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Discretization to Avoid Singularities in Vibration–Rotation Hamiltonians: A Bisector Embedding for AB_2 Triatomics

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Abstract

A previously proposed [Sutcliffe and Tennyson, Int. J. Quantum Chem. **29**, 183 (1991)] body-fixed Hamiltonian is applied to AB_2 systems in Radau coordinates with the x-axis embedded along the bisector of the angle. It is shown that by using a discrete variable representation for the angular coordinate it is possible to avoid singular regions of the Hamiltonian. A two-step variational procedure is used to obtain rotationally excited states of the system. The results of test calculations H_2S and D_2S with $J = 0$, 1, 5, and 10 are discussed along with computer-usage characteristics.

1. Introduction

In a recent paper [1], henceforth referred to as I, a general body-fixed Hamiltonian for the nuclear motion of triatomic species was derived. The internal motion part of the Hamiltonian was given in terms of two lengths, r_1 and r_2, chosen in a very general manner, and an included angle θ. This Hamiltonian also allowed for considerable flexibility in the choice of the orientation of the body-fixed axis system.

However, although the formalism for the general axis embedding was given in I, the only application was to cases where the z-axis was chosen parallel to either r_1 or r_2. This was because other choices were found to have singularities associated with the (linear) geometries $\theta = 0$ and π.

In I, one other special case was discussed. It was noted that when the molecule is placed in the x-z plane and the x-axis is placed along the bisector of the angle θ it is possible to restrict the singularity to only one θ value. The effective Hamiltonian in this embedding and the general coordinate system was derived but no applications were considered.

In fact, this special case is appropriate to an important class of triatomics, AB_2 molecules such as H_2O, H_2S, CH_2^+, and CO_2. It is only in a bisector embedding that fully symmetrized wave functions of rotationally excited states of the system can be developed in terms of internal coordinates generally used to represent

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these molecules. Indeed, recent calculations that did not employ the full symmetry of D_2S suffered from problems with intensity stealing between transitions linking nearly degenerate levels of different symmetry [2]. It is for these reasons that the bisector embedding has been used by Carter, Handy, and co-workers for extensive work on AB_2 systems [3–6], although their calculations appear to have paid little attention to the singularity at $\theta = 0$ implicit in their Hamiltonian.

In this paper, we present an alternative method of treating the bisector embedding for AB_2 systems. By using a finite element method, the discrete variable representation (DVR) [7–12], to treat the θ coordinate, it is possible to design a procedure that avoids sampling the region of the singularity. This procedure is valid as long as the singularity is in a region of space where the wave function is vanishingly small.

2. Theory

2.1. Coordinates

The Hamiltonians derived in I were obtained in terms of a very general set of coordinates, a subset of which are defined in Figure 1. To simplify the implementation of these coordinates, two geometric parameters g_1 and g_2 were defined as

$$g_1 = \frac{A_3 - P}{A_3 - A_2}; \qquad g_2 = \frac{A_3 - R}{A_3 - A_1}. \tag{1}$$

For AB_2 molecules were are interested in coordinate systems in which it is possible to represent symmetry. Thus, scattering or Jacobi coordinates, defined by ($g_1 = 0.5$, $g_2 = 0$), allow the symmetry to be carried by the θ coordinate. However, these coordinates, which represent the triatomic as a collision complex between a homonuclear diatomic and an atom, do not give a realistic representation of many chemically bound systems (see, e.g., [1, 13]).

Alternative coordinates that allow the symmetry to be represented by equal treatment of the radial coordinates are given by setting g_1 equal to g_2. Examples of such systems include bond-length–bond-angle coordinates ($g_1 = g_2 = 0$) and

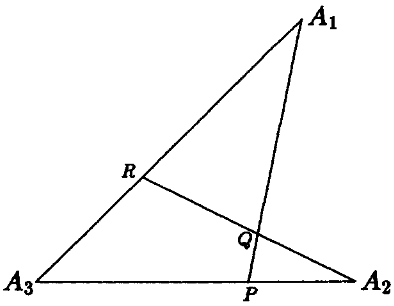

Figure 1. Coordinate system. A_i represents atom i. The coordinate system is defined by $r_1 = A_2 - R$, $r_2 = A_1 - P$, and $\theta = A_1\hat{Q}A_2$. The positions of points P and R can be defined arbitrarily.

Radau coordinates [14] ($g_1 = g_2 = \gamma$), where

$$\gamma = 1 + \frac{m_A}{m_B} - \left[\left(1 + \frac{m_A}{m_B}\right)^2 - 1\right]^{1/2} \tag{2}$$

and m_A/m_B is the ratio of the atomic masses. Note that $\gamma \simeq 0$ if this ratio is large.

The bisector embedding is appropriate for any coordinate system for which $g_1 = g_2$, and the theory will be developed in the following section for these coordinates. However, Radau coordinates have a particular advantage in that they generate a diagonal kinetic energy operator. Such coordinates are usually described as orthogonal. As will be shown below, this leads to a significant simplification of the kinetic energy operator. As the kinetic energy operator provides the off-diagonal coupling in the discrete variable representation [9,15], working with orthogonal coordinates leads to considerable computational savings. For this reason, only applications in Radau coordinates will actually be considered.

2.2 *Effective Hamiltonian*

Following I and earlier work [13,16], we consider an effective radial Hamiltonian operator

$$\hat{H}(r_1,r_2) = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + \hat{K}_{VR}^{(3)} + \delta_{k'k} V_{j'jk}(r_1,r_2). \tag{3}$$

This Hamiltonian is obtained by letting the full Hamiltonian of the problem act on the angular functions, multiplying from the left by the complex conjugate of these functions, and integrating over all angular variables. Appropriate angular functions are given by

$$|j,k\rangle = \Theta_{j,k}(\theta)\,|J,M,k\rangle, \tag{4}$$

where $\Theta_{j,k}(\theta)$ is a normalized associated Legendre polynomial with the Condon and Shortley [17] phase conventions. $|J,M,k\rangle$ is an angular momentum eigenfunction [18] given in terms of the Euler angles (α,β,γ), which are defined by the embedding. For the body-fixed axes in this case, we require x to bisect the angle θ, z to lie in the plane of the molecule perpendicular to x, and y to be such that (x,y,z) form a right-handed frame. This is equivalent to the $\alpha = \frac{1}{2}$ embedding of I.

In Eq. (4), J is the total angular momentum that is a good quantum number of the system; M is the projection of J on the space-fixed z-axis and will not be considered further; and k is the projection of J onto the body-fixed z-axis.

In Eq. (3), the effective vibrational kinetic energy operators, which are independent of the axis embedding, are given by

$$\hat{K}_V^{(1)} = \delta_{j'j}\,\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right] \tag{5}$$

$$\begin{aligned}\hat{K}_V^{(2)} = &-\delta_{j'j+1}\,\delta_{k'k}\,d_{jk}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} - \frac{j+1}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{j+1}{r_2}\right)\\ &- \delta_{j'j-1}\,\delta_{k'k}\,d_{j-1,k}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right),\end{aligned} \tag{6}$$

with

$$d_{jk} = \left[\frac{(j - k + 1)(j + k + 1)}{(2j + 1)(2j + 3)}\right]^{1/2}. \tag{7}$$

In the above, the reduced masses (the elements of the inverse metric) are given in terms of the atomic masses, m_i (numbering as in Fig. 1):

$$\begin{aligned} \mu_1^{-1} &= g_2^2 m_1^{-1} + m_2^{-1} + (1 - g_2)^2 m_3^{-1} \\ \mu_{12}^{-1} &= (1 - g_1)(1 - g_2) m_3^{-1} - g_2 m_1^{-1} - g_1 m_2^{-1} \\ \mu_2^{-1} &= m_1^{-1} + g_1^2 m_2^{-1} + (1 - g_1)^2 m_3^{-1}. \end{aligned} \tag{8}$$

It should be noted that for orthogonal coordinates, such as Radau coordinates, $\mu_{12}^{-1} = 0$. This removes the operator $\hat{K}_V^{(2)}$ and simplifies the effective vibration–rotation kinetic energy operators given below.

If the potential is expressed in a Legendre expansion

$$V(r_1, r_2, \theta) = \sum_\lambda V_\lambda(r_1, r_2)\Theta_{\lambda,0}(\tau), \tag{9}$$

then the angular integration described above can be performed analytically giving

$$V_{j'jk}(r_1, r_2) = \sum_\lambda \langle j'k'|\Theta_{\lambda,0}(\theta)|jk\rangle V_\lambda(r_1, r_2), \tag{10}$$

where the integral over θ gives the usual Gaunt coefficient [19]

$$\langle j'k'|\Theta_{\lambda,0}(\theta)|jk\rangle = \delta_{k'k}(-1)^k[(2j' + 1)(2j + 1)]^{1/2}\begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j' & \lambda & j \\ -k & 0 & k \end{pmatrix}. \tag{11}$$

This method of performing the angular integration over the potential is completely general as potentials that are not naturally expanded in Legendre polynomials can be so expressed for each (r_1, r_2) by using Gauss–Legendre quadrature [20].

For the bisector embedding, the effective vibration–rotation kinetic energy operators in Eq. (3) are given by

$$\begin{aligned} \hat{K}_{VR}^{(1)} = {} & \delta_{k'k}\frac{\hbar^2}{8}(J(J + 1) - 3k^2)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2}{\mu_{12} r_1 r_2}\right)I^{(1)}_{j',k,j,k} + \delta_{k'k}\frac{\hbar^2}{16} \\ & \times (J(J + 1) - k^2)\left(\delta_{j'j}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) + \frac{2}{\mu_{12} r_1 r_2}(\delta_{j'j+1} d_{jk} + \delta_{j'j-1} d_{j-1k})\right) \end{aligned} \tag{12}$$

$$\begin{aligned} \hat{K}_{VR}^{(2)} = {} & \delta_{k'k\pm1}\frac{\hbar^2}{4}C^\pm_{Jk}\left[\left(\frac{1}{\mu_2 r_2^2} - \frac{1}{\mu_1 r_1^2}\right)\left(\delta_{j'j}C^\pm_{jk} + \left(k \pm \frac{1}{2}\right)I^{(2)}_{j',k',j,k}\right)\right. \\ & \left. \pm \frac{1}{\mu_{12}}\left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2}\right)(\delta_{j'j+1} a_{j\pm k} - \delta_{j'j-1} b_{j\pm k})\right] \end{aligned} \tag{13}$$

and

$$\hat{K}_{VR}^{(3)} = \delta_{k'k\pm2}\frac{\hbar^2}{32}C_{Jk\pm1}^{\pm}C_{Jk}^{\pm}\left[\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)(2I_{j',k',j,k}^{(1)} - I_{j',k',j,k}^{(3)}) - \frac{2}{\mu_{12}r_1 r_2}(I_{j',k',j+1,k}^{(3)}d_{jk} + I_{j',k',j-1,k}^{(3)}d_{j-1k} + 2I_{j',k',j,k}^{(1)})\right], \tag{14}$$

where the integrals are defined by

$$I_{j',k',j,k}^{(1)} = \left\langle j'k'\left|\frac{1}{(1 - \cos\theta)}\right|jk\right\rangle \tag{15}$$

$$I_{j',k',j,k}^{(2)} = \left\langle j'k'\left|\frac{1 + \cos\theta}{\sin\theta}\right|jk\right\rangle \tag{16}$$

and

$$I_{j',k',j,k}^{(3)} = \langle j'k' \,|\, jk\rangle \tag{17}$$

and the angular factors are

$$C_{Jk}^{\pm} = [J(J + 1) - k(k \pm 1)]^{1/2} \tag{18}$$

$$a_{jk} = \left[\frac{(j + k + 1)(j + k + 2)}{(2j + 1)(2j + 3)}\right]^{1/2} \tag{19}$$

$$b_{jk} = \left[\frac{(j - k)(j - k - 1)}{(4j^2 - 1)}\right]^{1/2}. \tag{20}$$

Examination of the angular integrals in the above formulae shows that an angular divergence is encountered for terms arising from $\hat{K}_{VR}^{(1)}$ when $k = 0$. In this case, $I_{j',0,j,0}^{(1)}$ is logarithmically divergent at the limit $\theta = 0$. This divergence is effective only when $J(J + 1)$ is nonzero, for otherwise it is multiplied by k^2, which vanishes when $k = 0$. Thus, functions of the form (4) with $k = 0$ cannot strictly be allowed trial basis functions for the problem with $J \neq 0$. Any allowed function must vanish at $\theta = 0$ so as to eliminate the divergence. How such allowed functions can be achieved is discussed in Section 3.

2.3. Symmetry

An important aim of this work is the correct inclusion of symmetry in Hamiltonian (3). For an AB_2 system, two types of symmetry need to be considered: the interchange symmetry of the two like atoms and the symmetry of the rotational portion of the wave function.

Provided that coordinates are used for which $g_1 = g_2$ and identical basis functions are used for the r_1 and r_2 coordinates (denoted $|m\rangle$ and $|n\rangle$, respectively), then symmetrized radial functions can be written

$$|m,n,q\rangle = 2^{-1/2}(1 + \delta_{mn})^{-1/2}(|m\rangle|n\rangle + (-1)^q|n\rangle|m\rangle) \qquad m \geq n + q, \qquad q = 0,1. \tag{21}$$

For terms in the Hamiltonian diagonal in k, collectively denoted $\hat{H}_k$, it can be shown that the matrix elements of these symmetrized functions are

$$\langle m',n',q'|\hat{H}_k|m,n,q\rangle = \delta_{q'q}(1+\delta_{mn})^{-1/2}(1+\delta_{m'n'})^{-1/2} \\ (\langle m',n'|\hat{H}_k|m,n\rangle + (-1)^{q'}\langle m',n'|\hat{H}_k|n,m\rangle)\,. \tag{22}$$

However, inspection of the terms off-diagonal in k shows that the term coupling $k, k \pm 1$ is antisymmetric with respect to interchanging r_1 and r_2. This means that the true symmetry of the functions with respect to interchanging the two identical atoms is given by not $(-1)^q$ but by $(-1)^{q+k}$. Because of this, symmetrized matrix elements of $\hat{K}^{(2)}_{VR}$ have the form

$$\langle m',n',q'|\hat{K}^{(2)}_{VR}|m,n,q\rangle = \delta_{q'1-q}(1+\delta_{mn})^{-1/2}(1+\delta_{m'n'})^{-1/2} \\ (\langle m',n'|\hat{K}^{(2)}_{VR}|m,n\rangle + (-1)^{q'}\langle m',n'|\hat{K}^{(2)}_{VR}|n,m\rangle)\,, \tag{23}$$

while symmetrized matrix elements of $\hat{K}^{(3)}_{VR}$ have the same form as those of $\hat{H}_k$ above.

The rotational wave function is symmetrized by considering the behavior of the projection of the total angular momentum on the body-fixed z-axis, k, for the combined rotational and bending functions. The resulting symmetrized angular functions take the form

$$|j,k,p\rangle = 2^{-1/2}(1+\delta_{k0})^{-1/2}(|j,k\rangle + (-1)^p|j,-k\rangle) \qquad k \geq p, \qquad p = 0,1\,. \tag{24}$$

For these functions, the total parity is given by $(-1)^{J+p}$. For linear molecules, states with $p = 0$ and 1 are conventionally labeled e and f states, respectively [21]. The form (24) is often called the Wang form, and its use in conventional calculations is discussed in Papoušek and Aliev [22] and in Zare [23].

For terms diagonal in k, the matrix elements of these symmetrized functions are

$$\langle j',k,p'|\hat{H}_k|j,k,p\rangle = \delta_{p'p}\langle j',k|\hat{H}_k|j,k\rangle\,. \tag{25}$$

For the terms coupling k, $k \pm 1$, the matrix elements are

$$\langle j',k',p'|\hat{K}^{(2)}_{VR}|j,k,p\rangle = \delta_{p'p}(1+\delta_{k0})^{1/2}(1+\delta_{k'0})^{1/2}\langle j',k'|\hat{K}^{(2)}_{VR}|j,k\rangle\,. \tag{26}$$

In most cases, the k, $k \pm 2$ terms, given by operator $\hat{K}^{(3)}_{VR}$, again behave as the $k, k \pm 1$ terms in (26). However, there is one important special case. This is for k equal to 1. In this case, symmetrization of the rotational functions introduces an additional term into the diagonal, $k = 1, k' = 1$, block. This gives a contribution from the $\hat{K}^{(3)}_{VR}$ operator to the *diagonal* block

$$\langle j',k,p'|\hat{K}^{(3)}_{VR}|j,k,p\rangle = \delta_{p'p}(-1)^{1-p}\langle j',-k|\hat{K}^{(3)}_{VR}|j,k\rangle, \qquad k = 1\,. \tag{27}$$

3. Solution Strategy

3.1. Discrete Variable Representation

Above we have presented a fully symmetrized Hamiltonian for AB_2 systems. However, this Hamiltonian is singular for certain geometries, and, in particular, the integral $I^{(1)}$ over θ cannot be evaluated for the important $k = 0$ case. In this section, we show how a discrete variable representation (DVR) in the θ coordinate can be used to avoid this problem. DVRs in the angular variable have been used in a number of previous studies [7, 10–12, 15], but the treatment of the singularity presented here is novel.

A full discussion of the DVR can be found in a review article by Bačić and Light [9]. The basic idea is that one constructs a Hamiltonian matrix, as above, in terms of a finite basis representation (FBR). The FBR must comprise orthogonal polynomials. The FBR Hamiltonian matrix is then transformed to a finite element representation

$$H^{\text{DVR}} = T^T H^{\text{FBR}} T. \tag{28}$$

The feature that distinguishes the DVR from other finite element procedures is that the transformation matrix is based on the N points and weights of the N-point Gaussian quadrature derived from the orthogonal polynomials for the FBR. Thus, the appropriate transformation of the θ coordinate of $\hat{H}_k$ is

$$T^k_{j\alpha} = \omega^{1/2}_{k\alpha} \Theta_{jk}(\theta_{k\alpha}), \tag{29}$$

where θ_k and ω_k are the points and weights of Gauss-associated Legendre quadrature points for associated Legendre polynomials of order k.

This transformation procedure leads to certain formal similarities between the FBR and DVR [24]. However, the DVR allows the computationally important feature that a hierarchy of intermediate diagonalizations and truncations can be constructed that yield relatively small final Hamiltonian matrices with high information content [15]. In the current procedure, for example, separate two-dimensional Hamiltonians can be constructed and diagonalized for each angle of interest. Only the lowest solutions of these diagonalizations need be retained in constructing the full three-dimensional problem. It is this feature that allows us to avoid the singularity at $\theta = 0$. Provided the wave function can be taken as vanishingly small in this region, or, equivalently, this geometry is at high energy, then no solutions of the 2D problem with small θ need be retained in the full 3D calculation.

An important feature of the DVR is the so-called quadrature approximation, which is used to evaluate the contribution due to the potential

$$\sum_{j,j'=k}^{N+k-1} T^k_{j'\alpha'} \langle j'k | V(r_1, r_2, \theta) | jk \rangle_\theta T^k_{j\alpha} \simeq \delta_{\alpha\alpha'} V(r_1, r_2, \theta_{k\alpha}). \tag{30}$$

This makes evaluation of the potential matrix elements straightforward and means that all angular off-diagonal contributions arise from the kinetic energy operator. It is for this reason, and because transformations involving complicated off-diagonal matrix elements are computationally expensive, that all work performed using a DVR has employed orthogonal coordinates such as the Radau coordinates utilized here.

The transformation of the angular matrix elements in the vibrational kinetic energy term $\hat{K}^{(1)}_V$ has been extensively discussed elsewhere [10, 25]; we will therefore consider the new matrix elements arising from the vibration–rotation terms $\hat{K}_{VR}^{(i)}$ $i = 1, 3$. These new matrix elements are labeled $I^{(i)}$ above, again with $i = 1, 3$.

The crucial matrix element is $I_{j',k',j,k}^{(1)}$ as this integral is singular for the $k = k' = 0$ diagonal block. However, when $k = k'$, this integral can be evaluated using the quadrature approximation

$$\sum_{j,j'=k}^{N+k-1} T_{j'\alpha'}^{k} \left\langle j'k \left| \frac{1}{(1 - \cos\theta)} \right| jk \right\rangle_{\theta} T_{j\alpha}^{k} \simeq \delta_{\alpha\alpha'} \frac{1}{(1 - \cos\theta_{k\alpha})}. \tag{31}$$

Of course, the result is still singular at $\theta = 0$. However, if the wave function can be taken as vanishingly small in this region, a good approximation for many AB_2 triatomics for which the ABB linear geometry lies above the dissociation limit, then DVR points with small values of θ can simply be dropped from the calculation.

For the matrix elements of $I^{(1)}$ with $k \neq k'$, as well as $I^{(2)}$ and $I^{(3)}$, which only occur for $k \neq k'$, a different strategy is necessary. In this case, the integrals are first evaluated using an appropriate quadrature scheme and are then explicitly transformed to the DVR. In fact, by judicious use of Gauss–Jacobi quadrature [26], it is possible to design quadrature schemes that are effectively exact for all the off-diagonal matrix elements.

For example, consider the $2I^{(1)} - I^{(3)}$ term in $\hat{K}_{VR}^{(3)}$. First, we note that operators in the matrix elements can be summed to give

$$\frac{1 + x}{1 - x}, \qquad \text{where } x = \cos\theta.$$

Second, we note that this integral is only required for $k' = k + 2$ (because the secular matrix is symmetric, it is only necessary to consider $k' \geq k$). The nonpolynomial (i.e., $\sin\theta$) portion of $\langle j'k + 2|$ and $|jk\rangle$ differs only by a factor of $\sin^2\theta$, which can be incorporated in the operator to give $(1 + x)^2$. Evaluating this matrix element with Gaussian quadrature based on the zeros of associated Legendre polynomial Θ_{Nk} yields a purely polynomial expression to be treated numerically. In fact, all these integrals can be evaluated analytically; however, there appears to be no general expression for the integrals and it is therefore computationally simpler to evaluate them numerically.

3.2. *Rotational Excitation*

It is now widely recognized that the most efficient method of treating rotationally excited states is to perform the calculation in two steps [10–12, 25, 27, 28]. The first step of our procedure involves assuming that k is a good quantum number. This is equivalent to neglecting the off-diagonal Coriolis coupling for the embedding in question. This step thus involves solving $\hat{H}_k$ for each unique k. Usually [29], it is sufficient to solve for $k = 0, J$, but in the bisector embedding, the $k = 1$ case has to be treated separately for $p = 0$ and $p = 1$ because of the extra diagonal elements discussed above. The final step of the two-step procedure selects the lowest L solutions of the first step as a basis for solving the fully Coriolis coupled problem [30]. It is thus for this step that the integrals off-diagonal in k discussed above are needed.

This procedure has been found to be very efficient for two reasons: because only a small fraction of the first step solutions are usually required to converge the states of interest and because the resulting secular matrix has a sparse, blocked structure that can be diagonalized very efficiently [29].

In the bisector embedding, the presence of operators coupling both $k, k \pm 1$ and $k, k \pm 2$ means that approximately twice as many off-diagonal blocks need to be considered compared to the embedding used by us previously. However, this sparseness still leads to a saving of computer storage of a factor of about $J/2$ for large J calculations. Furthermore, the use of full symmetry and an embedding that reduces the Coriolis interactions leads to smaller secular matrices.

In previous work combining the two-step procedure and the DVR [10], it was found to be convenient to transform the solutions $\hat{H}_k^{\mathrm{DVR}}$ back to an FBR before solving the fully coupled problem. In the bisector embedding, this approach is no longer useful as it is only in the DVR that the region of the singularity can be rigorously avoided. Therefore, for the bisector embedding, it is necessary to treat the angular coordinate in the DVR. This, and the $I^{(i)}$ matrix elements, means that none of the off-diagonal Coriolis coupling terms are diagonal in any of the coordinates. This makes the resulting transformation of the matrix elements evaluated in terms of the first step basis functions, $|m, n, q\rangle$, and the DVR in θ into matrix elements of the second-step functions the slowest part of the calculation.

Some savings can be made by noting that the Hamiltonian matrices for a particular J, q but differing in p are the same, except (a) for $p = 1$, there are no blocks involving $k = 0$ and (b) blocks involving $k = 1$ differ because for this case the first-step solutions are not the same. Thus, the blocks involving higher k values can be saved from the $p = 0$ calculation and only the one or two blocks involving $k = 1$ need to be computed when performing a $p = 1$ calculation.

4. Sample Calculations

In recent benchmark calculations, Carter et al. [5] presented results for the $J = 0$ and 1 states for the four lowest vibrational states of H_2S using an ab initio potential energy surface due to Senekowitsch et al. [6]. We therefore chose this H_2S potential to provide an initial test of the work presented here. Calculations were performed in the bisector embedding and Radau coordinates with up to eight previously optimized [2] Morse oscillatorlike functions in each radial coordinate. The angular coordinate was discretized at 32 angles. For each k block, the 600 solutions lowest in energy were used to construct the Hamiltonian matrix. For calculations with $J > 0$, the molecule was prevented from sampling the HHS linear geometry. In practice, this meant that any solutions selected from the DVR point nearest $\theta = 0$ were removed from the basis. For the $J = 1$ calculations, the 350 lowest solutions from the first-step calculations were used in the second step.

These calculations were in excellent agreement with the results of Carter et al. [5]. With the exception of the $J = 1$ block with $p = 0$ and $q = 0$, we reproduced their results to all figures (i.e., to within 0.1 cm^{-1}). For the $J = 1, p = 0, q = 0$ case, we found three levels that were 0.1 cm^{-1} *lower* than quoted by Carter et al. This difference was due to the present calculations being better converged (to within 0.01 cm^{-1} compared to a claimed convergence of 0.1 cm^{-1} [5]), which led to changes in whether the last figure was rounded up or down.

More extensive comparisons were made with the finite basis representation (FBR) calculations of Miller et al. [2] on D_2S. The DVR calculations used similar basis sets to the H_2S calculations discussed above and the Morse parameters optimized by Miller et al. The FBR calculations of Miller et al. were actually performed with larger radial and angular basis sets and a final Hamiltonian of dimension 1600. Comparisons for $J = 0$ showed that the zero-point energy and 30 lowest band origins agreed to better than 0.1 cm^{-1} in all cases and to within 0.01 cm^{-1} for all but three levels. The DVR calculation was very much quicker than the FBR calculation, taking 32.5 s against 1776.2 s on a single processor of a Cray-XMP. This was due mainly to the smaller basis used in the DVR calculation, but must, in part, be a reflection of the greater efficiency of the DVR method for such calculations.

Further comparisons for D_2S were made for calculations with $J = 1, 5$, and 10. The $J = 10$ calculations are of particular interest because of the near degeneracies, in some cases to within 5×10^{-6} cm^{-1}, that occur between some levels differing only in q. The FBR calculations, which did not include symmetry with respect to interchange of the D atoms, represented by q, was found to blend these states causing strongly forbidden transitions apparently to become allowed. Comparison of the lowest 200 levels with $J = 10$ showed that the DVR and FBR results agreed to within 0.01 cm^{-1} in all cases, but that the very small splittings were not constant between the calculations. As the FBR basis for $J = 10$ by Miller et al. [2] was only half that used for the $J = 0$ calculations quoted above, the DVR eigenenergies were generally, but not always, lower than the FBR ones. Analysis of the $J = 1$ and five calculations showed a similar level of agreement.

As the $J > 0$ DVR calculations were performed using the full symmetry of the system, one might expect them to be computationally quicker—they certainly require considerably less computer memory. However, this is not the case. As was already observed for rotationally excited DVR calculations in scattering coordinates [10], the transformation step required by the rotational step of the calculation (see [31] for a discussion of computational aspects of the transformation step) is considerably slower in the DVR than in the FBR. This is because, first, the effective FBR basis is much bigger in the DVR than are basis sets actually used in FBR calculations and, second, because the transformation in the DVR is no longer diagonal in the angular coordinate [10]. This means that the DVR calculations took 6629 Cray-XMP seconds for $J = 10$ compared to 430 s for the FBR with a smaller vibrational basis set. However, it should be noted that although the time taken to perform the transformations is strongly dependent on the size of the effective vibrational basis it depends only linearly on J, which means that this problem is not a barrier to performing high J calculations.

5. Conclusions

We have shown how our recently formulated general triatomic Hamiltonian [1] can be used to perform calculations on AB_2 triatomics such H_2S with axes embedded along the symmetry axes. Although the resulting Hamiltonian is actually singular for the ABB linear geometry, use of a finite element procedure, the discrete variable representation (DVR), allows one to avoid the singularity that occurs in an energetically inaccessible region for many systems. Test calculations on H_2S and D_2S show that the method works well. It has also been successfully applied to the quasi-linear system H_2Si^+. Calculations using this procedure on H_2Si^+ [32] and H_2O [33] will be presented elsewhere.

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