Theor Chem Acc (2012) 131:1215
DOI 10.1007/s00214-012-1215-x

REGULAR ARTICLE

Is there an exact potential energy surface?

Brian Sutcliffe

Received: 15 February 2012 / Accepted: 25 March 2012 / Published online: 15 April 2012

Abstract Transition state theory was introduced in the 1930s to account for chemical reactions. Central to this theory is the idea of a potential energy surface (PES). It was assumed that quantum mechanical computation, when it became possible, would yield such surfaces, but for the time being they would have to be constructed empirically. The approach was very successful. Nowadays, quantum mechanical ab initio electronic structure calculations are possible and from their results PESs can be constructed. Such surfaces are now widely used in the explanation of chemical reactions in place of the traditional empirical ones. It is argued here that theoretical basis of such PESs is not quite as clear as is usually assumed and that, from a quantum mechanical perspective, certain puzzles remain.

Keywords Potential energy surface · Schrödinger Coulomb Hamiltonian · Permutational symmetry

1 Introduction

From the standpoint of quantum mechanics, the potential energy surface (PES) arises from treating the nuclear variables of a collection of electrons and nuclei, formally described by the Schrödinger Coulomb Hamiltonian, as parameters rather than variables. The basis for this approach is nowadays taken to be the work of Born, which is most conveniently found in [1] but is often referred to as "making the Born–Oppenheimer approximation". In order to introduce notation, a brief resume of this well-known approach will be given here.

Born's approach begins from Schrödinger's Hamiltonian for a system of N variables, $\mathbf{x}_i^{\mathrm{e}}$, describing the electrons and another set of A variables, $\mathbf{x}_i^{\mathrm{n}}$, describing the nuclei and $N_T = N + A$.

When the nuclei are clamped at a particular fixed geometry specified by the constant vectors $\mathbf{a}_i, i = 1, 2, \ldots, A$, these constant vectors can be regarded as arising by assigning the values $\mathbf{a}_i$ to the nuclear variables $\mathbf{x}_i^{\mathrm{n}}$, in the full Schrödinger Hamiltonian.

$$\mathsf{H}^{\mathrm{cn}}(\mathbf{a}, \mathbf{x}^{\mathrm{e}}) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{x}_i^{\mathrm{e}}) - \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{A}\sum_{j=1}^{N}\frac{Z_i}{|\mathbf{x}_j^{\mathrm{e}} - \mathbf{a}_i|} + \frac{e^2}{8\pi\epsilon_0}{\sum_{i,j=1}^{L}}'\frac{1}{|\mathbf{x}_i^{\mathrm{e}} - \mathbf{x}_j^{\mathrm{e}}|} \tag{1}$$

The clamped nucleus problem has solutions of the form

$$\mathsf{H}^{\mathrm{cn}}(\mathbf{a}, \mathbf{x}^{\mathrm{e}})\psi_p^{\mathrm{cn}}(\mathbf{a}, \mathbf{x}^{\mathrm{e}}) = E_p^{\mathrm{cn}}(\mathbf{a})\psi_p^{\mathrm{cn}}(\mathbf{a}, \mathbf{x}^{\mathrm{e}}) \tag{2}$$

In the present context, it is customary to incorporate the nuclear repulsion energy into the clamped nuclei problem and to use the Hamiltonian

$$\mathsf{H}^{bo} = \mathsf{H}^{\mathrm{cn}}(\mathbf{a}, \mathbf{x}^{\mathrm{e}}) + \frac{e^2}{8\pi\epsilon_0}{\sum_{i,j=1}^{A}}'\frac{Z_iZ_j}{|\mathbf{a}_i - \mathbf{a}_j|} \equiv \mathsf{H} + \mathsf{V}^{\mathrm{n}}(\mathbf{a}) \tag{3}$$

The extra term here is merely an additive constant and so does not affect the form of the electronic wavefunction. It affects the spectrum of the clamped nucleus Hamiltonian only trivially by changing the origin of the clamped nucleus electronic energy so that,

---

Published as part of the special collection of articles celebrating theoretical and computational chemistry in Belgium.

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

$$E_p^{\mathrm{cn}}(\mathbf{a}) \rightarrow E_p^{\mathrm{cn}}(\mathbf{a}) + \mathsf{V}^{\mathrm{n}}(\mathbf{a}) = \mathsf{V}_p^{\mathrm{cn}}(\mathbf{a}) \tag{4}$$

If the clamped nuclei solutions were known for all values that could be taken by **a**, they would constitute the solution set $\psi_p^{\mathrm{cn}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}})$.

The full Hamiltonian may be written as

$$\mathsf{H}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) = \mathsf{K}^{\mathrm{n}}(\mathbf{x}^{\mathrm{n}}) + \mathsf{H}^{\mathrm{bom}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) \tag{5}$$

where K^{n} is the kinetic energy operator for the nuclei, which can be written symbolically as

$$\sum_{k=1}^{A} \frac{\mathsf{p}_k^{\mathrm{n}2}}{2m_k}$$

and, although Born does not explicitly require it, the Hamiltonian H^{bo} is implicitly generalised to allow for nuclear motion as

$$\mathsf{H}^{\mathrm{bom}}(\mathbf{x}^{n}, \mathbf{x}) = \mathsf{H}^{\mathrm{cn}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) + \frac{e^2}{8\pi\epsilon_0} {\sum_{i,j=1}^{A}}' \frac{Z_i Z_j}{|\mathbf{x}_i^{\mathrm{n}} - \mathbf{x}_j^{\mathrm{n}}|} \tag{6}$$

The eigenfunctions of this Hamiltonian are assumed to be of the form $\psi_i^{\mathrm{n}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}})$ generalising those of (2) and to lead to a potential $\mathsf{V}_p^{\mathrm{bom}}(\mathbf{x}^{\mathrm{n}})$ generalising that of (4). It is this Hamiltonian which is often referred to as the *electronic Hamiltonian*.

Assuming that full problem had eigenstates such that

$$\mathsf{H}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}})\psi(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) = E\psi(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}), \tag{7}$$

then the solutions could be expanded as a sum of products of the form

$$\psi(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) = \sum_p \Phi_p(\mathbf{x}^{\mathrm{n}})\psi_p^{\mathrm{bom}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}}) \tag{8}$$

where $\Phi_p(\mathbf{x}^{\mathrm{n}})$ describes the nuclear motion and $\psi_i^{\mathrm{n}}(\mathbf{x}^{\mathrm{n}}, \mathbf{x}^{\mathrm{e}})$ is an eigenfunction of the electronic Hamiltonian (6). However, the status of the electronic function is not entirely clear as will be seen shortly.

2 The mathematics of the Born approach

In 1951, Kato [2] established that the full (Coulomb) Hamiltonian, H , is essentially self-adjoint.[1] This property, which is stronger than Hermiticity, guarantees that the time evolution

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

of a Schrödinger wavefunction is unitary and so conserves probability [3]. 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 [4] is of the radial momentum operator $-i\hbar\partial/\partial r$ acting on functions $\phi(r)$, $\phi(0) = 0$ with $0 \le r < \infty$.

What Kato showed in Lemma 4 of his paper was that for a Coulomb potential V 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

$$||\mathsf{V}f|| \le a||\mathsf{T}_0 f|| + b||f||$$

and that a can be taken as small as is liked. Thus, the potential energy is bounded relatively to the kinetic energy.

Given this result, he proved in Lemma 5 that the usual operator has a unique self-adjoint extension and thus is indeed, for all practical purposes, self-adjoint and is bounded from below. The sort of problems that can arise if an operator is not self-adjoint or does not have a unique self-adjoint extension are discussed in an accessible way in [5].

In the present context, the important point to note is that the Coulomb term is small only in comparison with the kinetic energy term involving the same set of variables. So the absence of one or more kinetic energy terms from the Hamiltonian means that the Coulomb potential term cannot be treated as small and the Hamiltonian will no longer be self-adjoint in the way demonstrated by Kato. This is not because it ceases to be intrinsically self-adjoint but because the Hamiltonian ceases to be self-adjoint on the domain of the complete kinetic energy operator. It is thus a problem of the extension. This is not to say that there is anything wrong with solutions to the clamped nuclei problem (3). Here the nuclei are fixed and the potential involves only the electronic variables, and the only requirement for self-adjointness is that there be an electronic kinetic energy term for each potential term. It does however mean the Hamiltonian (6) (the *soi-disant* electronic Hamiltonian) is *not* self-adjoint in the Kato sense. The problem is essentially one of domain and to deal with that, the differential equation approach to the electronic problem must be replaced with an approach that starts from the clamped nuclei Hamiltonian.

3 Defining an electronic Hamiltonian

The full Hamiltonian is invariant under all uniform translations of the variables, under all orthogonal transformations of the variables and under the permutation of all variables that correspond to particles of equal charge and mass. It is the first of these invariances that has the most immediate consequences. It implies that the full Hamiltonian has a completely continuous spectrum arising from the free motion of the whole system (atom, molecule, ion or whatever) through space. Any bound-states corresponding

---

[1] The work was completed in 1944 and was actually received by the journal in October 1948.

to discrete values in the spectrum will be clouded by this continuum, which must be removed before attention can be focused on square integrable eigenfunctions. This can be done easily by separating the centre-of-mass motion by choosing the centre-of-mass coordinate and $N_T - 1$ translationally invariant coordinates and transforming the Hamiltonian to have a part corresponding to the free motion of the centre-of-mass and a part H' composed from the translationally invariant coordinates. Although it was not mentioned earlier, this is actually what Kato did and it was the translationally invariant Hamiltonian that he showed to be essentially self-adjoint. He also pointed out that his proof permitted a trivial extension to cover the full Hamiltonian, so what has been said about self-adjointness previously needs no modification. The use of a translationally invariant form poses a problem, however, because one variable has been lost when translational motion has been removed and the translationally invariant coordinates can consist of linear combinations of all the laboratory coordinates. The spectrum of H' is independent of linear combination choice but rather special choices must be made in order to obtain a set of coordinates in which the electronic and nuclear parts can be recognised and the permutational invariances retained. The general problem is discussed in [6]. However, for present purposes in order to identify the electrons let the translationally invariant electronic coordinates be chosen with respect to the centre-of-nuclear mass.

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

in the case of the atom $A = 1$ and the origin is the nucleus. There is no need to specify the proposed $A - 1$ translationally invariant nuclear variables $\mathbf{t}^{\mathrm{n}}$ other than to say that are expressed entirely in terms of the laboratory nuclear coordinates by means of a A by $A - 1$ matrix $\mathbf{V}^{\mathrm{n}}$ in which the elements of each column sum to zero.

The electronic Hamiltonian now becomes

$$\begin{aligned}\mathsf{H}'^{\mathrm{e}}(\mathbf{x}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) = &-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{t}_i^{\mathrm{e}}) - \frac{\hbar^2}{2M}\sum_{i,j=1}^{N}\vec{\nabla}(\mathbf{t}_i^{\mathrm{e}})\cdot\vec{\nabla}(\mathbf{t}_j^{\mathrm{e}}) \\ &- \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{A}\sum_{j=1}^{N}\frac{Z_i}{|\mathbf{t}_j^{\mathrm{e}} - \mathbf{x}_i^{\mathrm{n}}|} \\ &+ \frac{e^2}{8\pi\epsilon_0}\left(\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_i^{\mathrm{e}} - \mathbf{t}_j^{\mathrm{e}}|} + \sum_{i,j=1}^{A}{}' \frac{Z_i Z_j}{|\mathbf{x}_i^{\mathrm{n}} - \mathbf{x}_j^{\mathrm{n}}|}\right)\end{aligned} \tag{9}$$

where it is understood that the $\mathbf{x}_i^{\mathrm{n}}$ are to be realised by a suitable linear combination of the $\mathbf{t}_i^{\mathrm{n}}$. The electronic Hamiltonian is properly translationally invariant and would yield the usual form were the nuclear masses to increase without limit. Were the nuclear positions to be chosen directly as a translationally invariant set, it would be those values that would appear in the place of the nuclear variables.

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

$$\mathsf{K}^{\mathrm{n}}(\mathbf{t}^{\mathrm{n}}) = -\frac{\hbar^2}{2}\sum_{i,j=1}^{A-1}\frac{1}{\mu_{ij}}\vec{\nabla}(\mathbf{t}_i^{\mathrm{n}}).\vec{\nabla}(\mathbf{t}_j^{\mathrm{n}}) \tag{10}$$

with the inverse mass matrix $\boldsymbol{\mu}$ defined in terms of the inverse nuclear masses and the elements of $\mathbf{V}^{\mathrm{n}}$.

The self-adjointness of (9) requires consideration according to the number of nuclei. For an atom, there is no nuclear kinetic energy part and, denoting the nuclear mass by m_{n}, the full Hamiltonian is simply the electronic Hamiltonian.

$$\begin{aligned}\mathsf{H}'^{\mathrm{e}}(\mathbf{t}^{\mathrm{e}}) = &-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{t}_i^{\mathrm{e}}) - \frac{\hbar^2}{2m_{\mathrm{n}}}\sum_{i,j=1}^{N}\vec{\nabla}(\mathbf{t}_i^{\mathrm{e}})\cdot\vec{\nabla}(\mathbf{t}_j^{\mathrm{e}}) \\ &- \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\frac{Z_i}{|\mathbf{t}_j^{\mathrm{e}}|} + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_i^{\mathrm{e}} - \mathbf{t}_j^{\mathrm{e}}|}\end{aligned} \tag{11}$$

The electronic problem for the atom (11) has exactly the same form as the full problem and as required by the Kato self-adjointness conditions, 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 were the nuclear mass to increase without limit. The atom is sometimes used as an illustration when considering the original form of the Born–Oppenheimer approximation 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 (11) 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 *diagonal Born–Oppenheimer* correction and it can be made exactly in the case of any one-electron atom. The Born–Oppenheimer approach therefore plays no important part in the consideration of the eigenfunctions of an atomic problem. For systems containing more than a single nucleus, (9) can never be properly self-adjoint even if the nuclear masses increase without limit and so it cannot be used directly in attempting solutions to the full problem.

To turn now to how an electronic Hamiltonian might be defined properly for a system with more than a single nucleus, let it be assumed that a chosen set of $\mathbf{A}$ nuclear positions generate a set $\mathbf{b}$ of $A - 1$ translationally invariant nuclear coordinates. It can be seen that the electronic Hamiltonian (9) commutes with each of the $A - 1$ nuclear position variables. Think now of the molecular bound state space $\mathfrak{H}$ as the square integrable sections in the trivial fibre bundle $\mathbf{R}^{3(A-1)} \otimes \mathcal{L}^2(\mathbf{R}^{3N})$. A fibre bundle is trivial if the two spaces have an associated Cartesian product space. If the base space is a manifold that is only locally a coordinate space, the bundle would be only locally trivial. Here, however, the bundle is globally trivial since the base space is a global coordinate space [7].

The nuclear operator (which is the bare kinetic energy operator) acts in the base space, that is upon functions defined on $\mathbf{R}^{3(A-1)}$ and the electronic Hamiltonian acts only upon the fibre defined by the choice of **b**. (In this case the fibre is a vector space $\mathcal{L}^2(\mathbf{R}^{3N};\mathbf{b})$ and so the fibre bundle in this context is often called a vector bundle. The spaces for different **b** values, are distinct.)

Now write the full electronic Hamiltonian as a direct integral over the fibres.

$$\mathsf{H}'^{\mathrm{e}}(\mathbf{t}^{\mathrm{e}}) = \int^{\oplus} \mathsf{H}'^{\mathrm{e}}(\mathbf{b},\mathbf{t}^{\mathrm{e}})\mathrm{d}\mathbf{b} \tag{12}$$

where the $\mathbf{t}^n$ have been replaced by **b** within the integral, to emphasise that it is over fixed points that the "sum" is occurring.

Modern mathematically secure accounts of the Born–Oppenheimer approximation are given in terms of the electronic Hamiltonian defined as a direct sum and as such do not explicitly consider the requirement that the solutions provide basis functions for the orthogonal group in three dimensions nor is spin symmetry considered. They do not either consider the permutational invariance of the full problem. The arguments can however easily be extended to cover spin and permutational symmetry in the electronic part of the problem. They cannot however be easily extended to cover the full angular momentum symmetry and the nuclear permutation symmetry, except for diatomic molecules. The arguments are based on the idea of a potential provided by the electrons, just as are the traditional arguments, but not directly upon the idea of PES everywhere defined. The arguments require only that it is possible to define a potential sufficiently close to a particular nuclear configuration. Making such assumptions, it is possible to estimate how closely a solution constructed from these forms approximates an exact solution in the region of interest. Serious difficulties arise in such approaches when a unique potential cannot be defined, the situation usually called *surface crossing*. But even where there is a unique potential, it is not possible to use perturbation theory, as is traditionally done, to make the estimation. The best that can be done is by means of an asymptotic expansion of the WKB type.

The original Born–Oppenheimer argument has been reconsidered in a mathematically rigorous way by Klein et al. [8] assuming the potential consists of a single isolated potential well such that the electronic wavefunction effectively vanishes outside it. This assumption corresponds exactly to the original assumption of Born and Oppenheimer. It is not at present clear how these arguments could be extended to deal with multiple minima resulting from permutational invariance. Since no explicit consideration of rotational motion has been attempted, nothing can be said about the rotational motion of the system, though the effects of inversion symmetry are considered. This work is perhaps most usefully seen as a justification of the original Born–Oppenheimer conclusions for a system in which the nuclei are treated as identifiable particles in which electronic motion is unaffected by the rotational motion of the whole system.

It is perfectly proper to perform clamped nuclei electronic structure calculations to obtain electronic energies and wavefunctions, and if it were possible to construct from these a set of electronic wave functions $\psi_n^{\mathrm{e}}(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}})$ covering the whole translationally invariant space, then it would be perfectly proper to attempt a variational solution of the full problem (8) using nuclear-motion wave functions obtained using potentials constructed from the electronic energies. But it would simply be a variational solution valid in the energy region relevant to the potential. Such a solution would not have any particular symmetry under the permutation of identical nuclei nor would it show any particular rotational symmetry were the potential to be treated as rotationally invariant thus making it simply a function of nuclear geometry. Its status as an approximation to an exact solution would thus be somewhat uncertain.

For the present, let this uncertainty be ignored, to consider what might be inferred about a PES were an exact solution to the translationally invariant form of the Schrödinger Coulomb Hamiltonian actually known.

4 The PES from an exact solution?

The presentation of a presumed exact bound state solution of the Schrödinger Coulomb Hamiltonian as a product of an electronic and a nuclear-motion part has been considered both by Hunter [9] and, more recently, by Gross [10]. For the present purposes, the Hunter approach will be employed on the translationally invariant form of the Hamiltonian, given earlier. Were the exact solution known, Hunter argues that it could be written in the form

$$\psi(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}}) = \chi(\mathbf{t}^{\mathrm{n}})\phi(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}}) \tag{13}$$

defining a nuclear wave function by means of

$$|\chi(\mathbf{t}^{\mathrm{n}})|^2 = \int \psi(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}})^*\psi(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}})\mathrm{d}\mathbf{t}^{\mathrm{e}} \tag{14}$$

then, providing this function has no nodes,[2] an "exact" electronic wavefunction could be constructed as

---

[2] A similar requirement must be placed on the denominator in equation (12) of [11] for the equation to provide a secure definition.

$$\phi(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) = \frac{\psi(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}})}{\chi(\mathbf{t}^{\mathrm{n}})} \tag{15}$$

if the normalisation choice

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

is made. In fact it is possible [12] to show that χ must be nodeless even though the usual approximate nuclear wavefunctions for vibrationally excited states do have nodes. The electronic wavefunction (15) is therefore properly defined and a potential energy surface could be defined in terms of it as

$$\mathsf{U}(\mathbf{t}^{\mathrm{n}}) = \int \phi(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}})^{*} \mathsf{H}'(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) \phi(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) \mathrm{d}\mathbf{t}^{\mathrm{e}} \tag{16}$$

with H' defined as the sum of (9) and (10) 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 [13] took such an accurate approximation for an excited vibrational state in the $J = 0$ rotational state of H_2 and computed $\mathsf{U}(R)$. They found strong spikes in the potential close to two positions at which the usual wave function would have nodes. To quote [13]

> 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 [14] that using the clamped nucleus Hamiltonian instead of the full one in (16) to define the potential might avoid the spikes but Hunter in [12] showed why this was unlikely to be the case and Cassam-Chenai [15] 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 [16].

Although Gross [10] does not approach the problem in quite this way, there is reason to believe that this sort of problem is bound to arise whatever the approach. To see this simply rewrite (13) to recognise that the exact states will actually have definite quantum numbers according to their orthogonal symmetry O, the electronic permutational symmetry l, the nuclear permutational symmetry j and the energy n so that it would be more realistic to write

$$\psi_{Oljn}(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) = \chi_{Oljn}(\mathbf{t}^{\mathrm{n}}) \phi_{Oljn}(\mathbf{t}^{\mathrm{n}}, \mathbf{t}^{\mathrm{e}}) \tag{17}$$

In the H_2 study cited, the first three quantum numbers are of no relevance, only n remains and here n labels the vibrational states. There is thus every reason to expect that the best that can be done from this approach is a distinct PES for each nuclear-motion state.

At this level, then it cannot be assumed that the potential surface calculated in the usual way is an approximation to anything exact but it remains open to see whether it is possible to associate it with the exact solution when rotational motion is taken into account.

5 Rotational motion in a polyatomic molecule

A transformation to internal coordinates and Eulerian angles can be made to produce a Hamiltonian in which the rotational motion is explicit. The cases of two and of three nuclei present particular and non-general features and so will not be considered here. For details of the transformation see [6] but it is sufficient to notice here that the Eulerian angles are to be chosen as defined by the nuclear variables alone. Such a transformation yields an electronic Hamiltonian whose potential terms depend only upon $3A - 6$ nuclear internal coordinates q_k which are invariant under all rotation-reflections of the translationally invariant coordinates. The electronic variables are simply transformed variables $\mathbf{r}$ where the transformation is an orthogonal one defined by the three angles ϕ_k, $k = 1, 2, 3$. The angular and internal motion parts of the Hamiltonian do not separate, and the electronic angular motion is coupled to the angular motion of the nuclei.

The complete Hamiltonian operator may be written as

$$\mathsf{H}(\mathbf{r}) + \mathsf{K}(\mathbf{q}, \mathbf{r}) + \mathsf{K}(\boldsymbol{\phi}, \mathbf{q}, \mathbf{r}) \tag{18}$$

The first term in (18) arises trivially from (9) simply by replacing the $\mathbf{t}^{\mathrm{e}}$ by the $\mathbf{r}$ and so is

$$\begin{aligned} \mathsf{H}(\mathbf{r}) = & -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2(\mathbf{r}_i) - \frac{\hbar^2}{2M} \sum_{i,j=1}^{N} \vec{\nabla}(\mathbf{r}_i) \cdot \vec{\nabla}(\mathbf{r}_j) \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{|\mathbf{r}_j - \bar{\mathbf{x}}_i^{\mathrm{n}}|} \\ & + \frac{e^2}{8\pi\epsilon_0} {\sum_{i,j=1}^{N}}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + {\sum_{i,j=1}^{A}}' \frac{Z_i Z_j}{|\mathbf{x}_i^{\mathrm{n}} - \mathbf{x}_j^{\mathrm{n}}|} \end{aligned} \tag{19}$$

and

$$\mathsf{K}(\boldsymbol{\phi}, \mathbf{q}, \mathbf{r}) = \frac{1}{2} \left(\sum_{\alpha\beta} \kappa_{\alpha\beta} \mathsf{L}_\alpha \mathsf{L}_\beta + \hbar \sum_{\alpha} \bar{\lambda}_\alpha \mathsf{L}_\alpha \right) \tag{20}$$

and

$$\mathsf{K}(\mathbf{q},\mathbf{r}) = -\frac{\hbar^2}{2}\left(\sum_{k,l=1}^{3A-6} g_{kl}\frac{\partial^2}{\partial q_k \partial q_l} + \sum_{k=1}^{3A-6} h_k \frac{\partial}{\partial q_k}\right) + \frac{\hbar^2}{2}\left(\sum_{\alpha\beta}\kappa_{\alpha\beta}\mathsf{l}_\alpha \mathsf{l}_\beta + \sum_{\alpha}\lambda_\alpha \mathsf{l}_\alpha\right) \tag{21}$$

L , the total angular momentum operator, involves only the angular variables, and the angular variables are defined in terms of the translationally invariant nuclear variables only. $\boldsymbol{\kappa}$ is an inverse generalised inertia tensor and, though expressible fully in terms of the q_k, is formally dependent upon the definition of the Eulerian angles. l is the electronic angular momentum operator divided by $\hbar$. The matrix $\mathbf{g}$ has elements that depend on the product of terms arising from the expression of $\frac{\partial q_k}{\partial t^{\mathrm{n}}_{\alpha i}}$ while $\mathbf{h}$ has elements that depend on the derivatives with respect to the q_k of these partial derivatives. The λ_α involves the operators $\frac{\partial}{\partial q_k}$ with coefficients which are elements of a matrix $\boldsymbol{\tau}$ which involves products of the first derivatives that form $\mathbf{g}$ and those arising as the same kind of derivative but with respect to the angular variables. $\overline{\lambda}_\alpha$ also contains the electronic angular momentum operator with coefficients that are elements of $\boldsymbol{\kappa}$. This term couples the electronic and angular motions.

The Jacobian for the transformation is

$$|\mathbf{D}|^{-1}|\boldsymbol{\kappa}|^{-\frac{1}{2}}|\mathbf{g}-\boldsymbol{\tau}\boldsymbol{\kappa}^{-1}\boldsymbol{\tau}^T|^{-\frac{1}{2}} \tag{22}$$

The factor $|\mathbf{D}|^{-1}$ is the angular part of the Jacobian and in the standard parameterisation $|\mathbf{D}|^{-1} = \sin\phi_2$ as required for the usual interpretation of the matrix elements.

Again the transformed space is a manifold and not a vector space. There will always be a region in which the Jacobian for the transformation vanishes for such difficulties will arise somewhere in any transformed coordinate set that involves angular coordinates to separate off the non-Cartesian rotational space S^3. Difficulties also arise in a suitable choice of internal coordinates. The interparticle distances constitute a properly invariant set from which to construct internal coordinates and a geometrical figure formed by a choice of clamped nuclei can be specified uniquely by specifying all the interparticle distances. However, for[3] $A > 4$ there are more interparticle distances than the $3A - 6$ internal coordinates allowed following the construction of the 3 angular coordinates. Thus, if 9 of the 10 possible interparticle distances are chosen as internal coordinates for the 5-nuclei problem, it is possible to construct two distinct geometrical figures which generate the same values of the chosen internal coordinates. To see this, imagine the nuclei of NH_3 clamped with the protons, numbered 1–3, in a plane and the nitrogen nucleus, numbered 4, on the z-axis. Let a fifth nucleus be placed equivalently either above or below the plane of the protons so that the value of its z-coordinate is either $\pm a$. If we choose nine interparticle coordinates r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34} and r_{35} as the independent internal coordinates, it is seen that the two possible positions of the fifth nucleus lead to exactly the same values of the chosen internal coordinates. Standard clamped nuclei electronic structure calculations, which can be performed at any geometry would, at each of the geometries, yield different electronic energies. If these energies were assumed to be achievable as a result of assigning coordinate values in a function of the internal coordinates, two energies would arise for a single set of coordinate values and the "function" would not really be a function since a function must be single valued. It is not that such geometries are not possible, it is just that with a particular choice of internal coordinates, they are not distinguishable. Of course if r_{45} was considered, then the two geometries would be distinguishable and other choices of internal coordinates are possible in which this problem can be avoided. But the problem is quite general, see [6] or [18]. If the number of nuclei is five or more, there are always two or more geometries which are distinct but have the same internal coordinate specification, whatever the choice of internal coordinates made.

6 Removing rotational motion in the frame fixed in the body

One can eliminate angular motion from the problem by allowing the operator to work on the function and multiplying from the left by its complex conjugate and integrating out over the angular variables. This yields an effective operator within any (J, M, k) rotation-reflection manifold that depends only on the internal coordinates.

To remove the rotational motion, we write (18) as

$$\mathsf{H}_I(\mathbf{q},\mathbf{z}) + \mathsf{K}_R(\boldsymbol{\phi},\mathbf{q},\mathbf{z}) \tag{23}$$

in which the first term, H_I, consists of the first two terms in (18). The matrix elements with respect to the angular variables of the operators that depend only on the q_k and the $\mathbf{z}_i$ are trivial. Thus

$$\langle J'M'k' \mid \mathsf{H}_I \mid JMk\rangle = \delta_{J'J}\delta_{M'M}\delta_{k'k}\mathsf{H}_I \tag{24}$$

In what follows, explicit allowance for the diagonal requirement on J and M will be assumed and the indices suppressed to save writing. Similarly, the fact that the integration implied is over $\boldsymbol{\phi}$ only will be left implicit.

---

[3] For $A = 4$ the internal coordinate part of the Jacobian becomes ferociously complicated [17] with singularities when $r_{12} = r_{34}$, $r_{13} = r_{24}$ and $r_{14} = r_{23}$. The Jacobian for the interparticle distances in the five particle case is probably even more complicated.

The second term in (23) becomes

$$
\begin{aligned}
&\langle JMk' \mid \mathsf{K}_R \mid JMk\rangle \\
&\quad= \frac{\hbar^2}{4}\left(b_{+2}C^{+}_{Jk+1}C^{+}_{Jk}\delta_{k'k+2} + b_{-2}C^{-}_{Jk-1}C^{-}_{Jk}\delta_{k'k-2}\right) \\
&\quad+ \frac{\hbar^2}{4}\left(C^{+}_{Jk}(b_{+1}(2k+1) + \overline{\lambda}_{+})\delta_{k'k+1}\right. \\
&\quad+ \left.C^{-}_{Jk}(b_{-1}(2k-1) + \overline{\lambda}_{-})\delta_{k'k-1}\right) \\
&\quad+ \frac{\hbar^2}{2}\left((J(J+1)-k^2)b + b_0k^2 + \overline{\lambda}_0 k\right)\delta_{k'k}
\end{aligned}
\tag{25}
$$

In this expression

$$
\begin{aligned}
&b_{\pm 2} = (\kappa_{xx} - \kappa_{yy})/2 \pm \kappa_{xy}/i \\
&b_{\pm 1} = \kappa_{xz} \pm \kappa_{yz}/i \\
&b = (\kappa_{xx} + \kappa_{yy})/2 \quad b_0 = \kappa_{zz}
\end{aligned}
\tag{26}
$$

and in terms of the $\overline{\lambda}_\alpha$ $\overline{\lambda}_0$ is $\overline{\lambda}_z$ and the $\overline{\lambda}_\pm$ are

$$
\overline{\lambda}_\pm = (\overline{\lambda}_x \pm \overline{\lambda}_y/i) \tag{27}
$$

The apparently odd positioning of the complex unit as $1/i$ when i might have been expected is because the standard commutation conditions have been chosen for the internal angular momentum components.

Thus, within any rotational manifold, it is the eigensolutions of the effective Hamiltonian given by (24) and (25) which are invariant to orthogonal transformations and it is these functions that will be used to consider the separation of electronic and nuclear motion.

7 The separation of electronic and nuclear motion in an embedded frame

The base manifold $R^{3A-6} \otimes S^3$ is clearly coordinatisable in the region in which the Jacobian (22) does not vanish. Over that region, it is, in principle, possible to construct fibre bundles, so it is, in principle, possible to extend mathematically rigorous arguments to the separation of electronic from nuclear motion even when rotational motion is explicitly considered. For any given J state, the Schrödinger Coulomb Hamiltonian is, however, now composed of $2J+1$ coupled differential equations. It should be remembered that the label k does not designate a good quantum number and that states of different k for a given J may couple extensively or not at all. Unfortunately, however, any coupling that there might be, involves the electronic motion because each of the $\overline{\lambda}_\alpha$ contain a term $(\boldsymbol{\kappa}\mathsf{l})_\alpha$. Although the form of $\boldsymbol{\kappa}$ depends upon the choice of embedding, for the Eckart embedding [19], which is the one usually chosen,

$$
\boldsymbol{\kappa} = \mathbf{I}''^{-1}\mathbf{I}^0\mathbf{I}''^{-1}
$$

where $\mathbf{I}^0$ is the inertia tensor for the molecule at the reference geometry and $\mathbf{I}''$ is of inertia tensor form and becomes the equilibrium inertia tensor when the nuclear variables take their equilibrium values. At the equilibrium values of the nuclear variables, $\boldsymbol{\kappa}$ becomes the inverse of the equilibrium inertia tensor. The notation is that of Watson [20]. Thus, with this embedding this part of coupling matrix will be small only if the matrix elements of the components of the electronic angular momentum between the different k labelled states are small.

There has been no detailed mathematical consideration of this matter but the most useful way to proceed would seem to be to assume that this part of the coupling is of small effect. It is natural then to think of the electronic part of the Hamiltonian as given by (19). This is however to ignore the last term in (21). It would be easy to imagine this term included in the electronic part of the Hamiltonian but for the fact that λ_α contains a term in the nuclear variable derivatives. If such a term is included, it is not the case that this part of the Hamiltonian commutes with the nuclear variables and so appropriate fibre bundles cannot be constructed over a base space defined by fixed values of the nuclear variables. In order to offer an account of the separation of motions analogous to that offered in the translationally invariant case, the second part of the last term in (21) cannot be included in the electronic part of the problem. Consistency would seem to require that the whole term be ignored for the purposes of an initial discussion. It might be argued too that the expectation values of the components of electronic angular momentum would be small is an assumption consistent with the neglect of their matrix elements discussed above. Whether or not all these reservations are valid, a potential can be calculated using the direct integral form with the part (19) of the Hamiltonian and it will be properly defined wherever the domain of the Hamiltonian is restricted to the region in which Jacobian is non-vanishing. Since this space is a manifold, care must be taken to make sure that it remains a proper coordinate space and that the potential is everywhere an analytic function of the chosen coordinates. A mathematical discussion in these sort of terms has been attempted only for a diatomic system in which the internal coordinates are just the internuclear variable R. In this case, two possible fibre bundles are constructible on this manifold and it is this possibility that gives rise to the Berry phase change which can arise when the internal coordinate R is transported around a circle of constant latitude. This is discussed in a mathematically sophisticated way for a rather simplified model of the diatomic molecule in [21]. The authors refer to their results as either "straight up" or "with a twist". If it can be safely assumed that a "straight up" choice has been made, then it can be assumed that at least locally, a potential $\mathsf{V}^{\mathrm{e}}(\mathbf{q})$ can be properly defined.

Assuming that a potential can be calculated from this part of the rotationally invariant Hamiltonian, then the nuclear-motion problem involves the Hamiltonian composed of the first part of (21) added to (25) and to the potential. The terms in (25) other than those involving $\overline{\lambda}_\alpha$ are simply multiplicative in the variables **q** and so it is natural to consider these as to be evaluated at fixed values of the nuclear variables and to be dealt with along with the potential. If it can be assumed that it is possible to choose the embedding so that for the energy range of interest k is almost a good quantum number, then the effective potential imagined in these terms would be

$$\mathsf{V}(\mathbf{q}) = \mathsf{V}^{\mathrm{e}}(\mathbf{q}) + \frac{\hbar^2}{2}((J(J+1) - k^2)b + b_0 k^2) \tag{28}$$

For fixed J and k, this extended potential is rotationally invariant so that the fibre bundle arguments used for the translationally invariant approach may simply be carried over. Even with the simplifying assumptions made here, in principle the potential should be affected by the rotational motion of the system, and for any given k, the higher the J value, the shallower the effective potential will become. This is exactly the behaviour observed in the case of H_2 [22] for the electronic Σ ground state of the molecule assumed to dissociate into two hydrogen atoms in their ground states. That work shows that, for example, the $J = 0$ state supports just 14 vibrational states while the $J = 15$ state supports 10 while the $J = 31$ supports only 1 state. Of course in a diatomic molecule, states of different k are states with differ in the electronic angular momentum and these results cannot be regarded as typifying the results for a polyatomic system. However, work on H_3^+ shows that in the case of $J = 0$ there are 1,280 vibrational states below dissociation [23] and that 46 is the highest value of J for which at least one vibrational state exists [24]. These figures should be taken as indicative rather than definitive, for the electronic structure calculations from which they result, though among the best available, do not have quite the accuracy that the calculations on H_2 cited above do. Nevertheless, it is clear that rotational dependence is not just relevant for diatomic molecules. However, in general the importance of the rotational terms will depend on the values of b and b_0. Both of these depend on the reciprocals of the nuclear masses and thus it is reasonable to expect their importance to become less as the constituent atomic masses increase for any given electronic potential. It is clear that a mathematically sound scheme could be developed for the separation of electronic and nuclear motion even when rotational motion is considered though it might be necessary to recognise rotational dependencies. However, it now becomes a much more difficult problem to consider permutational invariance.

8 The permutational invariance of the PES

For the purposes of this discussion, it is convenient to think of the translation-free nuclear cartesian coordinates $\mathbf{t}^{\mathrm{n}}$ as being related to a body-fixed set $\mathbf{z}^{\mathrm{n}}$ by

$$\mathbf{t}^{\mathrm{n}} = \mathbf{C}\mathbf{z}^{\mathrm{n}} \tag{29}$$

The body-fixed electronic variables can now be defined in terms of the transformation defined above by:

$$\mathbf{r}_i = \mathbf{C}^T \mathbf{t}_i^{\mathrm{e}} \quad i = 1, 2, \ldots N \tag{30}$$

The three orientation variables are specified by means of an orthogonal matrix **C**, parameterised by the three Euler angles ϕ_m, $m = 1, 2, 3$ as orientation variables. In the present case, the matrix **C** is specified entirely in terms of the A translation-free nuclear variables and so there will be just $3A - 6$ internal variables for the nuclei and so three relations among the $\mathbf{z}_i^{\mathrm{n}}$.

It is necessary to consider the behaviour of both the internal coordinates and the Euler angles under the permutation of identical nuclei. Because of the choices made in deriving equation (30), the permutation of electrons is standard and need not be explicitly considered. However, the effect on the nuclear variables of a permutation P with representative **P** in the laboratory coordinates induces in the translationally invariant space the $A \times A$ representative matrix

$$\mathbf{H} = \mathbf{V}^{\mathrm{n}-1}\mathbf{P}\mathbf{V}^{\mathrm{n}} \tag{31}$$

The matrix **H** is not in general in standard permutational form neither is it orthogonal even though it has determinant ± 1 according to the sign of det**P**.

Let the (redundant) set of $(A - 1)^2$ scalar products of the $\mathbf{t}_i$ be denoted by the square matrix **S**, of dimension $A - 1$. Then, using (31), it is seen that a permutation

$$\mathcal{P}\mathbf{t}^{\mathrm{n}} = \mathbf{t}^{\mathrm{n}}\mathbf{H} = \mathbf{t}'^{\mathrm{n}} \tag{32}$$

so that

$$\mathbf{S}' = \mathbf{H}^T\mathbf{S}\mathbf{H} \tag{33}$$

Making explicit the functional dependencies, (29) may be written as

$$\mathbf{t}^{\mathrm{n}} = \mathbf{C}(\boldsymbol{\phi})\mathbf{z}^{\mathrm{n}}(\mathbf{q}) \tag{34}$$

and using (32) and (33) two different expressions for the permuted translation-free coordinates may be obtained. The first follows at once from (34) and (32):

$$\mathbf{t}'^{\mathrm{n}} = \mathbf{t}^{\mathrm{n}}\mathbf{H} = \mathbf{C}(\boldsymbol{\phi})\mathbf{z}^{\mathrm{n}}(\mathbf{q})\mathbf{H} \tag{35}$$

and this gives the $\mathbf{t}'^{\mathrm{n}}_i$ as functions of ϕ and **q**.

Alternatively, the Euler angles and the internal coordinates can be expressed directly as functions of the $\mathbf{t}^{\mathrm{n}}$ and hence of the $\mathbf{t}'^{\mathrm{n}}$ according to:

$$\phi_m(\mathbf{t}^{\mathrm{n}}) = \phi_m(\mathbf{t}'^{\mathrm{n}}\mathbf{H}^{-1}) = \phi'_m(\mathbf{t}'^{\mathrm{n}}) = \overline{\phi}_m(\boldsymbol{\phi},\mathbf{q}) \tag{36}$$

and

$$q_k(\mathbf{S}) = q_k(\mathbf{H}^{-T}\mathbf{S}'\mathbf{H}^{-1}) = q'_k(\mathbf{S}') = \overline{q}_k(\mathbf{q}) \tag{37}$$

Notice that while the effect of the permutation on q_k can at most produce a function of the q_k, the effect of the permutation on ϕ_m can produce a function of both the ϕ_m and the q_k. If the permuted internal coordinates and Euler angles are used in (34), the resulting expression will be for the permuted translation- free variables thus:

$$\mathbf{t}'^{\mathrm{n}} = \mathbf{C}(\overline{\boldsymbol{\phi}}(\boldsymbol{\phi},\mathbf{q}))\mathbf{z}^{\mathrm{n}}(\overline{\mathbf{q}}(\mathbf{q})) \tag{38}$$

so that:

$$\mathbf{t}'^{\mathrm{n}} = \overline{\mathbf{C}}(\boldsymbol{\phi},\mathbf{q})\overline{\mathbf{z}}^{\mathrm{n}}(\mathbf{q}) \tag{39}$$

Equating (35) and (39) it follows that

$$\overline{\mathbf{z}}^{\mathrm{n}} = \overline{\mathbf{C}}^T\mathbf{C}\mathbf{z}^{\mathrm{n}}\mathbf{H} \tag{40}$$

and since this expression can be at most a function of the internal coordinates, it follows that the orthogonal matrix $\overline{\mathbf{C}}^T\mathbf{C}$ must have elements which are, at most, functions of the internal coordinates. Denoting this matrix by $\mathbf{U}$ (and from now on, since they will always be the original body-fixed ones, the variables will not be explicitly given), it follows that

$$\overline{\mathbf{z}}^{\mathrm{n}} = \mathbf{U}\mathbf{z}^{\mathrm{n}}\mathbf{H} \tag{41}$$

and

$$\overline{\mathbf{C}} = \mathbf{C}\mathbf{U}^T \tag{42}$$

giving a relationship (albeit implicit) between the permuted and unpermuted body-fixed variables. It is as well to state explicitly that there will be such a relationship for every distinct permutation, and so strictly the matrices should carry a designation to indicate which of the permutations is being considered. But that would be to overload the notation in a way that is not necessary here and so it will not be done.

Now that these relationships have been established, the effects of a permutation on the various parts of the wavefunction must now be worked out. To avoid overloading the notation again, the usual convention will be adopted in which the change (41) is written:

$$\mathbf{z}^{\mathrm{n}} \rightarrow \mathbf{U}^T\mathbf{z}^{\mathrm{n}}\mathbf{H}^{-1} \tag{43}$$

while (42) is written:

$$\mathbf{C} \rightarrow \mathbf{C}\mathbf{U} \tag{44}$$

when considering the change in a function upon the change of variables.

The angular momentum eigenfunction $|1Mk\rangle$ can be shown [25] to be writable as

$$|1Mk\rangle = \left(\frac{3}{8\pi^2}\right)^{\frac{1}{2}}(\mathbf{X}^T\mathbf{C}\mathbf{X})_{Mk} \tag{45}$$

Since the elements of $|JMk\rangle$ can be obtained by repeated vector coupling of the elements of $|1Mk\rangle$ it is sufficient to know how $|1Mk\rangle$ transforms in order to know the general result. Using (44) for the change in $\mathbf{C}$ it follows from (45) that:

$$\begin{aligned}|1Mk\rangle &\rightarrow \left(\frac{3}{8\pi^2}\right)^{\frac{1}{2}}(\mathbf{X}^T\mathbf{C}\mathbf{U}\mathbf{X})_{Mk}\\ &= \left(\frac{3}{8\pi^2}\right)^{\frac{1}{2}}(\mathbf{X}^T\mathbf{C}\mathbf{X}\mathbf{X}^{\dagger}\mathbf{U}\mathbf{X})_{Mk}\\ &= \sum_{n=-1}^{+1}|1Mn\rangle\mathcal{D}^1_{nk}(\mathbf{U})\end{aligned} \tag{46}$$

so that the change induced in the general symmetric-top function under $\mathcal{P}$ is:

$$|JMk\rangle \rightarrow \sum_{n=-J}^{+J}|JMn\rangle\mathcal{D}^J_{nk}(\mathbf{U}) \tag{47}$$

In this equation, $\mathcal{D}^J(\mathbf{U})$ is the matrix made up from the elements of $\mathbf{U}$ in exactly the same way that $\mathcal{D}^J$ is made up from the elements of $\mathbf{C}$. A precise account of how this is to be done is given in Section 6.9 of [26]. Should it turn out that $\mathbf{U}$ is a constant matrix, then $\mathcal{D}^J(\mathbf{U})$ is a constant matrix and (47) simply represents a linear combination. If $\mathbf{U}$ is a unit matrix, then $|JMk\rangle$ is invariant. It should be noted here that this coupling of rotations by the permutations can mean that certain rotational states are not allowed by the Pauli principle and this is important in assigning statistical weights to rotational states.

It is rather difficult to say anything precise about the change induced in the q_k under the permutation. Of course since the internal coordinates are expressible entirely in terms of scalar products[4] and the scalar products of the $\mathbf{t}^{\mathrm{n}}_i$ are identical to the scalar products of the $\mathbf{z}^{\mathrm{n}}_i$, the change is that given in (37) namely

$$\mathbf{q}(\mathbf{S}) \rightarrow \mathbf{q}(\mathbf{H}^{-T}\mathbf{S}\mathbf{H}^{-1}) \tag{48}$$

where the notation of (43) has been used and where $\mathbf{S}$ is regarded as a function of the q_k. However, the result has no general form and so the best that can be said is that a permutation of nuclei induces a general function change

$$\Phi^J_k(\mathbf{q},\mathbf{z}) \rightarrow \Phi'^J_k(\mathbf{q},\mathbf{z}) \tag{49}$$

where the precise nature of the function change depends on the permutation, the chosen form of the internal

---

[4] Because of this, the internal coordinates are invariant under inversion, which simply causes the $\mathbf{t}_i^{\mathrm{n}}$ to change sign. Thus, it is only the nuclear permutation group and not the permutation-inversion group which is relevant here.

coordinates and on the chosen functional form. Thus, the general change in the wavefunction induced by $\mathcal{P}$ can be written

$$\Psi^{J,M}(\boldsymbol{\phi},\mathbf{q},\mathbf{z}) \rightarrow \sum_{k=-J}^{+J}\sum_{n=-J}^{+J} \mathcal{D}^{J}_{nk}(\mathbf{U})\Phi'^{J}_{k}(\mathbf{q},\mathbf{z})|JMn\rangle$$
$$= \sum_{n=-J}^{+J} \overline{\Phi}^{J}_{n}(\mathbf{q},\mathbf{z})|JMn\rangle \qquad (50)$$

This expression will clearly be very difficult to handle for not only will a **U** be difficult to determine, but one must be found for each distinct permutation of the identical nuclei and in a problem of any size there will be a very large number of such permutations. It would obviously be desirable to choose a body-fixing matrix, **C**, that was invariant under all permutations of identical particles. This can be done by choosing **C** to be the matrix that diagonalises the translation-free instantaneous inertia tensor and this is how it was chosen in the two very first attempts to body-fix for molecules, [27] and [28], and it has been a choice made subsequently on many occasions, see for example, [29]. However, if this choice is made, then the resulting Hamiltonian is quite inappropriate for the study of molecules because the Jacobian for the transformation vanishes in regions of physical interest. Thus, for a molecule like ammonia, this happens at what is usually thought of as its equilibrium geometry. This was among the reasons that led Eckart to develop his body-fixing prescription, [19], which is the one that is generally taken as the basis for the interpretation of molecular spectra. The embedding defined in this approach is generally invariant only under the subset of permutations of the identical nuclei which correspond to point group operations on the equilibrium geometry figure (for more discussion of this, see [25] and [30]). Thus, it is clear that it is not always possible to avoid these difficulties and the fact that they can arise in the Eckart approach obviously poses some problems for the standard view of the separation of rotational and vibrational motion. These matters are discussed a little more in [31] and [32].

Why these broken symmetry solutions to the clamped nucleus problem turn out to be so effective in practice has been a vexing puzzle since the very beginning of molecular quantum mechanics. It has occasioned an enormous amount of work, particularly since the publication in 1963 of a paper by H. C. Longuet-Higgins [33] in which permutations were divided into *feasible* and *unfeasible* types and in which it was argued that it was necessary to consider only the (often rather small) set of feasible permutations in a given problem. A summary of much of the relevant work in the area of molecular spectroscopy is reviewed in the monographs by Ezra [25] and by Bunker [34] and in a more general context in [35] and [36].

The idea of unfeasibility seems to rest on the notion that the permutation is a real motion of particles in the potential computed from a clamped nucleus calculation. If between the typical geometry and the permuted geometry there is a high potential barrier, then the permutation is unfeasible. The idea that a permutation is a real motion of particles is an incongruous one, from a mathematical point of view, as is the idea of unfeasibility, outside the single product approximation for the wave function and hence a single uncoupled potential function. It might however be speculated, within the present context, that if the usual orbital electronic wavefunction for a typical geometry is projected so that it has the proper permutational invariance, then the elements in the projected function that are small and make only a small contribution to the electronic energy can be neglected without great loss in energy. It would be the permutations that produce these negligible terms that can perhaps properly be called unfeasible. Although calculations could not quite settle this matter, it would be very interesting to attempt some and to see what emerged. To do so however would necessitate a proper consideration of the permutation upon the internal and angular coordinates and it would not be sufficient simply to assume as is usually done, that the permutations can be realised in terms of the nuclear cartesian variables nor should inversion be invoked as relevant to internal motion.

9 Conclusions

This paper has been devoted to trying to "place" the potential energy function in the context of solutions to the full problem. As has been shown, this placing is more problematic than is commonly thought. It cannot therefore be said, with any confidence at present, to what question the potential energy function arising from a clamped nucleus calculation is the answer.

Acknowledgments I am grateful to Guy Woolley for reading some earlier drafts of this contribution. Some of the work reported here developed as part of ESA contract 21790/08/NL/HE and was carried out at the Universite Libre de Bruxelles. I thank the Fonds National de la Recherche Scientifique (F.R.S.-FNRS, contracts FRFC and IISN), the Universite libre de Bruxelles and the "Action de Recherches Concertees de la Communaute francaise de Belgique" for accommodation and the provision of library and computing facilities.

References

1. Born M, Huang K (1955) Dynamical theory of crystal lattices. Oxford University Press, Oxford
2. Kato T (1951) Trans Am Math Soc 70:195
3. Stone MH (1932) Proc Natl Acad Sci 16:172
4. Thirring W (1981) Quantum mechanics of atoms and molecules, vol 3 of A course in mathematical physics (trans: Harrell EM). Springer, Berlin

5. Perez JF, Arajuo VA, Coutinho FAB (2004) Am J Phys 72:203
6. Sutcliffe B (2000) Adv Chem Phys 114:97
7. Schutz B (1980) Geometrical methods of mathematical physics. Cambridge University Press, Cambridge
8. Klein M, Martinez A, Seiler R, Wang XP (1992) Commun Math Phys 143:607
9. Hunter G (1975) Int J Quantum Chem 9:237
10. Abedi A, Maitra NT, Gross EKU (2010) Phys Rev Lett 105:123002
11. Kutzelnigg W (2007) Mol Phys 105:2627
12. Hunter G (1981) Int J Quantum Chem 19:755
13. Czub J, Wolniewicz L (1978) Mol Phys 36:1301
14. Wilson E Bright (1979) Int J Quant Chem Symp 13:5
15. Cassam-Chenai P (2006) Chem Phys Lett 420:354
16. Pack RT, Hirschfelder JO (1970) J Chem Phys 52:521
17. Harris F (2004) Adv Quantum Chem 47:130
18. Collins MA, Parsons DF (1993) J Chem Phys 99:6756
19. Eckart C (1935) Phys Rev 47:552
20. Watson JKG (1968) Mol Phys 15:479
21. Herrin J, Howland JS (1997) Reviews in mathematical physics 9:467
22. Pachucki K, Komasa J (2009) J Chem Phys 130:164113
23. Henderson JR, Tennyson J, Sutcliffe BT (1993) J Chem Phys 98:7191
24. Miller S, Tennyson J (1988) Chem Phys Lett 145:117
25. Ezra G (1982) Symmetry properties of molecules, vol 28 of lecture notes in chemistry. Springer, Berlin
26. Biedenharn LC, Louck JC (1982) Angular momentum in quantum physics. Addison-Wesley, Reading, MA
27. Eckart C (1934) Phys Rev 46:384
28. Hirschfelder JO, Wigner E (1935) Proc Natl Acad Sci 21:113
29. Buck B, Biedenharn LC, Cusson RY (1979) Nucl Phys A 317:215
30. Louck JD, Galbraith HW (1976) Rev Mod Phys 48:69
31. Sutcliffe BT (1994) In: Kryachko ES, Calais JL (eds) Conceptual trends in quantum chemistry. Kluwer, Dordrecht, p 53
32. Sutcliffe BT (1991) In: Wilson S (ed) Methods of computational chemistry, vol 4. Plenum, New York and London, p 33
33. Longuet-Higgins HC (1963) Mol Phys 6:445
34. Bunker PR, Jensen P (1998) Molecular symmetry and spectroscopy, 2nd edn. NRC Research Press, Ottawa
35. Kaplan IG (1975) Symmetry of many-electron systems. Academic, London
36. Maruani J, Serre J (eds) (1983) Symmetries and properties of non-rigid molecules. Elsevier, Amsterdam