# An Introduction to the Electronic Structure of Atoms and Molecules

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# CHAPTER OVERVIEW

## 1: The Nature of the Problem

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# 1.1: Introduction

The understanding and prediction of the properties of matter at the atomic level represents one of the great achievements of twentieth-century science. The theory developed to describe the behavior of electrons, atoms and molecules differs radically from familiar Newtonian physics, the physics governing the motions of macroscopic bodies and the physical events of our everyday experiences. The discovery and formulation of the fundamental concepts of atomic physics in the period 1901 to 1926 by such men as Planck, Einstein, de Broglie and Heisenberg caused what can only be described as a revolution in the then-accepted basic concepts of physics.

The new theory is called quantum theory or quantum mechanics. As far as we now know this theory is able to account for all observable behaviour of matter and, with suitable extensions, for the interaction of matter with light. The proper formulation of quantum mechanics and its application to a specific problem requires a rather elaborate mathematical framework, as do proper statements and applications of Newtonian physics. We may, however, in this introductory account acquaint ourselves with the critical experiments which led to the formulation of quantum mechanics and apply the basic concepts of this new mechanics to the study of electrons.

Specifically the problem we set ourselves is to discover the physical laws governing the behaviour of electrons and then apply these laws to determine how the electrons are arranged when bound to nuclei to form atoms and molecules. This arrangement of electrons is termed the electronic structure of the atom or molecule. Furthermore, we shall discuss the relationship between the electronic structure of an atom and its physical properties, and how the electronic structure is changed during a chemical reaction.

Rutherford's nuclear model for the atom set the stage for the understanding of the structure of atoms and the forces holding them together.

From Rutherford's alpha-scattering experiments it was clear that the atom consisted of a positively-charged nucleus with negatively-charged electrons arranged in some fashion around it, the electrons occupying a volume of space many times larger than that occupied by the nucleus. (The diameters of nuclei fall in the range of l ´ 10-12 ® 1 ´ 10-13 cm, while the diameter of an atom is typically of the order of magnitude of 1 ´ 10-8 cm.) The forces responsible for binding the atom, and in fact all matter (aside from the nuclei themselves), are electrostatic in origin: the positively-charged nucleus attracts the negatively-charged electrons. There are attendant magnetic forces which arise from the motions of the charged particles. These magnetic forces give rise to many important physical phenomena, but they are smaller in magnitude than are the electrostatic forces and they are not responsible for the binding found in matter.

During a chemical reaction only the number and arrangement of the electrons are changed, the nucleus remaining unaltered. The unchanging charge of the atomic nucleus is responsible for retaining the atom's chemical identity through any chemical reaction. Thus for the purpose of understanding the chemical properties and behaviour of atoms, the nucleus may be regarded as simply a point charge of constant magnitude for a given element, giving rise to a central field of force which binds the electrons to the atom.

Rutherford proposed his nuclear model of the atom in 1911, some fifteen years before the formulation of quantum mechanics. Consequently his model, when first proposed, posed a dilemma for classical physics. The nuclear model, based as it was on experimental observations, had to be essentially correct, yet all attempts to account for the stability of such a system using Newtonian mechanics ended in failure.

According to Newtonian mechanics we should be able to obtain a complete solution to the problem of the electronic structure of atoms once the nature of the force between the nucleus and the electron is known. The electrostatic force operative in the atom is well understood and is described by Coulomb's law, which states that the force between two particles with charges $e_1$ and $e_2$ separated by a distance $R$ is given by:

$$F \propto \frac{e_1 e_2}{R^2}$$

There is a theorem of electrostatics which states that no stationary arrangement of charged particles can ever be in electrostatic equilibrium, i.e., be stable to any further change in their position. This means that all the particles in a collection of positively and negatively charged species will always have resultant forces of attraction or repulsion acting on them no matter how they are arranged in space. Thus no model of the atom which invokes some stationary arrangement of the electrons around the nucleus is possible. The electrons must be in motion if electrostatic stability is to be preserved. However, an electron moving in the field of a nucleus experiences a force and, according to Newton's second law of motion, would be accelerated. The laws of electrodynamics state that an accelerated charged particle should emit light and thus continuously lose energy. In this dynamical model of the atom,

all of the electrons would spiral into the nucleus with the emission of light and all matter would collapse to a much smaller volume, the volume occupied by the nuclei.

No one was able to devise a theoretical model based on Newtonian, or what is now called classical mechanics, which would explain the electrostatic stability of atoms. The inescapable conclusion was that the classical equations of motion did not apply to the electron. Indeed, by the early 1900's a number of physical phenomena dealing with light and with events on the atomic level were found to be inexplicable in terms of classical mechanics. It became increasingly clear that Newtonian mechanics, while predicting with precision the motions of masses ranging in size from stars to microscopic particles, could not predict the behavior of particles of the extremely small masses encountered in the atomic domain. The need for a new set of laws was indicated.

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# 1.2: Some Important Experiments with Electrons and Light

Certainly the early experiments on the properties of electrons did not suggest that any unusual behaviour was to be expected. Everything pointed to the electron being a particle of very small mass. The trajectory of the electron can be followed in a device such as a Wilson cloud chamber. Similarly, a beam of electrons generated by passing a current between two electrodes in a glass tube from which the air has been partially evacuated will cast the shadow of an obstacle placed in the path of the beam. Finally, the particle nature of the electron was further evidenced by the determination of its mass and charge.

Just as classical considerations placed electrons in the realm of particles, the same classical considerations placed light in the realm of waves with equal certainty. How can one explain diffraction effects without invoking wave motion?

In the years from 1905 to 1928 a number of experiments were performed which could be ***interpreted by classical mechanics*** only if it was assumed that electrons possessed a wave motion, and light was composed of a stream of particles! Such dualistic descriptions, ascribing both wave and particle characteristics to electrons or light, are impossible in a physical sense. The electron must behave either as a particle or a wave, but not both (assuming it is either). "Particle" and "wave" are both concepts used by ordinary or classical mechanics and we see the paradox which results when classical concepts are used in an attempt to describe events on an atomic scale. We shall consider just a few of the important experiments which gave rise to the classical explanation of dual behaviour for the description of electrons and light, a description which must ultimately be abandoned.

## The Photoelectric Effect

Certain metals emit electrons when they are exposed to a source of light. This is called the photoelectric effect. The pertinent results of this experiment are

i. The number of electrons released from the surface increases as the intensity of he light is increased, but the energies of the emitted electrons are independent of the intensity of the light.
ii. No electrons are emitted from the surface of the metal unless the frequency of the light is greater than a certain minimum value. When electrons are ejected from the surface they exhibit a range of velocities, from zero up to some maximum value. The energy of the electrons with the maximum velocity is found to increase linearly with an increase in the frequency of the incident light.

The first result shows that light cannot be a wave motion in the classical sense. As an analogy, consider waves of water striking a beach and hitting a ball (in place of an electron) at the water's edge. The intensity of a wave is proportional to the square of the amplitude (or height) of the wave. Certainly, even when the frequency with which the waves strike the beach remains constant, an increase in the amplitude of the waves will cause much more energy to be released when they strike the beach and hit the ball. Yet when light "waves" strike a substance only the number of emitted electrons increases as the intensity is increased; the energy of the most energetic electrons remains constant. This can be explained only if it is assumed that the energy in a beam of light is not transmitted in the manner characteristic of a wave, but rather that the energy comes in bundles or packets and that the size of the packet is determined by the frequency of the light. This explanation put forward by Einstein in 1905 relates the energy to the frequency - and not to the intensity of the light - as required by the experimental results. A packet of light energy is called a photon. The results of the photoelectric experiment show that the energy e of a photon is directly proportional to the frequency n of the light, or, calling the constant of proportionality h, we have:

$$\varepsilon = h v \tag{1.2.1}$$

Since the electron is bound to the surface of the metal, the photon must possess a certain minimum amount of energy, i.e., possess a certain minimum frequency $n_o$, just sufficient to free the electron from the metal. When an electron is ejected from the surface by a photon with a frequency greater than this minimum value, the energy of the photon in excess of the minimum amount appears as kinetic energy of the electron. Thus:

$$kinetic\ energy\ of\ electron = h v - h v_0 \tag{1.2.2}$$

where *hn* is the energy of the photon with frequency *n*, and *hn*$_o$ is the energy of the photon which is just sufficient to free the electron from the metal. Experimentally we can measure the kinetic energy of the electrons as a function of the frequency *n*. A plot of the kinetic energy versus the frequency gives a straight line whose slope is equal to the value of *h*, the proportionality constant. The value of *h* is found to be 6.6 ´ 10$^{-27}$ erg sec.

Equation 1.2.1 is revolutionary. It states that the energy of a given frequency of light cannot be varied continuously, (Click here for note.) as would be the case classically, but rather that it is fixed and comes in packets of a discrete size. The energy of light is said to be quantized and a photon is one quantum (or bundle) of energy.

It is tempting at this point, if we desire a classical picture of what is happening, to consider each bundle of light energy, that is, each photon, to be an actual particle. Then one photon, on striking an individual electron, scatters the electron from the surface of the metal. The energy originally in the photon is converted into the kinetic energy of the electron (minus the energy required for the electron to escape from the surface). This picture must not be taken literally, for then the diffraction of light is inexplicable. Nor, however, can the wave picture for diffraction be taken literally, for then the photoelectric effect is left unexplained. In other words, light behaves in a different way from ordinary particles and waves and requires a special description.

The constant $h$ determines the size of the light quantum. It is termed Planck's constant in honour of the man who first postulated that energy is not a continuously variable quantity, but occurs only in packets of a discrete size. Planck proposed this postulate in 1901 as a result of a study of the manner in which energy is distributed as a function of the frequency of the light emitted by an incandescent body. Planck was forced to assume that the energies of the oscillations of the electrons in the incandescent matter, which are responsible for the emission of the light, were quantized. Only in this way could he provide a theoretical explanation of the experimental results. There was a great reluctance on the part of scientists at that time to believe that Planck's revolutionary postulate was anything more than a mathematical device, or that it represented a result of general applicability in atomic physics. Einstein's discovery that Planck's hypothesis provided an explanation of the photoelectric effect as well indicated that the quantization of energy was indeed a concept of great physical significance. Further examples of the quantization of energy were soon forthcoming, some of which are discussed below.

## The Diffraction of Electrons

Just as we have found dualistic properties for light when its properties are considered in terms of classical mechanics, so we find the same dualism for electrons. From the early experiments on electrons it was concluded that they were particles. However, a beam of electrons, when passed through a suitable grating, gives a diffraction pattern entirely analogous to that obtained in diffraction experiments with light. In other words, not only do electrons and light both appear to behave in completely different and strange ways when considered in terms of our everyday physics, they both appear to behave in the same way! Actually, the same strange behaviour can be observed for protons and neutrons. All the fundamental particles and light exhibit behaviour which leads to conflicting conclusions when classical mechanics is used to interpret the experimental findings.

The diffraction experiment with electrons was carried out at the suggestion of de Broglie. In 1923 de Broglie reasoned that a relationship should exist between the "particle" and "wave" properties for light. If light is a stream of particles, they must possess momentum. He applied to the energy of the photon Einstein's equation for the equivalence between mass and energy:

$$\varepsilon = mc^2$$

where $c$ is the velocity of light and $m$ is the mass of the photon. Thus the momentum of the photon is $mc$ and:

$$\varepsilon = momentum \times c$$

If light is a wave motion, then of course it possesses a characteristic frequency $n$ and wavelength l which are related by the equation:

$$v = \frac{c}{\lambda}$$

The frequency and wavelength may be related to the energy of the photon by using Einstein's famous relationship:

$$\varepsilon = hv = \frac{hc}{\lambda}$$

By equating the two expressions for the energy:

$$\frac{hc}{\lambda} = momentum \times c$$

de Broglie obtained the following relationship which bears his name:

$$\lambda = \frac{h}{momentum} \tag{1.2.3}$$

However, de Broglie did not stop here. It was he who reasoned that light and electrons might behave in the same way. Thus a beam of electrons, each of mass *m* and with a velocity *u* (and hence a momentum *mu*) should exhibit diffraction effects with an apparent wavelength:

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

Using de Broglie's relationship, we can calculate that an electron with a velocity of $1 \times 10^9$ cm/sec should have a wavelength of approximately $1 \times 10^{-8}$ cm. This is just the order of magnitude of the spacings between atoms in a crystal lattice. Thus a crystal can be used as a diffraction grating for electrons. In 1927 Davisson and Germer carried out this very experiment and verified de Broglie's prediction. (See Problem 1 at the end of this section.)

## Line Spectra

A gas will emit light when an electrical discharge is passed through it. The light may be produced by applying a large voltage across a glass tube containing a gas at a low pressure and fitted with electrodes at each end. A neon sign is an example of such a "discharge tube." The electrons flowing through the tube transfer some of their energy to the electrons of the gaseous atoms. When the atomic electrons lose this extra energy and return to their normal state in the atom the excess energy is emitted in the form of light. Thus the gaseous atoms serve to transform electrical energy into the energy of light. The puzzling feature of the emitted light is that when it is passed through a diffraction grating (or a prism) to separate the light according to its wavelength, only certain wavelengths appear in the spectrum. Each wavelength appears in the spectrum as a single narrow line of coloured light, the line resulting from the fact that the emitted light is passed through a narrow slit (thus producing a thin "line" of light) before striking the grating or the prism and being diffracted. Thus a "line" spectrum rather than a continuous spectrum is obtained when atomic electrons are excited by an electrical discharge.

An example of such a spectrum is given in Fig. 1-1, which illustrates the visible spectrum observed for the hydrogen atom. This spectrum should be contrasted with the more usual continuous spectrum obtained from a source of white light which consists of a continuous band of colours ranging from red at the long wavelength end to violet at short wavelengths.
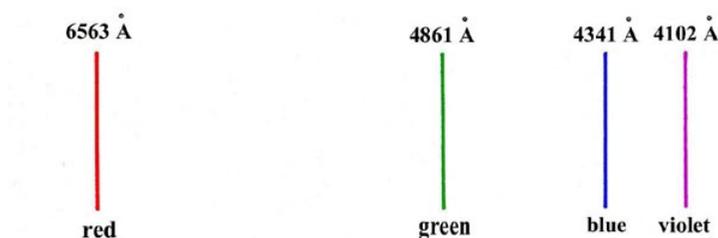


Fig. 1-1. The visible spectrum for hydrogen atoms (1Å = 1 Ångstrom = $1 \times 10^{-8}$ cm)

The energy lost by an electron as it is attracted by the nucleus appears in the form of light. If all energies were possible for an electron when bound to an atom, all wavelengths or frequencies should appear in its emission spectrum, i.e., a continuous spectrum should be observed. The fact that only certain lines appear implies that only certain values for the energy of the electron are possible or allowed. We could describe this by assuming that the energy of an electron bound to an atom is quantized. The electron can then lose energy only in fixed amounts corresponding to the difference in value between two of the allowed or quantized energy values of the atom. Since the energy of a photon is given by

$\varepsilon = hv$

and e must correspond to the difference between two of the allowed energy values for the electron, say *E* and *E'* {*E'* > *E*), then the value of the corresponding frequency for the photon will be given by

$$\frac{E' - E}{h} = v = \frac{\varepsilon}{h} \tag{1.2.4}$$

Obviously, if only certain values of *E* are allowed, only certain values of e or *n* will be observed, and a line spectrum rather than a continuous spectrum (which contains all values of *n*) will be observed.

Equation 1.2.4 was put forward by Bohr in 1913 and is known as Bohr's frequency condition. It was Bohr who first suggested that atomic line spectra could be accounted for if we assume that the energy of the electron bound to an atom is quantized. Thus the parallelism between the properties of light and electrons is complete. Both exhibit the wave-particle dualism and the energies of both are quantized.

## The Compton Effect

The results of one more experiment will play an important role in our discussions of the nature of electrons bound to an atom. The experiment concerns the direct interaction of a photon and an electron.

In order to determine the position of an object we must somehow "see" it. This is done by reflecting or scattering light from the object to the observer's eyes. However, when observing an object as small as the electron we must consider the interaction of an individual photon with an individual electron. It is found experimentally and this is the Compton effect that when a photon is scattered by an electron, the frequency of the emergent photon is lower than it was before the scattering. Since e = $hn$, and $n$ is observed to decrease, some of the photon's energy has been transmitted to the electron. If the electron was initially free, the loss in the energy of the photon would appear as kinetic energy of the electron. From the law of conservation of energy,

$$h v - h v' = \tfrac{1}{2} m v^2 = kinetic\ energy\ of\ electron$$

where $n'$ is the frequency of the photon after collision with the electron. This experiment brings forth a very important effect in the making of observations on the atomic level. We cannot make an observation on an object without at the same time disturbing the object. Obviously, the electron receives a kick from the photon during the observation. While it is possible to determine the amount of energy given to the electron by measuring $n$ and $n'$, we cannot however, predict in advance the final momentum of the electron. A knowledge of the momentum requires a knowledge of the direction in which the electron is scattered after the collision and while this can be measured experimentally one cannot predict the outcome of any given encounter. We shall illustrate later, with the aid of a definite example, that information regarding both the position and the momentum of an electron cannot be obtained with unlimited accuracy. For the moment, all we wish to draw from this experiment is that we must be prepared to accept a degree of uncertainty in the events we observe on the atomic level. The interaction of the observer with the system he is observing can be ignored in classical mechanics where the masses are relatively large. This is not true on the atomic level as here the "tools" employed to make the observation necessarily have masses and energies comparable to those of the system we are observing.

In 1926 Schrödinger, inspired by the concept of de Broglie's "matter waves," formulated an equation whose role in solving problems in atomic physic's corresponds to that played by Newton's equation of motion in classical physics. This single equation will correctly predict all physical behaviour, including, for example, the experiments with electrons and light discussed above. Quantization follows automatically from this equation, now called Schrödinger's equation, and its solution yields all of the physical information which can be known about a given system. Schrödinger's equation forms the basis of quantum mechanics and as far as is known today the solutions to all of the problems of chemistry are contained within the framework of this new mechanics. We shall in the remainder of this site concern ourselves with the behaviour of electrons in atoms and molecules as predicted and interpreted by quantum mechanics.

## 1.3: Units of Measurement used in Atomic Physics

The energies of electrons are commonly measured and expressed in terms of a unit called an ***electron volt***. An electron volt (ev) is defined as the energy acquired by an electron when it is accelerated through a potential difference of one volt.

Imagine an evacuated tube which contains two parallel separate metal plates connected externally to a battery supplying a voltage *V*. The cathode in this apparatus, the negatively-charged plate, is assumed to be a photoelectric emitter. Photons from an external light source with a frequency $n_o$ upon striking the cathode will supply the electrons with enough energy to just free them from the surface of the cathode. Once free, the electrons will be attracted by and accelerated towards the positively-charged anode. The electrons, which initially have zero velocity at the cathode surface, will be accelerated to some velocity u when they reach the anode. Thus the electron acquires a kinetic energy equal to ½ $mu^2$ in falling through a potential of *V* volts. If the charge on the electron is denoted by *e* this same energy change in ev is given by the charge multiplied by the voltage *V*:

| (5) | $$\frac{1}{2}mv^2 = eV$$ |
|-----|-------------------------|

For a given velocity u in cm/sec, equation (5) also (1.3.1) provides a relationship between the energy unit in the cgs (centimetre, gram, second) system, the erg, and the electron volt. This relationship is:

$$1\,ev = 1.602 \times 10^{-12}\,erg$$

The regular cgs system of units is inconvenient to use on the atomic level as the sizes of the standard units in this system are too large. Instead, a system of units called ***atomic units***, based on atomic values for energy, length, etc., is employed.

Atomic units are defined in terms of Planck's constant and the mass and charge of the electron:

$$Planck's\,constant = h = 6.625 \times 10^{-27}\,erg - sec$$
$$mass\,of\,electron = m = 9.108 \times 10^{-28}\,g$$
$$charge\,of\,electron = e = 4.8029 \times 10^{-10}\,esu$$

### Length.

$$1\,au = a_0 = \frac{h^2}{4\pi^2 me^2} = 0.52917 \times 10^{-8}\,cm$$

### Force.
Force has the dimensions of charge squared divided by distance squared or

$$1\,au = \frac{e^2}{a_0^2} = 8.2377 \times 10^{-3}\,dynes$$

### Energy.
Energy is force acting through a distance or

$$1\,au = \frac{e^2}{a_0} = 4.3592 \times 10^{-11}\,erg = 2.7210 \times 10^1\,ev$$

## 1.4: Further Reading

Any elementary introductory book on modern physics will describe the details of the experiments discussed in this section as well as other experiments, such as the Franck-Hertz experiment, which illustrate the quantum behaviour of atoms.

# 1.E: Exercises

## Q1.1

Atoms or ions in a crystal are arranged in regular arrays as typified by the simple lattice structure shown in Fig. 1-2.
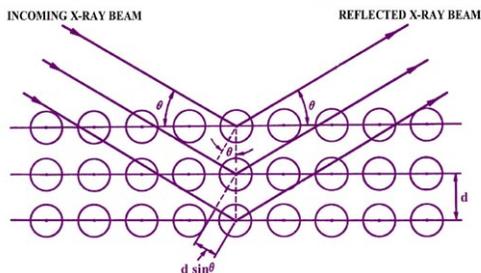


Fig. 1-2. A two-dimensional display of a simple crystal lattice showing an incoming and a reflected beam of X-rays.

This structure is repeated in the third dimension. X-rays are a form of light with a very short wavelength. Since the spacings between the planes of atoms in a crystal, denoted by *d*, are of the same order of magnitude of the wavelength of X-rays (~$10^{-8}$ cm), a beam of X-rays reflected from the crystal will exhibit interference effects. That is, the layers of atoms in the crystal act as a diffraction grating. The reflected beam of X-rays will be in phase if the difference in the path length followed by waves which strike succeeding layers in the crystal is an integral number of wavelengths. When this occurs the reflected X-rays reinforce one another and produce a beam of high intensity for that particular glancing angle q. For some other values of the angle q, the difference in path lengths will not be equal to an integral number of wavelengths. The reflected waves will then be out of phase and the resulting interference will greatly decrease the intensity of the reflected beam. The difference in path length traversed by waves reflected by adjacent layers is 2*d*sinq as indicated in the diagram. Therefore,

| (6) | $n\lambda = 2d\sin\theta$ |
|-----|---------------------------|

with $n = 1, 2, 3...$

which states that the reflected beam will be intense at those angles for which the difference in path length is equal to a whole number of wavelengths. Thus a diffraction pattern is produced, the intensity of the reflected X-ray beam varying with the glancing angle q.

### (a)

By using X-rays with a known wavelength and observing the angles of maximum intensity for the reflected beam, the spacings between the atoms in a crystal, the quantity *d* in equation (1.E.1) also (6), may be determined. For example, X-rays with a wavelength of 1.5420 C produce an intense first-order (n = 1 in equation (1.E.1) also (6)) reflection at an angle of 21.01° when scattered from a crystal of nickel. Determine the spacings between the planes of nickel atoms.

### (b)

Remarkably, electrons exhibit the same kind of diffraction pattern as do X-rays when reflected from a crystal; this provides a verification of de Broglie's prediction. The experiment performed by Davisson and Germer employed low energy electrons which do not penetrate the crystal. (High energy electrons do.) In their experiment the diffraction of the electrons was caused by the nickel atoms in the surface of the crystal. A beam of electrons with an energy of 54 ev was directed at right angles to a surface of a nickel crystal with *d* = 2.15 C. Many electrons are reflected back, but an intense sharp reflected beam was observed at an angle of 50° with respect to the incident beam.
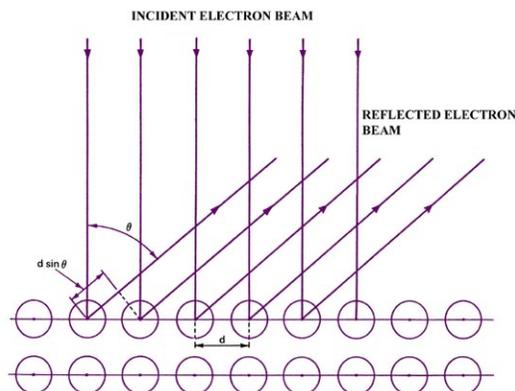


Fig. 1-3. The classic experiment of Davisson and Germer: the scattering of low energy electrons from the surface of a nickel crystal.

As indicated in Fig. 1-3 the condition for reinforcement using a plane reflection grating is

| (7) | $n\lambda = d\sin\theta$ | $n = 1, 2, 3, \ldots$ |
|-----|--------------------------|------------------------|

using equation **(1.E.2) also (7)** with $n = 1$ for the intense first-order peak. Observed at 50°, calculate the wavelength of the electrons. Compare this experimental value for l with that calculated using de Broglie's relationship.

**(8)**

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

The momentum $m$u may be calculated from the kinetic energy of the electrons using equation (5) in the website.

(c)

Even neutrons and atoms will exhibit diffraction effects when scattered from a crystal. In 1994 Professor Brockhouse of McMaster University shared the Nobel prize in physics with Professor Shull of MIT for their work on the scattering of neutrons by solids and liquids. Professor Brockhouse demonstrated how the inelastic scattering of neutrons can be used to gain information about the motions of atoms in solids and liquids. Calculate the velocity of neutrons which will produce a first-order reflection for q = 30° for a crystal with $d$ = 1.5 ´ 10$^{-8}$ cm. Neutrons penetrate a crystal and hence equation **(6) also (1.E.1)** should be used to determine l. The mass of the neutron is 1.66 ´ 10$^{-24}$ g.

(d)

The neutrons obtained from an atomic reactor have high velocities. They may be slowed down by allowing them to come into thermal equilibrium with a cold material. This is usually done by passing them through a block of carbon. The kinetic theory relationship between average kinetic energy and the absolute temperature,

$$\frac{1}{2}mv^{-2} = \frac{3}{2}kT$$

may be applied to the neutrons. Calculate the temperature of the carbon block which will produce an abundant supply of neutrons with velocities in the range required for the experiment described in (c).

## 2: The New Physics

Now that we have studied some of the properties of electrons and light and have seen that their behavior cannot be described by classical mechanics, we shall introduce some of the important concepts of the new physics, quantum mechanics, which does predict their behavior. For the study of chemistry, we are most interested in what the new mechanics has to say about the properties of electrons whose motions are in some manner confined, for example, the motion of an electron which is bound to an atom by the attractive force of the nucleus. An atom, even the hydrogen atom, is a relatively complicated system because it involves motion in three dimensions. We shall consider first an idealized problem in just one dimension, that of an electron whose motion is confined to a line of finite length. We shall state the results given by quantum mechanics for this simple system and contrast them with the results given by classical mechanics for a similar system, but for a particle of much larger mass. Later, we shall indicate the manner in which the quantum mechanical predictions are obtained for a system.

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# 2.1: A Contrast of the Old and New Physics

Consider an electron of mass $m = 9 \times 10^{-28}$ g which is confined to move on a line $L$ cm in length. $L$ is set equal to the approximate diameter of an atom, $1 \times 10^{-8}$cm = 1Å. Consider as well a system composed of a mass of 1 g confined to move on a line, say 1 metre in length. We shall apply quantum mechanics to the first of these systems and classical mechanics to the second.

## Energy

As either mass moves from one end of its line to the other, the potential energy (the energy which depends on the position of the mass) remains constant. We may set the potential energy equal to zero, and all the energy is then kinetic energy (energy of motion). When the electron reaches the end of the line, we shall assume that it is reflected by some force. Thus at the ends of the line the potential energy rises abruptly to a very large value, so large that the electron can never "break through." We can plot potential energy versus position $x$ along the line Fig. 2-1.
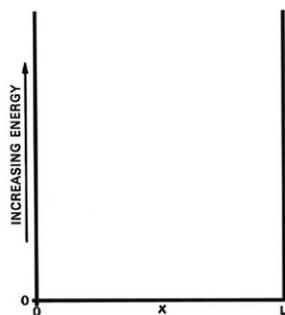


Fig. 2-1. Potential energy diagram for a particle moving on a line of lenght L. When the electron is at x = 0 or x = L the potential energy is infinite and for values of x between these limits (0< x < L ) the potential energy is zero.

We refer to the electron (or the particle of $m = 1$ g) as being in a potential well and we can imagine the abruptly rising potential at $x = 0$ and $x = L$ to be the result of placing a "wall" at each end of the line. First, what are the predictions of classical mechanics regarding the energy of the mass of 1 g? The total energy is kinetic energy and is simply:

$E = KE = \frac{1}{2}mv^2$

We know from experience that $u$, the velocity, can have any possible value from zero up to very large values. Since all values for $u$ are allowed, all values for $E$ are allowed. We conclude that the energy of a classical system may have any one of a continuous range of values and may be changed by any arbitrary amount. Let us contrast with this conclusion the prediction which quantum mechanics makes regarding the energy of an electron in a corresponding situation.

The quantum mechanical results are remarkable indeed, although they should not be surprising when we recall Bohr's explanation of the line spectra which are observed for atoms. Quantum mechanics predicts that there are only certain values of the energy which the electron confined to move on the line can possess. The energy of the electron is quantized. If this result could be observed for a massive particle, it would mean that only certain velocities were possible, say $u = 1$ cm/sec or 10 cm/sec but with no intermediate values! But then an electron is not really a particle. The expression for the allowed energies as given by quantum mechanics for this simple system is:

| (1) | $E_n = \dfrac{h^2 n^2}{8mL^2}$ | $n = 1, 2, 3, 4, \ldots.$ |
|-----|-------------------------------|----------------------------|

where again $h$ is Planck's constant and $n$ is an integer which may assume any value from one to infinity. Since only discrete values for $E$ are possible, the appearance of the index $n$ in equation (1) is necessary. A number such as $n$ which appears in the expression for the energy is called a quantum number. Each value of the quantum number $n$ fixes a value of $E_n$, one of the allowed energy values. We can indicate the possible values for the energy on an energy diagram. It is clear from equation (1) that for given values of $m$ and $L$, $E_n$ equals a constant ($K = h^2/8mL^2$) multiplied by $n^2$:

| (2) | $E_n = Kn^2$ | $n = 1, 2, 3, 4, \ldots.$ |
|-----|--------------|----------------------------|

Thus we can express the value of $E_n$ in terms of so many units of $K$.

Each line, called an energy level, in Fig. 2-2 denotes an allowed energy for the system and the figure is called an energy level diagram. Each level is identified by its value of $n$ as a subscript. A corresponding diagram for the case of the classical particle would consist of an infinite number of lines with infinitesimally small spacings between them, indicating that the energy in a classical system may vary in a continuous manner and may assume any value. The energy *continuum* of classical mechanics is replaced by a *discrete* set of energy levels in quantum mechanics.
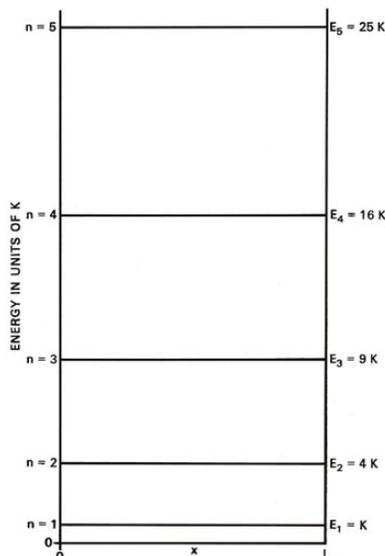


Fig. 2-2. Energy level diagram for an electron moving on a line of length L. Only the first few levels are shown.

Suppose we could give the electron sufficient energy to place it in one of the higher (excited) energy levels. Then when it "fell" back down to the lowest value of $E$ (called the ground level, $E_1$), a photon would be emitted. The energy e of the photon would be given by the difference in the values of $E_n$ and $E_1$ and, since e = $h\nu$ the frequency of the photon would be given by the relationship:

$$\nu = \frac{E_n - E_1}{h} \qquad n = 2, 3, 4, 5, \ldots$$

which is Bohr's frequency condition (I-4). Thus only certain frequencies would be emitted and the spectrum would consist of a series of lines.

We can illustrate the change in energy when the electron falls to the lowest energy level by connecting the upper level and the $n = 1$ level by an arrow in an energy level diagram. The frequency of the photon emitted during the indicated drop in energy is proportional to the length of the arrow, i.e., to the change in energy (Fig. 2-3). The line directly beneath each arrow represents the value of the frequency for that drop in energy. Since the differences in the lengths of the arrows increase as $n$ increases, the separations between the observed frequencies show a corresponding increase. The spectrum, therefore, consists of a series of lines, with the spacings between the lines increasing as $n$ increases. If the energy was not quantized and all values were possible, all jumps in energy would be possible and all frequencies would appear. Thus a continuum of possible energy values will produce a continuous spectrum of frequencies. A line spectrum, on the other hand, is a direct manifestation of the quantization of energy.
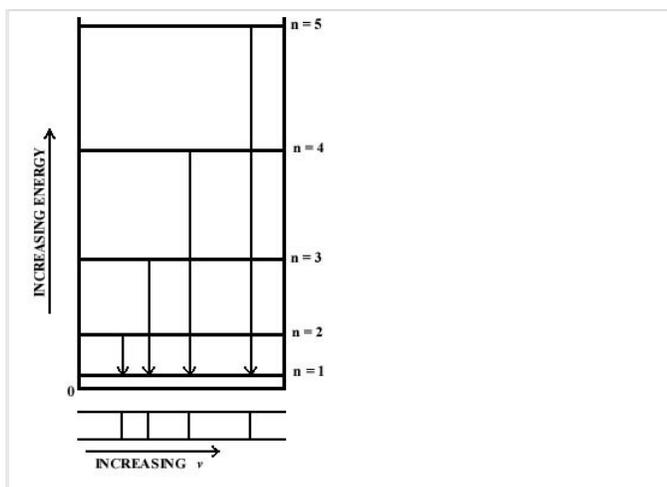
Fig. 2-3. The origin of a line spectra.

In the quantum case, as in the classical case, all of the energy will be in the form of kinetic energy. We may obtain an expression for the momentum of the electron by equating the total value of the energy $E_n$ to $p^2/2m$, where $p$ is the momentum (= $m$u) of the electron, ($p^2/2m$ is another way of expressing $2m$u$^2$.)

$$E_n = \frac{n^2 h^2}{8mL^2} = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

This gives:

| | | |
|---|---|---|
| | $p = \pm \frac{nh}{2L}$ | $n = 1, 2, 3, 4, \ldots$ |

A plus and a minus sign must be placed in front of the number which gives the magnitude of the momentum to indicate that we do not know and cannot determine the direction of the motion. If the electron moves from left to right the sign will be positive. If it moves from right to left the sign will be negative. The most we can know about the momentum itself is its average value. This value will clearly be zero because of the equal probability for motion in either direction. The average value of $p^2$, however, is finite.

Since the lowest allowed value of the quantum number $n$ in the quantum mechanical expression for the energy is unity, it is evident that the energy can never equal zero. ***A confined electron can never be motionless***. The expression for $E_n$ also indicates that the kinetic energy and the momentum increase as the length of the line $L$ is decreased. Thus the kinetic energy and momentum of the electron increase as its motion becomes more confined. This is both an important and a general result and will be referred to again.

## Position

The concept of a trajectory is fundamental to classical mechanics. Given a particular mass with a given initial velocity and a knowledge of the forces acting on it, we may use classical mechanics to predict the exact position and velocity of the particle at any future time. Thus we speak of the trajectory of the particle and we may calculate it to any desired degree of accuracy. It is also possible, within the framework of classical mechanics, to measure the position and velocity of a particle at any given instant of time. Thus classical mechanics correctly predicts what one can experimentally measure for massive particles.

We have previously mentioned the difficulties which are encountered when we attempt to determine the position of an electron. The results of the Compton effect indicate that part of the energy of the photon used in making the observation is transferred to the electron, and we invariably disturb the electron when we attempt to measure its position. Thus it is not surprising to find that quantum mechanics does not predict the position of an electron exactly. Rather, it provides only a ***probability*** as to where the electron will be found. When we consider the experiments which attempt to define the position of the electron, we shall find that this is the maximum information that can indeed be obtained even experimentally. The new mechanics again predicts only what can indeed be measured experimentally. We shall illustrate the probability aspect in terms of the system of an electron confined to motion along a line of length $L$. Quantum mechanical probabilities are expressed in terms of a distribution function which in this particular case we shall label $P_n(x)$.

Consider the line of length $L$ to be divided into a large number of very small segments, each of length D$x$. Then the probability that the electron is in one particular small segment D$x$ of the line is given by the product of D$x$ and the value of the probability

distribution function $P_n(x)$ for that interval. For example, the probability distribution function for the electron when it is in the lowest energy level, $n = 1$, is given by $P_1(x)$ (Fig. 2-4).
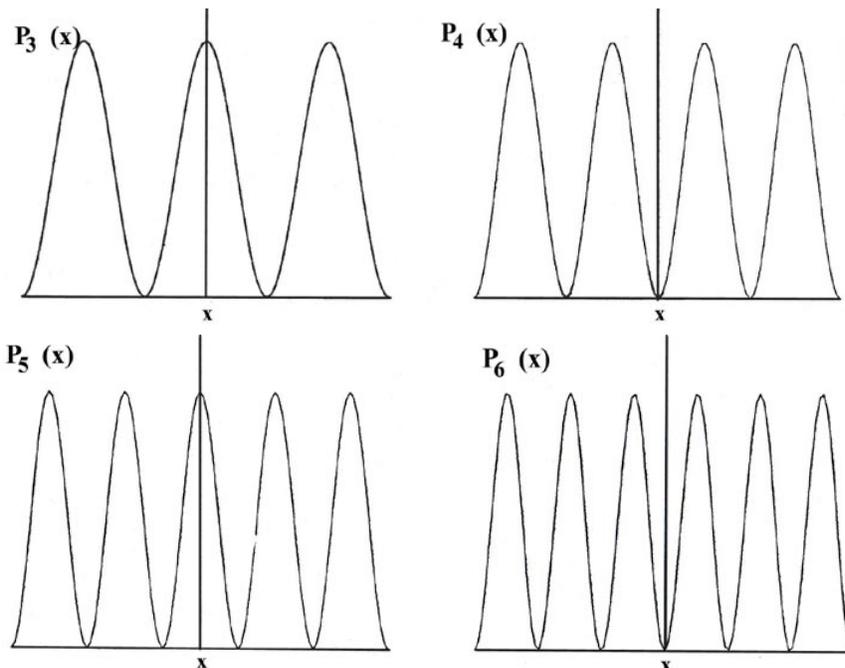


Fig. 2-4. Probability distributions $P_n(x)$ for an electron confined to move on a line of fixed length in the quantum levels with n = 1, 2, ..., 6. The area of each rectangle shown in the figure for $P_1(x)$ equals the probability that the electron is in the particular segment of the line D$x$ forming the base of the rectangle. The percentage shown in each rectangle is the percentage probability that the electron is in a particular segment D$x$. The total probability that the electron is somewhere on the line is given by the total area under the $P_1(x)$ curve, that is, by the sum of each small element of area $P_1(x)$D$x$ for each segment D$x$. This total area is made to equal unity for every $P_n(x)$ curve by expressing the values of $P_n(x)$ in units of (1/L). Thus by definition a probability of one denotes a certainty.

The probability that the electron will be in the particular small interval D$x$ indicated in Fig. 2-4 is equal to the shaded area, an area which in turn is equal to the product of D$x$ and the average value of $P_1(x)$ throughout the interval D$x$, called $P_1(x')$,

$$probability\ that\ electron\ is\ in\ segment \Delta x = P_1(x')\Delta x$$

The curve $P_1(x)$ may be determined in the following manner. We design an experiment able to determine whether or not the electron is in one particular segment D$x$ of the line when it is known to be in the quantum level $n = 1$. (One way in which this might be done is described below.) We perform the experiment a large number of times, say one hundred, for each segment and record the ratio of the number of times the electron is found in a particular segment to the total number of observations made for that segment. For example, an electron is found to be in the segment marked D$x$ (of length 0.1 $L$) in the figure for $P_1(x)$ in 18 out of 100 observations, or 18% of the time. In the other 82 observations the electron was in one of the other segments. Thus the average value of $P_1(x)$ for this segment, called $P_1(x')$ must be 1.8/$L$ since $P_1(x')$D$x$ = (1.8/L) (0.1 $L$) = 0.18 or 18%. A similar set of experiments is made for each of the segments D$x$ and in each case a rectangle is constructed with D$x$ as base and with a height equal to $P_1(x)$ such that the product $P_1(x)$D$x$ equals the fractional number of times the electron is found in the segment D$x$. The limiting case in which the total length $L$ is divided into a very large number of very small segments (D$x$ ® d$x$) would result in the smooth curve shown in the figure for $P_1(x)$.

There is a different probability distribution for each value of $E_n$, or each quantum level, as shown, for example, by the probability distributions for the energy levels with $n = 2, 3, 4, 5$ and 6 (Fig. 2-4). The probability of finding the electron at the positions where the curve touches the $x$-axis is zero. Such a zero is termed a **node**. The number of nodes is always $n$-1 if we do not count the nodes at the ends of each $P_n(x)$ curve.

Let us first contrast these results, particularly that for $P_1(x)$, with the corresponding classical case. Since a classical analysis allows us to determine the position of a particle uniquely at any instant, either theoretically or experimentally, the idea of a probability

distribution is foreign to a classical mechanical analysis. However, we still can determine the classical probability distribution for the particle confined to motion on a line. Since there are no forces acting on the particle as it traverses the line, it will be equally likely to be found at any point on the line (Fig 2-5). This probability will be the same regardless of the energy. There is again a striking difference between the classical and the quantum mechanics results. For the first quantum level, the graph of $P_1(x)$ indicates the electron will most likely be found at the midpoint of the line. Furthermore, the form of $P_n(x)$ changes with every change in energy. *Every allowed value of the of the energy has associated with it a distinct probability distribution for the electron*. Theses are the predictions of quantum mechanics regarding the position of a bound electron. Now let us investigate the experimental aspect of the problem to gain some physical reason for these predictions.
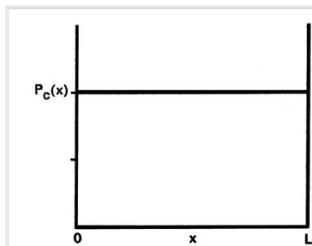


Fig. 2-5. The classical probability distribution for motion on a line. This is the result obtained when the particle is located a large number of times at random time intervals. The classical probability function $P_c(x)$ is the same for all values of $x$ and equals $1/L$, i.e., the particle is equally likely to be found at any value of $x$ between 0 and $L$

Let us design an experiment in which we attempt to pinpoint the position of an electron within a segment D$x$. The experiment is a hypothetical one in that we imagine that we are to observe the electron through a microscope by reflecting or scattering light from it. Imagine the lens of a microscope being placed above the line $L$ with the light entering from the side (Fig. 2-6 (a)). The electron, when illuminated with light, will act as a small source of light and will produce at $A$ an image in the form of a bright disc surrounded by a group of rings of decreasing intensity. Because of this effect, which is entirely analogous to the diffraction effect observed for a pinhole source of light, the centre of the image will appear bright even if the electron is not precisely located at the point marked $x$. It could equally well have been at any value of $x$ between the points $x'$ and $x''$ and produced an image visible to the eye at $A$ if the difference in the path lengths B$x'$ and C$x'$ (or B$x''$ and C$x''$) is less than one half of a wavelength. In other words the resolving power of a microscope is not unlimited but is instead determined by the wavelength of the light used in making the observation. The use of the microscope imposes an inherent uncertainty in our observation of the position of the electron. With the condition that the difference in the path lengths to the outside rim of the lens must be no greater than one half a wavelength and with the use of some geometry, the magnitude of the uncertainty in the position of the electron, $x'' - x' = $ D$x$, is found to be given approximately by:

**(3)**
$$\Delta x \sim \frac{\lambda}{2\sin\theta}$$

where q is the angle indicated in the diagram.
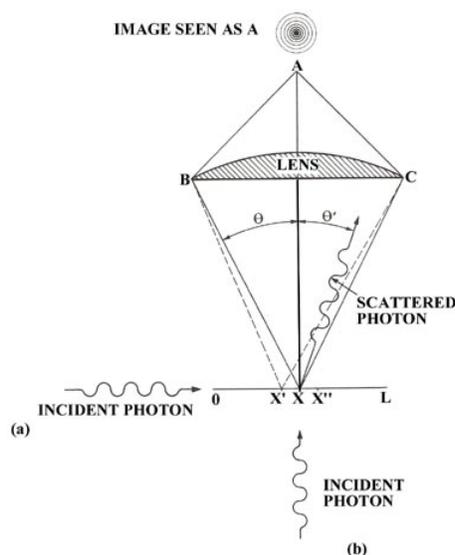
Fig. 2-6. An idealized experiment for detecting the position of an electron.

Remembering the Compton effect and bearing in mind that we wish to disturb the electron as little as possible during the observation, we shall inquire as to the results obtained when a single photon is scattered from the electron. A single photon will not yield the complete diffraction pattern at *A*, but will instead produce a single flash of light. A diffraction pattern is the result of many photons passing through the microscope and represents the probability distribution for the emergent photons when they have been scattered by an electron lying between *x'* and *x''*. A single photon, when scattered from an electron within the length D*x*, is however still diffracted and will produce a flash of light somewhere in one of the areas defined by the probability distribution produced by many photons passing through the system.

Thus even when we use but a single photon in our apparatus the uncertainty D*x* in our experimentally determined position of the electron will still be given by equation **(3)**. Obviously, if we want to locate an electron which is confined to move on a line to within a length that is small compared to the length of the line, we must use light which has a wavelength much less than *L*. This is exactly what equation **(3)** states: the shorter the wavelength of the light which is used to observe the electron, the smaller will be the uncertainty D*x*. That being the case, why not do the experiment with light of very short wavelength compared to the length *L*, say l = (1/100)*L*? Then we can hope to find the electron on one small segment of the line, each segment being approximately (1/100)*L* in length. Let us calculate the frequency and energy of a photon which has the required wavelength of l = (1/100)*L*. As before, we set *L* equal to a typical atomic dimension of 1 x $10^{-8}$ cm.

$$\varepsilon = hv = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{10^{-10}} = 2.0 \times 10^{-6} \, ergs$$

We are immediately in difficulty, because the energy of the electron in the first quantum level is easily found to be:

$$E_1 = \frac{(6.6 \times 10^{-27})^2}{9.1 \times 10^{-28} \times 8 \times 10^{-16}} = 6.0 \times 10^{-11} \, ergs = K$$

The energy of the photon is approximately 1 x $10^4$ times greater than the energy of the electron! We know from the Compton effect that the collision of a photon with an electron imparts energy to the electron. Thus the electron after the collision will certainly not be in the state *n* = 1. It will be excited to oneⵏwe don't know whichⵏof the excited levels with *n* = 2 (*E* = 4*K*) or *n* = 3 (*E* = 9*K*), etc. The result is clear. If we demand an intimate knowledge of what the position of the electron is in a given state, we can obtain this information only at the expense of imparting to the electron an unknown amount of energy which destroys the system, i.e., the electron is no longer in the *n* = 1 level but in one of the other excited levels. If this experiment was repeated a large number of times and a record kept of the number of times an electron was located in each segment of the line (roughly (1/100)*L*), a probability plot similar to Fig. 2-4 would be obtained.

We can ask another kind of question regarding the position of the electron: "How much information can be obtained about the position of the electron in a given quantum level without at the same time destroying that level?" The electron cannot accept energy in an amount less than that necessary to excite it to the next quantum level, *n* = 2. The difference in energy between $E_2$, and $E_1$, is

3$K$. Thus if we are to leave the electron in a state of known energy and momentum we must use light whose photons possess an energy less than 3$K$.

Let us calculate the wavelength of the light with e = 2$K$ and compare this value with the length $L$.

$$\lambda = \frac{hc}{\varepsilon} = \frac{6.6 \times 10^{-27} \times 3.0 \times 10^{10}}{12 \times 10^{-11}} = 1.7 \times 10^{-6} \, cm$$

The wavelength is greater than the length of the line $L$. From equation **(3)** it is clear that the uncertainty in the position of the particle will be of the order of magnitude of, or greater than, $L$ itself. The electron will appear to be blurred over the complete length of the line in a single experiment! Thus there are two interpretations which can be given to the probability distributions, depending on the experiment which is performed. The first is that of a true probability of finding the electron in a given small segment of the line using light of very short l relative to $L$. This experiment excites the electron, changes the system and leaves the electron with an unknown amount of energy and momentum. We have destroyed the object of our investigation. We now know where it was in a given experiment but not where it will be, in terms of energy or position.

Alternatively, we could use light with a l approximately equal to $L$. This does not excite the electron and leaves it in a known energy level. However, now the knowledge of the position is very uncertain. The photons are scattered from the system and give us directly the smeared distribution $P_1$ pictured in Fig. 2-4. In a real sense we must accept the fact that when the electron remains in a given state it is "smeared out" and "looks like" the pictures given for $P_n$. Thus we can interpret the $P_n$'s as instantaneous pictures of the electron when it is bound in a known state, and forgot their probability aspect. This "smeared out" distribution is given a special name; it is called the ***electron density distribution***. There will be a certain fraction of the total electronic charge at each point on the line, and when we consider a system in three dimensions, there will be a certain fraction of the total electronic charge in every small volume of space. Hence it is given the name electron density, the amount of charge per unit volume of space. The $P_n$'s represent a charge density distribution which is considered static as long as the electron remains in the $n$th quantum level. Thus the $P_n$ functions tell us either (a) the ***fraction of time*** the electron is at each point on the line for observations employing light of short wavelength, or (b) they tell us the ***fraction of the total charge*** found at each point on the line (the whole of the charge being spread out) when the observations are made with light of relatively long wavelength.

The electron density distributions of atoms, molecules or ions in a crystal can be determined experimentally by X-ray scattering experiments since X-rays can be generated with wavelengths of the same order of magnitude as atomic diameters (1 ´ 10$^{-8}$cm). In X-ray scattering the intensity of the scattered beam and the angle through which it is scattered are measured. The distribution of negative charge within the crystal scatters the X-rays and determines the intensity and angle of scattering. Thus these experimental quantities can be used to calculate the form of the electron density distribution.

There is a definite quantum mechanical relationship governing the magnitudes of the uncertainties encountered in measurements on the atomic level. We can illustrate this relationship for the one-dimensional system. Let us consider the minimum uncertainty in our observations of the position and the momentum of the electron moving on a line obtained in an experiment which leaves the particle bound in a given quantum level, say $n = 1$. This will require the use of light with l ~ $L$. We have seen that the use of light of this wavelength limits us to stating that the electron is somewhere on the line of length $L$. We can say no more than this with certainty unless we use light of much shorter l , and then we will change the quantum number of the electron. The uncertainty in the value of the position coordinate, which we shall call D$x$, is just $L$, the length of the line:

$$\Delta x = L$$

We have previously shown that the momentum of the electron in the $n$th quantum level is given by:

| | |
|---|---|
| $p_n = \pm \frac{nh}{2L}$ | $n = 1, 2, 3, \ldots$ |

the plus and minus signs denoting the fact that while we know the magnitude of the momentum we cannot determine whether the electron is moving from left to right (+$nh$/2$L$) or from right to left (-$nh$/2$L$). The minimum uncertainty in our knowledge of the momentum is the difference between these two possibilities, or for $n = 1$:

$$\Delta p = +\frac{h}{2L} - \left(\frac{-h}{2L}\right) = \frac{H}{L}$$

The product of the uncertainties in the position and the momentum is:

$$\Delta p \Delta x = L \frac{h}{L} = h$$

This result is a *particular example* of a general relationship governing the product of the uncertainties in the momentum and position known as ***Heisenberg's uncertainty principle***. In the general case, the equality sign in the above equation is replaced by the symbol "³" which denotes that the product in the uncertainties DpDx equals or exceeds the value of Planck's contant h, that is, the general statement is given by DpDx ³ h.

If we endeavour to decrease the uncertainty in the position coordinate (i.e., make D *x* small) there will be a corresponding increase in the uncertainty of the momentum of the electron along the same coordinate, such that the product of the two uncertainties is always equal to Planck's constant. We saw this effect in our experiments wherein we employed light of short l to locate the position of the electron more precisely. When we did this we excited the electron to one of the other available quantum states, thus making a knowledge of the energy and hence the momentum uncertain. We might also try to defeat Heisenberg's uncertainty principle by decreasing the length of the line *L*. By shortening *L*, we would decrease the uncertainty as to where the electron is. However, as was noted previously, the momentum increases as *L* is decreased and the uncertainty in *p* is always the same order of magnitude as *p* itself; in this case twice the magnitude of *p*. Thus the decrease in D*x* obtained by decreasing *L* is offset by the increase in D*p* which accompanies the increased confinement of the electron; the product D*x*D *p* remains unchanged in value.

We can illustrate the operation of Heisenberg's uncertainty principle for a free particle by referring again to our hypothetical experiment in which we attempted to locate the position of an electron by using a microscope. We imagine the electron to be free and travelling with a ***known momentum*** in the direction of the *x*-axis with a photon entering from below along the y-axis. When the photon is scattered by the electron it ***may*** transfer momentum to the electron and continue on a line which makes an angle q' to the y-axis (Fig. 2-6). The photon, in doing so, will acquire momentum in the direction of the *x*-axis, a direction in which it initially had none. Since momentum must be conserved, the electron will receive a recoil momentum, a momentum equal in magnitude but opposite in direction to that gained by the photon. This is the Compton effect. Thus our act of observing the electron will lead to an uncertainty in its momentum as the amount of momentum transferred during the collision is uncontrollable. We may, however, set limits on the amount transferred and in this way determine the uncertainty introduced into the value of the momentum of the electron.

The momentum of the photon before the collision is all directed along the y-axis and has a magnitude equal to *h*/l . After colliding with the electron the photon may be scattered to the left or to the right of the y-axis through any angle q' lying between 0 and q and still be collected by the lens of the microscope and seen by the observer at *A*. Thus every photon which passes through the microscope will have an uncertainty of 2(*h*/l)sinq in its component of momentum along the *x*-axis since it ***may*** have been scattered by the maximum amount to the left and acquired a component of -(*h*/l)sinq or, on the other hand, it ***may*** have been scattered by the maximum amount to the right and acquired a momentum component of +(*h*/l)sinq. Any *x*-component of momentum acquired by the photon must have been lost by the electron and the uncertainty introduced into the momentum of the electron by the observation is also equal to 2(*h*/l)sinq .

In addition to the uncertainty induced in the momentum of the electron by the act of measurement, there is also an inherent uncertainty in its position (equation (3)) because of the limited resolving power of the microscope. The product of the two uncertainties at the instant of measurement or immediately following it is:

$$\Delta p \Delta x \sim 2\frac{h}{\lambda}\sin\theta \times \frac{\lambda}{2\sin\theta} = h$$

Heisenberg's uncertainty relationship is again fulfilled. Our experiment employs only a single photon which, since light itself is quantized, represents the smallest packet of energy and momentum which we can use in making the observation. Even in this idealized experiment the act of observation creates an unavoidable disturbance in the system.

## Degeneracy

We may use an extension of our simple system to illustrate another important quantum mechanical result regarding energy levels. Suppose we allow the electron to move on the *x*-y plane rather than just along the *x*-axis. The motions along the *x* and y directions will be independent of one another and the total energy of the system will be given by the sum of the energy quantum for the motion along the *x*-axis plus the energy quantum for motion along the y-axis. Two quantum numbers will now be necessary, one to indicate the amount of energy along each coordinate. We shall label these as $n_x$ and $n_y$. Let us assume that the motion is confined to a length *L* along each axis, then:

$$E_{n_x, n_y} = \frac{h^2}{8mL^2}n_x^2 \ + \ \frac{h^2}{8mL^2}n_y^2 \ = \ \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right) \qquad\qquad n_{x,y} = 1, 2, 3, \ldots$$

Nothing new is encountered when the electron is in the lowest quantum level for which $n_x = n_y = 1$. The energy $E_{1,1}$ simply equals $2h^2/8mL^2$.

Since two dimensions ($x$ and $y$) are now required to specify the position of the electron, the probability distribution $P_{1,1}(x,y)$ must be plotted in the third dimension. We may, however, still display $P_{1,1}(x,y)$ in a two-dimensional diagram in the form of a contour map (Fig. 2-7). All points in the $x$-$y$ plane having the same value for the probability distribution $P_{1,1}(x,y)$ are joined by a line, a contour line. The values of the contours increase from the outermost to the innermost, and the electron, when in the level $n_x = n_y = 1$, is therefore most likely to be found in the central region of the $x$-$y$ plane.
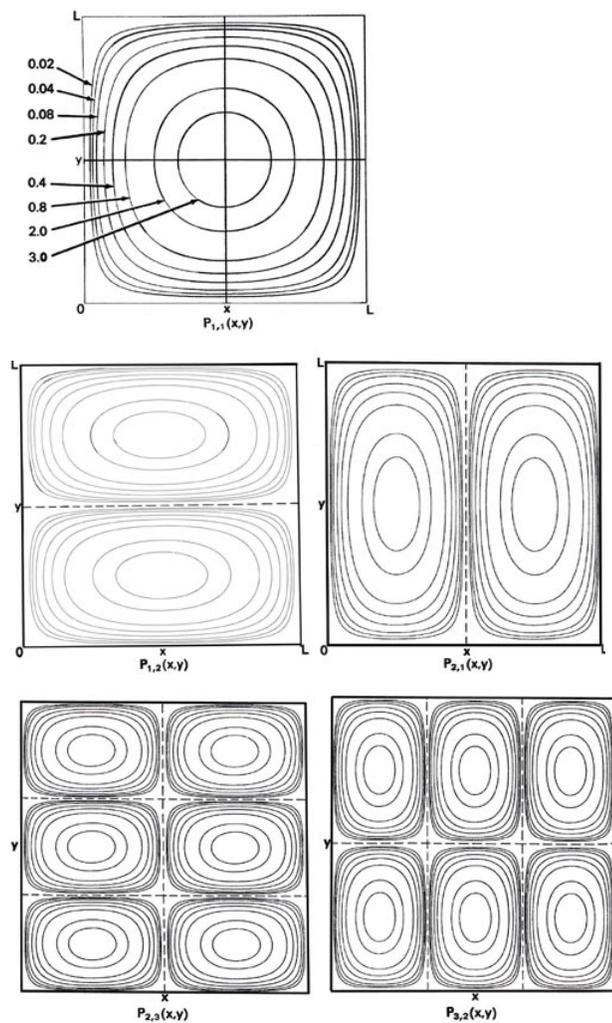
Fig. 2-7. Contour maps of the probability distributions $P_{nx, ny}(x,y)$ for an electron moving on the x-y plane. The dashed lines represent the postion of nodes, lines along which the probability is zero. $P_{1,2}(x,y)$ and $P_{2,1}(x,y)$ are distributions for one doubly-degenerate level; $P_{2,3}(x,y)$ and $P_{3,2}(x,y)$ are examples of distributions for another degenerate level of still higher energy. The same contours are shown in each diagram and their values (in units of $4/L^2$) are indicated in the diagram for $P_{1,1}(x,y)$.

A plot of $P_{1,1}(x,y)$ along either of the axes indicated in Fig. 2-7 (one parallel to the $x$-axis at $y = L/2$ and the other parallel to the y-axis at $x = L/2$) is similar in appearance to that for $P_1(x)$ shown in Fig. 2-4. That is, for a fixed value of y, the contribution to $P_{1,1}(x,y)$ from the motion along the y-axis is constant and

$$P_{1,1}(x, L/2) = constant \times P_1(x)$$

Thus, aside from the constant factor, $P_1(x)$ provides a profile, or if $P_{1,1}(x,y)$ were displayed in three dimensions, a cross section of the contour map of $P_{1,1}(x)$. A contour map is a display of the probability or density distribution in a plane; a profile is a display of the density distribution along a line.

Now consider the possibility of $n_x = 1$ and $n_y = 2$. Then

$$E_{1,2} = \frac{5h^2}{8mL^2}$$

We could also have the situation in which $n_x = 2$ and $n_y = 1$. This does not change the value of the total energy,

$$E_{2,1} = E_{1,2} = \frac{5h^2}{8mL^2}$$

but the probability distributions (Fig. 2-7) are different, $P_{1,1}(x,y)$ ¹$P_{2,1}(x,y)$. When $n_x = 1$ and $n_y = 2$, there must be a node on the y-axis, i.e., a zero probability of finding the electron at y = L/2. Thus a slice through $P_{1,2}(x\ y)$ at $x = L/2$ parallel to the y-axis must be similar to the figure for $P_2(x)$, while a slice parallel to the x-axis will still be similar to $P_1(x)$. Just the reverse is true for the case $n_x = 2$ and $n_y = 1$. In this case, whether or not we can distinguish experimentally between the x- and y-axes, there are two different arrangements for the distribution of the electron, both of which have the same energy. The energy level is said to be degenerate. ***The degeneracy of an energy level is equal to the number of distinct probability distribution for the system, all of which belong to this same energy level.***

The concept of degeneracy in an energy level has important consequences in our study of the electronic structure of atoms.

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# 2.2: Probability Amplitudes

In quantum mechanics, Newton's familiar equations of motion are replaced by Schrödinger's equation. We shall not discuss this equation in any detail, nor indeed even write it down, but one important aspect of it must be mentioned. When Newton's laws of motion are applied to a system, we obtain both the energy and an equation of motion. The equation of motion allows us to calculate the position or coordinates of the system at any instant of time. However, when Schrödinger's equation is solved for a given system we obtain the energy directly, but not the probability distribution functionCthe function which contains the information regarding the position of the particle. Instead, the solution of Schrödinger's equation gives only the amplitude of the probability distribution function along with the energy. The probability distribution itself is obtained by squaring the probability amplitude. (Click here for note.) Thus for every allowed value of the energy, we obtain one or more (the energy value may be degenerate) probability amplitudes.

The probability amplitudes are functions only of the positional coordinates of the system and are generally denoted by the Greek letter y (psi). For a bound system the amplitudes as well as the energies are determined by one or more quantum numbers. Thus for every En we have one or more yn's and by squaring the yn's we may obtain the corresponding Pn's.

Let us look at the forms of the amplitude functions for the simple system of an electron confined to motion on a line. For any system, y is simply some mathematical function of the positional coordinates. In the present problem which involves only a single coordinate x, the amplitude functions may be plotted versus the x-coordinate in the form of a graph. The functions yn are particularly simple in this case as they are sin functions.

| | $\psi_n(x) = \sqrt{2/L}\sin(n\pi x/L)$ | $n = 1, 2, 3, \ldots$ |
| --- | --- | --- |

The first few yn's are shown plotted in Fig. 2-8.
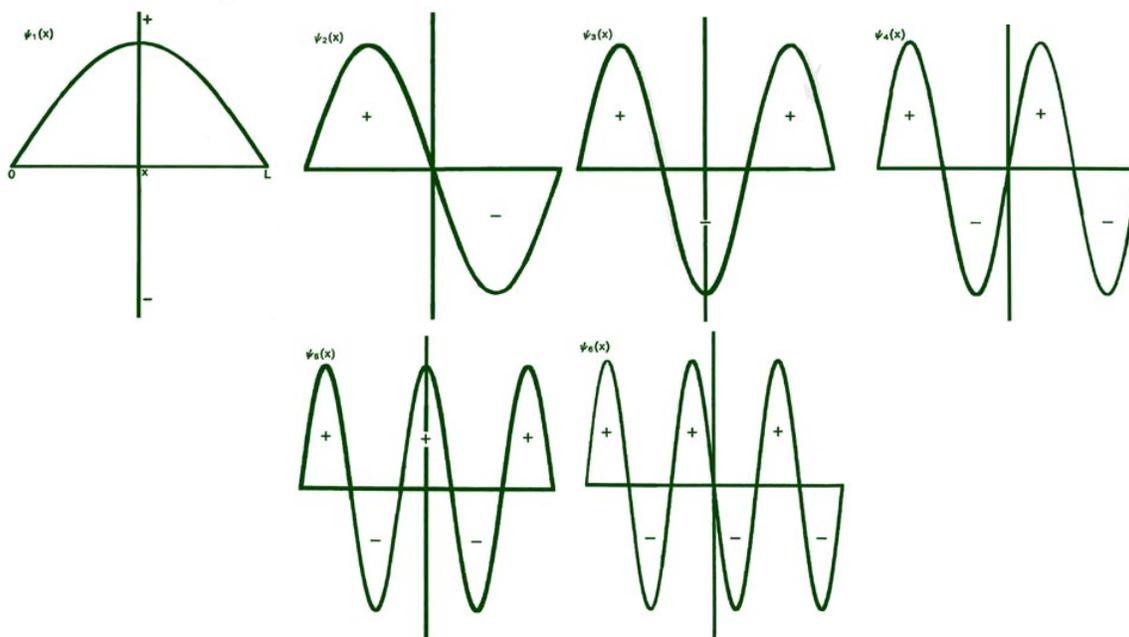


Fig. 2-8. The first six probability amplitudes yn(x) for an electron moving on a line of length L. Note the yn(x) may be negative in sign for certain values of x. The yn(x) are squared to obtain the probability distrubrition functions Pn(x), which are, therefore, positive for all values of x. Wherever yn(x) crosses the x-axis and changes sign, a node appears in the corresponding Pn(x).

Each of these graphs, when squared, yields the corresponding Pn curves shown previously. When n = 1,

| | $\psi_1(x) = \sqrt{2/L}\sin(\pi x/L)$ |
| --- | --- |

When x = 0,

$$\psi_1(0) = \sqrt{2/L}\,\sin(0) = 0$$

When x = L,

$$\psi_1(L) = \sqrt{2/L}\,\sin(\pi) = 0$$

When x = L/2,

$$\psi_1(L/2) = \sqrt{2/L}\,\sin(\pi/2) = \sqrt{2/L}$$

Thus y equals zero at x = 0 and x = L and is a maximum when x = L/2. When this function is squared, we obtain:

$$P_1(x) = (2/L)\sin^2(\pi x/L)$$

and the graph (Fig. 2-4) previously given for P1(x).

As illustrated previously in Fig. 2-4, the value of yn2(x) or Pn(x) multiplied by Dx, yn2(x)Dx, or Pn(x)Dx, is the probability that the electron will be found in some particular small segment of the line Dx. The constant factor of $\sqrt{2/L}$ which appears in every yn(x) is to assure that when the value of yn2(x)Dx is summed over each of the small segments Dx, the final value will equal unity. This implies that the probability that the electron is somewhere on the line is unity, i.e., a certainty. Thus the probability that the electron is in any one of the small segments Dx (the value of yn2(x)Dx or Pn(x)Dx evaluated at a value of x between 0 and L) is a fraction of unity, i.e., a probability less than one. (Click here for note.)

Each yn must necessarily go to zero at each end of the line, since the probability of the electron not being on the line is zero. This is a physical condition which places a mathematical restraint on the yn . Thus the only acceptable yn 's are those which go to zero at each end of the line. A solution of the form shown in Fig. 2-9 is, therefore, not an acceptable one. Since there is but a single value of the energy for each of the possible yn functions, it is clear that only certain discrete values of the energy will be allowed. The physical restraint of confining the motion to a finite length of line results in the quantization of the energy. Indeed, if the line is made infinitely long (the electron is then free and no longer bound), solutions for any value of n, integer or non-integer, are possible; correspondingly, all energies are permissible. Thus only the energies of bound systems are quantized.
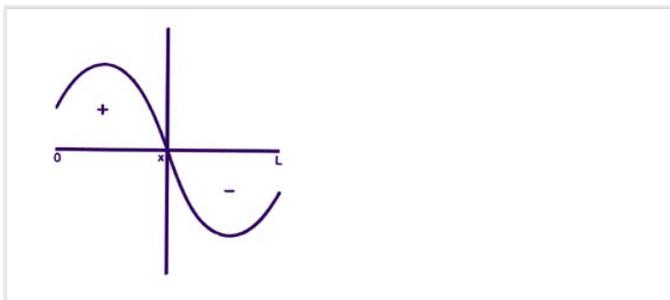


Fig. 2-9. An unacceptable form for yn(x).

The yn 's have the appearance of a wave in that a given value of yn(x) is repeated as x is increased. They are periodic functions of x. We may, if we wish, refer to the wavelength of yn. The wavelength of y1 is 2L since only one half of a wave fits on the length L. The wavelength for y2, is L since one complete wave fits in the length L. Similarly l3, = (2/3)L and l4 = (2/4)L. In general:

| | $\lambda_n = 2L/n$ | $n = 1, 2, 3, \ldots$ |
|---|---|---|

Because of the wave-like nature of the yn 's , the new physics is sometimes referred to as wave mechanics, and the yn functions are called wave functions. However, it must be stressed that a wave function itself has no physical reality. All physical properties are determined by the product of the wave function with itself. It is the product yn(x)yn(x) which yields the physically measurable probability distribution. Thus yn2 may be observed but not yn itself.

A $\psi_n$ does not represent the trajectory or path followed by an electron in space. We have seen that the most we can say about the position of an electron is given by the probability function $\psi_n^2$. We do, however, refer to the wavelengths of electrons, neutrons, etc. But we must remember that the wavelengths refer only to a property of the amplitude functions and not to the motion of the particle itself.

A number of interesting properties can be related to the idea of the wavelengths associated with the wave functions or probability amplitude functions. The wavelengths for our simple system are given by $l = 2L/n$. Can we identify these wavelengths with the wavelengths which de Broglie postulated for matter waves and which obeyed the relationship:

$$\lambda = h/p \ ?$$

The absolute value for the momentum (the magnitude of the momentum independent of its direction) of an electron on the line is nh/2L. Substituting this into de Broglie's relationship gives:

$$\lambda = h/p = \frac{h}{nh/2L} = 2L/n$$

So indeed the wavelengths postulated by de Broglie to be associated with the motions of particles are in reality the wavelengths of the probability amplitudes or wave functions. There is no need to postulate "matter waves" and the results of the electron diffraction experiment of Davisson and Germer for example can be interpreted entirely in terms of probabilities rather than in terms of "matter waves" with a wavelength $l = h/p$.

It is clear that as n increases, l becomes much less than L. For n = 100, $\psi_{100}$ and $P_{100}$ would appear as in Fig. 2-10. When L>>ln, the nodes in $P_n$ are so close together that the function appears to be a continuous function of x. No experiment could in fact detect nodes which are so closely spaced, and any observation of the position of the electron would yield a result for $P_{100}$ similar to that obtained in the classical case. This is a general result. When l is smaller than the important physical dimensions of the system, quantum effects disappear and the system behaves in a classical fashion. This will always be true when the system possesses a large amount of energy, i.e, a high n value. When, however, l is comparable to the physical dimensions of the system, quantum effects predominate.
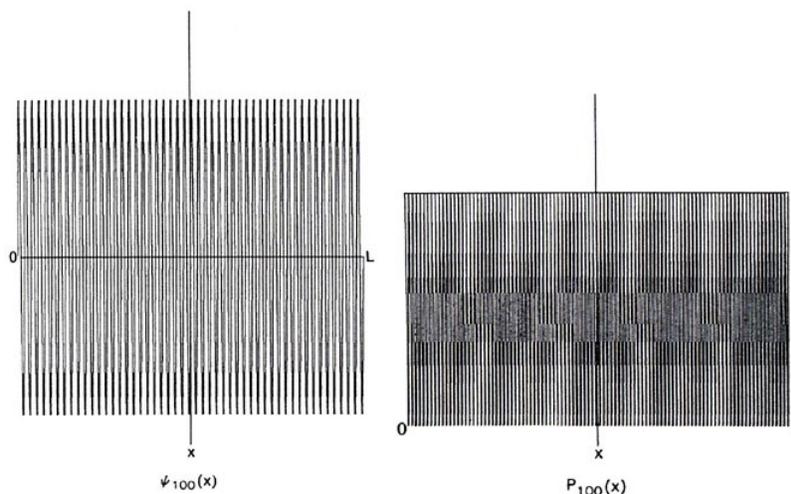


Fig. 2-10. The wave function and probability distribution for n = 100.

Let us check to see whether or not quantum effects will be evident for electrons bound to nuclei to form atoms. A typical velocity of an electron bound to an atom is of the order of magnitude of 109 cm/sec. Thus:

$$\lambda = \frac{6.6 \times 10^{-27}}{9.1 \times 10^{-28} \times 1 \times 10^{9}} = 10^{-8} \ cm$$

This is a short wavelength, but it is of the same order of magnitude as an atomic diameter. Electrons bound to atoms will definitely exhibit quantum effects because the wavelength which determines their probability amplitude is of the same size as the important

physical dimensionCthe diameter of the atom.

We can also determine the wavelength associated with the motion of the mass of 1 g moving on a line 1 m in length with a velocity of, say, 1 cm/sec:

$$\lambda = \frac{6.6 \times 10^{-27}}{1 \times 1} = 6.6 \times 10^{-27} \text{ cm}$$

This is an incredibly short wavelength, not only relative to the length of the line but absolutely as well. No experiment could detect the physical implications of such a short wavelength. It is indeed many, many times smaller than the diameter of the mass itself. For example, to observe a diffraction effect for such particles the spacings in the grating must be of the order of magnitude of 1 ´ 10-27 cm. Such a grating cannot be made from ordinary matter since atoms themselves are about 1019 times larger than this. Even if such a grating could be found, it certainly wouldn't affect the motion of a mass of 1 g as the size of the mass is approximately 1028 times larger than the spacings in the grating! Clearly, quantum effects will not be observed for massive particles. It is also clear that the factor which determines when quantum effects will be observed and when they will be absent is the magnitude of Planck's constant h. The very small magnitude of h restricts the observation of quantum effects to the realm of small masses.

## Contributors and Attributions

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## 2.3: Further Reading

W. Heisenberg, *The Physical Principles of the Quantum Theory*, University of Chicago Press, Chicago, Illinois, 1930.
This reference contains interesting discussions of the basic concepts of quantum mechanics written by a man who participated in the birth of the new physics.

## 2.E: Exercises

### Q.1

One of the more recent experimental methods of studying the nucleus of an atom is to probe the nucleus with very high energy electrons. Calculate the order of magnitude of the energy of an electron when it is bound inside a nucleus with a diameter $1 \times 10^{-12}$ cm. Compare this value with the order of magnitude of the energy of an electron bound to an atom of diameter $1 \times 10^{-8}$ cm.

### Q.2

Nuclear particles, protons or neutrons have masses approximately $2 \times 10^{3}$ times the mass of an electron. Estimate the average energy of a nuclear particle bound in a nucleus and compare it with the order of magnitude energy for an electron bound to an atom. This result should indicate that chemical changes which involve changes in the electronic energies of the system do not affect the nucleus of an atom.

## 3: The Hydrogen Atom

The study of the hydrogen atom is more complicated than our previous example of an electron confined to move on a line. Not only does the motion of the electron occur in three dimensions but there is also a force acting on the electron. This force, the electrostatic force of attraction, is responsible for holding the atom together.

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# 3.1: Introduction

The study of the hydrogen atom is more complicated than our previous example of an electron confined to move on a line. Not only does the motion of the electron occur in three dimensions but there is also a force acting on the electron. This force, the electrostatic force of attraction, is responsible for holding the atom together. The magnitude of this force is given by the product of the nuclear and electronic charges divided by the square of the distance between them. In the previous example of an electron confined to move on a line, the total energy was entirely kinetic in origin since there were no forces acting on the electron. In the hydrogen atom however, the energy of the electron, because of the force exerted on it by the nucleus, will consist of a potential energy (one which depends on the position of the electron relative to the nucleus) as well as a kinetic energy. The potential energy $V(r)$ arising from the force of attraction between the nucleus and the electron is:

$$V(r) = \frac{-e^2}{r}$$

Let us imagine for the moment that the proton and the electron behave classically. Then, if the nucleus is held fixed at the origin and the electron allowed to move relative to it, the potential energy would vary in the manner indicated in Fig. 3-1. The potential energy is independent of the direction in space and depends only on the distance $r$ between the electron and the nucleus. Thus Fig. 3-1 refers to any line directed from the nucleus to the electron. The $r$-axis in the figure may be taken literally as a line through the nucleus. Whether the electron moves to the right or to the left the potential energy varies in the same manner.
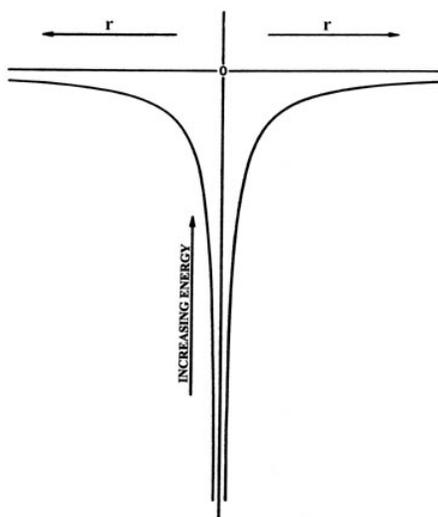


Fig. 3-1. The potential energy of interaction between a nucleus (at the origin) and an electron as a function of the distance r between them.

The potential energy is zero when the two particles are very far apart ($r = ¥$ ), and equals minus infinity when $r$ equals zero. We shall take the energy for $r = ¥$ as our zero of energy. Every energy will be measured relative to this value. When a stable atom is formed, the electron is attracted to the nucleus, $r$ is less than infinity, and the energy will be negative. A negative value for the energy implies that energy must be supplied to the system if the electron is to overcome the attractive force of the nucleus and escape from the atom. The electron has again "fallen into a potential well." However, the shape of the well is no longer a simple square one as previously considered for an electron confined to move on a line, but has the shape shown in Fig. 3-1. This shape is a consequence of there being a force acting on the electron and hence a potential energy contribution which depends on the distance between the two particles. This is the nature of the problem. Now let us see what quantum mechanics predicts for the motion of the electron in such a situation.

# 3.2: The Quantization of Energy

The motion of the electron in the hydrogen atom is not free. The electron is bound to the atom by the attractive force of the nucleus and consequently quantum mechanics predicts that the total energy of the electron is quantized. The expression for the energy is:

$$E_n = \frac{-2\pi^2 m e^4 Z^2}{n^2 h^2} \tag{3.2.1}$$

with $n = 1, 2, 3, 4...$

where $m$ is the mass of the electron, $e$ is the magnitude of the electronic charge, $n$ is a quantum number, $h$ is Planck's constant and $Z$ is the atomic number (the number of positive charges in the nucleus). Equation 3.2.1 applies to any one-electron atom or ion. For example, He$^+$ is a one-electron system for which $Z = 2$. We can again construct an energy level diagram listing the allowed energy values (Figure 3.2.1).
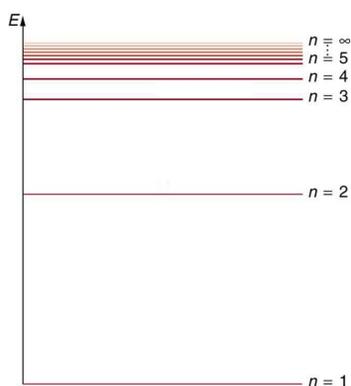


Figure 3.2.1: The energy level diagram for the H atom. Each line denotes an allowed energy for the atom. An energy-level diagram plots energy vertically and is useful in visualizing the energy states of a system and the transitions between them. This diagram is for the hydrogen-atom electrons.

These are obtained by substituting all possible values of $n$ into Equation 3.2.1. As in our previous example, we shall represent all the constants which appear in the expression for $E_n$ by a constant $K$ and we shall set $Z = 1$, i.e., consider only the hydrogen atom.

$$E_n = \frac{-K}{n^2} \tag{3.2.2}$$

with $n = 1, 2, 3, 4...$

Since the motion of the electron occurs in three dimensions we might correctly anticipate three quantum numbers for the hydrogen atom. But the energy depends only on the quantum number $n$ and for this reason it is called the ***principal quantum number***. In this case, the energy is inversely dependent upon $n^2$, and as $n$ is increased the energy becomes less negative with the spacings between the energy levels decreasing in size. When $n = 0$, then $E = 0$ and the electron is free of the attractive force of the nucleus. The average distance between the nucleus and the electron (the average value of $r$) increases as the energy or the value of $n$ increases. Thus energy must be supplied to pull the electron away from the nucleus.

The parallelism between increasing energy and increasing average value of $r$ is a useful one. In fact, when an electron loses energy, we refer to it as "falling" from one energy level to a lower one on the energy level diagram. Since the average distance between the nucleus and the electron also decreases with a decrease in $n$, then the electron literally does fall in closer to the nucleus when it "falls" from level to level on the energy level diagram.

The energy difference between $E_\infty$ and $E_1$:

$$E_{n=\infty} - E_{n=1} = 0 - (-K) = K = \frac{-2\pi^2 m e^4}{n^2 h^2} = \frac{e^2}{2a_o} \tag{3.2.3}$$

is called the ionization energy and is the energy required to pull the electron completely away from the nucleus and is, therefore, the energy of the reaction:

$$H \rightarrow H^+ + e^-$$
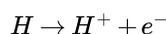
with $\Delta E = 13.60\,eV = 0.5\,a.\,u.$

This amount of energy is sufficient to separate the electron from the attractive influence of the nucleus and leave both particles at rest. If an amount of energy greater than $K$ is supplied to the electron, it will not only escape from the atom but the energy in excess of $K$ will appear as kinetic energy of the electron. Once the electron is free it may have any energy because all velocities are then possible. An electron which possesses and energy in this region of the diagram is a free electron and has kinetic energy of motion only.

## The Hydrogen Atom Spectrum

As mentioned earlier, hydrogen gas emits colored light when a high voltage is applied across a sample of the gas contained in a glass tube fitted with electrodes. The electrical energy transmitted to the gas causes many of the hydrogen molecules to dissociate into atoms:

$$H_2 \rightarrow H + H$$
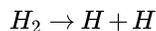
The electrons in the molecules and in the atoms absorb energy and are excited to high energy levels. Ionization of the gas also occurs. When the electron is in a quantum level other than the lowest level (with $n = 1$) the electron is said to be excited, or to be in an excited level. The lifetime of such an excited level is very brief, being of the order of magnitude of only $10^{-8}$ sec. The electron loses the energy of excitation by falling to a lower energy level and at the same time emitting a photon to carry off the excess energy. We can easily calculate the frequencies which should appear in the emitted light by calculating the difference in energy between the two levels and making use of Bohr's frequency condition ($E = h\nu$):

$$\nu = \frac{E_n' - E_n}{h}$$

with $n' > n$

Suppose we consider all those frequencies which appear when the electron falls to the lowest level, $n = 1$:

$$\nu = \frac{E_1 - E_n}{h} = \frac{K}{h}\left(\frac{1}{1} - \frac{1}{n^2}\right) \tag{3.2.4}$$

with $n = 2, 3, 4 \ldots$

very value of $n$ substituted into Equation 3.2.3 gives a distinct value for $v$. In Figure 3.2.1 we illustrate the changes in energy which result when the electron emits a photon by an arrow connecting the excited level (of energy $E_n$) with the ground level (of energy $E_1$). The frequency resulting from each drop in energy will be directly proportional to the length of the arrow. Just as the arrows increase in length as $n$ is increased, so $v$ increases. However, the spacings between the lines decrease as $n$ is increased, and the spectrum will appear as shown directly below the energy level diagram in Figure 3.2.1.
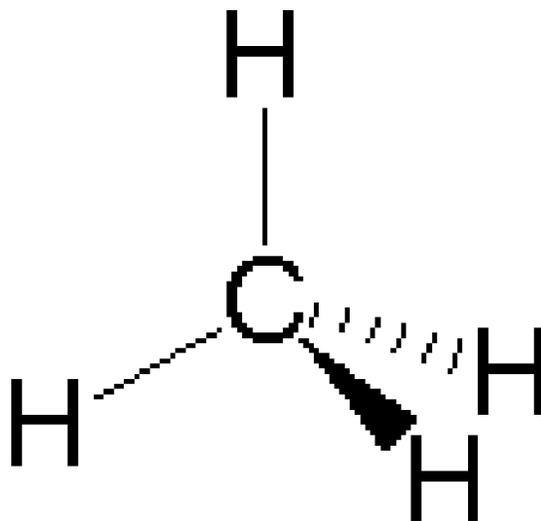
Figure 3.2.1: *The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)*

Each line in the spectrum is placed beneath the arrow which represents the change in energy giving rise to that particular line. Free electrons with varying amounts of kinetic energy ($\frac{1}{2}mu^2$) can also fall to the $n = 1$ level.

The energy released in the reversed ionization reaction (electron affinity):

$$H^+ + e^- \rightarrow H$$
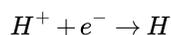
will equal $K$, the difference between $E_¥$ and $E_1$, plus $\frac{1}{2}mu^2$, the kinetic energy originally possessed by the electron. Since this latter energy is not quantized, every energy value greater than $K$ should be possible and every frequency greater than that corresponding to

$$\nu = \frac{K}{h}$$

should be observed. The line spectrum should, therefore, collapse into a continuous spectrum at its high frequency end. Thus the energy continuum above $E_¥$ gives rise to a continuum of frequencies in the emission spectrum. The beginning of the continuum should be the frequency corresponding to the jump from $E_¥$ to $E_1$, and thus we can determine $K$, the ionization energy of the hydrogen atom, from the observation of this frequency. Indeed, the spectroscopic method is one of the most accurate methods of determining ionization energies.

The hydrogen atom does possess a spectrum identical to that predicted by Equation 3.2.3, and the observed value for $K$ agrees with the theoretical value. This particular series of lines, called the Lyman series, falls in the ultraviolet region of the spectrum because of the large energy changes involved in the transitions from the excited levels to the lowest level. The first few members of a second series of lines, a second line spectrum, falls in the visible portion of the spectrum. It is called the Balmer series and arises from electrons in excited levels falling to the second quantum level. Since $E_2$ equals only one quarter of $E_1$, the energy jumps are smaller and the frequencies are correspondingly lower than those observed in the Lyman series. Four lines can be readily seen in this series: red, green, blue, and violet. Each color results from the electrons falling from a specific level, to the $n = 2$ level: red $E_3$ ® $E_2$; green, $E_4$® $E_2$; blue, $E_5$® $E_2$; and violet $E_6$ ®$E_2$. Other series, arising from electrons falling to the $n = 3$ and $n= 4$ levels, can be found in the infrared (frequencies preceding the red end or long wavelength end of the visible spectrum).

The fact that the hydrogen atom exhibits a line spectrum is visible proof of the quantization of energy on the atomic level.

# 3.3: The Probability Distribution of the Hydrogen Atom

## Crude Approximation of Electron Position in a Hydrogen Atom

To what extent will quantum mechanics permit us to pinpoint the position of an electron when it is bound to an atom? We can obtain an order of magnitude answer to this question by applying the uncertainty principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\approx h$$

to estimate $\Delta x$, which represents the minimum uncertainty in our knowledge of the position of the electron. The momentum of an electron in an atom is of the order of magnitude of $9 \times 10^{-19} \, g\,cm/sec$. The **uncertainty** in the momentum $Deltap$ must necessarily be of the same order of magnitude. Thus

$$\Delta x = \frac{7 \times 10^{-27}}{9 \times 10^{-19}} \approx 10^{-8} \, cm$$

The uncertainty in the position of the electron is of the same order of magnitude as the diameter of the atom itself. As long as the electron is bound to the atom, we will not be able to say much more about its position than that it is in the atom. Certainly all models of the atom which describe the electron as a particle following a definite trajectory or orbit must be discarded.

We can obtain an energy and one or more wavefunctions for every value of $n$, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes $\psi_n$, allows us to calculate the probability distributions for the electron in any given quantum level. When $n = 1$, the wave function and the derived probability function are independent of direction and depend only on the distance $r$ between the electron and the nucleus. In Figure 3.3.1, we plot both $\psi_1$ and $P_1$ versus $r$, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}$ cm.)
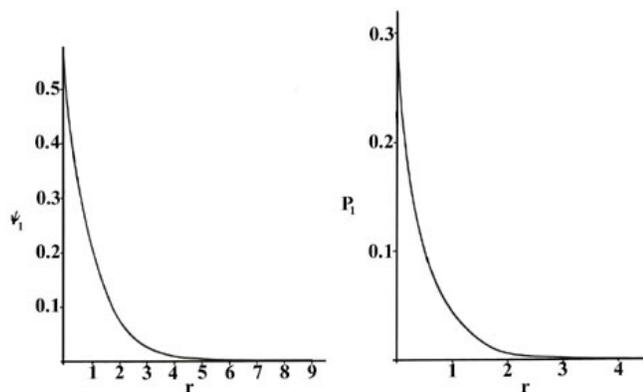


**Figure** $3.3.1$: *The wave function and probability distribution as functions of r for the n = 1 level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.*

Two interpretations can again be given to the $P_1$ curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure $3.3.1$ for $P_1$. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing $r$. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than $10^{-8}$ cm will be greater than $K$, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret $P_1$ as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of $P_n$ for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

When the electron is in a definite energy level we shall refer to the $P_n$ distributions as ***electron density distributions***, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, $e^-/V$. The volume $V$ is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then $e^-/a_0{}^3$. To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density $e^-/a_0{}^3$ = 6.7 electronic charges per cubic Ångstrom. That is, a cube with a length of $0.52917 \times 10^{-8}\ cm$, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

$P_1$ may be represented in another manner. Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius $r$ and an outer concentric sphere with a radius only infinitesimally greater, say $r + Dr$. The area of the inner sphere is $4pr^2$ and the thickness of the shell is D$r$. Thus the volume of the shell is $4\pi r^2 \Delta r$ and the product of this volume and the charge density $P_1(r)$, which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius $r$ and $r + Dr$. The product $4pr^2 P_n$ is given a special name, the radial distribution function, which we shall label $Q_n(r)$.

> 📌 Volume Element for a Shell in Spherical Coordinates
>
> The reader may wonder why the volume of the shell is not taken as:
>
> $$\frac{4}{3}\pi \left[ (r + \Delta r)^3 - r^3 \right]$$
>
> the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain
>
> $$\frac{4}{3}\pi \left( 3r^2 \Delta r + 3r\Delta r^2 + \Delta r^3 \right)$$
>
> and for very small values of $\Delta r$ the $3r\Delta r^2$ and $\Delta r^3$ terms are negligible in comparison with $3r^2 \Delta r$. Thus for small values of $\Delta r$, the two expressions for the volume of the shell approach one another in value and when $\Delta r$ represents an infinitesimal small increment in $r$ they are identical.

The radial distribution function is plotted in Figure $3.3.2$ for the ground state of the hydrogen atom.
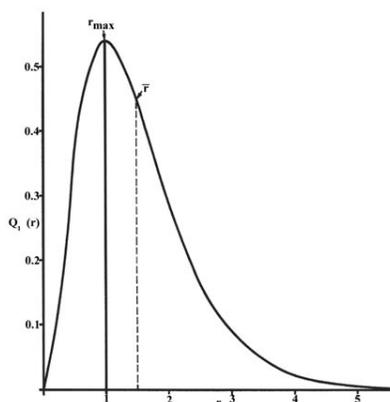


Figure $3.3.2$: The radial distribution function $Q_1(r)$ for an H atom. The value of this function at some value of r when multiplied by $\delta r$ gives the number of electronic charges within the thin shell of space lying between spheres of radius $r$ and $r + \delta r$ .

The curve passes through zero at $r = 0$ since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by $4pr^2$D$r$ increases. However, as shown in Figure $3.3.1$:, the absolute value of the electron density at a given point decreases with $r$ and the resulting curve must pass through a maximum. This maximum occurs at $r_{max} = a_0$. Thus more of the electronic charge is present at a distance $a_0$, out from the nucleus than at any other value of $r$. Since the curve is unsymmetrical, the average value of $r$, denoted by $\bar{r}$, is not equal to $r_{max}$. The average value of $r$ is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the $n = 1$ level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of $r$ is increased.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 3.3.1), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 3.3.3). Since the electron density depends only on $r$, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.
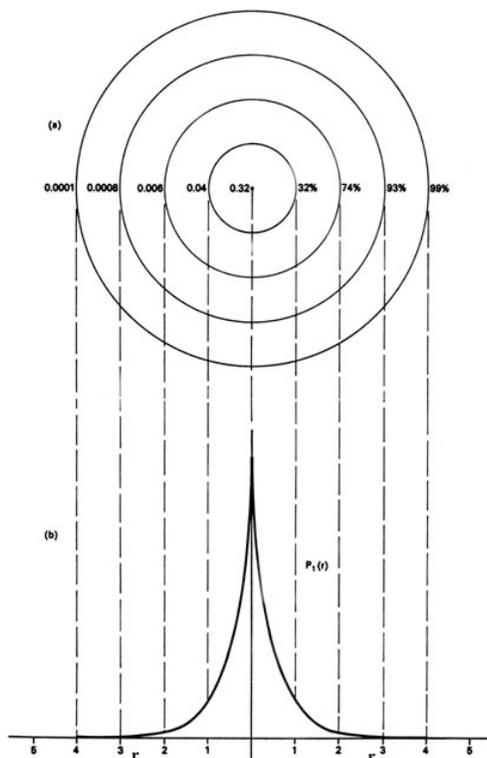


Figure 3.3.3: (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = $4.2 \times 10^{-8}$ $cm$ ). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure 3.3.1 for $P_1$, but now plotted from the nucleus in both directions.

This completes the description of the most stable state of the hydrogen atom, the state for which \(n = 1\). Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased to another of the allowed values, corresponding to a new value for $n$, $y_n$ and $P_n$ change as well. The wavefunctions $y_n$ for the hydrogen atom are given a special name, ***atomic orbitals***, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wavefunction which determines the motion of a single electron. If the one-electron wave function is for an atomic system, it is called an atomic orbital.

> *Do not confuse the word orbital with the classical word and notion of an orbit. First, an orbit implies the knowledge of a definite trajectory or path for a particle through space which in itself is not possible for an electron. Secondly, an orbital, like the wave function, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.*

For every value of the energy $E_n$, for the hydrogen atom, there is a degeneracy equal to $n^2$. Therefore, for $n = 1$, there is but one atomic orbital and one electron density distribution. However, for $n = 2$, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, $E_2$. Thus for all values of the principal quantum number $n$ there are $n^2$ different ways in which the electronic charge may be distributed in three-dimensional space and still possess

the same value for the energy. For every value of the principal quantum number, **one** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of $n = 1$. The other atomic orbitals for a given value of $n$ exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron density distributions are intimately connected with the angular momentum possessed by the electron.

## Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure $3.3.4$). Just as the ordinary momentum $m\vec{v}$ plays a dominant role in the analysis of straight line or linear motion, so angular momentum plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.
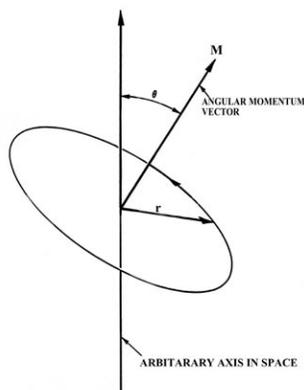


*Figure* $3.3.4$*:* The angular momentum vector for a classical model of the atom.

In Figure $3.3.4$, $m$ is the mass of the electron, **v** is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit as indicated in the figure) and $r$ is the radius of the orbit. The linear velocity **v** is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is **not** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius $r$ at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{M}| = m\nu r$$

The angular momentum vector $\vec{M}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($u$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along $r$; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector **v** would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{M}$, a **torque** is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system. Thus both the energy and the angular momentum are quantized for an atom.

*Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.*

There is a quantum number, denoted by $l$, which governs the magnitude of the angular momentum, just as the quantum number $n$ determines the energy. The **magnitude** of the angular momentum may assume only those values given by:

$$M = \sqrt{l(l+1)}\,\hbar$$

with $l = 0, 1, 2, 3, \ldots n-1$

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, *l* may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation ??? that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called *s* orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 1*s*, 2*s*, 3*s*, etc., atomic orbitals.

The preceding discussion referred to the 1*s* orbital since for the ground state of the hydrogen atom *n* = 1 and *l* = 0. This orbital, and all *s* orbitals in general, predict spherical density distributions for the electron as exemplified by Figure $3.3.2$ for the 1s density. Figure $3.3.5$ shows the radial distribution functions $Q(r)$ which apply when the electron is in a 2*s* or 3*s* orbital to illustrate how the character of the density distributions change as the value of $n$ is increased.

It is common usage to refer to an electron as being "in" an orbital even though an orbital is, but a mathematical function with no physical reality. To say an electron is in a particular orbital is meant to imply that the electron is in the quantum state which is described by that orbital. For example, when the electron is in the 2*s* orbital the hydrogen atom is in a state for which *n* = 2 and *l* = 0.
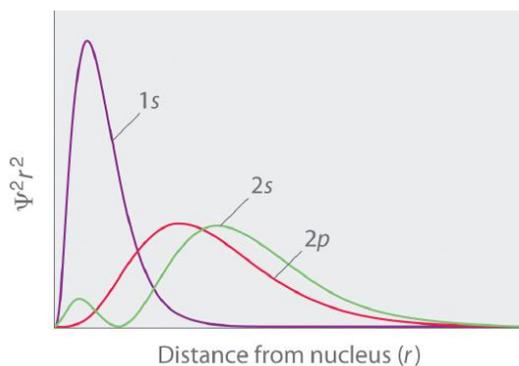


**Figure** $3.3.5$: *Radial distribution functions for the 1s, 2s, and 2p density distributions. Notice the number of nodes in each distribution.*

Comparing these results with those for the 1*s* orbital in Figure $3.3.2$ we see that as $n$ increases the average value of $r$ increases. This agrees with the fact that the energy of the electron also increases as $n$ increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of $r$ for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals $n-1$.

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of *l*, the electron density distribution assumes a characteristic shape Figure $3.3.6$.
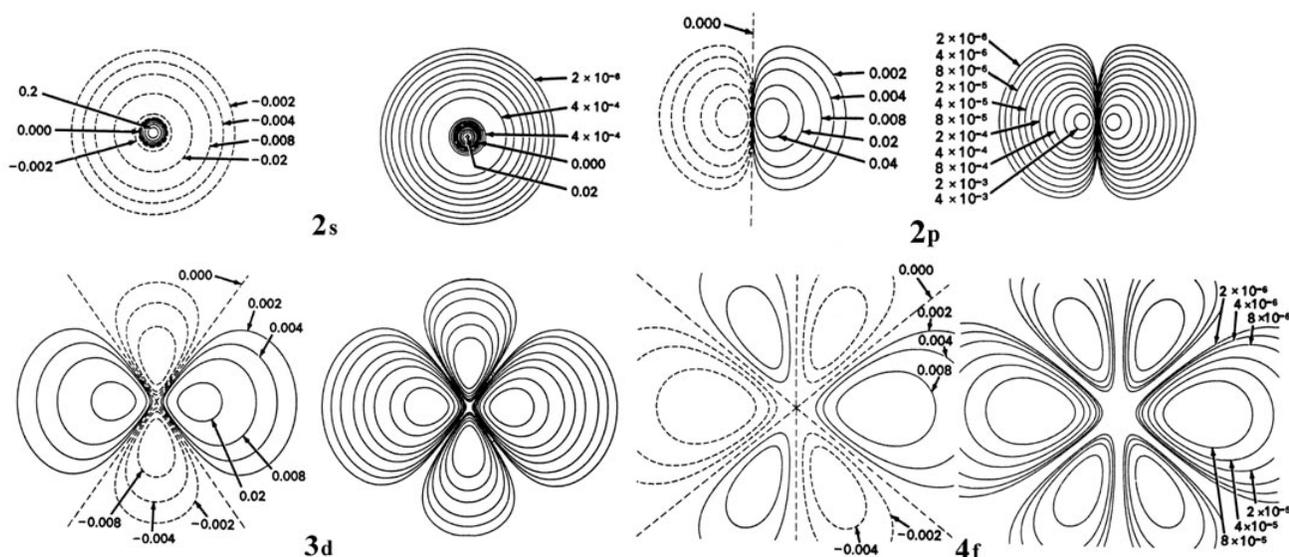
**Figure 3.3.6**: *Contour maps of the 2s, 2p, 3d and 4f atomic orbitals and their charge density distributions for the H atom. The zero contours shown in the maps for the orbitals define the positions of the nodes. Negative values for the contours of the orbitals are indicated by dashed lines, positive values by solid lines.*

When $l = 1$, the orbitals are called $p$ orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The 2$p$ orbital or wave function is positive in value on one side and negative in value on the other side of a plane which is perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a 2$p$ orbital does not place any electronic charge density at the nucleus. The electron density of a 1$s$ orbital, on the other hand, is a maximum at the nucleus. The same diagram for the 2$p$ density distribution is obtained for any plane which contains this axis. Thus in three dimensions the electron density would appear to be concentrated in two lobes, one on each side of the nucleus, each lobe being circular in cross section *Figure* **3.3.7**.
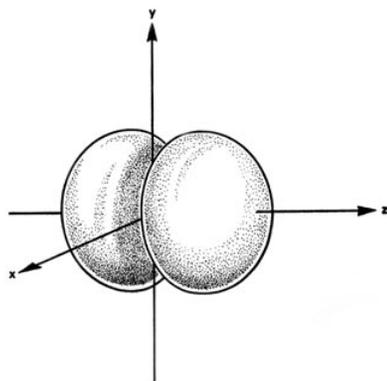


**Figure 3.3.7**: The appearance of the 2p electron density distribution in three-dimensional space.

When $l = 2$, the orbitals are called $d$ orbitals and Figure 3.3.7 shows the contours in a plane for a 3$d$ orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As a final example, **Figure 3.3.5** shows the contours of the orbital and electron density distribution obtained for a 4$f$ atomic orbital which occurs when $n = 4$ and $l = 3$. The point to notice is that as the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in $s$ orbitals with zero angular momentum give spherical density distributions and in addition place charge density at the position of the nucleus.

> There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of $\(l\)$ ($s, p, d, f$ for $l = 0, 1, 2, 3$). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter $s$ stood for sharp, $p$ for principal, $d$ for diffuse and $f$ for fundamental in characterizing spectral lines. From the letter $f$ onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, \ldots$.

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be $n^2$ for every value of $n$. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of $l$ is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an $s$ orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ of the total angular momentum which are physically distinguishable from one another. There are, therefore, three $p$ orbitals. Similarly there are five $d$ orbitals, $(2 \times 2+1)$, seven $f$ orbitals, $(2 \times 3 +1)$, etc. All of the orbitals with the same value of $n$ and $l$, the three $2p$ orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics predicts concerning the angular momentum of an electron in an atom.

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# 3.4: Angular Momentum of an Electron in a Hydrogen Atom

The simplest classical model of the hydrogen atom is one in which the electron moves in a circular planar orbit about the nucleus as previously discussed and as illustrated in Figure 3-7. The angular momentum vector **M** in this figure is shown at an angle qwith respect to some arbitrary axis in space. Assuming for the moment that we can somehow physically define such an axis, then in the classical model of the atom there should be an infinite number of values possible for the component of the angular momentum vector along this axis. As the angle between the axis and the vector **M** varies continuously from 0°, through 90° to 180°, the component of **M** along the axis would vary correspondingly from **M** to zero to -**M**. Thus the quantum mechanical statements regarding the angular momentum of an electron in an atom differ from the classical predictions in two startling ways. First, the magnitude of the angular momentum (the length of the vector **M**) is restricted to only certain values given by:

$$M = \sqrt{l(l+1)}\,\hbar$$

with $l = 0, 1, 2, \ldots$

The magnitude of the angular momentum is quantized. Secondly, quantum mechanics states that the component of **M** along a given axis can assume only $(2l + 1)$ values, rather than the infinite number allowed in the classical model. In terms of the classical model this would imply that when the magnitude of **M** is $\sqrt{2}\,(h/2\pi)$ (the value when $l = 1$), there are only three allowed values for q, the angle of inclination of **M** with respect to a chosen axis.

The angle q is another example of a physical quantity which in a classical system may assume any value, but which in a quantum system may take on only certain discrete values. You need not accept this result on faith. There is a simple, elegant experiment which illustrates the "quantization" of q, just as a line spectrum illustrates the quantization of the energy.

If we wish to measure the number of possible values which the component of the angular momentum may exhibit with respect to some axis we must first find some way in which we can physically define a direction or axis in space. To do this we make use of the magnetism exhibited by an electron in an atom. The flow of electrons through a loop of wire (an electric current) produces a magnetic field (Figure 3.4.1). At a distance from the ring of wire, large compared to the diameter of the ring, the magnetic field produced by the current appears to be the same as that obtained from a small bar magnet with a north pole and a south pole. Such a small magnet is called a magnetic dipole, i.e., two poles separated by a small distance.
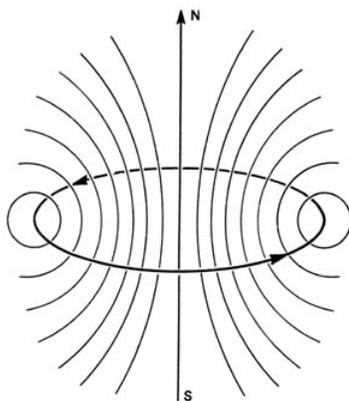


*Figure* $3.4.1$ *: The magnetic field produced by a current in a loop of wire.*

The electron is charged and the motion of the electron in an atom could be thought of as generating a small electric current. Associated with this current there should be a small magnetic field. The magnitude of this magnetic field is related to the angular momentum of the electron's motion in roughly the same way that the magnetic field produced by a current in a loop of wire is proportional to the strength of the current flowing in the wire.

The strength of the atomic magnetic dipole is given by m where:

$$\mu = \sqrt{l(l+1)}\,\beta_m \qquad\qquad (3.4.1)$$

Just as there is a fundamental unit of negative charge denoted by $e^-$ so there is a fundamental unit of magnetism at the atomic level denoted by b$_m$ and called the Bohr magneton. From Equation 3.4.1 we can see that the strength of the magnetic dipole will increase as the angular momentum of the electron increases. This is analogous to increasing the magnetic field by increasing the strength of the current through a circular loop of wire The magnetic dipole, since it has a north and a south pole, will define some direction in space (the magnetic dipole is a vector quantity). The axis of the magnetic dipole in fact coincides with the direction of the angular momentum vector. Experimentally, a collection of atoms behave as though they were a collection of small bar magnets if the electrons in these atoms possess angular momentum. In addition, the axis of the magnet lies along the axis of rotation, i.e., along the angular momentum vector. Thus the magnetism exhibited by the atoms provides an experimental means by which we may study the direction of the angular momentum vector.

> *Thus the magnetism exhibited by the atoms provides an experimental means by which we may study the direction of the angular momentum vector.*

If we place the atoms in a magnetic field they will be attracted or repelled by this field, depending on whether or not the atomic magnets are aligned against or with the applied field. The applied magnetic field ***will determine a direction in space***. By measuring the deflection of the atoms in this field we can determine the directions of their magnetic moments and hence of their angular momentum vectors with respect to this applied field. Consider an evacuated tube with a tiny opening at one end through which a stream of atoms may enter (Figure 3-12). By placing a second small hole in front of the first, inside the tube, we will obtain a narrow beam of atoms which will pass the length of the tube and strike the opposite end. If the atoms possess magnetic moments the path of the beam can be deflected by placing a magnetic field across the tube, perpendicular to the path of the atoms. The magnetic field must be one in which the lines of force diverge thereby exerting an unbalanced force on any magnetic material lying inside the field. This inhomogeneous magnetic field could be obtained through the use of N and S poles of the kind illustrated in Figure 3-12. The direction of the magnetic field will be taken as the direction of the $z$-axis.
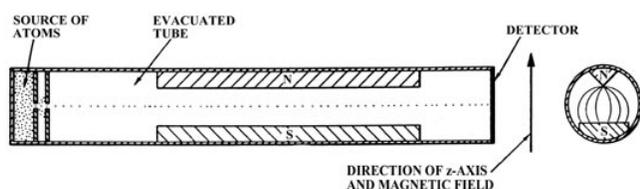


Figure 3-12. The atomic beam apparatus.

Let us suppose the beam consists of neutral atoms which possess $\sqrt{2}\,(h/2\pi)$ units of electronic angular momentum (the angular momentum quantum number $l = 1$). When no magnetic field is present, the beam of atoms strikes the end wall at a single ***point*** in the middle of the detector. What happens when the magnetic field is present? We must assume that before the beam enters the magnetic field, the axes of the atomic magnets are randomly oriented with respect to the $z$-axis. According to the concepts of classical mechanics, the beam should spread out along the direction of the magnetic field and produce a line rather than a point at the end of the tube (Figure 3-13a). Actually, the beam is split into three distinct component beams each of equal intensity producing three spots at the end of the tube (Figure 3-13b).
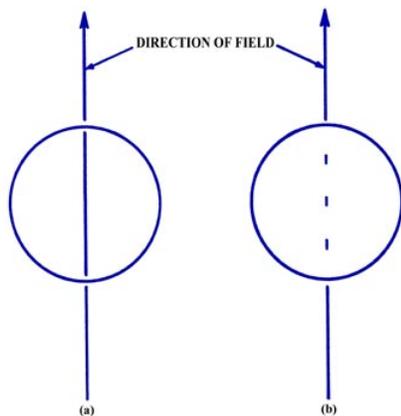


***Figure*** $3.4.3$ : (a) The result of the atomic beam experiment as predicted by classical mechanics, (b) The observed result of the atomic beam experiment.

The startling results of this experiment can be explained only if we assume that while in the magnetic field each atomic magnet could assume only one of three possible orientations with respect to the applied magnetic field (Figure 3-14).
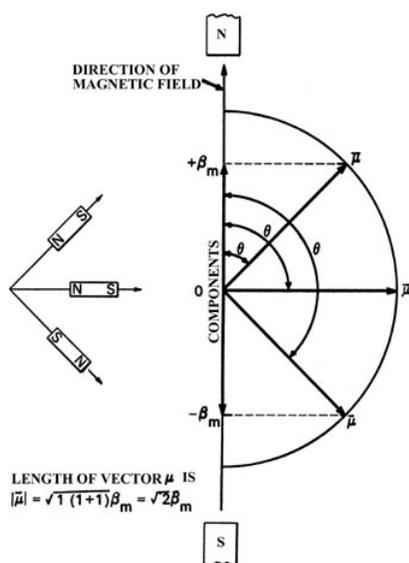


*Figure* $3.4.4$*: The three possible orientations for the total magnetic moment with respect to an external magnetic field for an atom with l =1.*

The atomic magnets which are aligned perpendicular to the direction of the field are not deflected and will follow a straight path through the tube. The atoms which are attracted upwards must have their magnetic moments oriented as shown. From the known strength of the applied inhomogeneous magnetic field and the measured distance through which the beam has been deflected upwards, we can determine that the component of the magnetic moment lying along the $z$-axis is only $b_m$ in magnitude rather than the value of $\sqrt{2}\beta_m$ This latter value would result if the axis of the atomic magnet was parallel to the z-axis, i.e., the angle q = 0°. Instead q assumes a value such that the component of the total moment $(\sqrt{l(l+1)}\beta_m)$ lying along the z-axis is just $lb_m$. Similarly the beam which is deflected downwards possesses a magnetic moment along the z-axis of $-b_m$ or $-lb_m$. The classical prediction for this experiment assumes that q may equal all values from 0° to 180°, and thus all values (from a maximum of $-\sqrt{2}\beta_m$ (q = 0°) to 0 (q =90°) to $-\sqrt{2}\beta_m$ (q = 180°)) for the component of the atomic moment along the z-axis would be possible. Instead, q is found to equal only those values such that the magnetic moment along the z-axis equals $+b_m$, 0 and $-b_m$.

The angular momentum of the electron determines the magnitude and the direction of the magnetic dipole. (Recall that the vectors for both these quantities lie along the same axis.) Thus the number of possible values which the component of the angular momentum vector may assume along a given axis must equal the number of values observed for the component of the magnetic dipole along the same axis. In the present example the values of the angular momentum component are $+1(h/2p)$, 0 and $-1(h/2p)$, or since $l = 1$ in this case, $+ l(h/2p)$, 0 and $-l(h/2p)$. In general, it is found that the number of observed values is always $(2l + 1)$ the values being:

$$-l\hbar, (-l+1)\hbar, \ldots 0, \ldots, (l-1)\hbar, l\hbar$$

for the angular momentum and

$$-l\beta_m, (l-1)\beta_m \ldots, 0, \ldots, (l-1)\beta_m, l\beta_m$$

for the magnetic dipole. The number governing the magnitude of the component of **M** and $\bar{\mu}$, ranges from a maximum value of $l$ and decreases in steps of unity to a minimum value of $-l$. This number is the third and final quantum number which determines the motion of an electron in a hydrogen atom. It is given the symbol $m$ and is called the magnetic quantum number.

In summary, the angular momentum of an electron in the hydrogen atom is quantized and may assume only those values given by:

| | |
|---|---|
| $\sqrt{l(l+1)}\,\dfrac{h}{2\pi}$ | $l = 0, 1, 2, \ldots, n\text{-}1$ |

https://chem.libretexts.org/@go/page/64673

Furthermore, it is an experimental fact that the component of the angular momentum vector along a given axis is limited to $(2l + 1)$ different values, and that the magnitude of this component is quantized and governed by the quantum number $m$ which may assume the values $l, l\text{-}1, \ldots, 0, \ldots, \text{-}l$. These facts are illustrated in for an electron in a $d$ orbital in which $l = 2$.

$$|\mathbf{M}| = \sqrt{2(2+1)} = \sqrt{6}$$
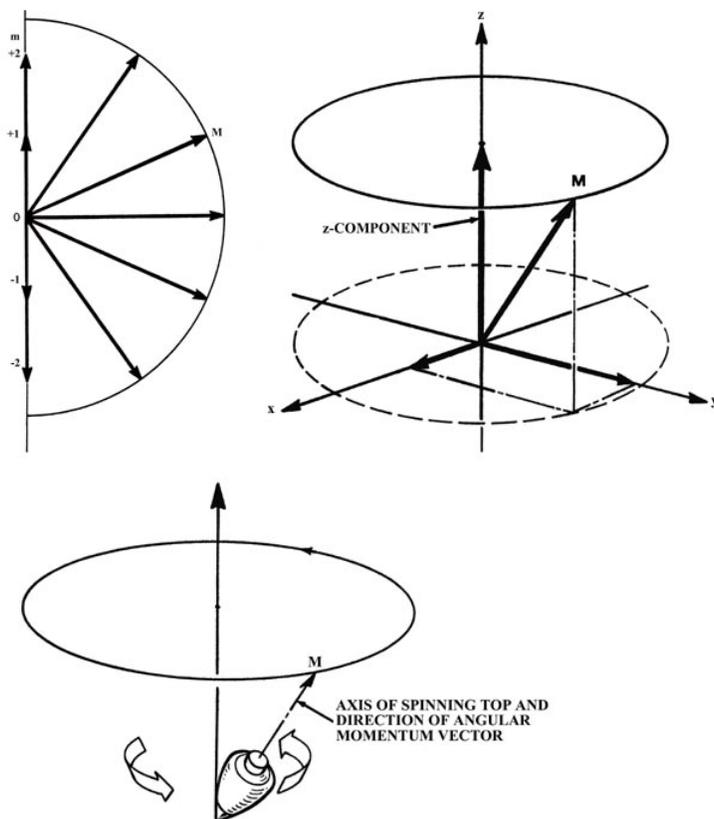


(a)
(b)

*Figure 3-15. Pictorial representation of the quantum mechanical properties of the angular momentum of a d electron for which l = 2. The z-axis can be along any arbitrary direction in space. Figure (a) shows the possible components which the angular momentum vector (of length $\sqrt{2(2+1)}\,(h/2\pi)$) may exhibit along an arbitrary axis in space. A d electron may possess any one of these components. There are therefore five states for a d electron, all of which are physically different. Notice that the maximum magnitude allowed for the component is less then the magnitude of the total angular momentum. Therefore, the angular momentum vector can never coincide with the axis with respect to which the observations are made. Thus the x and y components of the angular momentum are not zero. This is illustrated in Figure (b) which shows how the angular momentum vector may be oriented with respect to the z-axis for the case m = l = 2. When the atom is in a magnetic field, the field exerts a torque on the magnetic dipole of the atom. This torque causes the magnetic dipole and hence the angular momentum vector to precess or rotate about the direction of the magnetic field. This effect is analogous to the precession of a child's top which is spinning with its axis (and hence its angular momentum vector) at an angle to the earth's gravitational field. In this case the gravitational field exerts the torque and the axis of the top slowly revolves around the perpendicular direction as indicated in the figure. The angle of inclination of M with respect to the field direction remains constant during the precession. The z-component of M is therefore constant but the x and y components are continuously changing. Because of the precession, only one component of the electronic angular momentum of an atom an be determined in a given experiment.*

The quantum number $m$ determines the magnitude of the component of the angular momentum along a given axis in space. Therefore, it is not surprising that this same quantum number determines the axis along which the electron density is concentrated. When $m = 0$ for a $p$ electron (regardless of the $n$ value, $2p$, $3p$, $4p$, etc.) the electron density distribution is concentrated along the $z$-axis (see ) implying that the classical axis of rotation must lie in the $x$-$y$ plane. Thus a $p$ electron with $m = 0$ is most likely to be found along one axis and has a zero probability of being on the remaining two axes. The effect of the angular

momentum possessed by the electron is to concentrate density along one axis. When $m = 1$ or -1 the density distribution of a $p$ electron is concentrated in the $x$-$y$ plane with doughnut-shaped circular contours. The $m = 1$ and -1 density distributions are identical in appearance. Classically they differ only in the direction of rotation of the electron around the z-axis; counter-clockwise for $m = +1$ and clockwise for $m = -1$. This explains why they have magnetic moments with their north poles in opposite directions.

We can obtain density diagrams for the $m = +1$ and -1 cases similar to the $m = 0$ case by removing the resultant angular momentum component along the $z$-axis. We can take combinations of the $m = +1$ and -1 functions such that one combination is concentrated along the $x$-axis and the other along the $y$-axis, and both are identical to the $m = 0$ function in their appearance. Thus these functions are often labelled as $p_x$, $p_y$ and $p_z$ functions rather than by their $m$ values. The $m$ value is, however, the true quantum number and we are cheating physically by labelling them $p_x$, $p_y$ and $p_z$ . This would correspond to applying the field first in the $z$ direction, then in the $x$ direction and finally in the $y$ direction and trying to save up the information each time. In reality when the direction of the field is changed, all the information regarding the previous direction is lost and every atom will again align itself with one chance out of three of being in one of the possible component states with respect to the new direction.

We should note that the $r$ dependence of the orbitals changes with changes in $n$ or $l$, but the directional component changes with $l$ and $m$ only. Thus all $s$ orbitals possess spherical charge distributions and all $p$ orbitals possess dumb-bell shaped charge distributions regardless of the value of $n$.

*Table 3-1: The Atomic Orbitals for the Hydrogen Atom*

| $E_n$ | n | l | m | Symbol for orbital | |
|---|---|---|---|---|---|
| -K | 1 | 0 | 0 | 1s | |
| | 2 | 0 | 0 | 2s | |
| $-\frac{1}{4}K$ | 2 | 1 | 1 | $2p_{+1}$ | ö |
| | 2 | 1 | 0 | $2p_0$ | ý $p_x, p_y, p_z$ |
| | 2 | 1 | -1 | $2p_{-1}$ | þ |
| | 3 | 0 | 0 | 3s | |
| | 3 | 1 | 1 | $3p_{+1}$ | ö |
| | 3 | 1 | 0 | $3p_0$ | ý $p_x, p_y, p_z$ |
| | 3 | 1 | -1 | $3p_{-1}$ | þ |
| $-\frac{1}{9}K$ | 3 | 2 | 2 | $3d_{+2}$ | ö |
| | 3 | 2 | 1 | $3d_{+1}$ | \| |
| | 3 | 2 | 0 | $3d_0$ | ý $d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ |
| | 3 | 2 | -1 | $3d_{-1}$ | \| |
| | 3 | 2 | -2 | $3d_{-2}$ | þ |

Table 3-1 summarizes the allowed combinations of quantum numbers for an electron in a hydrogen atom for the first few values of $n$; the corresponding name (symbol) is given for each orbital. Notice that there are $n^2$ orbitals for each value of $n$, all of which belong to the same quantum level and have the same energy. There are $n$ - 1 values of $l$ for each value of $n$ and there are $(2l + 1)$ values of $m$ for each value of $l$. Notice also that for every increase in the value of $n$, orbitals of the same $l$ value (same directional dependence) as found for the preceding value of $n$ are repeated. In addition, a new value of $l$ and a new shape are introduced. Thus there is a repetition in the shapes of the density distributions along with an increase in their number. We can see evidence of a periodicity in these functions (a periodic re-occurrence of a given density distribution) which we might hope to relate to the

periodicity observed in the chemical and physical properties of the elements. We might store this idea in the back of our minds until later.

We can summarize what we have found so far regarding the energy and distribution of an electron in a hydrogen atom thus:

i. The energy increases as *n* increases, and depends only on *n*, the principal quantum number.
ii. The average value of the distance between the electron and the nucleus increases as *n* increases.
iii. The number of nodes in the probability distribution increases as *n* increases.
iv. The electron density becomes concentrated along certain lines (or in planes) as *l* is increased.

Some words of caution about energies and angular momentum should be added. In passing from the domain of classical mechanics to that of quantum mechanics we retain as many of the familiar words as possible. Examples are kinetic and potential energies, momentum, and angular momentum. We must, however, be on guard when we use these familiar concepts in the atomic domain. All have an altered meaning. Let us make this clear by considering these concepts for the hydrogen atom.

Perhaps the most surprising point about the quantum mechanical expression for the energy is that it does not involve *r*, the distance between the nucleus and the electron. If the system were a classical one, then we would expect to be able to write the total energy $E_n$ as:

$$E_n = KE = PE = \frac{1}{2}mv^2 - \frac{e^2}{r} \tag{3.4.2}$$

Both the *KE* and *PE* would be functions of *r*, i.e., both would change in value as *r* was changed (corresponding to the motion of the electron). Furthermore, the sum of the *PE* and *KE* must always yield the same value of $E_n$ which is to remain constant.
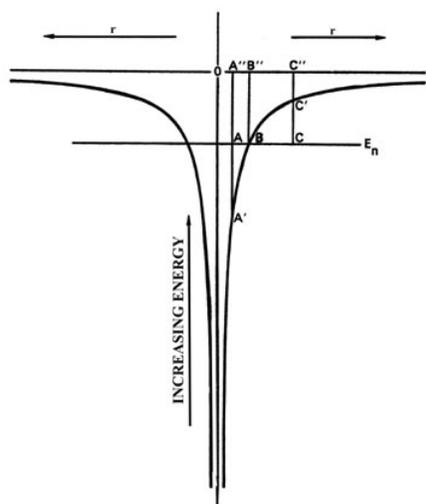


Figure3-16. The potential energy diagram for an H atom with one of the allowed energy values superimposed on it.

Fig 3-16 is the potential energy diagram for the hydrogen atom and we have superimposed on it one of the possible energy levels for the atom, $E_n$. Consider a classical value for *r* at the point *A*". Classically, when the electron is at the point *A*", its *PE* is given by the value of the *PE* curve at *A*'. The *KE* is thus equal to the length of the line *A* - *A*' in energy units. Thus the sum of *PE* + *KE* adds up to $E_n$.

When the electron is at the point *B*", its *PE* would equal $E_n$ and its *KE* would be zero. The electron would be motionless. Classically, for this value of $E_n$ the electron could not increase its value of *r* beyond the point represented by *B*". If it did, it would be inside the "potential wall." For example, consider the point *C*". At this value of *r*, the *PE* is given by the value at *C*' which is *now greater* than $E_n$ and hence the *KE* must be equal to the length of the line *C* - *C*'. But the *KE* must now be *negative* in sign so that the sum of *PE* and *KE* will still add up to $E_n$. What does a negative *KE* mean? It doesn't mean anything as it never occurs in a classical system. Nor does it occur in a quantum mechanical system. It is true that quantum mechanics does predict a finite probability for the electron being inside the potential curve and indeed for all values of *r* out to infinity. However, the quantum mechanical expression for $E_n$ does not allow us to determine the instantaneous values for the *PE* and *KE*. Instead, we can determine only their average values. Thus quantum mechanics does not give Equation 3.4.2 but instead states only that the *average* potential and kinetic energies may be known:

$$E_n = \langle PE \rangle = \langle KE \rangle \tag{3.4.3}$$

The bracket denotes the fact that the energy quantity has been averaged over the complete motion (all values of $r$) of the electron.

Why can $r$ not appear in the quantum mechanical expression for $E_n$, and why can we obtain only average values for the *KE* and *PE*? When the electron is in a given energy level its energy is precisely known; it is $E_n$. The uncertainty in the value of the momentum of the electron is thus at a minimum. Under these conditions we have seen that our knowledge of the position of the electron is very uncertain and for an electron in a given energy level we can say no more about its position than that it is bound to the atom. Thus if the energy is to remain fixed and known with certainty, we cannot, because of the uncertainty principle, refer to (or measure) the electron as being at some particular distance $r$ from the nucleus with some instantaneous values for its *PE* and *KE*. Instead, we may have knowledge of these quantities only when they are averaged over all possible positions of the electron. This discussion again illustrates the pitfalls (e.g., a negative kinetic energy) which arise when a classical picture of an electron as a particle with a definite instantaneous position is taken literally.

It is important to point out that the classical expressions which we write for the dependence of the potential energy on distance, -$e^2/r$ for the hydrogen atom for example, are the expressions employed in the quantum mechanical calculation. However, only the average value of the *PE* may be calculated and this is done by calculating the value of -$e^2/r$ at every point in space, taking into account the fraction of the total electronic charge at each point in space. The amount of charge at a given point in three-dimensional space is, of course, determined by the electron density distribution. Thus the value of $\overline{PE}$ for the ground state of the hydrogen atom is the electrostatic energy of interaction between a nucleus of charge +1$e$ with the surrounding spherical distribution of negative charge.

> ### 📌 Tunneling
>
> The penetration of a potential wall by the electron, into regions of negative kinetic energy, is known as "tunnelling." Classically a particle must have sufficient energy to surmount a potential barrier. In quantum mechanics, an electron may tunnel into the barrier (or through it, if it is of finite width). Tunnelling will not occur unless the barrier is of **finite height.** In the example of the H atom, the potential well is infinitely deep, but the energy of the electron is such that it is only a distance $E_n$ from the top of the well. In the example of the electron moving on a line we assumed the potential well to be infinitely deep regardless of the energy of the electron. In this case $y_n$ and hence $P_n$ must equal zero at the ends of the line and no tunnelling is possible as the potential wall is infinitely high.

We can say more about the $\overline{PE}$ and $\overline{KE}$ for an electron in an atom. Not only are these values constant for a given value of $(n)$, but also for any value of $(n)$,

$$\overline{KE} = \frac{1}{2}\overline{PE} = -E_n$$

Thus the $\overline{KE}$ is always positive and equal to minus one half of the $\overline{PE}$. Since the total energy $E_n$ is negative when the electron is bound to the atom, we can interpret the stability of atoms as being due to the decrease in the $\overline{PE}$ when the electron is attracted by the nucleus.

The question now arises as to why the electron doesn't "fall all the way" and sit right on the nucleus. When $r = 0$, the $\overline{PE}$ would be equal to minus infinity, and the $\overline{KE}$, which is positive and thus destabilizing, would be zero. Classically this would certainly be the situation of lowest energy and thus the most stable one. The reason for the electron not collapsing onto the nucleus is a quantum mechanical one. If the electron was bound directly to the nucleus with no kinetic energy, its position and momentum would be known with certainty. This would violate Heisenberg's uncertainty principle. The uncertainty principle always operates through the kinetic energy causing it to become large and positive as the electron is confined to a smaller region of space. (Recall that in the example of an electron moving on a line, the $\overline{KE}$ increased as the length of the line decreased.) The smaller the region to which the electron is confined, the smaller is the uncertainty in its position. There must be a corresponding increase in the uncertainty of its momentum. This is brought about by the increase in the kinetic energy which increases the magnitude of the momentum and thus the uncertainty in its value. In other words the bound electron must always possess kinetic energy as a consequence of quantum mechanics.

The $\overline{KE}$ and $\overline{PE}$ have opposite dependences on $\frac{1}{r}$. The $\overline{PE}$ decreases (becomes more negative) as $\frac{1}{r}$ decreases but the $\overline{KE}$ increases (making the atom less stable) as $\frac{1}{r}$ decreases. A compromise is reached to make the energy as negative as possible (the atom as

stable as possible) and the compromise always occurs when $\overline{KE} = -\frac{1}{2}\overline{PE}$. A further decrease in $\bar{r}$ would decrease the $\overline{PE}$ but only at the expense of a ***larger increase*** in the $\overline{KE}$. The reverse is true for an increase in $\bar{r}$. Thus the reason the electron doesn't fall onto the nucleus may be summed up by stating that "the electron obeys quantum mechanics, and not classical mechanics."

# 3.5: Some Useful Expressions

Listed below are a number of equations which give the dependence of $\bar{r}$, $\overline{PE}$ and $\overline{KE}$ on the quantum numbers $n$, $l$ and $m$. They refer not only to the hydrogen atom but also to any one-electron ion in general with a nuclear charge of $Z$. Thus $He^+$ is a one-electron ion with $Z = 2$, $Li^{+2}$ another example with $Z = 3$.

The average distance between the electron and the nucleus expressed in atomic units of length is:

$$r_{n,l,m} = \frac{n^2}{Z}\left[1 + \frac{1}{2}\left\{1 - \frac{l(l+1)}{n^2}\right\}\right]$$

Note that $\bar{r}_{n,l,m}$ is proportional to $n^2$ for $l = 0$ orbitals, and deviates only slightly from this for $l^1$ 0. The value of $\bar{r}_{n,l,m}$ decreases as $Z$ increases because the nuclear attractive force is greater. Thus $\bar{r}_{1,0,0}$ for $He^+$ would be only one half as large as $\bar{r}_{1,0,0}$ for H.

| $E_n = -\dfrac{Z^2}{n^2} K = -\dfrac{Z^2}{2n^2}$ au | $K = \dfrac{2\pi^2 me^4}{h^2} = \dfrac{e^2}{2a_0}$ |
|---|---|
| $\left(\overline{PE}\right)_{n,l,m} = -\dfrac{2Z^2}{n^2} K$ | $\left(\overline{KE}\right)_{n,l,m} = -E_n = +\dfrac{Z^2}{n^2} K$ |

# 3.E: Exercises

## Q1

In 1913 Niels Bohr proposed a model for the hydrogen atom which gives the correct expression for the energy levels $E_n$. His model was based on an awkward marriage of classical mechanics and, at that time, the new idea of quantization. In the Bohr model of the hydrogen atom the electron is assumed to move in a circular orbit around the nucleus, as illustrated in . The energy of the electron in such an orbit is: **(1)**

$$E = PE + KE = \frac{-e^2}{r} + \frac{1}{2}mv^2$$

where u is the tangential velocity of the electron in the orbit. Since the circular orbit is to be a stable one the attractive coulomb force exerted on the electron by the nucleus must be balanced by a centrifugal force, or: **(2)**

$$\frac{e^2}{r} = mr\omega^2 = \frac{mv^2}{r}$$

where w is the circular velocity of the electron. Up until this point the model is completely classical in concept. However, Bohr now postulated that only those orbits are allowed for which the angular momentum is an integral multiple of ($h/2$p). In other words, Bohr postulated that the angular momentum of the electron in the hydrogen atom is quantized. This postulate gives a further equation: **(3)**

$$\text{angular momentum} = mvr = \frac{nh}{2\pi} \quad n = 1, 2, 3, ...$$

   a. Show that by eliminating $r$ and u from these three equations you can obtain the correct expression for $E_n$.
   b. Show that Bohr's model correctly predicts that the $KE = -\frac{1}{2}PE$.
   c. Show that the radius of the first Bohr orbit is identical to the maximum value of $r$ for the $n = 1$ level of the hydrogen atom, $\bar{r}_{1,0,0}$, as calculated by quantum mechanics.
   d. Criticize the Bohr model in the light of the quantum mechanical results for the hydrogen atom.

## Q2

The part of the hydrogen atom spectrum which occurs in the visible region arises from electrons in excited levels falling to the $n = 2$ level. The quantum mechanical expression for the frequencies in this case, corresponding to equation **(3)** of the text for the Lyman series, is: **(4)**

$$\nu = \frac{K}{h}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, ...$$

The energy of an emitted photon for a jump from level $n$ to level 2 is: **(5)**

$$\varepsilon = h\nu = K\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, ...$$

Equation **(5)** predicts that a plot of the photon energies versus ($1/n^2$) should be a straight line. Furthermore, it predicts that the intercept of this line with the energy axis, corresponding to the value of $1/n^2 = 0$, i.e., n = ¥, should equal (¼)K where: **(6)**

$$K = \frac{2\pi^2 me^4}{h^2}$$

The point of this problem is to test these theoretical predictions against the experimental results.

Experimentally we measure the wavelength of the emitted light by means of a diffraction grating. A grating for the diffraction of visible light may be made by marking a glass plate with parallel, equally spaced lines. There are about 10,000 lines per cm. The spacings between the lines in the grating $d$ is thus about 1 ´$10^{-4}$ cm which is the order of magnitude of the wavelength of visible light. The diffraction equation is: **(7)**

$$n\lambda = d\sin\theta \quad n = 1, 2, 3, ...$$

as previously discussed in Problem I-1. We measure the angle q for different orders $n$ = 1, 2, 3, ... of the diffracted light beam. Since $d$ is known, l may be calculated. The experimentally measured values for the first four lines in the Balmer series are given below.

**Balmer Series**

| l(Å) | n |
|------|---|
| 6563 | 3 |
| 4861 | 4 |
| 4341 | 5 |
| 4102 | 6 |

The value of the principal quantum number $n$ which appears in equation (5) is given for each value of l. (This $n$ is totally unrelated to the $n$ of equation (7) for the experimental determination of l.) Calculate the energy of each photon from the value of its wavelength.

$$\varepsilon = h\nu = \frac{hc}{\lambda} = \frac{1.240 \times 10^{-4}}{\lambda} \text{ ev}$$

Plot the photon energies versus the appropriate value of $1/n^2$. Let the $1/n^2$ axis run from 0 to 0.25 and the energy axis run from 0 to 3.6 ev. Include as a point on your graph e = 0 for $1/n^2$ = 0.25, i.e., when $n$ = 2, the excited level and the level to which the electron falls coincide.

a. Do the points fall on a straight line as predicted?
b. Determine the value of $K$ by extending the line to intercept the energy axis. This intercept should equal $K$/4. Read off this value from your graph.
c. Compare the experimental value for $K$ with that predicted theoretically by equation (5). Use $e$ = 4.803 ´ $10^{-10}$ esu, express $m$ and $h$ in cgs units and the value of $K$ will be in ergs (1 erg = 6.2420 ´ $10^{11}$ ev). Recall that $K$ is the ionization potential for the hydrogen atom. An electron falling from the $n$ = ¥ level to the $n$ = 2 level will fall only (¼)$K$ in energy as is evident from the energy level diagram shown in Fig. 3-2.

## Q3

A beam of atoms with $l$ = 1 is passed through an atomic beam apparatus with the magnetic field directed along an axis perpendicular to the direc tion of the beam. The **undeflected beam** from this experiment enters a second beam apparatus in which the magnetic field is directed along an axis which is perpendicular to both the path of the beam and the direction of the field in the first experiment. Will this one component of the original beam be split in the second applied magnetic field? Explain why you think it will be, if this is indeed your answer.

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## 4: Many-Electron Atoms

The hydrogen atom is the *only* atom for which exact solutions of the Schrödinger equation exist. For any atom that contains two or more electrons, no solution has yet been discovered (so no solution for the helium atom exists!) and we need to introduce approximation schemes. The helium atom is a good example of a many-electron atom (that is, an atom which contains more than one electron). No fundamentally new problems are encountered whether we consider two or ten electrons, but a very important problem arises in passing from the one-electron to the two-electron case.

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# 4.1: Introduction

The helium atom is a good example of a many-electron atom (that is, an atom which contains more than one electron). No fundamentally new problems are encountered whether we consider two or ten electrons, but a very important problem arises in passing from the one-electron to the two-electron case. To see what this problem is, consider all the potential interactions found in a helium atom. Again, consider the electrons to be point charges and "freeze" them at some instantaneous positions in space (Figure 4.1.1).
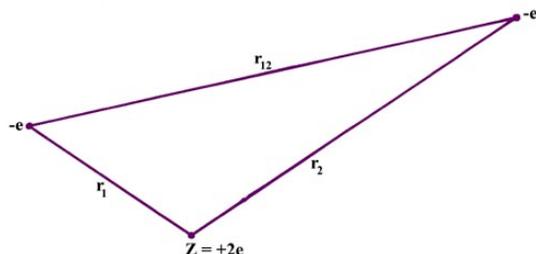


*Figure* **4.1.1** *: The potential interactions in an He atom. The electrons are labelled by their charge -e, and the nucleus by its charge Z = +2e.*

The potential energy, the average value of which is to be determined by quantum mechanics, is

$$V(r_1, r_2) = \frac{(+Ze)(-e)}{r_1} + \frac{(+Ze)(-e)}{r_2} + \frac{(-e)(-e)}{|r_1 - r_2|} \tag{4.1.1}$$

for the helium atom with $Z = 2$, equation 4.1.1 simplifies to

$$V_{He}(r_1, r_2) = \frac{-2e^2}{r_1} - \frac{2e^2}{r_1} + \frac{e^2}{|r_1 - r_2|}$$

The first and second terms in Equation 4.1.1 represent the attraction of the helium nucleus for electrons 1 and 2 respectively. The last term represents the repulsion between the two electrons. It is this last term which makes the problem of the helium atom, and of all many-electron atoms, difficult to solve. No direct solution to the problem exists, the reason being that there are too many interactions to consider simultaneously. We must make some approximation in our approach to this problem.

## 4.2: The Atomic Orbital Concept

Since the nuclear charge is twice the electronic charge, the electrostatic energy of repulsion between the electrons will be the smallest of the three terms in the potential energy expression of the helium atom when the interactions are averaged over all possible positions of the electrons. We could obtain an approximation to the electronic energy of the He atom by neglecting this small term. This is a good idea for another reason. If we ignore the repulsion between the electrons, then physically we are supposing that neither electron "realizes" the other electron is present. The problem is thus identical to that of the hydrogen atom, a problem which can be solved exactly, except that the nuclear charge is now +2 rather than +1.

The energy of each electron in the field of a nucleus of charge +2 is determined separately and the total energy is then simply the sum of the two energies. This is the first approximation to the energy. We will also obtain an approximation to the manner in which the electrons are distributed in space. With this latter knowledge, we can estimate the energy of repulsion between the electrons. That is, with the knowledge of how the electrons are distributed relative to one another we can pick up the term in the potential energy we originally neglected, the term $e^2/r_{12}$, and calculate its contribution to the energy.

> This method of calculating the electronic energy of atoms reduces a ***many-electron*** problem to many ***one-electron*** problems. Each electron (moving in the attractive field of the nucleus) is treated independently of the others. In addition, since the problem is now a set of one-electron problems, we may carry over and use all of the results obtained for the hydrogen atom.

We pointed out in our discussion of the hydrogen atom that the results we obtained could be applied to any one-electron system by setting $Z$ equal to the appropriate value in all of the formulae. The one-electron energies are easily calculated and are given by

$$E_n = -\frac{Z^2 R}{n^2}$$

with the Rydberg constant $R$ determined from basic constants:

$$R = \frac{m_e e^4}{8\varepsilon_0^2 h^2} = 13.6\,eV$$

More important, the concept of atomic orbitals, the one-electron wave functions for the hydrogen atom, may be employed in the many-electron case. When each electron is considered in turn, its motion and distribution in space will again be determined by an atomic orbital. The atomic orbitals will differ from the case of the hydrogen atom in that they will generally be more contracted In the previous chapter we pointed out that the average value of the distance between the nucleus and the electron, $\langle r \rangle$, decreased as the nuclear charge and hence the attractive force exerted by the nucleus was increased However, the orbitals will still be determined by the three quantum numbers $n$, $l$ and $m$. Increasing $Z$ contracts the orbital, but the symmetry of the problem is left unchanged, i.e., the attraction of the electron by the nucleus is still determined only by the distance between them and does not depend on the direction.

The $l$ and $m$ dependences of the orbitals, which determine the directional properties of the orbital and of the electron density distribution, remain unchanged. Thus we may still refer to "hydrogen-like" 1$s$, 2$s$, 2$p$ orbitals For example, the 1$s$ orbital is the most stable orbital (most negative $E$ value) for any value of $Z$, and we naturally assume that the most stable form of the helium atom will be obtained when **both** electrons are placed in the 1$s$ orbital. This information, telling us in which atomic orbital the electrons have been placed, is called an ***electron configuration***.

An abbreviated notation is used to denote the electron configuration For example, the lowest energy state of helium, in which two electrons are placed in the 1$s$ orbital, is written as 1$s^2$. (This is to be read as one-$s$-two and not as one-$s$-squared.) When one of the electrons is placed in an orbital of higher energy, an "excited" configuration is obtained. An example might be 1$s^1$2$p^1$ which one electron is in the 1$s$ orbital and one electron is in the 2$p$ orbital. It should be emphasized that the concept of assigning an electronto an atomic orbital is a rigorous and exact concept **only** for the hydrogen atom; for the many-electron case it is an approximation.

The atomic orbital approximation may be tested by applying it to the helium atom. We have seen that the energy of a single electron moving in the attractive field of a nucleus of charge $+Ze$ is

$$E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2} = -\frac{Z^2}{n^2} R \tag{4.2.1}$$

with $n = 1, 2, 3, 4...$

The energy of the two electrons in the helium atom, each considered to be independent of the other (this is a gross approximation, by the way), is simply

$$E_1 = -\left(\frac{2^2}{1}\right) R - \left(\frac{2^2}{1}\right) R = -8R$$

for the 1$s^2$ electron configuration. To this energy value must be added the energy of repulsion between the two electrons. Since both electrons have been placed in a 1$s$ atomic orbital, we know that the charge distribution for each electron must be spherical and centered on the helium nucleus. The two charge distributions will be completely intermingled and we must calculate the energy of repulsion between every small element of charge density of the one distribution with every small charge element of the second distribution. This calculation can be readily done by the methods of integral calculus and the value of the average energy repulsion is found to be

$$E_c = \frac{5}{4} ZR = \frac{5}{2} R \tag{4.2.2}$$

with $Z_{He} = 2$.

We label this energy $E_c$ as it is a correction to our first approximation to the energy. Notice from Equation 4.2.2 that in general $E_c$ depends directly on the value of $Z$. This makes physical sense, for the greater the value of $Z$, the more contracted and superimposed are the two charge distributions, and the greater is the energy of repulsion between them. Note as well that the correction $E_c$ is indeed smaller than $E_1$, an assumption we made in developing this method of approximating the electronic energy.

The estimate of the total electronic energy of helium atom is

$$E_{He} = E_1 + E_c = -8R + \frac{5}{2} R = \frac{11}{2} R$$

This total energy is called the electronic binding energy as it is the energy released when two initially free electrons are bound to the helium nucleus. Recall that -$K$ represents the binding energy of the most stable state of the hydrogen atom; thus the helium atom is five and one half times more stable than the hydrogen atom. This is not really a fair comparison because the value (11/2)$K$ is the energy required to remove **both** electrons from the helium atom (a double ionization)

$$He \rightarrow He^{+2} + 2e^-$$

with

$$\Delta E = \frac{11}{2} R$$

It is more interesting to compare the energy required to remove a single electron from helium with the energy required to remove the single electron in hydrogen. The energy of the reaction (i.e., the energy required to ionize an atom once) will be denoted by the letter $I_1$.

$$He \rightarrow He^+ + e^-$$

with

$$\Delta E = I$$

is easily calculated

$$I_1 = E_{He^+} + E_{e^-} - E_{He}$$

The energy of the $He^+$ ion using Equation 4.2.1 with $n = 1$ and $Z = 2$, is

$$E_{He^+} = -4R$$

as there is but a single electron left. The energy of the ionized electron $E_{e^-}$ is set equal to zero as it is assumed to be at rest infinitely far away from the ion and

$$E_{He} = -\left(\frac{11}{2}\right)R.$$

Thus $I_1$, the first ionization potential of helium, is equal to $1.5R$, or one and one half times larger than the energy required to ionize a hydrogen atom.

How well do our calculated values for the ionization potential and total energy agree with the experimental results? The energy required for the removal of both electrons is 78.98 eV. Since R = 13.61 eV, the calculated value is (11/2)13.61 = 74.86 eV. This is an encouraging result as the error is only about 5%. The experimental value for $I_1$ is 24.58 eV and our calculated value is (1.5)13.61 = 20.42 ev. The percentage error is larger for the latter case because the actual error is the same in both calculations but $I_1$ is smaller than $\Delta E$. However, the method seems promising. We have indeed predicted that it requires almost twice as much energy to remove an electron from helium as it does to remove one from hydrogen.
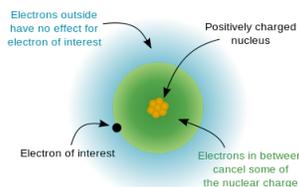
*Effective Nuclear Charge Diagram. (Public Domain)*

## Effective Nuclear Charge

The calculations outlined above may be improved by introducing the concept of an **effective nuclear charge**. Since there are two electrons present in the helium atom, neither electron experiences the full attractive force of the two positive charges on the helium nucleus. Each electron partially screens the nuclear charge from the other. We saw previously that the average value of the distance between an electron and the nucleus for a strictly hydrogen-like orbital varied as (1/Z). Thus by assuming that each electron moves in the field of the full nuclear charge of helium, we consider it to be in a 1s orbital with exactly one half the value of $\langle r \rangle$ as that found for a hydrogen 1s orbital. Since the electron on the average experiences a reduced nuclear charge (i.e., the effective nuclear charge) because of the screening effect of the second electron, we should place it in a 1s orbital which possesses an $\langle r \rangle$ value somewhere between that found for an orbital for the cases $Z = 1$ and $Z = 2$. In other words, the size of the orbital should be determined by an effective nuclear charge, rather than by the actual nuclear charge. This lowered value for $Z$ will obviously decrease the value of the average repulsion energy between the electrons as the two charge clouds will be more expanded and the average distance between the charge points in each distribution will increase. An increased value of $\langle r \rangle$ will also decrease the average kinetic energy of the electrons and thus again lead to an increase in the stability of the atom. On the other hand, an increase in $\langle r \rangle$ will lead to a less negative potential energy as the electrons will on the average be further away from the nucleus. Thus there is some best value for the effective nuclear charge and for $\langle r \rangle$, the value which gives the most stable description of the atom. For helium this "best" value for the effective nuclear charge is found to be 1.687 and the total energy of He is now calculated to be 77.48 ev. The error has been reduced to approximately 2%.

The effective nuclear charge value cannot be inserted into Equation 4.2.1 to determine the energy of the electron. The Z in Equation 4.2.1 refers to the actual nuclear charge, while the effective nuclear charge is a number, always less than the actual $Z$. which determines the optimum size of the orbital when other electrons are present. The value of $Z$ appearing in the equate for $E_c$ will be the effective nuclear charge value. The value of $E_c$ is indeed determined solely by the degree to which the two electron distributions are contracted and this is governed by the effective nuclear charge. It should be pointed out that the concept of an effective nuclear charge will be paramount in our future discussions concerning the electronic structures and properties of many-electron atoms.

## Excited States of the helium Atom

Just as the single electron in the hydrogen atom can be excited to higher quantum levels, so it should be possible to excite one of the electrons in the He atom to energy levels with quantum numbers greater than one. This will change the electron configuration from $1s^2$ to say, $1s^12s^1$ or $1s^12p^1$ etc. The excited electron may again lose the excitation energy in the form of light and fall back to the $1s$ level, giving the ground electronic configuration $1s^2$

$$1s^12p^1 \rightarrow 1s^2 + h\nu$$
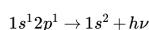
Thus the helium atom should emit a line spectrum when it is excited in an electrical discharge tube. Since only a single electron is excited at a given time although if is possible with the use of a laser to excite two electrons simultaneously, the spectrum for helium should be formally the same as that observed for hydrogen. However, since the nuclear charge experienced by the electron will always be greater than one, the lines in the helium spectrum should be observed at higher frequencies (shorter wavelengths) than those for hydrogen.

Table 4.2.1: The Wavelengths for the Balmer Series in H and the Wavelengths for the Corresponding One-Electron Transitions in He

| H | | | He | |
|---|---|---|---|---|
| n | l (Å) | | n | |
| 3 | 6563 | | 6 | |
| 4 | 4861 | | 4 | |
| 5 | 4340 | | 5 | |
| 6 | 4101 | | 6 | |

In Table 4.2.1, we compare two corresponding line spectra, one for hydrogen and one from helium. In both cases the excited electron fall from an upper $p$ energy level to the $2s$ energy level. In hydrogen the frequencies of the lines in the spectrum are determined by the energy differences between the configuration.

$$np^1 \rightarrow 2s^1$$

with $n = 3, 4, 5...$

This series of jumps from $E_n$ ($n$ = 3, 4, 5, 6, . . . ) to $E_2$ level generates the Balmer series of lines which we discussed earlier. We are now being more specific in stating that in this particular examples the excited electrons in in an $n$p orbital. The helium spectrum we wish to compare with this one arises from the transition between configurations

$$1s^1np^1 \rightarrow 1s^12s^1$$
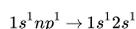
with $n = 3, 4, 5...$

Qualitatively the two spectra are the same, as our model predicted. In addition, the helium lines occur at shorter wavelengths (higher energies) than for hydrogen. In fact, for every series of lines (Lyman, Balmer, etc.) found for hydrogen, there is a corresponding series found at shorter wavelengths for helium. Our model, which uses hydrogen-like atomic orbitals to describe many-electron atoms, looks promising indeed. However, it is in the study of the spectrum of helium that we encounter the first shortcoming of this simple approach; there are two series of lines observed for helium for every single series of lines observed for hydrogen. Not only does helium possess the "Balmer" series, it has a second "Balmer"series starting at l = 3889A. That is, the whole series is repeated at

shorter wavelengths. Rather than abandon the atomic orbital approach for the many-electron atom, let us keep the above failure of the method in mind and proceed with an application to the lithium atom.

## The Lithium Atom

There are three electrons in the lithium atom ($Z = 3$) but the total repulsion energy between the electrons is still determined by considering the repulsions between a pair of electrons at a time. For this reason, three electrons are fundamentally no more difficult to treat than two electrons. There are simply more possible pairs and hence more repulsive interactions to consider than in the two-electron case. The dependence of the potential energy on the distances between the electrons and between the electrons and the nucleus is

$$V(r_1, r_2, r_3) = -\frac{3e^2}{r_1} - \frac{3e^2}{r_2} - \frac{3e^2}{r_3} + \frac{e^2}{|r_1 - r_2|} + \frac{e^2}{|r_1 - r_3|} + \frac{e^2}{|r_2 - r_3|}$$

where $|r_1 - r_2|$, is the distance between electrons 1 and 2, $|r_1 - r_3|$ the distance between electrons 1 and 3, and $|r_2 - r_3|$ the distance between electrons 2 and 3.

It is natural to assume that, as in the case of hydrogen or helium, the most stable energy of the lithium atom will be obtained when all three electrons are placed in the $1s$ atomic orbital giving the electronic configuration $1s^3$. Proceeding as in the case of helium we calculate the first approximation to the energy to be (using Equation 4.2.1)

$$E_1 = -3(3^3 R) = -27R$$

This represents the sum of the energies obtained when each electron is considered to move independently in the field of the nucleus of charge $+3$ in an orbital with $n = 1$. To this must be added the energy of repulsion between the electrons. The average repulsion energy between a pair of electrons is again given by $5/4ZR$. In lithium we must consider the repulsion between electrons 1 and 2, between electrons 1 and 3, and between electrons 2 and 3. Therefore the total repulsion energy which represents the correction to $E$ is estimated at (from Equation $ref3a$):

$$E_c = 3\left(\frac{5}{4}ZR\right) = \frac{45}{4}R$$

and the total electronic energy of the lithium atom is predicted to be

$$E = E_1 + E_c = -27R + \frac{45}{4}R = -15.75R = -214.4\,eV$$

Thus it should require 214.4 eV to remove all three electrons from the lithium atom. We can also calculate the energy required to remove a single electron from a lithium atom (the first ionization potential)

$$Li \rightarrow Li^+ + e^-$$
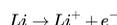
with

$$\Delta E = I_1 = E(Li^+) - E(Li)$$

$$= \underbrace{-2(3^3 K) + \left(\frac{15}{4}K\right)}_{E(Li^+)} - \underbrace{(-15.75\ K)}_{E(Li)} = +1.50\ R = +20.4\,eV$$

When the predicted values for lithium are compared with the corresponding experimental values, they are found to be in serious error. The lithium atom is not as stable as the calculations would suggest. Experimentally it requires 202.5 eV to remove all three electrons from lithium, and only 5.4 eV to remove one electron. Experimentally it requires less energy to ionize lithium than it does to ionize hydrogen, yet our calculation predicts an ionization energy one and one half times larger. The error in $I_1$ is 300%! We should expect a realistic model to do better than this. More serious than this, however, is that the kind of calculation we are doing should never predict the system to be more stable than it actually is. The method should always predict an energy less negative than is actually observed. If this is not found to be the case, then it means that an incorrect assumption has been made or that some physical principle has been ignored. It is also clear that if we were to continue this scheme of placing each succeeding electron in the $1s$ orbital as we increased the nuclear charge by unity we would never predict the most striking property of the elements: the property of periodicity.

We might recall at this point that there is a periodicity in the types of atomic orbitals found for the hydrogen atom. With every increase in $n$, all the preceding values of $l_1$ are repeated, and a new $l_1$ value is introduced. If we could discover a physical reason for not placing all of the electrons in the $1s$ orbital, but instead place succeeding electrons in the orbitals with higher $n$ values, we could expect to obtain a periodicity in our predicted electronic structures for the atoms. This periodicity in electronic structure would then explain the observed periodicity in their properties. There must be another factor governing the behavior of electrons and this factor must be one which determines the number of electrons that may be accommodated in a given orbital. To discover what this missing factor is and to find the physical basis for it, we must investigate further the magnetic properties of electrons.

# 4.3: The Magnetic Properties of the Electron

So far, the only motion we have considered for the electron is a motion in three-dimensional space. Since this motion is ultimately described in terms of an orbital wave function, we term this the orbital motion of the electron. However, the electron may possess an internal motion of some kind, one which is independent of its motion through space. Since the electron bears a charge, such an internal motion, if it does exist, might be expected to generate a magnetic moment. We have previously pointed out that when an electron is in an atomic orbital for which $l$ is not equal to zero, the resultant angular motion of the electron gives rise to a magnetic moment. We would anticipate then that an electron in an $s$ orbital ($l = 0$) should not exhibit any magnetic effects as its angular momentum is zero. If an electron in these circumstances did exhibit a magnetic effect, it would indicate that another type of motion was possible, presumably an internal one. Whether or not an electron in an $s$ orbital does possess a magnetic moment may be determined by means of an atomic beam experiment described below.
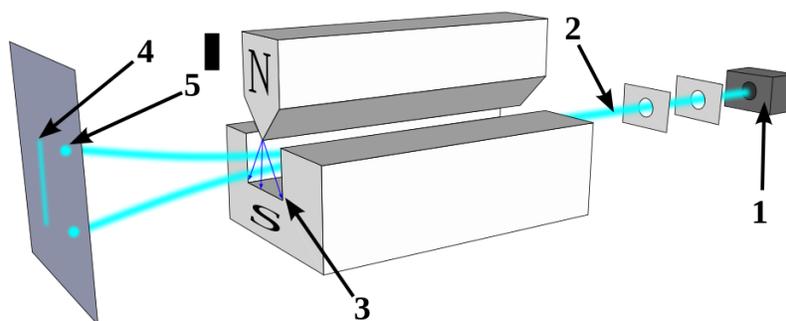


*Ground-state Hydrogen atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin (which is based on the electron spin). (1) the hydrogen atom source, (2) collimated atomic beam, (3) inhomogeneous magnetic field, (4) the observed bifurcation of the beam (5) the predicted spread for a classical atom with no intrinsic electron spin. (CC SA-BY 4.0; Tatoute).*

In the present experiment a beam of hydrogen atoms is passed through the apparatus. All of the hydrogen atoms in the beam will be in their ground state with $l = 0$ and hence they will not possess an orbital magnetic moment. However, when the magnetic field is applied, something does happen to the beam of atoms. It is split into two distinct beams, one of which is deflected to the N pole of the magnet and the other to the S pole. Thus even when atoms possess no magnetic moment because of the orbital motion of the electrons, they may still exhibit magnetic effects! As striking as the behaviour of the atoms as small magnets is the splitting of the beam into two distinct components. Let us consider first the origin of the magnetic effect, and second, the splitting of the beam into two distinct beams.

The observed magnetism of the hydrogen atoms must be due to some motion of the electrons. The nucleus of a hydrogen atom does possess a magnetic moment but its magnitude is too small, by a factor of roughly a thousand, to account for the deflections observed in this experiment. A magnetic moment will be observed only when the charged particle possesses angular momentum. Since the orbital angular momentum for an electron in the ground state of hydrogen is zero, we are forced to assume that the electron possesses some internal motion which has associated with it an angular momentum. A classical analogue of the internal angular momentum would be a spinning motion of the electron about its own axis. For this reason it is referred to as a ***spin angular momentum*** and the associated magnetic effect as a ***spin magnetic moment***. These effects are separate from, and in addition to, the orbital angular momentum of the electron (classically, the rotation of the electron around the nucleus) and its associated magnetic effects.

We are familiar enough with the predictions of quantum mechanics to anticipate that the spin angular momentum and its component along some axis will be quantized. As in the case of orbital angular momentum, the effect of the quantization will be to limit the number of values which the component of the spin magnetic moment may have along any given axis. The magnitude of the spin angular momentum will determine the number of possible values its component may have along a given axis. Each of the possible values will in turn cause some fraction of the total spin magnetic moment to be aligned along the same axis. In the case of the electron's orbital motion, we found that as $l$ and hence the orbital angular momentum was increased, the number of possible values for the component of the orbital magnetic moment along a given axis was increased, the number being equal to ($2l + 1$).

We can use a magnetic field to inquire into the nature of the spin angular momentum as well. In fact, we have already discussed the pertinent experiment. The beam of hydrogen atoms was split into just two components in the atomic beam experiment. This means that the component of the electron's spin magnetic moment (and spin angular momentum) along a given axis may have only one of two possible values; the component may be aligned with the field and hence be attracted, or it may be opposed to the field and be repelled. The electron's spin magnetic moment has been detected in many different kinds of experiments and the results are remarkable in that only two components of constant magnitude are ever observed. The electron is always either repelled by the field or attracted to it. This implies that the magnitude of the spin angular momentum for a single electron may have **only one possible value**. Since the number of possible values for the component of a given amount of angular momentum of any type in quantum mechanics is ($2l$ + 1), $l$ must equal ½ and only ½ for the spin angular momentum, and the values of $m$ for the electron spin, which assume values from a maximum of $l$ to a minimum of -$l$ in steps of unity, must equal +½ and -½. In this respect the spin angular momentum of the electron is quite different from its orbital angular momentum, which may have many possible values, as the value of $l$ for the orbital motion is restricted only in that it must equal zero or an integer.

It should be stressed that the splitting of the beam of hydrogen atoms into only two components is again evidence of quantization. If the atomic magnets (the hydrogen atoms) behaved according to classical mechanics, then the effect of the magnetic field would be simply to broaden the beam. The orientations of the atomic magnets would be random when they first entered the field of the magnet and classically the individual atomic magnets could be aligned at any and all angles with respect to the field, giving all possible components of the spin magnetic moment along the direction of the field. The inhomogeneous field would then exert a force proportional to the magnitude of the component, and the beam would broaden but not split.

Since the spin magnetic moment is an intrinsic property of the electron, even a beam of free electrons should be split into two components in a magnetic field. However, the charge possessed by the free electron also interacts with the magnetic field and the much smaller magnetic-magnetic interaction is masked by the usual deflection of a charge species in a magnetic field. By employing a neutral atom, the complications of the electronic charge may be avoided. The original experiment was performed on a beam of silver atoms by Stern and Gerlach in 1921. (We shall see shortly that the electrons in a silver atom do not possess any orbital angular momentum.)

Let us summarize what we have learned about this new property of the electron. Since an electron may exhibit a magnetic moment even when it does not possess orbital angular momentum, it must possess some internal motion. We call this motion the electron spin and treat it quantum mechanically as another kind of angular momentum. Experimentally, however, all we know is that the electron possesses an intrinsic magnetic moment. The remarkable feature of this intrinsic magnetic moment is that its magnitude and the number of components along a given axis are fixed. A given electron may exhibit only one of two possible components; it may be aligned with the field or against it. Experimentally, or theoretically, this is all we can know about the spin magnetic moment and the spin angular momentum. Hence only one quantum number is required to describe completely the spin properties of a single electron. We shall denote the value of this quantum number by or ¯, the upwards-pointing arrow signifying that the component of the magnetic moment is aligned with the field and the downwards-pointing arrow that this component is opposed to the field.

A total of four quantum numbers is required to specify completely the state of an electron when it is bound to an atom. The quantum numbers n, l and m determine its energy, orbital angular momentum and its component of orbital angular momentum. The fourth quantum number, the spin quantum number, summarizes all that can be known about the spin angular momentum of the electron. This final quantum number may have only one of two possible values corresponding to the magnetic moment component being (a) aligned with the field or (b) opposed to it.

## The Pauli Exclusion Principle

The consequences of the spin quantum number, when applied to the problem of the electronic structure of atoms, are not immediately obvious. The small magnitude of the electron's magnetic moment does not directly affect the energy of the electron to any significant degree. To see just how the spin of the electron does influence the problem, let us reconsider our atomic orbital model in the light of this new degree of freedom for the electron. In particular let us reconsider those instances in which our model failed to account for the observations.

If a beam of helium atoms is passed through a magnetic field, no splitting and no deflection is observed. The helium atom, unlike the hydrogen atom is not magnetic. We could account for the absence of a magnetic moment for helium if we assumed that of the two electrons in the helium 1$s$ orbital, one had its magnetic moment component up (↑) and the other down (¯). The two components would then cancel and there would be no resultant magnetic effect. Our complete description of the electronic

configuration of the helium atom would be $1s^2(\uparrow\downarrow)$, i.e., both electrons have $n = 1$, $l = 0$, $m = 0$ and one has a spin ($\uparrow$) and the other a spin ($\downarrow$).

You may wonder why the states of helium corresponding to the configurations $1s^2(\uparrow\uparrow)$ or $1s^2(\downarrow\downarrow)$ are not observed. These states should exhibit twice the magnetism possessed by a hydrogen atom. They are, however **not found to occur**. What about the excited states of the helium atom? An excited state results when one electron is raised in energy to an orbital with a higher $n$ value. The electrons are thus in different orbitals. The spin assignments for an excited configuration can be made in more than one way and are such as to predict the occurrence of both magnetic and non-magnetic helium. For example, the configuration $1s^12s^1$ could be $1s^1(\uparrow)2s^1(\downarrow)$ and be nonmagnetic or it could equally well be $1s^1(\downarrow)2s^1(\downarrow)$ or $1s^1(\uparrow)2s^1(\uparrow)$ and be magnetic.

> Care must be exercised in the use of the abbreviated notation $1s^1(\uparrow)2s^1(\downarrow)$ to indicate the configuration and spin of a many-electron atom. In the present example, all we mean to imply is that the total component of the spin is zero. We do not imply that the electron in the $1s$ orbital necessarily has a spin "up" and that in the $2s$ orbital a spin "down." The situation could equally well be described by the notation $1s^1(\downarrow)2s^1(\uparrow)$. There is no experimental method by which we can distinguish between electrons in an atom, or, for that matter, determine any property of an individual electron in a many-electron system. **Only the total magnetic moment, or total angular momentum, may be determined experimentally.**

**Both** the magnetic and non-magnetic forms are indeed found to occur for helium in an excited state. There are in fact two kinds of excited helium atoms, those which are non-magnetic and those which are magnetic. If the two forms of helium possess different energies even though they have the same orbital configuration (we shall see why this should be so later) then we have an explanation for the previously noted discrepancy that helium exhibits twice the number of line spectra as does hydrogen. For every set of lines in the spectrum which arises from the transition of the electron from the configurations $1s^1(\uparrow)np^1(\bar{\phantom{x}})$ to the configuration $1s^1(\uparrow)2s^1(\bar{\phantom{x}})$ for example, there will be another set of lines due to transitions from $1s^1(\uparrow)np^1(\bar{\phantom{x}})$ to $1s^1(\uparrow)2s^1(\bar{\phantom{x}})$.

The study of the magnetic properties of the ground and excited states of helium is sufficient to point out a general principle. For the ground state of helium, in which both electrons are in the same atomic orbital, **only the non-magnetic form exists**. This would imply that when two electrons are in the same atomic orbital their spins must be paired, that is, one up ($\uparrow$) and one down ($\bar{\phantom{x}}$). This is **an experimental fact** because helium is never found to be magnetic when it is in its electronic ground state. When the electrons are in different orbitals, then it is again an experimental fact that their spins may now be either paired ($\bar{\phantom{x}}\uparrow$) or unpaired, e.g., ($\uparrow$). Thus when two electrons are in the same orbital (i.e., they possess the same $n$, $l$ and $m$ values) their spins must be paired. When they are in different orbitals (one or more of their $n$, $l$ and $m$ values are different) then their spins may be paired or unpaired. We could generalize these observations by stating that "**no two electrons in the same atom may have all four quantum numbers the same.**" Stated in this way we see immediately that any given orbital may hold no more than two electrons. Since two electrons in the same orbital have the same values of $n$, $l$ and $m$, they can differ only through their spin quantum number. However, the spin quantum number may have only one of two possible values, and these possibilities are given by ($n$, $l$, $m$, $\uparrow$) or ($n$, $l$, $m$, $\bar{\phantom{x}}$).

We have indeed found the principle we were seeking, one which limits the occupation of an atomic orbital. This principle is known as the **Pauli exclusion principle**. One form of it, suitable for use within the framework of the orbital approximation, is the statement given in quotation marks above. The Pauli principle cannot be derived from, nor is it predicted by, quantum mechanics. It is a law of nature which must be taken into account along with quantum mechanics if the properties of matter are to be correctly described. The concept of atomic orbitals, as derived from quantum mechanics, together with the Pauli exclusion principle which limits the occupation of a given orbital, provides an understanding of the electronic structure of many-electron atoms. We shall demonstrate this by "predicting" the existence of the periodic table.

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# 4.4: The Electronic Basis of the Periodic Table

The hydrogen-like orbitals for a many-electron atom are listed in order of increasing energy in Fig. 4-2. This energy level diagram differs from the corresponding diagram for the hydrogen atom, a one-electron system. In the many-electron atom all orbitals with the same value of the principal quantum number $n$ do not have the same energy as they do in the case of hydrogen. For the many-electron atoms, the energy of an orbital depends on both $n$ and $l$, the energy increasing as $l$ increases even when $n$ is constant. For example, from Fig. 4-2 it is evident that the $3d$ orbital possesses a higher energy than does the $3p$ orbital which in turn has a higher energy than does the $3p$ orbital. The reason for this difference between the one- and the many-electron case will be discussed below. The energy of the orbital is still independent of the magnetic quantum number $m$. Thus when $l = 1$, there are three $p$ orbitals which are still degenerate (all possess the same energy) and this is indicated by the three open circles which are superimposed on each of the $p$ levels. The open circles thus represent the number of available orbitals or the degeneracy of each orbital energy level.
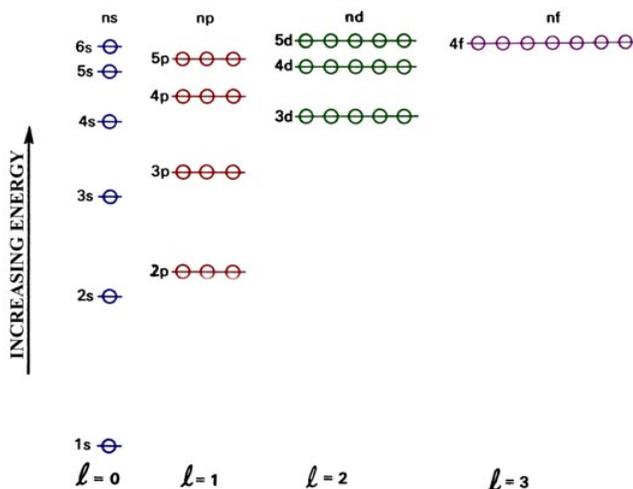


Fig. 4.2. An orbital energy level diagram for a many-electron atom.

With the aid of this energy level scheme and the Pauli principle we may proceed to build up the electronic structures of all the atoms. We do this by asssigning electrons one at a time to the vacant orbital which possesses the lowest energy. An orbital is "filled" when it contains two electrons with their spins paired.

**Hydrogen.** The nuclear charge is 1 and the single electron is placed in the $1s$ orbital. The electronic configuration is $1s^1$.

**Helium.** The nuclear charge is increased by one unit to 2 and the extra electron is again placed in the $1s$ orbital, with its spin opposed to that of the electron already present. The electronic configuration is $1s^2$.

**Lithium.** The nuclear charge is 3 and the third electron, because of the Pauli principle, must be placed in the 2s orbital as the 1s orbital is doubly occupied. The electronic configuration of lithium is therefore $1s^2 2s^1$.

We can now answer the question as to why the $2s$ orbital is more stable than the $2p$ orbital, i.e., why Li is described as $1s^2 2s^1$ and not as $1s^2 2p^1$. The two inner electrons of lithium (those in the $1s$ orbital) partially shield the nuclear charge from the outer elctron. Recall that as $n$ increases, the average distance between the electron and the nucleus increases. Thus most of tthe electron density of the electron with $n = 2$ will lie outside of the charge density of the two inner electrons which have $n = 1$. When the outer electron is at large distances from the nucleus and thus essentially outside of the inner shell of electron density it will experience a force from only one of the three positive charges on the lithium nucleus. However, as the outer electron does have a small but finite probability of being close to the nucleus, it will penetrate to some extent the tightly bound electron density of the two 1s electrons. In doing so it will "see" much more of the total nuclear charge and be more tightly bound. The closer the outer electron can get to the nucleus, that is, the more it can penetrate the density distribution of the inner shell electrons, the more tightly bound it will be.

An electron in an $s$ orbital has a finite probability of being found right at the nucleus. An electron in a $p$ orbital on the other hand has a node in its density distribution at the nucleus. Thus an $s$ electron penetrates the inner shell density more effectively than does a $p$ electron and is consequently more tightly bound to the atom. In a hydrogen atom, there are no inner electrons and both a $2s$ and $2p$ electron always experience the full nuclear charge and have the same energy. The crux of this penetration effect on the energy is that the inner shell electron density does possess a finite extension in space. Thus an outer electron can penetrate inner shell density

and the screening effect is reduced. If the inner shell density was contracted right onto the nucleus, then no matter how close the outer electron came to the lithium nucleus, it would always experience only a charge of +1. This dependence of the orbital energies on their *l* value is aptly called the penetration effect.

The electron density of a *d* electron is concentrated even further away from the nucleus than is that of a *p* electron. Consequently, the orbital energy of a *d* electron is even less stable than that of a *p* electron. In some atoms the penetration of the inner shell density by a *d* electron is so slight that its energy is raised even over that of the *s* electron with the next highest *n* value. For example, a 3*d* electron possesses a higher energy than does a 4*s* electron in the atoms Sc to Zn with the exceptions of Cr and Cu. The penetration effect in these elements overrides the principal quantum number for *d* electrons in determining their relative energies.

Notice that the configuration $1s^22s^1$ for lithium overcomes the difficulties of our earlier attempts to describe the electronic structure of this atom. The Pauli principle, of which we were ignorant in our previous attempt, forces the third electron to occupy the 2*s* orbital and forces in turn the beginning of a new quantum shell, that is, a new value of *n*. Thus lithium, like hydrogen, possesses one outer electron in an *s* orbital. Since it is only the outer electron density which in general is involved in a chemical change, lithium and hydrogen should have some chemical properties in common, as indeed they do. Hydrogen is the beginning of the first period (*n* = 1) and lithium marks the beginning of the second period (*n* = 2).

**Beryllium**. The nuclear charge is 4 and the electronic configuration is $1s^22s^2$.

**Boron.** *Z* = 5 and the electron configuration is $1s^22s^22p^1$.

**Carbon.** *Z* = 6. The placing of the sixth electron of carbon requires some comment. It will obviously go into a 2*p* orbital. But in which of the three should it be placed? Should it be placed in the 2*p* orbital which already possesses one electron, or should it be placed in one of the vacant 2*p* orbitals? If it is placed in the occupied 2*p* orbital its spin must be paired with that of the electron already present and the result would be a nonmagnetic carbon atom. If, however, it is placed in one of the vacant 2*p* orbitals it may be assigned a spin parallel to the first electron. The question is decided on the grounds of which situation gives the lowest energy. As a result of the Pauli principle, two electrons with parallel spins (both up or both down) have only a very small probability of being close to one another. In fact the wave function which describes the two-electron case for parallel spins vanishes when both electrons approach one another. When the wave function vanishes, the corresponding probability distribution goes to zero. On the average, then, electrons with parallel spins tend to keep out of each other's way. Two electrons with paired spins, whether in the same or different orbitals are not prevented by the Pauli principle from being close to one another. The wave function for this situation is finite even when they are on top of one another! Obviously, two electrons with parallel spins will have a smaller value for the electrostatic energy of repulsion between them than will two electrons with paired spins. This is a general result which holds almost without exception in the orbital approximation. It is known as one of Hund's rules as he was the first to state it. Thus the most stable electronic configuration of the carbon atom is $1s^22s^22p^2$() where we have emphasized the fact that the two 2*p* electrons have parallel spins and hence must be in different 2*p* orbitals.

**Nitrogen.** *Z* = 7. Because of Hund's rule the electronic configuration is

$$1s^22s^22p^3()$$
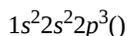
i.e., one electron in each of the 2*p* orbitals. The configuration with the largest possible component of the spin magnetic moment will be the most stable.

**Oxygen.** *Z* = 8. One of the 2*p* electrons must now be paired with the added electron, but the other 2*p* electrons will be left unpaired.

$$1s^22s^22p^4()$$
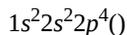
(Only the number of unpaired electrons is indicated by the arrows.)

**Fluorine.** *Z* = 9. The configuration will be

$$1s^22s^22p^5()$$
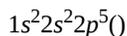
**Neon.** *Z* = 10. The tenth electron will occupy the last remaining vacancy in the second quantum shell (the set of orbitals with *n* = 2).

$$1s^22s^22p^6$$
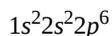
Thus neon represents the end of the second period and all the electrons have paired spins.

When all the orbitals in a given shell are doubly occupied, the resulting configuration is called a "closed shell." Helium and neon are similar in that they both possess closed shell configurations. Because neither of these elements possesses a vacancy in its outer shell of orbitals both are endowed with similar chemical properties. When the orbitals belonging to a given $l$ value contain either one electron each (are half-filled) or are completely filled, the resulting density distribution is spherical in shape. Thus the electron density distributions of nitrogen and neon, for example, will be spherical.

Reference to Fig. 4-2 indicates that the next element, sodium, will have its outer electron placed in the 3$s$ orbital and it will be the first element in the third period. Since its outer electronic structure is similar to that of the preceding elements, lithium and hydrogen, it is placed beneath them in the periodic table. It is obvious that in passing from sodium to argon, all of the preceding outer electronic configurations found in the second period ($n$ = 2) will be duplicated by the elements of the third period by filling the 3$s$ and 3$p$ orbitals. For example, the electronic structure of phosphorus ($Z$ = 15) will be

$$1s^22s^22p^63s^23p^3()$$
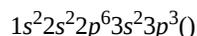
and thus resemble nitrogen.

**Argon.** $Z$ = 18. Argon will have filled 3$s$ and 3$p$ orbitals and will represent the end of a period. Argon, like helium and neon, possesses a closed shell structure and is placed beneath these two elements in the periodic table.

## The Transition Elements

The beginning of the fourth period will be marked by the single and double occupation of the 4$s$ orbital to give potassium and calcium respectively. However, reference to the orbital energy level diagram indicates that the 3$d$ orbital is more stable than the 4$p$ orbital. Since there are five $d$ orbitals they may hold a total of ten electrons. Thus the ten elements beginning with scandium ($Z$ = 21) will possess electronic structures which differ from any preceding them as they are the first elements to fill the $d$ orbitals. A typical electronic configuration of one of these elements is that of manganese: [Ar]4$s^2$3$d^5$. The symbol [Ar] is an abbreviated way of indicating that the inner shells of electrons on manganese possess the same orbital configuration as those of argon. In addition, the symbol 3$d^5$ indicates that there are five electrons in the 3$d$ orbitals, no distinction being made between the five different $d$ orbitals. This series of elements in which the 3$d$ orbitals are filled is called the ***first transition series***. The element zinc with a configuration [Ar]4$s^2$3$d^{10}$ marks the end of this series. The six elements from gallium to krypton mark the filling of the 4$p$ orbitals and the closing, with krypton, of the fourth quantum shell and the fourth period of the table.

While the 3$d$ orbitals are less stable than the 4$s$ orbitals in the neutral atom (with the exceptions of Cr and Cu) and are filled only after the 4$s$ orbitals are filled, the relative stability of the 4$s$ and 3$d$ orbitals is reversed in the ionic forms of the transition metals. For example, the configuration of the ion which results when the manganese atom loses two electrons is Mn$^{+2}$ [Ar]3$d^5$ and not [Ar]4$s^2$3$d^3$. This is a general result. The $d$ orbitals of quantum number $n$ are filled only after the $s$ orbital of quantum number ($n$ + 1) is filled in the neutral atom, but the $nd$ orbital is more stable than the ($n$ + l)$s$ orbital in the corresponding ion.

The fifth period begins with the filling of the 5$s$ orbital, followed by the filling of the 4$d$ orbitals, which generates the second transition series of elements. The period closes with the filling of the 5$p$ orbitals and ends with xenon.

## The lanthanide and actinide elements

The sixth period is started by the filling of the 6$s$ orbital. The next element, lanthanum, has the electronic configuration [Xe]6$s^2$5$d^1$. However, the next fourteen elements represent the beginning of another new series as the filling of the 4$f$ orbitals is now energetically favoured over a continued increase in the population of the 5$d$ orbitals. Note that the very small penetration effect possessed by the 4$f$ orbitals ($n$ = 4) delays their appearance until the sixth quantum shell has been partially filled. There are fourteen elements in this series, called the ***lanthanide series***, since there are seven 4$f$ orbitals ($l$ = 3 and 2 ´ 3+1 = 7).

The third transition series follows the lanthanide elements as the occupation of the 5$d$ orbitals is completed. This in turn is followed by the filling of the 6$p$ orbitals. The final period begins with the filling of the 7$s$ orbital and continues with the filling of the 5$f$ orbitals. This second series of elements with electrons in $f$ orbitals is called the ***actinide series***.

The concept of atomic orbitals in conjunction with the Pauli principle has indeed predicted a ***periodicity in the electronic structures of the elements***. The form of this periodicity duplicates exactly that found in the periodic table of the elements in which the periodicity is founded on the observed chemical and physical properties of the elements. Our next task will be to determine whether or not our proposed electronic structures will properly predict and explain the observed variations in the chemical and physical properties of the elements.

![LibreTexts logo]

# 4.5: Further Reading

R.M. Hochstrasser, *Behaviour of Electrons in Atoms*, W. A. Benjamin Inc., New York, N.Y., 1964.

The magnitude of the total angular momentum in a many-electron atom is governed by the same rules of quantization as apply to the motions of the individual electrons. Because of this, the addition of the angular momentum vectors of the individual electrons in an atom to give the total angular momentum quantum number denoted by $J$ is not arbitrary but must be carried out in such a way that the magnitude of the resultant vector is expressible in the form $\sqrt{J(J+1)}\,(h/2\pi)$ with $J$ = 0, 1, 2, 3 ... An elementary discussion of the manner in which the total angular momentum of an atom is determined by quantum mechanics is given in the above reference.

# 4.E: Exercises

## Problems

| | |
|---|---|
| 1. | Would you expect the spectrum of magnesium ($Z = 12$) to resemble that of He? Explain your answer. |
| 2. | The boron atom has the electronic configuration $1s^2 2s^2 2p^1$. The single unpaired electron in the $2p$ orbital will possess both orbital and spin angular momentum. Into how many distinct beams will a beam of boron atoms be split when it is passed through an atomic beam apparatus with an inhomogeneous magnetic field directed perpendicular to the direction of travel of the atoms? |
| 3. | When a test tube containing an aqueous solution of $Fe^{+3}$ ions is placed near the poles of a strong magnet, the test tube is attracted and pulled into the magnetic field. When a test tube containing a solution of $Zn^{+2}$ ions is placed near the magnetic field, it is **not** attracted into the field. Use the atomic orbital theory to account for the fact that the $Fe^{+3}$ solution is magnetic while the $Zn^{+2}$ solution is not. The atomic number of Fe is 26 and of Zn is 30. (Recall that the $3d$ orbitals are more stable than are the $4s$ orbitals in the ionic forms of the transition elements.) |
| 4. | Suppose you lived in a universe where all of the laws of quantum mechanics applied as they do in ours, but where the spin angular momentum quantum number of the electron had increased from ½ to some larger value. The new value must also be half-integer if the Pauli principle is to apply. Rather than use the general symbol "$l$"to denote an angular momentum quantum number, we shall reserve this symbol for orbital angular momentum and introduce a new symbol "$s$" to denote the spin angular momentum quantum number. In our universe, a beam of hydrogen atoms in their ground state (with $l = 0$) is split in two in an atomic beam apparatus when a magnetic field is applied. The number of quantized components of angular momentum is related to the angular momentum quantum number by the expression ($2l + 1$) for orbital momentum or ($2s + 1$) for spin momentum. Thus, since two components are observed, the value of the spin quantum number $s$ in our universe is ½. Recall that the magnetic quantum number $m$ governing the components of angular momentum assumes values from $l$ to $\lozenge$ $l$ in steps of unity or from $s$ to $\lozenge$ $s$ in the case of spin angular momentum. If we use $m_l$ and $m_s$ to denote the orbital and spin magnetic quantum numbers respectively, then the values of $m_s$ are + ½ and $\lozenge$ ½ in our universe. |

| | (a) | When a beam of hydrogen atoms with $l = 0$ is passed through an atomic beam apparatus in the new universe, the magnetic field causes the beam to split into four (4) separate beams. What is the value of the spin quantum number $s$ in the new universe and what are the possible values for the spin magnetic quantum number $m_s$? Since only the spin quantum number has undergone a change in the new universe, the atomic orbital model of electronic structure should still apply and each electron will be assigned to an orbital with some value of $n$, $l$ and $m_l$ and a given spin quantum number $m_s$. The statement of the Pauli principle as it applies to the orbital model is "no two electrons in the same atom may have all four quantum numbers the same." How many electrons may occupy an orbital with given values of $n$, $l$ and $m_l$ in the new universe? |
|---|---|---|
| | (b) | Clearly, the periodic table of the elements in the new universe will have a different structure from that in ours. State how many elements would appear in the first, second, third and fourth rows of the new table. What would be the ground state configurations of the elements with atomic numbers $Z = 7$ and 10 and what would their valencies be? Which element would be the first of the noble gases in the new universe? |
| 5. | | When a transition metal ion is place in solution, its magnetic moment generally changes from the value it had in the gas phase, indicating that the number of unpaired electron spins is different in the gas and solution phases. Transition metal ions $M^{2+}$ form a six-coordinated octahedral complex with $CN^-$ ions when placed in solution containing this ligand. The formation of the complex perturbs the d orbitals, changes their energy and partiallly removes their degeneracy. That is, the d-level which is five-fold degenerate in the gas phase is split into two or more levels with different energies. The new sets of levels can be dgenerate, but their degeneracies will necessarily be less than five. By measuring the magnetic moment of solution of the complexes $M(CN)_6^{-4}$ for various metal ions $M^{2+}$, one can determine the number of unpaired d electrons in the complex. With this information, use the orbital model to determine the number of levels into which the d-level is split and the degeneracy of each of the new levels. The solution of the $Fe^{2+}$ ion showed that no permanent magnetic moment was present - the solution was diamagnetic. The $V^{2+}$ and $Ni^{2+}$ solutions gave moments indicating the presence of three and two unpaired electrons respectively. The atomic numbers of the metal atoms are V:23, Fe:26 and Ni:28. You must show how your final answer is arrived. |

## 5: Electronic Basis for the Properties of the Elements

We shall now present an interpretation of the physical and chemical properties of the elements based on the atomic orbital description of their electronic structures. Our discussion of the properties of the atoms will be a qualitative one, but it should be pointed out that many of the properties of atoms can now be accurately predicted by quantum mechanical calculations employing a very extended version of the atomic orbital concept.

## 5.1: Introduction

We shall now present an interpretation of the physical and chemical properties of the elements based on the atomic orbital description of their electronic structures. Our discussion of the properties of the atoms will be a qualitative one, but it should be pointed out that many of the properties of atoms can now be accurately predicted by quantum mechanical calculations employing a very extended version of the atomic orbital concept.

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# 5.2: Horizontal Variations

The experimental values of the atomic radii and the first and second ionization potentials of the elements (labelled as $I_1$ and $I_2$ respectively) in the third row of the periodic table are listed in Table 5-1. A study of these values will indicate the basic trends observed as the number of electrons is increased one at a time until all the orbitals with a given value of $n$ are fully occupied.

Table 5-1:The Atomic Radii and Ionization Potentials* of Third Row Elements

| Element | Na | Mg | Al | Si | P | S | Cl | Ar |
|---|---|---|---|---|---|---|---|---|
| Radius (Å) | 1.86 | 1.60 | 1.48 | 1.17 | 1.0 | 1.06 | 0.97 | |
| $I_1$ (ev) | 5.14 | 7.64 | 5.98 | 8.15 | 11.0 | 10.4 | 13.0 | 15.8 |
| $I_2$ (ev) | 47.3 | 15.0 | 18.8 | 16.3 | 19.7 | 23.4 | 23.8 | 27.6 |

*The values for $I_1$ and $I_2$ are taken from C. E. Moore, *Atomic Energy Levels*, Vol. 1, N.B.S. Circular 467, Washington, D.C. (1949). $I_2$ is the energy required to remove an electron from the singly-charged ion, i.e., the energy required to ionize a second electron.

## Atomic radii

The diameter of an atom is difficult to define precisely as the density distribution tails off at large distances. However, there is a limit as to how close two atoms can be pushed together in a solid material. We shall take one half of the distance between the nuclei of two atoms in an elemental solid as a rough measure of the atomic radius. Any consistent method of defining the radius leads to the same trend we see in Table 5-1. The size of the atom in general decreases as the number of electrons in the quantum shell is increased. This observation, which at first sight might appear surprising, finds a ready explanation through the concept of an *effective nuclear charge*.

The electric field and hence the attractive force exerted by the nucleus on an electron in the outer quantum shell is reduced because of the screening effect of the other electrons which are present in the atom. An outer electron does not penetrate to any great extent the tightly bound density distribution of the inner shell electrons. Consequently each inner electron (an electron with an $n$ value less than the $n$ value of the electron in question) reduces the value of the nuclear charge experienced by the outer electron by almost one unit. The remaining outer electrons on the other hand are, on the average, all at the same distance away from the nucleus as is the electron under consideration. Consequently each outer electron screens considerably less than one nuclear charge from the other outer electrons. Thus the higher the ratio of outer shell to inner shell electrons, the larger will be the "effective nuclear charge" which is experienced by an electron in the outer shell.

All of the elements in a given row of the periodic table possess the same number of inner shell electrons. For example, the elements in the third row have the inner shell configuration of $1s^22s^22p^6$. As we move across the periodic table from left to right the nuclear charge increases, and each added electron is placed in the outer shell until a total of eight is reached and the quantum shell is full. The number of outer shell electrons increases along a given period, but the number of inner shell electrons remains fixed. Thus the effective nuclear charge increases from a minimum value for sodium, where the ratio of outer shell to inner shell electrons is 1:10, to a maximum value for argon where the same ratio is 8:10. The atomic radius undergoes a gradual decrease since the outer electrons become more tightly bound as the effective nuclear charge increases.

These features of the atomic density distributions are clearly evident in a graph of the radial distribution function, $Q(r)$. This function, it will be recalled, gives the number of electronic charges within a thin shell of space lying between two concentric spheres, one of radius $r$ and the other with a radius only slightly larger. The radial distribution functions for atoms may be determined experimentally by X-ray or electron diffraction techniques.

Plots of $Q(r)$ versus $r$ for sodium and argon (Fig. 5-1), the first and last members of the third row of the periodic table, clearly reveal the persistence of a "shell structure" in the many-electron atoms.
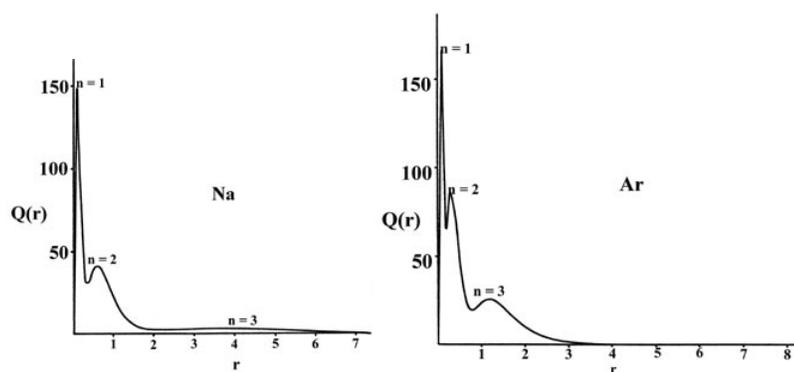
Fig. 5-1. The radial distribution functions $Q(r)$ for the Na and Ar atoms.

There are three peaks in the density distribution corresponding to the presence of three principal quantum shells in the orbital model of the electronic structure of sodium and argon. The peak closest to the nucleus may be identified with the charge density in the $1s$ orbital, the middle peak with that in the $2s$ and $2p$ orbitals and the outer peak with the charge density in the $3s$ orbital in sodium and in the $3s$ and $3p$ orbitals in argon. The maxima in $Q(r)$ occur at smaller values of $r$ for argon than for sodium as expected on the basis of a larger effective nuclear charge for argon than for sodium. Most of the $1s$ charge density is found within a very thin shell close to the nucleus in both cases as the inner shell density experiences the field of the full nuclear charge, $Z_{Na} = 11$ and $Z_{Ar} = 18$. The charge density in the $n = 2$ orbitals is confined to a shell which is narrower and closer to the nucleus in argon than in sodium. The electrons in this second shell experience a nuclear charge of approximately sixteen in argon but of only nine in sodium.

The most dramatic effect of the difference in the effective nuclear charges of argon and sodium is evidenced by the appearance of the electron density in the valence shell. In sodium this shell is broad and diffuse as there are ten inner electrons shielding eleven nuclear charges. In argon where there are ten inner electrons to shield eighteen nuclear charges the valence shell is more contracted and it peaks at roughly one third of the corresponding distance in sodium. The valence shell density is clearly more tightly bound in argon than in sodium.

Figure 5-2 shows the effect of an increase in the nuclear charge on the individual atomic orbital densities for elements in the same row of the periodic table, in this case sodium and chlorine. The total density distribution for the atom is obtained by summing the individual orbital densities. The summation of just the $1s$, $2s$ and three $2p$ densities yields the spherical inner shell densities indicated on the diagram as "core densities." It is the core density which shields the nuclear charge from the valence electrons. The outer density contour indicated for the inner shell or core densities defines a volume in space containing over 99% of the electronic charge of the inner shell electrons. Thus the effective nuclear charge experienced by the valence density beyond the indicated radii of the core densities is $Z_{Na} - 10 = 1$ for sodium and $Z_{Cl} - 10 = 7$ for chlorine. Notice that the radius of the core density is smaller for chlorine than it is for sodium and thus the attractive force exerted on the valence electrons by each of the unscreened nuclear charges will be greater in chlorine than in sodium.
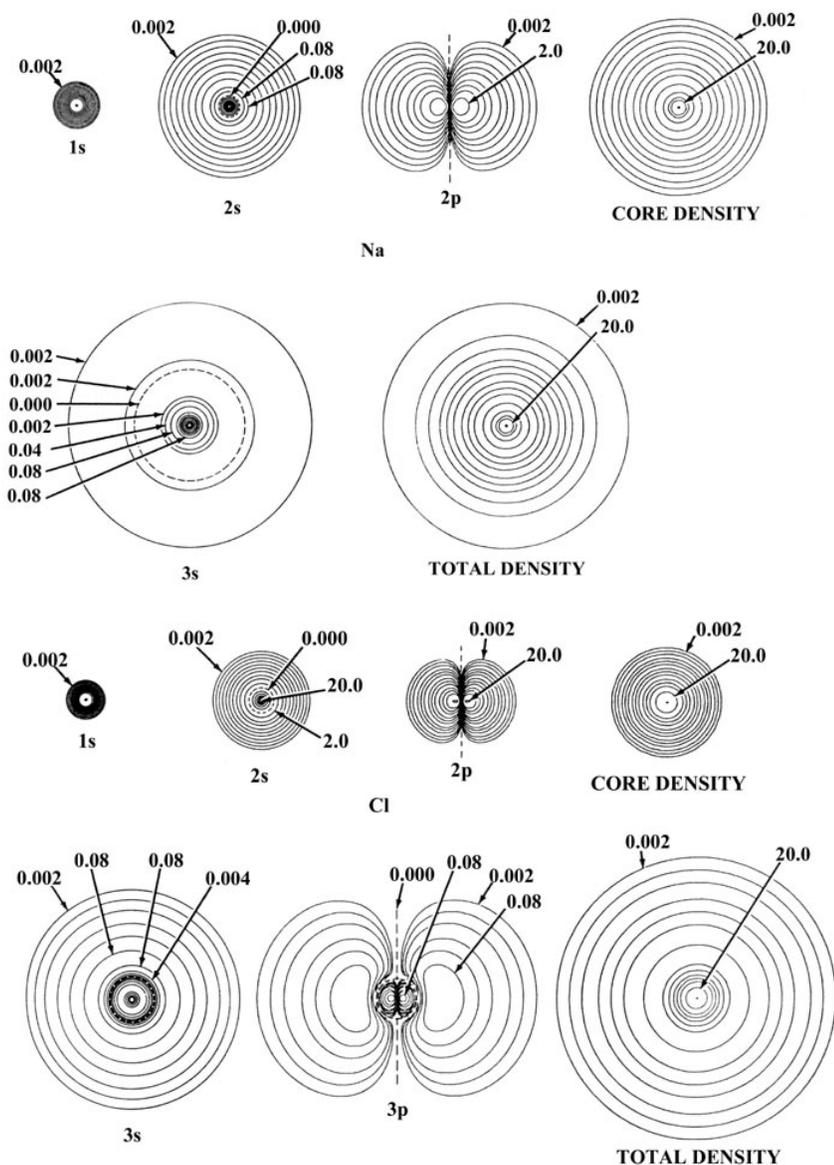
Fig. 5-2. Atomic orbital charge densities for the Na and Cl atoms. Only one member of a 2p or 3p set of orbitals is shown. The nodes are indicated by dashed lines. The inner node of the 3s orbital is too close to the nucleus to be indicated in the diagram. When two neighbouring contours have the same value, as for example the two outermost contours in the 3s density of Na, the charge density passes through some maximum value between the two contours, decreasing to zero at the nodal line. In terms of the outermost contour shown in the total density plots (0.002 au) the Cl atom appears to be larger than the Na atom. The outer charge density of Na is, however, very diffuse (as shown by the plot of Q(r) in Fig. 5-1) and in terms of density contours of value less than 0.002 au the Na atom is indeed larger than the Cl atom. The values of contours not indicated in the figure may be obtained by referring to the Table of Contour Values.

There is one exception to the trend of a decrease in diameter across a given row in that phosphorus has an atomic radius slightly smaller than that of sulphur which follows it in the table. The configuration of the outer electrons in phosphorus is $3s^2 3p^3$(). Each of the $p$ orbitals contains a single electron and according to Hund's rule all will have the same spin quantum number. Electrons with identical spins have smaller electron-electron repulsion energies than do electrons with paired spins, for reasons we have previously mentioned. Therefore, the larger the number of parallel spins in an atom, the smaller will be the average energy of repulsion between the electrons. Three is the maximum number of unpaired spins possible in any of the short periods as this corresponds to a half-filled set of $p$ orbitals. The stabilizing effect of the decreased energy of repulsion between the electrons is comparable to the effect obtained by increasing the effective nuclear charge by approximately one. This can be seen by comparing phosphorus with

sulphur. Sulphur has an increased nuclear charge but the added electron must be paired up with one of the electrons in the *p* orbitals. The number of unpaired electrons with parallel spins is thus reduced to two, the average energy of repulsion between the electrons is increased, and the sulphur atom is slightly larger than the phosphorus atom.

The decrease in energy which is obtained by maximizing the number of parallel spins is not sufficient to change the most stable outer configuration actually found for silicon, $3s^2(\overline{\phantom{x}})3p^2()$, to that in which all four outer electrons have parallel spins, $3s^1()3p^3()$. This latter configuration could be obtained only by promoting an electron from a 3*s* orbital to a 3*p* orbital. The 3*s* orbital is more stable than a 3*p* orbital because of the penetration effect, and the energy increase caused by the promotion of an electron from the 3*s* to a 3*p* orbital would not be offset by the energy decrease obtained by maximizing the number of parallel spins. It is interesting to note, however, that the reverse of this is true for some of the elements in the transition series. In these elements the 4*s* and 3*d* (or in general the *ns* and (*n* - l)*d* orbitals are the outer orbitals. The energy difference between an *ns* and an (*n* - 1)*d* orbital is much less than that between an *ns* and an *np* orbital. Thus the effect of maximizing the number of parallel spins can be overriding in these cases. The outer electronic structure of vanadium is $4s^2 3d^3$. (Recall that there are five *d* orbitals and hence the configuration $d^5$ will represent five electrons with parallel spins.) We would expect the outer electronic configuration of the next element, chromium, to be $4s^2 3d^4$ with four parallel spins. Instead, the configuration is actually $4s^1 3d^5$ resulting in a total of six parallel spins and a reduction in the energy of repulsion between the electrons.

## The Ionization Potentials

Reference to Table 5-1 indicates that in general the amount of energy required to remove one of the outer electrons increases as the effective nuclear charge increases. The increase in $I_1$ from approximately 5 ev for sodium to approximately 16 ev for argon dramatically illustrates the increase in the force which the nucleus exerts on the outer electrons as the nuclear charge and the number of **outer** electrons is increased. The effect of the half-filled set of *p* orbitals is again evident as $I_1$ is slightly larger for phosphorus than for sulphur. There is an apparent discrepancy in the value for $I_1$ observed for magnesium. The outer electronic configuration of magnesium is $3s^2$ and for aluminum is $3s^2 3p^1$. The value of 7.64 ev observed for magnesium is the energy required to remove a 3*s* electron, while the value quoted for aluminum is the energy required to remove a 3*p* electron. An *s* orbital is more stable than a *p* orbital because of its greater penetration of the inner core of electron density. Thus the penetration effect overrides the increase in the effective nuclear charge. We can test the validity of this explanation by comparing the energies required to remove a second electron ($I_2$) from the magnesium and aluminium atoms. The outer electronic configurations of the singly-charged magnesium and aluminum ions are $3s^1$ and $3s^2$. Thus a comparison of the second ionization potentials ($I_2$) will be free of the complication due to the penetration effect because we will be comparing the amount of energy required to remove an *s* electron in each case The values in Table 5-1 indicate that the removal of an *s* electron requires more energy in aluminum than in magnesium, a result which is consistent with the greater effective nuclear charge for aluminium than for magnesium. What explanation can be given to the second ionization potential of sulfur being almost equal to that for chlorine?

It is worthwhile noting the large value of the second ionization potential observed for sodium. The sodium ion has the electron configuration $1s^2 2s^2 2p^6$, i.e., there are no remaining outer electrons. The second ionization potential for sodium is, therefore, a measure of the amount of energy required to remove one of what were initially inner shell electrons in the neutral atom. The effective nuclear charge experienced by a 2*p* electron in the sodium ion will be very large indeed, because the number of inner shell electrons for an *n* = 2 electron is only two. That is, only the two electrons in the 1*s* orbital exert a large screening effect. Therefore, coupled to the fact that the ion bears a net positive charge, is the fact that the ratio of outer to inner shell electrons is 8:2, which is even more favourable than that obtained for argon. (Recall that in the neutral sodium atom the ratio is 1:10.) The value of $I_2$, for sodium again emphasizes the electronic stability of a closed shell, a stability which is a direct reflection of the large value of the effective nuclear charge operative in such cases.

---

# 5.3: Vertical Relationships

Table 5-2 lists the atomic radii and the ionization potentials of the elements found in the first column of the periodic table, the group I elements.

Table 5-2: Atomic Radii and Ionization Potentials of Group I Elements

| Element | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Radius (Å) | 1.50 | 1.86 | 2.27 | 2.43 | 2.62 |
| $I_1$ (ev) | 5.4 | 5.1 | 4.3 | 4.2 | 3.9 |

The average value of the distance between the electron and the nucleus increases as the value of the principal quantum number is increased. The increase in the atomic diameters down a given group in the periodic table is thus understandable. Each of the group I elements represents the beginning of a new quantum shell. There will be a very sharp decrease in the effective nuclear charge on passing from the preceding closed shell element to a member of group I, as the number of the inner shell electrons is increased by eight. This large sudden reduction in the effective nuclear charge and the fact that the electron, because of the Pauli exclusion principle, must enter a new quantum shell, causes the group I elements to be larger in size and much more readily ionized than the preceding noble gas elements. The decrease in the effective nuclear charge and the increase in the principal quantum number down a given family bring about a steady decrease in the observed ionization potentials. Thus the outer 6s electron in cesium is on the average, further from the nucleus than is the outer 2s electron in lithium. It is also more readily removed.

So far we have considered the periodic variations in the energy required to remove an electron from an atom:

| | |
|---|---|
| $M \rightarrow M^+ + e^-$ | $I_1$ = a positive value |
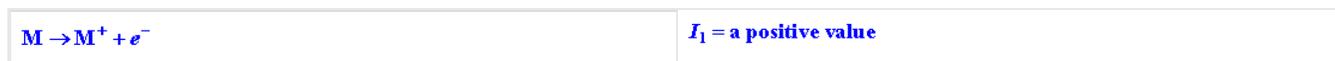
In some favourable cases it is possible to determine the energy released when an electron is added to an atom:

| | |
|---|---|
| $M + e^- \rightarrow M^-$ | $\Delta E$ = a negative value |

The magnitude of the energy released when an atom captures an extra electron is a measure of the atom's **electron affinity**.

It might at first seem surprising that a neutral atom may attract an extra electron. Indeed many elements do not have a detectable electron affinity. However, consider the outer electronic configuration of the group VII elements, the halogens:

## $ns^2np^5$
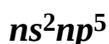
There is a single vacancy in the outer set of orbitals and the effective nuclear charge experienced by the valence electrons in a halogen atom is almost the maximum value possible for any given row. Because of the incomplete screening of the nuclear charge by the outer electrons, the remaining vacancy in the outer shell will, in effect, exert an attractive force on a free electron large enough to bind it to the atom.

The electron affinities for the rare gas atoms will be effectively zero even though the effective nuclear charge is a maximum for this group of elements there are no vacancies in the outer set of orbitals in a rare gas atom and as a result of the Pauli principle, an extra electron would have to enter an orbital in the next quantum shell. The electron in this orbital will experience only a very small effective nuclear charge as all of the electrons originally present in the atom will be in inner shells with respect to it. Elements to the left of the periodic table, the alkali metals for example, do have vacancies in their outer quantum shell but their effective nuclear charges are very small in magnitude. Thus these elements do not exhibit a measurable electron affinity. The electron affinity increases across a given row of the periodic table and reaches a maximum value with the group VII elements. This is a direct reflection of the variation in the effective nuclear charge.

The orbital vacancy in which the extra electron is placed is found at larger distances from the nucleus when the principal quantum number is increased. Thus the electron affinity should decrease down any given family of elements in the periodic table. For example, the electron affinities for the halogens should decrease in the order F > Cl > Br > I. (Click here for note.)

The variation in the ionization potentials across a given row is reflected in the values shown in the atomic orbital energy level diagram for the elements from hydrogen through to neon (Fig. 5-3).
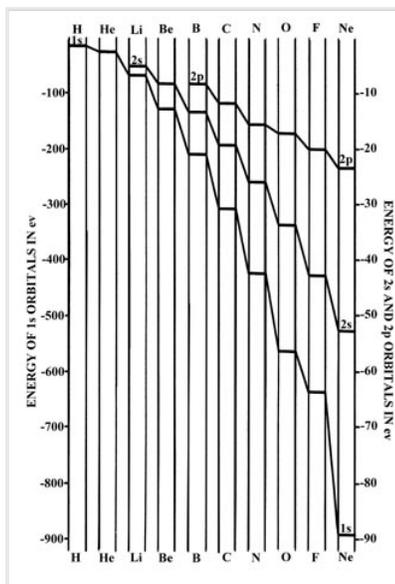
Fig. 5-3. An orbital energy level diagram for the elements H to Ne

(Note that the energy scale used for the 1$s$ orbital differs by a factor of ten from that for the 2$s$ and 1$p$ orbitals.) The orbital energies show a uniform decrease when the nuclear charge is increased, reflecting an increase in the binding of the electrons. The total energy of a many-electron atom is **not** simply the sum of the orbital energies. Summing the orbital energies does not take proper account of the repulsions between the electrons. The orbital energies do, however, provide **approximate** estimates of the ionization potentials. The ionization potential is the energy required to remove one electron from an atom, and an orbital energy is a measure of the binding of a **single electron** in a given orbital. Thus the ionization potential should be approximately equal to **minus** the orbital energy. For example, the ionization potential of lithium is 5.39 ev and the 2$s$ orbital energy is -5.34 ev. Similarly $I_1$, for neon is 21.56 ev and the 2$p$ orbital energy is -23.14 ev.

Shell structure is also evident in the ionization potentials and orbital energies of atoms. By exposing the atom to light of very short wavelength (in the X-ray region of the spectrum), it is possible to ionize one of the inner shell electrons, rather than a valence electron. That is, the energy of an X-ray photon is comparable to the binding energy of an inner shell electron. The resulting ion is in a very unstable configuration and after a very brief period of time an electron from the outer shell "falls" into the vacancy in the inner shell. In falling from an outer to an inner shell the binding of the electron is greatly increased and a photon is emitted. The energy of this photon should be **approximately** equal to the difference in energies of the outer shell and inner shell orbitals. For example, the photon emitted when neon loses an inner shell electron has an energy of 849 ev. The difference in energy between the 2$p$ and 1$s$ orbitals of neon is 869 ev. Photons with energies in this range occur in the X-ray region of the spectrum. It is apparent from the variation in the 1$s$ orbital energies shown in Fig. 5-3 that the energies and hence the frequencies of the X-ray photons will increase as the nuclear charge is increased. It was from a study of the X-ray photons emitted by the elements that Moseley was first able to determine the nuclear charges (the atomic numbers) of the elements.

# 5.4: Some Chemical Implications

A detailed study of the chemical implications of the orbital theory of electronic structure must await our discussion of the chemical bond. However, we can at this point correlate the gross chemical behaviour of the elements with the general results of the orbital theory.

The effective nuclear charge is a minimum for the group I elements in any given row of the periodic table. Therefore, it requires less energy to remove an outer electron from one of these elements than from any other element in the periodic table. The strong reducing ability of these elements is readily accounted for. The variation in the relative reducing power of the elements across a given period or within a given group will be determined by the variation in the effective nuclear charge. The ability of the elements in a given row of the periodic table to act as reducing agents should undergo a continuous decrease from group I to group VII, since the effective nuclear charge increases across a given row. Similarly, the reducing ability should increase down a given column (group) in the table since the effective nuclear charge decreases as the principal quantum number is increased. Anticipating the fact that electrons can be transferred from one atom (the reducing agent) to another (the oxidizing agent) during a chemical reaction, we expect the elements to the left of the periodic table to exhibit a strong tendency to form positively charged ions.

The ability of the elements to act as oxidizing agents should parallel directly the variations in the effective nuclear charge. Thus the oxidizing ability should increase across a given row (from group I to group VII) and decrease down a given family. These trends are, of course, just the opposite of those noted for the reducing ability. We can also relate the chemical terms "reducing ability" and "oxidizing ability" to the experimentally determined energy quantities, "ionization potential" and "electron affinity." The reducing ability should vary inversely with the ionization potential, and the oxidizing ability should vary directly with the electron affinity. The elements in groups VI and VII should exhibit a strong tendency for accepting electrons in chemical reactions to form negatively charged ions. Francium, which possesses a single outer electron in the 7$s$ orbital, should be the strongest chemical reducing agent and fluorine, with an orbital vacancy in the 2$p$ subshell, should be the strongest oxidizing agent.

A great deal of chemistry can now be directly related to the electronic structure of the elements. For example, the reaction

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

is explained chemically by stating that $Cl_2$ is a stronger oxidizing agent than $Br_2$. The electronic interpretation is that the orbital vacancy in Cl is in a 3$p$ orbital and closer to the nucleus than the 4$p$ orbital vacancy in Br. Thus the effective nuclear charge which attracts the extra electron is larger for the Cl atom than for the Br atom. We could of course interpret this same reaction by stating that the Br⁻ ion is a stronger reducing agent than is the Cl⁻ ion. In other words the extra electron in the Br⁻ ion is less tightly held than is the extra electron in the Cl⁻ ion. The explanation in terms of the relative effective nuclear charges is the same as that given above.

The decrease in the effective nuclear charge down the halogen family of elements leads to some interesting differences in their chemistry. For example, hydrogen chloride may be prepared from sodium chloride and sulphuric acid:

(1) $$2Cl^- + 2H^+ + SO_4^{-2} \rightarrow 2HCl + SO_4^{-2}$$
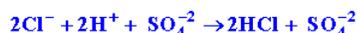
However, the same method cannot be employed in the preparation of hydrogen bromide or hydrogen iodide. In the preparation of hydrogen bromide from sodium bromide,

(2) $$2Br^- + 2H^+ + SO_4^{-2} \rightarrow SO_4^{-2} + 2HBr$$
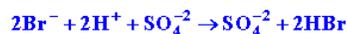
some of the HBr reacts further,

(3) $$2HBr + 2H^+ + SO_4^{-2} \rightarrow 2H_2O + SO_2 + Br_2$$
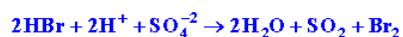
and the HBr is thus contaminated. In preparation of hydrogen iodide a further reaction again occurs:

(4) $$8HI + 2H^+ + SO_4^{-2} \rightarrow H_2S + 4I_2 + 4H_2O$$
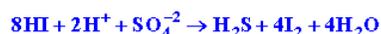
Reactions **(3)** and **(4)** are clearly redox reactions in which the halide ions reduce the sulphur in the $SO_4^{-2}$ anion to a lower oxidation state. Since Cl has the highest effective nuclear charge, the Cl$^-$ ion should be the weakest reducing agent of the three halide ions. Indeed, the Cl$^-$ ion is not a strong enough reducing agent to change the oxidation state of S in $SO_4^{-2}$. The Br$^-$ ion possesses an intermediate value for the effective nuclear charge and thus it is a stronger reducing agent than the Cl$^-$ ion. The Br$^-$ ion reduces the oxidation number of sulphur from (+6) to (+4). Since the I$^-$ ion binds the extra electron least of all (the electron is in an $n = 5$ orbital and the effective nuclear charge of iodine is the smallest of the three), it should be the strongest reducing agent of the three halide ions. The I$^-$ ion in fact reduces the sulphur from (+6) to (-2).

A word about oxidation numbers and electron density distributions is appropriate at this point. An oxidation number does not, in general, represent the formal charge present on a species. Thus S is not $S^{+6}$ in the $SO^{-2}$ ion, nor is it $S^{-2}$ in the $H_2S$ molecule. However, the average electron density in the direct vicinity of the sulphur atom does increase on passing from $SO_4^{-2}$ to $H_2S$. From their relative positions in the periodic table it is clear that oxygen will have a greater affinity for electrons than sulphur. Thus when sulphur is chemically bonded to oxygen the electron density in the vicinity of the sulphur atom is decreased over what it was in the free atom and increased in the region of each oxygen atom. Again it is clear from the relative positions of H and S in the periodic table that sulphur has a greater affinity for electrons than does hydrogen. Thus in the molecule $H_2S$, the electron density in the vicinity of the sulphur atom is increased over that found in the free atom. In changing the immediate chemical environment of the sulphur atom from that of four oxygen atoms to two hydrogen atoms, the electron density (i.e., the average number of electrons) in the vicinity of the sulphur atom has increased. The assignment of actual oxidation numbers is simply a bookkeeping device to keep track of the number of electrons, but the sign of the oxidation number does indicate the direction of the flow of electron density. Thus sulphur has a positive oxidation number when combined with oxygen (the sulphur atom has lost electron density) and a negative one when combined with hydrogen (the electron density around sulphur is now greater than in the sulphur atom).

The above are only a few examples of how a knowledge of the electronic structure of atoms may be used to understand and correlate a large amount of chemical information. It should be remembered, however, that chemistry is a study of very complex interactions and the few simple concepts advanced here cannot begin to account for the incredible variety of phenomena actually observed. Our discussion has been based solely on energy, and energy alone never determines completely the course of a reaction on a macroscopic level, i.e., when many molecules undergo the reaction. There are statistical factors, determined by the changes in the number of molecules and in the molecular dimensions, which must also be considered. Even so, the energy effect can often be overriding.

In the long form of the periodic table, families are labelled by both a number and by the letter A or B. Thus there is a IA family and a IB family. It will be noted that the elements in a B family all occur in the series of transition elements in which the $d$ orbitals are being filled. In the A families, however, the $d$ orbitals are either absent or are present as closed inner shells. For example, consider the electronic configurations of K (IA) and Cu (IB):

| | |
|---|---|
| **K** $[Ar]4s^1$ | **Cu** $[Ar]3d^{10}4s^1$ |

Note that the most stable configuration for Cu is not [Ar] $3d^94s^2$ as expected. By transferring one of the $4s$ electrons to the $3d$ vacancy, the $d$ subshell is filled and the electronic energy is lowered. The electron density distribution of the Cu atom is therefore a spherical one. Both K and Cu have one outer electron with a spherical charge distribution. They should have some properties in common, such as a tendency to lose one electron and form a positive ion. For this reason both families are labelled I. However, the shell underlying the outer electron in the K atom possesses a rare gas configuration, while in the Cu atom it is a set of filled $d$ orbitals. This difference in electronic structure is sufficient to cause considerable differences in their chemistry, hence the further labels A and B.

A rare gas configuration is always one of great stability, particularly when it occurs in a positive ion. (Recall that $I_2 = 47.3$ ev for sodium.) The species $K^{+2}$ is never observed in solution chemistry, and could be produced in the gas phase only by an expenditure of energy far in excess of that observed in ordinary chemical reactions. The Cu$^+$ ion, on the other hand, very readily loses a second electron to form the Cu$^{+2}$ ion. Indeed, Cu$^{+2}$ is the more common ionic form of copper. Thus the $d^{10}$ closed shell structure is more easily broken than a rare gas configuration, giving to Cu a variable valency of one or two.

# 5.E: Exercises

| | |
|---|---|
| 1. | Estimate the wavelength of the photon which is emitted when a 3p electron falls to a vacancy in the 1*s* orbital in a chlorine ion. The energies of the 1*s* and 3*p* orbitals in chlorine are -2.854 × $10^3$ ev and -13.77 ev respectively. |

| 2. | In his investigation of the X-ray spectra of the elements, Moseley found that the frequencies of the lines of shortest wavelength could be expressed as a function of the atomic number Z as |
| | $$\sqrt{v} = a(Z - \sigma)$$ |
| | where *a* and s are constants. Account for the general form of the relationship. What is the significance of the factor s? |

| 3. | (a) | On the basis of your knowledge of the electronic structure of the elements arrange the following substances in the order of their increasing ability to act as oxidizing agents. $He^+$, Cl, P, Na, $F^-$ |
|---|---|---|
| | (b) | Arrange the following substances in the order of their increasing ability to act as reducing agents. Cs, Li, C, S, Cl |

| 4. | Rationalize the following observations on the basis of the electronic structures of the halogen atoms and their ions. Iodide ions can be oxidized to elemental iodine by molecular oxygen $4HI + O_2 \to 2Li + 2H_2O$ but the corresponding reaction does not occur with HCl HCl + $O_2$ → no reaction |

| 5. | Account for the fact that the second ionization potential for oxygen is greater than that for fluorine. ($I_2$ for 0 is 35.15 ev and $I_2$ for F is 34.98 ev.) |

| 6. | Which atom or ion in the following pairs has the highest ionization potential? |
|---|---|
| | (a) N, P<br>(b) Mg, Sr<br>(c) Ge, As<br>(d) Ar, $K^+$ |

| 7. | Of the following substances: $F_2$, $F^-$, $I_2$, $I^-$ | |
|---|---|---|
| | (a) | Which is the best oxidizing agent? |
| | (b) | Which is the best reducing agent? |
| | (c) | Write **one** chemical equation for a reaction which will illustrate your answers to parts (a) and (b). |

## 6: The Chemical Bond

# 6.1: Introduction

With our knowledge of the electronic structure of atoms we are now in a position to understand the existence of molecules. Clearly, the force which binds the atoms together to form a molecule will, as in the atomic case, be the electrostatic force of attraction between the nuclei and electrons. In a molecule, however, we encounter a force of repulsion between the nuclei in addition to that between the electrons. To account for the existence of molecules we must account for the predominance of the attractive interactions. We shall give general arguments to show that this is so, first in terms of the energy of a molecule, relative to the energies of the constituent atoms, and secondly, in terms of the forces acting on the nuclei in a molecule.

In order to determine what attractive and repulsive interactions are possible in a molecule, consider an instantaneous configuration of the nuclei and electrons in a hydrogen molecule (Figure $6.1.1$). When the two atoms are initially far apart (the distance $R$ is very large) the only potential interactions are the attraction of nucleus A for electron number (1) and the attraction of nucleus B for electron number (2). When $R$ is comparable to the diameter of an atom (A and B are close enough to form a molecule) then new interactions appear. Nucleus A will now attract electron (2) as well as (1) and similarly nucleus B will attract electron (1) as well as (2). These interactions are indicated by the four solid lines in Figure $6.1.1$ connecting pairs of particles which attract one another.
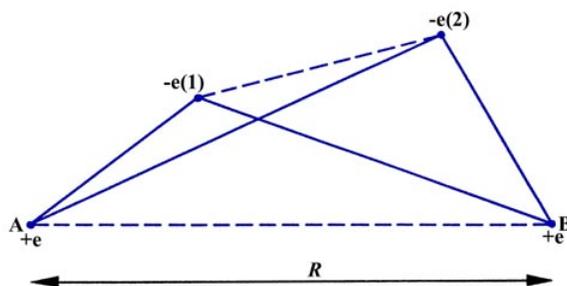


**Figure** $\mathbf{6.1.1}$ : *One possible set of the instantaneous relative positions of the electrons and nuclei in an $H_2$, molecule. The dashed lines represent the repulsive interactions between like charges and the solid lines indicate the attractive interactions between opposite charges.*

The number of attractive interactions has been doubled from what it was when the atoms were far apart. However, the reduction in $R$ introduces two repulsive interactions as well, indicated by the dashed lines joining charges of like sign in Figure $6.1.1$. The two electrons now repel one another as do the two nuclei. If the two atoms are to remain together to form a molecule, the attractive interactions must exceed the repulsive ones. It is clear from Figure $6.1.1$ that the new attractive interactions, nucleus A attracting electron (2) and nucleus B attracting electron (1), will be large only if there is a high probability of both electrons being found in the region between the nuclei. When in this region, both electrons are strongly attracted by both nuclei, rather than by just one nucleus as is the case when the atoms are far apart.

When the average potential energy is calculated by quantum mechanics, the attractive interactions are found to predominate over the repulsive ones because quantum mechanics does indeed predict a high probability for each electron being in the region between the nuclei. This general consideration of the energy demonstrates that electron density must be concentrated between the nuclei if a stable molecule is to be formed, for only in this way can the attractive interaction be maximized. We can be much more specific in our analysis of this problem if we discuss a molecule from the point of view of the forces acting on the nuclei. However, we must first state some general conclusions of quantum mechanics regarding molecular systems.

In the atomic case we could fix the position of the nucleus in space and consider only the motion of the electrons relative to the nucleus. In molecules, the nuclei may also change positions relative to one another. This complication can, however, be removed. The nuclei are very massive compared to the electrons and their average velocities are consequently much smaller than those possessed by the electrons. In a classical picture of the molecule we would see a slow, lumbering motion of the nuclei accompanied by a very rapid motion of the electrons. The physical implication of this large disparity in the two sets of velocities is that the electrons can immediately adjust to any change in the position of the nuclei. The positions of the nuclei determine the potential field in which the electrons move. However, as the nuclei change their positions and hence the potential field, the electrons can immediately adjust to the new positions. Thus the motion of the electrons is determined by where the nuclei are but not by how fast the nuclei are moving. We may, because of this fact, discuss the motions of the electrons and of the nuclei separately.

> *Thus the motion of the electrons is determined by where the nuclei are but not by how fast the nuclei are moving.*

For a given distance between the nuclei we obtain the energy, the wave function and the electron density distribution of the electrons, the nuclei being held in fixed positions. Then the distance between the nuclei is changed to a new value, and the calculation of the energy, wave function and electron density distribution of the electrons is performed again. This process, repeated for every possible internuclear distance, allows us to determine how the energy of the electrons changes as the distance between the nuclei is changed. More important for our present discussion, we may concern ourselves only with the motion of the electrons and hold the nuclei stationary at some particular value for the internuclear distance $R$.

The energy of the electrons in a molecule is quantized, as it is in atoms. When the nuclei are held stationary at some fixed value of $R$, there are a number of allowed energy levels for the electrons. There are, however, no simple expressions for the energy levels of a molecule in terms of a set of quantum numbers such as we found for the hydrogen atom. In any event we shall be concerned here only with the first or lowest of the energy levels for a molecule. As in the case of atoms, there is a wave function which governs the motion of all the electrons for each of the allowed energy levels. Each wave function again determines the manner in which the electronic charge is distributed in three-dimensional space.

The electron density distribution for a molecule is best illustrated by means of a contour map, of the kind introduced earlier in the discussion of the hydrogen atom. Figure $6.1.2$ shows a contour map of the charge distribution for the lowest, or most stable state of the hydrogen molecule. Imagine a hydrogen molecule to be cut in half by a plane which contains the nuclei. The amount of electronic charge at every point in space is determined, and all points having the same value for the electron density in the plane are joined by a line, a contour line. Also shown is a profile of the contour map along the internuclear axis. A profile illustrates the variation in the charge density along a single axis.
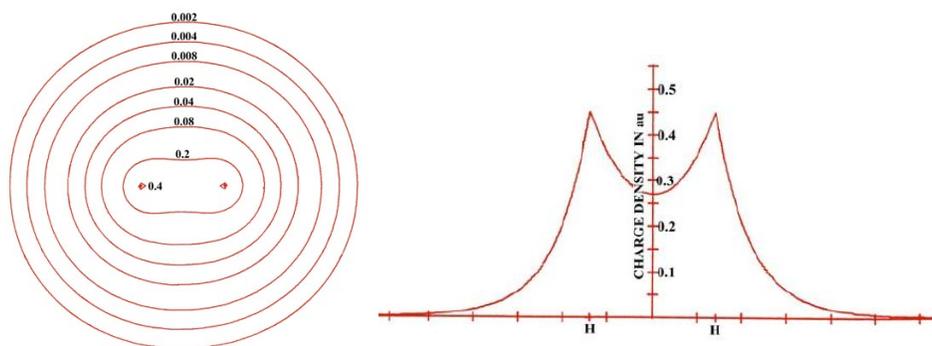


*Figure* $6.1.2$*: A contour map of the electron density distribution (or the molecular charge distribution) for H2 in a plane containing the nuclei. Also shown is a profile of the density distribution along the internuclear axis. The internuclear separation is 1.4 au. The values of the contours increase in magnitude from the outermost one inwards towards the nuclei. The values of the contours in this and all succeeding diagrams are given in au; 1 au = $e/a_o{}^3$ = 6.749 e/$Å^3$.*

The electron density contours of highest value are in the region of each nucleus. Thus the negative charge is concentrated in the region of the nuclei in a molecule as well as in an atom. The next highest concentration of negative charge is found in the region between the nuclei. It is the negative charge in this region which is strongly attracted by both nuclei and which results in the attractive interactions exceeding the repulsive ones in the formation of the molecule from the atoms. Most of the density contours envelope both nuclei. The density distributions of the two atoms have been merged together in the formation of the molecule.

The same contour map would be obtained for any plane through the nuclei. Therefore, in three-dimensional space the hydrogen molecule would appear to be an ellipsoidal distribution of negative charge. Most of the electronic charge is concentrated along the internuclear axis and becomes progressively more diffuse at large distances from the centre of the molecule. Recall that the addition of all the charge in every small volume element of space equals the total number of electrons which in the case of the hydrogen molecule is two. The volume of space enclosed by the outer contour in Figure $6.1.2$ contains over 99% of the total electronic charge of the hydrogen molecule.

# 6.2: An Electrostatic Interpretation of the Chemical Bond

## An Electrostatic Interpretation of the Chemical Bond

In the light of the above discussion of a molecular electron density distribution, we may regard a molecule as two or more nuclei imbedded in a rigid three-dimensional distribution of negative charge. There is a theorem of quantum mechanics which allows us to make direct use of this picture of a molecule. This theorem states that the force acting on a nucleus in a molecule may be determined by the methods of classical electrostatics. The nuclei in a molecule repel one another, since they are of like charge. This force of repulsion, if unbalanced, would push the nuclei apart and the molecule would separate into atoms. In a stable molecule, however, the nuclear force of repulsion is balanced by an attractive force exerted by the negatively-charged electron density distribution. The usefulness of this approach lies in the fact that we may account for and discuss the stability of molecules in terms of the classical concept of a balance between the electrostatic forces of attraction and repulsion. We can illustrate this method and arrive at some results of a general nature by considering in detail the forces acting on the nuclei in the hydrogen molecule.

The charge on a hydrogen nucleus is $+e$ and the force of repulsion acting on either nucleus is

$$F_n = +e^2/R^2$$

where $R$ is the internuclear distance. This force obviously acts to push the two nuclei apart (Fig. 6-3).
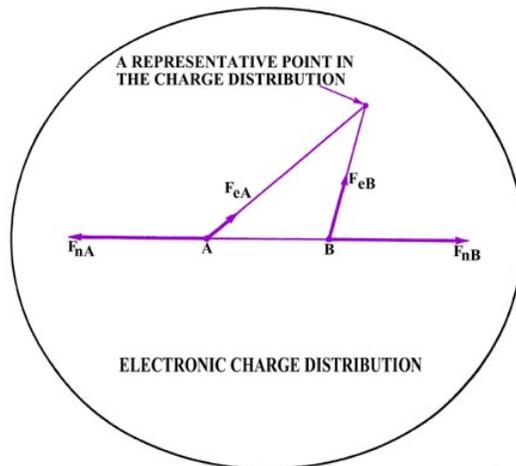


Fig. 6-3. The forces acting on the nuclei in $H_2$. Only one outer contour of the electron density distribution is shown. Over 99% of the total electronic charge is contained within this contour.

The attractive force which balances this force of repulsion and draws the nuclei together is exerted by the negatively-charged electron density distribution. The density distribution is treated as a ***rigid*** distribution of negative charge in space. Each small element of this charge distribution exerts a force on the nuclei, illustrated in Fig. 6-3 for one such small charge point. The forces it exerts on the nuclei are labelled $F_{eA}$ and $F_{eB}$. The total amount of negative charge in the electron density distribution must correspond to some integral number of electrons. However, the amount of negative charge in each small region of space will in general correspond to some fraction of one electronic charge.

The electronic force of attraction $F_{eA}$ or $F_{eB}$ may be equated to two components, one along the bond, and one perpendicular to it. The density distribution is symmetric with respect to the internuclear axis, i.e., for every charge point above the axis there must, by symmetry, be another point of equal charge at the corresponding place beneath the internuclear axis. The symmetrically related charge point will exert the same force along the bond, but the component perpendicular to the bond will be in the opposite direction. Thus the perpendicular forces of attraction exerted on the nuclei are zero (Fig. 6-4) and we may confine our attention to the components of the attractive force along the bond.
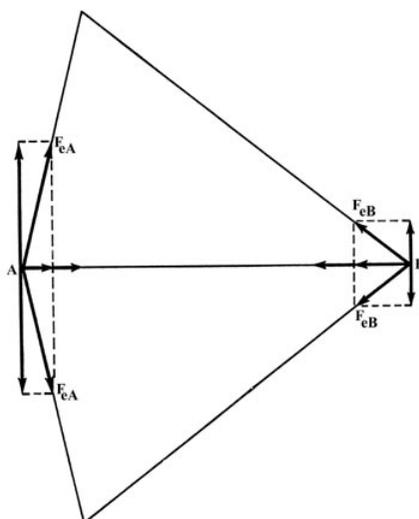
Fig. 6-4. The two components of force along the bond add together while the two perpendicular components cancel at both A and B.

It is obvious that all of the charge elements which are in the general region between the two nuclei will exert forces which draw the two nuclei together. The force exerted by the density in this region acts in opposition to the force of nuclear repulsion and binds the two nuclei together. It is also clear that a charge element in the region behind either nucleus will exert a force which tends to increase the distance between the nuclei (Fig. 6-5).
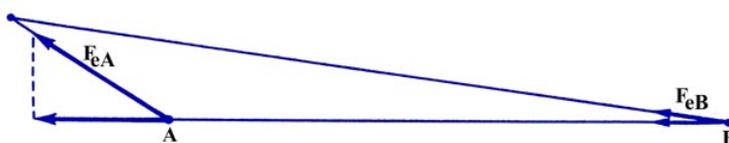


Fig. 6-5. The component of $F_{eA}$ along the bond is greater than the corresponding component of $F_{eB}$.

Since the charge element is closer to nucleus A than it is to nucleus B, the component of the force on A along the bond will be greater than the component of the force on B along the bond. Thus the effect of density in this region will be to separate the molecule into atoms.

There must also be a line on which the density exerts the same force on both nuclei and thus neither increases nor decreases $R$ because the charge density in one region draws the nuclei together and in another draws them apart. The charge element shown in Fig. 6-6 exerts the same force along the bond on both A and B even though it is closer to B than it is to A. Although the total force $F_{eB}$ is much larger than $F_{eA}$, $F_{eB}$ is directed almost perpendicular to the bond axis and thus its component along the bond is quite small and equal to the component of $F_{eA}$ along the bond. Charge density on either of the two curves shown in Fig. 6-6 exerts equal forces on both of the nuclei along the bond, and such charge density will not tend to increase or decrease the distance between the nuclei. Thus these two curves (surfaces in three dimensions) divide the space in a molecule into a binding region and an antibinding region. Any charge density between the two boundary curves, in the **binding region**, draws the two nuclei together while any charge density in the hatched region behind either curve, the **antibinding region**, exerts unequal forces on the nuclei and separates the molecule into atoms.
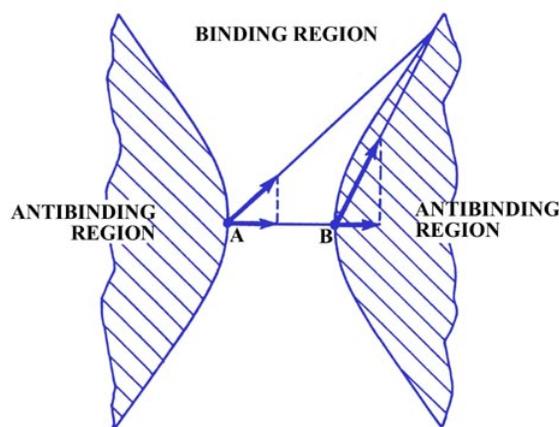
Fig. 6-6. The boundary curves which separate the binding from the antibinding regions in a homonuclear diatomic molecule.

*A chemical bond is thus the result of the accumulation of negative charge density in the region between the nuclei to an extent sufficient to balance the nuclear forces of repulsion.* This corresponds to a state of electrostatic equilibrium as the net force acting on each nucleus is zero for this one particular value of the internuclear distance. If the distance between the nuclei is increased from the equilibrium value, the nuclear force of repulsion is decreased. At the same time the force of attraction exerted by the electron density distribution is increased as the binding region is increased in size. Thus when $R$ is increased from its equilibrium value there are net forces of attraction acting on the nuclei which pull the two nuclei together again. A definite force would have to be applied to overcome the force of attraction exerted by the electron density distribution and separate the molecule into atoms. Similarly, if the value of $R$ is decreased from its equilibrium value, the force of nuclear repulsion is increased over its equilibrium value. At the same time, the attractive force exerted by the electron density is decreased, because the binding region is decreased in size. In this case there will be a net force of repulsion pushing the two nuclei apart and back to their equilibrium separation. There is thus one value of $R$ for which the forces on the nuclei are zero and the whole molecule is in a state of electrostatic equilibrium.

The division of the space around a molecule into a binding and an antibinding region shows where charge density must be concentrated in order to obtain a stable chemical bond. The next question which must be answered is, "How much charge must be placed in the binding region to achieve electrostatic equilibrium?" For example, we might consider the possibility of forming a molecule by bringing together two atoms, each with its own atomic distribution of charge, and simply allow the two atomic charge distributions to overlap without deforming in any way. This would result in the accumulation of approximately twice as much charge density in the binding region as in either of the antibinding regions behind the nuclei. Would this doubling of the charge density in the region between the nuclei be sufficient to balance the nuclear forces of repulsion? Let us answer this question for the simple case of two hydrogen atoms forming molecular hydrogen, but again the result will be general.

The most stable state of the hydrogen molecule is obtained when two hydrogen atoms, each in its most stable atomic state, approach one another. The ground state of a hydrogen atom is obtained when the electron is in the 1$s$ orbital. The density distribution around each hydrogren nucleus is the spherical one which we discussed previously in some detail. We shall first calculate the force on one of the hydrogen nuclei resulting when the two atoms are very far apart. The situation is represented in Fig. 6-7 where each atomic charge distribution is represented by a single outer circular contour. This contour is to define a sphere which in three-dimensions contains essentially all of the electronic charge of each atom.
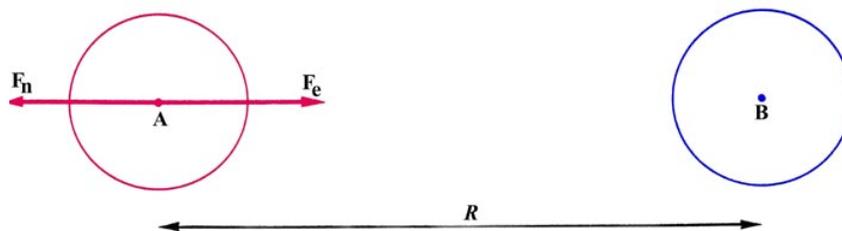


Fig. 6-7. The forces acting on nucleus A at a large internucleus distances, $R$.

Consider the forces exerted on nucleus A. The force of nuclear repulsion is just

$$F_n = (+e)(+e)/R^2 = e^2/R^2$$

The atomic charge density centred on nucleus A exerts no net force on this nucleus as it pulls equally in every direction because of its spherical symmetry. There is, however, a net force of attraction due to the single electronic charge dispersed in the atomic distribution of B. A theorem of classical electrostatics states that the force exerted by a spherical charge distribution on a point charge lying outside of the charge distribution is equal to the force which would be obtained if all the charge in the distribution were concentrated at its centre. Nucleus A is a point charge which lies outside of the spherical charge distribution centred on B. Thus the force exerted on nucleus A by this charge distribution is just

$$F_e = \frac{(-e)(+e)}{R^2} = -e^2/R^2$$

as the total amount of charge contained in the distribution is that of one electron. The total force acting on nucleus A is

$$F_n + F_e = e^2/R^2 - e^2/R^2 = 0$$

A zero force is the expected answer when the two atoms are very far apart.

Can we again balance the forces for a value of $R$ which is of the order of magnitude of an atomic diameter, i.e., typical of the values of $R$ found in molecules? At this value of $R$, each nucleus will have penetrated the charge density surrounding the other nucleus. Recall that in this calculation we insist upon the atomic charge densities remaining spherical and our molecular charge density is obtained by allowing the two rigid atomic charge distributions to overlap one another (Fig. 6-8).
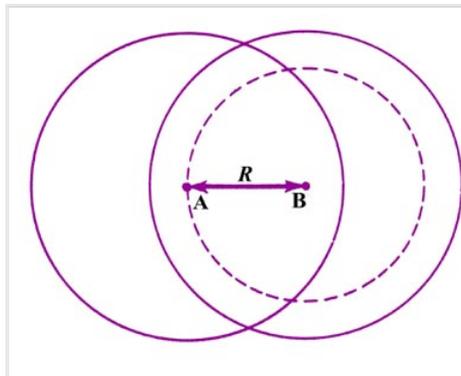


Fig. 6-8. The forces exterted on the nucleus A for the overlap of rigid atomic charge distributions. Only the charge density on B which is contained in the sphere of radius $R$ exerted a force on nucleus A.

The force of nuclear repulsion in this case is still given by

$$F_n = +e^2/R^2$$

where the value of $R$ is much less than in the previous calculation. Since the charge distribution on A is still spherical in shape, it exerts no net force on nucleus A. The force exerted on nucleus A by the charge density on B can again be calculated by the theorem referred to previously. However, nucleus A no longer lies outside of all the charge density on B. The value of $R$ is significantly less than the radius of the charge distribution on B. All the charge density on B which lies within the sphere defined by the bond length $R$ again exerts a force on nucleus A, equal to that obtained if all this density were situated at the B nucleus. The theorem referred to previously shows that the density on B which lies outside of this sphere defined by R exerts no net force on nucleus A.

Since $R$ is less than the diameter of the charge distribution, the amount of negative charge contained in a sphere of radius $R$ will be less than that of one electron. The observed value of $R$ for the hydrogen molecule is 1.4 au and reference to the data given previously for the 1$s$ orbital density for the hydrogen atom shows that a sphere of radius 1.4 would contain approximately one half of an electronic charge. The electrostatic force of attraction exerted on nucleus A is, therefore,

$$F_e = -0.5\,e^2/R^2$$

The net force on nucleus A is

$$F = F_n + F_e = +e^2/R^2 - 0.5\,e^2/R^2 = 0.5\,e^2/R^2$$

There is a net force of repulsion exerted on nucleus A under these conditions. If $R$ were decreased still further, nucleus A would penetrate the charge density around B to an even greater extent and "see" even more of the nuclear charge on B. The force on the nuclei will thus be repulsive for all finite values of $R$.

This is an important result as it shows that the density distribution in a molecule cannot be considered as the simple sum of the two atomic charge densities. The overlap of rigid atomic densities does not place sufficient charge density in the binding region to overcome the nuclear force of repulsion. We conclude that the original atomic charge distributions must be distorted in the formation of a molecule, and the distortion is such that charge density is concentrated in the binding region between the nuclei. A quantum mechanical calculation predicts this very result. The calculation shows that there is a continuous distortion of the original atomic density distributions, a distortion which increases as the internuclear distance decreases. This is illustrated in Fig. 6-9 for the approach of two hydrogen atoms to form the hydrogen molecule.
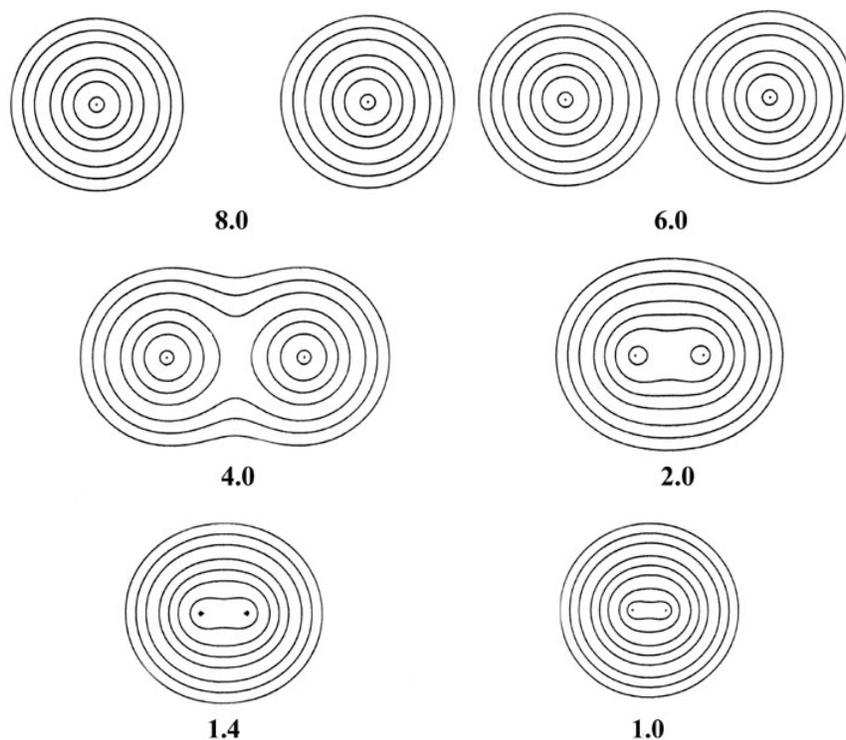


Fig. 6-9. A series of electron density contour maps illustrating the changes in the electron charge distribution during the approach of two H atoms to form $H_2$. The internuclear distance $R$ in units of au is indicated beneath each map. At $R = 8$ the atomic densities appear to be undistorted. At $R = 6$ the densities are distorted but still essentially separate. As $R$ is further decreased, charge density contours of increasing value envelope both nuclei, and charge density is accumulated at the positions of the nuclei and in the internuclear region. The values of the contours in au increase from the outermost to the innermost one in the order $2 \times 10^{-n}$, $4 \times 10^{-n}$, $8 \times 10^{-n}$, for decreasing values of $n$ beginning with $n = 3$. Thus the outermost contour in each case is 0.002 au and the value of the innermost contour for $R = 1.0$ au, for example, is 0.4.

The changes in the original atomic density distributions caused by the formation of the chemical bond may be isolated and studied directly by the construction of a ***density difference distribution***. Such a distribution is obtained by subtracting the density obtained from the overlap of the undistorted atomic densities separated by a distance $R$, from the molecular charge distribution evaluated at the same value of $R$. Wherever this density difference is positive in value it means that the electron density in the molecule is greater than that obtained from the simple overlap of the original atomic densities. Where the density difference is negative, it means that there is less density at this point in space in the molecule than in the distribution obtained from the overlap of the

original atomic distributions. Such a density difference map thus provides *a detailed picture of the net reorganization of the charge density of the separated atoms accompanying the formation of a molecule*.

We have just proven that the density distribution resulting from the overlap of the undistorted atomic densities does not place sufficient charge density in the binding region to balance the forces of nuclear repulsion. *The regions of charge increase in the density difference maps are, therefore, the regions to which charge is transferred relative to the separated atoms to obtain a state of electrostatic equilibrium and hence a chemical bond.* From this point of view a density difference map provides us with a picture of the "bond density."

Figure 6-10 shows a set of density difference or bond density maps for the approach of two hydrogen atoms to form the hydrogen molecule. At very large separations, for example at 8 au, the density distribution on each atom is polarized in the direction of the approaching atom. Charge density has been transferred from the antibinding region behind each nucleus to the binding region immediately in front of each nucleus. Thus even at large separations the atomic density distributions are no longer spherical. We noted in our discussion of the approach of two rigid hydrogen atoms that a spherical charge distribution does not exert a net force on the nucleus on which it is centred. Each polarized atomic charge distribution does, however, exert an attractive force on its nucleus. The polarized densities place more charge on the binding side of each nucleus than on the antibinding side. These long-range attractive forces, called van der Waals' or dispersion forces, could be aptly described as a "bootstrap effect" as each nucleus is pulled by its own charge density. All pairs of neutral molecules undergo this type of polarization as a result of the long-range interactions between them, and there are attractive forces operative between all pairs of molecules out to very large distances. Although the long-range polarizations and the resulting forces of attraction are very weak, they are of extreme importance. They are commonly referred to as van der Waals forces and are solely responsible for the binding observed in certain kinds of solids, solid helium for example. This will be discussed more fully later.
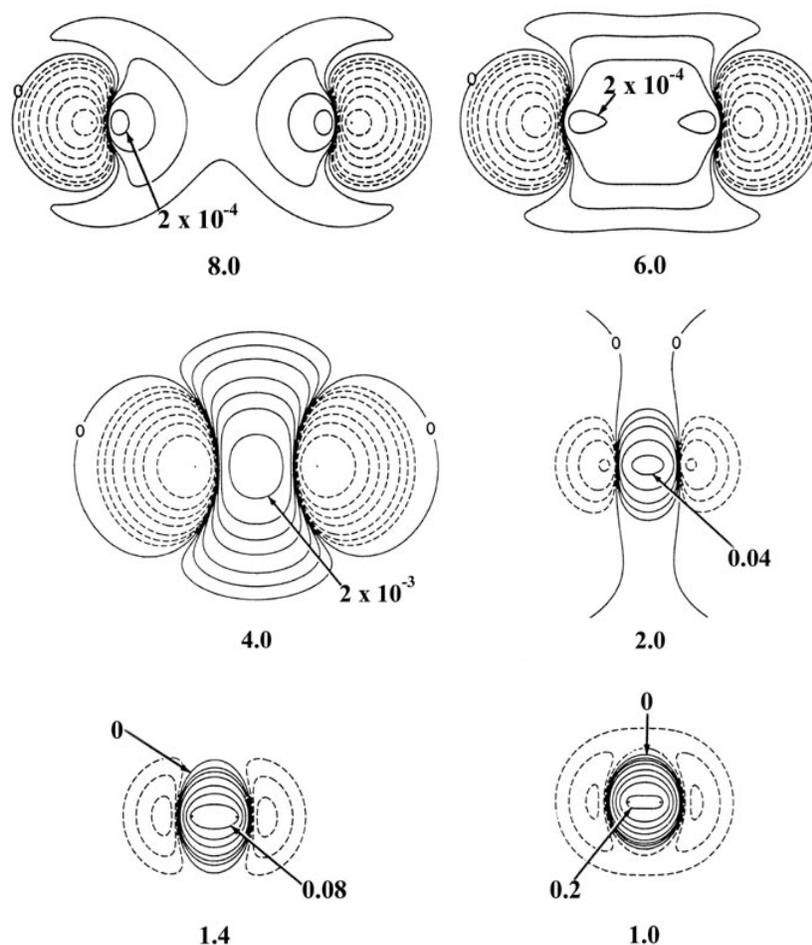


Fig. 6-10. Density difference distribution (molecular minus atomic) for the approach of two H atoms. These maps indicate the changes in the atomic densities caused by the formation of a molecule. The solid contours represent an increase in charge density

over the atomic case, while the dashed contours denote a decrease in the charge density relative to the atomic densities. Since the changes in the charge density are much smaller for large values of $R$ than for small values of $R$ two different scales are used. The solid and dashed contours increase (+) or decrease (-) respectively from the zero contour in the order $\pm 2 \times 10^{-n}$, $\pm 4 \times 10^{-n}$, $\pm 8 \times 10^{-n}$ au for decreasing values of $n$. The maps for $R = 8.0$, 6.0 and 4.0 au begin with $n = 5$ and those for $R = 2.0$, 1.4 and 1.0 au begin with $n = 3$. The zero contour and the value of the innermost positive contour are indicated in each case. Note the continuous increase in charge density in the region between the nuclei as $R$ is decreased.

At 6.0 au the density increase in the binding region is common to both nuclei, and for distances less than 6.0 au the system can no longer be described as two polarized hydrogen atoms. The distortions of the original densities caused by the transfer of charge to the binding region is so great that the individual character of the atomic densities is no longer discernible. The *magnitude* of the attractive force (which is negative in sign) exerted on the nuclei by this accumulation of charge density in the binding region increases rapidly for distances less than 4.5 au (Fig. 6-11).
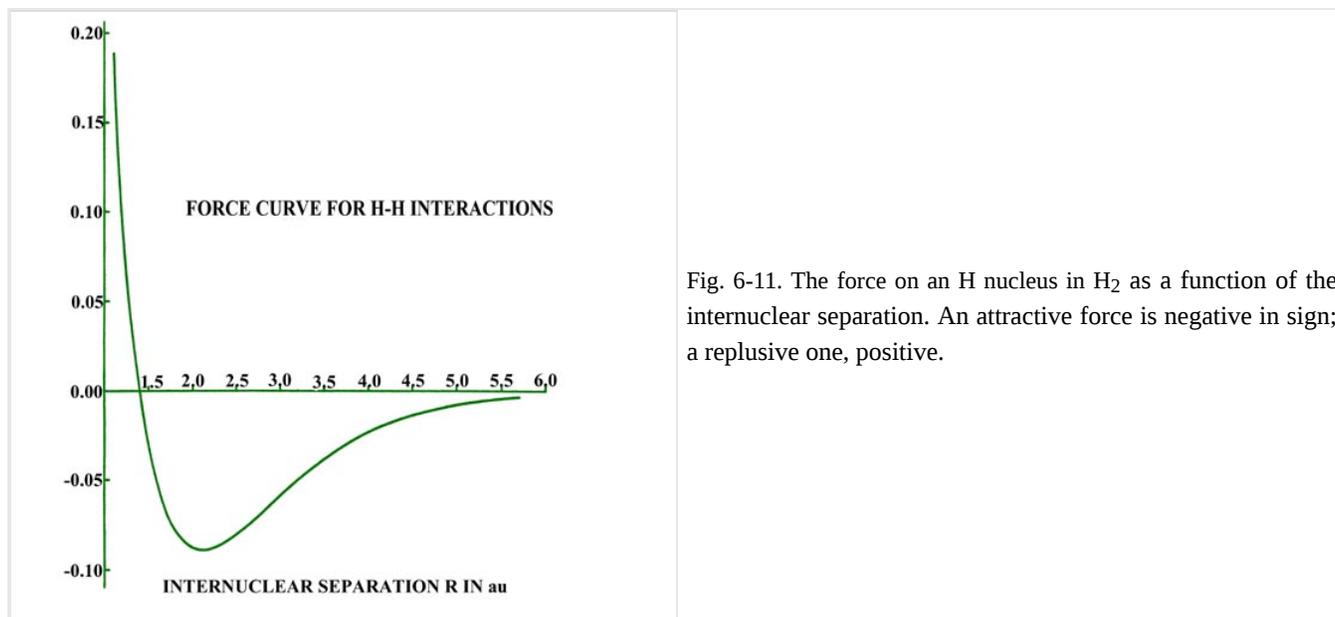


Fig. 6-11. The force on an H nucleus in $H_2$ as a function of the internuclear separation. An attractive force is negative in sign; a replusive one, positive.

The attractive force reaches a maximum at 2.1 au. The density difference diagrams indicate that for distances as small as 2.0 au, the density increase is confined to the region between the nuclei. For separations smaller than 2.0 au an increasing amount of charge density is transferred to the anti-binding regions behind each nucleus. Because of this, the attractive force on the nuclei decreases rapidly with a further decrease in $R$ until at $R = 1.4$ au, the net attractive force exerted by the charge density just balances the force of nuclear repulsion (Fig. 6-11). A state of electrostatic equilibrium is reached, and a chemical bond is formed. A further decrease in $R$ leads to a force of repulsion. More charge density is transferred to the antibinding regions, and the force exerted by this charge density, acting in concert with the increase in the force of nuclear repulsion, outweighs the attractive force exerted by the charge density in the binding region.

The same changes in density are depicted in Fig. 6-12, which is a series of profiles along the internuclear axis of the density difference maps shown in Fig. 6-10. The profile maps illustrate in a striking fashion the build-up of charge density in the region between the nuclei.
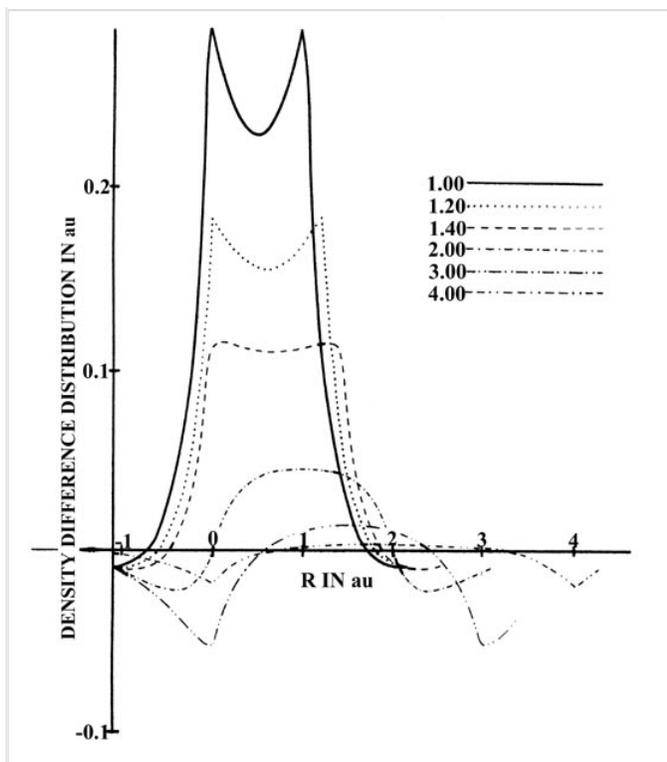
Fig. 6-12. Profiles of the density difference along the internuclear axis for $H_2$ at a series of internuclear separations. One nucleus is held fixed, and the other is moved relative to it. The separations are indicated on the diagram.

The formation of any chemical bond is qualitatively similar to the changes in the charge distribution and in the forces exerted on the nuclei as found for the hydrogen molecule. We must now inquire into the conditions which determine whether or not sufficient charge density can be accumulated in the binding region to yield a stable molecule. Since not all atoms form chemical bonds, clearly such conditions must exist.

# 6.3: The Effect of the Pauli Principle on Chemical Binding

The Pauli exclusion principle plays as important a role in the understanding of the electronic structure of molecules as it does in the case of atoms. The end result of the Pauli principle is to limit the amount of electronic charge density that can be placed at any one point in space. For example, the Pauli principle prevents the 1s orbital in an atom from containing more than two electrons. Since the 1s orbital places most of its charge density in regions close to the nucleus, the Pauli principle, by limiting the occupation of the 1s orbital, limits the amount of density close to the nucleus. Any remaining electrons must be placed in orbitals which concentrate their charge density further from the nucleus.

In an earlier discussion we pointed out that the reason the electron doesn't fall onto the nucleus is because it must possess kinetic energy if Heisenberg's uncertainty principle is not to be violated. This is one reason why matter doesn't collapse. The Pauli principle is equally important in this regard. The electron density of the outer electrons in an atom cannot collapse and move closer to the nucleus since it can do so only if the electrons occupy an orbital with a lower n value. If, however, the inner orbital contains two electrons, then the Pauli principle states that the collapse cannot occur. We must be careful in our interpretation of this aspect of the Pauli principle. The density from a 2s orbital has a small but finite probability of being found well within the density of the 1s orbital. Do not interpret the Pauli principle as implying that the density from an occupied orbital has a clearly defined and distinct region in real space all to its own. This is not the case. The operation of the Pauli principle is more subtle than this. In some simple cases, such as the ones we wish to discuss below, the limiting effect of the Pauli principle on the density distribution can, however, be calculated and pictured in a very direct manner.

The Pauli principle demands that when two electrons are placed in the same orbital their spins must be paired. What restriction is placed on the spins of the electrons during the formation of a molecule, when two orbitals, each on a different atom, overlap one another? For example, consider the approach of two hydrogen atoms to form a hydrogen molecule. Consider atom A to have the configuration *[Math Processing Error]* and atom B the configuration *[Math Processing Error]*. Even when the atoms approach very close to one another the Pauli principle would be satisfied as the spins of the two electrons are opposed. This is the situation we have tacitly assumed in our previous discussion of the hydrogen molecule. However, what would occur if two hydrogen atoms approached one another and both had the same configuration and spin, say *[Math Processing Error]*? When two atoms are relatively close together the electrons become **indistinguishable**. It is no longer possible to say which electron is associated with which atom as both electrons move in the vicinity of both nuclei. Indeed this is the effect which gives rise to the chemical bond. In so far as we can still regard the region around each atom to be governed by its own atomic orbital, distorted as it may be, two electrons with the same spin will not be able to concentrate their density in the binding region. This region is common to the orbitals on both atoms, and since the electrons possess the same spin they cannot both be there simultaneously. In the region of greatest overlap of the orbitals, the binding region, the presence of one electron will tend to exclude the presence of the other if their spins are parallel. Instead of density accumulating in the binding region as two atoms approach, electron density is removed from this region and placed in the antibonding region behind each nucleus where the overlap of the orbitals is much smaller. Thus the approach of two hydrogen atoms with parallel spins does not result in the formation of a stable molecule. This repulsive state of the hydrogen molecule, in which both electrons have the same spin and atomic orbital quantum numbers, can be detected spectroscopically.

We can now give the general requirements for the formation of a chemical bond. Electron density must be accumulated in the region between the nuclei to an extent greater than that obtained by allowing the original atomic density distributions to overlap. In general, the increase in charge density necessary to balance the nuclear force of repulsion requires the presence of two electrons.

> There are a few examples of "one-electron" bonds. An example is the *[Math Processing Error]* molecule-ion. This ion contains only one electron and is indeed a stable entity in the gas phase. It cannot, however, be isolated or stored in any way.

In the atomic orbital approximation we picture the bond as resulting from the overlap of two distorted atomic orbitals, one centered on each nucleus. When the orbitals overlap, both electrons may move in the field of either nuclear charge as the electrons may now exchange orbitals. Finally, the pair of electrons must possess opposed spins. When their spins are parallel, the charge density from each electron is accumulated in the antibinding rather than in the binding region. We shall now apply these principles to a number of examples and in doing so obtain a quantum mechanical definition of valency.

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# 6.4: The Quantum Mechanical Explanation of Valency

Helium atoms in their ground state do not form a stable diatomic molecule. In fact, helium does not combine with any neutral atom. Its valency, that is, its ability to form chemical bonds with other atoms, is zero. The electronic configuration of the helium atom is $1s^2(\downarrow\uparrow)$, a closed shell configuration.When two helium atoms are in contact, each electron on one atom encounters an electron on the other atom with a parallel spin. Because of the Pauli principle, neither electron on either atom can concentrate its density in the region they have in common, the region between the nuclei. Instead, the density is transferred to the antibinding regions behind each nucleus where the overlap of the two atomic density distributions is least. This is the same effect noted earlier for the approach of two hydrogen atoms with parallel spins.

Comparison of a series of density difference maps for the approach of two helium atoms (Figure *[Math Processing Error]*) with those given previously for $H_2$ (Fig. 6-10) reveals that one set is the opposite of the other. The regions of charge build-up and charge depletion are reversed in the two cases. The density difference diagrams are obtained by subtracting the distribution obtained by the overlap of the atomic charge densities from the molecular charge distribution. The former distribution, it will be recalled, does not place sufficient charge density in the binding region to balance the force of nuclear repulsion. Thus it is clear from Figure *[Math Processing Error]* that He$_2$ will be unstable because the molecular distribution places less charge density in the binding region than does the one obtained from the overlap of the atomic densities. The charge density in He$_2$ is transferred to the antibinding region where it exerts a force which, acting in the same direction as the nuclear force of repulsion, pulls the two nuclei apart. Repulsive forces will dominate in He$_2$ and no stable molecule is possible.
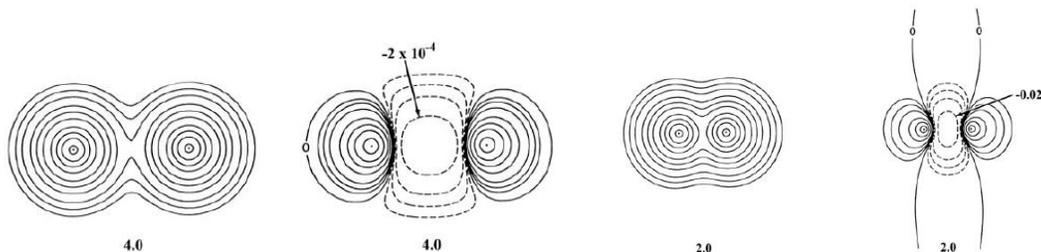


*Figure [Math Processing Error]: Contour maps of the total molecular charge density and of the density difference for two He atoms at internuclear separations of 4.0 au and 2.0 au. The scale of contour values for the total density maps are the same as used in Fig 6-9 for H2. The outermost contour is 0.002 au and the innermost one is 2.0 au for R = 4.0 and R = 2.0 au. The scale used in the density difference plots is the same as that given in Fig. 6-10 beginning with n = 5 for R = 4.0 au and with n = 3 for R = 2.0 au. Note the increase in the amount of charge density transferred from the binding to the antibinding regions as the separation between the two atoms is decreased.*

A comparison of the density diiference profiles for He$_2$ (Figure *[Math Processing Error]*) and H$_2$ (Fig. 6-12) provides a striking contrast of the difference between the charge redistributions which result in the formation of unstable and stable molecules.
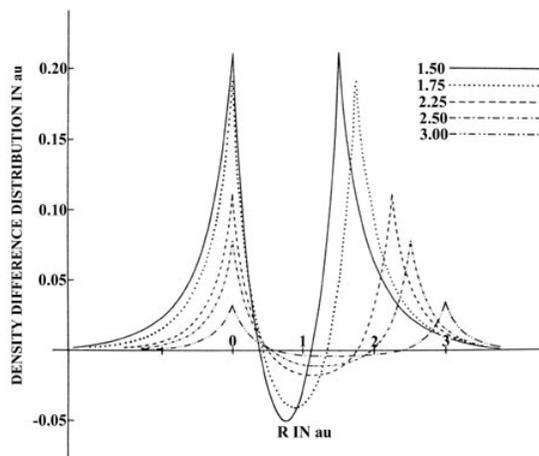


*Figure [Math Processing Error]: Profiles of the density difference maps along the internuclear axis for the approach of two He atoms. One nucleus is held stationary. This figure should be contrasted with Fig. 6-12, the corresponding one for H2.*

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The force on a helium nucleus in He$_2$ as a function of the internuclear separation is repulsive for the range of $R$ values indicated in Figure *[Math Processing Error]*.
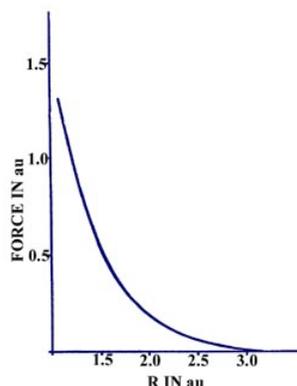


Figure *[Math Processing Error]*: Force an a *[Math Processing Error]* nucleus in *[Math Processing Error]* as a function of the internuclear separation. The general form of this curve is characturistic of an unstabe molecular species.

Unlike the force curve for H$_2$, there is no deep minimum in the curve which represents a range of \(R\) values for which the force is attractive. The force curve for *[Math Processing Error]* does cross the \(R\) axis at approximately 6 au (not indicated in Figure *[Math Processing Error]*) and becomes very slightly attractive for values of $R$ greater than this value. This weak attractive force has its origin in the long-range mutual polarization of the atomic density distributions which was discussed in detail for the approach of two hydrogen atoms. For large internuclear separations, where there is no significant overlap of the atomic orbitals and hence no need to invoke the Pauli exclusion principle, the atomic charge distributions of two approaching helium atoms are polarized in the same way as are the charge distributions for two approaching hydrogen atoms, and the force is attractive. At smaller internuclear separations, however, where the overlap of the orbitals is significant and the Pauli exclusion principle is operative, the direction of the charge transfer in He$_2$ is reversed and the force is rapidly transformed into one of repulsion. Were it not for the weak long-range attractive forces - the van der Waals forces - gaseous helium could not be condensed into a liquid or a solid phase. As it is, the force of attraction between two helium atoms is so weak that at a temperature of only 4.2°K they have sufficient kinetic energy to overcome the forces of attraction between them and escape into the gas phase.

> *The force of attraction between two helium atoms is so weak that at a temperature of only 4.2°K they have sufficient kinetic energy to overcome the forces of attraction between them.*

If it was not necessary to satisfy the demands of the Pauli principle, electron density would accumulate in the binding region of He$_2$, even for small values of $R$, as this region is of lower potential energy than is the antibinding region. However, when each electron detects another of like spin (when the orbitals overlap) they cannot concentrate their charge density in the region they have in common, the binding region. That it is indeed the Pauli principle which prevents the formation of He$_2$ is evident from the fact that He$_2^+$, which possesses one less electron, ***is stable***! When a helium atom approaches a helium ion, an orbital vacancy is present and the density from one pair of electrons (those with opposed spins) can be concentrated in the binding region.

All the rare gas atoms possess a closed shell structure and this accounts for their inertness in chemical reactions. No homonuclear diatomic molecules are found in this group of elements; all occur naturally in the atomic state. Compounds of Kr and Xe have been formed with fluorine, for the same reason that the formation of He$_2^+$ is possible. Fluorine has a very high electron affinity and a single vacancy in its outer quantum shell. Thus one of the electrons in the closed shell structure of Xe can be pulled into the orbital vacancy of the fluorine atom and density concentrated in the region between the nuclei.

Only an atom with a very high affinity for electrons will bond with a rare gas atom. The only species found with sufficient electron affinity to bind a helium atom (which holds its electrons the most tightly of all atoms) is a He$^+$ ion. If the helium atom has the highest ionization potential of all the elements, then the singly-charged He$^+$ ion must possess the highest electron affinity of all the neutral or singly-charged atoms.

## Second Row Elements

Let us now attempt to explain the variation in the valency exhibited by the elements in the second row of the periodic table. The

File failed to load: https://cdnjs.cloudflare.com/ajax/libs/mathjax/2.7.3/jax/output/HTML-CSS/jax.js ency of the hydrogen atom is unity as it possesses

one unpaired electron and one orbital vacancy. It can form one electron pair bond. Therefore, the valencies exhibited in the above hydrides must be 1, 2, 3, 4, 3, 2, 1, as this is the number of hydrogens bound in each case. (By the way, while the $BH_3$ molecule is predicted to be stable with respect to the separated boron and hydrogen atoms it cannot be isolated as such, but only in the form of its dimer $B_2H_6$).

We will consider HF first.

**Fluorine:** The electron configuration of F is $ls^2 2s^2 2p^5()$. Only one of the electrons in the $2p$ orbitals is unpaired. The $2p$ atomic orbital with the vacancy may overlap with the $1s$ atomic orbital of hydrogen, and if the spin of the electron on H is paired with the spin of the electron on F, all the requirements for the formation of a stable chemical bond will be met. The valency of F will be one as it possesses one unpaired electron and can form one electron pair bond.

**Oxygen:** The electronic configuration of oxygen is $ls^2 2s^2 2p^4()$. Oxygen has two unpaired electrons, both of which may pair up with an electron on a hydrogen atom. The valency of oxygen should be two as is observed. It is obvious that all the requirements for a chemical bond can be met for every unpaired electron present in the outer or "valency" shell of an atom. ***Thus valency may be defined as being equal to the number of unpaired electrons present in the atom.***

**Nitrogen:** The configuration of nitrogen is $ls^2 2s^2 2p^3()$, and its hydride should be $NH_3$ as is indeed the case.

**Carbon:** Since the most stable electron configuration of carbon is $1s^2 2s^2 2p^2()$ we predict its valency to be two. The molecule $CH_2$ (called methylene) is indeed known. However, $CH_2$ is very reactive and its products are not stable until four chemical bonds are formed to carbon as in the case of $CH_4$. Four, not two, is the common valency for carbon. How can our theory account for this fact? The energy of a $2p$ orbital is not much greater than that of a $2s$ orbital. Because of this, relatively little energy is required to promote an electron from the $2s$ orbital on carbon to the vacant $2p$ orbital:

$$C: ls^2 2s^2 2p^2() \text{®} C^* \ ls^2 2s^1()2p^3()$$

Carbon in the promoted state possesses four unpaired electrons and can now combine with four hydrogen atoms. Every bond to a hydrogen atom releases a large amount of energy. The energy required to unpair the $2s$ electrons and promote one of them to a $2p$ orbital is more than compensated for by the fact that ***two*** new C�H bonds are obtained.

**Boron:** Boron has the electronic configuration $ls^2 2s^2 2p^1()$. Its valency should be one and BH is known to exist. However, again through the mechanism of promotion, the valency of boron can be increased to three:

$$B^*: ls^2 2s^1()2p^2()$$
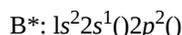
We might wonder why, with a $2p$ orbital still vacant, one of the $1s$ electrons is not promoted and thus give boron a valency of five. This does not happen because of the large difference in energy between the $1s$ and $2p$ orbitals as shown in the orbital energy level diagram (Fig. 5-3).

**Beryllium:** Beryllium has the configuration $ls^2 2s^2$ and should exhibit a valency of zero. The outer electron configuration of Be is similar to that of He, a closed shell of $s$ electrons. Indeed, the molecule $Be_2$ exists only as a weakly bound van der Waals molecule. However, Be differs from He in that there are vacant orbitals available in its ***valency*** shell. The observed valency of two in the molecule $BeH_2$ can be explained by a promotion to the configuration $ls^2 2s^1()2p^1()$.

**Lithium.** Lithium, with the configuration $ls^2 2s^1()$, should exhibit only a valency of one.

> *Thus valency may be defined as being equal to the number of unpaired electrons present in the atom.*

## Lewis Structures

The concept of an electron pair bond is not restricted to bonds with hydrogen. The only requirements are an unpaired electron on each atom (which is another way of saying there is an orbital vacancy on each atom) with their spins opposed. Thus two fluorine atoms may combine to form the fluorine molecule $F_2$ through the overlap of the singly-occupied $2p$ orbital on one atom with a similar orbital on the other. This will result in $F_2$ being described as F�F where the single line denotes that one pair of electrons forms the bond between the two atoms. Similarly, the three singly-occupied $2p$ orbitals on one nitrogen atom may overlap with those on another to form the $N_2$ molecule. Since three pairs of electrons are shared between the nuclei in this case, we represent the molecule by the symbol NºN. The electrons in the valence shell of an atom which are not involved in the formation of a chemical bond (as they are already paired in an orbital on the atom) may also be indicated and the resulting symbols are called ***Lewis***

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*structures*. Thus the three pairs of valency electrons on each F, ($2s^2 2p^4$), not involved in the bonding are often indicated by dots. For example,

| | | |
|---|---|---|
| H —— F̈: | :F̈ —— F̈: | Li —— F̈: |
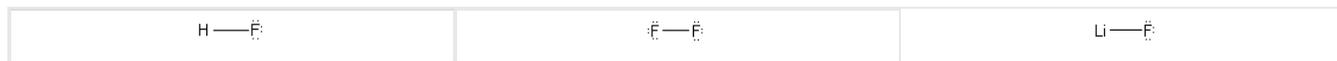
(Lithium has only one outer electron and it is shared in the bond.) In compounds with nitrogen we may indicate the 2*s* pair of electrons:

$$:NH_3 \quad \text{and} \quad :N\!\!\equiv\!\!N:$$
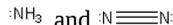
Recall that each line, since it denoted a bond in these diagrams, represents a pair of electrons shared between the two atoms joined by the line. If we add up the lines joined to each atom, multiply by two (to obtain the number of electrons) and add to this the number of dots which represents the remaining valence electrons, the number eight is obtained in many cases, particularly for the second-row elements (*n* = 2 valence orbitals). This so-called octet rule results from many elements having four outer orbitals ($nsnp_x np_y np_z$) which together may contain a total of eight electrons. Not all eight electrons belong to either atom in general as the electrons in a bond are shared (not necessarily equally as we shall see) between two atoms. Each bond contains two electrons with paired spins. Thus the orbital from one atom used to form the bond is, in a sense, filled as both spin possibilities are now accounted for.

The presence of an unshared pair of electrons in the valency shell of an atom can lead to the formation of another chemical bond. For example, the unshared pair of electrons in the 2*s* orbital on nitrogen in ammonia may attract and bind to the molecule another proton:

$$H_3N: + H^+ \circledR NH_4^+$$

A similar reaction occurs for the water molecule which possesses two unshared pairs of electrons:

$$H_2\ddot{O} + H^+ \circledR H_3O:^+$$
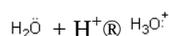
We must modify our previous rule regarding the requirements for the formation of an electron pair bond. Rather than both orbitals being half-filled, an orbital on one of the atoms may be filled if the orbital on the other atom is completely vacant. Molecules possessing an unshared pair of electrons, which may be used to bond another atom, are called **Lewis bases**. Only elements in groups V, VI and VII will exhibit this property. The elements in groups I to IV do not possess unshared pairs. Instead, the chemistry of the elements in groups II and III is largely characterized by the orbital vacancies which they possess in their valency shell.

The compound boron trifluoride represents the pairing of the three valence electrons of boron with the unpaired electrons on three F atoms. The boron is considered to be in the promoted configuration $ls^2 2s^1()2p^2()$ and $BF_3$ is represented as

$$\begin{array}{c} :\ddot{F}: \\ | \\ B \\ / \quad \backslash \\ :\ddot{F}: \quad :\ddot{F}: \end{array}$$
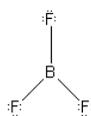
A 2*p* orbital on boron is vacant. It is not surprising to find that $BF_3$ may form another bond with a species which has an unshared pair of electrons, i.e., a Lewis base. For example,

*[Math Processing Error]*

Since $BF_3$ accepts the electron pair it is termed a **Lewis acid**. Further examples from Group 3 are

*[Math Processing Error]*

*[Math Processing Error]*

*[Math Processing Error]*

and from Group 2 (which have two orbital vacancies):

*[Math Processing Error]*

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# 6.5: Molecular Geometry

The theory of valency which we have been developing is known as *valence bond theory*. One further feature of this theory is that it may be used to predict (or in some cases, rationalize) the observed geometries of molecules By the geometry of a molecule we mean the relative arrangement of the nuclei in three-dimensional space. For example, assuming the two O-H bonds in the water molecule to be similar and hence of the same length, the angle formed by the two O-H bonds (the HOH angle could conceivably posess any angle from 180° to some relatively small value. All we demand of our simple theory is that it correctly predict whether the water molecule is linear (bond angle = 180°) or bent (bond angle less than 180°) Or as another example, it should predict whether the ammonia molecule is planar (a) or pyramidal (b).
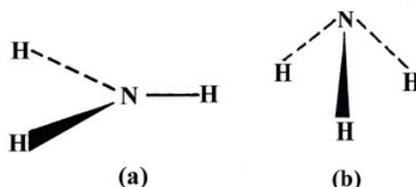
The observed geometry of a molecule is that which makes the energy of the system a minimum. Thus those geometries will be favoured which (i) concentrate the largest amount of charge density in the binding region and thus give the strongest individual bonds, and (ii) keep the nuclei as far apart as possible (consistent with (i)), and hence reduce the nuclear replusions. Consider again the two possibilities for the water molecule It is clear that the linear form (a) will have a smaller energy of nuclear repulsion from the hydrogens than will the bent form (b).

If the amount of electron density which could be concentrated in the regions between the nuclei in each *[Math Processing Error]* bond (i.e., the strength of each *[Math Processing Error]* bond) was independent of the bond angle, then clearly the linear form of the water molecule would be the most stable. This would be the situation if all the atomic orbitals which describe the motions of the electrons were rigidly spherical and centred on the nuclei. But this is not the case. As was stressed earlier in our discussion of atomic orbitals, the motion of electrons possessing angular momentum because they occupy orbitals with $l \, ^1 \, 0$ is concentrated along certain axes or planes in space. In particular the three $p$ orbitals are a maximum along the three perpendicular axes in space. The valence bond theory of the water molecule describes the two O-H bonds as resulting from the overlap of the H $1s$ orbitals with the two half-filled $2p$ orbitals of the oxygen atom. Since the two $2p$ orbitals are at right angles to one another, valence bond theory predicts a bent geometry for the water molecule with a bond angle of 90°.

The overlap of the orbitals is shown schematically in Fig. 6-16.
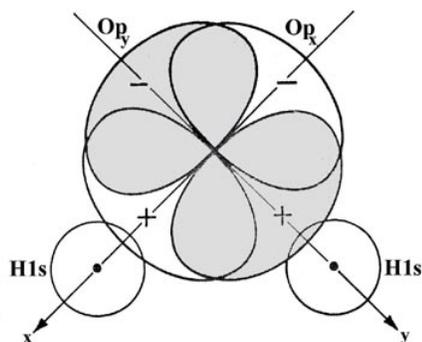
Fig. 6-16. A pictorial representation of the overlap of *[Math Processing Error]* and *[Math Processing Error]* orbitals on the oxygen with the 1s orbitals of two H atoms.

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The actual bond angle in the water molecule is 104.5°. The opening of the angle to a value greater than the predicted one of 90° can be accounted for in terms of a lessening of the repulsion between the hydrogen nuclei. The ***assumption*** we have made is that the maximum amount of electron density will be transferred to the binding region and hence yield the strongest possible bond when the hydrogen and oxygen nuclei lie on the axis which is defined by the direction of the $2p$ orbital. For a given internuclear separation, this will result in the maximum overlap of the orbitals. Because an orbital with $l$ $^1$ $0$ restricts the motion of the electron to certain preferred directions in space, bond angles and molecular geometry will be determined, ***to a first rough approximation***, by the inter-orbital angles.

In the valence bond description of ammonia, each N-H bond results from the overlap of an H $1s$ orbital with a $2p$ orbital on N. All three $2p$ orbitals on N have a vacancy and thus three bonds should be formed and each HNH angle should be 90°, i.e., ammonia should be a pyramidal and not a planar molecule. The $NH_3$ molecule is indeed pyramidal and the observed HNH angle is 107.3°. The actual bond angle is again larger than that predicted by the theory.

It might be argued that since the N atom possesses a half-filled $2p$ shell (its electronic configuration is $1s^2 2s^2 2p^3$), its density distribution is spherical and hence the N atom should not exhibit any directional preferences in its bonding. This argument is incorrect for the following reason. The density distribution is obtained by squaring the wave function. The wave function which properly describes the system must be obtained first, then squared to obtain the density. The wave function which describes the ammonia molecule consists of products of hydrogen $1s$ orbital functions with the nitrogen $2p$ orbital functions. (A product of orbitals is the mathematical statement of the phrase "overlap of orbitals" in valence bond theory.) The density distribution obtained by squaring the product of two orbitals is ***not*** the same as that obtained from the sum of the squares of the individual orbitals. Thus in the valence bond theory of molecular electronic structure the directional properties of the valence orbitals play an important role. By assuming that the most stable bond results when the two nuclei joined by the bond lie along the axis defined by the orbitals and considering the bonds to a first approximation to be independent of one another, we can predict the geometries of molecules.

## Hybridization

The $BeH_2$ molecule is linear and the two Be-H bonds are equivalent. The valence bond description of $BeH_2$ accounted for the two-fold valency of Be (which has the ground state configuration $1s^2 2s^2$) by assuming the bonding to occur with a promoted configuration of Be:

Be* $1s^2 2s()2p()$
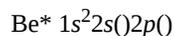
At first sight this suggests that the two Be-H bonds should be dissimilar and not necessarily 180° apart because one bond results from the overlap with a $2s$ orbital and the other with a $2p$ orbital on Be. We can, however, account for the equivalence of the two Be-H bonds and for the linearity of the molecule within the framework of the theory. There is no ***a priori*** reason for assuming that the one bond will result from the overlap with a $2s$ orbital and the other from the overlap with a $2p$ orbital. In the most general treatment of the problem, each bond to a hydrogen could involve both the $2s$ and the $2p$ orbitals. That is, we can "mix" or ***hybridize*** the valence orbitals on the Be atom. In fact, by taking each valence orbital on Be to be an equal part of $2s$ and $2p$, we can obtain two equivalent hybrid orbitals which are directed 180° apart. The two hybrid orbitals will form two equivalent bonds with the H $1s$ orbitals whose total bond strength will be larger than that obtained by forming one bond with a $2p$ and the other with a $2s$ orbital on Be.

The construction of the hybrid orbitals is accomplished by taking the sum and the difference of the $2s$ orbital and one of the $2p$ orbitals, say the $2p_x$ orbital, both orbitals being centred on the Be nucleus. This is illustrated in Fig. 6-17.

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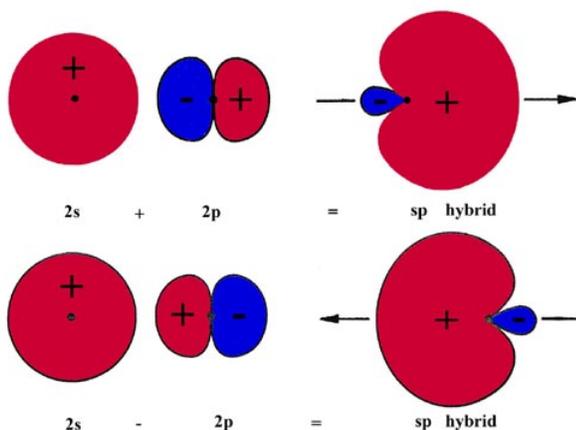
Fig. 6-17. The construction of sp hybrid orbitals from a 2s and 2p atomic orbital on Be.

Since the $2p$ orbital has a node at the nucleus the $2p$ orbital wave function has opposite signs on each side of the nodal plane indicated in the figure. Both orbitals are positive on one side and the orbital functions add at each point in space. On the other side of the nodal plane, the orbitals are of opposite sign and their sum yields the difference between the two functions at every point in space. The addition of a $2s$ and $2p_x$ orbital concentrates the wave function and hence the charge density on the positive side of the $x$-axis. Obviously the combination $(2s - 2p_x)$ will be similar in appearance but concentrated on the negative side of the $x$-axis. These combinations of the $2s$ and $2p$ orbitals yield **two** hybrid orbitals which are equivalent and oppositely directed. Since each of the hybrid orbitals is constructed from equal amounts of the $2s$ and $2p$ orbitals they are termed "$sp$ hybrid" orbitals.

The linear nature of $BeH_2$ can be explained if it is assumed (as is true) that the best overlap with both H $1s$ orbitals will result when the valence orbitals on the Be are $sp$ hybrids .
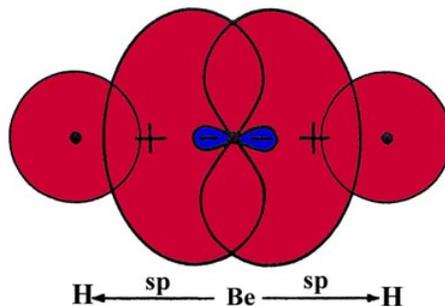


Fig 6-18. A pictorial representation of the overlap of two sp hybrid orbitals on Be with H 1s orbitals to form BeH2.

The three B-H bonds in $BH_3$ are equivalent and the molecule is planar and symmetrical:
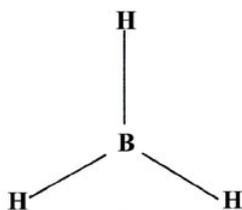


The promoted configuration of boron with three unpaired electrons is

B* $1s^2 2s()2p_x()2p_y()$
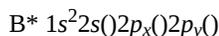
In this case we must construct three equivalent hybrid orbitals from the three atomic orbitals $2s$, $2p_x$, and $2p_y$, on boron. The $2p_x$ and $2p_y$ orbitals define a plane in space and the three hybrid orbitals constructed from them will be projected in this same plane. Since the hybrid orbitals are to be equivalent, each must contain one part $2s$ and two parts $2p$. They will be called "$sp^2$" hybrid

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orbitals. The three orbital combinations which have the above properties are indeed directed at 120° to one another. The planar, symmetrical geometry of $BH_3$ can be accounted for in terms of $sp^2$ hybridization of the orbitals on boron.

The four C-H bonds in $CH_4$ are equivalent and the molecule possesses a tetrahedral geometry:
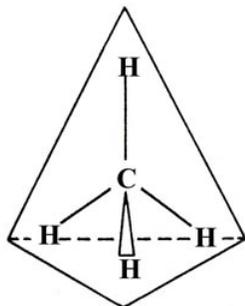


The promoted configuration of carbon with four unpaired spins is

$C^* \ 1s^2 2s()2p_x()2p_y()2p_z()$
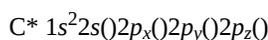
Four equivalent hybrid orbitals can be constructed from the $2s$ and the three $2p$ orbitals on carbon. Each orbital will contain one part $2s$ and three parts $2p$, and the hybrids are termed $sp^3$ hybrids. Only one such set of orbitals is possible and the angle between the orbitals is 109°28′, the tetrahedral angle. The tetrahedral geometry of $CH_4$ is described as resulting from the $sp^3$ hybridization of the valence orbitals on the carbon atom.

The three hybridization schemes which have been presented are sufficient to account for the geometries of all the compounds formed from elements of the first two rows of the periodic table (those with $n=1$ or $n = 2$ valence orbitals). Consider, for example, the unsaturated hydrocarbons. The ethylene molecule, $C_2H_4$, possesses the planar geometry indicated here,
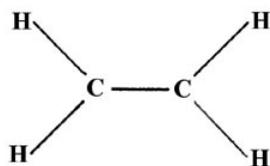


where the bond angles around each carbon nucleus are approximately 120°. Three bonds in a plane with 120° bond angles suggests $sp^2$ hybridization for the carbon atoms. Two of the $sp^2$ hybrids from each carbon may overlap with H $1s$ orbitals forming the four C-H bonds. The remaining $sp^2$ hybrids on each carbon may overlap with one another to form a bond between the carbons:
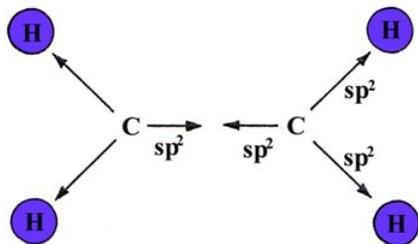


The $sp^2$ hybrids are denoted by arrows in the above diagram to indicate their directional dependence. If these bonds are formed in the $x$-$y$ plane, using the $2p_x$ and $2p_y$ orbitals of the carbon atoms, a singly-occupied $2p_z$ orbital will remain on each carbon. They will be directed in a plane perpendicular to the plane of the molecule:

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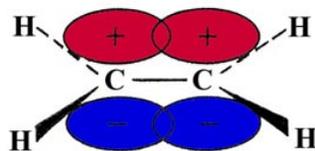
The overlap of the two $2p_z$ orbitals above and below the plane of the molecule will result in a second electron pair bond between the carbon atoms. The bonds formed in the plane of the molecule are called s (sigma) bonds, while those perpendicular to the plane are called p bonds. Since the overlap of the orbitals to form a p bond is not as great as the overlap obtained from s bonds (which are directed along the bond axis), p bonds in general are weaker than s bonds. A Lewis structure for the $C_2H_4$ molecule is expressed as
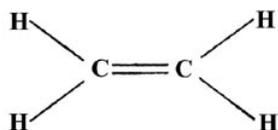


indicating that there is a double bond between the carbon atoms, i.e., the density from two pairs of electrons binds the carbon atoms.

The energy required to break the carbon-carbon double bond in ethylene is indeed greater than that required to break the carbon-carbon single bond in the ethane molecule, $H_3C-CH_3$. Furthermore, the chemical behaviour of ethylene is readily accounted for in terms of a model which places a large concentration of negative charge density in the region between the carbon atoms. The physical evidence thus verifies the valence bond description of the bonding between the carbons in ethylene.

Our final example concerns another important possible hybridization for the carbon atom. The acetylene molecule, $C_2H_2$, is a linear symmetric molecule: H-C-C-H. The linear structure suggests we try *sp* hybridization for each carbon, one hybrid overlapping with a hydrogen and the other with a similar hybrid from the second carbon atom. This will produce a linear s bond framework for the molecule:



The *sp* hybrids are denoted by arrows in the above diagram. If the *sp* hybrids are assumed to be directed along the *x*-axis, then the remaining singly-occupied $2p_y$ and $2p_z$ orbitals on each carbon may form p bonds. The $2p_y$ orbitals on each carbon may overlap to form a p bond whose density is concentrated in the *x-y* plane, with a node in the *x-z* plane. Similarly the $2p_z$ orbitals may form a second p bond concentrated in the *x-z* plane, with a node in the *x-y* plane. Acetylene will possess a triple bond, one involving three pairs of electrons, between the carbon atoms. The Lewis structure is drawn as



where it is understood that one of the C-C bonds is a s bond while the other two are of the p-type. The chemistry and properties of acetylene are consistent with a model which places a large amount of charge density in the region of the C-C bond.

Hybridization schemes involving *d* orbitals are also possible. They are important for elements in the third and succeeding rows of the periodic table. Although the elements of the third row do not possess occupied 3*d* orbitals in their ground electronic configurations, the 3*d* orbitals of phosphorus, sulphur and chlorine are low enough in energy that promoted configurations involving the 3*d* orbitals may be reasonably postulated to account for the binding in compounds of these elements. One consequence of the "availability" of the 3*d* orbitals is that there are many exceptions to the octet rule in compounds of the third row elements. For example, in $PCl_5$ there are ten valence electrons involved in the bonding of the five chlorines to the phosphorus. A hybridization scheme based on the promotion of one 3*s* electron of phosphorus to a 3*d* orbital to yield five "$dsp^3$" hybrid orbitals correctly predicts the trigonal bypyramidal structure of $PCl_5$:

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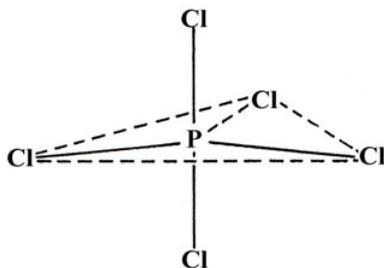
As a final example consider the molecule $SF_6$ in which all six S-F bonds are equivalent and the geometry is that of a regular octahedron (one F atom centred in each face of a regular cube):
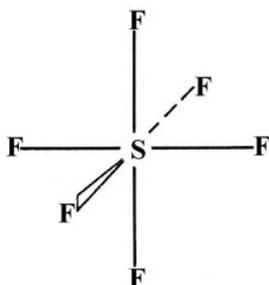


This geometry and number of bonds can be accounted for by assuming the promotion of one $3s$ and one $3p$ electron to two of the $3d$ orbitals on the sulphur atom. This hybridization yields six equivalent "$d^2sp^3$" hybrid bonds which are indeed directed as indicated in the structure for $SF_6$.

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# 6.6: Literature References

## Literature references

| | |
|---|---|
| 1. | The electrostatic method used in this book for the interpretation of chemical binding is based on the Hellmann-Feynman theorem. The theorem was proposed independently by both H. Hellmann and R. P. Feynman. Feynman's account of the theorem anticipates many of the applications to chemistry including the electrostatic interpretation of van der Waals forces. R. P. Feynman, Phys. Rev. *56*, 340 (1939). |
| 2. | The wave functions used in the calculation of the density distributions for $H_2$ were determined by G. Das and A. C. Wahl, J. Chem. Phys. *44*, 87 (1966). These wave functions include configuration interaction and hence provide suitable descriptions for the $H_2$ systems for large values of the internuclear separation. The wave functions for $He_2$ are from N. R. Kestner, J. Chem. Phys. *48*, 252 (1968). |

# 6.E: Exercises

## Q6.1

The element beryllium has an atomic number of four. Rationalize the following observations in terms of the valence bond theory of molecular structure.

 a. *[Math Processing Error]* does not exist except as a weakly bound van der Waals molecule.
 b. *[Math Processing Error]* can exhibit a valency of two in combination with a halogen, for example, $BeF_2$.
 c. *[Math Processing Error]* can undergo a further reaction with an excess of F$^-$ ions to give *[Math Processing Error]* In addition to explaining why this reaction occurs, predict the geometrical shape of the *[Math Processing Error]* ion.

## Q6.2

 a. Use valence bond theory to predict the molecular formula and geometrical structure of the most stable electrically neutral hydride of phosphorus.
 b. The hydride of phosphorus can react with HI to form an ionic crystal which contains the I$^-$ ion. Explain why this reaction can occur and give the formula and geometrical structure of the positive ion which contains phosphorus and hydrogen.

## Q6.3

The atomic number of silicon is fourteen. What is the electronic structure of Si in its ground state? Predict the molecular formula and geometrical shape of the most stable silicon-hydrogen compound using valence bond theory.

## Q6.4

The element vanadium (Z = 23) forms the compound $VCl_4$. Would a beam of $VCl_4$ molecules be deflected in an inhomogeneous magnetic field? Explain the reasoning behind your answer. 5. The $CH_2$ molecule may exist in two distinct forms. In the one case all the electrons are paired and the molecule does not possess a magnetic moment. In the second form the molecule exhibits a magnetism which can be shown to arise from the presence of two unpaired electrons. One of the forms of $CH_2$ is linear. Use valence bond theory to describe the electronic structures and geometries of both forms of $CH_2$. Which of the two will possess the lower electronic energy?

## Q6.6

 a. Write Lewis structures (structures in which each electron pair bond is designated by a line joining the nuclei and dots are used to designate unshared electrons in the valency shell) for $H_2O$, $CH_4$, $CO_2$, HF, $NH_4^+$, $H_2O_2$.
 b. Give a discussion of the bonding of the molecules listed in part (a) in terms of valence bond theory. Denote the use of hybrid orbitals by arrows and a label as to whether they are *sp*, *sp*$^2$, or *sp*$^3$ hybrids. You should predict that $H_2O$ and $H_2O_2$ are bent molecules, that $CH_4$ and $NH_4^+$ are tetrahedral and that $CO_2$ is linear.

## Q6.7

Sometimes it is possible to write a number of equivalent Lewis structures for a single species. For example, the bonding in the $NO_3^-$ ion can be described by:
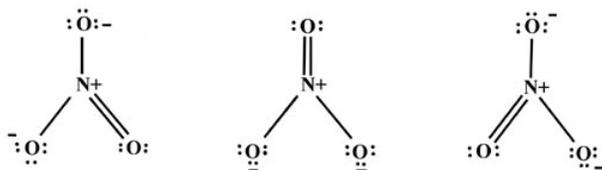


Each atom in these structures is surrounded by four pairs of electrons, the first cardinal rule in writing a Lewis structure. On the average, one electron of the pair in each bond belongs to one atom. Since there are only four bonds to N and no unshared valence pairs, N on the average has but four valence electrons in these three structures. The N atom initially possessed five electrons, and a plus sign is placed at N to denote that it has, on the average, one less electron in the $NO_3^-$ion. The two singly-bonded oxygens have on the average seven electrons in each structure, one more than a neutral oxygen atom. This is denoted by a minus sign. The

doubly-bonded O has on the average six electrons. Notice that the sum of these formal charges is minus one, the correct charge for the $NO_3^-$ ion.

The structure of the $NO_3^-$ ion is in reality planar and symmetrical, all of the NO bonds being of equal length. This could be indicated in a single Lewis structure by indicating that the final pair of electrons in the p bond between N and one O is actually spread over all three NO bonds simultaneously:
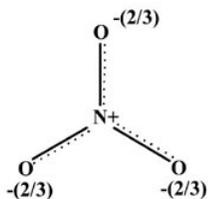


When one or more pairs of electrons are delocalized over more than two atoms, the Lewis method or the valence bond method of writing valence structures with bonds between pairs of atoms runs into difficulties. The compromise structure above correctly indicates that each NO bond in $NO_3^-$ is stronger and shorter than a N�O single bond, but not as strong as an N=O double bond.

a. Use the valence bond theory to account for the bonding and planar structure of the $NO_3^-$ ion.
b. Write Lewis structures and the corresponding valence bond structures for the $CO_3^{-2}$ ion and $SO_2$. Are there full S=O or C=O double bonds in either of these molecules?

## Q6.8

Draw valence bond structures for benzene, $C_6H_6$. This molecule has a planar hexagonal geometry:
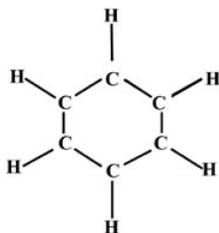


Are there any delocalized electron pairs in the benzene molecule?

## Q6.9

The carbon monoxide molecule forms stable complexes with many transition metal elements. Examples are (from the first transition metal series)

$Cr(CO)_6$, $(CO)_5Mn�Mn(CO)_5$, $Fe(CO)_5$, $Ni(CO)_4$
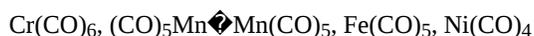
In each case the bond is formed between the metal and the unshared pair of electrons on the carbon end of carbon monoxide. The metal atom in these complexes obviously violates the octet rule, but can the electronic structures for the carbon monoxide complexes be rationalized on the basis of an expanded valency shell for the metal?

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# CHAPTER OVERVIEW

## 7: Ionic and Covalent Bonding

# 7.1: Introduction

## Ionic and Covalent Binding

The distribution of negative charge in a molecule will exhibit varying degrees of asymmetry depending on the relative abilities of the nuclei in the molecule to attract and bind the electronic charge density. The symmetry or asymmetry of the charge distribution plays a fundamental role in determining the chemical properties of the molecule and consequently this property of the charge distribution is used as a basis for the classification of chemical bonds.

We can envisage two extremes for the distribution of the valence charge density. An example of one of the extremes is obtained when a bond is formed between two identical atoms. The charge density of the valence electrons will in this case necessarily be delocalized equally over corresponding regions of each nucleus since both nuclei will attract the electron density with equal force. Such an equal *sharing of the charge* density is an example of *covalent binding* and is exemplified by the molecular charge distribution of $N_2$ (Fig. 7-1).
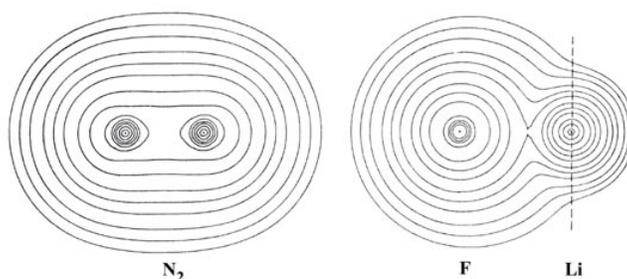


*Fig. 7-1. Contour maps of the molecular charge distributions of N2 and LiF at their equilibrium internuclear separations. The space to the right of the dashed line through the Li nucleus denotes the region of nonbonded charge density. The values of the contours increase from the outermost one to the innermost one. The specific values of the contours appearing in this and the following contour maps can be obtained by referring to the Table of Contour Values.*

The charge distribution of LiF (Fig. 7-1) provides an example of the other extreme, termed *ionic binding*, obtained when a bond is formed between two atoms with very different affinities for the electronic charge density. The very unsymmetrical distribution of charge in LiF is not simply a reflection of the fluorine atom possessing seven valence electrons to lithium's one. Instead the formation of the bond in LiF corresponds to the nearly complete transfer of the valence charge density of lithium to fluorine resulting in a molecule best described as $Li^+F^-$. We need only recall that initially a lithium atom is considerably larger than a fluorine atom to realize that a considerable transfer of charge has occurred in the formation of the LiF molecule.

In $N_2$ the valence charge density is delocalized over the whole molecule. The electronic charge is heavily concentrated in the internuclear region where it forms a bridge of high density between the two nuclei. Only the density of the $1s$ inner shell or "core" orbitals is strongly localized in the regions of the nuclei. In contrast to this, practically all of the charge density in the lithium fluoride molecule is localized in nearly spherical contours on the two nuclei in the manner characteristic of two separate closed-shell distributions. Only contours of very small value encompass both nuclei and the bridge of charge density joining the two spherical distributions is very low in value, being approximately one tenth of the value observed for $N_2$.

We may determine the total amount of electronic charge in an arbitrary region of space by summing the density in each small volume element within the region of interest (i.e., integrating the charge distribution over some particular volume of space):

$$\text{charge density } \times \text{ volume} = \left( e^- / a_o^3 \right) \times a_o^3 = e^-$$

A useful measure of the extent of charge transfer occurring on bond formation is obtained by determining the nonbonded charge on each nucleus. The nonbonded charge for a nucleus in a molecule is defined as occupying the volume of space on the nonbonded side of a plane perpendicular to the bond axis and through the nucleus in question. This is indicated by a dashed line for the Li nucleus in LiF (Fig. 7-1).

The nonbonded charge density of the lithium nucleus in LiF is 1.07 $e^-$ compared to 1.5 $e^-$ in the Li atom (i.e., one half of the total number of electronic charges in a Li atom). The nonbonded charge density of the F nucleus, on the other hand, is increased above its atomic value, being 5.0 $e^-$ as compared to 4.5 $e^-$ in the fluorine atom. Since the distributions centred on the nuclei in LiF are

nearly spherical, the total charge contained in each distribution will be approximately twice the value of the corresponding nonbonded charge. The total distribution of charge in LiF is, therefore, consistent with the ionic model $Li^+F^-$ corresponding to the transfer of the single 2$s$ valence electron of lithium to the fluorine. The radii of the nonbonded charge distributions (the distance measured along the bond axis from a nucleus to the outermost contour of its nonbonded density) are also consistent with the ionic model. The radius of the nonbonded charge density on lithium is 1.7 $a_o$, a value almost identical to the radius of a $Li^+$ ion (1.8 $a_o$) but much less than the radius of a Li atom (3.3 $a_o$). The value of 3.0 $a_o$ for the radius of the nonbonded charge density on fluorine is consistent with that of a fluoride ion distribution as it represents a slight increase over the atomic value for fluorine of 2.8 $a_o$.

By way of comparison, the nonbonded charge on the nitrogen nuclei in $N_2$ is increased above the atomic value of 3.5 $e^-$ to 3.68 $e^-$. This transfer of charge density to the nonbonded regions on bond formation is somewhat surprising when it is recalled that charge density must be accumulated in the binding region, the region between the nuclei, to achieve a chemical bond. We require a more detailed picture of the charge reorganization accompanying the formation of a bond to understand fully the distribution of the charge density in a molecule. In addition, many chemical bonds possess charge distributions which lie between the extreme of the perfect sharing of the valence charge density found in $N_2$ and its complete localization on one nucleus in LiF.

We consider next a method of classification of bonding in molecules, a classification which provides at the same time an understanding of the mechanism of the two binding situations in terms of the forces exerted on the nuclei.

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# 7.2: Classification of Chemical Bonds

To make a quantitative assessment of the type of binding present in a particular molecule it is necessary to have a measue of the extent of charge transfer present in the molecule relative to the charge distributions of the separated atoms. This information is contained in the density difference or bond density distribution, the distribution obtained by subtracting the atomic densities from the molecular charge distribution. Such a distribution provides a detailed measure of the net reorganization of the charge densities of the separated atoms accompanying the formation of the molecule.

The density distribution resulting from the overlap of the undistorted atomic densities (the distribution which is subtracted from the molecular distribution) does not place sufficient charge density in the binding region to balance the nuclear forces of repulsion. The regions of charge increase in a bond density map are, therefore, the regions to which charge is transferred relative to the separated atoms to obtain a state of electrostatic equilibrium and hence a chemical bond. Thus we may use the location of this charge increase relative to the positions of the nuclei to characterize the bond and to obtain an explanation for its electrostatic stability.

In covalent binding we shall find that the forces binding the nuclei are exerted by an increase in the charge density which is shared mutually between them. In ionic binding both nuclei are bound by a charge increase which is localized in the region of a single nucleus.

## Covalent Binding

The bond density map of the nitrogen molecule (Fig. 7-2) is illustrative of the characteristics of covalent binding.
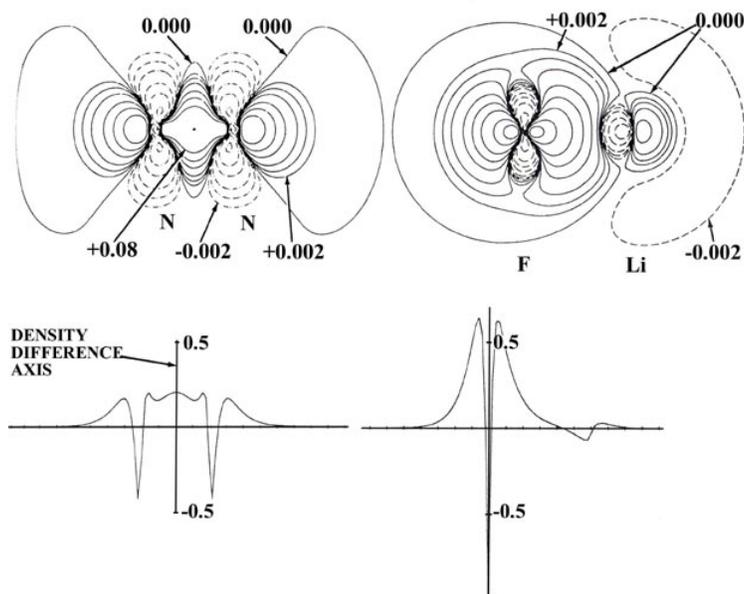


*Fig. 7-2. Bond density (or density difference) maps and their profiles along the internuclear axis for N2 and LiF. The solid and dashed lines represent an increase and a decrease respectively in the molecular charge density relative to the overlapped atomic distributions. These maps contrast the two possible extremes of the manner in which the original atomic charge densities may be redistributed to obtain a chemical bond. Click here for contour values.*

The principal feature of this map is a large accumulation of charge density in the binding region, corresponding in this case to a total increase of one quarter of an electronic charge. As noted in the study of the total charge distribution, charge density is also transferred to the antibinding regions of the nuclei but the amount transferred to either region, $0.13\ e^-$, is less than is accumulated in the binding region. The charge density of the original atoms is decreased in regions perpendicular to the bond at the positions of the nuclei. In three dimensions, the regions of charge deficit correspond to two continuous rings or roughly doughnut-shaped regions encircling the bond axis.

The increase in charge density in the antibinding regions and the removal of charge density from the immediate regions of the nuclei result in an increase in the forces of repulsion exerted on the nuclei, forces resulting from the close approach of the two atoms and from the partial overlap of their density distributions. The repulsive forces are obviously balanced by the forces exerted on the nuclei by the ***shared*** increase in charge density located in the binding region.

A bond is classified as covalent when the bond density distribution indicates that the charge increase responsible for the binding of the nuclei is shared by both nuclei. It is not necessary for covalent binding that the density increase in the binding region be shared equally as in the completely symmetrical case of $N_2$. We shall encounter heteronuclear molecules (molecules with different nuclei) in which the net force binding the nuclei is exerted by a density increase which, while shared, is not shared equally between the two nuclei.

The pattern of charge rearrangement in the bond density map for $N_2$ is, aside from the accumulation of charge density in the binding region, quite distinct from that found for $H_2$ (Fig. 6-10), another but simpler example of covalent binding. The pattern observed for nitrogen, a charge increase concentrated along the bond axis in both the binding and antibinding regions and a removal of charge density from a region perpendicular to the axis, is characteristic of atoms which in the orbital model of bonding employ $p$ atomic orbitals in forming the bond. Since a $p$ orbital concentrates charge density on opposite sides of a nucleus, the large buildup of charge density in the antibinding regions is to be expected.

In the orbital theory of the hydrogen molecule, the bond is the result of the overlap of $s$ orbitals. The bond density map in this case is characterized by a simple transfer of charge from the antibinding to the binding region since $s$ orbitals do not possess the strong directional or nodal properties of $p$ orbitals. Further examples of both types of charge rearrangements or polarizations will be illustrated below.

## Ionic Binding

We shall preface our discussion of the bond density map for ionic binding with a calculation of the change in energy associated with the formation of the bond in LiF. While the calculation will be relatively crude and based on a very simple model, it will illustrate that the complete transfer of valence charge density from one atom to another in forming a molecule is in certain cases energetically possible.

Lithium possesses the electronic configuration $1s^2 2s^1$ and is from group IA of the periodic table. It possesses a very low ionization potential and an electron affinity which is zero for all practical purposes. Fluorine is from group VIIA and has a configuration $1s^2 2s^2 2p^5$. It possesses a high ionization potential and a high electron affinity. The following calculation will illustrate that the $2s$ electron of Li could conceivably be transferred completely to the $2p$ shell of orbitals on F in which there is a single vacancy. This would result in the formation of a molecule best described as $Li^+F^-$, and in the electron configurations $1s^2$ for $Li^+$ and $1s^2 2s^2 2p^6$ for $F^-$.

We can calculate the energy change for the reaction

$$Li + F \rightarrow Li^+ R^-$$
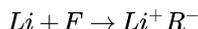
in stages. The energy which must be supplied to ionize the $1s$ electron on the Li atom is:

$$Li \rightarrow Li^+ e^- \tag{7.2.1}$$

with $E_1 = I_1 = 5.4 \, eV$.

The energy released when an electron combines with an F atom is given by the electron affinity of F:

$$F + e^- \rightarrow F- \tag{7.2.2}$$

with $E_2 = -3.7 \, eV$.

The two ions are oppositely charged and will attract one another. The energy released when the two ions approach one another from infinity to form the LiF molecule is easily estimated. To a first approximation it is simply $-e^2/R$ where $R$ is the final equilibrium distance between the two ions in the molecule:

$$\underbrace{Li^+ + F^-}_{\text{large distance apart}} \rightarrow \underbrace{Li^+ F^-}_{\text{at R}}$$

with $E_3 \approx -4 \, eV$.

The sum of these three reactions gives

$$Li + F \rightarrow Li^+ F^-$$
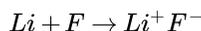
and the overall change in energy is the sum of the three energy changes, or approximately -2 ev. The species $Li^+F^-$ possesses a lower energy than the separated Li and F atoms and should therefore be a stable molecule.

The transfer of charge density from lithium to fluorine is very evident in the bond density map for LiF (Fig. 7-2). The charge density of the 2*s* electron on the lithium atom is a very diffuse distribution and consequently the negative contours in the bond density map denoting its removal are of large spatial extent but small in magnitude. The principal charge increase is nearly symmetrically arranged about the fluorine nucleus and is completely encompassed by a single nodal surface. The total charge increase on fluorine amounts to approximately one electronic charge. The charge increase in the antibinding region of the lithium nucleus corresponds to only 0.01 electronic charges. (The great disparity in the magnitudes of the charge increases on lithium and fluorine are most strikingly portrayed in the profile of the bond density map, also shown in Fig. 7-2) It is equally important to realize that the charge increase on lithium occurs within the region of the 1*s* inner shell or core density and not in the region of the valence density. Thus the slight charge increase on lithium is primarily a result of a polarization of its core density and not of an accumulation of valence density.

The pattern of charge increase and charge removal in the region of the fluorine, while similar to that for a nitrogen nucleus in $N_2$, is much more symmetrical, and the charge density corresponds very closely to the distribution obtained from a single 2*p*selectron. Thus the simple orbital model of the bond in LiF which describes the bond as a transfer of the 2*s* electron on lithium to the single 2*p*s vacancy on fluorine is a remarkably good one.

While the bond density map for LiF substantiates the concept of charge transfer and the formation of $Li^+$ and $F^-$ ions it also indicates that the charge distributions of both ions are polarized. The charge increase in the binding region of fluorine exceeds slightly that in its antibinding region (the $F^-$ ion is polarized towards the $Li^+$ ion) and the charge distribution of the $Li^+$ ion is polarized away from the fluorine. A consideration of the forces exerted on the nuclei in this case will demonstrate that these polarizations are a necessary requirement for the attainment of electrostatic equilibrium in the face of a complete charge transfer from lithium to fluorine.

Consider first the forces acting on the nuclei in the simple model of the ionic bond, the model which ignores the polarizations of the ions and pictures the molecule as two closed-shell spherical ions in mutual contact. If the charge density of the $Li^+$ ion is spherical it will exert no net force on the lithium nucleus. The $F^-$ ion possesses ten electrons and, since the charge density on the $F^-$ ion is also considered to be spherical, the attractive force this density exerts on the Li nucleus is the same as that obtained for all ten electrons concentrated at the fluorine nucleus. Nine of these electrons will screen the nine positive nuclear charges on fluorine from the lithium nucleus. The net force on the lithium nucleus is, therefore, one of attraction because of the one excess negative charge on F.

For the molecule to be stable, the final force on the lithium nucleus must be zero. This can be achieved by a distortion of the spherical charge distribution of the $Li^+$ ion. If a small amount of the 1*s* charge density on lithium is removed from the region adjacent to fluorine and placed on the side of the lithium nucleus away from the fluorine, i.e., the charge distribution is polarized away from the fluorine, it will exert a force on the lithium nucleus in a direction away from the fluorine. Thus the force on the lithium nucleus in an ionic bond can be zero only if the charge density of the $Li^+$ ion is polarized away from the negative end of the molecule.

A similar consideration of the forces exerted on the fluorine nucleus demonstrates that the $F^-$ ion density must also be polarized. The fluorine nucleus experiences a net force of repulsion because of the presence of the lithium ion. The two negative charges centred on lithium screen only two of its three nuclear charges. Therefore, the charge density of the $F^-$ ion must be polarized **towards** the lithium in order to exert an attractive force on the fluorine nucleus which will balance the repulsive force arising from the presence of the $Li^+$ ion. Thus both nuclei in the LiF molecule are bound by the increase in charge density localized in the region of the fluorine.

The charge distribution of a molecule with an ionic bond will necessarily be characterized not only by the transfer of electronic charge from one atom to another, but also by a polarization of each of the resulting ions in a direction counter to the transfer of charge, as indicated in the bond density map for LiF.

> *In a covalent bond the increase in charge density which binds both nuclei is shared between them. In an ionic bond both nuclei are bound by the forces exerted by the charge density localized on a single nucleus.*

The bond density maps for $N_2$ and LiF are shown side by side to provide a contrast of the changes in the atomic charge densities responsible for the two extremes of chemical binding. ***In a covalent bond the increase in charge density which binds both nuclei***

*is shared between them. In an ionic bond both nuclei are bound by the forces exerted by the charge density localized on a single nucleus.* It must be stressed that there is no fundamental difference between the forces responsible for a covalent or an ionic bond. They are electrostatic in each case.

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## 7.3: Molecular Charge Distribution of Homonuclear Diatomic Molecules

Contour maps of the charge distributions for the stable homonuclear diatomic molecules formed from the second-row atoms (Figure 7.3.1) provide further examples of covalent binding. The maps illustrate the relative tightness of binding of the density distributions, the density in $Li_2$ for example being much more diffuse than that in $N_2$. Two important physical dimensions for a molecule are the bond length and the molecular size. The bond length of a molecule may be directly determined (by X-ray diffraction techniques or by spectroscopic methods) but the size of a molecule cannot be as precisely defined or measured. However, molecular diameters may be inferred from measurements of the viscosity of gas phase molecules and from X-ray crystallographic studies on the structures of molecular crystals such as solid $N_2$ and $O_2$.
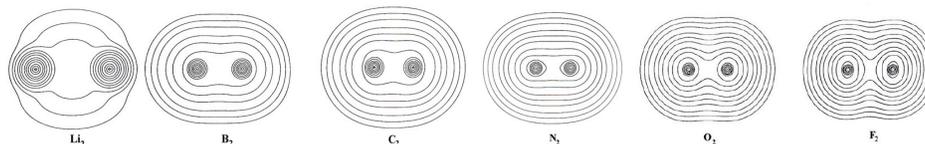


*Figure* 7.3.1: *Contour maps of the molecular charge distribution for the stable homonuclear diatomic molecules $Li_2$ to $F_2$. Click here for contour values.*

In general over 95% of the molecular charge lies within the 0.002 contour (the outermost contour illustrated in the density maps) and it has been found that the dimensions of this contour agree well with the experimental estimates of molecular sizes. The length and width of each molecule, defined respectively as the distance between the intercepts of the 0.002 contour on the molecular axis and on a line perpendicular to the axis and passing through its mid-point, are given in Table 7.3.1 along with the experimental bond lengths $R_e$

Table 7.3.1: Properties of the Total Charge Distributions*

| $A_2$ | $R_e$ | Length | Width | Nonbonded Ra |
|---|---|---|---|---|
| | | | | Molecule |
| $Li_2$ | 5.051 | 8.7 | 7.8 | 1.8 |
| $B_2$ | 3.005 | 9.8 | 7.2 | 3.4 |
| $C_2$ | 2.3481 | 8.5 | 7.0 | 3.1 |
| $N_2$ | 2.068 | 8.2 | 6.4 | 3.1 |
| $O_2$ | 2.282 | 7.9 | 6.0 | 2.8 |
| $F_2$ | 2.68 | 7.9 | 5.4 | 2.6 |

*All distances are given in units of $a_o = 0.52917$ Å.

There is only a rough correlation between the bond length and the overall length of the molecule. Thus the lengths of $N_2$ and $O_2$ are in the reverse order of their bond lengths, as is also roughly true experimentally. The lithium molecule has the largest bond length but a molecular length only slightly larger than that of $C_2$. There are two factors which must be considered in understanding the length of a molecule, the bond length and the rate at which the density falls off from the nucleus on the side away from the bond. Table 7.3.1 lists the distance from the nucleus to the 0.002 contour in the molecule, i.e., the radius of the nonbonded charge density, and the radius of the same contour in the isolated atom. With the exception of $Li_2$, this distance in the molecule is almost identical to the value in the isolated atom. Thus the contribution of the two end lengths, beyond the nuclear separation, to the overall length of a molecule is largely determined by how tightly the density is bound in the unperturbed atom.

The binding of the atomic densities increases from Li across to F, so that Li and Be are large and diffuse and N, 0, and F progressively tighter and more compact. Therefore $F_2$ is smaller in size than $N_2$ or $C_2$ even though it possesses a greater bond length because the density in the F atom is more tightly bound than that in the C or N atoms. The Li molecule differs from the others in that its length is considerably less than expected considering the diffuse nature of its atomic density. In this case the molecular length is not approximately equal to the sum of $R_e$ and twice the "atomic" radius. This is, however, easily understood since in the Li atom only one valence-shell electron is present and in the molecule the charge density of this electron is concentrated almost exclusively in the binding region. This is further illustrated by using instead of the 0.002 contour of Li the 0.002 contour of the $1s^2$ shell of $Li^+$, which is in fact equal to the value listed in Table 7.3.1 for the $Li_2$ molecule.

An estimate of the size of a peripheral atom in a molecule can thus be obtained by taking the sum of $\frac{1}{2}R_e$ from a suitable source and the atomic radius as defined by the 0.002 contour of the atom (except for Li, Na, etc., where the core radius should be used). The bond density maps for the second-row homonuclear diatomic molecules (Figure 7.3.2) indicate that the original atomic densities are distorted so as to place charge in the antibinding as well as in the binding regions.
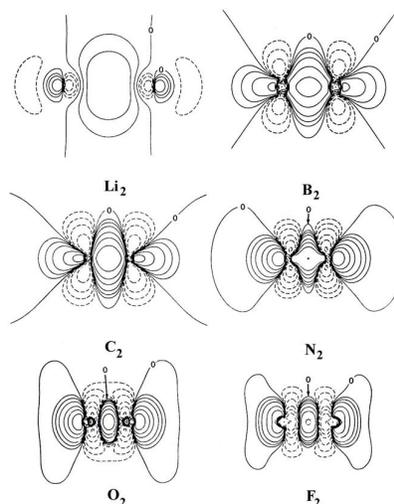


***Figure* 7.3.2**: *Bond density maps for the homonuclear diatomic molecules. Click here for contour values*

Apart from $Li_2$ the pattern of charge increase and charge removal in these molecules is similar to that discussed previously for $N_2$, a pattern ascribed to the participation of $2ps$ orbitals in the formation of the bond. Only $Li_2$ approximates the simple picture found for $H_2$ of removal of charge from the antibinding region and a buildup in the binding region. For the remaining molecules charge density is increasingly accumulated along the bond axis in both the binding and antibinding regions.

The total accumulation of electronic charge represented by the regions of positive contours in the binding and antibinding regions of the bond density maps are listed in Table 7.3.1.

Table 7.3.2: Charge Contained in the Regions of Increase in Bond Density Maps

| A$_2$ | Binding Region | Antibinding Region |
|---|---|---|
| Li$_2$ | 0.41 | 0.01 |
| B$_2$ | 0.30 | 0.05 |
| C$_2$ | 0.50 | 0.06 |
| N$_2$ | 0.25 | 0.13 |
| O$_2$ | 0.10 | 0.14 |
| F$_2$ | 0.08 | 0.10 |

These figures show that in O$_2$ and F$_2$ a greater amount of charge is transferred to the antibinding region of a single nucleus than to the binding region. It is evident, however, from the shapes of the contours that the charge increase in the binding region is concentrated along the bond axis where it exerts a maximum force of attraction on the nuclei while the buildup in the antibinding region is more diffuse.

The net forces on the nuclei are zero for each molecule. Therefore, the force exerted by the charge density in the binding region balances not only the force of nuclear repulsion but the force exerted by the charge buildup in the antibinding region as well. The nuclei are in each case bound by the charge increase which is shared equally by both nuclei.

An important physical property of a molecule is its bond energy, the amount of energy required to break the bond or bonds in a molecule and change it back into its constituent atoms. The bond energies of the second-row homonuclear diatomic molecules increase from either Li$_2$ or F$_2$ to a maximum value for the central member of the series, N$_2$ (Table 7.3.3).

Table 7.3.3: *Bond Energies for Homonuclear Diatomic Molecules*

| Molecule | Bond Energy (ev) | Number of electron pair bonds |
|---|---|---|
| Li$_2$ | 1.12 | 1 |
| B$_2$ | 3.0 | 1 |
| C$_2$ | 6.36 | 2 |
| N$_2$ | 9.90 | 3 |
| O$_2$ | 5.21 | 2 |
| F$_2$ | 1.65 | 1 |

We may rationalize the variation in the bond energies and the differences in the bond density maps in terms of the orbital theory of bonding. The simple bonding theory proposed in the preceding chapter equated the valency of an atom to its number of unpaired electrons. Thus the number of electron pair bonds formed between atoms in this series of molecules is predicted to be one for Li$_2$, B$_2$ and F$_2$, two for C$_2$ and O$_2$, and three for N$_2$. Reference to Table 7.3.3 reveals a parallelism between the bond energy and the number of electron pair bonds present in each molecule.

The detailed variation in bond energy through the series can be accounted for in terms of the type of bond (whether it is formed for *s* or *p* orbitals) present in each molecule, a feature which is clearly reflected in the bond density maps, and even more strikingly portrayed in their profiles (Figure 7.3.4).
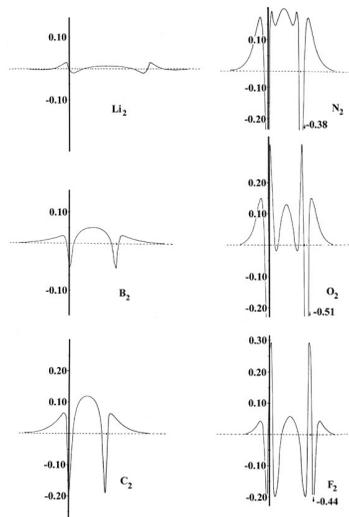


*Figure 7.3.4: Profiles of the bond density maps for the homonuclear diatomic molecules.*

The bond in Li$_2$ is formed primarily from the overlap of 2$s$ atomic orbitals on each lithium atom. The 2$s$ atomic density of lithium is a diffuse spherical distribution. These same characteristics are evident in the total charge distribution for Li$_2$ and particularly in its bond density map. The charge increase in the binding region, while large in amount (Table 7.3.2), is very diffuse and the bond density profile shows that relative to the other molecules, the charge increase is not concentrated along the bond axis. These are the very features expected for a bond resulting from the overlap of distorted, **nondirectional** *s* orbitals.

B$_2$ and F$_2$ also have but a single pair bond. However, the bonds in these two molecules are formed primarily from the overlap of 2$p$s orbitals. Since a $p$s orbital is directed along the bond axis, it is more effective than an *s* orbital at concentrating charge density along this same axis. This is particularly evident when we compare the profiles of the bond densities for F$_2$ and B$_2$ with the profile for Li$_2$. Similarly, the presence of two electron pair bonds and the still larger bond energies found for C$_2$ and O$_2$ are reflected in the larger increases in the charge densities along the internuclear axis in the binding region. Notice that while B$_2$ concentrates three times as much charge as O$_2$ in the binding region, it is not concentrated along the bond axis to as great an extent as in O$_2$, and consequently its bond energy is the smaller of the two.

The nitrogen molecule possesses three electron pair bonds and the largest bond energy of the molecules in this series. The charge increase in the binding region is concentrated along the bond axis to a far greater extent in this molecule than in any of the other molecules in the series. This concentration of the charge density gives N$_2$ a stronger bond than C$_2$ even though the total charge increase in its binding region is only one half as great as that for C$_2$.

The comparison of the bond energies in this series of molecules clearly illustrates that the strength of a bond is not simply related to the number of electronic charges in the binding region. As important as the *amount* of charge is the exact disposition of the charge density in the molecule, whether it is diffuse or concentrated.

# 7.4: Dipole Moments and Polar Bonds

Any chemical bond results from the accumulation of charge density in the binding region to an extent sufficient to balance the forces of repulsion. Ionic and covalent binding represent the two possible extremes of reaching this state of electrostatic equilibrium and there is a complete spectrum of bond densities lying between these two extremes. Since covalent and ionic charge distributions exhibit radically different chemical and physical properties, it is important, if we are to understand and predict the bulk properties of matter, to know which of the two extremes of binding a given molecule most closely approximates.

We can obtain an experimental measure of the extent to which the charge density is unequally shared by the nuclei in a molecule. The physical property which determines the asymmetry of a charge distribution is called the dipole moment. To illustrate the definition of the dipole moment we shall determine this property for the LiF molecule assuming that one electron is transferred from Li to F and that the charge distributions of the resulting ions are spherical.

The dipole moment is defined as the product of the total amount of positive or negative charge and the distance between their centroids The centroids of the positive and negative charges in a molecule are determined in a manner similar to that used to determine the center of mass of a system.

7.4.1
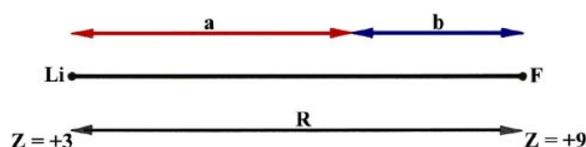


Figure $7.4.1$: diagram for the calculation of the centroids of positive and negative charge in LiF.

With reference to Figure $7.4.1$ the "center of gravity" of the positive charge in LiF is easily found from the following equations:

$$3a = 9b$$

$$a + b = R$$

Eliminating $b$ from these equations and solving for $a$ we find that

$$a = (3/4)R$$

Thus all the positive charge in the LiF molecule can be considered to be at a point one quarter of the bond length away from the fluorine nucleus. Similarly the centroid of negative charge, remembering that one electron has been transferred from Li to F, is found to lie at a point one sixth of the bond length away from the F nucleus. The centroids of positive and negative charge do not coincide, the negative centroid being closer to the F nucleus than the positive centroid. While the molecule is electrically neutral, there is a separation of charge within the molecule. Let us denote the distance between the centroids of charge by $l$ :

$$l = (5/6 - 3/4)R = (1/12)R$$

and since there are twelve electrons in LiF, the dipole moment denoted by m is

$$\mu = (12e)(1/12\,R) = eR$$

Thus, not surprisingly, the dipole moment in this case is numerically equal to one excess positive charge at the Li nucleus and one excess negative charge at the F nucleus, or one pair of opposite charges separated by the bond length.

We can easily calculate the value of the dipole moment. The value of $R$ for LiF is $1.53 \times 10^{-8}$ cm and the charge on the electron is $4.80 \times 10^{-10}$ esu. Thus

$$\mu = eR = 7.34 \times 10^{-18}\ \text{esu cm}$$

or
$$\mu = 7.34\ \text{debyes}$$

where 1 debye = 1 ´ 10$^{-18}$ esu cm. (The fundamental unit for dipole moments is called a debye in honour of P. Debye who was responsible for formulating the theory and method of measurement of this important physical quantity.) The experimental value of m for LiF is slightly smaller than the calculated value, being 6.28 debyes. The reason for the discrepancy is easily traced to the assumption made in the calculation that the charge distributions of the Li$^+$ and F$^-$ ions are spherical. We have previously indicated that the charge distributions of both the F$^-$ and Li$^+$ ions are polarized in a direction counter to the direction of transfer of the electron in order to balance the forces on the nuclei. The centroid of the ten negative charges on F is not at the F nucleus, but shifted slightly towards the Li, and the centroid of the charge density on Li$^+$ is correspondingly shifted slightly off the Li nucleus away from the F. Thus the centroid of negative charge for the whole molecule is not as close to the F nucleus as our simple calculation indicated and the dipole moment is correspondingly less.

Obviously from this discussion the dipole moment of a molecule with a covalent bond will be zero since the symmetry of the charge distribution will dictate that the positive and negative charge centroids coincide. Thus dipole moments can conceivably possess values which lie between the covalent limit of zero and the ionic extreme which approaches $neR$ in value ($n$ being the number of electrons transferred in the formation of the ionic bond).

The series of diatomic molecules formed by the union of a single hydrogen atom with each of the elements in the second row of the periodic table exemplifies both the extreme and intermediate types of binding, and hence of dipole moments. Table 7.4.2 lists the dipole moments and the values of $eR$ for the ionic extreme (assuming spherical ions) for the second-row diatomic hydride molecules.

Table 7.4.2: Dipole Moments and Bond Lengths of Second-row Hydrides

| AH | m*(debyes) | eR(debyes) | R(Å) |
|---|---|---|---|
| LiH | -6.002 | -7.661 | 1.595 |
| BeH | -0.282 | -6.450 | 1.343 |
| BH | 1.733 | 5.936 | 1.236 |
| CH | 1.570 | 5.398 | 1.124 |
| NH | 1.627 | 4.985 | 1.038 |
| OH | 1.780 | 4.661 | 0.9705 |
| FH | 1.942 | 4.405 | 0.9171 |

*The negative or positive signs for m imply that H is the negative or positive end of the dipole respectively.

All of these molecules exist as stable, independent species in the gas phase at low pressures and may be studied by spectroscopic methods or by molecular beam techniques. Only LiH and HF, however, are stable under normal conditions; LiH is a solid and HF a gas at room temperature. The remaining diatomic hydrides are very reactive since they are all capable of forming one or more additional bonds.

The variation of the dipole moment in this series of molecules provides a measure of the ***relative abilities*** of H and of each of the second-row elements to attract electrons. For example, the dipole moment for LiH illustrates that electron density is transferred from Li to H in the formation of this molecule. In HF, on the other hand, charge density is transferred from H to F. With the exception of BH, there is a steady increase in m from -6.0 debyes for LiH to +1.9 debyes for HF. Only LiH approaches the ionic limit of Li$^+$H$^-$. BeH appears to possess a close to equal sharing of the valence electrons. The remaining molecules, while exhibiting some degree of charge removal from H, are all far removed from the ionic extreme. They represent cases of molecular binding which lie between the two extremes, ionic and covalent. They are referred to as polar molecules.

We can best illustrate the variation in the chemical binding in this series of molecules by considering the properties of the molecular charge and bond density distributions (Figure 7-7 and 7-8). In LiH almost all of the molecular charge density is centerd on the two nuclei in nearly spherical distributions.
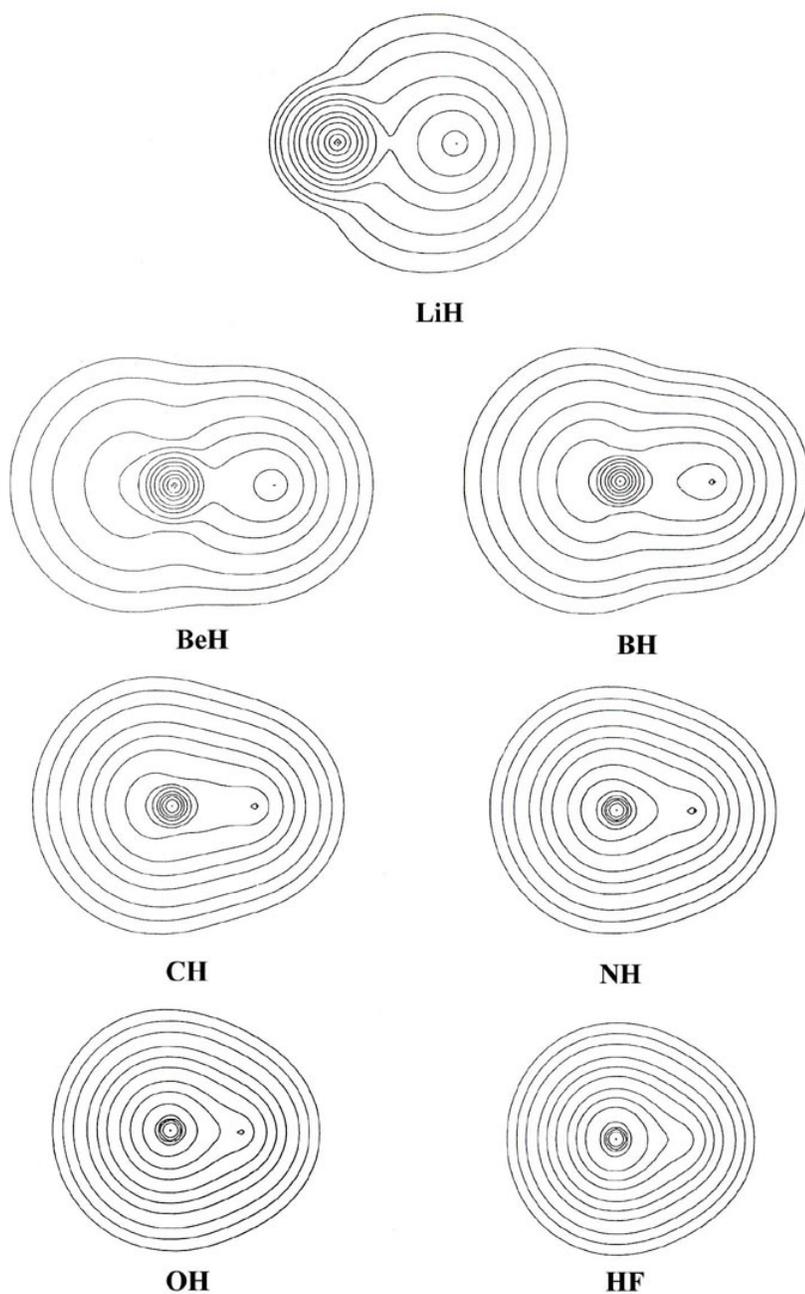
Figure 7.4.1 Contour maps of the molecular charge distrubution of the diatomic hydride molecules LiH to HF. The proton is the nucleus on the right-hand side in each case. Click here for contour values.
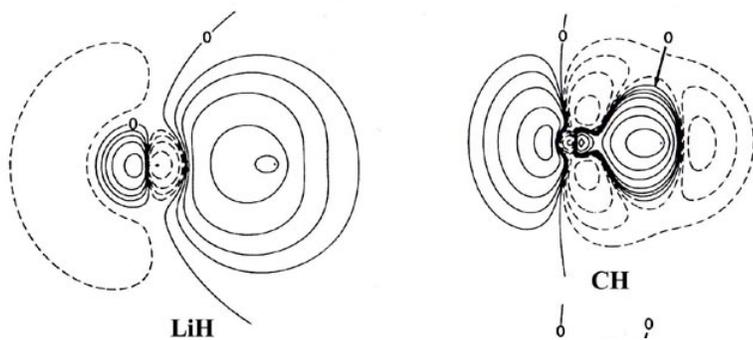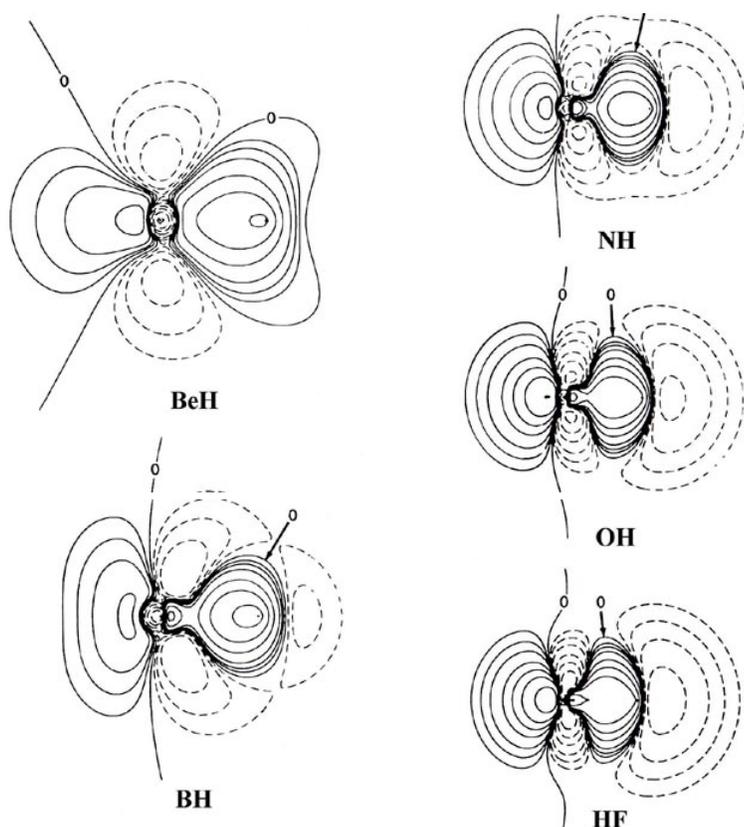
Figure $7.4.2$ Bond density maps for the diatiomic hydride molecules LiH to HF. The proton is on the right-hand side in each case. Click here for contour values.

The nonbonded charge and radius for lithium, 1.09 e⁻ and 1.7 $a_o$ respectively, are characteristic of the $1s^2$ inner shell distribution of Li⁺. Thus the molecular charge distribution for LiH indicates that the single valence electron of lithium is transferred to hydrogen and that the bond is ionic. (Recall that initially the Li **atom** is much larger than an H **atom**. The density map for LiH should be compared to that given previously for LiF, Figure 7-1.)

In BeH, the valence density has the appearance of being equally shared by the two nuclei. From BH through to HF a decreasing amount of density is centerd on the proton to the extent that the charge distribution of HF could be approximately described as an F⁻ ion distribution polarized by an imbedded proton.

The increase of the effective nuclear charge across a row of the periodic table is reflected not only in the amount of charge transferred to or from the hydrogen, but also in the relative sizes of the molecules. In BeH the density is diffuse and the molecule is correspondingly large. In HF the density is more compact and the molecule is the smallest in the series. The decrease in the size of the molecule from BH to HF parallels the decrease in the size of the atoms B to F. The intermediate size of LiH is a consequence of the one and only valence electron of lithium being transferred to hydrogen, and thus the size of LiH is a reflection of the size of the Li⁺ ion and not of the Li atom.

In general terms, the bond density maps provide a striking confirmation of the transfer of charge predicted by the relative electron affinities or by the relative effective nuclear charges of hydrogen and the second-row elements Li ® F. We may again employ the position of the charge increase in the bond density map to characterize the type of binding present in the molecule. The map for LiH exhibits the same characteristics as does the one for LiF (Figure 7-2), the contours in the region of the Li nucleus being remarkably similar in the two cases. The valence density is clearly localized about the proton just as it is about the fluorine nucleus in LiF. The $1s$ core density remaining on lithium is clearly polarized away from the proton, and the density increase localized on the proton is polarized towards the lithium as required in ionic binding.

The one principal difference between the LiH and LiF bond density maps concerns the shape of the contours representing the density increase on the proton and fluorine nucleus. In LiF the contours on fluorine are similar in shape to those obtained for a $2ps$ orbital density. In LiH the contours on the proton are nearly spherical. In terms of a simple orbital model we imagine the $2s$ electron of Li to be transferred to the $1s$ orbital of hydrogen in LiH and to the $2ps$ orbital of fluorine in LiF. The spherical and

double-lobed appearance of the density increases found for hydrogen and fluorine respectively show these orbital models of the binding to be reasonable ones.

From BeH through the rest of the series, the bond density maps show an increase in the amount of charge removed from the proton and transferred to the region of the other nucleus. This is evident from the increase in the number and diameter of the dashed contours in the nonbonded region of the proton. The pattern of charge increase and charge removal in the regions of the Be, B, C, N, O and F nuclei is similar to that found for these nuclei in their homonuclear diatomic molecules, and is characteristic of the participation of a $p$s orbital in the formation of the bond. The polarization of the density in the region of the hydrogen is of the simple dipolar type characteristic of a dominant $s$ orbital contribution. As previously discussed, the double-lobed appearance of the density increase in the region of fluorine in the bond density map for LiF can be viewed as characteristic of the ionic case when a 2$p$s orbital vacancy is filled in forming the bond. This limiting pattern is most closely approached in the hydride series by HF, the molecule exhibiting the largest degree of charge transfer from hydrogen. HF, of all the hydrides, is most likely to approach the limiting ionic extreme of $H^+F^-$. However, the charge increase in the region of fluorine in HF is not as symmetrical as that found for F in the LiF molecule. The proton in HF, unlike the $Li^+$ ion in LiF, is imbedded in one lobe of the density increase on F and distorts it. Thus, unlike the ionic extreme of LiF, the charge increase on F in HF is shared by both nuclei in the molecule.

Another important difference between the charge distributions of HF and LiF concerns the polarizations of the charge density in the immediate vicinities of the nuclei. In LiF (or LiH) the localized charge distributions are both polarized in a direction **opposite** to the direction of charge transfer Li ® F (or Li ® H). These polarizations are a consequence of the extreme charge transfer from lithium to fluorine, a transfer resulting in a force of attraction on the lithium nucleus and one of repulsion on the fluorine nucleus. In HF the charge density in the regions of the proton and the fluorine nucleus is polarized in the **same** direction as the direction of charge transfer from H ® F. Thus the amount of charge transferred to the vicinity of the fluorine in HF is not, unlike the situation in LiF, sufficient to screen the nuclear charge of fluorine and hence exert a net attractive force on the proton. Instead, the fluorine nucleus and its associated charge density exert a net repulsive force on the proton, one which is balanced by the inwards polarization of the charge density in the region of the proton.

The polarization of the charge density on the proton adds to and is contiguous with the charge increase in the binding region. Thus in HF and in the molecules BeH to OH for which the charge transfer is less extreme, the nuclei are bound by a shared density increase and the binding is covalent. From BeH through the series of molecules the sharing of the charge increase in the binding region becomes increasingly unequal and favours the heavy nucleus over the proton. The latter molecules in the series, NH, OH and HF, provide examples of polar binding which are intermediate between the extremes of perfect covalent and ionic binding as exhibited by the homo nuclear diatomics and LiF respectively.

In general, chemical bonds between identical atoms or between atoms from the same family in the periodic table will exhibit equal or close to equal sharing of the bond density and be covalent in character. Compounds formed by the union of elements in columns I or II with elements in columns VIA or VIIA will be ionic, as exemplified by LiF or BeO. We find a continuous change from covalent to ionic binding as the atoms joined by a chemical bond come from columns in the periodic table which are progressively further removed from one another. This is illustrated by the variation in the molecular charge distributions through the series of molecules shown in Figure 7.4.1.
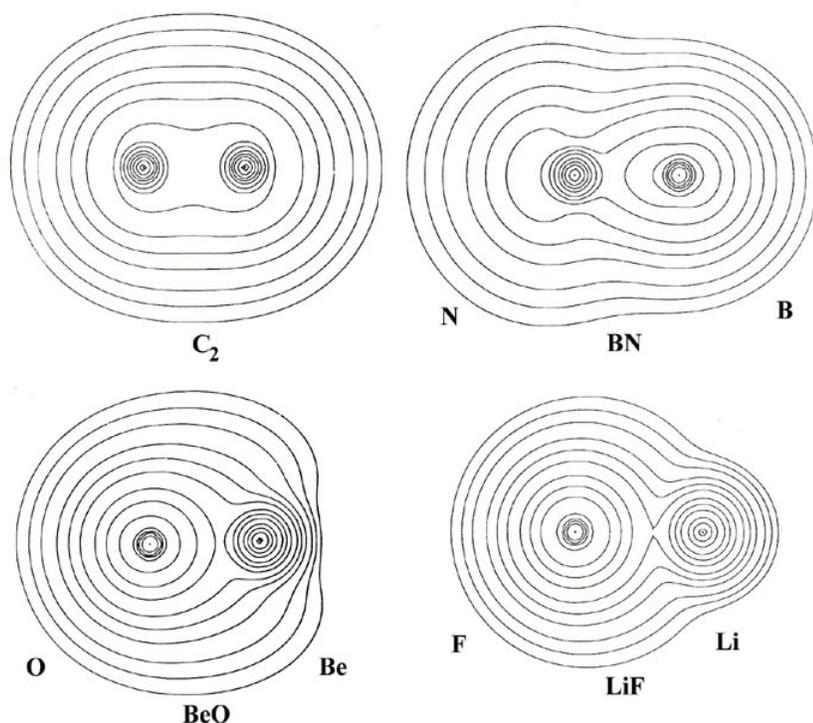
Figure $7.4.2$ Molecular charge distributions for the 12-electron isoelectronic series $C_2$, BN, BeO and LiF. Click here for contour values.

This series of molecules is formed (in an imaginary process) by the successive transfer of one nuclear charge from the nucleus on the left to the nucleus on the right, starting with the central symmetrical molecule $C_2$.
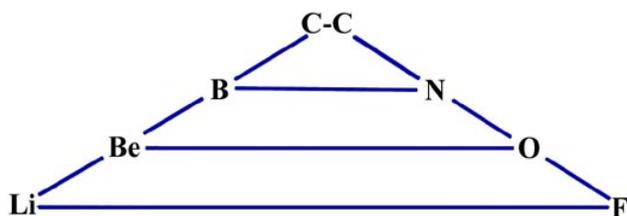


The molecules are said to form an isoelectronic series since they all contain the same number of electrons, twelve. The molecular charge distributions in this series illustrate how the charge distribution and binding for a constant number of electrons changes as the nuclear potential field in which the electrons move is made increasingly unsymmetrical.

In $C_2$ the nuclear charges are, of course, equal and the charge distribution is symmetrically shared by both nuclei in the manner characteristic of covalent binding. In the remaining molecules the valence charge density is increasingly localized in the region of the left-hand nucleus. This is particularly evident in the bond density maps and their profiles (Figure $7.4.1$) which show the increasing extent to which charge density is transferred from the region of the nucleus on the right (B, Be, Li) to its partner on the left (N, 0, F).
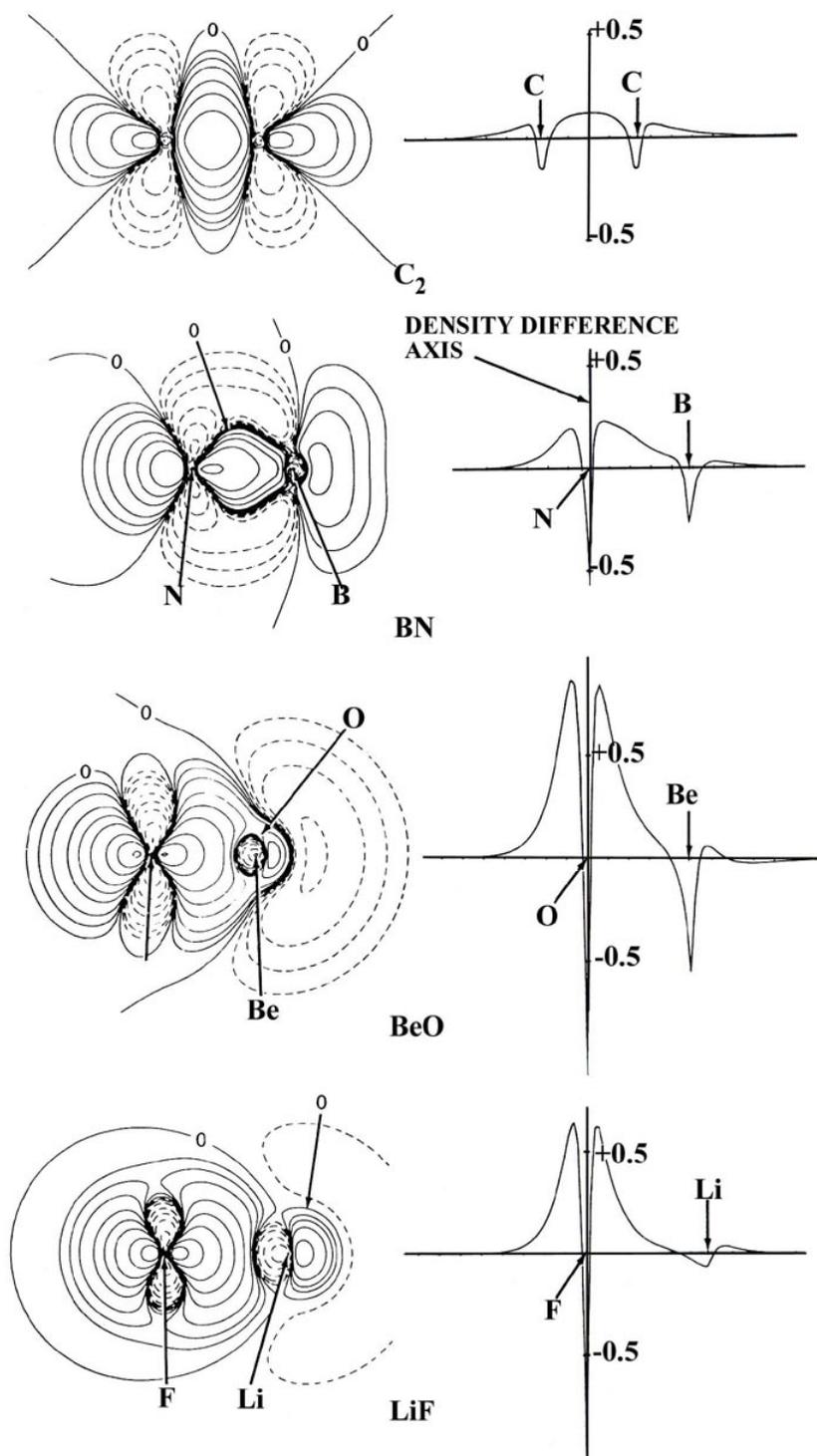
Figure $7.4.2$ Bond density maps and profiles along the internuclear axes for the 12-electron sequence of molecules $C_2$, BN, BeO and LiF. Click here for contour values.

The charge distribution of BN (with nuclear charges of five for boron and seven for nitrogen) is similar to that for $C_2$ in that charge is accumulated in the nonbonded regions of both nuclei as well as in the region between the nuclei. However, the buildup of charge behind the boron nucleus is smaller than that behind the nitrogen nucleus and the charge density shared between the nuclei is heavily shifted towards the nitrogen nucleus. Thus the binding in BN is predominantly covalent, but the bond density is polarized towards the nitrogen.

The charge transfer in BeO and LiF is much more extreme and the bond density maps show a considerable loss of charge from the nonbonded regions of both the Be and Li nuclei. Notice that except for contours of very low value the charge density in BeO, as in LiF, is localized in nearly spherical distributions on the nuclei, distributions which are characteristic of $Be^{+2}$ and $O^{-2}$ ions. A count of the number of electronic charges contamed within the spherical or nearly spherical contours centerd on the nuclei in BeO and LiF indicates that the charge distributions correspond to the formulae $Be^{+1.5}O^{-1.5}$ and $Li^{+1}F^{-1}$. That is, the binding is ionic and corresponds to the transfer of approximately one charge from Li to F and of one and one half charges from Be to O. Thus while the binding in LiF is close to the simple orbital model of $Li^+(1s^2)F^-(1s^22s^22p^6)$ as noted before, the binding in BeO falls somewhat short of the description $Be^{+2}(1s^2)O^{-2}(1s^22s^22p^6)$. Notice that the density contours on oxygen in BeO are more distorted towards the Be than the contours on F are towards Li in LiF. This illustrates that the oxygen anion is more polarizable than is the fluoride anion.

The radius of the charge distribution on the nonbonded side of the Be nucleus as measured along the bond axis is identical to that found for an isolated $Be^{+2}$ ion. (Recall that the radius of an atomic or orbital density decreases as the nuclear charge increases. Thus the $Li^{+1}$ ion is larger than the $Be^{+2}$ ion as indicated in Figure 7-9.) However, the radius of the Be charge density perpendicular to the bond axis is much greater than that for a $Be^{+2}$ ion. This shows, as does the actual electron count given above, that the two valence electrons of boron are not completely transferred to oxygen in the formation of the BeO molecule.

Hydrogen is an exception to the above set of generalizations regarding an element's position in the periodic table and the ionic-covalent nature of the bond it forms with other elements. It does not behave in a manner typical of family IA. The bond formed between hydrogen and another member of group IA, as exemplified by LiH, is ionic and not covalent. Here hydrogen accepts a single electron to fill the vacancy in its 1$s$ shell and thus resembles the members of family VIIA, the halogens. The bond in HF, however, is more polar than would be expected for the union of two adjacent members of the same family, and hydrogen is therefore not a typical member of family VIIA. This intermediate behaviour for H is understandable in that the values of its ionization potential and electron affinity are considerably greater than those observed for the alkali metals (IA) but are considerably less than those found for the halogens (VIIA).

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# 7.5: Electronegativity

It is important that we be able to predict the extent to which electronic charge will be transferred from one atom to another in the formation of a chemical bond, that is, to predict its polarity. The very detailed results given previously for the charge distributions of the diatomic hydrides are not generally available and there is a need for an empirical method which will allow us to estimate the polarity of any chemical bond. It is possible to define for an element a property known as its ***electronegativity***, which provides a qualitative estimate of the degree of polarity of a bond. Electronegativity is defined as the ability of an atom in a molecule to attract electrons to itself. The concept of an electronegativity scale for the elements was proposed by Pauling.

The electron affinity of an atom provides a direct measure of the ability of an atom to attract and bind an electron:

$$X + e^- \rightarrow X^-$$
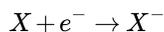
with $\Delta E = A_x$

here $A_X$ denotes the electron affinity of atom $X$. For the reactions of two elements, $X$ and $Y$, with free electrons, the relative values of the electron affinities $A_X$ and $A_Y$ provide a measure of the relative independent tendencies of X and Y to change into $X^-$ and $Y^-$. However, we are interested in the reaction of X ***with*** Y and in being able to predict whether the $X - Y$ bond will be polar in the sense $X^+ Y^-$ or $X^- Y^+$. The electron which is to be partially or wholly gained by $X$ or $Y$ is not a free electron but is bound to the atom Y or X respectively. Consequently we are interested in the relative energies of the following two processes:

$$X + Y \rightarrow X^+ + Y^- \tag{7.5.1}$$

with

$$\Delta E_1 = I_X + A_Y$$

and

$$X + Y \rightarrow X^+ + Y^- \tag{7.5.2}$$

with

$$\Delta E_2 = I_Y + A_X$$

For reaction 7.5.1 to be favored over reaction 7.5.2, not only must $Y$ have a high electron affinity, it is also necessary that X have a low ionization potential. We would expect the bonding electrons to be approximately equally shared in the $X - Y$ bond, if D$E_1$ = D$E_2$, as neither extreme structure is favored over the other. Thus the condition for a non-polar covalent bond is

$$I_X + A_Y = I_Y + A_X \tag{7.5.3}$$

or, collecting quantities for a given atom on one side of the equation,

$$I_X - A_X = I_Y - A_Y \tag{7.5.4}$$

Equation 7.5.4 states that a non-polar bond will result when the difference between the ionization potential and the electron affinity is the same for both atoms joined by the bond. If the quantity $I_X$ - $A_X$ is greater than $I_Y$ - $A_Y$, then the product X⁻Y⁺ will be energetically favoured over X⁺Y⁻. Thus the quantity ($I$ - $A$) provides a measure of the ability of an atom to attract electrons (or electronic charge density) to itself ***relative*** to some other atom. The electronegativity, denoted by the symbol $\chi$, is defined to be proportional to this quantity:

$$\chi_x \propto I_x - A_x$$

The electronegativities of the elements in the first few rows of the periodic table are given in Table 7.5.1.

> *Thus the quantity (I - A) provides a measure of the ability of an atom to attract electrons (or electronic charge density) to itself **relative** to some other atom.*

Table 7.5.1*: Some Electronegativity Values*

| H | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2.1 | | | | | | | |

| H | | | | | | |
|---|---|---|---|---|---|---|
| **Li** | **Be** | **B** | **C** | **N** | **O** | **P** |
| 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 6.5 | 4.0 |
| **Na** | **Mg** | **Al** | **Si** | **P** | **S** | **Cl** |
| 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 |
| **K** | **Ca** | | | | | Br |
| 0.8 | 1.0 | | | | | 2.8 |

As expected, the electronegativity increases from left to right across a given row of the periodic table and decreases down a given column. The greater the difference in the electronegativity values for two atoms, the greater should be the disparity in the extent to which the bond density is shared between the two atoms. Pauling has given empirical expressions which relate the electronegativity difference between two elements to the dipole moment and to the strength of the bond.

## 7.6: Interaction Between Molecules

The properties observed for matter on the macroscopic level are determined by the properties of the constituent molecules and the interactions between them. The polar or non-polar character of a molecule will clearly be important in determining the nature of its interactions with other molecules. There will be relatively strong forces of attraction acting between molecules with large dipole moments. To a first approximation, the energy of interaction between dipolar molecules can be considered as completely electrostatic in origin, the negative end of one molecule attracting the positive end of another.

The presence of intermolecular forces accounts for the existence of solids and liquids. A molecule in a condensed phase is in a region of low potential energy, a potential well, as a result of the attractive forces which the neighboring molecules exert on it. By supplying energy in the form of heat, a molecule in a solid or liquid phase can acquire sufficient **kinetic energy** to overcome the **potential energy** of attraction and escape into the vapor phase. The vapor pressure (the pressure of the vapor in equilibrium with a solid or liquid at a given temperature) provides a measure of the tendency of a molecule in a condensed phase to escape into the vapor; the larger the vapor pressure, the greater the escaping tendency. The average kinetic energy of the molecule in the vapor is directly proportional to the absolute temperature. Thus the observation of a large vapor pressure at a low temperature implies that relatively little kinetic energy is required to overcome the potential interactions between the molecules in the condensed phase.

> *By supplying energy in the form of heat, a molecule in a solid or liquid phase can acquire sufficient* **kinetic energy** *to overcome the* **potential energy** *of attraction and escape into the vapor phase.*

The only potential interactions possible between non-polar, covalently bonded molecules are of the van der Waals' type as previously discussed for the interaction between two helium atoms at large internuclear separations. Molecules such as $H_2$ and $N_2$ have closed shell electronic structures in the same sense that helium does; all of the valence electrons are paired and no further chemical bonding may occur. The small polarizations of the charge densities induced by the long-range interactions of closed shell atoms or molecules result in only weak forces of attraction. The low boiling points (the temperature at which the vapor pressure above the liquid phase equals one atmosphere) observed for substances composed of molecules which can interact only through a van der Waals' type force are, therefore, understandable. Table 7.6.1 lists the normal boiling points for a number of representative compounds.

Table 7.6.1: Normal Boiling Points (°K)

| Substance | BP | Substance | BP | Substance | BP |
|---|---|---|---|---|---|
| He | 4.2 | NH$_3$ | 240 | NaCl | 1686 |
| H$_2$ | 20.4 | HF | 292 | LiF | 1949 |
| N$_2$ | 77.4 | H$_2$O | 373 | BeO | 4100 |
| Ar | 87.4 | | | | |

An argon atom is larger than a helium atom and its outer charge density is not bound as tightly as that in helium. (Recall that the ionization potential for argon is less than that for helium.) Consequently, the charge density of argon is more polarizable than that of helium and the forces of attraction between argon atoms and hence its normal boiling point are correspondingly greater. These same forces do, of course, operate in the gas phase as well and are the cause of the observed deviations from ideal gas behaviour.

The interactions between polar molecules such as HF and $H_2O$ will be much larger and their normal boiling points greater than those observed for the non-polar molecules. When hydrogen is present at the positive end of a polar bond, the dipolar interactions are particularly strong and are given a special name, hydrogen-bonded interactions. The hydrogen bond increases in strength as the electronegativity of the atom to which the H is chemically bonded increases. (We noted previously that the dipole moment in the HA molecules increased as A was made more electronegative.) Liquid hydrogen fluoride consists of chains of molecules joined end to end; each hydrogen of one molecule is attracted to the fluorine of the next. In liquid water, each water molecule is hydrogen bonded to four other water molecules. This accounts for what appears to be an anomalously high boiling point for water when compared with the values observed for the neighboring hydride molecules $NH_3$ and HF.

The condensed phases so far considered are called molecular solids or molecular liquids because the identity of the individual molecule is largely retained. As the forces between the molecules become larger, the point of view of regarding a solid as a collection of individual, interacting molecules becomes less satisfactory. In the limiting case of the strong interactions which exist between the ions in an ionic crystal, the concept of a discrete molecule in the solid phase ceases to exist. In solid KCl, for example, the potassium and chloride ions exist as separate entities; each potassium ion is in contact with six chloride ions, which in turn are each in contact with six potassium ions. Each ion attracts its six neighboring ions equally and thus the structure is symmetrical and therefore cubic; six ions of one sign occupy the centers of the faces of a regular cube with an ion of opposite sign at its center.

The number of nearest neighbors a given ion has in an ionic crystal is determined by the relative sizes of the positive and negative species. The $Be^{+2}$ ion is considerably smaller than $O^{-2}$ and the basic structure of BeO is tetrahedral, each ion surrounded by four ions of opposite charge. The strong electrostatic forces between the ions in a crystal are reflected in the high boiling points recorded in Table 7.6.1 for the ionic compounds.

## 7.7: Literature References

More detailed discussions of the molecular charge distributions and the forces exerted on the nuclei will be found in the references given below. The sources of the wave functions used in the calculation of the density distributions are also given in these references.

| | |
|---|---|
| 1. | R. F. W. Bader, W. H. Henneker and P. E. Cade, J. Chem. Phys. *46*, 3341 (1967). (Homonuclear diatomic molecules.) |
| 2. | R. F. W. Bader, I. Keaveny and P. E. Cade, J. Chem. Phys. *47*, 3381 (1967). (The second-row diatomic hydrides, LiH ® HF.) |
| 3. | R. F. W. Bader and A. D. Bandrauk, J. Chem. Phys. *49*, 1653 (1968). (The 12- and 14-electron isoelectron series, $C_2$, BeO, LiF and No CO BF.) |
| 4. | P. E. Cade, R. F. W. Bader, I. Keaveny and W. H. Henneker, J. Chem. Phys. *50*, 5313 (1969). (The third-row diatomic hydrides NaH ® HC1.) |

# 7.8: Further Reading

L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1960, third edition.

# 7.A: Appendix

## A QUANTITATIVE DEFINITION OF ATOMIC CHARGE

Since the publication of this book in 1970, a theory of atoms in molecules (AIM) has been developed that enables one to define an atom in a molecule and all of its properties. The theoretical definition of an atom is based on the properties of the experimentally observable charge density. This theory is described elsewhere in this web site, but we present here a brief introduction to enable a quantitative definition of the charge on atom in a molecule. The theory is fully described and developed in the book "Atoms in molecules: a quantum theory", published by the University of Oxford Press, 1990.

A molecule, or a crystal, is partitioned into individual atoms in terms of surfaces that satisfy a particular condition on the electron density. The partitioning is a direct result of the density exhibiting a maximum at the position of each nucleus. As a consequence, the density passes through some minimum value before again attaining some maximum value at a neighbouring nucleus, as illustrated in the displays of the molecular density distributions shown in this book. This fundamental property of a charge distribution is illustrated in the accompanying figure, Fig. A1 which displays the electron density in a plane of the nuclei for the LiF molecule. The distribution is dominated by the two nuclear maxima. The point of minimum density along the line linking the two nuclei � the saddle point in the density � is a starting point for two paths of steepest descent away from this point, paths that define the boundary separating the atoms in this plane. The collection of such paths for all planes obtained by rotation about the axis defines the interatomic surface. The interatomic surfaces defined in this manner yield a �natural partitioning� of a molecule into atoms, as illustrated in Fig. A1 for LiF and in Figures A2a and A2b for the second- and third-row diatomic hydrides.

The properties of the atoms defined by these �natural� surfaces are determined by quantum mechanics. Thus, not only does quantum mechanics predict the properties of a molecule, it also predicts the properties of its individual constituent atoms. The theory of atoms in molecules (AIM) equates every property of a molecule to the sum of its atomic contributions. Among the properties of immediate interest is the charge on an atom. The electron population of an atom A - its average number of electrons - a quantity denoted by N(A), is obtained by integrating the electron density over the space of the atom up to its atomic boundaries, as given in equation A-1 where the electron density at a point denoted by the position vector $\mathbf{r}$ is denoted by r $(\mathbf{r})$

**A-1** $\qquad N(A) = \int_A \rho(\mathbf{r})d\mathbf{r}$

The subscript A on the integral means that the integration is carried out over the space of the atom A up to its atomic boundary, that is, its interatomic surface. The charge on the atom, q(A), is the difference between the nuclear charge $Z_A$ and its electron population, as given in equation A-2

**A-2** $\qquad q(A) = Z_A - N(A)$

Another useful property determined by the electron density is the atomic polarization. In a free atom the centroid of negative charge coincides with the nucleus and there is no dipole moment, that is, no separation of charge. When an atom is in chemical combination, its density becomes polarized, either towards or away from a neighbouring atom, as discussed and illustrated in this chapter. One can easily determine the displacement of the centroid of negative charge from the position of the nucleus by determining the average (vector) distance of every element of the electron density from the nucleus of the atom. This corresponds to integrating the product of the density at each position $\mathbf{r}$, with the vector distance of this point from the nucleus, a distance denoted by the vector $\mathbf{r}_A$ to obtain the atomic moment $\mathbf{M}(A)$. Its definition is given in equation A-3.

**A-3** $\qquad M(A) = \int_A \mathbf{r}_A \rho(\mathbf{r})\,d\mathbf{r}$

The atomic moment is a vector because it has a direction as well as a magnitude.

The dipole moment $\mathbf{m}$ of a diatomic molecule A-B, when expressed in terms of atomic contributions, is given by a charge transfer term, equal to the charge on atom B multiplied by $\mathbf{R}$, the vector distance from the nucleus of A and to that of B, and a polarization term given by the sum of the two atomic moments. The dipole moment of A-B is therefore given as in equation A-4

**A-4** $\qquad \mu = q(B)\mathbf{R} + M(A) + M(B)$

where all three terms are directed along the internuclear axis. The sign of the charge transfer term q(B)**R** is determined by the sign of q(B) = -q(A). The model expression for m given for LiF in the text assumes the complete transfer of one electron from Li to F and equates the dipole moment to the charge transfer term alone, that is, to the first term of equation **A-4**. We can use the molecular density distribution for LiF displayed in Fig. 7-9 or Fig. A1 to calculate the charges on the atoms and determine the atomic polarizations to illustrate how the atomic contributions determine the molecular dipole. The charge on F is q(F) = -0.938$e$, close to the value of -1$e$ assumed in the model calculation. As already discussed, the atoms are in general polarized in a direction counter to the direction of the charge transfer. In LiF the charge transfer is from Li ® F and hence the fluorine atom is polarized towards the lithium atom which in turn is polarized away from the fluorine atom. The length of the vector **R** in LiF is 1.564 Å and expressing the charge on the fluorine atom in esu, the charge transfer contribution to the dipole moment is � 7.05 debyes. The atomic polarizations are **M**(F) = +0.714 and **M**(Li) = +0.043 debyes to yield a dipole moment with a magnitude of 6.29 debyes, the experimental value being 6.28 debyes.
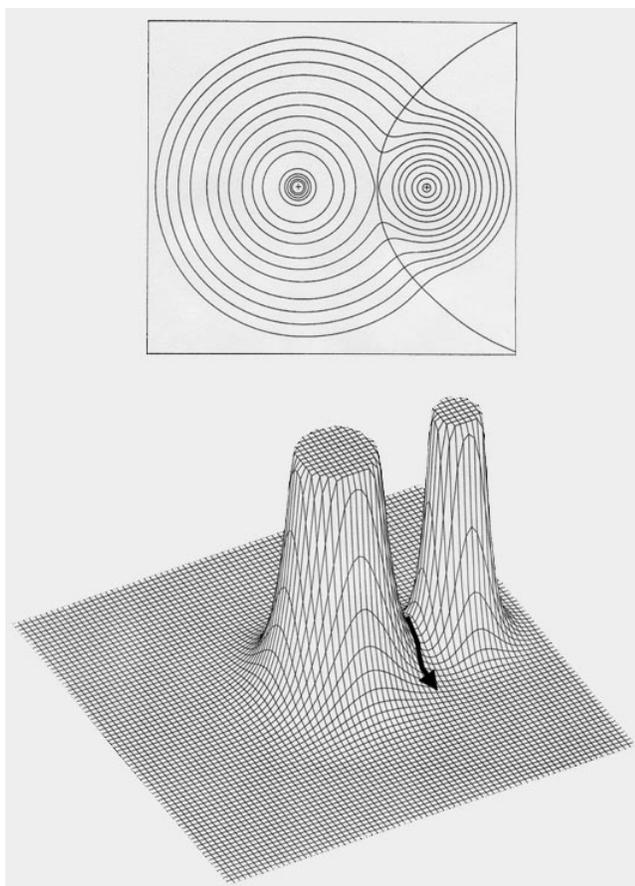


Fig. A1. Top diagram is a contour map of the electron density for the LiF molecule in a plane containing the nuclei. The outer contour has the value 0.001 au and the remaining contours increase in value as previously given. The boundary separating the basin of the F atom on the left, from the Li aton on the right, is also indicated. It is defined by the path of steepest descent from the point of minimum density along the Li-F internuclear axis indicated in the relief map of the density shown in the lower diagram.

## Properties Determined by the Electronic Charge Density

Pauling (1960) defined electronegativity to be 'the power of an atom in a molecule to attract electrons to itself.' This concept has proved to be extremely useful and it is reflected in the net charges on the atoms found in diatomic molecules, as determined by the theory of atoms in molecules. The atomic charges in a diatomic molecule are a direct measure of the relative abilities of the two atoms to attract and bind electronic charge within their basins. The variation in the charge on atom A in AB where A and B vary across the second row of the periodic table, Li ® F and including hydrogen are displayed in Fig. A2
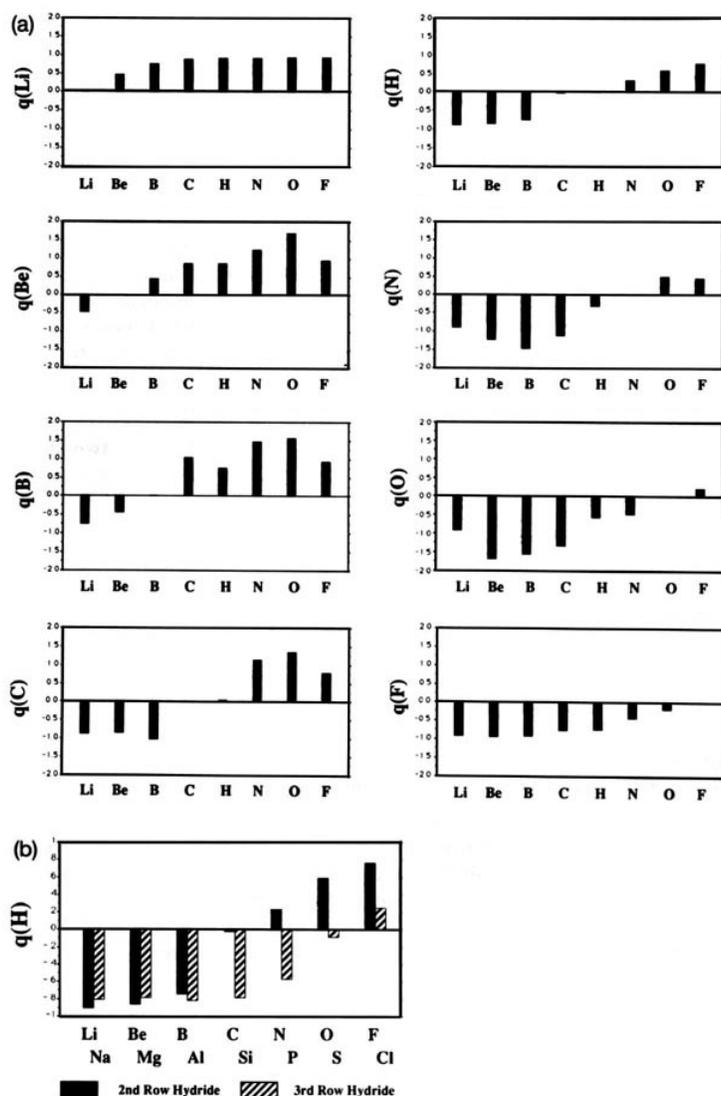
Fig. A2. (a) Bar graphs of the charges on the atoms in the ground states of the diatomic molecules AB where both A and B = Li, Be, B, C, H, N, O, F. This is the ordering of increasing electronegativity as determined by theory�all charges to the left of the position of the reference atom are negative, all those to its right are positive. (b) Bar graphs of the charge on hydrogen q(H), for the second- and third-row diatomic hydrides.

Each atom withdraws charge from elements to the left of it and donates charge to those on its right, with H appearing between C and N. The orderings are as anticipated with C and H possessing almost equal electronegativities. The electronegativity of C relative to H increases with the degree of unsaturation and with the extent of geometric strain. This result is anticipated on the basis of the orbital model which predicts the electronegativity of C to increase as the s character of its hybrid bonds to H increases. Most of the secondary variation in charges across the table are explicable in terms of the extent of charge transfer being limited by either the number of valence electrons on the donor or vacancies on the acceptor. The charges on the third-row elements Na ® Cl are also given relative to H in their hydrides and, as anticipated, H advances towards the electronegative end of the scale in this row relative to its position *vis-à-vis* the second-row elements. Unexpectedly, sodium and magnesium are slightly less electropositive than their second-row congeners.

The charge distributions of the second- and third-row hydrides are illustrated in Fig. A3a and b in the form of contour maps.

**(a)**

SCALE(au):
0  1  2  3  4  5

**(b)**



SCALE(au):
0  1  2  3  4  5
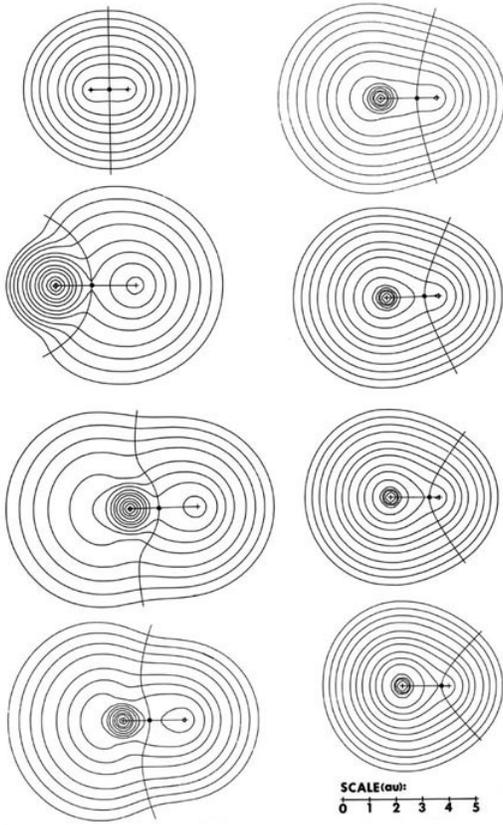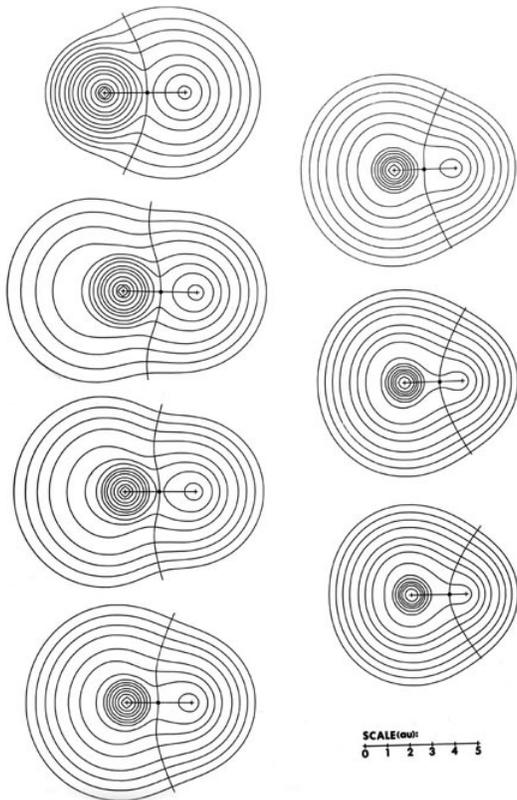
Fig. A3. Contour maps of the ground-state electronic charge distributions for the second- and third-row diatomic hydrides showing the positions of the interatomic surfaces. The first set of diagrams (a) also include a plot for the ground state of the $H_2$ molecule. The outer density contour in these plots is 0.001 au. The remaining contours increase in value according to the scale given in the table A1. (a) The left-hand side $H_2$, LiH, BeH , BH; right-hand side CH, NH, OH, HF. (b) The left-hand side: NaH, MgH, AlH, SiH; right-hand side PH, SH, HCl.

The extent and direction of charge transfer and its effect on the charge distribution are reflected in the behaviour of the interatomic surface which is indicated for each molecule. In LiH the surface envelops what is essentially a Li ion while in HF the total charge distribution is dominated by the forces exerted by the F nucleus. The charges $q$(H) of AH are also characteristic of the stable polyatomic species $AH_n$ the two values usually differing by less than 0.05 $e$, and they reflect the chemical behaviour of the hydrides. The hydrides of Li, Be, and B, for example, are all hydridic, expelling molecular hydrogen from water and, for all of these, $q$(H) < 0. There is a sharp break in the value of $q$(H) for methane for which $q$(H) » 0 and this is a faithful reflection of the non-polar nature of this molecule. It has a low solubility in water and does not dissociate. The remaining hydrides, $NH_3$, $H_2O$, and HF, are all increasingly polar with $q$(H) > 0 and the ordering of the charges accounts for the aqueous solution of ammonia being basic and that of HF being acidic.

The ability to determine the charge on an atom in a molecule removes the necessity of defining a numerical electronegativity scale. The concept, however, remains useful and one may use the atomic populations to demonstrate that they recover the basic idea underlying electronegativity�to predict the degree of charge transfer between two atoms. Since hydrogen can either donate or accept but a single electron, the electron population of hydrogen in AH may be used to define an electronegativity per electron of A relative to hydrogen. This electronegativity is given by $X$(A) = 1 - $N$(H)$_{AH}$, where $N$(H)$_{AH}$ is the population of H in AH. A positive or negative value for $X$(A) implies that A has a greater or lesser bonding electron affinity than does hydrogen, respectively. If the $X$(A) are meaningful, then the difference $|X(A) - X(B)|$ should determine the charge transfer per valence electron in AB. Using this concept, the population of A in AB is predicted to be

$$N(\mathbf{A})_{\mathbf{AB}} = [N(\mathbf{A})_{\mathbf{a}} - \{X(\mathbf{B}) - X(\mathbf{A})\}\mathbf{v}]$$

where v is the number of valence electrons on the donor A or the number of vacancies on the acceptor B, whichever value is limiting. $N$(A)$_a$ is the electron population of the isolated A atom. Examples of predicted and actual atomic populations for A are: NF, 6.56 (6.56); NO, 6.46 (6.50); CF, 5.21 (5.22); CO, 4.78 (4.65); CN, 4.94 (4.88); LiC, 2.12 (2.12). With the added stipulation that the charge transferred per vacancy, $|X(A) - X(B)|$, cannot exceed v, then all diatomic fluoride populations are predicted to within a maximum error of 0.08 electrons. This method of predicting the charge transfer between atoms yields significantly larger errors only for some compounds of the elements Be and B.

The charge distributions of the diatomic hydrides illustrate a general phenomenon�that a significant degree of interatomic charge transfer is accompanied by a polarization of the valence densities of the atoms in a direction counter to that of the charge transfer. The polarizations are in response to the electric field created by the charge transfer, the acceptor atom polarizing towards the positively charged donor atom which is itself polarized away from the negatively charged acceptor. This polarization of the donor atom is particularly pronounced when it possesses a greater number of valence electrons than there are vacancies on the acceptor atom, as illustrated by the data for the diatomic hydrides given in Table A2. This Table lists the atomic quantities that determine the molecular dipole moment, as given in equation A-4; the charges on the atoms (equation A-2 for q(A)), the atomic polarizations (equation A-3 for $\mathbf{M}$(A)), the charge transfer contribution to the molecular dipole moment under the heading $\mathbf{m}$(CT) = q(H)R = -q(A)R, the dipole moment for each molecule $\mathbf{m}$(AH) and the nonbonded radius of the A atom, $r_n$(A).

In general, the magnitude of the molecular dipole is less than that $\mathbf{m}$(CT), the charge transfer contribution, because of the opposing atomic polarizations. The polarizations of Li and Na in their hydrides are quite small as they correspond to tightly bound core densities. However, in some instances such as BH, the atomic polarizations determine the direction of the molecular moment. For the second row, the atomic polarizations are largest for the diffuse valence density on Be and B. They are larger still for their third-row congeners and Si where, because of the larger, 10-electron K-L core, the valence density is less tightly bound and more polarizable.

Attempts to assign atomic charges on the basis of measured dipole moments are unrealistic as such a procedure ignores the polarizations of the atomic densities. Such an attempt corresponds to assuming the molecular charge distribution to be composed of a set of spherically symmetric atomic densities, each centred on its own nucleus, a physically unacceptable model even in the limit of an ionic system. It should be evident from a comparison of the charge distribution in the non-bonded region of the A atoms that

the reduction in magnitude or reversal in sign of the dipole moment, which occurs after LiH in the second-row and after Na in the third-row, is a consequence of an atomic polarization and is not indicative of a sudden increase in the electronegativity of the A atom. The extent of the physical distortion of those atoms for which the atomic polarizations are greatest is reflected in the values of their non-bonded radii. A *non-bonded radius*, $r_n(\mathbf{W})$, is defined as the axial distance from a nucleus to an outer contour of the charge density on its non-bonded side. The 0.001au contour is chosen since the corresponding density envelopes provide good approximations to the experimentally determined van der Waals sizes and corresponding radii for molecules in the gas phase. The non-bonded radii for Li and Na are close to the values for the corresponding singly-charged ions while those for the strongly back-polarized atoms are all considerably greater than are their values in the free atomic state.

The presence of such a large and diffuse (weakly bound) charge distribution has important chemical consequences, imparting to the molecule the characteristics of a strong Lewis base. A classic example of this behaviour is the carbon atom in the CO molecule. This molecule has a near-zero dipole moment because of very pronounced polarizations of the atomic densities, particularly that of carbon, which oppose the considerable charge transfer moment. The charge on oxygen is - 1.33 e and the magnitudes of the opposing atomic dipoles are $|\mathbf{M}(O)| = 0.98$ au and $|\mathbf{M}(C)| = 1.72$ au with the non-bonded radius on carbon exceeding its free atomic value by 0.15 au. The physical importance of the atomic polarization of carbon is reflected in the ability of CO to act as a Lewis base, particularly in the formation of metal carbonyls. The considerable difference in the electronegativities of C and O is reflected in the relatively large dipole moment, $|\mathbf{m}| = 1.11$ au, of the formaldehyde molecule, $H_2C=O$. The charge transfer from C to O in formaldehyde where $q(O) = - 1.24$ $e$, is only slightly less than it is in CO. Unlike CO, however, the charge transfer contribution dominates the final moment in formaldehyde because of the close to halving of the atomic dipole on carbon which results from the use of its non-bonded density in the formation of non-polar bonds to the hydrogen atoms.

## Table of Contour Values

This table lists the values of the contours appearing in molecular density maps and bond density maps for those cases where the values are not given in the figure. In charge density maps the contours increase in value from the outermost one to the innermost one in the order indicated below. As an example, the reader may refer to Fig. 6-2, a contour map of the charge density for $H_2$ with the contours labelled in the order indicated by the table. In the bond density difference maps the contour values increase (solid lines) or decrease (dashed lines) from the zero lines indicated on cach contour map.

| Key to Charge Density Maps | | Key to Density Difference or Bond Density Maps | | |
|---|---|---|---|---|
| | | | Value of Contour | |
| Contour number beginning with outermost one | Value of contour in au | Contour number (from zero contour) | increase (solid contour) | decrease (dashed contour) |
| 1 | 0.002 | 1 | +0.002 | -0.002 |
| 2 | 0.004 | 2 | +0.004 | -0.004 |
| 3 | 0.008 | 3 | +0.008 | -0.008 |
| 4 | 0.02 | 4 | +0.02 | -0.02 |
| 5 | 0.04 | 5 | +0.04 | -0.04 |
| 6 | 0.08 | 6 | +0.08 | -0.08 |
| 7 | 0.2 | 7 | +0.2 | -0.2 |
| 8 | 0.4 | 8 | +0.4 | -0.4 |
| 9 | 0.8 | 9 | +0.8 | -0.8 |
| 10 | 2 | | | |
| 11 | 4 | | | |
| 12 | 8 | | | |
| 13 | 20 | | | |

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## 7.E: Exercises

| | |
|---|---|
| 1. | Arrange the following compounds in the order of the increasing polarity of their bonds:<br>CO, HF, NaCI, $O_2$ |
| 2. | Pauling introduced the idea of defining the percent ionic character possessed by a chemical bond. A covalent bond with equal sharing of the charge density has 0% ionic character, and a perfect ionic bond would of course have 100% ionic character. One method of estimating the percent ionic character is to set it equal to the ratio of the observed dipole moment to the value of eR,<br><br>$$\text{percent ionic character} = \left(\frac{\mu}{eR}\right)100$$<br><br>all multiplied by 100.<br>The value of eR is, it will be recalled, the value of the dipole moment when one charge is completely transferred in the formation of the bond and the resulting ions are spherical.<br>Use this method to determine the percent ionic character of the bonds in the diatomic hydrides, LiH to HF. Could any real molecule ever exhibit 100% ionic character according to this definition? |
| 3. | Pauling has proposed an empirical relationship which relates the percent ionic character in a bond to the electronegativity difference.<br><br>$$\text{percent ionic character} = \left(1 - e^{-(1/4)(\chi_A - \chi_B)}\right)100$$<br><br>From the electronegativity values given in Table 7-2, it is seen that the difference ($c_F$ - $c_H$) is greater than the value ($c_H$ - $c_{Li}$). Using the above relationship, we can calculate that the bond in HF should be 59% ionic while that in LiH should be only 26% ionic. Does the estimate of the relative ionic character in HF and LiH based on the electronegativity difference agree with that obtained by a comparison of the molecular charge density and density difference maps for these two molecules? |

# CHAPTER OVERVIEW

## 8: Molecular Orbitals

# 8.1: Introduction

There is a second major theory of chemical bonding whose basic ideas are distinct from those employed in valence bond theory. This alternative approach to the study of the electronic structure of molecules is called molecular orbital theory. The theory applies the orbital concept, which was found to provide the key to the understanding of the electronic structure of atoms, to molecular systems.

The concept of an orbital, whether it is applied to the study of electrons in atoms or molecules, reduces a many-body problem to the same number of one-body problems. In essence an orbital is the quantum mechanical description (wave function) of the motion of a single electron moving in the average potential field of the nuclei and of the other electrons which are present in the system. An orbital theory is an approximation because it replaces the instantaneous repulsions between the electrons by some average value. The difficulty in obtaining an accurate description of an orbital is the difficulty in determining the average potential field of the other electrons. For example, the $2s$ orbital in the lithium atom is a function which determines the motion of an electron in the potential field of the nucleus and in the average field of the two electrons in the $1s$ orbital. However, the $1s$ orbital is itself determined by the nuclear potential field and by the average potential field exerted by the electron in the $2s$ orbital. Each orbital is dependent upon and determined by all the other orbitals of the system. To know the form of one orbital we must know the forms of all of them. This problem has a mathematical solution; the exploitation of this solution has proved to be one of the most powerful and widely used methods to obtain information on the electronic structure of matter.

A molecular orbital differs from the atomic case only in that the orbital must describe the motion of an electron in the field of more than one nucleus, as well as in the average field of the other electrons. A molecular orbital will in general, therefore, encompass all the nuclei in the molecule, rather than being centred on a single nucleus as in the atomic case. Once the forms and properties of the molecular orbitals are known, the electronic configuration and properties of the molecule are again determined by assigning electrons to the molecular orbitals in the order of increasing energy and in accordance with the Pauli exclusion principle.

In valence bond theory, a single electron pair bond between two atoms is described in terms of the overlap of atomic orbitals (or in the mathematical formulation of the theory, the product of atomic orbitals) which are centred on the nuclei joined by the bond. In molecular orbital theory the bond is described in terms of a single orbital which is determined by the field of both nuclei. The two theories provide only a first approximation to the chemical bond.

We shall begin our discussion of molecular orbital theory by applying the theory to the discussion of the bonding in the homonuclear diatomic molecules.

---

## 8.2: Angular Momentum in Diatomic Molecules

The spatial symmetries of atomic orbitals and the number of each symmetry type are determined by the angular momentum of the electron. The orbitals are in fact labelled by the angular momentum quantum numbers, $l$ and $m$, which along with the principal quantum number $n$, completely specify the orbital. Angular momentum plays a similar role in determining the symmetries and number of orbitals of each symmetry species in the molecular case.

In an atom all of the angular momentum is electronic in origin. In the molecular case, the molecule as a whole rotates in space and the nuclei contribute to the total angular momentum of the system. The nuclei and the electrons of a diatomic molecule can rotate about both of the axes which are perpendicular to the bond axis (Fig. 8-1).
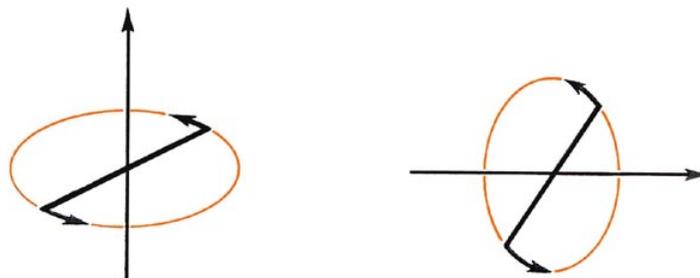


Fig. 8-1. Two rotational axis for a diatomic molecule.

In a classical analogue the electrons and the nuclei exchange angular momentum during these rotations and the angular momentum of the electrons is not separately conserved. Thus the magnitude of the total electronic angular momentum in a diatomic molecule, unlike the atomic case, is not quantized. Instead, the magnitude of the total angular momentum, nuclei and electrons, is quantized. Only the electrons, however, may rotate **about** the internuclear axis and this component of the angular momentum is entirely electronic in origin. As long as the molecule is left undisturbed, this one component of the angular momentum remains fixed in value and its magnitude, is, therefore, quantized.

The angular momentum **vector** for rotation about the bond will lie along the bond axis. This vector represents the component of the total angular momentum vector along the internuclear axis. As in the atomic case, quantum mechanics restricts the values of the component of the total angular momentum vector along a given axis to integral multiples of ($h$/2p). The quantum number in this case is denoted by the Greek letter l (lambda). It is analogous to the quantum number $m$ in the atomic case. The possible values for l are

$$\lambda = 0, 1, 2, 3, \ldots$$

Since the rotation may occur in the clockwise or anticlockwise sense about the axis, the angular momentum vector component may be pointed in either direction along the bond (Fig. 8-2).



+λ      −λ
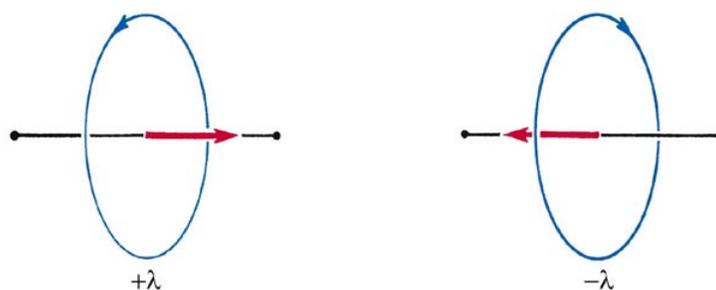
*Fig. 8-2. The two directions for the orbital angular momentum vector l for the rotation of an electron about the internuclear axis of a diatomic molecule.*

Correspondingly, the allowed values of the angular momentum about the internuclear axis are 0, ±1 ($h$/2p), ±2($h$/2p), etc., or in general, ±l($h$/2p). Thus when l is different from zero, each energy level is doubly degenerate corresponding to the two possible directions for the component l along the bond axis.

The molecular orbitals are labelled according to the values of the quantum number l. When l = 0, they are called s orbitals; when l = 1, p orbitals; when l = 2, d orbitals, etc. This is analogous to the labelling of the atomic orbitals as *s*, *p*, *d*, . . . , as determined by their *l* value.

We know less about the angular momentum of an electron in a diatomic molecule than in an atom. In the atomic case it is possible to determine the magnitude of the total angular momentum, as given by the quantum number *l*, and the magnitude of one of its components, as given by the quantum number *m*. In a linear molecule our knowledge is more restricted and we are limited to a single quantum number l, which determines only the component of angular momentum about the bond axis.

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# 8.3: Symmetry Considerations

The potential field of a nucleus in an atom is spherically symmetric, depending only on the distance between the nucleus and the electron. Consequently the spatial symmetries of atomic orbitals are completely determined by the angular momentum quantum numbers $l$ and $m$. When spherical polar coordinates rather than cartesian coordinates are used to describe the orbitals (Fig. 8-3) the dependence of the orbitals on the angles q and f is determined by their angular momentum quantum numbers.

**SPHERICAL POLAR COORDINATES**

$$x = r\sin\theta \cos\phi$$
$$y = r\sin\theta \sin\phi$$
$$z = r\cos\theta$$

**CYLINDICAL POLAR COORDINATES**

$$x = \rho \cos\phi$$
$$y = \rho \sin\phi$$
$$z = z$$
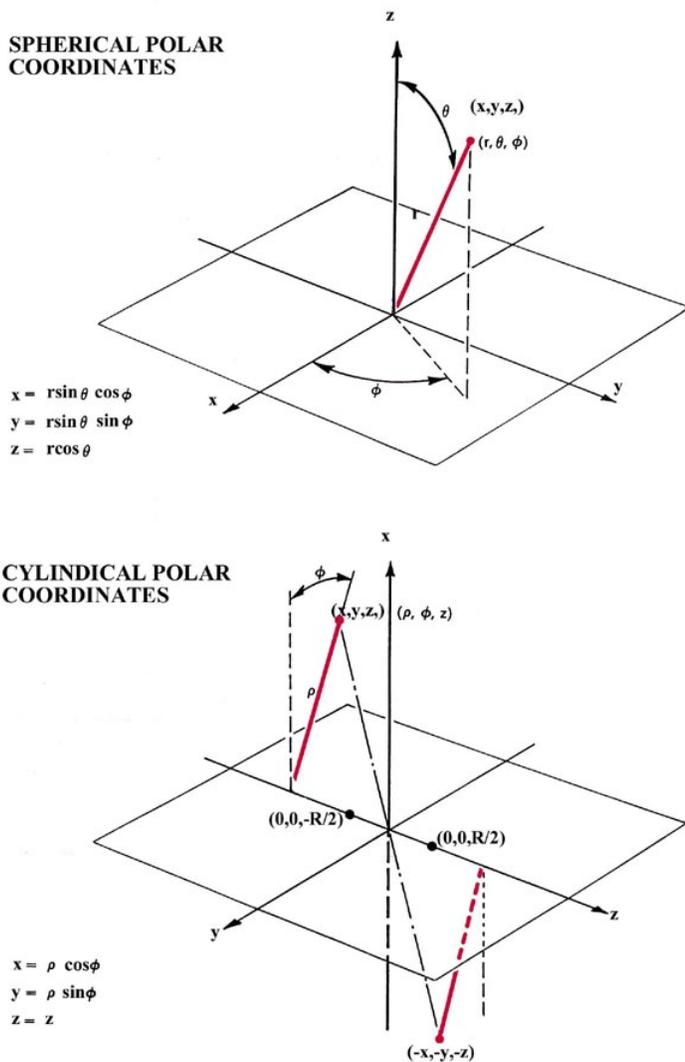
Fig. 8-3. The relationships of spherical polar and cylindrical polar coordinate systems to the Cartesian axes $x$, y and $z$. The inversion operation transforms the point $(x,y,z)$ into the point $(-x,-y,-z)$.

Only the radial dependence (the dependence of the orbital on the coordinate $r$, the distance between the nucleus and the electron) differs between orbitals with the same $l$ and $m$ values but different values of $n$.

The potential field of the nuclei in a linear molecule possesses cylindrical symmetry. In terms of a cylindrical coordinate system (Fig. 8-3) the single angular momentum quantum number l determines the dependence of the molecular orbitals on the anglef, a dependence determining the symmetry of the orbital for a rotation about the internuclear axis. The dependence of the molecular orbitals on r and $z$ is left undetermined.

The forms of the orbitals are not as fully determined by the angular momentum quantum numbers in a molecule as in an atom. However, we may further characterize and label the orbitals for a molecular system by taking advantage of the symmetry possessed by the molecule. The symmetry of the potential field in which an electron moves places very severe restrictions on the possible forms of the orbitals. This is a very general and powerful result. Indeed, the angular dependence of orbitals and wave functions and

their angular momentum quantum numbers may be completely determined solely by a consideration of the rotational symmetry of a system.

We may illustrate the role which symmetry plays in determining the form of an orbital by considering the symmetry properties of the orbitals obtained in Section 2 for the case of an electron restrained to move on a line of fixed length. Let us shift the origin of the x-axis in the plots of the orbitals (Fig. 2-8) to the mid-point of the line, thereby changing the values of the coordinates of the two end points from 0 and L to -L/2 and +L/2 respectively. Next let us denote by the symbol **R** the operation of reflection through the origin, an operation which replaces each value of x by -x. For example, the end points x = -L/2 and x = +L/2 are interchanged by the reflection operator **R**.

The first point to note about the operation of reflection is that its application leaves the physical system itself unchanged. The potential in which the electron moves is assumed to be of constant value along the x-axis. The reflection operator simply interchanges the two halves of the line leaving the system unchanged. The potential is said to be *invariant* to the operation of reflection through the origin.

What is the effect of **R** on the wave functions or orbitals? When **R** operates on $y_1(x)$ (that is, when $y_1(x)$ is reflected through the origin) the result is obviously to change $y_1(x)$ into itself:

$$\hat{R}|\psi_2(x)\rangle = \psi_2(-1x)\rangle = (+1)|\psi_2(x)\rangle$$

The reflected function $y_1(-x)$ is indistinguishable from $y_1(x)$.

The result of operating on $y_1(x)$ with the operator **R** is to leave the function *unchanged*. $y_1(x)$ is said to be *symmetric* with respect to a reflection through the origin. The operation of **R** on $y_2(x)$ yields a different result:

$$\hat{R}|\psi_2(x)\rangle = \psi_2(-x)\rangle = (-1)|\psi_2(x)\rangle$$

It is obvious from Fig. 2-8 that the reflection of $y_2(x)$ through the mid-point *changes its sign*, the reflected function $y_2(-x)$ is the negative of the unreflected function $y_2(x)$. Such a function is said to be *antisymmetric* with respect to a reflection at the origin. Every orbital for this system is either symmetric (those with odd n values) or antisymmetric (those with even n values) with respect to the symmetry operation of reflection.

Any orbital which was neither symmetric nor antisymmetric but was instead simply unsymmetrical with respect to reflection would when squared yield an unsymmetrical probability distribution. An unsymmetrical probability distribution implies that the electron is more likely to be found on one half of the x-axis than on the other. This is a physically unacceptable result since there are no forces acting on the electron which would favour one end of the line over the other. Only orbitals which are either symmetric or antisymmetric yield density distributions which properly reflect the symmetry of the system (Fig. 2-4), that is, density distributions which are themselves symmetrical with respect to reflection at the mid-point of the line.

Thus we conclude that the only wave functions resulting in physically acceptable probability distributions are those which are either symmetrical or antisymmetrical with respect to any symmetry operation which changes the physical system into itself. This statement is always true for non-degenerate wave functions, but must be amended somewhat for the action of some symmetry operations on a degenerate set of wave functions.

We shall use only one of the many symmetry elements possessed by a homonuclear diatomic molecule to further characterize and classify the molecular orbitals. A homonuclear diatomic molecule possesses a centre of symmetry and the corresponding operator is called the inversion operator. The action of this operator, denoted by the symbol **i**, is to replace the x, y, z coordinates of every point in space by their negatives -x, -y, -z. This corresponds to an inversion (or reflection) of every point through the origin or centre of symmetry of the molecule (Fig. 8-3).

The action of the inversion operator on the nuclear coordinates simply interchanges one nucleus for the other. Since the nuclei possess identical charges, the nuclear framework is left unchanged and the potential exerted by the nuclei is invariant to the operation of inversion. Thus every molecular orbital for a homonuclear molecule must be either symmetric or antisymmetric with respect to the inversion operator. Orbitals which are left unchanged by the operation of inversion (are symmetric) are labelled with a subscript g, while those which undergo a change in sign (are antisymmetric) are labelled u. The symbols g and u come from the German words "gerade" and "ungerade" meaning "even" and "odd" respectively.

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# 8.4: Molecular Orbitals for Homonuclear Diatomics

While the specific forms of the molecular orbitals (their dependence on r and $z$ in a cylindrical coordinate system) are different for each molecule, their dependence on the angle f as denoted by the quantum number l and their $g$ or $u$ behaviour with respect to inversion are completely determined by the symmetry of the system. These properties are common to all of the molecular orbitals for homonuclear diatomic molecules. In addition, the relative ordering of the orbital energies is the same for nearly all of the homonuclear diatomic molecules. Thus we may construct a molecular orbital energy level diagram, similar to the one used to build up the electronic configurations of the atoms in the periodic table. The molecular orbital energy level diagram (Figure 8.4.1) is as fundamental to the understanding of the electronic structure of diatomic molecules as the corresponding atomic orbital diagram is to the understanding of atoms.
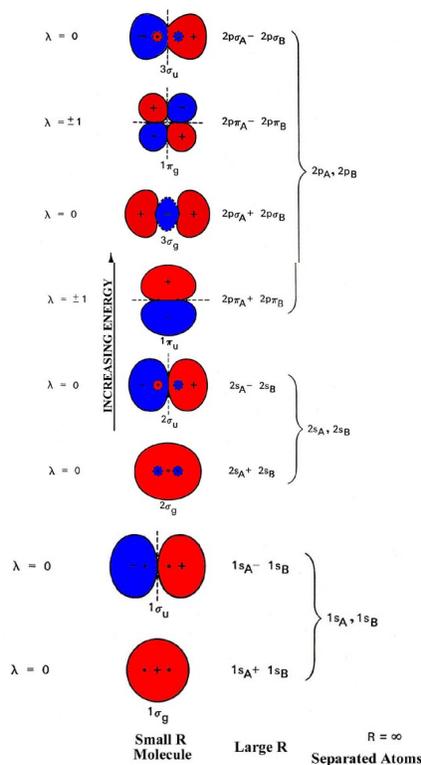


Figure 8.4.1: Molecular orbital energy level diagram for homonuclear diatomic molecules showing the correlation of the molecular orbitals with the atomic orbitals of the separated atoms. The schematic representation of the molecular orbitals is to illustrate their general forms and nodal properties (the nodes are indicated by dashed lines). Only one component of the degenerate 1pu and 1pg orbitals is shown. The second component is identical in form in each case but rotated 90° out of the plane. The ordering of the orbital energy levels shown in the figure holds generally for all homonuclear diatomic molecules with the exception of the levels for the 1pu and 3sg orbitals, whose relative order is reversed for the molecules after $C_2$.

Molecular orbitals exhibit the same general properties as atomic orbitals, including a nodal structure. The nodal properties of the orbitals are indicated inFigure 8.4.1. Notice that the nodal properties correctly reflect the $g$ and $u$ character of the orbitals. Inversion of a $g$ orbital interchanges regions of like sign and the orbital is left unchanged. Inversion of a $u$ orbital interchanges the positive regions with the negative regions and the orbital is changed in sign.

An orbital of a particular symmetry may appear more than once. When this occurs a number is added as a prefix to the symbol. Thus there are $1s_g$, $2s_g$, $3s_g$, etc. molecular orbitals just as there are $1s$, $2s$, $3s$, etc. atomic orbitals. The numerical prefix is similar to the principal quantum number $n$ in the atomic case. As $n$ increases through a given symmetry set, for example, $1s_g$, $2s_g$, $3s_g$, the orbital energy increases, the orbital increases in size and consequently concentrates charge density further from the nuclei, and finally the number of nodes increases as $n$ increases. All these properties are common to atomic orbitals as well.

We may obtain a qualitative understanding of the molecular orbital energy level diagram by considering the behaviour of the orbitals under certain limiting conditions. The molecular orbital must describe the motion of the electron for all values of the internuclear separation; from $R = ¥$ for the separated atoms, through $R = R_e$, the equilibrium state of the molecule, to $R = 0$, the united atom obtained when the two nuclei in the molecule coalesce (in a hypothetical reaction) to give a single nucleus. Hence a

molecular orbital must undergo a continuous change in form. At the limit of large $R$ it must reduce to some combination of atomic orbitals giving the proper orbital description of the separated atoms and for $R = 0$ it must reduce to a single atomic orbital on the united nucleus.

Consider, for example, the limiting behaviour of the $1s_g$ orbital in the case of the hydrogen molecule. The most stable state of $H_2$ is obtained when both electrons are placed in this orbital with paired spins giving the electronic configuration $1s_g^2$. For large values of the internuclear separation, the hydrogen molecule dissociates into two hydrogen atoms. Thus the limiting form of the $1s_g$ molecular orbital for an infinite separation between the nuclei should be a sum of $1s$ orbitals, one centred on each of the nuclei. If we label the two nuclei as A and B we can express the limiting form of the $1s_g$ orbital as

$$1\sigma_g \rightarrow (1s_A + 1s_b)$$

where $ls_A$ is a $1s$ orbital centered on nucleus A, and $ls_B$ is a $ls$ orbital centered on nucleus B. This form for the $1s_g$ orbital predicts the correct density distribution for the system at large values of $R$. Squaring the function ($1s_A + 1s_B$) we obtain for the density

$$1s_A 1s_A + 1s_B 1s_B + 2 \times 1s_A 1s_B$$

The first two terms denote that one electron is on atom A and one on atom B, both with 1s atomic density distributions. The cross term 2 ´ $ls_A$ ´ $ls_B$ obtained in the product is zero since the distance between the two nuclei is so great that the overlap of the orbitals vanishes. Notice as well that the function ($ls_A + ls_B$) has the same symmetry properties as does the $1s_g$ molecular orbital; it is symmetric with respect to both a rotation about the line joining the nuclei and to an inversion of the coordinates at the mid-point between the nuclei. The $1s_g$ orbital for the **molecule** is said to **correlate** with the sum of $1s$ orbitals, one on each nucleus, for the **separated atom case**.

Consider next the limiting case of the separated atoms for the helium molecule. Of the four electrons present in $He_2$ two are placed in the $1s_g$ orbital and the remaining two must, by the Pauli exclusion principle, be placed in the next vacant orbital of lowest energy, the $1s_u$ orbital. The electronic configuration of $He_2$ is thus $1s_g^2 1s_u^2$. The $1s_g$ orbital will correlate with the sum of the $1s$ orbitals for the separated helium atoms. Of the two electrons in the $1s_g$ molecular orbital one will correlate with the $1s$ orbital on atom A and the other with the $1s$ orbital on atom B. Since each helium atom possesses two $1s$ electrons, the $1s_u$ orbital must also correlate its electrons with $1s$ atomic functions on A and B. In addition, the correlated function in this case must be of $u$ symmetry. A function with these properties is

$$1\sigma_g \rightarrow (1s_A - 1s_b)$$

The limiting density distribution obtained by squaring this function places one electron in a $1s$ atomic distribution on A, the other in a $1s$ atomic distribution on B. The sum of the limiting charge densities for the $1s_g$ and $1s_u$ molecular orbitals places two electrons in $1s$ atomic charge distributions on each atom, the proper description of two isolated helium atoms.

Every diatomic homonuclear molecular orbital may be correlated with either the sum (for $s_g$ and $p_u$ orbitals) or the difference (for $s_u$ and $p_g$ orbitals) of like orbitals on both separated atoms. By carrying out this correlation procedure for every orbital we may construct a molecular orbital correlation diagram (Figure 8.4.2) which relates each of the orbital energy levels in the molecule with the correlated energy levels in the separated atoms. It is important to note that the symmetry of each orbital is preserved in the construction of this diagram. Consider, for example the molecular orbitals which correlate with the $2p$ atomic orbitals. The direction of approach of the two atoms defines a new axis of quantization for the atomic orbitals. The $2p$ orbital which lies along this axis is of s symmetry while the remaining two $2p$ orbitals form a degenerate set of p symmetry with respect to this axis. The sum and difference of the $2p$s orbitals on each center correlate with the $3s_g$ and $3s_u$ orbitals respectively, while the sum and the difference of the $2p$p orbitals correlate with the $p_u$ and $p_g$ orbitals (Figure 8.4.2).
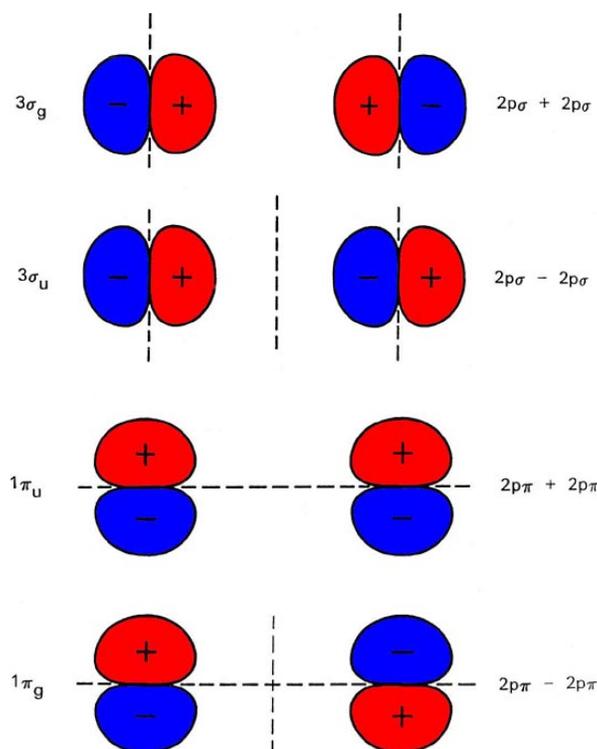
Figure 8.4.2: The correlated separated atom forms of the $3s_g$, $3s_u$, $1p_u$ and $1p_g$ molecular orbitals. The nodal planes are indicated by dashed lines. Only one component of each p orbital is shown.

For large values of the internuclear distance, each molecular orbital is thus represented by a sum or a difference of atomic orbitals centered on the two interacting atoms. As the atoms approach one another the orbitals on each atom are distorted by polarization and overlap effects. In general, the limiting correlated forms of the molecular orbitals are **not** suitable descriptions of the molecular orbitals for finite internuclear separations.

We are now in a position to build up and determine the electronic configurations of the homonuclear diatomic molecules by adding electrons two at a time to the molecular orbitals with the spins of the electrons paired, always filling the orbitals of lowest energy first. We shall, at the same time, discuss the effectiveness of each orbital in binding the nuclei and make qualitative predictions regarding the stability of each molecular configuration.

**Hydrogen.** The two electrons in the hydrogen molecule may both be accommodated in the $1s_g$ orbital if their spins are paired and the molecular orbital configuration for $H_2$ is $1s_g{}^2$. Since the $1s_g$ orbital is the only occupied orbital in the ground state of $H_2$, the density distribution shown previously in Figure 8.4.2 for $H_2$ is also the density distribution for the $1s_g$ orbital when occupied by two electrons. The remarks made previously regarding the binding of the nuclei in $H_2$ by the molecular charge distribution apply directly to the properties of the $1s_g$ charge density. Because it concentrates charge in the binding region and exerts an attractive force on the nuclei the $1s_g$ orbital is classified as a **bonding orbital**.

Excited electronic configurations for molecules may be described and predicted with the same ease within the framework of molecular orbital theory as are the excited configurations of atoms in the corresponding atomic orbital theory. For example, an electron in $H_2$ may be excited to any of the vacant orbitals of higher energy indicated in the energy level diagram. The excited molecule may return to its ground configuration with the emission of a photon. The energy of the photon will be given approximately by the difference in the energies of the excited orbital and the $1s_g$ ground state orbital. Thus molecules as well as atoms will exhibit a line spectrum. The electronic line spectrum obtained from a molecule is, however, complicated by the appearance of many accompanying side bands. These have their origin in changes in the vibrational energy of the molecule which accompany the change in electronic energy.

**Helium.** The electronic configuration of $He_2$ is $1s_g{}^2 \, 1s_u{}^2$. A $s_u$ orbital, unlike a $s_g$ orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1s_u$ orbital and all $s_u$ orbitals in general, because of this nodal property, cannot concentrate charge density in the binding region. It is instead concentrated in the antibinding region behind each nucleus (Figure 8.4.3).
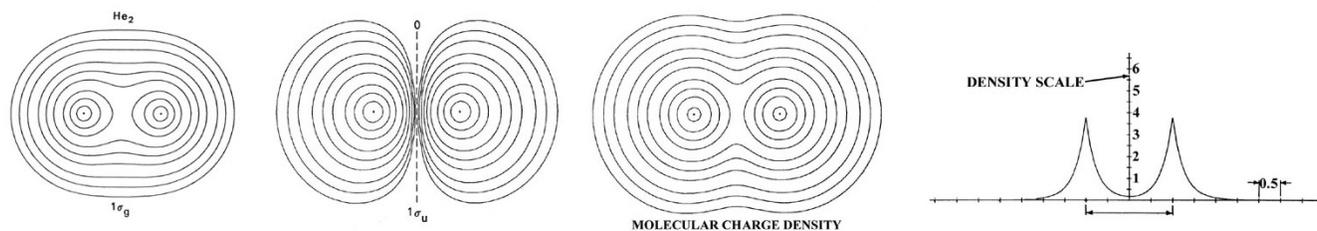
*Figure* 8.4.3: *Contour maps of the doubly-occupied* $1\sigma_g$ *and* $1\sigma_u$ *molecular orbital charge densities and of the total molecular charge distribution of* $He_2$ *at R = 2.0 au. A profile of the total charge distribution along the internuclear axis is also shown.* Click here for contour values.

The $s_u$ orbitals are therefore classified as ***antibonding***. It is evident from the form of density distribution for the $1s_u$ orbital that the charge density in this orbital pulls the nuclei apart rather than drawing them together. Generally, the occupation of an equal number of $s_g$ and $s_u$ orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the $s_g$ orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the $s_u$ orbitals. Thus molecular orbital theory ascribes the instability of $He_2$ to the equal occupation of bonding and antibonding orbitals. Notice that the Pauli exclusion principle is still the basic cause of the instability. If it were not for the Pauli principle, all four electrons could occupy a $s_g$-type orbital and concentrate their charge density in the region of low potential energy between the nuclei. It is the Pauli principle, and not a question of energetics, which forces the occupation of the $1s_u$ antibonding orbital.

The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for $He_2$ (Figure 8.4.3) is given by the sum of the $1s_g$ and $1s_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1s_u$ orbital has on the stability of $He_2$ is very evident in the total charge distribution. Very little charge density is accumulated in the central portion of the binding region. The value of the charge density at the mid-point of the bond in $He_2$ is only 0.164 au compared to a value of 0.268 au for $H_2$.

We should reconsider in the light of molecular orbital theory the stability of $He_2^+$ and the instability of the hydrogen molecule with parallel spins, cases discussed previously in terms of valence bond theory. $He_2^+$ will have the configuration $1s_g^2\ 1s_u^1$. Since the $1s_u$ orbital is only singly occupied in $He_2^+$, less charge density is accumulated in the antibinding regions than is accumulated in these same regions in the neutral molecule. Thus the binding forces of the doubly-occupied $1s_g$ density predominate and $He_2$ is stable. The electron configuration of $H_2$ is $1s_g^1()1s_u^1()$ when the electronic spins are parallel. The electrons must occupy separate orbitals because of the Pauli exclusion principle. With equal occupation of bonding and antibonding orbitals, the $H_2$ ()species is predicted to be unstable.

**Lithium.** The $Li_2$ molecule with the configuration $1s_g^2 1s_u^2 2s_g^2$ marks the beginning of what can be called the second quantum shell in analogy with the atomic case. Since the $1s_u$ antibonding orbital approximately cancels the binding obtained from the $1s_g$ bonding orbital, the bonding in $Li_2$ can be described as arising from the single pair of electrons in the $2s_g$ orbital. Valence bond theory, or a Lewis model for $Li_2$, also describes the bonding in $Li_2$ as resulting from a single electron pair bond. This is a general result. The number of bonds predicted in a simple Lewis structure is often found to equal the difference between the number of occupied bonding and antibonding orbitals of molecular orbital theory.

The forms of the orbital density distributions for $Li_2$ (Figure 8.4.4) bear out the prediction that a single electron pair bond is responsible for the binding in this molecule.
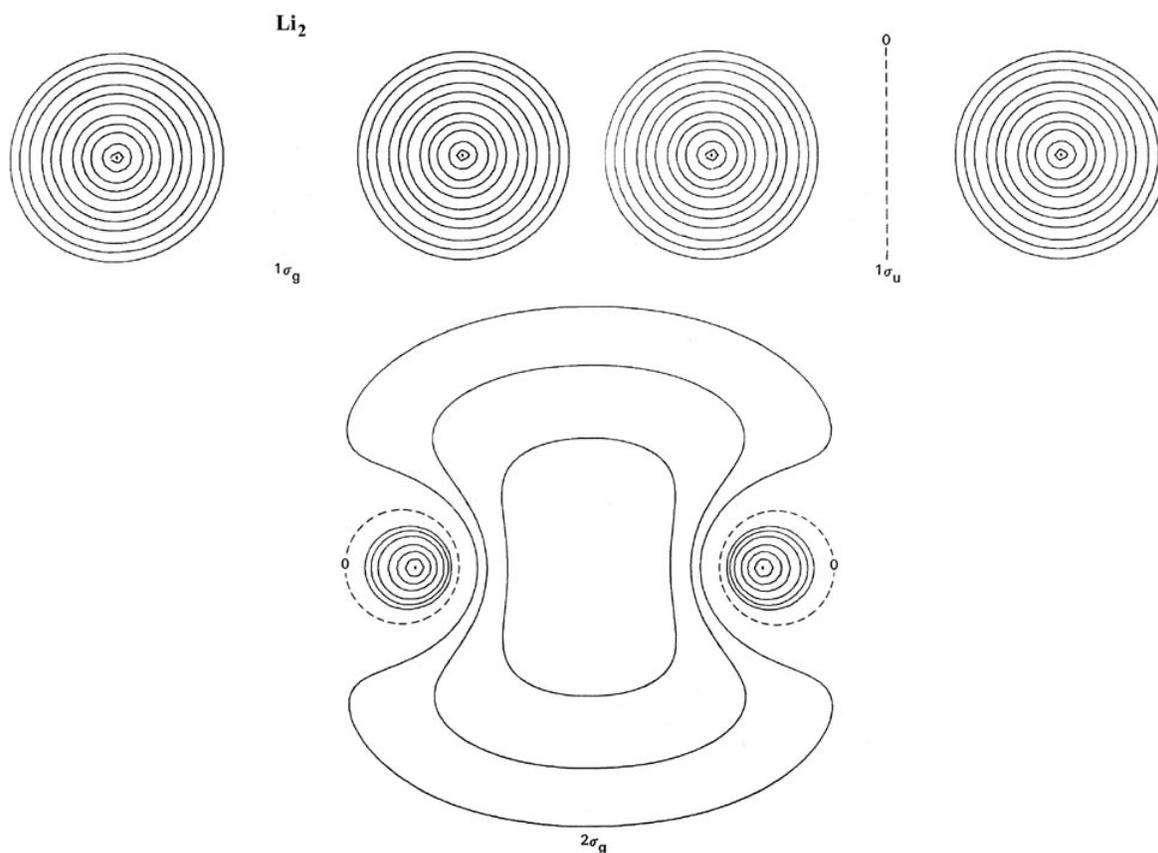
Figure 8.4.4: Contour maps of the doubly-occupied $1s_g$, $1s_u$ and $2s_g$ molecular orbital charge densities for $Li_2$ at $R = 5.051$ au, the equilibrium internuclear separation. Click here for contour values. The total molecular charge distribution for $Li_2$ is shown in Fig. 7-3.

The $1s_g$ and $1s_u$ density distributions are both strongly localized in the regions of the nuclei with spherical contours characteristic of $1s$ atomic distributions. The addition of just the doubly-occupied $1s_g$ and $1s_u$ orbital densities in $Li_2$ will yield a distribution which resembles very closely and may be identified with the doubly-occupied $1s$ or inner shell atomic densities on each lithium nucleus. Only the charge density of the pair of valence electrons in the $2s_g$ orbital is delocalized over the whole of the molecule and accumulated to any extent in the binding region.

Thus there are cases where the molecular orbitals even at the equilibrium bond length resemble closely their limiting atomic forms. This occurs for inner shell molecular orbitals which correlate with the inner shell atomic orbitals on the separated atoms. Inner shell $1s$ electrons are bound very tightly to the nucleus as they experience almost the full nuclear charge and the effective radii of the $1s$ density distributions are less than the molecular bond lengths. Because of their tight binding and restricted extension in space, the inner electrons do not participate to any large extent in the binding of a molecule. Thus with the exception of $H_2$ and $He_2$ and their molecular ions, the $1s_g$ and $1s_u$ molecular orbitals degenerate into non-overlapping atomic-like orbitals centred on the two nuclei and are classed as nonbonding orbitals.

**Beryllium.** The configuration of $Be_2$ is $1s_g^2 1s_u^2 2s_g^2 2s_u^2$ and the molecule is predicted to form a weakly bound van der Waals molecule like the helium dimer.

**Oxygen.** Since the method of determining electronic configurations is clear from the above examples, we shall consider just one more molecule in detail, the oxygen molecule. Filling the orbitals in order of increasing energy the sixteen electrons of $O_2$ are described by the configuration $1s_g^2 1s_u^2 2s_g^2 2s_u^2 3s_g^2 1p_u^4 1p_g^2$. The orbital densities are illustrated in Figure 8.4.5.
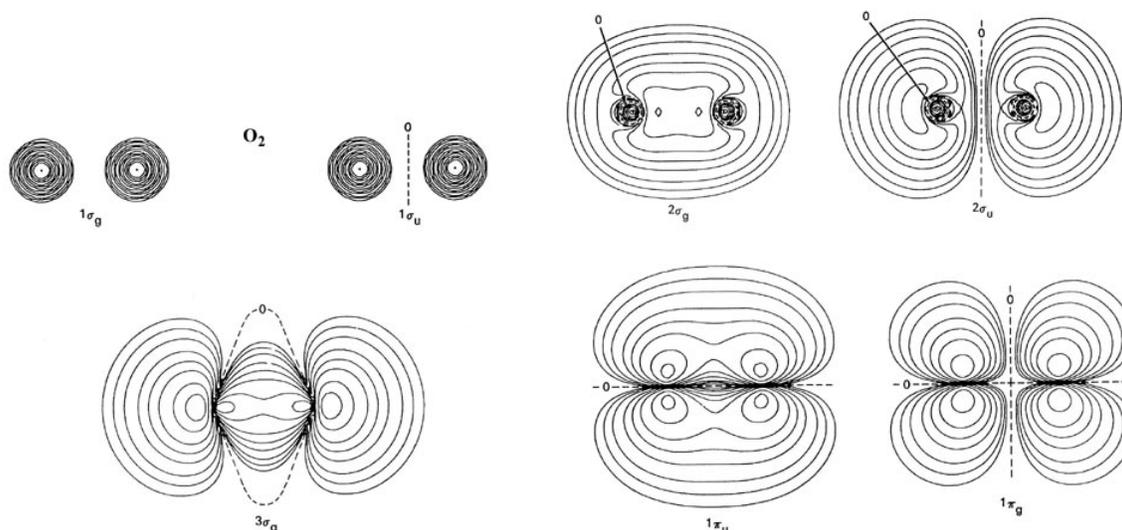
**Figure** 8.4.5: *Contour maps of the molecular orbital charge densities for $O_2$ at the equilibrium internuclear distance of 2.282 au. Only one component of the Ipg and 1pu orbitals is shown. All the maps are for doubly-occupied orbitals with the exception of that for 1pg for which each component of the doubly-degenerate orbital contains a single electron. The nodes are indicated by dashed lines. Click here for contour values.*

The molecular orbitals of p symmetry are doubly degenerate and a filled set of p orbitals will contain four electrons. The node in a $p_u$ orbital is in the plane which contains the internuclear axis and is not perpendicular to this axis as is the node in a $s_u$ orbital. (The nodal properties of the orbitals are indicated in Figure 8.4.5) The $p_u$ orbital is therefore bonding. A $p_g$ orbital, on the other hand, is antibonding because it has, in addition to the node in the plane of the bond axis, another at the bond mid-point perpendicular to the axis. The bonding and antibonding characters of the p orbitals have just the opposite relationship to their *g* and *u* dependence as have the s orbitals.

The $1s_g$ and $1s_u$ orbital densities have, as in the case of $Li_2$, degenerated into localized atomic distributions with the characteristics of $1s$ core densities and are nonbonding. The valence electrons of $O_2$ are contained in the remaining orbitals, a feature reflected in the extent to which their density distributions are delocalized over the entire molecule. Aside from the inner nodes encircling the nuclei, the $2s_g$ and $2s_u$ orbital densities resemble the $1s_g$ and $1s_u$ valence density distributions of $H_2$ and $He_2$. A quantitative discussion of the relative binding abilities of the $2s_g$, $3s_g$ and 1p orbital densities is presented in the following section.

One interesting feature of the electronic configuration of $O_2$ is that its outer orbital is not fully occupied. The two $p_g$ electrons could both occupy one of the $p_g$ orbitals with paired spins or they could be assigned one to each of the $p_g$ orbitals and have parallel spins. Hund's principle applies to molecules as well as to atoms and the configuration with single occupation of both $p_g$ orbitals with parallel spins is thus predicted to be the most stable. This prediction of molecular orbital theory regarding the electronic structure of $O_2$ has an interesting consequence. The oxygen molecule should be magnetic because of the resultant spin angular momentum possessed by the electrons. The magnetism of $O_2$ can be demonstrated experimentally in many ways, one of the simplest being the observation that liquid oxygen is attracted to the poles of a strong magnet.

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# 8.5: The Relative Binding Ability of Molecular Orbitals

We may determine the relative importance of each orbital density in the overall binding of the nuclei in a molecule through a comparison of the forces which the various molecular orbital charge distributions exert on the nuclei. In molecular orbital theory, the total charge density is given by the sum of the orbital charge densities. Thus the total force exerted on the nuclei by the electronic charge distribution will be equal to the sum of the forces exerted by the charge density in each of the molecular orbitals. It is of interest to compare the effectiveness of each orbital charge density in binding the nuclei with some standard case in which they all exhibit the same ability. The limiting forms of the molecular orbitals for the case of the separated atoms have this desired property. In addition, the properties of the separated atoms form a useful basis for the discussion of any molecular property from the point of view of determining the changes which have been brought about by the formation of the chemical bond.

Suppose we label the two nuclei of a homonuclear diatomic molecule as A and B and consider the forces exerted on the A nucleus by the pair of electrons in a molecular orbital when the orbital has assumed its limiting form for the separated atoms. At this limit, one electron correlates with an atomic orbital on nucleus A and the other with an identical orbital on nucleus B. The discussion of the forces exerted on the nuclei by such a limiting charge distribution is similar to the discussion given previously in Section 6 for the case of two separated hydrogen atoms. The charge density in the orbital on the A nucleus will not exert a force on that nucleus since an undistorted atomic orbital is centrosymmetric with respect to its nucleus. The charge density of the electron which correlates with the B nucleus will exert a force on the A nucleus equivalent to that obtained by concentrating the charge density to a point at the position of the B nucleus. The electron which correlates with the B nucleus will screen one of the nuclear charges of B from the A nucleus. Thus the force exerted on one of the nuclei by the pair of electrons in a molecular orbital for the limiting state of the separated atoms is equivalent to that obtained by placing one negative charge at the position of the second nucleus. *Of the pair of electrons in a given homonuclear molecular orbital, only one is effective in binding either nucleus in the limit of the separated atoms*.

If there are a total of $N$ electrons in the molecule, there will be $N/2$ occupied molecular orbitals since each molecular orbital contains a pair of electrons. Therefore, a total of $N/2$ electrons will correlate with each nucleus. The molecule dissociates into two neutral atoms each with a nuclear charge $Z = N/2$. Thus the $N/2$ electrons which correlate with each nucleus will exactly cancel the nuclear charge of both nuclei; the final force on the nuclei will be zero.

The limiting force exerted on the A nucleus by the pair of electrons in a molecular orbital is $(Z_A e^2/R^2)(-1)$, that is, **the force is equivalent to placing one negative charge at the position of the B nucleus**. Thus we may express the total limiting force on nucleus A as the product of $(Z_A e^2/R^2)$ with the difference between the number of positive charges on the B nucleus $(Z_B)$ and **the number of electronic charges which are effective in exerting a force on the A nucleus**, $(N/2)$:

$$F_A = \frac{Z_A e^2}{R^2}\left(Z_B - (N/2)\right)$$

The quantity $N/2$ is the ***charge equivalent*** of the electronic force, the number of charges which when placed at the position of one nucleus exerts the same force on the second nucleus as does the actual charge distribution. The zero force between the separated atoms may be viewed as a result of each electron screening one nuclear charge on one nucleus from the nuclear charge of the other atom.

As the atoms approach one another to form a chemical bond, the atomic distributions on each atom become increasingly distorted and charge density is transferred to the binding region between the nuclei. There is a net force of attraction on the nuclei. We may again express the electronic force on the A nucleus in terms of its charge equivalent by multiplying the electronic force of attraction by $R^2/Z_A e^2$. Because of the distortion of the atomic orbital densities and the formation of molecular orbitals concentrating charge density in the region between the nuclei, the charge density of more than just one electron in each molecular orbital is effective in binding the nuclei. Thus at intermediate $R$ values the charge equivalent of the electronic force exceeds its limiting value of $N/2$ required to screen the nuclear charge and the result is a force of attraction drawing the nuclei together.

When the distance between the nuclei is further decreased to its equilibrium value the force on the nuclei is again equal to zero. At this point, as when $R$ equals infinity, the charge equivalent of the electronic force equals the nuclear charge. However, the state of electrostatic equilibrium in the molecule does not correspond to the charge density in each molecular orbital effectively screening one nuclear charge as it did in the separated atoms. Instead the charge equivalent of the density in each molecular orbital may be less than, equal to, or greater than the limiting value of unity observed for the separated atoms.

An orbital which concentrates charge density in the binding region will exert a force on the nuclei with a charge equivalent greater than unity. Such an orbital is called **binding** as it does more than simply screen one unit of positive charge on each nucleus. The charge equivalent of an orbital which concentrates density in the antibinding regions will be less than the separated atom value of unity. Such an orbital is termed **antibinding** as the charge density does not screen one unit of positive charge on each nucleus. When the charge equivalent of the force equals unity, it implies that the orbital charge density plays the same role in the molecule as in the separated atoms, that of screening one nuclear charge on B from nucleus A. An orbital with this property is termed **nonbinding**.

Thus, by comparing the charge equivalent of the force exerted by the density in each molecular orbital with its separated atom value of unity, we may classify the orbitals as binding, antibinding or nonbinding:

| Binding orbital | � | charge equivalent > unity |
|---|---|---|
| Nonbinding orbital | � | charge equivalent ~ unity |
| Antibinding orbital | � | charge equivalent < unity |

Table 8-1. Charge Equivalents of the Orbital Forces in Homonuclear Diatomic Molecules

| Molecule | $1s_g$ | $1s_u$ | $2s_g$ | $2s_u$ | $1p_u$ | $3s_g$ | $1p_g$ | Sum = $Z_B$ | $R_e$ (au) |
|---|---|---|---|---|---|---|---|---|---|
| $He_2$ | 1.78 | -0.42 | | | | | | 1.36* | (1.750)* |
| $Li_2$ | 0.70 | 0.68 | 1.62 | | | | | 3.00 | 5.051 |
| $Be_2$ | 1.05 | 1.08 | 2.00 | -0.40 | | | | 3.68* | (3.500)* |
| $B_2$ | 0.98 | 0.98 | 2.32 | -0.48 | 1.20 | | | 5.00 | 3.005 |
| $C_2$ | 0.97 | 0.95 | 2.25 | -0.43 | 1.13� | | | 6.00 | 2.348 |
| $N_2$ | 1.15 | 1.08 | 2.67 | -0.47 | 1.21� | 0.15 | | 7.00 | 2.068 |
| $O_2$ | 1.23 | 1.14 | 2.94 | -0.52 | 1.30� | 0.18 | 0.43 | 8.00 | 2.282 |
| $F_2$ | 1.24 | 1.12 | 2.45 | -0.16 | 1.24� | 0.52 | 0.67� | 9.00 | 2.680 |

*$He_2$ and $Be_2$ form only weakly bound van der Waals molecules for relatively large internuclear seperations. The values of $R$ quoted for these molecules are the internuclear distances used in the calculation of the charge equivalents listed in the table.

�All of the values are quoted for double occupation of the orbitals for comparative purposes. The values marked by �are to be doubled to obtain the total electronic force as they refer to filled p orbitals.

The charge equivalents of the orbital forces for some homonuclear diatomic molecules are given in Table 8-1. Except for $He_2$ and $Be_2$ the sum of the charge equivalents equals the nuclear charge in each case as required for electrostatic equilibrium and the formation of a stable molecule. The charge equivalents of the orbital forces provide a quantitative measure of the role each orbital density plays in the binding of the nuclei in the molecule.

The $1s_g$ orbital in $He_2$ is binding. Of the two electronic charges in the $1s_g$ orbital, 1.78 of them are effective in binding the nuclei when $R$ = 1.75 $a_o$ as opposed to the one electronic charge which exerts a force when $R$ = ¥. The $1s_u$ charge density, however, is strongly antibinding. The transfer of charge density to the antibinding regions in the formation of the $1s_u$ orbital in $He_2$ is so great that the charge equivalent is negative in sign. The antibinding nature of this orbital is very evident in the form of its charge distribution (Fig. 8-6). Not only does the charge density in this orbital no longer screen a positive charge on one nucleus from the other, it actually exerts a repulsive force on the nuclei, one which pulls the nuclei further apart from one another. The total eletronic force exerted on a nucleus in $He_2$ at $R$ = 1.75 $a_o$ is equivalent to placing (1.78 - 0.42) = 1.36 negative charges at the position of the second nucleus. Since the nuclear charge on helium is 2.00, a total of (2.00 - 1.36) = 0.64 positive charges on the second nucleus are left unscreened by the charge density. The net force on the nuclei is thus a repulsive one.

The $1s_g$ and $1s_u$ molecular orbitals are inner shell orbitals in the remaining molecules, $Li_2$ to $F_2$. An idealized inner shell molecular orbital has a charge equivalent of unity, the same as the separated atom value. Each electron should be localized in an atomic-like distribution and screen one nuclear charge. This is illustrated by the $1s_g$ and $1s_u$ charge density maps for the $O_2$ molecule (Fig. 8-8).

The charge equivalents of the $1s_g$ and $1s_u$ orbital densities for $Li_2$ (Fig. 8-7) are significantly less than unity. While these orbitals are not as contracted around the nuclei in $Li_2$ as they are in $O_2$ (the nuclear charge for lithium is three compared to eight for oxygen), they are still atomic-like with no effective overlap between the two centres. The charge equivalents are less than the screening value of unity because each of the atomic-like distributions is polarized into the antibinding region and exerts an antibinding force on the nucleus on which it is centred. The charge equivalents for the $1s_g$ and $1s_u$ density distributions in the remaining molecules are close to unity indicating that they are essentially nonbinding inner shell orbitals. The slight binding character of the $1s_g$ charge density in $O_2$ and $F_2$ is the result of small inward polarizations of the atomic-like distributions.

The $2s_g$ molecular charge density is binding in every molecule. A comparison of the charge equivalents shows that the $2s_g$ charge density is the most binding of all the molecular orbitals in this series of molecules. The charge equivalent of the force exerted by the $2s_g$ density in $O_2$ is almost three times greater than it is for the separated oxygen atoms. This is a result of the large amount of charge density accumulated in the binding region by this orbital (Fig. 8-8).

The $2s_u$ orbital is uniformly strongly antibinding. The extreme concentration of charge density in the antibinding regions observed for the $2s_u$ orbital is typified by the $2s_u$ density plot for $O_2$ (Fig. 8-8). It is obvious that the density in this orbital, as that in the $1s_u$ orbital of $He_2$ will pull the nuclei away from one another rather than bind them together. Notice that $Be_2$ is analogous to $He_2$ except that the $2s_g$ and $2s_u$ orbitals rather than the $1s_g$ and $1s_u$ orbital densities are involved. In $Be_2$ the $1s_g$ and $1s_u$ densities are nonbinding and together simply screen two nuclear charges on each atom. The $2s_g$ density exerts a binding force equivalent to one electronic charge in excess of the simple screening effect. The $2s_u$ orbital density, however, leaves a single nuclear charge unscreened which cancels the net attractive force of the $2s_g$ density and in addition exerts an antibinding force equivalent to increasing the nuclear charge by 0.40 units. The beryllium molecule is therefore unstable at this value of R.

The $1p_u$ orbital density is binding in each case, but only weakly so. The charge density of a $p_u$ molecular orbital is concentrated around the internuclear axis rather than along it as in a $s_g$ molecular orbital. Consequently the $1p_u$ density distributions exert only weak binding forces on the nuclei. In fact, the inner shell $1s_g$ charge density in $F_2$ exerts as large a binding force on the nuclei as does a pair of electrons in the $1p_u$ orbital.

The charge equivalent of the $3s_g$ orbital density is less than unity in the three cases where it is occupied. Thus it is an antibinding orbital even though it is of $s_g$ symmetry. The charge density contours for this orbital in $O_2$ (Fig. 8-8) show that charge density is accumulated in the region between the nuclei as expected for an orbital of $s_g$ symmetry. However, the $3s_g$ orbital correlates with a $2ps$ atomic orbital on each nucleus. The strong participation of the $2ps$ orbitals in the molecular orbital is evidenced by the node at each nucleus and by the concentration of charge density on both sides of each nucleus. The concentration of charge in the antibinding regions nullifies the binding effect arising from the accumulation of charge density in the region between the nuclei. The net result is an attractive force considerably less than that required to screen one positive charge on each nucleus.

The $1p_g$ orbital density is only weakly antibinding just as the $1p_u$ density is only weakly binding. The formation of the $1p_g$ orbital results in the removal of charge density from the binding region, not from along the internuclear axis but instead from regions around the axis. Notice that unlike the $2s_u$ orbital densities, the $1p_g$ charge density is antibinding only in the sense that it does not screen its share of nuclear charge, not because it exerts a force which draws the nuclei apart.

# 8.6: Molecular Orbitals for Heteronuclear Molecules

The molecular orbitals which describe the motion of a single electron in a molecule containing two unequal nuclear charges will not exhibit the $g$ and $u$ symmetry properties of the homonuclear diatomic case. The molecular orbitals in the heteronuclear case will in general be concentrated more around one nucleus than the other. The orbitals may still be classified as s, p, d, etc. because the molecular axis is still an axis of symmetry.

In simple numerical calculations the molecular orbitals are sometimes approximated by the sum and difference of single atomic orbitals on each centre, their limiting form. The molecular orbital is said to be approximated mathematically by a linear combination of atomic orbitals and the technique is known as the LCAO-MO method. It must be understood that the LCAO-MO method using a limited number of atomic orbitals provides only an approximation to the true molecular orbital. The concept of a molecular orbital is completely independent of the additional concept of approximating it in terms of atomic orbitals, except for the case of the separated atoms. However, by using a large number of atomic orbitals centred on each nucleus in the construction of a single molecular orbital sufficient mathematical flexibility can be achieved to approximate the exact form of the molecular orbital very closely.

While the LCAO approximation using a limited number of atomic orbitals is in general a poor one for quantitative purposes, it does provide a useful guide for the prediction of the qualitative features of the molecular orbital. There are two simple conditions which must be met if atomic orbitals on different centres are to interact significantly and form a ***molecular orbital which is delocalized over the whole molecule***. Both atomic orbitals must have approximately the same orbital energy and they must possess the same symmetry characteristics with respect to the internuclear axis. We shall consider the molecular orbitals in LiH, CH and HF to illustrate how molecular orbital theory describes the bonding in heteronuclear molecules, and to see how well the forms of the orbitals in these molecules can be rationalized in terms of the symmetry and energy criteria set out above.

The $1s$ and $2s$ atomic orbitals and the $2p$ orbital which is directed along the bond axis are all left unchanged by a rotation about the symmetry axis. They may therefore form molecular orbitals of s symmetry in the diatomic hydride molecules. The $2p$ orbitals which are perpendicular to the bond axis will be of p symmetry and may form molecular orbitals with this same symmetry. The energies and symmetry properties of the relevant atomic orbitals and the electronic configurations of the atoms and molecules are given in Table 8-2.

Table 8-2.
Atomic Orbital Energies and Symmetry Properties

| Energy (au) | | | | | Symmetry |
|---|---|---|---|---|---|
| | H | Li | C | F | |
| $1s$ | -0.5 | -2.48 | -11.33 | -26.38 | s |
| $2s$ | | -0.20 | -0.71 | -1.57 | s |
| $2p$ | | | -0.43 | -0.73 | s and p |
| Atomic Configurations | | | | Molecular Configurations | |
| Li | $1s^2 2s^1$ | | | LiH | $1s^2 2s^2$ |
| C | $1s^2 2s^2 2p^2$ | | | CH | $1s^2 2s^2 3s^2 1p^1$ |
| F | $1s^2 2s^2 2p^5$ | | | HF | $1s^2 2s^2 3s^2 1p^4$ |

Density diagrams of the molecular orbitals for the LiH, CH, and HF molecules are illustrated in Fig. 8-9.
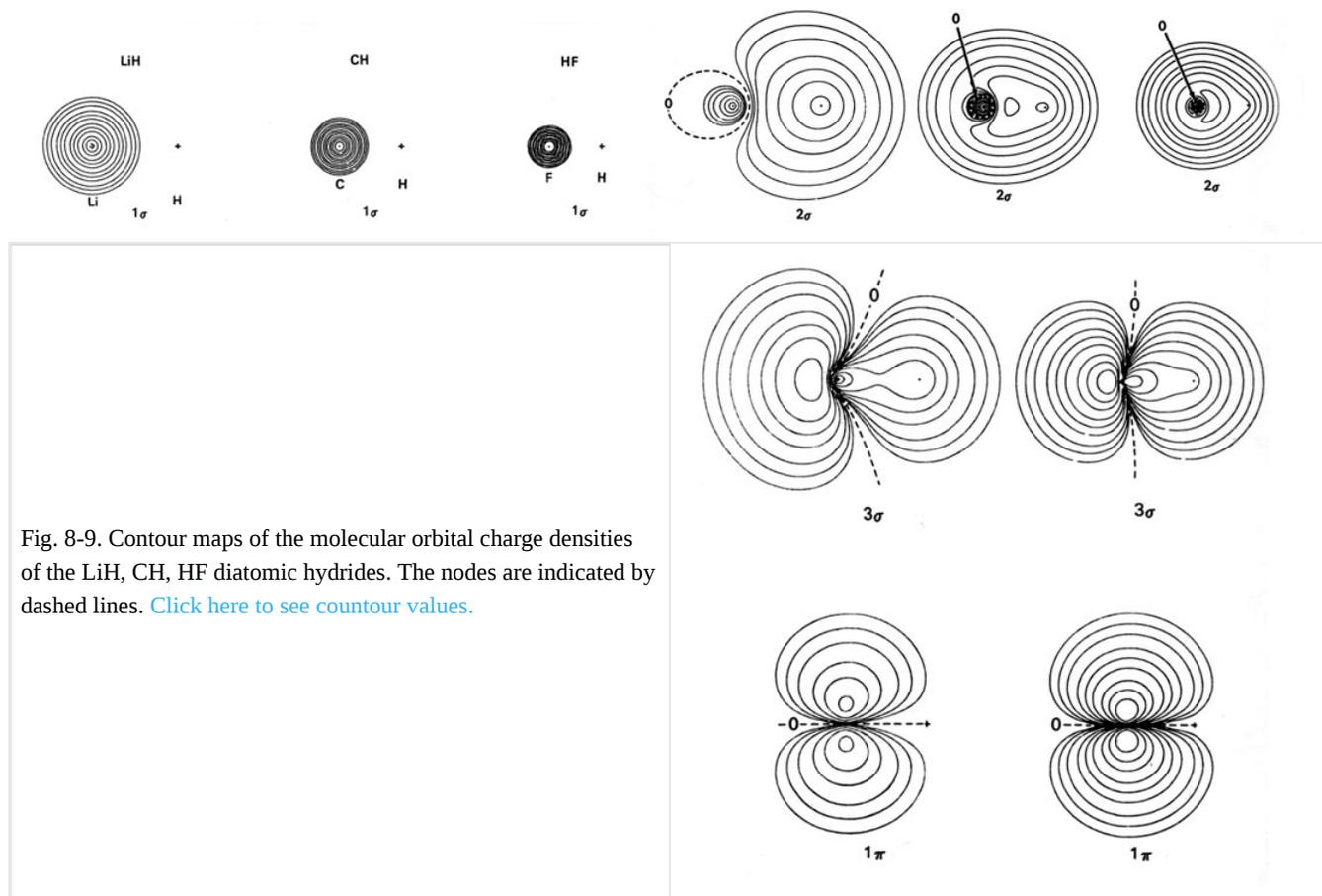
Fig. 8-9. Contour maps of the molecular orbital charge densities of the LiH, CH, HF diatomic hydrides. The nodes are indicated by dashed lines. Click here to see countour values.

The 1$s$ orbital energies of Li, C and F all lie well below that of the H 1$s$ orbital. The charge densities of these inner shell orbitals are tightly bound to their respective nuclei. They should not, therefore, be much affected by the field of the proton or interact significantly with the H 1$s$ orbital. The molecular orbital of lowest energy in these molecules, the ls molecular orbital, should be essentially nonbinding and resemble the doubly-occupied 1$s$ atomic orbital on Li, C and F respectively. These predictions are borne out by the ls orbital density distributions (Fig. 8-9). They consist of nearly spherical contours centred on the Li, C and F nuclei, the radius of the outer contour being less than the bond length in each case. The forces exerted on the proton by the lscharge distributions are equivalent to placing two negative charges at the position of the heavy nucleus in each case. The charge density in the ls molecular orbital simply screens two of the nuclear charges on the heavy nucleus from the proton. This same screening effect is obtained for the 1$s^2$ charge distribution when the molecules dissociate into atoms. Thus the 1$s$ atomic orbitals of Li, C and F are not much affected by the formation of the molecule and the ls charge density is nonbinding as far as the proton is concerned. The ls atomic-like distributions are slightly polarized. In LiH the ls density is polarized away from the proton to a significant extent while in CH and HF it is slightly polarized towards the proton. Thus the 1s charge density exerts an antibinding force on the Li nucleus and a small binding force on the C and F nuclei.

The energies of the 2$s$ atomic orbitals decrease (the electron is more tightly bound) from Li to F as expected on the basis of the increase in the effective nuclear charge from Li to F. The 2$s$ orbital on Li is large and diffuse and will overlap extensively with the 1$s$ orbital on H. However, the 2$s$ electron on Li is considerably less tightly bound than is the 1$s$ electron on H. Thus the charge density of the 2$s$ molecular orbital in LiH will be localized in the region of the proton corresponding to the transfer of the 2$s$electron on Li to the region of lower potential energy offered by the 1$s$ orbital on H. This is approximately correct as shown by the almost complete concentration of the charge density in the region of the proton in the 2s orbital density map for LiH. The small amount of density which does remain around the Li nucleus is polarized away from the proton. The 1s and 2s densities are polarized in a direction counter to the direction of charge transfer as required in ionic binding. The inwardly polarized accumulation of 2s charge density centred on the proton binds both nuclei.

The 1s molecular orbital in LiH is to a good approximation a polarized doubly-occupied 1$s$ orbital on Li, and the 2s molecular orbital is, to a somewhat poorer approximation, a doubly-occupied and polarized 1$s$ orbital on H. Our previous discussion of the bonding in LiH indicated that the binding is ionic, corresponding to the description Li$^+$(1$s^2$)H$^-$(1$s^2$). The molecular orbital description of an ***ionic bond*** is similar in that the molecular orbitals in the ionic extreme are localized in the regions of the individual nuclei, rather than being delocalized over both nuclei as they are for a covalent bond.

The matching of the 2$s$ orbital energy with the H 1$s$ orbital energy is closer in the case of C than it is for Li. Correspondingly, the 2s charge density in CH is delocalized over both nuclei rather than concentrated in the region of just one nucleus as it is in the LiH molecule. There is a considerable buildup of charge density in the binding region which is shared by both nuclei. The 2s charge density exerts a large binding force on both the H and C nuclei. This is the molecular orbital description of an interaction which is essentially covalent in character.

The 2$s$ orbital energy of F is considerably lower than that of the H 1$s$ orbital. The 2s orbital charge density in HF, therefore, approximately resembles a localized 2$s$ orbital on F. It is strongly polarized and distorted by the proton, but the amount of charge transferred to the region between the nuclei is not as large as in CH. The 2s orbital in HF plays a less important role in binding the proton than it does in CH.

The 3s molecular orbital in CH and HF will result primarily from the overlap of the 2$ps$ orbital on C and F, with the 1$s$ orbital on H. The 2$p$-like character of the 3s molecular orbital in both CH and HF is evident in the density diagrams (Fig. 8-9). In CH the 1$s$ orbital of H interacts strongly with both the 2$s$ and 2$ps$ orbitals on C. In terms of the forces exerted on the nuclei, the 2$s$ charge density is strongly binding for both C and H, while the 3s charge density is only very weakly binding for H and is actually antibinding for the C. This antibinding effect is a result of the large accumulation of charge density in the region behind the C nucleus.

In HF, the H 1$s$ orbital interacts only slightly with the 2$s$ orbital on F, but it interacts very strongly with the 2$ps$ orbital in the formation of the 3s molecular orbital. The 3s charge density exerts a large binding force on the proton. Thus the proton is bound primarily by the 2s charge density in CH and by the 3s charge density in HF. The 3s charge density in HF is primarily centred on the F nucleus and roughly resembles a 2$ps$ orbital. Although no density contours are actually centred on the proton, the proton is embedded well within the orbital density distribution. This is a molecular orbital description of a highly polar bond.

The 3s orbital charge density exerts a force on the F and C nuclei in a direction away from the proton. The molecular orbitals which involve $p$s orbitals are characteristically strongly polarized in a direction away from the bond in the region of the nucleus on which the $p$ orbital is centred. Compare, for example, the 3s orbitals of CH and HF with the 3s$_g$ molecular orbital of the homonuclear diatomic molecules.

When the C and H atoms are widely separated, we can consider the carbon atom to have one 2$p$ electron in the 2$ps$ orbital which lies along the bond axis, and the second 2$p$ electron in one of the 2$pp$ orbitals which are perpendicular to the bond. The F atom has five 2$p$ electrons and of these one may be placed in the 2$ps$ orbital; the remaining four 2$p$ electrons will then completely occupy the 2$pp$ orbitals. The singly-occupied 2$ps$ orbitals on F and C eventually interact with the singly-occupied 1$s$ orbital on H to form the doubly-occupied 3s molecular orbital in HF and CH. The remaining 2$p$ electrons, those of p symmetry, will occupy the 1p molecular orbital. The H atom does not possess an orbital of p symmetry in its valence shell and the vacant 2$pp$orbital on H is too high in energy (-0.125 au) to interact significantly with the 2$pp$ orbitals on C and F. Thus the 1p molecular orbital is atomic-like, centred on the F and C nuclei and is essentially nonbinding (Fig. 8-9). The 1p molecular orbital resembles a 2$pp$ atomic orbital in each case, but one which is polarized in the direction of the proton.

The 1p orbitals of CH and HF illustrate an interesting and general result. In the formation of a bond between different atoms, the charge density in the s orbitals is transferred from the least to the most electronegative atom. However, the charge density of p symmetry, if any is present, is invariably transferred, or at least polarized, in the opposite direction, towards the least electronegative atom. Although the amount of charge density transferred is less in the formation of the p orbitals than in the s orbitals, one effect increases with the other. Thus the polarization is more pronounced in HF than in CH.

The three examples considered above demonstrate the essential points of a molecular orbital description of the complete range of chemical bonding. In the ionic extreme of LiH the charge density of the bonding molecular orbital is localized around the proton. In CH the valence charge density is more evenly shared by both nuclei and the bond is covalent. The motions of the electrons in HF are governed largely by the potential field of the F nucleus. This is evidenced by the appearance of the molecular orbital charge distributions. The proton is, however, encompassed by the valence charge density and the result is a polar bond.

# 8.7: Molecular Orbitals for Polyatomic Molecules

The concept of a molecular orbital is readily extended to provide a description of the electronic structure of a polyatomic molecule. Indeed molecular orbital theory forms the basis for most of the quantitative theoretical investigations of the properties of large molecules.

In general a molecular orbital in a polyatomic system extends over all the nuclei in a molecule and it is essential, if we are to understand and predict the spatial properties of the orbitals, that we make use of the symmetry properties possessed by the nuclear framework. An analysis of the molecular orbitals for the water molecule provides a good introduction to the way in which the symmetry of a molecule determines the forms of the molecular orbitals in a polyatomic system.

There are three symmetry operations which transform the nuclear framework of the water molecule into itself and hence leave the nuclear potential field in which the electrons move unchanged (Fig. 8-10).
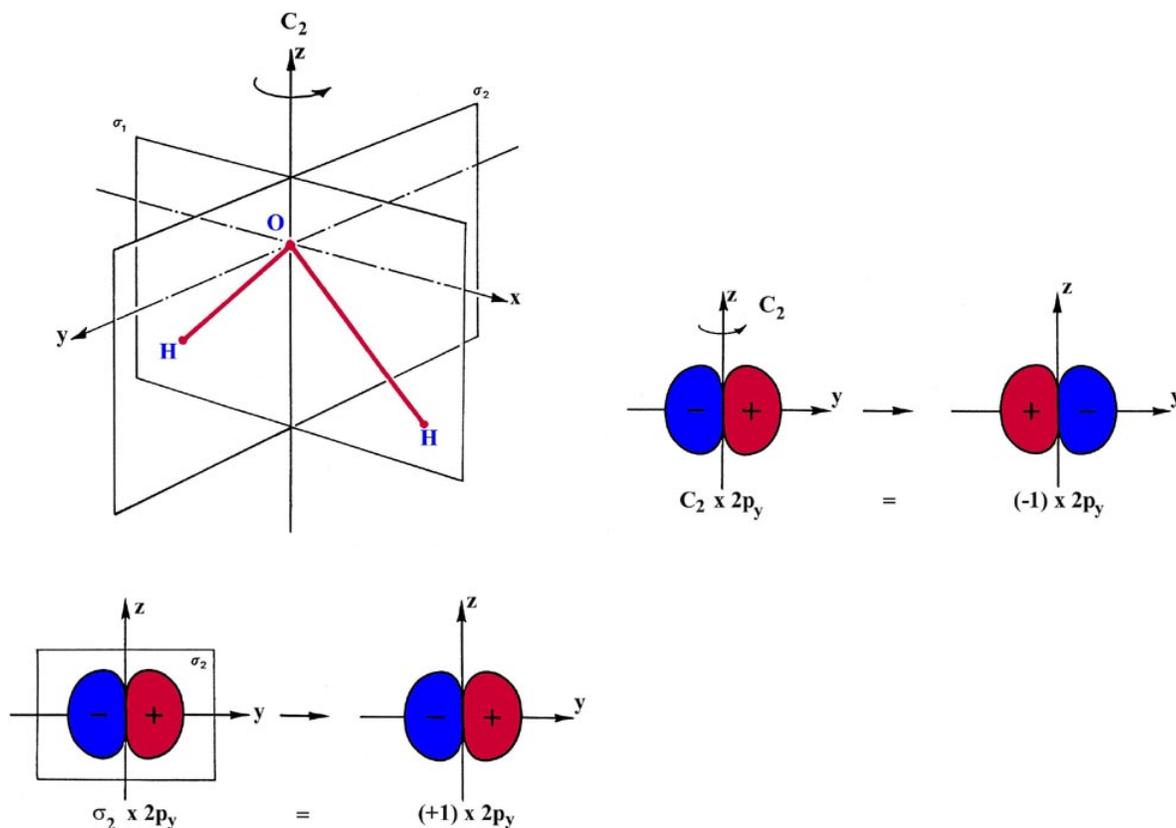


Fig. 8-10. Symmetry elements for $H_2O$. The bottom two diagrams illustrate the transformations of the $2p_y$ orbital on oxygen under the $C_2$ and $s_2$ symmetry operations.

For each symmetry operation there is a corresponding symmetry *element*. The symmetry elements for the water molecule are a two-fold axis of rotation $C_2$ and two planes of symmetry $s_1$ and $s_2$ (Fig. 8-10). A rotation of 180° about the $C_2$ axis leaves the oxygen nucleus unchanged and interchanges the two hydrogen nuclei. A reflection through the plane labelled $s_1$ leaves all the nuclear positions unchanged while a reflection through $s_2$ interchanges the two protons. The symmetry operations associated with the three symmetry elements either leave the nuclear positions unchanged or interchange symmetrically equivalent (and hence indistinguishable) nuclei. Every molecular orbital for the water molecule must, under the same symmetry operations, be left unchanged or undergo a change in sign.

Similarly we may use the symmetry transformation properties of the atomic orbitals on oxygen and hydrogen together with their relative orbital energy values to determine the primary atomic components of each molecular orbital in a simple LCAO approximation to the exact molecular orbitals. Only atomic orbitals which transform in the same way under the symmetry operations may be combined to form a molecular orbital of a given symmetry. The symmetry transformation properties of the

atomic orbitals on oxygen and hydrogen are given in Table 8-3. A value of +1 or -1 opposite a given orbital in the table indicates that the orbital is unchanged or changed in sign respectively by a particular symmetry operation.

Table 8-3: Symmetry Properties and Orbital Energies for the Water Molecule

| Atomic Orbitals on Oxygen | Symmetry Behaviour Under | | | Symmetry Classification | | Orbital Energy (au) |
|---|---|---|---|---|---|---|
| | $s_2$ | $s_1$ | $s_2$ | | | |
| $1s$ | +1 | +1 | +1 | $a_1$ | | -20.669 |
| $2s$ | +1 | +1 | +1 | $a_1$ | | -1.244 |
| $2p_z$ | +1 | +1 | +1 | $a_1$ | } | |
| $2p_x$ | -1 | +1 | -1 | $b_2$ | | -0.632 |
| $2p_y$ | -1 | -1 | +1 | $b_1$ | | |
| Atomic Orbitals on Hydrogen | | | | | | |
| $(1s_1 + 1s_2)$ | +1 | +1 | +1 | $a_1$ | } | |
| $(1s_1 - 1s_2)$ | -1 | +1 | -1 | $b_2$ | | -0.500 |

| Molecular Orbital Energies for $H_2O$ (au) | | | | |
|---|---|---|---|---|
| $1a_1$ | $2a_1$ | $1b_2$ | $3a_1$ | $1b_1$ |
| -20.565 | -1.339 | -0.728 | -0.595 | -0.521 |

The $1s$, $2s$ and $2p_z$ orbitals of oxygen are symmetric (i.e., unchanged) with respect to all three symmetry operations. They are given the symmetry classification $a_1$. The $2p_x$ orbital, since it possesses a node in the $s_2$ plane (and hence is of different sign on each side of the plane) changes sign when reflected through the $s_2$ plane or when rotated by 180° about the $C_2$ axis. It is classified as a $b_2$ orbital. The $2p_y$ orbital is antisymmetric with respect to the rotation operator and to a reflection through the $s_1$ plane. It is labelled $b_1$.

The hydrogen $1s$ orbitals when considered separately are neither unchanged nor changed in sign by the rotation operator or by a reflection through the $s_2$ plane. Instead both these operations interchange these orbitals. The hydrogen orbitals are said to be symmetrically equivalent and when considered individually they do not reflect the symmetry properties of the molecule. However, the two linear combinations $(1s_1 + 1s_2)$ and $(1s_1 - 1s_2)$ do behave in the required manner. The former is symmetric under all three operations and is of $a_1$ symmetry while the latter is antisymmetric with respect to the rotation operator and to a reflection through the plane $s_2$ and is of $b_2$ symmetry.

The molecular orbitals in the water molecule are classified as $a_1$, $b_1$ or $b_2$ orbitals, as determined by their symmetry properties. This labelling of the orbitals is analogous to the use of the s-p and $g$-$u$ classification in linear molecules. In addition to the symmetry properties of the atomic orbitals we must consider their relative energies to determine which orbitals will overlap significantly and form delocalized molecular orbitals.

The $1s$ atomic orbital on oxygen possesses a much lower energy than any of the other orbitals of $a_1$ symmetry and should not interact significantly with them. The molecular orbital of lowest energy in $H_2O$ should therefore correspond to an inner shell $1s$atomic-like orbital centred on the oxygen. This is the first orbital of $a_1$ symmetry and it is labelled $1a_1$. Reference to the forms of the charge density contours for the $1a$, molecular orbital (Fig. 8-11) substantiates the above remarks regarding the properties of this orbital.

**MOLECULAR CHARGE DISTRIBUTION**
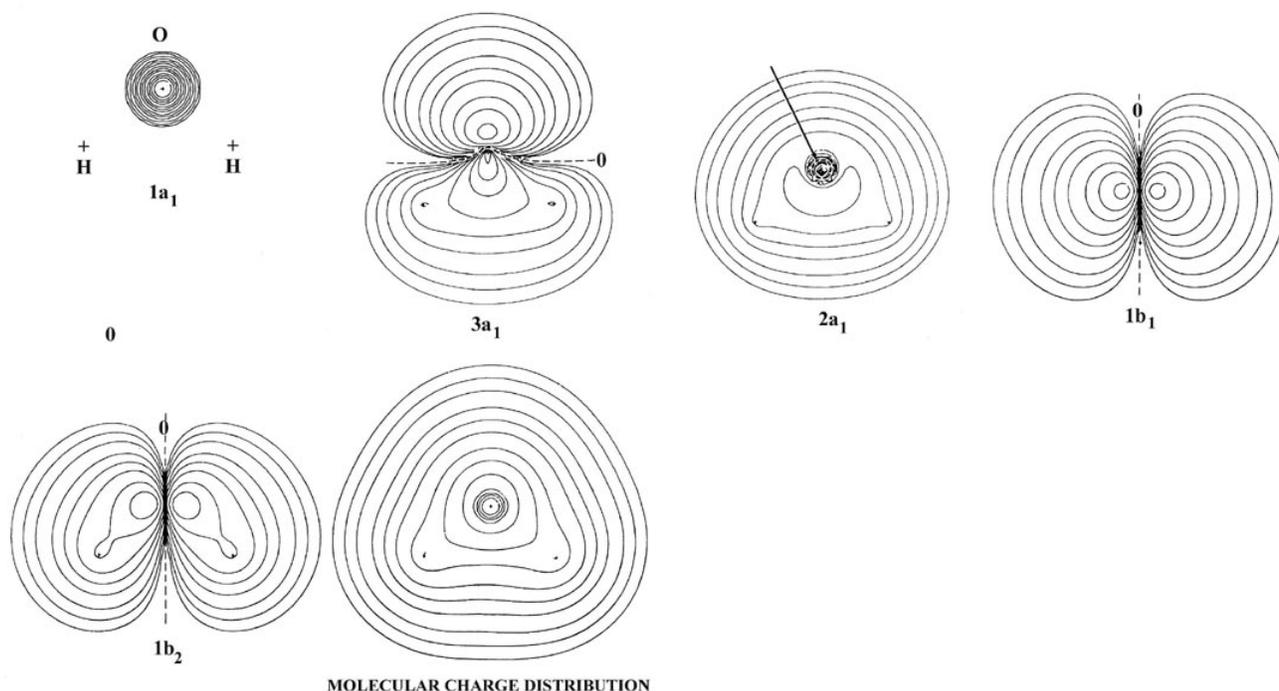
Fig. 8-11. Contour maps of the molecular orbital charge densities for $H_2O$. The maps for the $1a_1$, $2a_1$, $3a_1$ and $1b_2$ orbitals (all doubly-occupied) are shown in the plane of the nuclei. The $1b_1$ orbital has a node in this plane and hence the contour map for the $1b_1$ orbital is shown in the plane perpendicular to the molecular plane. The total molecular charge density for $H_2O$ is also illustrated. The density distributions were calculated from the wave function determined by R. M. Pitzer, S. Aung and S. I. Chan, J. Chem. Phys. *49*, 2071 (1968). Click here for contour values.

Notice that the orbital energy of the $1a_1$ molecular orbital is very similar to that for the $1s$ atomic orbital on oxygen. The $1a_1$ orbital in $H_2O$ is, therefore, similar to the $1s$ inner shell molecular orbitals of the diatomic hydrides.

The atomic orbital of next lowest energy in this system is the $2s$ orbital of $a_1$ symmetry on oxygen. We might anticipate that the extent to which this orbital will overlap with the $(1s_1 + 1s_2)$ combination of orbitals on the hydrogen atoms to form the $2a_1$ molecular orbital will be intermediate between that found for the 2s molecular orbitals in the diatomic hydrides CH and HF (Fig. 8-9). The 2s orbital in CH results from a strong mixing of the $2s$ orbital on carbon and the hydrogen $1s$ orbital. In HF the participation of the hydrogen orbital in the 2s orbital is greatly reduced, a result of the lower energy of the $2s$ atomic orbital on fluorine as compared to that of the $2s$ orbital on carbon.

Aside from the presence of the second proton, the general form and nodal structure of the $2a_1$ density distribution in the water molecule is remarkably similar to the 2s distributions in CH and HF, and particularly to the latter. The charge density accumulated on the bonded side of the oxygen nucleus in the $2a_1$ orbital is localized near this nucleus as the corresponding charge increase in the 2s orbital of HF is localized near the fluorine. The charge density of the $2a_1$ molecular orbital accumulated in the region between the three nuclei will exert a force drawing all three nuclei together. The $2a_1$ orbital is a binding orbital.

Although the three $2p$ atomic orbitals are degenerate in the oxygen atom the presence of the two protons results in each $2p$ orbital experiencing a different potential field in the water molecule. The nonequivalence of the $2p$ orbitals in the water molecule is evidenced by all three possessing different symmetry properties. The three $2p$ orbitals will interact to different extents with the protons and their energies will differ.

The $2p_x$ orbital interacts most strongly with the protons and forms an orbital of $b_2$ symmetry by overlapping with the $(1s_1 - 1s_2)$ combination of 1s orbitals on the hydrogens. The charge density contours for the $1b_2$ orbital indicate that this simple LCAO description accounts for the principal features of this molecular orbital. The $1b_2$ orbital concentrates charge density along each O-H bond axis and draws the nuclei together. The charge density of the $1b_2$ orbital binds all three nuclei. In terms of the forces exerted on the nuclei the $2a_1$ and $1b_2$ molecular orbitals are about equally effective in binding the protons in the water molecule.

The $2p_z$ orbital may also overlap with the hydrogen 1s orbitals, the $(1s_1 + 1s_2)$ $a_1$ combination, and the result is the $3a_1$ molecular orbital. This orbital is concentrated along the z-axis and charge density is accumulated in both the bonded and nonbonded sides of

the oxygen nucleus. It exerts a binding force on the protons and an antibinding force on the oxygen nucleus, a behaviour similar to that noted before for the 3s orbitals in CH and HF.

The $2p_y$ orbital is not of the correct symmetry to overlap with the hydrogen 1$s$ orbitals. To a first approximation the $1b_1$ molecular orbital will be simply a $2p_y$ atomic orbital on the oxygen, perpendicular to the plane of the molecule. Reference to Fig. 8-11indicates that the $1b_1$ orbital does resemble a $2p$ atomic orbital on oxygen but one which is polarized into the molecule by the field of the protons. The $1b_1$ molecular orbital of $H_2O$ thus resembles a single component of the 1p molecular orbitals of the diatomic hydrides. The $1b_1$ and the 1p orbitals are essentially nonbinding. They exert a small binding force on the heavy nuclei because of the slight polarization. The force exerted on the protons by the pair of electrons in the $1b_1$ orbital is slightly less than that required to balance the force of repulsion exerted by two of the nuclear charges on the oxygen nucleus. The $1b_1$ and 1p electrons basically do no more than partially screen nuclear charge on the heavy nuclei from the protons.

In summary, the electronic configuration of the water molecule as determined by molecular orbital theory is

$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$
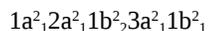
The la$_1$ orbital is a nonbinding inner shell orbital. The pair of electrons in the la$_1$ orbital simply screen two of the nuclear charges on the oxygen from the protons. The $2a_1$, $1b_2$ and $3a_1$ orbitals accumulate charge density in the region between the nuclei and the charge densities in these orbitals are responsible for binding the protons in the water molecule. Aside from being polarized by the presence of the protons, the lb$_1$ orbital is a non-interacting $2p_y$ orbital on the oxygen and is essentially nonbinding.

Before closing this introductory account of molecular orbital theory, brief mention should be made of the very particular success which the application of this theory has had in the understanding of the chemistry of a class of organic molecules called conjugated systems. Conjugated molecules are planar organic molecules consisting of a framework of carbon atoms joined in chains or rings by alternating single and double bonds. Some examples are



butadiene          benzene          naphthalene
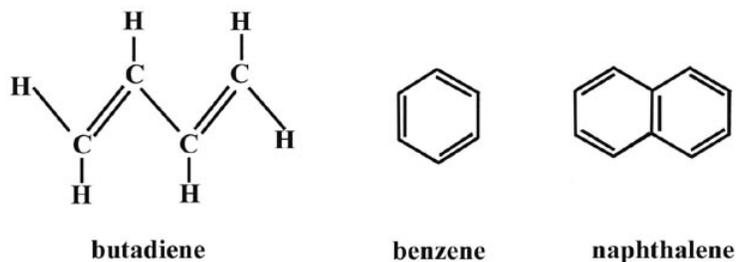
In the structural formulae for the cyclic molecules, e.g., benzene and naphthalene, it is usual not to label the positions of the carbon and hydrogen atoms by their symbols. A carbon atom joined to just two other carbon atoms is in addition bonded to a hydrogen atom, the C�H bond axis being projected out of the ring in the plane of the carbon framework and bisecting the CCC bond angle.

The notion of these molecules possessing alternating single and double bonds is a result of our attempt to describe the bonding in terms of conventional chemical structures. In reality all six C�C bonds in benzene are identical and the C�C bonds in the other two examples possess properties intermediate between those for single and double bonds. In other words, the pairs of electrons forming the second or p bonds are not localized between specific carbon atoms but are delocalized over the whole network of carbon atoms, a situation ideally suited for a molecular orbital description.

We may consider each carbon atom in a conjugated molecule to be s$p^2$ hybridized and bonded through these hybrid orbitals to three other atoms in the plane. This accounts for the bonding of the hydrogens and for the formation of the singly-bonded carbon network. The electrons forming these bonds are called s electrons. The axis of the remaining $2p$ orbital on each carbon atom is directed perpendicular to the plane of the molecule and contains a single electron, called a p electron. A simple adaptation of molecular orbital theory, called Hückel theory, which takes the s bonds for granted and approximates the molecular orbitals of the p electrons in terms of linear combinations of the $2p$p atomic orbitals on each carbon atom, provides a remarkably good explanation of the properties of conjugated molecules. Hückel molecular orbital theory and its applications are treated in a number of books, some of which are referred to at the end of this chapter.

# 8.8: Further Reading

| | |
|---|---|
| 1. | C. A. Coulson, *Valence*, Second Edition, Oxford University Press, 1961. |
| 2. | J. N. Murrell, S. F. A. Kettle and J. M. Tedder, *Valence Theory*, John Wiley and Sons Ltd., 1965. |
| 3. | L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, W. A. Benjamin Inc., 1966, Chapter 1. |

## 8.E: Exercises

| | | |
|---|---|---|
| 1. | (a) | Give the molecular orbital electronic configurations of the $N_2$ and $Ne_2$ molecules. |
| | (b) | Does the difference in the number of occupied bonding and anti-bonding orbitals agree with the number of electron pair bonds which a Lewis structure would predict for these two molecules? |
| 2. | | Complete the correlation diagram (Fig. 8-4) for the homonuclear diatomic molecular orbitals by correlating each molecular orbital with an atomic orbital of the united atom. The symmetry and nodal property of each orbital must be conserved in the correlation. Starting with the molecular orbital of lowest energy each molecular orbital will in turn correlate with the atomic orbital of lowest energy which possesses the same symmetry. All atomic orbitals with even $l$ values are of $g$ symmetry and those with odd $l$ values are of $u$ symmetry. |

The total and molecular orbital charge distributions of the bifluoride ion (FHF)⁻ are shown in Fig. 8-12.



TOTAL MOLECULAR CHARGE DISTRUBUTION



$2\sigma_g$     $2\sigma_u$



$3\sigma_g$     $3\sigma_u$



$1\pi_u$     $1\pi_g$

**ORBITAL CHARGE DISTRIBUTION**

3.
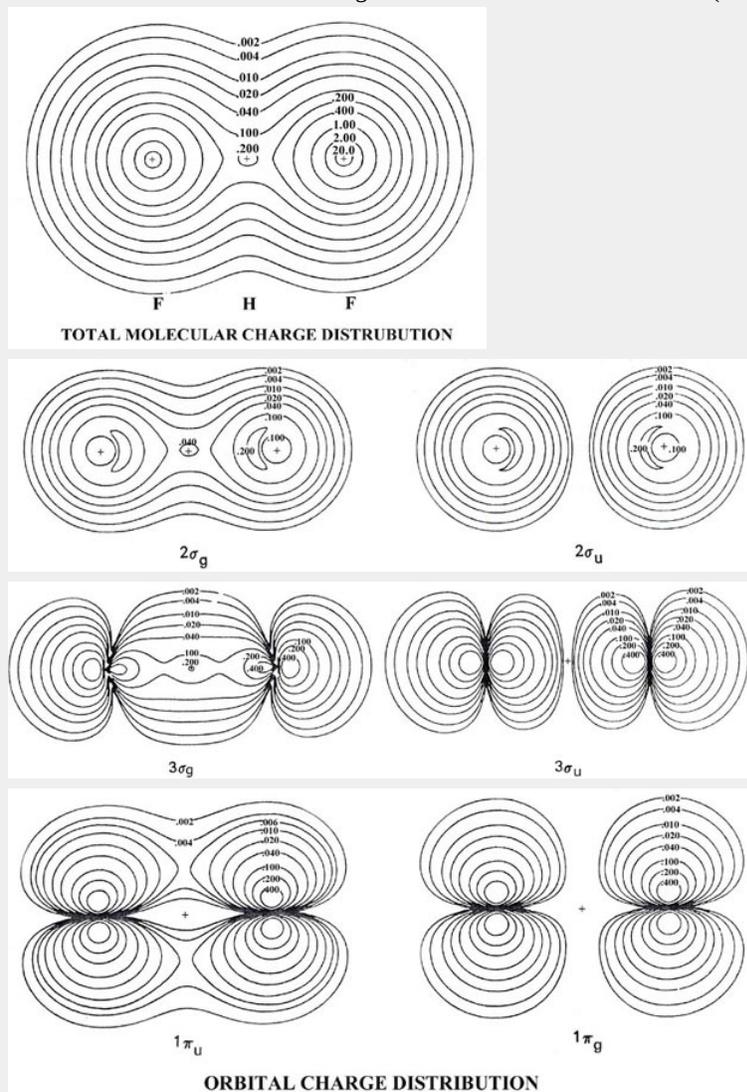
Fig. 8-12. Contour maps of the total molecular charge distribution and the molecular orbital densities for the (FHF)⁻ ion, which has the electronic configuration

$1s_g^2 1s_u^2 2s_g^2 2s_u^2 3s_g^2 1p_u^4 1p_g^4 3s_u^2$. Note that this electron configuration is formally identical to that for the unstable $Ne_2$ molecule. The binding properties of the orbitals in (FHF)⁻ are considerably altered from the homonuclear diatomic case by the presence of the proton, and the ion is a stable species. (The $1s_g$ and $1s_u$ densities are not shown.) (Click here for enlarged picture.)

This negatively-charged molecule results from the reaction of a fluoride ion with a hydrogen fluoride molecule. The molecule has a linear, symmetric structure with the proton forming a bond between the fluorines. The molecular orbitals thus have the same symmetry classification (s or p and *g* or *u*) as do the orbitals for the homonuclear diatomic molecules.

(a) Give a qualitative comparison of the forms and binding properties of the molecular orbitals for (FHF)⁻ with those for the homonuclear diatomic molecule $F_2$. (The molecular orbitals for $F_2$ are very similar to those shown in Fig. 8-8 for $O_2$. The $3s_u$ orbital is not occupied in the ground state of $F_2$.) The $1s_g$ and $1s_u$ molecular orbital densities for (FHF)⁻ are not illustrated since they, like the corresponding orbitals in the homonuclear diatomics, are simply inner shell $1s$ atomic-like distributions centred on the fluorine atom.

(b) Account for the general forms and the primary atomic orbital components of the molecular orbitals in (FHF)⁻ in terms of the simple LCAO approximation using symmetry properties and the relative energies of the orbitals on H and F.

| | |
|---|---|
| 4. | The $CO_2$ molecule is another linear symmetric triatomic molecule possessing the same symmetry properties as do the homonuclear diatomic molecules. The molecular orbitals will be of s or p and *g* or *u* symmetry. From a knowledge of the symmetries of the 1*s*, 2*s* and 2*p* atomic orbitals and their relative energies as given for C and O in Fig. 5-3 predict the electronic configuration of the $CO_2$ molecule in terms of molecular orbitals. |
| 5. | The CO molecule is isoelectronic with the $N_2$ molecule and can be thought of as being derived from $N_2$ by transferring one proton from one N nucleus to the other. The molecular orbitals of CO will be of s or p symmetry but will not exhibit any *g* or *u* dependence since the centre of symmetry has been lost. Derive the electronic configuration of CO by considering how each molecular orbital of $N_2$ will be changed as one N nuclear charge is increased by one unit and the other is decreased by one unit. As a hint, the $1s_g$ orbital of $N_2$ will become the 1s orbital of CO. Reference to Fig. 5-3 shows the 1*s* orbital of O to be considerably more stable than the 1*s* orbital of C. Thus the $1s_g$ orbital of $N_2$ which is concentrated equally in ls-like atomic orbitals on both N nuclei, becomes a 1*s*-like atomic orbital on O. Similarly the $1s_u$ orbital of $N_2$ becomes a 1*s*-like orbital on C. |
| 6. | Using the 1*s*, 2*s*, 2*p*s and 2*p*p atomic orbitals on C and the 1*s* orbital on H discuss the simple LCAO forms expected for the molecular orbitals of the linear form of methylene, $CH_2$. One can consider this problem from the point of view of how the molecular orbitals of CH given in the text would change if a second proton was brought up to the nonbonded side of the C atom. |
| 7. | Construct a correlation diagram for the HF molecule which relates the molecular orbitals with the orbitals of the separated atoms. Arrange the atomic orbitals of H and F on the right hand side of the diagram in order of increasing energy. The energies of the 1s, 2s, 3s, and 1p molecular orbitals in the HF molecule are -26.29 au, -1.60 au, -0.77 au and -0.65 au respectively. Is the energy of the 1*s* orbital on F much affected by the formation of the chemical bond with H? |
| 8. | Construct a correlation diagram for the CO molecule which relates the molecular orbitals with those of the separated atoms. Arrange the atomic orbitals of both C and O on the right hand side of the diagram in the order of increasing energy. Only atomic orbitals of the same symmetry can interact to form a molecular orbital and the resulting molecular orbital will have this same symmetry. The energies of the molecular orbitals in CO in au are 1s(-20.67), 2s(-11.37), 3s(-1.53) 4s(-0.81), 5s(-0.56), 1p(-0.65). Recall that the 2*p* atomic orbitals on C and O may form molecular orbitals of both s and p symmetry. |
| 9. | The correlation diagram in Problem 7 correlates the separated atom orbitals for R = ¥ with the molecular orbitals at $R_e$, the equilibrium internuclear distance in the molecule. Continue the correlation of the orbitals to the limiting case of R = 0, the united atom. When the distance between the F nucleus and the proton is decreased to zero the result is a neon nucleus and a neon atom. The electronic energy of each molecular orbital should correlate smoothly with an atomic energy level of the united atom, the symmetry again being conserved. For example, the 1s molecular orbital will correlate with the 1*s* atomic orbital of the Ne atom. Do the spacings between the energy levels for HF resemble those for the united or separated atoms more closely? That is, is the electronic structure of the HF best compared to that of the Ne atom or to that of perturbed energy levels of the F and H atoms? |

# 9: Preface to Calculations

The beginning student of chemistry must have a knowledge of the theory which forms the basis for our understanding of chemistry and he must acquire this knowledge before he has the mathematical background required for a rigorous course of study in quantum mechanics. The present approach is designed to meet this need by stressing the physical or observable aspects of the theory through an extensive use of the electronic charge density.

The manner in which the negative charge of an atom or a molecule is arranged in three-dimensional space is determined by the electronic charge density distribution. Thus, it determines directly the sizes and shapes of molecules, their electrical moments and, indeed, all of their chemical and physical properties.

Since the charge density describes the distribution of negative charge in real space, it is a physically measurable quantity. Consequently, when used as a basis for the discussion of chemistry, the charge density allows for a direct physical picture and interpretation.

In particular, the forces exerted on a nucleus in a molecule by the other nuclei and by the electronic charge density may be rigorously calculated and interpreted in terms of classical electrostatics. Thus, given the molecular charge distribution, the stability of a chemical bond may be discussed in terms of the electrostatic requirement of achieving a zero force on the nuclei in the molecule. A chemical bond is the result of the accumulation of negative charge density in the region between any pair of nuclei to an extent sufficient to balance the forces of repulsion. This is true of any chemical bond, ionic or covalent, and even of the shallow minimum in the potential curves arising from van der Waals' forces.

In this treatment, the classifications of bonding, ionic or covalent, are retained, but they are given physical definitions in terms of the actual distribution of charge within the molecule. In covalent bonding the valence charge density is distributed over the whole molecule and the attractive forces responsible for binding the nuclei are exerted by the charge density equally shared between them in the internuclear region. In ionic bonding, the valence charge density is localized in the region of a single nucleus and in this extreme of binding the charge density localized on a single nucleus exerts the attractive force which binds both nuclei.

This web page begins with a discussion of the need for a new mechanics to describe the events at the atomic level. This is illustrated through a discussion of experiments with electrons and light, which are found to be inexplicable in terms of the mechanics of Newton. The basic concepts of the quantum description of a bound electron, such as quantization, degeneracy and its probabilistic aspect, are introduced by contrasting the quantum and classical results for similar one-dimensional systems. The atomic orbital description of the many-electron atom and the Pauli exclusion principle are considered in some detail, and the experimental consequences of their predictions regarding the energy, angular momentum and magnetic properties of atoms are illustrated. The alternative interpretation of the probability distribution (for a stationary state of an atom) as a representation of a static distribution of electronic charge in real space is stressed, in preparation for the discussion of the chemical bond.

Chemical binding is discussed in terms of the molecular charge distribution and the forces which it exerts on the nuclei, an approach which may be rigorously presented using electrostatic concepts. The discussion is enhanced through the extensive use of diagrams to illustrate both the molecular charge distributions and the changes in the atomic charge distributions accompanying the formation of a chemical bond.

The above topics are covered in the first seven sections of this web page. The final section is for the reader interested in the extension of the orbital concept to the molecular cases. An elementary account of the use of symmetry in predicting the electronic structure of molecules is given in this section.

Hamilton, 1970

## Acknowledgement

The physical picture of chemical binding afforded by the study of molecular charge distributions has been forced to await the availability of molecular wave functions of considerable quality. The author, together with the reader who finds the approach presented in this volume helpful in his understanding of chemistry, is indebted to the people who overcame the formidable mathematical obstacles encountered in obtaining these wave functions.

<div align="center">This webpage is dedicated to Pamela, Carolyn, Kimberly and Suzanne.</div>

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# Detailed Licensing

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