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A General Treatment of Vibration-Rotation Coordinates for Triatomic Molecules

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Abstract

An exact, within the Born–Oppenheimer approximation, body-fixed Hamiltonian for the nuclear motions of a triatomic system is presented. This Hamiltonian is expressed in terms of two arbitrarily defined internal distances and the angle between them. The body-fixed axis system is related to these coordinates in a general fashion. Problems with singularities and the domain of the Hamiltonian are discussed using specific examples of axis embedding. A number of commonly used coordinate systems including Jacobi, bond-length-bond-angle, and Radau coordinates are special cases of this Hamiltonian. Sample calculations on the H_2S molecule are presented using all these and other coordinate systems. The possibility of using this Hamiltonian for reactive scattering calculations is also discussed.

1. Introduction

In a recent paper [1], a rather general body-fixed Hamiltonian for the nuclear motion of triatomic species was derived. The internal motion part of the Hamiltonian is given in terms of two lengths, r_1 and r_2, and an included angle θ. The coordinate r_1 is always the distance between particles 2 and 3, but r_2 is expressed in terms of a parameter g in the range $(0, 1)$ so that it can be chosen according to the physics of the problem. The value chosen for g essentially determines where the origin of the vector along r_2 lies on r_1. One particular choice gives r_2 as the distance between particles 2 and 1, whereas another makes r_2 the distance from the center-of-mass of particles 2 and 3 to particle 1 and so on. The first choice might be thought good for the description of normal triatomic molecules such as water, whereas the second choice might be thought good for collision complexes such as ArH_2 and other choices might fit other systems.

The advantage of this approach is that a number of physical situations can be encompassed in terms of a single piece of computer code [2] that uses g as an input. Its utility and efficiency in practice when dealing with a wide variety of triatomic systems has been shown in Ref. 3.

Since the appearance of Ref. 1, other papers have appeared (see e.g., [4, 5]) that also address themselves to the triatomic problem in general terms. It is the

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object of the present paper to present what is believed to be the most general Hamiltonian possible for a triatomic whose internal motion is expressed in terms of two lengths and an included angle and also to investigate its applicability.

2. The Construction of the Hamiltonian

As in Ref. 1, the general approach given in Ref. 7 will be used to derive the Hamiltonian. In this approach, a set of translation-free internal coordinates $\mathbf{t}_i$ are first constructed in terms of the laboratory-fixed coordinates $\mathbf{x}_i$ such that

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

or

$$\mathbf{t} = \mathbf{x}\mathbf{V}, \tag{1}$$

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

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

to ensure the invariance of the $\mathbf{t}_i$ under uniform translation. The $\mathbf{t}_i$ are often said to be a set of space-fixed coordinates. In terms of these coordinates, the translation-free part of the kinetic energy operator can be written as

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

where $\vec{\nabla}(\mathbf{t}_i)$ is the usual grad operator expressed in the variable $\mathbf{t}_i$ and where μ_{ij}^{-1} is

$$\mu_{ij}^{-1} = \sum_{k=1}^{N} m_k^{-1} V_{ki} V_{kj}, \tag{4}$$

in which the m_k are the particle masses. For ease of writing, the diagonal reduced masses, μ_{ii}, will be written simply as μ_i.

In the triatomic case, the most general $\mathbf{V}$ may be written as

$$\underline{V} = \begin{pmatrix} a_1 - b_1 & a_2 - b_2 \\ b_1 - c_1 & b_2 - c_2 \\ c_1 - a_1 & c_2 - a_2 \end{pmatrix}, \tag{5}$$

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

$$\mathbf{t}_i = a_i(\mathbf{x}_1 - \mathbf{x}_3) + b_i(\mathbf{x}_2 - \mathbf{x}_1) + c_i(\mathbf{x}_3 - \mathbf{x}_2). \tag{6}$$

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 two-by-two unit matrix. The matrix $\tilde{\mathbf{V}}$ is given formally by

$$\tilde{\mathbf{V}} =$$

$$D^{-1}\begin{bmatrix} m_3(b_2 - c_2) - m_2(c_2 - a_2) & m_1(c_2 - a_2) - m_3(a_2 - b_2) & m_2(a_2 - b_2) - m_1(b_2 - c_2) \\ m_2(c_1 - a_1) - m_3(b_1 - c_1) & m_3(a_1 - b_1) - m_1(c_1 - a_1) & m_1(b_1 - c_1) - m_2(a_1 - b_1) \end{bmatrix}, \tag{7}$$

with

$$D = \begin{vmatrix} m_1 & m_2 & m_3 \\ a_1 - b_1 & b_1 - c_1 & c_1 - a_1 \\ a_2 - b_2 & b_2 - c_2 & c_2 - a_2 \end{vmatrix}, \tag{8}$$

and so the inverse transformation exists as long as D is not zero.

The general form of the reciprocal reduced masses is, from Eqs. (5) and (4),

$$\begin{aligned} \mu_i^{-1} &= (a_i - b_i)^2 m_1^{-1} + (b_i - c_i)^2 m_2^{-1} + (c_i - a_i)^2 m_3^{-1} \qquad i = 1,2 \\ \mu_{12}^{-1} &= (a_1 - b_1)(a_2 - b_2)m_1^{-1} + (b_1 - c_1)(b_2 - c_2)m_2^{-1} \\ &\quad + (c_1 - a_1)(c_2 - a_2)m_3^{-1}. \end{aligned} \tag{9}$$

The $\mathbf{V}$ matrix used in [1] was a special case of (5) with the choices $a_1 = b_1 = 0$, $c_1 = 1$ and $a_2 = 1$, $b_2 = 0$, $c_2 = g$.

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

$$\mathbf{t} = \mathbf{C}\mathbf{z}. \tag{10}$$

To define fully the three Euler angles that specify $\mathbf{C}$, there must be three relations among the components of the $\mathbf{z}_i$ and, in consequence, the components of $\mathbf{z}$ must be specifiable in terms $3N$-6 rotationally invariant internal coordinates. In the present case, the three internal variables 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 $\mathbf{z}_2$). The matrix $\mathbf{C}$ is chosen to put the two $\mathbf{z}_i$ in the x–z plane, and the third relation is specified by requiring that the x- or the z-body fixed axis is 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,

$$\mathbf{z} = \mathbf{C}^T\mathbf{t} = \begin{pmatrix} z_{x1} & z_{x2} \\ 0 & 0 \\ z_{z1} & z_{z2} \end{pmatrix}, \tag{11}$$

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

$$\mathbf{z} = \begin{pmatrix} -r_1 \sin a\theta & r_2 \sin(1 - a)\theta \\ 0 & 0 \\ r_1 \cos a\theta & r_2 \cos(1 - a)\theta \end{pmatrix}, \tag{12}$$

whereas if the x-axis is chosen,

$$\mathbf{z} = \begin{pmatrix} r_1 \cos a\theta & r_2 \cos(1-a)\theta \\ 0 & 0 \\ r_1 \sin a\theta & -r_2 \sin(1-a)\theta \end{pmatrix}. \tag{13}$$

It is, of course, of no physical significance that the x–z plane has been chosen as the embedding plane; neither is Eq. (12) in any fundamental sense different from Eq. (13). Simple cyclic interchange of (xyz) will enable all other right-handed embeddings to be generated, but the chosen forms are convenient for relating the present to previous work. They also yield real matrix elements.

Using the techniques described in [7] and exemplified in [8], it may now be shown that the body-fixed kinetic energy operator may be written as

$$\hat{K} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}, \tag{14}$$

where

$$\begin{aligned} \hat{K}_V^{(1)} = -\frac{\hbar^2}{2}\biggl[&\frac{1}{\mu_1 r_1^2}\left(\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) \\ &+ \frac{1}{\mu_2 r_2^2}\left(\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\biggr] \end{aligned} \tag{15}$$

$$\begin{aligned} \hat{K}_V^{(2)} = +\frac{\hbar^2}{\mu_{12}}\biggl[&-\cos\theta\frac{\partial^2}{\partial r_1 \partial r_2} + \frac{\cos\theta}{r_1 r_2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) \\ &+ \sin\theta\left(\frac{1}{r_1}\frac{\partial}{\partial r_2} + \frac{1}{r_2}\frac{\partial}{\partial r_1} + \frac{1}{r_1 r_2}\right)\frac{\partial}{\partial\theta}\biggr] \end{aligned} \tag{16}$$

and

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

The internal coordinate part of the Jacobian for the transformation is $r_1^2 r_2^2 \sin\theta$ and that for the Euler angle part is $\sin\beta$, where β is the second Euler angle. The range of r_1 and r_2 is $(0, \infty)$ and of θ and β is $(0, \pi)$.

The $\hat{K}_V$ operators are the familiar ones for this choice of internal coordinates and have exactly the same form as that obtained in previous work [1]. In the operator $\hat{K}_{VR}$, the body-fixed angular momentum operators, $\hat{L}_\alpha$, obey the standard commutation relations and the elements $M_{\alpha\beta}$ of the inverse generalized inertiatensor are given by

$$
\begin{aligned}
M_{xx} &= \frac{1}{(r_1 r_2 \sin\theta)^2}\left(\frac{z_{x1}^2}{\mu_2} + \frac{z_{x2}^2}{\mu_1} - 2\frac{z_{x1}z_{x2}}{\mu_{12}}\right)\\
M_{yy} &= \frac{(1-a)^2}{\mu_1 r_1^2} + \frac{a^2}{\mu_2 r_2^2} + \frac{2a(1-a)\cos\theta}{\mu_{12} r_1 r_2}\\
M_{zz} &= \frac{1}{(r_1 r_2 \sin\theta)^2}\left(\frac{z_{z1}^2}{\mu_2} + \frac{z_{z2}^2}{\mu_1} - 2\frac{z_{z1}z_{z2}}{\mu_{12}}\right)\\
M_{xz} &= \frac{1}{(r_1 r_2 \sin\theta)^2}\left(\frac{z_{x1}z_{z1}}{\mu_2} + \frac{z_{x2}z_{z2}}{\mu_1} - \frac{z_{x1}z_{z2} + z_{x2}z_{z1}}{\mu_{12}}\right),
\end{aligned}
\tag{18}
$$

where the $z_{\alpha i}$ are to be realized according to Eq. (12) or (13) as appropriate.

If the body-fixed Hamiltonian is considered as operating on a manifold of functions that are products of internal coordinate functions and angular momentum eigenfunctions, then it may be replaced by an effective Hamiltonian that, within a particular rotational state manifold, operates only on the internal coordinate functions. This is possible because the angular momentum eigenfunctions depend on the Euler angles alone and the $\hat{L}_\alpha$ are also expressible entirely in terms of these angles. Thus, the effect of the $\hat{L}_\alpha$ on the angular eigenfunctions may be determined explicitly and the angular parts removed by integration. The resulting effective Hamiltonian is diagonal in J, the angular momentum quantum number, and is independent of M, the component of angular momentum along the space-fixed z-axis, but is generally non-diagonal in k, the component of angular momentum along the body-fixed z-axis.

In deriving this effective Hamiltonian, 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 Hermitian form. The process is equivalent to choosing an internal coordinate wave function $r_1^{-1} r_2^{-1}\,{}^J\Phi_{k,n}$ and obtaining an operator for ${}^J\Phi_{k,n}$ alone. The operators replacing $\hat{K}_V^{(1)}$ and $\hat{K}_V^{(2)}$ are thus

$$
\hat{K}_V^{(1)} = -\delta_{k'k}\frac{\hbar^2}{2}\left[\frac{1}{\mu_1 r_1^2}\frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2 r_2^2}\frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right] \tag{19}
$$

$$
\begin{aligned}
\hat{K}_V^{(2)} = +\delta_{k'k}\frac{\hbar^2}{\mu_{12}}\Bigg[&-\cos\theta\frac{\partial^2}{\partial r_1\,\partial r_2} + \left(\frac{1}{r_1}\frac{\partial}{\partial r_2} + \frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1 r_2}\right)\left(\sin\theta\frac{\partial}{\partial\theta} + \cos\theta\right)\\
&+ \frac{\cos\theta}{r_1 r_2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\Bigg],
\end{aligned}
\tag{20}
$$

while the operator replacing $\hat{K}_{VR}$ is

$$
\begin{aligned}
\hat{K}_{VR} = {}&\delta_{k'k\pm2}\frac{\hbar^2}{4}C_{Jk\pm1}^{\pm}C_{Jk}^{\pm}b_- + \delta_{k'k\pm1}\frac{\hbar^2}{2}C_{Jk}^{\pm}\lambda^{\pm}\\
&+ \delta_{k'k}\frac{\hbar^2}{2}(b_+(J(J+1) - k^2) + b_0 k^2).
\end{aligned}
\tag{21}
$$

Eqs. (19)–(21) are diagonal in J and this has not been explicitly noted. Because the potential energy is a function of the internal coordinates only, that too is diagonal in J and is also diagonal in k as in Eqs. (19) and (20). In Eq. (21),

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

and

$$b_{\pm} = (M_{xx} \pm M_{yy})/2, \qquad b_0 = M_{zz} \tag{23}$$

while

$$\begin{aligned} \lambda^{\pm} = {} & \frac{1}{\mu_1 r_1^2}\left[\mp(1 - a)\left(\frac{\partial}{\partial\theta} + \frac{\cot\theta}{2}\right) + \left(k \pm \frac{1}{2}\right)\frac{z_{x2}z_{z2}}{r_2^2\sin^2\theta}\right] \\ & + \frac{1}{\mu_2 r_2^2}\left[\pm a\left(\frac{\partial}{\partial\theta} + \frac{\cot\theta}{2}\right) + \left(k \pm \frac{1}{2}\right)\frac{z_{x1}z_{z1}}{r_1^2\sin^2\theta}\right] \\ & + \frac{1}{\mu_{12} r_1 r_2}\left[\mp(2a - 1)\left(\cos\theta\frac{\partial}{\partial\theta} + \frac{\csc\theta}{2}\right) - \left(k \pm \frac{1}{2}\right)\frac{(z_{x1}z_{z2} + z_{x2}z_{z1})}{r_1^2\sin^2\theta}\right] \\ & \mp \frac{\sin\theta}{\mu_{12}}\left[\frac{a}{r_2}\frac{\partial}{\partial r_1} - \frac{(1 - a)}{r_1}\frac{\partial}{\partial r_2} + \frac{(1 - 2a)}{r_1 r_2}\right], \end{aligned} \tag{24}$$

where again the terms in $z_{\alpha i}$ are to be supplied from Eq. (12) or (13) as required.

3. The Domain of the Hamiltonian

Because the construction of a body-fixed coordinate system is, in general, a mapping from R^{3N-3} to $R^{3N-6} \times S^3$, where R^M is the M-dimensional Euclidean manifold and S^3 is the spherical manifold, it must have singular regions identified by the vanishing of the Jacobian. In these regions, the transformation fails and the body-fixed Hamiltonian cannot properly be constructed. In a quantum mechanical context, this means that the domain of the body-fixed Hamiltonian can consist only of those functions that vanish very strongly in the singular regions. For any other kind of functions, the expectation values will diverge.

In the present case, the singular region of the transformation is defined by $r_1 = 0$, or $r_2 = 0$ or $\sin\theta = 0$, this last implying $\theta = 0$ or $= \pi$. The kind of difficulties that can arise in the singular region can be illustrated by considering the angular divergence.

In the embedding (13) (in which the x-axis divides the angle), explicit substitution in Eq. (23) gives

$$\begin{aligned} b_{\pm} = {} & \frac{1}{2\mu_1 r_1^2}\left(\frac{\cos^2(1 - a)\theta}{\sin^2\theta} \pm (1 - a)^2\right) + \frac{1}{2\mu_2 r_2^2}\left(\frac{\cos^2 a\theta}{\sin^2\theta} \pm a^2\right) \\ & - \frac{1}{\mu_{12} r_1 r_2}\left(\pm a(1 - a)\cos\theta - \frac{\cos a\theta\cos(1 - a)\theta}{\sin^2\theta}\right) \end{aligned} \tag{25}$$

$$b_0 = \csc^2\theta\left(\frac{\sin^2(1 - a)\theta}{\mu_1 r_1^2} + \frac{\sin^2 a\theta}{\mu_2 r_2^2} + \frac{2\sin a\theta\sin(1 - a)\theta}{\mu_{12} r_1 r_2}\right). \tag{26}$$

There will, in this embedding, be diagonal matrix elements involving products of operators of the form (a) cos $q\theta$/sin θ (from b_+) and (b) sin $q\theta$/sin θ (from b_0) where q can be a or $(1 - a)$, but, in general, lies between $(0,1)$. For operator (a) it is easy to see that the operator diverges at $\theta = 0$ whatever the value of q and that the operator also diverges at $\theta = \pi$ except when q is $\frac{1}{2}$. For operator (b), $q = 0$ and $q = 1$ are special cases; in the former the term vanishes, and in the latter, it is a constant. Otherwise, the term diverges at both $\theta = 0$ and $\theta = \pi$.

In the embedding (12), precisely the same integrals arise except in that case the cosine ones come from b_0 and the sine ones from b_+.

From the above discussion, it is clear that if, for example, $\mathbf{t}_1$ and $\mathbf{t}_2$ are chosen to lie along the bonds in a triatomic molecule so that θ is the bond angle, then care will have to be taken in using this Hamiltonian to describe states corresponding to large amplitude bending motion. However, whatever the precise physical significance of the chosen $\mathbf{t}_1$ and $\mathbf{t}_2$, and, hence, whatever meaning should be ascribed to the θ, trial functions that give rise to very large or small values of θ will need to be dealt with cautiously.

4. Effective Radial Hamiltonians

4.1 Vibrational Operators

It is convenient, as it was in earlier work, to construct an effective radial Hamiltonian. This can be obtained by allowing the internal coordinate Hamiltonian to act on the normalized associated Legendre functions (in the Condon and Shortley phase convention [6]) $\Theta_{jk}(\theta)$, multiplying from the left by $\Theta_{j'k'}(\theta)$ and integrating over θ yields

$$\hat{H}(r_1,r_2) = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_V^{(3)} + \hat{K}_{VR} + \delta_{k'k} V_{j'jk}(r_1,r_2), \tag{27}$$

where

$$\hat{K}_V^{(1)} = \delta_{j'j}\,\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right] \tag{28}$$

$$\begin{aligned}\hat{K}_V^{(2)} = &-\delta_{j'\,j+1}\,\delta_{k'k}\,d_{jk}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} - \frac{j+1}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{j+1}{r_2}\right)\\ &- \delta_{j'\,j-1}\,\delta_{k'k}\,d_{j-1,k}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right),\end{aligned} \tag{29}$$

with

$$d_{jk} = \left[\frac{(j-k+1)(j+k+1)}{(2j+1)(2j+3)}\right]^{1/2} \tag{30}$$

and

$$\hat{K}_V^{(3)} = -\delta_{k'k}\frac{\hbar^2 k^2}{2}\left(\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\langle j'k'|\frac{1}{\sin^2\theta}|jk\rangle - \frac{2}{\mu_{12} r_1 r_2}\langle j'k'|\frac{\cos\theta}{\sin^2\theta}|jk\rangle\right), \tag{31}$$

where the integration runs only over θ.

If the potential is expressed in a Legendre expansion

$$V(r_1,r_2,\theta) = \sum_\lambda V_\lambda(r_1,r_2)\Theta_{\lambda,0}(\theta), \tag{32}$$

then the angular integration described above can be performed analytically giving

$$V_{j'jk}(r_1,r_2) = \sum_\lambda \langle j'k'|\Theta_{\lambda,0}(\theta)|jk\rangle\, V_\lambda(r_1,r_2), \tag{33}$$

where the integral over θ gives the usual Gaunt coefficient [8]:

$$\langle j'k'|\Theta_{\lambda,0}(\theta)|jk\rangle = \delta_{k'k}(-1)^k[(2j'+1)(2j+1)]^{1/2}\begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j' & \lambda & j \\ -k & 0 & k \end{pmatrix}. \tag{34}$$

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 [9].

The "vibrational" terms in $\hat{H}(r_1,r_2)$ given above are valid for all choices of coordinates and embeddings discussed here. However, $\hat{K}_{VR}(r_1,r_2)$ depends on the embedding, chosen examples of which are given in the following subsections. The term $\hat{K}_V^{(3)}$ is included in the effective vibrational Hamiltonian despite the fact that it is null for $J = 0$ (as $|k| \leq J$) because it too is independent of the embedding. In practice, as will be seen below, this term is usually absorbed into the terms arising from $\hat{K}_{VR}$.

4.2. *Embeddings* a = *0 and* a = *1*

In earlier work [8], it was shown by choosing $\mathbf{t}_1$ and $\mathbf{t}_2$ to be scattering (or Jacobi) coordinates and by embedding the z-axis along either $\mathbf{t}_1$ or $\mathbf{t}_2$ ($a = 0$ or $a = 1$) that the divergence discussed in Section 3 could be explicitly avoided by choosing the angular part of the trial functions to be $\Theta_{jk}(\theta)$. In later work [1], it was shown how this approach could be extended somewhat by a more general choice of $\mathbf{t}_2$ but with the same embedding. From the present discussion, it should be clear that still further generalization is possible in terms of the same embedding but with the dependence of $\mathbf{t}_1$ and $\mathbf{t}_2$ given generally by Eqs. (1) and (5).

In this case, the operator $\hat{K}_V^{(3)}$ given above is cancelled exactly and the remaining vibration-rotation kinetic energy operators are

$$\hat{K}_{VR}^{(1)} = -\delta_{j'j}\,\delta_{k'k}\frac{\hbar^2}{2\mu_1 r_1^2}(J(J+1) - 2k^2) - \delta_{j'j}\,\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_1 r_1^2}C_{Jk}^{\pm}C_{jk}^{\pm} \tag{35}$$

$$\begin{aligned}\hat{K}_{VR}^{(2)} &= \delta_{j'j+1}\,\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{\pm}\frac{a_{j\pm k}}{r_1}\left(\frac{j+1}{r_2} - \frac{\partial}{\partial r_2}\right) \\ &+ \delta_{j'j-1}\,\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{\pm}\frac{b_{j\pm k}}{r_1}\left(\frac{j}{r_2} + \frac{\partial}{\partial r_2}\right),\end{aligned} \tag{36}$$

with the extra angular factors

$$a_{jk} = \left[\frac{(j + k + 1)(j + k + 2)}{(2j + 1)(2j + 3)}\right]^{1/2} \tag{37}$$

$$b_{jk} = \left[\frac{(j - k)(j - k - 1)}{(4j^2 - 1)}\right]^{1/2}. \tag{38}$$

These equations have the same form as eqs. (22)–(23) of Ref. 1, but here have been shown to apply to a very much more general coordinate set.

4.3. *Embedding $a = \frac{1}{2}$*

The present formalism also allows the generalization of some earlier work [10] in which $\mathbf{t}_2$ and $\mathbf{t}_2$ were chosen as bond lengths and in which a was chosen so that the z-axis bisects the angle between them. Here, embedding (13) is chosen with $a = \frac{1}{2}$ so that when bond-angle, bond-length coordinates are chosen the correspondence with Ref. 10 is exact. With these, choices Eqs. (25) and (26) specialize to

$$b_\pm = \frac{1}{4(1 - \cos\theta)}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2}{\mu_{12} r_1 r_2}\right) \pm \frac{1}{8}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} + \frac{2\cos\theta}{\mu_{12} r_1 r_2}\right) \tag{39}$$

$$b_0 = \frac{(1 - \cos\theta)}{2\sin^2\theta}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} + \frac{2}{\mu_{12} r_1 r_2}\right). \tag{40}$$

Similarly, Eq. (24) specializes to

$$\lambda^\pm = \left(\frac{1}{2\mu_2 r_2^2} - \frac{1}{2\mu_1 r_1^2}\right)\left(\hat{j}^\pm + \left(k \pm \frac{1}{2}\right)\frac{(1 + \cos\theta)}{\sin\theta}\right) \mp \frac{\sin\theta}{2\mu_{12}}\left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2}\right), \tag{41}$$

where

$$\hat{j}^\pm\Theta_{jk} = C_{jk}^\pm\Theta_{jk\pm1}, \tag{42}$$

with $C_{jk}^\pm$ given by Eq. (22).

If the result of the term in b_0 operating on the angular functions is combined with $\hat{K}_V^{(3)}$ from Eq. (31), the resulting term is then

$$-\delta_{k'k}\frac{\hbar^2}{4}k^2\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2}{\mu_{12} r_1 r_2}\right) I^{(1)}_{j',k,j,k}, \tag{43}$$

where

$$I^{(1)}_{j',k',j,k} = \langle j'k'|\frac{1}{(1 - \cos\theta)}|jk\rangle. \tag{44}$$

Adding this result to the remainder of the term in Eq. (21) that is diagonal in k leads to a contribution to the effective Hamiltonian

$$\hat{K}^{(1)}_{VR} = \delta_{k'k}\frac{\hbar^2}{8}(J(J+1) - 3k^2)\left(\frac{1}{\mu_1 r_2^2} + \frac{1}{\mu_2 r_2^2} - \frac{2}{\mu_{12} r_1 r_2}\right) I^{(1)}_{j',k,j,k}$$
$$+ \delta_{k'k}\frac{\hbar^2}{16}(J(J+1) - k^2)\left(\delta_{j'j}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) + \frac{2}{\mu_{12} r_1 r_2}(\delta_{j'j+1} d_{jk} + \delta_{j'j-1} d_{j-1k})\right). \tag{45}$$

The term depending on $\lambda^{\pm}$ in Eq. (21) leads to the contribution

$$\hat{K}^{(2)}_{VR} = \delta_{k'k\pm1}\frac{\hbar^2}{4}C^{\pm}_{jk}\left[\left(\frac{1}{\mu_2 r_2^2} - \frac{1}{\mu_1 r_1^2}\right)\left(\delta_{j'j}C^{\pm}_{jk} + \left(k \pm \frac{1}{2}\right)I^{(2)}_{j',k',j,k}\right)\right.$$
$$\left. \pm \frac{1}{\mu_{12}}\left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2}\right)(\delta_{j'j+1} a_{j\pm k} - \delta_{j'j-1} b_{j\pm k})\right], \tag{46}$$

where

$$I^{(2)}_{j',k',j,k} = \langle j'k' | \frac{1 + \cos\theta}{\sin\theta} | jk \rangle. \tag{47}$$

Finally, the remaining term in Eq. (21) gives rise to the effective operator

$$\hat{K}^{(3)}_{VR} = \delta_{k'k\pm2}\frac{\hbar^2}{32}C^{\pm}_{jk\pm1}C^{\pm}_{jk}\left[\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)(2I^{(1)}_{j',k',j,k} - I^{(3)}_{j',k',j,k})\right.$$
$$\left. - \frac{2}{\mu_{12} r_1 r_2} \times (I^{(3)}_{j',k',j+1,k} d_{jk} + I^{(3)}_{j',k',j-1,k} d_{j-1k} + 2I^{(1)}_{j',k',j,k})\right], \tag{48}$$

where

$$I^{(3)}_{j',k',j,k} = \langle j'k' | jk \rangle. \tag{49}$$

Examination of the angular integrals in the above formulae for $\hat{K}^{(i)}_{VR}$ shows that angular divergences are encountered only for terms arising from $\hat{K}^{(1)}_{VR}$ and then only when $k = 0$. In this case, $I^{(1)}_{j',0,j,0}$ is logarithmically divergent at the limit $\theta = 0$. This divergence is only effective when $J(J + 1)$ is non zero, for otherwise it is multiplied by k^2, which vanishes when $k = 0$. If r_1 and r_2 are chosen as bond lengths and θ as the bond angle, then *prima facie* it would seem that contributions with $\theta = 0$ may be unimportant because they have a very high energy. Thus, it might be expected that the divergence is of little physical consequence and should cause no trouble in calculation. Numerical experiments in Ref. 10 would seem to confirm that this is indeed the case.

It is perhaps appropriate to note here that if embedding (12) is chosen with $a = \frac{1}{2}$, the integral equivalent to $I^{(1)}_{j',0,j,0}$ has a logarithmic divergence at $\theta = \pi$. This choice of embedding with the specified angular functions would be inadequate to describe the more common case where large values of θ are important.

5. Application to H$_2$S

The coordinate system detailed in Section 2 is very general. We have programmed [11] a subset of the coordinates, given in Figure 1. These coordinates are obtained by setting

$$\begin{aligned} &a_1 = -g_2, b_1 = 0, c_1 = -1 && 0 \le g_2 \le 1 \\ &a_2 = 1, b_2 = 0, c_2 = g_1 && 0 \le g_1 \le 1. \end{aligned}$$

This is thus a generalization of the coordinates of [1] that can be obtained by setting $g_1 = g$ and $g_2 = 0$.

Orthogonal coordinates form a special class of coordinates systems. These coordinates have simpler, diagonal kinetic energy operators. They are thus particularly advantageous, if not essential, for finite element methods where the off-diagonal coupling is given by the kinetic energy rather than by the potential term. In our formalism, orthogonal coordinates are given by any combination satisfying the condition

$$\begin{aligned} \mu_{12}^{-1} = {} & (a_1 - b_1)(a_2 - b_2)m_1^{-1} + (b_1 - c_1)(b_2 - c_2)m_2^{-1} + (c_1 - a_1) \\ & \times (c_2 - a_2)m_3^{-1} = 0 \end{aligned} \tag{50}$$

or

$$-g_2 m_1^{-1} - g_1 m_2^{-1} + (1 - g_1)(1 - g_2)m_3^{-1} = 0 \tag{51}$$

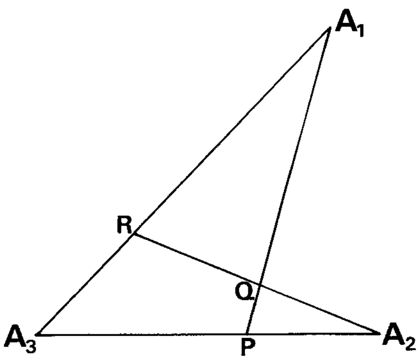

Figure 1. Coordinate system. A_i represents atom i. The coordinates in the text are given by $r_1 = A_2 - R$, $r_2 = A_1 - P$ and $\theta = A_1\hat{Q}A_2$. The geometric parameters are defined by

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

in the programmed coordinates. Clearly, there is a potentially infinite set of orthogonal coordinates.

In systems with identical particles, it is desirable for the coordinates to reflect this symmetry. For AB_2 molecules, scattering or Jacobi coordinates ($g_1 = 0.5$, $g_2 = 0$) allow the symmetry to be represented as reflections about $\theta = \pi/2$. Coordinates with $g_1 = g_2$ allow the interchange of r_1 and r_2 to carry this symmetry. One form of these coordinates, bond-length-bond-angle coordinates ($g_1 = g_2 = 0$) are well known [10]. Another form is Radau coordinates [12]. These orthogonal coordinates can be obtained for any system by setting

$$g_1 = 1 - \frac{\alpha}{\alpha + \beta - \alpha\beta} \qquad g_2 = 1 - \frac{\alpha}{1 - \beta + \alpha\beta}$$

$$\alpha = \left(\frac{m_3}{m_1 + m_2 + m_3}\right)^{1/2} \qquad \beta = \frac{m_2}{m_1 + m_2}. \tag{52}$$

For molecules where m_3 is very much bigger than m_1 or m_2, Radau coordinates mimic bond-length-bond-angle coordinates.

Table I presents results for a series of calculations on H_2S using several coordinate systems. To avoid difficulties with singularities and to enable comparison with previous results, all results are for the embedding of Section 4.2. H_2S has recently been used as a benchmark system for ro-vibrational calculations [13]. The calculations presented here used the same potential and other parameters as the previous calculations and are in very good agreement with them.

TABLE I. Calculated low-lying $J = 0$ and $J = 1$ energy levels, in cm^{-1}, for H_2S for several choices of internal coordinates.

	Quantum numbers			$g_2 = 0$ $g_2 = 0$	$g_1 = 0.0153$ $g_2 = 0.0153$	$g_1 = 0.25$ $g_2 = 0.25$	$g_1 = 0.5$ $g_2 = 0.0$
Band	J	K_a	K_c	$N_{vib} = 600$[a] $N_{rot} = 300$[b]	$N_{vib} = 600$ $N_{rot} = 300$	$N_{vib} = 1250$ $N_{rot} = 300$	$N_{vib} = 1051$ $N_{rot} = 200$
ν_0	0	0	0	3297.46	3297.46	3297.47	3297.46
	1	0	1	3311.15	3311.15	3311.15	3311.15
	1	1	1	3312.53	3312.53	3312.54	3312.54
	1	1	0	3316.79	3316.79	3316.79	3316.79
ν_2	0	0	0	4487.90	4487.90	4487.94	4487.90
	1	0	1	4501.72	4501.72	4501.72	4501.73
	1	1	1	4503.28	4503.28	4503.28	4503.28
	1	1	0	4507.79	4507.79	4507.79	4507.80
$2\nu_2$	0	0	0	5669.48	5669.48	5669.68	5669.50
	1	0	1	5683.45	5683.45	5683.45	5683.46
	1	1	1	5685.20	5685.20	5685.20	5685.21
	1	1	0	5689.78	5689.98	5689.98	5689.99

See text for an explanation of the coordinate system.

[a] Dimension of the vibrational secular matrix.

[b] Dimension of the largest rotational secular matrix.

These calculations were performed using programs TRIATOM and ROTLEVD [11] and our two-step variational procedure [14]. This procedure involves using the solutions of "vibrational" secular problems as basis functions for the fully coupled rotational problem. Given sufficient basis functions, of course, converged results should be obtained from any well-behaved coordinate system. However, the rate of convergence is dependent on a judicious choice of coordinates. Table I gives the size of both vibrational and rotational secular problems used.

Clearly, the bond-length-bond-angle ($g_1 = g_2 = 0$) and Radau ($g_1 = g_2 = 0.0153$) coordinates are most efficient for solving the vibrational problem. Of course, for H_2S, these coordinates are very similar. The arbitrarily defined coordinates ($g_1 = g_2 = 0.25$) proved the least efficient; indeed, an attempt to perform the calculation with a $g_1 = g_2 = 0.5$ coordinate system was abandoned because of poor convergence.

For the rotational problem, scattering coordinates ($g_1 = 0.5$, $g_2 = 0$) proved the most efficient. This is because the $a = 1$ embedding is not symmetric in the $g_1 = g_2$ coordinate systems, meaning that the calculations with rotational excitation cannot use the full symmetry of the system.

6. Conclusion

We have formulated a nuclear motion Hamiltonian for triatomic systems in terms of two arbitrarily defined internal distances and their included angle. We show how the body-fixed axis system can be placed at an arbitrary orientation with respect to the molecule, although most orientations have singularities that may cause difficulties in any numerical application. A nonsingular version of this Hamiltonian has been tested and been shown to give satisfactory results for a number of coordinate systems. This is now available as part of a program suite for the synthesis of ro-vibration spectra of triatomic systems [11].

Finally, it is worth mentioning a possible use of this Hamiltonian or reactive scattering calculations. If one considers the reaction $A + BC \rightarrow AB + C$, then both $A - BC$ and $C - AB$ scattering coordinates might give suitable representations for portions of the reaction. With the flexible coordinates presented here, one can define a coordinate system where r_1 and r_2 are the $A - BC$ and $C - AB$ distances. Other variations on this idea are also possible.

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