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Transition state theory was introduced in 1930s to account for chemical reactions. Central to this theory is the idea of a potential energy surface (PES). It was assumed that such a surface could be constructed using eigensolutions of the Schrödinger equation for the molecular (Coulomb) Hamiltonian but at that time such calculations were not possible. Nowadays quantum mechanical *ab initio* electronic structure calculations are routine and from their results PESs can be constructed which are believed to approximate those assumed derivable from the eigensolutions. It is argued here that this belief is unfounded. It is suggested that the potential energy surface construction is more appropriately regarded as a legitimate and effective modification of quantum mechanics for chemical purposes. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4755287]

I. INTRODUCTION

The principal aim of much of contemporary quantum chemical calculation is to calculate a potential energy surface from solutions of the Schrödinger equation for the clamped-nuclei electronic Hamiltonian which gives the electronic energy at a choice of nuclear positions. These electronic energies are then added to the clamped-nuclei classical Coulomb repulsion energy and the resulting "total" energies fitted to a functional form to provide a surface which, for a system of $A > 2$ nuclei, is of dimension $3A - 6$. Nuclear motion is treated as occurring on this surface.

The idea of a potential energy surface in such a role began with the work of Eyring and the almost contemporary work of Polanyi in the 1930s. Its basis is described in chapter 16 of the textbook by Eyring, Walter, and Kimball, published in 1944.[1] When describing the reaction between the hydrogen molecule and a hydrogen atom, the authors say:

> The properties of this system are completely determined by the Schrödinger equation governing it, that is by its eigenfunctions. The system itself may be represented by a point in four-dimensional space: three dimensions are required to express the relative positions of the nuclei, one additional dimension is required to specify the energy. (We assume here that the motion of the electrons is so rapid that the electrons form a static field for the slower nuclear motions.) The three internuclear distances... can conveniently be used to specify the configuration of the system.

They then give the name "potential energy surface" to the presumed calculated entity and go on to explain how transition probabilities for the hydrogen exchange reaction can be calculated using its characteristic shape. They take it as obvious that the nuclei can be treated as classical particles whose positions can be fixed and do not mention the work

of Born and Oppenheimer which, 17 years before the publication of their book, had argued that such a treatment of the nuclei could be justified if the potential energy surface had a unique minimum and that the nuclear motion involved only small departures from equilibrium.[2, 3]

In the textbook by Pauling and Wilson[4] the work of Born and Oppenheimer is quoted as justifying their use of a wavefunction which is a simple product of an electronic and a nuclear part in order to describe the vibration and rotation of molecules. They then introduce the potential energy function, which they call the "electronic energy function", for a diatomic system. In their description of a chemical reaction involving three atoms they attribute the idea of fixing the nuclei to the work of London who used such an approach in his 1928 paper.[5] It is interesting to note that London actually called this approach "adiabatic" saying that he assumed that as the nuclei moved they acted as adiabatic parameters in the electronic wavefunction.

Although treating the nuclei as classical particles that may be fixed in space to generate a potential energy surface is often now referred to as "making the Born-Oppenheimer approximation" it is something of a mis-attribution as can be seen from this discussion. This was indeed recognized by Born and in 1951 he published a paper[6] in which he presented a more general account of the separation of electronic and nuclear motion than that originally offered. It is to this later work by Born that the more general idea of a potential energy surface is regarded as owing its justification and it is that work that will be considered here.

We aim to show that the potential energy surface does not arise naturally from the solution of the Schrödinger equation for the molecular Coulomb Hamiltonian; rather its appearance requires the additional assumption that the nuclei can at first be treated as classical distinguishable particles and only later (after the potential energy surface has materialized) as quantum particles. In our view this assumption, although often very successful in practice, is *ad hoc*.

The outline of the paper is as follows. In Sec. II we review the main features of the standard Born-Oppenheimer

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and Born adiabatic treatments following Born and Huang's well-known book.[7] The key idea is that the nuclear kinetic energy contribution can be treated as a small perturbation of the electronic energy; the small parameter (κ) in the formalism is obtained from the ratio of the electronic mass (m) to the nuclear mass (M_o): $m/M_o = \kappa^4$. The argument leads to the expression of the molecular Hamiltonian as the sum of the "clamped-nuclei" electronic Hamiltonian (independent of κ) and the nuclear kinetic energy operator ($\propto \kappa^4$), Eq. (6).

In Sec. III we attempt a careful reformulation of the conventional Born-Oppenheimer argument drawing on results from the modern mathematical literature. The calculation is essentially concerned with the *internal motion* of the electrons and nuclei so we require the part of the molecular Hamiltonian that remains after the center-of-mass contribution has been removed. We show that it is possible to express the internal motion Hamiltonian in a form analogous to Eq. (6); however, the electronic part, independent of κ, is *not* the clamped-nuclei Hamiltonian. Instead, the exact electronic Hamiltonian can be expressed as a direct integral of clamped-nuclei Hamiltonians and necessarily has a *purely continuous spectrum of energy levels*; there are *no* potential energy surfaces. This continuum has nothing to do with the molecular centre-of-mass, by construction. The paper concludes (Sec. IV) with a discussion of our finding.

II. THE BORN-OPPENHEIMER APPROXIMATION

The original Born and Oppenheimer approximation[2,3] is summarized in the famous book by Born and Huang, and the later Born adiabatic method[6] is given in an appendix to that book.[7] Born and Huang use the same notation for both formulations and it is convenient to follow initially their presentation; the following is a short account focusing on the main ideas. They work in a position representation and for simplicity suppress all individual particle labels. Let us consider a system of electrons and nuclei and denote the properties of the former by lower-case letters (mass m, coordinates x, momenta p) and of the latter by capital letters (mass M, coordinates X, momenta P). The kinetic energy of the nuclei is the operator

$$T_N = \sum \frac{1}{2M}P^2 = -\sum \frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2}\right) \qquad (1)$$

and that of the electrons

$$T_e = \sum \frac{1}{2m}p^2 = -\sum \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right). \qquad (2)$$

The total Coulomb energy of the electrons will be represented by $U(x, X)$. We further introduce the abbreviation

$$T_e + U = H_o\left(x, \frac{\partial}{\partial x}, X\right). \qquad (3)$$

The full Hamiltonian for the molecule is then

$$H = T_e + U + T_N = H_o + T_N. \qquad (4)$$

The fundamental idea of Born and Oppenheimer is that the low-lying excitation spectrum of a typical molecule can be calculated by regarding the nuclear kinetic energy T_N as a

small perturbation of the Hamiltonian H_o. The physical basis for the idea is the large disparity between the mass of the electron and all nuclear masses. The expansion parameter must clearly be some power of m/M_o, where M_o can be taken as any one of the nuclear masses or their mean. They found that the correct choice is

$$\kappa = \left(\frac{m}{M_o}\right)^{\frac{1}{4}}$$

and therefore

$$T_N = \kappa^4 H_1\left(\frac{\partial}{\partial X}\right) = \sum\left(\frac{M_o}{M}\right)\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial X^2}\right). \qquad (5)$$

Thus the total Hamiltonian may be put in the form

$$H = H_o + \kappa^4 H_1 \qquad (6)$$

with Schrödinger equation

$$(H - E)\psi(x, X) = 0. \qquad (7)$$

In the original paper Born and Oppenheimer say at this point in their argument that:[3]

> If one sets $\kappa = 0 \ldots$ one obtains a differential equation in the x alone, the X appearing as parameters:
>
> $$\left[H_o\left(x, \frac{\partial}{\partial x}, X\right) - W\right]\psi = 0.$$
>
> This represents the electronic motion for stationary nuclei.

and it is perhaps to this statement that the idea of an electronic Hamiltonian with fixed nuclei as arising by letting the nuclear masses increase without limit, can be traced. In modern parlance H_o is customarily referred to as the "clamped-nuclei Hamiltonian".

Consider the unperturbed electronic Hamiltonian $H_o(x, X_f)$ at a fixed nuclear configuration X_f that corresponds to some molecular structure. The Schrödinger equation for H_o is
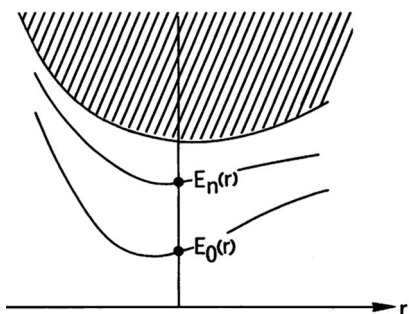
$$\left(H_o(x, X_f) - E^o(X_f)_m\right)\varphi(x, X_f)_m = 0. \qquad (8)$$

This Hamiltonian's natural domain, $\mathcal{D}_o$, is the set of square integrable electronic wavefunctions $\{\varphi_m\}$ with square integrable first and second derivatives; $\mathcal{D}_o$ is independent of X_f. We may suppose that the $\{\varphi_m\}$ are orthonormalized independently of X_f

$$\int dx\, \varphi(x, X_f)_n^* \varphi(x, X_f)_m = \delta_{nm}.$$

In the absence of degeneracies ("curve-crossing") they may be chosen to be real; otherwise there is a phase factor to be considered. For every X_f, H_o is self-adjoint on the electronic Hilbert space $\mathcal{H}(X_f)$, and therefore the set of states $\{\varphi(x, X_f)_m\}$ form a complete set for the electronic Hilbert space indexed by X_f.

The clamped-nuclei Hamiltonian can be analysed with the HVZ theorem which shows that it has both discrete and

FIG. 1. The spectrum $\sigma(r)$ for a diatomic molecule.[8]

continuous parts to its spectrum,[8–12]

$$\sigma(X_f) \equiv \sigma(H_o(x, X_f))$$

$$= \left[E^o(X_f)_0, \ldots E^o(X_f)_m \right) \bigcup \left[\Lambda(X_f), \infty \right), \quad (9)$$

where the $\{E^o(X_f)_k\}$ are isolated eigenvalues of finite multiplicities. $\Lambda(X_f)$ is the bottom of the essential spectrum marking the lowest continuum threshold. In the case of a diatomic molecule the electronic eigenvalues depend only on the internuclear separation r and have the form of the familiar potential curves shown in Fig. 1. For the general polyatomic molecule, the discrete eigenvalues are molecular potential energy surfaces.

Born and Oppenheimer used the set $\{\varphi_m\}$ to calculate approximate eigenvalues of the full molecular Hamiltonian H on the assumption that the nuclear motion is confined to a small vicinity of a special (equilibrium) configuration X_f^0. Their great success was in establishing that the energy levels of the low-lying states typical of small polyatomic molecules obtained from molecular spectroscopy could be written as an expansion in powers of κ^2

$$E_{nvJ} \approx V_n^{(0)} + \kappa^2 E_{nv}^{(2)} + \kappa^4 E_{nvJ}^{(4)} + \cdots, \quad (10)$$

where $V_n^{(0)}$ is the minimum value of the electronic energy which characterises the molecule at rest, $E_{nv}^{(2)}$ is the energy of the nuclear vibrations, and $E_{nvJ}^{(4)}$ contains the rotational energy.[2] The corresponding approximate wavefunctions are simple products of an electronic function φ_m and a nuclear wavefunction; this is known as *the adiabatic approximation*. In the original perturbation formulation the simple product form is valid through κ^4, but not for higher order terms.

About 25 years later Born observed that the results of molecular spectroscopy suggest that the adiabatic approximation has a wider application than predicted by the original theory, and he proposed an alternative formulation.[6,7] It is assumed that the functions $E^o(X)_m$ and $\varphi(x, X)_m$ arising from Eq. (8) which represent the energy and wavefunction of the electrons in the state m for a fixed nuclear configuration X are known. Born proposed to solve the wave equation (7) by an expansion

$$\psi(x, X) = \sum_m \Phi(X)_m \varphi(x, X)_m \quad (11)$$

with coefficients $\{\Phi(X)_m\}$ that play the role of nuclear wavefunctions. Substituting this expansion into the full Schrödinger equation (7), multiplying the result by $\varphi(x, X)_n^*$

and integrating over the electronic coordinates x leads to a system of coupled equations for the nuclear functions $\{\Phi\}$,

$$\left(T_N + E^o(X)_n - E \right) \Phi(X)_n + \sum_{nn'} C(X, P)_{nn'} \Phi(X)_{n'} = 0, \quad (12)$$

where the coupling coefficients $\{C(X, P)_{nn'}\}$ have a well-known form which we need not record here.[7] In this formulation the adiabatic approximation consists of retaining only the diagonal terms in the coupling matrix $\mathbf{C}(X, P)$, for then

$$\psi(x, X) \approx \psi(x, X)_n^{\text{AD}} = \varphi(x, X)_n \Phi(X)_n. \quad (13)$$

An obvious defect in this presentation, recognized by Born and Huang,[7] is that the kinetic energy of the overall center-of-mass is retained in the Schrödinger equation (7); this is easily corrected, either by the explicit separation of the center-of-mass kinetic energy operator (see Sec. III), or implicitly, as in the computational scheme proposed by Handy *et al.*[13,14] and Kutzelnigg.[15] For many years now these equations have been regarded in the theoretical molecular spectroscopy/quantum chemistry literature as defining the "Born-Oppenheimer approximation," the original perturbation method being relegated to the status of historical curiosity. Commonly they are said to provide an exact (in principle) solution[16–20] for the stationary states of the molecular Schrödinger equation (7), it being recognized that in practice drastic truncation of the infinite set of coupled equation (12) is required. In Sec. III we make a critical evaluation of this conventional account.

III. THE MOLECULAR SCHRÖDINGER EQUATION

We now start again and reconsider the Hamiltonian for a collection of electrons and nuclei, assuming that their interactions are restricted to the usual Coulombic form. The key idea in Sec. II is the decomposition of the molecular Hamiltonian (4) into a part containing all contributions of the nuclear momenta, and a remainder. This must be done in conjunction with a proper treatment of the center-of-mass motion. These two ideas guide the following discussion.

Let the position variables for the particles in a laboratory fixed frame be designated as $\{\mathbf{x}_i\}$. When it is necessary to distinguish between electrons and nuclei, the position variables may be split up into two sets, one set consisting of N coordinates, $\mathbf{x}_i^e$, describing the electrons with charge $-e$ and mass m, and the other set of A coordinates, $\mathbf{x}_g^n$, describing the nuclei with charges $+Z_g e$ and masses m_g, $g = 1, \ldots, A$; then $n = N + A$. We define corresponding canonically conjugate momentum variables $\{\mathbf{p}_i\}$ for the electrons and nuclei. With this notation, and after the usual canonical quantization, the Hamiltonian operator for a system of N electrons and A atomic nuclei with Coulombic interactions may be written as

$$\mathsf{H} = \sum_g^A \frac{\mathsf{p}_g^2}{2m_g} + \frac{e^2}{4\pi\epsilon_0} \sum_{g<h}^A \frac{Z_g Z_h}{\mathsf{r}_{gh}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^N \frac{1}{\mathsf{r}_{ij}}$$

$$+ \sum_i^N \left(\frac{\mathsf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_g^A \frac{Z_g}{\mathsf{r}_{ig}} \right). \quad (14)$$

It is easily seen that the Coulomb interaction is translation invariant. Thus the total momentum operator, which in

the present notation is

$$\mathbf{P} = \sum_i^n \mathbf{p}_i,$$

commutes with H. Physically the center-of-mass of the whole system, with position operator

$$\mathbf{R} = \frac{1}{M_T} \sum_i^n m_i \mathbf{x}_i, \quad M_T = \sum_i^n m_i$$

behaves like a free particle. It is then desirable to introduce $\mathbf{R}$ and its conjugate $\mathbf{P_R}$, together with appropriate internal coordinates, into H to make explicit the separation of the center-of-mass and the internal dynamics. Formally H may be written as a direct integral[21]

$$\mathsf{H} = \int_{\mathbf{R}^3}^{\oplus} H(P) \, dP, \qquad (15)$$

where[22]

$$H(P) = \frac{P^2}{2M_T} + \mathsf{H}' \qquad (16)$$

is the Hamiltonian at fixed total momentum P. This representation shows directly that H has purely continuous spectrum. The internal Hamiltonian H' is independent of the center-of-mass variables and acts on $L^2(\mathbf{R}^{3(n-1)})$; it is explicitly translation invariant.

There are infinitely many possible choices of internal coordinates that are unitarily equivalent, so that the form of H' is not determined uniquely, but whatever coordinates are chosen the essential point is that H' is the *same* operator specified by the decomposition (16). A simple procedure to make the internal Hamiltonian explicit is to refer the particle coordinates to a point moving with the system, for example, the center-of-mass itself, the center-of-nuclear-mass or one of the moving particles.[23]

As a result of the transformation to internal variables the kinetic energy operators are no longer diagonal in the particle indices and certain choices of the moving point, such as the choice of a single nucleus, result in an operator in which the nuclear and electronic indices are mixed. However the choice of the center-of-nuclear-mass as the point of origin avoids this mixing; the explicit equations for this choice were given in Sutcliffe and Woolley.[24] There are $A - 1$ translationally invariant coordinates $\mathbf{t}_i^n$ expressed entirely in terms of the original $\mathbf{x}_g^n$ that may be associated with the nuclei, and there are N translationally invariant coordinates for the electrons $\mathbf{t}_i^e$ which are simply the original electronic coordinates $\mathbf{x}_i^e$ referred to the center-of-nuclear-mass. There are corresponding canonically conjugate internal momentum operators. The classical total kinetic energy still separates in the form

$$\mathsf{T}_0 \equiv T_N + T_e = \mathsf{T}_{CM} + \mathsf{T}_{Nu} + \mathsf{T}_{el}$$

and the same is true after quantization. T_{CM} is the kinetic energy for the center-of-mass and, for example, T_{el} only involves electronic variables

$$\mathsf{T}_{el} = \frac{1}{2\mu} \sum_{i=1}^N \left(\boldsymbol{\pi}_i^e \right)^2 + \frac{1}{2M} \sum_{ij=1}^N {}' \left(\boldsymbol{\pi}_i^e \right) \cdot \left(\boldsymbol{\pi}_j^e \right) \qquad (17)$$

with

$$M = \sum_{g=1}^A m_g, \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}.$$

The nuclear kinetic energy term is like the second term in (17) expressed in terms of internal nuclear momentum variables $\{\boldsymbol{\Pi}_g^n\}$ with a mass factor in the denominator composed from the nuclear masses.

After this unitary transformation the original Coulomb Hamiltonian operator for the molecule can be rewritten in the form

$$\mathsf{H}(\mathbf{x}^e, \mathbf{p}^e, \mathbf{x}^n, \mathbf{p}^n) = \mathsf{T}_{CM} + \mathsf{T}_{Nu} + \mathsf{H}^{elec}, \qquad (18)$$

where H^{elec} is composed of (17) together with all the Coulomb interaction operators expressed in terms of the $\{\mathbf{t}^e, \mathbf{t}^n\}$ position operators.

The spectrum of the Coulomb operator H' formed by dropping T_{CM} from (18) was considered by Kato[26] who showed in Lemma 4 of his paper 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, $\mathcal{D}_V$, of the internal Hamiltonian H' contains $\mathcal{D}_0$ and there are two constants a, b such that

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

where a can be taken as small as is liked. This result is often summarised by saying that the Coulomb potential is small compared to the kinetic energy. Given this result he proved in Lemma 5 (the Kato-Rellich theorem) that the usual operator is indeed, for all practical purposes, self-adjoint and so is guaranteed a complete set of eigenfunctions, and is bounded from below.

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 may mean that the Coulomb potential term cannot be treated as small. Such a defective Hamiltonian will no longer be self-adjoint in the way demonstrated by Kato.

With our choice of coordinates the translationally invariant Hamiltonian may be written as the sum of the last two terms in (18) and the electronic Hamiltonian now becomes

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

$$- \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{|\mathbf{t}_j^e - \mathbf{x}_i^n|}$$

$$+ \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^N {}' \frac{1}{|\mathbf{t}_i^e - \mathbf{t}_j^e|} + \sum_{i,j=1}^A {}' \frac{Z_i Z_j}{|\mathbf{x}_i^n - \mathbf{x}_j^n|}, \qquad (19)$$

where it is understood that the $\mathbf{x}_i^n$ are to be realised by a suitable linear combination of the $\mathbf{t}_i^n$. The electronic Hamiltonian is properly translationally invariant and, were the nuclear masses to increase without limit, the second term in (19) would vanish and the electronic Hamiltonian would have the same form as that usually invoked in molecular electronic structure calculations. If the nuclear positions were

chosen directly as a translationally invariant set, it would be those values which would appear in the place of the nuclear variables. The nuclear part involves only kinetic energy operators and has the form

$$\mathsf{T}_{Nu} = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}} \vec{\nabla}\big(\mathbf{t}_i^{\mathrm{n}}\big) . \vec{\nabla}\big(\mathbf{t}_j^{\mathrm{n}}\big) \qquad (20)$$

with the inverse mass matrix $\boldsymbol{\mu}$ given in terms of the coefficients that define the translationally invariant coordinates and the nuclear masses.

$\mathsf{H}^{\mathrm{elec}}$ has the same invariance under the rotation-reflection group O(3) as does the full translationally invariant Hamiltonian H' and, in the case of the molecule containing some identical nuclei, it has somewhat extended invariance under nuclear permutations, since the nuclear masses appear only in symmetrical sums. In a position representation the Schrödinger equation for $\mathsf{H}^{\mathrm{elec}}$ may be written as

$$\mathsf{H}^{\mathrm{elec}} \Psi(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})_{\mathbf{m}} = \mathcal{E}_{\mathbf{m}} \Psi(\mathbf{t}^{\mathrm{e}}, \mathbf{t}^{\mathrm{n}})_{\mathbf{m}}, \qquad (21)$$

where $\mathbf{m}$ is used to denote a set of quantum numbers (*JMprk*) in which *J* and *M* are for the angular momentum state: *p* specifying the parity of the state: *r* specifying the permutationally allowed irreps within the group(s) of identical particles and *k* to specify a particular energy value.[24]

Before discussing (21) for the general case, let us consider a specific example for which high-quality computational results exist. It might be hoped, in the light of the claim in the original paper by Born and Oppenheimer quoted in Sec. II, that the solutions of (21) would actually be those that would have been obtained from an exactly solved problem by letting the nuclear masses increase without limit. Although there are no exactly solved molecular problems, the work of Frolov[25] provides extremely accurate numerical solutions for a problem with two nuclei and a single electron. Frolov investigated what happens when the masses of one and then two of the nuclei increase without limit in his calculations. To appreciate his results, consider 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, $\mathbf{x}_i^{\mathrm{n}}$ is simply of the form $\alpha_i \mathbf{t}$ where α_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 after the elimination of the center-of-mass contribution is

$$\mathsf{H}'^{\mathrm{e}}\big(\mathbf{t}^{\mathrm{e}}\big) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2\big(\mathbf{t}_i^{\mathrm{e}}\big) - \frac{\hbar^2}{2(m_1+m_2)} \sum_{i,j=1}^{N} \vec{\nabla}\big(\mathbf{t}_i^{\mathrm{e}}\big) \cdot \vec{\nabla}\big(\mathbf{t}_j^{\mathrm{e}}\big)$$

$$- \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^{N} \left(\frac{Z_1}{|\mathbf{t}_j^{\mathrm{e}} + \alpha_1 \mathbf{t}|} + \frac{Z_2}{|\mathbf{t}_j^{\mathrm{e}} + \alpha_2 \mathbf{t}|} \right)$$

$$+ \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_i^{\mathrm{e}} - \mathbf{t}_j^{\mathrm{e}}|} + \frac{Z_1 Z_2}{R}, \quad R = |\mathbf{t}| \qquad (22)$$

while the nuclear kinetic energy part is

$$\mathsf{T}_{Nu}(\mathbf{t}) = -\frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla^2(\mathbf{t}) \equiv -\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{t}). \qquad (23)$$

The full internal motion Hamiltonian for the three-particle system is then

$$\mathsf{H}'(\mathbf{t}^{\mathrm{e}}, \mathbf{t}) = \mathsf{H}'^{\mathrm{e}}(\mathbf{t}^{\mathrm{e}}) + \mathsf{T}_{Nu}(\mathbf{t}). \qquad (24)$$

It is seen from (23), 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 (24) remains self-adjoint in the Kato sense. Frolov's calculations showed that when one mass increased without limit (the atomic case), any discrete spectrum persisted but when two masses were allowed to increase without limit (the molecular case), the Hamiltonian ceased to be well-defined and this failure led to what he called *adiabatic divergence* in attempts to compute discrete eigenstates of (24). This divergence is discussed in some mathematical detail in the Appendix to Frolov.[25] It does not arise from the choice of a translationally invariant form for the electronic Hamiltonian; rather it is due to the lack of any kinetic energy term to dominate the Coulomb potential. Thus it is really essential to characterize the spectrum of $\mathsf{H}^{\mathrm{elec}}$ to see whether the traditional approach can be validated.

As before, the nuclear kinetic energy operator is proportional to κ^4, so after dropping the uninteresting center-of-mass kinetic energy term, (18) is seen to be of the same form as (6). There is however a fundamental difference between (6) and (18) which may be seen as follows; with the center-of-nuclear-mass chosen as the electronic origin $\mathsf{H}^{\mathrm{elec}}$ is independent of the nuclear momentum operators and so it commutes with the nuclear position operators

$$[\mathsf{H}^{\mathrm{elec}}, \mathbf{t}^{\mathrm{n}}] = 0.$$

They may therefore be simultaneously diagonalized and we use this property to characterize the Hilbert space $\mathcal{H}$ for $\mathsf{H}^{\mathrm{elec}}$. Let $\mathbf{b}$ be some eigenvalue of the $\mathbf{t}^{\mathrm{n}}$ corresponding to choices $\{\mathbf{x}_g = \mathbf{a}_g,\ g = 1, \ldots A\}$ in the laboratory-fixed frame; then the $\{\mathbf{a}_g\}$ describe a classical nuclear geometry. The set, X, of all $\mathbf{b}$ is $\mathbf{R}^{3(A-1)}$. We denote the Hamiltonian $\mathsf{H}^{\mathrm{elec}}$ evaluated at the nuclear position eigenvalue $\mathbf{b}$ as $\mathsf{H}(\mathbf{b}, \mathbf{t}^{\mathrm{e}})_o = \mathsf{H}_o$ for short; this H_o is very like the usual clamped-nuclei Hamiltonian but it is explicitly translationally invariant, and has an extra term, the second term in (17) (or (22)), which is often called the Hughes-Eckart term, or the mass polarization term. The Schrödinger equation for H_o is of the same form as (8), with eigenvalues $E^o(\mathbf{b})_k$ and corresponding eigenfunctions $\varphi(\mathbf{t}^{\mathrm{e}}, \mathbf{b})_k$, and with spectrum $\sigma(\mathbf{b})$ analogous to (9).

In general the symmetries of $\mathsf{H}(\mathbf{b}, \mathbf{t}^{\mathrm{e}})_o$ considered as a function of the electronic coordinates, $\mathbf{t}^{\mathrm{e}}$, are much lower than those of $\mathsf{H}^{\mathrm{elec}}$, since they are determined by the (point group) transformations that leave the geometrical figure defined by the $\{\mathbf{a}_g\}$ invariant. In a chiral structure there is no symmetry operation other than the identity so even space-inversion symmetry (parity) is lost.

At any choice of $\mathbf{b}$ the eigenvalues of H_o will depend only upon the shape of the geometrical figure formed by the $\{\mathbf{a}_g\}$ and not at all upon its orientation. For other than diatomic molecules, it is technically possible to produce a new coordinate system from the $\mathbf{b}$ with angular variables describing the orientation of the figure and 3A-6 internal variables describing its geometry. However this cannot be

done without angular momentum terms arising in which electronic and nuclear momentum operators are coupled. Thus the kinetic energy can no longer be expressed as a sum of separate electronic and nuclear parts. There are also many possible choices of angular and internal variables which span different (though often overlapping) domains, so it is not possible to produce a single account of the separation of electronic and nuclear motion, applicable to all choices.

As in Sec. II, H_o is self-adjoint on an electronic Hilbert space $\mathcal{H}(\mathbf{b})$, so we have a family of Hilbert spaces $\{\mathcal{H}(\mathbf{b})\}$ which are parameterized by the nuclear position vectors $\mathbf{b} \in X$ that are the "eigenspaces" of the family of self-adjoint operators H_o; from them we can construct a big Hilbert space as a direct integral over all the $\mathbf{b}$ values

$$\mathcal{H} = \int_X^\oplus \mathcal{H}(\mathbf{b})d\mathbf{b} \qquad (25)$$

and this is the Hilbert space for H^{elec} in (18). The internal molecular Hamiltonian H' in (16) and the clamped-nuclei like operator H_o just defined can be shown to be self-adjoint (on their respective Hilbert spaces) by reference to the Kato-Rellich theorem[9] because in both cases there are kinetic energy operators that dominate the (singular) Coulomb interaction; they therefore have a complete set of eigenfunctions. This argument cannot be made for H^{elec} because it contains nuclear position operators in some Coulombic terms but there are no corresponding nuclear kinetic energy terms to dominate those Coulomb potentials. It therefore cannot be thought of as being self-adjoint on the full Hilbert space of electronic and nuclear variables. Thus even though H^{elec} is evidently Hermitian symmetric, this is not sufficient to guarantee a complete set of eigenfunctions because the operator is unbounded, and an expansion analogous to (11) seems quite problematic.

However that may be, Eq. (25) leads directly to a fundamental result; since H^{elec} commutes with all the $\{t^n\}$, it has the direct integral decomposition

$$H^{elec} = \int_X^\oplus H(\mathbf{b}, \mathbf{t}^e)_o d\mathbf{b}. \qquad (26)$$

This result implies at once that the spectrum of H^{elec} is *purely continuous*

$$\sigma = \sigma(H^{elec}) = \bigcup_{\mathbf{b}} \sigma(\mathbf{b}) \equiv [V_0, \infty),$$

where V_0 is the minimum value of $E(\mathbf{b})_0$; in the diatomic molecule case this is the minimum value of $E_0(r)$ (see Fig. 1). H^{elec} has *no* normalizable eigenvectors. We conclude therefore that the decomposition of the molecular Hamiltonian into a nuclear kinetic energy operator contribution, proportional to κ^4, and a remainder *does not* yield molecular potential energy surfaces.

IV. DISCUSSION

The rigorous mathematical analysis of the original perturbation approach proposed by Born and Oppenheimer[2] for a molecular Hamiltonian with Coulombic interactions was initiated by Combes *et al.*[8,27,28] with results for the diatomic molecule. A perturbation expansion in powers of κ leads to a

singular perturbation problem because κ is a coefficient of differential operators of the highest order in the problem; the resulting series expansion of the energy is an *asymptotic* series, closely related to the WKB approximation. Some properties of the operator H^{elec}, (Eq. (26)), seem to have been first discussed in this work. Since the initial work of Combes, a considerable amount of mathematical work has been published using both time-independent and time-dependent techniques with developments for the polyatomic case; for a recent review of rigorous results about the separation of electronic and nuclear motions see Hagedorn and Joye[29] which covers the literature to 2006.

If it can be assumed that (a) the electronic wavefunction vanishes strongly outside a region close to a particular nuclear geometry and (b) that the electronic energy at the given geometry is an isolated minimum, then it is possible to present a rigorous account of the separation of electronic and nuclear motion which corresponds in some measure to the original Born-Oppenheimer treatment; such an account is provided for a polyatomic molecule by Klein *et al.*[30] Because of the continuous spectrum of the electronic Hamiltonian H^{elec}, it is not possible to use regular perturbation theory in the analysis; instead asymptotic expansion theory is used so that the result has essentially the character of a WKB approximation. Neither is it possible to consider rotational symmetry for the reasons outlined in Sec. III. However it is possible to impose inversion symmetry and the nature of the results derived under this requirement depend on the shape of the geometrical figure at the minimum energy configuration. If the geometry at the minimum is either linear or planar then inversion can be dealt with in terms of a single minimum in the electronic energy. If the geometry at the minimum is other than these two forms, inversion produces a second potential minimum and the problem must be dealt with as a two-minimum problem; then extra consideration is necessary to establish whether the two wells have negligible interaction so that only one of the wells need be considered for the nuclear motion. The nuclei are treated as distinguishable particles that can be numbered uniquely. The symmetry requirements on the total wavefunction that would arise from the invariance of the Hamiltonian operator under the permutation of identical nuclei are not considered.

It is similarly possible to consider such phenomena as Landau-Zener crossing by using a time-dependent approach to the problem and looking at the relations between the electronic and nuclear parts of a wave packet.[31] This is essentially a use of standard coherent state theory where again the nuclei are treated as distinguishable particles and the method is that of asymptotic expansion.

To summarize: what the rigorous work so far presented has done is to show that if an electronic wavefunction has certain local properties and if the nuclei can be treated as distinguishable particles then the eigenfunctions and eigenvalues of the molecular (Coulomb) Hamiltonian can be obtained in a WKB expansion in terms of κ to arbitrary order.

In this paper we have attempted to discuss the Born approach to the molecular theory in terms first set out by Combes.[27] The essential point is that the decomposition of the molecular Hamiltonian (with center-of-mass contribution

removed) into the nuclear kinetic energy, proportional to κ^4 and a remainder, is specified by Eq. (18), not by (6), or in other words, *Eq. (6) cannot be written with an = sign.* Allowing the nuclear masses to increase without limit in H^{elec} does not produce an operator with a discrete spectrum since this would just cause the mass polarisation term to vanish and the effective electronic mass to become the rest mass. It is thus not possible to reduce the molecular Schrödinger equation to a system of coupled differential equations of classical type for nuclei moving on potential energy surfaces, as suggested by Born, without a further approximation of an essentially empirical character. An *extra choice* of fixed nuclear positions must be made to give any discrete spectrum and normalizable L^2 eigenfunctions. In our view this choice, that is, the introduction of the clamped-nuclei Hamiltonian, by hand, into the molecular theory as in Sec. II is the essence of the "Born-Oppenheimer approximation"

$$\mathsf{H}^{elec} = \int_X^{\oplus} \mathsf{H}(\mathbf{b}, \mathbf{t}^e)_o \, d\mathbf{b}$$
$$\rightarrow \mathsf{H}(\mathbf{b}, \mathbf{t}^e)_o \quad \text{Born-Oppenheimer approximation.}$$
(27)

If the molecular Hamiltonian H were classical, the removal of the nuclear kinetic energy terms would indeed leave a Hamiltonian representing the electronic motion for stationary nuclei, as claimed by Born and Oppenheimer.[2,3] As we have seen, quantization of H changes the situation drastically, so an implicit appeal to the classical limit for the nuclei is required. The argument is a subtle one, for subsequently, once the classical energy surface has emerged, the nuclei are treated as quantum particles (though indistinguishability is rarely carried through); this can be seen from the complexity of the mathematical account given by Klein *et al.*[30]

We have long argued that the solutions of the time-independent Schrödinger equation for the molecular Hamiltonian are of limited interest for chemistry, being really only relevant to a quantum mechanical account of the physical properties (mainly spectroscopic) of atoms and diatomic molecules in the gas-phase. Towards the end of his life, P.-O. Löwdin made an extended study of a quantum mechanical definition of a molecule; in one of his late papers[32] he lamented

The Coulombic Hamiltonian H' does not provide much obvious information or guidance, since there is [*sic*] no specific assignments of the electrons occurring in the systems to the atomic nuclei involved - hence there are no atoms, isomers, conformations etc. In particular one sees no *molecular symmetry*, and one may even wonder where it comes from. Still it is evident that all this information must be contained somehow in the Coulombic Hamiltonian.

In our view it is not at all evident that the Coulombic Hamiltonian *on its own* will give rise to the chemically interesting features Löwdin required of it, nor will they be approachable by regular perturbation theory (supposedly convergent) starting from its eigenstates. Fundamental modifications of the quantum theory of the Coulomb Hamiltonian for a generic molecule have to be made for a chemically significant

account of dipole moments, functional groups and isomerism, optical activity and so on.[33–37] In other words one should not expect useful contact between the quantum theory of an *isolated* molecule (which is what the eigenstates of the Coulombic Hamiltonian refer to) and a quantum account of *individual* molecules, as met in ordinary chemical situations where *persistent interactions* (due to the quantized electromagnetic field, other molecules in bulk media) and finite temperatures are the norm.[38,39]

The usual practice in computational chemistry in which clamped-nuclei electronic energy calculations are used to define a potential energy surface upon which a quantum mechanical nuclear motion problem is solved, is a practice that is well defined mathematically. Solutions obtained to the equations formulated in this context do not have the symmetry of the full internal motion Hamiltonian and their relationship to solutions of that Hamiltonian is, as has been seen, uncertain.

That said, the conventional account, treating formally identical nuclei as identifiable particles when it seems chemically prudent to do so, has enabled a coherent and progressive account of much chemical experience to be provided. But it is not derived by continuous approximations from the eigensolutions of the Schrödinger equation for the molecular Coulomb Hamiltonian, requiring as it does an essential empirical input. The tremendous success of the usual practice might perhaps be best regarded as a tribute to the insight and ingenuity of the practitioners for inventing an effective variant of quantum theory for chemistry.

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note that each of the spaces $H(P)$ transforms under a different representation of the translation group in three dimensions—under translation by an amount a, an element of $H(P)$ is multiplied by the factor e^{iPa}. Thus the direct integral is the infinite-dimensional analogue of the decomposition of a finite-dimensional vector space on which a group acts as a direct sum of irreducible representations.

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