Reactive Scattering with Row-Orthonormal Hyperspherical Coordinates. 3. Hamiltonian and Transformation Properties for Pentaatomic Systems†

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Received: December 18, 2008; Revised Manuscript Received: January 28, 2009

The Hamiltonian for triatomic and tetraatomic systems in row-orthonormal hyperspherical coordinates has been derived previously. However, for pentaatomic systems this derivation requires nontrivial generalizations. These are presented in this paper, together with the corresponding Hamiltonian. Each of the twelve operators that contribute to this Hamiltonian is kinematic-rotation invariant. As for the triatomic and tetraatomic cases, these pentaatomic demcocratic coordinates are particularly well suited for calculations of reactive scattering in five atom systems.

1. Introduction

Major progress has been achieved in the concepts and methods for performing ab initio calculations of state-to-state cross sections of a large variety of simple but important bimolecular reactions over the last 15 years or so. These cross sections and the associated wave functions furnish deep insight into their molecular level mechanism, and greatly add to our understanding of these improtant chemical processes. Furthermore, such calculations furnish benchmarks against which to test the approximate methods which must be used to extend calculations to larger systems for which ab initio methods are not feasible.

The first accurate ab initio quantum mechanical calculation of state-to-state reaction cross sections was performed 33 years ago. Three recent reviews[3−5] and the references therein exemplify the progress achieved so far. The ab initio state-to-state work included the study of triatomic and tetraatomic systems, involving time-independent propagation and variational methods as well as time-dependent wave packet techniques. Progress in the latter has been impressive, having reached the level-to-level stage. None of these ab initio reactive scattering calculations have so far included systems of more than four atoms. There are at least two reasons for this exclusion. One is the very large amount of computational time such computations would entail. The other is the lack of efficient methodologies to perform them.

We have also over the last 15 years or so been developing the method of row-orthonormal hyperspherical coordinates (ROHC) to perform such computations by the time-independent approach[6] for triatomic and tetraatomic systems. In the present paper, we have extended this formalism to five-atom systems. Present state-of-the-art high performance computers should permit these ab initio calculations to be performed for carefully selected reactions of five-atoms, such as the $H_2 + H_3^+$ reaction and its isotopomers, which is important in interstellar processes[7] and for which an accurate potential energy surface has been calculated.[8]

In Section 2 we define the ROHC for N-atom systems, and in Section 3 the kinematic rotation matrix for the pentaatomic case. We introduce angular momentum operators in four-dimensional (4D) spaces in Section 4, and in Section 5 and 6 we derive the matrix gradient operator and Hamiltonian in ROHC for five atoms. The invariance properties of the operators for these systems are examined in Section 7, and in Section 8 we summarize and discuss these results.

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

The definition of the ROHC for general $N \geq 3$ has been given previously[9−12] and will only be summarized below. We consider a system of N toms and an associated set of $N - 1$ λ-arrangment mass-scaled Jacobi vectors $\mathbf{r}_\lambda^{(1)}, \mathbf{r}_\lambda^{(2)}, ..., \mathbf{r}_\lambda^{(N-1)}$. The corresponding space-fixed $3 \times (N - 1)$ Jacobi matrix $\rho_\lambda^{\rm sf}$ is defined by

$$\rho_\lambda^{\rm sf} = (\mathbf{r}_\lambda^{(1)}\mathbf{r}_\lambda^{(2)}...\mathbf{r}_\lambda^{(N-1)}) = \begin{pmatrix} x_{\lambda_1}^{(1)} & x_{\lambda_1}^{(2)} & ...x_{\lambda_1}^{(N-1)} \\ x_{\lambda_2}^{(1)} & x_{\lambda_2}^{(2)} & ...x_{\lambda_2}^{(N-1)} \\ x_{\lambda_3}^{(1)} & x_{\lambda_3}^{(2)} & ...x_{\lambda_3}^{(N-1)} \end{pmatrix} \quad (2.1)$$

where $x_{\lambda 1}^{(j)} \equiv x_\lambda^{(j)},\ x_{\lambda 2}^{(j)} \equiv y_\lambda^{(j)},\ x_{\lambda 3}^{(j)} \equiv z_\lambda^{(j)}$ are the Cartesian space-fixed components of r_{λ_j} ($j = 1,\ 2, ..., N - 1$). Because of the singular value decomposition theorem for real matrices,[13,14] for $N > 3$ $\rho_\lambda^{\rm sf}$ can be put in the form[15−17]

$$\rho_\lambda^{\rm sf} = (-1)^\chi \tilde{\mathbf{R}}(\mathrm{a}_\lambda)\rho\mathbf{N}(\theta, \phi)\bar{\mathbf{Q}}(\delta_\lambda) \quad (2.2)$$

where χ is a λ-independent chirality coordinate that can assume the values 0 or 1, $\mathrm{a}_\lambda \equiv (a_\lambda, b_\lambda, c_\lambda)$ are the Euler angles that rotate the space-fixed frame $Gxyz$ (G being the system's center of mass) to the principal-axes-of-inertia body-fixed frame $Gx_1^{I\lambda}x_2^{I\lambda}x_3^{I\lambda} \equiv Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ and $\tilde{\mathbf{R}}(\mathrm{a}_\lambda)$ is the transpose of the corresponding proper rotation matrix $\mathbf{R}(\mathrm{a}_\lambda)$[18]

† Part of the "George C. Schatz Festschrift".

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10.1021/jp811171p CCC: $40.75
Published on Web 04/16/2009

$$\mathbf{R}(a_\lambda) = \begin{pmatrix} \cos c_\lambda & \sin c_\lambda & 0 \\ -\sin c_\lambda & \cos c_\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos b_\lambda & 0 & -\sin b_\lambda \\ 0 & 1 & 0 \\ \sin b_\lambda & 0 & \cos b_\lambda \end{pmatrix} \times \begin{pmatrix} \cos a_\lambda & \sin a_\lambda & 0 \\ -\sin a_\lambda & \cos a_\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2.3)$$

These angles are confined to the ranges

$$0 \le a_\lambda, c_\lambda < 2\pi \qquad 0 \le b_\lambda \le \pi \quad (2.4)$$

In addition, $\delta_\lambda \equiv (\delta_\lambda^{(1)}, \delta_\lambda^{(2)},..., \delta_\lambda^{(3N-9)})$ is a set of $3N - 9$ hyperangles (whose ranges, for $N = 5$, are discussed in Section 3.3) and $\bar{\mathbf{Q}}(\delta_\lambda)$ is a $3 \times (N - 1)$ row-orthonormal matrix satisfying the relation

$$\bar{\mathbf{Q}}(\delta_\lambda)\tilde{\bar{\mathbf{Q}}}(\delta_\lambda) = \mathbf{I}^{(3)} \quad (2.5)$$

where $\mathbf{I}^{(3)}$ is the 3×3 identity matrix. $\bar{\mathbf{Q}}$ is called the kinematic rotation matrix. Furthermore, $\mathbf{N}(\theta,\phi)$ is the 3×3 diagonal matrix

$$\mathbf{N}(\theta, \phi) = \begin{pmatrix} \sin\theta\cos\phi & 0 & 0 \\ 0 & \sin\theta\sin\phi & 0 \\ 0 & 0 & \cos\theta \end{pmatrix} \quad (2.6)$$

where θ and ϕ are moment-of-inertia hyperangles whose ranges are

$$0 \le \phi \le \pi/4 \quad (2.7)$$

and

$$0 \le \theta \le \arcsin[1/(1 + \cos^2\phi)^{1/2}] \le \arcsin(2/3)^{1/2} \simeq 54.7° \quad (2.8)$$

They are related to the system's principal moments of inertia $I_{x^{I_\lambda}}$, $I_{y^{I_\lambda}}$, and $I_{z^{I_\lambda}}$ by

$$I_{x^{I_\lambda}} = \mu\rho^2(1 - N_{11}^2) \qquad I_{y^{I_\lambda}} = \mu\rho^2(1 - N_{22}^2) \qquad I_{z^{I_\lambda}} = \mu\rho^2(1 - N_{33}^2) \quad (2.9)$$

which are ordered according to

$$I_{z^{I_\lambda}} \ge I_{x^{I_\lambda}} \ge I_{y^{I_\lambda}} \quad (2.10)$$

the N_{ii} ($i = 1-3$) being the diagonal elements of eq 2.6. Finally, $\rho \ge 0$ is the system's λ-independent hyperradius defined by

$$\rho^2 = \sum_{j=1}^{N-1} (x_\lambda^{(j)^2} + y_\lambda^{(j)^2} + z_\lambda^{(j)^2}) \quad (2.11)$$

The set of $3N - 3$ quantities a_λ, ρ, θ, ϕ, δ_λ plus the chirality coordinate χ are called the ROHC of the system.

3. The Kinematic Rotation Matrix for $N = 5$

For pentaatomic systems, the $\bar{\mathbf{Q}}$ row-orthonomal matrix of eq 2.2 has dimensions 3×4. In view of eq 2.5, its 12 elements are interconnected by three row-normalization and three row-orthogonality relations, and as a result it has only 6 degrees of freedom, given by the 6 hyperangles $\delta_\lambda^{(l)}$ ($l = 1-6$). It is convenient to write $\bar{\mathbf{Q}}$ in the form[19]

$$\bar{\mathbf{Q}}(\delta_\lambda) = \mathbf{P}\mathbf{Q}(\delta_\lambda) \quad (3.1)$$

where $\mathbf{P}$ is the 3×4 row-orthogonal matrix

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (3.2)$$

and $\mathbf{Q}(\delta_\lambda)$ a 4×4 proper real orthogonal matrix which also has 6 degrees of freedom and is also called a kinematic rotation matrix and can therefore be defined in terms of the same hyperangles δ_λ as $\bar{\mathbf{Q}}$. The first 3 rows of $\bar{\mathbf{Q}}$ and $\mathbf{Q}$ are the same with the latter matrix having an extra row but not an extra angular degree of freedom. The use of the 4×4 orthogonal matrix $\mathbf{Q}$ in lieu of the 3×4 row orthogonal matrix $\bar{\mathbf{Q}}$ greatly simplifies the algebra needed to obtain the Hamiltonian for pentaatomic systems in ROHC, and is an important nontrivial generalization as this approach can be extended to $N > 5$ systems.

3.1. The Q Matrix for Tetraatomic Systems. The tetraatomic case is useful as a stepping stone toward the pentaatomic case of interest to this paper. For it, the $\mathbf{Q}$ matrix of eq 2.2 has dimensions 3×3, is proper orthogonal, and can be put in the form[11]

$$\bar{\mathbf{Q}} \equiv \mathbf{Q}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) = \mathbf{M}_{12}^{(3)}(\delta_\lambda^{(1)})\mathbf{M}_{13}^{(3)}(\delta_\lambda^{(2)})\mathbf{M}_{12}^{(3)}(\delta_\lambda^{(3)}) \quad (3.3)$$

where

$$\mathbf{M}_{12}^{(3)}(\omega) = \begin{pmatrix} \cos\omega & -\sin\omega & 0 \\ \sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{M}_{13}^{(3)}(\omega) = \begin{pmatrix} \cos\omega & 0 & \sin\omega \\ 0 & 1 & 0 \\ -\sin\omega & 0 & \cos\omega \end{pmatrix} \quad (3.4)$$

This $\mathbf{Q}^{(3)}$ is the transpose of the proper rotation matrix $\mathbf{R}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ defined by eq 2.3 (with a_λ, b_λ, c_λ replaced by $\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}$) and leads to a simple expression for the tetraatomic ROHC Hamiltonian in which the roles of the ordinary rotation Euler angles a_λ, b_λ, c_λ and the hyperangular kinematic rotation angles $\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}$ are analogous. This analogy is very useful and will serve as a guide for extension to the pentaatomic case.

Let us consider a three-dimensional mathematical space defined by the Cartesian axes $OX_1X_2X_3$. The subscripts of the $\mathbf{M}_{12}^{(3)}$ and $\mathbf{M}_{13}^{(3)}$ matrices of eq 3.4 indicate which of the Cartesian coordinates X_1, X_2, X_3 of a point in this space are affected by the associated rotation, namely X_1 and X_2 for $\mathbf{M}_{12}^{(3)}$ and X_1 and X_3 for $\mathbf{M}_{13}^{(3)}$, according to

$$\mathbf{M}_{12}^{(3)}\begin{pmatrix}X_1\\X_2\\X_3\end{pmatrix}=\begin{pmatrix}X_1\cos\omega-X_2\sin\omega\\X_1\sin\omega+X_2\cos\omega\\X_3\end{pmatrix}\qquad\mathbf{M}_{13}^{(3)}\begin{pmatrix}X_1\\X_2\\X_3\end{pmatrix}=\begin{pmatrix}X_1\cos\omega+X_3\sin\omega\\X_2\\-X_1\sin\omega+X_3\cos\omega\end{pmatrix}\tag{3.5}$$

$\mathbf{M}_{12}^{(3)}$ represents a rotation of the OX_1X_2 axes or plane around OX_3 in which the positive OX_2 axis moves toward the positive OX_1 axis by angle ω. This corresponds to a clockwise (rather than counterclockwise) rotation, which is used to take into account the transpose relation between $\mathbf{Q}^{(3)}$ and $\mathbf{R}$ mentioned after eq 3.4. This rotation and convention are convenient for extension to higher dimensional spaces, needed for systems of more than four atoms. Similar remarks for $\mathbf{M}_{13}^{(3)}$ are valid. It should be noticed that the matrix $\tilde{\mathbf{Q}}^{(3)}$ $(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ rotates the $OX_1X_2X_3$ frame into another frame designated by $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}$.

3.2. The *Q* Matrix for Pentaatomic Systems. In analogy to the tetraatomic case, we express the $\mathbf{Q}$ in the rhs of eq 3.1 as a product of six proper orthogonal matrices $\mathbf{M}_{ij}$, each depending on one of the six hyperangles $\delta_\lambda^{(l)}$ $(l = 1-6)$. We now define a 4D mathematical space whose Cartesian axes are $OX_1X_2X_3X_4$. Each of the 6 matrices $\mathbf{M}_{ij}$ represents a rotation in that space of the pair of axes (or plane) OX_iX_j around the remaining two axes, the sense of the rotation being defined by the positive OX_j axis moving toward the positive OX_i axis, as was the case for eq 3.5. Possible choices for these matrices, with $j > i$, are therefore

$$\mathbf{M}_{12}(\omega)=\begin{pmatrix}\cos\omega&-\sin\omega&0&0\\\sin\omega&\cos\omega&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\qquad\mathbf{M}_{13}(\omega)=\begin{pmatrix}\cos\omega&0&\sin\omega&0\\0&1&0&0\\-\sin\omega&0&\cos\omega&0\\0&0&0&1\end{pmatrix}$$
$$\mathbf{M}_{14}(\omega)=\begin{pmatrix}\cos\omega&0&0&-\sin\omega\\0&1&0&0\\0&0&1&0\\\sin\omega&0&0&\cos\omega\end{pmatrix}\qquad\mathbf{M}_{23}(\omega)=\begin{pmatrix}1&0&0&0\\0&\cos\omega&-\sin\omega&0\\0&\sin\omega&\cos\omega&0\\0&0&0&1\end{pmatrix}\tag{3.6}$$
$$\mathbf{M}_{24}(\omega)=\begin{pmatrix}1&0&0&0\\0&\cos\omega&0&\sin\omega\\0&0&1&0\\0&-\sin\omega&0&\cos\omega\end{pmatrix}\qquad\mathbf{M}_{34}(\omega)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&\cos\omega&-\sin\omega\\0&0&\sin\omega&\cos\omega\end{pmatrix}$$

We write $\mathbf{Q}$ as

$$\mathbf{Q}(\delta_\lambda)=\prod_{k=1}^{6}\mathbf{M}_{i_kj_k}(\delta_\lambda^{(k)})\tag{3.7}$$

where the six $(i_k j_k)$ pairs are chosen from the set (1,2), (1,3), (1,4), (2,3), (2,4), and (3,4) with not all necessarily distinct. However, their choice is constrained by the requirement that there be a one-to-one correspondence between $\rho_\lambda^{\mathrm{sf}}$ and the ROHC χ, a_λ, ρ, θ, ϕ, δ_λ that appear in the rhs of eq 2.2 (except for a subset of special geometries, such as coplanar and collinear), as was the case for $N = 4$.[11] This constraint also leads to specific ranges of the $\delta_\lambda^{(l)}$, as discussed in Section 3.3. One of its consequences is that no consecutive pair (i_l, j_l) and $(i_{l+1} j_{l+1})$ can be the same, since from eq 3.7 this leads to a $\mathbf{Q}$ that depends on $\delta_\lambda^{(l)}$ and $\delta_\lambda^{(l+1)}$ only through their sum $\delta_\lambda^{(l)} + \delta_\lambda^{(l+1)}$, which is in violation of this one-to-one correspondence. A choice of $\mathbf{Q}$ which satisfies this constraint is

$$\mathbf{Q}(\delta_\lambda)=\mathbf{M}_{12}(\delta_\lambda^{(1)})\mathbf{M}_{13}(\delta_\lambda^{(2)})\mathbf{M}_{12}(\delta_\lambda^{(3)})\mathbf{M}_{34}(\delta_\lambda^{(4)})\mathbf{M}_{24}(\delta_\lambda^{(5)})\mathbf{M}_{14}(\delta_\lambda^{(6)})\tag{3.8}$$

It should be remarked that the matrix $\mathbf{Q}(\delta_\lambda)$ rotates the $OX_1X_2X_3X_4$ frame to another 4D frame designated by $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}X_{\lambda_4}$. The selection of the first three matrices in the rhs of this expression is made in analogy to eq 3.3 and that of the last three by considerations related to the definition of the hyperangular momentum operators $\hat{L}_{\lambda_k}(\delta_\lambda)$ $(k = 1-6)$ associated with the set of hyperangles δ_λ, as discussed in Section 4.

3.3. The Ranges of the Hyperangles $\boldsymbol{\delta_\lambda}$. The δ_λ angles lie by definition in the $0-2\pi$ range. However, they are further restricted by the one-to-one correspondence mentioned after eq 3.7. To that effect, we seek to identify sets of ROHC corresponding to the same configuration (i.e., the same $\rho_\lambda^{\mathrm{sf}}$ matrix of eq 2.1) and to reduce them to a single set (except for the special geometries also mentioned after eq 3.7) by restricting the allowed ranges of the $\delta_\lambda^{(l)}$. To achieve this objective, we define, as for the tetraatomic case,[11] the 3×3 diagonal matrices $\mathbf{I}_p^{(3)}$ $(p = 0-3)$

$$\mathbf{I}_0^{(3)} \equiv \mathbf{I}^{(3)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{I}_1^{(3)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$
$$\mathbf{I}_2^{(3)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \mathbf{I}_3^{(3)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.9}$$

These $\mathbf{I}_p^{(3)}$ satisfy the relations

$$\mathbf{I}_p^{(3)^2} = \mathbf{I}^{(3)} \qquad \det\mathbf{I}_p^{(3)} = 1 \qquad p = 0-3 \tag{3.10}$$

With the help of eq 3.1, we can rewrite eq 2.2 as

$$\rho_\lambda^{\mathrm{sf}} = (-1)^\chi \tilde{\mathbf{R}}(\mathrm{a}_\lambda)\rho\mathbf{N}(\theta,\phi)\mathbf{P}\mathbf{Q}(\delta_\lambda) \tag{3.11}$$

Because of the diagonal nature of the $\mathbf{N}$ defined by eq 2.6, we may insert in eq 3.11 $\mathbf{I}_p^{(3)}$ after $\tilde{\mathbf{R}}$ and also before $\mathbf{P}$:

$$\rho_\lambda^{\mathrm{sf}} = (-1)^\chi \tilde{\mathbf{R}}(\mathrm{a}_\lambda)\mathbf{I}_p^{(3)}\rho\mathbf{N}(\theta,\phi)\mathbf{I}_p^{(3)}\mathbf{P}\mathbf{Q}(\delta_\lambda) \tag{3.12}$$

The definition of $\mathbf{P}$ by eq 3.2 and of $\mathbf{I}_p^{(3)}$ by eq 3.9 permits us to write

$$\mathbf{I}_p^{(3)}\mathbf{P} = \mathbf{P}\mathbf{I}_p \qquad p = 0-3 \tag{3.13}$$

where the $\mathbf{I}_p$ are the 4 × 4 diagonal matrices defined by

$$\mathbf{I}_0 \equiv \mathbf{I} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{I}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$
$$\mathbf{I}_2 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{I}_3 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{3.14}$$

$\mathbf{I}$ being the 4 × 4 identity matrix. As a result, eq 3.12 can be written as

$$\rho_\lambda^{\mathrm{sf}} = (-1)^\chi \tilde{\mathbf{R}}_p(\mathrm{a}_{\lambda_p})\rho\mathbf{N}(\theta,\phi)\mathbf{P}\mathbf{Q}_p(\delta_{\lambda_p}) \qquad p = 0-3 \tag{3.15}$$

where

$$\tilde{\mathbf{R}}_p(\mathrm{a}_{\lambda_p}) = \tilde{\mathbf{R}}(\mathrm{a}_\lambda)\mathbf{I}_p \qquad \mathbf{Q}_p(\delta_{\lambda_p}) = \mathbf{I}_p\mathbf{Q}(\delta_\lambda) \tag{3.16}$$

Because of the first of eq 3.16, we can, as for the $N = 4$ case,[11] express the a_{λ_p} ($p = 0-3$) in terms of the a_λ (which corresponds to $p = 0$) by equating the elements of the third row and column of of this expression[20] (where all a_λ and c_λ angles are expressed modulus 2π in order to simplify the resulting equations)

$$\begin{aligned} \mathrm{a}_{\lambda_0} &= (a_\lambda, b_\lambda, c_\lambda) \\ \mathrm{a}_{\lambda_1} &= (a_\lambda + \pi, \pi - b_\lambda, 2\pi - c_\lambda) \\ \mathrm{a}_{\lambda_2} &= (a_\lambda + \pi, \pi - b_\lambda, \pi - c_\lambda) \\ \mathrm{a}_{\lambda_3} &= (a_\lambda, b_\lambda, \pi + c_\lambda) \end{aligned} \tag{3.17}$$

From the second of eq 3.16, we can write the δ_{λ_p} ($p = 0-3$) in terms of the δ_λ, but doing so using the explicit expressions of the $\mathbf{Q}_p$ and $\mathbf{Q}$ matrices in terms of the 12 angles δ_{λ_p} and δ_λ is very cumbersome. In lieu of this explicit approach, we use an implicit one. We start by defining the additional 4×4 diagonal matrices $\mathbf{I}_4$ through $\mathbf{I}_7$ by

$$\mathbf{I}_4 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad \mathbf{I}_5 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$
$$\mathbf{I}_6 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad \mathbf{I}_7 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{3.18}$$

The set of eight matrices $\mathbf{I}_p$ ($p = 0 - 7$) satisfy

$$\mathbf{I}_\mathrm{p}^2 = \mathbf{I} \qquad \det \mathbf{I}_p = 1 \qquad p = 0-7 \tag{3.19}$$

They constitute a complete set of 4×4 diagonal matrices whose diagonal elements are ± 1 and whose determinants are 1. Replacing eq 3.8 in the rhs of the second of eq 3.16 and inserting $\mathbf{I}_{s_m}(m = 1-5)$ (where $\mathbf{I}_{s_m}$ is one of the $\mathbf{I}_p$ matrices) between the 5 consecutive pairs of $\mathbf{M}_{ij}$ products that appear in the resulting expression furnishes

$$\mathbf{Q}_p(\delta_{\lambda_p}) = \mathbf{I}_p\mathbf{M}_{12}(\delta_\lambda^{(1)})\mathbf{I}_{s_1}^2\mathbf{M}_{13}(\delta_\lambda^{(2)})\mathbf{I}_{s_2}^2\mathbf{M}_{12}(\delta_\lambda^{(3)})\mathbf{I}_{s_3}^2\mathbf{M}_{34}(\delta_\lambda^{(4)})\mathbf{I}_{s_4}^2\mathbf{M}_{24}(\delta_\lambda^{(5)})\mathbf{I}_{s_5}^2\mathbf{M}_{14}(\delta_\lambda^{(6)}) \tag{3.20}$$

Using the δ_{λ_p} version of eq 3.8 in the rhs of the expression above, it yields

$$\begin{aligned} &\mathbf{M}_{12}(\delta_\lambda^{(1)}) = \mathbf{I}_p\mathbf{M}_{12}(\delta_\lambda^{(1)}) && \mathbf{I}_{s_1}M_{13}(\delta_{\lambda_p}^{(2)}) = \mathbf{I}_{s_1}\mathbf{M}_{13}(\delta_\lambda^{(2)})\mathbf{I}_{s_2} \\ &\mathbf{M}_{12}(\delta_\lambda^{(3)}) = \mathbf{I}_{s_2}\mathbf{M}_{12}(\delta_\lambda^{(3)}) && \mathbf{I}_{s_3}\mathbf{M}_{34}(\delta_{\lambda_p}^{(4)}) = \mathbf{I}_{s_3}\mathbf{M}_{24}(\delta_\lambda^{(4)})\mathbf{I}_{s_4} \\ &\mathbf{M}_{24}(\delta_\lambda^{(5)}) = \mathbf{I}_{s_4}\mathbf{M}_{24}(\delta_\lambda^{(5)}) && \mathbf{I}_{s_5}\mathbf{M}_{14}(\delta_{\lambda_p}^{(6)}) = \mathbf{I}_{s_5}\mathbf{M}_{14}(\delta_\lambda^{(6)}) \end{aligned} \tag{3.21}$$

These equations furnish, for each $p = 0-3$, the relations between the $\delta_{\lambda_p}^{(l)}$ and the corresponding $\delta_\lambda^{(l)}$ ($l = 1-6$) angles. They also restrict the values that, for each p, the indices s_m ($m = 1-5$) can have. For example, for $p = 0$ the first of eq 3.6 and of eq 3.21 yield

$$\begin{pmatrix} \cos\delta_{\lambda_0}^{(1)} & -\sin\delta_{\lambda_0}^{(1)} & 0 & 0 \\ \sin\delta_{\lambda_0}^{(1)} & \cos\delta_{\lambda_0}^{(1)} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos\delta_\lambda^{(1)}(\mathbf{I}_{s_1})_{11} & -\sin\delta_\lambda^{(1)}(\mathbf{I}_{s_1})_{22} & 0 & 0 \\ \sin\delta_\lambda^{(1)}(\mathbf{I}_{s_1})_{11} & \cos\delta_\lambda^{(1)}(\mathbf{I}_{s_1})_{22} & 0 & 0 \\ 0 & 0 & (\mathbf{I}_{s_1})_{33} & 0 \\ 0 & 0 & 0 & (\mathbf{I}_{s_1})_{44} \end{pmatrix} \tag{3.22}$$

This requires that $(\mathbf{I}_{s_1})_{33} = (\mathbf{I}_{s_1})_{44} = 1$ and therefore, from eq 3.14, that s be either 0 or 3, corresponding to the two possible results where the first angle is either $\delta_\lambda^{(1)}$ or $\pi + \delta_\lambda^{(1)}$. We then proceed to the second of eq 3.21 and get the permissible values of s_2 and the associated expressions for the second delta angle, and so forth. The final results are the 8 sets of δ_{λ_0} given below

$$\begin{aligned} &\text{set1:} \quad \delta_{\lambda_0} = \delta_\lambda = (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ &\text{set2:} \quad \delta_{\lambda_0} = (\pi + \delta_\lambda^{(1)}, 2\pi - \delta_\lambda^{(2)}, \pi + \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ &\text{set3:} \quad \delta_{\lambda_0} = (\pi + \delta_\lambda^{(1)}, \pi - \delta_\lambda^{(2)}, 2\pi - \delta_\lambda^{(3)}, \pi - \delta_\lambda^{(4)}, \pi + \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ &\text{set4:} \quad \delta_{\lambda_0} = (\delta_\lambda^{(1)}, \pi + \delta_\lambda^{(2)}, \pi - \delta_\lambda^{(3)}, \pi - \delta_\lambda^{(4)}, \pi + \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ &\text{set5:} \quad \delta_{\lambda_0} = (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \pi + \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \pi - \delta_\lambda^{(5)}, \pi + \delta_\lambda^{(6)}) \\ &\text{set6:} \quad \delta_{\lambda_0} = (\pi + \delta_\lambda^{(1)}, 2\pi - \delta_\lambda^{(2)}, \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \pi - \delta_\lambda^{(5)}, \pi + \delta_\lambda^{(6)}) \\ &\text{set7:} \quad \delta_{\lambda_0} = (\pi + \delta_\lambda^{(1)}, \pi - \delta_\lambda^{(2)}, \pi - \delta_\lambda^{(3)}, \pi - \delta_\lambda^{(4)}, 2\pi - \delta_\lambda^{(5)}, \pi + \delta_\lambda^{(6)}) \\ &\text{set8:} \quad \delta_{\lambda_0} = (\delta_\lambda^{(1)}, \pi + \delta_\lambda^{(2)}, 2\pi - \delta_\lambda^{(3)}, \pi - \delta_\lambda^{(4)}, 2\pi - \delta_\lambda^{(5)}, \pi + \delta_\lambda^{(6)}) \end{aligned} \tag{3.23}$$

If the only constraint on the angles of the 8 δ_{λ_0} sets is that they be in the 0 to 2π range, these 8 sets together with the Euler angles $a_{\lambda_0} = a_\lambda$, the principal moment of inertia hyperangles θ, ϕ, the hyperradius ρ, and the chirality coordinate χ constitute 8 complete sets of ROHC all of which give the same ρ_λ^{sf} of eq 2.1 (for $N = 5$) and therefore the same configuration of the system. This violates the desired one-to-one correspondence between configurations and sets of ROHC. To introduce this correspondence, we must restrict the ranges of at least some of the $\delta_\lambda^{(l)}$ and of the corresponding angles in δ_{λ_0}. Let us start by restricting the range of $\delta_\lambda^{(2)}$ to 0 to π, as was done for tetraatomic systems.[11] The sets 2, 4, 6, and 8 are not allowed since $2\pi - \delta_\lambda^{(2)}$ and $\pi + \delta_\lambda^{(2)}$ are out of range. Further constraints are needed to eliminate three more of these sets. Let us therefore also constrain $\delta_\lambda^{(5)}$ to the 0 to π range. This eliminates sets 3 and 7 as $\pi + \delta_\lambda^{(5)}$ and $2\pi - \delta_\lambda^{(5)}$ are now out of range. Finally, constraining $\delta_\lambda^{(6)}$ to that range eliminates set 5, as $\pi + \delta_\lambda^{(6)}$ is out of range. Therefore, by constraining the $\delta_\lambda^{(2)}$, $\delta_\lambda^{(5)}$ and $\delta_\lambda^{(6)}$ angles to the 0 to π range, reduces the 8 sets of δ_{λ_0} angles to set 1. We now must repeat this procedure for $p = 1$, 2, and 3. Each of these values of p gives 8 δ_{λ_p} sets but the constraints on $\delta_\lambda^{(2)}$, $\delta_\lambda^{(5)}$ and $\delta_\lambda^{(6)}$ reduces each to a single set. We are therefore left with one acceptable set for each p, given by:

$$\begin{aligned} p = 0 \quad & \delta_{\lambda_0} = (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ p = 1 \quad & \delta_{\lambda_1} = (2\pi - \delta_\lambda^{(1)}, \pi - \delta_\lambda^{(2)}, \pi + \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ p = 2 \quad & \delta_{\lambda_2} = (\pi - \delta_\lambda^{(1)}, \pi - \delta_\lambda^{(2)}, \pi + \delta_\lambda^{(3)}\delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \\ p = 3 \quad & \delta_{\lambda_3} = (\pi + \delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}, \delta_\lambda^{(4)}, \delta_\lambda^{(5)}, \delta_\lambda^{(6)}) \end{aligned} \tag{3.24}$$

Constraining $\delta_\lambda^{(1)}$ to the 0 to π range eliminates the $p = 1$ and $p = 3$ sets, as $2\pi - \delta_\lambda^{(1)}$ and $\pi + \delta_\lambda^{(1)}$ are out of range. Finally, constraining $\delta_\lambda^{(3)}$ to this range eliminates the $p = 2$ set, as $\pi + \delta_\lambda^{(3)}$ is out of range. The desired ranges of the $\delta_\lambda^{(l)}$ that maintains the one-to-one correspondence between configurations and ROHC (except for the special geometries mentoned after eq 3.7) are therefore

$$\begin{aligned} 0 \le \delta_\lambda^{(l)} \le \pi \qquad & l = 1, 2, 3, 5, 6 \\ 0 \le \delta_\lambda^{(4)} < 2\pi & \end{aligned} \tag{3.25}$$

The equality in the rhs of the first of eq 3.25 results from the fact that for any l for which we set $\delta_\lambda^{(l)} = 0$ and $\delta_\lambda^{(l)} = \pi$, while maintaining the remaining 9 ROHC unchanged, results in two ρ_λ^{sf} that are distinct. The reason that $\delta_\lambda^{(4)}$ has not been constrained to a range narrower than 0 to 2π is that in all 32 sets of δ_{λ_p} discussed above (8 for each of the 4 values of p), the fourth hyperangle is either $\delta_\lambda^{(4)}$ or $\pi - \delta_\lambda^{(4)}$ and therefore constraining it to the 0 to π range would eliminate one-half of the allowed configurations of the system, making such $\delta_\lambda^{(4)}$-restricted ROHC incomplete, thereby violating the desired one-to-one correspondence. It should be noted that the inequality sign in the rhs of the second of eq 3.25 is required because if we set $\delta_\lambda^{(4)} = 0$ and $\delta_\lambda^{(4)} = 2\pi$, while maintaining the remaining 9 ROHC unchanged, we get two identical configurations, requiring that one of these two values of $\delta_\lambda^{(4)}$ be eliminated.

4. Definition and Properties of Angular Momentum Operators in 3D and 4D Spaces

In going from $N = 4$ to $N = 5$ systems, the $\mathbf{Q}(\delta_\lambda)$ matrix is changed from the $\mathbf{Q}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ of (3.3) to the $\mathbf{Q}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)},..., \delta_\lambda^{(6)})$ of eq 3.8. Associated to the former we have three orbital angular momentum operators $\hat{L}_{\lambda_k}^{(3)}$ ($k = 1-3$) defined in the 3D mathematical space $OX_1X_2X_3$ considered in Section 3.1. Similarly, associated with the $N = 5$ case we have six orbital angular momentum operators $\hat{L}_{\lambda_k}$ ($k = 1-6$) defined in the 4D mathematical space $OX_1X_2X_3X_4$ referred to in Section 3.2. In order to express the latter operators in terms of the $\partial/\partial\delta_\lambda^{(l)}$ ($l = 1-6$), it is convenient to first indicate how the corresponding expressions for $N = 4$ are obtained.

4.1. The Angular Momentum Operators in 3D Space. Consider a point in the mathematical 3D space of Cartesian coordinates X_1, X_2, X_3. The corresponding components of its angular momentum operators are

$$\hat{l}_k = \frac{\hbar}{i}\left(X_i\frac{\partial}{\partial X_j} - X_j\frac{\partial}{\partial X_i}\right) = \frac{\hbar}{i}\sum_{p,q=1}^{3} \epsilon_{pq}^{(k)} X_p \frac{\partial}{\partial X_q} \qquad i, j, k = 1, 2, 3 \tag{4.1}$$

where $i = \sqrt{-1}$ and $\epsilon_{pq}^{(k)} = \epsilon_{pqk}$ is the Levi-Civita density, also called the ε-tensor.[21,22] Its value is zero if any two indices are equal and 1 (−1) if p, q, k is an even (odd) permutation of 1, 2, 3. From eq 4.1, it can be shown[23] that the components $\hat{L}_{\lambda_k}^{(3)}$ ($k = 1-3$) of the total angular momentum of a system of such points in the frame $OX_1X_2X_3$ is related to the angles $\delta_\lambda^{(1)}$, $\delta_\lambda^{(2)}$, $\delta_\lambda^{(3)}$ used in eq 3.3 (which, as stated in Section 3.1, rotates $OX_1X_2X_3$ to $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}$ via $\tilde{\mathbf{Q}}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$) by

$$\frac{\hbar}{i}\begin{pmatrix} \partial/\partial\delta_\lambda^{(1)} \\ \partial/\partial\delta_\lambda^{(2)} \\ \partial/\partial\delta_\lambda^{(3)} \end{pmatrix} = \mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) \begin{pmatrix} \hat{L}_{\lambda_1} \\ \hat{L}_{\lambda_2} \\ \hat{L}_{\lambda_3} \end{pmatrix} \tag{4.2}$$

where

$$\mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) = \begin{pmatrix} 0 & 0 & 1 \\ -\sin\delta_\lambda^{(1)} & \cos\delta_\lambda^{(1)} & 0 \\ \cos\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \sin\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \cos\delta_\lambda^{(2)} \end{pmatrix} \tag{4.3}$$

It should be noted that the $\mathbf{C}$ in this expression is the inverse of the matrix formed from the rhs of eq 2.2.2 of ref 23.

We define the differential operator

$$\hat{d}_{3_\lambda} \equiv \sum_{l=1}^{3} d\delta_\lambda^{(l)} \frac{\partial}{\partial \delta_\lambda^{(l)}} \tag{4.4}$$

Replacement of eq 4.2 in this equation and comparison of the coefficients of the $\hat{L}_{\lambda_k}^{(3)}$ with the elments of the $(d\tilde{\mathbf{Q}}^{(3)})\,\tilde{\mathbf{Q}}^{(3)}$ matrix[11] results in

$$\hat{d}_{3_\lambda} = -\frac{i}{2\hbar} \sum_{i,j,k=1}^{3} \epsilon_{ijk} [(d\mathbf{Q}^{(3)})\tilde{\mathbf{Q}}^{(3)}]_{ij} \hat{L}_{\lambda_k} \tag{4.5}$$

In addition, we get the following explicit expression for the elements of $\mathbf{C}^{(3)}$ in terms of $\mathbf{Q}^{(3)}$:

$$\mathbf{C}_{lk}^{(3)} = \frac{1}{2}\mathrm{tr}[\epsilon^{(k)}\mathbf{B}^{(l)}] \tag{4.6}$$

$$\mathbf{B}^{(l)} = \frac{\partial \mathbf{Q}^{(3)}}{\partial \delta_\lambda^{(l)}} \tilde{\mathbf{Q}}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) \tag{4.7}$$

where $\epsilon^{(k)}$ and $\mathbf{B}^{(l)}$ are the skew-symmetric 3 × 3 matrices

$$\epsilon^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \quad \epsilon^{(2)} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \epsilon^{(3)} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.8}$$

$$\mathbf{B}^{(l)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) = \begin{pmatrix} 0 & -B_{21}^{(l)} & B_{13}^{(l)} \\ B_{21}^{(l)} & 0 & -B_{32}^{(l)} \\ -B_{13}^{(l)} & B_{32}^{(l)} & 0 \end{pmatrix} \tag{4.9}$$

The elements of $\mathbf{C}^{(3)}$ are then given in terms of those of $\mathbf{B}^{(l)}$ by

$$\mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) = \begin{pmatrix} B_{32}^{(1)} & B_{13}^{(1)} & B_{21}^{(1)} \\ B_{32}^{(2)} & B_{13}^{(2)} & B_{21}^{(2)} \\ B_{32}^{(3)} & B_{13}^{(3)} & B_{21}^{(3)} \end{pmatrix} \tag{4.10}$$

The $\hat{L}_{\lambda_k}^{(3)}$ resulting from eqs 4.2 and 4.3 satisfy the relation

$$\hat{L}_{\lambda_k}^{(3)}\mathbf{Q}^{(3)} = -\frac{\hbar}{i}\epsilon^{(k)}\mathbf{Q}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) \qquad k = 1-3 \tag{4.11}$$

Consider the following expression involving the $\hat{L}_{\lambda_k}^{(3)}$: eqs 4.2 (together with eqs 4.6 and 4.7), 4.5, and 4.11. It can be shown that they are equivalent, that is, that when using any of them as a definition of the $\hat{L}_{\lambda_k}^{(3)}$ $(k = 1-3)$, the other two are properties that can be derived.

4.2. The Angular Momentum Operators in 4D Space. We now consider $N = 5$ systems. As a result of the considerations just made, we define angular momentum operators $\hat{L}_{\lambda_k}$ $(k = 1-6)$ in the associated mathematical 4D space $OX_1X_2X_3X_4$ by

$$\frac{\hbar}{i}\frac{\partial}{\partial \delta_\lambda} = \frac{\hbar}{i}\begin{pmatrix} \partial/\partial\delta_\lambda^{(1)} \\ \partial/\partial\delta_\lambda^{(2)} \\ \vdots \\ \partial/\partial\delta_\lambda^{(6)} \end{pmatrix} = \mathbf{C}(\delta_\lambda)\hat{\mathbf{L}}_\lambda = \mathbf{C}(\delta_\lambda)\begin{pmatrix} \hat{L}_{\lambda_1} \\ \hat{L}_{\lambda_2} \\ \vdots \\ \hat{L}_{\lambda_6} \end{pmatrix} \tag{4.12}$$

where $\delta_\lambda = (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, ..., \delta_\lambda^{(6)})$ and $\mathbf{C}(\delta_\lambda)$ is a 6 × 6 matrix whose elements are given by

$$\mathbf{C}_{lk}(\delta_\lambda) = \frac{1}{2}\mathrm{tr}[\mathbf{a}^{(k)}\mathbf{B}^{(l)}(\delta_\lambda)]$$
$$\mathbf{B}^{(l)}(\delta_\lambda) = \frac{\partial \mathbf{Q}(\delta_\lambda)}{\partial \delta_\lambda^{(l)}}\tilde{\mathbf{Q}}(\delta_\lambda) \qquad k, l = 1-6 \tag{4.13}$$

In these expressions, $\mathbf{Q}(\delta_\lambda)$ is the 4 × 4 orthogonal matrix defined by eq 3.8 (such that $\tilde{\mathbf{Q}}(\delta_\lambda)$ rotates $OX_1X_2X_3X_4$ to $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}X_{\lambda_4}$) and the $\mathbf{a}^{(k)}(k = 1-6)$ are 4 × 4 generalizations of the 3 × 3 skew-symmetric Levi-Civita matrices $\epsilon^{(k)}(k = 1-3)$ of eq 4.8:

$$\mathbf{a}^{(1)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \mathbf{a}^{(2)} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$
$$\mathbf{a}^{(3)} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \mathbf{a}^{(4)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$
$$\mathbf{a}^{(5)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad \mathbf{a}^{(6)} = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \tag{4.14}$$

In addition, the $\mathbf{B}^{(l)}(\delta_\lambda)$ are 4 × 4 skew-symmetric matrices given by

$$\mathbf{B}^{(l)}(\delta_\lambda) = \begin{pmatrix} 0 & -B_{21}^{(l)} & B_{13}^{(l)} & B_{14}^{(l)} \\ B_{21}^{(l)} & 0 & -B_{32}^{(l)} & -B_{42}^{(l)} \\ -B_{13}^{(l)} & B_{32}^{(l)} & 0 & B_{34}^{(l)} \\ -B_{14}^{(l)} & B_{42}^{(l)} & -B_{34}^{(l)} & 0 \end{pmatrix} \tag{4.15}$$

The explicit expressions of their matrix elements in terms of the angles $\delta_\lambda^{(l)}$ $(l = 1-6)$ are easily obtained from the second of eq 4.13. The explicit expression of the corresponding $\mathbf{C}(\delta_\lambda)$ matrix in terms of the elements of the $\mathbf{B}^{(l)}(\delta_\lambda)$ matrices is given by

$$\mathbf{C}(\delta_\lambda) = \begin{pmatrix} B_{32}^{(1)} & B_{13}^{(1)} & B_{21}^{(1)} & B_{34}^{(1)} & B_{42}^{(1)} & B_{14}^{(1)} \\ B_{32}^{(2)} & B_{13}^{(2)} & B_{21}^{(2)} & B_{34}^{(2)} & B_{42}^{(2)} & B_{14}^{(2)} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ B_{32}^{(6)} & B_{13}^{(6)} & B_{21}^{(6)} & B_{34}^{(6)} & B_{42}^{(6)} & B_{14}^{(6)} \end{pmatrix} \tag{4.16}$$

Replacing this matrix in eq 4.12 and inverting the resulting expression gives the $\hat{L}_{\lambda_k}$ $(k = 1-6)$ operators in terms of the

Table 1

(i,j)	(1,2)	(2,3)	(3,1)	(2,4)	(4,1)	(4.3)
k	3	1	2	5	6	4

differential operators $\partial/\partial\delta_\lambda^{(l)}$ ($l = 1-6$). The 6 × 6 $\mathbf{C}^{-1}(\delta_\lambda)$ matrix can be calculated analytically, and explicit expressions for $\mathbf{C}(\delta_\lambda)$, $\mathbf{C}^{-1}(\delta_\lambda)$ and $\hat{L}_{\lambda_k}$ ($k = 1-6$) are given in Appendix A. The first three elements of $\hat{L}_{\lambda_k}$ are the same as those for the $N = 4$ case and can also be obtained from the inverse of eq 4.2. The remaining three are somewhat more complicated. However, the explicit expressions for those operators, although now known, are not needed for the derivation of the $N = 5$ ROHC Hamiltonian.

As a consequence of the definition of the $\hat{L}_{\lambda_k}$ ($k = 1-6$) given by eqs 4.12 through 4.14, it can be proven that the generalizations of eqs 4.5 and 4.11 to the $N = 5$ case are valid, namely that

$$\hat{d}_{3_\lambda} = \sum_{l=1}^{6} \mathrm{d}\delta_\lambda^{(l)} \frac{\partial}{\partial\delta_\lambda^{(l)}} = -\frac{\mathrm{i}}{2\hbar}\sum_{i,j=1}^{4}\sum_{l=1}^{6} \mathbf{a}_{ij}^{(l)}[(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}]_{ij}\hat{L}_{\lambda_l} \tag{4.17}$$

and

$$\hat{L}_{\lambda_k}\mathbf{Q} = -\frac{\hbar}{\mathrm{i}}\mathbf{a}^{(k)}\mathbf{Q}(\delta_\lambda) \qquad k = 1-6 \tag{4.18}$$

These two expressions are of importance for the derivation of the $N = 5$ ROHC Hamiltonian and are the justification for that definition of the $\hat{L}_{\lambda_k}$.

It should be noted that eq 4.1 can now be generalized to the 4D space with Cartesian coordinates X_1, X_2, X_3, X_4 by using the elements of $\mathbf{a}^{(k)}$ instead of those of $\epsilon^{(k)}$:

$$\hat{l}_k = \frac{\hbar}{\mathrm{i}}\left(X_i\frac{\partial}{\partial X_j} - X_j\frac{\partial}{\partial X_i}\right) = \frac{\hbar}{\mathrm{i}}\sum_{p,q=1}^{4}\mathbf{a}_{pq}^{(k)}X_p\frac{\partial}{\partial X_q} \tag{4.19}$$

where the correspondence between the k and the i, j pairs is given in Table 1. Thus these $\mathbf{a}^{(k)}$ matrices furnish a simple generalization of the concept of the cross product of two vectors in a 3D space to a 4D space. This generalization can easily be extended to n-dimensional spaces.

5. The Matrix Gradient Operator in ROHC for $N = 5$ Systems

Now that the angular momentum operators for $N = 5$ have been defined and some of its properties obtained, we proceed to derive the corresponding 3 × 4 matrix gradient operator, defined by[11]

$$\nabla_\lambda = \begin{pmatrix} \partial/\partial x_{\lambda_1}^{(1)} & \partial/\partial x_{\lambda_1}^{(2)} & \partial/\partial x_{\lambda_1}^{(3)} & \partial/\partial x_{\lambda_1}^{(4)} \\ \partial/\partial x_{\lambda_2}^{(1)} & \partial/\partial x_{\lambda_2}^{(2)} & \partial/\partial x_{\lambda_2}^{(3)} & \partial/\partial x_{\lambda_2}^{(4)} \\ \partial/\partial x_{\lambda_3}^{(1)} & \partial/\partial x_{\lambda_3}^{(2)} & \partial/\partial x_{\lambda_3}^{(3)} & \partial/\partial x_{\lambda_3}^{(4)} \end{pmatrix} \tag{5.1}$$

in terms of which the system's kinetic energy operator is given by

$$\hat{T}_\lambda = -\frac{\hbar^2}{2\mu}\mathrm{tr}(\nabla_\lambda\tilde{\nabla}_\lambda) \tag{5.2}$$

As shown previously, this operator is independent of the arrangement channel coordinates used to obtain it, that is, is invariant under kinematic rotations.[11] To express ∇_λ in ROHC, we will first consider the differential operator $\hat{d}$ associated with the independent variables of the system, which in Cartesian coordinates is given by

$$\hat{d}_{\mathrm{cart}} = \sum_{i=1}^{3}\sum_{j=1}^{4}\mathrm{d}x_{\lambda_i}^{(j)}\frac{\partial}{\partial x_{\lambda_i}^{(j)}} \tag{5.3}$$

and in ROHC by

$$\hat{d}_{\mathrm{ROHC}} = \hat{d}_{1_\lambda} + \hat{d}_2 + \hat{d}_{3_\lambda} \tag{5.4}$$

where

$$\hat{d}_{1_\lambda} = \mathrm{d}a_\lambda\frac{\partial}{\partial a_\lambda} + \mathrm{d}b_\lambda\frac{\partial}{\partial b_\lambda} + \mathrm{d}c_\lambda\frac{\partial}{\partial c_\lambda} \tag{5.5}$$

$$\hat{d}_2 = \mathrm{d}\rho\frac{\partial}{\partial\rho} + \mathrm{d}\theta_\lambda\frac{\partial}{\partial\theta} + \mathrm{d}\phi\frac{\partial}{\partial\phi} \tag{5.6}$$

with $\hat{d}_{3_\lambda}$ having been defined by eq 4.17. The operator $\hat{d}$ is invariant with respect to the choice of independent variables, that is

$$\hat{d} = \hat{d}_{\mathrm{cart}} = \hat{d}_{\mathrm{ROHC}} \tag{5.7}$$

This expression permits us to obtain the Cartesian derivatives $\partial/\partial x_{\lambda i}^{(j)}$ in terms of the ROHC and hence obtain ∇_λ in terms of these coordinates, as shown in the rest of this section.

5.1. Relation between $\hat{d}_{\mathrm{ROHC}}$ and $\mathbf{R}\mathrm{d}\rho_\lambda^{\mathrm{sf}}\tilde{\mathbf{Q}}$. To implement this approach we first establish a relation between $\hat{d}_{\mathrm{ROHC}}$ and the 3 × 4 matrix $\mathbf{R}\mathrm{d}\rho_\lambda^{\mathrm{sf}}\tilde{\mathbf{Q}}$. To that effect, we take the differential of eq 3.11

$$\mathrm{d}\rho_\lambda^{\mathrm{sf}} = (-1)^\chi[(\mathrm{d}\tilde{\mathbf{R}})(\rho\mathbf{N})\mathbf{PQ} + \tilde{\mathbf{R}}\,\mathrm{d}(\rho\mathbf{N})\mathbf{PQ} + \tilde{\mathbf{R}}\rho\mathbf{N}P\,\mathrm{d}\mathbf{Q}] \tag{5.8}$$

Left-multiplying this expression by $\mathbf{R}$ and right-multiplying it by $\tilde{\mathbf{Q}}$ gives

$$\mathbf{R}(\mathrm{d}\rho_\lambda^{\mathrm{sf}})\tilde{\mathbf{Q}} = (-1)^\chi[\mathbf{R}(\mathrm{d}\tilde{\mathbf{R}})(\rho\mathbf{N})\mathbf{P} + \mathrm{d}(\rho\mathbf{N})\mathbf{P} + (\rho\mathbf{N})\mathbf{P}(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}] \tag{5.9}$$

where $\mathbf{R}\,\mathrm{d}\tilde{\mathbf{R}}$ and $(\mathrm{d}\mathbf{Q})\,\tilde{\mathbf{Q}}$ are skew symmetric because both $\mathbf{R}$ and $\tilde{\mathbf{Q}}$ are orthogonal. The left hand side (lhs) of eq 5.9 as well as the three terms inside the square brackets on its rhs are retangular matrices of dimensions 3 × 4. The diagonal elements of the first and third of these terms are zeros whereas the only nonvanishing elements of $\mathrm{d}(\rho\mathbf{N})\,\mathbf{P}$ are its diagonal ones. Therefore, eq 5.9 can be decomposed into two equations:

$$\mathrm{d}(\rho\mathbf{N})\mathbf{P} = (-1)^{\chi}\mathrm{diag}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}] \quad (5.10)$$

$$\mathbf{R}(\mathrm{d}\tilde{\mathbf{R}})(\rho\mathbf{N})\mathbf{P} + (\rho\mathbf{N})\mathbf{P}(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}} = (-1)^{\chi}\mathrm{off\ diag}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}] \quad (5.11)$$

From eq 5.10, in complete analogy to eq 4.24 of ref 11 (which discusses the $N = 4$ system), we get

$$\hat{d}_{2_\lambda} = (-1)^{\chi}\sum_{i,j=1}^{3}[\mathbf{R}\,\mathrm{d}\rho_{\lambda}^{\mathrm{sf}}\tilde{\mathbf{Q}}]_{ij}\left(N_{ij}\frac{\partial}{\partial\rho} + N'_{\theta_{ij}}\frac{1}{\rho}\frac{\partial}{\partial\theta} + M_{\phi_{ij}}\frac{1}{\rho\sin\theta}\frac{\partial}{\partial\phi}\right) \quad (5.12)$$

where

$$\mathbf{N}'_{\theta}(\theta,\phi) = \frac{\partial\mathbf{N}}{\partial\theta} = \begin{pmatrix}\cos\theta\cos\phi & 0 & 0\\ 0 & \cos\theta\sin\phi & 0\\ 0 & 0 & -\sin\theta\end{pmatrix} \quad (5.13)$$

and

$$\mathbf{M}_{\phi}(\phi) = \frac{1}{\sin\theta}\frac{\partial\mathbf{N}}{\partial\phi} = \begin{pmatrix}-\sin\phi & 0 & 0\\ 0 & \cos\phi & 0\\ 0 & 0 & 0\end{pmatrix} \quad (5.14)$$

Again, in complete analogy to the $N = 4$ case, we have

$$\hat{d}_{1_\lambda} = -\frac{1}{2\hbar}\sum_{i,j,k=1}^{3}\epsilon_{ijk}(\mathbf{R}\,\mathrm{d}\tilde{\mathbf{R}})_{ij}\hat{J}_k^{I\lambda} \quad (5.15)$$

where $\hat{J}_k^{I\lambda}$ are the components of the system's total (orbital) angular momentum $\hat{\mathbf{J}}$ in the principal axes of inertia frame and are given by

$$\hat{\mathbf{J}}^{I\lambda} = \begin{pmatrix}\hat{J}_1^{I_\lambda}\\ \hat{J}_2^{I}\\ \hat{J}_3^{I_\lambda}\end{pmatrix} = \frac{\hbar}{\mathrm{i}}\begin{pmatrix}-\csc b_\lambda\cos c_\lambda & \sin c_\lambda & \cot b_\lambda\cos c_\lambda\\ \csc b_\lambda\sin c_\lambda & \cos c_\lambda & -\cot b_\lambda\sin c_\lambda\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\partial/\partial a_\lambda\\ \partial/\partial b_\lambda\\ \partial/\partial c_\lambda\end{pmatrix} \quad (5.16)$$

From eq 5.11, we can obtain the off-diagonal elements of the skew symmetric square matrices $\mathbf{R}\,\mathrm{d}\tilde{\mathbf{R}}$ and $(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}$. To do so we first consider the i, j elements (with $i \neq j$) and then the j, i (elements) for $(i, j) = (1, 2)$, $(1, 3)$, and $(2,3)$. We get two linear equations for each of these three pairs of indices which when solved yield

$$(\mathbf{R}\,\mathrm{d}\tilde{\mathbf{R}})_{ij} = \frac{(-1)^{\chi}}{\rho(N_{jj}^2 - N_{ii}^2)}\{N_{jj}(\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}})_{ij} + N_{ii}(\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}})_{ji}\} \qquad i \neq j \quad (5.17)$$

and

$$((\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}})_{ij} = -\frac{(-1)^{\chi}}{\rho(N_{jj}^2 - N_{ii}^2)}\{N_{ii}(\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}})_{ij} + N_{jj}(\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}})_{ji}\} \qquad i \neq j \quad (5.18)$$

These expression are analogous to the corresponding $N = 4$ ones.[11] However, we must in addition consider the $(i, j) = (1, 4)$, $(2, 4)$, and $(3,4)$ elements of $\mathbf{Q}\,\mathrm{d}\tilde{\mathbf{Q}}$, which did not exist in the $N = 4$ case. For them, eq 5.11 furnishes

$$[(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}]_{14} = \frac{(-1)^{\chi}}{\rho N_{11}^2}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}]_{14} \quad (5.19)$$

$$[(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}]_{24} = \frac{(-1)^{\chi}}{\rho N_{22}^2}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}]_{24} \quad (5.20)$$

$$[(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}]_{34} = \frac{(-1)^{\chi}}{\rho N_{33}^2}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}]_{34} \quad (5.21)$$

It should be noted that if we had right-multiplied eq 5.8 by the 3×4 matrix $\tilde{\bar{\mathbf{Q}}}$ instead of the 4×4 matrix $\tilde{\mathbf{Q}}$, we would in eq 5.18 have obtained an expression for the off-diagonal elements of the 3×3 matrix $(\mathrm{d}\bar{\mathbf{Q}})\,\tilde{\bar{\mathbf{Q}}}$ instead those for the 4×4 matrix $(\mathrm{d}\mathbf{Q})\,\tilde{\mathbf{Q}}$ and therefore not obtained eqs 5.19 through 5.21 which, as seen in eqs 5.29 and 6.23, are responsible for the appearance of the essential $\hat{L}_{\lambda_k}^{(3)}$ $(k = 4-6)$ operators. Therefore, the use of $\tilde{\mathbf{Q}}$ in lieu of $\tilde{\bar{\mathbf{Q}}}$ was crucial. Equations 5.19 through 5.21 encompass the important change in going from $N = 4$ to $N = 5$.

The expression for $\hat{d}_{3_\lambda}$ in terms of $(\mathrm{d}\mathbf{Q})\tilde{\mathbf{Q}}$ is given by eq 4.17. Replacement of eqs 5.17 through 5.21 in eqs 5.15 and 4.18 now gives $\hat{d}_{1_\lambda}$ and $\hat{d}_{3_\lambda}$ in terms of the 3×4 $\mathbf{R}\,\mathrm{d}\rho_{\lambda}^{\mathrm{sf}}\tilde{\mathbf{Q}}$ matrix, in analogy to eq 5.12 for $\hat{d}_{2_\lambda}$. As a result, replacing eqs 5.12, 5.15, and 5.17 through 5.21 in eq 5.4 we obtain

$$\hat{d}_{\mathrm{ROHC}} = (-1)^{\chi}\sum_{i}^{3}\sum_{j}^{3}[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}]_{ij}\left\{[\mathbf{N}\frac{\partial}{\partial\rho} + \mathbf{N}'_{\theta}\frac{1}{\rho}\frac{\partial}{\partial\theta} + \mathbf{M}_{\phi}\frac{1}{\rho\sin\theta}\frac{\partial}{\partial\phi}]_{ij} + \frac{\mathrm{i}}{\hbar}\sum_{k=1}^{3}\frac{N_{kk}\epsilon_{ijk}}{\rho(N_{jj}^2 - N_{ii}^2)}(N_{jj}\hat{J}_k^{I\lambda} - N_{ii}\hat{L}_{\lambda_k})\right\} - \frac{\mathrm{i}}{\hbar}\sum_{k=4}^{6}\frac{a_{ij}^{(k)}}{N_{ii}}\hat{L}_{\lambda_k} \quad (5.22)$$

The elements of $\mathbf{R}(\mathrm{d}\rho_{\lambda}^{sf})\tilde{\mathbf{Q}}$ can be written explicitly as

$$[\mathbf{R}(\mathrm{d}\rho_{\lambda}^{\mathrm{sf}})\tilde{\mathbf{Q}}]_{ij} = \sum_{m=1}^{3}\sum_{p=1}^{4}R_{im}\,\mathrm{d}x_m^{(p)}Q_{jp} \qquad i = 1-3, \quad j = 1-4 \quad (5.23)$$

Replacing eq 5.23 into eq 5.22 and identifying the coefficients of the Cartesian differentials in the resulting expression with those in eq 5.3 yields the elements of the matrix gradient operator ∇_λ defined by eq 5.1. The final result can be expressed as

$$\nabla_\lambda = (-1)^\chi[\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ} + \hat{\mathbf{U}}_\lambda] \quad (5.24)$$

where

$$\hat{\mathbf{A}} = \mathbf{N}\frac{\partial}{\partial\rho} + \mathbf{N}'_\theta\frac{1}{\rho}\frac{\partial}{\partial\theta} + \mathbf{M}_\phi\frac{1}{\rho\sin\theta}\frac{\partial}{\partial\phi} \quad (5.25)$$

is a 3 × 3 diagonal matrix operator which depends on the principal angles of inertia θ, ϕ and is the same as the one for the $N = 4$ case and $\hat{\mathbf{U}}_\lambda$ is a 3 × 4 matrix operator defined by

$$\hat{\mathbf{U}}_\lambda = \hat{\mathbf{F}}_\lambda - \hat{G}_\lambda^{(1)} + \hat{\mathbf{G}}_\lambda^{(2)} \quad (5.26)$$

where

$$(\hat{\mathbf{F}}_\lambda)_{ij} = -\frac{\mathrm{i}}{\hbar\rho}\sum_{m,p=1}^{3}\frac{R_{mi}Q_{pj}N_{pp}}{N_{pp}^2 - N_{mm}^2}\sum_{k=1}^{3}(\epsilon^{(k)}\mathbf{P})_{mp}\hat{J}_k^{I\lambda} \quad (5.27)$$

$$(\hat{\mathbf{G}}_\lambda^{(1)})_{ij} = -\frac{\mathrm{i}}{\hbar\rho}\sum_{m,p=1}^{3}\frac{R_{mi}Q_{pj}N_{mm}}{N_{pp}^2 - N_{mm}^2}\sum_{k=1}^{3}(\epsilon^{(k)}\mathbf{P})_{mp}\hat{L}_{\lambda_k} \quad (5.28)$$

$$(\hat{\mathbf{G}}_\lambda^{(2)})_{ij} = -\frac{\mathrm{i}}{\hbar\rho}\sum_{m=1}^{3}\sum_{p=1}^{4}\frac{R_{mi}Q_{pj}}{N_{mm}}\sum_{k=4}^{6}a_{mp}^{(k)}\hat{L}_{\lambda_k} \quad (5.29)$$

and $i = 1-3$, $j = 1-4$. These 3 × 4 pentaatomic $\hat{\mathbf{F}}_\lambda$ and $\hat{\mathbf{G}}_\lambda^{(1)}$ matrix operators are related to the corresponding tetraatomic 3 × 3 matrix operators by replacement in the latter the 3 × 3 $\mathbf{Q}^{(3)}$ matrix of eq 3.3 by the 4 × 4 $\mathbf{Q}$ matrix of eq 3.7, and by the introduction of the 3 × 4 matrix $\mathbf{P}$. In addition, however, the $N = 5$ ∇_λ contains the $\hat{\mathbf{G}}_\lambda^{(2)}$ matrix operator, which is absent in the $N = 4$ ∇_λ, and which incorporates the three additional internal angular momentum operators $\hat{L}_{\lambda_4}$, $\hat{L}_{\lambda_5}$, and $\hat{L}_{\lambda_6}$. All of the quantities in the rhs of eq 5.24 are given in terms of the ROHC, as desired. The approach developed in this section for obtaining ∇_λ for $N = 5$ has avoided the much more extensive algebra that would have been involved in using the chain rule together with eqs 2.1 and 2.2 to express the partial derivatives with respect to the Cartesian coordinates and inverting the resulting equations. The present approach is, in addition, generalizable to $N > 5$ systems.

6. The $N = 5$ Hamiltonain in ROHC

The Hamiltonain of the $N = 5$ system is given in terms of the kinetic energy operator $\hat{T}$ and potential energy function V by

$$\hat{H} = \hat{T} + V \quad (6.1)$$

where V is independent of the chirality χ and of the Euler angles a_λ, that is

$$V = V_\lambda(\rho, \theta, \phi, \delta_\lambda) \quad (6.2)$$

With the help of eqs 5.2 and 5.24 $\hat{T}$ can be written as

$$\hat{T} = -\frac{\hbar^2}{2\mu}\mathrm{tr}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ} + \hat{\mathbf{U}}_\lambda)^2 \quad (6.3)$$

As for the $N = 4$ case,[11] we express it as

$$\hat{T} = \sum_{a=1}^{4}\hat{T}_{\lambda_a} \quad (6.4)$$

where

$$\hat{T}_{\lambda_1} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j=1}^{4}[(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ})_{ij}]^2 \quad (6.5)$$

$$\hat{T}_{\lambda_2} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j=1}^{4}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ})_{ij}(\hat{\mathbf{U}}_\lambda)_{ij} \quad (6.6)$$

$$\hat{T}_{\lambda_3} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j=1}^{4}\hat{\mathbf{U}}_{\lambda_{ij}}(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ})_{ij} \quad (6.7)$$

$$\hat{T}_{\lambda_4} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j=1}^{4}[(\hat{\mathbf{U}}_\lambda)_{ij}]^2 \quad (6.8)$$

To evaluate the $\hat{T}_{\lambda_a}$ we use,

$$(\tilde{\mathbf{R}}\hat{\mathbf{A}}\mathbf{PQ})_{ij} = \sum_{m=1}^{3}\sum_{p=1}^{4}(\tilde{\mathbf{R}})_{im}(\hat{\mathbf{A}}\mathbf{P})_{mp}(\mathbf{Q})_{pj} \quad (6.9)$$

Since $\hat{\mathbf{A}}\mathbf{P}$ acts on ρ, θ and ϕ, whereas $\mathbf{R}(a_\lambda)$ and $\mathbf{Q}(\delta_\lambda)$ do not depend on these variables, we can change the order of $(\tilde{\mathbf{R}})_{im}$ and $(\hat{\mathbf{A}}\mathbf{P})_{mp}$ in this expression. Using this property as well as the diagonal nature of $\hat{\mathbf{A}}$ and $\mathbf{P}$ and the orthogonality of $\mathbf{R}$ and $\mathbf{P}$, we get from eqs 6.9 and 6.5

$$\hat{T}_{\lambda_1} = -\frac{\hbar^2}{2\mu}\mathrm{tr}\hat{\mathbf{A}}^2 = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\rho^2\frac{\partial}{\partial\rho} + \frac{\hat{K}^2}{2\mu\rho^2} \quad (6.10)$$

where

$$\hat{K}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \quad (6.11)$$

is an effective hyperangular momentum operator associated with the principal moments of inertia hyperangles θ and ϕ. Equations 6.10 and 6.11 are the same as the corresponding $N = 4$ expressions.[11] Similarly, performing the operations indicated in eq 6.6 and using eqs 5.26 through 5.29, we get

$$\hat{T}_{\lambda_2} = 0 \quad (6.12)$$

which is also the same result as for $N = 4$. The evaluation of $\hat{T}_{\lambda_3}$ given by eq 6.7 requires the use of the $\hat{J}^{I\lambda}$ counterpart of eq 4.11, namely[11]

$$\hat{J}_k^{I\lambda}\mathbf{R}(a_\lambda) = \frac{\hbar}{i}\epsilon^{(k)}\mathbf{R}(a_\lambda) \qquad k = 1-3 \tag{6.13}$$

as well as eq 4.18. After some extensive but otherwise straightforward algebra, we obtain the result

$$\hat{T}_{\lambda_3} = -\frac{\hbar^2}{\mu\rho}\sum_{i=1}^{3}\left[\frac{1}{2N_{ii}} + \sum_{j,k=1}^{3}\frac{\epsilon_{ijk}^2}{N_{ii}^2 - N_{jj}^2}\right]\hat{A}_{ii} \tag{6.14}$$

This is a relatively simple expression that differs from its $N = 4$ counterpart by the appearance of the $1/(2N_{ii})$ term in its rhs, which originated from the $\hat{L}_{\lambda_k}$ ($k = 4-6$) operators in eq 4.18. Finally, we use eq 6.8 to obtain $\hat{T}_{\lambda_4}$. This involves even more algebra but eventually furnishes

$$\hat{T}_{\lambda_4} = \frac{1}{2\mu\rho^2}\left\{\sum_{i,j,k=1}^{3}\left[\frac{\epsilon_{ijk}}{N_{jj}^2 - N_{ii}^2}(N_{jj}\hat{J}_k^{I\lambda} - N_{ii}\hat{L}_{\lambda_k})\right]^2 + \frac{1}{N_{33}^2}\hat{L}_{\lambda_4}^2 + \frac{1}{N_{22}^2}\hat{L}_{\lambda_5}^2 + \frac{1}{N_{11}^2}\hat{L}_{\lambda_6}^2\right\} \tag{6.15}$$

This expression differs from the corresponding $N = 4$ equation by the appearance the $\hat{L}_{\lambda_k}^2$ ($k = 4-6$) terms.

Replacement of eqs 6.10, 6.12, 6.14, and 6.15 in eq 6.4 gives the desired kinetic energy operator $\hat{T}$

$$\hat{T} = \hat{T}_\rho(\rho) + \frac{1}{2\mu\rho^2}\hat{\wedge}^2(a_\lambda, \theta, \phi, \delta_\lambda) \tag{6.16}$$

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

$$\hat{T}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^{11}}\frac{\partial}{\partial\rho}\rho^{11}\frac{\partial}{\partial\rho} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{11}{\rho}\frac{\partial}{\partial\rho}\right) \tag{6.17}$$

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

$$\hat{\wedge}^2 = \hat{K}^2(\theta,\phi) + \hat{B}(\theta,\phi) + \hat{C}^2(a_\lambda, \delta_\lambda;\theta,\phi) \tag{6.18}$$

with $\hat{K}^2$ given by eq 6.11 and $\hat{B}(\theta,\phi)$ and $\hat{C}^2(\theta,\phi)$ are defined by

$$\hat{B}(\theta,\phi) = -\hbar^2\left\{[c_\theta(\theta) + 2b_\theta(\theta,\phi)]\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}[c_\phi(\theta,\phi) + 2b_\phi(\theta,\phi)]\frac{\partial}{\partial\phi}\right\} \tag{6.19}$$

where

$$b_\theta(\theta,\phi) = \frac{N_{22}N'_{\theta_{22}} - N_{11}N'_{\theta_{11}}}{N_{22}^2 - N_{11}^2} + \frac{N_{33}N'_{\theta_{33}} - N_{22}N'_{\theta_{22}}}{N_{33}^2 - N_{22}^2} + \frac{N_{11}N'_{\theta_{11}} - N_{33}N'_{\theta_{33}}}{N_{11}^2 - N_{33}^2} \tag{6.20}$$

$$b_\phi(\theta,\phi) = \frac{N_{22}M_{\phi_{22}} - N_{11}M_{\phi_{11}}}{N_{22}^2 - N_{11}^2} - \frac{N_{22}M_{\phi_{22}}}{N_{33}^2 - N_{22}^2} + \frac{N_{11}M_{\phi_{11}}}{N_{11}^2 - N_{33}^2} \tag{6.21}$$

$$c_\theta(\theta) = 2\cot\theta - \tan\theta$$
$$c_\phi(\theta,\phi) = \frac{1}{\sin\theta}(\cot\phi - \tan\phi) \tag{6.22}$$

The b_θ and b_ϕ are the same as those for $N = 4$. However, eq 6.19 contains two new coefficients, c_θ and c_ϕ which did not appear in the $\hat{B}(\theta,\phi)$ operator for $N = 4$. The $\hat{C}^2$ operator is given by

$$\hat{C}^2(a_\lambda, \delta_\lambda;\theta,\phi) = \frac{(N_{22}J_3^{I\lambda} - N_{11}\hat{L}_{\lambda_3})^2 + (N_{11}J_3^{I\lambda} - N_{22}\hat{L}_{\lambda_3})^2}{(N_{22}^2 - N_{11}^2)^2} + \frac{(N_{33}\hat{J}_1^{I\lambda} - N_{22}\hat{L}_{\lambda_1})^2 + (N_{22}\hat{J}_1^{I\lambda} - N_{33}\hat{L}_{\lambda_1})^2}{(N_{33}^2 - N_{22}^2)^2} + \frac{(N_{11}\hat{J}_2^{I\lambda} - N_{33}\hat{L}_{\lambda_2})^2 + (N_{33}\hat{J}_2^{I\lambda} - N_{11}\hat{L}_{\lambda_2})^2}{(N_{11}^2 - N_{33}^2)^2} + \frac{1}{N_{33}^2}\hat{L}_{\lambda_4}^2 + \frac{1}{N_{22}^2}\hat{L}_{\lambda_5}^2 + \frac{1}{N_{11}^2}\hat{L}_{\lambda_6}^2 \tag{6.23}$$

The first three terms in eq 6.23 are the same as for the $N = 4$ $\hat{C}^2$, but in addition we have for $N = 5$ the three $\hat{L}_\lambda^2$ ($k = 4-6$) terms. The N_{ii}, $N'_{\theta_{ii}}$ and $M_{\phi_{ii}}$ in eqs 6.20, 6.21, and 6.23 are the diagonal elements of the 3×3 matrices $\mathbf{N}$, $\mathbf{N}'_\theta$ and $\mathbf{M}_\phi$ defined by eqs 2.6, 5.13, and 5.14, respectively.

The expressions for the $N = 4$ and $N = 5$ kinetic energy operator in ROHC are very similar. Their differences are:

(1) The exponent 11 in eq 6.17 is 8 for $N = 4$.

(2) The coefficients c_θ and c_ϕ are absent for $N = 4$.

(3) The terms in $\hat{L}_{\lambda_k}^2$ ($k = 4-6$) are absent for $N = 4$.

This similarity suggests that the $\hat{T}$ operators for $N > 5$ will be analogous to the one for $N = 5$.

The volume element for the $N = 5$ ROHC can be obtained using the methodology described for the $N = 4$ case.[11] The calculation is lengthy but straightforward and the result is

$$d\tau = \sin b_\lambda\, da_\lambda db_\lambda\, dc_\lambda\rho^{11}\, d\rho f(\theta,\phi)\sin\theta\, d\theta\, d\phi \times \sin\delta_\lambda^{(2)}\, d\delta_\lambda^{(1)}\, d\delta_\lambda^{(2)}\, d\delta_\lambda^{(3)}\cos^2\delta_\lambda^{(4)}|\cos\delta_\lambda^{(5)}|d\delta_\lambda^{(4)}\, d\delta_\lambda^{(5)}\, d\delta_\lambda^{(6)} \tag{6.24}$$

where

$$f(\theta,\phi) = \frac{1}{4}\sin^4\theta\cos\theta\sin 4\phi(\cos^2\theta - \sin^2\theta\sin^2\phi) \times (\cos^2\theta - \sin^2\theta\cos^2\phi) \tag{6.25}$$

7. Invariance Properties under Arrangement Channel Transformations

For a given configuration of a system of N particles we can define many sets of $N - 1$ mass-scaled Jacobi vectors connecting them. If λ and μ denote any two such sets, called clustering schemes, the corresponding Jacobi matrices are related by[9-11]

$$\rho_\nu^{sf} = \rho_\lambda^{sf}\mathbf{N}_{\lambda\nu} \tag{7.1}$$

where $\mathbf{N}_{\lambda\nu}$ is an $(N - 1)$-dimensional orthogonal square matrix whose elements depend only on the masses of the particles and the definitions of the Jacobi vectors $r_\lambda^{(j)}$ and $r_\nu^{(j)}$ ($j = 1,...,(N - 1)$). As a result of the orthogonality of $\mathbf{N}_{\lambda\nu}$, the $\lambda \to \nu$ mass-scaled Jacobi arrangement channel transformation is called a kinematic rotations.[24,25] Without loss of generality, we can restrict ourselves to kinematic rotations which are proper, that is, for which the determinant of $\mathbf{N}_{\lambda\nu}$ is 1. The reason is that if it is -1, by changing the sense of any one the $r_\nu^{(j)}$ it becomes 1.

We have previously shown for arbitrary $N \geq 4^{11}$, that ρ, θ, and ϕ are kinematic-rotation invariant. We have also shown, for $N = 4$, that each of the nine terms that contribute to the kinetic energy operator in ROHC are kinematic-rotation invariant (as is V). This is a very useful property for reactive scattering calculations. We now wish to show that an analogous property is valid for the 12 terms that contribute to $\hat{T}$ for the $N = 5$ case.

7.1. Transformation Properties of the Orbital Angular Momentum Operators. We know that for an arbitrary $N \geqslant 3$, the directions of the principal axes of inertia of the system are determined by the positions of the N particles only, and are invariant under kinematic rotations. Therefore, the directions of the corresponding axes of the frame $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ (introduced after eq 2.2) and of its ν counterpart $Gx^{I\nu}y^{I\nu}z^{I\nu}$ must be the same. In addition, both of these frames have, by definition, the same right-handness as the space-fixed frame $Gxyz$. As a result, either none or two of the senses of the $I\nu$ axes can differ from those of the corresponding $I\lambda$ ones. As a result, we must have

$$\mathbf{R}(\mathrm{a}_\nu) = \mathbf{I}^{(3)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}\mathbf{R}(\mathrm{a}_\lambda) \tag{7.2}$$

where

$$\mathbf{I}^{(3)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}} = \begin{pmatrix} (-1)^{n^{(1)}_{\lambda\nu}} & 0 & 0 \\ 0 & (-1)^{n^{(1)}_{\lambda\nu}+n^{(3)}_{\lambda\nu}} & 0 \\ 0 & 0 & (-1)^{n^{(3)}_{\lambda\nu}} \end{pmatrix} \tag{7.3}$$

is a 3×3 diagonal matrix in which $n^{(1)}_{\lambda\nu}$ and $n^{(3)}_{\lambda\nu}$ are each equal to 0 or 1. The matrix $\mathbf{I}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}$ rotates the $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ frame to $Gx^{I\nu}y^{I\nu}z^{I\nu}$ one. Consequently, the system's orbital angular momentum operator in the first of these is related to that in the second by

$$\hat{\mathbf{J}}^{I\nu} = \mathbf{I}^{(3)}_{n^{(1)}_{\lambda\nu}n^{(2)}_{\lambda\nu}}\hat{\mathbf{J}}^{I\lambda} \tag{7.4}$$

where $\hat{\mathbf{J}}^{I\lambda}$ was defined by eq 5.16, and a similar expression is valid for $\hat{\mathbf{J}}^{I\nu}$. Equation 7.4 gives the desired behavior of $\hat{\mathbf{J}}^{I\lambda}$ under kinematic rotations.

7.2. Transformation Properties of the Internal Angular Momentum Operator. To get the transformation properties of the $\hat{L}_{\lambda_k}(k = 1-6)$ defined by eq 4.12), we replace eq 3.11 and its ν counterpart in eq 7.1 and cancel the common terms on both sides

$$\tilde{\mathbf{R}}(\mathrm{a}_\nu)\mathbf{N}(\theta,\phi)\mathbf{P}\mathbf{Q}(\delta_\nu) = \tilde{\mathbf{R}}(\mathrm{a}_\lambda)\mathbf{N}(\theta,\phi)\mathbf{P}\mathbf{Q}(\delta_\lambda)\mathbf{N}_{\lambda\nu} \tag{7.5}$$

With the help of eq 7.2 and the proper orthogonality of $\mathbf{Q}(\delta_\lambda)$ and $\mathbf{Q}(\delta_\nu)$, we get

$$\mathbf{Q}_\nu(\delta_\nu) = \mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}\mathbf{Q}(\delta_\lambda)\mathbf{N}_{\lambda\nu} \tag{7.6}$$

where $\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}$ is the 4×4 diagonal matrix

$$\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}} = \begin{pmatrix} (-1)^{n^{(1)}_{\lambda\nu}} & 0 & 0 & 0 \\ 0 & (-1)^{n^{(1)}_{\lambda\nu}+n^{(3)}_{\lambda\nu}} & 0 & 0 \\ 0 & 0 & (-1)^{n^{(3)}_{\lambda\nu}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{7.7}$$

From eq 7.6, we obtain, using the orthogonality of $\mathbf{N}_{\lambda\nu}$

$$\mathrm{d}\mathbf{Q}(\delta_\nu)\tilde{\mathbf{Q}}(\delta_\nu) = \mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}\mathrm{d}\mathbf{Q}(\delta_\lambda)\tilde{\mathbf{Q}}(\delta_\lambda)\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}} \tag{7.8}$$

This indicates that the 4×4 skew-symmetric matrix $\mathrm{d}\mathbf{Q}(\delta_\lambda)\tilde{\mathbf{Q}}(\delta_\lambda)$ transforms as a tensor under the $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}X_{\lambda_4} \to OX_{\nu_1}X_{\nu_2}X_{\nu_3}X_{\nu_4}$ rotation, as discussed for the tensor $\mathscr{L}_\lambda(\delta_\lambda)$ of 7.23. On the other hand,

$$\mathrm{d}\mathbf{Q}(\delta_\lambda)\tilde{\mathbf{Q}}(\delta_\lambda) = \left[\sum_{l=1}^{6}\frac{\partial\mathbf{Q}(\delta_\lambda)}{\partial\delta_\lambda^{(l)}}\mathrm{d}\delta_\lambda^{(l)}\right]\tilde{\mathbf{Q}}(\delta_\lambda) = \sum_{l=1}^{6}\mathbf{B}^{(l)}(\delta_\lambda)\mathrm{d}\delta_\lambda^{(l)} \tag{7.9}$$

where $\mathbf{B}^{(l)}(\delta_\lambda)$ is the 4×4 skew-symmetric matrix defined by eqs 4.13 and 4.15, a similar expression being valid for the ν counterpart of eq 7.9:

$$\mathrm{d}\mathbf{Q}(\delta_\nu)\tilde{\mathbf{Q}}(\delta_\nu) = \sum_{l'=1}^{6}\mathbf{B}^{(l')}(\delta_\nu)\mathrm{d}\delta_\nu^{(l')} \tag{7.10}$$

Replacement of the last two expression in 7.8 furnishes

$$\sum_{l'=1}^{6}\mathbf{B}^{(l')}(\delta_\nu)\mathrm{d}\delta_\nu^{(l')} = \sum_{l=1}^{6}\bar{\mathbf{B}}^{(l)}(\delta_\lambda)\mathrm{d}\delta_\lambda^{(l)} \tag{7.11}$$

where

$$\bar{\mathbf{B}}^{(l)}(\delta_\lambda) = \mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}\mathbf{B}^{(l)}(\delta_\lambda)\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}} \qquad l = 1 - 6 \tag{7.12}$$

From eq 7.12, we get the following relation between six independent elements of the skew-symmetric 4×4 matrices $\bar{\mathbf{B}}^{(l)}(\delta_\lambda)$ and $\mathbf{B}^{(l)}(\delta_\lambda)$:

$$\begin{aligned}&\bar{B}_{32}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(1)}} B_{32}^{(l)}(\delta_\lambda) \qquad \bar{B}_{13}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}} B_{13}^{(l)}(\delta_\lambda)\\&\bar{B}_{21}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(3)}} B_{21}^{(l)}(\delta_\lambda) \qquad \bar{B}_{34}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(3)}} B_{34}^{(l)}(\delta_\lambda)\\&\bar{B}_{42}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}} B_{42}^{(l)}(\delta_\lambda) \quad \bar{B}_{14}^{(l)}(\delta_\lambda) = (-1)^{n_{\lambda\nu}^{(1)}} B_{14}^{(l)}(\delta_\lambda) \qquad l = 1-6\end{aligned} \tag{7.13}$$

These can be rewritten as

$$(\bar{\mathrm{B}}_{32}^{(l)}\ \ \bar{\mathrm{B}}_{13}^{(l)}\ \ \bar{\mathrm{B}}_{21}^{(l)}\ \ \bar{\mathrm{B}}_{34}^{(l)}\ \ \bar{\mathrm{B}}_{42}^{(l)}\ \ \bar{\mathrm{B}}_{14}^{(l)}) = (B_{32}^{(l)}\ \ B_{13}^{(l)}\ \ B_{21}^{(l)}\ \ B_{34}^{(l)}\ \ B_{42}^{(l)}\ \ B_{14}^{(l)})\mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}} \tag{7.14}$$

where $\mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}}$ is the 6 × 6 diagonal matrix defined by

$$\mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}} = \begin{pmatrix} (-1)^{n_{\lambda\nu}^{(1)}} & 0 & 0 & 0 & 0 & 0\\ 0 & (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}} & 0 & 0 & 0 & 0\\ 0 & 0 & (-1)^{n_{\lambda\nu}^{(3)}} & 0 & 0 & 0\\ 0 & 0 & 0 & (-1)^{n_{\lambda\nu}^{(3)}} & 0 & 0\\ 0 & 0 & 0 & 0 & (-1)^{n_{\lambda\nu}^{(1)}+n_{\lambda\nu}^{(3)}} & 0\\ 0 & 0 & 0 & 1 & 0 & (-1)^{n_{\lambda\nu}^{(1)}} \end{pmatrix} \tag{7.15}$$

Both sides of eq 7.11 are 4 × 4 skew-symmetric matrices, each having only six nonvanishing independent elements. As a result, it furnishes six independent scalar equations. Defining $\mathrm{d}\delta_\lambda$ and $\mathrm{d}\delta_\nu$ as the 6 × 1 column vectors whose elements are the $\mathrm{d}\delta_\lambda^{(l)}$ and $\mathrm{d}\delta_\nu^{(l)}$, respectively, and picking for the elements of the independent scalar equations the ones used in the rhs of eq 7.13, those equations can be written in matrix form as

$$\tilde{\mathbf{C}}(\delta_\nu)\mathrm{d}\delta_\nu = \mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}}\tilde{\mathbf{C}}(\delta_\lambda)\mathrm{d}\delta_\lambda \tag{7.16}$$

where $\mathbf{C}(\delta_\lambda)$ is the 6 × 6 matrix given by eq 4.16 and $\mathbf{C}(\delta_\nu)$ is its ν counterpart. Whereas eq 7.16 involves only 2 6 × 6 **C** matrices, eq 7.11 involves 12 4 × 4 **B** matrices. This compacting was made possible by the skew-symmetry of the **B** and greatly simplifies the algebra. We now use the relation

$$\mathrm{d}\delta_\nu = \frac{\partial\delta_\nu}{\partial\delta_\lambda}\mathrm{d}\delta_\lambda \tag{7.17}$$

where $\partial\delta_\nu/\partial\delta_\lambda$ is the Jacobian matrix of the $\delta_\nu \to \delta_\lambda$ transformation whose l, k element is $\partial\delta_\nu^{(k)}/\partial\delta_\lambda^{(l)}$ (l, k = 1−6). Left-multiplying eq 7.16 by $\tilde{\mathbf{C}}^{-1}(\delta_\nu)$ and identifying the result with eq 7.17 gives the following expression for that Jacobian:

$$\frac{\partial\delta_\nu}{\partial\delta_\lambda} = [\tilde{\mathbf{C}}(\delta_\nu)]^{-1}\mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}}\tilde{\mathbf{C}}(\delta_\lambda) \tag{7.18}$$

On the other hand we know that

$$\frac{\partial}{\partial\delta_\lambda} = \left(\frac{\partial\delta_\nu}{\partial\delta_\lambda}\right)^T\frac{\partial}{\partial\delta_\nu} \tag{7.19}$$

where $\partial/\partial\delta_\lambda$ is the column vector defined in eq 4.12, $\partial/\partial\delta_\nu$ is its ν counterpart, and $(\partial\delta_\nu/\partial\delta_\lambda)^T$ is the transpose of the Jacobian matrix. Replacing eq 7.18 in eq 7.19 and using eq 4.12 and its ν counterpart leads fairly directly to

$$\hat{\mathbf{L}}_\nu(\delta_\nu) = \mathbf{I}^{(6)}_{n_{\lambda\nu}^{(1)}n_{\lambda\nu}^{(3)}}\hat{\mathbf{L}}_\lambda(\delta_\lambda) \tag{7.20}$$

This is the desired transformation of the $\hat{L}_{\lambda_k}$ ($k = 1-6$) operators under kinematic rotations. More explicitly, it shows that

$$\hat{L}_{\nu_1} = (-1)^{n^{(1)}_{\lambda\nu}}\hat{L}_{\lambda_1} \qquad \hat{L}_{\nu_2} = (-1)^{n^{(1)}_{\lambda\nu}+n^{(3)}_{\lambda\nu}}\hat{L}_{\lambda_2} \qquad \hat{L}_{\nu_3} = (-1)^{n^{(1)}_{\lambda\nu}+n^{(3)}_{\lambda\nu}}\hat{L}_{\lambda_3} \qquad \hat{L}_{\nu_4} = (-1)^{n^{(3)}_{\lambda\nu}}\hat{L}_{\lambda_4}$$
$$\hat{L}_{\nu_5} = (-1)^{n^{(1)}_{\lambda\nu}+n^{(3)}_{\lambda\nu}}\hat{L}_{\lambda_5} \qquad \hat{L}_{\nu_6} = (-1)^{n^{(1)}_{\lambda\nu}}\hat{L}_{\lambda_6} \quad (7.21)$$

The first three of these expression are the same as those for the corresponding $\hat{J}_{\lambda_k}$ ($k = 1-3$), as seen from eqs 7.4 and 7.3. Equation 7.21 can be put in the tensor transformation form

$$\mathscr{L}_\nu(\delta_\nu) = \mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}\mathscr{L}_\lambda(\delta_\lambda)\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}} \quad (7.22)$$

where $\hat{\mathscr{L}}_\lambda$ is a skew-symmetric tensor operator of order 2 given by

$$\hat{\mathscr{L}}_\lambda(\delta_\lambda) = \begin{pmatrix} 0 & \hat{L}_{\lambda_3} & -\hat{L}_{\lambda_2} & -\hat{L}_{\lambda_6} \\ -\hat{L}_{\lambda_3} & 0 & \hat{L}_{\lambda_1} & \hat{L}_{\lambda_5} \\ \hat{L}_{\lambda_2} & -\hat{L}_{\lambda_1} & 0 & -\hat{L}_{\lambda_4} \\ \hat{L}_{\lambda_6} & -\hat{L}_{\lambda_5} & \hat{L}_{\lambda_4} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \hat{L}^{(1,2)}_\lambda & \hat{L}^{(1,3)}_\lambda & \hat{L}^{(1,4)}_\lambda \\ \hat{L}^{(2,1)}_\lambda & 0 & \hat{L}^{(2,3)}_\lambda & \hat{L}^{(2,4)}_\lambda \\ \hat{L}^{(3,1)}_\lambda & \hat{L}^{(3,2)}_\lambda & 0 & \hat{L}^{(3,4)}_\lambda \\ \hat{L}^{(4,1)}_\lambda & \hat{L}^{(4,2)}_\lambda & \hat{L}^{(4,3)}_\lambda & 0 \end{pmatrix} \quad (7.23)$$

with a similar expression being valid for the ν operators. The correspondence between the k and (i, j) in the $\hat{L}_{\lambda_k}$ and $\hat{L}^{(i,j)}_\lambda$ operators, (and in their ν counterparts) is given in Table 1. This transformation is the same as that for the quantity $d\mathbf{Q}(\delta_\lambda)\tilde{\mathbf{Q}}(\delta_\lambda)$ given by eq 7.8. Equation 7.22 indicates that the relation between the $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}X_{\lambda_4}$ and $OX_{\nu_1}X_{\nu_2}X_{\nu_3}X_{\nu_4}$ frames is, in either direction, a rotation described by the diagonal $\mathbf{I}^{(4)}_{n^{(1)}_{\lambda\nu}n^{(3)}_{\lambda\nu}}$ matrix, defined by eq 7.7, that is, the directions of the corresponding axes are the same, and the senses of the OX_{λ_4} and OX_{ν_4} axes are also the same. The senses of the remaining sets of three axes are either the same or pairwise opposite, as is the case for principal axes of inertia $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ and $Gx^{I\nu}y^{I\nu}z^{I\nu}$. It should be emphasized that the $\hat{L}^{(i,j)}_\lambda$ are the elements of the $\hat{\mathscr{L}}$ tensor in the $OX_1X_2X_3X_4$ frame rather than in the $OX_{\lambda_1}X_{\lambda_2}X_{\lambda_3}X_{\lambda_4}$ frame, that is, are space-fixed components in the 4D mathematical space, a similar statement being valid for the ν operators. This was also the case for $N = 4$ systems.[11]

7.3. Transformaton Properties of the Hamiltonian. As a result of eqs 7.4 and 7.21, we see that the operators $N_{jj}\hat{J}^{I\lambda}_k - N_{ii}\hat{L}_{\lambda_k}$ ($k = 1-3$), which appear in eq 6.23, can change sign under kinematic rotations but that their squares, 6 of which contribute to $\hat{\mathbf{C}}^2$, are kinematic- rotation invariant. The same is true for $\hat{L}^2_{\lambda_4}$, $\hat{L}^2_{\lambda_5}$, $\hat{L}^2_{\lambda_6}$, $\hat{T}_\rho(\rho)$, $\hat{K}^2$, and $\hat{B}$. Therefore, not only is $\hat{T}$ invariant under such transformations, but also each of the twelve contributing operators have this property, as posited just before Section 7.1. In addition, since ρ, θ, ϕ, δ_λ and ρ, θ, ϕ, δ_ν represent the same internal configuration of the pentaatomic system, we have

$$V_\lambda(\rho, \theta, \phi, \delta_\lambda) = V_\nu(\rho, \theta, \phi, \delta_\nu) = V \quad (7.24)$$

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 ROHC, is very convenient for both analytical and computational purposes. This justifies the designation of these coordinates as "democratic".

8. Summary and Conclusions

We have used in this paper a set of row-orthonormal hyperspherical coordinates (ROHC) for pentaatomic systems to derive the corresponding nuclear motion Hamiltonian. In the process, we developed a new mathematical methodology involving internal angular momentum operators and the corresponding tensor in a four-dimensional mathematical space. Every contributing term in that Hamiltonian is invariant under kinematic rotations, that is, under changes of the arrangement channel Jacobi vectors used in its derivation. This justifies calling these ROHC democratic. A single set of these coordinates permits the inclusion of all rearrangment collision processes in the crucial strong interaction regions of configuration space, eliminating supercompleteness problems. In the weak ineraction region of configuration space, other nondemocratic hyperspherical coordinates should be used to describe the nonreactive processes that occur in each separate arrangement channel. Attempts can now be made to use this approach to perform reactive scattering calculations for select systems, chosen to minimize the computational effort, using presently available high-performance computers.

The mathematical methodology used to derive the pentaatomic ROHC Hamiltonian is generalizable to an arbitrary number of atoms. The ROHC formalism can serve as a starting point for introducing approximations which preserve the important local feature characteristics of many polyatomic reactions.

Acknowledgment. The work described in refs 1 and 2 was part of George Schatz's Ph.D. thesis research. He was an extremely brilliant graduate student. The work in the present paper is an evolution of that early research. The present work was supported in part by NSF Grant CHE-138091. The author wishes to thank Dr. Desheng Wang for his expert help in preparing this manuscript.

Appendix A. Explicit expressions for $C(\delta_\lambda)$ and $L_\lambda(\delta_\lambda)$

Let us write the $\mathbf{C}(\delta_\lambda)$ 6 × 6 matrix defined by eq 4.12 in the form

$$\mathbf{C}(\delta_\lambda) = \begin{pmatrix} \mathbf{C}^{11}(\delta_\lambda) & \mathbf{C}^{12}(\delta_\lambda) \\ \mathbf{C}^{21}(\delta_\lambda) & \mathbf{C}^{22}(\delta_\lambda) \end{pmatrix} \tag{A.1}$$

where the $\mathbf{C}^{ij}(\delta_\lambda)$ $(i, j = 1, 2)$ are 3 × 3 matrices. With the help of eqs 4.16, 4.13, 3.8, and 3.6 we obtain in a straightforward manner the following explicit expressions for these matrices:

$$\mathbf{C}^{11}(\delta_\lambda) = \mathbf{C}^{(3)}(\delta_\lambda^1\delta_\lambda^2\delta_\lambda^3) \tag{A.2}$$

$$\mathbf{C}^{12}(\delta_\lambda) = 0 \tag{A.3}$$

$$\mathbf{C}^{21}(\delta_\lambda) = \begin{pmatrix} 0 & 0 & 0 \\ R_{11}\sin\delta_\lambda^{(4)} & R_{12}\sin\delta_\lambda^{(4)} & R_{13}\sin\delta_\lambda^{(4)} \\ R_{31}\sin\delta_\lambda^{(5)} + R_{21}\sin\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} & R_{32}\sin\delta_\lambda^{(5)} + R_{22}\sin\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} & R_{33}\sin\delta_\lambda^{(5)} + R_{23}\sin\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} \end{pmatrix} \tag{A.4}$$

$$\mathbf{C}^{22}(\delta_\lambda) = \begin{pmatrix} -R_{33} & R_{32} & -R_{31} \\ R_{23}\cos\delta_\lambda^{(4)} & -R_{22}\cos\delta_\lambda^{(4)} & R_{21}\cos\delta_\lambda^{(4)} \\ -R_{13}\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} & R_{12}\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} & -R_{11}\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)} \end{pmatrix} \tag{A.5}$$

The $\mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ matrix that appears in eq A.2 has been defined in eq 4.3 and the R_{ij} $(i, j = 1-3)$ quantities in eqs A.4 and A.5 are the elements of the $\mathbf{R}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ matrix defined by eq 2.3 with a_λ, b_λ, c_λ replaced by $\delta_\lambda^{(1)}$, $\delta_\lambda^{(2)}$, $\delta_\lambda^{(3)}$, respectively

$$\mathbf{R}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)}) = \begin{pmatrix} \cos\delta_\lambda^{(1)}\cos\delta_\lambda^{(2)}\cos\delta_\lambda^{(3)} - \sin\delta_\lambda^{(1)}\cos\delta_\lambda^{(3)} & \sin\delta_\lambda^{(1)}\cos\delta_\lambda^{(2)}\cos\delta_\lambda^{(3)} + \cos\delta_\lambda^{(1)}\sin\delta_\lambda^{(3)} & -\sin\delta_\lambda^{(2)}\cos\delta_\lambda^{(3)} \\ -\cos\delta_\lambda^{(1)}\cos\delta_\lambda^{(2)}\sin\delta_\lambda^{(3)} - \sin\delta_\lambda^{(1)}\cos\delta_\lambda^{(3)} & -\sin\delta_\lambda^{(1)}\cos\delta_\lambda^{(2)}\sin\delta_\lambda^{(3)} + \cos\delta_\lambda^{(1)}\cos\delta_\lambda^{(3)} & \sin\delta_\lambda^{(2)}\sin\delta_\lambda^{(3)} \\ \cos\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \sin\delta_\lambda^{(1)}\sin\delta_\lambda^{(2)} & \cos\delta_\lambda^{(2)} \end{pmatrix} \tag{A.6}$$

It is interesting to notice that $\mathbf{C}(\delta_\lambda)$ is independent of $\delta_\lambda^{(6)}$. This is a consequence of eqs 4.13, 3.8, and 3.6 which make $\mathbf{B}^{(l)}(\delta_\lambda)$ be a function of $\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, ..., \delta_\lambda^{(l-1)}$ only. Therefore, none of these matrices depend on $\delta_\lambda^{(6)}$ and, as a result, neither does $\mathbf{C}(\delta_\lambda)$. From eq 4.12, we have

$$\hat{\mathbf{L}}_\lambda(\delta_\lambda) = [\mathbf{C}(\delta_\lambda)]^{-1}\frac{\hbar}{i}\frac{\partial}{\partial\delta_\lambda} \tag{A.7}$$

Because of eqs A.2 and A.3, we can write

$$[\mathbf{C}(\delta_\lambda)]^{-1} = \begin{pmatrix} \mathbf{C}^{(3)^{-1}} & 0 \\ \mathbf{C}^{22^{-1}}\mathbf{C}^{21}\mathbf{C}^{(3)^{-1}} & \mathbf{C}^{22^{-1}} \end{pmatrix} \tag{A.8}$$

From eq 4.3, we get

$$[\mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})]^{-1} = \begin{pmatrix} -\cos\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & -\sin\delta_\lambda^{(1)} & \cos\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)} \\ -\sin\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & \cos\delta_\lambda^{(1)} & \sin\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)} \\ 1 & 0 & 0 \end{pmatrix} \tag{A.9}$$

In eq A.5, we can factor out at the left the diagonal matrix whose diagonal elements are 1, $\cos\delta_\lambda^{(4)}$, and $\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)}$. Noticing that the resulting matrix at the right is orthogonal, we get

$$[\mathbf{C}^{22}(\delta_\lambda)]^{-1}] = \begin{pmatrix} -R_{33} & R_{23}/\cos\delta_\lambda^{(4)} & -R_{13}/(\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)}) \\ R_{32} & -R_{22}/\cos\delta_\lambda^{(4)} & R_{12}/(\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)}) \\ -R_{31} & R_{21}/\cos\delta_\lambda^{(4)} & -R_{11}/(\cos\delta_\lambda^{(4)}\cos\delta_\lambda^{(5)}) \end{pmatrix} \tag{A.10}$$

Replacement of eqs A.9 and A.10 in eq A.8 gives $[\mathbf{C}(\delta_\lambda)]^{-1}$, and therefore $\hat{\mathbf{L}}_\lambda(\delta_\lambda)$ explicitly. In particular, for its first three elements we have

$$\begin{pmatrix} \hat{L}_{\lambda_1} \\ \hat{L}_{\lambda_2} \\ \hat{L}_{\lambda_3} \end{pmatrix} = \frac{i}{\hbar}[\mathbf{C}^{(3)}(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})]^{-1} \begin{pmatrix} \partial/\partial\delta_\lambda^{(1)} \\ \partial/\partial\delta_\lambda^{(2)} \\ \partial/\partial\delta_\lambda^{(3)} \end{pmatrix} \tag{A.11}$$

which are the same as for the corresponding $N = 4$ operators. The last three elements $\hat{L}_{\lambda_k}$ $(k = 4 - 6)$ involve all 6 differential operators $\partial/\partial\delta_\lambda^{(l)}$ $(l = 1 - 6)$ with coefficients which are explicit trigonometric functions of the first 5 $\delta_\lambda^{(l)}$ hyperangles.

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JP811171P