

Quantum dynamics of non-rigid systems comprising two polyatomic fragments

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We combine earlier treatments for the embedding of body-fixed coordinates in linear molecules with the close-coupling formalism developed for atom-diatom scattering and derive a hamiltonian which is most convenient for describing the nuclear motions in van der Waals complexes and other non-rigid systems comprising two polyatomic fragments, A and B . This hamiltonian can still be partitioned in the form $\hat{H}_A + \hat{H}_B + \hat{H}_{INT}$, just as the space-fixed hamiltonian. The body-fixed form, however, has several advantages. We discuss solution strategies for the rovibrational problem in non-rigid dimers, based on this partitioning of the hamiltonian. Finally, in view of the size of the general polyatomic-polyatomic case, we suggest problems which should be currently practicable.

1. INTRODUCTION

The search for suitable coordinate systems and hamiltonians for the polyatomic vibration-rotation problem has excited much scientific interest over the years [1-12]. For near-rigid systems, with localized or small amplitude vibrations, the use of Eckart coordinates has proved fruitful [1-5, 13, 14]. However, for one or more large amplitude internal motions the simple Eckart hamiltonian is unsatisfactory. This feature was recognized very early by Sayvetz [2] who modified the original approach of Eckart [1] to try and deal with the difficulties inherent in treating large amplitude internal motions.

The problems arise because the transformation that leads from the hamiltonian in the laboratory-fixed coordinate system to the internal hamiltonian, which is expressed in some suitably chosen body-fixed coordinate system, has a jacobian which is singular for some values of the coordinates. Thus the transformed internal hamiltonian is not everywhere well defined and, consequently, has a domain that is more restricted than all square-integrable functions of the body-fixed coordinates. The difficulties associated with this restriction of the domain usually manifest themselves in divergent expectation values of the internal hamiltonian between seemingly reasonable functions. Thus it is well known

[15–18] that if an attempt is made to treat a triatomic that has a large amplitude bending mode, in the Eckart approach, then divergence can occur in expectation values of functions that allow the system to become linear.

This sort of problem can be solved by using the Sayvetz modification of the Eckart approach and such a way out has been attempted [19–22]. It can also be solved by abandoning the Eckart approach altogether, based as it is on the idea of an equilibrium geometry for the system, and various different formulations have been given [6–10, 23–26]. However, because of the complexity of the problem, use of these hamiltonians has been restricted to triatomic systems and a few symmetric tetra-atomic $(AB)_2$ van der Waals complexes [6, 25–27]. With the exception of a recent calculation on HeHF [28], all these calculations have included some simplifying approximation involving the decoupling or freezing of certain vibrational modes.

A popular approach, applied to several van der Waals complexes [6, 7, 10, 23–28] as well as H_2O [29], KCN [10, 16], LiCN [30] and CH_2^+ [31], has been to work in so-called (di)atom–diatom collision coordinates. These are defined as the distance between the monomer centres of mass, the angles describing the orientations of the monomers, the internal monomer coordinates and the overall rotation angles. Several hamiltonians have been used to obtain the bound rovibrational states of systems treated as collision complexes using approaches which show strong analogies to atom– [32], diatom– [33] and electron– [34] diatom scattering problems. The main difference between the various hamiltonians is the embedding of the coordinate system. For atom–diatom systems alone, space fixed coordinates [7] and at least three different embeddings of body-fixed coordinates [8, 10, 30] have been used.

In recent work we have favoured the use of coordinates which have \mathbf{R} , the interaction or collision coordinate, embedded along the z -axis. This system has computational advantages over space-fixed coordinates and allows the simplifying approximation of neglect of off-diagonal Coriolis interactions, which has proved useful in many calculations [10, 26, 30, 35]. This embedding is favoured over one which fixes the axis(es) in one fragment of the complex, cf. Istomin *et al.* [8], as it is easier to generalize.

Fixing \mathbf{R} along the z -axis is not sufficient fully to body-fix the coordinates as it only defines two of three possible embedding Euler angles. A fully embedded hamiltonian for the atom–diatom problem was recently given by Tennyson and Sutcliffe [10], but as we show (in Appendix A) this is not convenient in larger systems. However, as shown by Tennyson and Sutcliffe, there is a strong equivalence between the matrix problems generated by the two embeddings.

In this paper, we present a general hamiltonian for the rovibrational (and scattering) problem of a system AB , where A and B are polyatomic molecules. This hamiltonian can be expressed in terms of fragment hamiltonians and an interaction hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{INT} \quad (1)$$

and it is derived in such a manner that \hat{H}_A and \hat{H}_B are the rovibrational hamiltonians of the isolated fragments for which conventional Eckart hamiltonians [1–5] are appropriate. Our hamiltonian is suitable for any system which contains two (near) rigid fragments undergoing large amplitude motions. Thus it is particularly convenient for van der Waals dimers.

By embedding the hamiltonian in this manner, we follow several earlier works on atom-diatom and diatom-diatom systems. Our hamiltonian extends to larger (polyatomic) molecules, however, and, moreover, we hope to clarify the situation with regard to the form and commutation relationships of the resulting pseudo-angular momentum operators (§ 2). In §§ 3 and 4 we discuss convenient and practical solution strategies for the problem.

An approach to the scattering of two polyatomic molecules which is similar to the present one has been proposed in 1953 by Curtiss [36], who based himself on the pioneering work by Hirschfelder *et al.* [37, 38]. Curtiss starts out in body-fixed coordinates (defined by three embedding angles). However, by rotating and recoupling his basis functions he actually derives the close-coupled equations in space-fixed coordinates.

2. HAMILTONIAN

Within the Born-Oppenheimer approximation, the hamiltonian for nuclear motion is

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_i^2(\mathbf{x}_i) + V, \quad (2)$$

where $\nabla_i^2(\mathbf{x}_i)$ is the laplacian for the i th nucleus and V the potential. If the N -nucleus system is divided into fragment A with N_A nuclei and fragment B with N_B nuclei, then the space (or laboratory) fixed coordinates can be ordered

$$\left. \begin{array}{l} \mathbf{x}_i, i = 1, 2 \dots N_A, N_A + 1, \dots, N. \\ 1, \dots, N_B. \end{array} \right\} \quad (3)$$

The overall translational motion is removed and the relative translation of the two monomers A and B is defined by the following transformation [36]

$$\left. \begin{array}{l} \mathbf{t}_i^A = \mathbf{x}_i - \mathbf{X}_A, \quad i = 1 \dots, N_A - 1 \\ \mathbf{t}_i^B = \mathbf{x}_{N_A+i} - \mathbf{X}_B, \quad i = 1 \dots, N_B - 1 \\ \mathbf{t}_0 = \mathbf{X}_A - \mathbf{X}_B, \\ \mathbf{X} = M^{-1}(M_A \mathbf{X}_A + M_B \mathbf{X}_B), \end{array} \right\} \quad (4)$$

with

$$\left. \begin{array}{l} \mathbf{X}_A = M_A^{-1} \sum_{i=1}^{N_A} m_i \mathbf{x}_i, \quad M_A = \sum_{i=1}^{N_A} m_i, \\ \mathbf{X}_B = M_B^{-1} \sum_{i=N_A+1}^N m_i \mathbf{x}_i, \quad M_B = \sum_{i=N_A+1}^N m_i, \\ M = M_A + M_B, \end{array} \right\} \quad (5)$$

where \mathbf{x}_i denotes a vector of coordinates in the original frame and \mathbf{t}_i in the new frame.

Use of the chain rule gives

$$\sum_{i=1}^N \frac{1}{m_i} \nabla^2(\mathbf{x}_i) = M^{-1} \nabla^2(\mathbf{X}) + \mu^{-1} \nabla^2(\mathbf{t}_0) + \sum_{F=A, B} \sum_{i, j=1}^{N_F-1} G_{ij}^F \nabla(\mathbf{t}_i^F) \cdot \nabla(\mathbf{t}_j^F), \quad (6)$$

where the terms in \mathbf{t}_i^F vanish if $N_F < 2$ and

$$\left. \begin{aligned} G_{ij}^F &= \delta_{ij} m_j^{-1} - M_F^{-1}, & (F = A, B), \\ \mu^{-1} &= M_A^{-1} + M_B^{-1}. \end{aligned} \right\} \quad (7)$$

The first term in (6), $M^{-1} \nabla^2(\mathbf{X})$, corresponds to the free translation of the centre of mass and can be separated off. The remaining terms form the kinetic energy operator of the rovibrational hamiltonian of the AB system, expressed in a coordinate frame which is body-fixed with respect to translations, but still parallel to the laboratory frame. This frame is usually called space-fixed.

If the separation of the monomer centres of mass is not done for all particles in one step, as in (4), but pairwise in $(N_F - 1)$ steps for each monomer F , which defines the so-called Jacobi coordinates \mathbf{t}_i , then the matrix \mathbf{G} becomes diagonal

$$G_{ij}^F = \delta_{ij} \mu_i^{-1}, \quad (F = A, B), \quad (7')$$

where μ_i is the mass of the i th reduced particle.

Next, we wish to separate off the overall rotations of the system by defining a body-fixed coordinate frame. The question is how to fix this frame on a non-rigid system, where the equilibrium structure, which could be used to define the Eckart embedding conditions [1], may not be meaningful. It seems natural to single out the vector $\mathbf{t}_0 = \mathbf{R}$ which connects the centres of mass of the two fragments A and B and to embed the body-fixed frame with the z -axis along \mathbf{R} (following the Pack and Hirschfelder [34] treatment of diatomic systems).

If \mathbf{R} has the polar angles (β, α) with respect to the space-fixed system, this embedding is achieved by the orthogonal transformation

$$\mathbf{z}_0 = \mathbf{C}^T \mathbf{t}_0 = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}, \quad (8a)$$

$$\mathbf{z}_i^F = \mathbf{C}^T \mathbf{t}_i^F, \quad (F = A, B), \quad (8b)$$

with the matrix \mathbf{C} , that corresponds to a rotation over two Euler angles, α and β , given by

$$\mathbf{C} = \begin{pmatrix} \cos \beta \cos \alpha & -\sin \alpha & \sin \beta \cos \alpha \\ \cos \beta \sin \alpha & \cos \alpha & \sin \beta \sin \alpha \\ -\sin \beta & 0 & \cos \beta \end{pmatrix}. \quad (9)$$

It is possible to define a third embedding angle γ but, as we show in Appendix A, this leads to a less convenient form of the hamiltonian.

We have to consider the effect of the rotation \mathbf{C} on the hamiltonian, in particular on the kinetic energy operator. In order to express the differential operators of the old coordinates (4) in the new ones, we have to use the chain rule. In applying this rule, however, it must be remembered that the embedding condition (8) makes each of the new coordinates \mathbf{z}_i^F a function of \mathbf{t}_0 , because the matrix \mathbf{C} depends on the angles α and β which occur in $\mathbf{t}_0 = \mathbf{R} = (R \sin \beta \cos \alpha, R \sin \beta \sin \alpha, R \cos \beta)$. Thus

$$\frac{\partial}{\partial t_{0,\xi}} = \frac{\partial R}{\partial t_{0,\xi}} \frac{\partial}{\partial R} + \frac{\partial \alpha}{\partial t_{0,\xi}} \frac{\partial}{\partial \alpha} + \frac{\partial \beta}{\partial t_{0,\xi}} \frac{\partial}{\partial \beta} + \sum_F \sum_{i=1}^{N_F-1} \sum_{\eta} \frac{\partial z_{i,\eta}^F}{\partial t_{0,\xi}} \frac{\partial}{\partial z_{i,\eta}^F} \quad (10)$$

and we can substitute

$$\left. \begin{aligned} \frac{\partial R}{\partial t_{0,\xi}} &= C_{\xi z}, \\ \frac{\partial \alpha}{\partial t_{0,\xi}} &= (R \sin \beta)^{-1} C_{\xi \nu}, \\ \frac{\partial \beta}{\partial t_{0,\xi}} &= R^{-1} C_{\xi x} \end{aligned} \right\} \quad (11)$$

and

$$\frac{\partial z_{i,\eta}^F}{\partial t_{0,\xi}} = \sum_{\zeta} \frac{\partial C_{\zeta \eta}}{\partial t_{0,\xi}} t_{i,\zeta}^F = \sum_{\zeta, \mu} \frac{\partial C_{\zeta \eta}}{\partial t_{0,\xi}} C_{\zeta \mu} z_{i,\mu}^F, \quad (12)$$

with

$$\frac{\partial C_{\zeta \eta}}{\partial t_{0,\xi}} = \frac{\partial C_{\zeta \eta}}{\partial \alpha} \frac{\partial \alpha}{\partial t_{0,\xi}} + \frac{\partial C_{\zeta \eta}}{\partial \beta} \frac{\partial \beta}{\partial t_{0,\xi}}. \quad (13)$$

The results of these substitutions can be written more simply in terms of the following angular momentum operators and their transformation properties ($\epsilon_{\lambda \mu \nu}$ is the Levi-Civita antisymmetric tensor; $\lambda, \mu, \nu = x, y$ or z)

$$\hat{i}_{\lambda}(\mathbf{t}_i^F) = \frac{\hbar}{i} \sum_{\mu, \nu} \epsilon_{\lambda \mu \nu} t_{i,\mu}^F \frac{\partial}{\partial t_{i,\nu}^F}, \quad (14 a)$$

$$\hat{\mathbf{j}}^F = \sum_{i=1}^{N_F-1} \hat{\mathbf{j}}(\mathbf{t}_i^F), \quad (14 b)$$

$$\hat{\mathbf{j}} = \sum_F \hat{\mathbf{j}}^F = \hat{\mathbf{j}}^A + \hat{\mathbf{j}}^B, \quad (14 c)$$

$$\hat{i}_{\lambda} = \frac{\hbar}{i} \sum_{\mu, \nu} \epsilon_{\lambda \mu \nu} t_{0,\mu} \frac{\partial}{\partial t_{0,\nu}} = \frac{\hbar}{i} \sum_{\mu, \nu} \epsilon_{\lambda \mu \nu} R_{\mu} \frac{\partial}{\partial R_{\nu}}, \quad (14 d)$$

and the total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{I}} + \hat{\mathbf{j}} = \hat{\mathbf{I}} + \hat{\mathbf{j}}^A + \hat{\mathbf{j}}^B. \quad (14 e)$$

The transformation of the operators $\hat{\mathbf{j}}(\mathbf{t}_i^F)$, $\hat{\mathbf{j}}^F$ and $\hat{\mathbf{j}}$ is easy because \mathbf{C} is not a function of the coordinates \mathbf{t}_i^F and we can write, using (8)

$$\begin{aligned} \frac{\partial}{\partial t_{i,\xi}^F} &= \sum_{\eta} \frac{\partial z_{i,\eta}^F}{\partial t_{i,\xi}^F} \frac{\partial}{\partial z_{i,\eta}^F} \\ &= \sum_{\eta} C_{\xi \eta} \frac{\partial}{\partial z_{i,\eta}^F}. \end{aligned} \quad (15)$$

Using this result and the transformation properties of the Levi-Civita tensor, this yields

$$\begin{aligned} \hat{\mathbf{j}}_\lambda(\mathbf{t}_i^F) &= \frac{\hbar}{i} \sum_{\mu, \nu} \sum_{\xi, \eta} \epsilon_{\lambda\mu\nu} C_{\mu\xi} C_{\nu\eta} z_{i,\xi}^F \frac{\partial}{\partial z_{i,\eta}^F} \\ &= \frac{\hbar}{i} \sum_{\zeta} C_{\lambda\zeta} \sum_{\xi, \eta} \epsilon_{\zeta\xi\eta} z_{i,\xi}^F \frac{\partial}{\partial z_{i,\eta}^F}, \end{aligned} \tag{16}$$

which shows that the components of $\hat{\mathbf{j}}$ transform as the components of a vector

$$\hat{\mathbf{j}}(\mathbf{t}_i^F) = \mathbf{C}\hat{\mathbf{j}}(\mathbf{z}_i^F), \tag{17}$$

with the same expressions (14 *a-c*) for $\hat{\mathbf{j}}$ holding in the body-fixed coordinates \mathbf{z}_i^F .

The transformation of $\hat{\mathbf{l}}$, equation (14 *d*), is more complicated because one must use the chain rule expressions (10) to (13).

First, we substitute (11) into (13) and rewrite (10) as

$$\begin{aligned} \frac{\partial}{\partial t_{0,\xi}} &= R^{-1} C_{\xi x} \left(\frac{\partial}{\partial \beta} - \frac{i}{\hbar} \hat{j}_y \right) + R^{-1} C_{\xi y} \left(\operatorname{cosec} \beta \frac{\partial}{\partial \alpha} - \cot \beta \frac{i}{\hbar} \hat{j}_z + \frac{i}{\hbar} \hat{j}_x \right) \\ &\quad + C_{\xi z} \frac{\partial}{\partial R}, \end{aligned} \tag{18}$$

with the angular momentum operator $\hat{\mathbf{j}} = \hat{\mathbf{j}}^A + \hat{\mathbf{j}}^B$ expressed in body-fixed coordinates \mathbf{z}_i^F . Then, using (8 *a*), it is straightforward to derive the angular momentum operator $\hat{\mathbf{l}}$, (14 *d*), also in body-fixed coordinates. Instead, we write the result for the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{l}} + \hat{\mathbf{j}}$, which is slightly simpler. Just as $\hat{\mathbf{j}}$, see (17), $\hat{\mathbf{J}}$ transforms as

$$\hat{\mathbf{J}}(\mathbf{t}_i) = \mathbf{C}\hat{\mathbf{J}}(\mathbf{z}_i), \tag{19}$$

with the components of $\hat{\mathbf{J}}$ in the body-fixed coordinates \mathbf{z}_i^F , α and β , given by

$$\left. \begin{aligned} \hat{J}_x &= -\frac{\hbar}{i} \operatorname{cosec} \beta \frac{\partial}{\partial \alpha} + \cot \beta \hat{j}_z, \\ \hat{J}_y &= \frac{\hbar}{i} \frac{\partial}{\partial \beta}, \\ \hat{J}_z &= \hat{j}_z. \end{aligned} \right\} \tag{20}$$

The form of this operator is unusual, it is different from the more familiar expression for $\hat{\mathbf{J}}$ in a body-fixed frame [34] which is embedded by three Euler angles, α , β and γ , rather than just two. We observe that its components do not even satisfy angular momentum commutation relations

$$\left. \begin{aligned} [\hat{J}_x, \hat{J}_z] &= [\hat{J}_y, \hat{J}_z] = 0, \\ [\hat{J}_x, \hat{J}_y] &= \frac{\hbar}{i} \cot \beta \hat{J}_x + \frac{\hbar}{i} \hat{j}_z, \end{aligned} \right\} \tag{21}$$

so that we must call $\hat{\mathbf{J}}$ a pseudo-angular momentum operator. Also, the components of $\hat{\mathbf{J}}$ do not commute with $\hat{\mathbf{j}}$

$$\left. \begin{aligned} [\hat{J}_x, \hat{j}_\lambda] &= -\frac{\hbar}{i} \cot \beta \epsilon_{z\lambda\mu} \hat{j}_\mu, \\ [\hat{J}_y, \hat{j}_\lambda] &= 0, \\ [\hat{J}_z, \hat{j}_\lambda] &= -\frac{\hbar}{i} \epsilon_{z\lambda\mu} \hat{j}_\mu \quad \text{with } \lambda, \mu = x, y, z. \end{aligned} \right\} \quad (22)$$

Watson [5], in his *isomorphic* hamiltonian for linear molecules, restores the usual body-fixed expressions for $\hat{\mathbf{J}}$ by introducing an artificial third rotation angle γ . In the next section we show that the action of our $\hat{\mathbf{J}}$ on a suitably chosen basis is actually quite simple, however, so that there is no need to invoke this extraneous angle. In Appendix A we demonstrate that embedding with three (physically defined, rather than extraneous) Euler angles only leads to a formalism which is less transparent and more difficult to apply.

After all this preliminary work it is not too tedious to write the kinetic energy operator (6) in body-fixed coordinates, $\alpha, \beta, R, \mathbf{z}_i^F$; we only have to substitute (15) for the derivatives $\nabla(\mathbf{t}_i^F)$ and (18) for $\nabla(\mathbf{t}_0)$. The derivatives $\nabla(\mathbf{t}_i^F)$ commute with the matrix \mathbf{C} and so we easily find (using $\mathbf{C}^T \mathbf{C} = \mathbf{1}$) that the terms

$$\hat{K}_F = -\frac{\hbar^2}{2} \sum_{i,j=1}^{N_F-1} G_{ij}^F \nabla(\mathbf{z}_i^F) \cdot \nabla(\mathbf{z}_j^F), \quad (F = A, B) \quad (23)$$

are form-invariant. If $N_F < 2$ these terms vanish.

Substituting (18) into $\nabla^2(\mathbf{t}_0)$ we must remember that \mathbf{C} depends on α and β (but it commutes with $\hat{\mathbf{j}}$) and the result becomes

$$\begin{aligned} \hat{K}_{\text{INT}} &= -\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{t}_0) \\ &= -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2} \left[(\hat{J}_x - \hat{j}_x)^2 + (\hat{J}_y - \hat{j}_y)^2 \right. \\ &\quad \left. + \frac{\hbar}{i} \cot \beta (\hat{J}_y - \hat{j}_y) \right]. \end{aligned} \quad (24)$$

This can still be simplified somewhat further. We note, after substituting (19) and (20), that also the expression for \hat{J}^2 has an unusual form in the body-fixed frame

$$\begin{aligned} \hat{J}^2(\mathbf{t}_i) &= \mathbf{C}\hat{\mathbf{J}}(\mathbf{z}_i) \cdot \mathbf{C}\hat{\mathbf{J}}(\mathbf{z}_i) = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \mathbf{C}(\hat{\mathbf{J}}\mathbf{C}^T) \cdot \hat{\mathbf{J}} \\ &= \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \frac{\hbar}{i} \cot \beta \hat{J}_y \\ &= \hat{J}_x^2 + \text{cosec } \beta \hat{J}_y \sin \beta \hat{J}_y + \hat{J}_z^2. \end{aligned} \quad (25)$$

If we use this form, in combination with the result that $\hat{J}_z = \hat{j}_z$ and the commutation relations (22), we obtain

$$\hat{K}_{\text{INT}} = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2} [\hat{J}^2 + \hat{j}^2 - 2\hat{\mathbf{j}} \cdot \hat{\mathbf{J}}] \quad (26)$$

with \hat{J}^2 given by (25).

So far we have only analysed the kinetic energy part of the hamiltonian (2). The potential is, of course, not in general separable, but it is always possible to define an interaction potential

$$V_{\text{INT}}(R, \mathbf{z}_i^A, \mathbf{z}_i^B) = V(R, \mathbf{z}_i^A, \mathbf{z}_i^B) - V_A(\mathbf{z}_i^A) - V_B(\mathbf{z}_i^B), \quad (27)$$

where $V_F(\mathbf{z}_i^F)$ is the potential function of the isolated fragment F . Equation (27) is in the spirit of the Sorbie–Murrell approach to potential energy surface fitting [39]. This allows the hamiltonian to be written in the form of (1) with

$$\hat{H}_F = \hat{K}_F + V_F, \quad (F = A, B, \text{INT}). \quad (28)$$

This form of the hamiltonian has been given for the atom-diatom case ($N_A = 2, N_B = 1$). However, little mention has been made of the unusual form of the pseudo-angular momentum operators $\hat{\mathbf{J}}$ and \hat{J}^2 , as given by (20)–(22) and (25). Indeed, the commutation relations have often been ignored leading to the loose expression $(\hat{J} - j)^2$ [20, 35] or even the incorrect one $(\hat{J}^2 + j^2 - 2\hat{\mathbf{J}} \cdot \mathbf{j})$, (29) and (30) of [24]. The latter expression becomes formally correct, however, if one introduces an extraneous third rotation angle, as Watson [5] does in his isomorphic hamiltonian for linear molecules.

Expressions similar to ours were given by Istomin *et al.* [8] for the atom-diatom case with the diatom bond vector embedded along the z -axis. Tennyson and van der Avoird used a hamiltonian with the form of \hat{H}_{INT} for their diatom-diatom calculations on the van der Waals dimer of nitrogen [26]. Hougen [40] and Howard and Moss [41] derived equivalent expressions for linear molecules by applying the Podolsky transformation to the classical expression.

3. MATRIX ELEMENTS

In this section we discuss a suitable solution strategy for the (two-angle) body-fixed hamiltonian just derived. We suggest basis functions which reflect the partitioning of this form of the hamiltonian. We start by looking at the rovibrational wavefunctions of the monomers A and B . If these monomers are more or less rigid molecules or fragments it is appropriate to write the monomer hamiltonians $\hat{H}_F = \hat{K}_F + \hat{V}_F(\mathbf{z}_i^F)$ in the Watson form [4] and to assume that the vibrational and rotational problems can be solved separately. A practical way to do this for triatomic molecules has been proposed by Whitehead and Handy [13] and described also by Tennyson and Sutcliffe [15]. In principle this method can be generalized to larger systems; in practice one will have to make further approximations to keep the calculations tractable. The method amounts to assuming that the monomer rovibrational wavefunctions can be written as products

$$\Phi_{v_F}(\mathbf{Q}_F) \sum_{k_F} d_{k_F} D_{\Omega_F, k_F}^{(j_F)^*}(\boldsymbol{\omega}_F), \quad (29)$$

where the vibrational wavefunctions Φ_{v_F} depend on the internal monomer coordinates \mathbf{Q}_F and the rotational functions are linear combinations of normalized rotation matrix elements in the convention of Brink and Satchler [42]. The rotation angles $\boldsymbol{\omega}_F = (\phi_F, \theta_F, \psi_F)$ describe the orientations of coordinate frames fixed on the monomers, for instance via the Eckart conditions [1], with respect to the body-fixed dimer frame introduced in § 2. The assumption of (29) is equivalent to stating that the monomer hamiltonians \hat{H}_F are diagonal in the vibrational functions Φ_{v_F} .

Taking the expectation values of \hat{H}_F over Φ_{v_F} leads to effective rotational hamiltonians [43]:

$$\begin{aligned} \hat{H}_F^{\text{ROT}} &= [A_{v_F}(\hat{j}_a^F)^2 + B_{v_F}(\hat{j}_b^F)^2 + C_{v_F}(\hat{j}_c^F)^2] \\ &= \frac{1}{2}[(A_{v_F} + B_{v_F})\hat{j}^{F2} + (2C_{v_F} - A_{v_F} - B_{v_F})\hat{j}_c^{F2} \\ &\quad + \frac{1}{2}(A_{v_F} - B_{v_F})(\hat{j}_+^{F2} + \hat{j}_-^{F2})]. \end{aligned} \quad (30)$$

Here it has been assumed that the vibrationally averaged inverse inertia tensor of monomer F (in vibrational state v_F) has been transformed to principal axes a, b and c ; the rotational constants A_{v_F}, B_{v_F} and C_{v_F} are its principal values. The quantum number k_F is the component of the angular momentum \hat{j}^F on the monomer c -axis, Ω_F its component on the dimer z -axis. The coefficients d_{k_F} in (29) could be determined for the free monomers by diagonalising the hamiltonians \hat{H}_F^{ROT} .

If the monomers are really strongly bound one might also describe their vibrations by the harmonic oscillator model and their rigid body rotations by the hamiltonian (30). The rigid rotor model implies that one replaces the vibrationally averaged rotational constants A_{v_F}, B_{v_F} and C_{v_F} by their values A_e, B_e and C_e at the equilibrium structure. This approximation has been made almost universally, even in calculations on atom-diatom systems. Its accuracy has been demonstrated for HeHF by Tennyson and Sutcliffe [28]. For larger molecules or fragments it will undoubtedly be required. The approach with the vibrationally averaged monomer geometries has been used by Le Roy and Van Kranendonk [7] for H_2 -rare gas van der Waals dimers in several H_2 vibrational states.

If we assume that there is no strong coupling between the internal monomer vibrations and the dimer modes, which is justified if the gap between the frequencies is sufficiently large, then we can also average the interaction potential over the monomer vibrational wavefunctions. This yields an effective potential for the dimer rovibrational problem with the monomers A and B in states v_A and v_B , respectively

$$\begin{aligned} V_{\text{INT}}(R, \omega_A, \omega_B) \\ = \langle \Phi_{v_A}(\mathbf{Q}_A)\Phi_{v_B}(\mathbf{Q}_B) | V_{\text{INT}}(R, \mathbf{z}_i^A, \mathbf{z}_i^B) | \Phi_{v_A}(\mathbf{Q}_A)\Phi_{v_B}(\mathbf{Q}_B) \rangle. \end{aligned} \quad (31)$$

For brevity the vibrational state labels v_A and v_B have been omitted from V_{INT} . If we consider rigid body interactions, then we can replace Φ_{v_A} and Φ_{v_B} by delta functions at the equilibrium structures.

In order to express explicitly the dependence of the potential (31) on the monomer orientations ω_A and ω_B , we can expand it in terms of a complete angular basis. A general formula for such an expansion has been given by van der Avoird *et al.* [44]

$$V_{\text{INT}}(R, \omega_A, \omega_B) = \sum_{\substack{L_A, K_A \\ L_B, K_B, L}} v_{L_A, K_A, L_B, K_B, L}(R) A_{L_A, K_A, L_B, K_B, L}(\omega_A, \omega_B). \quad (32)$$

In our body-fixed frame the angular basis functions of [44] simplify to

$$\begin{aligned} A_{L_A, K_A, L_B, K_B, L} \\ = 8\pi^2(2L+1)^{1/2} \sum_{M_A} \begin{pmatrix} L_A & L_B & L \\ M_A & -M_A & 0 \end{pmatrix} D_{M_A K_A}^{(L_A)*}(\omega_A) D_{-M_A K_B}^{(L_B)*}(\omega_B), \end{aligned} \quad (33)$$

where the brackets denote a 3- j symbol. The effective hamiltonian for the dimer rovibrational problem can now be written as

$$\hat{H} = \hat{H}_A^{\text{ROT}} + \hat{H}_B^{\text{ROT}} + \hat{K}_{\text{INT}} + \hat{V}_{\text{INT}} \quad (34)$$

with the terms \hat{H}_F^{ROT} ($F=A, B$), \hat{K}_{INT} and \hat{V}_{INT} given by (30), (26) and (32) respectively.

Next we wish to introduce a convenient basis for this hamiltonian. Let us start in the space-fixed frame again, just as in § 2. With respect to this frame the monomer A and B orientations are defined by three Euler angles each, which we denote by ω'_A and ω'_B , and the orientation of the relative position vector \mathbf{R} is given by the polar angles (β, α) . A complete angular basis would be

$$\sum_{m_j, m} \sum_{\Omega_A, \Omega_B} D_{\Omega_A k_A}^{(j_A)*}(\omega'_A) D_{\Omega_B k_B}^{(j_B)*}(\omega'_B) \langle j_A \Omega_A j_B \Omega_B | j m_j \rangle \times Y_{lm}(\beta, \alpha) \langle j m_j l m | J M \rangle. \quad (35)$$

We have coupled the angular functions by means of standard Clebsch-Gordan coefficients [42], because J and M are good quantum numbers for the overall dynamical problem. Now we transform this basis to the body-fixed frame by the two Euler rotations over α and β , which are represented in coordinate space by the matrix \mathbf{C} , (9). The orientations of local frames on A and B with respect to this dimer frame have been denoted before by ω_A and ω_B ; the polar angles of \mathbf{R} in this frame are $(0, 0)$. The result is

$$\sum_{\Omega} \sum_{m_j, m} \sum_{\Omega_A, \Omega_B} D_{\Omega_A k_A}^{(j_A)*}(\omega_A) D_{\Omega_B k_B}^{(j_B)*}(\omega_B) \langle j_A \Omega_A j_B \Omega_B | j m_j \rangle \times Y_{lm}(0, 0) \langle j m_j l m | J \Omega \rangle D_{M\Omega}^{(J)*}(\alpha, \beta, 0). \quad (36)$$

Remembering that $Y_{lm}(0, 0) = (2l+1/4\pi)^{1/2} \delta_{m0}$, we can simplify this result and, instead of the basis (36), use the equivalent body-fixed basis

$$\sum_{\Omega_A, \Omega_B} D_{\Omega_A k_A}^{(j_A)*}(\omega_A) D_{\Omega_B k_B}^{(j_B)*}(\omega_B) \langle j_A \Omega_A j_B \Omega_B | j \Omega \rangle \times D_{M\Omega}^{(J)*}(\alpha, \beta, 0). \quad (37)$$

This basis is very convenient indeed for calculating the angular matrix elements over the hamiltonian (34). The operators \hat{H}_F^{ROT} (30) work only on the monomer rotation functions $D_{\Omega_F k_F}^{(j_F)*}(\omega_F)$ and we get

$$\langle j'_A k'_A j'_B k'_B j' \Omega' | \hat{H}_A^{\text{ROT}} + \hat{H}_B^{\text{ROT}} | j_A k_A j_B k_B j \Omega \rangle = \delta_{j'_A j_A} \delta_{j'_B j_B} \delta_{j' j} \delta_{\Omega' \Omega} [\delta_{j'_B k'_B} h_{j_A k'_A k_A} + \delta_{k'_A k_A} h_{j_B k'_B k_B}] \quad (38 a)$$

with ($F=A, B$)

$$h_{j_F k'_F k_F} = \frac{\hbar^2}{2} \delta_{k'_F k_F} [(A+B)j_F(j_F+1) + (2C-A-B)k_F^2] + \frac{\hbar^2}{4} \delta_{k'_F, k_F+2} (A-B) C^+_{j_F k_F} C^+_{j_F k_F+1} + \frac{\hbar^2}{4} \delta_{k'_F, k_F-2} (A-B) C^-_{j_F k_F} C^-_{j_F k_F-1} \quad (38 b)$$

and

$$C_{j k}^{\pm} = [j(j+1) - k(k \pm 1)]^{1/2}. \quad (39)$$

The operator \hat{K}_{INT} is expressed by (26) in terms of the angular momentum operator $\hat{\mathbf{j}} = \hat{\mathbf{j}}^A + \hat{\mathbf{j}}^B$ and the pseudo-angular momentum operator $\hat{\mathbf{J}}$, given by

(20). It can be written in the form

$$\hat{K}_{\text{INT}} = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2} [\hat{J}^2 + j^2 - 2j_z \hat{J}_z - j_+ \hat{J}_+ - j_- \hat{J}_-] \quad (40)$$

with the shift operators defined as

$$\hat{j}_{\pm} = j_x \pm i j_y \quad \text{and} \quad \hat{J}_{\pm} = \hat{J}_x \mp i \hat{J}_y. \quad (41)$$

Despite the peculiar form of the components of \hat{J} , see (20), and also of \hat{J}^2 , see (25), it can be shown, see appendix B, that the operators occurring in (40) acting on the basis (37) obey the same relations as normal angular momentum operators.

Thus we find

$$\begin{aligned} &\langle j'_A k'_A j'_B k'_B j' \Omega' | \hat{K}_{\text{INT}} | j_A k_A j_B k_B j \Omega \rangle \\ &= \hbar^2 \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{j' j} \left[\delta_{\Omega' \Omega} \left\{ -\frac{1}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right. \right. \\ &\quad \left. \left. + \frac{J(J+1) + j(j+1) - 2\Omega^2}{2\mu R^2} \right\} + \frac{1}{2\mu R^2} \left\{ \delta_{\Omega', \Omega+1} C_{j\Omega}^+ + C_{J\Omega}^+ \right. \right. \\ &\quad \left. \left. + \delta_{\Omega', \Omega-1} C_{j\Omega}^- + C_{J\Omega}^- \right\} \right]. \quad (42) \end{aligned}$$

The angular matrix elements over the potential V_{INT} can be completely evaluated by vector coupling techniques if we expand this potential (32) in terms of the angular functions (33). The result is

$$\begin{aligned} &\langle j'_A k'_A j'_B k'_B j' \Omega' | V_{\text{INT}} | j_A k_A j_B k_B j \Omega \rangle \\ &= \delta_{\Omega' \Omega} \sum_{\substack{L_A, K_A \\ L_B, K_B, L}} v_{L_A K_A L_B K_B L}(R) \\ &\quad \times g_{L_A K_A L_B K_B L}(j'_A j'_B j'; j_A j_B j; k'_A k'_B k'_A k_B; \Omega), \quad (43) \end{aligned}$$

where the generalized Gaunt coefficient is

$$\begin{aligned} g = &(-1)^{j'+j'_A+j'_B+L_A+L_B-k'_A-k'_B-\Omega} \\ &\times [(2j'_A+1)(2j_A+1)(2L_A+1)(2j'_B+1)(2j_B+1)(2L_B+1) \\ &\times (2j'+1)(2j+1)(2L+1)]^{1/2} \\ &\times \begin{pmatrix} j'_A & L_A & j_A \\ k'_A & K_A & k_A \end{pmatrix} \begin{pmatrix} j'_B & L_B & j_B \\ k'_B & K_B & k_B \end{pmatrix} \begin{pmatrix} j' & L & j \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{Bmatrix} j'_A & j_A & L_A \\ j'_B & j_B & L_B \\ j' & j & L \end{Bmatrix} \quad (44) \end{aligned}$$

in terms of $3-j$ and $9-j$ symbols [42].

With all the angular matrix elements of \hat{H} completely evaluated we can immediately write down the close-coupled equations [24, 32, 33] for the radial wavefunctions $\Psi^{JM}_{j_A k_A j_B k_B j \Omega}(R)$ in a generalized collision complex in the body-fixed approach. The corresponding equations in space-fixed coordinates have been obtained by Curtiss [36]. The space-fixed equations are easier to derive, but our body-fixed formalism is finally simpler and has several advantages in practical applications.

There are three general methods of obtaining bound state solutions of the close-coupled equations. First, by direct numerical solution of the coupled differential equations, as done by Dunker and Gordon [45] and also by Shapiro and Balint-Kurti [46] in their artificial-channels-scheme, and recently by Danby and Flower [47]. This, however, is unlikely to be feasible for problems where a large number of channels must be included. Secondly, by expansion in a radial basis set

$$\Psi^{JM}_{j_A k_A j_B k_B j \Omega}(R) = \sum_n \chi_n(R) C^{JM}_{j_A k_A j_B k_B j \Omega; n} \quad (45)$$

and solving a matrix eigenvalue problem.

The radial basis $\chi_n(R)$ can be either numerical [16, 24, 30] or analytical [10, 26, 31, 48]; the radial matrix elements over \hat{K}_{INT} , (42) and over the potential expansion coefficients $v_{L_A K_A L_B K_B L}(R)$ in (43) can be calculated accordingly. This approach is called by Le Roy *et al.* [24] the secular equation method, whereas Tennyson and van der Avoird [26] have proposed the acronym LC-RAMP (Linear Combination of Radial and Angular Momentum Products). Thirdly, one can introduce further approximations such as BOARS (Born Oppenheimer Angular and Radial Separation) [49] and solve the effective radial equation numerically.

Clearly, whichever method is chosen, the problem will in general be very large. Without symmetry there are $(N+1)(16N^4 + 64N^3 + 96N^2 + 64N + 15)/15$ angular basis functions for a $J=0$ calculation which includes all allowed functions with $j_A, j_B \leq N$. For $N=6$, for example, this gives 17927 angular channels. Full calculations with $J>0$ will be even more expensive.

A simplification, which is only possible in the body-fixed formalism, is caused by the neglect of the off-diagonal Coriolis term, the last term in (42), which is the only one that couples basis functions with different Ω . This approximation makes solutions differing only in parity, degenerate and it has been made on several occasions [10, 26, 30, 35] since these Coriolis terms often appear to be small.

4. CONCLUSIONS

In the preceding sections we have derived a general rovibrational or scattering hamiltonian for a collision complex formed by two polyatomics. From our discussion of a possible solution strategy, it is clear that, even in the body-fixed frame where the close-coupled equations are simpler than their space-fixed counterparts, the solution of the most general problem is likely to remain prohibitively expensive for the foreseeable future. However, there are certain possibilities which make the problem tractable.

- (1) If the fragments A and B are identical, permutation symmetry can reduce the size of the problem. This, together with (2), has allowed the van der Waals complexes $(\text{HF})_2$ [25] and $(\text{N}_2)_2$ [26] to be tackled. For the ethylene dimer $(\text{C}_2\text{H}_4)_2$ there is a potential surface available also [50, 51] and the solution of the dynamical problem might be feasible.
- (2) If one of the fragments or both are either symmetric or linear, there is a corresponding reduction in the complexity of the problem. The symmetry, which involves the occurrence of identical nuclei, can be introduced via the group of *feasible* permutations [43, 52]. For linear

molecules $F = A, B$ we can set the labels k_F in the basis (37) and K_F in the potential (32) equal to zero and use the property that $D_{M0}^{(L)*}(\alpha, \beta, \gamma) = (4\pi/2L+1)^{1/2} Y_{LM}(\beta, \alpha)$. Also the rotation operator $\hat{H}_F^{\text{ROT}} = B j_F^2$ (30), and its matrix elements (38) become considerably simpler, $h_{j_F} = \hbar^2 B j_F(j_F+1)$. This suggests that CO-H₂, for which a full surface, including the monomer stretch coordinates, has recently been published [53], could reasonably be tackled.

- (3) If one of the fragments, say B , is an atom a very great simplification results ($L_B=0, L=L_A; j_B=0, j=j_A$). Although, to our knowledge only atom-diatom problems have been treated, atom-polyatom problems are certainly feasible. Examples are the motion of Tl around ReO₄, suggested by Istomin *et al.* [8] and SF₆-Ar, for which a surface has recently been published [54]. The $M^+LH_4^-$ problem has recently been treated in an approximation which involved freezing the distance R [55].
- (4) If the rotational constants for one of the fragments or both are large compared with the strength of the anisotropic contributions in the potential, then the number of basis functions required for that fragment is greatly reduced. This is the case with most hydrogenic systems such as H₂-H₂, H₂-rare gas, where the H₂ monomers are practically unperturbed internal rotors, and, to a smaller extent, also with HCl-Ar, etc.
- (5) Other simplifications can arise from constraints that can be put on the motions of the fragments A and B , due to the way in which the interaction potential depends upon their orientations. A simple example is the case where the relative motion of A and B is confined to one torsional angle around the \mathbf{R} -axis, such as the internal rotation around single bonds in molecules, for example ethane C₂H₆. Then, we can put $K_A=K_B=0$, use the quantum numbers $\Lambda_A=|M_A|, \Lambda_B=|M_B|$ and maintain one internal angle only, $\phi = \phi_B - \phi_A$, in the basis (37). This case has been treated by Hougen [56]. A similar case is the (semi-) rigid bender model of Bunker *et al.* [20, 21].

So, although the solution of the rovibrational problem for the interaction of two general polyatomics is still some way off, there are several interesting problems that can be tackled within the scope of the formalism presented here. It should be remembered, moreover, that before a rovibrational calculation can be performed it is necessary to have a potential surface for the system. This potential can be obtained from *ab initio* calculations [44] or from experimental data but, if it is to be in any way realistic, its construction is likely to be considerably more expensive than the rovibrational calculations which use it.

APPENDIX A

Three-angle embedding

In §§ 2 and 3 we have used a rotation over two angles, α and β , to define the body-fixed frame with respect to the space-fixed one. This leaves us free to define a third angle of rotation γ to fix completely the frame in the system AB .

We can choose that angle by embedding one of the particles, say the last particle of monomer A with coordinates $\mathbf{z}_{N_A-1}^A$ in the original (partly) body-fixed frame of § 2, in the xz plane of the new (completely) body-fixed frame. If the polar angles of this particle $\mathbf{z}_{N_A-1}^A = \mathbf{r}$ are (θ, ϕ) , the rotation angle γ must be equal to ϕ , so that

$$\mathbf{r}' = \mathbf{C}'^T \mathbf{r} = \begin{pmatrix} r & \sin \theta \\ & 0 \\ r & \cos \theta \end{pmatrix} \quad (\text{A } 1)$$

with

$$\mathbf{C}' = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (\text{A } 2)$$

The coordinates of the other particles in the new body-fixed frame are

$$\text{and } \left. \begin{aligned} \mathbf{z}_i'^A &= \mathbf{C}'^T \mathbf{z}_i^A, & \text{for } i = 1, \dots, N_A - 2, \\ \mathbf{z}_i'^B &= \mathbf{C}'^T \mathbf{z}_i^B, & \text{for } i = 1, \dots, N_B - 1. \end{aligned} \right\} \quad (\text{A } 3)$$

The transformation of the angular momentum operators proceeds along the same lines as in § 2. The gradients and angular momenta of all particles referred to by (A 3) retain the same expressions in the new coordinates, $\mathbf{z}_i'^A$ and $\mathbf{z}_i'^B$. It is convenient to define a new angular momentum operator

$$\hat{\mathbf{j}}' = \sum_{i=1}^{N_A-2} \hat{\mathbf{j}}(\mathbf{z}_i'^A) + \sum_{i=1}^{N_B-1} \hat{\mathbf{j}}(\mathbf{z}_i'^B) \quad (\text{A } 4)$$

which is different from $\hat{\mathbf{j}}$ in that the first summation is restricted to $(N_A - 2)$ particles on A . Using this definition, we obtain

$$\hat{\mathbf{j}}(\mathbf{z}_i) = \mathbf{C}' \hat{\mathbf{j}}(\mathbf{z}_i')$$

with the following expressions holding for the components of $\hat{\mathbf{j}}$ in the new coordinates \mathbf{z}_i'

$$\left. \begin{aligned} \hat{j}_x &= \hat{j}'_x + \cot \theta \left(\hat{j}'_z - \frac{\hbar}{i} \frac{\partial}{\partial \phi} \right), \\ \hat{j}_y &= \hat{j}'_y + \frac{\hbar}{i} \frac{\partial}{\partial \theta}, \\ \hat{j}_z &= \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \end{aligned} \right\} \quad (\text{A } 5)$$

The transformation for the total angular momentum operator is

$$\hat{\mathbf{J}}(\mathbf{z}_i) = \mathbf{C}' \hat{\mathbf{J}}(\mathbf{z}_i')$$

with in the new frame

$$\left. \begin{aligned} \hat{J}_x &= \frac{\hbar}{i} \left(\sin \phi \frac{\partial}{\partial \beta} - \operatorname{cosec} \beta \cos \phi \frac{\partial}{\partial \alpha} + \cot \beta \cos \phi \frac{\partial}{\partial \phi} \right), \\ \hat{J}_y &= \frac{\hbar}{i} \left(\cos \phi \frac{\partial}{\partial \beta} + \operatorname{cosec} \beta \sin \phi \frac{\partial}{\partial \alpha} - \cot \beta \sin \phi \frac{\partial}{\partial \phi} \right), \\ \hat{J}_z &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} = \hat{j}_z. \end{aligned} \right\} \quad (\text{A } 6)$$

This operator has now obtained its familiar form in a completely body-fixed frame [3, 4] and, in contrast with (21), its components satisfy the commutation relations usually called *anomalous* ($\xi, \eta, \zeta = x, y$ or z)

$$[\hat{J}_\xi, \hat{J}_\eta] = -\frac{\hbar}{i} \epsilon_{\xi\eta\zeta} \hat{J}_\zeta. \quad (\text{A } 7)$$

They are different from the commutation relations of the space-fixed components only by the minus sign. Also, we recover the relation

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \quad (\text{A } 8)$$

contrary to (25) in the partly body-fixed frame. On the other hand, we find that

$$\begin{aligned} \hat{i}^2(\mathbf{z}_i) &= \mathbf{C}' \hat{\mathbf{j}}(\mathbf{z}_i') \cdot \mathbf{C}' \hat{\mathbf{j}}(\mathbf{z}_i') \\ &= \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2 + \mathbf{C}'(\hat{\mathbf{j}}\mathbf{C}'^T) \cdot \hat{\mathbf{j}} \\ &= \hat{j}_x^2 + \operatorname{cosec} \theta \hat{j}_y \sin \theta \hat{j}_y + \hat{j}_z^2 \end{aligned} \quad (\text{A } 9)$$

and, analogously

$$\hat{\mathbf{j}} \cdot \hat{\mathbf{J}} = \hat{j}_x \hat{J}_x + \operatorname{cosec} \theta \hat{j}_y \sin \theta \hat{J}_y + \hat{j}_z \hat{J}_z. \quad (\text{A } 10)$$

Finally, we look at the transformation of the hamiltonian. First, we consider the monomer terms \hat{K}_F in the kinetic energy operator (6), which obtain the same expressions (23) in the partly body-fixed coordinates \mathbf{z}_i^F as they had in the space-fixed coordinates \mathbf{t}_i^F . If we use these expressions, then the result for monomer A will become very messy in the completely body-fixed frame. The reason is that all the (non-diagonal) $\nabla(\mathbf{z}_i^F) \cdot \nabla(\mathbf{z}_j^F)$ terms in (23) which involve the particle $\mathbf{z}_{N_A-1}^A$ will have to be replaced by complicated chain rule expressions. If, instead of the coordinates \mathbf{t}_i defined by (4), we define Jacobi coordinates \mathbf{t}_i' , which makes G_{ij} diagonal as in (7'), then all monomer A terms with $i = 1, \dots, N_A - 2$ remain form-invariant, as well as the monomer B terms $i = 1, \dots, N_B - 1$, and we have to use the chain rule only for the term with $i = N_A - 1$. For this term in \hat{K}_A we can write

$$\nabla^2(\mathbf{z}_{N_A-1}^A) = \nabla^2(\mathbf{r}) = r^{-2} \left[\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \left(\frac{i}{\hbar} \right)^2 \hat{j}^2(\mathbf{r}) \right] \quad (\text{A } 11)$$

and apply some of the results just obtained for the angular momenta

$$\left. \begin{aligned} \hat{\mathbf{j}}(\mathbf{r}) &= \hat{\mathbf{j}}(\mathbf{z}_{N_A-1}^A) = \hat{\mathbf{j}} - \hat{\mathbf{j}}' \\ \hat{i}^2(\mathbf{r}) &= \hat{j}^2 + \hat{j}'^2 - 2\hat{\mathbf{j}}' \cdot \hat{\mathbf{j}} \end{aligned} \right\} \quad (\text{A } 12)$$

with \hat{j}^2 given by (A 9).

So, let us assume at this point that all the transformed coordinates \mathbf{z}_i^F in (A 3) and \mathbf{r} in (A 1) actually originate from Jacobi coordinates \mathbf{t}_i' , where μ_r is the mass of the reduced particle $\mathbf{t}'_{N_A-1} = \mathbf{C}\mathbf{z}_{N_A-1}^A$. For the other kinetic energy term in the hamiltonian, \hat{K}_{INT} , see (26), we can directly use the angular momentum results, (A 8) to (A 10), and the final expression becomes, in completely body-fixed coordinates

$$\begin{aligned}
\hat{H} = & \sum_{i=1}^{N_A-2} -\frac{\hbar^2}{2\mu_i} \nabla^2(\mathbf{z}_i'^A) + \sum_{i=1}^{N_B-1} -\frac{\hbar^2}{2\mu_i} \nabla^2(\mathbf{z}_i'^B) \\
& -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} - \left[\frac{\hbar^2}{2\mu R^2} + \frac{\hbar^2}{2\mu_r r^2} \right] \text{cosec } \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \\
& + \frac{1}{2\mu R^2} [\hat{J}_x^2 + \hat{J}_y^2 + \cot^2 \theta \hat{J}_z^2 - \frac{\hbar}{i} \left(2 \frac{\partial}{\partial \theta} + \cot \theta \right) \hat{J}_y + \cot \theta (\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x) \\
& + \hat{j}_x'^2 + \hat{j}_y'^2 + \cot^2 \theta \hat{j}_z'^2 + \frac{\hbar}{i} \left(\frac{\partial}{\partial \theta} + \cot \theta \right) \hat{j}_y' + \cot \theta (\hat{j}_x' \hat{j}_z' + \hat{j}_z' \hat{j}_x') \\
& - 2(\hat{j}_x' \hat{J}_x + \hat{j}_y' \hat{J}_y + \cot^2 \theta \hat{j}_z' \hat{J}_z) - 2 \cot \theta (\hat{j}_x' \hat{J}_z + \hat{j}_z' \hat{J}_x) \\
& - \frac{\hbar^2}{2\mu_r r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{2\mu_r r^2} \text{cosec}^2 \theta [\hat{J}_z^2 + \hat{j}_z'^2 - 2\hat{j}_z' \hat{J}_z] + \text{V}. \tag{A 13}
\end{aligned}$$

This hamiltonian reduces to that obtained by Tennyson and Sutcliffe [10] for the atom-diatom problem by setting $N_A=2$ and $N_B=1$, that is, omitting the first two terms and all the terms with \hat{j}' . In the atom-diatom case it is convenient because r can be identified with the diatom bond length and we have no further internal monomer coordinates. Still, one has to be careful with the singularity at $\theta=0$.

For larger systems it is clear that this hamiltonian (A 13), although it contains only normal angular momentum operators $\hat{\mathbf{J}}$ and $\hat{\mathbf{j}}'$, is not as useful as the one obtained from the two-angle embedding, given in § 2. First, the separation $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{\text{INT}}$ is destroyed by taking one (Jacobi) coordinate out of monomer A and we can no longer follow the solution strategy outlined in § 3. Secondly, the symmetry between the two fragments A and B , although formally still present, is no longer reflected by the form of this hamiltonian. Especially when the two fragments are identical, this symmetry can be very helpful in simplifying the solution (see the conclusions in § 4). Thirdly, there is a singularity for $\theta=0$, that is, when the Jacobi coordinate $\mathbf{z}_{N_A-1}^A = \mathbf{r}$, that is chosen to fix the third embedding angle, see (A 1), lies along the vector \mathbf{R} between the centres of mass.

APPENDIX B

Action of pseudo-angular momentum operators on body-fixed basis

In order to derive the action of the components of the pseudo-angular momentum operator $\hat{\mathbf{J}}$, defined by (20) on the basis (37), we apply a simple coordinate transformation. In the body-fixed coordinate system of §§ 2 and 3 the orientations of the molecules A and B are given by the Euler angles $\omega_A = (\phi_A, \theta_A, \psi_A)$ and $\omega_B = (\phi_B, \theta_B, \psi_B)$, respectively, and the angles (β, α)

describe the overall rotations of the system. Instead of the angles ϕ_A and ϕ_B , we introduce the new angles $\gamma = \phi_A$ and $\phi = \phi_B - \phi_A$. The angle ϕ is actually a true internal angle of the dimer AB , while γ is the third overall rotation angle if we embed the body-fixed frame with its xz -plane containing the local c -axis of monomer A . We shall not perform the three-angle embedding transformation on the hamiltonian, however, since this leads to the problems outlined in appendix A.

It is easily proved that the basis (37) can be rewritten in terms of the new angles as follows

$$\sum_{\Omega_A, \Omega_B} D_{\Omega_A k_A}^{(J_A)^*}(0, \theta_A, \psi_A) D_{\Omega_B k_B}^{(J_B)^*}(\phi, \theta_B, \psi_B) \times \langle j_A \Omega_A j_B \Omega_B | j \Omega \rangle D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma). \quad (\text{B } 1)$$

The components of $\hat{\mathbf{J}}$ (20), contain the operator

$$\hat{j}_z = \hat{j}_z^A + \hat{j}_z^B = \frac{\hbar}{i} \left(\frac{\partial}{\partial \phi_A} + \frac{\partial}{\partial \phi_B} \right). \quad (\text{B } 2)$$

Using the chain rule again, we find that

$$\left. \begin{aligned} \frac{\partial}{\partial \phi_A} &= \frac{\partial \gamma}{\partial \phi_A} \frac{\partial}{\partial \gamma} + \frac{\partial \phi}{\partial \phi_A} \frac{\partial}{\partial \phi} = \frac{\partial}{\partial \gamma} - \frac{\partial}{\partial \phi} \\ \frac{\partial}{\partial \phi_B} &= \frac{\partial \gamma}{\partial \phi_B} \frac{\partial}{\partial \gamma} + \frac{\partial \phi}{\partial \phi_B} \frac{\partial}{\partial \phi} = \frac{\partial}{\partial \phi} \end{aligned} \right\} \quad (\text{B } 3)$$

so that \hat{j}_z in the new coordinates reads simply

$$\hat{j}_z = \frac{\hbar}{i} \frac{\partial}{\partial \gamma}. \quad (\text{B } 4)$$

Substituting this into the expressions (25) and (20) we observe that \hat{J}^2 and \hat{J}_z obtain their usual forms [42] in terms of the body-fixed frame angles α , β and γ . They only operate on the last factor in the basis (B 1) and they yield the regular results

$$\left. \begin{aligned} \hat{J}^2 D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma) &= \hbar^2 J(J+1) D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma), \\ \hat{J}_z D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma) &= \hbar \Omega D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma). \end{aligned} \right\} \quad (\text{B } 5)$$

The operators $\hat{J}_{\pm} = \hat{J}_x \mp i \hat{J}_y$ defined by (41) we can call pseudo-shift operators. Substituting the result (B 4) for \hat{j}_z again and comparing them with the regular expressions for step-up and step-down operators \hat{J}'_{\pm} [42], we observe that they are related to the latter by

$$\hat{J}_{\pm} = \exp(\mp i \gamma) \hat{J}'_{\pm}. \quad (\text{B } 6)$$

Acting with those operators on the last factors in the basis (B 1)

$$\begin{aligned} \hat{J}_{\pm} D_{M \Omega}^{(J)^*}(\alpha, \beta, \gamma) &= \exp(\mp i \gamma) \hbar C_{J \Omega}^{\pm} D_{M \Omega \pm 1}^{(J)^*}(\alpha, \beta, \gamma) \\ &= \hbar C_{J \Omega}^{\pm} D_{M \Omega \pm 1}^{(J)^*}(\alpha, \beta, 0) \exp(i \Omega \gamma) \end{aligned} \quad (\text{B } 7)$$

substituting this result back into (B 1) again and re-expressing γ and ϕ in ϕ_A and ϕ_B , we obtain the desired result for the action of \hat{J}_{\pm} on the original basis (37).

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