THE CHEMICAL BOND

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Preface

The advance and extension of that organized body of knowledge which is physical science involves an interplay between experiment and observation on the one hand and theory with its deductions and predictions on the other. In the development of some branches of science there are periods when theory lags behind experiment: this is characterized by the accumulation of facts which have seemingly little relationship to one another. The measurement of the frequencies of atomic spectral lines in the period just before the work of Balmer in 1885, and later before the development of the Bohr quantum theory in 1913, is a good example. There are other periods when experiment has lagged behind theory: some aspects of astronomy before the age of radio telescopes and space probes would typify this.

Whilst not wishing to underplay the importance in experimental science of lucky accidents which often initiate new areas of study, it would be generally agreed that experiments should be undertaken with specified objectives and with a reasonable expectation of achieving those objectives. In the broadest sense it is theory which provides the basis for these expectations. Theory can be anything from a highly developed and mathematically based model capable of giving a quantitative prediction of the result of the experiment, to a qualitative expectation based upon past experience with similar experiments.

Chemistry, or perhaps one should take a wider brief and say molecular science, is not for the most part susceptible to accurate quantitative predictions. For many scientists that is one of its attractions. It is nevertheless clear that chemists are extraordinarily successful in the development of their subject and ingenious in the new directions which they take. The two growth industries of the past thirty years, of polymers and pharmaceuticals, are evidence of that. In the field of organic chemistry over a million distinguishable compounds have been prepared and characterized and their number is increasing by several hundred each year, yet this development has occurred in a period when we cannot predict with accuracy the rate of a simple chemical reaction and we are in many cases uncertain about its course.

The majority of advances in chemistry have therefore been made with the support of qualitative theories. In many cases there would appear to be no theory at all in the usual sense in which we use that term, but if we have some 'explanation' or 'understanding' of an experimental result then that is a theory in its simplest form. We can say that in this respect a theory is part of the language of scientific communication. The concepts or ideas on which we rationalize our observations become our jargon. In the development of science this jargon changes partly by fashion but mainly by whether particular ideas are widely accepted as useful for communication. Concepts are continually being tested against new experiments or the results of more fundamental and reliable theories.

The language of modern chemistry stems largely from the beginning of this century and the formulation of atomic theory. Our understanding of molecular structure and reactivity is based upon the distribution of electrons in molecules, their movement in chemical reactions, and the energies associated with these distributions. In the 1920s modern quantum theory provided for the first time the basis for a quantitative description of molecular properties, and yet it was not until the 1960s that one could say that for molecular electron energy levels the results of this theory were fully tested against accurate experimental results. This was achieved through the agreement, within experimental accuracy, of the experimental and calculated dissociation energy of the hydrogen molecule.

The period 1930–1960 was one in which the basic equations that described molecular phenomena and the methods of solving them were known but their solution was beyond the ability of computational technology. However, it was not a period of inaction on the theoretical front. In retrospect it appears that the failure to solve the equations was a stimulus to the development of approximate solutions or models for which exact solutions could be found.

It is in this period that many of our concepts associated with the chemical bond and molecular structure were introduced. In contrast, during the past 15 years, in which the emphasis in theoretical chemistry has been to obtain computer based solutions of the quantum mechanical equations of increasing accuracy, few new concepts have been introduced. Some of the earlier ideas have failed the test of this recent period, but perhaps surprisingly a large number have maintained their usefulness to chemistry. The concept of hybridization is one example of an established and widely used concept of chemistry which has, however, little role in modern computer based calculations.

Most books on the chemical bond adopt a historical development of the subject in which the two basic theories of valence, molecular orbital and valence bond, are introduced and applied in the first place to simple systems like H_2^+ and H_2 for which a mathematically rigorous treatment was possible even in the 1930s. Such texts usually proceed with the discussion of empirical theories such as Hückel theory and ligand field theory, and, depending on the level at which the books are written, some of the more advanced empirical and non-empirical theories developed in recent years may be described. Our book *Valence Theory* published in 1965 was written to this pattern.

In this book, which is intended as an introduction to the subject at the undergraduate level, we adopt a different approach. We shall concentrate on those concepts of the subject which can be considered important within chemistry as a whole, but we will examine the validity of the concepts in the light of the most recent quantitative calculations. Although the computational techniques by which these calculations are made are not relevant at this level of the subject the principles underlying such calculations are no more difficult to understand than those on which the simple empirical theories are founded. The mathematical requirements for a reading of this book are not as high as those needed for *Valence Theory*, as the only computational technique which will be carried through in detail is the solution of a set of linear simultaneous equations.

Constants and Units

Physical constants

Constant	Symbol	Value	Units (SI)	Units (c.g.s.)
Speed of light in vacuum	c	2.998 x	10^{8} m s^{-1}	10^{10} cm s^{-1}
Electronic charge	$-e$	−1.602	10^{-19} C	10^{-20} e.m.u.
		−4.803		10^{-10} e.s.u.
Electron rest mass	m_e	9.110	10^{-31} kg	10^{-28} g
Proton rest mass	m_p	1.673	10^{-27} kg	10^{-24} g
Planck's constant	h	6.626	10^{-34} J s	10^{-27} erg s
	$\hbar = h/2\pi$	1.055	10^{-34} J s	10^{-27} erg s
Bohr radius	a_0	5.292	10^{-11} m	10^{-9} cm
Boltzmann's constant	k	1.381	10^{-23} J K^{-1}	10^{-16} erg K^{-1}
Avogadro's number	N_A	6.022	10^{23} mol^{-1}	10^{23} mol^{-1}
Permittivity of free space	ϵ_0	8.854	10^{-12} F m^{-1}	

Other common units:

Length: Angstrom, Å = 10^{-10} m

Energy: Electron volt, 1 eV = 1.602 x 10^{-19} J

Calorie, 1 cal = 4.184 J

Energy per mole: 1 eV per molecule is equivalent to 96.49 kJ mol^{-1}

kT at 300 K is equivalent to 2.494 kJ mol^{-1}

Wavenumber (reciprocal wavelength): 1 eV is equivalent to 8066 cm^{-1} based upon $E = hc/\lambda$

Dipole moment: debye = 10^{-18} e.s.u. cm = 3.334 x 10^{-30} C m

Atomic units

This system of units is chosen to avoid cluttering the quantum-mechanical equations with fundamental constants. It is based upon the choice $\hbar = m_e = e = 1$. The principal quantities of interest in this system are:

Unit of length: Bohr radius, a_0 = 5.292 x 10^{-11} m = 0.529 2 Å

Unit of energy; the hartree, E_H = 27.21 eV, which is equivalent to 2 626 kJ mol^{-1}

Contents

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

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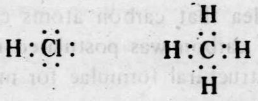
[†] Frankland, *Phil. Trans.*, 67, 417 (1852).

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



$$\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:} \qquad \mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{C}}:H}$$

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.

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†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 (3×10^8 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.

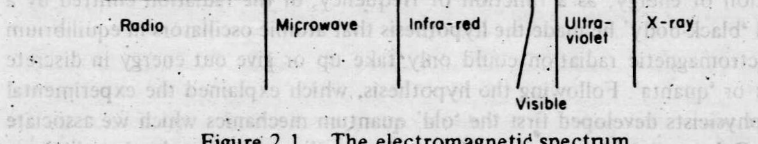

Figure 2.1 The electromagnetic spectrum.

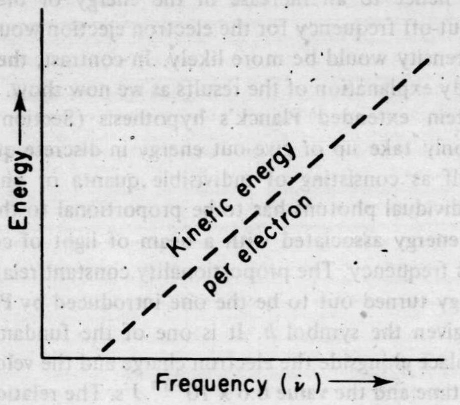

Figure 2.2 The relationship between the kinetic energy of the electrons emitted from a metal surface and the frequency of the light incident upon it.

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 energy 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 × time and the value 6.6×10^{-34} J s. The relationship

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

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:

$$h\nu = A + \tfrac{1}{2}mv^2 \tag{2.2}$$

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

$$p = c^{-1}\sqrt{E^2 - m_0^2 c^4}\,. \tag{2.3}$$

Therefore, for the photon with zero rest mass

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}\,. \tag{2.4}$$

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