Incorporating the Geometric Phase Effect in Triatomic and Tetraatomic Hyperspherical Harmonics†

Aron Kuppermann*

Arthur Amos Noyes Laboratory of Chemical Physics, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125

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Hyperspherical harmonics in the democratic row-orthonormal hyperspherical coordinates are very appropriate basis sets for performing reactive scattering calculations for triatomic and tetraatomic systems. The mathematical conditions for incorporating the geometric phase effect in these harmonics are given. These conditions are implemented for triatomic systems, and their explicit analytical expressions in terms of Jacobi polynomials, in both the absence and presence of the geometric phase effect, are given.

1. Introduction

One of the approaches used to perform accurate quantum reactive scattering calculations for *N*-atom systems involves solving the corresponding time-independent Schrödinger equation expressed in democratic coordinates that span the configuration space equivalently, without favoring any arrangement channel region over any other. One such set of coordinates is the row-orthonormal hyperspherical coordinates (ROHC), based on the singular-value decomposition of the system's mass-scaled Jacobi matrix.[1−3] This decomposition leads automatically to a principal axis of inertia body-fixed frame. In general, the Hamiltonian of a system is invariant under changes of arrangement channel Jacobi vectors. In addition, however, using these ROHC for triatomic and tetraatomic systems, each individual term in the corresponding Hamiltonian is invariant under such transformations.[2−3] It is this property that makes such coordinates democratic, and greatly facilitates scattering calculations for these systems in the strong interaction region of configuration space, where all atoms are sufficiently close to each other to interact strongly. For the weak interaction region, where pairs of molecules interact weakly, different nondemocratic hyperspherical coordinates, which favor those pairs, should be used instead.[4]

The approach chosen in such scattering calculations is to employ local hyperspherical surface functions (LHSF), which are eigenfunctions of the system's Hamiltonian at a set of constant values of the hyperradius. In addition, they are eigenfunctions of the square of the total angular momentum, $\hat{J}^2$, its space-fixed *z* component, $\hat{J}_z$, and the inversion through the center-of-mass, $\hat{O}_{\hat{i}}$, operators. These LHSF constitute an excellent basis set for expanding the system's partial wave functions. The hyperangular part of the LHSF kinetic energy operator is the same as that of the total Hamiltonian and of the grand-canonical angular momentum operator, $\hat{\Lambda}^2$, and has poles at all configurations for which two of the three principal moments of inertia of the system are equal. It is very important to use methods to determine the LHSF that ascertain that they are regular at those poles. One approach that satisfies this condition involves expanding the LHSF in ROHC hyperspherical harmonics (HH), which are simultaneous eigenfunctions of $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{J}_z$, and $\hat{O}_{\hat{i}}$ and additional hyperangular momentum operators that commute with the latter.[5−7] These ROHC HH satisfy that regularity condition and, in the absence of conical intersections, they have recently been determined analytically by an efficient computer-algebra approach.[5,6] This approach is based on the fact that the eigenfunctions of the system's kinetic energy operator, $\hat{T}$, with zero eigenvalue are single-valued homogeneous polynomials of the space-fixed Cartesian coordinates of the system's mass-scaled Jacobi vectors, and the properties of these polynomials are central to this method.[8]

In the presence of conical intersections, however, the wave function no longer needs to be single-valued and must instead satisfy a geometric phase (GP) boundary condition upon pseudorotations of the system around such intersections.[9,10] A consequence of this condition is that the eigenfunctions of $\hat{T}$ with zero eigenvalue no longer need to be polynomials of those Cartesian coordinates, and a different approach is required for the analytical determination of the corresponding GP HH. In this paper we describe such an approach for triatomic systems of the A_3 type and tetraatomic systems of the A_3B type. In Section 2 we summarize the definition and properties of the ROHC, and in Section 3 we give explicit expressions for the corresponding kinetic energy and grand-canonical angular momentum operators for triatomic and tetraatomic systems. In Section 4 we define pseudorotations for A_3 and A_3B systems. The ROHC HH for these systems are defined, and their general properties are given in Section 5. The parities of the grand-canonical angular momentum quantum number, *n*, and the principal moment of inertia internal angular momentum quantum number, *L*, for triatomic systems, which are important for determining the properties of the corresponding HH, are described in Section 6 in both the absence and presence of the GP effect. In Section 7 we give explicit analytical expressions for the HH of triatomic systems in both the absence and presence of the GP effect. Finally, in Section 8, we give a summary and some conclusions.

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

The ROHC used in this paper and their properties have been described previously[1−3] and will only be summarized here.

Consider a system of *N* atoms and an associated set of $N-1$ λ-arrangement mass-scaled Jacobi vectors, $\mathbf{r}_\lambda^{(1)}, \mathbf{r}_\lambda^{(2)}, ..., \mathbf{r}_\lambda^{(N-1)}$.

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* Corresponding author. E-mail: aron@caltech.edu.

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The corresponding space-fixed 3 by $(N-1)$ Jacobi matrix, ρ_λ^{sf}, is defined by

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

where $x_\lambda^{(j)}$, $y_\lambda^{(j)}$, and $z_\lambda^{(j)}$ ($j = 1, 2, ..., N-1$) are the Cartesian space-fixed coordinates of $\mathbf{r}_\lambda^{(j)}$. Because of the singular value decomposition theorem for real matrices,[11,12] ρ_λ^{sf} can, for $N > 3$, be put in the form[3,4,13]

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

where χ_λ is a chirality coordinate that can assume the values 0 or 1, $\boldsymbol{a}_\lambda \equiv (a_\lambda, b_\lambda, c_\lambda)$ 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 $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ and $\tilde{R}(\boldsymbol{a}_\lambda)$ is the corresponding proper rotation matrix.[14] In addition, $\delta_\lambda \equiv (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, ... \delta_\lambda^{(3N-9)})$ are a set of $3N-9$ hyperspherical coordinates and $\mathbf{Q}$ is a 3 by $(N-1)$ row-orthonormal matrix satisfying

$$\mathbf{Q}\tilde{\mathbf{Q}} = \mathbf{I} \quad (2.3)$$

$\boldsymbol{N}(\theta, \phi)$ is the 3×3 diagonal matrix

$$\mathbf{N}(\theta,\phi) = \begin{pmatrix} \sin\theta\cos\phi & 0 & 0 \\ 0 & \sin\theta\sin\phi & 0 \\ 0 & 0 & \cos\theta \end{pmatrix} \quad (2.4)$$

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

$$0 \le \phi \le \pi/4 \quad (2.5)$$

and

$$0 \le \theta \le \arcsin[1/(1+\cos^2\phi)^{1/2}] \le \arcsin(2/3)^{1/2} \cong 54.7^\circ \quad (2.6)$$

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

$$I_{x^{I\lambda}} = \mu\rho^2(1-N_{11}^2) \quad I_{y^{I\lambda}} = \mu\rho^2(1-N_{22}^2) \quad I_{z^{I\lambda}} = \mu\rho^2(1-N_{33}^2) \quad (2.7)$$

which are ordered according to

$$I_{z^{I\lambda}} \le I_{x^{I\lambda}} \le I_{y^{I\lambda}} \quad (2.8)$$

Finally, $\rho \ge 0$ is the system's λ-independent hyperradius defined by

$$\rho^2 = \sum_{j-1}^{N-1} (x_\lambda^{(j)^2} + y_\lambda^{(j)^2} + z_\lambda^{(j)^2}) \quad (2.9)$$

The set of quantities χ_λ, $\boldsymbol{a}_\lambda$, ρ, θ, ϕ, and δ_λ is called the ROHC of the system.

For tetraatomic systems, $\mathbf{Q}$ depends on three internal hyperangles $\delta_\lambda \equiv (\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ and is chosen to be $\tilde{\mathbf{R}}(\delta_\lambda)$ where the ranges of these angles are given by

$$0 \le \delta_\lambda^{(1)}, \delta_\lambda^{(3)} < \pi \quad 0 \le \delta_\lambda^{(2)} \le \pi \quad (2.10)$$

and the chirality coordinate is λ-independent and given by

$$(-1)^x = \text{sign det } \rho_\lambda^{sf} \quad (2.11)$$

For triatomic systems, eq 2.2 is replaced by

$$\rho_\lambda^{sf} = \tilde{\mathbf{R}}(\boldsymbol{a}_\lambda)\, \rho \mathrm{N}(\theta)\, \mathbf{Q}(\delta_\lambda) \quad (2.12)$$

where $\mathbf{N}(\theta)$ is given by eq 2.4 with $\phi = 0$, that is

$$\mathbf{N}(\theta) = \begin{pmatrix} \sin\theta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \cos\theta \end{pmatrix} \quad (2.13)$$

where

$$0 \le \theta \le \pi/4 \quad (2.14)$$

and

$$\mathbf{Q}(\delta_\lambda) = \begin{pmatrix} \cos\delta_\lambda & \sin\delta_\lambda \\ 0 & 0 \\ -\sin\delta_\lambda & \cos\delta_\lambda \end{pmatrix} \quad (2.15)$$

with the range of δ_λ given by

$$0 \le \delta_\lambda \le \pi \quad (2.16)$$

The ranges of the δ_λ angles in eqs 2.10 and 2.16 are chosen to satisfy the requirement that, except for some special geometries of the systems, there should be a one-to-one correspondence between the ROHC and the corresponding set of Jacobi vectors, that is, the systems' configuration.

3. Kinetic Energy and Grand Canonical Angular Momentum Operators for Triatomic and Tetraatomic Systems

For any system of coordinates associated with the λ-arrangement Jacobi vectors $\mathbf{r}_\lambda^{(j)}$ ($j = 1, 2, ..., N-1$), which includes ρ, the kinetic energy operator, $\hat{T}$, can be expressed in terms of the grand-canonical angular momentum operator, $\hat{\Lambda}^2$, by[7]

$$\hat{T} = \hat{T}_\rho(\rho) + \frac{\hat{\Lambda}^2}{2\mu\rho^2} \quad (3.1)$$

where

$$\hat{T}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^{3N-4}}\frac{\partial}{\partial\rho}\rho^{3N-4}\frac{\partial}{\partial\rho} \quad (3.2)$$

3.1. $\hat{\Lambda}^2$ for Triatomic Systems. For triatomic systems, $\hat{\Lambda}^2$ is given by[2]

$$\hat{\Lambda}^2 = \frac{1}{\cos^2\theta}\hat{J}_x^{I\lambda 2} + \frac{1}{\cos^2 2\theta}\hat{J}_y^{I\lambda 2} + \frac{1}{\sin^2\theta}\hat{J}_z^{I\lambda 2} + \frac{1}{\cos^2 2\theta}\hat{L}^2 + \hat{K}^2 - 2\frac{\sin 2\theta}{\cos^2 2\theta}\hat{L}\,\hat{J}_y^I - 4i\hbar\cot 4\theta\,\hat{K} \quad (3.3)$$

where

$$\hat{L} = \frac{\hbar}{i}\frac{\partial}{\partial\delta_\lambda} \quad (3.4)$$

and

$$\hat{K} = \frac{\hbar}{i}\frac{\partial}{\partial\theta} \tag{3.5}$$

The $\hat{J}_x^{I\lambda}$, $\hat{J}_y^{I\lambda}$, and $\hat{J}_z^{I\lambda}$ operators are the components of the system's total angular momentum operator, $\hat{\boldsymbol{J}}$, along the principal-axes-of-inertia frame $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ expressed in terms of the Euler angles, $\boldsymbol{a}_\lambda$, as

$$\begin{pmatrix}\hat{J}_x^{I\lambda}\\ \hat{J}_y^{I\lambda}\\ \hat{J}_z^{I\lambda}\end{pmatrix} = \frac{\hbar}{i}\begin{pmatrix}-\csc b_\lambda\cos c_\lambda & \sin c_\lambda & \cot b_\lambda\cos c_\lambda\\ \csc b_\lambda\sin c_\lambda & \cos c_\lambda & -\cot b_\lambda\sin c_\lambda\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\partial/\partial a_\lambda\\ \partial/\partial b_\lambda\\ \partial/\partial c_\lambda\end{pmatrix} \tag{3.6}$$

and act only on those angles. Arrangement channel coordinate transformations are a particular kind of kinematic rotations,[1,15] and those two designations will be used interchangeably in this paper. The $Gy^{I\lambda}$ axis is invariant under such transformations, whereas $Gx^{I\lambda}$ and $Gx^{I\lambda}$ are either invariant or both change sense together. In addition, $\hat{L}$ and $\hat{K}$ are also invariant under those rotations. As a result, not only is $\hat{\Lambda}^2$ invariant under them but so is every one of the seven terms in the rhs of eq 3.3. This justifies the designation of these triatomic ROHC as democratic. This property makes the ROHC for the strong interaction region of triatomic systems particularly useful because any arrangement channel, λ, can be chosen to perform scattering calculations in this region, and from them the result for any other λ can be obtained easily.

3.2. $\hat{\Lambda}^2$ for Tetraatomic Systems. For tetraatomic systems, $\hat{\Lambda}^2$ is given by[3]

$$\hat{\Lambda}^2 = \hat{K}^2(\theta,\phi) + \hat{B}(\theta,\phi) + \hat{C}^2(\boldsymbol{a}_\lambda, \delta_\lambda; \theta, \phi) \tag{3.7}$$

where

$$\hat{K}^2(\theta,\phi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{3.8}$$

$$\hat{B}(\theta,\phi) = -2\hbar^2\left(b_\theta(\theta,\phi)\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}b_\phi(\theta,\phi)\frac{\partial}{\partial\phi}\right) \tag{3.9}$$

$$b_\theta(\theta,\phi) = \frac{\mathrm{N}_{22}\mathrm{N}'_{\theta_{22}} - \mathrm{N}_{11}\mathrm{N}'_{\theta_{11}}}{\mathrm{N}_{22}^2 - \mathrm{N}_{11}^2} + \frac{\mathrm{N}_{33}\mathrm{N}'_{\theta_{33}} - \mathrm{N}_{22}\mathrm{N}'_{\theta_{22}}}{\mathrm{N}_{33}^2 - \mathrm{N}_{22}^2} + \frac{\mathrm{N}_{11}\mathrm{N}'_{\theta_{11}} - \mathrm{N}_{33}\mathrm{N}'_{\theta_{33}}}{\mathrm{N}_{11}^2 - \mathrm{N}_{33}^2} \tag{3.10}$$

$$b_\phi(\theta,\phi) = \frac{\mathrm{N}_{22}\mathrm{M}_{\phi_{22}} - \mathrm{N}_{11}\mathrm{M}_{\phi_{11}}}{\mathrm{N}_{22}^2 - \mathrm{N}_{11}^2} - \frac{\mathrm{N}_{22}\mathrm{M}_{\phi_{22}}}{\mathrm{N}_{33}^2 - \mathrm{N}_{22}^2} + \frac{\mathrm{N}_{11}\mathrm{M}_{\phi_{11}}}{\mathrm{N}_{11}^2 - \mathrm{N}_{33}^2} \tag{3.11}$$

and

$$\hat{C}^2(\boldsymbol{a}_\lambda, \delta_\lambda; \theta, \phi) = \frac{(\mathrm{N}_{22}\hat{J}_z^{I\lambda} - \mathrm{N}_{11}\hat{L}_{\lambda 3})^2 + (\mathrm{N}_{11}\hat{J}_z^{I\lambda} - \mathrm{N}_{22}\hat{L}_{\lambda 3})^2}{(\mathrm{N}_{22}^2 - \mathrm{N}_{11}^2)^2} + \frac{(\mathrm{N}_{33}\hat{J}_x^{I\lambda} - \mathrm{N}_{22}\hat{L}_{\lambda 1})^2 + (\mathrm{N}_{22}\hat{J}_x^{I\lambda} - \mathrm{N}_{33}\hat{L}_{\lambda 1})^2}{(\mathrm{N}_{33}^2 - \mathrm{N}_{22}^2)^2} + \frac{(\mathrm{N}_{11}\hat{J}_y^{I\lambda} - \mathrm{N}_{33}\hat{L}_{\lambda 2})^2 + (\mathrm{N}_{33}\hat{J}_y^{I\lambda} - \mathrm{N}_{11}\hat{L}_{\lambda 2})^2}{(\mathrm{N}_{11}^2 - \mathrm{N}_{33})^2} \tag{3.12}$$

The N_{ii} ($i = 1, 2, 3$) in these expressions are the diagonal elements of the $\mathbf{N}(\theta, \phi)$ matrix of eq 2.4 and the $\mathrm{N}'_{\theta_{11}}$ and $\mathrm{M}'_{\phi_{ii}}$ are given, respectively, by

$$\mathrm{N}'_{\theta_{11}} = \cos\theta\cos\phi \quad \mathrm{N}'_{\theta_{22}} = \cos\theta\sin\phi \quad \mathrm{N}'_{\theta_{33}} = -\sin\theta \tag{3.13}$$

$$\mathrm{M}_{\phi_{11}} = -\sin\phi \quad \mathrm{M}_{\phi_{22}} = \cos\phi \tag{3.14}$$

The $\hat{J}_x^{I\lambda}$, $\hat{J}_y^{I\lambda}$, and $\hat{J}_z^{I\lambda}$ are defined as for triatomic systems and are given by eq 3.6. Similarly, $\hat{L}_{\lambda_1}$, $\hat{L}_{\lambda_2}$, and $\hat{L}_{\lambda_3}$ are the components of an internal angular momentum operator, $\hat{\boldsymbol{L}}_\lambda$, in a space-fixed-type mathematical frame and are given by

$$\begin{pmatrix}\hat{L}_{\lambda_1}\\ \hat{L}_{\lambda_2}\\ \hat{L}_{\lambda_3}\end{pmatrix} = \frac{\hbar}{i}\begin{pmatrix}-\cos\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & -\sin\delta_\lambda^{(1)} & \cos\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)}\\ -\sin\delta_\lambda^{(1)}\cot\delta_\lambda^{(2)} & \cos\delta_\lambda^{(1)} & \sin\delta_\lambda^{(1)}\csc\delta_\lambda^{(2)}\\ 1 & 0 & 0\end{pmatrix}\begin{pmatrix}\partial/\partial\delta_\lambda^{(1)}\\ \partial/\partial\delta_\lambda^{(2)}\\ \partial/\partial\delta_\lambda^{(3)}\end{pmatrix} \tag{3.15}$$

The axes of $Gx^{I\lambda}y^{I\lambda}z^{I\lambda}$ are either invariant under arrangement channel coordinate transformations or two of them change sense together. As a result, a similar property holds for the $I\lambda$ components of $\hat{\boldsymbol{J}}$. The components of $\hat{\boldsymbol{L}}_\lambda$ are similarly invariant or change sign concurrently with the corresponding components of $\hat{\boldsymbol{J}}$ and, therefore, each of the products $\hat{J}_x^{I\lambda}\hat{L}_{\lambda 1}$, $\hat{J}_y^{I\lambda}\hat{L}_{\lambda 2}$, and $\hat{J}_z^{I\lambda}\hat{L}_{\lambda 3}$ are invariant under those transformations as are the six square operators that appear in the numerators of the rhs of eq 3.12. As a result, each of the 11 terms that appear in the rhs of eq 3.7 (namely, $\hat{K}^2$, $\hat{B}$, and the nine terms resulting from eq 3.12) are invariant under arrangement channel coordinate transformations, in analogy to the seven terms of the triatomic $\hat{\Lambda}^2$ of eq 3.3. For this reason, the tetraatomic ROHC are also called democratic. As for the triatomic case, they are very useful for performing tetraatomic reactive scattering calculations in the strong interaction region of configuration space. For the weak interaction region, different hyperspherical coordinates and HH should be used.[4]

4. Effect of Pseudorotations on Triatomic and Tetraatomic ROHC

The geometric phase (GP) effect is associated with conical intersections between electronically adiabatic potential energy surfaces of polyatomic systems.[16,17] Loops in nuclear configuration space are called pseudorotations. When a system traverses such a loop, inside of which there is an odd number of conical intersection geometries, their electronic wave function, if required to be real and change continuously, undergoes a discontinuous change of sign at the end of the loop, with respect to their values at the beginning of the loop, and as a result that electronic wave function is not single-valued. To preserve the single-valuedness of the complete electronuclear wave function, the corresponding nuclear wave function must undergo a compensating change of sign.[9] This results in effects on bound[18] and scattering[19] states of the system, which have recently been shown to affect observable state-to-state reactive scattering differential cross sections[20] for the H_3 system. If there are no or an even number of conical intersections inside a pseudorotation loop, both the system's electronic and nuclear wave functions do not display a discontinuity at the end of the loop; that is, they are single valued.

In this paper, we consider special pseudorotations for triatomic and tetraatomic systems. For triatomic systems, they start with the configuration whose ROHC are a_λ, b_λ, c_λ, ρ, θ, $\delta_\lambda = 0$. We

then allow δ_λ to change continuously from 0 to π, while $\rho \neq 0$ and $\theta \neq \pi/2$ are maintained constant and the Euler angles are made to depend linearly on δ_λ as $a_\lambda + \delta_\lambda$, $b_\lambda + (1 - b_\lambda/\pi)\delta_\lambda$, $c_\lambda + (1 - c_\lambda/\pi)\delta_\lambda$, so that on completion of the loop the ROHC of the system are $a_\lambda + \pi$, $\pi - b_\lambda$, $\pi - c_\lambda$, ρ, θ, $\delta_\lambda = \pi$. From eq 2.12 it is straightforward to show that the system's configuration at the beginning and the end of this path are the same, and that the configuration $\boldsymbol{a}_\lambda$, ρ, $\theta = \pi/2$ and arbitrary δ_λ corresponds to a point inside that path, which is therefore a loop around that configuration. Furthermore, if the system is of the type A_3, involving three identical atoms, such as H_3, that $\theta = \pi/2$ configuration corresponds to an equilateral triangle. When A_3 systems have conical intersections, their configurations are usually equilateral triangles and in this case the pseudorotation just defined would be a loop around a conical intersection geometry.

Let us now consider tetraatomic systems of the type A_3B, such as H_3O. The corresponding conical intersections, when they exist, usually have configurations corresponding to regular pyramid geometries, whose base is an equilateral triangle, A_3. Let us define the arrangement channel coordinates $\lambda = 1$, as those for which $\mathbf{r}_1^{(1)}$ is the Jacobi mass-scaled vector between two of the A atoms, $\mathbf{r}_1^{(2)}$ that form their center of mass to the third A atom, and $\mathbf{r}_1^{(3)}$ that from the center of mass of A_3 to the B atom. The corresponding ROHC for regular pyramid configurations are $\phi = \pi/4$, $\delta_1^{(3)} = 0$ and arbitrary χ, a_1, b_1, c_1, ρ, θ, $\delta_1^{(1)}$, $\delta_1^{(2)}$ with $\rho \neq 0$ and $\theta \neq 0$. Let us consider the path in nuclear configuration space starting at a point whose ROHC are χ, a_1, b_1, c_1, ρ, θ, $\delta_1^{(1)} = 0$, $\delta_1^{(2)}$, $\delta_1^{(3)}$ with all coordinates except $\delta_1^{(1)}$ arbitrary but subject to the conditions $\rho \neq 0$, $\theta \neq 0$, $\phi \neq \pi/4$, $\delta_1^{(3)}$. We now maintain χ, a_1, b_1, ρ, θ, ϕ, $\delta_1^{(2)}$, and $\delta_1^{(3)}$ constant while changing $\delta_1^{(1)}$ from 0 to π and making the third external Euler angle depend linearly on δ_λ as $c_1 + \delta_\lambda$. Upon completion of the path the ROHC of the system are a_1, b_1, $c_1 + \pi$, ρ, θ, ϕ, $\delta_1^{(1)} = \pi$, $\delta_1^{(2)}$, and $\delta_1^{(3)}$. From eqs 2.2, 2.4, and the choice of $\mathbf{Q}$ mentioned before eq 2.10, one can show that the configurations corresponding to the initial and final points of this path are the same and that it encircles the associated regular pyramid configuration point a_1, b_1, c_1, θ, $\phi = \pi/4$, $\delta_1^{(1)}$, $\delta_1^{(2)}$, $\delta_1^{(3)} = 0$. Therefore, that path is a pseudorotation, which could enclose a conical intersection configuration. This pseudorotation differs from the one defined in ref 3, which was in error.

The special pseudorotations just defined for triatomic and tetraatomic systems will be useful for incorporating the GP effect in the hyperspherical harmonics for these systems, as shown in Section 5.

5. ROHC Hyperspherical Harmonics With and Without the Geometric Phase

We will now define the ROHC hyperspherical harmonics (HH) without and including the GP for triatomic and tetraatomic systems.

5.1. Triatomic Systems. For triatomic systems, the five operators $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{J}_z^{sf}$, $\hat{L}$, and $\hat{O}_{\hat{\mathscr{I}}}$ commute with each other. $\hat{\Lambda}^2$ was defined by eq 3.1, $\hat{J}^2$, and $\hat{J}_z^{sf}$ are, respectively, the square and the space-fixed z component of the total angular momentum operator $\hat{\mathbf{J}}$, $\hat{\mathscr{I}}$ is the associated operator that inverts the system through its center of mass, and $O_{\hat{\mathscr{I}}}$ is the associated operator that acts on functions of the system's coordinates. The corresponding F HH is defined as the simultaneous eigenfunction of those operators.

$$\hat{\Lambda}^2 F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) = n_{s\Pi}(n_{s\Pi}+4)\hbar^2 F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) \tag{5.1}$$

$$\hat{J}^2 F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) = J(J+1)\hbar^2 F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) \tag{5.2}$$

$$\hat{J}_z^{sf} F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) = M_J \hbar F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) \tag{5.3}$$

$$\hat{L} F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) = L_{s\Pi}\hbar F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) \tag{5.4}$$

$$\hat{O}_{\hat{\mathscr{I}}} F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) = (-1)^{\Pi} F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(\Theta_\lambda) \tag{5.5}$$

which is regular at their poles. Θ_λ represents the six ROHC $\boldsymbol{a}_\lambda$, ρ, θ, δ_λ. The quantum numbers $n_{s\Pi}$, J, M_J, $L_{s\Pi}$, and Π are integers subject to the constraints

$$n_{s\Pi} \geq 0 \quad 0 \leq J \leq n_{s\Pi} \quad -J \leq M_J \leq J \quad -n_{s\Pi} \leq L_{s\Pi} \leq n_{s\Pi} \quad \Pi = 0, 1 \tag{5.6}$$

and D is a degeneracy number equal to the total number of linearly independent F functions with the same values of s, Π, $n_{s\Pi}$, $L_{s\Pi}$, J, and M_J. d designates which of these D functions is being considered. In addition, F satisfies the pseudorotation condition

$$F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(a_\lambda + \pi, \pi - b_\lambda, \pi - c_\lambda, \theta, \delta_\lambda = \pi) = (-1)^s F^{s\Pi n_{s\Pi} L_{s\Pi}\, J\ D}_{M_J\ d}(a_\lambda, b_\lambda, c_\lambda, \theta, \delta_\lambda = 0) \tag{5.7}$$

where $s = 0$ means NGP (no geometric phase, i.e., no or an even number of conical intersections encircled by the corresponding pseudorotation defined in Section 4) and $s = 1$ means GP (geometric phase, i.e., and odd number of conical intersections encircled by that pseudorotation). $L_{s\Pi}$ and $n_{s\Pi}$ have the parity of $s + \Pi$, as shown in Section 6. For the GP case, the F HH changes sign under the associated pseudorotation, whereas for the NGP case it is single valued, that is, has the same value at the beginning and end of that pseudorotation.

The D degeneracy stems from the fact that a system of three free particles in a center-of-mass frame has five angular degrees of freedom, a_λ, b_λ, c_λ, θ, and δ_λ, and as a result has five simultaneously knowable angular constants of the motion, but F has been required to be an eigenfunction of only four differential operators in these angular variables. The subscript d varies from 1 to D and can be considered to be a fifth quantum number.

5.2. Tetraatomic Systems. For the tetraatomic systems, the six operators $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{J}_z^{sf}$, $\hat{L}^2$, $\hat{L}_{\lambda_3}^{bf}$, and $\hat{O}_{\hat{\mathscr{I}}}$ commute with each other. The first three and the last one are similar to the ones defined in Section 5.1, $\hat{L}^2$ is the square of the internal angular momentum operator, $\hat{\boldsymbol{L}}_\lambda$, and $\hat{L}_{\lambda_3}^{bf}$ is a body-fixed type component of $\hat{\boldsymbol{L}}_\lambda$ that differs from its space-fixed-type component displayed in eq 3.15. It is given by

$$\hat{L}_{\lambda_3}^{bf} = \frac{\hbar}{i}\frac{\partial}{\partial \delta_\lambda^{(3)}} \tag{5.8}$$

The corresponding F HH is defined as a simultaneous eigenfunction of those six operators that is regular at their poles

$$\hat{\Lambda}^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = n(n+7)\hbar^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.9}$$

$$\hat{J}^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = J(J+1)\hbar^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.10}$$

$$\hat{J}^{sf}_z F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = M_J \hbar F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.11}$$

$$\hat{L}^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = L(L+1)\hbar^2 F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.12}$$

$$\hat{L}^{bf}_{\lambda_3} F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = M_{L_\lambda} \hbar F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.13}$$

$$\hat{O}_{\hat{\mathscr{T}}} F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) = (-1)^{\Pi} F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_\lambda}\ d}(\chi, \Theta_\lambda) \tag{5.14}$$

Θ_λ the nine hyperspherical coordinates $\boldsymbol{a}_\lambda$, ρ, θ, ϕ, δ_λ. The six quantum numbers n, J, M_J, L, M_{L_λ}, and Π are integers subject to the constraints

$$n \geq 0 \quad 0 \leq J,L \leq n \quad -J \leq M_J \leq J \quad -L \leq M_{L_\lambda} \leq L$$

$$\Pi = 0, 1 \tag{5.15}$$

Symbols D and d have meanings similar to the ones given for triatomic systems and appear for similar reasons. In addition, F satisfies the pseudorotation condition

$$F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_1}\ d}(\chi, a_1, b_1, c_1 + \pi, \rho, \theta, \phi, \delta_1^{(1)} = \pi, \delta_1^{(2)}, \delta_1^{(3)}) = (-1)^s F^{s\Pi n\ J\ L\ D}_{M_J\ M_{L_1}\ d}(\chi, a_1, b_1, c_1, \rho, \theta, \phi, \delta_1^{(1)} = 0, \delta_1^{(2)}, \delta_1^{(3)}) \tag{5.16}$$

where, as for triatomic systems, $s = 0$ corresponds to the NGP case and results in a single-valued F and $s = 1$ corresponds to the GP case and the corresponding F changes sign (discontinuously) between the end and the beginning of the tetraatomic pseudorotation defined in Section 4. The consequences of eq 5.16 will not be examined in the present paper.

6. Parities of $L_{s\pi}$ and $n_{s\pi}$ for Triatomic Systems

The general solution of eqs 5.1 through 5.6 is

$$F^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{M_J\ d}(\Theta_\lambda) = N^{s\Pi n_{s\Pi} L_{s\Pi}}\ {}^{D}_{d} e^{iL_{s\Pi}\delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D_{M_J\Omega_{J_\lambda}}(\boldsymbol{a}_\lambda)\, G^{s\Pi n_{s\Pi} L_{s\Pi}\Omega^J_{J_\lambda}\ D}_{\ d}(\theta) \tag{6.1}$$

where $D^J_{M_J\Omega_{J_\lambda}}$ is Davydov's[21] Wigner rotation function. The $G(\theta)$ functions are called G HH. $\Pi = 0(1)$ corresponds to symmetric (antisymmetric) solutions with respect to inversion through the system's center of mass. We wish to prove that $L_{s\Pi}$ and $n_{s\Pi}$ have the parity of $s + \Pi$. For $L_{s\Pi}$, this can be achieved easily using the parity Wigner functions defined by

$$D^{J\Pi}_{M_J\Omega_{J_\lambda}}(\boldsymbol{a}_\lambda) = N^{J\Omega_{J_\lambda}}[D^J_{M_J\Omega_{J_\lambda}}(\boldsymbol{a}_\lambda) + (-1)^{J+\Pi+\Omega_{J_\lambda}} D^J_{M_J,-\Omega_{J_\lambda}}(\boldsymbol{a}_\lambda)] \tag{6.2}$$

where

$$N^{J\Omega_{J_\lambda}} = \left[\frac{2J+1}{16\pi^2(1+\delta_{\Omega_{J_\lambda}0})}\right]^{1/2} \tag{6.3}$$

These functions satisfy

$$\hat{O}_{\hat{\mathscr{T}}} D^{J\Pi}_{M_J\Omega_{J_\lambda}}(a_\lambda, b_\lambda, c_\lambda) = D^{J\Pi}_{M_J\Omega_{J_\lambda}}(a_\lambda + \pi, \pi - b_\lambda, \pi - c_\lambda) = (-1)^{\Pi} D^{J\Pi}_{M_J\Omega_{J_\lambda}}(a_\lambda, b_\lambda, c_\lambda) \tag{6.4}$$

and in terms of them the F HH can be written as

$$F^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{M_J\ d}(\Theta_\lambda) = N'^{s\Pi n_{s\Pi} L_{s\Pi} J} e^{iL_{s\Pi}\delta_\lambda} \sum_{\Omega_{J_\lambda}=0}^{J} D^{J\Pi}_{M_J\Omega_{J_\lambda}}(a_\lambda, b_\lambda, c_\lambda) G'^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{\Omega_{J_\lambda}\ d}(\theta) \tag{6.5}$$

The G' HH are related to the G HH for $\Omega_{J_\lambda} \geq 0$ by[6]

$$G'^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{\Omega_{J_\lambda}\ d}(\theta) = (1 + \delta_{\Omega_{J\lambda}0})^{-1/2} G^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{\Omega_{J_\lambda}\ d}(\theta) \tag{6.6}$$

$$N'^{s\Pi n_{s\Pi} J L_{s\Pi}} = \left[\frac{2J+1}{16\pi^2}\right]^{1/2} N^{s\Pi n_{s\Pi} J L_{s\Pi}} \tag{6.7}$$

whereas the G HH for $\Omega_{J_\lambda} < 0$ are related to those for $\Omega_{J_\lambda} > 0$ by

$$G^{s\Pi n_{s\Pi} L_{s\Pi} J}_{-\Omega_{J_\lambda}\ d}(\theta) = (-1)^{(J+s+L_{s\Pi}+\Omega_{J_\lambda})} G^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{\Omega_{J_\lambda}\ d}(\theta) \tag{6.8}$$

Therefore, the replacement of $D^J_{M_J}\Omega_{J_\lambda}(\boldsymbol{a}_\lambda)$ by $D^{J\Pi}_{M\Omega_{J_\lambda}}(a_\lambda)$ limits the sum over Ω_{J_λ} to nonnegative values only and changes the normalization constant of the F HH. Replacing eq 6.5 into eq 5.7 and using

$$D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda) = e^{iM_J a_\lambda} d^J_{M_J\Omega_{J_\lambda}}(b_\lambda) e^{i\Omega_J c_\lambda} \tag{6.9}$$

results in

$$(-1)^{\Pi + L_{s\Pi}} = (-1)^s \tag{6.10}$$

which furnishes

$$(-1)^{L_{s\Pi}} = (-1)^{s+\Pi} \text{ Q.E.D.} \tag{6.11}$$

The proof that $n_{s\Pi}$ also has the parity of $s + \Pi$ is more elaborate. From eqs 6.1, 3.1, and 3.2 it is easy to prove that the function $\rho^n F^{s\Pi n_{s\Pi} L_{s\Pi}\ J\ D}_{M_J\ d}(\Theta_\lambda)$ is *harmonic* for both $s = 0$ and $s = 1$, that is, that

$$\nabla^2[\rho^{n_{s\Pi}} F^{s\Pi n_{s\Pi} L_{s\Pi}}_{M_J\ J\ d}{}^{D}(\Theta_\lambda)] = 0 \tag{6.12}$$

where ∇^2 is the six-dimensional Laplacian of the system. For the NGP case, it is also a **homogeneous polynomial of degree $n_{s\Pi}$** in the six space-fixed Cartesian coordinates of the Jacobi vectors $\mathbf{r}^{(1)}_\lambda$ and $\mathbf{r}^{(2)}_\lambda$.[6] Because the operator $\hat{\mathscr{T}}$ changes the signs of all of these coordinates, that polynomial and therefore $F^{s\Pi n_{s\Pi} L_{s\Pi}}_{M_J\ J\ d}{}^{D}$ has the parity of $n_{s\Pi}$ in addition to having the parity of Π. Therefore, for $s = 0$ $n_{s\Pi}$ has the parity of $s + \Pi$, QED. For $s = 1$ $\rho^n F$ is still harmonic but *no longer* a polynomial. To prove that for this case $n_{s\Pi}$ still has the parity of $s + \Pi$ we use the explicit expression for $G^{\Pi n_\Pi L_\Pi}\ {}^{J\alpha}_{\Omega_{J_\lambda}}(\theta)$ given in Section 7.1. Those functions satisfy a system of coupled differential equations in θ,[7] which depend only on the validity of eqs 5.1 through 5.6 and whose derivation does not invoke eq 5.7. Therefore, that explicit expression is valid for both $s = 0$ and $s = 1$. In eqs 7.4 and 7.17, Jacobi polynomials of integer order $\eta - J + m + \epsilon$ appear, where η is given by eqs 7.9 and 7.22 for $n_{s\Pi}$ and J having the same or opposite parities, respectively. In addition, ϵ is given by eq 7.11 for both cases.

Finally m equals m_1 plus an integer, where m_1 is given by eq 7.13 also for both cases. The requirement that $\eta - J + m + \epsilon$ be an integer, both for $s = 0$ and $s = 1$, leads directly to the requirement that $n_{s\Pi}$ and $L_{s\Pi}$ have the same parity. Because from eq 6.11 the latter has the parity of $s + \Pi$, so does the former,that is

$$(-1)^{n_{s\Pi}} = (-1)^{L_{s\Pi}} = (-1)^{s+\Pi} \tag{6.13}$$

We conclude that the parities of $L_{s\Pi}$ and $n_{s\Pi}$ are equal to each other both for $s = 0$ and $s = 1$, and that the *only* but *crucial* difference between the NGP and GP cases is that that parity is the parity of Π for the former and the opposite of that parity for the latter. This important conclusion will permit the explicit expressions for G given in Section 7 to be used for both the NGP and GP cases.

7. Explicit Determination of the G HH for Triatomic Systems

7.1. NGP Case. For the NGP case, the theory of harmonic polynomials can be used to determine the G functions analytically. This has been done using two different methods: (a) A recursion relation between a complete set $\{G^n\}$ of G functions for a given n and another complete set $\{G^{n+1}\}$ for $n + 1$ was derived. This relation was implemented with a Mathematica program to obtain all G functions up to $n = 40$, about 2.3 million of them.[6,22] (b) A sophisticated complex variable harmonic projection method together with very extensive manual algebra was used to obtain explicit expressions for the G functions in terms of Jacobi polynomials for arbitrary n and total angular momentum quantum number J.[23]

For the purpose of obtaining GP functions, it is more convenient to use the results of method b. Those results were obtained using different hyperspherical coordinates and principal axes of inertia than the ROHC used in method a. The method b coordinates and axes were the same as those designated as LPK in ref 2. It's z axis is perpendicular to the triatom plane, whereas the z axis of method a and of the present paper lies in that plane. In addition, the Wigner rotation functions used in method b are those of Rose,[24] whereas the ones used in method a and in eq 6.1 are those of Davydov.[21] The present principal axes of inertia are more convenient for performing reactive scattering calculations than the ones of method b because, as $\rho \rightarrow \infty$, the present z axis approaches the Jacobi body-fixed axis, which is the vector from the center of mass of the product diatom to the product atom, which is the helicity axis for quantizing the component of that diatom's angular momentum. For this reason, we converted the results of ref 23 to the present axes, ROHC, and Wigner rotation functions. In the resulting expressions, degeneracy indices D and d were replaced by the single index α that, for a given J, and all allowed values of n_Π and L_Π is expressed explicitly by eqs 7.12 and 7.25. It should be noted that D is equal to the number of values that α can have for given J, n_Π, and L_Π and the analytical expression for D in terms of these three variables is known[25,26] and is not repeated in the present paper.

In this NGP case ($s = 0$) L and n have the same parity as Π and will be designated simply as L_Π and n_Π respectively, with the subscript s omitted. The G functions of eq 6.1 are then given by

$$G^{\Pi n_\Pi L_\Pi\ J\alpha}_{\qquad\ \Omega_{J_\lambda}}(\theta) = (-1)^{L_\Pi/2} i^{\Omega_{J\lambda}} \sum_{\Omega'_{J_\lambda\Pi}=-J}^{J} (-1)^{\Omega'_{J\lambda\Pi}} d^J_{\Omega_{J\lambda}\Omega'_{J\lambda\Pi}}(\pi/2)\, \mathscr{G}^{\Pi n_\Pi L_\Pi\ J\alpha}_{\qquad\ \Omega'_{J_\lambda\Pi}}(\theta) \tag{7.1}$$

where the values of $\Omega'_{J_\lambda\Pi}$ in the summation include only those that have the same parity as Π[27] and the $\mathscr{G}$ function depends on the parity of J and Π, as indicated below:

(1) For J and Π having the same parity, it is given by

$$\mathscr{G}^{\Pi n_\Pi L_\Pi\ J\alpha}_{\qquad\ \Omega_{J_\lambda\Pi}}(\theta) = [(J + \Omega_{J_\lambda\Pi})!(J - \Omega_{J_\lambda\Pi})!]^{-1/2} \sum_{\mu=-J/2}^{J/2} \times \varphi^J_{\Omega_{J\lambda\Pi}\mu}(\theta) W^{\Pi n_\Pi L_\Pi\ J\alpha}_{\qquad\ \mu}(\theta) \tag{7.2}$$

where

$$\varphi^J_{\Omega_{J_\lambda}\Pi\mu}(\theta) = (-1)^{(1/2)(J-\Omega_{J\lambda\Pi})}(J/2 + \mu)!(J/2 - \mu)! \times \sum_{k_1k_2u_1u_2} (k_1!k_2!u_1!u_2!)^{-1}[\cos(\pi/4 - \theta)]^{k_1+u_2} \times [\sin(\pi/4 - \theta)]^{k_2+u_1} \tag{7.3}$$

and

$$W^{\Pi n_\Pi L_\Pi\ J\alpha}_{\qquad\ \mu}(\theta) = (-1)^\eta (\cos 2\theta)^{|L_\Pi/2-\mu|} \times \sum_{m=m_1}^{m_2} \binom{J/2+\alpha}{m+(1/2)(\alpha+\mu+\epsilon)} \times \binom{J/2-\alpha}{m-(1/2)(\alpha+\mu-\epsilon)} \times \frac{m!\Gamma(m+\epsilon+1/2)}{(\xi+m-J)!} \sum_{i=0}^{m} \frac{(-1)^i(\xi+i)!}{(m-i)!i!\Gamma(i+\epsilon+1/2)} \times (-1)^{\eta-J+m+\epsilon} P^{(J-m+i,|L_\Pi/2-\mu|)}_{\eta-J+m+\epsilon}(\cos 4\theta) \tag{7.4}$$

The several parameters in these two equations are defined by

$$k_1 + u_1 = J/2 + \mu \tag{7.5}$$

$$k_2 + u_2 = J/2 - \mu \tag{7.6}$$

$$k_1 + k_2 = (1/2)(J + \Omega_{J_\lambda\Pi}) \tag{7.7}$$

$$u_1 + u_2 = (1/2)(J - \Omega_{J_\lambda\Pi}) \tag{7.8}$$

$$\eta = (1/4)(n + J) - (1/2)(|L_\Pi/2 - \mu| + \epsilon) \tag{7.9}$$

$$\xi = (1/4)(n + J) + (1/2)(|L_\Pi/2 - \mu| + \epsilon) \tag{7.10}$$

$$\epsilon = \begin{cases} 0 \text{ for } \alpha + \mu \text{ even} \\ 1 \text{ for } \alpha + \mu \text{ odd} \end{cases} \tag{7.11}$$

For a given J, and all allowed values of n_Π and L_Π, α is given by

$$2\alpha = -J, -J + 2, \ldots, J - 2, J \tag{7.12}$$

In addition,

$$m_1 = (1/2)(|\alpha + \mu| - \epsilon) \tag{7.13}$$

$$m_2 = (1/2)(J - |\alpha - \mu| - \epsilon) \tag{7.14}$$

In eq 7.4 and in eq 7.17 below, $P_{\gamma}^{(\alpha,\beta)}$ is the Jacobi polynomial of non-negative integer degree γ.[28]

Quantities k_1, k_2, u_1, and u_2 in eqs 7.5 through 7.8 are restricted to be nonnegative integers. In addition, three of these four relations are linearly independent and, as a result, the 4-fold sum in eq 7.4 reduces to a single sum.

(2) For J and Π having opposite parity, it is given by

$$\mathcal{G}^{\Pi n_\Pi L_\Pi\, J\alpha}_{\Omega_{J_\lambda}\Pi}(\theta) = [(J+\Omega_{J_\lambda\Pi})!\,(J-\Omega_{J_\lambda\Pi})!]^{-1/2} \times \sum_{\mu=-(J-1)/2}^{(J-1)/2} \sqrt{2}\sin 2\theta\, \varphi^{J-1}_{\Omega_{J_\lambda}\Pi\mu}(\theta) W^{\Pi n_\Pi L_\Pi\, J\alpha}_{\mu}(\theta) \quad (7.15)$$

where

$$\varphi^{J-1}_{\Omega_{J\lambda}\Pi\mu}(\theta) = (-1)^{(1/2)(J-1-\Omega_{J\lambda\Pi})}[(J-1)/2+\mu]![(J-1)/2-\mu]! \sum_{k_1k_2u_1u_2} (k_1!k_2!u_1!u_2!)^{-1}[\cos(\pi/4-\theta)]^{k_1+u_2} \times [\sin(\pi/4-\theta)]^{k_2+u_1} \quad (7.16)$$

and

$$W^{\Pi n_\Pi L_\Pi\, J\alpha}_{\mu}(\theta) = (-1)^{\eta}(\cos 2\theta)^{|L_\Pi/2-\mu|} \times \sum_{m=m_1}^{m_2} \binom{(J-1)/2+\alpha}{m+(1/2)(\alpha+\mu+\epsilon)} \binom{(J-1)/2-\alpha}{m-(1/2)(\alpha+\mu-\epsilon)} \frac{m!\Gamma(m+\epsilon+1/2)}{(\xi+m-J)!} \times \sum_{i=0}^{m} \frac{(-1)^i(\xi+i)!}{(m-i)!i!\Gamma(i+\epsilon+1/2)} \times (-1)^{\eta-J+m+\epsilon} P^{(J-m+i,\,|L_\Pi/2-\mu|)}_{\eta-J+m+\epsilon}(\cos 4\theta) \quad (7.17)$$

with the associated parameters defined by

$$k_1 + u_1 = (J-1)/2 + \mu \quad (7.18)$$

$$k_2 + u_2 = (J-1)/2 - \mu \quad (7.19)$$

$$k_1 + k_2 = (1/2)(J-1+\Omega_{J\lambda}) \quad (7.20)$$

$$u_1 + u_2 = (1/2)(J-1-\Omega_{J\lambda}) \quad (7.21)$$

$$\eta = (1/4)(n+J+1) - (1/2)(|L_\Pi/2-\mu|+\epsilon) \quad (7.22)$$

$$\xi = (1/4)(n+J+1) + (1/2)(|L_\Pi/2-\mu|+\epsilon) \quad (7.23)$$

Quantities ϵ and m_1 are still given by eqs 7.11 and 7.13, respectively. However, 2α is now expressed, for a given J, and all allowed values of n_Π and L_Π, by

$$2\alpha = -(J-1), -(J-3), \ldots, (J-1) \quad (7.24)$$

and m_2 is given by

$$m_2 = (1/2)(J-1-|\alpha-\mu|-\epsilon) \quad (7.25)$$

The remarks made in the paragraph after eq 7.14 are also applicable to this case in which J and n_Π have opposite parities.

As a particular case, we get from these expressions, for $J = 0$ (and except for a constant phase), the following previously known simple result[6]

$$G^{\Pi=0 n_\Pi L_\Pi\, J=0\ \alpha=0}_{\Omega_{J_\lambda}=0}(\theta) = (\cos 2\theta)^{|L_\Pi/2|} P^{(0,\,|L_\Pi|/2)}_{(1/4)(n_\Pi-|L_\Pi|)}(\cos 4\theta) \quad (7.26)$$

with n_Π and L_Π even, and $(1/4)(n_\Pi - |L_\Pi|)$ equal to a nonnegative integer.

7.2. GP Case. As stated in the last paragraph of Section 6, the central difference between the NGP and GP cases is: (a) For NGP: $s = 0$ and $L_{s\Pi}$ and $n_{s\Pi}$ have the same parity as Π. (b) For GP: $s = 1$ and $L_{s\Pi}$ and $n_{s\Pi}$ have the opposite parity of Π. As a result, all of the explicit NGP expressions for the G HH of Section 7.1 are **equally valid** for the GP case, but with L_Π and n_Π replaced by $L_{s\Pi}$ and $n_{s\Pi}$, respectively, and required to have the opposite parity of Π (i.e., $s = 1$ in eq 6.12). In addition, $L \geqslant J$. The powers of $\cos(\pi/4-\theta)$ and $\sin(\pi/4-\theta)$ in eqs 7.3 and 7.16 are still nonnegative integers in the GP case. For example, for $J = 0$, (eq 7.26) is still valid with this replacement. However, because for this case the only allowed parity is $\Pi = 0$ (because the $D^{J\Pi}_{M_J\Omega_{J_\lambda}}$ of eq 6.4 is now independent of a_λ, b_λ, and c_λ), the only allowed values of $L_{s\Pi}$ and $n_{s\Pi}$ are odd. As a result, the multiplicative factor for the Jacobi polynomial in that expression is a half-odd-integer power of $\cos 2\theta$, resulting in a G HH that is no longer a homogeneous polynomial of degree n in the two variables $x = \cos\theta$ and $y = \sin\theta$ and an F HH that is no longer that kind of a polynomial in the space-fixed Cartesian coordinates $x^{(1)}_\lambda$, $y^{(1)}_\lambda$, $z^{(1)}_\lambda$, $x^{(2)}_\lambda$, $y^{(2)}_\lambda$, $z^{(2)}_\lambda$ of the two Jacobi vectors $\mathbf{r}^{(1)}_\lambda$ and $\mathbf{r}^{(2)}_\lambda$ as stated, for arbitrary J, after eq 6.12.

8. Summary and Conclusions

Hyperspherical harmonics (HH) in democratic row-orthonormal hyperspherical coordinates (ROHC) are eigenfunctions of the grand-canonical angular momentum operator, $\hat{\Lambda}^2$, and therefore of the hyperangular part of the kinetic energy operator for N atom systems, and behave regularly at the poles of that kinetic energy operator. In addition, they are independent of the system's hyperradius. As such, they are excellent basis functions for expanding the time-independent scattering wave functions, once they are known. We have shown how to incorporate the geometric phase (GP) effect into these functions for triatomic and tetraatomic systems and have given explicit analytical expressions for the HH for triatomic systems for arbitrary values of the total angular momentum quantum number. These triatomic HH expressions are somewhat complicated but easily programmable, and the associated computational effort is negligible compared to the computation time required for propagation of the scattering equations. They are expressed in terms of powers of $\sin\theta$, $\cos\theta$, and $\cos 2\theta$ and of Jacobi polynomials of $\cos 4\theta$, where θ is the principal moment of inertia hyperangle, which is invariant under arrangement channel coordinate transformations. The difference between the triatomic NGP and GP HH expressions is minor (but very important). In both cases, the quantum numbers n of $\hat{\Lambda}^2$ and L of the principal moment of inertia internal angular momentum operator $\hat{L}$ have the same parity. For the NGP case that parity is the parity of Π, whereas for the GP case it is the opposite one. The coupling in the scattering equations using ROHC HH is entirely because of the system's potential energy function, V, because all Coriolis-coupling effects are incorporated into those HH. Use of their analytical expressions, both with and without inclusion of the geometric phase, should significantly simplify and accelerate reactive scattering calculations, both for triatomic and tetraatomic systems.

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