

## PERMUTATIONAL SYMMETRY AND MOLECULAR STRUCTURE CALCULATIONS

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*Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.*

In a paper published in 1985 (Katriel J., Paldus J., Pauncz R.: *Int. J. Quantum Chem.* **1985**, *28*, 181) Paldus and his colleagues considered explicit relations between the permutational symmetry and the spin operators for systems of identical particles. The principal concern of this paper was with particles for which  $\sigma = 1/2$  but there is some consideration of the case of particles for which  $\sigma = 1$ . This latter consideration was developed by Katriel (Katriel J.: *J. Mol. Struct. (THEOCHEM)* **2001**, *547*, 1) in a paper honouring Prof. Paldus on the occasion of his 65th birthday. The present paper attempts a consideration of aspects of permutational symmetry, not explicitly considered in those two papers, as they affect the interpretation of the results of molecular structure calculations.

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I shall begin by trying to summarise what is known about bound state solutions to the full molecular problem, nuclear motion included, posed in terms of the standard Schrödinger equation with just Coulomb forces acting. What I shall argue is that permutational symmetry makes Dirac's celebrated dictum 1929<sup>1</sup> "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." not quite as obviously true as is sometimes supposed.

### THE COULOMB HAMILTONIAN

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

$$H = \sum_g^A \frac{p_g^2}{2m_g} + \frac{e^2}{4\pi\epsilon_0} \sum_{g<h}^A \frac{Z_g Z_h}{r_{gh}} + \sum_i^N \left( \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_g^A \frac{Z_g}{r_{ig}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^N \frac{1}{r_{ij}}. \quad (1)$$

This operator is essentially self-adjoint and bounded from below. It has, however, a completely continuous spectrum  $[0, \infty]$ . The fact that it is completely continuous is because of the centre-of-mass motion and to see any discrete spectrum this motion must be removed as

$$H = \frac{\hbar^2 \nabla^2(\xi)}{2M_T} + H' = T_\xi + H', \quad (2)$$

where  $\xi$  denotes the three-component cartesian coordinate of the centre-of-mass and  $M_T$  is the total mass of the system.

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

$$T(\xi)\Psi(\mathbf{t}), \quad (3)$$

where  $\Psi(\mathbf{t})$  is a wave function for the Hamiltonian  $H'(\mathbf{t})$  which we will refer to as the translationally invariant Hamiltonian. The  $N + A - 1$  coordinates  $\mathbf{t}_i$  are themselves translationally invariant and are typically chosen as a set of inter-particle distance vectors. The translationally invariant Hamiltonian is that which we must use when considering the separation of nuclear from electronic motion.

There are infinitely many possible choices of translationally invariant coordinates, so that the form of  $H'$  is not determined, but whatever coordinates are chosen the essential point is that all  $H'$  have the same spectrum. More detailed accounts of the spectral properties of the Coulomb Hamiltonian that will be cited below can be found in<sup>2,3</sup> and briefly but fully in<sup>4</sup>. It is the fact that the Coulomb potential, though unbounded, is small compared with the kinetic energy, that enables many of results that follow, to be proved. Interestingly enough, equivalent results in classical mechanics are not generally provable.

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 classifi-

cation most useful in molecular physics is into discrete and essential parts. The discrete spectrum  $\sigma_d(A)$  is the subset of the pure point spectrum that consists of isolated eigenvalues of finite multiplicity. The essential spectrum  $\sigma_{\text{ess}}(A)$  is the complement of the discrete spectrum.

$$\sigma_{\text{ess}}(A) = \sigma(A) \setminus \sigma_d(A) \quad (4)$$

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 bottom of the essential spectrum is located by means of the famous Hunzicker–Van Winter–Zhislin (HVZ) theorem. It is obtained by looking at the lowest energy of all possible separated clusters. It can be shown that the lowest possible energy arises from a two-cluster decomposition.

The problem is: what is the extent of the discrete spectrum in any particular case?

For a neutral or positively charged “atomic” system the essential spectrum begins at the first ionization energy. The discrete spectrum is infinite and begins at a negative energy value. This result is independent of the “nuclear” mass. For the hydrogen atom the discrete spectrum ends where the energy is zero. The essential spectrum of the hydrogen atom begins at zero. 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 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.

For a negatively charged “atomic” system there are, at most, a finite number of bound states. ( $\text{H}^-$  has just one bound state, see<sup>5</sup>.)

The clamped nuclei electronic Hamiltonian is just like an “atomic” Hamiltonian but the form of the discrete spectrum depends upon the nuclear geometry.

Almost nothing is known about “molecular” systems in a way that is mathematically rigorous.

The origin of the essential spectrum has been located only for the hydrogen molecule.

It is known that the hydrogen molecule has at least one bound state. It is also known that if a system becomes “too” negative (or positive) it has no bound states. If a trial wave function can be found whose expected energy is below the start of the essential spectrum, then the system has at least one bound state.

If the beginning of the essential spectrum is at a point where the two clusters have opposite charges, then there are an infinite number of bound states: if the two clusters are neutral then there are only a finite number of bound states.

The results recorded above were proved with no consideration of any symmetry restrictions upon the solutions. But subsequent work, especially by Balslev<sup>6</sup>, established that the atomic results remained true even after requiring the electronic states to obey the Pauli Principle and to be angular momentum eigenfunctions.

In extending these considerations to molecules, however, certain technical problems arise in showing that the HVZ theorem can be maintained allowing for permutational symmetry. This is because the separating clusters may well contain identical particles. These technical problems arise because from the  $N + A$  variables  $\mathbf{x}$  defined in the laboratory fixed frame, only  $N + A - 1$  translationally invariant variables  $\mathbf{t}$  may be used to define  $H'(\mathbf{t})$ . This means that it is not possible to define a set of translationally invariant coordinates that can be associated each with a nuclear field point,  $\mathbf{x}_g^n$  and simultaneously, a set each associated with an electronic field point,  $\mathbf{x}_i^e$  as expressed in the laboratory fixed frame. Such problems of “coordinate mixing” are tricky technical ones but they can be surmounted. The HVZ theorem remains valid allowing for permutational symmetry. The spectrum of  $H'(\mathbf{t})$  is independent of any particular coordinate choice and if one knew the exact solutions then one could express them in any chosen coordinate set, to taste. However one has to make a coordinate choice in ignorance and what these results show is that it is not always possible to keep “electronic” and “nuclear” variables separate in a uniformly useful way.

Of course the effectiveness of calculations including both electronic and nuclear motions on small molecular systems in yielding approximate solu-

tions which appear to be bound, makes us feel easy about future mathematical progress to establish their existence.

### PERMUTATIONAL SYMMETRY

The eigenfunctions of the Coulomb Hamiltonian will provide irreps for the permutation group  $S$  of the system. This group comprises the direct product of the permutation group  $S_N$  for the electrons with the permutation groups  $S_{A_g}$  for each set of identical nuclei  $g$  comprising  $A_g$  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 invariance groups 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.

It should be emphasised that the variables  $\mathbf{x}(t)$  simply specify field points, and cannot actually be particle coordinates because of the indistinguishability of sets of identical particles. Weyl stresses 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. 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 *The Theory of Groups and Quantum Mechanics*<sup>7</sup>. 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 indi-

viduals 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. Indeed it is obvious that no single operator from such a set commutes with the Hamiltonian operator and so it cannot have a definite value as long as the energy remains definite.

If a particular irreducible representation of the symmetric group of degree  $N$  is denoted as  $[\lambda]^N$  and the conjugate representation as  $[\tilde{\lambda}]^N$  then, for electrons (or any spin 1/2 particles), the representation of the symmetric group carried by the spin-eigenfunctions  $\Theta_{S, M_S, k}$  must be one described by a no more than two-rowed Young diagram, that is  $[\lambda]^N \equiv [\lambda_1, \lambda_2]$  where

$$\lambda_1 = N/2 + S, \quad \lambda_2 = N/2 - S. \quad (5)$$

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

$$f_S^N = \frac{(2S+1)N!}{(N/2+S+1)!(N/2-S)!}. \quad (6)$$

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 ten 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  $[\tilde{5}, 5]$  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  $[2,1]$  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 and such extensions were begun in the work of Paldus et al.<sup>8</sup> and in the further work by Katriel<sup>9</sup> cited earlier. But the argument in these cases becomes quite tricky. It is much harder in the general case than it is with particles of spin  $1/2$ , to associate the spin eigenfunctions with their space parts to produce functions of appropriate symmetry. Although it is true that the spin wave functions for 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.

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  $[28,28]$  for the singlet state, given by the Wigner number  $f_s^N$  with  $N = 56$  and  $S = 0$ , is

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

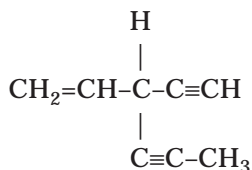
so that for this rather simple system one can expect the eigenfunctions, if any, in the discrete spectrum of  $H'(t)$  to be very extensively degenerate even without considering any degeneracies arising from the nuclear variables.

Interestingly enough such a possibility may have troubled Born and Oppenheimer. In their discussion of Eq. (15) in Part I of the paper they write  $V_n$  as arising from the sum of the electronic energy resulting from a solution of the clamped-nuclei Hamiltonian for the  $n$ -th electronic state and the classical nuclear repulsion energy at the clamped nuclei geometry at all values of the nuclear positions and say: "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 de-

generacy, 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.”

It seems unreasonable, considering possible permutational degeneracies, to assume that  $V_n$  would be a non-degenerate eigenvalue, but even if it were, or if any degeneracies could really be dealt with by using degenerate perturbation theory, it will leave behind those degeneracies arising from rotation-reflection symmetry and it will also leave unconsidered degeneracy arising from permutational symmetry in the nuclear part of the problem. To see the sort of problems to which this can lead consider an example of the way in which isomers are usually accounted for.

The Coulomb Hamiltonian  $H'(t)$  for  $C_8H_8$  is the molecular Hamiltonian for cubane, cyclooctatetraene, vinylbenzene and many other compounds, too. Indeed it is even the molecular Hamiltonian for a system with optical isomers, 3-vinylhexa-1,4-diyne, which has the molecular formula



and in which the central carbon is clearly chiral by the conventional rules.

The irrep of the nuclear permutation group that corresponds to an antisymmetric singlet state for the protons and a symmetric singlet state for the carbons is of dimension 14, that which corresponds to a triplet state for the protons with same carbon spin state is of dimension 28 and so on.

This apparent “confusion” of molecules 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  $H'$ , perhaps with different nuclear spin states. 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, given that the wave function must belong to a subspace of definite permutational symmetry.

If we write the variables corresponding to the carbon nuclei in  $C_8H_8$  as  $\mathbf{x}_g^n$ ,  $g = 1, \dots, 8$  and those corresponding to the protons as  $\mathbf{x}_{g+8}^n$ ,  $g = 1, \dots, 8$  then a particular CH interparticle distance is

$$x_{gh}^{\text{CH}} = \left| \mathbf{x}_{g+8}^n - \mathbf{x}_h^n \right|. \quad (7)$$



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 that  $x_{gh}^{\text{CH}}$  is not a proper observable. Its product with a function lying in a particular permutational subspace carries the function outside the subspace and so out of quantum mechanical utility.

The only possible operator incorporating these distances is the symmetrical sum

$$\sum_{g,h=1}^8 x_{gh}^{\text{CH}} \quad (8)$$

and all that can be inferred from its expectation value is that, on average, all the CH interparticle distances are the same.

It is thus not possible to identify an isomer in terms of a set of distinct geometrical parameters computed as expectation values. Neither would it be possible using pair correlation functions for the CH bond because, for any eigenfunction of the Coulomb Hamiltonian, there would be only one CH pair correlation function.

This is not to suppose that the average value or the pair correlation function 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 isomer identification in classical chemical structure theory.

It does not seem possible to treat the full molecular Hamiltonian with permutational invariance properly considered and to get out anything that a chemist would think of as a molecule. So this was not perhaps the "fundamental law" that Dirac was thinking of.

It seems likely from the context that Dirac was actually thinking of chemistry as explained using the clamped nuclei Hamiltonian, treating the nuclei as identifiable particles. Here one computes energy differences between various classical isomeric forms of the molecule under consideration and constructs isomerization paths between them and so on. But if the nuclei are to be treated as indistinguishable particles, then it must be shown that one can work back from the position that one is left in at the end of a clamped nuclei calculation to a solution of the full problem, at least to a very good approximation. Ideally one would like to be able to construct from a clamped nuclei start, a very good (anti)symmetrised approximate wave function for the whole system and to show that classical molecular structure can be recovered from it as a single term, without any significant

loss of energy. This would be similar to the sort of thing that is done in computing inter-molecular forces within the clamped nuclei approximation. 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 wave function by the product of two individually antisymmetric wave functions 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. If such a separation approach were effective, then it might be possible too, to account for isomers in the manner first proposed by Hund to explain chirality<sup>10</sup> in terms of long-lived non-stationary states. 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.

#### SEPARATING ELECTRONIC AND NUCLEAR MOTION

Either the classical 1927 work of Born and Oppenheimer<sup>11</sup> or the 1950s approach by Born as presented in App. VIII of Born and Huang<sup>12</sup> is supposed to provide the connection between the clamped nuclei approach and the full problem. The original work here, however, considers neither the translational symmetry or any of the permutational symmetries. The Born and Oppenheimer work uses perturbation theory to expand the wave function about a minimum in the potential  $V_n$ . The aim is to account for the standard spectroscopic picture of the freely rotating semi-rigid molecule executing small harmonic vibrations. The work described in the book by Born and Huang is to formulate the full problem in terms of an electronic potential, closely similar to  $V_n$ , and electron-nuclear coupling terms which, it is hoped, may often be treated as small. The aim is to account for the transition state theory of chemical reactions and similar potential-surface based theories.

To put the original Born-Oppenheimer approach in context, the translationally invariant part of the Coulomb Hamiltonian  $H'(t)$ , can be expressed in terms of two sets of coordinates. One set consists of  $A - 1$  translationally invariant coordinates  $\mathbf{t}_i^n$  is expressed entirely in terms of the original coordinates of field points associated with nuclei,  $\mathbf{x}_i^n$ :

$$\mathbf{t}_i^n = \sum_{j=1}^A \mathbf{x}_j^n V_{ji}^n, \quad i = 1, 2, \dots, A - 1, \quad (9)$$

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

$$V_{iA}^n = M^{-1} m_i, \quad M = \sum_{i=1}^A m_i, \quad (10)$$

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 to ensure translational invariance. The other set comprises  $N$  translationally invariant "electronic" coordinates whose origin is the centre-of-nuclear mass

$$\mathbf{t}_i^e = \mathbf{x}_i^e - \mathbf{X}. \quad (11)$$

For generality<sup>+</sup> the systems that we shall consider must have  $A \geq 4$ . The inverse relations are

$$\mathbf{x}_i^e = \mathbf{X} + \mathbf{t}_i^e \quad (12)$$

$$\mathbf{x}_i^n = \mathbf{X} + \sum_{j=1}^{A-1} \mathbf{t}_j^n \left( (\mathbf{V}^n)^{-1} \right)_{ji} \quad (13)$$

with

$$\left( (\mathbf{V}^n)^{-1} \right)_{Ai} = 1 \quad i = 1, 2, \dots, A - 1, \quad (14)$$

while the inverse requirement on the remaining rows gives

$$\sum_{i=1}^A \left( (\mathbf{V}^n)^{-1} \right)_{ji} m_i = 0, \quad j = 1, 2, \dots, A - 1. \quad (15)$$

The translationally invariant Coulomb Hamiltonian now takes the form:

$$H'(\mathbf{t}) \rightarrow H^e(\mathbf{t}^e) + H^n(\mathbf{t}^n) + V^{en}(\mathbf{t}^n, \mathbf{t}^e). \quad (16)$$

<sup>+</sup> The cases  $A = 1$ ,  $A = 2$  and  $A = 3$  (the nuclear configurations that define a point, a line and a plane, respectively) 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

$$H^e(\mathbf{t}^e) = -\frac{\hbar^2}{2\mu} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|} \quad (17)$$

with

$$1/\mu = 1/m + 1/M, \quad (18)$$

while the part that can be associated with nuclear motion is

$$H^n(\mathbf{t}^n) = \frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(\mathbf{t}_i^n) \cdot \vec{\nabla}(\mathbf{t}_j^n) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)}, \quad (19)$$

where  $r_{ij}(\mathbf{t}^n)$  is defined as

$$r_{ij}(\mathbf{t}^n) = \left( \sum_{\alpha} \left( \sum_k (\mathbf{V}^n)^{-1}_{kj} - (\mathbf{V}^n)^{-1}_{ki} \right) t_{\alpha k}^n \right)^2 \Big)^{1/2} \quad (20)$$

and the inverse mass matrix is similarly specialised as

$$1/\mu_{ij}^n = \sum_{k=1}^A m_k^{-1} V_{ki}^n V_{kj}^n, \quad i, j = 1, 2, \dots, A-1. \quad (21)$$

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

$$V^{\text{en}}(\mathbf{t}^n, \mathbf{t}^e) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^n \frac{Z_i}{r'_{ij}(\mathbf{t}^n, \mathbf{t}^e)} \quad (22)$$

and the electron-nucleus distance expression becomes

$$|\mathbf{x}_i^n - \mathbf{x}_j^e| \equiv r'_{ij} = \left| \sum_{k=1}^{A-1} \mathbf{t}_k^n (\mathbf{V}^n)^{-1}_{ki} - \mathbf{t}_j^e \right|. \quad (23)$$

The full electronic Hamiltonian arising from (16) is

$$H^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) = H^e(\mathbf{t}^e) + V^{\text{en}}(\mathbf{t}^n, \mathbf{t}^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)}. \quad (24)$$

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 of the electronic Hamiltonian appropriate to a particular classical nuclear geometry and

$$H^{\text{elec}}(\mathbf{t}^n, \mathbf{t}^e) \rightarrow H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e) . \quad (25)$$

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 Eq. (17), which is often called either the Hughes–Eckart or the mass polarisation term.

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  $\mathbf{t}_i^n$  alone. It makes  $H^e(\mathbf{t}^e)$  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  $V^{\text{en}}(\mathbf{t}^n, \mathbf{t}^e)$  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, this one is convenient for the purposes of the present discussion. However it should be noted that it would not be convenient for a discussion of the asymptotic problem. As the system separates, the present coordinate choice describes naturally a system of bare nuclei with electronic variables still referred to the centre-of-nuclear mass. This choice of coordinates would not be very useful in considering the Born–Huang approach to separation because there a potential surface needs to be described towards the asymptotes, not just locally. To get asymptotes that naturally describe separate atoms, it is necessary to refer some electronic origins to different nuclei.

It might now be reasonably hoped that for a particular choice of nuclei and electrons, there were discrete solutions of the form

$$H'(\mathbf{t})\Psi_n(\mathbf{t}) = E_n\Psi_n(\mathbf{t}) \quad (26)$$

among which molecules might be identified. Here  $\mathbf{n}$  is used to denote a set of quantum numbers:  $J$  and  $M$  for the angular momentum state:  $p$  specifying the parity of the state:  $\mathbf{r}$  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.

Allowing the nuclear masses to increase without limit, yields

$$H_f^e(\mathbf{t}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|}, \quad (27)$$

while Eq. (19) becomes

$$H_f^n(\mathbf{t}^n) = \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^n)} \quad (28)$$

and Eq. (22) remains unchanged as

$$V_f^{\text{en}}(\mathbf{t}^n, \mathbf{t}^e) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{r'_{ij}(\mathbf{t}^n, \mathbf{t}^e)} \quad (29)$$

and

$$H'(\mathbf{t}) \rightarrow H'_f(\mathbf{t}),$$

so  $H'_f(\mathbf{t})$  is simply the electronic Hamiltonian (24) without the mass polarisation term.

The passage to infinite nuclear mass, while removing the nuclear kinetic energy terms, leaves unchanged the form of the potential terms involving the nuclei. There is, therefore, no intrinsic argument for treating these terms as other than multiplicative operators involving nuclear coordinates. There is no inherent reason from this analysis to treat the nuclear coordinates simply as fixed vectors.  $H'_f(\mathbf{t})$ , although closely similar to the electronic Hamiltonian, is quite distinct from  $H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$ . The domain of the operator  $H'_f$  is  $\mathcal{L}^2[\mathbf{R}^{3N} \oplus \mathbf{R}^{3A}]$  while that of  $H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$  is restricted to  $\mathcal{L}^2[\mathbf{R}^{3N}]$ . This is because the nuclear repulsion operator simply becomes a number multiplier and just determines an origin for the energy. As in the original clamped nuclei formulation, the choice of the nuclear positions as constant vectors is an additional choice.

The equivalent form to Eq. (26) would now be

$$H'_f(\mathbf{t})\Psi_n^f(\mathbf{t}) = E_n \Psi_n^f(\mathbf{t}) \quad (30)$$

but this form cannot be a legitimate one since the operator  $H'_f$  contains a bare Coulomb operator involving the nuclear variables alone with no kinetic energy terms at all. The operator cannot, in this context, be regarded as small. It is unbounded and it has a completely continuous spectrum and so the operator  $H'_f$  is unbounded and has no discrete spectrum. It is therefore not possible to pass from the full problem to the clamped nuclei problem, simply by treating the nuclear masses as increasing without limit: an extra choice of fixed nuclear positions has to be made. This analysis is quite independent of any particular coordinate choice. If fixed nuclear positions are chosen, there is no problem. Discrete solutions of the Schrödinger equation associated with  $H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e)$  are possible, whether or not the mass polarization term is included.

It is the observation that the spectrum of the infinite nuclear mass Hamiltonian with unclamped nuclei is completely continuous, that means that Born and Oppenheimer's original discussion cannot be mathematically sound, no matter how persuasive it may seem. They illegitimately use ordinary perturbation theory to pursue the clamped nuclei solutions across a singular divide. In the case of the diatomic molecule Combes, Duclos and Seiler<sup>13</sup> in the 1970s, using singular perturbation theory about the potential minimum, with the fourth root of the ratio of the electronic to a typical nuclear mass as the parameter, showed in a mathematically sound way for the diatomic molecule (the only form that is explicitly considered in the original paper) that the Born–Oppenheimer approach led to asymptotic solutions for the full problem.

It has not proved possible to consider the polyatomic molecule using singular perturbation theory. In 1992 however, it was shown by Klein et al.<sup>14</sup> that if it is assumed that Eq. (25) has a discrete eigenvalue which has a minimum as a function of the  $\mathbf{t}_g^n$  in the neighborhood of some values  $\mathbf{t}_g^n = \mathbf{b}_g$  that 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 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. So it is properly established that the Born–Oppenheimer approach leads to asymptotic solutions for the full problem, but interestingly usually the potential is 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 antisymmetric. On this understanding, it is perfectly reasonable to assume that  $V_m$ , as previously defined, 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 wave functions whose energy is close to a minimum in the potential  $V_m$ .

At present there has been no direct consideration of the Born and Huang 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 to the asymptotes, 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<sup>15</sup>. 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 wave function could be expanded. Hagedorn's work has not formally been extended to polyatomic molecules (but see<sup>16</sup>) though it certainly could be, by deploying the same sort of techniques that are used by Klein et al.<sup>14</sup> in their work on polyatomics. It seems safe to say that current computational chemical practice in the treatment of nuclear motion on an isolated potential surface is well justified for identifiable nuclei. 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<sup>17</sup> Hagedorn puts some aspects of the work that has been done here in the context of more chemically-oriented level-crossing ideas.

It still remains, however, to deal with nuclear permutational symmetry having separated electronic and nuclear motions.

If the nuclei are treated as identifiable particles and a particular set of nuclear coordinates is chosen so that the nuclear repulsion term becomes a pure number, the nuclear repulsion term can be dropped from the translationally invariant formulation of the clamped nuclei Hamiltonian (25) and

$$H^{\text{elec}}(\mathbf{b}, \mathbf{t}^e) \rightarrow H_f^{\text{cne}}(\mathbf{b}, \mathbf{t}^e),$$

then solutions of the form

$$H_f^{\text{cne}}(\mathbf{b}, \mathbf{t}^e) \Psi^{\text{cne}}(\mathbf{b}, \mathbf{t}^e) = E^{\text{cne}}(\mathbf{b}) \Psi^{\text{cne}}(\mathbf{b}, \mathbf{t}^e) \quad (31)$$

are possible by making specific choices of the molecular geometry. Such solutions are the ones whose spectral distribution is essentially like that of an atom. But the symmetry properties of the solutions are diminished from those of the fuller problem. The only variables in the problem formulated here are those describing the electrons. The choice of nuclear positions is merely to specify a parameter set. 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 which can be obtained from a given choice by means of a rotation-reflection, will generate the same geometrical figure. It is easily seen that only rotation-reflections of the electronic variables which are such that, if they were effected on the parametric geometry, would leave it invariant, leave  $H_f^{\text{cne}}$  invariant. The only other invariance remaining is that of the permutation of the electrons.

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  $E^{\text{cne}}$ . However two equivalent geometries so generated generally correspond to a different coordinate choice. So, regarding  $E^{\text{cne}}$  as contributing to the energy at a particular point on a potential surface expressed in terms of the  $\mathbf{t}_g^n$  is rather too restrictive. It actually contributes to as many points as are generated by permutations of particles with identical charges. This point was made at least as long ago as 1985 by Schmelzer and Murrell<sup>18</sup> and developed in a series of papers by Collins and his group<sup>19</sup>. If the chosen point corresponds to a minimum on

the potential surface then it corresponds to a multiple minimum with as many wells as there are permuted positions.

It should be possible 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

$$\mathbf{a}_i \rightarrow P\mathbf{a}_i, \quad \forall P \in S_A.$$

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<sup>20</sup> 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. There do not seem to be any 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 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 this is to neglect some of the permutational symmetry of the problem.

The work by Longuet-Higgins<sup>21</sup> 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 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<sup>22</sup>.

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. These arguments count with equal force against the Hund theory<sup>10</sup> of isomers.

### CONCLUSIONS

It seems to be the case that what is usually done in quantum chemical calculations to interpret molecular spectra can be properly justified mathematically just so long as identical nuclei are treated as distinguishable particles. The description of molecular scattering can similarly be justified as long as the potential is an isolated one. Anything involving potential surface crossings remains problematic, even though much work has been done and is being done here. It would not seem unreasonable, however, to suggest that some sort of resolution of the crossing problem might well be arrived at. But at present there is no satisfactory account of why identical particle permutational symmetry can be ignored. And there seems no way forward except by trying to construct trial wave functions of the proper symmetry and seeing how they relate to the usual ones with incomplete symmetry. This means considering systems with at least four nuclei and this would be a quite formidable task. But, who knows, it might be possible to celebrate Professor Paldus' 80th birthday with a paper providing just such a justification of what we all usually do.

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