The Quantum Dynamics of a System of Two Polyatomic Fragments†

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The Hamiltonian designed to describe the quantum dynamics of a nonrigid system comprising two polyatomic molecules in terms of the separation of their centers of mass is somewhat generalized in an attempt to make it more useful for dealing with systems in which the potential can be specified only incompletely.

1. Introduction

In their paper,[1] Brocks et al. showed that the kinetic energy operator for a system composed of $N > 3$ nuclei each with mass m_i and with Cartesian coordinates defined in a laboratory frame of reference x_{α_i} ($\alpha = x, y, z$, $i = 1, 2, 3, ..., N$),

$$\hat{T} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2 \equiv -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\sum_{\alpha}\frac{\partial^2}{\partial x_{\alpha i}\partial x_{\alpha i}} \tag{1}$$

can be written as (using $\vec{\nabla}$ as the usual vector gradient operator)-with

$$\hat{T} = -\frac{\hbar^2}{2M}\nabla^2(\mathbf{X}) - \frac{\hbar^2}{2\mu}\nabla^2(\mathbf{t}_0) - \frac{\hbar^2}{2}\sum_{F=\mathrm{A,B}}\sum_{i,j=1}^{N_F-1} G_{ij}^F\vec{\nabla}(\mathbf{t}_i^F)\cdot\vec{\nabla}(\mathbf{t}_j^F) \tag{2}$$

$$1/\mu = 1/M_\mathrm{A} + 1/M_\mathrm{B} \tag{3}$$

$$G_{ij}^F = \delta_{ij}/m_j^F - 1/M_F, \quad F = \mathrm{A, B} \tag{4}$$

by identifying two groups A and B in the system, dividing the coordinates into two sets, and making the translationally invariant coordinate choices

$$\mathbf{t}_i^F = \mathbf{x}_i^F - \mathbf{X}_F, \quad i = 1, 2, ..., N_F - 1, \quad F = \mathrm{A, B} \tag{5}$$

$$\mathbf{t}_0 = \mathbf{X}_\mathrm{A} - \mathbf{X}_\mathrm{B} \tag{6}$$

where $\mathbf{X}_F$ is the group center of mass coordinate so that the total mass of the system is $M = M_\mathrm{A} + M_\mathrm{B}$ and the total center of mass coordinate is $\mathbf{X} = M^{-1}(M_\mathrm{A}\mathbf{X}_\mathrm{A} + M_\mathrm{B}\mathbf{X}_\mathrm{B})$.

The the first term in eq 2 represents the center of nuclear mass motion. It is unimportant in the discussion and is separated off. The simplicity of the remaining terms depends crucially on the choice of the separation coordinate made in eq 6. However, as van der Avoird, Wormer, and Moszynski point out in their review,[2] although the choice of separation coordinate $\mathbf{t}_0$ made by Brocks et al. leads to a neat and elegant form for the kinetic energy operator, it is not always the choice that is most appropriate for computation. This is because the group center of mass coordinates involve all of the coordinates necessary to specify the geometry and orientation of the group. The group separation coordinate therefore involves all of these coordinates of both groups. It is thus not possible to express a computed potential in terms of the group separation coordinate unless it is known in terms of all of the group coordinates. But in practice, we often want to consider a simplified problem in which the potential is expressed in terms of an arbitrary separation coordinate. Here, we show that a simple transformation of the Brocks et al. form leads to an account of the problem in which the separation coordinate can be chosen in an essentially arbitrary way, and the formulation that we shall present contains the previous work as a special case. The price paid for the freedom gained by this tactic (and what is newly derived here) is a more complicated kinetic energy operator than in the original case, part of which represents an extra element of "vibration−rotation" interaction. In considering this term, we shall also exhibit, rather more explicitly than previously, precise forms of the angular momentum operators.

What follows can also be seen as generalizing the diatomic molecule Hamiltonian as presented, for example, in Kolos and Wolniewicz's treatment.[3] In the present work, the fragments correspond to a pair of electrons in a diatomic and the angular momentum of the polyatomic fragments plays the same formal role as does the electronic angular momentum in the diatomic case.

2. The Translationally Invariant Kinetic Energy Operators for the Dimer in Terms of an Arbitrary Separation Coordinate

An arbitrary separation coordinate **t** can be written in terms of the transla- tionally invariant coordinates introduced above as

$$\mathbf{t} = \mathbf{t}_0 + \sum_{F=\mathrm{A,B}}\sum_{i=1}^{N_F-1} u_i^F\mathbf{t}_i^F \tag{7}$$

For the translationally invariant part of the kinetic energy operator, simple use of the chain rule leads to the expression

$$-\frac{\hbar^2}{2\bar{\mu}}\nabla^2(\mathbf{t}) - \frac{\hbar^2}{2}\sum_{F=\mathrm{A,B}}\sum_{i,j=1}^{N_F-1} G_{\mathrm{ij}}^F\vec{\nabla}(\mathbf{t}_i^F)\cdot\vec{\nabla}(\mathbf{t}_j^F) - \frac{\hbar^2}{2}\sum_{F=\mathrm{A,B}}\sum_{j=1}^{N_F-1}\frac{1}{\mu_j^F}(\vec{\nabla}(\mathbf{t})\cdot\vec{\nabla}(\mathbf{t}_j^F) + \vec{\nabla}(\mathbf{t}_j^F)\cdot\vec{\nabla}(\mathbf{t})) \tag{8}$$

where

$$1/\bar{\mu} = 1/\mu + 1/\mu_\mathrm{A} + 1/\mu_\mathrm{B} \tag{9}$$

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with

$$1/\mu_F = \sum_{i,j=1}^{N_F-1} G_{ij}^F u_i^F u_j^F \tag{10}$$

and

$$\frac{1}{\mu_i^F} = \sum_{j=1}^{N_F-1} G_{ij}^F u_j^F = \frac{u_i^F}{m_i^F} - \frac{1}{M_F}\sum_{j=1}^{N_F-1} u_j^F \tag{11}$$

3. The Kinetic Energy Operators Expressed in the Dimer Frame

Following Brocks et al., we write the intergroup distance vector **t** in polar coordinates (R, β, α), where $t_z = R\cos\beta$. Then, the orthogonal matrix

$$\mathbf{C} = \begin{pmatrix} \cos\beta\cos\alpha & -\sin\alpha & \sin\beta\cos\alpha \\ \cos\beta\sin\alpha & \cos\alpha & \sin\beta\sin\alpha \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \tag{12}$$

is such that

$$\mathbf{z} = \mathbf{C}^{\mathrm{T}}\mathbf{t} = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix} \tag{13}$$

and the remaining Cartesian variables are transformed to variables in the frame defined by **C**, the dimer frame, as

$$\mathbf{z}_i^F = \mathbf{C}^{\mathrm{T}}\mathbf{t}_i^F, \quad i = 1, 2, ..., N_F - 1, \quad F = \mathrm{A}, \mathrm{B} \tag{14}$$

If we treat **t** as defined here in the way that Brocks et al. treated $\mathbf{t}_0$, we can rewrite the kinetic energy operators expressed in the dimer frame. The second part of eq 8, which refers to the fragments alone, changes only trivially to become

$$-\frac{\hbar^2}{2}\sum_{F=\mathrm{A},\mathrm{B}}\sum_{i=1}^{N_F-1} G_{ij}^F \vec{\nabla}(\mathbf{z}_i^F)\cdot\vec{\nabla}(\mathbf{z}_j^F) \tag{15}$$

The first part becomes

$$\hat{K}_1^{\mathrm{INT}} \rightarrow -\frac{\hbar^2}{2\bar{\mu}R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\bar{\mu}R^2}\hat{D}_1(\alpha,\beta,\mathbf{z}^F) \tag{16}$$

and the last part becomes

$$\hat{K}_2^{\mathrm{INT}} = \frac{\hbar}{i}\frac{\partial}{\partial R}\hat{v}_z + \frac{1}{2R}\hat{D}_2(\alpha,\beta,\mathbf{z}^F) \tag{17}$$

where the components of the velocity operator are given by

$$\hat{v}_\alpha = \frac{\hbar}{i}\sum_{F=\mathrm{A},\mathrm{B}}\sum_{j=1}^{N_F-1}\frac{1}{\mu_j^F}\frac{\partial}{\partial z_{\alpha j}^F} = \sum_{F=\mathrm{A},\mathrm{B}}\hat{v}_\alpha^F$$

Using the angular momentum operators as defined in ref 1, we may write the $\hat{D}_i$

$$\hat{D}_1(\alpha,\beta,\mathbf{z}^F) = \left[(\hat{J}_x - \hat{\jmath}_x)^2 + (\hat{J}_y - \hat{\jmath}_y)^2 + \frac{\hbar}{i}\cot\beta(\hat{J}_y - \hat{\jmath}_y)\right]$$

or

$$\hat{D}_1(\alpha,\beta,\mathbf{z}^F) = [\hat{J}^2 + \hat{\jmath}^2 - 2\hat{\jmath}_z\hat{J}_z - \hat{\jmath}^+\hat{J}^+ - \hat{\jmath}^-\hat{J}^-]$$

and

$$\hat{D}_2(\alpha,\beta,\mathbf{z}^F) = \frac{2\hbar}{i}\hat{v}_z + \left(\hat{J}_y - \hat{\jmath}_y - \frac{i\hbar}{2}\cot\beta\right)\hat{v}_x + \hat{v}_x\left(\hat{J}_y - \hat{\jmath}_y - \frac{i\hbar}{2}\cot\beta\right) - ((\hat{J}_x - \hat{\jmath}_x)\hat{v}_y + \hat{v}_y(\hat{J}_x - \hat{\jmath}_x))$$

The operator $\hat{D}_1$ is exactly as in ref 1 and thus may be manipulated as in that paper. However, it is useful to rewrite it and $\hat{D}_2$ explicitly in terms of the angular derivatives so that direct comparison may be made with the equivalent diatomic forms.

$$\hat{D}_1 = -\hbar^2\left[\frac{\partial^2}{\partial\beta^2} + \cot\beta\frac{\partial}{\partial\beta} + \frac{1}{\sin^2\beta}\frac{\partial^2}{\partial\alpha^2} - \frac{1}{\sin^2\beta}\left(\frac{\hat{\jmath}_z}{\hbar} + 2i\cos\beta\frac{\partial}{\partial\alpha}\right)\frac{\hat{\jmath}_z}{\hbar} + \frac{\hat{\jmath}_z}{\hbar}\left(\frac{\hat{\jmath}_z}{\hbar} + 1\right) - \frac{\hat{\jmath}^+\hat{\jmath}^-}{\hbar^2} + \frac{\hat{\jmath}^+}{\hbar}\left(-\frac{\partial}{\partial\beta} + \cot\beta\frac{\hat{\jmath}_z}{\hbar} + \frac{i}{\sin\beta}\frac{\partial}{\partial\alpha}\right) + \frac{\hat{\jmath}^-}{\hbar}\left(\frac{\partial}{\partial\beta} + \cot\beta\frac{\hat{\jmath}_z}{\hbar} + \frac{i}{\sin\beta}\frac{\partial}{\partial\alpha}\right)\right] \tag{18}$$

$$\hat{D}_2 = \frac{\hbar}{i}\left[\hat{v}^+\left(\frac{\partial}{\partial\beta} - \frac{i}{\sin\beta} - \cot\beta\frac{\hat{\jmath}_z}{\hbar}\right) + \hat{v}^-\left(\frac{\partial}{\partial\beta} + \frac{i}{\sin\beta} + \cot\beta\frac{\hat{\jmath}_z}{\hbar}\right) + \left(\hat{v}^+\frac{\hat{\jmath}^-}{\hbar} - \hat{v}^-\frac{\hat{\jmath}^+}{\hbar}\right)\right] \tag{19}$$

The operators $\hat{\jmath}^\pm$ are the standard raising and lowering operators for the fragment wave function, and $\hat{v}^\pm$ are defined just like $\hat{\jmath}^\pm$ but using the components of the velocity operator.

$\hat{D}_1$ and $\hat{D}_2$ are essentially identical with the angular parts of eqs 12 and 13, respectively, in Kolos and Wolniewicz's treatment of the diatomic molecule.[3] In the present work, the angular momentum of the polyatomic fragments plays the same formal role as does the electronic angular momentum in the diatomic case.

4. The Construction of Wavefunctions and Matrix Elements

A reasonable form for trial wave functions for the problem is

$$\Phi_{nmjp}^J(\alpha,\beta,R,\mathbf{z}^A,\mathbf{z}^B) = \sqrt{\frac{1}{2\pi}}\,\mathrm{e}^{in\alpha}\sqrt{\frac{2}{2J+1}}d_{nm}^J(\beta)\psi_{mjp}^J(R,\mathbf{z}^A,\mathbf{z}^B) \tag{20}$$

where d_{nm}^J, is a term in a standard rotation matrix element as defined in ref 4 or equivalently in either ref 5 or 6.

If ψ_{mjp}^J is chosen to be an eigenfunction of $\hat{\jmath}_z$ with eigenvalue $\hbar m$ and an eigenfunction of $\hat{\jmath}^2$ with eigenvalue $\hbar^2 j(j+1)$ then

$$\hat{D}_1\Phi_{nmjp}^J \rightarrow \hbar^2 N_J\,\mathrm{e}^{in\alpha}[d_{nm}^J(\beta)\psi_{mjp}^J(J(J+1) + j(j+1) - 2m^2) - c_{Jm}^+c_{jm}^+d_{nm+1}^J(\beta)\psi_{m+1jp}^J - c_{Jm}^-c_{jm}^-d_{nm-1}^J(\beta)\psi_{m-1jp}^J] \tag{21}$$

and

$$\hat{D}_2\Phi_{nmjp}^J \rightarrow \frac{\hbar}{i}N_J\,\mathrm{e}^{in\alpha}[d_{nm}^J(\beta)(c_{jm}^-\hat{v}^+\psi_{m-1jp}^J - c_{jm}^+\hat{v}^-\psi_{m+1jp}^J) + (c_{Jm}^-d_{nm-1}^J(\beta)\hat{v}^- - c_{Jm}^+d_{nm+1}^J(\beta)\hat{v}^+)\psi_{mjp}^J] \tag{22}$$

where the normalization factor in eq 20 is denoted by N_J and $c_{ls}^\pm$ is defined in the standard manner.

It should noted that the phase conventions adopted here are not the same as those used in ref 3, so there are some sign differences between this work and that.

If it is supposed, as it was in ref 1, that each of the two groups is described in a local coordinate system oriented with respect to the frame fixed in the body by a matrix $\mathbf{C}^F$ specified by local Euler angles denoted collectively as ω^F, then the wave function for the group may be written generally as

$$\sum_{k_F=-j_F}^{j_F} \Phi_{k_F}^{j_F}(\mathbf{q}^F)|j_F m_F k_F\rangle \tag{23}$$

Here, $\mathbf{q}^F$ symbolizes the $3N_F - 6$ internal coordinates for the fragment, and the angular momentum eigenfunction is assumed to be expressed in terms of the Euler angles given collectively by ω^F. It will be assumed that the functions for one fragment are orthogonal to those of the other fragment and that within a fragment the functions form an orthonormal set. The angular parts for the two groups may be coupled as

$$|j_A k_A j_B k_B j_m\rangle = \sum_{m_A,m_B} \langle j_A j_B m_A m_B|jm\rangle |j_A m_A k_A\rangle |j_B m_B k_B\rangle \tag{24}$$

using the Clebsch−Gordan coefficients as defined in ref 4. The total angular momentum eigenfunctions may be written in terms of the products

$$|Jnj_A k_A j_B k_B jm\rangle = |j_A k_A j_B k_B jm\rangle N_J \, e^{in\alpha} d^J_{nm}(\beta) \tag{25}$$

The quantum number m (m_F) is the component of j (j_F) along the z axis between the two groups, and the quantum number n is the component of J along the z axis of the frame fixed in the laboratory, Although there is no upper limit to the value of j, subject to the value being properly composable from the j_F values, the maximum value of m is J. The functions ψ^J_{mjp} may be imagined expressed in terms of appropriately coupled products of functions of the form in eq 23. With the use of eq 21, the matrix elements of eq 16 in this basis with respect to the angular variables are of the form

$$\langle J'n'j'_A k'_A j'_B k'_B j'm'|\hat{K}_1^{\mathrm{INT}}|Jnj_A k_A j_B k_B jm\rangle = \delta_{j'_A j_A}\delta_{k'_A k_A}\delta_{j'_B j_B}\delta_{k'_B k_B}\delta_{j'j}\hbar^2$$
$$\left[\delta_{m'm}\left(-\frac{1}{2\bar{\mu}R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}+\frac{(J(J+1)+j(j+1)-2m^2)}{2\bar{\mu}R^2}\right)-\frac{1}{2\bar{\mu}R^2}(\delta_{m'm+1}c^+_{Jm}c^+_{jm}+\delta_{m'm-1}c^-_{Jm}c^-_{jm})\right] \tag{26}$$

That these are also diagonal in J and in n has been left implicit because all matrix elements in this formulation are diagonal in these two quantum numbers. This would be the same as eq 42 of ref 1 but for a mistake in that equation (its last term should be negative). It is given correctly in eq 26.

The matrix elements arising from eq 17 are not altogether straightforward to construct in the absence of a specific choice of coordinates to describe the individual group wave functions and the velocity operator. Of course, because the components of the velocity operator are writable in terms of the standard components of a rank 1 irreducible tensor operator, ${}^1\mathbf{v}$, as ${}^1v_0 = v_z$ and ${}^1v_\pm = \mp v^\pm/\sqrt{2}$, the form of the angular part of their matrix elements can be constructed using the Wigner−Eckart theorem. The problem is to get a form for the reduced matrix elements. Without becoming too specific however, it is possible to get a little further because rather general arguments (see ref 7) can be used to show that the Cartesian form of the first derivative operator in a given coordinate system may be expressed in a coordinate system related to it by an orthogonal transformation $\mathbf{C}$ as follows

$$\frac{\partial}{\partial \mathbf{t}_i} = \mathbf{C}\left(\mathbf{\Omega}^i\mathbf{D}\frac{\partial}{\partial\phi}+\mathbf{Q}^i\frac{\partial}{\partial\mathbf{q}}\right) \tag{27}$$

The matrix $\mathbf{D}$ is a function of the Euler angles only and the matrices $\mathbf{\Omega}^i$ and $\mathbf{Q}^i$ are functions of the internal coordinates $\mathbf{q}$ only. The angular momentum operator in the system specified by $\mathbf{C}$ is

$$\hat{\mathbf{L}}(\phi) = \frac{\hbar}{i}\mathbf{D}\frac{\partial}{\partial\phi} \tag{28}$$

The components of this operator obey the standard commutation conditions. Of course, specific choices will have to be made to give definite form to this result. However, if we imagine that we have made a choice of $\mathbf{C}$ as $\mathbf{C}^F$ moving from the dimer frame to the frame local to the group and that a suitable set of internal coordinates has been chosen, then for $\mathbf{v}^F$ we can write

$$\mathbf{v}^F = \mathbf{C}^F\left(\mathbf{\Omega}^F\hat{\mathbf{j}}^F+\frac{\hbar}{i}\mathbf{Q}^F\frac{\partial}{\partial\mathbf{q}^F}\right) \tag{29}$$

where

$$\mathbf{\Omega}^F = \sum_{i=1}^{N_F-1}\frac{1}{\mu_i^F}\mathbf{\Omega}^i, \quad \mathbf{Q}^F = \sum_{i=1}^{N_F-1}\frac{1}{\mu_i^F}\mathbf{Q}^i$$

and $\hat{\mathbf{j}}^F$ is the form that $\hat{\mathbf{L}}$ takes in this context.

It can be shown[5] that, whatever the parametrization, for any $\mathbf{C}$ in $SO(3)$, the appropriate Wigner $\mathscr{D}^1$ matrix can be written as

$$\mathscr{D}^1 = \mathbf{X}^\dagger\mathbf{C}\mathbf{X} \tag{30}$$

with

$$\mathbf{X} = \begin{pmatrix} -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ -i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 1 & 0 \end{pmatrix} \tag{31}$$

provided that $C_{\alpha\beta}$ is ordered α, $\beta = x, y, z$ and the indices on $\mathscr{D}^1$ run $+1$, 0, -1 across each row and down each column.

Dropping the superscripts on the matrixes in eq 29, multiplying from the left by $\mathbf{X}^{\mathrm{T}}$, and inserting the unit matrix appropriately gives

$$\mathbf{X}^{\mathrm{T}}\mathbf{v} = {}^1\mathbf{v} = \mathbf{X}^{\mathrm{T}}\mathbf{C}\mathbf{X}^*\left(\mathbf{X}^{\mathrm{T}}\mathbf{\Omega}\mathbf{X}^*\mathbf{X}^{\mathrm{T}}\hat{\mathbf{j}}+\frac{\hbar}{i}\mathbf{X}^{\mathrm{T}}\mathbf{Q}\frac{\partial}{\partial\mathbf{q}}\right)$$

or

$${}^1\mathbf{v} = \mathscr{D}^1*\left({}^1\Omega^1\hat{\mathbf{j}}+\frac{\hbar}{i}{}^1\mathbf{Q}\frac{\partial}{\partial\mathbf{q}}\right)$$

It is possible to develop this somewhat because the results of the components of ${}^1\hat{\mathbf{j}}$ operating on the angular functions are known and because

$$\langle j'm'k'|\mathscr{D}^1_{sp}*|jmk\rangle = (-1)^{m'}(2j'+1)^{1/2}\begin{pmatrix} j' & 1 & j \\ -m' & s & m\end{pmatrix}(-1)^k(2j+1)^{1/2}\begin{pmatrix} j' & 1 & j \\ k' & p & -k\end{pmatrix} \tag{32}$$

where the $3-j$ symbols are as defined in ref 4.

The expected values of the components of the rank 1 tensor operator with respect to the angular variables are therefore

$$\langle j'm'k'|{}^1v_s|jmk\rangle = (-1)^{m'}(2j'+1)^{1/2}\begin{pmatrix} j' & 1 & j \\ -m' & s & m \end{pmatrix}(2j+1)^{1/2}$$
$$(-1)^k\hbar\sum_{p=-1}^{+1}\left(\begin{pmatrix} j' & 1 & j \\ k' & p & -(k+1) \end{pmatrix}\frac{c_{jk}^{+1}\Omega_{p1}}{\sqrt{2}} + \begin{pmatrix} j' & 1 & j \\ k' & p & -k \end{pmatrix}k^1\Omega_{p0} - \begin{pmatrix} j' & 1 & j \\ k' & p & -(k-1) \end{pmatrix}\frac{c_{jk}^{-1}\Omega_{p-1}}{\sqrt{2}} + \begin{pmatrix} j' & 1 & j \\ k' & p & -k \end{pmatrix}\frac{1}{i}\left({}^1\mathbf{Q}\frac{\partial}{\partial \mathbf{q}}\right)_p\right) \quad (33)$$

The first three terms in eq 33 are exactly what would be expected from the Wigner−Eckart theorem. These connect states with a given j not only to states with the same j but also to those with $j \pm 1$. The states with given m can also be connected to those with $m \pm 1$ depending on the value of s. Because no angular momentum coupling is performed on the indices k, the $3-j$ symbols involving k in eqs 32 and 33 will be relevant to one or another of the fragments according to the **C** matrix from which the Wigner matrix originates. The matrix elements associated with a particular fragment will be diagonal in the k value of the other fragment. The matrix elements that are dependent on k have no dependence on m or s and are the reduced matrix elements expected from the Wigner−Eckart theorem. Thus eq 33 may be rewritten in a slightly different somewhat more explicit way using the functional form given in eq 24 as

$$\langle j'_A,k'_A,j'_B,k'_B,j',m'|{}^1v^A{}_s + {}^1v^B{}_s|j_A,k_A,j_B,k_B,j,m\rangle = (-1)^{m'}(2j'+1)^{1/2}\begin{pmatrix} j' & 1 & j \\ -m' & s & m \end{pmatrix}(2j+1)^{1/2}\hat{g}(j'_A,k'_A,j_A,k_A:\mathbf{q}^A;j'_B,k'_B,j_B,k_B:\mathbf{q}^B) \quad (34)$$

with

$$\hat{g}(j'_A,k'_A,j_A,k_A:\mathbf{q}^A;j'_B,k'_B,j_B,k_B:\mathbf{q}^B) = \hat{g}_A(j'_A,k'_A;j_A,k_A:\mathbf{q}^A)\delta_{j'_Bj_B}\delta_{k'_Bk_B} + \hat{g}_B(j'_B,k'_B;j_B,k_B:\mathbf{q}^B)\delta_{j'_Aj_A}\delta_{k'_Ak_A} \quad (35)$$

where $\hat{g}_F(j'_F,k'_F;j_F,k_F:\mathbf{q}^F)$ is composed as are the last two lines of eq 33 but with reference to the individual fragments. Because the velocity operator has been expressed in a local coordinate system, eq 34 can now be used to give at least formal expressions for their matrix elements. The matrix elements of eq 17 are

$$\langle J'n'j'_Ak'_Aj'_Bk'_Bj'm'|\hat{K}_2^{INT}|Jnj_Ak_Aj_Bk_Bjm\rangle = \frac{\hbar}{i}(2j'+1)^{1/2}(2j+1)^{1/2}\hat{g}(j'_A,k'_A,j_A,k_A:\mathbf{q}^A;j'_B,k'_B,j_B,k_B:\mathbf{q}^B)(-1)^m \left[\delta_{m'm}\begin{pmatrix} j' & 1 & j \\ -m & 0 & m \end{pmatrix}\frac{\partial}{\partial R} - \frac{\delta_{m'm}}{\sqrt{2}R}\left(c_{jm}^+\begin{pmatrix} j' & 1 & j \\ -m & -1 & m+1 \end{pmatrix} + c_{jm}^-\begin{pmatrix} j' & 1 & j \\ -m & +1 & m-1 \end{pmatrix}\right) - \frac{1}{\sqrt{2}R}\left(\delta_{m'm+1}c_{Jm}^+\begin{pmatrix} j' & 1 & j \\ -(m+1) & +1 & m \end{pmatrix} + \delta_{m'm-1}c_{Jm}^-\begin{pmatrix} j' & 1 & j \\ -(m-1) & -1 & m \end{pmatrix}\right)\right] \quad (36)$$

The parameters arising from the angular integrations may be evaluated by standard procedures, and provided that the derivatives can be evaluated effectively, the remaining radial matrix elements should prove no more difficult than those involved in the integrations over the potential required in all approaches.

5. Conclusions

A formalism for a two-fragment polyatomic dimer has been given that is not subject to stringent separation coordinate requirements. Although the new kinetic energy term that must be added to achieve such freedom makes this Hamiltonian more complicated than the traditional one, it does seem likely that it can form at least a basis for well-founded model calculations.

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