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REGULAR ARTICLE

An analysis of the role of the Born–Oppenheimer approximation in calculating rotational–vibrational interactions in molecules

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Abstract It is argued that whether the use of the Born–Oppenheimer approximation is thought to require consideration of the potential energy surface in the context of a full Coulomb Schrödinger Hamiltonian in which translational and rotational motions are explicitly considered, and then it is inconsistent to treat that surface without allowing for the rotational motion of the molecule. Some of the implications of this upon the calculation of partition functions are considered.

Keywords Born–oppenheimer · Vibration–rotation interaction · Potential energy surface

1 Introduction

In an previous presentation [1], it was argued that because the potential calculated from the standard clamped-nuclei electronic Hamiltonian is usually taken to be rotationally and translationally invariant, and then any attempt to place this potential in the context of the full Schrödinger Coulomb Hamiltonian must be made with this Hamiltonian expressed in terms of translationally and rotationally invariant coordinates with the electronic coordinates explicit. Ways in which such a Hamiltonian might be constructed were discussed in the study by [2] and in that by [3]. In what follows the account given in [3] will be used.

2 Treating rotational and translational motion

The detailed derivation of the equations used in the following summary can be found in the study by [3] but in what follows the special case is chosen in which the N translationally invariant electronic coordinates $\mathbf{t}^{\mathrm{e}}$ have their origin at the center-of-nuclear mass. This choice is most likely to be effective in a region close to the equilibrium molecular geometry and is unlikely to be useful in describing dissociation. The translationally invariant nuclear coordinates $\mathbf{t}^{\mathrm{n}}$ may be chosen in any convenient way provided that only the original nuclear variables are involved. Diatomic species are not included in the following discussion.

The nuclear cartesian coordinates $\mathbf{t}^{\mathrm{n}}$ are considered related to a set $\mathbf{z}^{\mathrm{n}}$ by

$$\mathbf{t}^{\mathrm{n}} = \mathbf{C}\mathbf{z}^{\mathrm{n}} \tag{1}$$

so the matrix $\mathbf{C}$ may be thought of as a direction cosine matrix, relating the laboratory frame to the frame fixed in the body.

The electronic variables fixed in the body are then defined in terms of the above-mentioned transformation by

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

in which the superscript on the electronic variables fixed in the body has been dropped. Equations (1) and (2) *define* in the frame fixed in the body by means of $\mathbf{C}$, the cartesian form of the variables. Thus, *any* orthogonal transformation of the translationally invariant coordinates (including inversion) leaves them, by definition, unchanged.

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

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The internal coordinates q_k must be invariant to any orthogonal transformation of the translationally invariant coordinates and so must be expressible in terms of scalar products of the translationally invariant nuclear coordinates.

The translationally invariant angular momentum operator becomes

$$\mathsf{L}(\mathbf{t}) = -\frac{\hbar}{i}|\mathbf{C}|\mathbf{C}\mathbf{D}\frac{\partial}{\partial\boldsymbol{\phi}} = -|\mathbf{C}|\mathbf{C}\mathsf{L}(\boldsymbol{\phi}) \tag{3}$$

where $|\mathbf{C}|$ is either plus or minus one according to whether $\mathbf{C}$ corresponds to a proper rotation or to an improper rotation.

There is at this stage an element of choice for the definition of the angular momentum in the frame fixed in the body, and in Eq. (3), it can be seen that we have chosen

$$\mathsf{L}(\boldsymbol{\phi}) = \frac{\hbar}{i}\mathbf{D}\frac{\partial}{\partial\boldsymbol{\phi}} \tag{4}$$

Often, indeed perhaps more usually, the negative of this operator is chosen. However, a little algebra shows that in either case $\mathsf{L}^2(\boldsymbol{\phi}) \equiv \mathsf{L}^2(\mathbf{t})$ and that $\mathsf{L}_z(\boldsymbol{\phi})$ and $\mathsf{L}_z(\mathbf{t})$ commute with L^2 so one can find a complete set of angular momentum eigenfunctions $|JMk>$ such that

$$\begin{aligned}\mathsf{L}^2(\mathbf{t})|JMk> &= \mathsf{L}^2(\boldsymbol{\phi})|JMk> = \hbar^2 J(J+1)|JMk> \\ \mathsf{L}_z(\mathbf{t})|JMk> &= \hbar M|JMk> \\ \mathsf{L}_z(\boldsymbol{\phi})|JMk> &= \hbar k|JMk>\end{aligned} \tag{5}$$

The functions $|JMk>$ are often called *symmetric-top* eigenfunctions.

The complete kinetic energy operator may be written as

$$\mathsf{K}(\mathbf{z}) + \mathsf{K}(\mathbf{q},\mathbf{z}) + \mathsf{K}(\boldsymbol{\phi},\mathbf{q},\mathbf{z}) \tag{6}$$

Where

$$\mathsf{K}(\mathbf{z}) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{z}_i) - \frac{\hbar^2}{2M}\sum_{i,j=1}^{N}\vec{\nabla}(\mathbf{z}_i).\vec{\nabla}(\mathbf{z}_j) \tag{7}$$

The part of the Hamiltonian involving nuclear motion is

$$\mathsf{K}(\boldsymbol{\phi},\mathbf{q},\mathbf{z}) = \frac{1}{2}\left(\sum_{\alpha\beta}\kappa_{\alpha\beta}\mathsf{L}_\alpha\mathsf{L}_\beta + \hbar\sum_{\alpha}\bar{\lambda}_\alpha\mathsf{L}_\alpha\right) \tag{8}$$

and

$$\mathsf{K}(\mathbf{q},\mathbf{z}) = \mathsf{K}_A + \frac{\hbar^2}{2}\left(\sum_{\alpha\beta}\kappa_{\alpha\beta}\mathsf{l}_\alpha\mathsf{l}_\beta + \sum_{\alpha}\lambda_\alpha\mathsf{l}_\alpha\right) \tag{9}$$

where

$$\mathsf{K}_A = \frac{\hbar^2}{2}\left(\sum_{k,l=1}^{3A-6} g_{kl}\frac{\partial^2}{\partial q_k\partial q_l} + \sum_{k=1}^{3A-6} h_k\frac{\partial}{\partial q_k}\right) \tag{10}$$

In the above, m is the electronic mass and M is the total nuclear mass. Detailed definition of the various coefficients of the derivative terms in the Hamiltonian can be found in the study by [3]. For the moment, it is sufficient to note that $\boldsymbol{\kappa}$ depends upon the moments of inertia $\mathbf{I}$ of the rotating body. It is shown in [3] that

$$\boldsymbol{\kappa} = \mathbf{I}^{-1} + \boldsymbol{\tau}^T\mathbf{g}^{-1}\boldsymbol{\tau} \tag{11}$$

where the elements of $\mathbf{g}$ are the g_{kl} in Eq. (10) and the elements of $\boldsymbol{\tau}$ are part of the definition of λ_α. This last involves a part dependent upon derivatives of the q_k and a multiplicative term v_α/i while

$$\bar{\lambda}_\alpha = \lambda_\alpha + 2(\boldsymbol{\kappa}\mathsf{l})_\alpha$$

where l is the electronic angular momentum operator. The potential energy operator is

$$\begin{aligned}V(\mathbf{q},\mathbf{z}) = {}& \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{z}_j - \mathbf{z}_i|} + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{A}{}' \frac{Z_iZ_j}{r_{ij}(\mathbf{z}^{\mathrm{n}})} \\ & - \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{A}\sum_{j=1}^{N}\frac{Z_i}{r'_{ij}(\mathbf{z}^{\mathrm{n}},\mathbf{z}^{\mathrm{e}})}\end{aligned}$$

or

$$V(\mathbf{q},\mathbf{z}) = V^{\mathrm{e}}(\mathbf{z}) + V^{\mathrm{n}}(\mathbf{q}) - V^{\mathrm{en}}(\mathbf{q},\mathbf{z}) \tag{12}$$

Here, r'_{ij} is the electron-nucleus distance.

Although both $\mathsf{L}_z(\boldsymbol{\phi})$ and $\mathsf{L}_z(\mathbf{t})$ commute with L^2, only $\mathsf{L}_z(\mathbf{t})$ and L^2 commute with the Hamiltonian, so that the eigenfunctions $\Psi^{J,M}(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}})$ written in the form

$$\Psi^{J,M}(\mathbf{t}^{\mathrm{n}},\mathbf{t}^{\mathrm{e}}) \to \Psi^{J,M}(\boldsymbol{\phi},\mathbf{q},\mathbf{z}) = \sum_{k=-J}^{+J}\Phi_k^J(\mathbf{q},\mathbf{z})|JMk> \tag{13}$$

where the $|JMk>$ are angular momentum eigenfunctions and where the internal coordinate function on the right side cannot depend on M because, in the absence of a field, the energy of the system does not depend on M. Eigenfunctions of this kind form a basis for irreducible representations of $SO(3)$, as required.

It is argued in [1] that the ordinary clamped-nuclei electronic Hamiltonian should be mapped on to the Hamiltonian formed from the sum of Eq. (7) and the potential Eq. (12) but with the coordinates $\mathbf{q}$ taken at the fixed values arising from the geometry chosen when clamping the nuclei.

A linear transformation of the laboratory coordinates leads to a translationally invariant set of coordinates so the Jacobian for such a transformation is simply a constant. Thus, the spectrum of the resulting Hamiltonian remains invariant, no matter what choice of translationally invariant coordinates is made. However, the transformation to body-fixed coordinates is to a manifold and not a Cartesian space and so has a Jacobian that vanishes in some region of space. In fact it can be shown (see the discussion in [3]) that at least two choices of body-fixed coordinates must be made in order to cover the Cartesian space defined by translationally invariant coordinates and, furthermore, in any one choice, a single choice of orthogonally invariant internal coordinates is not sufficient to describe unambiguously all possible nuclear geometries. It is thus to be expected that a given body-fixed Hamiltonian will have a spectrum that describes only part of the full spectrum.

3 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, the Hamiltonian is written as

$$\mathsf{K}_I + \mathsf{K}_R + \mathsf{V} \tag{14}$$

in which the first term, K_I, consists of the first two terms and K_R is the third term in Eq. (6). V is Eq. (12).

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.

The matrix elements of this Hamiltonian with respect to the angular variables are

$$\begin{aligned}
&< JMk' \mid \mathsf{K}_I + V + \mathsf{K}_R \mid JMk > \\
&= \frac{\hbar^2}{4}(b_{+2}C^+_{Jk+1}\,C^+_{Jk}\delta_{k'k+2} + b_{-2}C^-_{Jk-1}C^-_{Jk}\delta_{k'k-2}) \\
&\quad + \frac{\hbar^2}{4}(C^+_{Jk}(b_{+1}(2k+1) + \overline{\lambda}_+)\delta_{k'k+1} + C^-_{Jk}(b_{-1}(2k-1) \\
&\quad + \overline{\lambda}_-)\delta_{k'k-1}) + \frac{\hbar^2}{2}((J(J+1) - k^2)b + b_0k^2 + \overline{\lambda}_0 k)\delta_{k'k} \\
&\quad + (\mathsf{K}_I + V)\delta_{k'k}
\end{aligned} \tag{15}$$

In this expression

$$\begin{aligned}
&b_{\pm 2} = (\kappa_{xx} - \kappa_{yy})/2 \pm \kappa_{xy}/i \\
&b_{\pm 1} = \kappa_{xz} \pm \kappa_{yz}/i \\
&b = (\kappa_{xx} + \kappa_{yy})/2 \quad b_0 = \kappa_{zz}
\end{aligned} \tag{16}$$

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

$$\overline{\lambda}_\pm = (\overline{\lambda}_x \pm \overline{\lambda}_y/i) \tag{17}$$

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 Eq. (15) which are invariant to orthogonal transformations, and it is these functions that will be used to consider the separation of electronic and nuclear variables.

4 Constructing effective operators for nuclear motion in a product function basis

An approximate solution to the effective Hamiltonian is expressed in terms of a sum of products of the form

$$\Phi^J_{kp}(\mathbf{q})\psi_p(\mathbf{q},\mathbf{z}) \tag{18}$$

where p labels the electronic state and the sum is over p. The explicit variables in which ψ_p is imagined expressed are electron nucleus separation variables. Technically, this means that ψ_p is an implicit function of the $\mathbf{q}$ and the $\mathbf{z}$. But it is probably clearer to use the terminology that is appropriate when a fixed value is chosen for $\mathbf{q}$ and say that the explicit variables are the $\mathbf{z}$ and that the $\mathbf{q}$ are parameters in the function. It should be stressed that this separation is simply a computational strategy because the system of differential equations implied by the Hamiltonian is obviously stiff because of the very great differences in size between the mass terms that coefficient the Laplacians.

In this approach, the approximating functions including angular momentum are taken to be of the form.

$$\psi_p(\mathbf{q},\mathbf{z})\sum_{k=-J}^{+J}\Phi^J_{kp}(\mathbf{q})|JMk> \tag{19}$$

If we consider the effective internal motion operator working on a product function, we get

$$\begin{aligned}
&\Phi^J_{kp}(\mathbf{q})(\mathsf{K}(\mathbf{z}) + V^{\mathrm{e}}(\mathbf{z}) - V^{\mathrm{ne}}(\mathbf{q},\mathbf{z}) + V^{\mathrm{n}}(\mathbf{q}))\psi_p(\mathbf{q},\mathbf{z}) \\
&\quad + \mathsf{K}(\mathbf{q},\mathbf{z})\Phi^J_{kp}(\mathbf{q})\psi_p(\mathbf{q},\mathbf{z})
\end{aligned} \tag{20}$$

As explained before, this equation is, within any rotational manifold, diagonal in J, M but this will be left implicit in future. The nuclear function has been moved through the expression as far as is possible, but the electronic function may not be moved at all, since it depends on all the variables in the problem at this stage.

In the standard approach, it is stipulated that the set of known functions, $\psi_p(\mathbf{q},\mathbf{z})$, should be chosen as exact solutions of the electronic problem

$$\begin{aligned}
&(\mathsf{K}(\mathbf{z}) + V^{\mathrm{e}}(\mathbf{z}) - V^{\mathrm{ne}}(\mathbf{q},\mathbf{z}))\psi_p(\mathbf{q},\mathbf{z}) \\
&\equiv \mathsf{H}^{\mathrm{elec}}(\mathbf{q},\mathbf{z})\psi_p(\mathbf{q},\mathbf{z}) = E_p(\mathbf{q})\psi_p(\mathbf{q},\mathbf{z})
\end{aligned} \tag{21}$$

However, as argued in [1], the operator in this equation is not self-adjoint and so has no proper eigenfunctions.

However, if the nuclei are clamped, then the equation does have proper eigenfunctions and a well-formed electronic Hamiltonian can be defined over these fixed points using the theory of fiber-bundles. At each and every point in the nuclear position space, these eigenfunctions may be chosen as an orthogonal set each with eigenvalue $E_p(\mathbf{a})$ where the choice of fixed nuclear geometry **a**, yields a fixed value of the internal coordinates. The theory of fiber-bundles may be used to define a potential $V_p(\mathbf{q})$ arising from the properly defined electronic Hamiltonian plus the classical nuclear repulsion. The potential could in principle be calculated at any point, but in practice this potential is known only at a finite number fixed values of the nuclear geometry. These may be chosen in a manner required in advance of the calculation but often the chosen points are fitted to a functional form. Ideally, any fit should be checked to show that the value of the potential at any point not used in the fit is close enough to the eigenvalue computed at that point. The whole internal coordinate space does not admit a global potential because the internal coordinates are built on a manifold which is not globally Cartesian.

A set of electronic functions covering all the internal coordinate space arising from a properly defined electronic motion problem can be postulated. These functions may then be imagined as $\psi_p(\mathbf{q}, \mathbf{z})$ then Eq. (20) may be worked through remembering that the product rule must be used when considering the effect of derivative operators with respect to the q_k because *both* terms in the product Eq. (18) depend on the **q** variables. The effective nuclear motion Hamiltonian, depending only on the **q**, can be obtained by multiplying the resulting expression from the left by $\psi_{p'}(\mathbf{q}, \mathbf{z})$ and integrating over the **z**. Doing this yields an equation with coupling between different electronic states, labeled by p. The effective internal motion operator is then:

$$
\begin{aligned}
&< JMk'p' \mid \mathsf{H} \mid JMkp >_{\mathbf{z}}\\
&= \frac{\hbar^2}{4}(b_{+2}C^{+}_{Jk+1}\,C^{+}_{Jk}\delta_{k'k+2} + b_{-2}C^{-}_{Jk-1}C^{-}_{Jk}\delta_{k'k-2})\delta_{p'p}\\
&\quad + \frac{\hbar^2}{4}\big(C^{+}_{Jk}(b_{+1}(2k+1) + \lambda_{+})\delta_{k'k+1}\\
&\quad + C^{-}_{Jk}(b_{-1}(2k-1) + \lambda_{-})\delta_{k'k-1}\big)\delta_{p'p}\\
&\quad + \frac{\hbar^2}{4}\Big(C^{+}_{Jk}\gamma^{+}_{p'p}(\mathbf{q})\delta_{k'k+1} + C^{-}_{Jk}\gamma^{-}_{p'p}(\mathbf{q})\delta_{k'k-1}\Big)\\
&\quad + \frac{\hbar^2}{2}\big((J(J+1) - k^2)b + b_0k^2 + \lambda_0 k\big)\delta_{k'k}\delta_{p'p}\\
&\quad + \frac{\hbar^2}{2}\delta_{k'k}k\gamma^{0}_{p'p}(\mathbf{q})\\
&\quad + \ \delta_{p'p}\delta_{k'k}\big(\mathsf{K}_A + E_p(\mathbf{q}) + V^{\mathrm{n}}(\mathbf{q})\big) + \delta_{k'k}\gamma_{p'p}(\mathbf{q}) \qquad (22)
\end{aligned}
$$

The definitions of the γ terms can again be found in [3] but it is sufficient here to note that they are all simply multiplicative functions of the internal coordinates and can couple different electronic states.

If it were the case that a single electronic state dominated in the energy range of interest and that within that state for a given J only a single value of k dominated then, to a first approximation the Hamiltonian

$$\big(\mathsf{K}_A + E_p(\mathbf{q}) + V^{\mathrm{n}}(\mathbf{q})\big)$$

would determine the vibrational motion, and since the b and b_0 values are simply multipliers, the Hamiltonian

$$\frac{\hbar^2}{2}\big((J(J+1) - k^2)b + b_0k^2\big)$$

would determine the rotational motion if any contribution from λ_0 can be ignored. This separation forms the basis for the standard description of vibration–rotation motion in which the vibrational levels are treated as primary levels having rotational sublevels.

4.1 The valid utilization of a product function basis

If the electronic functions calculated at each fixed point were members of a set of functions with known explicit dependence on **q** specifiable over the whole range of the internal coordinate space, then it would be possible to calculate all the derivatives required to evaluate the γ terms. If a single electronic state was considered, a set of internal motion functions could be taken as the basis for a secular problem defined, within any J manifold, by matrix elements of the Hamiltonian defined by Eq. (22). The resulting internal motion eigenfunctions could be combined with the electronic functions and used as a basis for a secular problem, again within any J manifold, defined by the full Hamiltonian. This would result in variationally exact solutions to the full problem. The results could then be improved if necessary by means of the usual computational strategies.

In practice, this approach has not yet proved possible. The best that can be done is to determine the internal motion functions using a suitable potential and then to treat the γ terms as perturbations with the derivative terms estimated as accurately as possible around the fixed points at which the electronic functions are known. If the ordinary clamped-nuclei Hamiltonian is to be used to determine this potential, then since this can be mapped only onto the first term in Eq. (7), consistency requires that the second term in Eq. (7) should be treated as a perturbation and added to the clamped nuclei result. In what follows $\mathsf{V}_p(\mathbf{q})$ denotes the clamped-nuclei result and v_p denotes the addition.

If it were anticipated that a single electronic state and a single value of k was going to provide an adequate approximation for determining the internal nuclear motion, then it would seem appropriate to use as a potential the effective form:

$$\mathsf{V}_p(\mathbf{q}) + \mathsf{v}_p + \frac{\hbar^2}{2}\left((J(J+1) - k^2)b + b_0k^2\right) \tag{23}$$

The extra terms in Eq. (23) arise from the purely product terms in Eq. (22) and involve no derivatives with respect to the internal variables. This can be compared with the effective potential commonly used in diatomic calculations namely

$$\mathsf{V}_p(\mathbf{q}) + \mathsf{v}_p + \frac{\hbar^2}{2\mu_{ab}}\frac{1}{R^2}\left(J(J+1) - 2k^2\right)$$

The coefficients of the terms in J and k in Eq. (23) depend on the choice of a particular body-fixed frame just as they do for the diatomic Hamiltonian. In the case of three or more nuclei, however, more than one choice of body-fixing can be made and, as noted earlier, at least two choices must be made if it is wished to cover all the Cartesian space $R^{3A\text{-}3}$ formed by the translationally invariant coordinates. If it is wished to investigate the spectrum up to the lowest dissociation level of a polyatomic molecule, although the so-called HVZ theorem (Theorem XIII.17 in [5]) provides a secure theoretical basis for recognizing that level as the top of the discrete spectrum of the operator, but, as discussed in [4], it seldom provides a secure basis for identifying it in advance except in the case of neutral atoms. Although the continuous spectrum begins at the lowest dissociation level, since this level is below zero (where zero is defined in the standard spectral theory manner, as the energy of the infinitely separated components, so only hydrogen-like atoms dissociate at zero energy), then there will be resonant states above the dissociation level which may well contribute to the discrete spectrum. Thus, it is not known in advance whether a particular state is accessible with the chosen body-fixed coordinate system because the Jacobian of the transformation may vanish in the coordinate domain in which the required states can be described.

In the diatomic case, there are no such troubles because with the choice illustrated earlier with μ_{ab} the reduced nuclear mass and R the bond length, and for the electronic variables to carry the z component of internal angular momentum, it is only at dissociation into atoms or ions that uncertainties arise. For diatomic states of different k correspond to different electronic states and thus, up to the lowest dissociation level, the mixing of states of different k will be very small in molecules composed of atoms in the first two rows of the periodic table, (exhibited as so-called lambda doubling), and it is sufficient to consider only the single value of $|k|$ that is determined by the clamped nucleus electronic structure calculation when determining the potential. So, though $2J + 1$ states of different k can be associated with a given J, it is not usually necessary to consider all of them and for any electronic state. For homonuclear diatomic molecules, it is known that the lowest dissociation level is at the energy of two neutral atoms in their electronic ground states.

The role of k in the polyatomic case is, unfortunately, much more involved. The form of the coupling terms in Eq. (22) makes it clear that for any electronic state, any given J state can have $2J + 1$ different k states coupled by nuclear motion. So investigating states of high J is liable to involve a very extensive domain of trial functions and to make great care necessary to construct feasible computational schemes. It is therefore the case that, from the present position, the potential must be regarded not only as depending upon J but also upon the way in which angular motion is realized in a given formulation.

However, k is defined for a particular J, and it is clear that potential will become more and more shallow for any given k as J increases. Precisely how important this is depends upon the size of b which is indirectly related through Eq. (11) to the inverse of the instantaneous inertia tensor.

It is useful then to examine particular examples to obtain some idea of how important the proposed modification of the potential to allow for the effects of rotational motion is likely to prove. It is already known [6] that for the hydrogen molecule dissociating into two hydrogen atoms in their ground states, the $J = 0$ state supports 14 vibrational states, the state $J = 15$, supports 10 and for $J = 31$, only 1. In fact, there are just 301 states that can be associated with the lowest electronic state of the hydrogen molecule. So it is clear that here the number of vibrational states possible is strongly associated with the rotational state. Furthermore, the energy levels are inter-twined. Thus, for example, in the ground vibrational state, the rotational state with $J = 9$ has a higher energy than the $J = 0$ state has in the second vibrational state.

This is, of course, not the usual way in which these calculations are presented for, just as described earlier in the polyatomic case, the rotational levels are shown as sublevels of a vibrational state. Thus, the ground vibrational state is associated with 31 rotational sublevels even though the sublevel $J = 9$ has an energy above that of the $J = 0$ level of first excited vibrational state.

Since the proton nuclear masses are the smallest nuclear masses, it might be expected that the effects of rotational motion would be most marked in the case of molecules made up only of protons so it seems sensible to examine what happens in H_3^+ a molecule involving only protons and, with only two electrons, one on which very accurate electronic structure calculations can be made.

5 The vibration–rotation spectrum of H_3^+

It is known that the lowest dissociation products of H_3^+ are H^+ and H_2 in its ground electronic state so that the upper limit of the discrete spectrum is known pretty accurately. It is common in very accurate calculations of the vibration–rotation states of H_3^+ use a formulation of the vibration–rotation Hamiltonian developed in [7] for triatomic systems generally. Because only two distinct translationally invariant coordinates, call them $\mathbf{t}_1$ and $\mathbf{t}_2$ can be chosen, this formulation is not able explicitly to support the full nuclear permutational symmetry, but provided that the electronic potential used is invariant under all the nuclear permutations the full symmetry can be accommodated. In this formulation, where the three nuclei define the $x - z$ plane with the y axis chosen to make the frame right handed, Eq. (23) simplifies a little to

$$\mathsf{V}_p(\mathbf{q}) + \mathsf{v}_p + \frac{\hbar^2}{2}((J(J+1) - k^2)b + b_0 k^2) \tag{24}$$

with

$$b = (\kappa_{xx} + \kappa_{yy})/2, \quad b_0 = \kappa_{zz}$$

If now a special choice of coordinate system is made so that $\mathbf{t}_1$ is the vector joining two protons and $\mathbf{t}_2$ is chosen with its origin at the center-of-mass of the proton pair and pointing toward the remaining proton and the angular trial functions are chosen to be associated Legendre polynomials $\Theta_{j,k}(\theta)$ then even further simplification is possible to yield

$$\mathsf{V}_p(\mathbf{q}) + \mathsf{v}_p + \frac{\hbar^2}{2\mu_1 r_1^2}((J(J+1) - 2k^2)) \tag{25}$$

where r_1 is the length of the vector joining the two protons and μ_1 is the reduced mass of the proton pair. This choice results in a formulation of the Hamiltonian which is valid even when the system becomes linear. It seems that the molecule becomes linear at an excitation energy of about 12,000 cm^{-1} above its vibrational ground state which is at about 2,394 cm^{-1}. Its dissociation energy is at about 35,000 cm^{-1}. The divergence at $r_1 = 0$, though of theoretical consequence, is easily avoided by a suitable choice of trial function.

It should be emphasized that the choice of the $\mathbf{t}_i$ to be bond-length vectors would give a very different forms for b and b_0 and that b, on integration over θ, would give rise to a term (see Sect. 4.3 of [7])

$$I^{(1)}_{j',k',j,k} = <j'k' \mid \frac{1}{(1 - \cos\theta)} \mid jk>$$

This term diverges logarithmically when $k' = k = 0$ and thus can result in a divergent term in the Hamiltonian for states for which $J > 0$, $k = 0$. The remark made earlier can thus be seen to be a matter of consequence. The potential depends not just upon J but upon the way in which the angular motion is realized in a given formulation.

In the case of $J = 0$ in the chosen formulation, it is estimated that there are 1,280 vibrational states below dissociation [8]. It seems that 46 is the highest value of J for which at least one vibrational state exists [9] but 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. What information there is would seem to indicate that for $J = 11$ and above there will be overlap between the rotational states assigned to the lowest vibrational state and the $J = 0$ states of the higher vibrational states, just like the inter-twining that occurs in the hydrogen molecule case. As can be seen from the upper limit for $J = 0$ states given previously, many states exist at energies above which the molecule becomes linear. A discussion of this can be found in [10].

It has not yet proved possible to calculate all the vibration–rotation states of H_3^+ at a highly accurate level but an attempt has been made [11] to calculate the partition function using accurate energy levels for all states up to 15,000 cm^{-1} above the ground state including all rotational states up to $J = 20$ and using an extrapolation scheme above these. The scheme assumed that J did not exceed 46, as indicated in accurate calculations, and modeled states up to the dissociation limit taken to be 35,000 cm^{-1}. The treatment of the rotational levels in their extrapolation scheme is based on the Eckart [12] approach to the treatment of rotational motion which is the most generally used formulation for considering nuclear motion in molecules, and it is that approach to be considered next.

6 An analysis of the effect of rotational motion on the potential in the Eckart formulation

This formulation of the vibration–rotational problem is the one that forms the basis for the treatment of vibrations and rotations as independent motions and so forms the basis for what is usually done in calculating vibration–rotation partition functions. The Eckart Hamiltonian for nuclear motion was put into quantum mechanical form by Watson [13] with the angular momentum operators obeying the anomalous commutation conditions. For consistency with what has gone before, a reformulation of Watson's form will be used, with angular momentum operators that obey the standard commutation conditions. Details may be found in [3], and it is sufficient to note here that $\mathbf{a}_i$ is used to denote the position of the i-th nucleus expressed in the

Eckart frame and z_i to denote its instantaneous position, and the skew-symmetric matrix $\hat{\mathbf{x}}_i$ is

$$\hat{\mathbf{x}}_i = \begin{pmatrix} 0 & -x_{zi} & x_{yi} \\ x_{zi} & 0 & -x_{xi} \\ -x_{yi} & x_{xi} & 0 \end{pmatrix} \tag{26}$$

where $\mathbf{x}$ denotes any of the coordinate variables.

The form of the potential in the Eckart case is slightly different in form from the triatomic form Eq. (24) because incorporation of the internal coordinate part of the Jacobian into the trial wavefunction generates an extra term, the so-called Watson term

$$-\frac{\hbar^2}{8}\sum_{\alpha}\kappa_{\alpha\alpha}$$

Here, the matrix $\boldsymbol{\kappa}$ from which b and b_0 are derived is:

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

where $\mathbf{I}^0$ is the inertia tensor for the molecule at the reference geometry

$$\mathbf{I}^0 = \sum_{i=1}^{H} m_i \hat{\mathbf{a}}_i^T \hat{\mathbf{a}}_i$$

and so is a constant matrix and

$$\mathbf{I}'' = \sum_{j=1}^{H} m_j \hat{\mathbf{z}}_j^{nT} \hat{\mathbf{a}}_j \tag{27}$$

When the nuclear displacements from the equilibrium geometry are small ones

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

and the inertia tensor can be put into principal axis form without loss of generality and yields the usual rotational Hamiltonian

$$\mathsf{H}^{\mathrm{rot}} = \frac{1}{2}\left(\kappa_{xx}\mathsf{L}_x^2 + \kappa_{yy}\mathsf{L}_y^2 + \kappa_{zz}\mathsf{L}_z^2\right)$$

When expressing the expectation value of the Hamiltonian in this form, the terms arising from the $1/2\kappa_{\alpha\,\alpha}$ are usually denoted A, B and C with $A \geq B \geq C$ and refered to as the rotational constants and quoted in cm^{-1}. This Hamiltonian forms the starting point for the discussion of microwave spectra.

In the case of H_3^+, the equilibrium geometry is that of an oblate symmetric-top ($A = B > C$) and the second part of Eq. (24) is usually written as

$$hc(BJ(J+1) + (C-B)k^2)$$

If this form is used to interpret the experimental spectrum, then, in cm^{-1}, $B = 43.56$ and $C = 20.61$ [11]. These are quite small quantities and would lead only to a small Watson term in the $J = 0$ state for vibrational states that result in only a small departure from the equilibrium geometry.

In the extrapolation scheme used in [11], the energies of the upper states are estimated using a formula

$$E_n = E_n(J=0) + E_{gs}(J,K)$$

in which the last term on the right is a function of the symmetric-top energy given above, determined by fitting the rotational states up to $J = 20$ of the lowest vibrational state.

However, the calculations discussed earlier show that there are many vibrational states in the $J = 0$ state that reach a linear geometry, and for these states, it is easy to see that one of the moments of inertia vanishes and so B and C increase without limit and the Watson term becomes divergent.

It is thus not possible to justify, from a theoretical point of view, the usual treatment of vibrational and rotational motions in the calculation of partition functions for this system because in the usual formulation, it is assumed that any vibrational level can be achieved for any rotational level, and this cannot be the case here, even for the $J = 0$ state.

Although extrapolation scheme outlined previously uses the Eckart form of the symmetric-top rotational energy, it is used merely as a fitting device and its form is chosen at the start of the fitting and so any actual divergence is irrelevant to its use. However, it might be thought that for states that are substantially linear, a rigid rotor might form a better model for extrapolation.

7 Conclusions

To put matters in perspective but still confining attention to the bound eigenstates of the Coulomb Hamiltonian:

When calculating bound state energy for atoms all that is necessary is to separate the translational motion of the atom as a whole and then to express choose the internal coordinates to be the spherical polar coordinates for each of the electrons with the atomic nucleus as the origin. There is no need to approximate the nuclear motion and so the Born–Oppenheimer approximation is irrelevant in this case, and there is only an electronic structure problem. Approximate solutions may easily be chosen in a form in which both the orbital and spin angular momentum are definite without any approximation. However, the nuclear mass can be allowed to increase without limit, so effectively clamping the nucleus, while preserving a self-adjoint Hamiltonian, and if this is done, the Hamiltonian is slightly simplified to the one that is used most often in electronic structure calculations. The difference between the energy levels as calculated with the two Hamiltonians is very small. The problem is exactly soluble for the hydrogen atom and for any hydrogen-like ion and, as has been seen, using the exact energy levels leads to partition function which diverges. Even though exact solutions cannot be obtained for many electron atoms, it is demonstrable that all neutral atoms or positively charged ions have an infinite number of energy levels terminating at the first ionization energy. The partition function for any of them will therefore diverge in exactly the same way as for the hydrogen atom. There is no agreement about how this divergence should be dealt with.

When calculating the bound state energy for a any molecule once the translational motion has been separated, there remains the problem of dealing with the nuclear motion as well as the electronic motion and it is here that the clamped-nuclei approach plays an important part. There is no molecule for which exact eigenfunctions are known but for the diatomic H_2^+ very accurate solutions are known without using the clamped-nuclei approach and similarly accurate solutions are known for the hydrogen molecule in its lowest energy state. It has not so far proved possible to calculate any other state of the hydrogen molecule or of any state of any other molecule without using the clamped-nuclei approach. The Hamiltonian produced by clamping the nuclei is properly self-adjoint and, if the molecule is neutral or positively charged, has an infinite number of bound electronic states just like an atom or positive ion. However, it is known that the full problem has bound states only up to the lowest energy state at which the eigenfunction corresponds to the dissociation into two parts. In general, this level is not known, but for H_2^+, it is known to be $H + H^+$ and for the hydrogen molecule it is known to be two hydrogen atoms both in their ground electronic state. Unless both of the dissociated parts are oppositely charged, the number of bound states can be shown to be finite [14, 15]. The Born–Oppenheimer approximation consists of choosing the clamped-nuclei electronic state in terms of which the lower rotational and vibrational states of the full problem can be most closely approximated. It is thought that for most molecules, the lowest dissociation level is into neutral parts and so it is anticipated that only a finite number of bound states need to be considered in calculating the partition function. It has been seen that for the hydrogen molecule in the clamped-nuclei approach that the Born–Oppenheimer approximation leads to an excellent separation between electronic and nuclear motion and that only one electronic state lies below the first dissociation level. However, the potential in which vibrational nuclear motion occurs is strongly dependent upon the rotational state of the molecule and so the Born–Oppenheimer approximation is not applicable here in its usual form in which the rotations and vibrations are treated independently. A detailed analysis of this case has already been presented.

In the present work, the polyatomic case in which the most accurate calculations are possible has been considered. The Born–Oppenheimer approximation for the separation of electronic and nuclear motion has once more, seemed to be a good one but, again, the separation of rotational and vibrational motion does not seem justified, because the potential for nuclear vibrational motion has been shown to depend strongly on the rotational motion of the molecule. The precise form of this dependence has been shown to depend upon the way in which the rotating axes are fixed in the molecule, and it is thus much less clear than in the diatomic case, how this failure to separate ought to be handled. There is an additional complication in polyatomic systems because all $2J + 1$ states of different k can be achieved within a given electronic potential, so that the variational problem in any approximate calculation of vibrational motion grows rapidly in size with increasing J.

The molecules that have been considered in the work reported for this project are "worst cases" in the sense that they have the smallest possible nuclear masses and thus will give rise to kinetic energy operators which are the closest possible to the electronic ones and thus will lead to the greatest possible interaction between the electronic and nuclear motions. What has been shown, however, is that even in such cases, calculations using the clamped nuclei approach can lead to potentials in which nuclear motion can be effectively calculated if the rotational and vibrational motions are treated as coupled.

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