

# To what question is the clamped-nuclei electronic potential the answer?

Brian Sutcliffe

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**Abstract** An examination is made of how the nuclear motion Hamiltonian arises from a consideration of solutions to the eigenvalue problem for the full Coulomb Hamiltonian and the role played by the usual clamped-nuclei electronic Hamiltonian in the construction of such solutions.

## 1 Introduction

In a paper of which Prof. Hinze was one of the authors [1], the results of accurate clamped nuclei calculations on the hydrogen molecule were deployed to try and decide precisely how a potential for nuclear motion might be defined and if the nuclear masses should be treated differently in dealing with rotations and vibrations in calculated spectral assignments for  $\text{H}_3^+$ . Since the publication of that paper, the question has been considered by others among whom one might cite Refs. [2–4]. The present paper, which is offered in warm memory of Prof. Hinze, is an attempt to examine the basis of some of the arguments offered in that paper and the later ones. Central to the examination is an attempt to decide precisely how the clamped-nuclei Hamiltonian might be positioned in relation to solutions of the full problem.

## 2 The clamped nucleus approximation

Quantum mechanical molecular structure calculations are most commonly attempted by first clamping the nuclei at

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This work is dedicated to the memory of Professor Jürgen Hinze and published as part of the Hinze Memorial Issue.

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B. Sutcliffe (✉)  
Service de Chimie quantique et Photophysique,  
Université Libre de Bruxelles, 1050 Bruxelles, Belgium  
e-mail: bsutclif@ulb.ac.be

fixed positions and then performing electronic structure calculations treating the clamped nuclei as providing the field for electronic motion. Schrödinger's Coulomb Hamiltonian for a system of  $N$  variables,  $\mathbf{x}_i^e$ , describing the electrons and another set of  $A$  variables,  $\mathbf{x}_i^n$  describing the nuclei and  $N_T = N + A$ , when the nuclei are clamped at a particular fixed geometry specified by the constant vectors  $\mathbf{x}_i^n = \mathbf{a}_i$ ,  $i = 1, 2, \dots, A$ , takes the form

$$\begin{aligned} H^{\text{cn}}(\mathbf{a}, \mathbf{x}^e) = & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{x}_i^e) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{|\mathbf{x}_j^e - \mathbf{a}_i|} \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{x}_i^e - \mathbf{x}_j^e|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{|\mathbf{a}_i - \mathbf{a}_j|} \end{aligned} \quad (1)$$

Although the only variables in the problem are the electronic ones, it is customary to incorporate the nuclear repulsion energy into the electronic equation. The nuclear repulsion term is merely an additive constant and so does not affect the form of the electronic wavefunction: it affects the spectrum of the clamped nuclei Hamiltonian only trivially by changing the origin of the energy.

The clamped nuclei problem can have solutions of the form

$$H^{\text{cn}}(\mathbf{a}, \mathbf{x}^e) \psi_p^{\text{cn}}(\mathbf{a}, \mathbf{x}^e) = E_p^{\text{cn}}(\mathbf{a}) \psi_p^{\text{cn}}(\mathbf{a}, \mathbf{x}^e) \quad (2)$$

The full Coulomb Hamiltonian may be written as

$$\begin{aligned} H(\mathbf{x}^n, \mathbf{x}^e) = & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{x}_i^e) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{x}_i^e - \mathbf{x}_j^e|} \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{|\mathbf{x}_j^e - \mathbf{x}_i^n|} \\ & - \frac{\hbar^2}{2} \sum_{k=1}^A \frac{\nabla^2(\mathbf{x}_k^n)}{m_k} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{|\mathbf{x}_i^n - \mathbf{x}_j^n|} \end{aligned} \quad (3)$$

It is easily established that the Coulomb Hamiltonian is invariant under the coordinate transformations that correspond to uniform translations, rotation-reflections and permutations of particles with identical masses and charges.

Kato [5] established that the Coulomb Hamiltonian,  $\mathbf{H}$ , is essentially self-adjoint. This means that it has a unique self-adjoint extension and that the domain of the operator is identical with the domain of its adjoint.<sup>1</sup> This property includes Hermiticity but is stronger than Hermiticity, and guarantees that the time evolution

$$\Psi(t) = \exp(-i\mathbf{H}t/\hbar)\Psi(0)$$

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 [6] is of the radial momentum operator  $-i\hbar\partial/\partial r$  acting on functions  $\phi(r)$ ,  $\phi(0) = 0$  with  $0 \leq r < \infty$ .

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 unobvious 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 range of potentials  $V$  including Coulomb ones, 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

$$\|\mathbf{V}f\| \leq a\|T_0f\| + b\|f\|$$

and that  $a$  can be taken as small as is liked. This result is often summarized 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.

Because of the symmetry of the Hamiltonian, its eigenfunctions will be basis functions for irreducible

representations (irreps) of the translation group in three dimensions, the orthogonal group in three dimensions and for the various symmetric groups corresponding to the sets of identical particles.

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

$$\begin{aligned} \mathbf{H}^{\text{nn}}(\mathbf{x}^n, \mathbf{x}^e) = & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{x}_i^e) - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{|\mathbf{x}_j^e - \mathbf{x}_i^n|} \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{x}_i^e - \mathbf{x}_j^e|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^A \frac{Z_i Z_j}{|\mathbf{x}_i^n - \mathbf{x}_j^n|} \end{aligned} \quad (4)$$

It would seem to have solutions, by analogy with Eq. 2,

$$\mathbf{H}^{\text{nn}}(\mathbf{x}^n, \mathbf{x}^e)\psi_p^{\text{nn}}(\mathbf{x}^n, \mathbf{x}^e) = E_p^{\text{nn}}(\mathbf{x}^n)\psi_p^{\text{nn}}(\mathbf{x}^n, \mathbf{x}^e) \quad (5)$$

Assuming that full problem had eigenstates such that

$$\mathbf{H}(\mathbf{x}^n, \mathbf{x}^e)\psi(\mathbf{x}^n, \mathbf{x}^e) = E\psi(\mathbf{x}^n, \mathbf{x}^e) \quad (6)$$

then, if the solutions of Eq. 5 were well defined, it would seem that they could be expanded as a sum of products of the form

$$\psi(\mathbf{x}^n, \mathbf{x}^e) = \sum_p \Phi_p(\mathbf{x}^n)\psi_p^{\text{nn}}(\mathbf{x}^n, \mathbf{x}^e) \quad (7)$$

In the Hamiltonian Eq. 4, the nuclear variables are free and not constant and there are no nuclear kinetic energy operators to dominate the potential operators involving these free nuclear variables. The Hamiltonian thus specified cannot be self-adjoint in the Kato sense. The Hamiltonian can be made self-adjoint by clamping the nuclei because the electronic kinetic energy operators can dominate the potential operators which involve only electronic variables. The Hamiltonian Eq. 1 is thus a proper one and the solutions of Eq. 2 are well defined. But, because the Hamiltonian Eq. 4 is not self-adjoint it is not clear how the proposed solutions of Eq. 5 could be properly defined. But assuming that they can be defined, it was observed more than 30 years ago [7] that the arguments for an expansion of Eq. 7 are quite formal because the Coulomb Hamiltonian has a completely continuous spectrum arising from the possibility of uniform translational motion and so its solutions cannot be properly approximated by a sum of this kind. This means too that the arguments of Born and Oppenheimer [8] and by Born [9] for his later approach to representations of this kind are also quite formal.

As a basis for the Born-Oppenheimer and the Born approach, it is commonly assumed that it is possible to construct an analytic potential function  $V(\mathbf{x}^n)$  such that

<sup>1</sup> The work was completed in 1944 and was actually received by the journal in October 1948.

$$E_p^{\text{cn}}(\mathbf{a}) = \mathbf{V}(\mathbf{a}), \text{ for some } p \text{ and for all } \mathbf{a} \quad (8)$$

and that this potential forms an adequate starting point for a discussion of the nuclear motion part of the full problem. Examination of the form 1 makes it clear, however, that  $E_p^{\text{cn}}(\mathbf{a})$  takes the same value for all choices of  $\mathbf{a}$  that differ from a given choice merely by a uniform translation. Similarly, it remains unchanged if the  $\mathbf{a}$  differ only by a constant orthogonal transformation. Thus, any potential formed according to Eq. 8 will have some variables under any change of which no change in the potential will be described. In the context of calculations of molecular spectra, these variables are often referred to as *redundant* ones. It is also the case that  $E_p^{\text{cn}}(\mathbf{a})$  is invariant under the permutation of any nuclei with the same charge (nuclear mass does not enter into Eq. 2). This means that the potential in Eq. 8 will have the same value for all geometries that can be obtained from a given geometry by means of a permutation of nuclei with the same charge. Should the potential have any minima at all, it always has as many as there are permutations of nuclei with the same charge. This would seem to make the assumption of a single isolated minimum in the potential, which is essential to the usual account of the Born-Oppenheimer approximation, a rather too restrictive one for comfort, except perhaps in the case of the diatomic system.

It is thus not at all clear to precisely which questions the clamped-nuclei Hamiltonian provides the answer and a further discussion of the properties of the Coulomb Hamiltonian is required before the clamped nuclei problem can be put into a form proper for yielding a potential. There are two main ways in which such a discussion can be attempted. If it is desired to stay with the Coulomb Hamiltonian in its laboratory-fixed form then the solutions must be expressed in coherent states (wave-packet) form to allow for their continuum nature. If the solutions are required as discrete forms, then the translational motion must be separated from the Coulomb Hamiltonian and the solutions of the remaining translationally invariant part must be used. It is in this last approach that it is easiest to make contact with the arguments of [1] and which will be considered in the following section.

## 2.1 The separation of translational motion

All that is needed to remove the centre of mass motion from the full molecule Hamiltonian is a linear point transformation symbolized by

$$(\mathbf{t}\xi) = \mathbf{x}\mathbf{V} \quad (9)$$

In Eq. 9  $\mathbf{t}$  is a 3 by  $N_T - 1$  matrix ( $N_T = N + A$ ) and  $\xi$  is a 3 by 1 matrix, so that the combined (bracketed) matrix on the left of Eq. 9 is 3 by  $N_T$ .  $\mathbf{V}$  is an  $N_T$  by  $N_T$  matrix which,

from the structure of the left side of Eq. 9, has a special last column whose elements are

$$V_{iN_T} = M_T^{-1}m_i, \quad M_T = \sum_{i=1}^{N_T} m_i \quad (10)$$

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

$$\xi = M_T^{-1} \sum_{i=1}^{N_T} m_i \mathbf{x}_i \quad (11)$$

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

$$\sum_{i=1}^{N_T} V_{ij} = 0, \quad j = 1, 2, \dots, N_T - 1 \quad (12)$$

on each remaining column of  $\mathbf{V}$  and it is easy to see that Eq. 12 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

$$\mathbf{x} = (\mathbf{t}\xi)\mathbf{V}^{-1} \quad (13)$$

exists. Every element of the bottom row of  $\mathbf{V}^{-1}$  must be the same and constant because of Eq. 12 and, without loss of generality, may be required to be

$$(\mathbf{V}^{-1})_{N_T i} = 1 \quad i = 1, 2, \dots, N_T \quad (14)$$

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

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

The Hamiltonian Eq. 3 in the new coordinates becomes

$$\begin{aligned} H(\mathbf{t}, \xi) &= -\frac{\hbar^2}{2} \sum_{i=1}^{N_T-1} \frac{1}{\mu_{ii}} \nabla^2(\mathbf{t}_i) - \frac{\hbar^2}{2} \sum_{i,j=1}^{N_T-1} \frac{1}{\mu_{ij}} \vec{\nabla}(\mathbf{t}_i) \cdot \vec{\nabla}(\mathbf{t}_j) \\ &\quad + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N_T} \frac{Z_i Z_j}{r_{ij}(\mathbf{t})} - \frac{\hbar^2}{2M_T} \nabla^2(\xi) \\ &= H'(\mathbf{t}) - \frac{\hbar^2}{2M_T} \nabla^2(\xi) \end{aligned} \quad (16)$$

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

$$1/\mu_{ij} = \sum_{k=1}^{N_T} m_k^{-1} V_{ki} V_{kj}, \quad i, j = 1, 2, \dots, N_T - 1 \quad (17)$$

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

$$r_{ij}(\mathbf{t}) = \left( \sum_{\alpha} \left( \sum_{k=1}^{N_T-1} \left( (\mathbf{V}^{-1})_{k\alpha} - (\mathbf{V}^{-1})_{ki} \right) t_{\alpha k} \right)^2 \right)^{1/2} \quad (18)$$

In Eq. 16 the  $\vec{\nabla}(\mathbf{t}_i)$  are gradient operators expressed in the Cartesian components of  $\mathbf{t}_i$  and the last term represents the

centre-of-mass kinetic energy. Because 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

$$T(\xi)\Psi(\mathbf{t}) \quad (19)$$

where  $\Psi(\mathbf{t})$  is a wavefunction for the Hamiltonian  $H'(\mathbf{t})$ , Eq. 16, which will be referred to as the *translationally invariant* Hamiltonian. The eigenfunctions of this Hamiltonian will be basis functions for irreps of the orthogonal group in three dimensions and for the various symmetric groups of the sets of identical particles.

It should be emphasized 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 Eqs. 10 and 12. In particular, it is perfectly possible to put the kinetic energy operator into diagonal form by choosing an orthogonal matrix  $\mathbf{U}$  that diagonalizes 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 Eq. 18, the practical problem with any choice of  $\mathbf{V}$  is the complicated form given to the potential operator.

## 2.2 Choosing electronic and nuclear variables in the translationally invariant Hamiltonian

In order to identify the electrons, let the translationally invariant electronic coordinates be chosen with respect to the centre-of-nuclear mass

$$\mathbf{t}_i^e = \mathbf{x}_i^e - \mathbf{X}, \quad \mathbf{X} = M^{-1} \sum_{i=1}^A m_i \mathbf{x}_i^n, \quad M = \sum_{i=1}^A m_i$$

in the case of the atom  $A = 1$  and the origin is the nucleus. Other coordinate choices are possible, but this choice avoids a term in the kinetic energy operator coupling the electronic and nuclear variables and which allows the electronic part of the potential to be written in terms of the electronic variables and the clamped nuclei positions (see [2, 10, 11]).

There is no need to specify the proposed  $A-1$  translationally invariant nuclear variables  $\mathbf{t}^n$  other than to say that they are expressed entirely in terms of the laboratory nuclear coordinates by means of a matrix  $\mathbf{V}^n$  exactly like  $\mathbf{V}$  in Eq. 9, but with side  $A$  and with  $M$  in the place of  $M_T$  and  $\mathbf{X}$  in the place of  $\xi$ . It is also sometimes useful to define a set of redundant Cartesian coordinates

$$\bar{\mathbf{x}}_i^n = \mathbf{x}_i^n - \mathbf{X}, \quad i = 1, 2, \dots, A, \quad \text{so that } \sum_{i=1}^A m_i \bar{\mathbf{x}}_i^n = 0 \quad (20)$$

Of course the laboratory nuclear variable  $\mathbf{x}_i^n$  cannot be completely written in terms of the  $A-1$  translationally invariant coordinates arising from the nuclei, but in the electron-nucleus attraction and in the nuclear repulsion terms the centre-of-nuclear mass term appears in both variables in the term and cancels. For ease of writing,  $\mathbf{x}_i^n$  will continue to be used in those terms but it should be remembered that what is written in such a term is really a function of the translationally invariant coordinates defined by the nuclear coordinates. On making this choice of electronic coordinates the electronic part of Eq. 16 is

$$\begin{aligned} H^e(\mathbf{x}^n, \mathbf{t}^e) = & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{|\mathbf{t}_j^e - \bar{\mathbf{x}}_i^n|} \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{|\mathbf{t}_i^e - \mathbf{t}_j^e|} + \sum_{i,j=1}^A \frac{Z_i Z_j}{|\bar{\mathbf{x}}_i^n - \bar{\mathbf{x}}_j^n|} \quad (21) \end{aligned}$$

The electronic Hamiltonian is properly translationally invariant and would yield the usual form where the nuclear masses increase without limit. It has been noted [4] that to take Eq. 21 as the electronic Hamiltonian is inconsistent with a power series solution in terms of the inverse nuclear mass because the Hamiltonian itself already contains a term in the first power of the inverse nuclear mass. There is however no need to consider this term at the first stage of development of a solution to the full problem and it can be included at the point where terms of similar magnitude are considered. The remaining part of Eq. 21 is then exactly the same as the clamped nuclei form. The clamped nuclei form can be deployed consistently in an account of solutions to the full problem only if a uniform translational factor is included in the full solution or if the translational motion of the centre-of-mass is subtracted, as in the work of Nakai [12] (see also [13]), to yield a problem from which the continuous spectrum has been removed.

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

$$K^n(\mathbf{t}^n) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}(\mathbf{t}_i^n) \cdot \vec{\nabla}(\mathbf{t}_j^n) \quad (22)$$

with the inverse mass matrix defined as a special case of Eq. 17 involving only the original nuclear variables.

Both Eqs. 21 and 22 are invariant under any orthogonal transformation of both the electronic and nuclear variables. If the nuclei are clamped in Eq. 21 then invariance remains

only under those orthogonal transformations of the electronic variables that can be re-expressed as changes in the positions of nuclei with identical charges while maintaining the same nuclear geometry. The form of Eq. 21 remains invariant under all permutations of the electronic variables and is invariant under permutation of the variables of those nuclei with the same charge. Thus, if an electronic energy minimum is found at some clamped nuclei geometry there will be as many minima as there are permutations of identically charged nuclei.

The kinetic energy operator of Eq. 22 is invariant under all orthogonal transformations of the nuclear variables and under all permutations of the variables of nuclei with the same mass.

The splitting of the Hamiltonian into two parts breaks the symmetry of  $H'(\mathbf{t})$  for each part exhibits only a sub-symmetry of the full problem. If wavefunctions derived from approximate solutions to Eq. 21 are to be used to construct solutions to the full problem utilizing Eq. 22, care will be needed to couple the sub-symmetries to yield solutions with full symmetry.

### 2.2.1 Atoms

For the atom there is no nuclear kinetic energy part and, denoting the nuclear mass by  $m_n$ , the full Hamiltonian is simply the electronic Hamiltonian.

$$H^e(\mathbf{t}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2m_n} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) - \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \frac{Z_i}{|\mathbf{t}_j^e|} + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N'} \frac{1}{|\mathbf{t}_i^e - \mathbf{t}_j^e|} \quad (23)$$

The electronic problem for the atom of Eq. 23 has exactly the same form and symmetry as the full problem and meets the requirements for Kato self-adjointness, for there is a kinetic energy operator in all of the variables that are used to specify the potential terms. This would continue to be the case where the nuclear mass increases without limit.

The atom is sometimes used as an illustration when considering the original form of the Born-Oppenheimer approximation, as in [14], but the only aspect of the approximation that can be thus illustrated is the translational motion part and that is easily considered in first order by treating the second term in Eq. 23 as a perturbation to the solution obtained using an infinite nuclear mass. The inclusion of this term in this way is analogous to making the usual *diagonal Born-Oppenheimer* correction that can be made exactly in the case of any one-electron atom (see [15]). As noted in Ref. [1], it is usually made approximately simply by including the diagonal part of the mass

polarization term (the second term on the right in Eq. 23) to produce an electronic reduced mass

$$1/\mu_e = 1/m_n + 1/m$$

in the place of  $1/m$ .

The Hamiltonian Eq. 23 maintains full symmetry and is invariant under electronic permutations and under rotation-reflections of the electronic coordinates. Trial functions are usually constructed from atomic orbitals and from their spin-orbitals. Permutational antisymmetry is achieved by forming from the spin-orbitals, Slater determinants. Rotational symmetry is usually realized using orbitals that form bases for representations of the rotation group  $SO(3)$  by subsequent vector-coupling. Spin-eigenfunctions too are achieved by vector coupling.

### 2.2.2 Molecules

For a molecule there is always a nuclear kinetic energy part to the operator and therefore self-adjointness must be achieved by explicit construction. Although the discussion that follows is, for the most part, quite general, explicit consideration is confined to the diatomic in order to avoid overburdening the exposition with details. For a system with two nuclei, the natural nuclear coordinate is the internuclear distance which will be denoted here simply as  $\mathbf{t}$ . When needed to express the electron-nuclei attraction terms,  $\mathbf{x}_i^e$  is simply of the form  $\alpha_i \mathbf{t}$  where  $\alpha_i$  is a signed ratio of the nuclear mass to the total nuclear mass. In the case of a homonuclear system  $\alpha_i = \pm \frac{1}{2}$ . The di-nuclear electronic Hamiltonian is

$$H^e(\mathbf{t}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2(m_1 + m_2)} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) - \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \left( \frac{Z_1}{|\mathbf{t}_j^e + \alpha_1 \mathbf{t}|} + \frac{Z_2}{|\mathbf{t}_j^e + \alpha_2 \mathbf{t}|} \right) + \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N'} \frac{1}{|\mathbf{t}_i^e - \mathbf{t}_j^e|} + \frac{Z_1 Z_2}{R}, \quad R = |\mathbf{t}|, \quad (24)$$

while the nuclear kinetic energy part is:

$$-\frac{\hbar^2}{2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \nabla^2(\mathbf{t}) \equiv -\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{t}). \quad (25)$$

The electronic part is not self-adjoint in the manner prescribed by Kato because it contains no kinetic energy terms involving the nuclear variable which would dominate the potential energy terms. The full Hamiltonian would not be Kato self-adjoint if both nuclear masses were to increase without limit either. It is seen from Eq. 25, however, that if only one nuclear mass increases without limit then the kinetic energy term in the nuclear variable remains in the

full problem and so the Hamiltonian remains self-adjoint in the Kato sense.

The di-nuclear case has been considered numerically by Frolov [16] in a study of the hydrogen molecular ion. In extremely accurate calculations on the discrete states of this system, he investigated what happened when first one and then two nuclear masses are increased without limit. He showed that when one mass increased without limit, any discrete spectrum persisted but when two masses were allowed to increase without limit, the Hamiltonian ceased to be well defined and this failure led to what he called *adiabatic divergence* in attempts to compute discrete eigenstates. This sort of behaviour would certainly be anticipated from the present discussion.

Irrespective of any choices made for the nuclear masses, the electronic Hamiltonian Eq. 24 becomes self-adjoint in the Kato sense if the nuclei are clamped for then the nuclear variables in the potential terms become constants and the only variables are the electronic ones. So the clamped nuclei potential is properly dominated by the electronic kinetic energy. Thus, the usual practice of clamped nuclei electronic structure calculations is a perfectly proper one.

Writing the variable  $\mathbf{t}$  in spherical polar coordinates,  $R$ ,  $\beta$  and  $\alpha$  where  $t_z = R \cos \beta$ , where the clamped nucleus Hamiltonian is to be used to define a potential, it is easily seen that for  $\mathbf{t} = \mathbf{a}$ ,  $R = a$  then

$$E^{\text{cn}}(\mathbf{a}) = V(a) \quad (26)$$

so that the potential has the form  $V(R)$ . But the potential is not just a curve, it is a series of spherical shells of rotation swept out by the curve by all choices of  $\beta$  and  $\alpha$ . It is thus a genuine central-field potential. If the internuclear distance is fixed but  $\mathbf{a}$  allowed to rotate or invert then  $E^{\text{cn}}(\mathbf{a})$  is a sphere of constant energy as swept out by the variables  $\beta$  and  $\alpha$  at radius  $a$ . If  $\mathbf{a}$  is oriented so as to define a  $z$ -axis then  $E^{\text{cn}}(\mathbf{a})$  will take the same value at  $+a_z$  and  $-a_z$  so that there is a minimum at  $+a_z$  then there will be another at  $-a_z$ . The electronic Hamiltonian is not invariant under inversion of the nuclear variables alone unless the two nuclei have identical charges in which case inversion and permutation will have identical effects. In differential geometry terms, the potential is homeomorphic to  $S^2$ .

The Hamiltonian Eq. 24 is invariant under all rotations of the electronic coordinates about the internuclear axis and all reflections in a plane containing the internuclear axis. The electronic states can be labelled by a quantum number  $m$  which can take the values  $0, \pm 1, \pm 2$  and so on corresponding to  $z$ -component of the electronic angular momentum about the internuclear axis.

It is easily seen that the potential will tend to increase without limit as  $R \rightarrow 0$  but the behaviour as  $R \rightarrow \infty$  presents a problem. To see this, consider the asymptotic behaviour

of the electron–nucleus potential terms in the case of the one-electron homonuclear di-hydrogen molecule. The electronic coordinate is

$$\mathbf{t}^e = \mathbf{x} - \frac{1}{2}(\mathbf{x}_1^n + \mathbf{x}_2^n) \quad (27)$$

where  $\mathbf{x}$  is the laboratory coordinate of the electron.

As the internuclear distance becomes very large, the nuclear repulsion term becomes very small and one would expect the trial wave function to approach the wave function for a one-electron ion corresponding to one of the atoms. Thus, one might expect the lowest energy wavefunction to be of the form

$$N e^{-cr}, \quad \mathbf{r} = \mathbf{x} - \mathbf{x}_1^n, \quad r = |\mathbf{r}|$$

for instance. However, working in the chosen coordinate set

$$\mathbf{r} = \mathbf{t}^e - \frac{1}{2}\mathbf{t}$$

so that the expected asymptotic electronic solution could be expressed only in terms of both the electronic and nuclear variables. This does not, of course, mean that the potential cannot approach the required value. It simply means that it cannot do so in any calculation in which the trial functions are confined to electronic functions whose variable origin is at the centre-of-nuclear-mass.

This sort of difficulty is a general one and obviously not confined simply to one-electron diatomic molecules. It would clearly be unwise to attempt to approximate solutions for molecules at energies close to their dissociation limits in terms of electronic coordinates with origin at the centre-of-nuclear-mass. A trial function for the general case of the Born-Huang form

$$\psi(\mathbf{t}^n, \mathbf{t}^e) = \sum_p \Phi_p(\mathbf{t}^n) \psi_p(\mathbf{t}^n, \mathbf{t}^e) \quad (28)$$

where the  $\mathbf{t}^e$  have an origin at the centre-of-nuclear mass could, therefore, approximate only a limited region of the spectrum of the full problem.

This difficulty cannot be solved by working in the laboratory frame. The solution to the full problem would be defined in terms of a three-dimensional subspace expressed in terms of a translation variable and a  $3(N_T - 1)$ -dimensional subspace expressible in terms of translationally invariant variables. Translationally invariant variables must involve at least a pair of variables and so there must be at least one such variable which involves a laboratory frame electron and a laboratory frame nuclear variable. All this can be easily illustrated by considering the exact ground-state wavefunction of the hydrogen atom, as is seen in [4].

This point is developed in more detail by Hunter [17] in a paper considering to what extent a separation of electronic and nuclear motion would be possible if the exact

solution to the full problem was actually known wherever the exact solution is known, Hunter argues [18] that it could be written in the form

$$\psi(\mathbf{t}^n, \mathbf{t}^e) = \chi(\mathbf{t}^n)\phi(\mathbf{t}^n, \mathbf{t}^e) \quad (29)$$

defining a nuclear wave function by means of

$$|\chi(\mathbf{t}^n)|^2 = \int \psi(\mathbf{t}^n, \mathbf{t}^e)^* \psi(\mathbf{t}^n, \mathbf{t}^e) d\mathbf{t}^e$$

then, provided this function has no nodes,<sup>2</sup> an “exact” electronic wavefunction could be constructed as

$$\phi(\mathbf{t}^n, \mathbf{t}^e) = \frac{\psi(\mathbf{t}^n, \mathbf{t}^e)}{\chi(\mathbf{t}^n)} \quad (30)$$

if the normalization choice

$$\int \phi(\mathbf{t}^n, \mathbf{t}^e)^* \phi(\mathbf{t}^n, \mathbf{t}^e) d\mathbf{t}^e = 1$$

is made. In fact, it is possible [17] to show that  $\chi$  must be nodeless even though the usual approximate nuclear wavefunctions for vibrationally excited states do have nodes. The electronic wavefunction of Eq. 30 is therefore properly defined and a potential energy surface could be defined in terms of it as

$$U(\mathbf{t}^n) = \int \phi(\mathbf{t}^n, \mathbf{t}^e)^* H'(\mathbf{t}^n, \mathbf{t}^e) \phi(\mathbf{t}^n, \mathbf{t}^e) d\mathbf{t}^e \quad (31)$$

with  $H'$  defined as in Eq. 16 with  $\mathbf{t}$  composed of  $\mathbf{t}^e$  and  $\mathbf{t}^n$ . Although no exact solutions to the full problem are known for a molecule, some extremely good approximate solutions are known for excited vibrational states of  $H_2$  and Czub and Wolniewicz [19] took such an accurate approximation for an excited vibrational state in the  $J = 0$  rotational state of  $H_2$  and computed  $U(R)$ . They found strong spikes in the potential close to two positions at which the usual wave function would have nodes. To quote [19]

This destroys completely the concept of a single internuclear potential in diatomic molecules because it is not possible to introduce on the basis of non-adiabatic potentials a single, approximate, mean potential that would describe well more than one vibrational level.

It is obvious that in the case of rotations the situation is even more complex.

Bright Wilson suggested [20] that using the clamped nucleus Hamiltonian instead of the full one in Eq. 31 to define the potential might avoid the spikes, but Hunter in [17] showed why this was unlikely to be the case and

<sup>2</sup> A similar requirement must be placed on the denominator in Eq. 12 of Ref. [4] for the equation to provide a secure definition.

Cassam-Chenai [21] repeated the work of Czub and Wolniewicz using an electronic Hamiltonian and showed that exactly the same spiky behaviour occurred. However, Cassam-Chenai showed, as Hunter had anticipated, that if one simply ignored the spikes, the potential was almost exactly the same as would be obtained by deploying the electronic Hamiltonian in the usual way. This would seem to be consistent too with the earlier work of Pack and Hirschfelder [22].

Although the spiky nature of an “exact” potential has been demonstrated explicitly only for  $J = 0$  states of a small diatomic molecule, there is no reason to suppose that their occurrence is not general. Matters would be further complicated by rotational motion. Thus, the demonstrably smooth potentials generated by solving an electronic problem are simply computationally useful intermediates in a solution to the full problem. It would therefore seem unwise to assign too much weight to them in explaining chemical structure.

In the standard approach to solving the nuclear motion part of the diatomic problem, the potential  $V(R)$  is chosen and the nuclear motion Hamiltonian becomes

$$-\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{t}) + V(R) \quad (32)$$

Expressing this Hamiltonian in spherical polar coordinates, one obtains the usual form

$$-\frac{\hbar^2}{2\mu} \left( \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} L^2 + V(R) \quad (33)$$

where  $L$  is the operator for the angular part of the nuclear motion. The angular part of the solution is known analytically and the solution of the nuclear motion problem involves only the variable  $R$ .

The eigensolutions to this problem are quite naturally eigenvalues of the nuclear angular momentum and can easily be chosen with the required permutational symmetry. But things are not quite so clear for the electronic part of the problem because one does not in practice have a form which is explicit in the nuclear variables as it is computed only at fixed nuclear geometries. It is easy to achieve the correct permutational symmetry for the electronic part of the function at each and every nuclear geometry, but it is not at all easy to see how the electronic angular momentum of the functions could be coupled to the nuclear angular momentum to produce the required total angular momentum eigenfunctions.

In trying to deal with the rotational motion, it is possible to reformulate the diatomic problem to exhibit explicitly the angular symmetry of the Hamiltonian. As shown in [23] and, in a somewhat more general way in [24] it is possible to define an internal coordinate system by a transformation that makes the internuclear vector  $\mathbf{t}$  the  $z$ -axis in a

right-handed coordinate system and in this system the electronic Hamiltonian Eq. 24 becomes

$$-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{r}_i) - \frac{\hbar^2}{2(m_1 + m_2)} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{r}_i) \cdot \vec{\nabla}(\mathbf{r}_j) + V(R, \mathbf{r}) \quad (34)$$

with

$$V(R, \mathbf{r}) = \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N \frac{1}{r_{ij}} + \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_2}{R} - \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \left( \frac{Z_1}{r_{j1}(R)} + \frac{Z_2}{r_{j2}(R)} \right) \quad (35)$$

where the  $\mathbf{r}_i$  is the electronic variables expressed in the transformed system. In this formulation the  $\mathbf{t}$  orients freely and “clamping the nuclei” comes down to simply choosing  $R = a$ . A clamped nuclei solution of Eq. 34 would lead to a clamped nucleus energy

$$E^{\text{cn}}(a) = V(a) \quad (36)$$

rather than the form given by Eq. 26. Thus, any minima in  $V(a)$  would not be duplicated by the requirement of rotational invariance. Inversion is achieved by means of

$$\beta \rightarrow \pi - \beta, \alpha \rightarrow \pi + \alpha$$

and thus involves just the angular part of the formulation. An identical operation achieves the nuclear permutation. The electronic Hamiltonian is invariant under neither operation unless the nuclei have identical charge.

The nuclear kinetic energy operator of Eq. 25 becomes

$$-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2} D_1(\alpha, \beta, \mathbf{r}) \quad (37)$$

with

$$D_1(\alpha, \beta, \mathbf{r}) = \left[ (\mathbf{J}_x - l_x)^2 + (\mathbf{J}_y - l_y)^2 + \frac{\hbar}{i} \cot \beta (\mathbf{J}_y - l_y) \right]$$

where the electronic angular momentum is

$$l = \sum_{i=1}^N l(i) = \frac{\hbar}{i} \sum_{i=1}^N \mathbf{r}_i \times \frac{\partial}{\partial \mathbf{r}_i} \quad (38)$$

and the total angular momentum operator is denoted  $\mathbf{J}$  and involves both the electronic and nuclear variables in such a way that  $\mathbf{J}_z = l_z$ . The Jacobian for this transformation is

$$R^2 \sin \beta$$

It is seen that in this formulation any solution of the clamped nuclei form of the electronic Hamiltonian Eq. 34 will give rise to a potential which is simply a curve and not a surface of rotation. However, the angular part of the nuclear kinetic energy operator now involves the electronic

angular momentum so that the electronic motion and the overall rotational motion are coupled.

The electronic wave function in this case has the same axial symmetry as in the previous case and is characterized by the quantum number  $m$ . However, the states can no longer be regarded as occurring in degenerate pairs for  $m > 0$ . This is because in the diatomic  $l_z$  is the  $z$ -component of the *total* angular momentum so  $m$  can take integer values lying between  $J$  and  $-J$  where  $J$  is the *total* angular momentum. There is no a priori reason to believe that these states are degenerate, or degenerate in pairs. In fact the coupling of the electronic and nuclear angular momenta lifts the  $m$  degeneracy and the Hamiltonian becomes a system of  $2J + 1$  coupled partial differential equations. The phenomenon of  $\Lambda$  doubling in the molecular spectrum of a diatomic is explained by this coupling.

Although the interchange of the nuclear variables would change neither  $\mu$  nor  $R$  even if the nuclear masses were distinct, it would change  $\alpha$  and  $\beta$  as seen above and would change the angular part of the operator Eq. 37 and the operator is not invariant under such changes unless the nuclear masses are the same.

In the first of the two possible ways of looking at the diatomic, one remains in the Cartesian product space  $R^3 \times R^{3N}$  and it is thus necessary to give some explicit consideration to the angular properties of solutions to the electronic part of the problem. If the usual approach were taken to approximating solutions to the nuclear motion Hamiltonian using sums of products of electronic and nuclear parts, a typical term in the sum used as trial function for the form 33 would be

$$\phi_{pm}(\mathbf{r}^e, R)^L \Phi_{pm}(R) \Theta_{Lm}(\beta, \alpha) \quad (39)$$

where  $p$  denotes an electronic state and  $L$  the nuclear angular momentum quantum number. There are no operators in the nuclear motion part of the problem which explicitly couple the electronic and nuclear motions. It is thus possible to represent for any electronic state, any number of rotational states specified by values of  $L$ , without considering any coupling.  $L$  in Eq. 24 is not the total angular momentum operator and so a description of rotational motion given in these terms yields only an approximate quantum number.

If one transforms to the manifold  $R_+ \times S^2 \times R^{3N}$  then one can consider explicitly the rotational coupling of electronic and angular motions. The fact that the transformation is to a manifold rather than a vector space means that any operator built using coordinates defined on the manifold will be well defined only where the Jacobian for the transformation does not vanish. This does not cause great problems here because the only places where the Jacobian vanishes are when  $R = 0$  and where  $\beta = 0$  and



$\beta = \pi$ . The region around  $R = 0$  is inaccessible because of the nuclear repulsion term and the exact angular wavefunctions take care of the problem with  $\beta$ .

It would not be consistent to use only a single term in a product approximation for a trial for the form 37 with a potential  $V(R)$  except in considering a  $J = 0$  state. Here, the minimum consistent product approximation is

$$\sum_{m=-J}^J \phi_{pm}(\mathbf{r}, R)^J \Phi_{pm}(R) \Theta_{Jm}(\beta, \alpha). \quad (40)$$

It is only for  $J = 0$  states that the forms 39 and 40 are the same.

Of course the angular momentum coupling in Eq. 40 implies a coupling of different electronic states, between  $\Sigma$  and  $\Pi$  states or  $\Sigma$  and  $\Delta$  states for example. To allow explicitly for that possibility, Eq. 40 should really be extended to

$$\sum_{m=-J}^J \sum_{pm} \phi_{pm}(\mathbf{r}, R)^J \Phi_{pm}(R) \Theta_{Jm}(\beta, \alpha) \quad (41)$$

where the electronic state is denoted as  $pm$  to indicate that the state must have quantum number  $m$ . Thus for  $J = 2$ , one would need at least five electronic states.

### 3 Which is the “correct” clamped-nuclei Hamiltonian?

There is clearly a choice between the forms 24 and 34, and although in the clamped nuclei approximation both would yield the same energies for any chosen internuclear separation  $a$ , the resulting energy would be a potential for two quite different situations.

To generalize from the diatomic case, if the usual approach was taken to approximating solutions to the nuclear motion Hamiltonian using sums of products of electronic and nuclear parts a typical term in the sum used as trial function for the form 33 would be

$$\phi_p(\mathbf{t}^e, \mathbf{t}^n) \Phi_p(\mathbf{t}^n) \quad (42)$$

where  $p$  denotes an electronic state. The solutions are on the Cartesian product space  $R^{3A-3} \times R^{3N}$ . There is again no explicit coupling of the nuclear motion to the electronic and it is thus possible to represent for any electronic state, any number of rotational states. It is only in the diatomic case that the nuclear angular momentum can be realized explicitly as part of the nuclear kinetic energy so it is neither generally possible to choose  $\Phi$  directly as an eigenfunction of the nuclear angular momentum, nor is it possible to choose  $\phi$  directly as an eigenfunction of the electronic angular momentum.  $\phi$  as usually computed belongs to the totally symmetric representation of the symmetric group of each set of nuclei with identical

charges.  $\Phi$  could then be a basis function for an irreducible representation of the symmetric group for each set of particles with identical masses if the permutational symmetry was properly considered in solving the nuclear motion problem.

Clamped nuclei calculations are usually undertaken so as to yield a potential that involves no redundant coordinates. Thus, a translationally invariant electronic Hamiltonian like Eq. 24 would actually generate a more general potential than this. A clamped nuclei potential is therefore more properly associated with the electronic Hamiltonian after the separation of rotational motion like Eq. 34 than with the merely translationally invariant one. With this choice again, the minimum consistent product approximation is

$$\sum_{m=-J}^J \phi_{pm}(\mathbf{r}, \mathbf{R})^J \Phi_{pm}(\mathbf{R}) |JMm\rangle \quad (43)$$

where  $\mathbf{R}$  represents the  $3A-6$  internal coordinates invariant under all orthogonal transformations of the  $\mathbf{t}^n$  and  $|JMm\rangle$  is an angular momentum eigenfunction. The general solutions are on the manifold  $R^{3A-6} \times S^3 \times R^{3N}$  though for triatomic because the three nuclear positions define a plane, the internal coordinate part of the manifold is confined to  $R_+ \times R^2$ . It is only in the diatomic case that the electronic variables play a direct part in the specification of the angular momentum eigenfunctions and therefore there is only one internal coordinate. However, the Coriolis coupling terms in the angular part of the Hamiltonian contain terms in the electronic angular momentum so coupling of the electronic motion to the angular motion would still be anticipated (see Sections V and VI of Ref. [11]). It is only for  $J = 0$  states that the forms 39 and 40 are the same. Although the angular momentum coupling could imply a coupling of different electronic states, as it certainly does in a diatomic, it is not obviously implied in the general case. To achieve permutational symmetry in the nuclear motion part of the wave function would in the general case be very tricky. The nuclei are identified in the process of defining a body-fixed frame to describe the rotational motion, even if they are identical. If only a subset of a set of identical nuclei were used in such a definition, some permutation of the nuclear variables would induce a change in the definition of the body-fixed frame and thus spoil the rotational separation. Thus, permutations of identical nuclei are considered usually only if such permutations correspond to point-group operations which leave the body-fixing choices invariant.

If one considers the clamped nuclei Hamiltonian as providing input for the full Hamiltonian in which the rotational motion is made explicit, the basic nuclear motion problem should be treated as a  $2J + 1$ -dimensional

problem. If this is done then the translational and rotational symmetries of the full problem are properly dealt with. However, the solutions are not generally basis functions for irreps of the symmetric groups of sets of identical nuclei except for such sub-groups as constitute the point groups used in frame fixing. This restriction of the permutations is usually assumed justified by appealing to the properties of the potential surface. The idea here was introduced by Longuet-Higgins [25] and is widely used in interpreting molecular spectra.

As noted earlier, the original attempts to justify the Born-Oppenheimer and the Born approaches from the full Coulomb Hamiltonian lack secure mathematical foundations. So far there have been no attempts to make the foundations of the Born approach mathematically secure. However, the coherent states approach has been used to give mathematically secure accounts of surface crossings and a review of the work here can be found in [26]. It seems very unlikely that it would be possible to provide a secure foundation for the Born approach in anything like manner in which it is usually presented.

The Born-Oppenheimer approximation, whose validity depends on there being a deep enough localized potential well in the electronic energy, has however been extensively treated. The mathematical approaches depend upon the theory of fiber bundles and the electronic Hamiltonian in these approaches is defined in terms of a fiber bundle. It is central to these approaches, however, that the fiber bundle should be trivial, that is that the base manifold and the basis for the fibers be describable as a direct product of Cartesian spaces. This is obviously possible with the decomposition choice made for Eq. 42 but not obviously so in the choice made for Eq. 43.

The Born-Oppenheimer approach has been put on a secure foundation for diatomics with solutions of the form 39 in work which is described in a helpful context in [27]. For solutions like Eq. 40, it is possible that more than one vector (coordinate) space can be constructed on it because the transformation is to a manifold. In fact, two-coordinate spaces are possible on  $S^2$  a trivial one and a twisted one, the latter associated with the possibility of an electronic wavefunction with a Berry phase and the “twisted” solutions are accounted for in [28].

A mathematically satisfactory account for polyatomics in an approach based on the Eq. 43 has not yet been provided but it has proved possible to provide one based on the Eq. 42 (see [29]). Because the nuclear kinetic energy operator in the space  $R^{3A-3}$  cannot be expressed in terms of the nuclear angular momentum, it is not possible in this formulation to separate the rotational motion from the other internal motions. This work also considers the possibility that there are two minima in the potential as indeed there would be because of inversion symmetry if the potential

minimum were at other than a planar geometry. It does not, however, consider the possibility of such multiple minima as might be induced by permutational symmetry. It might be possible to extend the two minima arguments to the multiple minima case and perhaps provide a mathematically secure account of the Longuet-Higgins approach to ignore some of the inconvenient permutations. This has not so far been attempted.

For a secure account to be given in terms of the separation (Eq. 43), which is what is really required if one is to use the clamped-nuclei electronic Hamiltonian, it would be necessary to consider more than one coordinate space. On the manifold  $S^3$ , at least two-coordinate spaces are required to span the whole manifold. The internal coordinates within any coordinate space for five or more particles are such that it is possible to construct two distinct molecular geometries at the same internal coordinate specification, so that a potential expressed in the internal coordinates cannot be analytic everywhere [30]. Even for triatomic systems, problems can arise [31].

It is also not clear at present that a multiple minima argument could be constructed to account for point-group symmetry in this context. It is possible to show (see Section IV of [11]) that in the usual Eckart form of the Hamiltonian for nuclear motion, permutations can be such as to cause the body-fixed frame definition to fail completely.

## 4 Conclusions

If it is wished to perform a clamped nuclei calculation on a molecule containing three or more nuclei, avoiding translations and rigid rotations, it is necessary to fix the values of six of the  $3A$  nuclear variables. In practice, this is usually done by choosing one nucleus,  $\mathbf{x}_1^n$ , at the origin, one nucleus,  $\mathbf{x}_2^n$ , defining an axis and a third,  $\mathbf{x}_3^n$ , defining a plane. Every possible geometry of the molecule can be specified with this choice, except those geometries in which the three nuclei are co-linear, but not every component of the  $3A$  variables will appear in the clamped nuclei electronic energy as six of them have been chosen to be zero. This means that even though the clamped nuclei electronic energy can be specified in terms of a molecular geometry in which the positions of  $A$  points can be given, the energy itself is a function of only the relative positions of a subset of the nuclei. Thus performing clamped nuclei calculations will not make possible the expression of the electronic energy in anything other than internal coordinates and the electronic energy when expressed in any set of internal coordinates, cannot be analytic everywhere. Thus, there cannot really be a “global” potential energy surface. In any case, as has been seen, the potential, even locally, cannot be regarded as an approximation to

anything in particular and thus should be treated simply as a convenient peg on which to hang further calculations. From this perspective, the further calculations should properly be ones in which the electronic Hamiltonian results from the full Hamiltonian in which the rotational motion has been made explicit. Such Hamiltonians have only a local validity and can be defined only where the Jacobian for the transformation to the rotational variables does not vanish. However, at present there is no satisfactory account of how nuclear permutational symmetry should be treated from this perspective, there is neither any secure mathematical justification of the Born-Oppenheimer approximation nor of the Born approach.

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

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