

QUANTUM THEORY OF THE CHEMICAL BOND

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INTRODUCTION

The present text is a rational analysis of the concept of the chemical bond by means of the principles of wave mechanics. The discussion of the material has been arranged so as to render its main content comprehensible for readers who may not have had previous training in quantum mechanics.

The text comprises three major parts. It begins with an exposition of the fundamental ideas. In this section the principles are reviewed from which de Broglie developed his mechanics; this allows the book to be read by chemistry majors and freshmen alike. However, we believe that it may also be of interest to university- and college teachers who must include certain aspects of quantum chemistry into their courses while being insufficiently familiar with the subject. It may even be of interest to science teachers in secondary schools. Finally, having been a witness to the evolution of these notions for over a quarter of a century, we present certain concepts from a particular point of view which might prove attractive to chemists of all kinds, perhaps even quantum chemists.

The second, more technical part summarizes the methods of constructing wave functions that describe the electrons in molecules. This section can only be fully appreciated by those readers who are familiar with some aspects of the algorithms used in quantum mechanics.

On the other hand, we have expended considerable effort on writing the third part of this book in such a way that reference is only occasionally made to the techniques described in the second part. Hence it should be possible to study part three without having read part two. Some applications of the quantum theory of the chemical bond are presented in this last section.

In order to stress the multitude of areas where this theory demonstrates its value, we shall treat problems of reaction mechanisms and subjects of interest to biochemistry, biology, pharmacology as well as questions relevant to industrial chemistry.

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CHAPTER I

FUNDAMENTAL IDEAS

1. Introduction

Only three years separate the birth of wave mechanics [1]* from its application to the study of the chemical bond [2a, b]. I shall therefore try to report here some of the principal results obtained in the course of the subsequent forty years, during which the methods of mathematical physics penetrated into the field of chemistry. In our opinion it is useful first of all to place certain epistemological aspects of this amalgamation in perspective.

As in every other domain of mathematical physics, one stands in witness of the origin of a notion shaped by the intimate contact between an applied rationalism and a technical materialism [3]. The dialogue between the theoretician and the experimenter who in the initial stages of his research often operates on a qualitative, intuitive level, is carried on until an ensemble of mathematical concepts has been brought to bear on an ensemble of notions derived from the experiment though appearing in a quantitative structure. We shall examine in more detail how such a connection is established.

Concepts in physics and chemistry alike tend to become increasingly *operational* in the sense of Bridgman [4].

In order to find the length of an object we have to execute certain physical operations. The concept of length is then established when the operations measuring length have been fixed, i.e. the concept of length is not more and not less than the ensemble of operations measuring the length. In general, a concept is nothing more than an ensemble of operations: the concept is synonymous with its corresponding operations.

Is it not precisely so with the length of a chemical bond? Which chemist can pretend to have 'seen' such a length? And, strictly speaking, how is a number ultimately determined if not by the set of operations eventually leading to this number? We intend to show that such a number which is situated at the point where applied rationalism and technical materialism flow together, acquires the dualism of simultaneously being true and real. Its reality stems from the engendering material operations practised by the physical chemist, and the multitude

* Numbers in brackets refer to the list of references on p. 105.

of paths converging on the same number. It is as in the case that two series of operations as different as electron diffraction and microwave spectroscopy lead to the same number within experimental error. Then its reality stems from the fact that when one solves the wave equation associated with the molecule in question, the same number is found again. Here one applies a sequence of purely rational operations and relies on pencil and paper only to support one's short-term memory. One cannot emphasize often enough the miracle of such concurrent findings which give the scientist the feeling of security so characteristic of the mature scientific method. Operationalism induces the real and the true to bring forth the same entity: the number. Pythagoras must have had a presentiment when he noticed a numerical and harmonic duality in reality; and, in fact, the number remains the only indisputable point where applied rationalism and technical materialism flow together. The theory is allright by definition when for the calculation of a quantity it leads to a sequence of operations providing the same number as the experimental manipulations eventually measuring it. Theory and experiment derive their very affinity from the efforts made by the theoreticians and the experimenters in their attempts to arrive at the same numerical values. When the theoretical concepts are given careful scrutiny, it will soon become evident that they are of a very distinct kind. One should bear in mind that the first step in the sequence of operations creating the concepts, is to associate an entire molecule with an equation, the wave equation. The principles of wave mechanics provide the precise rules according to which such association can be conveniently carried out. The solution of the wave equation is a function, the total wave function, which enables us to calculate all those characteristic quantities that otherwise cannot be determined. The fundamental concepts which form the subject matter of the first part of this book will be grouped around the total wave function with its dependence on all the electrons of the molecule. Unfortunately, there are no practicable means to find an exact wave function, except in the case of extremely simple molecules. For this reason the quantum theory of the chemical bond utilizes numerous approximation methods. Moreover, there is the remarkable fact that some concepts are defined only by means of approximate wave functions, and gradually vanish the more exact the wave function becomes. For example, the charge distribution in a molecule, bond orders and free valencies are such concepts. It is evident that such concepts have a technical rather than a physical flavour, that they are based on cognition rather than on physical reality; they will be encountered in the second part of this book.

Among the procedures for the construction of wave functions the most common one is that which develops the function from a basis of orbitals. It will be shown that this method is largely analogous to the representation of a vector by its components in a coordinate system. It is possible to rotate the

basis of the orbitals leaving the approximate wave function invariant, though changing its expression in terms of the orbitals. This is similar to a rotation of the coordinate axes whereby the components of the vector are altered. Strangely enough, some concepts have been defined so as to be dependent on the choice of the orbital basis of the wave function. The exchange energy belongs to this class. One senses that such concepts are bound to be physically meaningless; they can never coincide with measurable quantities, and populate physical parlance with dangerous expressions suggesting many false notions to the minds of those not yet immunized by a period of prolonged asceticism. We will call attention to such ambiguous concepts as soon as they appear, since it is just as intolerable not to give a feeling of the physical meaning behind a concept as it is to make others believe that there is a meaning hidden behind a concept actually devoid of such meaning.

2. Wave Mechanics

Differences are worthwhile since they create the most beautiful harmony, for everything is shaped by struggle. (...) They do not understand how the differences are reconciled; the harmony of opposite tensions like those of the arch and the lyra.

Thus wrote Heraclitus of Ephesus five centuries before our era. Wave mechanics gives a view of the world with the discontinuous and the continuous living in harmony, like the particle and the wave, the certain and the uncertain. For the benefit of readers untrained in such usage, the principal ideas upon which the present theoretical structure is based, will be brought together.

THE DE BROGLIE WAVE AND THE PARTICLE

A study of light will very quickly reveal its dual nature, continuous and discontinuous. In the geometrical theory of Descartes, which associates each bundle of light with a collection of straight lines, rays, it is considered as continuous. Isaac Newton already considered each brilliant object as a generator of light particles, grains with a very small weight and forcefully ejected into space. Applying the principles of his mechanics to this discontinuous phenomenon, Newton gave an elegant interpretation of reflection and refraction. The discovery of interference fringes and diffraction effects forced Fresnel to treat light as though it were a transverse wave propagating along the rays.

Only this structure, continuous again, permitted him to understand why a doubly illuminated area may appear dark. Finally the interpretation of the experimental data on the photo-electric effect led Einstein to the rehabilitation of the light corpuscle while preserving its wave character. In this theory a monochromatic radiation appears as a kind of undulatory fluid characterized

by a certain frequency ν with its energy concentrated in particles called photons.

In the meantime, Planck was led to assume that the exchange of energy between radiation and matter could take place in small, distinct quantities only, i.e. in quanta W proportional to the frequency ν of the wave-like intermedium. Such a hypothesis permitted a theoretical derivation of the distribution of the radiation frequencies emitted by a black body. The factor h , connecting W and ν , bears Planck's name. As a natural consequence of this Einstein supposed that the energy of a photon guided by a wave, should be expressed by

$$W = h\nu.$$

This relation enabled him to give a quantitative explanation of the fundamental laws of the photo-electric effect. Fresnel's wave-theory associates every light ray travelling along the x -axis, with a wave

$$\Psi(x, t) = a \cos 2\pi[\nu t - x/\lambda],$$

where λ = wavelength.

According to Fresnel, this is equivalent to the complex form

$$\Psi(x, t) = a \exp[2\pi i(\nu t - x/\lambda)].$$

Furthermore, light intensity is proportional to the square of the amplitude a^2 , i.e. to the square of the modulus of Ψ . According to Einstein's hypothesis which reduces the energy to a collection of identical corpuscles, the light intensity must be proportional to the volume density of those corpuscles. In view of this the volume density of the photons must be proportional to a^2 or to $|\Psi|^2$.

In 1923 Louis de Broglie became convinced that the wave-particle dualism is not an exclusive attribute of the photon, but rather that every particle can be associated with a wave. He clearly anticipated the wave character of electricity. Davisson and Germer's experiments in 1927 proved the correctness of that idea when these scientists proved that an electron beam produces diffraction fringes just like a light beam does. In 1924 Louis de Broglie had already defined distinct links between waves and particles. In particular, he showed that for the classical trajectory of a particle with mass m and velocity v to coincide with an associated wave within the limits of the approximations of geometrical optics, the wavelength should be selected so as to obey the relation

$$\lambda = h/mv,$$

which is de Broglie's formula. The wavelength calculated with this formula for the electrons in Davisson and Germer's experiments, accounted quantitatively for the structure of the observed diffraction pattern. So far we have been interested in light rays associated with waves, and hence in large numbers of photons. When we have the intention to study the chemical bond, the wave

function must describe very small numbers of photons. We must therefore scrutinize the significance of an associated wave relative to decreasing numbers of particles associated with it. We noted that for large numbers the square of the modulus of the wave, $|\Psi(M, t)|^2$, represents the volume density of the particles at point M at time t . In the extreme case of a wave associated with one electron only, it is obvious that $|\Psi(M, t)|^2$ can no longer represent the number of electrons in one unit volume at point M , since this number would be zero everywhere except at the very point where the electron happens to be. Brief reflection yields the recognition of a probability as the only possible link between wave and particle. Let us therefore assume that the probability dp of finding the electron in a volume dv around point M at time t , shall be given by

$$dp = |\Psi(M, t)|^2 dv.$$

This means that

$$dp/dv = |\Psi(M, t)|^2$$

represents a probability density; this becomes an ordinary density when the number of particles becomes large, and by virtue of the laws of large numbers these probabilities will turn into certainties.

THE WAVE EQUATION

It can easily be seen that the wave travelling along the x -axis,

$$\Psi = a \exp[2\pi i (vt - x/\lambda)]$$

obeys the equation

$$d^2\Psi/dx^2 = v^{-2}\lambda^{-2} d^2\Psi/dt^2$$

In the general context of classical wave optics it can be shown that a light wave

$$\Psi(M, t) = a(M) \exp[2\pi i (vt - \varphi(M))]$$

obeys d'Alembert's equation

$$\partial^2\Psi/\partial x^2 + \partial^2\Psi/\partial y^2 + \partial^2\Psi/\partial z^2 = v^{-2}\lambda^{-2} \partial^2\Psi/\partial t^2$$

which can be written in a more concise form as*

$$\nabla\Psi = v^{-2}\lambda^{-2} \partial^2\Psi/\partial t^2.$$

* The symbol ∇ (nabla) identifies the Laplace operator, defined as the summation of second derivatives:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

(for simplicity's sake ∇ is used instead of the customary ∇^2).

We note that

$$\frac{\partial \Psi}{\partial t} = 2\pi i v \Psi; \quad \frac{\partial^2 \Psi}{\partial t^2} = -4\pi^2 v^2 \Psi.$$

Substitution of the latter expression into d'Alembert's equation yields

$$\nabla^2 \Psi = - (4\pi^2 / \lambda^2) \Psi. \quad (1.1)$$

Suppose now that the wave Ψ is associated with an electron and that its total energy E can be separated into a potential energy $F(M)$ and a kinetic energy $mv^2/2$. Then

$$E = F(M) + \frac{1}{2}mv^2.$$

But since

$$\lambda = h/mv$$

we may write

$$E = F(M) + h^2/(2m\lambda^2)$$

and so

$$\lambda^{-2} = (2m/h^2) (E - F(M))$$

which then is substituted into (1):

$$\nabla^2 \Psi = - (8\pi^2 m/h^2) (E - F(M)) \Psi$$

or

$$- (h^2/8\pi^2 m) \nabla^2 \Psi + F(M) \Psi = E \Psi.$$

This is the so-called Schrödinger equation. Its solution gives the exact form of the function $\Psi(M, t)$ representing the distribution of the wave over space and time, thus permitting us to calculate at any moment the probability of finding the particle in any selected domain of space.

STATIONARY STATES

Let us briefly review the fundamental ideas encountered so far. We shall associate a wave of frequency ν with a particle of energy E , such that

$$E = h\nu.$$

At point M and time t this may be written

$$\Psi(M, t) = a(M) \exp 2\pi i \nu t.$$

(One should notice that the quantity $\exp 2\pi i \nu t$ can always be absorbed into $a(M)$.)

When this wave describes a particle with mass m and subject to such inter-

actions as to give it a potential energy $F(M)$, the wave obeys the equation

$$-(\hbar^2/8\pi^2m) \nabla^2 \Psi + F(M) \Psi = E\Psi.$$

The probability dp of finding the particle in a volume dv at time t is given by the expression

$$dp = |\Psi(M, t)|^2 dv.$$

This is why the derivative

$$dp/dv = |\Psi(M, t)|^2$$

is called the probability density. Essentially, the wave appears to have the nature of a probability; it is a probability wave. Note that, according to the well-known properties of exponential functions

$$|\Psi(M, t)|^2 = |a(M)|^2.$$

Consequently, the probability of finding the particle in the volume element dv is independent of time. Hence, the wave in question describes a stable state, a state not changing with time: it is a *stationary state*. Notice also that since the particle cannot fail to be found in space somewhere, the summation of the probabilities dp corresponding with all the volume elements dv of that space must be the same as a certainty, i.e. must equal 100% or 1. This means that,

$$\int_{\text{space}} dp = \int_{\text{space}} |\Psi(M, t)|^2 dv = 1.$$

The wave function $\Psi(M, t)$ is normalized to unity. Next we wish to point out that with

$$H = -(\hbar^2/8\pi^2m) \nabla^2 + F$$

the Schrödinger equation becomes

$$H\Psi = E\Psi,$$

which clearly shows that the operations performed by the operator H on the function Ψ must lead to a simple multiplication of the function by a constant, the energy E of the particle. The function Ψ is called the *eigenfunction* of the operator H and the energy E is the corresponding *eigenvalue*. These ideas will now be applied to the movements of a particle with mass m and confined to a segment of a straight line with length l (Figure 1).



Fig. 1.

The x -axis is chosen collinear with the segment, one end of which is in the origin. In order to prevent the particle from leaving the segment, it is subjected to a potential which is constant along the segment and infinitely repulsive beyond its end points. The wave equation is then simply

$$-(\hbar^2/8\pi^2 m) d^2\Psi/dx^2 + F(x) \Psi = E\Psi$$

with $F(x)$ =Constant for all x on the segment, but infinite for all x outside of the segment. This equation will now be solved for the open interval $(0, l)$. Within this interval the potential energy is defined apart from a constant which can always be taken so as to obey

$$F(x)=0 \text{ for all } x \text{ in the open interval } (0, l).$$

Within the interval we have

$$-(\hbar^2/8\pi^2 m) d^2\Psi/dx^2 = E\Psi,$$

where

$$\Psi = a(x) \exp 2\pi i v t.$$

It follows quite easily that

$$-(\hbar^2/8\pi^2 m) (d^2a/dx^2) = Ea \tag{1.2}$$

and from this

$$a = k \sin (Ax + B). \tag{1.3}$$

The calculation of A and B is easy:

$$(d^2a/dx^2) = -A^2a$$

which after substitution into (1.2) leads to

$$(\hbar^2 A^2/8\pi^2 m) = E.$$

Now the equation's behaviour must be examined for the case that $x \rightarrow 0$. Write

$$-(\hbar^2/8\pi^2 m) (d^2a/dx^2) + aF(x) = Ea.$$

The right hand side, Ea , remains finite because a is a continuous function. Consequently, the left hand side must also remain finite. The first term fulfills that requirement. The second term must behave likewise. Since $F(x) \rightarrow \infty$ it is necessary that $a \rightarrow 0$. And so for $x=0$

$$a = k \sin (Ax + B) = 0.$$

Hence

$$\sin B = 0; \quad B = p\pi.$$

So we may let $B=0$ without imposing restrictions on the generality of the

discussion, and the function becomes

$$a = k \sin Ax \quad \text{with} \quad (h^2 A^2 / 8\pi^2 m) = E. \quad (1.4)$$

The same kind of reasoning shows that when $x \rightarrow l$ it is necessary that $a \rightarrow 0$, and consequently

$$0 = k \sin Al; \quad Al = n\pi \quad \text{with} \quad n = \text{integer}.$$

Substitution of this value of A into (1.4) eventually yields

$$E = (h^2 n^2 / 8ml^2) \quad (1.5)$$

and

$$a = k \sin (n\pi/l) x. \quad (1.6)$$

This result indicates that the energy of the particle can only assume one of the values given by formula (1.5). It cannot vary continuously. It undergoes discontinuous changes only, passing from one value of the set defined by (1.5) to another value in the same set. The energy is said to be *quantized* and dependent on the *quantum number* n .

It will be clear, however, that the wave's amplitude is a sinusoidal function of x . So it equals zero for a series of values x , and passes through maxima for other values x . The wave possesses *nodes* and *antinodes*. This resembles the classical stationary waves (e.g. Melde's experiment, resonance of sound waves in a tube). For $n=1$ there is one node at each end of the segment and a maximum at the center. The best chances to find the particle are in the center. It will never go to the very ends since that is forbidden. For $n=2$ a third node appears in the middle of the segment; the particle is no longer allowed to be there. The maximum of the probability density corresponds with

$$x = \frac{1}{4}l \quad \text{and} \quad x = \frac{3}{4}l.$$

One observes that with increasing n , i.e. with increasing energy, the number of nodes increases. The distribution of the probability density depends on the energy.

WAVE MECHANICS AS A SET OF THEOREMS

The essentials of wave mechanics can be condensed to three principles.

(a) *The Principle of the Associated Wave*

Each particle with mass m and subjected to a force field giving it a potential energy $F(M)$ at point M , is associated with a wave (M, t) . This wave is a solution of

$$-(h^2/8\pi^2 m) \nabla^2 \Psi + F(M) \Psi = (h/2\pi i) \partial \Psi / \partial t. \quad (1.7)$$