

What mathematicians know about the solutions of Schrodinger Coulomb Hamiltonian. Should chemists care?

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Abstract An attempt is made to determine the relationship between the full Schrödinger Coulomb Hamiltonian and the clamped nuclei form that is usually the basis of electronic structure calculations, without treating identical nuclei as distinguishable. It is concluded that it is not at present possible to establish such a relationship in a mathematically secure way.

Keywords Schrödinger · Coulomb · Hamiltonian · Permutational symmetry · Moving nuclei

1 Introduction

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

$$\begin{aligned} H = & \sum_g^A \frac{\mathbf{p}_g^2}{2m_g} + \frac{e^2}{8\pi\epsilon_0} \sum_{g,h=1}^A \frac{Z_g Z_h}{r_{gh}} + \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{g=1}^A \frac{Z_g}{r_{ig}} \right) \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{r_{ij}} \end{aligned} \quad (1)$$

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where the individual terms have obvious classical interpretations; the charges and masses of the electrons and nuclei are regarded as parameters to be taken from experimental data. N and A are undetermined positive integers.¹

In 1951 Kato [2] established that the Coulomb Hamiltonian, H , is essentially self-adjoint.² This property, which is stronger than Hermiticity, guarantees that the time evolution

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

of a Schrödinger wavefunction is unitary, and so conserves probability. This is not true for operators that are Hermitian but not self-adjoint. It is easy enough to construct examples of such operators; an example given by Thirring [3] is of the radial momentum operator $-i\hbar\partial/\partial r$ acting on functions $\phi(r)$, $\phi(0) = 0$ with $0 \leq r < \infty$.

2 What Kato did?

The first thing that Kato did was to separate out the centre-of-mass motion from the problem. All that is needed to remove the centre of mass motion from the full molecule Hamiltonian is a linear point transformation symbolised by

$$(\mathbf{t} \xi) = \mathbf{x} \mathbf{V} \quad (2)$$

In (2) \mathbf{t} is a 3 by $N_T - 1$ matrix ($N_T = N + A$) and ξ is a 3 by 1 matrix, so that the combined (bracketed) matrix on the left of (2) is 3 by N_T . \mathbf{V} is an N_T by N_T matrix which, from the structure of the left side of (2), has a special last column whose elements are

$$V_{iN_T} = M_T^{-1} m_i, \quad M_T = \sum_{i=1}^{N_T} m_i \quad (3)$$

Hence ξ is the standard centre-of-mass coordinate

$$\xi = M_T^{-1} \sum_{i=1}^{N_T} m_i \mathbf{x}_i \quad (4)$$

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

$$\sum_{i=1}^{N_T} V_{ij} = 0, \quad j = 1, 2, \dots, N_T - 1 \quad (5)$$

¹ This Hamiltonian results from the standard canonical quantization of electrodynamics if it is assumed particle speeds are negligible compared to the speed of light, and all charge–photon interactions are discarded; the Coulomb gauge condition must also be imposed [1].

² The work was completed in 1944 and was actually received by the journal in October 1948.

on each remaining column of \mathbf{V} and it is easy to see that (5) 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

$$\mathbf{x} = (\mathbf{t} \boldsymbol{\xi}) \mathbf{V}^{-1} \quad (6)$$

exists. The structure of the right side of (6) shows that the bottom row of \mathbf{V}^{-1} is special and, without loss of generality, its elements may be required to be

$$(\mathbf{V}^{-1})_{N_T i} = 1 \quad i = 1, 2, \dots, N_T \quad (7)$$

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

$$\sum_{i=1}^{N_T} (\mathbf{V}^{-1})_{ji} m_i = 0 \quad j = 1, 2, \dots, N_T - 1 \quad (8)$$

The Hamiltonian (1) in the new coordinates becomes

$$\begin{aligned} H(\mathbf{t}, \boldsymbol{\xi}) &= -\frac{\hbar^2}{2} \sum_{i=1}^{N_T-1} \frac{1}{\mu_{ii}} \nabla^2(\mathbf{t}_i) - \frac{\hbar^2}{2} \sum_{i,j=1}^{N_T-1} \frac{1}{\mu_{ij}} \vec{\nabla}(\mathbf{t}_i) \cdot \vec{\nabla}(\mathbf{t}_j) \\ &\quad + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N_T} \frac{Z_i Z_j}{r_{ij}(\mathbf{t})} - \frac{\hbar^2}{2M_T} \nabla^2(\boldsymbol{\xi}) \\ &= H'(\mathbf{t}) - \frac{\hbar^2}{2M_T} \nabla^2(\boldsymbol{\xi}) \end{aligned} \quad (9)$$

Here the positive constants $1/\mu_{ij}$ are given by

$$1/\mu_{ij} = \sum_{k=1}^{N_T} m_k^{-1} V_{ki} V_{kj}, \quad i, j = 1, 2, \dots, N_T - 1 \quad (10)$$

The operator r_{ij} is the interparticle distance operator expressed as a function of \mathbf{t}_i . Thus

$$r_{ij}(\mathbf{t}) = \left(\sum_{\alpha} \left(\sum_{k=1}^{N_T-1} ((\mathbf{V}^{-1})_{kj} - (\mathbf{V}^{-1})_{ki}) t_{\alpha k} \right)^2 \right)^{1/2} \quad (11)$$

In (9) 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

$$T(\boldsymbol{\xi}) \Psi(\mathbf{t}) \quad (12)$$

where $\Psi(\mathbf{t})$ is a wavefunction for the Hamiltonian $H'(\mathbf{t})$, Eq. 9, which will be referred to as the *translationally invariant* Hamiltonian. It should be emphasised that different choices of \mathbf{V} are unitarily equivalent so that the spectrum of the translationally invariant Hamiltonian is independent of the particular form chosen for \mathbf{V} , provided that it is consistent with (3) and (5). In particular it is perfectly possible to put the kinetic energy operator into diagonal form by choosing an orthogonal matrix \mathbf{U} that diagonalises the positive definite symmetric matrix of dimension $N_T - 1$ formed from the $1/\mu_{ij}$ and then replacing elements of the originally chosen \mathbf{V} according to

$$V_{ij} \rightarrow \sum_{k=1}^{N_T-1} V_{ik}U_{kj}, \quad j = 1, 2, \dots, N_T-1$$

As can be seen from (11), the practical problem with any choice of \mathbf{V} is the complicated form given to the potential operator.

Kato considers just the translationally invariant part of the problem and he actually uses a coordinate system in which the kinetic energy can be written in the form

$$\frac{\hbar^2}{2} \sum_{i=1}^{N_T-1} \frac{1}{\mu_{ii}} \nabla^2(\mathbf{r}_i) + \frac{\hbar^2}{2\mu_0} \left| \sum_{i=1}^{N_T-1} |\vec{\nabla}(\mathbf{r}_i)| \right|^2$$

where \mathbf{t} is replaced by \mathbf{r} to agree with Kato in describing the coordinates. Each individual \mathbf{r}_i is thought of as being composed of three cartesian coordinates (x_i, y_i, z_i) with $r_i = \sqrt{(x_i^2 + y_i^2 + z_i^2)}$

He points out that if μ_0 increases without limit then something in the form of the original Hamiltonian is obtained but for one “particle” less, so that there is no loss of generality in choosing this form. But the finding is general.

He specifies the potential energy as expressible in the form

$$V(\mathbf{r}) = V'(\mathbf{r}) + \sum_{i=1}^{N_T-1} V_{0i}(\mathbf{r}) + \sum_{i,j}^{N_T-1} V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{13}$$

For a mathematician the specification of differential operator thus far leaves the problem vague and as Kato says, “we cannot expect such an obscure operator to be self-adjoint in the literal sense.” To remove this vagueness one must specify the domain of the operator, that is say what sort of functions it is supposed to operate on and one must specify the behaviour of the potential.

So what Kato does is to say

- H must be a symmetric (Hermitian) operator
- H can be applied on all functions of the form

$$g(\mathbf{r}) = P(\mathbf{r}) \exp\left(-\left(\sum_{i=1}^{N_T-1} r_i^2\right)/2\right)$$

where P is a polynomial.

Notice, this does not mean to say that it can be applied *ONLY* to such a sort of functions but that it must produce meaningful results when applied to such functions. This choice is made because Kato is going to work in momentum space and this class of functions have nice Fourier transforms. Any such function belongs to a Hilbert space \mathfrak{H} denoted \mathcal{L}^2 of square integrable functions. Thus for the whole operator to make any sense the product function Vg must belong to the same Hilbert space.

To ensure this Kato requires that for two real constants C and R

•

$$|V(\mathbf{r})| \leq C$$

•

$$\int_{r \leq R} |V_{ij}(\mathbf{r})|^2 dx dy dz \leq C^2$$

•

$$|V_{ij}(\mathbf{r})| \leq C(r > R)$$

These are pretty mild requirements and are satisfied by all inverse power potentials of the form r^{-m} provided that m is positive and less than $3/2$. It does NOT hold for potentials like r^{-2} and this is what makes relativistic calculations so tricky to be sure about.

It is not necessary to specify the domain of H' more closely than this because these conditions on the functions and the potential enable Kato to show that the operator defined on the restricted domain has a unique self-adjoint extension and that this extension is the operator that we know and love!

It was pretty obvious to applied mathematicians, that the kinetic energy operator alone is indeed self-adjoint because of their classical mechanical experience. It was shown by Stone in the 1930s that multiplicative operators of the kind specified above are also self-adjoint but it was entirely un-obvious that the sum of the operators would be self-adjoint because the sum of the operators is defined only on the intersection of their domains.

What Kato showed in Lemma 4 of his amazing paper was that for a potential so specified and for any function f in the domain \mathcal{D}_0 of the full kinetic energy operator T_0 , the domain of full problem \mathcal{D}_V contains \mathcal{D}_0 and there are two constants a , b such that

$$\|Vf\| \leq a\|T_0f\| + b\|f\|$$

and that a can be taken as small as liked. This result is often summarised by saying that the Coulomb potential is small compared to the kinetic energy.

Given this result he proved in Lemma 5 that the usual operator is indeed, for all practical purposes, self-adjoint and is bounded from below.

Why worry about this? Well if the operator is not self-adjoint then it could support solutions interpretable as a particle falling into a singularity or getting to infinity in a finite time and these are unacceptable as physical solutions. Curiously enough these are possible solutions in the classical mechanics of three bodies. Thus one can expect that un-physical solutions will not arise from solving the problem specified by the Coulomb Hamiltonian.

It thus makes sense to suppose that one can get all that one wants by considering eigen-solutions of the problem (to return to our notation) of the form

$$H'(\mathbf{t})\Psi(\mathbf{t}) = E\Psi(\mathbf{t}) \quad (14)$$

One does know at this stage that the eigenvalue E lies on the real line but one does not know if it is isolated point or part of a continuum. One does not know either whether Ψ lies in the Hilbert space \mathcal{L}^2 or not.

By extending some work of Friedrichs from the 1930s Kato showed that Ψ has continuous derivatives of the second order in a region S of configuration space where $V(\mathbf{r})$ is sufficiently regular and where the potential satisfies the (classical) wave equation. For the case of the Coulomb potential this means that problems arise only at singular points of the potential where the derivatives result in delta functions. Later work by Kato [4] established the *cuspid conditions* on the behaviour of Coulomb wave functions in many of the singular cases.

The spectral properties of the Coulomb Hamiltonian have been established in the years since the initial work of Kato, and so what is said here is not at all new but it is perhaps not yet well represented in the theoretical chemistry literature and a brief summary of the fundamental results and reference to some books may be helpful. Chapter XIII of the book *The Analysis of Operators* by Reed and Simon [5] contains proofs of many of the required results but in it, 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 Sect. VII of [6] and Sect. X of [7]. An alternative source of similarly relevant material is the book by Thirring [8], who also provides a useful summary, expressed in accessible language and without too much detail, in his contribution to the Schrödinger centenary volume [3].

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

$$\sigma_{\text{ess}}(\mathbf{A}) = \sigma(\mathbf{A}) \setminus \sigma_d(\mathbf{A}) \quad (15)$$

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

The spectrum of H' may (but need not) have a discrete part, and the start of the essential part is established by means of so-called HVZ theorem (Theorem XIII.17 in [5]) which demonstrates that the essential spectrum can be written as $\sigma_{ess}(H') = [\Sigma, \infty)$ where Σ is the energy of the lowest two-body cluster decomposition of the N_T -particle system. A valuable discussion of the HVZ theorem from a geometrical point of view can be found in [9].

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

However the extent of the discrete spectrum is by no means obvious and for a Coulomb Hamiltonian describing a given collection of electrons and nuclei the difficult technical problem is to find out if there is any discrete spectrum at all before the start of the essential spectrum. This requires the demonstration of a so-called 'binding condition', first obtained by Zhislin [10]. For a collection of N electrons and A fixed nuclei with total (positive) charge Ze , the bottom of the spectrum of H' is a genuine N -particle bound state that satisfies the Schrödinger equation with some energy E_0 for each choice of the locations of the nuclei, provided $N < Z + 1$. The same result has recently been obtained when account is taken of the ever-present quantized electromagnetic field [11].

It was also shown by Zhislin [10], and later by Uchiyama [12], that in the single nucleus case there are an infinite number of bound states if the atom is electrically positive or neutral. Proofs of this are accessible in Thirring [8] and Simon [13]. If the system has an overall negative charge then it has at most a finite number of bound states as, again, was first shown by Zhislin [14]. For example Nyden Hill [15] showed explicitly that the H^- ion had only one bound state. If the system has more than one nucleus then, as shown in Thirring, with the nuclei treated as clamped, the Hamiltonian has spectral properties just like those of an atom but the form of the spectrum depends upon the choice of the nuclear geometry. At one extreme the spectrum will be that of the united atom and at the other, that of the separated atoms.

There is the following fundamental theorem due to Weyl: if one has a trial wave function Φ with an expectation value $\langle H' \rangle$ which is below the bottom of the essential spectrum, then H' has at least one discrete negative eigenvalue. A proof of this result can be found in [5] where it is shown to follow easily from the linear variation theorem. But it is a rather limited result: to make use of it in any particular system the start of the essential spectrum must be determined and a trial function found that bounds this start from below. Both are very difficult to do. At present the most that has been proved is that the hydrogen molecule has at least one bound state (Richard et al. [16]).

Ordinary chemical experience makes it seem likely that there are some atomic combinations that do not have any bound states but, so far, there are no rigorous results that enable it to be said that a particular kind of neutral system has no bound states.

It is known that if a system gets either too positive or too negative it does not have any bound states at all, [17, 18]. Simon [19] argued very persuasively that a neutral system will have an infinite number of bound states only if the position of the bottom of the essential spectrum is determined by break-up into a pair of oppositely charged ionic clusters; if the clusters are neutral there will be, at most, only a finite number of bound states. Subsequently Vugal'ter and Zhislin [20] showed rigorously that Simon's conjecture about the spectrum in the case of neutral clusters was well founded, and Evans et al. [21] were able to show that his belief about the charged clusters was too.

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

2.1 The symmetries of the Coulomb Hamiltonian

It should be emphasised that the variables t_i or x_g , used to designate particles, simply specify field points, and cannot actually be particle coordinates because of the indistinguishability of sets of identical particles. Weyl [22] and later Mackey [23] 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 is a more restricted space than that considered so far but Balslev [24] showed that all the results stated above on the wider space continue to hold on the restricted space.

The requirement that an operator be totally symmetric means that the effect of an operator on a function in the sub-space of a particular permutational symmetry must be to produce another function in the sub-space. To put it slightly differently: it is easy to see that an operator which is unsymmetric in form could not possibly commute with the Hamiltonian, which is symmetric, and so could not be simultaneously definite with the energy of the system.

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 Sect. C 9 of Chapter IV of [22]. 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 interparticle distance when chosen from a set describing more than two identical particles. If \mathbf{P} represents a permutation of particles in the space defined by the \mathbf{x}_i treating the collection of coordinates as a three by N_T row matrix, then the centre-of-mass coordinate is unchanged by such a permutation and the translationally invariant coordinates \mathbf{t}_i , treated as a three by $N_T - 1$ row matrix, are transformed by a matrix \mathbf{H} where

$$(\mathbf{H})_{ij} = (\mathbf{V}^{-1}\mathbf{P}\mathbf{V})_{ij}, \quad i, j = 1, 2, \dots, N_T - 1 \quad (16)$$

Any permutation of particles with the same mass and charge, identical particles, will leave the translationally invariant Hamiltonian unchanged. The matrix \mathbf{H} however is not necessarily in standard permutational form nor is it orthogonal, even though it has determinant ± 1 according to the sign of $|\mathbf{P}|$; thus under any permutation of particles, the translationally invariant coordinates will transform into linear combinations of themselves. Any chosen transformed coordinate will, generally, involve coordinates associated with both electrons and nuclei in the original formulation. If it is desired to identify electrons with a particular set of translationally invariant coordinates, specialised coordinate choices must be made to avoid such mixing.

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 $O(3)$. This requirement further restricts the space but the spectral results given earlier remain valid as again proved by Balslev [24]. 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.

For molecules, descriptions of rotation-reflection 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. The process of making these choices is often called *fixing* or *embedding a frame in the body*. To construct the frame fixed in the body it is supposed that the three orientation variables are specified by means of an orthogonal matrix \mathbf{C} , the elements of which are expressed as functions of three Eulerian angles ϕ_m , $m = 1, 2, 3$ which are orientation variables. The the matrix \mathbf{C} is specified in terms of the translationally invariant coordinates \mathbf{t} . Thus the cartesian coordinates \mathbf{t} are considered related to a set \mathbf{z} by

$$\mathbf{t} = \mathbf{Cz} \quad (17)$$

so the matrix \mathbf{C} may be thought of as a direction cosine matrix, relating the laboratory frame to the frame fixed in the body. The laboratory frame may always be chosen as a right handed frame but it is not always the case that there is the freedom to choose the frame fixed in the body as a right handed one. Since \mathbf{z} are fixed in the body, not all their $3N_T - 3$ components are independent, for there must be three relations between them. Hence components of \mathbf{z}_i must be writable in terms of $3N_T - 6$ independent internal coordinates $q_i, i = 1, 2, \dots, 3N_T - 6$. Some of the q_i may be components of \mathbf{z}_i but generally the q_i are expressible in terms of scalar products of the \mathbf{t}_i (and equally of the \mathbf{z}_i) since scalar products are the most general constructions that are invariant under orthogonal transformations of their constituent vectors. 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 internal 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. This would seem to mean that the idea of a *global* potential surface will not fit easily into this account.

The eigenfunctions will also 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. In general the relevant spatial 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 among the eigenfunctions of the translationally invariant Hamiltonian.³ It is perhaps informative to consider the possible extent of such degeneracy for a relatively simple hydrocarbon with empirical formula C_8H_8 . Consider just the 56 electrons for which it can be shown [25] that the dimension of the permutationally allowed representation for the singlet state is given by the Wigner formula f_S^N with $N = 56$ and $S = 0$ and is:

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

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

³ See the discussion of Theorem XIII.46 in [5].

3 Looking for molecules

In view of the discussion in the arguments advanced by Born and Oppenheimer [26], it may be helpful to express $H'(t)$ in terms of two sets of coordinates.⁴ One set consists of $A - 1$ translationally invariant coordinates \mathbf{t}_i^n expressed entirely in terms of the coordinates used originally to describe the nuclei, \mathbf{x}_i^n ,

$$\mathbf{t}_i^n = \sum_{j=1}^A \mathbf{x}_j^n V_{ji}^n, \quad i = 1, 2, \dots, A - 1 \quad (18)$$

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

$$V_{iA}^n = M^{-1} m_i, \quad M = \sum_{i=1}^A m_i \quad (19)$$

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 ‘electronic’ coordinates defined in terms of the initially chosen electronic variables \mathbf{x}^e and whose origin is the centre-of-nuclear mass

$$\mathbf{t}_i^e = \mathbf{x}_i^e - \mathbf{X} \quad (20)$$

The inverse relations are

$$\mathbf{x}_i^e = \mathbf{X} + \mathbf{t}_i^e \quad (21)$$

$$\mathbf{x}_i^n = \mathbf{X} + \sum_{j=1}^{A-1} \mathbf{t}_j^n ((\mathbf{V}^n)^{-1})_{ji} \quad (22)$$

with

$$((\mathbf{V}^n)^{-1})_{Ai} = 1, \quad i = 1, 2, \dots, A \quad (23)$$

while the inverse requirement on the remaining rows gives

$$\sum_{i=1}^A ((\mathbf{V}^n)^{-1})_{ji} m_i = 0, \quad j = 1, 2, \dots, A - 1 \quad (24)$$

⁴ The discussion below is aimed at the general polyatomic case. The cases $A = 1$, $A = 2$, $A = 3$ (the nuclear configurations that define, respectively, a point, a line and a plane) may be dealt with by special techniques which are not considered here as it would deflect the main thrust of the argument.

With this choice of coordinates the translationally invariant Coulomb Hamiltonian takes the form,

$$H'(\mathbf{t}) \rightarrow H^e(\mathbf{t}^e) + H^n(\mathbf{t}^n) + H^{en}(\mathbf{t}^n, \mathbf{t}^e) \tag{25}$$

The part of the Hamiltonian which can be associated with electronic motion can be written as either

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

or

$$H^e(\mathbf{t}^e) = -\frac{\hbar^2}{2\mu} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|} \tag{26}$$

with

$$1/\mu = 1/m + 1/M \tag{27}$$

while the part that can be associated with nuclear motion is

$$H^n(\mathbf{t}^n) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(\mathbf{t}_i^n) \cdot \vec{\nabla}(\mathbf{t}_j^n) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)} \tag{28}$$

where $r_{ij}(\mathbf{t}^n)$ is defined just as in the general case (11) but using the \mathbf{t}_i^n and $(\mathbf{V}^{n-1})^{-1}$, that is

$$r_{ij}(\mathbf{t}^n) = \left(\sum_{\alpha} \left(\sum_{k=1}^{A-1} ((\mathbf{V}^{n-1})_{kj} - (\mathbf{V}^{n-1})_{ki}) t_{\alpha k}^n \right)^2 \right)^{1/2} \tag{29}$$

and the inverse mass matrix is similarly specialised as

$$1/\mu_{ij}^n = \sum_{k=1}^A m_k^{-1} V_{ki}^n V_{kj}^n, \quad i, j = 1, 2, \dots, A - 1 \tag{30}$$

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

$$H^{en}(\mathbf{t}^n, \mathbf{t}^e) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{r'_{ij}(\mathbf{t}^n, \mathbf{t}^e)} \tag{31}$$

and the electron–nucleus distance expression becomes

$$|\mathbf{x}_i^n - \mathbf{x}_j^e| \equiv r'_{ij} = \left| \sum_{k=1}^{A-1} \mathbf{t}_k^n (\mathbf{V}^n)^{-1}_{ki} - \mathbf{t}_j^e \right| \quad (32)$$

For reasons that are explained fully in [27] this form of the Hamiltonian is only really useful when the internuclear distances are relatively small but since it is molecules that are being considered here, it is an appropriate form. It would not be very useful when considering a scattering problem.

It might now be reasonably hoped that for some set of nuclei and electrons there were discrete solutions of the form

$$\mathbf{H}'(\mathbf{t})\Psi_{\mathbf{n}}(\mathbf{t}) = E_{\mathbf{n}}\Psi_{\mathbf{n}}(\mathbf{t}) \quad (33)$$

among which molecules might be identified. Here \mathbf{n} is used to denote a set of quantum numbers ($J M p r n$): J and M for the angular momentum state: p specifying the parity of the state: r specifying the permutationally allowed irreps within the groups of identical particles and n to specify a particular energy value. For a given J such solutions will be degenerate for all $2J + 1$ values of M , and the permutational irreps can be, as has been seen, extensively degenerate too.

It might also be hoped that a first approximation to a solution of (33) could be constructed in terms of product functions in which one portion of each product was obtained from a problem in which the electronic motion was treated as primary, and the other portion described the nuclear motion in the electronic field derived from the first part of the product. This is the standard technique for treating a system of coupled differential equations in which one group of equations represent fast motions and another slow motions. Most chemists get their familiarity with this technique by considering the kinetics of sequential chemical reactions. It is this technique that underlies the Born and Oppenheimer programme in which the electronic motion is approached in a frame fixed in the laboratory with an electronic Hamiltonian in which the nuclear motion is at first ignored.

By analogy, the electronic Hamiltonian arising from (25) on ignoring the nuclear motion is

$$\mathbf{H}^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) = \mathbf{H}^e(\mathbf{t}^e) + \mathbf{V}^{\text{en}}(\mathbf{t}^n, \mathbf{t}^e) + \frac{e^2}{8\pi\epsilon_0} \sum'_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)} \quad (34)$$

It is the sum of (26) and (31) together with the last term from (28). So that the full Hamiltonian can now be written as:

$$\mathbf{H}'(\mathbf{t}) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(\mathbf{t}_i^n) \cdot \vec{\nabla}(\mathbf{t}_j^n) + \mathbf{H}^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) \quad (35)$$

If the \mathbf{t}^n were assigned values, \mathbf{b} say, based upon choices $\mathbf{x}_g^n = \mathbf{a}_g$ in the laboratory-fixed frame, then this would be the translationally invariant form of the electronic Hamiltonian appropriate to a particular classical nuclear geometry and

$$H^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) \rightarrow H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e) \quad (36)$$

This Hamiltonian is very like the usual clamped-nuclei one but it is explicitly translationally invariant and has an extra term, the second term in (26), which is often called either the Hughes–Eckart or the mass polarisation term. The domain of $H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$ consists of functions on \mathbf{R}^{3N} because the nuclear repulsion operator becomes a number multiplier and just determines an energy zero and the electron–nucleus interaction terms have fixed origins. The Hamiltonian can be shown to have discrete solutions $\Psi_p^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$ below the HVZ threshold by an extension of the argument used to show this property for the clamped nucleus Hamiltonian. The only tricky point in this extension arises from the fact that the Hughes–Eckart term need not be positive [8].

The Hamiltonian $H^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e)$ has the same invariance under the rotation-reflection group $O(3)$ as does the full translationally invariant Hamiltonian (9) and it has a somewhat extended invariance under nuclear permutations, since it contains the nuclear masses only in symmetrical sums. Since it contains the translationally invariant nuclear coordinates as multiplicative operators, its domain is of functions on $\mathbf{R}^{3N} \otimes \mathbf{R}^{3(A-1)}$. It contains a bare Coulomb operator involving the nuclear variables alone with no kinetic energy terms at all and the potential operator cannot, in this context, be regarded as small; there must therefore be some question about its self-adjointness. The operator seems to be unbounded and to have a completely continuous spectrum of a very unpleasant kind given that eigenfunctions of the cartesian position operators are Dirac δ functions.

It is often assumed that the electronic problem can be written as if the potential for nuclear motion arose from:

$$H^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) \Psi_p^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) = E_p^{\text{elec}}(\mathbf{t}^n) \Psi_p^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) \quad (37)$$

but from the forgoing discussion the problems in such an identification are apparent, even without considering nuclear permutations. It is clearly unwise to start off on such dangerous ground if one hopes to try and move further.

Progress can be made by noting that electronic Hamiltonian (34) commutes with each of the $A - 1$ nuclear position variables. Think now of the molecular bound state space \mathfrak{H} as the square integrable sections in the trivial fiber bundle $\mathbf{R}^{3A-6} \otimes \mathcal{L}^2(\mathbf{R}^{3N})$. In this case the nuclear operator (which is the bare kinetic energy operator) acts in the base space, that is upon functions defined on \mathbf{R}^{3A-6} and the electronic Hamiltonian acts only upon the fiber defined by the choice of \mathbf{b} . (In this case the fiber is a vector space and so the fiber bundle in this context is often called a vector bundle.) Now write the full electronic Hamiltonian as a direct integral over the fibers.

$$H^{\text{elec}}(\infty, \mathbf{t}^e) = \int_{\oplus} H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e) d\mathbf{b} \quad (38)$$

where the \mathbf{t}^n have been replaced by \mathbf{b} within the integral, to emphasise that it is over fixed points that the “sum” is occurring and by ∞ on the left, to symbolise that this is the form that the electronic Hamiltonian would have were the nuclear masses allowed to increase without limit and the nuclear positions to cover all of \mathbf{R}^{3A-3} . This is, of course to redefine the electronic Hamiltonian but in a perfectly reasonable way and one which avoids the pitfalls of trying to deal directly with (34). It is a perfectly decent operator but there are some aspects of it that need a bit more discussion.

It should be noted that $\Psi^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$ as a solution to the Schrödinger Eq. 37 with \mathbf{t}^n replaced by \mathbf{b} , is defined only up to a phase factor of the form

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

where w is any single-valued real function of the \mathbf{b}_k and can be different for different electronic states. Specific phase choices must therefore be made when tying this part to the nuclear part of the product wave function. It is only by making suitable phase choices that the electronic wave function is made a continuous function of the formal nuclear variables, \mathbf{b} , and the complete product function, made single valued. This is the origin of the Berry phase in clamped nuclei calculations involving intersecting potential energy surfaces; for a discussion of these matters see [28]. It is worth noting explicitly that notions of molecular Berry phases and conical intersections of PE surfaces are tied to the clamped nuclei viewpoint. They are only ‘observable’ to the extent that experimental data are interpreted within that framework. According to quantum mechanics the eigensolutions of (33) are single-valued functions by construction with arbitrary phases (rays) so one does not expect any Berry phase phenomena.

If it is decided to treat the system by specifying a set of three rotation angles and $3N_T - 6$ internal coordinates then problems arise with the vector bundle idea. This is because such a separation requires that the the vector space \mathbf{R}^{3N_T-3} is decomposed into the manifold $\mathbf{S}^3 \otimes \mathbf{R}^{3N_T-6}$. But this manifold cannot be coordinatised globally, of course, so any account of electronic structure given in this way can at best be only local.

It is possible to decompose the full space leaving the electrons described in a vector space, if there are more than two nuclei, by splitting the whole space as $\mathbf{R}^{3N} \otimes \mathbf{S}^3 \otimes \mathbf{R}^{3A-6}$. Although with such a splitting the form of the electronic Hamiltonian remains unchanged, because the matrix \mathbf{C} in (17) will be a function only of the nuclear coordinates, it couples the electronic motion to the angular motion and leaves the notion of the electronic Hamiltonian as a direct integral, a local idea.

However the useful angular momentum operators can be constructed on \mathbf{R}^{3N_T-3} and so one can suppose that the angular momentum eigenfunctions are constructed by the standard coupling methods used in atomic theory and thus side-step the problems raised by the manifold division when constructing possible solutions. The direct integral form of the electronic Hamiltonian will still be invariant under the operations of $O(3)$.

If a solution of the electronic problem is to be used in a solution of the full problem then the solution must be one invariant under the permutation of identical nuclei. The direct integral form is indifferent to whether or not individual nuclei are identified and it is thus perfectly possible to regard formally identical nuclei as distinguishable

particles simply by a suitable labelling of the points specified by \mathbf{b} . However it is equally possible that the direct integral properly reflect the permutational symmetry by requiring that if \mathbf{b}' results from a permutation of identical nuclei specified by \mathbf{b} both sets be included in the same way in the direct integral.

4 The status of the Born–Oppenheimer approximation

The observations made above must make it clear that Born and Oppenheimer's original discussion cannot be mathematically sound, no matter how persuasive it may seem. They started from an equivalent of (37) for a diatomic molecule and used ordinary perturbation theory. They give no fully explicit account of the polyatomic molecule problem at all. Combes et al. [29] using the fiber bundle approach and singular perturbation theory about an assumed non-degenerate minimum in the potential $V^{\text{elec}}(\mathbf{t}^n)$, with the fourth root of the ratio of the electronic to a typical nuclear mass as the perturbation parameter, κ , showed in the 1970s that this approach for the diatomic molecule led in a mathematically sound way to *asymptotic solutions* for the full problem, just like those anticipated by Born and Oppenheimer. That is, they were able to show that asymptotically the energy could be written as the sum of an electronic, a vibrational and rotational part. The electronic part was the value of the potential at the minimum, the vibrational part was given by the Harmonic oscillator eigenvalues with the force constant determined by the second derivative of the electronic energy at the potential minimum and the rotational energies were given by those of a rigid rotor whose extension was the value of the internuclear separation at the potential minimum. That it is the Harmonic oscillator that provides the vibrational energies is, as the authors note, “a miracle” because the range of the internuclear distance operator is only $[0 \infty)$ while that of the Harmonic oscillator variable is $(-\infty +\infty)$. But they show that this is justified if the vibrational eigenfunctions vanish quickly enough away from the equilibrium extension and that such vanishing is a consequence of a potential minimum deep enough to validate the general argument.

It has not proved possible to consider the polynuclear molecule using singular perturbation theory nor by separating out rotation-inversion symmetry. In 1992 however, it was shown by Klein et al. [30], again treating the full problem in terms of a fiber bundle, that if it is assumed that (36) has a discrete eigenvalue which has a minimum as a function of the \mathbf{t}_g^n in the neighborhood of some values $\mathbf{t}_g^n = \mathbf{b}_g$, then because of the rotation-inversion invariance such a minimum exists on a three dimensional sub-manifold for all \mathbf{b}_g such that

$$\mathbf{b}_g \rightarrow \mathbf{R}\mathbf{b}_g, \quad \mathbf{R} \in \text{O}(3)$$

The \mathbf{b}_g 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 $\text{SO}(3)$ while if it is non-planar then it is diffeomorphic to $\text{O}(3)$ and so the well is actually a symmetric double well. In either case, Klein et al. show that the eigenvalues and eigenfunctions for a polynuclear molecule can be obtained as WKB-type expansions to all orders⁵ of

⁵ The eigenfunctions expand in integer powers of κ ; most of the eigenvalues expand in even powers of κ .

the parameter κ . So it is properly established that the Born–Oppenheimer approach leads to asymptotic solutions for the full problem but, interestingly, the potential is usually a double-well one.

Just as permutational symmetry was not considered in the work of Born and his collaborators, neither is it considered in the later work. With the choice of translationally invariant coordinates made above, it is a simple matter to incorporate electronic permutational symmetry and, without any diminution of mathematical generality, to require that the electronic part of the wave function include spin and be properly anti-symmetric. On this understanding, it is perfectly reasonable to assume that the potential at the minimum should not be degenerate. If it seems sufficient to treat the nuclei as distinguishable particles then it can confidently be asserted that the Born–Oppenheimer approach offers a perfectly satisfactory account of molecular wavefunctions whose energy is close to a minimum in the potential.

At present there has been no direct consideration of the Born and Huang [31] approach by mathematicians. To remove the translational motion from the problem and so make possible the formal expansion at the heart of this method, while still allowing a useful approach as the nuclei became widely separated, seems a vain hope. However, in the time-dependent coherent states (wave-packet) approach to a freely moving system, it is possible to use the laboratory-fixed coordinate system and hence to deal with all the asymptotes, while avoiding problems arising from the pure translational continuum. Among the first to use this approach on a molecule was Hagedorn [32]. For diatomics he was able to show that, in the limit of large nuclear masses, the electrons move adiabatically and determine an effective potential in which the nuclei, treated as identifiable particles, move semi-classically if the potential surface is isolated. These results do not depend upon there being a minimum in the potential. The results of the Born and Oppenheimer work cited above would not be valid if there were not a minimum around which the wavefunction could be expanded. Hagedorn's work has not been formally extended to polynuclear molecules (but see [33]) though it certainly could be, by deploying the same sort of techniques that are used by Klein et al. [30] in their work on polynuclear systems. However the approximation breaks down when the potential surface fails to remain isolated from the rest of the electronic energy spectrum. There is so far no mathematically satisfactory resolution of the general level crossing problem but in a later paper [34] Hagedorn puts some aspects of the work that has been done here in the context of more chemically-oriented level-crossing ideas. If it becomes possible to deal with level crossing, then what is usually done in quantum chemical calculations can be regarded as soundly based mathematically; however to relate the product-like solutions obtained from such calculations to eigenfunctions of the Hamiltonian for the moving nucleus problem, it still remains to deal with nuclear permutational symmetry.

4.1 Permutational invariance of the effective electronic Hamiltonian

If the nuclei are treated as identifiable particles and a particular set of nuclear coordinates is chosen, say $\mathbf{x}_g^n = \mathbf{a}_g$, then within the chosen set of translationally invariant coordinates this will generate the set \mathbf{b}_g corresponding to the \mathbf{t}_g^n . A particular

choice of nuclear coordinates will specify a geometrical figure \mathbf{F} at whose vertices are placed the nuclei. Any choice of nuclear coordinates that can be obtained from a given choice by means of a rotation-reflection will generate the same geometrical figure. If the nuclear coordinate choice \mathbf{a} generates a geometry \mathbf{F} , then any nuclear coordinate choice that arises from a permutation of nuclei with the same charge, will give rise to the same energy V^{elec} . However two equivalent geometries so generated usually correspond to a different coordinate choice. So, regarding V^{elec} as specifying a particular point on a potential surface expressed in terms of the \mathbf{t}_g^n is rather too restrictive. It actually corresponds to as many points as are generated by permutations of particles with identical charges. This observation was made at least as long ago as 1985 by Schmelzer and Murrell [35] and developed in a series of papers by Collins and his group [36]. If the chosen point is located at a minimum on the potential surface then it corresponds to a multiple minimum with as many wells as there are permuted positions.

It is perhaps useful to provide an example of what is meant here. Suppose that one was dealing with the molecule H_2O_2 and began by specifying four nuclear coordinates in the full problem as \mathbf{x}_g^n , $g = 1, 2, 3, 4$ with 1 and 3 as labels for the protons, and 2 and 4 for the oxygens. The internal coordinates might be chosen as

$$\mathbf{t}_1^n = \mathbf{x}_2^n - \mathbf{x}_1^n, \quad \mathbf{t}_2^n = \mathbf{x}_2^n - \mathbf{x}_4^n, \quad \mathbf{t}_3^n = \mathbf{x}_4^n - \mathbf{x}_3^n$$

and thought of as one OH bond vector, an OO bond vector and another OH bond vector, respectively. Now imagine a specific choice \mathbf{a} made for the \mathbf{x}^n then such a choice would specify a point in the coordinate space. The permutation (13) would transform the OH bond vectors and produce new coordinates corresponding to crossed OH bonds vectors. These crossed forms would require a linear combination of all three of the original coordinates to express them. They would therefore, when the specific choice has been made, locate a different position in the coordinate space than that originally specified, but one at which the electronic energy had the same value.

Were there to be a minimum in the potential for some particular choice of the \mathbf{b} then in this example there would be four minima simply as a result of permutational symmetry. If these minima occurred at a non-planar configuration there would be eight because of inversion symmetry. Any point group symmetry would be subsumed in the permutational symmetry. The nuclear motion problem tackled along the lines of the Born–Oppenheimer programme would thus involve establishing that the usual solutions were asymptotic solutions to a problem with a many-well potential. It would also involve constructing permutationally allowed trial functions for nuclear motion. No mathematical work that attempts to follow the Born and Oppenheimer or the Born programme along this path appears to have been done.

The work mentioned above, [35] and [36], and later work [37] is devoted to describing a potential surface in terms of coordinates that are invariant under permutations of identical nuclei and is not directly a help in the matters considered here. However the use made of classical invariant theory as described in Weyl [38] in these discussions is very illuminating and may perhaps provide a way forward, as perhaps does the work of Helffer and Sjöstrand [39] dealing with multiple well potentials. The potentials considered in all of these works are invariant under the operations of the rotation-reflection group in three dimensions, $O(3)$. The discussion given is thus at a

level somewhat different from that given above, where only translational invariance has been considered explicitly. No matter which internal motion space is chosen, it will still be necessary to deal with both fermion and boson particles. Methods for dealing with spin 1/2 fermions are well enough known but the treatment of fermions with higher spins and bosons generally is much less studied. The work of Paldus and his colleagues [40] and that of Katriel [41] may perhaps provide a useful start here.

It should be pointed out that if one is considering potentials invariant under the operations of the rotation-reflection group in three dimensions, $O(3)$, then it is possible that a permutation of identical particles may result in a redefinition of the Eulerian angles. Since the internal coordinates are defined in terms of scalar products of the translationally invariant coordinates, it is clear that a permutation of the original coordinates will transform any internal coordinate into, at most, a function of internal coordinates. However, since the Eulerian angles are defined by orienting a coordinate frame in the translationally invariant coordinate space, it is equally clear that, unless the orientation is such that all indistinguishable particles are treated symmetrically, a permutation will result in the Eulerian angles being transformed into functions of the original Eulerian angles and the internal coordinates. Thus if the matrix \mathbf{C} were chosen according to the Eckart prescription [42], which is the one generally used by molecular spectroscopists and does not usually involve all nuclei of equal mass symmetrically, then permutations often mix the Eulerian and internal coordinates. Nuclear motions in the Eckart prescription are defined in terms of displacements from a fixed nuclear geometry and only permutations that correspond to point group operations for that geometry, leave the Eulerian angles unchanged.

If it were possible to construct from a clamped nuclei start, a very good approximate wave function for the whole system, having all the required symmetry properties and including nuclear motion, then it might be possible to consider in a proper manner in what sense it could be approximated by a wavefunction arising from the same clamped nuclei start but leaving the nuclei identified and ignoring any nuclear permutation symmetry. This could be by means of an approach similar to that which is used in computing inter-molecular forces within the clamped nuclei approximation. Here, if one considers two interacting molecules then the system of electrons formed by the two combined must be represented by an antisymmetric wave function. The system is a 'super-molecule'. But as the two molecules are separated, then the representation of the totally antisymmetric wavefunction by the product of two individually antisymmetric wavefunctions becomes perfectly adequate in energy terms. Thus some consequences of the full symmetry requirements of the problem become unimportant from an energetic point of view. Of course if one were looking for Einstein–Podolsky–Rosen correlation effects, the full symmetry of the problem might well remain important in understanding the results of some experiment, even where it is unimportant energetically.

The work by Longuet–Higgins [43] offered a justification of this sort of neglect of nuclear permutational symmetry 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 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 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 [44].

If the analysis given here 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.

It would seem that it is not at present possible to give a satisfactory account of how the usual clamped nuclei approach leads to a solution of the moving nuclei problem. It is thus appropriate to consider proceeding in the other direction to see if a moving nuclei approach can lead to solution of the clamped nuclei problem.

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