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The *ab initio* calculation of the vibrational-rotational spectrum of triatomic systems in the close-coupling approach, with KCN and H_2Ne as examples

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A Hamiltonian for the vibration-rotation motions of atom–diatom systems is derived in body-fixed coordinates and a method for its solution as a close-coupled secular problem is formulated. The radial coordinate is expanded in Morse oscillator functions. Calculations on KCN and H_2Ne are presented. For KCN the neglect of Coriolis interactions is found to have little effect. Extensions of the method to problems in more dimensions are suggested.

I. INTRODUCTION

The problem of the rotation-vibration spectrum of triatomic systems is one of great theoretical interest. It has been much studied since the early days of quantum mechanics and recent interest is strong in the context of triatomics formed by atom–diatom molecular beams, especially van der Waals molecules. A review of recent experimental and theoretical work on van der Waals molecules is given by Le Roy and Carley.[1] Carney, Sprandel, and Kern[2] provide a more general review of variational methods used for solving the dynamical problem for triatomics. Solutions for larger systems are still almost unknown.[3]

The close-coupling approach was originally formulated for the scattering of an atom by a diatom[4] and its use for bound state problems has largely been confined to loosely bound van der Waals molecules.[1,5,6] The approach, however, is applicable to any triatomic system whose potential can conveniently be expressed as an expansion in Legendre polynomials,

$$V(R, r, \theta) = \sum_{\lambda} V_{\lambda}(R, r) P_{\lambda}(\cos\theta) , \qquad (1)$$

where R, r, and θ are suitable internal coordinates. Indeed, a close-coupling method has recently been successfully applied to water.[7] Such a method can be expected to perform well for any molecule which performs large amplitude librations in the bending (θ) coordinate.

Le Roy and Van Kranendonk[5] implemented a close-coupling method in space-fixed coordinates which uses a numerically generated radial basis. They utilized this method for H_2–X systems for which it is particularly appropriate as the basis is nearly saturated by only one basis function.[8,9] For systems with less isotropic potentials, however, the use of inconveniently large angular basis sets becomes necessary.[10]

Istomin, Stepanov, and Zhilinski[11] developed a body-fixed method for triatomic molecules with two large amplitude coordinates. However, their method requires the potential in a special form in order that all integrals may be evaluated analytically. They attempted only problems with model potentials. Both their radial and angular basis sets are developed by solving suitable one dimensional problems. They found, however, that their hindered rotor functions developed for localized bending states gave a poor description of the highly excited states lying above the barrier to free internal rotation. For this reason, we use only uncontracted free rotor functions although their use can lead to larger secular problems if a good description of only low lying localized states is required.

The aim of the present work is to obtain a compact and useful expression for the Hamiltonian for the triatomic system regarded as a collision complex, in a completely body-fixed coordinate system and to attempt approximate solutions of the resulting eigenvalue problems for potential functions written in the form of Eq. (1) using a basis set expansion of the radial coordinate function.

Body-fixed coordinates not only provide a more natural way of representing the problem and a convenient starting point for approximations such as separation of the vibration and rotation problem, they also have considerable computational advantages. The analytic angular integration is considerably simpler; for the atom–diatom, only 3-j symbols are required compared with 6-j symbols in space fixed coordinates. Furthermore, these 3-j symbols have to be calculated only for certain diagonal blocks of the problem when J, the total angular momentum quantum number, is greater than 0. If the method is to be extended, as is our aim, to the diatom–diatom problem, this saving on the angular integration will be very important.

Whilst the use of numerical basis sets has advantages in speed of convergence, especially for highly isotropic problems, they are not without their drawbacks in terms of computer storage and integration time. It would be very difficult, e.g., to solve the full triatomic problem using two numerical basis sets generated by explicit integration of two separate pseudodiatomic problems. By the use of a set of flexible orthogonal polynomials as a basis we hope to obtain a method which will not only perform well for the atom-rigid diatom problem, but

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can also be extended to the full triatomic problem in three dimensions.

As exemplary systems, we use two molecules which, while both being "floppy" in the bending coordinate, have very different behavior in the stretching direction. While KCN can be expected to have several hundred bound vibrational states, it is known from experiment that H_2–Ne does not support any vibrationally excited states and only a few rotationally excited ones.[12] This will enable us to assess the performance of our method on two very dissimilar systems.

The pure rotational spectrum of KCN has been well studied experimentally.[13] In contrast the only direct measurement of the gas-phase vibrational spectrum was largely inconclusive,[14] although vibrational fundamentals have been reported from a matrix isolation study.[15] An *ab initio* potential energy surface for KCN in two dimensions has been calculated by Wormer and Tennyson.[16] Furthermore, calculations on this system have been carried out by the authors,[17] using the conventional Eckart Hamiltonian due to Watson,[18] and by Tennyson and van der Avoird[10] using a space-fixed Hamiltonian. Both calculations utilized the Wormer–Tennyson potential, so that detailed comparisons can be made between these and the present calculations.

The H_2Ne van der Waals complex has been well studied experimentally and all its bound states have been assigned from its hyperfine spectrum by Reuss and coworkers.[2] These results suggest that the potential of Andreas *et al.*,[19] obtained from measurements of differential cross-sections, is the most accurate; it reproduces the hyperfine spectrum with only a slight correction, which, for our purposes, is insignificant. Potentials due to Carley[6] and Tang and Toennies[20] are also available. Carley used the space-fixed method of Le Roy and Van Kranendonk[5] to obtain the bound states of his potential. We will compare his results with space and body-fixed close-coupling calculations on the potential of Andres *et al.* and assess the vector model proposed by Waaijer, Jacobs, and Reuss.[21]

II. THE HAMILTONIAN

If the electrons are considered simply as providing an effective field for nuclear motion then the Hamiltonian for a triatomic system is

$$\hat{H} = \frac{-\hbar^2}{2} \sum_{i=1}^{3} \frac{1}{m_i} \nabla_i^2(\mathbf{x}_i) + V . \tag{2}$$

Here $\nabla^2(\mathbf{x}_i)$ is the Laplacian for the ith nucleus and the potential V is the sum of the electronic energy and nuclear repulsion energy. Since V is invariant under uniform translations and rotations, H can be regarded as specified in an arbitrary axis frame.

To remove the translational motion from the kinetic energy operator the following coordinate transformation is chosen:

$$\begin{aligned} \mathbf{t}_1 &= \mathbf{x}_1 - \mathbf{x}_d , \\ \mathbf{t}_2 &= \mathbf{x}_3 - \mathbf{x}_2 , \\ \mathbf{X} &= M^{-1} \sum_{i=1}^{3} m_i \mathbf{x}_i , \end{aligned} \tag{3}$$

where $\mathbf{x}_i$ denotes a column vector of coordinates in the original frame and $\mathbf{t}_i$ denotes a column vector of new coordinates in the same axis frame. The other symbols in Eq. (3) are defined as follows:

$$\begin{aligned} m_d &= m_2 + m_3 , \\ M &= m_1 + m_d , \\ \mathbf{x}_d &= m_d^{-1}(m_2\mathbf{x}_2 + m_3\mathbf{x}_3) . \end{aligned} \tag{4}$$

Clearly, $\mathbf{x}_d$ represents the coordinates of the center-of-mass of a diatomic system [atoms 2 and 3] and X is the total center-of-mass. The coordinate system can be thought of as describing the "collision" of an atom [atom 1] and a diatomic system.

The Jacobian for this transformation is a constant and so may be neglected. Straightforward use of the chain rule shows that the translation-free part of the Hamiltonian (2) can be written in the new coordinates as

$$\hat{H}' = \frac{-\hbar^2}{2\mu_1} \nabla^2(\mathbf{t}_1) - \frac{\hbar^2}{2\mu_2} \nabla^2(\mathbf{t}_2) + V , \tag{5}$$

where

$$\begin{aligned} \mu_1^{-1} &= m_1^{-1} + m_d^{-1} , \\ \mu_2^{-1} &= m_2^{-1} + m_3^{-1} . \end{aligned} \tag{6}$$

This corresponds to the so-called "space-fixed" Hamiltonian referred to in the previous section.

To make the rigid rotational motions in Eq. (5) explicit, it is necessary to embed an axis frame in the system and relate this frame to the original frame by means of an orthogonal transformation. The three variables (Euler angles, say) that parametrize this transformation are then the three variables that describe the rigid rotations. Three more internal coordinates must then be chosen to describe the remaining motions. Thus, if the original axis frame is denoted by the right-hand side set of Cartesian unit vectors, $\hat{e}_\alpha$ ($\alpha = x, y, z$) and the embedded frame by $\hat{\epsilon}_\alpha$, then

$$\hat{\boldsymbol{\epsilon}} = \hat{\mathbf{e}}\mathbf{C} , \tag{7}$$

where the vectors have been collected together as row matrices.

Any vector can be written in the original frame as

$$\vec{\mathbf{t}}_i = \hat{\mathbf{e}}\mathbf{t}_i \tag{8}$$

and is equal to the vector expressed in the embedded frame

$$\vec{\mathbf{z}}_i = \hat{\boldsymbol{\epsilon}}\mathbf{z}_i , \tag{9}$$

if

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

In this work, the internal coordinates will be chosen as R, the length of $\mathbf{t}_1$ and the distance from the center of diatomic mass to the atom, r the length of $\mathbf{t}_2$ and the diatomic bond length and θ the angle between $\mathbf{t}_1$ and $\mathbf{t}_2$. Thus, if the polars of $\mathbf{t}_1$ are (R, γ, δ) and of $\mathbf{t}_2(r, \alpha, \beta)$, then

$$\cos\theta = \sin\gamma \sin\alpha \cos(\beta - \delta) + \cos\gamma \cos\alpha . \tag{11}$$

The frame will be embedded such that the system lies in a plane with R as the z axis in that plane and θ the polar angle of r, thus,

$$\mathbf{z}_1 = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}, \quad \mathbf{z}_2 = r \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}, \tag{12}$$

where $\mathbf{t}_i$ is related to $\mathbf{z}_i$ by Eq. (10) above. The conditions (12) implicitly define the required Euler angles on the additional requirement that $\mathbf{C}$ is a pure rotation and the range of θ is $(0, \pi)$.

We note that this embedding is necessarily arbitrary, although it arises naturally from analogy with atom–diatom scattering problems. In contrast, Istomin *et al.*[11] chose to fix their diatom along the z axis. This choice makes little difference to the resultant secular equations for the triatomic but is difficult to generalize to larger collision complexes.

It is now possible to transform Eq. (2) to the new coordinate system but as the algebra involved is rather intricate and tedious, it will not be considered further here. An outline of the method is given in Appendix A or more fully by Sutcliffe,[22] and the final result is

$$\hat{H} = \hat{K}_{VR} + \hat{K}_V + V(R, r, \theta), \tag{13}$$

where

$$\hat{K}_V = \frac{-\hbar^2}{2\mu_1 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2\mu_2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2}\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right), \tag{14}$$

$$\hat{K}_{VR} = \frac{1}{2}\left[\frac{1}{\mu_1 R^2}(\Pi_x^2 + \Pi_y^2) + \left(\frac{\cot^2\theta}{\mu_1 R} + \frac{\operatorname{cosec}^2\theta}{\mu_2 r^2}\right)\Pi_z^2 + \frac{\cot\theta}{\mu_1 R^2}(\Pi_x\Pi_z + \Pi_z\Pi_x)\right] + \frac{\hbar}{i}\frac{1}{\mu_1 R^2}\left(\frac{\partial}{\partial\theta} + \frac{\cot\theta}{2}\right)\Pi_y. \tag{15}$$

In Eq. (15) the quantities Π_α are total angular momentum operators, depending only on the Euler angles, defined so that

$$\mathbf{L} = -\mathbf{C}\Pi, \tag{16}$$

where Π is a column vector of components and the L_α are the components of the total angular momentum operator expressed in $\mathbf{t}_i$ coordinates. It should be noticed that the negative sign in Eq. (16) ensures that the components of Π obey standard commutation conditions.

The internal coordinate part of the Jacobian for the transformation is $r^2 R^2 \sin\theta$ and the Euler angle part is the sine of the second Euler angle.

Any eigenfunction of the problem specified by the Hamiltonian (13) can be written as a sum of products of internal functions and rotational eigenfunctions

$$\sum_{k=-J}^{J} \Psi_{Jk}(r, R, \theta)\mathfrak{D}^J_{Mk}. \tag{17}$$

Here, $\mathfrak{D}^J_{Mk}$ is a rotation matrix element in the convention of Brink and Satchler[23] and is a function only of the three Euler angles of the transformation. In the absence of magnetic fields, the energy is independent of M and $\mathfrak{D}^J_{Mk}$ is an ordinary angular momentum eigenfunction such that

$$\Pi^2\mathfrak{D}^J_{Mk} = \hbar^2 J(J+1)\mathfrak{D}^J_{Mk},$$
$$\Pi_z\mathfrak{D}^J_{Mk} = \hbar k\mathfrak{D}^J_{Mk}, \tag{18}$$
$$\Pi_\pm\mathfrak{D}^J_{Mk} = \hbar C^\pm_{Jk}\mathfrak{D}^J_{Mk\pm1},$$

with

$$\Pi_\pm = \Pi_x \pm i\Pi_y,$$
$$C^\pm_{Jk} = [J(J+1) - k(k\pm1)]^{1/2}. \tag{19}$$

If the Hamiltonian (13) is allowed to operate on Eq. (17), then multiplying from the left-hand side by a set of angular functions $\mathfrak{D}^{J*}_{Mk'}$ and integrating over Euler angles, an effective Hamiltonian is obtained which operates on Ψ_{JK}. This Hamiltonian has the same form as Eq. (13) and the part arising from $\hat{K}_{VR}$ is

$$\delta_{k',k+1}C^+_{Jk}\frac{\hbar^2}{2\mu_1 R^2}\left(-\frac{\partial}{\partial\theta} + k\cot\theta\right) + \delta_{k',k-1}C^-_{Jk}\frac{\hbar^2}{2\mu_1 R^2}\left(\frac{\partial}{\partial\theta} + k\cot\theta\right) + \delta_{k,k'}\frac{\hbar^2}{2}\left\{\frac{[J(J+1) - k^2]}{\mu_1 R^2} + k^2\operatorname{cosec}^2\theta\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\right\}, \tag{20}$$

while the part arising from $\hat{K}_V$ is $\hat{K}_V$ itself multiplied by $\delta_{k'k}$. In this form the Hamiltonian is essentially the same as that derived for the special case of the triatomic from the more general expression developed by Hirschfelder, Curtis, and Adler.[24]

The form of the coordinate system is clearly appropriate to a description of the "collision" of an atom (nucleus 1) with a diatomic species [nuclei 2 and 3] in a close-coupled molecule and similar Hamiltonians have been used for atom–diatom scattering calculations,[4] although in practice additional approximations are often made, see, e.g., Ref. 25. In these circumstances a sensible expansion of Ψ_{Jk} has the form

$$\Psi_{Jk}(r, R, \theta) = \sum_{n,l} \psi_n(r, R)\Theta_{lk}(\theta), \tag{21}$$

where Θ_{lk} is a standard normalized associated Legendre polynomial with the Condon and Shortley phase conventions.[26] It is assumed that Ψ_n is independent of the rotations and that all the close-coupling occurs through the θ dependence.

Letting the effective Hamiltonian operate on functions of this form, then multiplying from the left-hand side by $\Theta_{l'k'}$ and integrating over θ leads to another effective Hamiltonian operating on $\psi_n(r, R)$, namely,

$$\hat{H} = \hat{H}_V + \hat{K}_{\text{VIB ROT}}, \tag{22}$$

where

$$\hat{H}_V = \delta_{kk'}\delta_{ll'}\left[\frac{-\hbar^2}{2\mu_1 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2\mu_2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2}{2}\, l(l+1)\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\right]$$

$$+\,\delta_{kk'}\langle\Theta_{l'k}|V(r,R,\theta)|\Theta_{lk}\rangle_\theta\ , \tag{23}$$

the potential integral being only over θ, and

$$\hat{K}_{\mathrm{VIBROT}} = -\delta_{k',k+1}\delta_{l',l}C^+_{JK}C^+_{lk}\hbar^2/(2\mu_1R^2) - \delta_{k',k-1}\delta_{l',l}C^-_{Jk}C^-_{lk}\hbar^2/(2\mu_1R^2) + \delta_{k',k}\delta_{l',l}\hbar^2[J(J+1)-2k^2]/(2\mu_1R^2)\ . \tag{24}$$

The secular equations appropriate to the operator (22) are called the close-coupled equations.[4] It can be seen that the choice of Eq. (21) is such that terms arising from the last expressions in Eqs. (14) and (20) cancel each other, enabling the vibration-rotation of the effective operator (24) to be expressed entirely in terms of the radial coordinates of the "atom" in the problem.

Le Roy and Carley[1] derive, but do not apply, a similar "body-fixed" Hamiltonian by transforming their space-fixed Hamiltonian (5) over the two Euler angles necessary to embed z_1 [Eq. (12)]. They, however, do not perform the final transformation over ϕ to fix z_2. This gives them basis functions partitioned between internal and rotational functions of the form

$$\sum_{k=-J}^{+J}\sum_{l,n}\psi_n(r,R)Y_{lk}(\theta,\phi)\mathfrak{D}^J_{Mk}(\alpha',\beta',0)\ , \tag{25}$$

where α' and β' are the relevant Euler angles and Y_{lk} is a spherical harmonic.[23] We note, however, that the relationship

$$\Theta_{lk}(\theta)\mathfrak{D}^J_{Mk}(\alpha',\beta',\phi) = Y_{lk}(\theta,\phi)\mathfrak{D}^J_{Mk}(\alpha',\beta',0) \tag{26}$$

means that the two basis sets are equivalent. Differences in the approaches arise only if some approximate partitioning between rotational and vibrational problems is attempted.

In the present work, the further assumption is made that the diatomic portion of the system is very stiff and can be assumed rigid allowing r to be replaced by a suitable "equilibrium" value r_0. This causes all differential operators in r to vanish and reduces H_V to a pseudodiatomic operator of the form

$$\hat{H}_V = \delta_{k'k}\delta_{l'l}\left[-\frac{\hbar^2}{2\mu_1R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{\hbar^2 l(l+1)}{2\mu_1R^2} + \frac{\hbar^2 l(l+1)}{2\mu_2 r_0^2}\right] + \delta_{kk'}\langle\Theta_{l'k}|V(R,r_0,\theta)|\Theta_{lk}\rangle_\theta\ . \tag{27}$$

If the potential can be expanded in the form of Eq. (1), the angular integration over the potential can be done by standard means so that the last term in Eq. (27) can be replaced by

$$\sum_\lambda g_\lambda(l',l,k)\,V_\lambda(R)\ , \tag{28}$$

where the g_λ are the Gaunt coefficients given by[27]

$$g_\lambda(l',l,k) = (-1)^k[(2l'+1)(2l+1)]^{1/2}\begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & \lambda & l \\ -k & 0 & k\end{pmatrix}, \tag{29}$$

where the 3-j symbols are standard.[23]

With these assumptions the problem has been reduced to a one-dimensional one and it remains only to choose a tractable set of functions of R and to solve the secular problem predicted by Eq. (22). Given the form of the Hamiltonian, a suitable choice for the functions ψ_n would be

$$\psi_n(r_0,R) = R^{-1}H_n(R)\ , \tag{30}$$

where the constant part of the function arising from the r_0 dependence has been ignored. Functions of this form remove the R^2 term arising from the Jacobian in the volume element of the integration. The effective Hamiltonian operating on $H_n(R)$ consists of Eqs. (27) plus (24) with the differential operator in Eq. (27) replaced by

$$\frac{-\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R^2}\ . \tag{31}$$

The symmetry of the rotational problem under inversion allows each set of close-coupled secular equations, for which J and M are good quantum numbers, to be subdivided into blocks symmetric and antisymmetric with respect to a sign change in k. This is done by transforming the angular basis functions into $\phi^\pm_{Jkl}$ (dropping the redundant quantum number M),

$$\phi^\pm_{Jkl} = 2^{-1/2}(\mathfrak{D}^J_{Mk}\Theta_{lk} \pm \mathfrak{D}^J_{M-k}\Theta_{l-k})\ , \tag{32}$$

with $k \ge 1$. For $k=0$, $\phi^-_{J0l}=0$ and $\phi^+_{J0l}=\mathfrak{D}^J_{M0}\Theta_{l0}$. All the relevant integrals of the form $\langle\phi^+_{Jkl}|\hat{O}|\phi^-_{Jk'l'}\rangle$ are identically zero. Those within each block for $\hat{K}_{\mathrm{VIBROT}}$ are unchanged with the exception

$$\langle\phi^+_{J0l}|\hat{K}_{\mathrm{VIBROT}}|\phi^+_{J1l}\rangle = -2^{1/2}C^+_{J0}C^+_{l0}\frac{\hbar^2}{2\mu_1R^2}\ . \tag{33}$$

However, even with this additional partitioning the dimensions of the secular problem increase linearly with J. This makes calculation of rotationally excited states prohibitively expensive unless some further approximation is made. In body-fixed coordinates, it is only the Coriolis and angular momentum terms like those of Eq. (33) which link blocks with differing k values. If these terms are neglected k becomes a good quantum number and no secular problem larger than that of the $J=0$ state needs to be solved in order to obtain the rotationally excited states. A similar approximation has been used in scattering problems.[28] Holmgren *et al.*[29] found that the neglect of Coriolis interactions on had a small effect on the energy levels of the "floppy" van der Waals molecule Ar–HCl. Our previous calculations[17] showed that, at least for the vibrational ground state, rotation-vibration coupling could also be neglected for KCN. In Sec. IV we explore the effect of neglecting terms off-diagonal in k for KCN, but first we develop radial basis functions.

III. CHOICE OF RADIAL FUNCTIONS

If the system is in a $J=0$ state the effective Hamiltonian for $H_n(R)$ becomes

$$\hat{H} = -\frac{\hbar^2}{2\mu_1}\frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu_1 R^2} + \sum_\lambda g_\lambda(l', l, \lambda)\, V_\lambda(R) , \tag{34}$$

where the term due to the rigid rotation of the diatomic has been dropped and the Kronecker deltas are regarded as implicit. It is this pseudodiatomic Schrödinger equation given by this Hamiltonian acting on $H_n(R)$ with $\lambda=0$ that Le Roy and Van Kranendonk[5] solve explicitly to get their numerical radial basis functions.

We choose to approach the problem in terms of known solutions for diatomic molecules. If the potential has a minimum at some value R_e of R, it is not unreasonable to assume a Morse-oscillator form for the functions[30]

$$H_n(y) = \beta^{1/2} N_{n\alpha} \exp(-y/2)\, y^{b/2} L_n^\alpha(y) , \tag{35}$$

where

$$y = A \exp[-\beta(R-R_e)] \tag{36}$$

and where $N_{n\alpha} L_n^\alpha(y)$ are normalized associated Laguerre polynomials for which the definition of Gradshteyn and Ryzhik[31] is adopted.

If the potential in Eq. (34) has exactly the Morse form[30]

$$V_0(R) = D_e\{1-\exp[-\beta(R-R_e)]\}^2 - D_e , \tag{37}$$

it is possible to write the scaling parameters in Eq. (36) in terms of the dissociation energy D_e and the energy of the fundamental vibration ω_e,

$$A = 4D_e/\omega_e , \quad \beta = \omega_e(\mu_1/2D_e)^{1/2} . \tag{38}$$

In practice, these parameters can be adjusted for each problem to give an optimal basis set expansion.

For the Morse potential (37), b equals α, and α, the index on $L_n^\alpha(y)$ in Eq. (35), is equal to $A-(2n+1)$, where n is the order of the polynomial and the degree of vibrational excitation. As α must be greater than -1, the number of bound states supported by a particular Morse potential is $A/2-1$.

In the new variable system of Eq. (36) the differential operator in Eq. (34) becomes

$$\beta^2\left(y^2\frac{d^2}{dy^2} + y\frac{d}{dy}\right) , \tag{39}$$

the Jacobian for the transformation is $-\beta^{-1}y^{-1}$ and the inverse transformation is

$$R = \beta^{-1}\ln(A/y) + R_e . \tag{40}$$

As first pointed out by ter Haar,[32] the Morse oscillators do not obey the correct boundary conditions at $R=0$. Here the function $H_n(y_0)$ should vanish, where

$$y_0 = A\exp(\beta R_e) . \tag{41}$$

The wave function should also vanish as R tends to ∞, that is as y tends to 0. Clearly, the second boundary condition is satisfied by Eq. (35), if $\beta \geq 0$, but the first is not. It will be remembered, however, that it is possible to get a very good account of diatomic vibrational motion using such a function even though it does violate the boundary conditions, because typically values of a 100 or more can be assigned to y_0. Thus, because of the exponential in Eq. (35), the function has effectively vanished by the time y reaches y_0.

It will be assumed that this sort of behavior can be expected in the present problem and that without loss of accuracy y_0 may be replaced by ∞ in all integral limits. This means that the overlap and kinetic energy integrals between functions like Eq. (35) may be written in terms of the integral

$$I(n,\alpha;n',\alpha';m) = N_{n\alpha}N_{n'\alpha'}\int_0^\infty e^{-y}\, y^m L_n^\alpha(y) L_{n'}^{\alpha'}(y)\, dy , \tag{42}$$

which can be evaluated analytically. The algebra involved is lengthy and is summarized in Appendix B. The final result is

$$I(n,\alpha,n',\alpha';m) = (-1)^{n+n'} N_{n\alpha}N_{n'\alpha'} \times \sum_{\sigma=0}^{n'} \binom{m-\alpha}{\tau+\sigma}\binom{m-\alpha'}{\sigma} \times \Gamma\frac{(m+n'-\sigma+1)}{(n'-\sigma)!} , \tag{43}$$

where the notation is conventional and

$$\tau = n-n' \geq 0 , \quad m > -1 . \tag{44}$$

Formula (43) is general, but in practice we have used only integer values of m and α. The normalization constants $N_{n\alpha}$ have been retained in the formula as they have the effect of reducing all factorials which depend on α to ratios. As α can be of order several hundred this is important in any practical application. Yutsever *et al.*[33] have recently published a similar formula for a Sturmian basis.

From this result it is seen that if α is regarded as a constant for the problem and b is chosen as $(\alpha+1)$, then the set of functions (35) form a complete orthonormal set for all n. Such a set is convenient for calculations and makes the explicit inclusion of continuum functions, which has led to the placing of artificial walls in the potential function[21,34] unnecessary. Such a basis set with α fixed at the integer value of A will be used in the following.

The kinetic energy integrals within this basis can be evaluated analytically. Use of the recurrence relationships for Laguerre polynomials and formula (43) gives

$$\frac{-\hbar^2}{2\mu_1}\int_0^\infty H_{n'}(R)\frac{d^2}{dR^2}H_n(R)\, dR = \frac{\hbar^2\beta^2}{8\mu_1}\{\delta_{nn'}[2n(\alpha+n+1)+\alpha+1] - \delta_{n,n'+2}[(\alpha+n)(\alpha+n+1)n(n-1)]^{1/2}\} , \quad n \geqslant n' , \tag{45}$$

which has only one off-diagonal element.

The integral associated with the inverse moment-of-inertia operator [the second term in Eq. (34)] is

TABLE I. Diagonal ($n = n'$) elements of the integral of Eq. (46) evaluated by M point Gauss–Laguerre integration in a.u. ×10^6.[a]

n	0	1	2	3	4
$M = 4$	0.670 110	0.673 482	0.675 700	···	···
5	0.670 110	0.673 482	0.676 868	0.678 703	···
6	0.670 110	0.673 482	0.676 868	0.680 268	0.681 715
7	0.670 110	0.673 482	0.676 868	0.680 268	0.683 683
8	0.670 110	0.673 482	0.676 868	0.680 268	0.683 683
15	0.670 110	0.673 482	0.676 868	0.680 268	0.683 683

[a] Units: hartree bohr^{-2}. 1 hartree (E_h) = 4.3598 aJ, 1 bohr (a_0) = 5.291 77 × 10^{-11} m.

$$N_{n\alpha} N_{n'\alpha} \frac{\hbar^2}{2\mu_1\beta} \times \int_0^\infty e^{-y} y \left[R_e + \beta^{-1} \ln(A/y)\right]^{-2} L_n^\alpha(y) L_{n'}^\alpha(y)\, dy \, . \tag{46}$$

Clearly, this integrand diverges at $y = y_0$ and so the integral makes no sense unless the vanishing of the functions refered to above is sufficiently strong.

The integral (46) resists analytic evaluation (although asymptotic forms have been suggested for it[35]) as, in general, do the radial integrals over the potential function $V_\lambda(R)$. However, the general form of the integrals suggest that Gauss–Laguerre quadrature may well be a suitable technique for their evaluation.

The integrals are best evaluated by a scheme based on the zeros of $L_M^\alpha(x)$, since for $M > n$ this guarantees the correct evaluation of overlap integrals. To do this it is necessary to generate Gauss–Laguerre integration points and weights for arbitrary α. Such a program has been given by Stroud and Secrest,[36] but only works without numerical difficulties for $\alpha < 30$. However, if the integrals are taken between *normalized* Laguerre polynomials and the normalization constants are included in the formula for the weights, the weight for the *i*th integration point x_i reduces to

$$w_i = M! \left[\frac{dL_M^\alpha(x_i)}{dx} \, L_{M-1}^\alpha(x_i) \right]^{-1} \tag{47}$$

for M point integration. This form is numerically stable for small M (< 20), and α up to several thousand. Stroud and Secrest's empirical extrapolation formula between integration points

$$\frac{x_{k+2} - x_{k+1}}{x_{k+1} - x_k} \approx \frac{1}{(1+0.3\alpha)} \, \frac{1+2.55k}{1.9k} + \frac{1.26k\alpha}{1+3.5k} \, , \qquad k = 1, 2, \ldots, M-2 \, , \tag{48}$$

was found to provide a good first guess, even for large α, but in this case it is necessary to find the lowest two zeros of L_M^α by a direct search.

Table I shows diagonal ($n = n'$) terms of integral (46) between basis functions optimized for KCN, $\alpha = 547$. The integral is stable for $M \geq n + 3$. The potential integrals were found to behave similarly and the off-diagonal elements in both cases to be even more stable. All further calculations presented are for numerical integration schemes based on $M = n_{\max} + 3$, where $n_{\max}$ is the maximum order of radial basis function included in the basis.

A suitable solution strategy is, therefore, to guess physically reasonable values for the parameters D_e, ω_e, and R_e and hence a suitable α. These can then be improved by minimizing the eigenvalues of a problem solved with $J = 0$, since it is assumed that the radial functions do not depend on J. This basis set can then be used for the full vibration-rotation problem. In the next two sections, we present calculations on KCN and H_2Ne which demonstrate the application of this strategy.

IV. KCN

Both experiment[13] and *ab initio* calculation[16,37,38] have shown KCN to be triangular. Furthermore, calculations at the SCF level predict a low barrier to inversion at the linear isocyanide KCN geometry. In particular, Wormer and Tennyson (WT)'s surface,[16] fitted in the form of Eq. (1), has a barrier of 503.9 cm^{-1}.

This surface has been the subject of a series of dynamical calculations which we will refer to as paper I and paper II. In paper I,[17] the present authors applied the method of Whitehead and Handy[39] to KCN. In paper II,[10] Tennyson and van der Avoird compared these calculations to ones performed with the space-fixed close-coupling method of Le Roy and Van Kranendonk.[5] There is good agreement between papers I and II for low-lying states, but the method of Whitehead and Handy was found to perform poorly for higher states. This can be attributed to the singularity exhibited by Watson's Hamiltonian for nonlinear molecules[18] at the barrier. Recently, an attempt has been made to circumvent this problem in the case of CH_2^+[40] by using Watson's form of the Hamiltonian for linear molecules.[41]

Thus, KCN should provide an interesting testing ground for our method. In order to optimize our radial basis, we started from the values $R_e = 5.055a_0$ and $D_e = 39\,086$ cm^{-1} (relative to K$^+$ and CN$^-$ ions) suggested by WT's potential, and $\omega_e = 294$ cm^{-1} the fundamental stretching frequency of paper II. For the cyanide, we used WT's SCF optimized bond length of $2.186a_0$, so as to be consistent with the previous calculations.

Optimization of the radial basis set for a calculation with $J = 0$, with 5 radial functions ($n_{\max} = 4$) and 11 angular functions ($l_{\max} = 10$) showed the ground state energy to be insensitive to the parameters D_e and ω_e. It was, thus, only necessary to change the value of R_e used to $5.130a_0$ to give an optimized radial basis for this calculation. Table II gives our vibrational spectrum ($J = 0$) for KCN and compares it with those of papers I and II. These calculations use a radial basis of 12 functions ($n_{\max} = 11$) which, we found, saturated the radial coordinate. This is the same number of functions used in paper II to converge the numerical basis set required by the method of Le Roy and Van Kranendonk.[5]

In the body-fixed problem, using all angular basis functions up to $l_{\max}$ is equivalent to including all allowed functions up to $j_{\max}$ (the quantum number associated with rotations of the diatomic) = $l_{\max}$ in the space-fixed approach. Thus, as $j_{\max} = 23$ was found to provide a saturated angular basis in paper II, we can expect $l_{\max} = 23$ to do the same for our body-fixed calculations. It is clear from Table II that almost exact agreement is

TABLE II. Comparison of ground state energies (in cm^{-1})[a] and $J=0$ vibrational spectrum (in cm^{-1}) for this work ($l_{\max}=23$), paper I (Ref. 17) ($j_{\max}=23$) and paper II (Ref. 10).

		This work	II	I
Ground state energy		−38 861.40	−38 861.40	−38 863.2[b]
Band origin	1	116.1	116.1	119.7
	2	217.7	217.8	241.9
	3	294.3	294.3	302.7
	4	314.6	314.6	382.9
	5	380.0	379.6	438.6
	6	421.2	420.5	524.0
	7	451.8	448.4	588.3
	8	499.7	494.9	616.7
	9	533.4	530.4	···

[a] $1\ \mathrm{cm}^{-1} = 11.9625\ \mathrm{J\,mol}^{-1}$.

[b] Corrected for $1064.9\ \mathrm{cm}^{-1}$ zero-point energy for the CN stretch.

found between the two sets of close-coupling calculations.

The agreement between the close-coupling calculations and those of paper I, performed using harmonic oscillator functions of normal coordinates in the method Whitehead and Handy,[39] is not so good. Once an allowance is made for the zero-point energy of the CN stretch, which is present in the full three-dimensional calculation of paper I, there is fair agreement for the ground and first three excited states. For the higher excited states, however, the band origins of paper I are severe overestimates. This problem was analyzed in paper II and is associated with tunneling by states which lie as much as $70\ \mathrm{cm}^{-1}$ below the barrier to inversion. This tunneling is accompanied by a shift in average geometry towards a linear KCN structure which means that the molecule in its excited states is no longer vibrating about its minimum energy structure. Thus, the results of paper I, while variationally correct, cannot be relied upon for the higher excited states.

Table III gives a comparison of the known experimental and theoretical data for the KCN stretching and bending fundamentals. From this we exclude the results of Istomin *et al.*[11] as their calculations were only performed on a model KCN potential with no coupling between R and Θ. Furthermore, this potential was derived assuming an equilibrium isocyanide ($\Theta = 180°$) geometry for KCN.

In Table III, the calculations were all performed on WT's surface and show a good measure of agreement. In contrast, the experimental results can only be regarded as inconclusive. Recently, Marsden has performed configuration interaction calculations on NaCN.[38] He found that inclusion of electron correlation could substantially alter the shape of the NaCN surface and concluded that this would also be true of KCN. If this is so, then one would expect fundamentals obtained using an SCF level surface to be in error. However, calculations of a potential energy surface for KCN at the configuration interaction level using extended basis from SCF is prohibitively expensive and smaller basis sets yield unrealistic results.[38]

Table IV shows the $J=0 \rightarrow 1$ transition energies of the vibrational ground state. The close-coupling calculations are all for $j_{\max} = l_{\max} = 18$. For these rotational transitions, all the theoretical calculations are in excellent agreement. This shows that neglect of the Coriolis interactions has only a slight effect. This approximation means that no secular problem larger than that of the $J=0$ problem needs to be solved to obtain the rotational spectrum. The complete separation of vibrational and rotational problems used in paper I also works well, at least for the vibrational ground state. This approximate separation allowed rotational levels up to $J=25$ to be calculated in just 11 s on an IBM 370/158, although 10 min CPU time was required to compute the necessary vibrationally averaged inertia tensor.

For the full close-coupling calculations the $J=1$ energies are obtained as solutions of a 444 dimensional secular problem. Using our method the secular matrix took 21.5 s to construct in contrast with 249.2 s required by the method of Le Roy and Van Kranendonk.[5] However, in both cases, in core diagonalization required a further 622 s CPU time. The computation of higher rotational states with these close-coupling methods becomes rapidly more time consuming. By neglecting the terms off-diagonal in k, however, the calculations become tractable without serious loss of accuracy.

The *ab initio* and experimental results in Table IV agree only to within about 10%. This problem was analyzed in paper I and is associated with inaccuracies in WT's potential energy surface. In particular, their SCF calculations overestimate the equilibrium values of R and θ, and underestimate the optimum value of r_0 compared with experiment. The inclusion of electron correlation should rectify these faults.[38]

It is clear, however, from Tables II–IV, that our method is capable of producing results in good agreement with other *ab initio* approaches.

V. H_2–Ne

H_2-inert gas van der Waals molecules have been much studied both theoretically[1,5,6,9] and experimental-

TABLE III. K–CN stretch and bend fundamental energies (in cm^{-1}), comparison of theoretical and experimental results.

Stretch	Bend	Reference	Method
294.3	116.1		This work
294.3[a]	116.1[a]	paper II (Ref. 10)	Le Roy and Van Kranendonk (Ref. 5).
302.7	119.7	paper I (Ref. 17)	Whitehead and Handy (Ref. 39)
285[b]	···	(Ref. 42)	Morse oscillators (Ref. 42)
···	···	(Ref. 14)	Gas-phase infrared[c]
288	139	(Ref. 15)	Matrix isolation study
···	157	(Ref. 13)	Microwave spectroscopy[d]

[a] Results with $r_0 = 2.186 a_0$.

[b] From the isotropic potential.

[c] One (unassigned) band observed at $207 \pm 20\ \mathrm{cm}^{-1}$.

[d] Inferred from inertial defect of the pure rotation spectrum.

TABLE IV. $J=0\rightarrow 1$ transition energies (in cm^{-1}) for the vibrational ground state of KCN. The parity labeling is for blocks given by Eq. (32).

Parity	This work	This work[a]	Paper II (Ref. 10)	Paper I (Ref. 17)	(Ref. 42)	Experiment (Ref. 13)
ϕ^-	2.3262	2.3262	2.3429	2.3277	···	2.0933
ϕ^+	0.2877	0.2988	0.2877	0.2879	0.2874	0.3158
ϕ^+	2.3161	2.3262	2.3328	2.3377	···	2.1068

[a] Neglecting Coriolis interactions.

ly.[1,12,19–21,43] In particular, the H_2–Ne system has been well characterized experimentally.[12] In this section, we present calculations on the empirical potential of Andres *et al.*,[19] with a slight correction due to Waaijer and Reuss,[11] which reproduces all the known data on H_2Ne.[43] These calculations were performed using the method presented in Secs. 2 and 3, and that of Le Roy and Kranendonk,[5] whose method is particularly suited to the near isotropic H_2–X systems. Furthermore, the large separation of the rotational levels of the H_2 diatom has led to the so-called vector model,[21,44] which neglects all angular basis functions associated with rotational excitation of H_2. We also test this model for H_2Ne.

In the case of a homonuclear diatomic, symmetry considerations dictate that only even terms in λ appear in the Legendre expansion of Eq. (1). The symmetry of the Gaunt coefficient (29) causes the secular problem to be factorized into l (even) and l (odd) blocks. These blocks correspond to para- and ortho-H_2, respectively. This allows p-H_2Ne and o-H_2Ne to be treated as separate problems.

Basis set optimization was performed on $J=0$, p-H_2 Ne with a basis of one radial function ($n=0$) and 3 angular functions ($l=0, 2, 4$); results are given in Table V. Experience with both KCN and H_2Ne suggests that R_e is the critical parameter in basis set optimization. For H_2Ne, the minimum of the isotropic potential lies at $R_e=6.2a_0$,[19] but calculations with this parameter value fail to give any bound states. Clearly, the anharmonicity in the potential shifts the center of vibration outwards.

TABLE V. Basis set optimization for para-H_2Ne. D_e is the dissociation energy; ω_e the vibrational transition energy and R_e equilibrium atom–diatom distance.

R_e/a_0	D_e/cm^{-1}	$\omega_e/\mathrm{cm}^{-1}$	Ground state energy/cm^{-1}
7.5	25.0	22.0	+3.77
8.0	···	···	−3.40
8.5	···	···	−2.74
7.8	···	···	−2.11
8.2	···	···	−3.56
8.1	···	···	−3.58
8.15	···	···	−3.60
8.15	25.0	19.8	−3.52
···	···	24.2	−2.97
···	···	20.9	−3.60
8.15	28.5	20.9	−3.30
···	21.9	···	−3.56
···	24.1	···	−3.59
···	optimized	···	···
8.15	25.0	20.9	−3.60

Table VI shows the effect of increasing both angular and radial basis sets using the optimized radial basis of Table V. This shows the radial basis set to be slowly convergent. However, reoptimization of the basis with $n_{\max}=4$ (5 functions) and $l=0, 2, 4$ gave an energy of $-4.67\ \mathrm{cm}^{-1}$ with the parameters $R_e=9.5a_0$, $\omega_e=20.9\ \mathrm{cm}^{-1}$ and $D_e=25.0\ \mathrm{cm}^{-1}$. The H_2 bond length r_0 was taken as $1.4a_0$ in all calculations.

Tables VII and VIII show all the bound states of H_2Ne found with this basis. For comparison we show the energies obtained with the method of Le Roy and Van Kranendonk[5] and the vector model.[21] All three methods

TABLE VI. Ground state H_2Ne energy level in cm^{-1} with increase in $n_{\max}$ (radial basis set) and $l_{\max}$ (angular basis set).

$n_{\max}$	$l_{\max}$	Ground state energy/cm^{-1}
0	4	−3.60
1	4	−3.60
2	4	−3.78
3	4	−4.08
4	4	−4.50
5	4	−4.55
8	4	−4.59
14	4	−4.66
5	0	−4.54
5	2	−4.55
5	4	−4.55
5	6	−4.55

TABLE VII. Energies (in cm^{-1}) of para-H_2Ne bound states for (1) optimized basis set (see the text), (b) using the method of Le Roy and Kranendonk,[a] (3) using the vector model,[b] (4) due to Carley,[c] and (1), (2), and (3) use the potential of Andres *et al.*[d]

J	(1)	(2)	(3)	(4)
0	−4.67	−4.70	−4.66($L=0$)	−4.06
1	−3.52	−3.56	−3.51($L=1$)	−2.98
2	−1.30	−1.36	−1.30($L=2$)	−0.92

[a] Reference 5.

[b] Reference 21.

[c] Reference 6.

[d] Reference 19.

TABLE VIII. Energies (in cm^{-1}) or ortho-H_2Ne bound states relative to separated o-H_2 and Ne. o-H_2 is taken to lie 121.93 cm^{-1} above p-H_2. Columns (1), (2), and (3) are as for Table VII.

J	(1)	(2)	(3)
0	−3.79	−3.80	−3.78($L=1$)
1	−4.69	−4.70	−4.68($L=0$)
	−3.40	−3.44	−3.40($L=1$)
	−1.43	−1.46	−1.43($L=2$)
2	−3.56	−3.59	−3.56($L=1$)
	−1.18	−1.24	−1.17($L=2$)
3	−1.35	−1.39	−1.35($L=2$)

are in excellent agreement. Clearly, for H_2 the large rotational separation (~350 cm^{-1}) means that higher ($l\neq 0$ for p-H_2 and $l\neq 1$ for o-H_2) angular functions have little influence. This has allowed Waaijer *et al.* to perform calculations on the o-H_2–p-H_2 system by treating p-H_2 as an atom.[44] Within this model, L (the rotational quantum number of the complex) is a good quantum number and the energies in Tables VII and VIII have been labeled accordingly. As found experimentally[12,21] all states with $L\leq 2$ are bound.

Also shown in Table VII are the results of Carley[6] who used the method of Le Roy and Van Kranendonk[5] on his own potential. His results, which are only for p-H_2Ne, show that his potential is slightly more repulsive than that of Andres *et al.*[19] favored by the experimentalists.[12,21] The differences in Table VII show that the potential used is of greater significance than the method. Again our method gives results in close agreement with those methods used previously.[5,6,21]

VI. CONCLUSION

In the previous sections, we have demonstrated a close-coupling method which *ab initio* can provide reliable results for the dynamics of atom-rigid diatom systems. The method uses body-fixed coordinates which allow the simplyfing approximation that Coriolis-like interactions can be neglected. This and the use of a flexible radial basis of orthogonal polynomials suggests that the method can be easily extended to theoretically more demanding systems.

In future publications, we hope to extend this method. Firstly, to diatom–diatom systems,[45] where the angular integration is three dimensional and the body-fixing of coordinates, with the resulting reduction in complexity of the angular integration, has significant advantages. Secondly, to the full triatomic problem in coordinates (R, r, θ).[46] The radial basis set of Eq. (30) can easily be generalized to

$$\Psi_{mn}(r,R)=r^{-1}R^{-1}H'_m(r)H_n(R)\ , \tag{49}$$

and the parameters of the coordinate transformations (36) optimized separately. This should allow us to test the validity of freezing the vibrational mode associated with the diatom and could provide insight into the much studied problem of vibrational predissociation in van der Waals molecules.[5,9,47] It will also enable us to study "floppy" AB_2 systems such as CH_2^+.[40,48]

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APPENDIX A

The Hamiltonian (13) was obtained from a general formula whose derivation is outlined below. A more detailed account of the genesis of the formula can be found in Sutcliffe.[22]

Any linear transformation from laboratory fixed to center-of-mass fixed coordinates such as that from $\mathbf{x}_i$ to $\mathbf{t}_i$ in Eq. (3) is such as to introduce a constant metric matrix $\tilde{\mathrm{G}}$ into the kinetic energy part of the operator. Thus,

$$-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla^2(\mathbf{x}_i)\rightarrow-\frac{\hbar^2}{2}\sum_{i,j=1}^{N-1}\tilde{G}_{ij}\nabla(\mathbf{t}_i)\cdot\nabla(\mathbf{t}_j) \tag{A1}$$

after the removal of center-of-mass motion.

A further orthogonal transformation from the $\mathbf{t}_i$ to a set of body-fixed coordinates $\mathbf{z}_i$ according to [cf. (10)]

$$\mathbf{t}_i=\mathrm{C}\mathbf{z}_i\ ,\quad \mathrm{CC}^T=\mathrm{E}_3 \tag{A2}$$

can then be made. The $\mathbf{z}_i$ must be completely expressible in terms of $3N$-6 internal coordinates q_k and the elements of C can be defined by three relations of the form

$$f_m(\mathbf{z}_i)=0\ ,\quad m=1,\ 2,\ 3\ . \tag{A3}$$

If the $\mathbf{z}_i$ in Eq. (A3) are expressed in terms of the $\mathbf{t}_i$ and C then Eq. (A3) can be thought of as a set of constraining equations through which the three Euler angles that parametrize C are expressed as functions of the $\mathbf{t}_i$. If these angles are known and the $\mathbf{z}_i$ are expressed in terms of the q_k in Eq. (A3) then three constraint equations are satisfied as identities for any suitable set of q_k. The q_k are, in general, not unique for a given choice of the Euler angles.

If it is assumed that the Jacobian and its inverse exist for a particular transformation $\mathbf{t}_i\rightarrow\phi_n,\ q_k$ (where the ϕ_n are the Euler angles), then straightforward if rather tedious use of the chain rule enables the following results for the elements Jacobian and its inverse to be derived

$$\frac{\partial\phi_m}{\partial t_{\alpha i}}=(\mathrm{C}\Omega^i\,\mathrm{D})_{\alpha m}\ ,\quad \frac{\partial q_k}{\partial t_{\alpha i}}=[\mathrm{C}(\mathrm{Q}^i+\Omega^i N)]_{\alpha k}\ , \tag{A4}$$

and

$$\frac{\partial t_{\alpha i}}{\partial\phi_m}=(\mathrm{D}^{-1}\hat{\mathbf{z}}^i\,\mathrm{C}^T)_{m\alpha}\ ,\quad \frac{\partial t_{\alpha i}}{\partial q_k}=(\mathrm{C}\bar{\mathrm{Q}}^i)_{\alpha k}\ . \tag{A5}$$

In the above formula $\hat{\mathbf{z}}^i$ is a "vector-product" matrix composed of the elements of $\mathbf{z}_i$, thus,

$$\hat{\mathbf{z}}_i = \begin{pmatrix} 0 & -z_{zi} & z_{yi} \\ z_{zi} & 0 & -z_{xi} \\ -z_{yi} & z_{xi} & 0 \end{pmatrix} , \qquad \text{(A6)}$$

and

$$Q^i_{\alpha k} = \frac{\partial q_k}{\partial z_{\alpha i}} , \quad \bar{Q}^i_{\alpha k} = \frac{\partial z_{\alpha i}}{\partial q_k} , \qquad \text{(A7)}$$

$$N_{\alpha k} = \sum_{j=1}^{N-1} \sum_{\epsilon} \hat{z}^j_{\alpha \epsilon} Q^j_{\epsilon k} . \qquad \text{(A8)}$$

It should be noted that the constraint conditions (A3) may well be fulfilled by the identical vanishing of some component of $\mathbf{z}_i$. In such cases the relevant elements of $\mathbf{Q}^i$ and $\bar{\mathbf{Q}}^i$ are zero.

The matrices $\mathbf{\Omega}^i$ and D arise from the Euler angle differentiation. From the requirement that C be an orthogonal matrix it follows at once that the derivative of C with respect to any parameter on which it depends, can be expressed in terms of a product a skew-symmetric ("vector-product") matrix and C itself. Thus,

$$\frac{\partial \mathbf{C}^T}{\partial t_{\alpha i}} = \hat{\omega}^{\alpha i} \mathbf{C}^T , \qquad \text{(A9)}$$

where $\hat{\omega}^{\alpha i}$ is the skew symmetric matrix [like Eq. (A6)] with nonzero elements $\omega^{\alpha i}_{\delta}$. Without loss of generality the $\omega^{\alpha i}_{\delta}$ may be expressed as

$$\omega^{\alpha i}_{\delta} = \sum_{\gamma} C_{\alpha \lambda} \omega^i_{\gamma \delta} , \qquad \text{(A10)}$$

and using this form and writing the ϕ_m as implicit functions of the elements of C leads, after some algebra to the first term in Eq. (A4) with

$$(\Omega^i)_{\gamma\delta} = \omega^i_{\gamma\delta} \qquad \text{(A11)}$$

and

$$D_{\alpha m} = \sum_{\delta} \left(C_{\delta\beta} \frac{\partial \phi_m}{\partial C_{\delta\gamma}} - C_{\delta\gamma} \frac{\partial \phi_m}{\partial C_{\delta\gamma}} \right) , \qquad \text{(A12)}$$

$\alpha, \beta, \gamma = xyz$ and cyclic .

It is easy to see that D is a function of the Euler angles alone and it is possible to show that Ω^i is a function of the q_k only.

Very similar arguments to those used above can be used in deriving the first term in Eq. (A5), but in this connection it is worthwhile remembering that any skew-symmetric matrix can be decomposed in terms of the "angular-momentum" matrices

$$\mathbf{H}^x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} , \quad \mathbf{H}^y = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} ,$$

$$\mathbf{H}^z = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \qquad \text{(A13)}$$

so that skew-symmetric form equivalent to Eq. (A9) for ϕ_m can be written

$$\frac{\partial \mathbf{C}}{\partial \phi_m} = \sum_{\beta} \omega^m_{\beta} (\mathbf{C}\mathbf{H}^{\beta}) , \qquad \text{(A14)}$$

where the ω^m_{β} are the equivalents of $\hat{\omega}^{\alpha i}_{\delta}$. In this form it is easy to identify the ω^m_{β} as $(D^{-1})_m$ by means of the requirement that

$$\sum_{\alpha\beta} \frac{\partial C_{\gamma\beta}}{\partial \phi_m} \frac{\partial \phi_n}{\partial C_{\gamma\beta}} = \delta_{nm} . \qquad \text{(A15)}$$

Using these results it follows (using a rather obvious matrix notation) that

$$\frac{\partial}{\partial \mathbf{t}_i} = \mathbf{C} \left(\mathbf{\Omega}^i \mathbf{D} \frac{\partial}{\partial \phi} + (\mathbf{Q}^i + \mathbf{\Omega}^i \mathbf{N}) \frac{\partial}{\partial \mathbf{q}} \right) . \qquad \text{(A16)}$$

If the components L_{α} of the angular momentum in the center-of-mass fixed frame are written as a column matrix L then from Eq. (A16) and the expression (A2) for $\mathbf{z}_i$ in terms of $\mathbf{t}_i$ it can be shown that

$$\mathbf{L} = - |\mathbf{C}| \mathbf{C} \Pi , \qquad \text{(A17)}$$

where

$$\Pi = \frac{\hbar}{i} \mathbf{D} \frac{\partial}{\partial \phi} . \qquad \text{(A18)}$$

With the aid of Eq. (A14) it can be shown that the components of Π obey the ordinary (*not* the anomalous) angular momentum commutation relations and that $L^2 = \Pi^2$.

It is usual to rewrite Eq. (A16) as

$$\frac{\partial}{\partial \mathbf{t}} = \mathbf{C} \left(\frac{i}{\hbar} \mathbf{\Omega}^i \bar{\Pi} + \mathbf{Q}^i \frac{\partial}{\partial \mathbf{q}} \right) , \qquad \text{(A19)}$$

where

$$\bar{\Pi} = \Pi + \pi , \qquad \text{(A20)}$$

with

$$\pi = \frac{\hbar}{i} \mathbf{N} \frac{\partial}{\partial \mathbf{q}} . \qquad \text{(A21)}$$

π is a Coriolis term and though closely associated with the angular momentum, it does not in general obey angular momentum commutation rules.

The expression on the right-hand side of Eq. (A1) may now be converted to the new coordinates by straightforward if rather tedious algebra. The result is

$$\frac{1}{2} \sum_{\alpha\beta} M_{\alpha\beta} \bar{\Pi}_{\alpha} \bar{\Pi}_{\beta} - \frac{\hbar^2}{2} \sum_{kl} G_{kl} \frac{\partial^2}{\partial q_k \partial q_l}$$
$$+ \frac{\hbar^2}{2i} \sum_k \sum_{\alpha} \left(W_{k\alpha} \bar{\Pi}_{\alpha} \frac{\partial}{\partial q_k} + W_{k\alpha} \frac{\partial}{\partial q_k} \bar{\Pi}_{\alpha} \right)$$
$$+ \frac{\hbar}{i} \sum_{\alpha} \nu_{\alpha} \bar{\Pi}_{\alpha} - \frac{\hbar^2}{2} \sum_k \tau_k \frac{\partial}{\partial q_k} . \qquad \text{(A22)}$$

In Eq. (A22),

$$\mathbf{M} = \sum_{i,j=1}^{N-1} \tilde{G}_{ij} \mathbf{\Omega}^{iT} \mathbf{\Omega}^j , \qquad \text{(A23)}$$

$$\mathbf{G} = \sum_{i,j=1}^{N-1} \tilde{G}_{ij} \mathbf{Q}^{iT} \mathbf{Q}^j , \qquad \text{(A24)}$$

$$\mathbf{W} = \sum_{i,j=1}^{N-1} \tilde{G}_{ij} \mathbf{Q}^{iT} \mathbf{\Omega}^j . \qquad \text{(A25)}$$

The ν_{δ} and τ_k in Eq. (A22) arise on taking the second derivatives, from the dependence of C on the ϕ_n and from the dependence (possibly) of Ω^i, $\mathbf{Q}^i$ on the internal coordinates. The terms arising from C can be worked out, in general, using (A14). Their contribution to ν_β is

$$\frac{1}{2}\sum_{i,j=1}^{N-1} \tilde{G}_{ij} \sum_\alpha (\Omega^{iT}\,\mathbf{H}^\alpha\,\Omega^j)_{\alpha\beta} \;, \tag{A26}$$

and to τ_k is

$$\sum_{i,j=1}^{N-1} \tilde{G}_{ij} \sum_\alpha (\Omega^{iT}\,\mathbf{H}^\alpha\,\mathbf{Q}^j)_{\alpha k} \;. \tag{A27}$$

The contribution to ν_β from the remaining terms is

$$\frac{1}{2}\sum_{i,j=1}^{N-1} \tilde{G}_{ij} \sum_\alpha \sum_l (\mathbf{Q}^i + \Omega^i\mathbf{N})_{\alpha l}\,\frac{\partial}{\partial q_l}\,\Omega^j_{\alpha\beta} \;, \tag{A28}$$

and to τ_k is

$$\sum_{i,j=1}^{N-1} \tilde{G}_{ij} \sum_\alpha \sum_l (\mathbf{Q}^i + \Omega^i\mathbf{N})_{\alpha l}\,\frac{\partial}{\partial q_l}\,Q^j_{\alpha k} \;. \tag{A29}$$

The Jacobian for the transformation may be determined (to within a sign) as the square root of the metric of the transformation and thus in terms of the quantities (A23)–(A25) above. In this form the Jacobian turns out to be (to within a constant factor)

$$\begin{aligned} J &= |\mathbf{D}|^{-1}\,|\mathbf{M}|^{-1/2}\,|\mathbf{G}+\mathbf{W}\mathbf{M}^{-1}\mathbf{W}^T|^{-1/2} \\ &= |\mathbf{D}|^{-1} j \;. \end{aligned} \tag{A30}$$

The portion of this function involving $|\mathbf{D}|$ is the volume element for angular integration and may be assumed incorporated into any angular integrals. Since $L^2 \equiv \Pi^2$ and L_z commute with the Hamiltonian and Π_z commutes with L^2 and L_z solutions to the Hamiltonian may be expressed in terms of sums of standard (symmetric-top) rotational functions. The incorporation of $|\mathbf{D}|^{-1}$ into integrals over the function means that standard integral expressions may be used. Thus, it is not necessary to know D in any particular case. This result would have been anticipated from group theoretical arguments. The internal part j of the Jacobian must be carried through however in all subsequent integrations over internal coordinates.

In the present case, it is easy to show that

$$\tilde{G}_{ij} = \delta_{ij}/\mu_i \;, \tag{A31}$$

and that the three constant relations like Eq. (A3) are [cf. (1.12)]

$$\mathbf{z}_1 = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix} = \mathbf{C}^T\,\mathbf{t}_1 \;, \quad \mathbf{z}_2 = r\begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix} = \mathbf{C}^T\,\mathbf{t}_2 \;. \tag{A32}$$

Differentiation with respect to $t_{\alpha i}$ of the three identically zero terms in these expressions yields expressions for the elements of Ω^1 and Ω^2 according to Eqs. (A9) and (A10). The results are

$$\Omega = \begin{pmatrix} 0 & -R^{-1} & 0 \\ R^{-1} & 0 & R^{-1}\cot\theta \\ 0 & 0 & 0 \end{pmatrix} \;,$$

$$\Omega^2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -r^{-1}\operatorname{cosec}\theta \\ 0 & 0 & 0 \end{pmatrix} \;. \tag{A33}$$

The elements of the $\mathbf{Q}^i$ follow from differentiating the elements of Eq. (A32) with respect to the $z_{\alpha i}$ and the results are, on identifying R with q_1, r with q_2 and θ with q_3,

$$\mathbf{Q}^1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \;, \quad \mathbf{Q}^2 = \begin{pmatrix} 0 & \sin\theta & r^{-1}\cos\theta \\ 0 & 0 & 0 \\ 0 & \cos\theta & -r^{-1}\sin\theta \end{pmatrix} \;. \tag{A34}$$

N follows at once from Eq. (A8) and is

$$\mathbf{N} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \;. \tag{A35}$$

With the aid of these results it can be established that

$$\mathbf{M} = \begin{pmatrix} 1/M_1R^2 & 0 & \cot\theta/M_1R^2 \\ 0 & 1/M_1R^2 & 0 \\ \cot\theta/M_1R^2 & 0 & (\cot^2\theta/M_1R^2 + \operatorname{cosec}^2\theta/M_2r^2) \end{pmatrix} \;, \tag{A36}$$

$$\mathbf{G} = \begin{pmatrix} \mu_1^{-1} & 0 & 0 \\ 0 & \mu_2^{-1} & 0 \\ 0 & 0 & \mu_2^{-1}r^{-2} \end{pmatrix} \;, \tag{A37}$$

and

$$\mathbf{W} = 0 \;. \tag{A38}$$

In this case, the contribution to ν_β arises from Eq. (A26) alone and is

$$\nu_\beta = \delta_{\beta y}\cot\theta/2\mu_1 R^2 \;, \tag{A39}$$

while contributions to τ_k arise from Eqs. (A27) and (A29) to give

$$\tau_1 = 2/\mu_1 R \;, \quad \tau_2 = 2/\mu_2 r \;, \quad \tau_3 = \cot\theta/r^2 \;. \tag{A40}$$

The internal Jacobian j (A22) is

$$j = R^2 r^2 \sin\theta \;. \tag{A41}$$

Substituting the results (A35)–(A40) into Eq. (A22) yields Eq. (13), as required.

APPENDIX B

The integral on the right-hand side of Eq. (42),

$$J(n,\alpha;n',\alpha';m) = \int_0^\infty e^{-y}\,y^m\,L_n^\alpha(y)\,L_{n'}^{\alpha'}(y)\,dy \;, \tag{B1}$$

does not seem to appear in any of the standard tabulations.

It can, however, be evaluated with the aid of the generating function for the Laguerre polynomial

$$(1-z)^{-\alpha-1}\exp(y/z-1) = \sum_{n=0}^\infty L_n^\alpha(y)\,z^n \;, \tag{B2}$$

and a brief summary of how this is done is given in this Appendix, in case the result has never been recorded.

Using Eq. (B2) it follows that:

$$\sum_{n,n'=0}^{\infty} z_1^n z_2^n J(n, \alpha; n', \alpha'; m) = V_1^{-\alpha-1} V_2^{-\alpha'-1} \int_0^{\infty} e^{-(\gamma+1)y} y^m \, dy \ , \tag{B3}$$

$$\gamma = z_1/V_1 + z_2/V_2 \ , \quad V_i = (1 - z_i) \ . \tag{B4}$$

The integral on the right-hand side of Eq. (B3) can be rewritten as

$$\delta^{-t} \int_0^{\infty} x^{t-1} e^{-x} \, dx = \delta^{-t} \, \Gamma(t) \ , \quad \text{if } t > 0 \ , \tag{B5}$$

where

$$\delta = (\gamma + 1) \ , \quad t = m + 1 \ . \tag{B6}$$

The right-hand side of Eq. (B3) may therefore be rewritten as

$$(1 - z_1)^{t-\alpha-1} (1 - z_2)^{t-\alpha'-1} (1 - z_1 z_2)^{-t} \, \Gamma(t) \ . \tag{B7}$$

Expanding the brackets in Eq. (B7) using the binomial theorem and collecting powers of z_1 and z_2 yields, for the coefficient of $\Gamma(t)$,

$$\sum_{k,j,l} (-1)^{k+j} \cdot \binom{t - \alpha - 1}{k} \binom{t - \alpha' - 1}{j} \binom{t + l - 1}{l} z_1^{k+l} z_2^{j+l} \ . \tag{B8}$$

Equating powers of $z_1 z_2$ on both sides of Eq. (B3) and simplifying leads at once to the result

$$J(n, \alpha; n', \alpha'; m) = (-1)^{n+n'} \sum_{\sigma=0}^{n'} \binom{m - \alpha}{\tau + \sigma} \binom{m - \alpha'}{\sigma} \frac{\Gamma(m + n' - \sigma + 1)}{(n' - \sigma)!} \ , \tag{B9}$$

$$\tau = n - n' \geqslant 0 \ , \quad m > -1 \ ,$$

which, in turn, leads to the result (43).

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