1 Introduction

Lavoisier was the first person to publish an account of how the weight relationships of reagents and products in chemical reactions could serve as the basis of a systematic analytical approach to chemistry [1]. Measurements of changes in weight are a characteristic feature of the quantitative study of chemical reactions; such measurements reveal one of the most important facts about the chemical combination of substances, namely that it generally involves fixed and definite proportions by weight of the reacting substances, and invariably leads to products consistent with the laws of conservation of mass, and of definite proportions.

A knowledge of the proportions by weight of the elements in a given pure substance is not sufficient information to fix the chemical identity of the substance since there may be several, or many, compounds with the same proportions by weight of their elemental constituents; this is true of many hydrocarbon substances which are chemically distinct yet contain one part by weight of hydrogen to twelve parts by weight of carbon, for example, acetylene, benzene, vinylbenzene, cyclooctatetraene etc. In these cases there are distinct compounds formed by two elements that exhibit constant chemical equivalents.

At the beginning of the nineteenth century, the chemical elements were given a new interpretation in terms of Dalton’s atomic hypothesis that marks the beginning of microscopic chemical theory. Henceforth the elements were to be regarded as being composed of microscopic building-blocks, atoms, which were indestructible and had invariable properties, notably weight, characteristic of the individual elements. Similarly, compounds came to be thought of in terms of definite combinations of atoms that we
now call molecules. All molecules of a given chemical substance are exactly similar as regards size, mass etc. If this were not so it would be possible to separate the molecules of different types by chemical processes of fractionation, whereas Dalton himself found that successively separated fractions of a gaseous substance were exactly similar.

Nearly 50 years of confusion followed Dalton until the Sicilian chemist Cannizzaro outlined a method whereby one could reliably determine a consistent set of weights of different kinds of atoms from the stoichiometric data associated with a set of chemical reactions, and he used this to define the atomic composition of molecules. It is important to note that the atom is the smallest unit of matter required in the description of chemical processes. Cannizzaro’s argument was based on Avogadro’s hypothesis that equal volumes of gases at the same pressure and temperature contain equal numbers of molecules. From the mathematical point of view the problem is indeterminate in the sense that one cannot exclude the possibility that the ‘true’ atomic weights are integer submultiples of those proposed. Cannizzaro offered a partial remedy by observing that the probability that one has the ‘true’ weights is increased by increasing the amount of data about stoichiometric relations. A complete account of the mathematical relations that represent stoichiometry does not require any assumption about the nature of atoms.

An evident limitation of stoichiometry is that it is only concerned with the changes in weight that occur in chemical reactions; it says nothing about the changes in other properties that accompany chemical transformations. Equally, the original atomic theory could say nothing about the chemical affinity of atoms, why some atoms combine and others do not, nor give any explanation of the restriction to simple fractions in the laws of chemical combination of atoms. In order to keep track of the growth of experimental results, more and more transformations of compounds into other compounds, some further development of the theoretical framework was needed. In the nineteenth century the only known forces of attraction that might hold atoms together were the electromagnetic and gravitational forces, but these were seen to be absolutely useless for chemistry, and so were given up in favour of a basic structural principle.

In 1875 van ’t Hoff published a famous booklet which marks the beginning of stereochemistry. Following a suggestion of Wislicenus, van ’t Hoff proposed that molecules were microscopic material objects in the ordinary 3-dimensional space of our sensory experience with physicochemical properties that could be accounted for in terms of their 3-dimensional structures. For example, if the four valencies of the carbon atom were supposed to be directed towards the corners of a tetrahedron, there was a perfect correspondence between predicted and experimentally prepared isomers, and a beautiful structural explanation for the occurrence of optical activity. It is natural to extend this hypothesis to all molecules and to suppose that optically active molecules are simply distinguished from other species in that they possess structures that are dissymmetric.

Here there is a clear implication for the dimensionality of the ‘molecular space’. In a two-dimensional world there would be two forms of the molecule CH2X2, whereas only one such compound is known. On the other hand molecules such as C-abde exist in two
forms; these facts require a three-dimensional arrangement of the ‘bonds’. Evidently no picture of the atom is required for this construction; indeed molecular structures can be reduced to suitably labelled points (atoms) joined by lines (bonds). Moreover van ’t Hoff’s identification of ordinary physical space as the space supporting these structures is optional; any Euclidean 3-space will do.

The development of the interpretation of chemical experiments in terms of molecular structure was a highly original step for chemists to take since it had nothing to do with the then known physics based on the Newtonian ideal of the mathematical specification of the forces responsible for the observed motions of matter (the mechanical philosophy). It was one of the most far-reaching steps ever taken in science. G.N. Lewis once wrote

No generalization of science, even if we include those capable of exact mathematical statement, has ever achieved a greater success in assembling in a simple way a multitude of heterogeneous observations than this group of ideas which we call structural theory.

Thus over a period of many years chemists developed a language - a system of signs and conventions for their use - which gave them a representation of their fundamental postulate that atoms are the building-blocks of matter; molecules are built up using atoms like the letters of an alphabet. A molecule in classical chemistry is also seen as a structure, as a semi-rigid collection of atoms held together by chemical bonds. So not only do we count the numbers of different kinds of atoms in a molecule, but also we say how they are arranged with respect to each other, and so we can draw pictures of molecules. In more abstract terms this account has a topological quality that can be represented diagrammatically using ‘trees’ or ‘graphs’. The laws that govern the relative dispositions of the atoms in 3-dimensional space are the classical valency rules which provide the syntax of chemical structural formulae. Valency, the capacity of an atom for stable combination with other atoms, is thus a constitutive property of the atom.

The proposed atomic constitution of matter seems first to have been related to valency when both Mendeléev and Meyer observed, independently, in 1869 how valency was correlated with position in the periodic table. There was however no agreement between chemistry and physics about the nature of atoms. In the same year as van ’t Hoff inaugurated stereochemistry with his advocacy of the tetrahedral bonding about the carbon atom, the contributor of the entry ‘ATOM’ in the Encyclopaedia Britannica, (generally believed to be James Clerk Maxwell) gave strong support to Lord Kelvin’s vortex model of the atom because it offered an atomic model which had permanence in magnitude, the capacity for internal motion or vibration (which the author linked to the spectroscopy of gases), and a sufficient amount of possible characteristics to account for the differences between atoms of different kinds.

To each pure substance there corresponds a structural molecular formula, and conversely, to each molecular formula there corresponds a unique pure substance. It is absolutely fundamental to the way chemists think that there is a direct relationship...
between specific features of a molecular structure and the chemical properties of the substance to which it corresponds. Of especial importance is the local structure in a molecule involving a few atoms coordinated to a specified centre, for this results in the characteristic notion of a functional group; the presence of such groups in a molecule expresses the specific properties of the corresponding substance (acid, base, oxidant etc.) which however is only realized experimentally in an appropriate reaction context.

Each pure substance can be referred to one or several categories of chemical reactivity, and can be transformed into other substances which fall successively in other categories. The classical structural formula of a molecule summarizes or represents the connection between the spatial organization of the atoms and a given set of chemical reactions that the corresponding substance may participate in. This set includes not only the reactions required for its analysis and for its synthesis, but also potential reactions that have not yet been carried out experimentally. This leads to a fundamental distinction between the chemical and physical properties of substances; while the latter can be dealt with by the standard ‘isolated object’ approach of physics, the chemical properties of a substance only make sense in the context of the network that describes its chemical relationships, actual and potential, with other substances. Of course, the chemical properties are constrained by the physical requirements of the conservation of mass, and the competition between energy and entropy expressed through the thermodynamic notion of ‘free energy’.

A notable consequence of the structural account of chemical facts is that identical atoms can play distinguishable roles, that is the fundamental permutation symmetry of the elemental atoms is not generally preserved in molecular structures. Thus there are ‘hydroxyl hydrogens’, ‘methyl hydrogens’, ‘aromatic hydrogens’ etc., and this poses formidable conceptual problems for an ‘isolated object’ type of description. Nevertheless, this has been the standard approach in the physical description of molecules, as we now describe.

2 The physical model of molecules

Although we have seen that chemistry relies on the atom as its basic unit, there is no sufficient theoretical account of interactions between atoms, and the conventional approach is to invoke sub-atomic structure. Thus chemical physics and quantum chemistry rely on Schrödinger’s equation and an appropriate Hamiltonian for atoms and molecule which are taken to be composed of charged particles. The wave equation for the hydrogen atom with the Hamiltonian based on purely electrostatic (Coulombic) forces between the charged particles, yields definite formulae for the atom’s energy levels expressed in terms of fundamental constants including values for the electron and proton masses and their charges; if we substitute the experimentally determined values (obtained from other

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1 Since there is no apparent limit in principle to the (exponential) growth in the number of new substances the chemical network is an unbounded domain.
On observing that there is a formal relation between this [Schrödinger] wave equation and the classical energy equation for a system of two particles of different masses and charges, we seize on this as providing a simple, easy, and familiar way of describing the system, and we say that the hydrogen atom consists of two particles, the electron and proton, which attract each other according to Coulomb’s inverse-square law. Actually we do not know that the electron and proton attract each other in the same way that two macroscopic electrically charged bodies do, inasmuch as the force between two particles in a hydrogen atom has never been directly measured. All that we do know is that the wave equation for the hydrogen atom bears a certain formal relation to the classical dynamical equations for a system of two particles attracting each other in this way.

Having emphasized the formal nature of this correlation and of the usual description of wave mechanical systems in terms of classical concepts, let us now point out the extreme practical importance of this procedure. It is found that satisfactory wave equations can be formulated for nearly all atomic and molecular systems by accepting the descriptions of them developed during the days of the classical and old quantum theory and translating them into quantum mechanical language by the methods discussed above. Indeed, in many cases the wave mechanical expressions for values of experimentally observable properties of systems are identical with those given by the old quantum theory, and in other cases only small changes are necessary. Throughout the following chapters we shall make use of such locutions as “a system of two particles with inverse square attraction” instead of “a system whose wave equation involves six coordinates and a function $e^{2/r_{12}}$, etc.

Since we are dealing with charged particles, a fundamental theory of atoms and molecules must presumably be based on their electrodynamics, and so we require electrodynamics formulated in terms of Hamiltonian dynamics, since this is the route to Schrödinger’s equation. It is conventional to begin with a classical description knowing that the canonical quantization scheme due to Dirac is a standard procedure for obtaining a quantum theory from a classical analogue that has been cast in Hamiltonian form. It has long been recognized however that the scheme involves analogy which may not be reliable, since the resulting quantum theory may or may not turn out to be satisfactory. The classical theory is thus no more than a recognizable starting point towards a quantum theory, the required endpoint.

The usual discussion in the literature of classical electrodynamics concentrates on the Lorentz force law for the dynamics of the charges, with fields obtained from the relevant (retarded) solutions of the Maxwell equations; much of the discussion is concerned with
aligning the theory with special relativity which is an obvious priority in general physics. In classical electrodynamics the limiting case of point charged particles is pathological, and a major goal of the theory is the treatment of the infinities that arise. For example, the Coulomb energy is divergent for a classical point charge. In some sense this means that the notion of a point particle carrying electric charge is simply inconsistent with classical physics. We now know from quantum mechanics that classical physics cannot be used for lengths shorter than about the reduced Compton wavelength ($\lambda_C = \hbar/m_0c$) for the particle; according to the uncertainty principle this corresponds to energies greater than the rest-mass energy of the particle, that is above the pair production threshold. It is known that maintaining explicit Lorentz invariance and gauge invariance provides the best route to making sense of the divergences that plague the electrodynamics of point charged particles.

Atoms and molecules are characterized minimally by the specification of a definite number of nuclei and electrons (molecules have ‘classical structures’ which is a separate problem that will concern us below). There is no known theory of a system with a fixed finite number of particles interacting through the electromagnetic force that is covariant under Lorentz transformations, so that any general account of atoms and molecules will be ‘non-relativistic’ to some degree. It is usually accepted that the first step in transforming to a Hamiltonian description is to ensure that Newton’s law of motion for the charges with the Lorentz force, and the Maxwell equations for the field, are recovered as Lagrangian equations of motion. There is then a standard calculation for the determination of the associated Hamiltonian.

It is important to note that the customary starting point for classical Lagrangian electrodynamics involves symbols for the electric charges $\{e_n\}$ and masses $\{m_n\}$ of the particles which are merely parameters that cannot be assumed to have the experimentally determined values. There is a subtle change of viewpoint here; the original equations of motion, modelled on macroscopic classical electrodynamics, describe the electromagnetic fields associated with prescribed sources through Maxwell’s equations, while Newton’s laws are used to describe the motion of charged particles in a prescribed electromagnetic field. The Lagrangian formalism however describes a closed system for which $\partial L/\partial t = 0$, so that by the usual arguments the Hamiltonian $H$ is the constant energy of the whole system.

For comparison with experimental data the parameter $e$ is required to be the experimentally observed charge of a particle; a gauge invariant theory guarantees charge conservation and at non-relativistic energies there are no physical processes that can modify the value of $e$. This is true in both classical and quantum theories. The situation with the mass parameter $m$ for a particle is quite different since there is a charge-field interaction that leads to an arbitrary ‘electromagnetic mass’ additional to the ‘mechanical mass’ $m$. It is possible for the ‘electromagnetic mass’ (due to self-interaction) to become arbitrarily large and this requires $m$ to be negative so that the observed mass = mechanical mass + electromagnetic mass has its observed (positive) value. This pathology certainly occurs in the point charge limit, and is the origin of so-called ‘runaway’
The physical model of molecules

solutions in the classical equations of motion for the charged particles. A feature of the runaway solution is that it has an essential singularity at \( e = 0 \), so there is no possibility of constructing solutions of the interacting charge and field system that pass smoothly into the solutions of the non-interacting system as \( e \to 0 \). Some of these problems are inherited by the quantum theory resulting from canonical quantization of non-relativistic classical electrodynamics.

The origins of the approach employed in modern atomic and molecular theory can be found in the model of the hydrogen atom proposed by Bohr in 1913 to account for the spectrum of hydrogen. Of course the model did not survive the discovery of quantum mechanics but it left a seemingly permanent imprint; the quantum mechanics that developed from it is fundamentally spectroscopic in nature (energy levels, transition matrix elements, the S-matrix, response functions etc.). In the present context it is perhaps worth keeping in mind an aphorism by the late Hans Primas, “Chemistry is not spectroscopy” [11]. Bohr’s model is mainly remembered for his introduction of Planck’s constant, \( h \), and the resulting quantization of the angular momentum. Much less remarked on today is that Bohr made a decisive break with classical electrodynamics. In modern terms the idea is this; formally one fixes the gauge of the vector potential, \( a \), by the Coulomb gauge condition

\[
\nabla \cdot a = 0
\]

and it then follows easily that the longitudinal part of the electric field strength due to the electrons and nuclei can be expressed entirely in terms of their coordinates and gives rise to the familiar static Coulomb potential in the Hamiltonian \( H \). ‘Radiation reaction’ due to the transverse part of their electromagnetic field is discarded, and the role of the radiation field is demoted to the status of an ‘external’ perturbation inducing transitions between Bohr’s stationary states. Whether one can really separate charged particles from their own fields in a gauge-invariant fashion is another matter entirely.

The intrinsically quantum mechanical nature of the description can be seen in the characteristic interaction parameter, the fine structure constant \( \alpha \), which is inversely proportional to \( h \), and so makes no sense in a classical description in which \( h \) plays no role (formally \( h = 0 \)). Thus one is lead to the notion of an isolated atom or molecule with a specified number of electrons and nuclei in free space interacting through purely Coulombic forces according to quantum mechanics. This framework was well-known to Schrödinger and he too chose to formulate his quantum theory of the hydrogen atom in terms of the singular Coulomb potential; most mathematicians were astonished that it seemed to work since the classical version of the model (Newtonian gravity) has pathological solutions. It was immediately attractive to those studying atoms and molecules, and as molecules had traditionally ‘belonged’ to chemists, it was attractive to them too.

In most textbooks of physical chemistry there is, somewhere, a section on quantum mechanics. In it there are usually examples of the use of the Schrödinger equation to solve a few standard problems, at least for their bound states. These are then used to

\[2\text{In dimensionless form } \alpha = e^2 / 4\pi\epsilon_0 hc.\]
motivate the proposition that in quantum mechanics can be found the theoretical basis of chemistry. Although such direct assertions are seldom to be found in textbooks of organic chemistry, quite often such quantum mechanical constructs as ‘orbitals’ or ‘potential energy surfaces’ supplement the traditional constructs of ‘bonds’ and ‘structures’. From time to time, both ‘spin’ and ‘the exclusion principle’ also get a mention. Although some of the ideas of quantum mechanics in the Schrödinger formulation seem to have got into chemistry quite quickly, they were only employed in a qualitative fashion. It is only with the growth in widely available computational power that the discipline of computational quantum chemistry became possible. This discipline claims to have justified Dirac’s original claim that quantum mechanics could be used directly and quantitatively to describe traditional chemical concepts, if only the computation could be done. Let us remind ourselves of what Dirac wrote and its context. Dirac started by remarking that (in 1929) quantum mechanics had been nearly completed, the remaining problem being essentially its relationship with relativity ideas [12]. He continued:

These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

The evidence for such a claim was really rather slight, probably amounting to little more than the work of Heitler and London on the electronic structure of the hydrogen molecule, but nevertheless it has been regarded as ‘received wisdom’ ever since. Today we know that there is a well developed quantum theory for both the bound states and the continuum states of diatomic systems which make no contact with typical chemical ideas. As we shall see, an evident irony is that the claim was made in the introduction to a justly famous paper showing the far reaching implications of permutation symmetry in the new mechanics for systems of identical particles. More of that later (§4.3).

However that might be, it is Dirac’s claim that has interested philosophers of science. We are not philosophers but, nevertheless, we hope that we can be helpful to them by explaining, in a not too technical way, the mathematical basis of that claim and then putting it in a fuller context. We shall not provide detailed references for the mathematical assertions that we make, but we provide a few references in which the technical details are considered and from which the original work can be identified [13]-[16].

In the following we shall restrict the discussion to a consideration of the bound states of the normal, neutral case of what may be termed the ‘generic’ molecule. Hence we

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3Doubtless Dirac was aware of the then recent work of Born and Oppenheimer (1927).
will say nothing about atomic and diatomic systems, and will also exclude from certain parts of the discussion, molecules with either three or four nuclei. How calculations are or might be done is not the concern here. We shall leave spin properties implicit and will not consider any relativistic effects.

The Coulomb Hamiltonian for a system of $N$ electrons with position variables, $x^e_i$, and a set of $A$ nuclei with position variables $x^n_i$ corresponding to a given molecular formula, may be written, in the Schrödinger representation, as

$$H(x^n, x^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2(x^e_i) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N} \frac{1}{|x^e_i - x^e_j|} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{|x^e_i - x^e_j|}$$

$$-\frac{\hbar^2}{2} \sum_{k=1}^{A} \frac{\nabla^2(x^n_k)}{m_k} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{A} \frac{Z_i Z_j}{|x^n_i - x^n_j|}$$

in which the position operators are simple time-independent multiplicative operators acting on functions of the coordinate variables (‘wavefunctions’). The primes on the second and last summations require the diagonal ($i = j$) terms to be omitted; they represent the infinite self-energy of each charge referred to above. It is assumed that the charge and mass parameters are the experimentally observed values for the particles. This Hamiltonian, together with its associated Schrödinger equation

$$H(x^n, x^e)\Psi_n(x^n, x^e) = E_n\Psi_n(x^n, x^e)$$

are taken to be the foundational equations of the quantum mechanical account of chemistry. When, subsequently we speak of “the full problem” we shall mean the theory defined by equations (2) and (3). A short account of its properties will be the subject of §4.

### 3 Computational Quantum Chemistry

In computational quantum chemistry calculations are accomplished by first clamping the nuclei at fixed positions and then performing electronic structure calculations treating the nuclei as providing a classical potential field for the electronic motion. Thus the nuclear momentum operators must first be removed from (2). In the second step it is proposed to reintroduce the nuclear momentum and position variables as quantum mechanical operators so as to accommodate the quantum properties of the nuclei.

With the nuclei at a particular fixed geometry specified by the constant vectors $x^n_i = a_i$, $i = 1, 2, \ldots, A$, this modified Hamiltonian takes the form

$$H^{cm}(a, x^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2(x^e_i) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{|x^e_i - a_i|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N} \frac{1}{|x^e_i - x^e_j|}$$

$$+ \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{A} \frac{Z_i Z_j}{|a_i - a_j|}.$$
The Schrödinger equation for the clamped-nuclei Hamiltonian is then

$$H_{cn}(\mathbf{a}, \mathbf{x}^e) \psi_{cn}^{\text{p}}(\mathbf{a}, \mathbf{x}^e) = E_{cn}^{\text{p}}(\mathbf{a}) \psi_{cn}^{\text{p}}(\mathbf{a}, \mathbf{x}^e)$$

(5)
in which the eigenvalues (‘electronic energies’) have a parametric dependence on the constant nuclear position vectors \(\mathbf{a} = \{a_i\}\). It is customary to omit the last term (the nuclear repulsion energy) from equation (4) since it is merely an additive constant and so does not affect the form of the electronic wavefunctions. Its inclusion modifies the spectrum of the clamped-nuclei Hamiltonian only trivially by changing the origin of the energy.

The electronic energies are regarded as providing the energies of chemical interest at a particular nuclear geometry specified by the set of nuclear position vectors \(\{a_i\}\). Thus if the electronic energy has a minimum at a particular nuclear geometry, then this is regarded as the geometry of a stable system. Computing the electronic energies in the nuclear region around that minimum, is regarded as describing a potential in which nuclei can vibrate, while the geometry at the minimum determines the axes about which the system can rotate. The possibility of there being a number of minima in the potential so calculated, means that ‘reactants’ and ‘products’ can be described in terms of these minima and hence transition states and the like. Although the subsequent discussion will often seem to be in terms of exact solutions, the actual outcome of quantum chemical calculations will be solutions that approximate the exact ones.

However that may be, it can be shown that if the system described by the clamped-nuclei Hamiltonian is either neutral or positively charged, then it has an infinite number of bound states (an infinite set of square-integrable eigenfunctions) whatever the nuclear geometry. With appropriate charge and mass parameters it could thus certainly describe all molecules and even a system of two equal but oppositely charged parts. However a negatively charged system can have at most a finite number of bound states, so it is not clear if it could describe an isolated negatively charged ion. It has been possible to show that \(H^-\) has just one bound state but not much else is known. In any case the spectrum is bounded from below so it is always possible to identify any minima in the energy.

It should be noted that the eigenfunctions \(\{\psi_{cn}^{\text{p}}(\mathbf{a}, \mathbf{x}^e)\}\) of the Hamiltonian, equation (5), are defined only up to phase factors of the form

$$\exp[iw(\mathbf{a})]$$

where \(w\) is any single-valued real function of the \(\{a_i\}\) and can be different for different electronic states. It is only by making suitable phase choices that the electronic wavefunction is made a continuous function of the formal nuclear variables, \(\mathbf{a}\). According to quantum mechanics the eigenfunctions of (2) are single-valued functions by construction with arbitrary phases (rays). Thus care must be taken to make phase-independent comparisons when attempting to tie the clamped-nuclei Hamiltonian to the full Coulomb one.

\(^4H_{cn}\) is also commonly referred to as the ‘electronic’ Hamiltonian.
From a mathematical point of view the eigenfunctions of the clamped-nuclei Hamiltonian at a particular geometry, constitute a vector bundle defined on the base space of which \( a \) is a point. To achieve properly defined eigenfunctions for any nuclear geometry, a suitable base space must be defined. This can be done in the present context by defining its origin by choosing one of the \( a_i \) to be zero and by choosing the rest of the \( \{a_i\} \) to constitute a Cartesian space. This ensures that base space is translationally invariant and that the required vector bundle is a trivial one. The resulting eigenfunctions are then, in terms of the nuclear variables, single-valued and well-behaved. This space is larger than is required to describe a geometry, for it also allows description of all orientations and inversions of any geometrical figure. In this space therefore, each eigenvalue of the electronic Hamiltonian remains the same on a spherical shell described by the rotation-inversion of a defined geometry. From this point of view, the electronic Hamiltonian obviously has a completely continuous spectrum, bounded from below.

In computational quantum chemistry practice no calculations are made on any configuration of the nuclei which differs simply by a rotation-inversion from a configuration at which a calculation has actually been made. So in practice computational quantum chemistry is carried out on a sub-space of the full Cartesian base space which is invariant under translations and rotation-inversions of the variables \( a_i \). This restriction however renders the base space non-Cartesian. The relevant restricted base space for the nuclear variables will be of dimension \( 3A-6 \) and to cover it, all the internuclear distances, of which there are \( A(A-1)/2 \), are required. It is not required to choose the inter-particle distances as internal coordinates explicitly, and any functions of them, \( q_i(r_{ij}) \), may be used. Complete cover is possible up to \( A=4 \), but beyond that no choice of the \( q \) can cover all of the internal motion space. Care must be taken with the general internal coordinates for not only do they describe a restricted space, but two distinct geometries might be described by a single choice of internal coordinates.

It is at this level that calculations in computational quantum chemistry are made over a range of values, 1,2,3,...,s,... of the \( \{a_s\} \) to yield a sequence of energies, \( E^{cn}_p(a_s) \). These values, for fixed \( p \), are then fitted to construct a ‘surface’, \( V(q) \); if, for a given geometry, a value \( a_s \) that was not in the original list, is mapped on to a value \( q_p \) then the calculated electronic energy, \( E^{cn}_p(a_s) \) should be the same as \( V(q_p) \). The function \( V(q) \) is often called a ‘potential energy surface’ (PES) and is treated as a basis for considering nuclear motion associated with the electronic state labelled by the index \( p \).

Any consideration of nuclear motion must involve extending the restricted space to the full space because the nuclear kinetic energy operators are expressed in the full space of \( 3A \) dimensions. This can be done by using a Cartesian variable \( R \) to describe the translation of the \( a \) and a set of three Eulerian angles \( \{\phi_m\} \) to describe their rotation-inversion. This provides the 6 extra variables required to fill the space. In standard electronic structure calculations the translational motion is fixed, as explained above, by fixing the value of one \( a_i \), and so a choice of \( R \) is inherent in such calculations. However some other choice might prove more suitable in considering the full problem. The choice of a particular set of Eulerian angles, however it is made, must involve a
non-linear transformation from the Cartesian space. Thus the relationship of the space described using the \( \{ \phi_m \} \), to the Cartesian base space, can be an invertible one only where the Jacobian for the transformation does not vanish.

For example in dealing with a triatomic it is possible to require that the three nuclei define a triangle and hence a plane. The Eulerian angles are defined to achieve that end and the internal coordinates may be chosen as two sides \((r_1, r_2)\) and the included angle \((\theta)\) of the triangle. The part of the Jacobian that arises from the internal coordinate choice is \(r_1^2 r_2^2 \sin \theta\) which vanishes when any of its elements become zero. So when, say, \(\theta\) is 0 or \(\pi\) the transformation ceases to be defined. This failure shows up by terms in the Hamiltonian expressed in the chosen coordinates becoming singular. These singularities will, among other things, close off any part of the internal coordinate space in which the nuclei form a linear system.

The Hamiltonian (11) has an invariance group composed of the electronic permutation group \(S_N\) and of the point group, if present, which when considered as acting in the space \(a\) simply interchanges the positions of nuclei with equal charges. The requirement that the electronic wavefunction satisfy the Pauli principle can be achieved without explicit consideration of spin as an extra variable, because it is possible to specify, given the spin-state of the system, the irreducible representation of the symmetric group \(S_N\) that is then required to satisfy the Pauli principle. Since the nuclei are regarded as identifiable in computational quantum chemistry practice, the Pauli principle is not relevant to permutations on the space \(a\). This is somewhat at odds with the usual practice of treating the nuclear kinetic energy operators as quantum mechanical operators, when considering nuclear motion.

So computational quantum chemistry can be used to describe not only the electronic but also the nuclear motions. However the electronic problem must be addressed before addressing the nuclear problem. From a mathematical standpoint, the processes used are perfectly well defined, providing that care is taken when moving from the restricted to the full space. An account of the full problem in a restricted region can therefore be properly be provided using the computational quantum chemistry approach. Thus, for example, the electric dipole moment of a molecule is defined by first computing the expected value of electronic position operators with the clamped-nuclei electronic wavefunction at the equilibrium geometry, and then adding to it the classical electric dipole moment of the nuclei.

If the sequence of Hamiltonians (the electronic one and the subsequent nuclear motion one) used in computational quantum chemistry are regarded as quantum mechanical then there is no doubt that the theoretical basis of chemical ideas can be found in quantum mechanics. It is certainly the case that the Coulomb Hamiltonian is a quantum mechanical object and if it can be shown that the computational quantum chemical scheme can be accommodated to a correct usage of that Hamiltonian, then there can be no doubt about the theoretical basis of chemical ideas.

It is to such a consideration that we turn next.
4 The Coulomb Hamiltonian and the ‘Isolated Molecule model’

In this section we try to show what features exact solutions of the Schrödinger equation for the Coulomb Hamiltonian for a molecular system must have even though we don’t actually have any explicit solutions at our disposal. We also try to place the solutions obtained in computational quantum chemistry practice in a mathematically proper relationship to the exact solutions.

Since the nearest we have to exact solutions of a molecular problem are those for the hydrogen atom, we think that it may be helpful to begin by looking at them. But to go further is inevitably to involve some quite sophisticated mathematical ideas; our aim is to make these ideas as plain as possible. We hope that what we say may be sufficient, even if only skimmed, to make the conclusions to which we come, both comprehensible and plausible.

4.1 The hydrogen atom

The first thing to notice is that the eigenvalues of the problem depend only on the principal quantum number, usually written \( n \), and not on the angular quantum number \( l \). This was a surprise to the chemists who first thought about it, since they felt that the energy should depend upon angular motion as well as radial motion. They thus called it an *accidental degeneracy*. This \( n^2 \)-fold degeneracy at each level might well have been anticipated for it had been noted by Pauli in his 1926 treatment of the atom. It arises in the present context because an operator corresponding to the classical Runge-Lenz vector, commutes with the Hamiltonian and its symmetry is such that the \( n^2 \)-fold degeneracy is expected. The point that is to be made here is that a full solution of the problem recognises the full symmetry of the problem, even if we do not.

For the hydrogen atom the expected value of \( r \) (in Bohr radius units \( a_0 \approx 10^{-10} \) m) for the level labelled by \( n \) and \( l \) is

\[
\bar{r} = \frac{1}{2} (3n^2 - l(l + 1)) \approx n^2, \quad n \text{ large}
\]

and for \( n = 10^5 \) this is about 0.5 m. This is a macroscopic dimension so it might be expected that the probability of finding the atom in this state is very small. To compute that probability one might use the standard statistical mechanics approach. Here the partition function is defined to normalise the total probability assuming that the levels are randomly distributed in a Boltzmann manner.

The partition function is defined in terms of a set of discrete energy levels as

\[
Q = \sum_n e^{-E_n/k_B T}
\]

where \( k_B \) is Boltzmann’s constant and \( T \) the thermodynamic temperature, and each energy \( E_n \) is counted as often as it occurs. Working in Hartree atomic units (one
Hartree atomic unit $E_h$ is about 27 eV or, equivalently, about 2625 kJ/mol) and writing $\beta = 1/k_B T$ the general term in the partition function is:

$$2 \times (n^2) \exp(-\beta/2n^2) \rightarrow 2 \times (n^2) \quad \text{as} \quad n \rightarrow \infty.$$ 

The partition function thus diverges if one tries to compute the sum. So one cannot use it to estimate probabilities.

It is clear that precisely the same sort of divergence is going to arise for any neutral atom or, indeed, for any neutral molecule if the nuclei are treated as being clamped. This is because for such systems the number of bound states is infinite and the energy levels tend to 0 as the first ionization energy is approached so that the exponential tends to 1 but the sum does not terminate. It is usually argued that this divergence can be ignored because the probability of any of the higher atomic levels being occupied is negligible. (At 298 K the second term in the sum for the hydrogen atom has a value of about $10^{-172}$.) But the series is really divergent and a choice of stopping point is quite arbitrary. These troubles arise because the system is being treated as isolated and in an infinite space. In the physical world no system is isolated and the space available is not infinite. We shall discuss this further in §4.2.

It is quite often said that bound-state eigenfunctions are continuous, differentiable everywhere and form a complete set but that is not always the case.

In the hydrogen atom problem the effect of the kinetic energy operator on the eigenfunction can be seen explicitly to produce a term proportional to $1/r$ that cancels out the potential term and thus the Hamiltonian is well-defined, even at the divergence point $r = 0$. This must imply that the eigenfunction behaves oddly around this point. In fact the eigenfunctions are continuous at the origin but they are not differentiable there, as can easily be seen by examining the explicit functions. This might be taken as a warning that it is perilous to neglect a kinetic energy operator in the Hamiltonian, for its presence seems essential to overcome the singularities in the potential.

As for completeness, if a radial function is chosen which is of the same kind as, but not among the bound state radial eigenfunctions, then it is easy to calculate the overlap integrals between the chosen function and the eigenfunctions. One can subsequently construct the linear combination of eigenfunctions that maximise the eigenfunction overlap. If the set were complete, then the value 1 would be found. In typical cases, the value is about 0.6. This might be taken as a warning that the Coulomb eigenfunction problem has rather special features. So a result that depends on an expansion assuming the eigenfunctions form a complete set is not always safely derived.

The hydrogen atom Hamiltonian is separable in four distinct sets of orthogonal coordinates: spherical polar, paraboloidal, ellipsoidal and sphericonical sets. The shapes and nodal properties of the eigenfunctions expressed in each of these coordinate sets differ considerably, as do the way that their quantum numbers relate to the principal one. It is only in the spherical polar system that the traditional orbitals appear and so the adoption of the orbital as a chemical object might seem to be the consequence of a
simple accident of coordinate choice. But no matter which set is chosen, the eigenvalues remain the same.

The point here is that the way the eigenfunctions of the Hamiltonian look is entirely a matter of coordinate choice. It is the eigenvalues and operator expectation values that are constants of the problem. It is thus perhaps unwise to attempt physical explanations in terms of the way eigenfunctions look.

4.2 The full problem

In many computational quantum chemistry papers the use of the clamped-nuclei Hamiltonian as described in the previous section is claimed to be related to use of the full Coulomb Hamiltonian by appeal to the work either of Born and Oppenheimer or Born and Huang. Were those claims supportable then this section could be a very short one. Unfortunately the works quoted lack proper mathematical foundation. We shall examine these claims later.

The mathematical properties of the quantum mechanical Coulomb Hamiltonian are discussed at length in [17], and we give only a summary account. In 1951 Kato established that the Coulomb Hamiltonian, $H$, (2), is essentially self-adjoint [18]. The proof involved showing that the kinetic energy operator dominated the potential energy operator. From what has been seen in the discussion of the hydrogen atom this observation will come as no surprise. The property of self-adjointness, which is stronger than Hermiticity, guarantees that the time evolution

$$\Psi(t) = \exp(-iHt/\hbar)\Psi(0)$$

of a Schrödinger wavefunction is unitary, and so conserves probability. This is not true for operators that are Hermitian but not self-adjoint, and this reminds us of the importance of boundary conditions in the full specification of a physical model. An example given by Thirring is of the radial momentum operator $-i\hbar \partial/\partial r$ acting on functions $\phi(r)$, $\phi(0) = 0$ with $0 \leq r < \infty$ which is not self-adjoint on the infinite half-line. Thus one cannot simply say ‘the momentum operator, $-i\hbar d/dx$ is self-adjoint’; one must specify the domain of the operator as well.

It is customary to assume ‘free’ boundary conditions for the Coulomb Hamiltonian so that the configuration space is unbounded. Then the full Galilean symmetry group of an isolated system can be realized, and the Hamiltonian (2) is recognized as the time-translation generator in that group; the other generators are the vector operators describing space translations (the total momentum $P$), space rotations (the total angular momentum $J$), and the relationship between reference frames moving at different velocities (the ‘booster’ $K$). They can all be constructed as simple sums over all the constituent particles in the system. Furthermore they can be separated into centre-of-mass and internal contributions which are uncoupled, so that the dynamics of the centre-of-mass can be discussed quite separately from the internal (‘spectroscopic’) dynamics of the particles. We refer to this specification as the ‘isolated atom’ ($A = 1$) or
The Coulomb Hamiltonian and the ‘Isolated Molecule model’

‘isolated molecule’ \((A > 1)\) model. It is evidently an ideal since in the physical world one cannot avoid confinement as well as interactions. The hope is that their effects are sufficiently small that they can be regarded as ‘weak perturbations’. But one has to exercise care since an unsuspecting assumption of an infinite configuration space can lead to pathologies, as in the H-atom example in the previous section.

The first thing that Kato did was to make an explicit separation of the centre-of-mass motion and the internal motions. That is essential in any search for bound states since \(H\) is invariant under uniform translations; the translation group has only continuous irreducible representations (irreps) so that \(H\) must have a completely continuous spectrum. Let us denote the translationally invariant Hamiltonian as \(H'\). It can be written in terms of \(N_T - 1\) Cartesian (vector) variables where \(N_T = N + A\). These can be constructed by a non-singular linear transformation of the original Cartesian variables. As might be expected from the discussion above, whatever the choice of coordinates made, it has absolutely no effect on the eigenvalues of \(H'\). This freedom makes it possible, whenever it is convenient for us, to choose \(A - 1\) Cartesian coordinates \(t^n_i\) constructed entirely from the original nuclear coordinates and to retain \(N\) coordinates to describe the electrons simply by setting their origins at the centre-of-nuclear mass. These will be denoted \(t_e\). With this choice made for atoms, only the electronic coordinates survive and the centre-of-nuclear mass becomes the mass of the single nucleus. This is why the clamped-nucleus hydrogen atom Hamiltonian differs from \(H'\) for the hydrogen atom only by the replacement of the electronic mass with its reduced mass equivalent.

There are various ways in which the spectrum \(\sigma(A)\) of a self-adjoint operator \(A\) may be classified. The classification most useful in molecular physics is into discrete and essential parts. The discrete spectrum \(\sigma_d(A)\) is the subset of the pure point spectrum that consists of isolated eigenvalues of finite multiplicity. The essential spectrum \(\sigma_{\text{ess}}(A)\) is the complement of the discrete spectrum

\[
\sigma_{\text{ess}}(A) = \sigma(A) \setminus \sigma_d(A).
\]

The discrete spectrum and the essential spectrum are, by definition, disjoint; however, although the essential spectrum is always closed, the discrete spectrum need not be. The essential spectrum of the Coulomb Hamiltonian consists of the absolutely continuous spectrum and may contain a portion of the pure point spectrum. The operator \(H'\) has no singular continuous spectrum. The essential spectrum describes scattering states of the system while the discrete spectrum describes bound states.

The spectrum of \(H'\) may (but need not) have a discrete part, and the start of the essential part is established by means of the so-called HVZ theorem which demonstrates that the essential spectrum can be written as \(\sigma_{\text{ess}}(H') = [\Sigma, \infty)\) where \(\Sigma\) is the energy of the lowest two-body cluster decomposition of the \(N_T - 1\) particle system.

Even without recourse to detailed mathematics, it is clear that the essential spectrum of the hydrogen atom begins at zero energy. It is absolutely continuous and does not contain any pure point members; it describes the scattering states of a single electron and a nucleus. For all other atoms the first ionization energy is such that the essential
spectrum begins at somewhat below zero energy. It contains states describing the scattering of an electron from a singly ionized atom, two electrons from a doubly ionized atom and so on. These states occur at energies below zero. This part of the spectrum is often said to describe the bound states in the continuum but is perhaps more accurately designated as describing resonances. At energies above zero, the spectrum is absolutely continuous and describes the scattering of the electrons by the nucleus. This sort of description can be generalised to the formal Hamiltonian appropriate to any molecular formula.

However the extent of the discrete spectrum is by no means obvious and for a Coulomb Hamiltonian describing a given collection of electrons and nuclei the difficult technical problem is to find out if there is any discrete spectrum at all before the start of the essential spectrum.

There is the following fundamental theorem due to Weyl; if one has a trial wavefunction $\Phi$ with an expectation value $\langle \Phi | H' | \Phi \rangle$ which is below the bottom of the essential spectrum, then $H'$ has at least one discrete negative eigenvalue. But it is a rather limited result; to make use of it in any particular system the start of the essential spectrum must be determined and a trial function found that bounds this start from below. Both are very difficult to do. At present the most that has been proved is that the hydrogen molecule has at least one bound state. Ordinary chemical experience makes it seem likely that there are some atomic combinations that do not have any bound states but, so far, there are no rigorous results that enable it to be said that a particular kind of neutral system has no bound states.

An examination of tables of experimental values of electron affinities and ionisation energies leads to the conclusion that it is very unlikely that any diatomic molecule has an infinite number of bound states. This observation is not inconsistent with spectroscopic experience. The awkward problem in the moving nuclei case is to know whether a neutral system has any bound states at all, although, as mentioned above, the equivalent result in the clamped-nuclei case is known.

### 4.3 The symmetries of the Coulomb Hamiltonian

It should be emphasised that the position variables in equation (2) simply specify field points, and cannot generally be identified as particle coordinates because of the indistinguishability of sets of identical particles. Weyl and later Mackey, both stress that in the case of sets of identical particles, in addition to supporting the canonical quantum conditions, the space on which quantum mechanical operators act must be confined to a sub-space of the full Hilbert space of definite permutational symmetry. This means that the effect of any operator on a function in this sub-space must be to produce another function in the subspace. Multiplication of a properly symmetrised function by a single coordinate variable produces a new function which is not in the symmetrised sub-space. Thus only operators symmetric in all the coordinates of identical particles can properly be deployed in the calculation of expectation values that represent observables. Weyl
Physical quantities have only an objective significance if they depend \textit{symmetrically} on the two individuals.

and he then goes on to generalise this conclusion to the symmetrical form for the quantities constructed from the variables of \( N \) identical particles. He closes his discussion by looking at the two electron problem. He says that although it might be supposed that the electrons as a pair of twins could be named “Mike” and “Ike”

it is impossible for either of these individuals to retain his identity so that one of them will always be able to say “I’m Mike” and the other “I’m Ike”. Even in principle one cannot demand an alibi of an electron! In this way the Leibnizian principle of \textit{coincidentia indiscernibilium} holds in quantum mechanics.

This discussion holds for identical particles of any kind that are to be described by quantum mechanics and it precludes the specification of, for example, the expected value of a particular coordinate chosen from a set describing many identical particles.

The Hamiltonian \( H' \) is also invariant under all rotations and rotation-reflections of the translationally invariant coordinates; it will have eigenfunctions which provide a basis for irreducible representations (irreps) of the orthogonal group in three dimensions \( O(3) \). Thus the eigenfunctions are expected to be of two kinds classified by their parity; each kind consists of eigenfunction sets, each with degeneracy \( 2J + 1 \), according to the irrep \( J = 0, 1, 2, \ldots \) of \( SO(3) \) to which the eigenfunctions belong. The representations of \( O(3) \) are distinct for each parity, and so there is no group theoretical reason to expect eigenfunctions with different parity to be degenerate.

Simultaneously the eigenfunctions will provide irreps for the permutation group \( S \) of the system. This group comprises the direct product of the permutation group \( S_N \) for the electrons with the permutation groups \( S_{A_i} \) for each set of identical nuclei \( i \) comprising \( A_i \) members. The physically realisable irreps of this group are restricted by the requirement that, when spin is properly incorporated into the eigenfunctions, the eigenfunctions form a basis only for the totally symmetric representation, if bosons (spin 0, 1, 2 \textit{etc.}) or of the antisymmetric representation, if fermions (spin 1/2, 3/2, 5/2 \textit{etc.}). Both of these representations are one-dimensional. We shall speak of irreps of the translationally invariant Hamiltonian which correspond to physically realisable states as \textit{permutationally allowed}. In general such irreps will be many dimensional and so we would expect to have to deal with degenerate sets of eigenfunctions in attempting to identify a molecule in the solutions to the translationally invariant problem. Unfortunately the dimensions of the permutationally allowed representations are very large and so it is necessary to consider eigenvalue sets of extensive degeneracy. To look for the singlet spin of a 22 electron system, say \( C_3H_4 \), would involve dealing with a degenerate set of size \( 6 \times 10^6 \).
Our primary concern here is not with the extent of the electronic degeneracy, but that of the nuclei and to what extent the requirements of nuclear permutations are consistent with the occurrence of isomers. It has already been shown that isomers may be treated explicitly in the clamped-nuclei approach because molecular structure can be recognised there. Consideration of these matters in the context of solutions of $H'$ will next be considered.

4.4 Molecular structure and isomers

The most severe problem associated with the formal quantum mechanical description perhaps is the fact that the Coulomb Hamiltonian $H$ is one and the same for all possible isomers associated with a given chemical formula. In the words of P.-O. Löwdin echoing Dirac’s claim (§2) [20]:

The Coulombic Hamiltonian $H$ does not provide much obvious information or guidance, since there is [sic] no specific assignments of the electrons occurring in the systems to the atomic nuclei involved - hence there are no atoms, isomers, conformations etc. In particular one sees no molecular symmetry, and one may even wonder where it comes from. Still it is evident that all this information must be contained somehow in the Coulombic Hamiltonian.

A natural element of classical molecular structure theory is to assign static dipoles to particular molecules so as to account for the difference between ‘non-polar’ and ‘polar’ molecules demonstrated by the temperature behaviour of their electric susceptibilities (the Langevin-Debye law). Such assignments are often made in terms of vector sums of bond dipole moments, so that bonds are deemed to play an important role in static molecular dipoles. However the Coulomb Hamiltonian commutes with the inversion operator, so its eigenstates must be parity eigenstates and hence must have zero expectation values for the static electric dipole operator. But if an eigenstate corresponds to a molecule with structure then, it follows, that the molecule cannot have a static electric dipole moment. The result cannot be doubted, but it has a very paradoxical flavour. There is a quantum-mechanical account of the Langevin-Debye law, given many years ago by van Vleck [21, 22]. Its ingredients are: expectation values of the square of the electric dipole operator, transition matrix elements of the dipole operator and the energy level separations of states supporting fully allowed dipole transitions, and the thermal energy $k_BT$. van Vleck’s calculation makes no reference to bond dipoles, nor ‘structures’ and probably for that reason is now much less well known than his analogous treatment of magnetic susceptibilities.

A similar argument leads to the conclusion that the existence of stereo-isomers cannot be accounted for in terms of eigensolutions of the Schrödinger equation for the Coulomb Hamiltonian, for the optical rotation angle is a pseudoscalar observable (Hund’s paradox). Clearly then, an eigenstate of $H'$ does not correspond to a classical molecule.
with structure! And if one responds that chemistry is of course concerned with time-dependent states, the observation invites the question: what are the equations that determine the time-dependent quantum states of molecules? Unless one simply accepts the clamped-nuclei approach to the problem, we have no idea.

There are more difficulties; in classical structural chemistry, different isomers mean different geometries and the idea of a distinct geometry is problematic for the stationary states of the Coulomb Hamiltonian. If we write the variables corresponding to the carbon nuclei in a generic case such as the hydrocarbon $C_8H_8$ as $x^n_i$, $j = 1, \ldots 8$ and those corresponding to the protons as $x^n_{i+8}$, $i = 1, \ldots 8$ then a particular CH interparticle distance is

$$x^{CH}_{ij} = |x^n_{i+8} - x^n_j|.$$  

One might be tempted to suppose that the calculation of the expected values of such interparticle distances with a particular eigenfunction of $H'$ would determine the geometry; however $x^{CH}_{ij}$ is not a proper observable. As noted earlier, the only possible operator incorporating these distances is the symmetrical sum

$$\sum_{i,j=1}^{8} x^{CH}_{ij}$$

and all that can be inferred from its expectation value is that, on average, all the CH interparticle distances are the same. This is not to suppose that this average value is the same for all the eigenfunctions of $H'$ that might be investigated in a search for isomers, it is simply that what differences there might be, cannot support the detailed geometrical interpretation which is characteristic of classical chemical structure theory.

It is possible to define an electronic charge density by integrating the squared modulus of the total wave function over all but one of the electronic space coordinates and all of the electronic spin coordinates and all of the nuclear variables. This process would yield an electronic charge density function corresponding to expected values of the nuclear variables. This would seem to be the closest that one might get to a clamped-nuclei result. The density so calculated here would reflect precisely the nuclear permutational symmetry alluded to above and so knowledge of the charge density would not help identify a molecular structure or pattern of bonding any more than the inter-nuclear distances can do in systems in which, using classical considerations, isomers are possible. Likewise, the electronic energy of the problem as a function of the translationally invariant nuclear variables can be determined, as the expected value of the electronic part of the full Hamiltonian [2] obtained by integrating over all the electronic space and spin coordinates. But the electronic energy function will be invariant under any permutation of like nuclei, so there will be no unique minimum in it to be associated with an equilibrium geometry. The electronic charge density and the electronic energy derived from the full wave-function seem, therefore, to have properties quite different from those that they have in the clamped-nuclei approximation. So, for the time being at least, it does not seem that any charge density methods for identifying bonds, can be regarded as properly based in the full problem.
It would seem that one cannot extract from the solutions of the full problem many of those features that are desirable for chemical explanations, but one can extract them from the clamped-nuclei picture. However if it were possible to establish that the clamped-nuclei Hamiltonian were an effective approximation to $H'$, that might be thought enough.

### 4.5 Clamping the nuclei

It is sometimes asserted that the clamped-nuclei Hamiltonian can be obtained from the Coulomb Hamiltonian by letting the nuclear masses increase without limit. The Hamiltonian that would result if this were done would be

$$H_{nn}(x^n, x^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2(x^n_i) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{|x^e_j - x^n_i|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{A'} \frac{1}{|x^n_i - x^n_j|}$$

with formal Schrödinger equation, by analogy with (5),

$$H_{nn}(x^n, x^e)\psi_{nn}^p(x^n, x^e) = E_{nn}^p(x^n)\psi_{nn}^p(x^n, x^e).$$

Given that the Coulomb Hamiltonian has eigenstates such that

$$H(x^n, x^e)\psi(x^n, x^e) = E\psi(x^n, x^e)$$

then, if the solutions of (8) were well defined, it would seem that the eigenstates in (9) could be expanded as a sum of products of the form

$$\psi(x^n, x^e) = \sum_{p} \Phi_p(x^n)\psi_{nn}^p(x^n, x^e)$$

where the $\{\Phi\}$ play the role of ‘nuclear wavefunctions’.

In the Hamiltonian (7) the nuclear variables are free and not constant and there are no nuclear kinetic energy operators to dominate the potential operators involving these free nuclear variables. The Hamiltonian thus specified cannot be self-adjoint in the Kato sense. It is certainly not the case either, that the nuclei variables become constants, as asserted in Born and Oppenheimer. The Hamiltonian can be made self-adjoint by clamping the nuclei because the electronic kinetic energy operators can dominate the potential operators which involve only electronic variables. The Hamiltonian (4) is thus a proper one. But since the Hamiltonian (7) is not self adjoint it is not at all clear that the hoped for eigensolutions of (8) form a complete set suitable for the expansion (10). However that may be, it was observed more than 30 years ago and as we have already seen here, that the arguments for an expansion (10) are quite formal because the Coulomb Hamiltonian has a completely continuous spectrum arising from the possibility...
of uniform translational motion and so its solutions cannot be properly approximated by a sum of this kind. This means too that the arguments of Born and Oppenheimer and of Born for his later approach to representations of this kind, are also quite formal [15, 16].

There is no need to specify the proposed \( A - 1 \) translationally invariant nuclear variables \( t^n \) other than to say that they are expressed entirely in terms of the laboratory nuclear coordinates. Of course the laboratory nuclear variable \( x^n_i \) cannot be completely written in terms of the \( A - 1 \) translationally invariant coordinates arising from the nuclei, but in the electron-nucleus attraction and in the nuclear repulsion terms the centre-of-nuclear mass \( X \) cancels out. The symbol \( x^n_i \) will still be used to denote the nuclear variables but it should be remembered that the nuclear potentials are functions of the translationally invariant coordinates defined by the nuclear coordinates.

On making this choice of electronic coordinates the Coulomb Hamiltonian (2) is transformed so that the electronic part becomes:

\[
H'(x^n, t^n) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2(t^n_i) - \frac{\hbar^2}{2M} \sum_{i,j=1}^{N} \vec{\nabla}(t^n_i) \cdot \vec{\nabla}(t^n_j) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i |t^n_i - x^n_i|}{|t^n_j - x^n_j|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N} \frac{1}{|t^n_i - t^n_j|} + \sum_{i,j=1}^{A, j} Z_i Z_j |x^n_i - x^n_j|.
\]  

This electronic Hamiltonian is translationally invariant and would yield the usual form were the nuclear masses to increase without limit.

The nuclear part of the transformed Hamiltonian involves only kinetic energy operators and has the form:

\[
K^n(t^n) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(t^n_i) \cdot \vec{\nabla}(t^n_j)
\]  

with the inverse mass matrix suitably defined involving only the original nuclear variables.

Both (11) and (12) are invariant under any orthogonal transformation of both the electronic and nuclear variables. If the nuclei are clamped in (11) then invariance remains only under those orthogonal transformations of the electronic variables that can be re-expressed as changes in the positions of nuclei with identical charges while maintaining the same nuclear geometry. The form (11) remains invariant under all permutations of the electronic variables and is invariant under permutation of the variables of those nuclei with the same charge. Thus if an electronic energy minimum is found at some clamped nuclei geometry there will be as many minima as there are permutations of identically charged nuclei. The kinetic energy operator (12) is invariant under all orthogonal transformations of the nuclear variables and under all permutations of the variables of nuclei with the same mass.

The splitting of the translationally invariant Hamiltonian \( H'(t) \) into two parts breaks its symmetry, since each part exhibits only a sub-symmetry of the full problem. If
wavefunctions derived from approximate solutions to (11) are to be used to construct solutions to the full problem (9) utilizing (12) care will be needed to couple the sub-symmetries to yield solutions with full symmetry.

If the usual approach were taken to approximating solutions to the nuclear motion Hamiltonian using sums of products of electronic and nuclear parts a typical term in the sum used as trial function for the form would be

$$\phi_p(t^e, t^n)\Phi_p(t^n)$$

where $p$ denotes an electronic state. The solutions are on the Cartesian product space $R^{3A-3} \times R^{3N}$. There is no explicit coupling of the nuclear motion and electronic motions and it is thus possible to represent for any electronic state, any number of rotational states. It is not generally possible to choose $\Phi$ directly as an eigenfunction of the nuclear angular momentum, neither is it possible to choose $\phi$ directly as an eigenfunction of the electronic angular momentum. $\phi$ as usually computed belongs to the totally symmetric representation of the symmetric group of each set of nuclei with identical charges. $\Phi$ could then be a basis function for an irrep of the symmetric group for each set of particles with identical masses if the permutational symmetry were properly considered in solving the nuclear motion problem.

Clamped-nuclei calculations are usually undertaken so as to yield a potential that involves no redundant coordinates. Thus a translationally invariant electronic Hamiltonian, as noted previously, would actually generate a more general potential than this. A clamped-nuclei potential is therefore more properly associated with the electronic Hamiltonian after the separation of rotational motion than with the merely translationally invariant one. With this choice again,

$$\sum_{m=-J}^{J} J \phi_{pm}(r, R) J \Phi_{pm}(R)|JMm>$$

where $R$ represents the $3A - 6$ internal coordinates invariant under all orthogonal transformations of the $t^n$ and $|JMm>$ is an angular momentum eigenfunction. The general solutions are on the manifold $R^{3A-6} \times S^3 \times R^{3N}$.

To achieve permutational symmetry in the nuclear motion part of the wavefunction would in the general case be very difficult. The nuclei are identified in the process of defining a body-fixed frame to describe the rotational motion, even if they are identical. If only a subset of a set of identical nuclei were used in such a definition, some permutation of the nuclear variables would induce a change in the definition of the body-fixed frame and thus spoil the rotational separation. Thus permutations of identical nuclei are considered usually only if such permutations correspond to point-group operations which leave the body-fixing choices invariant.

If one considers the clamped-nuclei Hamiltonian as providing input for the full Hamiltonian in which the rotational motion is made explicit, the basic nuclear motion problem should be treated as a $2J + 1$ dimensional problem. If this is done then the translational
and rotational symmetries of the full problem are properly dealt with. However the solutions are not generally basis functions for irreps of the symmetric groups of sets of identical nuclei except for such sub-groups as constitute the point groups used in frame fixing. This restriction of the permutations is usually assumed to be justified by appealing to the properties of the potential surface. The idea here is widely believed and used in interpreting molecular spectra.

As noted earlier, the original attempts to justify the Born-Oppenheimer and the Born approaches from the full Coulomb Hamiltonian, lack rigorous mathematical foundations. So far there have been no attempts to make the foundations of the Born approach mathematically secure. However the coherent states approach has been used to give mathematically rigorous accounts of surface crossings. It seems very unlikely that it would be possible to provide a secure foundation for the Born approach in anything like the manner in which it is usually presented.

The Born-Oppenheimer approximation, whose validity depends on there being a deep enough localized potential well in the electronic energy, has however been extensively treated. The mathematical approaches depend upon the theory of fibre bundles and the electronic Hamiltonian in these approaches is defined in terms of a fibre bundle. It is central to these approaches however that the fibre bundle should be trivial, that is that the base manifold and the basis for the fibres be describable as a direct product of Cartesian spaces.

A mathematically satisfactory account of the Born-Oppenheimer approximation for polyatomic in an approach based on (14) has not yet been provided but it has proved possible to provide one based on (13). Because the nuclear kinetic energy operator in the space $R^{3A-3}$ cannot be expressed in terms of the nuclear angular momentum, it is not possible in this formulation to separate the rotational motion from the other internal motions. This work also considers the possibility that there are two minima in the potential as indeed there would be because of inversion symmetry if the potential minimum were at other than a planar geometry. It does not, however, consider the possibility of such multiple minima as might be induced by permutational symmetry. It might be possible to extend the two minima arguments to the multiple minima case and perhaps provide a mathematically secure account of the potential energy surface properties approach to ignoring some of the inconvenient permutations. This has not so far been attempted.

At the same proper mathematical level it has been more recently shown that almost any of the eigenvalues of the Coulomb Hamiltonian can be approximated by eigenvalues of the clamped-nuclei Hamiltonian. The correspondence does not depend on the clamped-nuclei eigenvalue being one that corresponds to an electronic energy minimum.

There have also been claims that a bound-state wavefunction of the Coulomb Hamiltonian can be written exactly as a single product rather than the sum (10). But for exactly the same reasons that the initial formulations of the Born-Oppenheimer and the Born approaches are purely formal, so is this approach. It might be urged that this approach would succeed if the translation motion were removed and the arguments
based on the use of $H'(t)$ and the product $[13]$ considered. But so far no mathematically sound formulation has been made and there is a mathematically sound view that such a formulation is very unlikely.

For a secure account to be given in terms of the separation $[14]$, which is what is really required if one is to use the clamped-nuclei electronic Hamiltonian, it would be necessary to consider more than one coordinate space. On the manifold $S^3$ as explained before, once there are more than four particles, at least two coordinate spaces are required to span the whole manifold because it is possible to construct two distinct molecular geometries with the same internal coordinate specification within a coordinate space, so that a potential expressed in the internal coordinates cannot be analytic everywhere. It would therefore seem to be an impossible job. But even if it were to be accomplished it seems very unlikely that a multiple minima argument could be constructed to account for point-group symmetry in this context. It is possible to show, that in the usual form of the Hamiltonian for nuclear motion, where the axes are defined in terms of a given nuclear geometry, permutations can be such as to cause the body-fixed frame definition to fail completely.

Naturally any extension of the trial wave function for the full Coulomb Hamiltonian problem from a single term to a many term form must be welcomed as an advance; it is however simply a technical advance and it might prove premature to load that technical advance with too much physical import.

At present it is not possible properly to place the clamped-nuclei electronic Hamiltonian in the context of the full problem, including nuclear motion. However if the nuclei were treated as distinguishable particles, even when formally identical, then some of difficulties that arise from the consideration of nuclear permutations would not occur. But it would still be necessary to be able to justify the choice of sub-sets of permutations among identical particles when such seem to be required to explain experimental results. A particular difficulty arises here for it is not possible to distinguish between isomers nor is it possible to specify a molecular geometry, unless it is possible to distinguish between formally identical particles.

But regarding the nuclei as distinguishable would not avoid the difficulty of constructing total angular momentum eigenfunctions from the nuclear and electronic parts. Such treatment of the nuclei would not make the traditional demonstrations of the Born-Oppenheimer or the Born approximations mathematically sound either. However it would ensure that the mathematically sound presentations of the Born-Oppenheimer approximation mentioned earlier need no further extension to include permutations of identical nuclei. There is, unfortunately, little good to be said, from a mathematical point of view, of the traditional Born argument. This is troubling because the Born approach is assumed to provide the basis for the consideration of chemical reactions on and between potential energy surfaces. However it is clear that the clamped-nuclei (electronic) Hamiltonian can be usefully deployed in nuclear motion calculations if the nuclei are considered identifiable.
5 Discussion

We have suggested in the foregoing that using the clamped-nuclei Hamiltonian, treating the nuclei as classical particles while calculating electronic wavefunctions, and then using the electronic functions as a basis for a semiclassical treatment of nuclear motion, will lead to a coherent picture that is compatible with classical chemical explanation.

At the start of the 21st century Simon presented a list of open problems in mathematical physics among which Problem 12 is of relevance here [23]:

**Problem 12**: Is there a mathematical sense in which one can justify from first principles current techniques for determining molecular configurations?

This problem, although stated in mathematically vague terms, should be viewed as asking for some precise way to go from fundamental quantum theory to configurations of molecules; evidently Simon did not see *ab initio* electronic structure theory as a complete answer. We do not know exactly what Simon envisaged with “from first principles”, but it is plausible he had the Coulomb Hamiltonian in mind. In our view, and contrary to Löwdin’s expectation, §4.4, we see no reason to suppose that chemistry can be founded on the Coulomb Hamiltonian. Let us first summarize briefly what we see as the outstanding difficulties.

We should note at the outset that in our account of quantum chemistry, we have not mentioned any aspects of special relativity except, incidentally, spin. Spin provides the basis for some spectroscopic methods of chemical importance such as nuclear magnetic resonance, but such behaviour can be treated perfectly adequately by first-order perturbation theory so our discussion can be regarded as complete. Other relativistic considerations seem irrelevant to chemical explanation. Indeed we have no idea of how a quantum mechanical account of a defined collection of electrons and nuclei - as required for the minimal specification of a molecule - with electromagnetic interactions, that is Lorentz invariant, can be developed.

The most that can be shown is that, over a limited energy range, certain of the bound-state energies of the Coulomb Hamiltonian can be well-approximated by eigenvalues of the clamped-nuclei Hamiltonian; however the conventional product of the electronic wavefunctions (from the clamped-nuclei Hamiltonian) and associated nuclear wavefunctions lack the symmetry properties of Coulomb Hamiltonian eigenfunctions and this difference has not been explained. It will be a matter of some mathematical difficulty to show that the full allowed nuclear permutation group has irreps which can be approximated by the irreps of the permutational sub-group which characterises a given nuclear geometry. It will be a project of similar difficulty to show that the full rotation-inversion group has irreps that are approximated by the results obtained from the combined nuclear and electronic treatment arising from the clamped-nuclei Hamiltonian. Such results will have rotation-inversion symmetry only by accident and so irreps are not usually definable. In neither case is it likely that a general demonstration will be possible and the expectation is that any results must be achieved on a case by case basis. It is quite
clear that the eigenvalues/eigenfunctions of the Coulomb Hamiltonian itself do not lend themselves to classical chemical explanations. So the best that can be hoped for in the relationship between chemical explanation and explanation in terms of results from the Coulomb Hamiltonian, is a rather tenuous one.

In some contexts the quantum mechanical properties of nuclei are crucial; in other situations they are simply dropped, and nuclei are treated as classical, distinguishable particles. Thus, for example, the fact that the deuteron, D, and the N\textsuperscript{14} nucleus are \textit{boson} particles can be recognized from characteristic features in the band spectra of D\textsubscript{2} and N\textsubscript{2} respectively. The spectra of diatomic molecules are traditionally described using the clamped-nuclei approach (§3) in terms of potential energy curves and the spin of the nuclei has to be added \textit{ad hoc}; however it is perfectly possible to use a moving-nuclei description (§1.2) of diatomic molecules in which the boson/fermion classification of nuclei sits comfortably.

In most of chemistry however there is no reference to this basic aspect of quantum mechanics. As an example\footnote{This is \textit{not} an isolated special case; it is generic.} there are three familiar isomers of formula C\textsubscript{3}H\textsubscript{4}; the structural principle predicts correctly that replacement of two hydrogen atoms by two deuterium atoms leads to seven distinct species, two of which are predicted to be optically active. All seven have been synthesized in the laboratory, including the resolved enantiomers. About that quantum mechanics based on the Coulomb Hamiltonian (§4) apparently has nothing to say.

This suggests that the Coulomb Hamiltonian on its own (the ‘isolated molecule model’) is not an adequate basis for a quantum mechanical account of chemistry, and so one is led to consider the role of persistent interactions of an environment with the charged particles constituting a molecule. Various suggestions as to how the ‘environment’ is to be characterized can be found in the literature, for example: other molecules, ‘thermal baths’, the quantized electromagnetic field \textit{etc.}, together with finite temperatures; such discussions largely focus on models far removed from the Coulomb Hamiltonian\cite{13, 14, 21, 23}. None of them really explain, in quantum mechanical terms, how one gets from indistinguishable identical particles to (classical) distinguishable particles, other than by putting the requisite answer in by hand.

Our account, which we believe is an accurate and impartial one, is deeply puzzling. One could of course elucidate matters by saying that there must be another theory. But that wouldn’t help at the moment and it seems a sensible use of epistemological imagination on the puzzle would be very welcome. But that is a matter in which we believe philosophers of science are much more capable that are we.

References

[1] A. Lavoisier, (1789), \textit{Traité élémentaire de chimie} in \textit{Oeuvres de Lavoisier}, (1862), Paris, Imprimerie Imperiale; English translation republished by Dover Publications
[2] S. Cannizzaro, (1858), Nuovo Cimento, 7, 321
[3] R.G. Woolley, (1995), Mol. Phys. 85, 539
[4] J.H. van ’t Hoff, La Chimie dans l’Espace, (Bazendijk, Amsterdam 1875)
[5] G.N. Lewis, Valence and the Structure of Atoms and Molecules, (Chemical Catalog Co., New York 1923)
[6] R.G. Woolley, (1998), J. Math. Chem. 23, 3
[7] D. Mendeleéev, The principles of chemistry, Vol. 2, p.16, footnote (Longmans Green, London 1891)
[8] W. Thomson, (Session 1866 - 67), Proc. Roy. Soc. Edinburgh, 94
[9] J.C. Maxwell, (1875), Entry for ‘ATOM’ in Encyclopaedia Britannica, 9th Edition, 3, 36
[10] L. Pauling and E.B. Wilson, Introduction to Quantum Mechanics, (McGraw-Hill Book Company, Inc. New York 1935), p. 56
[11] H. Primas in NATO ASI Series B57 (Physics), Quantum Dynamics of Molecules: The New Experimental Challenge to Theorists, Ed. R.G.Woolley, p. 105 (Plenum Publishing Corporation 1980)
[12] P.A.M. Dirac, (1929), Proc. Roy. Soc. Lond. A123, 714
[13] B.T. Sutcliffe and R.G. Woolley, (2005), Phys. Chem. Chem. Phys. 7, 3664-3676
[14] B.T. Sutcliffe and R.G. Woolley, Handbook of Computational Chemistry, Ed. J. Lesczynski, (Springer, 2012), pp. 13-54
[15] B.T. Sutcliffe and R.G. Woolley, (2012), J. Chem. Phys. 137, 22A544
[16] B.T. Sutcliffe and R.G. Woolley, (2014), J. Chem. Phys. 140, 037101
[17] W. Hunziker and I.M. Sigal, (2000), J. Math. Phys. 41, 3448
[18] T. Kato, (1951), Trans. Amer. Math. Soc. 70, 212
[19] H. Weyl, The Theory of Groups and Quantum Mechanics, 2nd Edition, Tr. H.P. Robertson, (Dover, New York, 1931)
[20] P.O. Löwdin, (1989), Pure and Appl. Chem. 61, 2065
[21] J.H. van Vleck, The Theory of Electric and Magnetic Susceptibilities, (Oxford, Clarendon Press, 1932), p.186ff
[22] R.G. Woolley, (1976), Adv. Phys. 25, 27

[23] B. Simon, in Mathematical Physics, Eds. A. Fokas, A. Grigoryan, T. Kibble and B. Zegarlinski (Imperial College Press, London, 2000), p. 283

[24] R.G. Woolley and B.T. Sutcliffe, P.-O. Löwdin and the quantum mechanics of molecules, Fundamental World of Quantum Chemistry: A Tribute to the Memory of Per-Olov Löwdin, E.J.Brändas and E.S.Kryachko, Eds, (Kluwer Academic Publishers, 2003), pp. 21-65

[25] E.B. Davies, (1995), J. Phys. A: Math. Gen. 28, 4025