The Construction and Fitting of Molecular Potential Energy Surfaces and Their Use in Vibration-rotation Calculations

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Abstract

The state-of-the-art in non-empirical calculations of potential energy surfaces for small molecules is discussed, as is the present position with respect to the analytic fitting of such surfaces. The results of some nonempirical vibration-rotation calculations performed on such analytic surfaces are presented and compared with experimental results. An attempt is made to assess the extent to which present methods of electronic structure calculation and present analytic fitting methods are adequate to produce surfaces for the interpretation of high-resolution spectral data.

Introduction

In the past decade computational quantum chemistry has developed, as computers have developed, to the position where it is possible, almost as a matter of routine, to obtain very accurate and extensive potential energy surfaces from electronic structure calculations for systems consisting of 3 or 4 nuclei and up to about 10 electrons. There have also been parallel developments in the rather less accurate calculation of such surfaces for larger systems with more nuclei and more electrons. It is, however, the first sort of calculation on which interest will be centered in this paper, for it is these calculations that offer the best basis for nonempirical calculations of whole-molecule wave functions; that is, calculations of not only electronic structure but of nuclear motion behavior too. The interest in such calculations lies not only in the role that they play in interpreting the rotation-vibration spectra of molecules, but also in the role that they might play in understanding chemical reactions. Thus, if one could find methods of dealing with very highly excited vibration and rotational states, where the molecule is on the verge of dissociation, then one would be approaching from below the elusive region of chemical reaction, which is approached from above by scattering and collision theory.

The work described in this article represents only a modest step toward the

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goal of describing the reactive domain, but it does illustrate what can be done by purely nonempirical means to describe quite highly excited vibration and rotation states of small systems.

The Theoretical Basis

The complete non relativistic molecular Hamiltonian expressed in a laboratory-fixed frame has the form

$$\hat{H} = \hat{K}_{\mathrm{n}} + \hat{K}_{\mathrm{e}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{en}} + \hat{V}_{\mathrm{ee}}, \tag{1}$$

where the subscripts e and n designate the electrons and nuclei, respectively, and the symbols are otherwise conventional.

In electronic structure calculations it is usual simply to ignore $\hat{K}_{\mathrm{n}}$, to treat V_{nn} as a classical quantity, and to try to obtain solutions to the problem specified by

$$\hat{H}_{\mathrm{elec}} = \hat{K}_{\mathrm{e}} + \hat{V}_{\mathrm{en}} + \hat{V}_{\mathrm{ee}} \tag{2}$$

as functions of the nuclear geometry. Thus if there are $N(>2)$ nuclei in the problem, the electronic energy $E(\mathbf{R})$ associated with $\hat{H}_{\mathrm{elec}}$ is a function of $3N - 6$ internal variables (denoted collectively as $\mathbf{R}$). These variables must be chosen so that $\hat{H}_{\mathrm{elec}}$ is invariant to translation and rigid rotation of the system, but otherwise may be chosen at will. V_{nn}, considered as a classical quantity, can also be expressed in terms of these internal variables, and the sum of $E(\mathbf{R})$ and $V_{\mathrm{nn}}(\mathbf{R})$ is the potential energy surface (or function) for the system. As is well known, if there is a minimum in this surface at some geometry $\mathbf{R}_0$, then the energy at this minimum is generally, to a very good approximation, the true total energy of the bound system with equilibrium geometry $\mathbf{R}_0$.

In the standard formalism for moving beyond the electronic structure calculation, it is assumed that the whole-system wave function can be written as a sum of products:

$$\psi = \sum_n \chi_n \Phi_n, \tag{3}$$

where Φ_n is an electronic wave function expressed as a function of electronic variables and of nuclear geometry, and χ_n is a nuclear motion function.

Clearly, the situation is not quite straightforward here, because one must be able to express χ_n in (3) in terms of the chosen internal variables used in Φ_n and six more variables, three of which describe the translation of the system and three its rigid rotations, thus covering the motion of the whole system. To put this another way, if χ_n is to occur as a solution to an "effective" problem arising from (1) after electronic motion has been integrated out, then it is essential that the Hamiltonian (1) be reexpressed in terms of the chosen internal coordinates, with three coordinates to describe translations and three more to describe rigid rotations of the system as a whole.

This is a technically formidable task whose solution was first convincingly tackled by Eckart [1] for the case where the stable system has a very deep minimum at some unique equilibrium geometry, $\mathbf{R}_0$, and where at that minimum, the other electronic states in the expansion (3) are, energetically, well separated from the state of primary interest. In this case careful analysis shows that, if the nuclei exhibit only small-amplitude motions, it is sufficient to consider just one electronic state, and the influence of the electrons on the nuclear motion can be incorporated via the potential energy function alone. This is usually called the Born-Oppenheimer approximation.

The conditions given by Eckart [1] may be used to express the Hamiltonian in terms of three translations, three rotation and $3N - 6$ translation- and rotation-free internal coordinates, and after a great deal of algebra, it may be shown that the effective Hamiltonian for nuclear motion (ignoring the translational term, which may be factorized off) is:

$$\hat{H} = \sum_{\alpha,\beta} \mu_{\alpha\beta}(L_\alpha - \pi_\alpha)(L_\beta - \pi_\beta) - \frac{\hbar^2}{2}\sum_{k=1}^{3N-6}\frac{\partial^2}{\partial Q_k^2} - \frac{\hbar^2}{8}\sum_\alpha \mu_{\alpha\alpha} + V(\mathbf{Q}) \tag{4}$$

This form was first given by Watson [2], and there a detailed explanation of the terms can be found. It is sufficient to note here that the internal coordinates Q_k are usually normal coordinates, the L_α are angular momentum operators for the whole system (and depend only on the angular variables), the π_α are the coriolis coupling operators, and the matrix $\boldsymbol{\mu}$ is a matrix closely related to the inverse of the moment-of-inertia tensor for the problem. The term $V(\mathbf{Q})$ is the potential energy function expressed in terms of the coordinates Q_k, which are chosen such that at the equilibrium geometry the Q_k are all zero.

For small amplitude motions the Q_k are small, the π_α negligible, and the intertia tensor well approximated by its equilibrium value. The potential $V(\mathbf{Q})$ can be expanded in a Taylor series about the minimum, so that the second order

$$V(\mathbf{Q}) = V(\mathbf{O}) + \frac{1}{2}\sum_{k,\ell=1}^{3N-6} F_{k\ell}Q_kQ_\ell, \tag{5}$$

where $\mathbf{F}$ is the so-called force-constant matrix, whose elements can be determined by computing the second derivatives of $V(\mathbf{Q})$ and evaluating them at $\mathbf{Q} = \mathbf{O}$. Thus, for sufficiently small-amplitude motion (4) can be well approximated as the sum of rigid-rotor plus simple-harmonic oscillator Hamiltonians. The solution of the problem in this approximation is of the form

$${}^J\psi_n = \Phi_n(\mathbf{Q}) \sum_{k=-J}^{+J} C_k^J|Jk\rangle, \tag{6}$$

where $\Phi_n(\mathbf{Q})$ is a product of harmonic-oscillator functions and $|Jk\rangle$ are the symmetric-top eigenfunctions with arbitrary quantization along the space-fixed axis.

Now if the whole sequence of approximations that lead to a solution of the form (6) are adequate, then the calculation of whole-molecule properties, although tricky, need actually involve only a relatively few electronic structure calculations, in fact just enough to locate the minimum of the potential energy-surface and to get the second derivatives at the minimum. The advantages that flow from this are clear. A good nonempirical calculation of an electronic energy is a formidably expensive and lengthy undertaking, even with the best techniques that are now available, so the fewer such energies that are needed the better. Furthermore, in this approach it is not necessary to have any particular view about the shape of the potential energy surface near the minimum, for purely numerical methods can be used to calculate the first and second derivatives.

It was early discovered however that, unfortunately, this simple procedure did not in general lead to very accurate results, and the deficiency was identified as lying in the approximation for the potential (5) and the consequent approximation in the nuclear motion wave function, (6).

To transcend the approximation (5) is formally easy. It is simply necessary to determine $V(\mathbf{Q})$ over a suitable range, to extend the trial wave function to be a sum of vibration functions (possibly J and k dependent), and to use the linear variation theorem. In practice, however, two difficulties arise. In the first place it is feasible to calculate V only at a set of points; it is not clear at the outset of the calculation how these points should be chosen. Neither is it clear how the function should be continued (or "fitted") between the calculated points. Furthermore, because of the expense and labor of such calculations, it is imprudent to engage in indiscriminate calculation. It is also, in general, difficult to calculate matrix elements of the Hamiltonian between the functions that form the linear-variation basis. Even if a suitable choice of basis is made so that analytic expressions are obtainable for the kinetic energy integrals, it is not easy to avoid numerical integration for the matrix elements involving V and the elements of $\boldsymbol{\mu}$, and $3N - 6$ dimensional quadrature is a difficult and time-consuming business.

Pioneering attempts in this area were made, for triatomic systems, by Whitehead and Handy [3,4] and Carney and Porter [5,6]. Whitehead and Handy argued that it was advantageous to avoid explicit fitting of the surface, but rather to decide on a quadrature scheme in advance and simply to evaluate the potential at the required quadrature points. In their work they found the normal coordinates by solving the usual problem with a nonempirical $\mathbf{F}$ matrix, chose as basis functions products of simple-harmonic oscillator functions, and used Gauss–Hermite quadrature. The course of action that they advocated is equivalent to assuming that the potential energy surface can be fitted as a sum of products of Hermite polynomials. It can thus be regarded as a special case of a more general technique in which the potential energy surface is fitted by products of general orthogonal polynomials, a technique used explicitly in, for example, Bartholomae et al.[7].

Carney and Porter, on the other hand, fitted the potential directly, adopting a somewhat more physically motivated approach to describing it, recognizing in their functional form both the nature of the bonds involved and their dissociation behavior. They did this by modifying a fitting technique introduced for diatomics and linear triatomics by Simons, Parr, and Finlan (SPF) [8]. (A similarly physically motivated approach to fitting the potential was also suggested, a little later, by Sorbie and Murrell [9]). The matrix elements of the potential were evaluated by means of a generalized three-dimensional gaussian quadrature scheme adapted to the form of the potential and the chosen basis functions.

It was apparent from the early calculations that the results obtained were sensitive not only to the quality of the ab-initio calculation itself but also to the method (implicit or explicit) of fitting the potential energy. It is of course possible to quantify the defects in a fit by calculating the root-mean-square error, but this is only a measure of how well the fit matches the calculated points. It is obviously at least equally important to know how well a fit interpolates between the calculated points, and this can be done only by using the fitting function to estimate uncalculated values and comparing the estimate with actual calculations. The expense of actually calculating fresh points is generally so great that this is seldom done, and all calculated points are deployed in making the fit, so that most fitted surfaces are, in a sense, untested. It is thus not unusual, as will be seen, for distinctly different results to be obtained in nuclear-motion calculations that are nominally on the same potential energy surface but in which different fits have been made of the potential.

Besides the problems discussed above, associated with the potential energy functions and the evaluation of matrix elements, there is another problem that arises from the actual Hamiltonian for nuclear motion expressed in body fixed coordinates. It is the case (see, for example, Ref. 10) that the separation of rotational motion from the other motions always results in a Hamiltonian containing terms that are incipiently singular. In the Eckart Hamiltonian (4) μ is such a term, for it is the inverse of a matrix that can become singular for sufficiently large amplitude vibrations: for example, when a bent triatomic becomes almost linear. The underlying reason for this kind of singularity is the impossibility of parameterizing the proper rotation group, SO(3), in such a way that the parameterization function is analytic everywhere. In the present context that means that in a "nonrigid" system it is not always possible to define properly the Euler angles that determine the angular momentum operators.

The possibility of such a difficulty was anticipated early by Sayvetz [11], who suggested ways in which the Eckart Hamiltonian could be modified to avoid the more usual problems, such as free internal rotation and vibration to linear or planar configurations. This seminal work has led to many developments in the theory of what are now called semi- or nonrigid molecules (see, for example, Refs. 12 and 13), but in the work to be described here another path has been taken with a view to coping simultaneously with the incipient singularities in highly-excited triatomics and dealing with the problems of potential fitting and matrix element evaluation in an efficient way.

Calculations on Triatomic Systems

It is clear that in describing highly excited nuclear motion states of triatomics, it is not a good approximation to assume that the molecule executes only small amplitude vibrations about an equilibrium configuration; nor is it sensible to assume that the molecule rotates approximately as a rigid body. The states of interest may, for example, be described better in terms of the collision process of an atom with a diatomic, and thus in terms of the standard scattering coordinates as used, for example, by Arthurs and Dalgarno [14]. Such coordinates are appropriate for van der Waals complexes, where the potential in the region of interest can be fitted in terms of functions of such scattering coordinates.

It is equally the case, however, that in certain energy regions the molecule is perhaps better described in terms of a more traditional bond-length, bond-angle system of coordinates. It is clearly something of a problem to obtain a Hamiltonian that describes the various possibilities in a coherent and uniform way without making any assumptions about the rigidity of the system.

However, the authors have recently shown [15] how a suitable Hamiltonian may be constructed that allows for at least some of the possibilities. For this Hamiltonian it is assumed that the three laboratory-fixed coordinates $\mathbf{x}_i$ of the nuclei are transformed to a space-fixed set of two translation-free coordinates, $\mathbf{t}_i$, by the transformations

$$\mathbf{t}_i = \sum_{j=1}^{3} \mathbf{x}_j V_{ji} \tag{7}$$

with

$$\mathbf{V} = \begin{bmatrix} 0 & 1 \\ -1 & -g \\ 1 & g-1 \end{bmatrix} \tag{8}$$

From (7) it is seen that $\mathbf{t}_1$ is the bond-length vector from particle 2 to particle 3. By choosing $g = 1$ in (7), $\mathbf{t}_2$ becomes the bond-length vector from particle 2 to particle 1, and by choosing $g = m_2(m_2 + m_3)^{-1}$, $\mathbf{t}_2$ becomes the vector from the center of mass of the diatomic system 2-3 to the particle 1, so that in this case the $\mathbf{t}_1$ and $\mathbf{t}_2$ are the space-fixed scattering coordinates. Clearly other choices are possible by varying g.

The body-fixed system is defined by an orthogonal transformation $\mathbf{C}$ such that

$$\mathbf{C}^T\mathbf{t}_1 = r_1 \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad \mathbf{C}^T\mathbf{t}_2 = r_2 \begin{bmatrix} \sin\theta \\ 0 \\ \cos\theta \end{bmatrix} \tag{9}$$

where r_1 and r_2 are the lengths of $\mathbf{t}_1$ and $\mathbf{t}_2$, respectively. θ is the angle between $\mathbf{t}_1$ and $\mathbf{t}_2$ with range 0–π, and the embedded coordinate system is chosen to be right handed. An alternative embedding is obtained by swapping $\mathbf{t}_1 \leftrightarrow \mathbf{t}_2$ and $r_1 \leftrightarrow r_2$.

The scheme outlined in [16] may be used to construct the body-fixed Hamiltonian. This Hamiltonian is then allowed to operate on the manifold of rotational functions $|Jk\rangle$ and the results multiplied from the right by $\langle Jk'|$. On integrating out over the rotational variables, the following effective form containing internal coordinates only is obtained

$$\hat{H} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + V \tag{10}$$

with

$$\begin{aligned} K_V^{(1)} = \delta_{k'k} \frac{-\hbar^2}{2} \Bigg(& \frac{1}{\mu_1 r_1^2} \left(\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right) \\ & + \frac{1}{\mu_2 r_2^2} \left(\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right) \Bigg) \end{aligned} \tag{11}$$

$$\begin{aligned} K_V^{(2)} = \delta_{k'k} \frac{\hbar^2}{\mu_{12}} \Bigg(& -\cos\theta \frac{\partial^2}{\partial r_1 \partial r_2} + \frac{\cos\theta}{r_1 r_2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right) \\ & + \sin\theta \left(\frac{1}{r_1} \frac{\partial}{\partial r_2} + \frac{1}{r_2} \frac{\partial}{\partial r_1} + \frac{1}{r_1 r_2} \right) \frac{\partial}{\partial\theta} \Bigg) \end{aligned} \tag{12}$$

$$\begin{aligned} K_{VR}^{(1)} = {} & \delta_{k'k} \frac{\hbar^2}{2} \left(\frac{J(J+1) - 2k^2}{2\mu_1 r_1^2} + \mathrm{k}^2 \mathrm{cosec}^2\theta \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2\cos\theta}{\mu_{12} r_1 r_2} \right) \right) \\ & + \delta_{k',k+1} \frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{+} \left(-\frac{\partial}{\partial\theta} + \mathrm{k}\cot\theta \right) + \delta_{k',k-1} \frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{-} \left(\frac{\partial}{\partial\theta} + \mathrm{k}\cot\theta \right) \end{aligned} \tag{13}$$

$$\begin{aligned} K_{VR}^{(2)} = {} & \delta_{k',k+1} \frac{\hbar^2}{2\mu_{12} r_1 r_2} \left(\cos\theta \left(\frac{\partial}{\partial\theta} - \mathrm{k}\cot\theta \right) + \left(r_2 \frac{\partial}{\partial r_2} - k \right) \sin\theta \right) \\ & + \delta_{k',k-1} \frac{\hbar^2 C_{Jk}^{-}}{2\mu_{12} r_1 r_2} \left(-\cos\theta \left(\frac{\partial}{\partial\theta} + \mathrm{k}\cot\theta \right) - \left(r_2 \frac{\partial}{\partial r_2} + k \right) \sin\theta \right) \end{aligned} \tag{14}$$

The above form is for $\mathbf{t}_1$ chosen as defining the z axis of the body-fixed system. The form for z chosen along $\mathbf{t}_2$ is obtained by the exchange $r_1 \leftrightarrow r_2$, $\mu_1 \leftrightarrow \mu_2$. The kronecker deltas show the couplings within the rotational manifold.

In (11)–(14)

$$\begin{aligned} \mu_1^{-1} &= m_2^{-1} + m_3^{-1} \\ \mu_{12}^{-1} &= g(m_2^{-1} + m_3^{-1}) - m_3^{-1} \\ \mu_2^{-1} &= m_1^{-1} + g^2 m_2^{-1} + (1 - g)^2 m_3^{-1}. \end{aligned}$$

and

$$C_{Jk}^{\pm} = (J(J+1) - k(k \pm 1))^{1/2} \tag{15}$$

It should be noted that if scattering coordinates are chosen, μ_{12}^{-1} is zero, and hence the operators $K_V^{(2)}$ and $K_{VR}^{(2)}$ are null operators. The Hamiltonian thus reduces to the standard one used by the authors in the previous work [17]. If the bond-length bond-angle coordinates are chosen, the Hamiltonian is that of Hagstrom and Lai [18]. The general Hamiltonian takes a volume element of integration $r_1^2 r_2^2 \sin\theta dr_1 dr_2 d\theta$.

For systems in which this coordinate representation is appropriate, the potential may be expanded as

$$V(r_1,r_2,\theta) = \sum_{\lambda} V_{\lambda}(r_1,r_2)P_{\lambda}(\theta), \tag{16}$$

where P_λ is a standard Legendre polynomial. The V_λ may be obtained exactly from this assumed form by $(\lambda + 1)$-point Gauss–Legendre quadrature over θ for any choice of r_1,r_2. A computer program to do this is available [19]. With this form then the explicit fitting problem is reduced to fitting the $V_\lambda(r_1,r_2)$.

It is seen that, as expected, the Hamiltonian (10) also has incipient singularities arising possibly from the r_i^{-2} terms and from the terms in $\operatorname{cosec}^2\theta$ as θ tends to 0 and π. That the effect of these singularities can be mitigated without abandoning any physically significant information is shown in detail in [15]. Essentially what is done is to choose a basis of products of the form

$$\psi^J_{nkj}(r_1,r_2)\Theta_{jk}(\theta) \tag{17}$$

where the Θ_{jk} are standard normalized associated Legendre functions defined in the convention of Condon and Shortley [20] and the ψ^J_{nkj} are chosen as products of central-field functions (for example Morse or spherical oscillator functions). If the effective operator derived above is applied to functions of the type (17), it can be seen that the $\operatorname{cosec}^2\theta$ terms in $K^{(1)}_{VR}$ cancel with those that arise from the operation of the derivative terms in $K^{(1)}_V$ and $K^{(2)}_V$ upon the Θ_{jk}. The incipient divergences are thus removed, and the results of the operation may be multiplied by $\Theta_{j'k'}$ and integrated over θ to yield an effective operator that operates only on a basis of radial functions. In constructing this radial operator it is convenient to incorporate the radial portion of the jacobian into the operator to put it in what is often called a manifestly hermitian form. This process is equivalent to choosing radial functions of the form $r_1^{-1}r_2^{-1}\Phi^J_{nkj}(r_1,r_2)$, and the resulting operator determines the Φ^J_{nkj}. The volume element of integration thus becomes $\sin\theta d\theta dr_1 dr_2$, and the form of the kinetic energy operator is

$$K^{(1)}_V = \delta_{j'j}\delta_{k'k}\left(-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right) \tag{18}$$

$$\begin{aligned} K^{(2)}_V = {} & \frac{-\hbar^2}{\mu_{12}} d_{jk}\delta_{j',j+1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} - \frac{(j+1)}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{(j+1)}{r_2}\right) \\ & \frac{-\hbar^2}{\mu_{12}} d_{j-1,k}\delta_{j',j-1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right) \end{aligned} \tag{19}$$

$$K^{(1)}_{VR} = \delta_{k'k}\delta_{j'j}\frac{\hbar^2}{2\mu_1 r_1^2}(J(J+1)-2k^2) - \delta_{j'j}\frac{\hbar^2}{2\mu_1 r_1^2}(\delta_{k',k+1}C^+_{Jk}C^+_{jk} + \delta_{k',k-1}C^-_{Jk}C^-_{jk}) \quad (20)$$

$$\begin{aligned} K^{(2)}_{VR} = {} & \delta_{k',k-1}\delta_{j',j+1}\frac{\hbar^2}{2\mu_{12}}C^+_{Jk}\frac{a_{jk}}{r_1}\left(\frac{(j+1)}{r_2}-\frac{\partial}{\partial r_2}\right) \\ & + \delta_{k',k+1}\delta_{j',j-1} -\frac{\hbar^2}{2\mu_{12}}C^+_{Jk}\frac{b_{jk}}{r_1}\left(\frac{j}{r_2}+\frac{\partial}{\partial r_2}\right) \\ & + \delta_{k',k-1}\delta_{j',j+1}\frac{\hbar^2}{2\mu_{12}}C^-_{Jk}\frac{a_{j-k}}{r_1}\left(\frac{(j+1)}{r_2}-\frac{\partial}{\partial r_2}\right) \\ & + \delta_{k',k-1}\delta_{j',j-1}\frac{\hbar^2}{2\mu_{12}}C^-_{Jk}\frac{b_{j-k}}{r_1}\left(\frac{j}{r_2}+\frac{\partial}{\partial r_2}\right) \end{aligned} \quad (21)$$

The potential in the form (17) leads to terms of the form

$$\delta_{k'k}V_{j',jk}(r_1,r_2) \quad (22)$$

where $V_{j'jk}$ are just sums over λ of products of Gaunt coefficients and the $V_\lambda(r_1,r_2)$ (see, e.g. Ref. 15). The auxilliary quantities in the kinetic energy operators are defined as

$$d_{jk} = [(j-k+1)(j+k+1)/(2j+1)(2j+3)]^{1/2} \quad (23)$$

$$a_{jk} = [(j+k+1)(j+k+2)/(2j+1)(2j+3)]^{1/2} \quad (24)$$

$$b_{jk} = [(j-k)(j-k-1)/(4j^2-1)]^{1/2} \quad (25)$$

and are easily seen to be simply related to Clebsch–Gordon coefficients. The kronecker deltas show the coupling within the complete angular manifold.

The Hamiltonian as given above is not divergent over a suitable basis of radial functions and can accommodate the most extreme of bending motions. It is therefore eminently suitable for describing highly excited vibrational and rotational states. The computer program [19] mentioned above can be used to perform complete calculations with this Hamiltonian in its scattering coordinate form.

Results and Discussion

It is appropriate first to put in context what can be expected in the way of absolute accuracy from vibration-rotation calculations on triatomics. The very best potential energy surface calculations that have been done on the simplest of all triatomics, namely H_3^+, yield an energy at the minimum that is between 150 and 200 cm^{-1} higher than the absolute energy minimum found in the best one point calculation. This one point calculation is that of Mentsch and Anderson [21], which was performed using a random walk method that yields results that are, arguably, exact. It would be extremely difficult to construct a surface from points so calculated however, for the errors in such calculations differ from point to point. It would also be very expensive even if the error problem could be obviated. However, as will be seen, modern high-accuracy CI calculations seem able to get the shape of the potential energy surface correct, that is to have about the same error at all the points of interest. This means that predicted rotation-vibration spectra turn out to be rather accurate because the relative positions of the energy levels are well predicted, although it must be admitted that the finer details of the rotational spectrum do appear to be rather sensitive to quite small changes in the predicted geometry at the potential minimum.

Within the context outlined above, the kind of accuracy that can be expected from the fundamental vibrational calculations ($J = 0$) are exhibited in Table I, where results arising from various fits to the same potential energy surface and to different surfaces for H_3^+ are compared with each other and with experiment. Although the agreement between the calculated and observed results is good for all the calculations, the differences between calculations on the same surface, but that correspond to different fits, are somewhat disconcerting. It is very difficult indeed to see a way out of this problem other than by increasing the density of calculated potential energy surface points so that all points are sufficiently close for a standard interpolation scheme to be used between any pair of them. In some ways that would be to return to the kind of scheme first advocated by Whitehead and Handy [5]. To use such a dense set would ameliorate, but not obviate, the difficulty of deciding in advance just where the points on the potential energy surface that are to be calculated should lie. In most current calculations the number that can be afforded is distributed almost by art across the surface with a view to the kind of fitting technique that is to be used. If a dense set could be afforded, it would be possible to start from a sparse, perhaps randomly distributed, set to interpolate between pairs of points and then to calculate at the interpolated points and so continue until the interpolation was shown to be essentially exact. This sort of task is ideally suited

TABLE I. Comparison of ab initio calculations of the band origins in cm^{-1} of H_3^+.

Electronic Calculation	Fit Used	Vibrational Calculation	H_3^+	
			ν_1	ν_2
Burton et al [30]	SPF[a] [30]	Burton et al [30]	3189	2509
	SPF[a] [30]	Tennyson & Sutcliffe [31]	3188	2508
	SPF [25]	Martire & Burton [25]	3176	2519
	SPF [25]	Tennyson & Sutcliffe [31]	3175	2518
Meyer et al [32]	Morse [32]	Meyer et al [32]	3178	2519
Dykstra and Swope [33]	Morse [32]	Meyer et al [32]	3186	2521
	SPF [34]	Carney et al [34]	3180	2522
	Morse [25]	Martire & Burton [25]	3185	2522
Observed [35]			—	2521

[a] This corresponds to the SPF$^+$ fit of Table 4 of Ref. 30.

to parallel computation, and as parallel vector-processing computers develop, this course of action will perhaps become a possibility at least for triatomics. Currently, however, it must be recognized that this side of nuclear motion calculations is in a rather unsatisfactory state.

We turn now to the sort of accuracy that can be achieved on any assumed potential energy surface. In the calculations performed by the authors, analytical forms were chosen for the radial (central-field) functions, usually Morse oscillator-like functions. It is of course possible to choose these functions by direct numerical integration of an artificial one-dimensional problem (see, for example, Ref. 22), but such a course of action means that the kinetic energy integrals must be calculated numerically, and a very dense multi-dimensional quadrature must be done over the potential. It is not yet clear that the extra effort involved is worthwhile. The angular expansion functions were taken up to a prespecified j value depending on the range of λ required for the potential expansion in (16) and on the k values possible with a given j. For high j values this means a very extensive set of j, and recently Carter and Handy [23] have suggested an ingenious method whereby suitable angular functions may be determined self-consistently, which will perhaps prove helpful in shortening such expansions.

Because the method of calculating solutions in the present approach is variational, its accuracy can be assessed by examining the convergence of the calculations under increase in basis size. In Table II are shown the results for a selection of vibrational states ($J = 0$) of D_3^+ taken from recent work by the authors [24]. The results are calculated using the scattering coordinate form of the Hamiltonian (where r represents the diatomic coordinate and R the coordinate from the diatomic center of mass to the atom). The radial basis chosen

TABLE II. Vibrational band origins, in cm^{-1}, for D_3^+ calculated using the BVDH potential of Martire and Burton [25]. (a) Simple product basis, (b) perturbation selected basis.

Quantum Numbers				Simple Product Basis ($m \leq 7$, $n \leq 9$, $j \leq 19$)		Perturbation Selected Basis ($N = 800$)	
ν_1	ν_2	l	Symmetry	j even	j odd	j even	j odd
0	1	1	E′	1831.07	1831.07	1831.07	1831.07
1	0	0	E′	2297.49		2297.49	
0	2	0	A_1'	3523.24		3523.23	
0	2	2	E′	3647.43	3647.40	3647.40	3647.40
1	1	1	E′	4052.65	4052.60	4052.61	4052.60
2	0	0	A_1'	4549.89		4549.88	
3	0	1	E′	5208.17	5206.71	5207.17	5206.71
3	0	3	A_1'	5400.25		5399.28	
3	0	3	A_2'		5470.59		5468.39
1	2	0	A_1'	5704.28		5703.90	
1	2	2	E′	5791.20	5788.69		5788.71
Zero point energy				3102.230		3102.230	

is one of products of the Morse-like oscillators $H_m(r)H_n(R)$, and the potential is that of Martire and Burton [25].

The results on the left of the table were calculated using all possible products of a truncated set of central-field functions, while the results on the right were calculated using basis functions selected by a first-order perturbation technique. The agreement between the levels is excellent and suggests a high degree of convergence. However as can be seen, a very large number of expansion functions (800 in each case) are needed to get reasonably accurate energies in the $J = 0$ case, and clearly to deal with high J states is going to prove a very difficult problem, for the size of the secular problem increases as $2J + 1$. The problem here is essentially one of immediate-access computer storage size, for the actual time taken by nuclear motion calculations is negligible compared with the time taken to calculate an electronic energy.

Recently, however, the authors [26] have developed a secondary variational method with which it has proved possible to get up to $J = 20$ for the various isotopomers of H_3^+. The method is similar to that proposed by Chen et al. [27] but differs in that the base Hamiltonian has a dependence on J but is diagonal in k. In this way the base problem remains tractable but also allows for shifts in geometry caused by centrifugal terms in the potential which, as experience has shown, are large for high J states. Table III shows some results taken from this work for $J = 10$ states of H_2D^+ on the potential surface of Schinke, Dupuis, and Lester [28] that allow the convergence of the proposed method to be assessed. It is interesting to observe that the lower levels do not necessarily converge most quickly. This is because the Coriolis terms for states with low k are considerably stronger than for those with high k, as would be expected from the form of the Hamiltonian. It is seen, too, that the convergence at $N = 160$ is about 0.1 cm^{-1}, which is a satisfactory level of accuracy. However, for larger J at $N = 160$ the convergence is less good, and with present machines this makes $J = 20$ about the highest level for which sensible results can be obtained. The difficulty is that, unlike conventional CI electronic structure, where one usually needs a few of the lowest roots, here one needs $2J + 1$ roots for each vibrational state of interest, so that a single-root iterative dia-

TABLE III. Convergence of some levels of H_2D^+ with $J = 10^e$ (j even) with increasing vibrational basis, N. Energies, in cm^{-1}, are all relative to $E_0 = -32962.24$. Values of k, the projection of J along R, taken from the no-Coriolis calculations.

Level number	1	2	3	7	8	9
k =	0	2	4	1	0	3
No Coriolis	2928.04	3007.67	3234.84	4993.32	5177.72	5202.43
N = 40	1982.24	2570.61	2937.70	4191.53	4406.52	4621.42
80	1977.14	2568.93	2937.12	4191.37	4392.96	4608.68
120	1976.66	2568.77	2937.05	4191.35	4391.01	4606.93
140	1976.56	2568.75	2937.04	4191.35	4390.68	4606.71
160	1976.53	2568.74	2937.04	4191.34	4390.55	4606.64

gonalizer is not very efficient. However, since the matrices involved are rather sparse, it may be possible to increase the value of J that can be considered, and work in this area is in active progress. It should be noted that at high J it is almost impossible to maintain the idea of vibration-rotation separation, for the rotational splittings become larger than the vibrational splittings. This causes no problems in the computational scheme outlined here, but it does cause problems of identification and selection for comparison of calculated results with experiments that are currently being performed (see, for example, Ref 29).

Conclusions

The work described in this paper does seem to offer a way forward in the treatment of highly excited rotation-vibration states of triatomic molecules, but despite its success, there remain problems. The most important of these is that of the accurate representation of the electronic potential energy surface, and to that problem there seems to be no easy solution. It seems that only the calculation of more points will suffice, and such many-point calculations will become routinely possible only with the further development of parallel processing computers. There is also the problem of solving the large secular problems that arise in this work for many roots. In this area there is much active development, and it does not seem unlikely that, with modern numerical techniques dealing with sparse matrices and modern vector-processors with increased store size, it might be possible to consider states with $J \sim 100$ in the near future.

The overall picture is then a hopeful one, and the theory of nuclear motion in triatomic systems seems on the verge of a substantial advance.

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