MOLECULAR PHYSICS, 1986, VOL. 58, NO. 6, 1053–1066

A generalized approach to the calculation of ro-vibrational spectra of triatomic molecules

by BRIAN T. SUTCLIFFE
Chemistry Department, University of York, Heslington,
York YO1 5DD, England

and JONATHAN TENNYSON
Department of Physics and Astronomy, University College London,
Gower Street, London WC1E 6BT, England

(*Received 12 March 1986; accepted 28 March 1986*)

A generalization of the well known atom–diatom scattering hamiltonian to a coordinate system of two lengths and an angle is derived, another special case of which is a previously known bond angle–bond length hamiltonian. Different axis embeddings are also considered. The formalism is applied to the ro-vibrational levels of D_2H^+, CH_2^+ and HDHe ($A\,^1A'$) and the advantage of a judicious choice of coordinates demonstrated. The vibrational band origins for HDHe*, the first predictions for this system for which previous calculations had failed, are obtained using a new geometrically defined coordinate system. It is suggested that these coordinates might be used to represent isotopically substituted van der Waals complexes.

1. INTRODUCTION

Recently there has been much interest in the *ab initio* calculation of the vibration–rotation spectra of triatomic systems as experimental interest in such systems has turned to those for which extremely good electronic structure calculations are possible. Perhaps foremost amongst such systems are H_3^+ and its isotopomers [1]. Naturally many of the nuclear motion calculations have been made using the traditional Eckart hamiltonian [2] in its quantum mechanical form as given by Watson [3]. However it has long been realized that this hamiltonian was inappropriate for large amplitude vibrations. As attention has focused on higher energy regions where all vibrational motion becomes large, calculations have been made with using specially constructed hamiltonians which, it was argued, were particularly appropriate to the problem at hand. This has led to an increasing number of candidate hamiltonians and complementary solution strategies being suggested for even the relatively simple triatomic problem.

It is of course a relatively straightforward and well understood matter to compare and to evaluate the results of different calculations using the same hamiltonian but it is a much more vexed matter to compare calculations using different hamiltonians. In particular, although one knows that one's choice of coordinates, embedding and consequent hamiltonian should be determined by the potential of the problem [4], the best choice is rarely obvious *a priori*.

In a series of papers [5–10] we have developed and applied a solution strategy based upon the use of body-fixed scattering coordinates. This method has proved sufficiently robust to give reliable results for problems for which these coordinates cannot be thought of natural (e.g. [8]). Meanwhile other workers have developed similar procedures based upon the use of different coordinates, for example the bond length–bond angle approach of Carter and Handy [11–14]. This proliferation of hamiltonians and methods is understandable but not desirable particularly when one considers polyatomic systems for which the number of plausible coordinate systems increases alarmingly.

The object of the present paper is to show how the two hamiltonians mentioned above can be simply related to each other as special cases of a continuum of hamiltonians expressed in terms of two lengths and an included angle. We show that the choice of hamiltonian can be reduced to the definition of a single parameter to define the coordinate system and another to define the embedding of the axes. These parameters can be part of the data input for a generalized computer program. We also discuss the way in which a third well-known hamiltonian might also be related to these two. We present the results of calculations on several systems using the various hamiltonians, including another special case, a geometrically defined hamiltonian that has not previously been suggested, in order to show how a comparison and evaluation of them can be effected.

2. THE CONSTRUCTION OF THE HAMILTONIANS

A rather general method for the construction of hamiltonians in body-fixed coordinates has recently been described [15]. In this method a set of translation-free internal coordinates t_i are first constructed in terms of the laboratory fixed coordinates x_i such that

$$\left.\begin{aligned} \mathbf{t}_i &= \sum_{j=1}^{N} \mathbf{x}_j V_{ji}, \quad i = 1, 2, \ldots, N-1; \\ \text{or} \qquad \mathbf{t} &= \mathbf{x}\mathbf{V}, \end{aligned}\right\} \tag{1}$$

where N is the total number of particles and the elements of $\mathbf{V}$ are chosen such that

$$\sum_{i=1}^{N} V_{ij} = 0 \quad \text{all } j = 1, 2, \ldots, N-1 \tag{2}$$

to ensure the invariance of the $\mathbf{t}_i$ under uniform translations. In terms of these coordinates the translation-free part of the kinetic energy operator can be written as

$$\hat{K} = -\frac{1}{2} \sum_{i,j=1}^{N-1} \bar{G}_{ij} \nabla(\mathbf{t}_i) \cdot \nabla(\mathbf{t}_j) \tag{3}$$

where $\nabla(\mathbf{t}_i)$ is the usual grad operator expressed in the variables $\mathbf{t}_i$ and where the matrix $\bar{G}$ has elements

$$\bar{G}_{ij} = \sum_{k=1}^{N} m_k^{-1} V_{ki} V_{kj} \tag{4}$$

in which the m_k are the particle masses.

The translation-free internal coordinates are now transformed by an orthogonal transformation **C** so that

$$\mathbf{t}_i = \mathbf{C}\mathbf{z}_i \tag{5}$$

and among the $\mathbf{z}_i$ there are three relations

$$f_m(\mathbf{z}_1, \mathbf{z}_2, \ldots, \mathbf{z}_{N-1}) = 0, \quad m = 1, 2, 3 \tag{6}$$

that define the way in which the coordinate frame is fixed in the system. The matrix **C** is parameterizible in terms of three Euler angles (α, β, γ) and the coordinates $\mathbf{z}_i$ are expressible in terms of $3N-6$ independent rotation- and translation-free internal coordinates, q_k. The body-fixed hamiltonian can then be written in terms of the angular momentum operators (involving α, β, γ) and of operators and functions of the q_k. Precisely how this is to be done is outlined in [15] and shown in some detail for a particular choice of triatomic coordinates in [5] so that algebraic detail will not be given in the present paper.

Consider now a translation-free set of coordinates such that $\mathbf{t}_1$ is the bond length vector from particle 2 to particle 3 and $\mathbf{t}_2$ is a proper combination of all three laboratory-fixed coordinates. Thus the form of **V** is

$$\mathbf{V} = \begin{pmatrix} 0 & 1 \\ -1 & -g \\ 1 & g-1 \end{pmatrix}, \quad 0 \leqslant g \leqslant 1. \tag{7}$$

Among the translation-free coordinate sets that have such a form is one in which $\mathbf{t}_2$ is the bond length vector from particle 2 to particle 1, obtained by setting $g = 1$. Also possible is the collision or scattering coordinate set in which $\mathbf{t}_2$ is the vector from the centre-of-mass of the diatomic 2–3 to particle 1. For this case

$$g = m_2 m_{\rm d}^{-1}, \quad m_{\rm d} = m_2 + m_3. \tag{8}$$

The $\bar{\mathbf{G}}$ matrix generated by **V** as given in equation (7) has elements

$$\left.\begin{aligned} \bar{G}_{11} &= \mu_1^{-1} = m_2^{-1} + m_3^{-1}, \\ \bar{G}_{12} &= \mu_{12}^{-1} = g(m_2^{-1} + m_3^{-1}) - m_3^{-1}, \\ \bar{G}_{22} &= \mu_2^{-1} = m_1^{-1} + g^2 m_2^{-1} + (1-g)^2 m_3^{-1}. \end{aligned}\right\} \tag{9}$$

A suitable set of internal coordinates in this approach is r_1, the length of $\mathbf{t}_1$; r_2, the length of $\mathbf{t}_2$ and θ, the angle between $\mathbf{t}_1$ and $\mathbf{t}_2$. The matrix **C** may be defined by choosing it so that the embedded z-axis lies either along $\mathbf{t}_1$ or $\mathbf{t}_2$ and the remaining coordinate has a range of keep it in the positive x half of the xz plane, with the additional requirement that the three body-fixed axes form a right-handed set. Thus if the coordinate chosen to define the z-axis is denoted by **a** and the other coordinate by **b** then

$$\mathbf{C}^{\rm T}\mathbf{a} = a\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{C}^{\rm T}\mathbf{b} = b\begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}, \tag{10}$$

where a is either r_1 or r_2 and b is either r_2 or r_1 according to the embedding chosen. Which of these embeddings is used is unimportant in a full calculation, but will be important if approximations, such as the neglect of off-diagonal Coriolis interactions are to be made [7].

It is now possible to write down the hamiltonian for the system in terms of the angular momentum operators, and operators and functions involving only the internal coordinates by following the prescription given in [15] and illustrated in [5]. As explained in [15], the angular momentum operators can then be eliminated from the expression. This is done by allowing the operator to act on a manifold of functions which are products of functions of the internal coordinates and standard angular momentum eigenfunctions and then integrating over the angular variables. Because the energy does not depend upon the projection, M, of the total angular momentum, J, along the space-fixed z-axis, it is sufficient simply to consider the projection, k, of J along the body-fixed z-axis. Of course k is not in general a good quantum number and the resulting operator consists of $2J + 1$ coupled terms, the kinetic energy part of which can be written as

$$\hat{K} = \hat{K}_{\mathrm{V}}^{(1)} + \hat{K}_{\mathrm{V}}^{(2)} + \hat{K}_{\mathrm{VR}}^{(1)} + \hat{K}_{\mathrm{VR}}^{(2)}, \tag{11}$$

with

$$\hat{K}_{\mathrm{V}}^{(1)} = -\frac{\hbar^2}{2}\left[\frac{1}{\mu_1 r_1^2}\left(\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\mu_2 r_2^2}\left(\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right], \tag{12}$$

$$\hat{K}_{\mathrm{V}}^{(2)} = \frac{\hbar^2}{\mu_{12}}\left[-\cos\theta\frac{\partial^2}{\partial r_1\,\partial r_2} + \frac{\cos\theta}{r_1 r_2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \sin\theta\left(\frac{1}{r_1}\frac{\partial}{\partial r_2} + \frac{1}{r_2}\frac{\partial}{\partial r_1} + \frac{1}{r_1 r_2}\right)\frac{\partial}{\partial\theta}\right], \tag{13}$$

$$\hat{K}_{\mathrm{VR}}^{(1)} = \delta_{k'k}\hbar^2\left[\frac{(J(J+1) - 2k^2)}{2\mu_1 r_1^2} + \frac{k^2}{2}\operatorname{cosec}^2\theta\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2\cos\theta}{\mu_{12} r_1 r_2}\right) + \delta_{k'k+1}\frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{+}\left(-\frac{\partial}{\partial\theta} + k\cot\theta\right) + \delta_{k'k-1}\frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{-}\left(\frac{\partial}{\partial\theta} + k\cot\theta\right)\right], \tag{14}$$

$$\hat{K}_{\mathrm{VR}}^{(2)} = \delta_{k'k+1}\frac{\hbar^2}{2\mu_{12} r_1 r_2} C_{Jk}^{+}\left(\cos\theta\left(\frac{\partial}{\partial\theta} - k\cot\theta\right) + \left(r_2\frac{\partial}{\partial r_2} - k\right)\sin\theta\right) + \delta_{k'k-1}\frac{\hbar^2}{2\mu_{12} r_1 r_2} C_{Jk}^{-}\left(-\cos\theta\left(\frac{\partial}{\partial\theta} + k\cot\theta\right) + \left(r_2\frac{\partial}{\partial r_2} + k\right)\sin\theta\right). \tag{15}$$

The form given above is appropriate for the z-axis embedded along $\mathbf{t}_1$. The embedding along $\mathbf{t}_2$ is obtained simply by making the exchanges $r_1 \leftrightarrow r_2$ and $\mu_1 \leftrightarrow \mu_2$. In using the operator in this form any integral over the internal coordinates must be performed with the volume element $r_1^2 r_2^2 \sin\theta\, dr_1\, dr_2\, d\theta$. The range of r_i is $(0, \infty)$ and that of θ $(0, \pi)$. The coefficients $C^{\pm}_{Jk}$ are the usual step up and down coefficients

$$C^{\pm}_{Jk} = (J(J+1) - k(k \pm 1))^{1/2}. \tag{16}$$

It is easily seen that if the scattering coordinates are used then μ_{12}^{-1} vanishes and $\hat{K}$ reduces to the standard form often used in describing atom–diatom collisions (e.g. [5]). If the bond length–bond angle embedding is used so that r_1 is the 2–3 bond, r_2 the 2–1 bond and the z-axis is placed along $\mathbf{t}_1$ then

$$\mu_1 = m_3^{-1} + m_2^{-1}, \quad \mu_2 = m_1^{-1} + m_2^{-1}, \quad \mu_{12} = m_2^{-1} \tag{17}$$

and the hamiltonian reduces to the form attributed to Hagstrom and Lai [16] (see also [4] and [17]). Clearly other forms are possible too, for example one in which g is chosen as $\frac{1}{2}$, so placing the origin for particle 1 at the geometric centre of the diatomic 2–3. In this case (with the z-axis along $\mathbf{t}_1$)

$$\mu_1 = m_2^{-1} + m_3^{-1}, \quad \mu_2 = m_1^{-1} + \tfrac{1}{4}(m_2^{-1} + m_3^{-1}), \quad \mu_{12} = \tfrac{1}{2}(m_2^{-1} - m_3^{-1}) \tag{18}$$

and naturally this coordinate system is identical with the scattering coordinates in the case of a homonuclear diatomic 2–3.

The given form of the kinetic energy operator is often called the 'non-hermitian' form but this is a somewhat misleading appelation. It must be remembered that hermiticity is defined only with respect to a specified manifold of functions and in terms of integration between products of such functions, given that the effect of the operator on a function is to produce another function that is also in the manifold. If a suitable manifold is chosen and the jacobian in the volume element for integration is properly included then it is easy to show that a given operator is hermitian. The choice of a suitable manifold is a matter of some delicacy in the present case, for inspection of the operator indicates that unless the functions are rather carefully chosen then divergent integrals could be encountered arising from terms in r_i^{-2} as $r_i \to 0$ and those in $\operatorname{cosec}^2 \theta$ as $\theta \to 0$ or π. Certainly the operator could not be hermitian on any manifold that permitted such behaviour. It is easy to accomplish what is necessary to avoid the possible difficulties with the radial variables because the singularity is of no higher order than that which occurs in the central field problem after the angular motion is separated off. Thus a suitable manifold of radial functions can be constructed from products of central field functions with the form $r_1^{-1} r_2^{-1} \Phi(r_1, r_2, \theta)$, to require that Φ is normalizable using the volume element $dr_1\, dr_2 \sin \theta\, d\theta$ and to re-write the kinetic energy operator so that Φ is a suitable trial function. This process corresponds to incorporating the radial part of the jacobian into the operator (in the manner described, for example, by Kemble [18]). The resulting operator is often said to be in 'hermitian form'. This form is given below for the present operator.

The problem with θ is a little more difficult to deal with. To describe what is to be done it is convenient to imagine that each of the standard angular-momentum functions, $D^J_{Mk}(\alpha, \beta, \gamma)$ [19], which are used above in the derivation of (11) are supplemented for any chosen J, k by a standard associated Legendre function $\theta_{jk}(\theta)$ as defined by Condon and Shortley [20]. Clearly, the maximum value of $|k|$ is J, and j must be such that it admits the chosen k. The manifold of functions on which the original hamiltonian operates may be thought of as consisting of the products

$$r_1^{-1} r_2^{-1} \quad \Psi^J_{mnkj}(r_1, r_2) \quad \theta_{jk}(\theta) \quad D^J_{Mk}(\alpha, \beta, \gamma). \tag{19}$$

If the integrals over the angular variables that lead to equations (12)–(15) are now extended to involve integration over θ, it is seen that each of the terms in $\hat{K}_V^{(1)}$ and $\hat{K}_V^{(2)}$ that involve derivatives of θ give rise to terms in $k^2 \operatorname{cosec}^2 \theta$ that exactly cancel the term in $k^2 \operatorname{cosec}^2 \theta$ in $\hat{K}_{VR}^{(1)}$. Thus, providing that the manifold consists of functions like (19), there is no possibility of divergence and the operator is hermitian on such a manifold. Choosing the radial functions as in (19) or, equivalently incorporating the radial part of the jacobian into the operator, and integrating over all the angular variables leads to an effective operator which works only on functions of the radial variables. This operator, which is manifestly hermitian, has the form:

$$\hat{K}_V^{(1)} = \delta_{j'j}\delta_{k'k}\left[\frac{-\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} \frac{-\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2} j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right], \tag{20}$$

$$\begin{aligned} \hat{K}_V^{(2)} = &-\frac{\hbar^2}{\mu_{12}} d_{jk}\delta_{j'j+1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} - \frac{(j+1)}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{(j+1)}{r_2}\right) \\ &-\frac{\hbar^2}{\mu_{12}} d_{j-1,k}\delta_{j'j-1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right), \end{aligned} \tag{21}$$

$$\begin{aligned} \hat{K}_{VR}^{(1)} = &\ \delta_{k'k}\delta_{j'j}\frac{\hbar^2}{2\mu_1 r_1^2}(J(J+1) - 2k^2) \\ &-\delta_{j'j}\frac{\hbar^2}{2\mu_1 r_1^2}(\delta_{k'k+1}C^+_{Jk}C^+_{jk} + \delta_{k'k-1}C^-_{Jk}C^-_{jk}), \end{aligned} \tag{22}$$

$$\begin{aligned} \hat{K}_{VR}^{(2)} = &\ \delta_{k'k+1}\delta_{j'j+1}\frac{\hbar^2}{2\mu_{12}} C^+_{Jk}\frac{a_{jk}}{r_1}\left(\frac{(j+1)}{r_2} - \frac{\partial}{\partial r_2}\right) \\ &+ \delta_{k'k+1}\delta_{j'j-1}\frac{\hbar^2}{2\mu_{12}} C^+_{Jk}\frac{b_{jk}}{r_1}\left(\frac{j}{r_2} + \frac{\partial}{\partial r_2}\right) \\ &+ \delta_{k'k-1}\delta_{j'j+1}\frac{\hbar^2}{2\mu_{12}} C^-_{Jk}\frac{a_{j-k}}{r_1}\left(\frac{(j+1)}{r_2} - \frac{\partial}{\partial r_2}\right) \\ &+ \delta_{k'k-1}\delta_{j'j-1}\frac{\hbar^2}{2\mu_{12}} C^-_{Jk}\frac{b_{j-k}}{r_1}\left(\frac{j}{r_2} + \frac{\partial}{\partial r_2}\right). \end{aligned} \tag{23}$$

In the above, the embedding is for z along $\mathbf{t}_1$ and the auxiliary quantities are defined as follows

$$d_{jk} = [(j+k-1)(j+k+1)/(2j+1)(2j+3)]^{1/2}, \tag{24}$$

$$a_{jk} = [(j+k+1)(j+k+2)/(2j+1)(2j+3)]^{1/2}, \tag{25}$$

$$b_{jk} = [(j-k)(j-k-1)/(4j^2-1)]^{1/2} \tag{26}$$

which are special cases of Clebsch–Gordan coefficients.

If scattering coordinates are used then μ_{12}^{-1} vanishes. $\hat{K}_{\mathrm{V}}^{(2)}$ and $\hat{K}_{\mathrm{VR}}^{(2)}$ are thus absent from the kinetic energy operator and it reduces to the form used by the authors in some of their previous work (e.g. [7, 8]).

It can be seen from the form of the kinetic energy operator given above that it would be possible to take matrix elements once and for all over a given set of radial functions. These matrix elements could then be combined at will with the appropriate mass factors to give full elements for a problem with any choice of internal coordinates and embedding of the axes. This formal possibility is, unfortunately, of little practical consequence because, as detailed in the next section, the potential appears to be different with each of the internal coordinate choices. This apparent difference determines the details of an optimum expansion function choice and thus in practice the radial matrix elements must be calculated afresh for each choice. However, the actual computer code necessary to evaluate these matrix elements is not dependent on these details provided that the same type of radial functions are used in each case. This means, as asserted in the introduction, that a single program can be used for all cases with the choice of coordinates and embedding simply being signalled as part of the input data.

3. Matrix elements

Two considerations need to be addressed in the calculation of matrix elements. Firstly, in § 2 we integrated the kinetic energy operator over all angular coordinates, but did not consider the potential. Secondly, for an actual calculation is it necessary to solve for the radial coordinates. We choose to do this by defining radial basis functions and thus need to compute the resulting radial matrix elements. This procedure implies the construction and diagonalization of a secular matrix and is fully variational.

The electronic potential is purely a function of the internal coordinates, $V(r_1, r_2, \theta)$. If this potential is expressed as a Legendre expansion in cos θ,

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_{\lambda}(r_1, r_2) P_{\lambda}(\cos\theta) \tag{27}$$

matrix elements over the potential for the angular basis functions defined above can be computed analytically

$$\langle j', k' | P_{\lambda}(\cos\theta) | j, k\rangle = \delta_{k'k}(-1)^k[(2j'+1)(2j+1)]^{1/2}\begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j' & \lambda & j \\ -k & 0 & k \end{pmatrix}, \tag{28}$$

where the integral is over all the angular coordinates and the $3-j$ symbols in the Gaunt coefficient are conventional [19]. In the atom–diatom scattering coordinates the potential is often given in a Legendre expansion, but this is unlikely to be generally the case. However Gauss–Legendre integration has been used successfully to express a general potential function in the form of equation (27) [7, 8]. This procedure, which has been shown to have distinct computational advantages [21], is equally applicable to the generalized coordinates considered here.

In previous work it has not generally been found necessary to use radial functions in (19) that depend explicitly on J, j and k (for an exception see [7]) and it has proved sufficient to express them as sums of products of one-variable radial functions. Of the various radial functions that have been tested in previous calculations [5–10], the Morse oscillator-like functions [5] have proved the most durable as they are both flexible and computationally tractable in multi-dimensional calculations. The normalized Morse oscillator-like functions are given by

$$\left.\begin{aligned} |n\rangle &= H_n(r) = \beta^{1/2} N_{n,\alpha} \exp(-y/2) y^{(\alpha+1)/2} L_n^\alpha(y), \\ y &= A \exp[-\beta(r - r_e)], \end{aligned}\right\} \tag{29}$$

where

$$A = \frac{4D_e}{\beta}, \qquad \beta = \omega_e \left(\frac{\mu}{2D_e}\right)^{1/2}, \qquad \alpha = \text{Integer}(A) \tag{30}$$

and the parameters r_e, ω_e and D_e can be associated with the equilibrium separation, fundamental frequency and dissociation energy of the coordinate respectively. In practice they are usually treated as variational parameters and optimized accordingly [10]. $N_{n,\alpha} L_n^\alpha$ is a normalized Laguerre polynomial [22].

The kinetic energy operator derived in § 2 contains four radial operators, two of which arise in the scattering coordinate calculation considered previously, r^{-2} and $\partial^2/\partial r^2$, and two of which are new, r^{-1} and $\partial/\partial r$. Using the technique given [5] (in which it is assumed that the range of y is $(0, \infty)$) it is possible to derive analytic closed forms for matrix elements of the differential operators

$$\begin{aligned} \langle n' | \frac{\partial^2}{\partial r^2} | n \rangle = \frac{\beta^{1/2}}{4} (\delta_{n'n} [2n(\alpha + n + 1) + \alpha + 1]^{1/2} \\ - \delta_{n'n-2} [(\alpha + n)(\alpha + n - 1) n(n - 1)]^{1/2} \\ - \delta_{n'n+2} [(\alpha + n + 2)(\alpha + n + 1)(n + 2)(n + 1)]^{1/2}) \end{aligned} \tag{31}$$

$$\begin{aligned} \langle n' | \frac{\partial}{\partial r} | n \rangle = \frac{\beta}{2} (\delta_{n'n+1} [(n - 1)(\alpha + n - 1)]^{1/2} \\ - \delta_{n'n-1} [(n - 2)(\alpha + n - 2)]^{1/2}). \end{aligned} \tag{32}$$

There is no simple closed form for the matrix elements of r^{-1}, but these integrals are easily evaluated using Gauss–Laguerre integration as has been done for the operator r^{-2} previously [5]. Integration over the radial coordinates in the potential can be performed in an analogous fashion.

4. SYMMETRY

In ro-vibrational calculations it is desirable to make the greatest possible use of symmetry, for this simplifies both the calculation and the interpretation of results. In two special cases of the generalized hamiltonian, scattering coordinates, equation (8) and bond length–bond angle coordinate, equation (17), there is the possibility that the basis set can be symmetrized to account for AB_2 systems. Additionally the angular basis may also be symmetrized to take account of the total parity of a given ro-vibrational state. This is achieved by transforming the angular functions to

$$\left.\begin{aligned} |j, k, p\rangle &= 2^{-1/2}[|j, k\rangle + (-1)^p |j, -k\rangle]^{1/2}, \quad k > 0, \quad p = 0, 1, \\ &= |j, k\rangle, \qquad\qquad\qquad\qquad\qquad k = 0, \quad p = 0, \end{aligned}\right\} \tag{33}$$

where $|j, k\rangle = \theta_{jk} D^J_{Mk}$ is the full angular function described in §2 above. The total parity of the state is given by $(-1)^{J+p}$. The matrix elements in the symmetrized angular basis are

$$\langle j', k', p' | \hat{K} | j, k, p\rangle = \delta_{p'p} f(k', k) \langle j', k' | \hat{K} | j, k\rangle, \tag{34}$$

where

$$\left.\begin{aligned} f(k', k) &= 1, \qquad k', k > 0 \qquad\quad \text{or} \quad k' = k = 0, \\ &= 2^{1/2}, \quad k' = 0, \ \ k > 0 \quad \text{or} \quad k' > 0, \ \ k = 0. \end{aligned}\right\} \tag{35}$$

In scattering coordinates, the symmetrization for an AB_2 system is well known [10] and simple, as the basis splits between associated Legendre functions with j even and j odd. In the bond length–bond angle case this symmetry is carried by the interchange of the radial coordinates. As we have so far assumed a simple product basis for the radial functions

$$\Psi^J_{mnkj}(r_1, r_2) = |m, n\rangle = H_m(r_1) H'_n(r_2), \tag{36}$$

it is necessary to symmetry adapt the basis in this case. This can be achieved by the transformation

$$\left.\begin{aligned} |m, n, q\rangle &= 2^{-1/2}[H_m(r_1)H_n(r_2) + (-1)^q H_n(r_1) H_m(r_2)], \quad m \neq n, \quad q = 0, 1, \\ &= H_m(r_1) H_n(r_2), \qquad\qquad\qquad\qquad\qquad\qquad m = n, \quad q = 0, \end{aligned}\right\} \tag{37}$$

where it has been assumed that the same basis sets have been used for both radial coordinates. With these symmetrized functions it is easy to show that the matrix elements have the form

$$\begin{aligned} \langle m', n', q' | \hat{K} | m, n, q\rangle = \delta_{q'q} (1 + \delta_{mn})^{-1/2} (1 + \delta_{m'n'})^{-1/2} \\ \times [\langle m', n' | \hat{K} | m, n\rangle + (-1)^q \langle m', n' | \hat{K} | n, m\rangle], \end{aligned} \tag{38}$$

provided that

$$\hat{K}(r_1, r_2) = \hat{K}(r_2, r_1). \tag{39}$$

For $\hat{K}_V$ this condition is satisfied, but for $\hat{K}_{VR}$ it is not. As $\hat{K}_{VR}$ is null for $J = 0$, this means that with the present formalism this symmetrization can only be achieved for the rotational ground state (pure vibrational states). Physically this situation arises because, while there is nothing inherently asymmetric about the coordinate system, there is about the embedding of the body-fixed z-axis along one of the bonds.

A symmetric embedding can be achieved by choosing the body-fixed axis to lie along the bisector of the internal angle, θ. This was the proposal made by Carter *et al.* [12, 13] following Bhatia and Temkin [23]. Not surprisingly this leads to kinetic energy operators which are identical with $K^{(1)}_V$ and $K^{(2)}_V$ ((12) and (13)) but to distinctly different forms for the K_{VR} terms (14) and (15), whose treatment requires somewhat different considerations from those used above. The terms are such that we have not so far been able to show the analytic cancellation of potentially divergent terms. In consequence, the hamiltonian in such a form cannot easily be incorporated into the present scheme and more detailed consideration of it is deferred until a later publication. We note, however, that numerical work with these kinetic energy terms would seem to indicate that they cause no trouble [12, 13].

5. SPECIMEN CALCULATIONS

In order to test the theory given above we performed trial calculations on three molecular systems for which calculations in scattering coordinates had been previously attempted. Results for the molecules D_2H^+, CH_2^+ and HDHe* are given in tables 1 to 3 respectively. In these tables, the energy of the rotational and vibrational ground states are given relative to dissociation and the vibrational band origins are given relative to the (0, 0, 0) level. In table 1 the rotational frequencies are relative to the $J = 0$ level with the same vibrational quantum numbers. The calculations were performed with program TRIATOM [24], a generalization of ATOMDIAT/ATOMDIAT2 [9].

Column (*a*) of table 1 reproduces a scattering coordinate calculation from table 6 of [25]. The potential used was Martire and Burton's BVDH potential [26].

Column (*b*) is for a coordinate system for which r_1 was the HD separation and r_2 linked the geometric midpoint of HD with the other D atom. This coordinate system is not a sensible choice as the calculation does not take advantage of the permutation symmetry of the like D nuclei. However, it gives a numerical test of our generalized hamiltonian. The energies obtained from this calculation are in good agreement with those given in column (*a*) although, since the calculations are variational, they are inferior. This is to be expected as the coordinates are

Table 1. Energy levels of D_2H^+, in cm^{-1}, for calculations using (*a*) scattering coordinates, equation (8), (*b*) midpoint coordinates, equation (18) with H–D as the diatomic and (*c*) DHD^+ bond length–bond angle coordinates, equation (17). The maximum number of basis functions used in each coordinate is shown for comparison.

			Wavenumbers/cm^{-1}		
(v_1, v_2, v_3)	J	k	(*a*)	(*b*)	(*c*)†
0 0 0	0		−71477·482	−71477·371	−71477·385
	1	0^e	49·151	49·140	
	1	1^e	34·820	34·829	
0 1 0	0		1964·943	1964·849	1965·104
	1	0^e	45·886	46·067	
	1	1^e	30·344	30·477	
0 0 1	0		2075·080	2076·167	2077·053
	1	0^e	50·191	50·132	
	1	1^e	40·290	40·023	
	$j^{\max}$		14	14	28
	$m^{\max}$		4	4	4
	$n^{\max}$		4	4	4

† Basis functions parameters: $r_e = 1{\cdot}89a_0$, $\omega_e = 0{\cdot}0116E_h$, $D_e = 0{\cdot}115E_h$.

Table 2. Vibrational band origins of CH_2^+, in cm^{-1}, calculated using (*a*) scattering coordinates, equation (8) and (*b*) HCH^+ bond length–bond angle coordinates, equation (17). The maximum number of basis functions used in each coordinate is shown for comparison.

		Wavenumbers/cm^{-1}	
(v_1, v_2, v_3)	*j*†	(*a*)	(*b*)‡
0 0 0	e	−70400·48	−70400·61
0 2 0	e	718·6	718·4
0 4 0	e	1612·1	1611·4
0 6 0	e	2774·7	2772·7
1 0 0	e	2999·0	2998·9
0 0 1	o	3271·5	3270·7
0 8 0	e	3680·5	3678·6
0 2 1	o	3969·1	3966·9
	j^{max}	17	14
	m^{max}	7	4
	n^{max}	5	4

† Parity with respect to interchange of the H atoms: e = even, o = odd.

‡ Basis functions parameters: $r_e = 2{\cdot}18a_0$, $\omega_e = 0{\cdot}014E_h$, $D_e = 0{\cdot}25E_h$.

Table 3. Vibrational band origins for the two isomers of HeHD($A\,^1A'$), in cm^{-1}, for a calculation using diatom midpoint coordinates, equation (18). (*a*) short He–D, long He–H isomer and (*b*) short He–H, long He–D isomer. Basis set parameters for r_1: $r_e = 4{\cdot}245a_0$, $\omega_e = 0{\cdot}007E_h$, $D_e = 0{\cdot}4E_h$; for r_2: $r_e = 2{\cdot}0a_0$, $\omega_e = 0{\cdot}004E_h$, $D_e = 0{\cdot}02E_h$. Column (*c*) shows the corresponding levels of $HeH_2(A\,^1A')$ [30] for comparison. The absolute minimum in the potential is −12,756 cm^{-1}.

	Wavenumbers/cm^{-1}		
(v_1, v_2, v_3)	(*a*)	(*b*)	(*c*)
0 0 0	−9978·4	−9559·9	−9394·4
0 1 0	1116	920	1162
0 0 1	1253	1361	1438
0 2 0	2207	1825	2292
0 1 1	2339	2282	2575
0 0 2	2503	2657	2814
1 0 0	3035		3869
0 3 0	3300	2724	3410
j^{max}	34		33
m^{max}	4		5
n^{max}	4		5

non-optimal and we did not specifically optimize the radial basis set for this case, but used functions optimized previously [1] for the D_3^+ ion.

Column (*c*) gives results obtained using the bond length–bond angle coordinate system, but only for the vibrational band origins because of the difficulty with symmetrization in this coordinate system. Again the results are in good agreement with, but variationally inferior to, the scattering coordinate calculation of column (*a*). Furthermore, while the calculations of columns (*a*) and (*b*) used the same number of basis functions, it was necessary to use twice as many angular functions to obtain reasonable convergence in this coordinate representation.

The scattering coordinate calculation on CH_2^+ given in column (*a*) of table 2 is taken from table 6 of [8] which used Carter and Handy's [27] representation of the potential of Bartholomae *et al.* [28]. By contrast, the bond length–bond angle coordinate calculation of column (*b*), which gives results variationally superior to column (*a*), used a basis set less than half as big as the one used for the scattering coordinate calculation.

Table 3 gives results for a vibrational calculation on the first electronically excited state of HDHe. Although the electronic ground state of H_2He shows only a weak Van der Waals minimum, the electronically excited state shows a deep minimum for a highly asymmetric, bent geometry where the He is much closer to one H [29]. Previous ro-vibrational calculations on H_2He^* showed small splittings between the two symmetry related minima due to tunnelling [30], but failed for HDHe* because of the difficulty of obtaining a suitable radial basis set which gave a good representation of both minima simultaneously [31]. The previous calculations used scattering coordinates, but test calculations by us using bond length–bond angle coordinates failed for the same reason. We note that the vibrational assignments given in table 3 must be regarded as tentative, but are supported by scattering-coordinate calculations which only stabilized states for one minimum.

6. Discussion and conclusion

The three sets of calculations presented in the previous section provide a useful insight into the behaviour of our hamiltonian in different coordinate systems. For D_2H^+ the scattering coordinate calculation proved easily the most efficient of those tested. D_2H^+ is a highly bent molecule with a bond angle of 60°. In contrast CH_2^+ is quasi-linear and was represented much more efficiently in the bond length–bond angle coordinates. This behaviour was noted by Carter and Handy [11] who found that their methodology was more suited to (near) linear molecules than strongly bent ones.

The calculations on HDHe* demonstrate the usefulness of our hamiltonian for a problem where other procedures fail. Of course, one could perform separate calculations for each minimum using an Eckart hamiltonian but that would mean neglecting the tunnelling interaction of the states from the two minima.

The coordinates system in which r_2 measures the distance of He from the HD geometric midpoint does not suffer from this problem as the two minima have the same (r_1, r_2) coordinates. We were thus able to stabilize vibrational levels for the molecules with a short He–D bond and a long He–H bond (the more stable isomer) and a short He–H bond and a long He–D bond simultaneously. Physically, the isotopic substitution leaves the potential unaltered, but creates extra off-diagonal elements in the kinetic energy operator. Our calculation recognizes this by not transforming to a new set of coordinates which breaks the symmetry of the potential.

A situation where this commonly arises is for the van der Waals complexes formed between homonuclear diatomics (e.g. H_2) and rare gas atoms. The potentials of these systems are usually represented as Legendre expansions. We suggest that use of our hamiltonian in diatomic midpoint coordinates would provide more insight into the behaviour of such complexes upon asymmetric isotopic substitution than does the usual procedure [32] of transforming the potential.

The strength of the Coriolis forces in a system is an artifact of the coordinate choice and the embedding of the axes in the internal coordinate frame. It is desirable to minimize these Coriolis interactions as this can lead to useful simplifications. Indeed this is the basis of the second Eckart condition [2]. In deriving our generalized hamiltonian we have allowed for some flexibility in the choice of embedding as this allows one to choose the appropriate body-fixed axes for a particular problem. This is particularly important if there is a partitioning between the vibrational and rotational steps in the calculation [33].

In summary we have derived a hamiltonian expressed in terms of a generalized internal coordinate system and with options about the embedding used. This hamiltonian is a unification of several hamiltonians which have previously found favour. By performing test calculations on three triatomic problems of interest we show how the choice of coordinates strongly effects the effort involved in obtaining results—or even the possibility of doing so. The methodology we have developed, which gives one flexibility in choosing the appropriate coordinates, has been implemented as general computer program which will be published [24].

REFERENCES

[1] TENNYSON, J., and SUTCLIFFE, B. T., 1986, *J. chem. Soc. Faraday II* (in the press).
[2] ECKART, C., 1935, *Phys. Rev.*, **47,** 552.
[3] WATSON, J. K. G., 1968, *Molec. Phys.*, **15,** 476.
[4] SUTCLIFFE, B. T., 1983, *Molec. Phys.*, **48,** 561.
[5] TENNYSON, J., and SUTCLIFFE, B. T., 1982, *J. chem. Phys.*, **76,** 5710.
[6] TENNYSON, J., and SUTCLIFFE, B. T., 1983, *J. chem. Phys.*, **79,** 43.
[7] TENNYSON, J., and SUTCLIFFE, B. T., 1983, *J. molec. Spectrosc.*, **101,** 71.
[8] TENNYSON, J., and SUTCLIFFE, B. T., 1984, *Molec. Phys.*, **51,** 887.
[9] TENNYSON, J., 1983, *Comput. Phys. Commun.*, **29,** 307; 1984, *Ibid.*, **32,** 109.
[10] TENNYSON, J., 1986, *Comput. Phys. Rep.* (in the press).
[11] CARTER, S., and HANDY, N. C., 1982, *Molec. Phys.*, **47,** 1445; 1986, *Ibid.*, **52,** 175.
[12] CARTER, S., HANDY, N. C., and SUTCLIFFE, B. T., 1983, *Molec. Phys.*, **49,** 745.
[13] CARTER, S., and HANDY, N. C., 1984, *Molec. Phys.*, **52,** 1367.
[14] CARTER, S., 1984, Report CCP1/84/2, Daresbury Laboratory.
[15] SUTCLIFFE, B. T., 1982, *Current Aspects of Quantum Chemistry*, edited by R. Carbo (Studies in Theoretical Chemistry, Vol. 21), p. 99.
[16] LAI, E. K. C., 1975, Masters Thesis, Department of Chemistry, Indiana University.
[17] BURDEN, F. R., and QUINEY, H. M., 1984, *Molec. Phys.*, **53,** 917.
[18] KEMBLE, E. C., 1937, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill).
[19] BRINK, D. M., and SATCHLER, G. R., 1968, *Angular Momentum*, 2nd edition (Clarendon Press).
[20] CONDON, E. U., and SHORTLEY, G. H., 1935, *The Theory of Atomic Spectra* (Cambridge University Press).
[21] TENNYSON, J., 1985, *Comput. Phys. Commun.*, **38,** 39.
[22] GRADSHTEYN, I. S., and RYZHIK, I. H., 1980, *Tables of Integrals, Series and Products* (Academic).
[23] BHATIA, A. K., and TEMKIN, A., 1965, *Phys. Rev.* A, **137,** 1335.
[24] TENNYSON, J., *Comput. Phys. Commun.* (in the press).
[25] TENNYSON, J., and SUTCLIFFE, B. T., 1985, *Molec. Phys.*, **56,** 1175.
[26] MARTIRE, B., and BURTON, P. G., 1985, *Chem. Phys. Lett.*, **121,** 479.
[27] CARTER, S., and HANDY, N. C., 1982, *J. molec. Spectrosc.*, **95,** 9.
[28] BARTHOLOMAE, R., MARTIN, D., and SUTCLIFFE, B. T., 1981, *J. molec. Spectrosc.*, **87,** 367.

[29] FARANTOS, S. C., THEODORAKOPOULOS, G., and NICOLAIDES, C. A., 1983, *Chem. Phys. Lett.*, **100,** 263.
[30] FARANTOS, S. C., and TENNYSON, J., 1985, *J. chem. Phys.*, **82,** 2163.
[31] FARANTOS, S. C., and TENNYSON, J. (unpublished work).
[32] KREEK, H., and LE ROY, R. J., 1975, *J. chem. Phys.*, **63,** 338. LIU, W.-K., GRABENSTETTER, J. E., LE ROY, R. J., and MCCOURT, F. R., 1978, *J. chem. Phys.*, **68,** 5028.
[33] TENNYSON, J., and SUTCLIFFE, B. T., 1986, *Molec. Phys.*, **58,** 1067.