 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. It gets even worse when f -orbitals begin to fill!

Because these relative energies can vary even for the same atom in different chemical environments, most instructors will not expect you to memorize them.

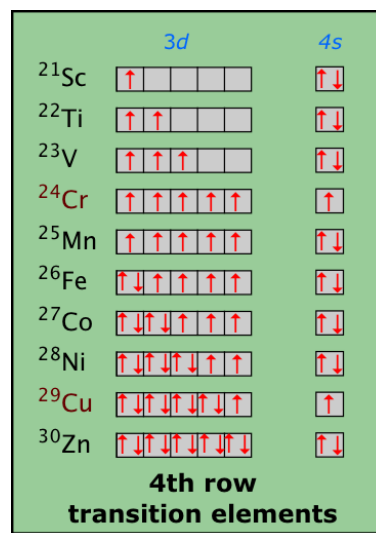


Fig. 18: $3d$ - $4s$ orbitals

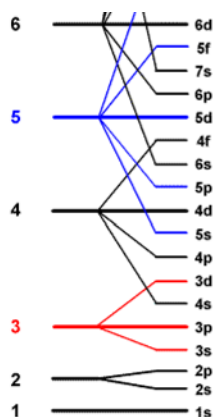


Fig. 19: Overlap of orbital energies

This diagram shows how the atomic orbitals corresponding to different principal quantum numbers become interspersed with one another at higher values of n . The actual situation is more complicated than this; calculations show that the energies of d and f orbitals vary with the atomic number of the element.

5.4 The periodic table

The relative orbital energies illustrated above and the Pauli exclusion principle constitute the fundamental basis of the periodic table of the elements which was of course worked out empirically late in the 19th century, long before electrons had been heard of.

IA 1	"representative elements"										IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIA 18		
H	Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB 3		IVB 4	VB 5	VIB 6	VIIA 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Cs	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Rb	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	"main group elements"								
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Lanthanides		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Actinides		

S.K. Lower

Fig. 20: Organization of the periodic table

The periodic table of the elements is conventionally divided into sections called *blocks*, each of which designates the type of "sub-orbital" (*s*, *p*, *d*, *f*) which contains the highest-energy electrons in any particular element. Note especially that

- The non-metallic elements occur only in the *p*-block;
- The *d*-block elements contain the so-called transition elements;
- The *f*-block elements go in between Groups 3 and 4 of the *d*-block.

The above diagram illustrates the link between the electron configurations of the elements and the layout of the periodic table. Each row, also known as a *period*, commences with two *s*-block elements 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. At n values of 2 and 3, *d*- and *f*-block element sequences are added.

The table shown above is called the *long form* of the periodic table; for many purposes, we can use a "short form" table in which the *d*-block is shown below the *s*- and *p*-block "representative elements" and the *f*-block does not appear at all. Note that the "long form" would be even longer if the *f*-block elements were shown where they actually belong, between La-Hf and Ac-Db.

Check your understanding of this chapter

- State the principle feature of that distinguishes the energies of the excited states of a single-electron atom from atoms containing more than one electron.
- Explain why the first ionization energy of the helium atom is smaller than twice the first ionization of the hydrogen atom.
- Be able to write a plausible electron configuration for any atom having an atomic number less than 90.

6 • Chemical periodicity

As you saw in the illustration of the periodic table on the preceding page, the two *f* blocks are written at the bottom merely to keep the table from becoming inconveniently wide; these two blocks actually go in between La-Hf and Ac-Db, respectively, in the *d* block.

6.1 More on the organization of the periodic table

To understand how the periodic table is organized, imagine that we write down a long horizontal list of the elements in order of their increasing atomic number. It would begin this way:

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca...

Now if we look at the various physical and chemical properties of these elements, we would find that their values tend to increase or decrease with Z in a manner that reveals a repeating pattern—that is, a periodicity. For the elements listed above, these breaks can be indicated by the vertical bars as shown here:

H He | Li Be B C N O F Ne | Na Mg Al Si P S Cl Ar | K Ca ...

Periods

To construct the table, we place each sequence in a separate row, which we call a *period*. The rows are aligned in such a way that the elements in each vertical column possess certain similarities. Thus the first short period elements H and He are chemically similar to the elements Li and Ne at the beginning and end of the second period, the first period is split in order to place H above Li and He above Ne.

The “block” nomenclature shown in 20 refers to the *sub-orbital type* (quantum number l , or *s-p-d-f* classification) of the highest-energy orbitals that are occupied in a given element. 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 the second period ($n=2$) 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.

Groups

Each column of the periodic table is known as a *group*. The elements belonging to a given group bear a strong similarity in their chemical behaviors.

In the past, two different systems of Roman numerals and letters were used to denote the various groups. North Americans added the letter *B* to denote the *d*-block groups and *A* for the others; this is the system shown in 20.) The rest of the world adopted *A* for the *d*-block ele-

ments and *B* for the others. In 1985, a new international system was adopted in which the columns were simply labeled 1-18. 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.

Families

Chemists have long found it convenient to refer to the elements of different groups, and in some cases of spans of groups by the names indicated in the table shown below. The two of these that are most important for you to know are the *noble gases* and the *transition metals*.

IA 1	IIA 2	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18
H	He	B	C	N	O	F	Ne
Li	Be	Al	Si	P	S	Cl	Ar
Na	Mg	Zn	Ga	Ge	As	Se	Br
K	Ca	Sc	Ti	V	Cr	Mn	Fe
Cs	Sr	Y	Zr	Nb	Mo	Tc	Ru
Rb	Ba	La	Hf	Ta	W	Re	Os
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs
		Ce	Pr	Nd	Pm	Sm	Eu
		Th	Pa	U	Np	Pu	Am
		Tm	Yb	Lu			
		Er	Dy	Tb	Gd	Sm	Pm
		No	Md	Fm	Es	Cf	Bk
		Lr					

Fig. 21: Element families

6.2 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 of which consists of the highest-principal quantum number orbitals (always *s*- and *p*-orbitals) that contain at least one electron. 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. The principal simplification here is that it deals only with the main group elements of the *s*- and *p*-blocks, omitting the *d*- and *f*-block elements whose properties tend to be less closely tied to their group numbers.

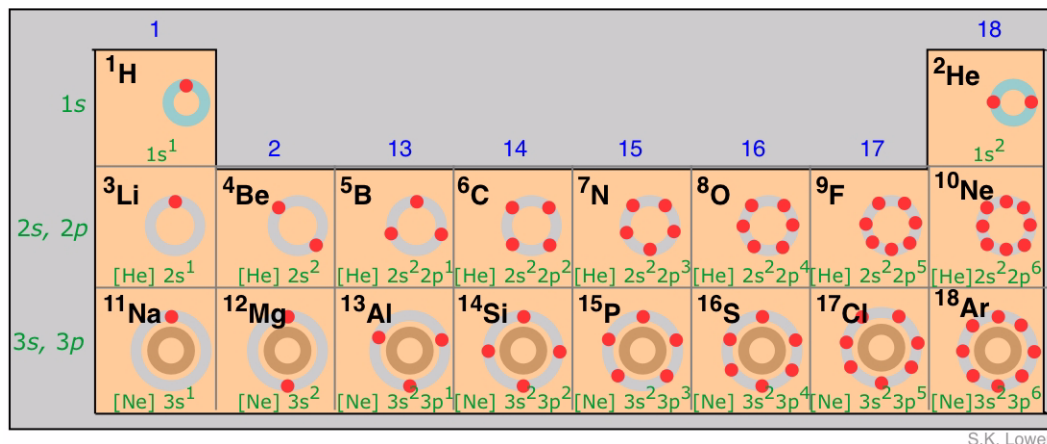


Fig. 22: Shell model of the atom

The red dots depict the electrons in the outermost shells of the first eighteen elements.

The electrons in the outer-most shell of an atom are the ones that interact most readily with other atoms, and thus play a major role in governing the chemistry of an element. Notice the use of noble-gas symbols to simplify the electron-configuration notation.

In particular, the number of outer-shell electrons (which is given by the rightmost digit in the group number) is a major determinant of an element's "combining power", or *valence*. The general trend is for an atom to gain or lose electrons, either directly (leading to formation of ions) or by sharing electrons with other atoms so as to achieve an outer-shell configuration of s^2p^6 . This configuration, known as an *octet*, corresponds to that of one of the noble-gas elements of Group 18.

- the elements in Groups 1, 2 and 13 tend to give up their valence electrons to form positive ions such as Na^+ , Mg^{2+} and Al^{3+} , as well as compounds NaH , MgH_2 and AlH_3 . The outer-shell configurations of the metal atoms in these species correspond to that of neon.
- elements in Groups 15-17 tend to acquire electrons, forming ions such as P^{3-} , S^{2-} and Cl^- or compounds such as PH_3 , H_2S and HCl . The outer-shell configurations of the P, S, and Cl atoms correspond to that of argon.
- the Group 14 elements do not normally form ions at all, but share electrons with other elements in tetravalent compounds such as CH_4 .

The above diagram shows the first three rows of what are known as the *representative elements*— that is, the *s*- and *p*-block elements only. As we move farther down (into the fourth row and below), the presence of *d*-electrons exerts a complicating influence which allows elements to exhibit multiple valences. This effect is especially noticeable in the transition-metal elements, and is the reason for not including the *d*-block with the representative elements at all.

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 the atomic number 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 $Z_{\text{effective}}$ is due to 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 or “screening” effect on the valence electrons.

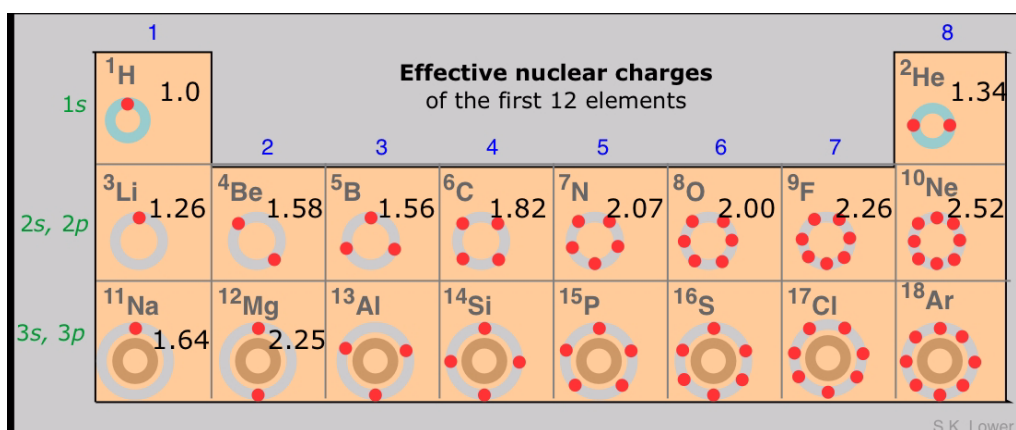


Fig. 23:
effective nuclear
charge

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.

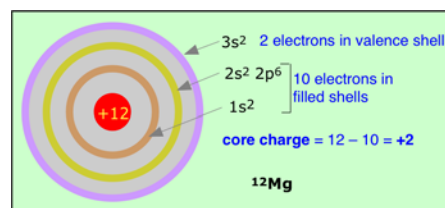
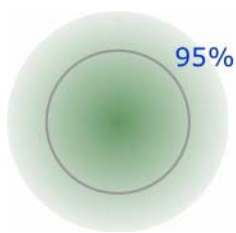


Fig. 24: Core charge

6.3 Sizes of atoms and ions

What do we mean by the “size” of an atom?



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; the best we can do is to define a spherical shell within whose radius some arbitrary percentage of the electron density can be found.

When an atom is combined with other atoms in a solid element or compound, an effective radius can be determined by observing the distances between adjacent rows of atoms in these solids. This is most commonly carried out by X-ray scattering experiments. Because of the different ways in which atoms can aggregate together, several different kinds of atomic radii can be defined.

Distances on the atomic scale have traditionally been expressed in Ångstrom units

($1\text{Å} = 10^{-8}\text{ cm}$), but nowadays the picometer is preferred;

$1\text{ pm} = 10^{-12}\text{ m} = 10^{-10}\text{ cm} = 100\text{ Å}$. The radii of atoms and ions are typically in the range 70-400 pm.

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 $2r$. 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 .

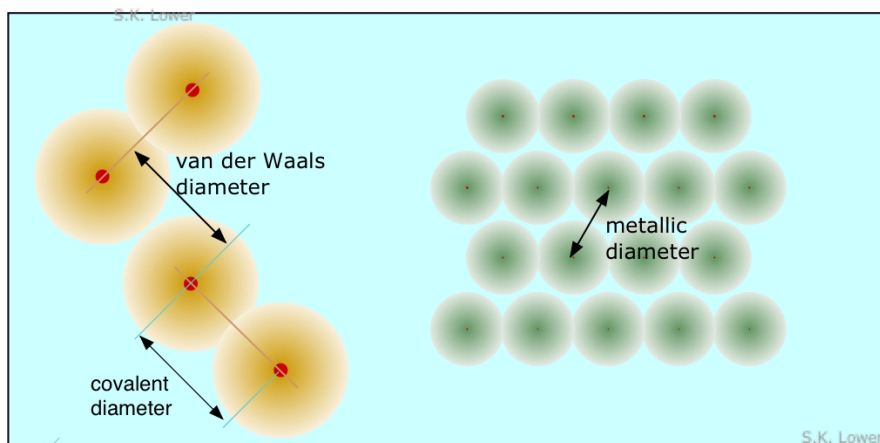
Although the radius of an atom or ion cannot be measured directly, in most cases it can only be inferred from measurements of the distance between adjacent nuclei in a crystalline solid. This is most commonly carried out by X-ray scattering experiments. Because such solids fall into several different classes, several kinds of atomic radius are defined. 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 such as NaCl .

Fig. 25: Atomic radii

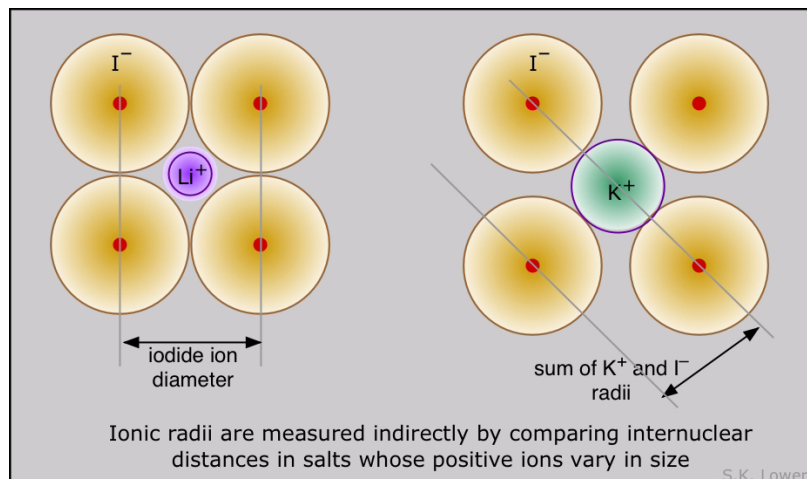
The **metallic radius** is half the distance between nuclei in a metallic crystal.

The **covalent radius** is half the distance between like atoms that are bonded together in a molecule.

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.



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 portions 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.

**Fig. 26: Ionic radii**

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

Periodic trends in atomic size

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.

Fig. 27: Covalent radii

The covalent radii are represented by the sizes of the circles. 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 estimates from those of nearby elements.

Covalent radii - pm																	
3.7 H																	.93 He
13.4 Li	9.0 Be											.82 B	.87 C	.75 N	.73 O	.72 F	1.31 Ne
15.4 Na	13.0 Mg											1.18 Al	1.11 Si	1.06 P	1.02 S	.99 Cl	1.74 Ar
19.6 K	17.4 Ca	14.4 Sc	13.6 Ti	V	Cr	Mn	Fe	Co	Ni	1.38 Cu	1.31 Zn	1.26 Ga	1.22 Ge	1.19 As	1.16 Se	1.14 Br	1.74 Kr
21.1 Rb	19.2 Sr	16.2 Y	14.8 Zr	Nb	Mo	Tc	Ru	Rh	Pd	15.3 Ag	14.8 Cd	14.4 In	14.1 Sn	13.8 Sb	13.5 Te	13.3 I	20.9 Xe
22.5 Cs	19.8 Ba	16.9 La	Hf	Ta	W	Re	Os	Ir	Pt	15.0 Au	14.9 Hg	14.8 Tl	14.7 Pb	14.6 Bi	Po	At	21.4 Rn

Comparison of covalent and 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.

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.

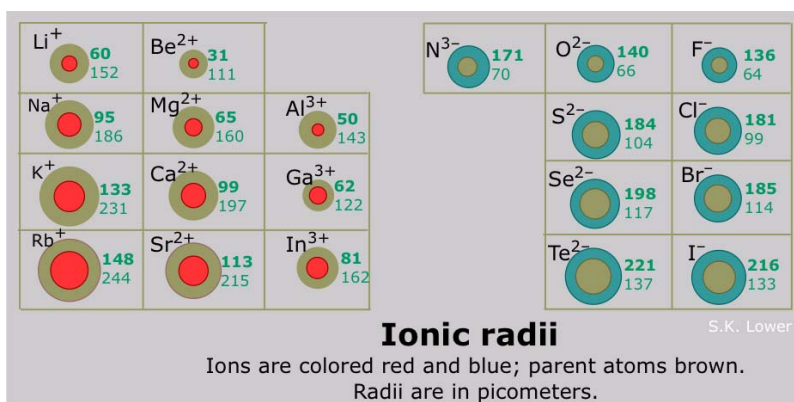


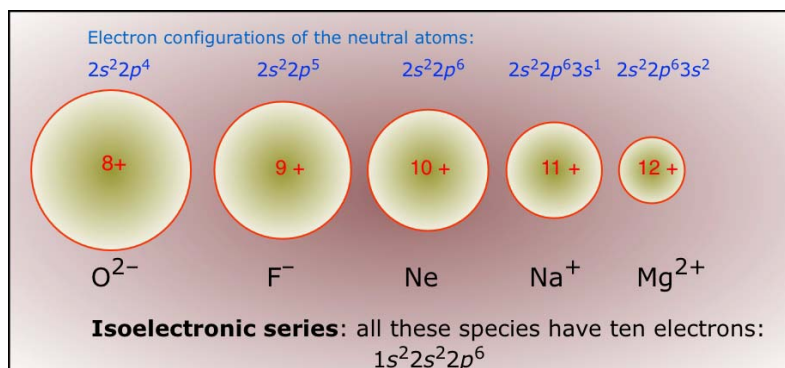
Fig. 28: Atomic and ionic radii compared

Positive ions are always smaller than their parent ions, while negative ions are larger. The differences in each case are due to changes in electron-electron repulsion and, in some cases, to changes in the number of occupied shells.

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. Of course, only one member of such a sequence can be a neutral atom (neon in the series shown below.) The effect of increasing nuclear charge on the radius is clearly seen.

Fig. 29: An isoelectronic series

Each of the species shown here has the electronic configuration of neon; only the nuclear charges (atomic numbers Z) are different.

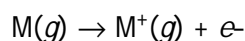


6.4 Periodic trends in ion formation

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, lose or share 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 exothermic process



in which $M(g)$ stands for any isolated (gaseous) atom.

An atom has as many ionization energies as it has electrons. Electrons are always removed from the highest-energy occupied orbital. An examination of the successive ionization energies of the first ten elements (right) provides experimental confirmation that the binding of the two innermost electrons ($1s$ orbital) is significantly different from that of the $n=2$ electrons. Successive ionization energies of an atom increase rapidly as reduced electron-electron repulsion causes the electron shells to contract, thus binding the electrons even more tightly to the nucleus. Notice especially the large jumps in energy required to remove electrons from the $n=1$ shells from atoms of the second-row elements (Li-Ne).

	H	He	Li	Be	B	C	N	O	F	Ne
E1	1.3	2.4	0.5	0.9	0.8	1.1	1.4	1.3	1.7	2.1
E2		5.3	7.3	1.7	2.4	2.3	2.8	3.4	3.4	4.0
E3			12	15	3.7	4.6	4.6	5.3	6.0	6.1
E4				21	25	6.2	7.5	7.5	8.4	9.4
E5					33	38	9.4	11	11	12
E6						47	53	13	15	15
E7							64	71	18	19
E8								84	92	23
E9									106	115
E10										130

Fig. 30: Successive ionization energies (MJ/mol)

Ionization energies increase with the nuclear charge Z as we move across the periodic table. 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 .

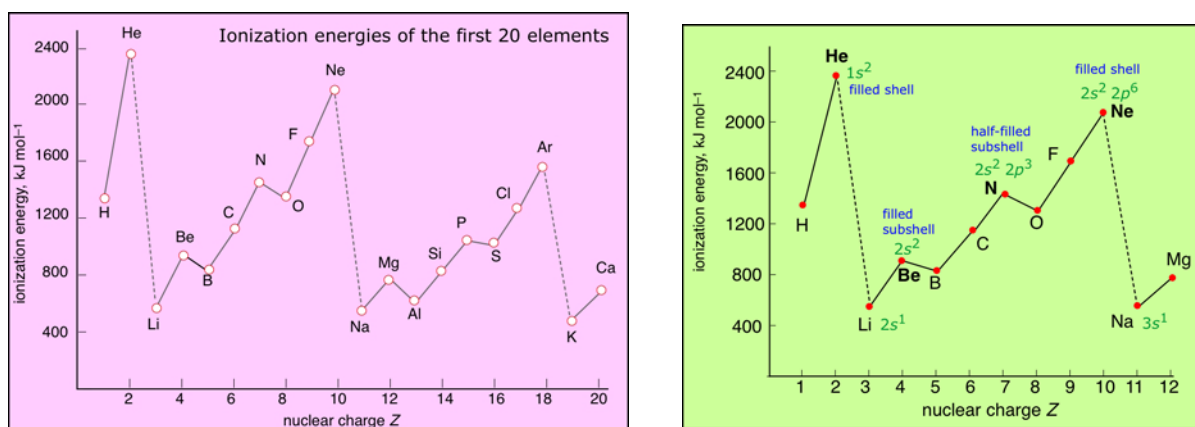


Fig. 31: Ionization energies as a function of Z

The more detailed plot on the right reveals some interesting irregularities that can be related to the slightly lower energies (greater stabilities) of electrons in half-filled (spin-unpaired) and completely-filled subshells.

Finally, a more comprehensive survey of the ionization energies of all the main group elements is shown below.

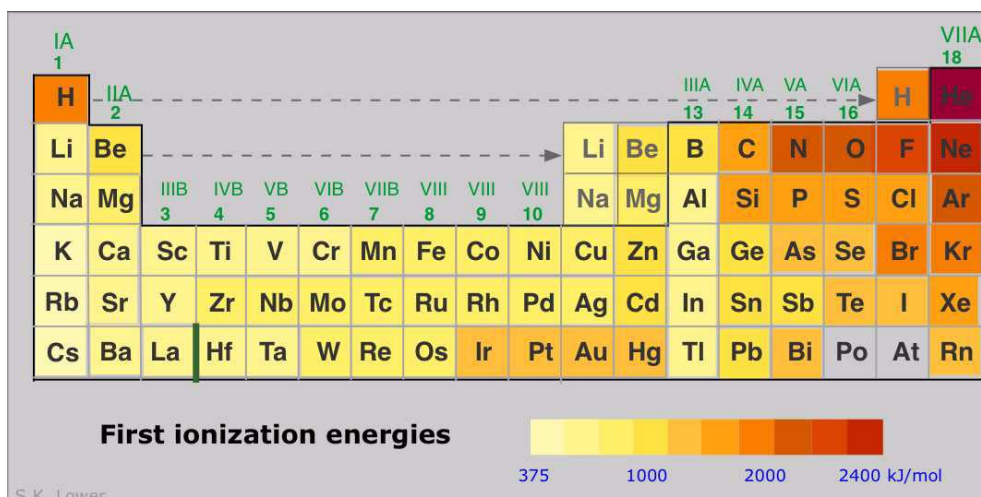


Fig. 32: Periodic trends in ionization energies

Some points to note:

- The noble gases have the highest IE's of any element in the period. This has nothing to do with any mysterious "special stability" of the noble gas s^2p^6 electron configuration; it is simply a matter of the high nuclear charges acting on more contracted orbitals.
- IE's (as well as many other properties) tend not to vary greatly amongst the *d*-block elements. This reflects the fact that as the more-compact *d* orbitals are being filled, they exert a screening effect that partly offsets that increasing nuclear charge on the outermost *s* orbitals of higher principal quantum number.
- Each of the Group 13 elements has a lower first-IE than that of the element preceding it. The reversal of the IE trend in this group is often attributed to the more easy removal of the single outer-shell *p* electron compared to that of electrons contained in filled (and thus spin-paired) *s*- and *d*-orbitals in the preceding elements.

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 released is a measure of the *electron affinity* of the atom. For some atoms, the electron affinity appears to be slightly negative, suggesting that electron-electron repulsion is the dominant factor in these instances.

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.

Fig. 33: Electron affinities of the elements

Electron affinities in kJ released per mole of mononegative ions formed																																		
IA 1	IIA 2												IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18																
H 73	Li 60	Be -19											B 27	C 122	N -7	O 141	F 328	Ne -21																
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 16	Fe 64	Ni 112	Cu 118	Zn -47	Ga 29	Ge 116	As 78	Se 195	Br 325	Kr -39										
Cs 47	Sr 30	Y 41	Zr 86	Nb 72	Mo 53	Tc 101	Ru 110	Rh 54	Pd 126	Ag -32	Cd 29	In 116	Sn 103	Sb 190	Te 295	I -41	Xe -41	Rb 45	Ba 31	La 79	Hf 14	Ta 106	W 101	Os 205	Ir 223	Pt -61	Au 20	Hg 35	Tl 91	Pb 183	Bi 270	Po -41	At -41	Rn -41
Fr 44	Ra	Ac	Db	Jl	Rf	Bh	Hn	Mt																										

S.K. Lower

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.

Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more *electronegative*. 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 here, 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.

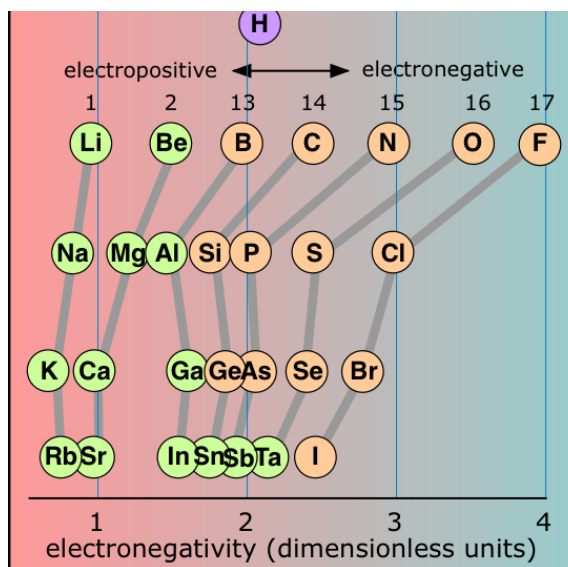


Fig. 34: Electronegativities

The location of **hydrogen** on this scale reflects some of the significant chemical properties of this element. Although it acts like a metallic element in many respects (forming a positive ion, for example), it can also form hydride-ion (H^-) solids with the more electropositive elements, and of course its ability to share electrons with carbon and other *p*-block elements gives rise to a very rich chemistry, including of course the millions of organic compounds.

Check your understanding of this chapter

- You should be able to sketch out the **general form of the periodic table** and identify the various *blocks* and identify the *groups* corresponding to the *alkali metals*, the *transition elements*, the *halogens*, and the *noble gases*.
- For the first eighteen elements, you should be able to **predict the formulas of typical binary compounds** they can be expected to form with hydrogen and with oxygen.
- Comment on the concept of the “**size**” of an atom, and give examples of how radii are defined in at least two classes of substances.
- Define *ionization energy* and *electron affinity*, and explain the periodic general trends.
- State the meaning and significance of *electronegativity*.