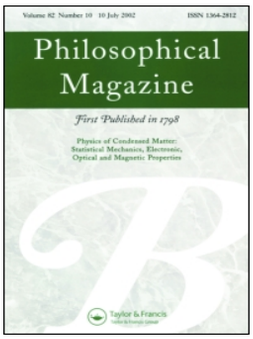

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Philosophical Magazine B

ISSN: 1364-2812 (Print) 1463-6417 (Online) Journal homepage: www.tandfonline.com/journals/tphb20

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To cite this article: James R. Henderson, Jonathan Tennyson & Brian T. Sutcliffe (1994) The calculation of molecular spectra using finite-element methods, Philosophical Magazine B, 69:5, 1027-1036, DOI: 10.1080/01418639408240171

To link to this article: https://doi.org/10.1080/01418639408240171

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PHILOSOPHICAL MAGAZINE B, 1994, VOL. 69, NO. 5, 1027–1036

The calculation of molecular spectra using finite-element methods

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[*Received 7 August 1992*† *and accepted 16 December 1992*]

ABSTRACT

The body-fixed Hamiltonian for a triatomic molecule as given by Sutcliffe and Tennyson in 1991 had the molecule define the x–z plane. Here the relationship between this Hamiltonian and those in which the molecule defines other planes is exhibited. It is shown that in the Sutcliffe–Tennyson approach the original embedding is preferred. In this embedding the relative effectiveness of the finite-basis representation and the discrete-variable representation as a means of approximate solution are considered for rotationally excited states of water.

§ 1. INTRODUCTION

Since the pioneering work of the early 1970s (for a review see Carney, Sprandel and Kern (1978)) there have been extensive developments in non-empirical calculations, within the Born–Oppenheimer approximation, of the vibration–rotation spectra of triatomic molecules. As part of these developments the present authors have proposed (Sutcliffe and Tennyson 1991) a rather general body-fixed Hamiltonian for such systems and have also (Tennyson and Sutcliffe 1992) shown how the discrete-variable representation (DVR) method can be used to manage the singularities that are an inescapable feature of any body-fixed formulation.

In the present paper, which is dedicated to Professor Norman March on the occasion of his 65th birthday, the discussion of the body-fixed Hamiltonian is extended to show how to allow for different axis embeddings and to illustrate the relationship of the results obtained using it, with those obtained using more conventional formulations. In this context the DVR method is used to show the utility of the approach.

§ 2. THE BODY-FIXED HAMILTONIAN

2.1. *Geometric coordinate: z in the plane*

In order to put the discussion in context it is appropriate briefly to recapitulate the results of Sutcliffe and Tennyson (1991) on the triatomic Hamiltonian. The context in which that work is cast can be found in the review by Sutcliffe (1992).

Let the laboratory-fixed coordinates for the three particles be denoted as $\mathbf{x}_i$, $i = 1, 2, 3$ where $\mathbf{x}_i$ is a 3×1 column matrix of cartesian components $\mathbf{x}_{\alpha i}$, $\alpha = x, y$ or z. The

† Received in final form 22 October 1992.

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translational motion is separated from the full Hamiltonian by using the centre-of-mass coordinate **X** and two translational-free internal coordinates $\mathbf{t}_i$:

$$\mathbf{t}_i = \sum_{j=1}^{3} \mathbf{x}_j V_{ji}, \qquad i = 1, 2, \tag{1}$$

with

$$\mathbf{V} = \begin{pmatrix} a_1 - b_1 & a_2 - b_2 \\ b_1 - c_1 & b_2 - c_2 \\ c_1 - a_1 & c_2 - a_2 \end{pmatrix}, \tag{2}$$

corresponding to a choice for $\mathbf{t}_i$ of

$$\mathbf{t}_i = a_i(\mathbf{x}_1 - \mathbf{x}_3) + b_i(\mathbf{x}_2 - \mathbf{x}_1) + c_i(\mathbf{x}_3 - \mathbf{x}_2). \tag{3}$$

The a_i, b_i, and c_i may be chosen at will but, whatever the choice, the $\mathbf{t}_i$ are clearly translationally invariant. This choice is proper as long as the inverse transformation $\tilde{\mathbf{V}}$ exists such that $\tilde{\mathbf{V}}\mathbf{V} = \mathbf{E}_2$ where $\mathbf{E}_2$ is the 2×2 unit matrix.

The translationally invariant part of the kinetic energy operator is

$$\hat{K} = -\tfrac{1}{2}\hbar^2 \sum_{i,j=1}^{2} \frac{1}{\mu_{ij}} \nabla(\mathbf{t}_i) \cdot \nabla(\mathbf{t}_j), \tag{4}$$

where $\nabla(\mathbf{t}_i)$ is the usual grad operator expressed in the variable $\mathbf{t}_i$ and where $1/\mu_{ij}$ is given by

$$\begin{aligned} \frac{1}{\mu_i} &= (a_i - b_i)^2 m_1^{-1} + (b_i - c_i)^2 m_2^{-1} + (c_i - a_i)^2 m_3^{-1}, \qquad i = 1, 2, \\ \frac{1}{\mu_{12}} &= (a_1 - b_1)(a_2 - b_2) m_1^{-1} + (b_1 - c_1)(b_2 - c_2) m_2^{-1} + (c_1 - a_1)(c_2 - a_2) m_3^{-1}, \end{aligned} \tag{5}$$

and where μ_{ii} has been abbreviated as μ_i. Note that $\mu_{12}^{-1} = 0$ defines an orthogonal coordinate system.

The translationally invariant coordinates $\mathbf{t}_i$ are now transformed to a body-fixed set $\mathbf{z}_i$ by means of an orthogonal matrix **C** according to

$$\mathbf{t} = \mathbf{C}\mathbf{z}. \tag{6}$$

In order to define fully the three Euler angles that specify **C**, there must be three relations among the components of the $\mathbf{z}_i$ and, in consequence, the components of **z** must be specifiable in terms of $3N - 6$ rotationally invariant internal coordinates. In the present case, $N = 3$; so there are three internal variables which are chosen to be r_i, the length of $\mathbf{t}_i$ (and of $\mathbf{z}_i$) and θ the angle between $\mathbf{t}_1$ and $\mathbf{t}_2$ (and $\mathbf{z}_1$ and $\mathbf{z}_2$). In the earlier work, the matrix **C** was chosen to put the two $\mathbf{z}_i$ in the x–z plane and the third relation was specified by requiring that the x- or the z-body fixed axis should be such that r_1 makes with it an angle $a\theta$ and r_2 an angle $(1-a)\theta$ with a in the interval (0, 1). It is further required that $|\mathbf{C}| = +1$ in order to keep a right-handed coordinate frame.

Thus in general

$$\mathbf{z} = \mathbf{C}^{\mathrm{T}}\mathbf{t} = \begin{pmatrix} z_{x_1} & z_{x_2} \\ 0 & 0 \\ z_{z_1} & z_{z_2} \end{pmatrix} \tag{7}$$

and, if the z axis is chosen to divide the angle,

$$\mathbf{z}=\begin{pmatrix} -r_1\sin(a\theta) & r_2\sin[(1-a)\theta] \\ 0 & 0 \\ r_1\cos(a\theta) & r_2\cos[(1-a)\theta] \end{pmatrix} \tag{8}$$

while, if the x axis is chosen,

$$\mathbf{z}=\begin{pmatrix} r_1\cos(a\theta) & r_2\cos[(1-a)\theta] \\ 0 & 0 \\ r_1\sin(a\theta) & -r_2\sin[(1-a)\theta] \end{pmatrix}. \tag{9}$$

In the earlier work these two forms were carried through separately and the Hamiltonian was realized in terms of the internal coordinates and angular momentum operators appropriate to each set. However, there is between them no deep difference and it would clearly be both more elegant and more physically satisfying to be able to give just one expression and to specify how it transforms. It turns out to be possible to do this. Consider two possible sets of $\mathbf{z}$ related by an orthogonal transformation $\mathbf{R}$ such that

$$\bar{\mathbf{z}}=\mathbf{R}\mathbf{z}. \tag{10}$$

Thus, if $\mathbf{z}$ was given by eqn. (9) then $\bar{\mathbf{z}}$ would be given by eqn. (8) if $\mathbf{R}$ were chosen to be

$$\mathbf{R}=\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \tag{11}$$

Now it is possible to write $\mathbf{t}$ in terms of either of these choices simply by writing

$$\mathbf{t}=\mathbf{C}\mathbf{z}=\mathbf{C}\mathbf{R}^{\mathrm{T}}\mathbf{R}\mathbf{z}=\bar{\mathbf{C}}\bar{\mathbf{z}}. \tag{12}$$

$\bar{\mathbf{C}}$ can be regarded as an orthogonal matrix which is determined by three new Euler angles appropriate to the new choice of axis embedding while there is no essential change in $\bar{\mathbf{z}}$ from $\mathbf{z}$ since they are expressed in terms of the same internal coordinates. Thus one would expect the potential energy and that part of the kinetic energy that depends only on the internal coordinates to be invariant under this change while the part of the kinetic energy operator that contains angular momentum terms would be changed. This is indeed the case. To see precisely what happens, it is necessary to consider the general expression for the part of the kinetic energy that depends on the angular momentum operators and this is (Sutcliffe 1992)

$$\hat{K}(\phi,\mathbf{q})=\frac{1}{2}\left(\sum_{\alpha\beta}M_{\alpha\beta}\hat{L}_\alpha\hat{L}_\beta+\hbar\sum_\alpha\gamma_\alpha\hat{L}_\alpha\right). \tag{13}$$

Here the $\hat{L}_\alpha$ are the components of the body-fixed angular momentum operators and are chosen to obey the standard commutation conditions. They depend only upon the Euler angles denoted collectively by ϕ. The matrix $\mathbf{M}$ is a generalized inverse inertia tensor and depends, as do the operator components λ_α, only on the internal coordinates denoted here collectively as $\mathbf{q}$. The passage to the changed form is rather complicated if $\mathbf{R}$ is allowed to have elements which are functions of the internal coordinates but, if the elements are constants as in eqn. (11) above, then the forms are simple and can be

obtained from eqn. (13) by replacing $\mathbf{M}$ by $\bar{\mathbf{M}}$ and the components λ_α by the components $\bar{\lambda}_\alpha$ according to

$$\bar{\mathbf{M}} = \mathbf{R}\mathbf{M}\mathbf{R}^{\mathrm{T}}, \tag{14}$$

$$\bar{\lambda} = |\mathbf{R}|\lambda\mathbf{R}^{\mathrm{T}}, \tag{15}$$

where λ is a row matrix of components and $|\mathbf{R}|$ is ± 1 according to whether $\mathbf{R}$ is a proper or an improper rotation. Of course the angular momentum operators too are changed, because they now refer to a changed set of Euler angles but that change need not be explicitly expressed, for all angular behaviour is removed from the problem by allowing the operator to operate on the appropriate angular momentum eigenfunctions and then integrating out over the Euler angles to give an effective Hamiltonian in terms of the internal coordinates only. This effective operator is diagonal in J, the total angular momentum quantum number, and in M, the component of angular momentum along the space-fixed z axis, but not in k, the component along the body-fixed z axis.

For the triatomic problem, the kinetic energy operator obtained in the earlier work had the form

$$\hat{K} = \hat{K}_{\mathrm{V}}^{(1)} + \hat{K}_{\mathrm{V}}^{(2)} + \hat{K}_{\mathrm{VR}}, \tag{16}$$

where the $\hat{K}_{\mathrm{V}}$ operators contain no references to the angular momentum and so are invariant under the change, as was established in previous work and so need not be considered further here. The operator $\hat{K}_{\mathrm{VR}}$ corresponds to the general operator given in eqn. (13) and so is not invariant. It is given by

$$\begin{aligned}\hat{K}_{\mathrm{VR}} = \tfrac{1}{2}[&M_{xx}\hat{L}_x^2 + M_{yy}\hat{L}_y^2 + M_{zz}\hat{L}_z^2 + M_{xz}(\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x)] \\ &+ \frac{\hbar}{i}\left[\left(\frac{1-a}{\mu_1 r_1^2} - \frac{a}{\mu_2 r_2^2}\right)\left(\frac{\partial}{\partial\theta} + \frac{\cot\theta}{2}\right) + \frac{2a-1}{\mu_{12} r_1 r_2}\left(\cos\theta\frac{\partial}{\partial\theta} + \frac{1}{2\sin\theta}\right)\right. \\ &\left. + \frac{\sin\theta}{\mu_{12}}\left(\frac{a}{r_2}\frac{\partial}{\partial r_1} - \frac{1-a}{r_1}\frac{\partial}{\partial r_2}\right)\right]\hat{L}_y.\end{aligned} \tag{17}$$

It is seen that only λ_y is non-zero with this choice while all off-diagonal elements involving a y subscript in the inverse generalized inertia tensor vanish. The non-vanishing elements of this tensor, with the choice of z as given by eqn. (9) are

$$\begin{aligned}M_{xx} &= \frac{1}{\sin^2\theta}\left(\frac{\cos^2[(1-a)\theta]}{\mu_1 r_1^2} + \frac{\cos^2(a\theta)}{\mu_2 r_2^2} - 2\frac{\cos(a\theta)\cos[(1-a)\theta]}{\mu_{12} r_1 r_2}\right), \\ M_{yy} &= \frac{(1-a)^2}{\mu_1 r_1^2} + \frac{a^2}{\mu_2 r_2^2} + \frac{2a(1-a)\cos\theta}{\mu_{12} r_1 r_2}, \\ M_{zz} &= \frac{1}{\sin^2\theta}\left(\frac{\sin^2[(1-a)\theta]}{\mu_1 r_1^2} + \frac{\sin^2(a\theta)}{\mu_2 r_2^2} - 2\frac{\sin(a\theta)\sin[(1-a)\theta]}{\mu_{12} r_1 r_2}\right), \\ M_{xz} &= \frac{1}{\sin^2\theta}\left(-\frac{\cos[(1-a)\theta]\sin[(1-a)\theta]}{\mu_1 r_1^2} + \frac{\cos(a\theta)\sin(a\theta)}{\mu_2 r_2^2} - \frac{\sin[(2a-1)\theta]}{\mu_{12} r_1 r_2}\right).\end{aligned} \tag{18}$$

In the present case with $\mathbf{R}$ given by eqn. (11), the transformed elements of inertia tensor are

$$\bar{M}_{xx} = M_{zz},\ \bar{M}_{yy} = M_{yy},\ \bar{M}_{zz} = M_{xx},\ \bar{M}_{xz} = -M_{xz}, \tag{19}$$

while $\bar{\lambda}_y = \lambda_y$ so that the term linear in $\hat{L}_y$ in eqn. (17) is unchanged. These results agree exactly with the previously obtained results in which the embeddings were treated separately.

It is possible to use this approach to determine the change to be made under *any* constant reorientation of the axis system and, in particular, to see what happens if the body-fixed axis system is oriented so that the z axis is perpendicular to the molecular plane. This choice is of interest because it is often seen as the 'natural' choice if the molecule is approximately a symmetric top. Before considering this in more detail let the general problem of removing the rotational motion, mentioned above, be considered rather more generally.

To remove the rotational motion from the part of the Hamiltonian that depends only on the internal coordinates is perfectly straightforward. If we denote that part by $\hat{K}_I(\mathbf{q}) + V(\mathbf{q})$ then the effective operator arising from that is just

$$\langle J'M'k'|\hat{K}_I + V|JMk\rangle = \delta_{J'J}\delta_{M'M}\delta_{k'k}(\hat{K}_I + V), \tag{20}$$

where the $|JMk\rangle$ are angular momentum eigenfunctions that are appropriate to the choice of angular momentum operators and the integration implied is over the Euler angles ϕ only. It follows from this that the $\hat{K}_V$ operators are essentially unchanged by this process and so again need not be considered further here.

To deal similarly with the term (13) is considerably more complicated, however, and is best done by re-expressing the components of $\hat{\mathbf{L}}$ in terms of $L_\pm(\phi)$ and $\hat{L}_z(\phi)$. When this is done,

$$\begin{aligned}\langle JMk'|\hat{K}(\phi,\mathbf{q})|JMk\rangle = {}& \tfrac{1}{4}\hbar^2\{b_{\pm 2}C^{\pm}_{Jk\pm 1}C^{\pm}_{Jk}\delta_{k'k\pm 2} + C^{\pm}_{Jk}[b_{\pm 1}(2k\pm 1)+\lambda_\pm]\delta_{k'k\pm 1}\} \\ & + \tfrac{1}{2}\hbar^2\{[J(J+1)-k^2]b_+ + b_0k^2 + \lambda_0 k\}\delta_{k'k}.\end{aligned} \tag{21}$$

In this expression,

$$C^{\pm}_{Jk} = [J(J+1)-k(k\pm 1)]^{1/2} \tag{22}$$

and

$$\begin{aligned} b_{\pm 2} &= \tfrac{1}{2}(M_{xx}-M_{yy}) \pm \frac{M_{xy}}{\mathrm{i}}, \\ b_{\pm 1} &= M_{xz} \pm \frac{M_{yz}}{\mathrm{i}}, \\ b_\pm &= \tfrac{1}{2}(M_{xx} \pm M_{yy}), \qquad b_0 = M_{zz}, \end{aligned} \tag{23}$$

and, in terms of the λ_α in eqn. (13), λ_0 is λ_z and the $\lambda_\pm$ are

$$\lambda_\pm = \lambda_x \pm \frac{\lambda_y}{\mathrm{i}}. \tag{24}$$

All the terms above are diagonal in J and M but that has been left implicit.

In constructing the effective triatomic Hamiltonian for the embedding given by eqn. (9) it is convenient also to eliminate the factor $r_1^2 r_2^2$ from the Jacobian so that the results appear in what is often called manifestly a Hermitian form. The operator replacing $\hat{K}_{VR}$ according to eqn. (21) is then

$$\hat{K}_{VR} = \delta_{k'k\pm 2}\tfrac{1}{4}\hbar^2 C^{\pm}_{Jk\pm 1}C^{\pm}_{Jk}b_- + \delta_{k'k\pm 1}\tfrac{1}{2}\hbar^2 C^{\pm}_{Jk}\lambda^\pm + \delta_{k'k}\tfrac{1}{2}\hbar^2 b_+[J(J+1)-k^2] + b_0k^2, \tag{25}$$

where the same name is used for the effective operator as for the full operator since confusion is unlikely because only the effective form is used in future. In eqn. (25), $b_\pm$ and b_0 are as before, while

$$\lambda^\pm = \frac{1}{\mu_1 r_1^2}\left[\mp(1-a)\left(\frac{\partial}{\partial\theta}+\frac{\cot\theta}{2}\right)+(k\pm\tfrac{1}{2})\frac{\sin[(1-a)\theta]\cos[(1-a)\theta]}{\sin^2\theta}\right]$$
$$+\frac{1}{\mu_2 r_2^2}\left[\pm a\left(\frac{\partial}{\partial\theta}+\frac{\cot\theta}{2}\right)+(k\pm\tfrac{1}{2})\frac{\sin(a\theta)\cos(a\theta)}{\sin^2\theta}\right]$$
$$+\frac{1}{\mu_{12} r_1 r_2}\left[\mp(2a-1)\left(\cos\theta\frac{\partial}{\partial\theta}+\frac{\operatorname{cosec}\theta}{2}\right)-(k\times\tfrac{1}{2})\frac{\sin[(2a-1)\theta]}{\sin^2\theta}\right]$$
$$\mp\frac{\sin\theta}{\mu_{12}}\left[\frac{a}{r_2}\frac{\partial}{\partial r_1}-\frac{1-a}{r_1}\frac{\partial}{\partial r_2}+\frac{1-2a}{r_1 r_2}\right]. \tag{26}$$

Some simplifications of form have been made in notation here, from the full notation of eqn. (21). These are possible in the present case because only λ_y is non-zero and no off-diagonal terms of the form $\mathbf{M}_{\alpha y}$ survive either.

2.2. *Geometric coordinate: z out of the plane*

Consider what happens when $\mathbf{z}$, as given by eqn. (9), is related to

$$\bar{\mathbf{z}} = \begin{pmatrix} r_1\cos(a\theta) & r_2\cos[(1-a)\theta] \\ -r_1\sin(a\theta) & r_2\sin[(1-a)\theta] \\ 0 & 0 \end{pmatrix} \tag{27}$$

by

$$\bar{\mathbf{z}} = \mathbf{R}\mathbf{z} \tag{28}$$

so that $\mathbf{R}$ is given by

$$\mathbf{R} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{29}$$

That is, the embedding is rotated so that the molecule lies in the x–y plane with the x axis still dividing the angle in the same way as previously and the z axis is perpendicular to the molecular plane.

The change corresponding to eqn. (19) is, in this case,

$$\bar{M}_{xx} = M_{xx},\ \bar{M}_{yy} = M_{zz},\ \bar{M}_{zz} = M_{yy},\ \bar{M}_{xy} = -M_{xz}, \tag{30}$$

and all off-diagonal elements with a z subscript vanish, while $\bar{\lambda}_z = \lambda_y$ and $\bar{\lambda}_x = \bar{\lambda}_y = 0$. These changes result in substantial changes in to the form of $\hat{K}_{\mathrm{VR}}$ in eqn. (25) and necessitate a return to the rather fuller notation of eqn. (21). It is easily seen that both $\bar{\lambda}_\pm$ and $\bar{b}_{\pm 1}$ vanish, so that the second term in eqn. (25) is absent from the transformed form while b_- has to be extended as $\bar{b}_{\pm 2}$ with $\bar{b}_{-2} = b^*_{+2}$ with

$$\bar{b}_{+2} = \frac{\exp(2ia\theta)}{2\sin^2\theta}\left(\frac{\exp(-2i\theta)}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}-2\frac{\exp(-i\theta)}{\mu_{12} r_1 r_2}\right). \tag{31}$$

Similarly, in the last term in eqn. (25), b_+ has to be replaced by $\bar{b}$ which is given by

$$\bar{b}=\frac{1}{2\sin^2\theta}\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}-2\frac{\cos\theta}{\mu_{12} r_1 r_2}\right), \tag{32}$$

while b_0 becomes

$$\bar{b}_0=\frac{(1-a)^2}{\mu_1 r_1^2}+\frac{a^2}{\mu_2 r_2^2}+2\frac{a(1-a)\cos\theta}{\mu_{12} r_1 r_2} \tag{33}$$

and an extra term $\bar{\lambda}_0 k$ must be added in the last term of eqn. (25) as in the last term of eqn. (21). The operator is given by (see the last term in eqn. (17))

$$\begin{aligned}\bar{\gamma}_0=\frac{2}{\mathrm{i}}\Bigg[&\left(\frac{1-a}{\mu_1\mu_1^2}-\frac{a}{\mu_2 r_2^2}\right)\left(\frac{\partial}{\partial\theta}+\frac{\cot\theta}{2}\right)\\&+\frac{2a-1}{\mu_{12} r_1 r_2}\left(\cos\theta\frac{\partial}{\partial\theta}+\frac{\operatorname{cosec}\theta}{2}\right)+\frac{\sin\theta}{\mu_{12}}\left(\frac{a}{r_2}\frac{\partial}{\partial r_1}-\frac{1-a}{r_1}\frac{\partial}{\partial r_2}\right)\Bigg]\end{aligned} \tag{34}$$

to give a changed form of $\hat{K}_{\mathrm{VR}}$:

$$\hat{K}_{\mathrm{VR}}=\delta_{k'k\pm2}\tfrac{1}{4}\hbar^2 C^{\pm}_{Jk\pm1}C^{\pm}_{Jk}\bar{b}_{\pm2}+\delta_{k'k}\tfrac{1}{2}\hbar^2\{\bar{b}[J(J+1)-k^2]+\bar{b}_0 k^2+\bar{\lambda}_0 k\}. \tag{35}$$

Even though the two forms (25) and (35) look so different, it must be stressed they are precisely equivalent. Indeed all body-fixed Hamiltonians are equivalent to each other in their common domains and in this case, since the transformation matrix is a constant matrix, the domains of both forms are identical. Thus exact solutions of the problem in either form would yield exactly the same energies and wavefunctions differing only by a coordinate transformation. From a practical point of view, one form is preferred to another if it is particularly suggestive of an approximation scheme or if it puts the inevitable singularities in the kinetic energy operator outside a region of interest. Thus a preferred form could be one that allowed easy and efficient calculation of matrix elements in a chosen basis. Similarly in the triatomic case an attractive form is one in which there is no divergence as the molecule became linear.

In the present case the form (25) is much more convenient than the form (35) because the operators are real and so allow for a basis of real trial functions. Furthermore a very efficient form for the expansion of the angular part of the problem has been shown to be possible using eqn. (25) whereas there seems no obvious comparable possibility for eqn. (35). It is possible too (Tennyson and Sutcliffe 1992) to ameliorate the effects of singularities by special choices of a in the form (25). This does not seem possible in the form (35). Finally, since eqn. (35) has no closer relationship to the traditional 'natural' form than has eqn. (25), there is no reason for preferring it on those grounds either.

Thus the form developed in the earlier work remains the form of choice from a computational point of view and will continue to be used here.

§3. Rotationally excited states of water

As a comparison of the embeddings discussed above and of the finite-basis representation (FBR) against the DVR, we have performed a number of calculations on rotationally excited water. The Hamiltonian developed in the earlier work is used and a choice will be made for the form of **V** to yield Radau coordinates. Various choices for a will be made and the embeddings (8) and (9) will both be used as is convenient.

The most efficient method of treating rotational excitation in variational calculations is in two steps (Tennyson and Sutcliffe 1986). In the first step it is assumed that

the projection k of the total angular momentum J along the body-fixed z axis is conserved. Selected solutions of this calculation are used to solve the full problem in the second step. It is because the number of solutions required for the second step decreases greatly if k is indeed nearly conserved that we have put so much effort into investigating different axis embeddings and hence definitions of k.

We have developed a number of programs for treating the triatomic rovibrational problem in both FBR and DVR. TRIATOM (first step) and ROTLEVD (second step) (Tennyson, Miller and Le Sueur (1993)) employ a FBR in all three internal coordinates and can only use axis embeddings defined by $a=0$ or 1. These embeddings are equivalent to taking the z axis parallel to either r_1 or r_2. DVR1D (Henderson and Tennyson 1993) uses a FBR for the radial coordinates and a DVR for the θ coordinate. By transforming from the DVR to the FBR (Tennyson and Henderson 1989), DVR1D can be used as the first step driving ROTLEVD with embeddings $a=0$ or 1.

For an AB_2 molecule, such as water, represented by Radau coordinates, DVR1D can also drive ROTLEV2 (Henderson and Tennyson 1993) in which case the embedding is defined by $a=\frac{1}{2}$; this bisector embedding places the z axis at an angle $\frac{1}{2}\theta$ to either of the radial coordinates (Tennyson and Sutcliffe 1992).

For water, the advantage of the bisector embedding, which has been extensively used by Carter and Handy (for example Carter and Handy (1986)), is that it preserves the permutation symmetry of the molecule. This is important not only because use of the full symmetry is computationally, at least in principle, more efficient but also because levels with different permutation symmetry have different nuclear spin degeneracies which need to be considered when generating synthetic spectra. Conversely rotationally excited states in Radau coordinates with $a=0$ or 1 are not easily symmetrized with respect to the interchange of two like atoms.

The table summarizes the results of a series of calculations on $J=9$ rotational manifold of the vibrational ground state of water. The calculations use the spectroscopically determined potential of Jensen (1989) and previously optimized basis sets used by Fernley, Miller and Tennyson (1991) for looking at the $J=1$ and 2 levels of water. The unsymmetrized calculations, those which drove ROTLEVD, diagonalized ten Hamiltonians (each k from 0 to J) of dimension 800 in the first step and chose the lowest 1500 solutions of these in the second. An approximately equivalent symmetrized calculation was performed which diagonalized the 11 Hamiltonians ($k=1$ has to be done twice (Tennyson and Sutcliffe 1992)) of dimension 450 in the first step and used the lowest 800 solutions of these to drive ROTLEV2. A large symmetrized run diagonalizing Hamiltonians of dimension 1250 in the first step and using the lowest 800 solutions to drive ROTLEV2 was performed for comparison.

All the calculations give very similar answers and the comparison with the large calculation, and other test runs using larger second-step basis sets, demonstrates a very high level of convergence. Comparison with the experimental results (Flaud, Camy-Peyret and Maillard 1976) shows that agreement with the term values worsens with increasing K_a. These states sample bending regions of the potential which were poorly characterized by the data used to fit the potential (Jensen 1989).

What is markedly different between the various methods of doing the calculation is the central processing unit (CPU) requirement. The comparisons based on the ground vibrational state will tend to favour the FBR over the DVR approach. This is because small calculations are not generally feasible with the DVR which performs much more efficiently when one is seeking many vibrational states (Tennyson 1992). In practice this means that, because of the pre-diagonalizations and truncations involved in the DVR

Calculated ground vibrational state $J=9$ rotational term values for water.

		Calculated rotational term (cm^{-1})				
K_a	K_c	Observed (Flaud *et al.* 1976)	TRIATOM ROTLEVD $a=0$	DVR1D ROTLEVD $a=0$	DVR1D ROTLEV2 $a=\frac{1}{2}$	DVR1D ROTLEV2 $a=\frac{1}{2}$
0	9	920·169	920·033	920·034	920·032	920·032
1	9	920·211	920·074	920·074	920·073	920·073
1	8	1079·080	1078·979	1078·979	1078·978	1078·978
2	8	1080·386	1080·246	1080·246	1080·245	1080·245
2	7	1201·922	1202·072	1202·072	1202·072	1202·072
3	7	1216·232	1216·063	1216·063	1216·063	1216·063
3	6	1282·919	1283·281	1283·281	1283·280	1283·280
4	6	1340·886	1340·477	1340·477	1340·477	1340·477
4	5	1360·236	1360·178	1360·178	1360·178	1360·178
5	5	1474·981	1474·030	1474·030	1474·030	1474·030
5	4	1477·298	1476·416	1476·416	1476·416	1476·416
6	4	1631·251	1629·539	1629·539	1629·539	1629·539
6	3	1631·384	1629·682	1629·682	1629·682	1629·682
7	3	1810·584	1807·986	1807·986	1807·986	1807·986
7	2	1810·589	1807·991	1807·991	1807·991	1807·991
8	2	2009·805	2006·196	2006·196	2006·196	2006·196
8	1	2009·805	2006·196	2006·196	2006·196	2006·196
9	1	2225·468	2220·725	2220·725	2220·725	2220·725
9	0	2225·468	2220·725	2220·725	2220·725	2220·725
Size of first step			800	800	450	1250
Size of second step			1500	1500	800	800
CPU time, first step (s)			90	584	235	2555
CPU time, second step (s)			65	372	19973	25450

calculation, diagonalization of a Hamiltonian of a given size will converge many more vibrational levels than will the corresponding FBR calculation using a rather simple-minded basis selection procedure (Tennyson 1986). However, it is still possible to make some useful observations.

It is immediately apparent from the table that the symmetrized procedure, using ROTLEV2, is actually much *slower* than the seemingly less efficient methods using ROTLEVD. In part this is due to the extra matrix elements which need to be evaluated in the bisector Hamiltonian, but the main difference is the loss of simplicity in the Coriolis coupling matrix elements in the DVR compared with the FBR. One of the reasons that the two-step procedure works so efficiently (Tennyson, Miller and Sutcliffe 1989) is that the angular contribution to the off-diagonal Coriolis coupling matrix element is diagonal. In the DVR this is not so and the result is to increase considerably the time required to transform the matrix elements calculated in the first step to the representation of the second step. It is therefore more efficient to transform between a first step calculated in the DVR and a second step in an FBR as advocated by Tennyson and Henderson (1989).

§4. Conclusion

We have extended our previous body-fixed internal-coordinate Hamiltonian by considering a number of ways of embedding the axes system into the molecule. In particular we discuss the potentially useful case where the z axis is taken perpendicular

to the plane of the molecules. Unfortunately the innate problems with this Hamiltonian suggest that it will be of little use in actual calculations.

Comparisons are made between ways of performing calculations for highly rotationally excited states of water using different z-axis embeddings. Perhaps surprisingly we find that an embedding in which the off-diagonal Coriolis coupling terms are sparse is much more computationally efficient than one which allows the full symmetry of the molecule to be used in the calculation.

ACKNOWLEDGMENTS

We thank Steven Miller for help with the FBR calculations reported here. J.R.H. thanks the Science and Engineering Research Council (SERC) for a Fellowship. This work was supported by SERC Grant No. GR/H41744.

REFERENCES

CARNEY, G. D., SPRANDEL, L. L., and KERN, C. W., 1978, *Adv. chem. Phys.*, **37**, 305.
CARTER, S., and HANDY, N. C., 1986, *Comput. Phys. Rep.*, **5**, 117.
FERNLEY, J. A., MILLER, S., and TENNYSON, J., 1991, *J. molec. Spectrosc.*, **150**, 597.
FLAUD, J.-M., CAMY-PEYRET, C., and MAILLARD, J. P., 1976, *Molec. Phys.*, **32**, 499.
HENDERSON, J. R., and TENNYSON, J., 1993, *Comput. Phys. Commun.*, **75**, 365.
JENSEN, P., 1989, *J. molec. Spectrosc.*, **133**, 438.
SUTCLIFFE, B. T., 1992, *Methods of Computational Chemistry*, Vol. 4, edited by S. Wilson (London: Plenum), p. 33.
SUTCLIFFE, B. T., and TENNYSON, J., 1991, *Int. J. quant. Chem.*, **39**, 183.
TENNYSON, J., 1986, *Comput. Phys. Rep.*, **4**, 1; 1992, *J. Chem. Soc., Faraday Trans.*, **88**, 3287.
TENNYSON, J., and HENDERSON, J. R., 1989, *J. chem. Phys.*, **91**, 3815.
TENNYSON, J., MILLER, S., and SUTCLIFFE, B. T., 1989, *Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules*, NATO Advanced Study Institute Series C, Vol. 277 edited by A. Lagana (Dordrecht: Kluwer), p. 261.
TENNYSON, J., MILLER, S., and LE SUEUR, C. R., 1993, *Comput. Phys. Commun.*, **75**, 339.
TENNYSON, J., and SUTCLIFFE, B. T., 1986, *Molec. Phys.*, **58**, 1067; 1992, *Int. J. quant. Chem.*, **42**, 941.