

## **Atoms and the Interactions between them**

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We discuss in a simple, qualitative way, the properties of atoms, the interaction between atoms and the properties of the simplest compound systems. We concentrate on four fundamental problems: why do stable atoms exist? Why do particular combinations of atoms form molecules and others not? Why are the sizes of atoms and simple molecules of the order of  $10^{-8}$  cm?

Discutimos, de uma forma simples e qualitativa, as propriedades dos átomos, de suas interações, dos sistemas compostos mais simples. Concentramo-nos em quatro problemas fundamentais: Por que existem átomos estáveis? Por que certas combinações de átomos formam moléculas e outras não? Por que as dimensões de átomos e moléculas simples são da ordem de  $10^{-8}$  cm?

### **1. INTRODUCTION**

During the 19th century, it was established that matter is made of atoms. The atomic size was known to be of the order of  $10^{-8}$  cm, and the atomic mass of the order of  $10^{-22}$  gm. It was assumed that there were nearly 100 kinds of atoms, each kind corresponding to a particular chemical element. There was no understanding of what kept all atoms of an element so unalterably alike or what made the atoms of different elements so unlike. Such ignorance could be tolerated provided atoms are assumed to be the elementary, indivisible constituents of matter, but at the end of the 19th century it became clear that atoms are not indivisible. In particular the discovery of radioactive elements and the dis-

covery of the electron, a particle which is considerably less massive than an atom, indicated that atoms are composite structures. Thus the outstanding problem confronting physics at the turn of the century was to explain the properties of atoms in terms of their own more fundamental constituents.

We begin this article by describing how atomic and quantum physics developed in the years 1900 to 1930. During this period it became possible, in principle if not in practice, to calculate almost every chemical and physical property of matter. In particular it led to a solution of such question as:

Why do stable atoms exist?

Why do particular combinations of atoms form molecules and others not? (the rules of valence).

Why are the sizes of atoms of the order of  $10^{-8}$  cm?

How much energy is needed to disrupt atoms and molecules?

The aim of this article is to answer these questions

## 2. THE DEVELOPMENT OF ATOMIC PHYSICS 1900 TO 1930

The initial problem was to describe the distribution within the atom of the light negatively charged electrons. Several models were proposed, all sensibly constructed so as to allow for a stable configuration of the negative and positive charges. The most favoured was the model, proposed by J.J. Thomson, in which the electrons were embedded in a sphere of uniform positive charge having the dimensions of the atom. On the basis of these models it was expected that a fast and massive projectile, such as an  $\alpha$ -particle would be only slightly deflected as it passes through small quantities of matter. However, on performing a series of experiments in which  $\alpha$ -particles were fired at a very thin metallic foil, Rutherford and his collaborators were amazed to find that, while most of them did just this, a few were deflected through very large angles indeed (e.g. about 1 in  $10^4$  through an angle greater than  $90^\circ$ ). It was to quote Rutherford "almost as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you".

To account for the phenomenon Rutherford proposed a new model for the atom. He proposed that most of the mass of the atom is concentrated in a tiny, positively charged nucleus of radius about  $10^{-12}$  cm and that the light negatively charged electrons move in the electrostatic field of this nucleus in orbits extending out to a distance comparable with the atomic size.

This model is simple, but very puzzling, since according to classical physics it is unstable: the moving electrons would radiate electromagnetic waves, lose energy and fall into the nucleus. The earlier atomic models, such as the one proposed by J.J. Thomson, were deliberately constructed so as to allow for a stable configuration of the electrons, but they were at variance with the  $\alpha$ -particle scattering experiments. In contrast, if the Rutherford model is adopted, one can account for these experiments, but only at the expense of rejecting classical physics.

The structure of the atom was not the only case where classical physics was in conflict with experiment. Earlier it had become apparent that it predicted that a body at a particular temperature radiates an infinite amount of energy. To get a more reasonable result, Planck had assumed that radiation was emitted or absorbed in discrete lumps, or quanta, the energy of each quantum being related to the frequency of the radiation by the equation

$$E = h\nu \tag{2.1}$$

The idea that the energy of the radiation is related to its frequency is foreign to classical physics. The number,  $h$ , which relates the energy and frequency, is called Planck's constant. It is a universal constant which when expressed in the units of macroscopic physics is extremely small

$$h = 1.05 \times 10^{-27} \text{ ergs sec} \tag{2.2}$$

Thus when we are concerned with large amounts of radiant energy we can usually ignore Planck's quantisation of the radiation.

Niels Bohr acknowledged the failure of classical physics and attempted to incorporate Planck's ideas into Rutherford's picture of the

atom. In a classic paper published in 1913 Bohr wrote "whatever the alteration in the laws of motion of the electrons may be, it seems necessary to introduce into the laws in question a quantity foreign to the classical electrodynamics, i.e. Planck's constant. By the introduction of this quantity the question of the stable configuration of the electron in the atom is essentially changed". By introducing Planck's constant Bohr was able to incorporate features which were beyond the scope of classical physics. In particular, he introduced the concept of the quantum state which restricted the electron to certain well defined modes or configurations around the nucleus; the quantum states were defined as states with orbital angular momenta which were multiples of  $\hbar$ . This mixture of Planck's ideas with classical physics provided an intuitive but powerful way of understanding the structure of the hydrogen atom. However, the Bohr model, although a very important step forward, is a hybrid of inconsistent ideas; it offers no real understanding of the "quantum state".

The first clue to the significance of this concept emerged when it became clear that it was intimately connected with the experimental fact that electrons, in addition to acting like particles, can in other circumstances appear to act like waves. The reasons for the existence of both wave and particle states of motion were only understood when the ideas of quantum mechanics, and in particular the Heisenberg uncertainty principle, were developed between 1922 and 1930.

### 3. SOME CONCEPTS OF QUANTUM PHYSICS

We shall now discuss those concepts of quantum physics which are basic to the study of atoms and molecules. The most important of these is the uncertainty principle which implies that there is a limit beyond which it becomes a poor approximation to describe a system in terms of the concepts of classical physics. The classical state of motion of a particle at a given moment in time is determined by stating the position and momentum of that particle, both of which can, in principle, be specified simultaneously and with absolute precision. According to quantum mechanics a state with these precisely known properties

cannot exist. There is a fundamental minimal uncertainty in the simultaneous values of the momentum and the position of a particle; if the uncertainty in the momentum is  $\Delta p$  and the uncertainty in its position is  $\Delta x$ , then

$$\Delta x \Delta p \geq \hbar \quad (3.1)$$

Thus the magnitudes of the uncertainties and, hence, the limits of the applicability of classical physics, are determined by Planck's constant.

Since Planck's constant is small the uncertainty principle may be safely ignored if we are dealing with large objects; the motion of a baseball presents no problems to a classical physicist. In contrast the uncertainty principle and the magnitude of  $\hbar$  imply that the motion of an electron in an atom or molecule is beyond the scope of classical physics. For example, if we make a measurement of the distance  $r$  of the electron from the nucleus we cannot say in advance what the result will be. However, if we make the same measurement on a very large number of identical atoms, we will obtain a continuous distribution of values centred about some  $r$ -value and with a spread of the order of  $\Delta r$ . In atomic and molecular systems the spread, or the uncertainty, in the radius is comparable with the actual radius; that is

$$\Delta r \sim r$$

Thus there is no way of knowing where the electron is within the atom; however there is a definite probability of finding the electron at any particular point. Because of this it is sometimes useful to think of the electron in an atom as a diffuse cloud of negative charge distributed over a region having the dimensions of the atom. This cloud represents the possible positions of the electron at any instant.

Clearly the classical description of a moving electron as a precise trajectory is inappropriate in atomic or molecular systems. In fact the variation with time of the continuous distribution of the possible electron positions is conveniently represented by a wave motion - the form of motion appropriate to any continuous distribution. This is the origin of the wave like properties of electrons mentioned earlier. Further in the case of atoms and molecules we are dealing with wave mo-

tion in a space limited by the size of the atom. Accordingly we expect certain discrete modes of vibration. This is the origin of the discrete quantum states introduced by Bohr: they are the vibrational modes of electron waves confined in the region around the nucleus, just like modes of vibration of air confined in an organ pipe. However if the different quantum states have different energies and angular momenta, and if we consider a sequence of these states with increasing energy and angular momentum, the uncertainty demanded by the uncertainty principle becomes less significant; and for states of angular momentum much greater than Planck's constant, the uncertainty becomes negligible and the classical picture of a precise trajectory becomes appropriate.

As we shall see the uncertainty principle leads to an explanation of the existence of stable atoms and the structure of the simplest of them. However it cannot account for the variations in the degree of stability of the different elements. To do this we will have to use a further fundamental principle of quantum physics, the Pauli principle, which can be important when there are several electrons present, and is closely connected with the fact that all electrons are exactly alike. In those cases where the ideas of classical physics are a good approximation - when the uncertainties in the electron co-ordinates are negligibly small compared to their separations, so that their motions lie on trajectories which can be continuously followed and used to identify the various electrons - the effects of this are unimportant. However if the separation between the trajectories is comparable with the uncertainties in their locations, the possible positions of an electron in the other state. In this situation the electrons are no longer distinct; their identity can have important consequences. The Pauli principle specifies the way in which these must be taken into account. In fact for the purposes of this discussion we need concern ourselves with only one consequence of the exclusion principle which we will regard for the rest of this article as a statement of the principle. It is that no more than two electrons may be associated with a quantum state of specific energy and orbital angular momentum\*.

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\* That two are allowed, rather than one, is a consequence of the existence of the electron spin.

#### 4. THE SCALE OF ATOMIC PROPERTIES

Before going on to apply these ideas to atomic properties in detail, we will first show how the scales of atomic sizes and energies are set by three basic constants.

The mass of an atom is almost entirely concentrated in its central core. This central core, or nucleus, carries a positive charge of magnitude  $Ze$ . Here  $e$  is the magnitude of the charge of the electron, and  $Z$  is the Atomic Number of the atom; empirically, the more massive the atom then the larger the value of  $Z$ . The whole atom is rendered electrically neutral by  $Z$  electrons of charge  $-e$  which surround the nucleus and interact with it via the Coulomb force. Now the electrons and the nucleus are subjected to forces of similar magnitude, but the nucleus is much less mobile because of its large mass. Thus to understand the atom we have to consider the problem of the motion of electrons around a charged nucleus which is almost stationary. Thus we expect three fundamental constants to determine this motion of the electrons and hence the properties of the atom.

(a) Planck's constant,

$$\hbar = 1.05 \times 10^{-27} \text{ erg. sec} \quad (4.1)$$

enters because of the role of quantum mechanics in determining the motion. The notion of each electron is not the precisely defined trajectory of classical physics, but rather a form of motion in which the instantaneous position and momentum are uncertain. This uncertainty has a magnitude which is characterized by  $\hbar$ .

(b) The magnitude of the electron charge,

$$e = 4.80 \times 10^{-10} \text{ esu} \quad (4.2)$$

is important since it determines the strength of the force between the constituents of the atom; this is the Coulomb or electrostatic force between charged particles.

(c) The mass of the electron,

$$m = 9.1 \times 10^{-28} \text{ gm} \quad (4.3)$$

clearly plays a central role in determining the electron motion.

Because of the role played by  $h$ ,  $e$  and  $m$  in determining the properties of atoms, the size of the atom is expected to be comparable with a length constructed directly from  $h$ ,  $e$  and  $m$ . Such a length is the Bohr radius,

$$a_0 = \hbar^2/me^2 = 0.54 \times 10^{-8} \text{ cm} \quad (4.4)$$

Similarly we can construct an energy, called the Rydberg energy, from  $h$ ,  $e$  and  $m$ ;

$$R_\infty = e^2/2a_0 = e^4m/2\hbar^2 = 2.18 \times 10^{-11} \text{ ergs} \quad (4.5)$$

The Rydberg is expected to be a useful measure for atomic binding energies\*. This is more apparent when we note that the Rydberg is the energy of an electron in the electric potential given by a charge  $e$  at a distance  $2a_0$ . In equations (3.4) and (3.5) we have expressed  $a_0$  and  $R_\infty$  in c.g.s. units. As these are clearly inappropriate for atomic physics, we shall often express atomic distances in  $\text{\AA}$ (angstroms),

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

and atomic energies in, eV, electrons volts (the energy of an electron in an electric potential of one volt).

$$1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg.}$$

In these units  $a_0 = 0.53 \text{ \AA}$  and  $R = 13.6 \text{ eV}$ . Even though an eV is a very small amount of energy the binding energy stored in everyday quantities of matter is large. For example chemists deal with substances in terms of gram moles (e.g. 18 grams of water) which contain  $N_0 = 6.025 \times 10^{23}$  molecules. Thus if in some reaction each molecule loses 1 eV,

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\* The factor of 2 is completely insignificant at the present level of discussion. It is merely inserted for later convenience.



it is easy to calculate that the total energy release is 23.06 kilocal per gram mole. It is no accident that this is typical of the order of magnitude of the energies absorbed or released in chemical reactions.

The reader may wonder why we have not used the velocity of light,  $c$ , to construct lengths and energies which may be relevant to atomic physics. In fact the electrons in an atom move with velocities which are small compared with the velocity of light, and the effects of special relativity, and hence  $c$ , are unimportant. To see this we anticipate the following sections and assume that electron energies in atoms are indeed of the order of  $R_\infty$ . The ratio of the Rydberg energy to the electron rest energy is

$$\frac{R_\infty}{mc^2} = \frac{1}{2} (e^2/\hbar c)^2$$

Since the dimensionless number

$$e^2/\hbar c = 1/137$$

is small, the kinetic and potential energies of electrons in atoms are a small fraction of the electron rest energy. Thus electrons in atoms are non-relativistic; the relativistic corrections are fine structure effects. This is an important general property, true for all the lighter atoms, and in addition, for the molecules they form. It is not true for some of the inner electrons (electrons close to the nucleus) of the atoms of heavy elements, such as lead. However, we shall see that the chemical properties are controlled by the outer electrons and these are always non-relativistic,

## 5. THE HYDROGEN ATOM

To see how the ideas of section 3 work in practice, we shall consider in detail the properties of a few simple atoms. The simplest is the hydrogen atom. This has atomic number  $Z=1$ , and hence has just one electron. First let us consider a classical state of the electron and nucleus. To this end we assume that the separation,  $r$ , between the electron and the nucleus is large enough so that the effects of the uncertainty principle can be neglected and classical physics can be used.

Since the electron and nucleus have opposite charges they are attracted to each other by a force of magnitude  $e^2/r^2$ . Therefore the potential energy can be taken as

$$V = -e^2/r \quad (5.1)$$

The kinetic energy is

$$\begin{aligned} T &= p^2/2m = p_r^2/2m + (\vec{r} \times \vec{p})^2/2mr^2 \\ &= p_r^2/2m + L^2/2mr^2 \end{aligned} \quad (5.2)$$

where  $\vec{p}$  is the electron momentum,  $p_r$  is its radial component and  $L^2$  is the square of the electron angular momentum. For a circular orbit,  $p_r = 0$  and the electrostatic force is balanced by the centrifugal force when

$$r = L^2/me^2 \quad (5.3)$$

At this radius the total energy of the system has the minimum value

$$E = T + V = -\frac{1}{2} e^2/r = -\frac{1}{2} me^4/L^2 \quad (5.4)$$

The magnitude of  $E$ ,  $me^4/2L^2$ , represents the **binding energy** of the system, the energy needed to remove the electron from the orbit of radius  $r$  to a point at infinity. This situation would be stable, just as a planetary orbit is stable, **if it** were not for the electromagnetic energy radiated by the accelerating electron. As a result of this, the system loses both energy and angular momentum, and the electron spirals in towards the nucleus. Under the laws of classical physics this spiraling would continue until the electron came to rest with zero momentum at  $r=0$ . We know from the discussion in Section 3 that a precise position ( $r=0$ ) and momentum ( $p=0$ ) would violate the uncertainty principle. Thus the electron cannot spiral into the nucleus; but reaches a stable "quantum" state in which the average distance from the nucleus is finite. This corresponds to the lowest energy or ground state of the hydrogen atom.

It is a simple matter to use the uncertainty principle to estimate the size and energy of the ground state of the hydrogen atom. As we have seen, the electron cannot be definitely localised at  $r=0$ , but

will be distributed about this point with a positional uncertainty  $\Delta x$ . This uncertainty is of the order of the size of the atom. Similarly its radial momentum is distributed about zero with a mean square value governed by the uncertainty principle. If we represent the size of the atom by  $r_0$ ,

$$p_r^2 \sim (\Delta p_r)^2 > (\hbar/\Delta x)^2 \sim (\hbar/r_0)^2 \quad (5.5)$$

Thus the minimal energy of the electron moving in the electrostatic potential of the nucleus, with orbital momentum  $L$ , and localised in a region of dimension  $r_0$ , is

$$E \sim \hbar^2/2mr_0^2 + L^2/2mr_0^2 - e^2/r_0 \quad (5.6)$$

Hence we see that in quantum mechanics there are two effects which work against the electrostatic attraction and thereby prevent the electron from falling towards the nucleus; the orbital angular momentum,  $L$ , gives rise to a centrifugal potential  $L^2/2mr_0^2$  as in classical mechanics, and the uncertainty principle gives rise to an additional effective repulsion whose minimum value is approximately  $\hbar^2/2mr_0^2$ . Clearly the state of lowest energy has zero orbital angular momentum  $L^2 = 0$ , with only the delocalising effect of the uncertainty principle balancing the electrostatic attraction. The energy is given by the minimum value of

$$E \sim \hbar^2/2mr_0^2 - e^2/r_0 \quad (5.7)$$

This minimum is equal to minus the Rydberg energy and occurs when  $r_0$  is equal to the Sohr radius; i.e.

$$r_0 = a_0 = \hbar^2/me^2 \text{ and } E = -R = -e^4m/2\hbar^2 \quad (5.8)$$

As expected the atomic size is given by  $a_0$  and the binding energy by  $R_\infty$ . Of course this calculation is crude, and the results must be considered as estimates. In this case they happen to agree with the results of the exact calculation.

We have previously discussed the classical states of the electron and nucleus. These are excited states of the hydrogen atom, with

well defined radii which are much larger than the average radius of the quantum ground state.

$$r = L^2/me^2 \gg a_0 \quad (5.9)$$

Between the classical states and the ground state is a sequence of states with discrete values of energy and angular momentum.

It can be shown that the energies of all the hydrogen atom states are given by

$$E_n = -\frac{1R_\infty}{n^2} \quad (5.10)$$

where  $n = 1, 2, 3 \dots$  etc. The state with  $n = 1$  is the ground state. As  $n$  increases the binding energy decreases and the radius increases - for  $n=2$  the binding energy is four times smaller and the average radius is typically four times greater than in the ground state. In addition, if  $r$  is greater than one the orbital angular momentum can take on values other than zero. In fact,

$$L^2 = \ell(\ell + 1) \hbar^2 \quad (5.11)$$

- where  $\ell$  can equal 0, 1, 2, ... etc. up to  $(n-1)$ . We note that for small values of  $n$ , there is a marked difference in energy between adjacent states; for example, the energies of the ground state ( $n=1$ ) and the first excited ( $n=2$ ) states are  $-R_\infty$  and  $-R_\infty/4$ . However as  $n$  increases the levels get closer together until for large  $n$  they can effectively be regarded as a continuum. Further, if  $n$  is large the maximum angular momentum is

$$L^* = n(n-1) \hbar^2 \sim n^2 \hbar^2$$

so that the energy (5.10) approaches the expression (5.4), i.e.

$$E_n = -\frac{\hbar^2}{L^2} R_\infty = -\frac{1}{2} me^4/L^2$$

Thus the states with large  $n$  and the maximum angular momentum correspond to the classical circular orbits considered previously.

This discussion of the states of the hydrogen atom extends also to the so-called hydrogen-like ions, which have a structure similar to that of the hydrogen atom. An ion is the electrically charged enti-

ty obtained by removing or adding electrons to a neutral atom. For example if there is one electron moving around a nucleus with charge  $Ze$  then we have a singly charged helium ion, ( $\text{He}^+$ ). In general, a hydrogen-like ion has one electron and a nucleus of charge  $Ze$ . The potential energy is now

$$V = -Ze^2/r_0 \quad (5.12)$$

and if we use this in equation (5.6), etc., we find for the energies and radii of the ground states,

$$E_1 = -Z^2 R_\infty \quad \text{and} \quad r_0 = a_0/Z \quad (5.13)$$

Thus the lowest energy of the singly charged helium ion is  $E_1(\text{He}^+) = 14 R_\infty$  and the doubly charged Lithium ion has a energy of  $E_1(\text{Li}^{++}) = -9 R_\infty$ . These numbers will come in useful later. Finally the energy of the excited states of hydrogen-like ions are given by a trivial generalization of (5.10),

$$E_n = -Z^2 R_\infty / n^2 \quad (5.14)$$

## 6. ATOMS AND IONS WITH MORE THAN ONE ELECTRON

First we consider systems with two electrons. The most important ones are the helium (He) atom which has two electrons bound to a nucleus with  $Z=2$ , the  $\text{H}^-$  ion, which has two electrons surrounding a hydrogen nucleus ( $Z=1$ ), and the lithium ion  $\text{Li}^+$  which has two electrons bound to the nucleus of lithium with  $Z=3$ . We can estimate the binding energies for these systems by using the uncertainty principle. If both electrons are localized within a distance  $r_0$  from the nucleus, the minimum kinetic energy is

$$T = p_1^2/2m + p_2^2/2m \sim \hbar^2/mr_0^2 \quad (6.1)$$

and the potential energy is approximately

$$V = -2Ze^2/r_0 + e^2/r_{12} \quad (6.2)$$

Here  $r_{12}$  is the average distance between the electrons. To represent

the tendency of the electrons to stay apart from one another, we make the rough approximation

$$r_{12} \sim 2r_0$$

The total energy of the system is then

$$E = \hbar^2/mr_0^2 - \left(\frac{4Z-1}{2}\right) e^2/r_0 \quad (6.3)$$

Minimising we find

$$E = -\left(\frac{4Z-1}{8}\right) 2R_\infty, \quad \text{and} \quad r_0 = \left(\frac{4}{4Z-1}\right) a_0 \quad (6.4)$$

Thus for the neutral helium atom with  $Z=2$ , we find a binding energy of  $49R_\infty/8 \sim 83 \text{ eV}$

Actually as we shall see, the total binding energy, the energy required to remove all the electrons to infinity is not the most interesting quantity to consider. We shall be interested in the ionization energy, which is the energy required to remove one electron from an atom (or ion) to infinity. For hydrogen, this is just the binding energy of  $1 R_\infty$ . For helium, it is the difference between the binding energy of helium itself and that of  $\text{He}^+$ . From (5.13) and (6.4) we obtain an ionization energy for helium of about  $17R_\infty/8$  or 28.9 eV. Thus the electrons are much more tightly bound in helium than in hydrogen, a fact which will become more significant later.

The term "the electron affinity" of an atom or ion is directly related to an ionization energy. Adding an extra electron to the atom or ion sometimes results in the lowering of the energy; the additional electron is bound and its binding energy is called the "electron affinity". Clearly if the ionization energy of the helium atom is 28.9 eV, the electron affinity of  $\text{He}^+$  is 28.9 eV. As another example we can use (6.4) to calculate the total energy of the  $\text{H}^-$  ion, and hence we can find the ionization energy of  $\text{H}^-$  or equivalently the electron affinity of the hydrogen atom. The result is 1.7 eV, indicating that the second electrons in  $\text{H}^-$  is just bound.

To consider atoms with more than two electrons we must remember a further fundamental principle of quantum physics, the Pauli

exclusion principle. In the two electron systems each electron was assumed to have the same minimal kinetic energy

$$T = \hbar^2 / 2mr_0^2 \quad (6.6)$$

when localized in a region of dimension  $r_0$ . When a similar assumption is made for each of the electrons in a many electron system we obtain nonsense. For example, the lithium atom, which has  $Z=3$  and three electrons, is predicted to have a higher ionization energy than helium, just as helium has a higher ionization energy than hydrogen. Moreover, it is predicted that this sequence of increasing stability with increasing  $Z$  continues through the whole series of elements. This prediction is in gross contradiction with known experimental facts; lithium, for example, it is known to have a small ionization energy, being loosely bound.

The key to understanding Lithium and other more complex atoms is the Pauli exclusion principle, which limits the number of electrons in any orbital state to two. As a result, in Lithium only two of the electrons can exist in a state of minimal kinetic energy, corresponding roughly to the  $n=1$ , ground state of a hydrogen-like one electron system. The third must go into an  $n=2$  state with lower binding energy and larger radius. In fact this electron has a radius which is sufficiently large for the two inner electrons to be regarded as lying completely inside it, giving an effective charge of  $(Z-2)e = +e$ . The energy and average radius of this third electron will be roughly like those of the one electron state with  $n=2$ ,  $l=1$ , i.e. the  $n=2$  state of hydrogen. Thus using the values of these from (5.14), for the ionization energy and radius of Lithium we obtain

$$E(\text{Li}^+) - E(\text{Li}) \sim \frac{1}{4} R_\infty \sim 3.4 \text{ eV} \quad (6.7)$$

and

$$r(\text{Li}) \sim 4a_0 \sim 2.1 \text{ \AA} \quad (6.8)$$

These numbers are of course rough estimates: the accurate values are 5.4 eV and 1.5 \AA.

Table I lists our results in the one, two and three-electron systems. The calculated ionization energies are obtained using equa-

tions (5.13), (6.4) and (6.7). We see that our simple estimates are quite successful in reproducing the main features of the experimental results

We see from Table I that the two-electron atom or ion is the most stable; for example, it is harder to remove an electron from a helium atom than it is from an atom of hydrogen or lithium. The stability of the two-electron system occurs because the exclusion principle allows two electrons to be in states of low energy; if a third electron is added it can only occupy a state of higher energy. Thus the helium atom cannot readily lose or gain electrons, and as a result it does not react with itself or with other atoms to form compounds. Lithium, on the other hand, can readily lose one electron; only 5.4 eV are needed to remove the outer electron. However, a second electron cannot easily be removed since  $\text{Li}^+$  has a stable two-electron structure with an ionization energy of 75.6 eV. As a result lithium can react with other atoms but with an interaction which is mediated by just one electron. Lithium is said to be mono-valent. By applying similar arguments to the next atom Beryllium (Be) with  $Z=4$ , the reader should be able to convince himself that two electrons are comparatively loosely bound. Beryllium is said to be di-valent.

**Table I**

Atom	No. of Electrons	Ionization Energy in eV	
		Calculated	Experimental
H	1	13.6 eV	13.6 eV
He	2	28.9	24.6
Li	3	3.4	5.4
$\text{He}^+$	1	54.4	54.4
$\text{Li}^+$	2	83.3	75.6
$\text{Be}^+$	3	13.6	18.2
$\text{H}^-$	2	1.7	
$\text{He}^-$	3	0	



In this brief account of the structure of the simplest atoms and ions we have introduced all the basic ideas that are necessary to understand all the elements of the periodic table. We shall merely discuss the variation in the ionization energies and electron affinities of the different elements, and show how this variation can be used to group the elements into classes having distinct chemical properties.

We have seen that lithium has two electrons tightly bound to the nucleus and a third which is loosely bound. If there was no repulsion between the electrons, the tightly bound electrons would be indistinguishable to the  $n=1$  ground state of the one electron ion discussed in section 5. The loosely bound electron would be in an  $n=2$  state. In addition the average distance of an  $n=2$  electron from the nucleus is much greater than that of the  $n=1$  electrons. Thus the electrons of lithium occupy two "shells"; the  $n=1$  shell has two electrons and the  $n=2$  shell one.

In this case the  $n=1$  shell is 'complete' (it has the maximum number of electrons allowed by the exclusion principle). To decide how many electrons are required to complete the  $n=2$  shell we must know how many states it contains - there will be more than one since we now have the possibility of non-zero angular momentum as pointed out in section 5. When the implications of this are worked out in detail it is found that there are four states in the  $n=2$  shell, so that according to the exclusion principle it may contain up to eight electrons. It is complete in the element neon, which has ten electrons, two in the closed  $n=1$  shell and eight in the closed  $n=2$  shell. There is little tendency for neon to acquire an extra electron. Such an electron will have to go into a state corresponding to  $n=3$ ; it will be more distant from the nucleus than the electrons in the  $n=1$  and  $n=2$  shells, and will to a large extent be shielded from the nuclear charge by all ten electrons. On the other hand it is difficult to remove an electron from neon, since this would have to come from the  $n=2$  shell, and so is strongly bound to the nucleus. Hence neon, like helium, has a small electron affinity and a high ionization energy.

On the other hand sodium, which has eleven electrons, is similar to lithium. The first ten electrons occupy the  $n=1$  and 2 shells,

and the eleventh is in a loosely bound state which corresponds to  $n=3$ . Thus the energy needed to form a  $\text{Na}^+$  ion is small. Furthermore, only one electron can easily be removed from sodium since  $\text{Na}^+$  has a stable closed-shell structure similar to that of the neon atom. Therefore, sodium is a mono-valent element like lithium. The actual electron distribution of these ions  $\text{Li}^+$ ,  $\text{Na}^+$  is shown in figure 1, together with the analogous  $\text{K}^+$  ion, which as well as complete  $n=1, 2$  shells has eight electrons in the  $n=3$  shell. The first three shells on which we have been basing our discussion can be clearly seen, although they overlap so that it is only an approximation to regard them as distinct. The averaged distance from the nucleus is seen to increase with  $n$  and decrease with  $Z$  as expected.

Variations in stability similar to those whose origins we have just discussed occur throughout the periodic table. This is illustrated in figure 2 which gives the ionization energies for all the elements up to barium. The peaks correspond to the most stable elements, the noble gases: helium, neon, argon, krypton and xenon. We note that xenon is the least stable and, hence the least inert, of the noble gases.

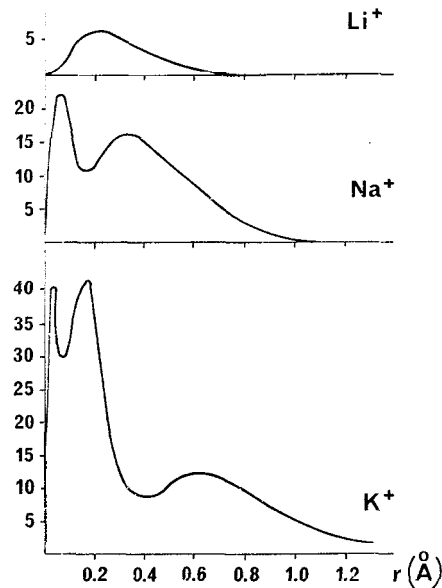


Fig.1 - The electron density distribution as a function of the distance  $r$  from the nucleus for singly ionised lithium ( $\text{Li}$ ,  $Z=3$ ), sodium ( $\text{Na}$ ,  $Z=11$ ) and potassium ( $\text{K}$ ,  $Z=19$ ) ions.

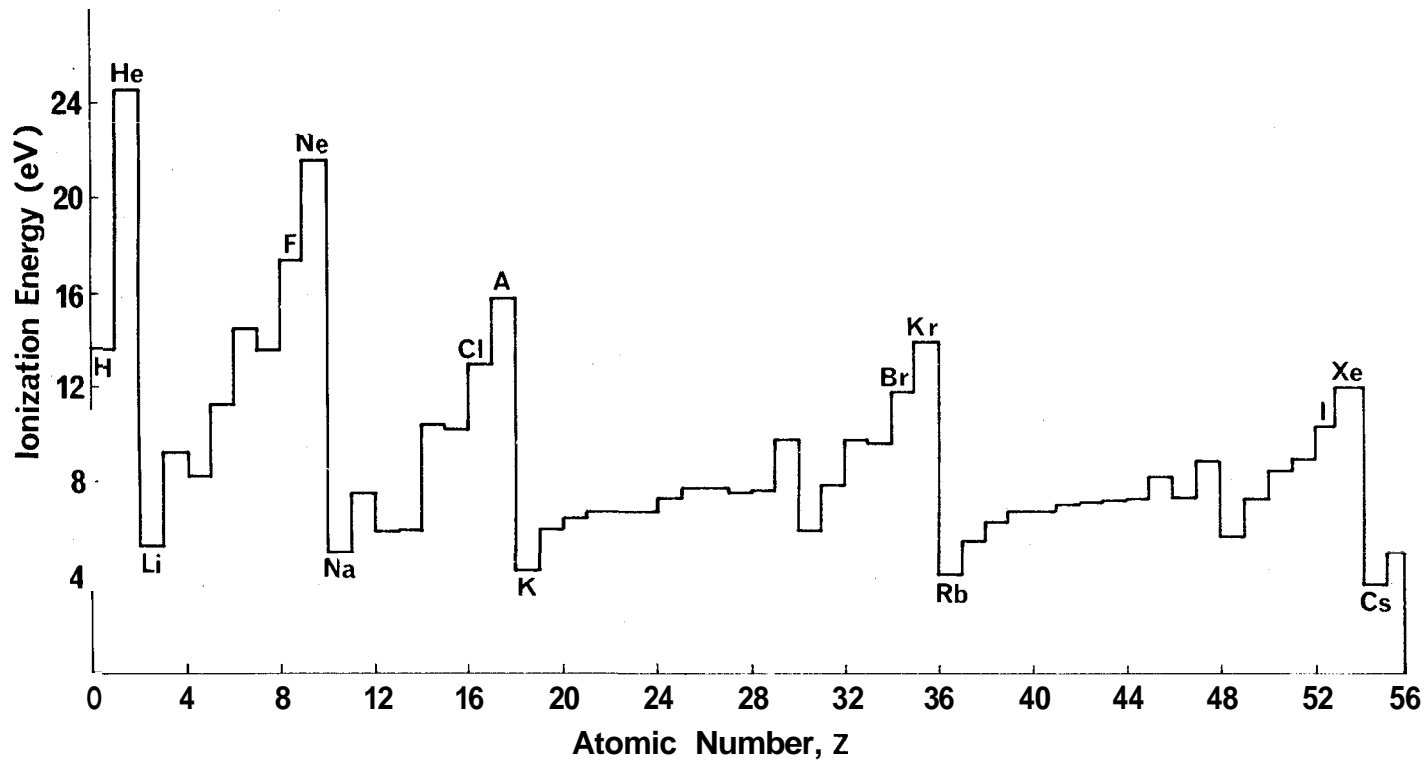


Fig.2 • Ionization energies of the elements.

ses. The elements immediately after the noble gases are the mono-valent metals, lithium, sodium, potassium, rubidium and cesium; they are chemically active because of their low ionization energies. The elements immediately preceding each noble gas are the halogens: fluorine, chlorine, bromine, and iodine. These have large ionization energies but nevertheless are chemically active. This is because they have large electron affinities, and readily acquire an extra electron to form negative ions which have the stable closed shell structure of a noble gas; for example, the  $F^-$  ion, like the  $Na^+$  ion, has the same electron structure as the Ne atom.

This completes our discussion of atoms and the variations in their stability with regard to the gain or loss of electrons. This is closely related to the variations in their chemical activity - their ability to form stable molecules. We go on to discuss how (and when) this occurs, and other features of the interactions between atoms in terms of the same basic ideas, in the following section.

## 7. FORCES BETWEEN ATOMS AND THE FORMATION OF MOLECULES

In this section we consider how atoms interact with each other. The origin of the interaction is the electrostatic force between the charged constituents of the atoms. We have a complicated system of moving electrons and nuclei. But since the nuclei and the electrons are subjected to forces of similar magnitude, the electrons, being the less massive, are much more mobile and play the major role in determining the interaction. We shall see how the exclusion principle determines whether the interaction is attractive or repulsive. We shall also see how the chemical activity of an atom is measured by the ease with which it can lose or gain an electron.

Let us first consider the short range repulsion between atoms which ultimately is responsible for the rigidity of matter. As two atoms get closer, the mobile electrons move so as to minimize the energy of the system. In particular, at short distances, the electrons tend to screen the two nuclei from each other, thereby reducing the electrosta-

tic potential energy. Thus the electrons tend to be localized in the small region between the nuclei. The uncertainty principle implies that this localization is only possible at the expense of increasing the electron kinetic energy. If  $R$  is the distance between the two nuclei, an electron localized over this region has a minimum kinetic energy of the order of

$$T \approx \hbar^2/2mR^2$$

Moreover the exclusion principle imposes a limit on the number of electrons that can have this minimum kinetic energy. In fact, a maximum of two electrons can have this energy, and the kinetic energy of a third electron must be at least of the order of

$$T \approx 4(\hbar^2/2mR^2)$$

Clearly when the distance between the atoms,  $R$ , becomes sufficiently small, the kinetic energy of the electrons becomes greater than the kinetic energy in the isolated atoms. Eventually, the decrease in the potential energy caused by the screening of the nuclei, must be accompanied by a larger increase in the kinetic energy, the total energy of the system increases, and there is a tendency for the two atoms to repel each other. Since the electron kinetic energy in an isolated atom is comparable with

$$T \approx \hbar^2/2mr^2$$

where  $r$  is a measure of the atomic size, the repulsion becomes effective when the separation  $R$  becomes comparable with  $r$ .

In general there is a tendency for two atoms to repel each other when their electron clouds appreciably overlap. However, in many cases when the atoms first begin to overlap, the outer electron or electrons can be arranged so as to give an attraction, i.e. form a chemical bond. Provided there is sufficient attraction, the atoms form a bound state called a molecule. The basic condition for atoms to form a stable molecule is that the total energy of the atoms, when they are separated by a distance of the order of one or two atomic radii, is smaller than the energy of the isolated atoms. This is possible if the outer electrons can form a configuration which screens the nuclei and thereby reduce the potential energy; but at the same time the kinetic energy of

the electrons must not be appreciably greater than their kinetic energy in the isolated atoms. The condition for the existence of a stable molecule is determined by the exclusion principle and is that the atoms have incomplete outer shells. If one or more of the atoms has a complete outer shell the mechanism described above for the short range repulsion becomes effective as soon as the atoms touch. Thus hydrogen and lithium can form molecules but not helium can form molecules.

The nature of the chemical bond is determined by the complicated distribution of the electrons in the molecule. It is useful to conceive of two types of bond, called ionic and co-valent, each of which corresponds to a simple electron distribution. In some molecules the chemical bond is clearly ionic or co-valent. But in others the bond is more complicated, and lies between these two extremes.

The ionic bond is fairly simple to understand. Here the electrons are arranged so that the molecule can be viewed as negative and positive ions, held together by electrostatic attraction. Clearly the key to understanding ionic binding lies in the ionization energies and electron affinities of the atoms involved.

The ionization energies for some simple elements are listed in Table I. Let us use these results to explore the energy changes involved in forming the lithium hydride molecule by ionic bonding. To remove an electron from a lithium atom to form a  $\text{Li}^+$  ion requires the expenditure of energy equal to the ionization energy of lithium. When an electron is added to hydrogen to form a  $\text{H}^-$  ion, energy equal to the electron affinity of hydrogen is gained. (We remind the reader that the electron affinity of hydrogen equals the ionization energy of H-). Thus if an electron is removed from a lithium atom and added to a hydrogen atom, the energy of the system changes. If the atoms are separated by an infinite distance, the energy increase is the difference of the ionization energy of lithium and the electron affinity of hydrogen, i.e. 5 eV or so. Now let us assume that the  $\text{Li}^+$  and  $\text{H}^-$  ions are separated by a finite distance  $R$ . The resultant electrostatic attraction between the ions lowers the energy of the system by  $e^2/R$ . If  $R$  is less than  $2.8 \times 10^{-8}$  cm, the energy is lowered by more than 5 eV and hence can compensate for the energy expended in forming the ions. Thus the ener-

gy of  $\text{Li}^+ \text{H}^-$  system can be less than the energy of the isolated Li and H atoms, and a molecule can exist. Clearly there is a limit to the decrease in the potential energy. If the separation between the ions becomes too small, the motion of the inner electrons is disturbed and the short range repulsion mentioned earlier becomes effective.

In practice this picture of lithium hydride as an ionic molecule is extremely crude; the outer electron from the lithium atom cannot be definitely associated with a hydrogen ion. Sodium chloride (common salt) provides a better example of ionic bonding. The energy rise when an electron is transferred from a sodium to a chlorine atom is only 1.3 eV. The fall in the potential energy can compensate for this if the separation of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions is less than  $11 \text{ \AA}$ . This distance is large compared with the distance at which the ions begin to overlap and thereby repel each other.

An important feature of ionic bonding is that it is unsaturated. In sodium chloride many  $\text{Cl}^-$  ions can be attracted by a single  $\text{Na}^+$  ion and repelled by a single  $\text{Cl}^-$  ion. Hence the binding energy per ion can be increased by an arrangement in which each positive ion is surrounded by a number of negative ions and vice versa. In the case of  $\text{Na}^+ \text{Cl}^-$  this is achieved by the arrangement shown in figure 3. Thus ionic binding gives rise to crystalline solids; the whole crystal is a single structure with each ion tightly bound to all its neighbours.

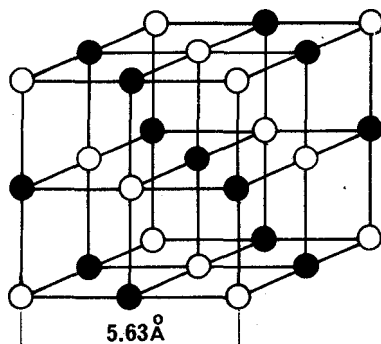


Fig.3 - A 'unit cell' of the crystal structure of sodium chloride. The  $\bigcirc$  (Na) and  $\bullet$  (Cl) symbols are used to indicate the location of the nuclei of the atoms only - the size of the  $\bigcirc, \bullet$  drawn is of no significance. The pattern shown repeats itself very many times over the entire space occupied by the crystal.

This ionic crystalline structure is the normal form of common salt at room temperature: there are no discrete Na Cl molecules. However if sufficient heat is applied the extended structure breaks down to some extent - salt melts at 804°C - and eventually discrete diatomic Na Cl molecules can be found in the vapour phase. In these molecules the internuclear distance is slightly smaller than in the crystalline case - 2.5 Å as opposed to 2.8 Å - a first clue that the nature of the binding has changed. In fact if we assume that we are still dealing with spherical ions the electrostatic potential energy between them at this distance is easily calculated to be

$$-e^2/2.5 \text{ \AA} = -4.2 \text{ eV}$$

Remembering that 1.3 eV are required to remove an electron from an Na atom to a Cl atom at infinity, the binding energy of an Na Cl molecule is calculated to be 2.9 eV. This is a typical value - a fraction of a Rydberg - for the binding energy of a diatomic molecule. However the experimental value is 3.6 eV, indicating that while the assumption of ionic binding is roughly correct, it is not precise. The outer electron from the sodium atom is only partially transferred to the chlorine atom. Moreover the inner electrons of each atom are affected by the presence of the other atom.

We now consider a second type of chemical bond, the covalent bond. The molecules H<sub>2</sub> and Cl<sub>2</sub> are due to covalent bonds. HCl is also covalent but in addition exhibits certain ionic characteristics. In covalent and in ionic bonds the potential energy is reduced by a particular arrangement of the outer electrons of the atoms. In an ionic bond this is achieved by forming a system of positive and negative ions. In a covalent bond the potential energy is reduced by arranging the electrons in the space between a pair of atoms; i.e. the electrons are shared. In general any stable arrangement which lowers the potential energy of a system of atoms also increases the kinetic energy. To ascertain whether a bond is possible one has to check that the increase in kinetic energy is less than the decrease in potential energy. This task is more difficult for a covalent than for an ionic bond. Accordingly we shall have to be content with arguments which merely show that covalent bonds are more likely in some cases than in others. As an example let us



consider the existence of the hydrogen molecule,  $H_2$ , and the non-existence of the "helium molecule",  $He_2$ .

Let us assume that, as two hydrogen or two helium atoms approach each other, the mobile electrons arrange themselves predominantly in the region between the nuclei so as to reduce the potential energy; for simplicity we assume that the electrons are localized in a region of dimension  $R$ , where  $R$  is the distance between the nuclei and of the order of one to two atomic radii so that the atoms are starting to overlap. This rearrangement of the electrons can be equally effective in reducing the potential energy of the two hydrogen or the two helium atoms. However, by virtue of the exclusion principle the accompanying change in the kinetic energies in the two cases are significantly different. The average kinetic energy of each electron in the two hydrogen atom case is of the order  $\hbar^2/2mR^2$ . In the case of the two helium atoms only two electrons can have kinetic energies of magnitude  $\hbar^2/2mR^2$ ; the exclusion principle requires the other two electrons to be in different states each with a higher kinetic energy of the order  $4(\hbar^2/2mR^2)$ . The non-existence of the helium molecule is a consequence of this large kinetic energy. In contrast the decrease in the potential energy can and does compensate for the small change in the kinetic energy when two hydrogen atoms approach one another, and leads to the formation of the hydrogen molecule. Given the existence of such a molecule its internuclear separation is comparable with  $r = a_0$ , the Bohr radius, and its binding energy is clearly some fraction of  $\hbar^2/2ma_0^2$  or the Rydberg energy.

Of course if in the above discussion we make  $R$  smaller than the atomic size ( $R < r$ ) we arrive at the short range repulsion discussed earlier, even for hydrogen, because of the rapid growth in the kinetic energy terms  $\hbar^2/2mR^2$ . The behaviour of the energy as a function of  $R$  is shown in figure 4, starting with the short range repulsion for  $R < r$ , the attractive (A) (or repulsive (B)) interaction in the intermediate range  $r < R < 2r$ , which decreases gradually for larger  $R$  until at infinite  $R$  we have two neutral, isolated atoms\*. The energy shown is

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\* For very large  $R \gg r$ , the interaction for both cases A, B always becomes weakly attractive and goes to zero like  $R^{-7}$  (the Van der Waals for-

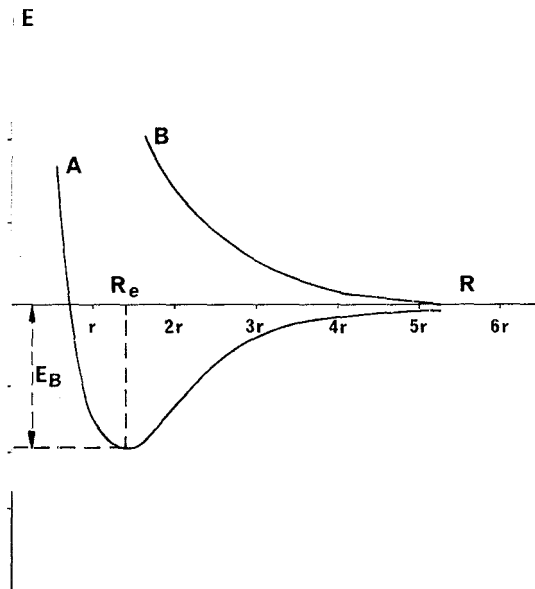


Fig.4 - Typical energy curves for a diatomic system as a function of the internuclear separation  $R$ . The unit  $r$  is the atomic radius (or average radius if the atoms are different). Curve B corresponds to a repulsive case (e.g. 2 helium atoms), curve A to a case in which a molecule occurs at internuclear distance  $R \approx R_e$  with binding energy  $E_B$  (ignoring nuclear motion). For  $H_2$  for example,  $E_B \sim 4.5 \text{ eV} \sim 0.33 R_\infty$  and  $R_e \sim 1.39 a_0 = 1.39 \times 0.74 \text{ \AA}$ .

the difference between the total energy  $E$  and  $R = R_e$ , with binding energy  $E_B$ , which is the situation in the ground state of the molecule, neglecting the nuclear motion<sup>t</sup>.

The binding that occurs in the region  $R \sim R_e$  does so because the electrons are able to arrange themselves around the two nuclei so that the total energy is lower than it would be in two isolated atoms. We have discussed two possible arrangements that can lead to such an effect. In an ionic bond an electron is transferred from one atom to the other to give rise to two ions, which attract each other electro-

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ce). This is important for some considerations, for example the deviations of the behaviour of real gases from the ideal gas laws  $PV = RT$ , but is unimportant for the topics discussed here.

<sup>t</sup> In fact this is not completely negligible, and the nuclei will vibrate slightly about this equilibrium position and the binding energy will not quite equate  $E_B$ . However these effects though present, are only small corrections.

tatically. This will lead to a dipole moment of the molecule. If we assume the ions are spherical, then we effectively have two charges  $\pm e$  at a distance  $R_e$ , so that the dipole moment is

$$D = e R_e \text{ (a } 4.8 \times 10^{-10} \text{ esu if } R_e \sim 1 \text{ \AA )}$$

In a covalent bond the electrons are shared equally, there is no dipole moment,  $D = 0$ . Thus if we define a parameter

$$x = D/e R_e$$

then for a covalent bond  $x = 0$ , for an ionic  $x = 1$ . In nature the electrons cannot only arrange themselves in these two simple distributions but also in intermediate distributions, the particular distribution being such as to give the lowest energy in each case. This is brought out clearly by examining the  $x$  values, which do not fall neatly into two groups  $x = 0, 1$  but range themselves in the region spanning these two extremes. The measured values for some examples are  $x = 0$  ( $H_2$ ), .05 (HI, hydrogen iodide), .35 (NaI, sodium iodide), .43 (HF, hydrogen fluoride), .60 (KF, potassium fluoride) and .77 (KBr, potassium bromide). The purely ionic extreme is most closely approached, not in the case of diatomic molecules when it would give  $x = 1$ , but in the crystalline solid cases like sodium chloride. In fact at room temperature NaI, KF and KBr all form crystalline solids of the sodium chloride structure in which the ionic nature of the binding is greatly enhanced over that for the vapour phase, diatomic molecules whose  $x$  values are given above. ( $H_2$ , HF and HI are gases at room temperature and pressures.) Thus ionic and covalent bonding are not magic mechanisms, but idealised cases of a whole range of binding types, which arise from the arrangement of the electrons around the nuclei so as to achieve the lowest energy.

## 8. CLOSING REMARKS

We have discussed the properties of atoms, the interaction between atoms, and the properties of the simplest compound systems—the diatomic molecules and ionic crystals. We have discussed how these

phenomena can be understood in terms of the distribution of electrons moving in the electric fields of atomic nuclei. The motion is governed by the laws of non-relativistic quantum physics and the simple use of just two quantum physics concepts, the uncertainty principle and the exclusion principle, has been sufficient to illustrate many of the consequences of this motion. In particular it has led to an understanding of the four fundamental problems posed in the introduction, i.e.

Why do stable atoms exist?

Why do particular combinations of atoms form molecules and others not?

Why are the sizes of atoms and simple molecules of the order of  $10^{-8}$  cm?

and

How much energy is needed to disrupt atoms and molecules?