Reactive Scattering with Row-Orthonormal Hyperspherical Coordinates. 2. Transformation Properties and Hamiltonian for Tetraatomic Systems

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The formalism for tetraatomic reactive scattering using row-orthonormal hyperspherical coordinates is presented. The transformation properties of these coordinates under kinematic rotations and symmetry operations are derived, as are the corresponding Hamiltonian and volume element. Each of the nine operators which contribute to this Hamiltonian is kinematic-rotation invariant. Continuity conditions appropriate for the absence and presence of the geometric phase associated with conical intersections are described. It is concluded that the row-orthonormal hyperspherical coordinates are particularly well suited for calculations of reactive scattering in tetraatomic systems.

1. Introduction

I first met Yuan T. Lee 30 years ago, in the spring of 1967, when he was a postdoctoral fellow working with Dudley Herschbach at Harvard. He was in the middle of designing the first crossed molecular beam machine which used a "universal" mass spectrometer detector. I was greatly impressed by his design skills, which were just one manifestation of his enormous scientific ability. My admiration of his work grew continuously over the years as he demonstrated exquisite scientific taste and made a profound mark on modern chemical dynamics. It is with great pleasure that I dedicate this paper to him in celebration of his 60th birthday, and in honor of over 30 years of major accomplishments in the elucidation of the dynamics of elementary chemical reactions.

Recent *ab initio* calculations of converged integral and differential cross sections for atom−diatomic molecules at total energies up to 2.6 eV using a propagation approach to solve the time-independent Schrödinger equation have all been done with some form of symmetrized hyperspherical coordinates.[1−6] These coordinates have also permitted inclusion of the effect of the geometric phase associated with conical intersections.[4−10] The geometric phase effect is apt to play an important role in many systems displaying such intersections. In addition, many propagation calculations involving a limited number of partial waves have also been done,[11−21] only one of which did not employ hyperspherical coordinates of one variety or another.[11] This indicates the effectiveness of the hyperspherical coordinate propagation method.

For the last 8 years or so an alternative approach to performing accurate quantum mechanical reactive scattering integral and differential cross section calculations using variational methods has been very successfully applied.[22−49] In addition, two new methods have been recently developed. One of them involves a time-dependent wave packet approach with absorbing walls[50−52] and the other a time-independent method as well as absorbing walls.[53] A further interesting new method for time-dependent wave packet propagation involving complex potentials to absorb and re-emit wave functions in regions separating the reactant from the product arrangements has been proposed[54] and extended to time-independent wave packet calculations.[55] All of these methods have their individual strengths and are worth pursuing further.

Extension of accurate *ab initio* reactive scattering calculations of state-to-state integral and differential cross sections to tetraatomic systems is not only highly desirable but has become feasible with the advent of massively parallel high-performance computers. It has already been shown that multiple-instruction multiple-data (MIMD) distributed memory computers are very well suited for reactive scattering calculations which use symmetrized hyperspherical coordinates and hyperradial propagation.[20] Furthermore, recent results on tetraatomic systems have been published in most of which some of the degrees of freedom were treated exactly and others approximately,[56−59] except for three that used a time-dependent wave packet approach and for which all degrees of freedom were treated exactly in the $J = 0$ partial wave only.[60−62] A fourth one was proposed which employs a propagation method based on the use of different hyperradial coordinates in different arrangement channels and treats all partial waves exactly.[63] In order to use the permutation symmetries of the system effectively, it would be desirable to generalize the concept of symmetrized hyperspherical coordinates[64] (which proved so useful for triatomic systems) to tetraatomic systems. Such a generalization has been recently developed,[65] but the system's Hamiltonian in those coordinates is complicated. A different approach is to use row-orthonormal hyperspherical coordinates.[65,66] For triatomic systems these two kinds of coordinates are related in a very simple manner[64,65] but for tetraatomic systems this relation is significantly more complex.[65] In spite of this, the Hamiltonian in row-orthonormal coordinates is relatively simple both for triatomic systems[67] and for tetraatomic ones,[68] and its terms display useful invariance properties under kinematic rotations and symmetry operations. The purpose of this paper is to derive this Hamiltonian and its properties. A summary of some of the results have been given previously.[68] Recently, a related set of hyperspherical coordinates and the associated Hamiltonian has also been proposed.[69]

In section 2 we define row-orthonormal hyperspherical coordinates for N-atom systems. In section 3 the transformation properties of these coordinates under kinematic rotations and symmetry operations are examined. This is followed in section 4 by a derivation of the Hamiltonian of such systems, of the associated volume element, and of the Hamiltonian's transformation properties. In section 5 we discuss the continuity conditions for the system's eigenfunctions with and without inclusion of the geometric phase effect, and in section 6 we summarize the results.

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2. Row-Orthonormal Hyperspherical Coordinates for *N*-Atom Systems

We will consider in this section the general case $N \geq 3$ and particularize it to $N = 4$ in later sections. The definitions of quantities of interest and their properties have been given in detail elsewhere[65,67] and will only be summarized here.

2.1. Jacobi Matrices and Their Products. Let the nuclei of the atoms comprising the system be P_i and the corresponding nuclear masses be $m_i = (i = 1, 2 ..., N)$. We locate them in physical space by N Jacobi vectors $\boldsymbol{R}_G$, $\boldsymbol{r}'^{(1)}_\lambda$, ..., $\boldsymbol{r}'^{(N-1)}_\lambda$, where $\boldsymbol{R}_G$ is the position vector of the center of mass G of the system of nuclei with respect to a space-fixed origin O, $\{\boldsymbol{r}'^{(j)}_\lambda | j = 1, 2, ..., N-1\}$ is a set of relative position vectors of the centers of mass of the nuclei for a clustering scheme λ[65,67] and $\boldsymbol{r}'^{(N-1)}_\lambda$ passes through G. Associated with these vectors and masses we define another set of masses μ, $\mu^{(1)}_\lambda$, $\mu^{(2)}_\lambda$, ..., $\mu^{(N-1)}_\lambda$ and define the Jacobi mass-scaled coordinates by[65,70,71]

$$\mathbf{r}^{(j)}_\lambda = [\mu^{(j)}_\lambda/\mu]^{1/2}\mathbf{r}'^{(j)}_\lambda \tag{2.1}$$

where μ is an effective reduced mass of the system and is independent of the clustering scheme λ. The kinetic energy operator $\hat{T}$ of the total relative motion of the nuclei is given in terms of these mass-scaled coordinates by

$$\hat{T} = -(\hbar^2/2\mu)\sum_{j=1}^{N-1}\nabla^2_{\mathbf{r}^{(j)}_\lambda} \tag{2.2}$$

We now define the $3 \times (N-1)$ Jacobi matrix[72]

$$\rho^{sf}_\lambda = (\mathbf{r}^{(1)}_\lambda \mathbf{r}^{(2)}_\lambda ... \mathbf{r}^{(N-1)}_\lambda) = \begin{pmatrix} x^{(1)}_{\lambda_1} & x^{(2)}_{\lambda_1} ... & x^{(N-1)}_{\lambda_1} \\ x^{(1)}_{\lambda_2} & x^{(2)}_{\lambda_2} ... & x^{(N-1)}_{\lambda_2} \\ x^{(1)}_{\lambda_3} & x^{(2)}_{\lambda_3} ... & x^{(N-1)}_{\lambda_3} \end{pmatrix} \tag{2.3}$$

where $x_{\lambda_1}(j) \equiv x^{(j)}_\lambda$, $x^{(j)}_{\lambda 2} \equiv y^{(j)}_\lambda$, and $x^{(j)}_{\lambda 3} \equiv z^{(j)}_\lambda$ are the components of $\boldsymbol{r}^{(j)}_\lambda$ in either of the space-fixed Cartesian frames $Oxyz \equiv Ox_1x_2x_3$ or $Gxyz \equiv Gx_1x_2x_3$ whose corresponding axes have parallel directions and equal senses. If ν is another clustering scheme, the corresponding ρ^{sf}_ν is related to ρ^{sf}_ν by

$$\rho^{sf}_\nu = \rho^{sf}_\lambda \mathbf{N}_{\lambda\nu} \tag{2.4}$$

where $\mathbf{N}_{\lambda\nu}$ is an $(N-1)$ -dimensional orthogonal square matrix whose elements depend only on the masses of the atoms and the clustering schemes λ and ν. As a result of the orthogonality of $\mathbf{N}_{\lambda\nu}$, the $\lambda \rightarrow \nu$ mass-scaled Jacobi coordinate transformation is called a kinematic rotation.[73] We can, without loss of generality, restrict ourselves to kinematic rotations which are proper, i.e., for which the determinant of $\mathbf{N}_{\lambda\nu}$ is $+1$. As a result of (2.4), the right-hand side of (2.2) is λ-independent, as is the hyperradius $\rho \geq 0$. It is useful to introduce the products of Jacobi matrices[65]

$$\mathbf{S}_\lambda = \tilde{\rho}^{sf}_\lambda \rho^{sf}_\lambda \tag{2.5}$$

and

$$\mathbf{K} = \rho^{sf}_\lambda \tilde{\rho}^{sf}_\lambda \tag{2.6}$$

$\tilde{\mathbf{A}}$ means the transpose of matrix $\mathbf{A}$, $\mathbf{S}_\lambda$ is a symmetric square matrix of dimensions $(N-1)$, and $\mathbf{K}$ is a 3×3 non-negative definite symmetric square matrix. The elements of $\mathbf{S}_\lambda$ are the scalar products $\mathbf{r}^{(j)}_\lambda \cdot \mathbf{r}^{(k)}_\lambda$ and it is called the scalar product matrix.[65] The matrix $\mathbf{K}$ is related to the system's moment of inertia tensor $\boldsymbol{I}$ by[74]

$$\boldsymbol{I} = \mu(\rho^2\mathbf{I} - \boldsymbol{K}) \tag{2.7}$$

(where $\mathbf{I}$ is the 3×3 identity matrix) and is called the moment of inertia product matrix.

Under kinematic rotations $\mathbf{S}_\lambda$ transforms according to the similarity transformation

$$\mathbf{S}_\nu = \tilde{\mathbf{N}}_{\lambda\nu}\mathbf{S}_\lambda\mathbf{N}_{\lambda\nu} \tag{2.8}$$

and is invariant under space rotations. On the other hand, $\mathbf{K}$ displays a reverse behavior, i.e., it is invariant under kinematic rotations and changes according to a similarity transformation to a matrix $\bar{\mathbf{K}}$ under space rotations.[65,67] As a result of these properties the following relations can be easily derived:

$$\det \mathbf{S}_\nu = \det \mathbf{S}_\lambda \tag{2.9}$$

$$\mathrm{tr}\, \mathbf{S}_\nu = \mathrm{tr}\, \mathbf{S}_\lambda = \rho^2 \tag{2.10}$$

$$\det \bar{\mathbf{K}} = \det \mathbf{K} \tag{2.11}$$

$$\mathrm{tr}\, \bar{\mathbf{K}} = \mathrm{tr}\, \mathbf{K} = \rho^2 \tag{2.12}$$

where det $\mathbf{A}$ and tr $\mathbf{A}$ mean respectively the determinant and the trace of the square matrix $\mathbf{A}$.

The eigenvalues K_1, K_2, and K_3 of $\mathbf{K}$ are real and non-negative and are placed for subsequent convenience in the order

$$K_3 \geq K_1 \geq K_2 \geq 0 \tag{2.13}$$

In view of the kinematic rotation invariance of $\mathbf{K}$ and of (2.12) and (2.13), we may define the λ-independent moment of inertia hyperangles θ and ϕ by

$$K_1^{1/2} = \rho \sin\theta \cos\phi \tag{2.14}$$

$$K_2^{1/2} = \rho \sin\theta \sin\phi \tag{2.15}$$

$$K_3^{1/2} = \rho \cos\theta \tag{2.16}$$

where[75]

$$0 \leq \phi \leq \pi/4 \tag{2.17}$$

$$0 \leq \theta \leq \arcsin[1/(1+\cos^2\phi)^{1/2}] \leq \arcsin\left(\frac{2}{3}\right)^{1/2} \cong 54.7^\circ \tag{2.18}$$

2.2. Row-Orthonormal Form of Jacobi Matrices and Row-Orthonormal Hyperspherical Coordinates. For $N \geq 4$ the number of columns of ρ^{sf}_λ is equal to or greater than the number 3 of its rows and can be, according to the singular value decomposition theorem for real matrices,[76,77] put in the form

$$\rho^{sf}_\lambda = \mathbf{A}_\lambda \mathbf{B} \mathbf{Q}_\lambda \tag{2.19}$$

where $\mathbf{A}_\lambda$ is a 3×3 orthogonal matrix, $\mathbf{B}$ is the diagonal matrix whose diagonal elements are $K_1^{1/2}$, $K_2^{1/2}$, and $K_3^{1/2}$ respectively, and $\mathbf{Q}_\lambda$ is a $3 \times (N-1)$ row-orthogonal matrix. When the K_i are all different, the matrices $\mathbf{A}_\lambda$, $\mathbf{B}$, and $\mathbf{Q}_\lambda$ are essentially unique once the ordering (2.13) is adopted; the slight lack of uniqueness is discussed in section 3. The determinant of $\mathbf{A}_\lambda$ can be $+1$ or -1, i.e., $\mathbf{A}_\lambda$ can be proper or improper. Once $\mathbf{A}_\lambda$ has been determined from ρ^{sf}_λ, one can define an associated *proper* orthogonal matrix $\mathbf{A}'_\lambda$ by

$$\mathbf{A}'_\lambda = \mathbf{A}_\lambda \det \mathbf{A}_\lambda \tag{2.20}$$

in terms of which ρ^{sf}_λ becomes

$$\rho^{sf}_\lambda = (-1)^{\chi_\lambda} \mathbf{A}'_\lambda \mathbf{B} \mathbf{Q}_\lambda \tag{2.21}$$

where χ_λ is 0 if det $\mathbf{A}_\lambda = +1$ and 1 if det $\mathbf{A}_\lambda = -1$. The matrices of $\mathbf{A}'_\lambda$, $\mathbf{B}$, and $\mathbf{Q}_\lambda$ can be expressed in terms of row-orthonormal hyperspherical coordinates as

$$\mathbf{A}'_\lambda = \tilde{\mathbf{R}}\,(a_\lambda, b_\lambda, c_\lambda) \tag{2.22}$$

$$\mathbf{B} = \rho \mathbf{N}\,(\theta\phi) = \rho \begin{pmatrix} \sin\theta\cos\phi & 0 & 0 \\ 0 & \sin\theta\sin\phi & 0 \\ 0 & 0 & \cos\theta \end{pmatrix} \tag{2.23}$$

$$\mathbf{Q}_\lambda = \mathbf{Q}\,(\delta^{(1)}_\lambda, \delta^{(2)}_\lambda, \ldots, \delta^{(3N-9)}_\lambda) \tag{2.24}$$

The angles a_λ, b_λ, and c_λ are the Euler angles which rotate the space-fixed frame $Gxyz$ to the principal-axes-of-inertia body-fixed frame $Gx^{\lambda}y^{\lambda}z^{\lambda}$, and $\mathbf{R}\,(a_\lambda, b_\lambda, c_\lambda)$ is the corresponding proper rotation matrix.[78] Although the directions of the axes of the body-fixed frame are λ-independent, their senses, as shown in section 3.2 for $N = 4$, are generally not. These Euler angles have the usual ranges of definition

$$0 \le a_\lambda, c_\lambda < 2\pi \qquad 0 \le b_\lambda \le \pi \tag{2.25}$$

In addition, $\{\delta^{(i)}_\lambda | i = 1, 2, \ldots, 3N - 9\}$ is a set of internal configuration space hyperangles and $\mathbf{Q}$ is a $3 \times (N - 1)$ row-orthonormal matrix, i.e., satisfies the condition

$$\mathbf{Q}\,\tilde{\mathbf{Q}} = \mathbf{I} \tag{2.26}$$

For tetraatomic systems, $\mathbf{Q}$ depends on three internal hyperangles $\delta^{(1)}_\lambda$, $\delta^{(2)}_\lambda$, and $\delta^{(3)}_\lambda$ and can be chosen to be the proper three-dimensional square orthogonal matrix

$$\mathbf{Q} = \tilde{\mathbf{R}}\,(\delta^{(1)}_\lambda, \delta^{(2)}_\lambda, \delta^{(3)}_\lambda) \tag{2.27}$$

For such systems ρ^{sf}_λ is a 3×3 square matrix and (2.21) can be rewritten as

$$\rho^{sf}_\lambda = (-1)^{\chi}\, \tilde{\mathbf{R}}\,(a_\lambda, b_\lambda, c_\lambda)\, \rho \mathbf{N}\,(\theta, \phi)\, \tilde{\mathbf{R}}\,(\delta^{(1)}_\lambda, \delta^{(2)}_\lambda, \delta^{(3)}_\lambda) \tag{2.28}$$

with

$$(-1)^{\chi} = \text{sign}\,(\boldsymbol{r}^{(1)}_\lambda \times \boldsymbol{r}^{(2)}_\lambda \cdot \boldsymbol{r}^{(3)}_\lambda) = \text{sign det}\, \rho^{sf}_\lambda \tag{2.29}$$

where the sign of zero is considered to be $+$. This χ has been written without the index λ because it is invariant under proper kinematic rotations since ρ^{sf}_λ and ρ^{sf}_ν have equal determinants, as can be seen from (2.4). Its value is 0 (1) if $\mathbf{r}^{(1)}_\lambda$, $\mathbf{r}^{(2)}_\lambda$, and $\mathbf{r}^{(3)}_\lambda$ comprise a right-handed (left-handed) set of vectors. For $N = 3$ (i.e., triatomic systems), ρ^{sf}_λ has dimensions 3×2 and the singular value decomposition theorem is still valid with $\chi = 0$, $\mathbf{Q}_\lambda$ being now a row-orthogonal but not row-orthonormal matrix. This special case has been considered in detail previously.[67]

Equation 2.21, with $\mathbf{A}'_\lambda$, $\mathbf{B}$, and $\mathbf{Q}_\lambda$ given by (2.22) through (2.24) is called[65,67] the row-orthonormal form of the Jacobi matrix ρ^{sf}_λ. The method used previously to arrive at it[65] was essentially a rederivation of the singular value decomposition theorem. The quantities a_λ, b_λ, c_λ, χ, ρ, θ, ϕ, $\delta^{(1)}$, $\delta^{(2)}_\lambda$, ..., $\delta^{(3N-9)}_\lambda$ are called the λ row-orthonormal hyperspherical coordinates of the N-atom system. They consist of the chirality coordinate χ, the hyperradius ρ, and $3N - 4$ angles of which three are the "external" Euler angles $\boldsymbol{a}_\lambda \equiv (a_\lambda, b_\lambda, c_\lambda)$ and $\theta, \phi, \delta_\lambda \equiv (\delta^{(1}_\lambda, \delta^{(2)}_\lambda, \ldots, \delta^{(3N-9)}_\lambda)$ are $3N - 7$ "internal" hyperangles (which reduce to two angles θ and δ_λ for triatomic systems since in this case $\phi = 0$ and this angle does not count as a coordinate but $\mathbf{Q}$ still depends on the one internal hyperangle δ_λ[67]). In the Born−Oppenheimer single electronically-adiabatic state approximation, the corresponding potential energy function V_λ is independent of χ and $\boldsymbol{a}_\lambda$ but depends on ρ and on the set of internal hyperangles $\theta, \phi, \delta_\lambda$.

The ranges of the $\delta^{(i)}_\lambda$ appearing in (2.24) are determined by the requirement that for general geometries of the system (which exclude some special geometries as discussed in section 5 for tetraatomic systems) the correspondence between the λ row-orthonormal hyperspherical coordinates and ρ^{sf}_λ be one-to-one. For tetraatomic systems, (2.27) limits the ranges of the $\delta^{(i)}_\lambda$ ($i = 1, 2, 3$) to

$$0 \le \delta^{(1)}_\lambda, \delta^{(3)}_\lambda < 2\pi \qquad 0 \le \delta^{(2)}_\lambda \le \pi \tag{2.30}$$

However, this one-to-one correspondence, as shown in section 3.1, further limits these ranges to[79]

$$0 \le \delta^{(1)}_\lambda, \delta^{(3)}_\lambda < \pi \qquad 0 \le \delta^{(2)}_\lambda \le \pi \tag{2.31}$$

Once this one-to-one correspondence between ρ^{sf}_λ and the total set of hyperspherical coordinates $\boldsymbol{a}_\lambda$, χ, ρ, θ, ϕ, δ_λ is established, a similar one-to-one correspondence results between the scalar product matrix $\mathbf{S}_\lambda$ and the internal hyperspherical coordinates ρ, θ, ϕ, δ_λ, except for some special geometries, as discussed in section 5.

3. Transformation Properties of Row-Orthonormal Hyperspherical Coordinates for Tetraatomic Systems

In this section we determine the ranges of the $\delta^{(i)}_\lambda$ hyperangles and describe how row-orthonormal hyperspherical coordinates for tetraatomic systems transform under kinematic rotations, inversion through the system's center of mass, and permutation of identical particles.

3.1. The Ranges of the Hyperangles $\boldsymbol{\delta}_\lambda$. Given ρ^{sf}_λ (i.e., $\mathbf{r}^{(1)}_\lambda$, $\mathbf{r}^{(2)}_\lambda$, and $\mathbf{r}^{(3)}_\lambda$), (2.29) furnishes χ uniquely. As a result, (2.28) can be considered as a system of nine scalar equations in the nine unknowns $\boldsymbol{a}_\lambda$, ρ, θ, ϕ, δ_λ. It was possible to solve the corresponding equations for triatomic systems explicitly (see sections 4.1 and 4.2 of ref 67). For the tetraatomic case, the (analytical) solution of (2.28) is very cumbersome. Nevertheless, as stated in the next-to-the-last paragraph of section 2.2, the ranges of these tetraatomic hyperspherical coordinates can be determined from the requirement of a one-to-one correspondence between them and ρ^{sf}_λ, taking (2.28) to be an implicit definition of these coordinates.

As stated in section 2.2, the matrices $\mathbf{A}_\lambda$, $\mathbf{B}$, $\mathbf{Q}_\lambda$ which appear in (2.19), and as a result the matrix $\mathbf{A}'_\lambda$ of (2.20), are essentially unique as long as the eigenvalues of (2.6) are nondegenerate and placed in a specific order, such as (2.13). The only lack of uniqueness are phase factors equal to $+1$ or -1 for the columns of $\mathbf{A}'_\lambda$ and rows of $\mathbf{Q}_\lambda$. Indeed, let $\mathbf{I}_j$ ($j = 1, 2, 3$) be the 3×3 diagonal matrices defined by

$$\mathbf{I}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \mathbf{I}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \mathbf{I}_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.1}$$

These matrices have the properties

$$\mathbf{I}_j^2 = \mathbf{I} \qquad \det \mathbf{I}_j = +1 \qquad j = 1, 2, 3 \tag{3.2}$$

The diagonality of **B** allows their insertion into (2.21) as

$$\rho_\lambda^{sf} = (-1)^{\chi_\lambda}\, \mathbf{A}'_\lambda \mathbf{I}_j \mathbf{B} \mathbf{I}_j \mathbf{Q}_\lambda$$

$$j = 1,2,3 \tag{3.3}$$

All four right-hand sides of (2.21) and (3.3) are equal. We now define the matrices $\mathbf{A}'_\lambda$ and $\mathbf{Q}_{\lambda_j}$ by

$$\mathbf{A}'_{\lambda_j} = \mathbf{A}'_\lambda \mathbf{I}_j \qquad \mathbf{Q}_{\lambda_j} = \mathbf{I}_j \mathbf{Q}_\lambda \qquad j = 1,2,3 \tag{3.4}$$

The $\mathbf{A}'_{\lambda_j}$ are 3×3 proper orthogonal matrices, and the $\mathbf{Q}_{\lambda_j}$ are $3 \times (N-1)$ row-orthonormal matrices. The four matrices $\mathbf{A}'_\lambda$ and $\mathbf{A}'_{\lambda_j}$ are distinct as are $\mathbf{Q}_\lambda$ and $\mathbf{Q}_{\lambda_j}$. This leads to the lack of uniqueness mentioned above and is applicable for arbitrary $N \geq 3$.

For the tetraatomic case, (3.4) becomes

$$\tilde{\mathbf{R}}(\boldsymbol{a}_{\lambda_j}) = \tilde{\mathbf{R}}(\boldsymbol{a}_\lambda)\mathbf{I}_j \qquad \tilde{\mathbf{R}}(\delta_{\lambda_j}) = \mathbf{I}_j \tilde{\mathbf{R}}(\delta_\lambda) \tag{3.5}$$

We can easily express the $\boldsymbol{a}_{\lambda_j}$ in terms of $\boldsymbol{a}_\lambda$ and the δ_{λ_j} in terms of δ_λ by equating the third row and column elements of the right- and left-hand sides of (3.5). The result is

$$\boldsymbol{a}_{\lambda_1} = ((\pi + a_\lambda) \bmod 2\pi, \pi - b_\lambda, (\pi - c_\lambda) \bmod 2\pi)$$

$$\delta_{\lambda_1} = ((2\pi - \delta_\lambda^{(1)}) \bmod 2\pi, \pi - \delta_\lambda^{(2)}, (\pi + \delta_\lambda^{(3)}) \bmod 2\pi) \tag{3.6}$$

$$\boldsymbol{a}_{\lambda_2} = ((\pi + a_\lambda) \bmod 2\pi, \pi - b_\lambda, (2\pi - c_\lambda) \bmod 2\pi)$$

$$\delta_{\lambda_2} = ((\pi - \delta_\lambda^{(1)}) \bmod 2\pi, \pi - \delta_\lambda^{(2)}, (\pi + \delta_\lambda^{(3)}) \bmod 2\pi) \tag{3.7}$$

$$\boldsymbol{a}_{\lambda_3} = (a_\lambda, b_\lambda, (\pi + c_\lambda) \bmod 2\pi)$$

$$\delta_{\lambda_3} = ((\pi + \delta_\lambda^{(1)}) \bmod 2\pi, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) \tag{3.8}$$

If the $\delta_\lambda^{(i)}$ are permitted to assume arbitrary values in the ranges defined by (2.30), the generally distinct four sets of row-orthonormal coordinates $\boldsymbol{a}_\lambda, \chi, \rho, \theta, \phi, \delta_\lambda$ and $\boldsymbol{a}_{\lambda_j}, \chi, \rho, \theta, \phi, \delta_{\lambda_j}$ ($j = 1, 2, 3$) furnish the same Jacobi matrix ρ_λ^{sf}, leading to a 4 to 1 correspondence between ρ_λ^{sf} and distinct sets of hyperspherical coordinates. This can be reduced to a one-to-one correspondence by restricting the allowed ranges of the $\delta_\lambda^{(i)}$, as the following analysis indicates.

Let us consider a δ_λ space whose Cartesian coordinate axes are $O\delta_\lambda^{(1)}$, $O\delta_\lambda^{(2)}$, $O\delta_\lambda^{(3)}$. Equations (2.30) define a parallelopiped in this space, which can be partitioned into four cubes C, C_j ($j = 1, 2, 3$) whose edges have length π, as indicated in Figure 1. As we allow a point $P \equiv (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ to scan the internal region of cube C, points $P_j \equiv (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ scan the internal regions of cubes C_j. Therefore, we must limit the range of the $\delta_\lambda^{(j)}$ to that of cube C. Consideration of the surface of C indicates that points on its $\delta_\lambda^{(1)} = \pi$ and $\delta_\lambda^{(3)} = \pi$ faces, including the corresponding edges, should be omitted, whereas points on all other faces and edges should be allowed. These results are expressed by (2.31). The ranges of χ, ρ, θ, ϕ, and the $\boldsymbol{a}_\lambda$ are still those given by $\chi = 0, 1$, $\rho \geq 0$, and (2.17), (2.18), and (2.25). These ranges span all possible ρ_λ^{sf}, and reciprocally, ρ_λ^{sf} spans these ranges. Although, for a given set of such row-orthonormal hyperspherical coordinates, a single ρ_λ^{sf} is obtained, it should be remembered that for some special geometries of the four-particle system more than one set of hyperspherical coordinates satisfying (2.31) can be obtained (see section 5). As a result, when using these coordinates for solving scattering problems, special attention should be paid to these geometries.

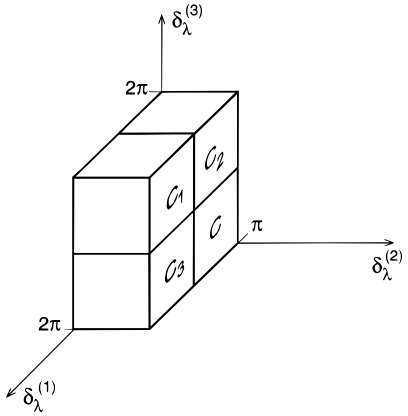

Figure 1. Ranges of definition of the $\delta_\lambda^{(i)}$ ($i = 1, 2, 3$) row-orthonormal hyperspherical coordinates for tetraatomic systems. The set of cubes C, C_j ($j = 1, 2, 3$) yields a 1 to 4 correspondence between Jacobi matrices ρ_λ^{sf} and sets of such coordinates. Limiting their range to that of cube C (see (2.31) and section 3.1) makes this correspondence become 1 to 1, except for the special geometries considered in section 5.

3.2. Kinematic Rotations. We will now derive the effect of kinematic rotations on the row-orthonormal hyperspherical coordinates for tetraatomic systems. For triatomic systems, it was possible to obtain this effect by using one of two methods:[67] one based on the explicit dependence of such coordinates on ρ_λ^{sf} and the other based on the implicit dependence described by the expression for ρ_λ^{sf} as a function of those coordinates. For tetraatomic systems only the implicit method will be used since, as mentioned at the beginning of section 3.1, the explicit dependence is very cumbersome.

We already showed, after (2.29), that χ is invariant under proper kinematic rotations. The matrix **K** defined by (2.6) is also invariant under such rotations[65,67] and, therefore, so are the ρ, θ, ϕ coordinates given by (2.14) through (2.16). Replacing (2.28) and its ν counterpart into (2.4) and using these kinematic-rotation-invariant properties results in

$$\tilde{\boldsymbol{R}}\,(\boldsymbol{a}_\nu)\, \boldsymbol{N}\,(\theta,\phi)\, \tilde{\boldsymbol{R}}\,(\delta_\nu) = \tilde{\boldsymbol{R}}\,(\boldsymbol{a}_\lambda)\, \boldsymbol{N}\,(\theta,\phi)\, \tilde{\boldsymbol{R}}\,(\delta_\lambda)\, \boldsymbol{N}_{\lambda\nu} \tag{3.9}$$

We know that the directions of the principal axes of inertia are determined by the positions of the four particles and are invariant under kinematic rotations. Since both principal axes frames $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ and $Gx^{I\nu}y^{I\nu}z^{I\nu}$ must have the same right-handedness as the space-fixed frame, either none or two of the senses of the $I\nu$ axes can differ from the corresponding $I\lambda$ ones. As a result, we must have

$$\mathbf{R}\,(\boldsymbol{a}_\nu) = \mathbf{I}_j \mathbf{R}\,(\boldsymbol{a}_\lambda) \tag{3.10}$$

where $\mathbf{I}_j$ ($j = 0, ..., 3$) stands for the identity matrix for $j = 0$ and the matrices defined by (3.1) for $j = 1, 2, 3$. Replacement of (3.10) into (3.9) leads to

$$\tilde{\boldsymbol{R}}\,(\delta_\nu) = \mathbf{I}_j\, \tilde{\boldsymbol{R}}\,(\delta_\lambda)\, \boldsymbol{N}_{\lambda\nu} \tag{3.11}$$

This equation has a solution in the range (2.30) for each of the values of j. However, from considerations similar to those in the last paragraph of section 3.1 we are assured that one and only one of these lies in the range (2.31). In this manner δ_λ

TABLE 1: Relation between j and $n_{\lambda\nu}^{(1)}$, $n_{\lambda\nu}^{(3)}$

j	$n_{\lambda\nu}^{(1)}$	$n_{\lambda\nu}^{(1)}$
0	0	0
1	0	1
2	1	1
3	1	0

TABLE 2: Relation between $n_{\lambda\nu}^{(1)}$, $n_{\lambda\nu}^{(3)}$, δ_ν, and $\bar{\delta}_\nu$

		$n_{\lambda\nu}^{(1)}$	$n_{\lambda\nu}^{(3)}$	$\delta_\nu^{(1)}$	$\delta_\nu^{(2)}$	$\delta_\nu^{(3)}$
$0 \le \bar{\delta}_\nu^{(3)} \le \pi$	$0 \le \bar{\delta}_\nu^{(1)} \le \pi$	0	0	$\bar{\delta}_\nu^{(1)}$	$\bar{\delta}_\nu^{(2)}$	$\bar{\delta}_\nu^{(3)}$
	$\pi < \bar{\delta}_\nu^{(1)} < 2\pi$	1	0	$\bar{\delta}_\nu^{(1)} - \pi$	$\bar{\delta}_\nu^{(2)}$	$\bar{\delta}^{(3)}$
$\pi < \bar{\delta}_\nu^{(3)} < 2\pi$	$0 \le \bar{\delta}_\nu^{(1)} \le \pi$	1	1	$\pi - \bar{\delta}_\nu^{(1)}$	$\pi - \bar{\delta}_\nu^{(2)}$	$\bar{\delta}_\nu^{(3)} - \pi$
	$\pi < \bar{\delta}_\nu^{(1)} < 2\pi$	0	1	$2\pi - \bar{\delta}_\nu^{(1)}$	$\pi - \bar{\delta}_\nu^{(2)}$	$\bar{\delta}_\nu^{(3)} - \pi$

TABLE 3: Relation between a_ν and $n_{\lambda\nu}^{(1)}$, $n_{\lambda\nu}^{(3)}$, and a_λ and the Senses of the $Gx^{I\nu}y^{I\nu}z^{I\nu}$ Axes in Terms of Those of $Gx^{I\lambda}Gy^{I\lambda}Gz^{I\lambda}$

$n_{\lambda\nu}^{(1)}$	$n_{\lambda\nu}^{(3)}$	a_ν[a]	b_ν	c_ν[a]	$Gx^{I\nu}$	$Gy^{I\nu}$	$Gz^{I\nu}$
0	0	a_λ	b_λ	c_λ	+	+	+
1	0	a_λ	b_λ	$\pi + c_\lambda$	−	−	+
1	1	$\pi + a_\lambda$	$\pi - b_\lambda$	$\pi - c_\lambda$	−	+	−
0	1	$\pi + a_\lambda$	$\pi - b_\lambda$	$2\pi - c_\lambda$	+	−	−

[a] The relations between the ν and λ Euler angles are given modulo 2π.

and $\boldsymbol{N}_{\lambda\nu}$ together with (3.11) uniquely determine j and δ_ν, and use of (3.10) and a knowledge of j and $\boldsymbol{a}_\lambda$ uniquely determine $\boldsymbol{a}_\nu$.

All four matrices $\mathbf{I}_j$ can be put in the form

$$\mathbf{I}_j = \mathbf{I}_{n_{\lambda\nu}^{(1)} n_{\lambda\nu}^{(3)}} = \begin{pmatrix} (-1)^{n_{\lambda\nu}^{(1)}} & 0 & 0 \\ 0 & (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}} & 0 \\ 0 & 0 & (-1)^{n_{\lambda\nu}^{(3)}} \end{pmatrix} \quad (3.12)$$

where $n_{\lambda\nu}^{(1)}$ and $n_{\lambda\nu}^{(3)}$ are 0 or 1 and depend on δ_λ in a stepwise manner. Their relation to j is given in Table 1. We now define $\bar{\delta}_\nu$ as the unique solution of

$$\tilde{\mathbf{R}}(\bar{\delta}_\nu) = \tilde{\mathbf{R}}(\delta_\lambda)\,\mathbf{N}_{\lambda\nu} \quad (3.13)$$

in range (2.30). In Table 2 we give $n_{\lambda\nu}^{(1)}$, $n_{\lambda\nu}^{(3)}$, and δ_ν in terms of this $\bar{\delta}_\nu$.

In Table 3, we give the values for $\boldsymbol{a}_\nu$ in terms of $n_{\lambda\nu}^{(1)}$, $n_{\lambda\nu}^{(3)}$, and $\boldsymbol{a}_\lambda$, as well as the senses of the $Gx^{I\nu}y^{I\nu}z^{I\nu}$ axes in terms of those of $Gx^{I\nu}y^{I\nu}z^{I\nu}$ as the plus or minus signs according to

$$Gx^{I\nu} = (-1)^{n_{\lambda\nu}^{(1)}}\, Gx^{I\lambda}$$

$$Gy^{I\nu} = (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}}\, Gy^{I\lambda}$$

$$Gz^{I\nu} = (-1)^{n_{\lambda\nu}^{(3)}}\, Gz^{I\lambda} \quad (3.14)$$

3.3. Inversion through the Center of Mass. Let us now consider the effect of inverting the tetraatomic system through its center of mass. Representing the inversion operator by $\hat{\mathcal{I}}$, we have

$$\hat{\mathcal{I}}\rho_\lambda^{sf} = -\rho_\lambda^{sf} \quad (3.15)$$

From this expression we get

$$\det(\hat{\mathcal{I}}\rho_\lambda^{sf}) = -\det\rho_\lambda^{sf} \quad (3.16)$$

and, in view of (2.29)

$$(\hat{\mathcal{I}}\chi) = \chi + 1 \bmod 2 \quad (3.17)$$

As a result of (2.5) and (3.15) **K** is inversion-invariant, and in view of (2.14) through (2.16), so are ρ,θ,ϕ

$$\hat{\mathcal{I}}(\rho,\theta,\phi) = \rho,\theta,\phi \quad (3.18)$$

Furthermore, (2.7) shows that **K** determines the moment of tensor $\boldsymbol{I}$ and therefore the directions of the principal axes of inertia, but not their senses. Those directions are therefore inversion-invariant, and since the senses of either none or two of the axes of the $\hat{\mathcal{I}}(Gx^{I\lambda}y^{I\lambda}z^{I\lambda})$ frame can be different from those of the $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ frame, we must have, in analogy with (4.10)

$$\mathbf{R}(\hat{\mathcal{I}}\boldsymbol{a}_\lambda) = \mathbf{I}_j\mathbf{R}(\boldsymbol{a}_\lambda) \quad (3.19)$$

We now write

$$\hat{\mathcal{I}}\rho^{sf} = (-1)^{\hat{\mathcal{I}}\chi}\,\tilde{\mathbf{R}}(\hat{\mathcal{I}}\boldsymbol{a}_\lambda)\,(\hat{\mathcal{I}}\rho)\,\mathbf{N}(\hat{\mathcal{I}}\theta,\hat{\mathcal{I}}\phi)\,\tilde{\mathbf{R}}(\hat{\mathcal{I}}\delta_\lambda) \quad (3.20)$$

Replacement of (2.28), (3.19), and (3.20) into (3.15) and use of (3.17) and (3.18) leads to

$$\tilde{\mathbf{R}}(\hat{\mathcal{I}}\delta_\lambda) = \mathbf{I}_j\tilde{\mathbf{R}}(\delta_\lambda) \quad (3.21)$$

Similarly to (3.11), (3.21) has a solution in the range (2.31) for one and one only of the four possible values of j, and that solution is

$$\hat{\mathcal{I}}\delta_\lambda = \delta_\lambda \quad (3.22)$$

corresponding to $j = 0$. When replaced in (3.19), it yields

$$\hat{\mathcal{I}}\boldsymbol{a}_\lambda = \boldsymbol{a}_\lambda \quad (3.23)$$

We conclude that $\hat{\mathcal{I}}$ changes the chirality of the system, while leaving the remaining row-orthonormal hyperspherical coordinates unchanged.

3.4. Permutations of Identical Nuclei. Of the four nuclei P_i ($i = 1, ..., 4$) comprising the tetraatomic system, all, some, or none can be identical. We should therefore consider the four kinds of systems A_4, A_3B, A_2B_2, A_2BC and ABCD, where A through D stand for distinct nuclei. Possible examples are the H_4, H_2OH, H_2O_2, HOCO, and HOCN, respectively. It is useful to determine the effect of the permutations of identical P_i on the row-orthonormal hyperspherical coordinates for the purpose of decoupling the associated nuclear motion equations—scattering or bound—according to the irreducible representations of the corresponding permutation groups.

Generally speaking we have either no, one, or two sets of identical particles: ABCD; A_4,A_3B and A_2BC; and A_2B_2, respectively. For the ABCD case, no permutations are considered. For A_4, A_3B, and A_2BC we consider the permutations comprising the S_4, S_3, and S_2 permutation groups, respectively.[80] Finally, for A_2B_2 we must consider the direct product group $S_2 \otimes S_2$. For the sake of brevity, we will only discuss explicitly the A_3B case, appropriate for the H_2OH system; generalization to the other cases is however straightforward.

Let the nuclei P_1, P_2, and P_3 be identical to each other and distinct from P_4. We define the $\lambda = 1$ arrangement Jacobi coordinates as the one in which $\mathbf{r}_1'^{(1)}$ is the vector from P_1 to P_2, $\mathbf{r}_1'^{(2)}$ that from the center of mass of the P_1, P_2 pair to P_3 and $\mathbf{r}_1'^{(3)}$ the one connecting the center-of-mass of the $P_1P_2P_3$ triplet to P_4. We will consider the effect of the S_3 permutations on the corresponding ρ_1^{sf} Jacobi matrix. This group is isomorphic with the point group C_{3v} of an equilateral triangle.[81] For this reason it is convenient to use the notation

$$\hat{E} \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} \quad \hat{\sigma}_1 \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \quad \hat{\sigma}_2 \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}$$

$$\hat{\sigma}_3 \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} \quad \hat{C}^+ \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \quad \hat{C}^- \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \tag{3.24}$$

where the permutation

$$\begin{pmatrix} 1 & 2 & 3 \\ i & j & k \end{pmatrix}$$

replaces 1 by i, 2 by j, and 3 by k, with i,j,k being an arbitrary permutation of 1,2,3. The permutations $\hat{E}$, $\hat{C}^+$, and $\hat{C}^-$ have even parity and $\hat{\sigma}_1$, $\hat{\sigma}_2$, and $\hat{\sigma}_3$ have odd parity. We will designate a general operation of S_3 or C_{3v} by $\hat{g}$. The effect of $\hat{g}$ on ρ_1^{sf} can be written as

$$\hat{g}\rho_1^{sf} = \rho_1^{sf}\mathbf{N}_{\hat{g}} \tag{3.25}$$

where $\mathbf{N}_{\hat{g}}$ is a 3×3 orthogonal matrix given by[82]

$$\mathbf{N}_{\hat{g}} = \begin{pmatrix} (-1)^g \cos\beta_{\hat{g}} & \sin\beta_{\hat{g}} & 0 \\ -(-1)^g \sin\beta_{\hat{g}} & \cos\beta_{\hat{g}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.26}$$

where $(-1)^g = +1$ for the even parity $\hat{g}$ and $(-1)^g = -1$ for the odd parity $\hat{g}$. The angles $\beta_{\hat{g}}$ are defined by

$$\beta_{\hat{E}} = \beta_{\hat{\sigma}_3} = 0 \quad \beta_{\hat{C}^+} = \beta_{\hat{\sigma}_1} = \frac{2\pi}{3} \quad \beta_{\hat{C}^-} = \beta_{\hat{\sigma}_2} = \frac{4\pi}{3} \tag{3.27}$$

Equations 3.25 through 3.27 result from the definition of the $\mathbf{r}_\lambda^{(i)}$ for $\lambda = 1$ and the fact that P_1, P_2, and P_3 have equal masses. We see from (3.26) that

$$\det\mathbf{N}_{\hat{g}} = (-1)^g \tag{3.28}$$

and therefore that $\mathbf{N}_{\hat{g}}$ is proper (improper) for even (odd) parity $\hat{g}$.

Replacement of (3.25) into (2.6) shows that $\mathbf{K}$ is invariant under all $\hat{g}$ and therefore that ρ, θ, and ϕ are unaffected by these operations:

$$\hat{g}(\rho,\theta,\phi) = (\rho,\theta,\phi) \tag{3.29}$$

To determine the effect of $\hat{g}$ on χ we use (2.29), its $\hat{g}\rho_1^{sf}$ counterpart and (3.28). The result is

$$\hat{g}\chi = \chi + g \bmod 2 \tag{3.30}$$

which means that even (odd) permutations $\hat{g}$ do not (do) change the chirality coordinate χ. To obtain the effect of $\hat{g}$ on δ_1 and $\boldsymbol{a}_1$ we use (2.28) with $\lambda = 1$ and its $\hat{g}\rho_1^{sf}$ counterpart and proceed as in section 3.2, remembering that permutations of identical nuclei cannot change the directions of the principal axes of inertia. The result is

$$\mathbf{R}(\hat{g}\delta_1) = (-1)^g \tilde{\mathbf{N}}_{\hat{g}} \mathbf{R}(\delta_1) \mathbf{I}_{n_{\hat{g}}^{(1)} n_{\hat{g}}^{(3)}} \tag{3.31}$$

$$\mathbf{R}(\hat{g}\boldsymbol{a}_1) = \mathbf{I}_{n_{\hat{g}}^{(1)} n_{\hat{g}}^{(3)}} \mathbf{R}(\boldsymbol{a}_1) \tag{3.32}$$

where $\mathbf{I}_{n_{\hat{g}}^{(1)} n_{\hat{g}}^{(3)}}$ is given by (3.12) with the subscripts $\lambda\nu$ replaced by $\hat{g}$. The two expressions above yield

$$(-1)^{n_{\hat{g}}^{(1)}} = \text{sign}\sin(\delta_1^{(3)} - \beta_{\hat{g}}) \quad (-1)^{n_{\hat{g}}^{(3)}} = (-1)^{n_{\hat{g}}^{(1)}+g} \tag{3.33}$$

$$\cos(\hat{g}\delta_1^{(1)}) = (-1)^{n_{\hat{g}}^{(3)}} \cos\delta_1^{(1)} \quad \sin(\hat{g}\delta_1^{(1)}) = \sin\delta_1^{(1)} \tag{3.34}$$

$$\cos(\hat{g}\delta_1^{(2)}) = (-1)^{n_{\hat{g}}^{(1)}} \cos\delta_1^{(2)} \quad \sin(\hat{g}\delta_1^{(2)}) = \sin\delta_1^{(2)} \tag{3.35}$$

$$\cos(\hat{g}\delta_1^{(3)}) = (-1)^{n_{\hat{g}}^{(3)}} \cos(\delta_1^{(3)} - \beta_{\hat{g}})$$
$$\sin(\hat{g}\delta_1^{(3)}) = (-1)^{n_{\hat{g}}^{(1)}} \sin(\delta_1^{(3)} - \beta_{\hat{g}}) \tag{3.36}$$

From these equations, valid for all $\hat{g}$, we obtain the values of $(-1)^{n(1)\hat{g}}$ and $(-1)^{n(3)\hat{g}}$ given in Table 4 and the following detailed expressions for $\hat{g}\delta_1$ and $\hat{g}\mathbf{a}_1$:

$$\hat{E}\delta_1 = \delta_1 \quad \hat{E}\boldsymbol{a}_1 = \boldsymbol{a}_1 \tag{3.37}$$

$$\hat{\sigma}_1\delta_1 = \begin{cases} \left(\delta_1^{(1)}, \pi - \delta_1^{(2)}, \frac{2\pi}{3} - \delta_1^{(3)}\right) & \text{for } 0 \le \delta_1^{(3)} \le \frac{2\pi}{3} \\ \left(\pi - \delta_1^{(1)}, \delta_1^{(2)}, \frac{5\pi}{3} - \delta_1^{(3)}\right) & \text{for } \frac{2\pi}{3} < \delta_1^{(3)} < \pi \end{cases} \tag{3.38}$$

$$\hat{\sigma}_1\hat{\boldsymbol{a}}_1 =$$

$$\begin{cases} (a_1, b_1, (\pi + c_1) \bmod 2\pi) & \text{for } 0 \le \delta_1^{(3)} \le \frac{2\pi}{3} \\ ((\pi + a_1) \bmod 2\pi, \pi - b_1, (2\pi - c_1) \bmod 2\pi) & \text{for } \frac{2\pi}{3} < \delta_1^{(3)} < \pi \end{cases} \tag{3.39}$$

$$\hat{\sigma}_2\delta_1 = \begin{cases} \left(\pi - \delta_1^{(1)}, \delta_1^{(2)}, \frac{\pi}{3} - \delta_1^{(3)}\right) & \text{for } 0 \le \delta_1^{(3)} \le \frac{\pi}{3} \\ \left(\delta_1^{(1)}, \pi - \delta_1^{(2)}, \frac{4\pi}{3} - \delta_1^{(3)}\right) & \text{for } \frac{\pi}{3} < \delta_1^{(3)} < \pi \end{cases} \tag{3.40}$$

$$\hat{\sigma}_2\boldsymbol{a}_1 =$$

$$\begin{cases} ((\pi + a_1) \bmod 2\pi, \pi - b_1, (2\pi - c_1) \bmod 2\pi) & \text{for } 0 \le \delta_1^{(3)} \le \frac{\pi}{3} \\ (a_1, b_1, (\pi + c_1) \bmod 2\pi) & \text{for } \frac{\pi}{3} < \delta_1^{(3)} < \pi \end{cases} \tag{3.41}$$

$$\hat{\sigma}_3\delta_1 = (\pi - \delta_1^{(1)}, \delta_1^{(2)}, \pi - \delta_1^{(3)}) \tag{3.42}$$

$$\hat{\sigma}_3\boldsymbol{a}_1 = ((\pi + a_1) \bmod 2\pi, \pi - b_1, (2\pi - c_1) \bmod 2\pi) \tag{3.43}$$

$$\hat{C}^+\delta_1 =$$

$$\begin{cases} \left(\pi - \delta_1^{(1)}, \pi - \delta_1^{(2)}, \frac{\pi}{3} + \delta_1^{(3)}\right) & \text{for } 0 \le \delta_1^{(3)} < \frac{2\pi}{3} \\ \left(\delta_1^{(1)}, \delta_1^{(2)}, \delta_1^{(3)} - \frac{2\pi}{3}\right) & \text{for } \frac{2\pi}{3} \le \delta_1^{(3)} \le \pi \end{cases} \tag{3.44}$$

$$\hat{C}^+\boldsymbol{a}_1 =$$

$$\begin{cases} ((\pi + a_1) \bmod 2\pi, \pi - b_1, (2\pi - c_1) \bmod 2\pi) & \text{for } 0 \le \delta_1^{(3)} < \frac{2\pi}{3} \\ (a_1, b_1, c_1) & \text{for } \frac{2\pi}{3} \le \delta_1^{(3)} < \pi \end{cases} \tag{3.45}$$

$$\hat{C}^-\delta_1 =$$

$$\begin{cases} \left(\delta_1^{(1)}, \delta_1^{(2)}, \frac{2\pi}{3} + \delta_1^{(3)}\right) & \text{for } 0 \le \delta_1^{(3)} < \frac{2\pi}{3} \\ \left(\pi - \delta_1^{(1)}, \pi - \delta_1^{(2)}, \delta_1^{(3)} - \frac{\pi}{3}\right) & \text{for } \frac{\pi}{3} \le \delta_1^{(3)} < \pi \end{cases} \tag{3.46}$$

$$\hat{C}^-\boldsymbol{a}_1 =$$

$$\begin{cases} (a_1, b_1, c_1) & \text{for } 0 \le \delta_1^{(3)} < \frac{\pi}{3} \\ ((\pi + a_1) \bmod 2\pi, \pi - b_1, (\pi - c_1) \bmod 2\pi) & \text{for } \frac{\pi}{3} \le \delta_1^{(3)} < \pi \end{cases} \tag{3.47}$$

TABLE 4: Values of $(-1)^{n_g^{(1)}}$ and $(-1)^{n_g^{(3)}}$

$\hat{g}$	range of $\delta_1^{(3)}$	$(-1)^{n_g^{(1)}}$	$(-1)^{n_g^{(3)}}$
$\hat{E}$	$0 \le \delta_1^{(1)} < \pi$	1	1
$\hat{\sigma}_1$	$0 \le \delta_1^{(3)} \le 2\pi/3$	−1	1
	$2\pi/3 < \delta_1^{(3)} < \pi$	1	−1
$\hat{\sigma}_2$	$0 \le \delta_1^{(3)} \le \pi/3$	1	−1
	$\pi/3 < \delta_1^{(3)} < \pi$	−1	1
$\hat{\sigma}_3$	$0 < \delta_1^{(3)} < \pi$	1	−1
C^+	$0 \le \delta_1^{(3)} < 2\pi/3$	−1	−1
	$2\pi/3 \le \delta_1^{(3)} < \pi$	1	1
C^-	$0 \le \delta_1^{(3)} < \pi/3$	1	1
	$\pi/3 \le \delta_1^{(3)} < \pi$	−1	−1

These results are relatively simple and bear a close resemblance to the corresponding ones in ref 67. The reason for this simplicity is the ordering of $\mathbf{r}_1^{(1)}$, $\mathbf{r}_1^{(2)}$, and $\mathbf{r}_1^{(3)}$ adopted in (2.3).[72]

4. The Hamiltonian for Tetraatomic Systems and Its Transformation Properties

We now derive the nuclear motion Hamiltonian operator for tetraatomic systems in row-orthonormal hyperspherical coordinates as well as the corresponding volume element and transformation properties under the symmetry operations of the system.

4.1. The Hamiltonian. We assume that all matrix elements of the first and second derivative operators in the electronically-adiabatic representation vanish and therefore that the motion of the nuclei occurs on a single electronically-adiabatic potential energy surface V. In addition we neglect spin-containing terms in the system's nuclear motion Hamiltonian, which is taken to be

$$\hat{H} = \hat{T}_\lambda + V_\lambda(\rho,\theta,\phi,\delta_\lambda) \tag{4.1}$$

where $\hat{T}_\lambda$ is the nuclear motion kinetic energy operator and V_λ depends only on the relative position of the nuclei, and therefore on ρ,θ,ϕ and δ_λ only. The kinetic energy of the motion of the center of mass of the system has already been excluded from $\hat{T}_\lambda$. The formalism can of course be augmented[10] to include multiple potential energy surfaces, angular momentum coupling between nuclear and electronic spin and orbital motions, other relativistic effects, and mass polarization effects, to make it as accurate as desired. This, however, transcends the objectives of this paper. Our goal is to obtain $\hat{T}_\lambda$ in row-orthonormal hyperspherical coordinates for tetraatomic systems and analyze the properties of the resulting expression.

In analogy to the triatomic case,[67] we define the matrix gradient operator ∇_λ by

$$\nabla_\lambda = \begin{pmatrix} \partial/\partial x_{\lambda_1}^{(1)} & \partial/\partial x_{\lambda_1}^{(2)} & \dots & \partial/\partial x_{\lambda_1}^{(N-1)} \\ \partial/\partial x_{\lambda_2}^{(1)} & \partial/\partial x_{\lambda_2}^{(2)} & \dots & \partial/\partial x_{\lambda_2}^{(N-1)} \\ \partial/\partial x_{\lambda_3}^{(1)} & \partial/\partial x_{\lambda_3}^{(2)} & \dots & \partial/\partial x_{\lambda_3}^{(N-1)} \end{pmatrix} \tag{4.2}$$

We can express $\hat{T}_\lambda$ in terms of ∇_λ as

$$\hat{T}_\lambda = -\frac{\hbar^2}{2\mu}\,\mathrm{tr}(\nabla_\lambda\,\tilde{\nabla}_\lambda) \tag{4.3}$$

where, even though the matrix operator ∇_λ depends on λ, the scalar operator $\hat{T}_\lambda$ does not, as can easily be shown from kinematic rotation transformation property (2.4). From now on we will drop the subscript λ on the latter. We will first determine ∇_λ and then $\hat{T}$. The approach used is very similar in spirit to the one employed previously by Öhrn and Linderberg to determine the kinetic energy functional for four-particle systems.[66]

4.1.1. The Matrix Gradient Operator. The elements of ∇_λ are the coefficients of the expansion of the total nine-dimensional differential operator $\hat{d}$ in terms of the Cartesian coordinate differentials

$$\hat{d} = \sum_{i,j=1}^{3} dx_{\lambda_i}^{(j)} \frac{\partial}{\partial x_{\lambda_i}^{(j)}} \tag{4.4}$$

To obtain ∇_λ in terms of the row-orthonormal hyperspherical coordinates, we also expand $\hat{d}$ in terms of the latter, and identify both expansions. To that effect we write $\hat{d}$ as

$$\hat{d} = \hat{d}_{1_\lambda} + \hat{d}_2 + \hat{d}_{3_\lambda} \tag{4.5}$$

where

$$\hat{d}_{1_\lambda} = da_\lambda \frac{\partial}{\partial a_\lambda} + d\theta \frac{\partial}{\partial b_\lambda} + \mathrm{d}c_\lambda \frac{\partial}{\partial c_\lambda} \tag{4.6}$$

$$\hat{d}_2 = d\rho \frac{\partial}{\partial \rho} + db_\lambda \frac{\partial}{\partial \theta} + d\phi \frac{\partial}{\partial \phi} \tag{4.7}$$

$$\hat{d}_{3_\lambda} = \sum_{l=1}^{3} d\delta_\lambda^{(l)} \frac{\partial}{\partial \delta_\lambda^{(l)}} \tag{4.8}$$

It is useful to express the operator $\hat{d}_{1\lambda}$ in terms of the components $J^{I\lambda}{}_1, J^{I\lambda}{}_2, J^{I\lambda}{}_3$ of the nuclear motion angular momentum operator $\hat{\mathbf{J}}$ along the $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ principal-moment-of-inertia body-fixed axes. Inverting the relation

$$\begin{pmatrix} \hat{J}_1^{I\lambda} \\ \hat{J}_2^{I\lambda} \\ \hat{J}_3^{I\lambda} \end{pmatrix} = \frac{\hbar}{i} K_\lambda \begin{pmatrix} \partial/\partial a_\lambda \\ \partial/\partial b_\lambda \\ \partial/\partial c_\lambda \end{pmatrix} =$$

$$\frac{\hbar}{i} \begin{pmatrix} -\csc b_\lambda \cos c_\lambda & \sin c_\lambda & \cot b_\lambda \cos c_\lambda \\ \csc b_\lambda \sin c_\lambda & \cos c_\lambda & -\cot b_\lambda \sin c_\lambda \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \partial/\partial a_\lambda \\ \partial/\partial b_\lambda \\ \partial/\partial c_\lambda \end{pmatrix} \tag{4.9}$$

we get, as in the triatomic case[67]

$$\begin{pmatrix} \partial/\partial a_\lambda \\ \partial/\partial b_\lambda \\ \partial/\partial c_\lambda \end{pmatrix} = \frac{i}{\hbar} \begin{pmatrix} -\sin b_\lambda \cos c_\lambda & \sin b_\lambda \sin c_\lambda & \cos b_\lambda \\ \sin c_\lambda & \cos c_\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{J}_1^{I\lambda} \\ \hat{J}_2^{I\lambda} \\ \hat{J}_3^{I\lambda} \end{pmatrix} \tag{4.10}$$

which permits us to rewrite (4.6) as

$$\hat{d}_{1_\lambda} = \frac{\hbar}{i} [(-\sin b_\lambda \cos c_\lambda da_\lambda + \sin c_\lambda db_\lambda)\, \hat{J}_1^{I\lambda} +$$

$$(\sin b_\lambda \sin c_\lambda da_\lambda + \cos c_\lambda db_\lambda)\, \hat{J}_2^{I\lambda} + (\cos b_\lambda da_\lambda + dc_\lambda)\, \hat{J}_3^{I\lambda}] \tag{4.11}$$

A comparison of the coefficients of the angular momentum operators in this expression with the elements of the $\mathbf{R}d\tilde{\mathbf{R}}$ matrix shows that (4.11) can be written as

$$\hat{d}_{1_\lambda} = -\frac{i}{2\hbar} \sum_{i,j,k=1}^{3} \epsilon_{ijk} (\mathbf{R}d\tilde{\mathbf{R}})_{ij}\, \hat{J}_k^{I\lambda} \tag{4.12}$$

where ϵ_{ijk} is the Levi−Civita density (also called the alternating tensor, the isotropic tensor of rank 3, or the ϵ-tensor).[83,84] This is a convenient form of $\hat{d}_{1\lambda}$ which is valid for all $N > 2$.

To express $\hat{d}_2$ and $\hat{d}_{3\lambda}$ in a more useful form, we take the differential of (2.28). The result is

$$d\rho_\lambda^{sf} = (-1)^\chi[(d\tilde{\mathbf{R}})\rho\mathbf{N}\mathbf{Q} + \tilde{\mathbf{R}}\, d(\rho\mathbf{N})\mathbf{Q} + \tilde{\mathbf{R}}\,\rho\mathbf{N}d\mathbf{Q}] \quad (4.13)$$

where $\mathbf{Q}$ is given by (2.27). Left-multiplying this expression by $\mathbf{R}$, right-multiplying it by $\hat{\mathbf{Q}}$, and using the orthogonality property of these matrices we get

$$\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}} = (-1)^\chi\,[\mathbf{R}(d\tilde{\mathbf{R}})\rho\mathbf{N} + d(\rho\mathbf{N}) + \rho\mathbf{N}(d\mathbf{Q})\tilde{\mathbf{Q}}] \quad (4.14)$$

Due to that orthogonality, both $\mathbf{R}d\tilde{\mathbf{R}}$ and $(d\mathbf{Q})\ \tilde{Q}$ are skew-symmetric matrices (of dimensions 3×3) and as a result their diagonal elements vanish. On the other hand, $\rho\mathbf{N}$ and therefore its differential are diagonal matrices. Consequently,

$$d(\rho\mathbf{N}) = (-1)^\chi\,\mathrm{diag}[\mathbf{R}(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}] \quad (4.15)$$

$$\mathbf{R}(d\tilde{\mathbf{R}})\,\rho\mathbf{N} + \rho\mathbf{N}(d\mathbf{Q})\tilde{\mathbf{Q}} = (-1)^\chi\,\mathrm{off\ diag}[\mathbf{R}(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}] \quad (4.16)$$

where diag$\mathbf{A}$ is a diagonal matrix whose diagonal elements are equal to the corresponding ones of the square matrix $\mathbf{A}$ and off diag$\mathbf{A}$ is a matrix whose diagonal elements vanish and whose off-diagonal elements are equal to the corresponding ones of $\mathbf{A}$. The first of these expressions yields a convenient form for $\hat{d}_2$ and the second one for $\hat{d}_{3\lambda}$.

From (4.15) we get

$$\mathbf{N}d\rho + \rho\mathbf{N}'_\theta d\theta + \rho\,\sin\theta\,\mathbf{M}_\phi d\phi = (-1)^\chi\,\mathrm{diag}[\mathbf{R}(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}] \quad (4.17)$$

where

$$\mathbf{N}'_\theta\,(\theta,\phi) = \frac{\partial\mathbf{N}}{\partial\theta} = \begin{pmatrix}\cos\theta\cos\phi & 0 & 0\\ 0 & \cos\theta\sin\phi & 0\\ 0 & 0 & -\sin\theta\end{pmatrix} \quad (4.18)$$

and

$$\mathbf{M}_\phi(\phi) = \frac{1}{\sin\theta}\frac{\partial\mathbf{N}}{\partial\phi} = \begin{pmatrix}-\sin\phi & 0 & 0\\ 0 & \cos\phi & 0\\ 0 & 0 & 0\end{pmatrix} \quad (4.19)$$

The matrices N, N'_θ, and $\mathbf{N}_\phi$ have the properties

$$\mathrm{tr}\mathbf{N}^2 = \mathrm{tr}\mathbf{N}'^2_\theta = \mathrm{tr}\mathbf{M}^2_\phi = 1$$
$$\mathrm{tr}\mathbf{N}\mathbf{N}'_\theta = \mathrm{tr}\mathbf{N}\mathbf{M}_\phi = \mathrm{tr}\mathbf{N}'_\theta\mathbf{M}_\phi = 0 \quad (4.20)$$

As a consequence, left-multiplying (4.17) by $\mathbf{N}$ and taking the traces of both sides we obtain

$$d\rho = (-1)^\chi\sum_{i,j=1}^{3} N_{ii}[\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}]_{ii} = \sum_{i,j=1}^{3} N_{ij}[\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}]_{ij} \quad (4.21)$$

Similarly, left-multiplying (4.17) by $\mathbf{N}'_\theta$ or $\mathbf{M}_\phi$ and taking the traces of both sides results in

$$d\theta = (-1)^\chi\frac{1}{\rho}\sum_{i,j=1}^{3} N'_{\theta_{ij}}[\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}]_{ij} \quad (4.22)$$

$$d\phi = (-1)^\chi\frac{1}{\rho\,\sin\theta}\sum_{i,j=1}^{3} M_{\phi_{ij}}[\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}]_{ij} \quad (4.23)$$

Replacement into (4.7) now furnishes

$$\hat{d}_2 = (-1)^\chi\sum_{i,j=1}^{3}[\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}]_{ij}\left[N_{ij}\frac{\partial}{\partial\rho} + N'_{\theta_{ij}}\frac{1}{\rho}\frac{\partial}{\partial\theta} + M_{\phi_{ij}}\frac{1}{\rho\,\sin\theta}\frac{\partial}{\partial\phi}\right] \quad (4.24)$$

which is the desired convenient form for $\hat{d}_2$. This form is also valid for $N > 4$.

We now consider (4.16), which will permit us to express the nonvanishing (i.e., off-diagonal) elements of the skew-symmetric matrices $\mathbf{R}d\,\tilde{\mathbf{R}}$ and $(d\mathbf{Q})\ \tilde{\mathbf{Q}}$ in terms of the off-diagonal elements of $\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}$. Obtaining these expressions is useful because $\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}$ appears in $\hat{d}_2$ (see (4.24)) and as a result it would be desirable to have this same matrix appear in the expressions for $\hat{d}_{1\lambda}$ and $\hat{d}_{3\lambda}$. In view of the diagonality of $\mathbf{N}$, we obtain from the off-diagonal elements of both sides of (4.16) the relation

$$[\mathbf{R}d\tilde{\mathbf{R}}]_{ij}\rho N_{jj} + \rho N_{ii}[(d\mathbf{Q})\tilde{\mathbf{Q}}]_{ij} = (-1)^\chi[\mathbf{R}\,(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ij} \qquad i \neq j \quad (4.25)$$

Interchanging i and j in this expression and using the skew-symmetry of $\mathbf{R}\ (d\tilde{\mathbf{R}})$ and $(d\mathbf{Q})\ \tilde{\mathbf{Q}}$ gives

$$-[\mathbf{R}d\tilde{\mathbf{R}}]_{ij}\rho N_{ii} - \rho N_{jj}[(d\mathbf{Q})\tilde{\mathbf{Q}}]_{ij} = (-1)^\chi[\mathbf{R}(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ji} \qquad i \neq j \quad (4.26)$$

These two expressions can be considered as a system of two linear equations in the two quantities $[\mathbf{R}\ (d\mathbf{R})]_{ij}$ and $[(d\mathbf{Q})\ \tilde{\mathbf{Q}}]_{ij}$ which permit us to obtain them in terms of $[\mathbf{R}\ (d\rho_\lambda^{sf})\ \tilde{\mathbf{Q}}]_{ij}$ and $[\mathbf{R}\ (d\rho_\lambda^{sf})\ \tilde{\mathbf{Q}}]_{ji}$ as

$$[\mathbf{R}d\tilde{\mathbf{R}}]_{ij} = \frac{(-1)^\chi}{\rho(N_{jj}^2 - N_{ii}^2)}\{N_{jj}[\mathbf{R}(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ij} + N_{ii}[\mathbf{R}(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ji}\} \qquad i \neq j \quad (4.27)$$

$$[(d\mathbf{Q})\tilde{\mathbf{Q}}]_{ij} = -\frac{(-1)^\chi}{\rho(N_{jj}^2 - N_{ii}^2)}\{N_{ii}[\mathbf{R}(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ij} + N_{jj}[\mathbf{R}(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ji}\} \qquad i \neq j \quad (4.28)$$

Replacement of (4.27) into (4.12) results in an expression for $\hat{d}_{1\lambda}$ in terms of the matrix $\mathbf{R}\ (d\rho_\lambda^{sf})\ \tilde{\mathbf{Q}}$ and the operators $J_k^{l\lambda}$. In view of (2.28), δ_λ should play a similar role to that of $\boldsymbol{a}_\lambda$. Therefore, associated to δ_λ we wish to define a hyperangular momentum vector operator $\hat{\mathbf{L}}_\lambda$ with components $\hat{L}_{\lambda_1},\hat{L}_{\lambda_2},\hat{L}_{\lambda_3}$. We must notice, however, that whereas from (4.27) we get $[\mathbf{R}\ (\boldsymbol{a}_\lambda)\ d\ \tilde{\mathbf{R}}\ (\boldsymbol{a}_\lambda)]_{ij}$, from (4.28) we get $\{[d\mathbf{Q}\ (\delta_\lambda)]\ \tilde{\mathbf{Q}}\ (\delta_\lambda)\}_{ij}$, which, in view of (2.27), is the same as $\{[d\ \tilde{\mathbf{R}}\ (\delta_\lambda)]\mathbf{R}\ (\delta_\lambda)\}_{ij}$. The matrices $\mathbf{R}d\tilde{\mathbf{R}}$ and $(d\tilde{\mathbf{R}})\ \mathbf{R}$ are different since $\mathbf{R}$ is not symmetric. As a result, a useful definition of $\hat{\mathbf{L}}_\lambda$ in terms of δ_λ should have a form for which, after an expression for $\hat{d}_{3_\lambda}$ similar to (4.12) is obtained, the elements of $(d\tilde{\mathbf{R}})\ \mathbf{R}$ (i.e., $(d\mathbf{Q})\ \tilde{\mathbf{Q}}$) appear rather than those of $\mathbf{R}d\ \tilde{\mathbf{R}}$. This objective can be accomplished if, rather than the body-fixed components of $\hat{\mathbf{J}}^{l\lambda}$ used in (4.9), we introduce the *space-fixed type* components of $\mathbf{L}_\lambda$ defined by[85]

$$\begin{pmatrix}\hat{L}_{\lambda_1}\\ \hat{L}_{\lambda_2}\\ \hat{L}_{\lambda_3}\end{pmatrix} = \frac{\hbar}{i} P_\lambda \begin{pmatrix}\partial/\partial\delta_\lambda^{(1)}\\ \partial/\partial\delta_\lambda^{(2)}\\ \partial/\partial\delta_\lambda^{(3)}\end{pmatrix} =$$

$$\frac{\hbar}{i}\begin{pmatrix}-\cos\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & -\sin\delta_\lambda^{(1)} & \cos\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)}\\ -\sin\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & \cos\delta_\lambda^{(1)} & \sin\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)}\\ 1 & 0 & 0\end{pmatrix}\begin{pmatrix}\partial/\partial\delta_\lambda^{(1)}\\ \partial/\partial\delta_\lambda^{(2)}\\ \partial/\partial\delta_\lambda^{(3)}\end{pmatrix} \tag{4.29}$$

which, upon inversion, yields

$$\begin{pmatrix}\partial/\partial\delta_\lambda^{(1)}\\ \partial/\partial\delta_\lambda^{(2)}\\ \partial/\partial\delta_\lambda^{(3)}\end{pmatrix} =$$

$$\frac{i}{\hbar}\begin{pmatrix}0 & 0 & 1\\ -\sin\delta_\lambda^{(1)} & \cos\delta_\lambda^{(1)} & 0\\ \cos\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \sin\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \cos\delta_\lambda^{(2)}\end{pmatrix}\begin{pmatrix}\hat{L}_{\lambda_1}\\ \hat{L}_{\lambda_2}\\ \hat{L}_{\lambda_3}\end{pmatrix} \tag{4.30q}$$

The difference between the body-fixed character of $\hat{\mathbf{J}}^{I\lambda}$ and the space-fixed character of $\hat{\mathbf{L}}_\lambda$ as encompassed in (4.9) and (4.29), respectively, is important and stems from the fact that the $\tilde{\mathbf{R}}(\boldsymbol{a}_\lambda)$ in (2.28) appears at the left of $\mathbf{N}$, whereas $\tilde{\mathbf{R}}(\delta_\lambda)$ appears at its right. Substituting (4.30) into (4.8) we get

$$\hat{d}_{3_\lambda} = \frac{\hbar}{i}[(-\sin\delta_\lambda^{(1)}\, d\delta_\lambda^{(2)} + \cos\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)}\, d\delta_\lambda^{(3)})\hat{L}_{\lambda_1} + (\cos\delta_\lambda{}^{(2)} d\delta_\lambda^{(2)} + \sin\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} d\delta_\lambda^{(3)})\hat{L}_{\lambda_2} + (d\delta_\lambda^{(1)} + \cos\delta_\lambda^{(2)} d\delta_\lambda^{(3)})\hat{L}_{\lambda_3}] \tag{4.31}$$

As for (4.11), a comparison of the coefficients of the $\hat{L}_{\lambda_k}$ ($k = 1, 2, 3$) in this expression with the elements of the $(d\mathbf{Q})\,\tilde{\mathbf{Q}}$ matrix shows that (4.31) can be rewritten as

$$\hat{d}_{3_\lambda} = -\frac{i}{2\hbar}\sum_{i,j,k=1}^{3}\epsilon_{ijk}[(d\boldsymbol{Q}))\tilde{\mathbf{Q}}]_{ij}\hat{L}_{\lambda_k} \tag{4.32}$$

where the $[(d\mathbf{Q})\tilde{\mathbf{Q}}]_{ij}$ are given by (4.28). Equation 4.32 has the same structure as (4.12).

We now replace (4.27) into (4.12) and (4.28) into (4.32) and the resulting equations, together with (4.24), into (4.5). After some simple algebraic manipulations we get the important expression

$$\hat{d} = (-1)^\chi \sum_{i,j=1}^{3}[\mathbf{R}\,(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ij} \times \left\{\left[\mathbf{N}\frac{\partial}{\partial\rho} + \mathbf{N}'_\theta\frac{1}{\rho}\frac{\partial}{\partial\theta} + \mathbf{M}_\phi\frac{1}{\rho\sin\theta}\frac{\partial}{\partial\phi}\right]_{ij} - \frac{i}{\hbar}\sum_{k=1}^{3}\frac{\epsilon_{ijk}}{\rho(N_{jj}^2 - N_{ii}^2)}(N_{jj}\hat{J}_k^{I\lambda} - N_{ii}\hat{L}_{\lambda_k})\right\} \tag{4.33}$$

The quantity $\epsilon_{ijk}/(N_{jj}^2 - N_{ii}^2)$ which appears in (4.33) vanishes by definition (as does ϵ_{ijk}) for $i = j$. We now write the elements of $\mathbf{R}\,(d\rho_\lambda^{sf})\,\tilde{\mathbf{Q}}$ explicitly as

$$[\mathbf{R}\,(d\rho_\lambda^{sf})\tilde{\mathbf{Q}}]_{ij} = \sum_{k,l=1}^{3} R_{ik}\, dx_k^{(l)} Q_{jl} \tag{4.34}$$

Replacing (4.34) into (4.33) and identifying the coefficients of the Cartesian differentials in the resulting expression with those in (4.4) yields the elements of the matrix gradient operator ∇_λ defined by (4.2). The final result can be expressed as

$$\nabla_\lambda = (-1)^\chi[\tilde{\mathbf{R}}\,\hat{\mathbf{A}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda] \tag{4.35}$$

where $\hat{\mathbf{A}}$ is a 3×3 diagonal matrix operator defined by

$$\hat{\mathbf{A}} = \mathbf{N}\frac{\partial}{\partial\rho} + \mathbf{N}'_\theta\frac{1}{\rho}\frac{\partial}{\partial\theta} + \mathbf{M}_\phi\frac{1}{\rho\sin\theta}\frac{\partial}{\partial\phi} \tag{4.36}$$

and $\hat{\mathbf{P}}_\lambda$ is a 3×3 matrix operator given by

$$\hat{\mathbf{P}}_\lambda = \hat{\mathbf{F}}_\lambda - \hat{\mathbf{G}}_\lambda \tag{4.37}$$

with

$$\hat{F}_{\lambda_{ij}} = -\frac{i}{\hbar\rho}\sum_{l,m=1}^{3}\frac{R_{li}Q_{mj}N_{mm}}{N_{mm}^2 - N_{ll}^2}\sum_{k=1}^{3}\epsilon_{lmk}\hat{J}_k^{I\lambda} \tag{4.38}$$

$$\hat{G}_{\lambda_{ij}} = -\frac{i}{\hbar\rho}\sum_{l,m=1}^{3}\frac{R_{li}Q_{mj}N_{ll}}{N_{mm}^2 - N_{ll}^2}\sum_{k=1}^{3}\epsilon_{lmk}\hat{L}_{\lambda_k} \tag{4.39}$$

It is possible to put (4.38) and (4.39) in matrix operator form with the help of the matrix operator $\hat{\mathbf{A}}_{\hat{\mathbf{B}}}$ defined by

$$(\hat{\mathbf{A}}_{\hat{\mathbf{B}}})_{lm} = \sum_{k=1}^{3}\frac{\epsilon_{lmk}\hat{B}_k}{N_{mm}^2 - N_{ll}^2} \tag{4.40}$$

where $\hat{\mathbf{B}}$ is a column vector operator with components $\hat{B}_1$, $\hat{B}_2$, and $\hat{B}_3$. This matrix operator is symmetric and its diagonal elements vanish. It is given explicitly by

$$\hat{\mathbf{A}}_{\hat{\mathbf{B}}} = \begin{pmatrix}0 & \dfrac{\hat{B}_3}{N_{22}^2 - N_{11}^2} & \dfrac{\hat{B}_2}{N_{11}^2 - N_{33}^2}\\ \dfrac{\hat{B}_3}{N_{22}^2 - N_{11}^2} & 0 & \dfrac{\hat{B}_1}{N_{33}^2 - N_{22}^2}\\ \dfrac{\hat{B}_2}{N_{11}^2 - N_{33}^2} & \dfrac{\hat{B}_1}{N_{33}^2 - N_{22}^2} & 0\end{pmatrix} \tag{4.41}$$

In terms of it (4.38) and (4.39) can be expressed as

$$\hat{\mathbf{F}}_\lambda = -\frac{i}{\hbar\rho}\tilde{\mathbf{R}}\,\hat{\mathbf{A}}_{\hat{\mathbf{J}}I\lambda}\mathbf{N}\mathbf{Q} \tag{4.42}$$

$$\hat{\mathbf{G}}_\lambda = \frac{i}{\hbar\rho}\tilde{\mathbf{Q}}\,\mathbf{N}\hat{\tilde{\mathbf{A}}}_{\hat{\mathbf{L}}_\lambda}\mathbf{R} \tag{4.43}$$

Great care must be taken in manipulating this last expression since if $\hat{\mathbf{B}}(\mathbf{x})$ is a matrix of operators which act on variable $\mathbf{x}$ and $\mathbf{C}(\mathbf{x})$ is another matrix which depends on $\mathbf{x}$, then in general

$$\overline{(\hat{\mathbf{B}}\mathbf{C})}\psi(\mathbf{x}) \neq (\tilde{\mathbf{C}}\hat{\tilde{\mathbf{B}}})\psi(\mathbf{x}) \tag{4.44}$$

where $\psi(\mathbf{x})$ is a scalar function of $\mathbf{x}$. Treating $\hat{\mathbf{B}}\mathbf{C}$ as a matrix

operator, (4.44) means that

$$\overline{\hat{\mathbf{B}}\mathbf{C}} \neq \tilde{\mathbf{C}}\hat{\tilde{\mathbf{B}}} \tag{4.45}$$

As a result, it is safer to use (4.38) and (4.39) instead of (4.42) and (4.43).

4.1.2. The Kinetic Energy Operator. To evaluate $\hat{T}$ we replace (4.35) into (4.3):

$$\hat{T} = -\frac{\hbar^2}{2\mu}\,\mathrm{tr}[(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda)(\tilde{\mathbf{R}}\hat{\tilde{\mathbf{A}}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda)] \tag{4.46}$$

In view of the remarks made after (4.43), it is better to rewrite this expression in the "safe" form

$$\hat{T} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda)_{ik}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda)_{ik} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}(\hat{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q} + \hat{\mathbf{P}}_\lambda)_{ik}^2 \tag{4.47}$$

From it we get

$$\hat{T} = \sum_{a=1}^{4}\hat{T}_{\lambda_a} \tag{4.48}$$

with the $\hat{T}_{\lambda_a}$ ($a = 1$ through 4) defined by

$$\hat{T}_{\lambda_1} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik}^2 \tag{4.49}$$

$$\hat{T}_{\lambda_2} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik}\hat{\mathbf{P}}_{\lambda_{ik}} \tag{4.50}$$

$$\hat{T}_{\lambda_3} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}\hat{\mathbf{P}}_{\lambda_{ik}}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik} \tag{4.51}$$

$$\hat{T}_{\lambda_4} = -\frac{\hbar^2}{2\mu}\sum_{i,k=1}^{3}(\hat{\mathbf{P}}_\lambda)_{ik}^2 \tag{4.52}$$

We now proceed to evaluate the $\hat{T}_{\lambda_a}$. The operator $(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik}$ can be expressed as

$$(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik} = \sum_{l,m=1}^{3}(\tilde{\mathbf{R}})_{il}(\hat{\mathbf{A}})_{lm}(\mathbf{Q})_{mk} = \sum_{l,m=1}^{3}R_{li}\hat{A}_{ll}\delta_{lm}Q_{mk} = \sum_{l=1}^{3}R_{li}\hat{A}_{ll}Q_{lk} \tag{4.53}$$

The matrix elements R_{li} and Q_{lk} depend on $\boldsymbol{a}_\lambda$ and δ_λ, respectively, whereas as indicated by (4.36) the operator $\hat{A}_{ll}$ acts on ρ, θ, and ϕ only. Therefore, $\hat{A}_{ll}$ commutes with both R_{li} and Q_{lk} and we can put (4.53) in the form

$$(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q})_{ik} = \sum_{l=1}^{3}R_{li}Q_{lk}\hat{A}_{ll} = \sum_{l=1}^{3}\hat{A}_{ll}R_{li}Q_{lk} \tag{4.54}$$

Replacement of this expression into (4.49) and use of the orthogonality properties of **R** and **Q** and of the definition of $\hat{\mathbf{A}}$ given by (4.36) yields

$$\hat{T}_{\lambda_1} = -\frac{\hbar^2}{2\mu}\,\mathrm{tr}\hat{\mathbf{A}}^2 = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\rho^2\frac{\partial}{\partial\rho} + \frac{\hat{K}^2}{2\mu\rho^2} \tag{4.55}$$

where $\hat{K}^2$ is an effective hyperangular momentum operator associated with the principal moment of inertia hyperangles θ, ϕ

$$\hat{K}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{4.56}$$

Similarly it is straightforward to show that

$$\hat{T}_{\lambda_2} = -\frac{\hbar^2}{2\mu}\mathrm{tr}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{Q}\hat{\mathbf{P}}_\lambda) = 0 \tag{4.57}$$

The evaluation of $\hat{T}_{\lambda_3}$ is similarly straightforward, albeit lengthier. The result is

$$\hat{T}_{\lambda_3} = -\frac{\hbar^2}{\mu\rho}\sum_{l,m,k=1}^{3}\frac{N_{mm}\epsilon_{lmk}^2}{N_{mm}^2 - N_{ll}^2}\hat{A}_{mm} \tag{4.58}$$

The evaluation of $\hat{T}_{\lambda_4}$ is more complicated because the operators $\hat{\mathbf{J}}^{I\lambda}$ and $\hat{\mathbf{L}}_\lambda$ act on the angles $\boldsymbol{a}_\lambda$ and δ_λ, respectively, which appear in $\mathbf{R}$ ($\boldsymbol{a}_\lambda$) and $\mathbf{Q}$ (δ_λ). To that effect it is useful to use the relations

$$\hat{J}_k^{I\lambda}\mathbf{R}(\boldsymbol{a}_\lambda) = \frac{\hbar}{i}\epsilon^{(k)}\mathbf{R}(\boldsymbol{a}_\lambda) \qquad k = 1,2,3 \tag{4.59}$$

and

$$\hat{L}_{\lambda_k}\mathbf{R}(\delta_\lambda) = \frac{\hbar}{i}\mathbf{R}(\delta_\lambda)\epsilon^{(k)} \qquad k = 1,2,3 \tag{4.60}$$

where $\epsilon^{(k)}$ is the 3×3 skew-symmetric matrix defined by

$$[\epsilon^{(k)}]_{lm} = \epsilon_{klm} \qquad k,l,m = 1,2,3 \tag{4.61}$$

With their help and some extensive but otherwise straightforward algebra we get:

$$\hat{T}_{\lambda_4} = \frac{1}{2\mu\rho^2}\sum_{l,m,k=1}^{3}\left[\frac{\epsilon_{lmk}}{N_{mm}^2 - N_{ll}^2}(N_{mm}\hat{J}_k^{I\lambda} - N_{ll}\hat{L}_{\lambda_k})\right]^2 \tag{4.62}$$

Substituting (4.55), (4.57), (4.58), and (4.62) into (4.48) leads to the expression for the kinetic energy operator in the row-orthonormal hyperspherical coordinates $\boldsymbol{a}_\lambda$, χ, ρ, θ, ϕ, δ_λ,

$$\hat{T} = \hat{T}_\rho(\rho) + \frac{1}{2\mu\rho^2}\hat{\Lambda}^2(\boldsymbol{a}_\lambda,\theta,\phi,\delta_\lambda) \tag{4.63}$$

where $\hat{T}_\rho(\rho)$ is the system's hyperradial kinetic energy operator

$$\hat{T}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} \tag{4.64}$$

and $\hat{\Lambda}^2$ its grand conical angular momentum operator

$$\hat{\Lambda}^2 = \hat{K}^2(\theta,\phi) + \hat{B}(\theta,\phi) + \hat{C}^2(\boldsymbol{a}_\lambda,\delta_\lambda;\theta,\phi) \tag{4.65}$$

The operator $\hat{K}^2$ was defined in (4.56) and $\hat{B}$ and $\hat{C}^2$ are given by

$$\hat{B}(\theta,\phi) = -2\hbar^2\left[b_\theta(\theta,\phi)\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}b_\phi(\theta,\phi)\frac{\partial}{\partial\phi}\right] \tag{4.66}$$

where

$$b_\theta(\theta,\phi) = \frac{N_{22}N'_{\theta_{22}} - N_{11}N'_{\theta_{11}}}{N_{22}^2 - N_{11}^2} + \frac{N_{33}N'_{\theta_{33}} - N_{22}N'_{\theta_{22}}}{N_{33}^2 - N_{22}^2} + \frac{N_{11}N'_{\theta_{11}} - N_{33}N'_{\theta_{33}}}{N_{11}^2 - N_{33}^2} \quad (4.67)$$

$$b_\phi(\theta,\phi) = \frac{N_{22}M_{\phi_{22}} - N_{11}M_{\phi_{11}}}{N_{22}^2 - N_{11}^2} - \frac{N_{22}M_{\phi_{22}}}{N_{33}^2 - N_{22}^2} + \frac{N_{11}M_{\phi_{11}}}{N_{11}^2 - N_{33}^2} \quad (4.68)$$

and

$$\hat{C}^2(\boldsymbol{a}_\lambda,\delta_\lambda;\theta,\phi) = \frac{(N_{22}J_3^{I\lambda} - N_{11}\hat{L}_{\lambda_3})^2 + (N_{11}J_3^{I\lambda} - N_{22}\hat{L}_{\lambda_3})^2}{(N_{22}^2 - N_{11}{}^2)^2} + \frac{(N_{33}\hat{J}_1^{I\lambda} - N_{22}\hat{L}_{\lambda_1})^2 + (N_{22}\hat{J}_1^{I\lambda} - N_{33}\hat{L}_{\lambda_1})^2}{(N_{33}^2 - N_{22}^2)^2} + \frac{(N_{11}\hat{J}_2^{I\lambda} - N_{33}\hat{L}_{\lambda_2})^2 + (N_{33}\hat{J}_2^{I\lambda} - N_{11}\hat{L}_{\lambda_2})^2}{(N_{11}^2 - N_{33})^2} \quad (4.69)$$

The N_{ii}, $N'_{\theta_{ii}}$, and $M_{\phi_{ii}}$ in these equations are the diagonal elements of the matrices N, N'_θ, and $\mathbf{M}_\phi$ defined by (2.23), (4.18), and (4.19), respectively.

The nuclear motion Schrödinger equation for the system associated with (5.1) is

$$\hat{H}\Psi(\chi,\boldsymbol{a}_\lambda,\rho,\theta,\phi,\delta_\lambda) = E\Psi \quad (4.70)$$

In view of the expression for the four-particle volume element derived in section 4.2, it is convenient to perform the dependent variable change defined by

$$\Psi = \frac{\psi}{\rho^4 g^{1/2}(\theta,\phi)} \quad (4.71)$$

where g (θ,ϕ) is given by (4.102). The Schrödinger equation satisfied by ψ is

$$\hat{H}\psi = E\psi \quad (4.72)$$

where the new nuclear motion Hamiltonian $\hat{H}$ is given by

$$\hat{H} = \hat{\mathscr{T}} + V_{\lambda_{\text{eff}}} \quad (4.73)$$

with

$$\hat{\mathscr{T}} = \hat{\mathscr{T}}_\rho(\rho) + \frac{1}{2\mu\rho^2}\hat{\lambda}^2(\boldsymbol{a}_\lambda,\theta,\phi,\delta_\lambda) \quad (4.74)$$

$$\hat{\mathscr{T}}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\rho^2} \quad (4.75)$$

$$\hat{\lambda}^2 = \hat{K}^2(\theta,\phi) + \hat{C}^2(\boldsymbol{a}_\lambda,\delta_\lambda;\theta,\phi) \quad (4.76)$$

$V_{\lambda_{\text{eff}}}$ is an effective potential defined as

$$V_{\lambda_{\text{eff}}} = V_\lambda(\rho,\theta,\phi,\delta_\lambda) + V_{\lambda_{\text{cent}}}(\rho,\theta,\phi) \quad (4.77)$$

with the centrifugal potential $V_{\lambda_{\text{cent}}}$ being

$$V_{\lambda_{\text{cent}}}(\rho,\theta,\phi) = -\frac{\hbar^2}{2\mu\rho^2}\left[\frac{1}{\sin^2\theta\cos^2 2\phi} + \frac{1}{\sin^2\theta\cos^2\phi - \cos^2\theta} + \frac{1}{\sin^2\theta\sin^2\phi - \cos^2\theta} + \frac{2\cos^2\theta}{(\sin^2\theta\sin^2\phi - \cos^2\theta)^2} + \frac{2\cos^2\theta}{(\sin^2\theta\cos^2\phi - \cos^2\theta)^2}\right] \quad (4.78)$$

The operator $\hat{C}^2$ is positive-definite and can be written as

$$\hat{C}^2 = \hat{\tilde{\mathbf{C}}}_\lambda\,\hat{\mathbf{C}}_\lambda \quad (4.79)$$

where $\hat{\mathbf{C}}_\lambda$ is a 6-dimensional column vector operator whose elements $\hat{C}_{\lambda_i}$ $(i = 1, ..., 6)$ are

$$\hat{C}_{\lambda_1} = \frac{N_{22}\hat{J}_1^{I\lambda} - N_{33}\hat{L}_{\lambda_1}}{N_{22}^2 - N_{33}^2}$$

$$\hat{C}_{\lambda_2} = \frac{N_{33}\hat{J}_2^{I\lambda} - N_{11}\hat{L}_{\lambda_2}}{N_{33}^2 - N_{11}^2}$$

$$\hat{C}_{\lambda_3} = \frac{N_{11}\hat{J}_3^{I\lambda} - N_{22}\hat{L}_{\lambda_3}}{N_{11}^2 - N_{22}^2}$$

$$\hat{C}_{\lambda_4} = \frac{N_{33}\hat{J}_1^{I\lambda} - N_{22}\hat{L}_{\lambda_1}}{N_{33}^2 - N_{22}^2}$$

$$\hat{C}_{\lambda_5} = \frac{N_{11}\hat{J}_2^{I\lambda} - N_{33}\hat{L}_{\lambda_2}}{N_{11}^2 - N_{33}^2}$$

$$\hat{C}_{\lambda_6} = \frac{N_{22}\hat{J}_3^{I\lambda} - N_{11}\hat{L}_{\lambda_3}}{N_{22}^2 - N_{11}^2} \quad (4.80)$$

As will be shown in section 4.3, although the signs of the $\hat{C}_{\lambda_i}$ are λ-dependent (i.e., may change under $\lambda \rightarrow \nu$ transformations), $\hat{C}^2$ is kinematic-rotation-invariant. The form of the kinetic energy operator $\hat{\mathscr{T}}$ given by (4.74) through (4.76) is particularly simple and appropriate for using in reactive scattering calculations of tetraatomic systems.

In view of (2.7), $\boldsymbol{I}$ and $\mathbf{K}$ have equal eigenvector matrices and their eigenvalues are inter-related by

$$I_i = \mu(\rho^2 - K_i) = \mu\rho^2(1 - N_{ii}^2)$$
$$i = 1,2,3 \quad (4.81)$$

As a result of this equation and of (2.13), the principal moments of inertia I_i are ordered according to

$$I_2 \geq I_1 \geq I_3 \geq 0 \quad (4.82)$$

From (4.81) we obtain the following relations between the differences which appear in the denominators of (4.69) and the differences between pairs of principal moments of inertia

$$N_{22}^2 - N_{11}^2 = \frac{1}{\mu\rho^2}(I_1 - I_2) = -\sin^2\theta\cos 2\phi \leq 0 \quad (4.83)$$

$$N_{33}^2 - N_{22}^2 = \frac{1}{\mu\rho^2}(I_2 - I_3) = \cos^2\theta - \sin^2\theta\sin^2\phi \geq 0 \tag{4.84}$$

$$N_{11}^2 - N_{33}^2 = \frac{1}{\mu\rho^2}(I_3 - I_1) = \sin^2\theta\cos^2\phi - \cos^2\theta \leq 0 \tag{4.85}$$

Therefore, for nuclear configurations for which any two of the system's principal moments of inertia become degenerate, the Hamiltonian operator has a pole (the well-known Eckart singularities[86,87]), as does the centrifugal potential. It should be noted that in view of (4.82), we can only have $I_2 = I_3$ if both these moments of inertia are equal to I_1. The corresponding geometries are discussed after (5.3). In solving the Schrödinger equation, special attention must be paid to those poles.

4.2. The Volume Element. In what follows, it becomes useful to define the two sets of nine coordinates x_{λ_l} and σ_{λ_l} (l = 1, ..., 9) by

$$x_{\lambda_1} = x_{\lambda_1}^{(1)} \quad x_{\lambda_2} = x_{\lambda_2}^{(1)} \quad x_{\lambda_3} = x_{\lambda_3}^{(1)}$$

$$x_{\lambda_4} = x_{\lambda_1}^{(2)} \quad x_{\lambda_5} = x_{\lambda_2}^{(2)} \quad x_{\lambda_6} = x_{\lambda_3}^{(2)}$$

$$x_{\lambda_7} = x_{\lambda_1}^{(3)} \quad x_{\lambda_8} = x_{\lambda_2}^{(3)} \quad x_{\lambda_9} = x_{\lambda_3}^{(3)} \tag{4.86}$$

and

$$\sigma_{\lambda_1} = \rho \quad \sigma_{\lambda_2} = \theta \quad \sigma_{\lambda_3} = \phi$$

$$\sigma_{\lambda_4} = a_\lambda \quad \sigma_{\lambda_5} = b_\lambda \quad \sigma_{\lambda_6} = c_\lambda$$

$$\sigma_{\lambda_7} = \delta_\lambda^{(1)} \quad \sigma_{\lambda_8} = \delta_\lambda^{(2)} \quad \sigma_{\lambda_9} = \delta_\lambda^{(3)} \tag{4.87}$$

and the two 9 × 1 column vectors $\mathbf{x}_\lambda$ and σ_λ by

$$(\mathbf{x}_\lambda)_l = x_{\lambda_l} \quad (\sigma_\lambda)_l = \sigma_{\lambda_l} \quad l = 1, ..., 9 \tag{4.88}$$

Let furthermore $d\tau$ and $d\sigma_\lambda$ be the nine-dimensional volume elements

$$d\tau = \prod_{l=1}^{9} dx_{\lambda_l} = \prod_{i,j=1}^{3} dx_{\lambda_i}^{(j)} \tag{4.89}$$

and

$$d\sigma_\lambda = \prod_{l=1}^{9} d\sigma_{\lambda_l} \tag{4.90}$$

Let G_λ be the 9 × 9 nonorthogonal Jacobian matrix of the $\chi,\sigma_\lambda \rightarrow \mathbf{x}_\lambda$ transformation defined by

$$(G_\lambda)_{kl} = G_{\lambda_{kl}} = (-1)^\chi \frac{\partial\sigma_{\lambda_k}}{\partial x_{\lambda_l}}$$

$$k,l = 1, 2, ..., 9 \tag{4.91}$$

In terms of it we can write

$$d\tau = \frac{d\sigma_\lambda}{|\det G_\lambda|} \tag{4.92}$$

In order to obtain $d\tau$ in terms of the row-orthonormal hyperspherical coordinates χ,σ_λ we seek an expression for $\det G_\lambda$ as a function of those coordinates. It is expected that, in view of the structure of (2.28), in which ρ_λ^{sf} is expressed as a product of 3 × 3 matrices, G_λ will have some rows which are orthogonal to each other, i.e., that the 9 × 9 matrix $F_\lambda = G_\lambda\tilde{G}_\lambda$ will have a block-diagonal structure. In order to exploit this possibility, we use the following identity to evaluate $\det G_\lambda$, which is valid whether or not such a structure occurs:

$$|\det G_\lambda| = [\det(G_\lambda\tilde{G}_\lambda)]^{1/2} = [\det F_\lambda]^{1/2} \tag{4.93}$$

We now proceed to evaluate F_λ. Let $\bar{\nabla}_\lambda$ be the 9 × 1 vector gradient operator defined by

$$(\bar{\nabla}_\lambda)_l = \frac{\partial}{\partial x_{\lambda_l}} \qquad l = 1,2,...,9 \tag{4.94}$$

It has the same elements as those of the 3 × 3 matrix gradient operator ∇_λ defined by (4.2) and can be obtained from the latter by stacking its columns under each other. As a result of (4.91), the kth row of G is the 1 × 9 row vector of $\bar{\tilde{\nabla}}_\lambda\sigma_{\lambda k}$ and the lth column of $\tilde{G}_\lambda$ is the 9 × 1 column vector $\nabla_{\tilde{\lambda}}\sigma_{\lambda_l}$, and therefore

$$(F_\lambda)_{kl} = (\bar{\tilde{\nabla}}_\lambda\sigma_{\lambda_k})(\bar{\nabla}_\lambda\sigma_{\lambda_l}) = \mathrm{tr}[(\tilde{\nabla}_\lambda\sigma_{\lambda_k})(\nabla_\lambda\sigma_{\lambda_l})]$$

$$k,l = 1, 2, ..., 9 \tag{4.95}$$

The evaluation of F_λ has thus been reduced to the evaluation of the nine 3 × 3 matrices $\nabla_\lambda\sigma_{\lambda l}$, which can be accomplished in a straightforward manner with the help of (4.35). The eventual result is that F_λ has the expected block-diagonal structure

$$F_\lambda = \begin{pmatrix} F_{\lambda_1} & 0 \\ 0 & F_{\lambda_2} \end{pmatrix} \tag{4.96}$$

where F_{λ_1} and F_{λ_2} are square matrices of dimensions 3 × 3 and 6 × 6 respectively given by

$$F_\lambda = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\rho^2 & 0 \\ 0 & 0 & 1/(\rho^2\sin^2\theta) \end{pmatrix} \tag{4.97}$$

and

$$F_{\lambda_2} = \frac{1}{\rho^2}\begin{pmatrix} \tilde{K}_\lambda & 0 \\ 0 & P_\lambda \end{pmatrix}\begin{pmatrix} U & W \\ W & U \end{pmatrix}\begin{pmatrix} K_\lambda & 0 \\ 0 & P_\lambda \end{pmatrix} \tag{4.98}$$

The matrices K_λ and P_λ appearing in this expression were defined in (4.9) and (4.29), respectively, and U and W are 3 × 3 matrices defined by

$$U(\theta,\phi) = \begin{pmatrix} \dfrac{N_{22}^2 + N_{33}^2}{(N_{22}^2 - N_{33}^2)^2} & 0 & 0 \\ 0 & \dfrac{N_{33}^2 + N_{11}^2}{(N_{33}^2 - N_{11}^2)^2} & 0 \\ 0 & 0 & \dfrac{N_{11}^2 + N_{22}^2}{(N_{11}^2 - N_{22}^2)^2} \end{pmatrix} \tag{4.99}$$

and

$$W(\theta,\phi) = -2\begin{pmatrix} \frac{N_{22}N_{33}}{(N_{22}^2 - N_{33}^2)^2} & 0 & 0 \\ 0 & \frac{N_{33}N_{11}}{(N_{33}^2 - N_{11}^2)^2} & 0 \\ 0 & 0 & \frac{N_{11}N_{22}}{(N_{11}^2 - N_{22}^2)^2} \end{pmatrix} \quad (4.100)$$

Relations (4.96) through (4.100), together with (2.23), (4.9), (4.29), and (4.83) through (4.85) eventually yield

$$\det F_\lambda = [\rho^{16} \sin^2 b_\lambda \sin^2 \delta_\lambda^{(2)} g^2(\theta,\phi) \sin^2 \theta]^{-2} \quad (4.101)$$

where

$$g(\theta,\phi) = \sin^2 \theta \cos 2\phi(\cos^2 \theta - \sin^2 \theta \sin^2 \phi) \times (\cos^2 \theta - \sin^2 \theta \cos^2 \phi)$$
$$= \frac{1}{\mu^3 \rho^6}(I_2 - I_1)(I_2 - I_3)(I_1 - I_3) \geq 0 \quad (4.102)$$

Substitution of (4.101) and (4.93) into (4.92) gives the desired final result

$$d\tau = \sin b_\lambda da_\lambda db_\lambda dc_\lambda \rho^8 d\rho g(\theta,\phi) \sin\theta d\theta d\phi \sin \delta_\lambda^{(2)} d\delta_\lambda^{(1)} d\delta_\lambda^{(2)} d\delta_\lambda^{(3)}$$
$$= \sin b_\lambda da_\lambda db_\lambda dc_\lambda \rho^2 d\rho \frac{1}{\mu^3}(I_2 - I_1)(I_2 - I_3) \times (I_1 - I_3) \sin\theta d\theta d\phi \sin \delta_\lambda^{(2)} d\delta_\lambda^{(1)} d\delta_\lambda^{(2)} d\delta_\lambda^{(3)} \quad (4.103)$$

4.3. Transformation Properties. The system's Hamiltonian must, of course, be invariant under the operations considered in sections 3.2 through 3.4. In the present section we examine how each individual term in (4.63) through (4.69) transforms under these operations.

4.3.1. Kinematic Rotations. As shown in section 3.2, whereas χ, ρ, θ, ϕ are invariant under kinematic rotations, $\boldsymbol{a}_\lambda$ and δ_λ are not. We wish to determine the effect of such rotations on the operators $\hat{\mathbf{J}}^{I\lambda}$ and $\hat{\mathbf{L}}_\lambda$ which act on these coordinates.

As indicated after (3.9) the ν and λ principal axes of inertia frames are related through

$$Gx^{I\nu}y^{I\nu}z^{I\nu} = \mathbf{I}_{n_{\lambda\nu}^{(1)} n_{\lambda\nu}^{(3)}} Gx^{I\lambda}y^{I\lambda}z^{I\lambda} \quad (4.104)$$

where $\mathbf{I}_{n_{\lambda\nu}^{(1)} n_{\lambda\nu}^{(3)}}$ is given by (3.12). As a result, $\hat{\mathbf{J}}^{I\lambda}$ and $\hat{\mathbf{J}}^{I\lambda}$ are related through the equivalent expression

$$\hat{\mathbf{J}}^{I\nu} = \mathbf{I}_{n_{\lambda\nu}^{(1)} n_{\lambda\nu}^{(3)}} \hat{\mathbf{J}}^{I\lambda} \quad (4.105)$$

This means that either these two operators are equal or two of its components differ in sign:

$$\hat{J}_1^{I\nu} = (-1)^{n_{\lambda\nu}^{(1)}} \hat{J}_1^{I\lambda} \quad \hat{J}_2^{I\nu} = (-1)^{n_{\lambda\nu}^{(1)} + n_{\lambda\nu}^{(3)}} \hat{J}_2^{I\lambda} \quad \hat{J}_3^{I\nu} = (-1)^{n_{\lambda\nu}^{(3)}} \hat{J}_3^{I\lambda} \quad (4.106)$$

The values of $n_{\lambda\nu}^{(1)}$ and $n_{\lambda\nu}^{(3)}$ have been given in Table 2.

Let us consider the angular momenta associated with the δ internal hyperspherical angles. For that purpose, the diagram depicted in Figure 2 is very useful. In it, GXYZ and $G\bar{X}\bar{Y}\bar{Z}$ are auxiliary coordinate systems. The matrices associated with the arrows are the transformation matrices between the corresponding frames, and the vector operators $\hat{\mathbf{F}}$, $\hat{\bar{\mathbf{F}}}$, $\hat{\mathbf{L}}_\lambda$, and $\hat{\mathbf{L}}_\nu$ are the representation of a hypothetical angular momentum in each of the corresponding frames. This diagram was chosen to be consistent with (3.11) and (3.13), i.e., those equations can be derived from that diagram. It therefore appropriately reflects the algebra associated with the $\lambda \rightarrow \nu$ transformation. From it we get the desired transformation property

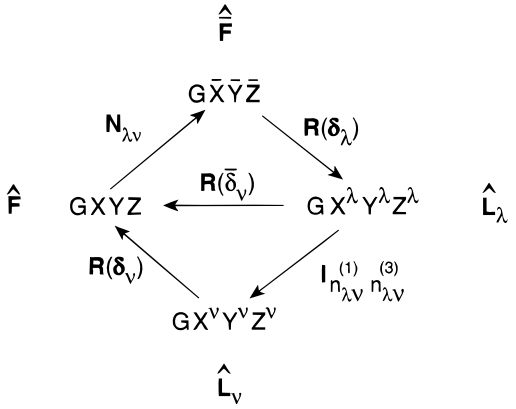

Figure 2. Systems of different mathematical frames GXYZ, $G\bar{X}\bar{Y}\bar{Z}$, $GX^\lambda Y^\lambda Z^\lambda$, and $GX^\nu Y^\nu Z^\nu$, the associated hyperangular momentum vector operators $\hat{\mathbf{F}}$, $\hat{\bar{\mathbf{F}}}$, $\hat{\mathbf{L}}_\lambda$, and $\hat{\mathbf{L}}_\nu$, and the rotation matrices which inter-relate them. This diagram summarizes the transformation properties of these operators.

$$\hat{\mathbf{L}}_\nu = \mathbf{I}_{n_{\lambda\nu}^{(1)} n_{\lambda\nu}^{(3)}} \hat{\mathbf{L}}_\lambda \quad (4.107)$$

which, when compared with (4.105), indicates that $\hat{\mathbf{L}}_\lambda$ transforms under kinematic rotations the same way that $\hat{\mathbf{J}}^{I\lambda}$ does, and as a result, that $GX^\lambda Y^\lambda Z^\lambda$ transforms the same way as $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ does. The correctness of (4.107) has been independently verified by a much more laborious direct calculation starting with (4.29) and its ν counterpart and using (3.11) and the chain rule to obtain $\hat{\mathbf{L}}_\nu$ in terms of $\hat{\mathbf{L}}_\lambda$.

As a result of (4.105) and (4.107) we see that the operators $N_{jj'k}^{I\lambda} - N_{ii}\hat{L}_{\lambda k}$ which appear in (4.69) can change sign under kinematic rotations but that their squares, six of which contribute to $\hat{C}^2$, are kinematic-rotation-invariant, as are $\hat{T}_\rho$, $\hat{K}^2$, and $\hat{B}$. Therefore, not only is $\hat{T}$ invariant under such transformations but also each of nine contributing operators have this property. In addition, since $\rho,\theta,\phi,\delta_\lambda$ and $\rho,\theta,\phi,\delta_\nu$ represent the same internal configuration of the tetraatomic system, we have

$$V_\lambda(\rho,\theta,\phi,\delta_\lambda) = V_\nu(\rho,\theta,\phi,\delta_\nu) = V \quad (4.108)$$

and all the contributions to the system's Hamiltonian are individually kinematic-rotation-invariant. Such term-by-term independence that $\hat{H}$ displays when expressed in row-orthonormal hyperspherical coordinates is very convenient for both analytical and computational purposes.

4.3.2. Inversion through the Center of Mass. As stated after (3.23), the only coordinate affected by the inversion operation $\hat{\mathcal{I}}$ is the chirality coordinate χ. Since, however, this coordinate does not appear in $\hat{H}$, we conclude that every term of the Hamiltonian is invariant under $\hat{\mathcal{I}}$.

4.3.3. Permutations of Identical Nuclei. We consider here the case in which P_1, P_2, and P_3 are identical to each other and distinct from P_4 and use the arrangement channel coordinates $\lambda = 1$ described in section 3.4. In view of (3.37) through (3.47) we conclude that $\hat{H}$ is term-by-term invariant under all symmetry operations of S_3. This is a very useful property.

5. Continuity Conditions for the Tetraatomic Schrödinger Equation

Under the electronically-adiabatic conditions spelled out at the beginning of section 4.1, the wave function describing a

physical state of a molecular system is the product of an electronic wave function, which depends parametrically on the position of the nuclei, and a nuclear wave function. This product must be single-valued with respect to the positions of the nuclei, but its individual factors need not satisfy such a condition. Nevertheless, the electronic wave function is usually chosen to be a single-valued function of the nuclear geometry, in which case so is the nuclear wave function. However, if the electronically-adiabatic potential energy surface being considered displays a conical intersection, the electronic wave function, if required to be real and to depend on the nuclear coordinates in a manner which is as continuous as possible, changes sign as the system traverses a closed loop around the conical intersection in nine-dimensional nuclear configuration space.[10] In order that the electronuclear wave function be everywhere single-valued, the corresponding nuclear wave function must in such a case undergo a compensating change of sign, called the geometric phase effect.[4−10] The consequences of this effect have been detected in atom−diatom chemical reactions.[6]

To implement the single-valuedness condition in the absence of a conical intersection, or to include the geometric phase effect in the presence of one, it is convenient to utilize coordinates bearing one-to-one correspondences with the configurations of the system. The space-fixed mass-scaled Jacobi Cartesian coordinates $x_{\lambda i}^{(j)}$ ($i = 1, 2, 3$; $j = 1, 2, ..., N - 1$) of (2.3) display this kind of one-to-one correspondence for all possible configurations (including different orientations in space for a given internal geometry). However, whenever angular coordinates are introduced, such correspondence breaks down for special arrangements of the nuclei. In this section we consider these special geometries for tetraatomic systems when using the row-orthonormal hyperspherical coordinates $\boldsymbol{a}_\lambda, \chi, \rho, \theta, \phi, \delta_\lambda$. This is conveniently done with the help of the symmetrized internal configuration space mapping vector $\mathbf{X}_\lambda$ defined by[65]

$$\mathbf{X}_\lambda = \frac{1}{\rho}\begin{pmatrix} \left(\frac{1}{2}\right)[r_\lambda^{(3)^2} + r_\lambda^{(2)^2} - 2r_\lambda^{(1)^2}] \\ \left(\frac{\sqrt{3}}{2}\right)[r_\lambda^{(3)^2} - r_\lambda^{(2)^2}] \\ \sqrt{3}\mathbf{r}_\lambda^{(3)}\cdot\mathbf{r}_\lambda^{(2)} \\ \sqrt{3}\mathbf{r}_\lambda^{(3)}\cdot\mathbf{r}_\lambda^{(1)} \\ \sqrt{3}\mathbf{r}_\lambda^{(2)}\cdot\mathbf{r}_\lambda^{(1)} \\ \rho X_6 \end{pmatrix} \tag{5.1}$$

where

$$X_6 = (-1)^\chi[|\mathbf{r}_\lambda^{(3)} \times \mathbf{r}_\lambda^{(2)}|^2 + |\mathbf{r}_\lambda^{(3)} \times \mathbf{r}_\lambda^{(1)}|^2 + |\mathbf{r}_\lambda^{(2)} \times \mathbf{r}_\lambda^{(1)}|^2]^{1/2} \tag{5.2}$$

This vector undergoes a six-dimensional proper rotation under $\lambda \rightarrow \nu$ transformations and displays a one-to-one correspondence with internal configurations of the system. As a consequence of (2.28), its components can be expressed as functions of the internal hyperspherical coordinates $\chi, \rho, \theta, \phi, \delta_\lambda$. Replacement of (2.28) into (2.5) furnishes

$$\mathbf{S}_\lambda = \mathbf{R}(\delta_\lambda)\rho^2\mathbf{N}^2(\theta,\phi)\tilde{\mathbf{R}}(\delta_\lambda) \tag{5.3}$$

from which we can calculate the $r_\lambda^{(i)2}$ and the $\mathbf{r}_\lambda^{(i)}\cdot\mathbf{r}_\lambda^{(j)}$ needed to evaluate the components X_{λ_l} ($l = 1, 2, ..., 5$) of $\mathbf{X}_\lambda$. Since $|\mathbf{X}_\lambda| = \rho$, the magnitude of X_6 can be obtained from these first five components, and its sign is $(-1)^\chi$. In this manner, given χ, ρ, θ, ϕ, and δ_λ, we can calculate $\mathbf{X}_\lambda$. There is a one-to-one correspondence between the elements of $\mathbf{S}_\lambda$ and the components of $\mathbf{X}_\lambda$ (except for the sign of X_6) and therefore between $\mathbf{S}_\lambda$ and the internal configurations of the system, excluding its chirality. As a result, the special geometries of interest can be derived from an analysis of (5.3). This analysis is performed keeping (2.13) through (2.16) and (2.23) in mind, considering the values of θ,ϕ for which (a) $N_{11} = N_{22} < N_{33}$ (prolate symmetric top rotor), (b) $N_{11} = N_{33} > N_{22}$ (oblate symmetric top rotor), and (c) $N_{11} = N_{22} = N_{33}$ (spherical top rotor), and examining the corresponding $\mathbf{S}_\lambda$ and $\mathbf{X}_\lambda$. Cases a and c lead to special geometries whereas case b does not. The results are:

1. $\theta = 0$. $\mathbf{X}_\lambda$ is independent of ϕ and $\delta_\lambda^{(1)}$.
2. $\phi = \pi/4$ and $\theta \neq \arcsin(2/3)^{1/2}$. $\mathbf{X}_\lambda$ is independent of $\delta_\lambda^{(1)}$.
3. $\theta = \arcsin(2/3)^{1/2} \cong 54.7°$ and $\phi = \pi/4$. $\mathbf{X}_\lambda$ is independent of δ_λ.

In addition, due to the structure of matrix $\mathbf{R}$,[78] if $\delta_\lambda^{(2)} = 0$ ρ_λ^{sf} depends on $\delta_\lambda^{(1)}$ and $\delta_\lambda^{(3)}$ through their sum only, a similar property being valid for a_λ and c_λ if $b_\lambda = 0$. At all of these geometries, the volume element $d\tau$ of (4.103) vanishes. For cases 1 and 2 we have $N_{11} = N_{22} < N_{33}$, with the moments of inertia I_1 and I_2 being equal to each other and greater than I_3. For case 1, the four nuclei lie on a straight line. For case 2, if $\delta_\lambda^{(2)}$ is set equal to zero, the vectors $\mathbf{r}_\lambda^{(j)}$ ($j = 1, 2, 3$) are orthogonal to each other and $r_\lambda^{(1)} = r_\lambda^{(2)}$. If the three nuclei P_{λ_1}, P_{λ_2}, and P_{λ_3} have equal masses, the geometry is that of a regular trigonal pyramid, and $\mathbf{X}_\lambda$ is independent of $\delta_\lambda^{(1)}$ and $\delta_\lambda^{(3)}$ but depends on θ. For case 3, $N_{11} = N_{22} = N_{33}$, the system's three moments of inertia are equal, and all three vectors $\mathbf{r}_\lambda^{(j)}$ have equal lengths in addition to being orthogonal to each other. The first five components of $\mathbf{X}_\lambda$ vanish in this case, and the sixth one equals $(-1)^\chi \rho$, independently of δ_λ. If the four nuclei are identical, the geometry of the configuration is a regular tetrahedron. Associated to all these special geometries, there are distinct sets of values of the row-orthonormal hyperspherical coordinates which lead to the same ρ_λ^{sf}, and the system's electronuclear wave function must have the same value at those degenerate sets. This boundary condition must be fulfilled regardless of whether or not the system displays a conical intersection and can be imposed through a judicious choice of basis functions (either analytical or numerical) in the $\theta, \phi, \delta_\lambda$ hyperangular coordinates.

Let us consider a system in which the nuclei P_1, P_2, and P_3 are identical to each other and distinct from P_4. Let us adopt the $\lambda = 1$ arrangement channel coordinates of section 3.4 and consider the motion of the system on an electronically-adiabatic potential energy surface which displays a conical intersection with another such surface for configurations for which P_1, P_2, and P_3 are on the vertices of an equilateral triangle and P_4 is on the trigonal axis of symmetry of that triangle. When the system traverses a closed loop in 9D nuclear configuration space that, in 6D internal configuration space surrounds the locus of points representing such regular pyramid configurations, the 9D nuclear wave function must change sign. A loop L, going through an arbitrary configuration of the system defined by $\mathbf{a}_1$, χ, ρ, θ, ϕ, and δ_1, can be chosen in general as follows. We maintain $\chi^L, \rho^L, \theta^L, \phi^L, \delta_1^{(2)L}$, and $\delta_1^{(3)L}$ for points on L constant and equal to $\chi, \rho, \theta, \phi, \delta_1^{(2)}$ and $\delta_1^{(3)}$, respectively, and vary $\delta_1^{(1)L}$ from $\delta_1^{(1)}$ to $\delta_1^{(1)} + \pi$, modulo π. At the same time, we change the Euler angles a_1^L, b_1^L, and c_1^L with $\delta_1^{(1)L}$ from a_1, b_1, and c_1, to $(a_1 + \pi)$ mod2π, $\pi - b_1$, and $(\pi - c_1)$ mod2π, respectively. The reason for choosing $\delta_1^{(1)L}$ as the parametric variable which spans L is that the components of $\mathbf{X}_\lambda$ are linear functions of $\sin 2\delta_\lambda^{(1)}$ and $\cos 2\delta_\lambda^{(1)}$.

If, on the other hand, the system does not display a conical intersection, its nuclear wave function must have the same value

at the beginning and end of that loop. Such continuity conditions on the nuclear wave functions may be imposed by an appropriate choice of basis functions in θ, ϕ, and δ_λ. For $\phi = \pi/4$, $\delta_\lambda^{(2)} = 0$ and in the presence of a conical intersection, the condition that the electronuclear wave function not diverge at the geometries of that intersection forces the corresponding nuclear wave function to vanish at those geometries. In the absence of a conical intersection, the nuclear wave function at those values of ϕ and $\delta_\lambda^{(2)}$ is independent of $\delta_\lambda^{(1)}$ and $\delta_\lambda^{(3)}$ sum only. In either case, the resulting electronuclear wave function satisfies the single-valuedness condition discussed two paragraphs earlier.

Generally speaking, once a given system of coordinates is chosen, the corresponding continuity conditions must be determined before a scattering calculation can be performed.

6. Conclusions

We have considered in this paper a set of row-orthonormal hyperspherical coordinates for tetraatomic systems and derived the corresponding nuclear motion Hamiltonian. The simple transformation properties of the terms of the latter under kinematic rotations and symmetry operations make those coordinates a very promising candidate for performing efficient accurate *ab initio* reactive scattering calculations.

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