

Chapter 1

P.-O. LÖWDIN AND THE QUANTUM MECHANICS OF MOLECULES[†]

R. G. Woolley

*Dept. of Chemistry and Physics,
Nottingham Trent University,
Nottingham NG11 8NS, UK.
guy.woolley@ntu.ac.uk*

B. T. Sutcliffe

*Laboratoire de Chimie Physique Moléculaire,
Université Libre de Bruxelles,
B-1050 Bruxelles, Belgium
bsutclif@ulb.ac.be*

Abstract It is surely no exaggeration to say that all Per-Olov Löwdin's career was devoted to the quantum mechanics of molecules. But late in his career he began detailed consideration of a formal definition of the term *molecule* within quantum mechanics. The authors first heard him talk of such matters at a meeting held in honour of Prof. Raymond Daudel in 1986. The paper arising from this talk appeared in 1988 and was followed during the next six or so years by others in the same vein. In tribute to Per-Olov we should like here to examine the work in these papers.

1. Introduction

Towards the end of his scientific career, Per-Olov Löwdin actively devoted time to foundational questions of quantum chemistry. He gave many talks at conferences and workshops in which he surveyed the whole

[†]This article appeared in *E. J. Brändas and E. S. Kryachko (eds.), Fundamental World of Quantum Chemistry, Vol. 1 21-65, 2003 Kluwer Academic Publishers.*

range of theoretical techniques employed in quantum chemistry. He also drew attention to what he saw as significant problems that his generation had not succeeded in resolving, and expressed the hope that the next generation of leaders in the field of quantum chemistry would take up the challenge; some of these talks were written up and published. In the following we refer only to the published work [1]–[6] that we have located [7], and concentrate on his attempts to give a quantum definition of a molecule.

His approach is presented fairly fully in just two of the papers [1, 2] which have much common material that we describe below, whereas the other papers [3]–[6] give only summary discussion, and draw attention to some of the unsolved problems. We have felt it appropriate to summarize Per-Olov’s views (Section 3) very much in his own words which we have taken freely from these papers. We start with a summary account of the historical perspective as a background to Löwdin’s concerns. The development of quantum chemistry is a well-known story. It is generally accepted that because of the great difference in the masses of electrons and nuclei it is a good approximation to treat the electronic and nuclear motions as being essentially independent. Thus the electronic states can be determined at different nuclear geometries by treating the nuclei as fixed sources of a potential for the electronic motion. The charge distribution of the electrons is then a function of the nuclear positions and determines the nuclear motion [8, 9]. Our main concern is to emphasize how its procedures require identical nuclei to be treated as distinguishable particles. We take this feature to be the defining characteristic of quantum chemistry.

It is clear that Löwdin was not satisfied with the traditional account. In [2] he starts with the famous Dirac quotation about the theoretical basis for the whole of chemistry being known with the completion of quantum mechanics (see Section 2 below), but reminds us that the situation in quantum mechanics is just the same as with Newton’s laws; these laws regulate the planetary motion but do not describe the planetary system itself - the various planets, their masses, the actual initial conditions appropriate to the solar system. He notes that “quantum chemistry is to a large extent still based on a great deal of chemical and physical insight of mostly experimental nature”, and that there is a very long road from the statement that a molecule is a collection of electrons and nuclei, subject to the laws of quantum mechanics, to an account of chemistry, longer perhaps than Dirac ever imagined. The first steps on this road involve an examination of the quantum mechanics of a molecule that is not based on the Born-Oppenheimer approximation. At the WATOC90 conference in Toronto, Löwdin declared “One of the

most urgent problems of modern quantum chemistry is to treat the motions of the atomic nuclei and the electrons on a more or less equivalent basis” [5]. The motivation for such a step had been identified in his earlier lecture in Paris [1]: “In this way, we may have a somewhat better chance to try to eliminate - or at least minimize - the elements of chemical insight derived from experimental experience which are now so essential as starting points of the theory.”

His programme (Section 3) is to start with the non-relativistic Hamiltonian¹, H , for a collection of electrons and nuclei interacting via Coulombic forces, and to use the results of modern mathematical analysis to see how far he can go with the characterization of the properties of H . The relevant branch of mathematics is the functional analysis for operators on a Hilbert space; this subject is now very extensive and there is a wealth of results, as well as recognized open problems, relevant to the quantum mechanics of the Coulomb Hamiltonian [10, 11]. We attempt here to draw this information together as a development of the approach Löwdin sketched in his late papers [1]–[6].

2. Quantum chemistry: the historical perspective

In 1929 Dirac wrote famously [12]

The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

Whatever might have been felt by the Chemists of the day about Dirac’s claim (and about this, see Simões [13]), there can be no doubt that quantum mechanical ideas began to be very influential in chemistry from the early 1930s onwards. Not only did Pauling’s quantum mechanically based, if still qualitative, valence bond ideas begin to supplement the traditional Lewis and Langmuir account of bonding but also the work of Hückel, Hund and Mulliken led to the idea of molecular orbitals. The molecular orbital approach led to simplifications in the complex equations of quantum theory in such a way as to enable certain kinds of model calculations to be made on molecules. The results of such calculations could be correlated with experimental observations, and quantitative developments along these lines continued throughout the 1940s. With the development of electronic computers, however, the complexity of the equations began to seem rather less of a problem and from the early

¹The *Coulomb Hamiltonian*

1950s onwards there were attempts to understand some of the molecular aspects of chemistry by means of quantum mechanical electronic structure calculations. These were performed within the clamped nuclei scheme using linear combinations of atomic orbitals and aimed to evaluate computationally the molecular integrals that arise when this is done.

In this context it is interesting to recall what Coulson said in his Tilden lecture given in October 1951 [14]. He quotes Dirac as above but then goes on to say

Yet the true contribution of wave mechanics is not here, as I have to remind myself when I am being urged to start immense schemes for the numerical evaluation of molecular integrals. But if it is not here, where is it? The answer is simple. Wave mechanics has shown us what is going on, and at the deepest possible level. We shall find, . . . , that it has taken the concepts of the experimental chemist—the imaginative perception that those who had lived in their laboratories and allowed their minds to dwell creatively upon the facts that they found—and it has shown how they all fit together; how, if you wish, they have one single rationale; and how this hidden relationship to each other can be brought out.

What Coulson seems to be saying here is that Dirac was wrong in supposing that all that there was to chemistry could be comprehended if only we could solve the equations of wave mechanics. Coulson sees chemistry as a much more complicated and imaginative enterprise than Dirac apparently does; instead he suggests that wave mechanics has provided a rationalising underpinning to many chemical ideas. He did not, in 1951 anyway, believe that the most important contribution that quantum mechanics could make to chemistry was by means of computation. Nevertheless, although computational quantum chemistry comprised and continues to comprise only a small part of chemistry, it has grown in influence and utility, as was recognized explicitly in the award in 1998 of the Nobel Prize for Chemistry to Kohn and Pople. It is the citation for Pople that is of particular relevance here:

John Pople is rewarded for developing computational methods making possible the theoretical study of molecules, their properties and how they act together in chemical reactions. These methods are based on the fundamental laws of quantum mechanics as defined by, among others, the physicist E. Schrödinger. A computer is fed with particulars of a molecule or a chemical reaction and the output is a description of the properties of that molecule or how a chemical reaction may take place. The result is often used to illustrate or explain the results of different kinds of experiment. Pople made his computational techniques easily accessible to researchers by designing the GAUSSIAN computer program. The first version was published in 1970. The program has since

been developed and is now used by thousands of chemists in universities and commercial companies the world over.

As this citation makes clear, many aspects of chemical behaviour can be rationalized in terms of molecular electronic structure calculations made in the clamped nuclei approach.

In the clamped nuclei approach, the nuclei form a geometrical figure whose shape and size are disposable. The nuclei generate an attractive potential for electronic motion, and this potential is invariant under all uniform translations and all orthogonal transformations of the figure. The Coulomb Hamiltonian for electronic motion is solved with this potential to yield the electronic wavefunction and electronic energy for particular choices of the nuclear geometry. The classical molecular structure is taken to be that nuclear geometry at which the sum of electronic energy and the classically calculated nuclear repulsion energy is a minimum. The vibration-rotation spectrum can be understood in terms of the structure so calculated, freely rotating while the nuclei perform small vibrations. Technically this outcome is achieved by treating the sum of the electronic energy and the nuclear repulsion energy as a potential with a minimum at the classical structure and solving the quantum mechanical vibration-rotation problem for nuclear motion about this minimum. This is a development of the approach first proposed by Eckart [15]. By constructing this potential as the nuclei are separated in various ways, nuclear collision calculations can be made, in terms of which many kinds of simple chemical reactions can be understood. The basis of the scheme is found in the work of Born and Oppenheimer [16] who gave a quantum mechanical justification for the treatment of the nuclei, in first approximation, simply as providers of a potential for electronic motion.

Eckart's work is in the context of classical mechanics and so makes no reference to the work of Born and Oppenheimer; however they share the same classical viewpoint, namely that in a stable molecule the nuclei undergo only small oscillations about an equilibrium configuration. Eckart proposes a coordinate frame fixed in the molecule which is such that the equilibrium positions of the nuclei are A constant vectors \mathbf{a}_i . The potential energy for the nuclei may be expressed in terms of displacement coordinates

$$\rho_i(\mathbf{z}_i) = \mathbf{z}_i - \mathbf{a}_i$$

which vanish when the molecule is at its equilibrium configuration; here the \mathbf{z}_i are nuclear coordinates expressed relative to the centre of nuclear mass in the frame fixed in the molecule.

It is possible, by perfectly standard methods, to transform a classical Hamiltonian into a quantum mechanical one. Equally, Eckart's Hamiltonian may be derived directly from the Schrödinger equation for

a system of A nuclei moving in the specified potential [17]. The resulting quantum mechanical Hamiltonian must, if it is to be regarded as arising from the Coulomb Hamiltonian, be invariant under any permutation of identical particles. Consider, however, the changes induced in the displacement coordinates by the permutation of identical nuclei. If a particular permutation induces the transposition $\mathbf{z}_i \leftrightarrow \mathbf{z}_j$ then the displacement coordinates transform as

$$\rho_i(\mathbf{z}_i) \rightarrow \rho_i(\mathbf{z}_j), \quad \rho_j(\mathbf{z}_j) \rightarrow \rho_j(\mathbf{z}_i)$$

and are usually different from the initial ones. So in general one cannot expect the Eckart Hamiltonian to be invariant under the permutation of identical nuclei. In fact the Eckart Hamiltonian is invariant only under that sub-group of permutations that can be realised by the operations comprising the point group of the equilibrium framework. An extreme example of the difference between the Coulomb Hamiltonian, and the Eckart model Hamiltonian is afforded by a chiral molecule for which the only symmetry operation is the identity (point group C_1). Most chiral molecules contain some identical nuclei of course.

Historically it was found that the Eckart approach in classical form worked pretty well to describe molecular spectra and that it worked well in quantum mechanical form too, provided that the symmetry of the problem was restricted to that of the point group of the equilibrium framework, that is, to the point group of the classical molecular geometry. It thus appears that the quantum mechanical form of the Eckart Hamiltonian is appropriate if the displacement coordinates can be regarded as describing distinguishable particles. The more extended kinds of potential energy surface needed to describe simple chemical reactions have to be similarly symmetry restricted.

It would thus seem necessary for the success of the standard approaches that the nuclei be treated as identifiable particles, just as they are in classical chemical structure theories. In the original work by Born and Oppenheimer both the electrons and the nuclei are assumed at the outset to be treated as quantum mechanical particles. In Section 3 of their paper [16] one reads (in a translation by S. M. Blinder [18]):

An arbitrary configuration of electrons and nuclei cannot always be treated by a general approximation procedure. We will here consider only states which correspond to a stable molecule. We will begin with the following question:

Is there a system of values of the relative nuclear coordinates ξ_i such that the eigenfunctions ψ_n of the energy operator (6), in so far as they depend on the ξ_i , have values significantly different from zero only in a small neighborhood of this set?

This wave-mechanical requirement corresponds obviously to the classical condition that the nuclei undergo only small oscillations about the equilibrium configuration; the $|\psi_n|^2$ is the probability of finding a certain configuration of given energy.

The energy operator referred to here as (6) is just the full Coulomb Hamiltonian in which the A nuclear coordinates are assumed expressible in terms of the $3A - 6$ relative nuclear coordinates ξ_i and 6 more coordinates which denote the position and orientation of the relative nuclear configuration. In the discussion to establish an answer to the question that they pose in the second paragraph above, they do not require the wave functions to have any particular permutational symmetry. But if the nuclei and the electrons were to be treated on an equal footing in a Coulomb Hamiltonian for the whole molecular system, which of course was the starting point of the work of Born and Oppenheimer, any identical nuclei would be indistinguishable and any wavefunction involving them would have to reflect the symmetries required by such indistinguishability. Thus in using the clamped nuclei Hamiltonian to construct a potential, by holding the nuclei in fixed relative positions and hence identifying them, we are discarding a fundamental symmetry of the full problem. This point appears to have been first recognised in the literature by Berry [19].

3. Löwdin's definition of a molecule

Although Löwdin fully accepted the tremendous range and utility of modern quantum chemistry it is evident in his late writings that he was sensitive to the fact that its foundation, particularly as regards 'molecular symmetry', relies substantially on practical chemical experience. He hoped that a fundamental analysis of the Coulomb Hamiltonian for a molecule would help reduce this dependence on chemical insights, and initiated such a study in the paper [1]. In the following we review the problem taking Löwdin's study as our starting point.

The Hamiltonian operator for a system of N electrons and A atomic nuclei may be written as

$$H = \sum_g^A \frac{\mathbf{p}_g^2}{2m_g} + e^2 \sum_{g<h}^A \frac{Z_g Z_h}{r_{gh}} + \sum_i^N \left(\frac{\mathbf{p}_i^2}{2m} - e^2 \sum_g^A \frac{Z_g}{r_{ig}} \right) + e^2 \sum_{i<j}^N \frac{1}{r_{ij}} \quad (1.1)$$

where the individual terms have obvious physical interpretations. The most basic operator property of H is that it is *essentially self-adjoint*, as famously proved by Kato in 1951. The first, second and last terms on

the rhs of (1.1) are positive, and the crude estimate [1]

$$\sum_i^N \left(\frac{\mathbf{p}_i^2}{2m} - e^2 \sum_g^A \frac{Z_g}{r_{ig}} \right) \geq -\frac{me^4 AN}{2\hbar^2} \sum_g^A Z_g^2 \quad (1.2)$$

confirms that \mathbf{H} is *bounded from below*; thus the spectrum has a lowest eigenvalue E_0 , so that

$$\mathbf{H} \geq E_0 \mathbf{1} \quad (1.3)$$

For normalized wavefunctions in the L^2 -Hilbert space one then has the variation principle,

$$\langle \mathbf{H} \rangle = \frac{\langle \Phi | \mathbf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0 \quad (1.4)$$

and by using a scaling argument originally due to Hylleraas, it can be shown that

$$\langle \mathbf{H} \rangle \leq 0 \quad (1.5)$$

i.e. E_0 is always negative. Löwdin notes that a density matrix (or as he prefers to say 'system operator') formulation is equally possible with

$$\langle \mathbf{H} \rangle = \text{Tr}[\mathbf{H}\Gamma], \quad \text{Tr}[\Gamma] = 1, \quad \text{etc.} \quad (1.6)$$

The lowest eigenvalue E_0 , however, lies at the *bottom of a continuum*, and so the associated eigenfunction describes a *scattering* state. The reason for this is easily found by examining the symmetries of \mathbf{H} . The Coulomb Hamiltonian has the following constants of the motion [1, 2]:

i) The total momentum²

$$\mathbf{P} = \sum_k \mathbf{p}_k \quad (1.7)$$

ii) The total angular momentum

$$\mathbf{L} = \sum_k \mathbf{r}_k \times \mathbf{p}_k \quad (1.8)$$

iii) The permutations \mathcal{P} of the electronic coordinates \mathbf{x}_i which lead with the Pauli Principle [12] to the antisymmetry property of the wavefunctions

$$\mathcal{P}\Psi = (-1)^P \Psi \quad (1.9)$$

²The sums are now taken over *all* the particles in the system.

iv) The permutations of such nuclear coordinates as are associated with nuclei of the same mass.

As a consequence of i) the centre-of-mass of the whole system, with coordinate vector

$$\boldsymbol{\xi} = \frac{1}{M} \sum_k m_k \mathbf{r}_k, \quad M = \sum_k m_k \quad (1.10)$$

moves like a *free particle* having an energy spectrum covering the interval $[0, \infty]$, and so E_0 must be at the bottom of a continuum. Thus it is desirable to separate out the centre-of-mass motion by writing

$$H = \frac{P_{\boldsymbol{\xi}}^2}{2M} + H' = T_{\boldsymbol{\xi}} + H' \quad (1.11)$$

and shift the focus of the investigation to the internal Hamiltonian H' which may have both discrete and continuous eigenvalues. There are infinitely many possible choices of internal coordinates, so that the form of H' is not determined, but whatever coordinates are chosen the essential point is that H' is the *same* operator specified by the decomposition (1.11).

Since the total angular momentum is constant, and can be written in the form

$$L = L_{\boldsymbol{\xi}} + L_{int} \quad (1.12)$$

where both terms are separately conserved, one could further transform H' by making its rotational invariance explicit. Löwdin however does not pursue this further, and contents himself with the remark that the angular momentum operators have discrete spectra, and so do not alter the analysis. At this point in the discussion, in both [1] and [2], he observes that there are in any case other difficulties that - for the moment at least - must be given higher priority. He writes [2] "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. In this situation, it is possible to proceed in two completely different ways." Firstly, there is the traditional approach based on the Born-Oppenheimer argument which emerged from physical and chemical insights of essentially experimental nature as to the existence of molecules, their shapes, symmetry etc. Most quantum chemistry is of this type and is hence still highly dependent on empirical experience.

One may also use mathematical analysis; in order to show the existence of a molecule in its ground state, one has to show that the lowest eigenvalue E_0 of the associated Hamiltonian H' is discrete and corresponds to a *closed state*.

That this statement can be true follows from two fundamental results. Firstly, a classical theorem asserts that, given a self-adjoint operator such as H' and a trial wavefunction that yields an expectation value $\langle H' \rangle$ which is below the bottom of the essential spectrum, H' has at least one discrete negative eigenvalue. Secondly, the location of the bottom of the essential spectrum is defined by the famous Hunzicker-Van Winter-Zhislin (HVZ) theorem. It is obtained by looking at the lowest energy of all possible separated clusters. Taken together these two theorems confirm the validity of a *conjecture* on which quantum chemistry was originally founded; namely if one can find an expectation value $\langle H' \rangle$ which is a lower energy than the lowest energy of all possible separated clusters then there exists a bound ground state. Löwdin cites the study by Hylleraas of the energy of the He atom, the study of the H_2 molecule by James and Coolidge and other examples [1, 2].

There are still formidable problems however, of which the most severe perhaps is the fact that the Coulomb Hamiltonian (1.1) is one and the same for all possible isomers associated with a given chemical formula. Löwdin proposes a general energy surface that may provide a description of isomerism [1, 2]; the energy surface is constructed by writing

$$\mathfrak{E}(\boldsymbol{\alpha} \langle H' \rangle) = \frac{\langle \Phi | H' | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad (1.13)$$

where $\Phi = \Phi(\mathbf{X}, \mathbf{Q}, \boldsymbol{\alpha})$; \mathbf{X} and \mathbf{Q} stand for all the electronic and nuclear variables and are integrated out in the evaluation of $\langle H' \rangle$. Then \mathfrak{E} depends on a set of parameters $\boldsymbol{\alpha} = \alpha_1, \alpha_2, \dots, \alpha_p$, and its minima might be associated with stable isomers in a way familiar from the standard classical discussion of potential energy surfaces; this calculation can also be formulated in a density matrix framework. He concludes that the calculation of the hypersurface $\mathfrak{E}(\boldsymbol{\alpha})$ is a computational effort much bigger than anything yet undertaken in quantum chemistry, and that a new computer architecture might be required. On the other hand molecular structure itself is problematic in this setting [1]. Suppose the molecule contains A nuclei which, to simplify the discussion, are taken to be distinguishable, and that one nuclear coordinate is fixed in the process of elimination of the centre-of-mass motion. There are then $(3A - 3)$ coordinates to be determined, whereas there are $1/2A(A - 1)$ internuclear distances in a 'structure', and so for $A > 6$ the system is over-determined. There must therefore be further constraints to make the additional in-

ternuclear distances compatible with the others. Hence the existence of specific ‘molecular structures’ cannot be taken for granted³.

Finally, in Per-Olov’s last published paper devoted to these questions [6], the fundamental problem for a quantum theory of molecules is identified as: *where does molecular symmetry come from ?* The tenor is very much of handing over unsolved problems to a new generation: in his words “It is definitely not easy to *go beyond* the conventional Born-Oppenheimer approximation and - even if some scientists have tackled the problem with a certain amount of success - it seems evident that some new fundamental ideas may be needed.”

4. The spectrum of the Coulomb Hamiltonian

In this section we develop further the ideas that Löwdin introduced in his discussion of the bound states of the Coulomb Hamiltonian and their identification as molecules. Nothing that is said here is at all new but it is perhaps not yet well represented in the theoretical chemistry literature so a brief summary of the fundamental results may be helpful. In [1] Löwdin acknowledges the help he received from correspondence with Prof. Barry Simon and draws attention to the book [20] *The Analysis of Operators* by Reed and Simon. Chapter XIII of that book contains proofs of many of the results cited by Löwdin. In [20] some necessary results arising from the spectral theory of self-adjoint operators are simply quoted; details may be found in earlier volumes by the same authors, particularly in Section VII [21] and Section X of [22]. An alternative source of similarly relevant material is the book by Thirring [23], who also provides a useful summary, expressed in accessible language and without too much detail, in his contribution to the Schrödinger centenary volume [24].

In 1951 Kato [25] established that the Coulomb Hamiltonian, H , is essentially self-adjoint. This property, which is stronger⁴ 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. It is easy enough to construct examples of such operators; an example given by Thirring [24] is of the radial momentum operator $-i\hbar\partial/\partial r$ acting on functions $\phi(r)$, $\phi(0) = 0$ with $0 \leq r < \infty$. He comments

³If rotation is also separated off [5] there are $(3A - 6)$ coordinates and the condition for over-determination becomes $A > 4$.

⁴They are the same for finite-dimensional operators

Having been confronted with these facts of life one might wonder whether Schrödinger by writing down a formal Hamiltonian without specifying its domain has actually predicted anything about atoms and molecules. That he has actually done so comes from the fact that the Coulomb potential, though unbounded, is small compared with the kinetic energy.

It is the smallness of the Coulomb potential that is used to establish that H is bounded from below, see (1.3).

There are various ways in which the spectrum $\sigma(A)$ of a self-adjoint operator A may be classified. From the point of view of measure theory the natural decomposition is into *pure point*, *absolutely continuous* and *singular continuous* parts. The sets are closed but need not be disjoint. 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 $\sigma_{ess}(A)$ is the complement of the discrete spectrum and is the infinite dimensional part.

$$\sigma_{ess}(A) = \sigma(A) \setminus \sigma_d(A)$$

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. $\sigma_{ess}(A)$ includes the absolutely continuous spectrum $\sigma_{ac}(A)$ and the singular continuous spectrum, $\sigma_{sc}(A)$ this last consisting of infinitely degenerate eigenfunctions. As we shall see, for the Coulomb Hamiltonian the singular continuous spectrum is empty, $\sigma_{sc}(H) = \emptyset$.

The absolutely continuous spectrum describes states in which the particles leave a bounded region in a finite time; these are the scattering states of the system. The discrete spectrum describes bound states in which the particles stay infinitely long in a bounded region. This is the part of the spectrum that is most usefully investigated in the search for the molecule. If one considers the spectrum of the Coulomb Hamiltonian for the Helium atom then the essential spectrum clearly begins at the first ionisation energy, an energy E somewhat below zero. Between this beginning and zero there are an infinite number of states corresponding to those of the hydrogen-like system remaining after the ionisation, together with a free electron. Such states are part of the essential and not of the discrete spectrum. At energies above zero the system consists of a freely moving nucleus and two free electrons. Thus in the case of the Helium atom $\sigma_d(H') = [E_0, E)$ and $\sigma_{ess}(H') = [E, \infty)$. This sort of description can be generalised to the formal Hamiltonian appropriate to any molecular formula, as we now describe.

An extremely powerful technique for the investigation of eigenvalues (the discrete spectrum) of an operator is the *min-max* principle pio-

neered by Weyl and Courant [26]. This characterizes the (exact) eigenvalues in terms of an extremum property of the operator. A modern formulation is Theorem XIII.1 in [20]; a self-adjoint operator A that is bounded from below, that is $A \geq cI$ for some finite c , has eigenvalues $\lambda_n(A)$ that can be expressed as

$$\lambda_n(A) = \sup U_A(\phi_1, \phi_2, \dots, \phi_{n-1}) \quad (1.14)$$

where

$$U_A(\phi_1, \phi_2, \dots, \phi_m) = \inf \langle \psi | A | \psi \rangle \quad (1.15)$$

and $\langle \psi | \psi \rangle = 1$, $\psi \in [\phi_1, \dots, \phi_m]^-$

$$[\phi_1, \dots, \phi_m]^- = \{\psi | \langle \psi | \phi_i \rangle = 0, i = 1, 2, \dots, m\} \quad (1.16)$$

Then for each fixed n , either

- a) there are n eigenvalues below $\sigma_{ess}(A)$, and λ_n is the n th eigenvalue or
- b) λ_n is the bottom of $\sigma_{ess}(A)$, and there are at most $(n - 1)$ eigenvalues below $\sigma_{ess}(A)$. The significance of this result is that if $\sigma_{ess}(A) = [a, \infty)$ for some a and we know that $\lambda_n < a$, there must be at least n eigenvalues [20].

On the other hand if the variation in (1.14)-(1.16) is restricted to a n -dimensional subspace of the domain of the operator A described by an orthogonal projection P , then the min-max principle can be used to characterize the eigenvalues $\hat{\lambda}_n$ of PAP, and this leads to

$$\lambda_n \leq \hat{\lambda}_n \quad (1.17)$$

which is the *Rayleigh-Ritz* principle. This is essentially the result that Löwdin [1, 2] attributes to Weyl⁵, for if a variational calculation with some trial function yields an expectation value $\langle A \rangle$ below the bottom of $\sigma_{ess}(A)$, there must be at least one eigenvalue below $\langle A \rangle$, by (1.17).

We noted in Section 1 that the operator H_∞ obtained from (1.1) by taking the limit $\{m_g \rightarrow \infty, \forall g\}$ is the basis of modern quantum chemistry; it is of course the familiar electronic Hamiltonian. Suppose we have found the energy eigenvalues $U_m(\mathbf{x}^n)$, $\mathbf{x}^n = (\mathbf{x}_1^n, \mathbf{x}_2^n, \dots, \mathbf{x}_A^n)$ and corresponding eigenfunctions $\Psi_m(\mathbf{x}^e, \mathbf{x}^n)$ of H_∞ . The energies are to be used as effective potentials in the Schrödinger equation for the nuclear motion,

$$\left[\sum_g^A \frac{p_g^2}{2m_g} + U_m(\mathbf{x}^n) \right] \Phi(\mathbf{x}^n)_i = \mathcal{E}_{mi} \Phi(\mathbf{x}^n)_i \quad (1.18)$$

⁵But Löwdin was mistaken in his attribution to Weyl's paper [27], which contains fundamental results about σ_{ess} for bounded self-adjoint operators.

to yield molecular energies $\{\mathcal{E}_{mi}\}$. The approximate ground-state energy \mathcal{E}_{11} found in this way provides a *lower bound* to the true ground state energy E_0 , according to the operator inequality

$$\mathbf{H} \geq U_1(\mathbf{x}^n) + \sum_g^A \frac{p_g^2}{2m_g} \geq \mathcal{E}_{11} \quad (1.19)$$

On the other hand, if the product wavefunction $\Psi(\mathbf{x}^e, \mathbf{x}^n)_1 \Phi(\mathbf{x}^n)_1$ is used in a Rayleigh-Ritz calculation, the energy so obtained is an upper bound to E_0 , so we have the estimates

$$\mathcal{E}_{11} \leq E_0 \leq \mathcal{E}_{11} + \sum_g^A \frac{c_g^2}{2m_g} \quad (1.20)$$

where the constants c_g are independent of the nuclear masses [24, 28, 29, 30].

In order to use these results as information about the ground-state however we need quantitative information also about the bottom of $\sigma_{ess}(\mathbf{A})$; this is much harder for the general N -particle Coulomb Hamiltonian. A theorem of Weyl, [27] shows that if \mathbf{A} is self-adjoint and an operator \mathbf{B} differs from it by only a compact perturbation, $\sigma_{ess}(\mathbf{A}) = \sigma_{ess}(\mathbf{B})$. The essential spectrum of the kinetic energy operator, $-\nabla^2$, is easily seen to be $\sigma_{ess}(-\nabla^2) = [0, \infty]$ (e.g. consider its Fourier transform); Weyl's theorem suffices to prove that $\sigma_{ess}(-\nabla^2 + V) = \sigma_{ess}(-\nabla^2) = [0, \infty)$ for a large class of two-body Schrödinger operators (after removal of the centre-of-mass contribution) with $V \rightarrow 0$ at infinity, including the case of the Coulomb interaction $1/r$. Suppose we write

$$\mathbf{H} = \mathbf{H}_0 + V \quad (1.21)$$

and define the resolvents of \mathbf{H} and \mathbf{H}_0 by

$$R(E) = \frac{1}{\mathbf{H} - E} \quad R_0(E) = \frac{1}{\mathbf{H}_0 - E} \quad (1.22)$$

Then by standard manipulations [31]

$$R(E) = R_0(E) - R_0(E)V R(E) \quad (1.23)$$

In the two-body Coulombic case where $\mathbf{H}_0 = -\nabla^2$, and $V = 1/r$, the crucial result is that $R_0(E)V$ is a compact operator, and so is bounded [30].

This property fails in the N -body case where V is a sum over two-particle interactions

$$V = \sum_{i < j} V_{ij}(\mathbf{x}_i - \mathbf{x}_j)$$

which are such that $V_{ij}(\mathbf{X}) \rightarrow 0$ as $X \rightarrow \infty$, where X is the ij relative distance coordinate. Then even though the two-body potential is well-behaved at infinity, V fails to go to zero at infinity in tubes where

$$\sum_{i=1}^{n-1} |\mathbf{x}_i - \mathbf{x}_n|^2 \rightarrow \infty$$

while some $|\mathbf{x}_i - \mathbf{x}_j|$ remain finite. As a result, $R_0(E)V$ is not compact, and Weyl's theorem is no longer applicable. During the 1960's and 1970's a different decomposition of the resolvent was discovered and utilized in scattering theory, and this culminated finally in the proof of the so-called HVZ theorem (Theorem XIII.17 in [20]) which demonstrates that the essential spectrum of the internal Coulombic Hamiltonian H' can be written as $\sigma_{ess}(H') = [\Sigma, \infty)$ where Σ is the energy of the lowest two-body⁶ cluster decomposition of the N -particle system. Subsequently a rather different method of proof based on geometrical ideas was developed; a valuable discussion of the HVZ theorem from this point of view can be found in [30].

The Coulomb interaction belongs to a special class of two-body potentials that are called *dilatation analytic*. Indeed, suppose that $V_{ij}(\mathbf{X})$ has the property that the operator

$$J(\theta) = V(e^\theta \mathbf{X})(-\nabla^2 + 1)^{-1}$$

is compact and has an analytic continuation from real θ to $\{\theta, |Im \theta| < \epsilon\}$ for some $\epsilon > 0$. This suffices to guarantee that any eigenvalues of the internal Hamiltonian H' are of finite multiplicity and can only accumulate at thresholds [32]; physically, the thresholds correspond to fragmentation energies. The exploitation of the dilatation analyticity of the Coulombic interaction is commonly referred to as the complex coordinate rotation technique [32, 33, 34]. It allows a particularly vivid visualization of the entire spectrum of H' , and generalizes the description of the Helium atom we gave earlier. The continuous spectrum of H' lies above a certain (possibly infinite) number of discrete states which are bound stationary states of the N -particle cluster (atom or molecule). The singular continuous spectrum of H' is empty, $\sigma_{sc}(H') = \emptyset$. In the complex energy plane the continuous spectrum is a branch cut on the real E axis starting at some value Σ and extending to $+\infty$; it is rich in structure having numerous sets of other bound states embedded in it. These are associated with the fragments that the N -particle cluster

⁶It is necessary to consider the two-cluster threshold only, since the three-cluster threshold can be shown (see result (20b) of XIII.5 of [20]) to be above the two-cluster one and so on.

can break up into. A new cluster fragment does not appear until the energy has exceeded a characteristic threshold value. This description of the spectrum is what one would expect intuitively from the facts of mass spectrometry.

Let \mathbf{x} and \mathbf{p} stand collectively for all the coordinate and momentum operators of the N particles described by H , and write a position space wavefunction as $\psi^N(\mathbf{x})$ with $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, where as discussed previously, Section 3, only $(N - 1)$ of the \mathbf{x}_i are independent of the centre-of-mass coordinate $\boldsymbol{\xi}$. Now introduce a dilatation transformation with a unitary operator parameterized by an angle θ such that

$$U(\theta)\psi^N(\mathbf{x}) = e^{i3(N-1)\theta/2}\psi^N(\mathbf{x}e^{i\theta})$$

The effect of $U(\theta)$ is simply to transform \mathbf{x} and \mathbf{p} as

$$\mathbf{x} \rightarrow \mathbf{x}e^{i\theta} \quad \mathbf{p} \rightarrow \mathbf{p}e^{i\theta}$$

Then we can construct the unitary transform of the molecular Hamiltonian H under $U(\theta)$

$$\mathcal{H} = U(\theta)HU(\theta)^{-1}$$

With the assumption of Coulombic interactions between the particles the following conclusions can then be stated [34]:

- i Bound-state eigenvalues of \mathcal{H} are independent of θ , and identical to those of H , for $|\theta| < \pi/2$;
- ii scattering thresholds corresponding to the possibility of fragmentation into all possible cluster fragments in different states of excitation are also independent of θ for $|\theta| < \pi/2$;
- iii the segments of continua beginning at each scattering threshold rotate by an angle 2θ into the lower half plane ($\theta \geq 0$), each about its own threshold,
- iv in addition, discrete eigenvalues of \mathcal{H} may appear in the sector $0 > \arg(z - \Sigma) > -2\theta$ where z is the complex energy and Σ is the bottom of $\sigma_{ess}(H)$ - these are associated with bound states with finite lifetimes (resonances).

5. Symmetry in the Coulomb Hamiltonian

It would seem pertinent before we consider molecular symmetry further, to analyse more fully the consequences of the symmetries of the Coulomb Hamiltonian identified in Section 3.

Let us initially look at the translational symmetry and let the position variables in the problem be designated as \mathbf{x}_i which will be treated as a column matrix of three cartesian components $x_{\alpha i}$, $\alpha = x, y, z$. We regard the \mathbf{x}_i collectively as the 3 by N_T matrix \mathbf{x} . When it is necessary

to distinguish between electrons and nuclei, the variables may be split up into two sets, one set consisting of N variables, \mathbf{x}_i^e , describing the electrons and the other set of A variables, \mathbf{x}_i^n , describing the nuclei with $N_T = N + A$. Each of the particles has mass m_i and charge $Z_i e$. The charge-numbers Z_i are positive integers for a nucleus and minus one for an electron. In a neutral system the charge-numbers sum to zero.

All that is needed to remove the centre of mass motion from the full molecule Hamiltonian is a coordinate transformation symbolised by

$$(\mathbf{t} \boldsymbol{\xi}) = \mathbf{x} \mathbf{V} \quad (1.24)$$

In (1.24) \mathbf{t} is a 3 by $N_T - 1$ matrix and $\boldsymbol{\xi}$ is a 3 by 1 matrix, so that the combined (bracketed) matrix on the left of (1.24) is 3 by N_T . \mathbf{V} is an N_T by N_T matrix which, from the structure of the left side of (1.24), has a special last column whose elements are

$$V_{iN_T} = M_T^{-1} m_i, \quad M_T = \sum_{i=1}^{N_T} m_i \quad (1.25)$$

Hence $\boldsymbol{\xi}$ is the standard centre-of-mass coordinate

$$\boldsymbol{\xi} = M_T^{-1} \sum_{i=1}^{N_T} m_i \mathbf{x}_i \quad (1.26)$$

As the coordinates \mathbf{t}_j , $j = 1, 2, \dots, N_T - 1$ are to be translationally invariant, we require

$$\sum_{i=1}^{N_T} V_{ij} = 0, \quad j = 1, 2, \dots, N_T - 1 \quad (1.27)$$

on each remaining column of \mathbf{V} and it is easy to see that (1.27) forces $\mathbf{t}_j \rightarrow \mathbf{t}_j$ as $\mathbf{x}_i \rightarrow \mathbf{x}_i + \mathbf{a}$, all i .

The \mathbf{t}_i are independent if the inverse transformation

$$\mathbf{x} = (\mathbf{t} \boldsymbol{\xi}) \mathbf{V}^{-1} \quad (1.28)$$

exists. The structure of the right side of (1.28) shows that the bottom row of \mathbf{V}^{-1} is special and, without loss of generality, we may require its elements to be

$$(\mathbf{V}^{-1})_{N_T i} = 1, \quad i = 1, 2, \dots, N_T \quad (1.29)$$

The inverse requirement on the remainder of \mathbf{V}^{-1} implies that

$$\sum_{i=1}^{N_T} (\mathbf{V}^{-1})_{ji} m_i = 0, \quad j = 1, 2, \dots, N_T - 1 \quad (1.30)$$

When we write the column matrix of the cartesian components of the partial derivative operator as $\partial/\partial\mathbf{x}_i$, the coordinate change (1.24) gives

$$\frac{\partial}{\partial\mathbf{x}_i} = \sum_{j=1}^{N_T-1} V_{ij} \frac{\partial}{\partial\mathbf{t}_j} + m_i M_T^{-1} \frac{\partial}{\partial\xi} \quad (1.31)$$

and when it seems more convenient this column matrix of derivative operators will also be denoted as the vector grad operator $\vec{\nabla}(\mathbf{x}_i)$.

If a second set \mathbf{t}' of translationally invariant coordinates is constructed it may be related to the original set by

$$(\mathbf{t}' \xi) = (\mathbf{t} \xi) \bar{\mathbf{V}}, \quad \bar{\mathbf{V}} = \mathbf{V}^{-1} \mathbf{V}' \quad (1.32)$$

where \mathbf{V}' is the transformation matrix that defines \mathbf{t}' . The matrix $\bar{\mathbf{V}}$ is

$$\begin{pmatrix} \mathbf{G} & \mathbf{0} \\ \mathbf{0} & 1 \end{pmatrix}, \quad G_{ij} = (\bar{\mathbf{V}})_{ij}, \quad i, j = 1, 2, \dots, A-1 \quad (1.33)$$

It is easily seen that the form of (1.31) is preserved under a change from \mathbf{t} to \mathbf{t}' . It is thus the case that any set of translationally invariant coordinates can be related to any other set by means of a linear transformation.

The Hamiltonian (1.1) in the new coordinates becomes

$$\begin{aligned} \mathbf{H}(\mathbf{t}, \xi) &= -\frac{\hbar^2}{2} \sum_{i,j=1}^{N_T-1} \frac{1}{\mu_{ij}} \vec{\nabla}(\mathbf{t}_i) \cdot \vec{\nabla}(\mathbf{t}_j) + \frac{e^2}{8\pi\epsilon_o} \sum_{i,j=1}^{N_T} \frac{Z_i Z_j}{r_{ij}(\mathbf{t})} - \frac{\hbar^2}{2M_T} \nabla^2(\xi) \\ &= \mathbf{H}'(\mathbf{t}) - \frac{\hbar^2}{2M_T} \nabla^2(\xi) \end{aligned} \quad (1.34)$$

Here

$$1/\mu_{ij} = \sum_{k=1}^{N_T} m_k^{-1} V_{ki} V_{kj}, \quad i, j = 1, 2, \dots, N_T - 1 \quad (1.35)$$

The $N_T - 1$ dimensional square matrix composed of all the $1/\mu_{ij}$ is denoted as $\boldsymbol{\mu}^{-1}$. The operator r_{ij} is the interparticle distance operator expressed as a function of \mathbf{t}_i . Thus

$$r_{ij}(\mathbf{t}) = \left(\sum_{\alpha} \left(\sum_{k=1}^{N_T-1} ((\mathbf{V}^{-1})_{kj} - (\mathbf{V}^{-1})_{ki}) t_{\alpha k} \right)^2 \right)^{1/2} \quad (1.36)$$

In (1.34) the $\vec{\nabla}(\mathbf{t}_i)$ are grad operators expressed in the cartesian components of \mathbf{t}_i and the last term represents the centre-of-mass kinetic energy. Since the centre-of-mass variable does not enter the potential energy term, the centre-of-mass motion may be separated off completely so that the eigenfunctions of H are of the form

$$T(\boldsymbol{\xi})\Psi(\mathbf{t}) \tag{1.37}$$

where $\Psi(\mathbf{t})$ is a wavefunction for the Hamiltonian $H'(\mathbf{t})$ (1.34) in (1.11) which we will refer to as the *translationally invariant* Hamiltonian.

It should be emphasised that the \mathbf{x}_i simply specify field points, and cannot actually be particle coordinates because of the indistinguishability of sets of identical particles. Weyl [35] and later Mackey [36] 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 discusses this in Section C 9 of Chapter IV of [35]. He says of the two particle case:

Physical quantities have only an objective significance if they depend *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 *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. To avoid periphrasis we shall, however, continue to speak of the variables as if they were particle coordinates.

It is straightforward to enumerate the other symmetries of the translationally invariant Hamiltonian. The general permutation of identical particles can be written as

$$\mathcal{P}(\mathbf{x}^e \mathbf{x}^n) = (\mathbf{x}^e \mathbf{x}^n) \begin{pmatrix} \mathbf{P}^e & \mathbf{0} \\ \mathbf{0} & \mathbf{P}^n \end{pmatrix} \equiv \mathbf{xP} \quad (1.38)$$

where \mathbf{P}^e and \mathbf{P}^n are standard permutation matrices. They are orthogonal with determinant ± 1 according to whether the permutation is of even or odd parity. The matrix \mathbf{P}^n will have non-zero entries only for each group of identical atomic nuclei and is most conveniently visualised as having block diagonal form, one block for each group of identical nuclei. The effect of this permutation on the translationally invariant coordinates is:

$$\mathcal{P}(\mathbf{t} \boldsymbol{\xi}) = (\mathbf{t} \boldsymbol{\xi}) \begin{pmatrix} \mathbf{H} & \mathbf{0} \\ \mathbf{0} & 1 \end{pmatrix} \quad (1.39)$$

where

$$(\mathbf{H})_{ij} = (\mathbf{V}^{-1} \mathbf{P} \mathbf{V})_{ij}, \quad i, j = 1, 2, \dots, N_T - 1 \quad (1.40)$$

The matrix \mathbf{H} is not necessarily in standard permutational form neither is it orthogonal, even though it has determinant ± 1 according to the sign of $|\mathbf{P}|$. Thus under any permutation of like particles, the translationally invariant coordinates will transform into linear combinations of themselves. Any chosen transformed coordinate will, generally, involve both \mathbf{P}^e and \mathbf{P}^n in its definition. If it is desired to identify electrons with a particular set of translationally invariant coordinates, specialised coordinate choices must be made to avoid \mathbf{P}^n becoming involved in the definition of their transformed forms, and even more specialised choices must be made to ensure that members of the chosen set transform only into each other under \mathbf{P}^e .

Because the translationally invariant Hamiltonian 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 $J = 0, 1, 2, \dots$ 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 \mathcal{S} of the system. This group comprises the direct product of

the permutation group \mathcal{S}_N for the electrons with the permutation groups \mathcal{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 etc) or of the antisymmetric representation, if fermions (spin 1/2, 3/2, 5/2 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 *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.⁷

Since all possible sets of translationally invariant coordinates can be related by linear transformations, the spectrum of the translationally invariant Hamiltonian is quite independent of the choice of translationally invariant coordinates made. It is, however, clear from the form of (1.36) that the asymptotic form of any particular $H'(\mathbf{t})$ for a given interparticle configuration, will not in general be expressible at all simply in terms of the chosen set of the \mathbf{t}_i . Further, any linear transformations of the \mathbf{t}_i that may be induced by permutations according to (1.39), will complicate further the expression of asymptotic behaviour. Thus extreme care must be exercised in any attempt to describe cluster decomposition for any given Coulomb Hamiltonian, and so situate the bottom of its essential spectrum. These problems have been addressed by Balslev⁸ [37] who was able to show that the essential spectrum of the translationally invariant Coulomb Hamiltonian started at the lowest two-cluster threshold with compatible symmetry. In particular he showed that for the atomic Coulomb Hamiltonian there were infinite sequences of discrete eigenvalues for each symmetry type. It is the case then, that the HVZ theorem that Löwdin [1, 2] referred to, still holds when all symmetries are considered. However, actually to describe a given cluster decomposition it is, in general, necessary to perform linear transformations of the translationally invariant coordinates so that the interparticle asymptotes may be properly represented and also preserve permutational symmetry. This last is important because there may be particles of the same kind in each of the clusters.

⁷See the discussion of Theorem XIII.46 in [20].

⁸see also Notes to Section XIII.5 in [20]

5.1 Symmetry and asymptotic behaviour

As an example of what is involved in cluster decomposition consider a neutral system with two nuclei and N electrons. Let the two nuclei have masses m_b and m_c , and charges Z_b and Z_c and be located by coordinates \mathbf{x}_b and \mathbf{x}_c . Then if one is investigating this system as if it were a diatomic molecule, it is customary to define a relative nuclear variable as

$$\mathbf{t}^n = \mathbf{x}_b - \mathbf{x}_c \quad (1.41)$$

A set of translationally invariant electronic variables may be written as

$$\mathbf{t}_i^e \equiv \mathbf{t}_i = \mathbf{x}_i^e + v_b \mathbf{x}_b + v_c \mathbf{x}_c, \quad i = 1, 2, \dots, N, \quad v_b + v_c = -1 \quad (1.42)$$

The inverse transformation is

$$\begin{aligned} \mathbf{x}_b &= m_c M^{-1} \mathbf{t}^n + \mathbf{X} \\ \mathbf{x}_c &= -m_b M^{-1} \mathbf{t}^n + \mathbf{X} \\ \mathbf{x}_i^e &= \mathbf{t}_i + \frac{(m_b v_c - m_c v_b)}{M} \mathbf{t}^n + \mathbf{X} \end{aligned} \quad (1.43)$$

where $M = m_b + m_c$ and $\mathbf{X} = M^{-1}(m_b \mathbf{x}_b + m_c \mathbf{x}_c)$ is the usual centre-of-nuclear mass coordinate. It is seen that generally the definition of \mathbf{t}_i will be changed if \mathbf{x}_b and \mathbf{x}_c are interchanged, so if permutations of the nuclear coordinates are to have no effect on the translationally invariant electronic coordinates, v_b and v_c must be chosen to be the same for identical nuclei. This is just the sort of coordinate choice that seems to have been made by Born and Oppenheimer [16] in Part VIII of their paper where they offer an independent treatment of the diatomic molecule⁹.

The nuclear-electronic distances have to be supplied from (1.43) according to the particular choices made for v_b and v_c . A natural choice for a homonuclear diatomic, and a possible one for a heteronuclear one too, is to choose both v_b and v_c to be $-1/2$, giving

$$\mathbf{t}_i = \mathbf{x}_i^e - \frac{1}{2}(\mathbf{x}_b + \mathbf{x}_c) \quad (1.44)$$

$$\mathbf{x}_i^e = \mathbf{t}_i + \frac{(m_c - m_b)}{2M} \mathbf{t}^n + \mathbf{X} \quad (1.45)$$

⁹It is not quite clear from the paper precisely how the electronic coordinates were chosen.

so that in the homonuclear case we get

$$(\mathbf{x}_b - \mathbf{x}_j^e) = \left(\frac{\mathbf{t}^n}{2} - \mathbf{t}_j\right), \quad (\mathbf{x}_c - \mathbf{x}_j^e) = \left(\frac{\mathbf{t}^n}{2} + \mathbf{t}_j\right)$$

Let us consider the asymptotic behaviour of the electron-nucleus potential terms here. As \mathbf{t}^n becomes very large, the nuclear repulsion term becomes very small and, for any fixed values for the \mathbf{t}_i , the electron-nucleus attraction terms become small too, while the electronic repulsion terms remain constant. Thus the asymptotes of the problem so formulated are a pair of bare nuclei with the ionised electrons referred to a point midway between them. This is clearly not a very good candidate for the lowest two-cluster decomposition.

A much better choice for the lowest two-cluster decomposition would be into a pair of neutral atoms. In these circumstances it would be reasonable to define

$$\begin{aligned} \mathbf{t}'_i &= \mathbf{x}_i^e - \mathbf{x}_b, \quad i = 1, 2, \dots, Z_b \\ \mathbf{t}'_i &= \mathbf{x}_i^e - \mathbf{x}_c, \quad i = Z_b + 1, \dots, N \end{aligned} \quad (1.46)$$

Notice that with this choice, the definition of the translationally invariant electronic coordinates is changed, if the nuclei are permuted. The inverse of this transformation for the nuclei is as above in (1.43) while that for the electrons is

$$\begin{aligned} \mathbf{x}_i^e &= \mathbf{t}'_1 + \frac{m_c}{M} \mathbf{t}^n + \mathbf{X}, \quad i = 1, 2, \dots, Z_b \\ \mathbf{x}_i^e &= \mathbf{t}'_2 - \frac{m_b}{M} \mathbf{t}^n + \mathbf{X}, \quad i = Z_b + 1, \dots, N \end{aligned}$$

If i and j are in different clusters then

$$(\mathbf{x}_i^e - \mathbf{x}_j^e) = (\mathbf{t}_i - \mathbf{t}_j \pm \mathbf{t}^n)$$

so that the inter-electronic part of the potential has a dependence upon the translationally invariant nuclear coordinates. The coordinates of the electron-nucleus attraction terms take the form:

$$(\mathbf{x}_i^e - \mathbf{x}_b) = (\mathbf{t}_i), \quad (\mathbf{x}_i^e - \mathbf{x}_c) = (\mathbf{t}_i + \mathbf{t}^n)$$

if i is in the first cluster and

$$(\mathbf{x}_i^e - \mathbf{x}_c) = (\mathbf{t}_i), \quad (\mathbf{x}_i^e - \mathbf{x}_b) = (\mathbf{t}_i - \mathbf{t}^n) \quad (1.47)$$

if i is in the second cluster. It is easily seen that this choice does allow the dissociation into a pair of separate atoms but at the cost of making the

electronic repulsion term dependent upon what is formally, a nuclear variable and also of considerably complicating the description of the permutational symmetry of the electrons.

The two sets (1.44) and (1.46) of translationally invariant coordinates are related by

$$\begin{aligned} \mathbf{t}'_i &= \mathbf{t}_i - \frac{1}{2}\mathbf{t}^n, \quad i = 1, 2, \dots, Z_b \\ \mathbf{t}'_i &= \mathbf{t}_i + \frac{1}{2}\mathbf{t}^n \quad i = Z_b + 1, \dots, N \end{aligned} \quad (1.48)$$

and obviously, any wave function obtained in one set of coordinates can be re-expressed, though perhaps not at all conveniently, in the other. This establishes that the exact solutions to the problem expressed in either set of coordinates yield the same energies, provided that the same boundary conditions are imposed, in spite of having different looking wave functions; it is this fact that makes it possible to establish the HVZ theorem while restricting the permutational symmetry of the solutions.

Clearly a somewhat different approach is necessary when considering how rotation-reflection symmetry can be maintained asymptotically. The translationally invariant coordinates are not immediately adapted to describe such symmetry. Descriptions of this kind of symmetry are usually offered in terms of three angular coordinates and a parity specification, together with $3N_T - 6$ *internal* coordinates, which are invariant under all rotation-reflections. There are many rather delicate topological problems raised by such a choice. The space defined is a quotient manifold that is only locally Euclidean and so coordinates can be defined only locally. In fact it always takes more than one coordinate system to cover the quotient manifold, and this complicates greatly any explicit account of the rotation-reflection symmetry at the asymptotes. We shall follow Löwdin in his discussion of angular momentum (rotational symmetry) and take the view that there are other difficulties that for the moment must be given higher priority.

5.2 Symmetry and particle identity

In view of the above discussion and the arguments advanced by Born and Oppenheimer [16], it may be helpful to express $H'(\mathbf{t})$ in terms of two sets of coordinates. One set consists of $A - 1$ translationally invariant coordinates \mathbf{t}_i^n expressed entirely in terms of the original \mathbf{x}_i^n :

$$\mathbf{t}_i^n = \sum_{j=1}^A \mathbf{x}_j^n V_{ji}^n, \quad i = 1, 2, \dots, A - 1 \quad (1.49)$$

here \mathbf{V}^n is a non-singular matrix whose last column is special, with elements

$$V_{iA}^n = M^{-1}m_i, \quad M = \sum_{i=1}^A m_i \quad (1.50)$$

so that the coordinate \mathbf{X} , defined by its last column, is the coordinate of the centre-of-nuclear mass. The elements in the first $A - 1$ columns of \mathbf{V}^n each sum to zero, exactly as in the general case, to ensure translational invariance. The other set comprises N translationally invariant coordinates of the form

$$\mathbf{t}_i^e = \mathbf{x}_i^e + \sum_{j=1}^A v_j \mathbf{x}_j^n \quad (1.51)$$

For definiteness we shall choose $v_i = -m_i/M$ so that the translationally invariant electronic coordinates are the original electronic coordinates expressed relative to the centre-of-nuclear-mass. For generality¹⁰ the systems that we shall consider must have $A \geq 4$. The inverse relations are

$$\mathbf{x}_i^e = \mathbf{X} + \mathbf{t}_i^e \quad (1.52)$$

$$\mathbf{x}_i^n = \mathbf{X} + \sum_{j=1}^{A-1} \mathbf{t}_j^n ((\mathbf{V}^n)^{-1})_{ji} \quad (1.53)$$

with

$$((\mathbf{V}^n)^{-1})_{Ai} = 1, \quad i = 1, 2, \dots, A \quad (1.54)$$

while the inverse requirement on the remaining rows gives

$$\sum_{i=1}^A ((\mathbf{V}^n)^{-1})_{ji} m_i = 0 \quad j = 1, 2, \dots, A - 1 \quad (1.55)$$

The centre-of-mass and the centre-of-nuclear-mass are related by

$$\boldsymbol{\xi} = \mathbf{X} + \frac{m}{M_T} \sum_{i=1}^N \mathbf{t}_i^e \quad (1.56)$$

The translationally invariant Coulomb Hamiltonian now takes the form:

$$\mathbf{H}'(\mathbf{t}) \rightarrow \mathbf{H}^e(\mathbf{t}^e) + \mathbf{H}^n(\mathbf{t}^n) + \mathbf{H}^{en}(\mathbf{t}^n, \mathbf{t}^e) \quad (1.57)$$

¹⁰The cases $A = 1$, $A = 2$ and $A = 3$ (the nuclear configurations that define, respectively, a point, a line and a plane) must be given special attention and to consider them here would deflect us from the main thrust of the argument.

The part of the Hamiltonian which can be associated with electronic motion is

$$\mathbf{H}^e(\mathbf{t}^e) = -\frac{\hbar^2}{2\mu} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|} \quad (1.58)$$

with

$$1/\mu = 1/m + 1/M \quad (1.59)$$

while the part that can be associated with nuclear motion is

$$\mathbf{H}^n(\mathbf{t}^n) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(\mathbf{t}_i^n) \cdot \vec{\nabla}(\mathbf{t}_j^n) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)} \quad (1.60)$$

where $r_{ij}(\mathbf{t}^n)$ is defined just as in the general case (1.36) but using the \mathbf{t}_i^n and $(\mathbf{V}^n)^{-1}$, that is

$$r_{ij}(\mathbf{t}^n) = \left(\sum_{\alpha} \left(\sum_{k=1}^{A-1} ((\mathbf{V}^n)^{-1})_{kj} - (\mathbf{V}^n)^{-1}_{ki} t_{\alpha k}^n \right)^2 \right)^{1/2} \quad (1.61)$$

and the inverse mass matrix is similarly specialised as

$$1/\mu_{ij}^n = \sum_{k=1}^A m_k^{-1} V_{ki}^n V_{kj}^n, \quad i, j = 1, 2, \dots, A-1 \quad (1.62)$$

The electronic and nuclear motion are coupled only via a potential term:

$$\mathbf{H}^{en}(\mathbf{t}^n, \mathbf{t}^e) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{r'_{ij}(\mathbf{t}^n, \mathbf{t}^e)} \quad (1.63)$$

and the electron-nucleus distance expression becomes

$$|\mathbf{x}_i^n - \mathbf{x}_j^e| \equiv r'_{ij} = \left| \sum_{k=1}^{A-1} \mathbf{t}_k^n (\mathbf{V}^n)^{-1}_{ki} - \mathbf{t}_j^e \right| \quad (1.64)$$

It follows from (1.39) that this choice of translationally invariant coordinates is such that the \mathbf{t}_i^e transform under a permutation of the \mathbf{x}_i^e exactly as do the \mathbf{x}_i^e and remain unchanged under any permutation of the \mathbf{x}_i^n . The \mathbf{t}_i^n are invariant under any permutation of the \mathbf{x}_i^e while a permutation of the \mathbf{x}_i^n produces a transformation among the \mathbf{t}_i^n just as in (1.39) but with the variables restricted to the \mathbf{t}_i^n , the permutations only among the identical nuclei and with transformation matrices involving only the nuclear variables. This choice makes $\mathbf{H}^e(\mathbf{t}^e)$ trivially

invariant under permutations of the original electronic coordinates and independent of any particular choice of translationally invariant nuclear coordinates. Similarly $H^n(\mathbf{t}^n)$ is independent of any particular choice of translationally invariant electronic coordinates and is also invariant under any permutation of the original coordinates of identical nuclei. The interaction operator $H^{en}(\mathbf{t}^n, \mathbf{t}^e)$ is obviously invariant under a permutation of the original electronic coordinates and is also invariant under a permutation of the original coordinates of identical nuclei.

Although, for a given choice of boundary conditions, the spectrum of the translationally invariant Hamiltonian is precisely the same with this choice of coordinates as it would be for any other choice, we might hope to recognise in these coordinates an eigenfunction corresponding to a molecule, rather more easily than we would in some other choices. We might hope too, that if we find a suitably localised eigenfunction $\Psi(\mathbf{t}^n, \mathbf{t}^e)$ then it might be possible to write it in good approximation in the electron-nuclear product form $\Phi(\mathbf{t}^n)\psi(\mathbf{t}^e, r_{ij}(\mathbf{t}^n))$ in the spirit of the Born and Oppenheimer analysis. It should be noted explicitly that the choice of a product form to approximate the exact eigenfunction does not mean that any permutational symmetry of the problem is being neglected here or will in future be neglected in this context.

Let us consider now the behaviour of such functions under identical particle permutations. Let a particular irreducible representation of the symmetric group of the electronic coordinates be denoted as $[\boldsymbol{\lambda}]^N$ and let the conjugate representation be denoted as $[\tilde{\boldsymbol{\lambda}}]^N$. For electrons (or any spin 1/2 particles) the representation of the symmetric group carried by the spin-eigenfunctions $\Theta_{S, M_S, i}$ must be one described by a no more than two-rowed Young diagram, that is $[\boldsymbol{\lambda}]^N \equiv [\lambda_1, \lambda_2]$ where

$$\lambda_1 = N/2 + S, \quad \lambda_2 = N/2 - S$$

The representations are independent of the choice of M_S and i labels the rows (columns) of the representation. The dimension of the representation is given by the Wigner number

$$f_S^N = \frac{(2S + 1)N!}{(N/2 + S + 1)!(N/2 - S)!}$$

Assuming that the translationally invariant part of the Coulomb Hamiltonian for the chosen system has eigenfunctions in the discrete spectrum then, among them, there will be a degenerate set that provides a basis for the representation conjugate to that for the chosen spin-eigenfunctions. The representation and the conjugate representation have the same dimension and a basis of space-spin products can be formed which belongs to the antisymmetric representation of the symmetric group and hence

satisfies the Pauli Principle. For example, suppose that a 10 electron system, such as ammonia, was being considered and it was hoped to identify a singlet state. In this case (ignoring for the moment the nuclear variables) one would be looking for a set of 42 degenerate eigenfunctions of the Coulomb Hamiltonian which provided a basis for the irrep $\widetilde{[5, 5]}$ under permutations of electronic variables. These would be functions of the kind earlier called *permutationally allowed*.

One could provide precisely similar arguments to deal with protons and so to describe ammonia, for example, one might look for a nuclear spin doublet arising from the protons and then $[\lambda]^A$ would just be $[2, 1]$ and one would be looking for a pair of degenerate functions to provide a basis for the irrep $\widetilde{[2, 1]}$ under permutation of the protons. Thus to describe ammonia in a singlet electronic spin state with a doublet nuclear spin state one would have to find a degenerate set of 84 eigenfunctions among the eigenfunctions of the Coulomb Hamiltonian to provide a basis for the permutationally allowed irrep of $S_N(10) \times S_A(3)$.

This sort of argument could be extended to particles with spins other than 1/2 and with Bose rather than Fermi statistics. To do so is, however, much more difficult and, so far as the authors know, has never been systematically attempted. The difficulties arise because it is much harder in the general case than it is with particles of spin 1/2, to associate the spin functions with their space parts to produce functions of appropriate symmetry. Although it is true that particles of spin s can provide a basis for representations of the symmetric group corresponding to Young diagrams with, at most, only $2s + 1$ rows, it is not in general possible to determine the lengths of these rows simply from the total S and N values in the problem. One cannot then make any simple association between particular spin-eigenfunctions and a matched spatial function. To achieve the required results it is necessary to deploy the formal machinery of the symmetric group in constructing a Clebsch-Gordan series from the full set of space-spin products in order to isolate in the direct product space either the antisymmetric irreps for fermions, or symmetric irreps for bosons. For the present, it will have to be sufficient to know that it could be done.

If one moves from ammonia to a larger molecule, for example, the simple hydrocarbon with empirical formula C_8H_8 , then a host of other problems begin to emerge. Consider first the 56 electrons. It is easy, though tedious, to show that the dimension of the permutationally allowed representation $\widetilde{[28, 28]}$ for the singlet state, given by the Wigner formula f_S^N with $N = 56$ and $S = 0$, is

$$53 \times 47 \times 44 \times 43 \times 41 \times 37 \times 35 \times 34 \times 31 \simeq 2.6 \cdot 10^{14}$$

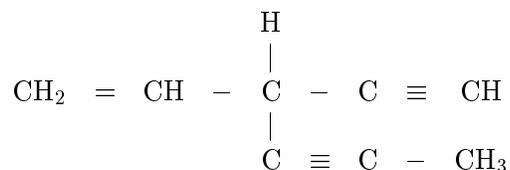
so that for this rather simple system one can expect the eigenfunctions, if any, in the discrete spectrum of $H'(\mathbf{t})$ to be very extensively degenerate even without considering any degeneracies arising from the nuclear variables.

Interestingly enough such a possibility may have troubled Born and Oppenheimer [16]. In their discussion of equation (15) in Part I of the paper they write V_n as the sum of the electronic and nuclear repulsion energy for the n th electronic state and say [18]:

Moreover we assume that V_n is a non-degenerate eigenvalue. As a matter of fact, this is never the case, since, because of the indistinguishability of the electrons the resonance degeneracy, discovered by Heisenberg and Dirac, enters; But since we are concerned here only with the systematics of the approximation procedure, we will not consider these degeneracies. Their consideration would require higher approximations in the secular equation.

The work of Dirac referred to in this quotation is from Section 3 of [12] but nowhere is the sheer extent of the likely degeneracy at all discussed.

Our primary concern here is not with the extent of the degeneracy, but rather the occurrence of *isomers*. The Coulomb Hamiltonian $H'(\mathbf{t})$ for C_8H_8 is the molecular Hamiltonian for cubane, cyclooctatetrene, vinylbenzene and many other compounds too. Indeed it is even the molecular Hamiltonian for a system with optical isomers, 3-vinyl hexa-1,4-diyne, which has the molecular formula



and in which the central carbon is clearly chiral by the conventional rules. For a chiral molecule the only symmetry operation is the identity (point group C_1).

This might not seem too serious a matter for it might be argued that the different isomers corresponded simply to different eigenstates of the same Hamiltonian, H' . But in classical structural chemistry, different isomers mean different geometries and it is the idea of a distinct geometry that is problematic in quantum mechanics. If we write the variables corresponding to the carbon nuclei in C_8H_8 as \mathbf{x}_j^n , $j = 1, \dots, 8$ and those corresponding to the protons as \mathbf{x}_{i+8}^n , $i = 1, \dots, 8$ then a particular CH interparticle distance is

$$x_{ij}^{CH} = |\mathbf{x}_{i+8}^n - \mathbf{x}_j^n|$$

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 we have seen in Section 5 that x_{ij}^{CH} is not a proper observable. The only possible operator incorporating these distances is the symmetrical sum

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

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.

However, one might hope to get somewhere with the idea of a geometrical structure by considering the development of the definition to deal with a system described in a frame fixed in the body. Since we are interested only in a localised region of configuration space in which we hope to identify the molecule, it is reasonable to start from the Hamiltonian (1.57). The idea here is to somehow fix a coordinate frame in the system and to define its orientation by means of 3 Eulerian angles, ϕ_m defined entirely in terms of the $A - 1$ translationally invariant \mathbf{t}_i^n . The remaining motions of the system are then described in terms of $3A - 6$ internal coordinates q_k which are so defined as to be invariant to any orthogonal transformations of the \mathbf{t}_i^n , together with the \mathbf{z}_i which are the \mathbf{t}_i^e expressed in the frame fixed in the body.

In such a coordinate system the Hamiltonian takes the general form

$$H = H_{rot} + H_{vib} + H_{rv}$$

where the particular forms of each term depend on how the choices are made for the Eulerian angles and the internal coordinates. But if we can make choices here such that the rotational part of this Hamiltonian looks something like

$$H_{rot} = \frac{L_x^2}{2I_{xx}^0} + \frac{L_y^2}{2I_{yy}^0} + \frac{L_z^2}{2I_{zz}^0}$$

where the L_α are the components of the total angular momentum operator and $I_{\alpha\alpha}^0$ are the nuclear principal moments of inertia then we are some way towards identifying a chemical molecule. One thinks this because in traditional molecular spectroscopy, the molecule is identified by

its rotational characteristics, even if vibrational motion is also involved, and its rotational characteristics are explained in terms of moments of inertia of a geometrical figure composed of point masses.

Starting from the Coulomb Hamiltonian, to arrive at a Hamiltonian which had an angular part of this form, a neutral and natural choice would seem to be to choose the Eulerian angles to define an orthogonal matrix \mathbf{C} that diagonalises the nuclear inertia tensor. This yields moments of inertia and puts the Hamiltonian in principal axis form, just the form appropriate to describe a rigid rotator in classical mechanics. The principal axis approach to the molecule was attempted in classical mechanics by Eckart [38] in 1934, shortly before the approach [15] that we have referred to in Section 2. It was tried too, almost simultaneously, by Hirschfelder and Wigner [39] using quantum mechanics. It has been used on many subsequent occasions, even in nuclear structure theory [40]. It leads to a rotational Hamiltonian of the form

$$H_{rot} = \frac{I_{xx}L_x^2}{2(I_{zz} - I_{yy})^2} + \frac{I_{yy}L_y^2}{2(I_{xx} - I_{zz})^2} + \frac{I_{zz}L_z^2}{2(I_{yy} - I_{xx})^2}$$

This is not at all like the rigid rotor operator given above. Here the operator is divergent whenever two nuclear moments of inertia are the same. It is thus quite impossible to describe a symmetric top molecule in this formulation. It seemed to pose such a severe problem that Eckart observed in the abstract of his paper [38] that:

The ordinary moments of inertia appear in the Lagrangian kinetic energy but these are replaced by other functions of the radii of gyration in the Hamiltonian. This throws doubt upon all molecular configurations assigned on the basis of empirical values of moments of inertia.

Indeed it turns out more generally, inspite of some heroic efforts by van Vleck [41], that the Hamiltonian so derived is largely ineffective in describing molecules in terms of their traditional geometrical structures and so it found no use in the elucidation of molecular spectra. As we have seen, Eckart [15], got round this difficulty by defining a frame fixed in the body so that in that frame, a particular chosen geometrical shape, the reference geometry for the molecule, could be composed from constant vectors. This choice led to the rotational part of his Hamiltonian having exactly the classically expected form when the nuclei occupied their equilibrium positions. Furthermore Eckart was able to show that when this happened, the interaction part H_{rv} of his Hamiltonian, vanished. Of course, Eckart did not derive his form from the Coulomb Hamiltonian, he simply used what he knew about classical molecular structure to build an appropriate potential and it is unsurprising that the results of using that Hamiltonian confirm the assumptions used in its construction.

It should be noticed that in the principal axis form, no permutational symmetry has been disregarded and the Hamiltonian remains invariant under any permutation of identical particle coordinates. In the later Eckart form, some permutational symmetry has been disregarded. It is often assumed that this disregard can be justified if the potential energy surface that arises from making the Born Oppenheimer approximation to solutions of the Coulomb Hamiltonian, has certain features. This view originates in some work [42] of Longuet-Higgins in the early 1960s but it has been much extended and developed since then. It is to an examination of this view that we turn in the next section.

6. The Born Oppenheimer approximation and the potential energy surface.

As was pointed out by us in 1976, [43], the general arguments made by Born and Oppenheimer in [16] are really quite formal. This is equally true of the later work by Born which is described in appendix VIII of his book with Huang [44]. To make the arguments mathematically precise and to estimate errors, it is necessary to find a way of dealing with the mathematical problems raised by the invariance of the Hamiltonian to uniform translations, orthogonal transformations and permutations of the variables, while preserving a plausible distinction between electronic and nuclear variables. A suitable translationally invariant Hamiltonian has been given in (1.57) but as we have seen, it is not an appropriate one for the description of the atomic dissociation asymptotes of the problem. This Hamiltonian is relevant for the purposes of describing electrons and nuclei separately, only in respect of eigenfunctions which are suitably localised, and, as we shall see, it is the Hamiltonian that has been used to provide a mathematical underpinning for the Born-Oppenheimer approach. So far as is known at present, it cannot be used to provide a similar underpinning for the later approach of Born [44] and we shall not consider this further here. It is recognised, of course, that it is this later Born approach which provides the basis for the standard descriptions of molecular dissociation and other reactions.

The full electronic Hamiltonian arising from (1.57) is obtained as

$$H^{elec} = H^e(\mathbf{t}^e) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{r_{ij}'(\mathbf{t}^n, \mathbf{t}^e)} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)} \quad (1.65)$$

and this is the Hamiltonian used by Klein *et al* [45] in their consideration of the precise formulation of the Born-Oppenheimer approximation for

polyatomic systems¹¹. This Hamiltonian is invariant under all orthogonal transformations of coordinates so that its eigenfunctions, if any, are angular momentum eigenstates with definite parity. It is also invariant under the permutation of the variables of any set of identical particles.

In [45] it is assumed that (1.65) has a discrete eigenvalue which has a minimum as a function of the \mathbf{t}_i^n in the neighborhood of some values $\mathbf{t}_i^n = \mathbf{a}_i$. Because of the rotation-inversion invariance, such a minimum exists on a three dimensional sub-manifold for all \mathbf{a}_i such that

$$\mathbf{a}_i \rightarrow \mathbf{R}\mathbf{a}_i, \quad \mathbf{R} \in O(3)$$

The \mathbf{a}_i therefore define the geometrical shape of the minimum in the usual way. If the minimum figure is a plane then the potential well is diffeomorphic to $SO(3)$ while if it is non-planar then it is diffeomorphic to $O(3)$ and so the well is actually a symmetric double well. In either case, Klein *et al* show that the eigenvalues and eigenfunctions of the full problem can be obtained as WKB-type expansions to all orders of the expansion parameter, the square root of the ratio of the electronic to a typical nuclear mass. Because of the way the Hamiltonian is formulated the invariance of the Hamiltonian under permutations of the electronic variables is readily considered and the electronic wavefunction can easily be chosen in permutationally allowed form, no matter what the nuclear geometry happens to be. However it is rather less easy to consider permutational invariance when some of the nuclei are identical and, in fact, such permutations are not considered in [45].

In our view it would be very desirable to attempt to extend the arguments of Klein *et al* to include invariance under the permutation of identical nuclear variables in a way analogous to that in which rotational invariance is considered. It would have to be assumed that the required minimum exists on an appropriate sub-manifold for all \mathbf{a}_i such that

$$\mathbf{a}_i \rightarrow \mathcal{P}\mathbf{a}_i, \quad \forall \mathcal{P} \in \mathcal{S}_A$$

This requirement would, presumably, result in a multi-well problem to be solved. Quantum mechanical problems of this form have been studied, at least in the semi-classical limit by Helffer and Sjöstrand [47] for example. The eigenfunctions of the full Hamiltonian with such a multi-well potential would, again presumably, be viewable as superpositions of various rotationally invariant forms associated with particular nuclear geometries. But, on average, there would be only one interparticle distance for like particles. It should be stressed however, that this is speculative and

¹¹A detailed consideration of the diatomic system can be found in [30, 46].

we have no firm mathematical results to support such a view. However that may be, such a multiple minimum view is not the one usually taken in spectroscopic calculations. Rather, as we have seen in our discussion of the Eckart Hamiltonian, a single specific assignment of molecular geometry is made in which the nuclei are identified. In the context of the present discussion this might be considered as a choice of geometry that defines just one of the permutationally equivalent minima and, as we have also seen, this is to neglect some of the permutational symmetry of the problem. The work by Longuet-Higgins [42] offered a justification of this in terms of the idea of a *feasible* permutation. If, within the chosen well on the potential energy surface, a permutation of identical nuclei could be described by a point group operation on the nuclear framework then such a permutation was *feasible*. If such a permutation could be described only by an energetically demanding dismantling and re-assembling of the the molecular model, then such a permutation would not be a feasible one. What permutations are feasible depends upon the energy range being considered. Such non-point group operations as rotation about a single bond are often considered feasible operations in this context and there is nowadays a pretty complete theory of the symmetry feasible operations, usually called the theory of the the Nuclear Permutation Inversion Group. A critical account of this theory and an exposition of others in the same vein, can be found in the monograph by Ezra [48].

If our analysis of the problem is correct, however, these approaches cannot be considered fully satisfactory. The arguments given above imply that in order to construct the potential well in terms of which feasible operations can be defined, it is necessary largely to ignore the permutational symmetry that feasible operations are invoked to restore at least in part. There is also something of a logical difficulty in such approaches. The permutations of the variables of identical particles are simply mathematical operations in the quantum theory: they do not correspond to physical operations. However, once the idea of feasibility is associated with a permutation then some physical effect seems inevitably to be implied. So it is not clear if the idea of a feasible permutation is equivalent to the more abstract mathematical idea in the underlying theory.

Our position here can be summarised by saying that we believe that the work of Klein *et al* [45] and of others, for example Hagedorn [49], has put the Born-Oppenheimer approximation on a firm foundation but without considering fully the permutational invariances of the problem. We think that such invariances might well be included without seriously affecting the arguments used and that the basic intuition of Born and Oppenheimer, that wave functions of electron-nuclear product form are

adequate approximations in the circumstances specified, will remain a correct one. If we are right however, there will be a major difference between the solutions to the traditional and our extended formulation of the Born-Openheimer problem. The solutions to the extended formulation will provide basis functions for irreps of \mathcal{S} , the full permutation group of the system. This is because all the permutational symmetry has been included in posing the extended problem. But with such solutions, as we have seen, the idea of molecular structure ceases to have its usual meaning and any definition of the term ‘molecule’ becomes problematic.

7. Discussion

In the preceding sections we have attempted to describe some of the basic properties of the Coulomb Hamiltonian for a collection of electrons and nuclei. Per-Olov Löwdin sought to found a mathematical definition of a molecule on such a discussion, but recognized that the theory was far from completion. We may mention several aspects of the quantum mechanics of molecules that he left as problems for the future (Section 3); firstly his suggestion of an ‘energy surface’ as an account of isomerism has an *ad hoc* character, for the nature of the parameters α was left entirely obscure from the point of view of the fundamental theory. Then, what is the mathematical nature of the constraints required to make the $\frac{1}{2}A(A-1)$ interatomic distances in a system containing A nuclei consistent with a definite molecular structure Γ Finally we recall that we noted earlier that, from the perspective of the theory of the Coulomb Hamiltonian for a system of electrons and nuclei, Löwdin found the occurrence of isomerism and molecular symmetry a mystery whose unravelling would require new ideas. Recently, Simon has presented a list of open problems in mathematical physics [11], among which Problem 12 is of relevance here:

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 does not see *ab initio* electronic structure theory as a complete answer.

The characteristic feature of any molecular structure is the identification of particular atoms with specific locations in the molecule. Typically this entails that identical nuclei are treated as distinguishable entities (‘methyl hydrogens’, ‘hydroxyl hydrogens’ etc.). How then can identical particles be regarded as distinguishable in a quantum theory Γ It is clear

that no continuous approximation can lead to a change in the symmetry group of any given Hamiltonian, since symmetries are either present or absent. It is also clear that a *linear* Schrödinger equation for a *finite* system cannot generate states that exhibit spontaneously broken symmetries. Symmetry breaking is a familiar occurrence in quantum field theories [50] and we leave open the possibilities that either the system of electrons and nuclei can be considered to be macroscopic (N the number of particles $\rightarrow \infty$) with molecules appearing as *quasi-particles*, or, if finite, is coupled to a quantized field that represents its “environment” as in discussions of decoherence; however we do not wish to pursue this line here beyond noting that the properties of the Coulomb Hamiltonian are likely to be important in such discussions [56, 57, 58].

Let us, with Löwdin [2], confine attention to the Coulomb Hamiltonian for a molecule, equation (1.1), on the assumption that somehow all the information about molecular symmetry is contained within it. Several observations seem pertinent. We know that the treatment of identical particles is a matter of fundamental difference between classical and quantum mechanics. In classical mechanics we describe motion by specifying the orbits of the individual particles under the given classical dynamical law. Even though the particles may be identical, if the initial conditions have been set, it makes perfect sense to say that at a given instant in time, t , particle 1 is moving along orbit 1, particle 2 is moving along orbit 2 and so on. Any permutation of the identical particles will also be a solution of the dynamical problem, since the classical equations of motion are invariant under such permutations, but this solution belongs to *another set of initial conditions* i.e to a distinct physical situation [31]. So a classical description of a molecular structure involving identical nuclei in terms of an association between a specified particle and a specified potential well in which it is localized is perfectly natural.

The characteristic features of the quantum mechanical treatment of permutation symmetry can be seen in the simple case of two identical particles. Given a set of single-particle states $\{\phi_k(\mathbf{x})\}$, which we may take to be orthonormal, a general state of a two-particle system can be constructed as the superposition

$$\Psi(1,2) = \sum_{k,k'} c_{k,k'} \phi_k(\mathbf{x}_1) \phi_{k'}(\mathbf{x}_2) \quad (1.66)$$

according to the usual rules of quantum mechanics the coefficients $\{c_{k,k'}\}$ have the interpretation that $|c_{k,k'}|^2$ is the probability that particle 1 is in state k , while particle 2 is in state k' . Let P_{12} be the linear operator

that permutes the variables of particles 1 and 2, such that acting on $\Psi(1,2)$ it gives the state

$$\Phi(1, 2) \equiv P_{12} \Psi(1, 2) = \sum_{k,k'} c_{k,k'} \phi_k(\mathbf{x}_2) \phi_{k'}(\mathbf{x}_1) \quad (1.67)$$

Now the probability that particle 1 is in state k while particle 2 is in state k' is $|c_{k',k}|^2$ which in general is different from $|c_{k,k'}|^2$, so that the state $\Phi(1,2)$ resulting from the action of P_{12} is a *different* vector in the Hilbert space.

However if the two particles are *identical*, $\Phi(1,2)$ and $\Psi(1,2)$ should be states representing the *same* physical situation, and hence can differ at most by a sign; equivalently the probabilities $|c_{k,k'}|^2$ and $|c_{k',k}|^2$ must be equal and so [31]

$$c_{k,k'} = \pm c_{k',k}$$

The + sign here means that the state Ψ is *symmetric* in the particle variables

$$\Psi(1, 2) = \Psi(2, 1)$$

while the – sign is associated with an *antisymmetric* state

$$\Psi(1, 2) = - \Psi(2, 1)$$

in turn, these are eigenstates of the permutation operator P_{12} with eigenvalues +1 and –1 respectively. As shown by Dirac [12] the permutation P_{12} can be considered to be a dynamical variable in quantum mechanics; P_{12} , considered as a dynamical variable, has no classical limit, and there is no analogous quantity in classical mechanics.

If the particles are identical all physical observables Ω_i must be symmetric functions of the variables, and so will commute with the permutation operator

$$[P_{12}, \Omega_i] = 0$$

one of the Ω_i will be the Hamiltonian H of course, and thus P_{12} is a constant of the motion

$$\dot{P}_{12} = \frac{i}{\hbar} [H, P_{12}] = 0$$

The eigenstates of H will be simultaneous eigenstates of P_{12} . Thus the dynamical evolution of the system cannot cause transitions from one subspace to the other i.e. they are incoherent spaces and are never mixed

in superpositions. The restriction of the possible states of the system to lie in either the symmetric subspace or the antisymmetric subspace is therefore consistent with the equations of motion. It is also reasonable to suppose that if the two particles are perturbed by some interaction V it cannot disturb the permutation symmetry of the system,

$$[P_{12}, V] = 0$$

since, following Weyl's whimsical example referred to in Section 5, no perturbation can distinguish between "Mike" and "Ike" [35]. The textbook discussion of the states of the Helium atom is a paradigmatic example of these ideas, but they are of course quite generally applicable to any identical particles (in any numbers) in a quantum mechanical system. The exchange degeneracy characteristic of identical particles in quantum mechanics is associated with the occurrence of superpositions such as (1.66). Thus it seems essential to find reasons why such superpositions can be suppressed, so that the state reduces to something like a Hartree product

$$\Psi(1, 2) = \psi(1, 2) \approx \alpha_k(\mathbf{x}_1) \alpha_{k'}(\mathbf{x}_2)$$

A clue to the nature of the functions $\alpha_k(\mathbf{x})$ may perhaps be gleaned from a remark attributed to Pauli: "No description of the motion of an electron in an atom in space and time is given.....this is clear from the fact that, outside the domain of validity of geometrical optics it is impossible to construct 'rays' that can be considered as orbits of particles." [51] In the context of a quantum mechanical theory, geometrical optics corresponds to the semiclassical limit ($\hbar \rightarrow 0$) i.e. the WKB approximation. Of course \hbar has a definite value depending on the system of units used, and has the dimensions of action (or angular momentum), and $\hbar = 0$ *cannot* be realized in the physical world. What we mean by the semiclassical limit is the situation where, if S a typical classical action in the system under consideration, there is a parameter $\delta = (\hbar/S)$ that is negligibly small.

The quantum mechanical Hamiltonian for a N -particle system in a coordinate representation is

$$H = -\hbar^2 \sum_i \frac{\nabla_i^2}{2m_i} + V(\mathbf{x})$$

with Schrödinger equation

$$H \psi(\mathbf{x}) = E \psi(\mathbf{x})$$

The limits $\hbar \rightarrow 0$ or $m_i \rightarrow \infty$ for some i are closely related; they lead to *singular* perturbation problems since in the limit the coefficient of the *highest-order* differential operator in the Schrödinger equation is put to zero. Thus in quantum mechanics, $\hbar = 0$ is a point of singularity; if it were not, the semiclassical limit would be trivial for we could solve the quantum mechanical problem with \hbar as a parameter and then set $\hbar = 0$ at the end. The discrete spectrum of the Hamiltonian is associated with infinitely long-lived states, and the semi-classical limit is further complicated by the conjunction of the two limits $t \rightarrow \infty$, $\hbar \rightarrow 0$ which do *not* commute; on the other hand, it is precisely this fact that leads to a remarkable richness of physically relevant phenomena [52, 53]. This suggests that a possibly crucial contribution to Löwdin's programme is the detailed exploration of the asymptotic behaviour of the Schrödinger equation for the Coulomb Hamiltonian, with the consequences of the occurrence of identical nuclei being fully accounted for.

Suppose that the quantum mechanical Hamiltonian is written

$$H = H(\mathbf{x}, \mathbf{p})$$

and consider its transform with an unitary operator U that is purely a function of the coordinates,

$$U = e^{iS(\mathbf{x})/\hbar}$$

so that

$$H(\mathbf{x}', \mathbf{p}') = U H U^{-1} = H(\mathbf{x}, \mathbf{p} + \nabla S) \quad (1.68)$$

The traditional derivation of the semiclassical limit [54] is that since $\mathbf{p} \rightarrow -i\hbar\nabla$, the momentum drops out of the Hamiltonian in the limit $\hbar \rightarrow 0$ and the Schrödinger equation reduces to the classical Hamilton-Jacobi (HJ) equation

$$H(\mathbf{x}, \nabla S) = E$$

The solutions of the HJ equation determine the dynamics of the classical system described by H ; the WKB approximation says that for a partially (or completely) integrable system there is a *regular spectrum* of energy levels that can be obtained by imposing the Einstein-Brillouin-Keller or Maslov conditions on the action integrals over closed curves C_k on invariant N -tori, [55]

$$\oint_{C_k} \mathbf{p} \cdot d\mathbf{x} = (n_k + \gamma) h, \quad k = 1, \dots, N \quad (1.69)$$

A limitation of this formulation, for our purposes, is that it is based on picking out particular classical solutions according to the EBK quantization condition (1.69), that is, it approximates the quantum solution from the *classical side* of the singular limit $\hbar \rightarrow 0$, for which there is no permutation operator as a dynamical variable. However the semiclassical limit *can* be studied in a Hilbert space setting; for example the *microscope transformation* used by Combes and Seiler [30] to give a rigorous version of the Born-Oppenheimer theory of a diatomic molecule is essentially a semiclassical theory. It is applicable if there is a minimum in the potential $V_{min} = V(\mathbf{x}_0)$ associated with a particular configuration of the particles¹² that is deep enough for the lowest energy eigenstates to be localized about \mathbf{x}_0 . One can look at these states with a ‘microscope’ with a certain resolving power that depends on Planck’s constant - loosely speaking, this means that it is possible to study the limit $\hbar \rightarrow 0$ from the *quantum side* of the problem, and it is possible that the consequences for permutation symmetry can be studied in this setting. As yet this has not been done, as far as we are aware.

The microscope transformation is based on a unitary transformation of the form

$$U_\lambda = e^{iS_\lambda(\mathbf{x},\mathbf{p})/\hbar}, \quad S_\lambda^* = S_\lambda$$

where λ is a parameter to be determined. The usual rules yield

$$\begin{aligned} \Psi_\lambda &= U_\lambda^{-1} \psi, & H_\lambda &= U_\lambda^{-1} H U_\lambda \\ \mathbf{x}_\lambda &= \mathbf{x} - \frac{\partial S_\lambda}{\partial \mathbf{p}}, & \mathbf{p}_\lambda &= \mathbf{p} + \frac{\partial S_\lambda}{\partial \mathbf{x}} \end{aligned}$$

The Hermitian operator S_λ is chosen so that the transformation produces a translation to make \mathbf{x}_0 the origin of the coordinates, and a dilation (scale transformation)

$$\frac{\partial S_\lambda}{\partial \mathbf{p}} = (1 - \lambda)(\mathbf{x} - \mathbf{x}_0), \quad \frac{\partial S_\lambda}{\partial \mathbf{x}} = \frac{(1 - \lambda)}{\lambda} \mathbf{p} \quad (1.70)$$

These relations show that S_λ is a *non-integrable* function of the phase-space variables (\mathbf{x}, \mathbf{p}) , that is, it doesn’t have a definite value at (\mathbf{x}, \mathbf{p}) , but it does have well-defined derivatives given by equation (1.70) *except* at $\lambda = 0$; at this point the transformation equations have a singularity.

Under this transformation a Hamiltonian of the form

¹²The multiminima case can also be treated in this way.

$$H = \sum_i \frac{p_i^2}{2m_i} + V(\mathbf{x})$$

is transformed to

$$H_\lambda = V(\mathbf{x}_0) + \lambda^2 K(\lambda)$$

where

$$K(\lambda) = - \frac{\hbar^2}{\lambda^4} \sum_i \frac{\nabla_i^2}{2m_i} + \frac{1}{\lambda^2} (V(\mathbf{x}_0 + \lambda(\mathbf{x} - \mathbf{x}_0)) - V(\mathbf{x}_0))$$

We now put $\lambda = \sqrt{\hbar}$ so as to eliminate λ from the kinetic energy term in $K(\lambda)$; with this choice for λ , unitary equivalence of the spectrum implies that the eigenvalues of the original Hamiltonian H are related to those of $K(\lambda)$ by

$$E_n = V(\mathbf{x}_0) + \hbar \mu_n(\lambda)$$

Provided V is analytic in λ it can be expanded about $\lambda = 0$, and this puts $K(\lambda)$, in lowest order, into the form of a sum of coupled oscillators so that the first approximation for the eigenvalue function μ_n is

$$\mu_n \approx \sum_k \omega_k \left(n_k + \frac{1}{2} \right)$$

In the Born-Oppenheimer calculation for the diatomic molecule [30], analyticity of V in λ could be proven, and the role of $\sqrt{\hbar}$ was taken by the usual BO expansion parameter $\kappa = (m_e/M_{Nu})^{\frac{1}{4}}$.

The singular nature of the transformation is demonstrated by the modification of the spectrum associated with the limit $\kappa \rightarrow 0$. The spectrum of the Coulomb Hamiltonian for a molecule was discussed in Section 4; for the diatomic molecule, $\sigma_{ess}(H)$ starts at the lowest two-body threshold $\Sigma = \lambda_A(m_A) + \lambda_B(m_B)$ given by the minimal value of the sums of pairs of binding energies for atoms A and B with finite masses m_A and m_B respectively. On the other hand the spectrum of the electronic Hamiltonian, H_∞ , is purely continuous, $\sigma(H_\infty) = [V_{min}, \infty)$. In the limit $m_A, m_B \rightarrow \infty$, Σ does not generally converge to V_{min} ; instead the missing part of the continuous spectrum $[V_{min}, \lambda_A(\infty) + \lambda_B(\infty)]$ is provided by an accumulation of bound states in this interval [59].

While the microscope transformation is formally applicable to the polyatomic case, it may not be sufficient to control the asymptotic behaviour. The work of Klein et al. was based on a powerful symbolic

operator method, the *pseudodifferential calculus* [45, 60]. Interestingly, these investigations utilize a formalism closely associated with Löwdin, namely the partitioning technique. The complement of the adiabatic subspace can be used to fold the non-adiabatic terms into a modified Hamiltonian acting on the adiabatic subspace, as an energy dependent operator. This turns out to be a useful procedure because bounds can be established for its contribution. Whether these techniques are sufficient to investigate the consequences of treating identical nuclei explicitly remains to be seen however. In our view the intrinsically quantal nature of indistinguishability of particles is the major hurdle that must be cleared if Löwdin's programme is to be developed further.

8. Dedication

This paper is dedicated to the memory of Per-Olov Löwdin.

References

- [1] P-O. Löwdin in *Molecules in Physics, Chemistry and Biology II*, Ed. J. Maruani, Kluwer, Dordrecht, 1988, p 3.
- [2] P-O. Löwdin, 1989, *Pure and Applied Chemistry*, **61**, 2065.
- [3] P-O. Löwdin, *Studies in Physical and Theoretical Chemistry*, **62**, Elsevier, Amsterdam, 1989, p.605.
- [4] P-O. Löwdin, *Int. J. Quant. Chem.*, **38**, 741 (1990).
- [5] P-O. Löwdin, *J. Mol. Struct. (Theochem)*, **230**, 13 (1991).
- [6] P-O. Löwdin, *Int J. Quant Chem.*, **51**, 473 (1994).
- [7] P-O. Löwdin, List of published papers, provided by Prof. E. Brandas, Institute for Quantum Chemistry, Uppsala University, Sweden.
- [8] B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules*, Longmans, London 1983.
- [9] A. Messiah, *Quantum Mechanics*, Vol. II North-Holland, Amsterdam, 1960.
- [10] B. Simon, *J. Math. Phys.* **41**, 3523 (2000).
- [11] B. Simon, in *Mathematical Physics 2000*, Eds. A. Fokas, A. Grigoryan, T. Kibble and B. Zegarlinski, Imperial College Press, London, 2000, p.283.
- [12] P. A. M. Dirac, *Proc. Roy. Soc. A* **123**, 714 (1929).
- [13] A. Simões, *Physics in Perspective*, **4**, 253, (2002).
- [14] C. A. Coulson, *J. Chem. Soc.*, 2069 (1955).
- [15] C. Eckart, *Phys. Rev.*, **47**, 552 (1935).
- [16] M. Born and J. R. Oppenheimer, *Ann. der Phys.*, **84**, 457 (1927).
- [17] J. C. Louck, *J. Mol. Spec.*, **61**, 107 (1976).
- [18] S. M. Blinder at www.ulb.ac.be/cpm/people/scientists/bsutclif/welcome.html
- [19] R. S. Berry, *Rev. Mod. Phys.*, **32**, 447 (1960).
- [20] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, IV, Analysis of Operators*, Academic Press, New York, 1978.
- [21] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, I, Functional Analysis*, revised and enlarged edition, Academic Press, New York, 1980.
- [22] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, II, Fourier Analysis, Self-Adjointness*, Academic Press, New York, 1975.

- [23] W. Thirring, *A Course in Mathematical Physics, 3, Quantum Mechanics of Atoms and Molecules*, Tr. E. M. Harrell, Springer-Verlag, New York, 1981.
- [24] W. Thirring in *Schrödinger, centenary celebrations of a polymath*, Ed. C. W. Kilminster CUP, Cambridge, 1987, p 65.
- [25] T. Kato, *Trans. Am. Math. Soc.*, **70**, 212 (1951).
- [26] R. Courant and D. Hilbert, *Methods of Mathematical Physics*, Vol. 1, Interscience Publishers, Inc. New York, 1953.
- [27] H. Weyl, *Rend. Circ. Mat. Palermo*, **27**, 373 (1909).
- [28] V. F. Brattsev, *Soviet Physics - Doklady*, **10**, 44 (1965).
- [29] S. Epstein, *J. Chem. Phys.*, **44**, 836 and 4062 (1966).
- [30] J.-M. Combes and R. Seiler, in *Quantum Dynamics of Molecules*, Ed. R. G. Woolley, NATO ASI B57, Plenum Press, New York, 1980, p.435.
- [31] P. Roman, *Advanced Quantum Theory*, Addison-Wesley Publishing Co., Reading, Mass., 1965.
- [32] E. Balslev and J.-M. Combes, *Commun. Math. Phys.* **22**, 280 (1973).
- [33] J. Aguilar and J.-M. Combes, *Commun. Math. Phys.* **22**, 269 (1973).
- [34] W. P. Reinhardt, *Ann. Rev. Phys. Chem.* **33**, 223 (1982).
- [35] H. Weyl, *The Theory of Groups and Quantum Mechanics*, 2nd Edition, Tr. H. P. Robertson, Dover, New York, 1931.
- [36] G. Mackey, *The Mathematical Foundations of Quantum Mechanics*, Benjamin, New York, 1963.
- [37] E. Balslev, *Ann. Phys.(N.Y.)*, **73**, 49 (1972).
- [38] C. Eckart, *Phys. Rev.*, **46**, 384 (1934).
- [39] J. O. Hirschfelder and E. Wigner, *Proc. Nat. Acad. Sci.*, **21**, 113 (1935).
- [40] B. Buck, L. C. Biedenharn and R. Y. Cusson, *Nucl. Phys*, **A 317**, 215 (1979).
- [41] J. H. van Vleck, *Phys. Rev.*, **47**, 487 (1935).
- [42] H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).
- [43] R. G. Woolley and B. T. Sutcliffe, *Chem. Phys. Lett.*, **45**, 393 (1976).
- [44] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* , Oxford University Press, Oxford, 1955.

- [45] M. Klein, A. Martinez, R. Seiler, and X. P. Wang, *Commun. Math. Phys.*, **143**, 607 (1992).
- [46] J.-M. Combes, P. Duclos and R. Seiler in *Rigorous atomic and molecular physics*, Eds. G. Velo and A. Wightman, Plenum, New York, 1981, p. 185.
- [47] B. Helffer and J. Sjöstrand, *Commun. Partial Differ. Equations* **9**, 337 (1984).
- [48] G. Ezra, *Symmetry properties of molecules*, Lecture Notes in Chemistry **28**, Springer, Berlin, 1982.
- [49] G. Hagedorn, *Commun. Math. Phys.*, **77**, 1 (1980).
- [50] P. W. Anderson, *Basic Notions in Condensed Matter Physics*, Benjamin/Cummings/Addison-Wesley, New York (1984).
- [51] W. Pauli, quoted by B. L. van der Waerden, in *The Physicist's Conception of Nature*, Ed. J. Mehra, Reidel, Dordrecht, 1973, p.282.
- [52] M. V. Berry, in *Les Houches Lecture series 52*, Eds. M. J. Giannoni, A. Voros and J. Zinn-Justin, North-Holland, Amsterdam, 1991.
- [53] M. V. Berry, in *Quantum Mechanics: Scientific perspectives on divine action* Eds: R. J. Russell, P. Clayton, K. Wegter-McNelly and J. Polkinghorne, Vatican Observatory CTNS publications, Rome, 2001, p.41.
- [54] P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th Edition revised, Oxford University Press, Oxford, 1967.
- [55] I. C. Percival, *J. Phys. B Atom. Molec. Phys.* **6**, L229, (1973).
- [56] R. G. Woolley, *Israel. J. Chem.* **19**, 30 (1980).
- [57] R. G. Woolley, *Structure and Bonding*, **52**, 1 (1982).
- [58] R. G. Woolley, *J. Mol. Struct. (Theochem)*, **230**, 17 (1991).
- [59] J.-M. Combes, *Acta Phys. Austr.* **17**, Suppl., 139 (1977)
- [60] C. L. Feffermann, *Bull. Am. Math. Soc.*, **9**, 129 (1983)