

The
Chemical Bond

SECOND EDITION

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Chapter 1

The Chemical Bond – Early Concepts

‘When the formulae of inorganic compounds are considered even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorous, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements, and it is in these proportions that their affinities are best satisfied.’

This comment by Frankland in 1852† illustrates the body of knowledge which was available to chemists in the middle of the 19th century and which led to rapid advances in the concept of valence. The rapid development of organic chemistry at that time led Kekulé in 1857 to deduce that carbon was tetravalent, and he also introduced the important idea that carbon atoms could form bonds with one another. The tetravalence of carbon was postulated independently by Couper in 1858 and he made use of structural formulae for molecules with lines between atoms linked together.

The existence of multiple links between carbon atoms was postulated by Kekulé in 1859, and in 1865 he gave a structural formula for benzene consisting of a flat hexagonal ring of carbon atoms with alternating single and double bonds.

One of the successes of Kekulé’s formula for benzene was in explaining isomerism. Disubstituted benzenes, for example, have three isomeric forms. The next important development in molecular structure also came from a study of isomerism, in this case the optical isomerism of tartaric acid and similar compounds which had been investigated by Pasteur. The interpretation of Pasteur’s results was given independently by van’t Hoff and le Bel in 1874 with their model of the tetrahedral orientation of the valences of carbon. According to van’t Hoff: ‘In the case where four affinities of an atom of carbon are saturated by four different univalent groups, two and only two different tetrahedra can be obtained of which one is the mirror image of the other’. This development marked the beginning of our picture of a molecule of atoms joined by bonds: what one might call a ball and stick model. A satisfactory theory of valence must explain the number of bonds, their length and the angles between them.

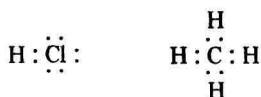
The early attempts at an electronic theory of valence, following Thomson’s discovery of the electron in 1897, suffered from the limitation that the electrons

† Frankland, *Phil. Trans.*, 67, 417 (1852).

were considered to be at rest. Electron sharing within such a model conflicts with the electrostatic result that particles carrying like charges repel one another.

It was not until 1913 that Bohr introduced a dynamic model for the electrons in an atom which gave a satisfactory explanation of many features of atomic spectral lines. This model was based upon the laws of classical (Newtonian) dynamics, but the new principle introduced by Bohr was that only certain orbits of the electrons around the nucleus were allowed. Although a recipe was given for identifying these stable orbits, Bohr theory must be considered as fundamentally unsatisfactory because no explanation for the stability was forthcoming from within classical dynamics. Nevertheless, the work of Bohr indicated that an explanation for the chemical bond could be found in a dynamical model of the electron although no quantitatively satisfactory results were ever obtained. These had to await the development of the new principles of wave mechanics as we shall see in the next chapter.

The early electronic theories of bonding supported by the Bohr model of electron dynamics were successfully developed by Lewis into a broad rationalization of chemical bonding types. This work can be said to culminate in the publication of his book *Valence and the Structure of Atoms and Molecules* in 1923. In this book Lewis developed a symbolism for the electronic bonding in which electrons are represented as dots. Dots between atoms represented shared electrons thus



This symbolism was universally adopted by chemists for many years and is even now used in elementary texts.

In the Lewis theory of valence† there are two main types of chemical bond: ionic and covalent. The driving force for bond formation is identified as the pairing of electrons between atoms so as to obtain stable octets: the inert gas electronic structure. This idea of electron pairing had an important influence on the first quantitatively successful theories of the chemical bond which were a description of electron sharing in wave mechanical terms. As we shall see in later chapters, electron pairing is closely identified with a property of the electron which was unrecognized in 1923, namely its spin. Before we discuss the modern view of the concepts used by Lewis we must examine the development of new ideas in physics in the period 1900–1930.

†We should not ignore the contributions of others like Langmuir, Kossel, and Sidgwick to what is generally called Lewis theory.

Chapter 2

Matter Waves

2.1. Wave mechanics

In this chapter we introduce the concept of the wave nature of atomic particles. This is the foundation of the mathematical discipline of wave mechanics from which we can understand and predict the properties of molecules as individual entities (the so-called microscopic state). The properties of molecules in bulk (the macroscopic state) can be obtained by applying statistical techniques to these microscopic results.

Wave mechanics plays for atomic particles the role that classical mechanics plays for material objects. We interpret the motion of celestial bodies and we can predict the trajectories of space probes from the equations of classical mechanics developed by Newton, Lagrange, and Hamilton. We can understand and predict the properties of the hydrogen molecule from the equations of wave mechanics developed by de Broglie, Schrödinger, and Dirac. For both classical and atomic systems success in these endeavours depends to a large extent on the computational technology available at the time: the ability to land a man on the moon depended as much on the development of the digital computer as on the development of the rocket motor. Present computational resources are sufficient to enable us to understand many aspects of molecular behaviour for quite complicated molecules and to make accurate predictions for the smallest molecules, but they are insufficient for us to make accurate predictions for most larger molecules of interest to chemists. It is, however, important to appreciate that the scientific limitations we face at present do not suggest that the fundamental concepts of wave mechanics are inadequate or that the equations of wave mechanics are wrong.

We can identify the birth of wave mechanics either with the year 1924, when de Broglie postulated that material particles would show wave-like characteristics, or with the year 1926, when Schrödinger introduced an equation to define these characteristics. The conception, however, occurred much earlier, and is probably identified with the work of Planck in 1900. In attempting to explain the distribution of energy, as a function of frequency, of the radiation emitted by a so-called 'black-body' he made the hypothesis that atomic oscillators in equilibrium with electromagnetic radiation could only take up or give out energy in discrete amounts or 'quanta'. Following the hypothesis, which explained the experimental results, physicists developed first the 'old' quantum mechanics which we associate with the Bohr model of the atom, and then the 'new' quantum mechanics which we

associate mainly with the work of Heisenberg. We shall have little need in this book to make specific reference to the ideas inherent in the Heisenberg approach to quantum mechanics but it is perhaps worth noting that in 1930 Dirac showed that the mathematical approaches of wave and quantum mechanics were complementary: which is not to say they are equally easy to apply.

The revolutionary postulate of de Broglie received direct experimental verification in 1927 by Davisson and Germer. They showed that mono-energetic electrons scattered from crystalline nickel foil gave a diffraction pattern analogous to that shown by X-rays. Similar experiments were carried out independently by G. P. Thomson, and later Stern showed that beams of heavier particles (H_2 , He, etc.) showed diffraction patterns when reflected from the surfaces of crystals. De Broglie's expression for the wavelength of these matter waves, which we shall meet in the next section, was confirmed with high accuracy.

In retrospect, de Broglie's postulate was not such a bold step, as it was strongly suggested by the position that had been reached at that time regarding the nature of light or electromagnetic radiation. For this reason a brief interlude on the nature of light is appropriate.

2.2. The wave-particle duality of light

A satisfactory scientific description of light has presented a challenge to physicists over several centuries. In the 17th century there was a great controversy between the schools of Newton and Huygens over whether light was a stream of particles or a wave.

The fact that light travels in straight lines, is reflected and refracted and has the ability to impart momentum to anything it strikes, suggests a particulate (corpuscular) model. In contrast, the phenomena of diffraction and interference are most readily explained by a wave model. At the time when quantum theory was proposed the wave model was dominant because what was known at that time about the particulate behaviour of light could be largely understood from the wave model, although the carrier of the wave, the 'ether', was proving rather elusive.

Visible light is one part of a family of electromagnetic radiation whose members include X-rays, infrared, and ultraviolet radiation. The speed of light in a vacuum is a constant ($3 \times 10^8 \text{ m s}^{-1}$) independent of its frequency (ν) or wavelength (λ). Figure 2.1 shows the part of the electromagnetic spectrum of interest to scientists today, and we show the common names associated with different wavelength regions. Note that visible light is a very small band of the whole spectrum.

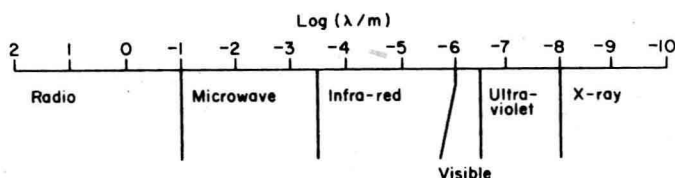


Figure 2.1 The electromagnetic spectrum.

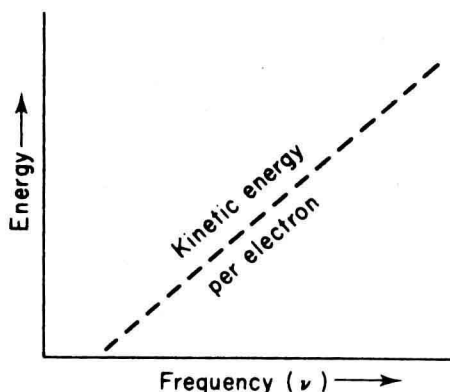


Figure 2.2 The relationship between the kinetic energy of the electrons emitted from a metal surface and the frequency of the light incident upon it.

The word electromagnetic is used to describe this radiation because its wave description is represented by electric and magnetic fields which fluctuate with the frequency of the radiation. Light is absorbed or scattered by matter either through the interaction of its electric field with the electric charges of atomic particles or through the interaction of its magnetic field with the magnetic moments of atomic particles. The former is by far the stronger effect and when in this book we consider the absorption of light by matter it is only the electric interaction that is important.

In the last few years of the 19th century the wave model of light was to experience a challenge to its superior position by experiments related to the observation that light is able to cause electrons to be ejected from the surface of metals. This so-called photoelectric effect was not only to have a big impact on the development of quantum theory, but, as we shall see in Chapter 5, it has been developed in recent years as an important tool for probing the electron energies of molecules.

The importance of the photoelectric effect became apparent when Lenard in 1902 published his investigation of the relationship between the frequency and the intensity of light on the one hand and the number and kinetic energy of the ejected electrons on the other. Figure 2.2 shows the relationship between the frequency and the kinetic energy per electron. No electrons are emitted until the frequency of the light exceeds a value characteristic of the metal, and above this the number increases rapidly but then levels off to a constant value. In the latter region the kinetic energy of the electrons is increasing linearly with ν , but not their number; the number of electrons released depends on the intensity of the light but not its frequency.

These results are not explicable in terms of the wave description of light, for which an increase in intensity should lead to an increase in the magnitude of the

electric field and hence to an increase in the energy of the ejected electrons. Further, a lower cut-off frequency for the electron ejection would not be expected; a lower cut-off intensity would be more likely. In contrast, the corpuscular model of light gives a ready explanation of the results as we now show.

In 1905 Einstein extended Planck's hypothesis (Section 2.1) that atomic oscillators could only take up or give out energy in discrete quanta, by regarding the radiation itself as consisting of indivisible quanta or photons. The energy associated with individual photons has to be proportional to the frequency of the light because the energy associated with a beam of light of constant intensity is proportional to its frequency. The proportionality constant relating the energy of a photon to its frequency turned out to be the one introduced by Planck in his theory. This constant is given the symbol h . It is one of the fundamental constants of nature, taking its place alongside the electron charge and the velocity of light. It has the units energy \times time and the value 6.6×10^{-34} J s. The relationship

$$E = h\nu, \quad (2.1)$$

is usually called the Planck-Einstein relationship.

The particulate interpretation of the photoelectric effect is straightforward. Each photon absorbed by a metal can lead to emission of one electron providing that the energy of the photon, when transferred to the electron, is sufficient to enable the electron to escape from the surface of the metal. Increasing the intensity of the light increases the number of photons but not their energy and so will lead to an increase in the number of electrons escaping but not to an increase in their energy.

Remembering Einstein's result, that the energy of the incident photon is given by $h\nu$, where ν is the frequency of the incident light, and that the kinetic energy of the ejected electron will be $\frac{1}{2}mv^2$, where m is the mass of the electron and v its velocity, we may write an equation for the energy balance in the experiment:

$$h\nu = A + \frac{1}{2}mv^2, \quad (2.2)$$

where A is an energy characteristic of the metal surface. For several years this expression provided the best method of evaluating the magnitude of Planck's constant.

This interpretation of the photoelectric effect restored the balance between the wave and particle models for light, and the position adopted today is that light has a wave-particle duality and that for any experiment one uses whichever model leads to the simpler interpretation. For example, the so-called Compton scattering of X-rays by the electrons in solids is best treated as a collision of two particles, the photon and the electron. There is no conflict here: light is light and it is only for convenience that we use familiar terms like wave and particle.

An important aspect of the treatment of the Compton effect is the conservation of the momentum of the colliding particles. But how can a photon, which has no mass, have momentum? Similarly, in writing the energy of the photon in equation (2.2) as $h\nu$ we avoided any discussion of the form of this energy. If a photon has momentum can it not also have kinetic energy? The fact that the photon has

momentum but no mass can be understood within the framework of relativity. In general, for a particle of rest mass m_0 , the momentum is

$$p = c^{-1} \sqrt{E^2 - m_0^2 c^4}. \quad (2.3)$$

Therefore, for the photon with zero rest mass

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}. \quad (2.4)$$

When de Broglie postulated that material particles would show wave-like characteristics, expression (2.4), which relates the momentum to the wavelength, was taken to apply not only to photons but to matter waves also. However, although the de Broglie postulate appears to give a close parallelism between light and matter, one must not lose sight of the essential difference that matter has mass and the photon does not. With this proviso however we can now examine the wave equation that applies to matter waves.

2.3. The Schrödinger equation

In discussions of elementary mechanics, one commonly starts by making definitions — such as defining force as the rate of change of linear momentum. This approach tends to conceal the fact that what is really involved is a postulate; a postulate which is accepted because it leads to results which agree with the measurements we make on large bodies. Similarly there is no way of deducing by strict logic the form of the equation that describes matter waves. Any relationship which we may obtain has to be tested, like any other fundamental equation of physics, by the fact that the results obtained from it are in accord with experiment. In the present case one can either derive the wave equation starting from certain postulates or, alternatively, argue by analogy with other established principles of physics. We shall adopt the latter approach. Our derivation is not the most general or elegant one to the fundamental equations of quantum mechanics but it has the advantage of relative simplicity and is sufficient for the objectives of this book.

First let us rehearse the characteristics of the equation which we are seeking. Most important of all is the fact that it is a wave equation and so may be expected to have some of the characteristics of more familiar wave equations, such as those describing the vibrations of a violin string. However, for the most part we shall not be interested in time-dependent quantities associated with the systems to which we shall apply our equation. So, we shall be interested in the allowed energy levels of an atom or molecule but will not consider whether a level only persists for a short time because the atom or molecule emits radiation or some other energy-changing process occurs. It follows, then, that the wave equation will not be time-dependent. In particular, it will not contain quantities differentiated with respect to time (in contrast to the more common mathematical description of the wave motion of systems such as a vibrating violin string). Another feature which we expect to find is that all of those quantities which we would have included in a classical

treatment — the kinetic energies of the particles, the repulsions between particles of like electrical charge and the attraction between those of opposite charge — will have their counterparts in the wave treatment. Finally, and in the light of our earlier discussion, we would expect that the de Broglie relationship (equation 2.4) will be in some way involved.

Let us write down a general expression for the sort of wave that we are considering but, for simplicity, consider a wave motion along only one coordinate axis. Note that the wave will be a stationary one, that is, for a given wave motion the nodes will not move with time. The reader may find it easiest to visualize this equation as representing, for example, the relative amplitude of excursion of points along a vibrating violin string at any instant in time (note that these relative amplitudes are themselves time independent); but the equation is really much more general than this. A suitable expression is

$$y(x) = A \sin \frac{2\pi x}{\lambda} \quad (2.5)$$

In this expression x is the coordinate axis along which the wave motion occurs with wavelength λ . The relative amplitude of the wave at any point along x is represented by the function $y(x)$, and as the maximum value of $\sin(2\pi x/\lambda)$ is unity, A represents the maximum amplitude of vibration. We shall refer to a function like $y(x)$ as a *wavefunction*. In equation (2.5) we have chosen the origin from which we measure x to lie at a node of the wave (for instance, one end of a violin string). A more general point could have been chosen as origin but there would have been an additional, constant, term on the right hand side of equation (2.5).

We next derive a differential equation for y by twice differentiating each side of (2.5) with respect to x , obtaining

$$\frac{d^2 y}{dx^2} = -\frac{4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda}, \quad (2.6)$$

or

$$\frac{d^2 y}{dx^2} = -\frac{4\pi^2}{\lambda^2} y. \quad (2.7)$$

This equation has an infinite number of solutions like (2.5). Firstly, equation (2.7) in no way places any limitations on A so that an infinite number of acceptable values exist. Secondly, the equation does not limit λ in any way. Thirdly, we note that a solution of equation (2.7) more general than (2.5) is

$$y(x) = A \sin \frac{2\pi}{\lambda} (x + \varphi), \quad (2.8)$$

where φ is a phase angle which can have any value. However, we can remove this freedom by the specification that $y(0) = 0$ so that

$$A \sin \frac{2\pi}{\lambda} (0 + \varphi) = 0. \quad (2.9)$$

It follows that we may set φ equal to 0 as in the function (2.5).

We can restrict the infinite number of values of λ which are acceptable as solutions in a similar manner by specifying the relative amplitude at some other point along the x axis. The simplest way of doing this is to require there to be a node at another specified value of x , say at l , so that $y(l) = 0$.

A general solution of

$$y(l) = A \sin \frac{2\pi l}{\lambda} = 0 \quad (2.10)$$

is

$$\frac{2\pi l}{\lambda} = n\pi, \quad (2.11)$$

where n is an integer. It follows that

$$\lambda = \frac{2l}{n}. \quad (2.12)$$

Thus in fixing the ends of a violin string and forcing these points to be nodes we restrict the value of the wavelengths which can be excited when the string is played. We refer to conditions which constrain the form of the wave function as *boundary conditions*. Boundary conditions are important in wave mechanics because as we shall see they are the origin of the quantization of energy: quantization is analogous to the requirement that n be an integer in equations (2.11) and (2.12).

We have gone into some detail over the form of equation (2.7) and its solutions because the pattern is followed closely for matter waves to which we now turn. The derivation is a simple one: we merely replace the wavelength, λ , by the momentum, p , in equation (2.7) using the de Broglie relationship (2.4). For a single particle moving in a one-dimensional space (x) with momentum p_x , we therefore have a wave function [which is traditionally represented by the Greek letter psi (ψ)] which satisfies the equation

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{h^2} p_x^2 \psi. \quad (2.13)$$

Equation (2.13) is not yet of such a form that its solutions will give directly the energy levels of the system because it does not yet contain any description of the forces acting on the particle. Force is defined by the derivative of the potential energy and hence we need to introduce into (2.13) some function of the potential energy. The momentum of the particle is related to its kinetic energy (T) by the expression

$$T = \frac{1}{2} mv^2 = \frac{p^2}{2m}, \quad (2.14)$$

where m is the mass of the particle. The kinetic energy is the difference between the total energy (E) and the potential energy (V)

$$T = E - V, \quad (2.15)$$

hence the momentum in (2.13) can be replaced according to the expression

$$p_x^2 = 2m(E - V), \quad (2.16)$$

to give the equation

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2m}{h^2}(E - V)\psi, \quad (2.17)$$

which on rearrangement gives

$$\frac{-h^2}{8\pi^2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi. \quad (2.18)$$

Equation (2.18) is the equation proposed by Schrödinger for a particle moving in one dimension in a potential V . To be more useful we need to extend the equation to three-dimensional space and we also require an equation which is applicable to more than one particle. The extension to three dimensions is made by letting ψ be a function of the three Cartesian coordinates and writing the appropriate partial derivatives instead of the complete derivatives in (2.17) as follows

$$\frac{-h^2}{8\pi^2m} \left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \right) + V\psi = E\psi. \quad (2.19)$$

Equation (2.19) can be written in a more compact form as

$$\mathcal{H}\psi = E\psi, \quad (2.20)$$

where \mathcal{H} is defined by

$$\mathcal{H} = \frac{-h^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V, \quad (2.21)$$

and is called the Hamiltonian of the system for reasons which will soon be clear. Note that \mathcal{H} contains differential operators $\partial^2/\partial x^2$ etc. and for this reason it makes no sense to cancel the ψ from both sides of equation (2.20).

Having established the general structure of Schrödinger's equation for atomic particles as (2.20) it is not difficult to give its precise form for any number of particles, by comparison with the corresponding equations that would describe the motion of the particles in classical mechanics.

2.4. The Hamiltonian

A link must exist between the equations which describe the motion of atomic (quantum) particles and those which describe the motion of heavy (classical)

particles because the results obtained by applying the quantum equations to heavy particles must be the same as those obtained from the classical equations. This idea was first proposed by Bohr in what is referred to as the correspondence principle.

The function which represents the total energy of a system in classical mechanics expressed in terms of the coordinates and momenta of all the particles is called Hamilton's function.† For a particle having mass m and moving under the influence of a potential V which is a function of the position of the particle, Hamilton's function is

$$\mathcal{H} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z), \quad (2.22)$$

the first term being the kinetic energy according to expression (2.14). We can set up a correspondence between Hamilton's function (2.22) and the operator \mathcal{H} , defined as the Hamiltonian in (2.21), if we make the substitution

$$p_x \rightarrow \frac{-i\hbar}{2\pi} \frac{\partial}{\partial x}, \quad (2.23)$$

or

$$p_x^2 \rightarrow \frac{-\hbar^2}{4\pi^2} \frac{\partial^2}{\partial x^2}. \quad (2.24)$$

It has been found that the connection (2.23) provides a general recipe for constructing the quantum mechanical Hamiltonian for any number of particles from the appropriate Hamilton function. It is because of this relationship that the Schrödinger equation is formally written as (2.20) and the operator \mathcal{H} is called the Hamiltonian. For example, for a set of i particles of mass m_i interacting with a potential energy V which is a function of the relative position of the particles, Hamilton's function will be

$$\mathcal{H} = \sum_i \frac{1}{2m_i} (p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) + V(x_i, y_i, z_i), \quad (2.25)$$

the total kinetic energy being a sum of the kinetic energies of each particle. The appropriate many-particle Hamiltonian is obtained by making the substitution in accord with (2.24)

$$\mathcal{H} = - \sum_i \frac{\hbar^2}{8\pi^2 m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + V(x_i, y_i, z_i). \quad (2.26)$$

† Hamilton was born in Dublin in 1805. According to the Dictionary of National Biography he had by the age of twelve studied Hebrew, Latin, Greek, and the four leading continental languages and could profess a knowledge of Syriac, Persian, Arabic, Sanskrit, Hindustani, and Malay. The choice of languages owed much to his father's intention to obtain for him a clerkship in the East India Company. In mathematics he appears to have been mainly self-taught. In 1823 he became a student of Trinity College, Dublin, and was first in all subjects and at all examinations. In 1824 when only a second year student Hamilton read a paper on Caustics (the shapes produced by focused light rays) before the Royal Irish Academy. In 1827 he was appointed Andrews Professor of Astronomy and superintendent of the observatory and soon after Astronomer Royal for Ireland.

The Schrödinger equation for such a system is then simply

$$\mathcal{H}\psi = E\psi. \quad (2.27)$$

The solutions, ψ , of such an equation are called the *eigenfunctions* of \mathcal{H} and the associated energies, E , are the *eigenvalues*.

2.5. The physical significance of the wavefunction

The wavefunction of a particle, ψ , is clearly an important quantity which is the amplitude of the particle wave in three-dimensional space. But just what is its connection to measurable properties of the particle? The step from a classical, particulate, to a wave picture (the step from equation (2.16) to (2.18)) makes the representation unclear. We gain some insight by looking at the wave nature of light. Suppose a beam of monochromatic light is incident on two narrow, closely spaced, slits. If one of the slits is covered, part of the beam of light will pass through the open slit, which itself acts as a secondary source, and illuminates a screen placed behind the slit. If we now cover this slit but open up the adjacent one a similar illumination of the screen will result. How will the illumination of the screen be altered when both slits are open? It is well known that an interference pattern will be seen on the screen. To describe this effect the wave amplitudes originating in each slit must be summed, leading to constructive interference when their phases are identical and destructive interference when they are of opposite phase. The light intensity and therefore the distribution of energy density on the screen is given by the *square* of the function which results when the wave amplitude from the two slits are summed: this energy density must always be positive.

There are similar interpretations of other phenomena related to wave motion and so we are led to look for a connection between the *squares* of the particle-wavefunctions ψ which are solutions of the Schrödinger equation and some physical quantity. In particular, we have to give a physical interpretation of the connection between ψ^2 , a continuous (cloud like) function† distributed in space, and the position of the particle. This interpretation was given by Born in 1926 and is now generally accepted. Born suggested that ψ^2 is interpreted as a *probability distribution* for the particle such that the probability of finding the particle in a small element of space dv is proportion to $\psi^2 dv$. The proportionality constant can be evaluated when we recognize that there is unit probability of finding the particle somewhere in space. That is, the integral of the probability density over all space must be unity

$$\int \psi^2 dv = 1. \quad (2.28)$$

Expression (2.28) is called the *normalization* condition for the wavefunction. It can be seen from equation (2.27) that the energy of the particle is unaffected by this

†Or $\psi^*\psi$ if ψ is a complex quantity as in some situations it may be. We shall assume in this book that wave functions are real unless we specify otherwise.

normalization. If ψ is a solution of (2.27) so too is $k\psi$ where k is any constant. If we have any solution of (2.27) which is not normalized, it is easy to normalize it by multiplying by the number N defined by

$$N^{-2} = \int \psi^2 dv. \quad (2.29)$$

We must recognize that the interpretation of $\psi^2 dv$ as a probability distribution means that we cannot say exactly where the particle is at any specific time. Although the point is not clear from the derivation we have used in this chapter it is a fundamental aspect of quantum mechanics that there are limitations to the accuracy with which some quantities can be measured which have nothing to do with the accuracy of the instruments we use in their measurement. The position of an electron (or any other atomic particle) is one such quantity. The physical rationale is simple enough. In order to measure the position of an electron (assumed stationary) we would have to bounce something off it (like a photon) and then observe the photon. Unfortunately, the collision would impart some momentum to the electron and so observation of the photon would only tell us where the electron was when it collided (some time ago) with the photon, not where it is now (when we observe the photon). Even this discussion simplifies the problem because one such measurement would not be sufficient to locate uniquely a point in space. What is clear, however, is that in this example uncertainty in position and changes (and, therefore, uncertainty) in momentum are linked.

A mutual and simultaneous uncertainty in the position and momentum of atomic particles is an integral part of quantum mechanics. This was first stated formally in 1927 by Heisenberg with his famous *Uncertainty Principle*. He proved that the product of the limits to our knowledge of the position of a particle and the limits to our knowledge of its momentum is of the order of Planck's constant h .

There has been much philosophical debate over whether the Uncertainty Principle is inherent in nature or only a consequence of our attempts to make measurements on nature (Einstein held the latter view). Such debates can never be more than philosophical; in this book we are concerned with our understanding of atomic and molecular structures based on measurements made on these systems. For us, then, it is good to know that this uncertainty is covered by our theory; in particular we note that the wavefunction which is a continuous function in three dimensional space provides us with all the information that can be determined about the particle by experimental observation.

Chapter 3

Atomic Orbitals

3.1. The Schrödinger equation for the hydrogen atom

The wavefunctions which are the solutions of the Schrödinger equation for atoms and molecules are in general functions of extreme complexity. We note from expression (2.26) that the Schrödinger equation involves a summation over all the particles of the system and hence the solution of this equation leads to wavefunctions ψ which are functions of the positions of all the particles. Even if we had knowledge of such functions this would not be of any great interest to us. From the square of the wavefunction $\psi^2(x_i, y_i, z_i)$ we determine the probability of finding particle 1 at the point with coordinates x_1, y_1, z_1 , particle 2 at x_2, y_2, z_2 , etc.† However, there is no physical measurement that could possibly test whether such a probability distribution would be correct or not. The type of distribution we *can* test from experiment is the distribution of the net charge of a molecule in space. In other words, we are interested in probability distributions in real 3-dimensional space rather than in abstract $3n$ -dimensional space for n particles.

There is no exact relationship between the total n -particle wavefunction and individual wavefunctions for each particle, but, as we shall see later, an approximate relationship does exist. The theory of the electron distribution and energies of atoms and molecules is based upon such an approximate relationship and we shall have no cause in this book to look beyond such an approximation. In other words, our concern is primarily with one-particle wavefunctions and the way in which we build up approximate many-particle wavefunctions from these.

For a full description of molecular properties we must be concerned with the wavefunctions of both nuclei and electrons. In Chapter 5 we shall show that because nuclei are several thousand times heavier than electrons their motion in a molecule is slow compared with the electronic motion, and we can obtain electronic wavefunctions by assuming that the nuclei are at rest. For atoms we have only a single nucleus and we are therefore only interested in the position of the electrons relative to the nucleus. The one-electron wavefunctions for atoms which define these positions are called *atomic orbitals*.

We shall, in later chapters, examine the one-electron wavefunctions for molecules, which are called *molecular orbitals*, and shall find that there are important similarities between atomic and molecular orbitals.

† More precisely the probability that particle 1 is between x_1 and $x_1 + dx_1$, y_1 and $y_1 + dy_1$, etc.