Analytical Derivation of Row-Orthonormal Hyperspherical Harmonics for Triatomic Systems†

Desheng Wang and Aron Kuppermann*

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

Received: July 9, 2009; Revised Manuscript Received: October 15, 2009

Hyperspherical harmonics for triatomic systems as functions of row-orthonormal hyperspherical coordinates, (also called democratic hyperspherical harmonics) are obtained explicitly in terms of Jacobi polynomials and trigonometeric functions. These harmonics are regular at the poles of the triatomic kinetic energy operator, are complete, and are not highly oscillatory. They constitute an excellent basis set for calculating the local hyperspherical surface functions in the strong interaction region of nuclear configuration space. This basis set is, in addition, numerically very efficient and should permit benchmark-quality calculations of state-to-state differential and integral cross sections for those systems. The approach used for their derivation is new and should be applicable to systems of more than three atoms.

1. Introduction

Quantum reaction dynamics is an important and active field whose state has been summarized in a number of reviews.[1−5] One of its main objectives is the calculation of state-to-state differential cross sections of electronically adiabatic elementary bimolecular reactions, as a function of scattering angle and energy, using ab initio methods. This can be accomplished by two complementary but distinct approaches. One is to solve the nuclear motion time-dependent Schrödinger equation using an initial wave packet covering a spread of relative translational energies but only one rovibrational state of the reagents at a time. The other is to solve the nuclear motion time-independent Schrödinger equation for one total energy at a time, but including all possible open rovibrational states of the reagents simultaneously. These two approaches have different computational characteristics, and one or the other is chosen, depending on the objectives of the calculation. They have been used extensively for studying reactions in triatomic systems and, to a more limited extent, tetraatomic systems. The latter are computationally much more challenging because of the larger number of degrees of freedom and quantum states involved.

In this paper, we focus attention on the time-independent approach, and in particular the use of row-orthonormal hyperspherical harmonics (ROHH) for solving the corresponding Schrödinger equation. The general theory has been described previously.[6] It is based on the use of row-orthonormal hyperspherical coordinates (ROHC)[7−9] to describe the strong interaction region of configuration space. These kinds of coordinates have been labeled "democratic" by Whitten and Smith,[10] as they span that space "democratically", without favoring any one arrangement channel over another. This is an important property for the description of chemical reactions among any subsets of atoms of the system. For a system of N atoms, after the motion of the center of mass is removed, the Hamiltonian depends on a hyperradius ρ and $3N - 4$ angles. A difficulty associated with these angles is that the corresponding kinetic energy operator has angular poles for special configurations of the system, as is generally the case for any system of angular coordinates. The scattering wave function must behave regularly at those poles. To achieve this property, we expand it in a basis set of local hyperspherical surface functions (LHSF) which are eigenfunctions of the system's Hamiltonian at a fixed value of ρ, and of the square $\hat{J}^2$ of the total angular momentum operator $\hat{J}$, of its space-fixed z component $\hat{J}_z^{\mathrm{sf}}$ and of the operator $\hat{O}_{\mathscr{I}}$ associated with the inversion $\hat{\mathscr{I}}$ of the system through its center of mass. The angular poles of this surface Hamiltonian are the same as those of the total Hamiltonian. We now define the F ROHH as the eigenfunctions F of the grand canonical angular momentum operator $\hat{\wedge}^2$ and of additional operators that commute with it and that include $\hat{J}^2$, $\hat{J}_z^{\mathrm{sf}}$ and $\hat{O}_{\mathscr{I}}$. $\hat{\wedge}^2$ is a function of all the ROHC angles and also has the same angular poles as the system's Hamiltonian. The F harmonics are required to be regular at those poles and constitute a complete set of linearly independent functions of those angles. This regularity guarantees that the LHSF obtained by expansion in the F set will have this property, as will the scattering wave function obtained by expansion in the LHSF. As a result, the ROHH play a very important role in calculations using ROHC, for both reactive and bound state problems. It should be noted that ROHC and the associated harmonics can also be used in time-dependent calculations.[11]

A significant number of ab initio quantum-dynamical converged state-to-state integral and differential cross sections of triatomic systems have been performed using some version of hyperspherical coordinates and a propagation approach to solve the corresponding time-independent Schrödinger equation, a few of which are referred to here.[12−25] In addition, some bound state calculations have been performed.[26,27] In the latter, as well as in some of these scattering calculations, ROHH were used. However, no converged calculations of this kind have been reported for tetraatomic systems so far. An important constraint in the use of this methodology is the lack of explicit analytical expressions for the corresponding ROHH, which are easy to use and efficient to calculate. For triatomic systems, explicit ROHH were derived for the total angular momentum quantum number J equal to 0,[28] 1,[29,30] and 2.[30] In addition, several

† Part of the "Vincenzo Aquilanti Festschrift".

* To whom correspondence should be sent. E-mail address: aron@caltech.edu.

10.1021/jp906473n CCC: $40.75
Published on Web 12/23/2009

approaches have been used for obtaining such ROHH for arbitrary values of J and of the grand canonical angular momentum quantum number n, having those ease and efficiency characteristics.[31−33] All of them almost achieve those characteristics, but each has some shortcoming. Wolniewicz's method[31] requires the numerical solution of an overdetermined set of equations by a weighted least-squares method. Mukhtarova and Efros' method[32] is completely analytical, but the resulting expressions for the ROHH involve cumbersome 4-fold summations. In addition, their approach seems to be limited to three-particle systems. The completely analytical method of Wang and Kuppermann,[33] based on the theory of harmonic polynomials,[34] uses a recursion relation that requires that, if a hyperspherical harmonic for a given J and n (which must satisfy the condition $0 \le J \le n$) are needed, the harmonics for all $J \le n$ must be obtained at the same time whether needed or not. Since the computational effort involved scales as n^4, this makes the method not be as efficient as desired, especially if the highest value of J to be used in a calculation is significantly smaller than the largest value of n required for convergence, as is frequently the case for reactive scattering calculations. Another approach, of Lepetit and co-workers,[27,35] that uses basis function expansions of the ROHH, is also partly numerical, and requires eigen solutions.

In the present paper we describe a completely analytical method to generate, for triatomic systems, ROHH that are simultaneous eigenfunctions of the four operators $\hat{O}_{\mathscr{G}}$, $\hat{\wedge}^2$, $\hat{J}$, and $\hat{J}_z^{\mathrm{sf}}$ defined above as well as of $\hat{L}$, which is an internal hyperangular momentum operator associated with one of the internal hyperangles. These harmonics are linearly independent and can be calculated, for any desired set of the corresponding quantum numbers, without requiring the calculation of harmonics for additional quantum numbers. This eliminates the inefficiency of the recursion method mentioned in the previous paragraph. In addition, this approach is generalizable to systems of more than 3 particles. In section 2 we describe those operators in greater detail and summarize the ROHC used and the corresponding Hamiltonian,[7] and in section 3 we define the associated hyperspherical harmonics. In section 4 we derive an analytical expression for these harmonics. Some representative results are presented in section 5, and a discussion is given in section 6. Finally, a summary and conclusions are given in section 7.

2. Coordinates and Kinetic Energy Operator

The ROHC used in this paper, as well as their properties, have been described previously[7−9] for N-particle systems, but we summarize them below for the sake of completeness. We consider the particular case of a system of three particles whose mass-scaled λ-arrangement-channel Jacobi vectors in a space-fixed frame $\mathrm{O}x^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ are $\mathbf{r}_\lambda^{(i)}$, $i = 1, 2$. The corresponding Jacobi matrix is defined as

$$\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = \begin{pmatrix} x_\lambda^{(2)} & x_\lambda^{(1)} \\ y_\lambda^{(2)} & y_\lambda^{(1)} \\ z_\lambda^{(2)} & z_\lambda^{(1)} \end{pmatrix} \tag{2.1}$$

The 6 ROHC

$$\gamma_\lambda \equiv (\rho, \boldsymbol{\Theta}_\lambda^{\mathrm{bf}}) \tag{2.2}$$

where $\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}$ represents the 5 body-fixed angles

$$\boldsymbol{\Theta}_\lambda^{\mathrm{bf}} \equiv (\mathbf{a}_\lambda, \theta, \delta_\lambda) \tag{2.3}$$

are defined by the relation

$$\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = \tilde{\mathbf{R}}(\mathbf{a}_\lambda)\, \rho \mathbf{N}(\theta)\, \mathbf{Q}(\delta_\lambda) \tag{2.4}$$

In this expression, $\mathbf{a}_\lambda \equiv (a_\lambda, b_\lambda, c_\lambda)$ are the Euler angles that rotate the space-fixed frame into the principal-axes-of-inertia body-fixed frame $\mathrm{O}x^{I_\lambda}y^{I_\lambda}z^{I_\lambda}$. The quantity ρ is the usual hyperradius which, together with the two internal hyperangles θ and δ_λ, determine the internal configuration of the system. The $\mathbf{R}$ in eq 2.4 is the proper orthogonal 3×3 matrix associated with that rotation, and $\mathbf{N}(\theta)$ is a 3×3 diagonal matrix whose diagonal elements are

$$N_{11} = \sin\theta \quad N_{22} = 0 \quad N_{33} = \cos\theta \tag{2.5}$$

Finally, $\mathbf{Q}(\delta_\lambda)$ is the 3×2 row-orthogonal matrix

$$\mathbf{Q}(\delta_\lambda) = \begin{pmatrix} \cos\delta_\lambda & \sin\delta_\lambda \\ 0 & 0 \\ -\sin\delta_\lambda & \cos\delta_\lambda \end{pmatrix} \tag{2.6}$$

The Euler angles $\mathbf{a}_\lambda$ have the usual ranges of definition

$$0 \le a_\lambda, c_\lambda < 2\pi \quad 0 \le b_\lambda \le \pi \tag{2.7}$$

To obtain a one-to-one correspondence between $\boldsymbol{\rho}_\lambda^{\mathrm{sf}}$ and the 6 ROHC (except for some special geometries), we limit the range of δ_λ to

$$0 \le \delta_\lambda < \pi \tag{2.8}$$

and of θ to

$$0 \le \theta \le \pi/4 \tag{2.9}$$

The latter results in

$$N_{22} \le N_{11} \le N_{33} \tag{2.10}$$

The hyperangle θ is related to the system's principal moments of inertia I_1, I_2, and I_3 by

$$I_1 = \mu\rho^2 N_{33}{}^2 = \mu\rho^2 \cos^2\theta \tag{2.11}$$

$$I_2 = \mu\rho^2 \tag{2.12}$$

$$I_3 = \mu\rho^2 N_{11}{}^2 = \mu\rho^2 \sin^2\theta \tag{2.13}$$

and, as a result of eq 2.10, are ordered according to

$$I_2 \ge I_1 \ge I_3 \ge 0 \tag{2.14}$$

In terms of these ROHC, the kinetic energy operator is given by

$$\hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 = \hat{T}_\rho(\rho) + \frac{\hat{\wedge}^2}{2\mu\rho^2} \tag{2.15}$$

where ∇^2 is the system's mass-scaled 6-dimensional Laplacian, $\hat{\wedge}^2$ is the grand-canonical hyperangular momentum operator

$$\hat{\wedge}^2 = \frac{1}{\cos^2\theta}\hat{J}_x^{I_\lambda 2} + \frac{1}{\cos^2 2\theta}\hat{J}_y^{I^2} + \frac{1}{\sin^2\theta}\hat{J}_z^{I_\lambda 2} + \frac{1}{\cos^2 2\theta}\hat{L}^2 + \hat{K}^2 - 2\frac{\sin 2\theta}{\cos^2 2\theta}\hat{L}\hat{J}_y^{I} - 4i\hbar\cot 4\theta\hat{K} \tag{2.16}$$

$\hat{T}_\rho(\rho)$ is the hyperradial kinetic energy operator

$$\hat{T}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} \tag{2.17}$$

and $\hat{K}$ and $\hat{L}$ are internal hyperangular momentum operators defined by

$$\hat{K} = \frac{\hbar}{i}\frac{\partial}{\partial\theta} \tag{2.18}$$

and

$$\hat{L} = \frac{\hbar}{i}\frac{\partial}{\partial\delta_\lambda} \tag{2.19}$$

The $\hat{J}_x^{I_\lambda}$, $\hat{J}_y^{I}$, and $\hat{J}_z^{I_\lambda}$ operators in eq 2.16 are the components of the nuclear motion orbital angular momentum operator $\hat{\boldsymbol{J}}$ in the body-fixed frame $Ox^{I_\lambda}y^{I_\lambda}z^{I_\lambda}$ and are explicit functions of the Euler angles $\mathbf{a}_\lambda$.[7]

A very important property of the ROHC is that each one of the 7 terms in eq 2.16 as well as the $\hat{T}_\rho(\rho)$ of eq 2.17 are invariant under a $\lambda \rightarrow \nu$ change in Jacobi coordinates,[7] called a kinematic rotation.[10,36] This property is an additional justification for the designation of "democratic" for these coordinates.

The grand-canonical hyperangular momentum operator of eq 2.16, and therefore the kinetic energy operator of eq 2.15, has singularities at collinear configurations of the 3-particle system, corresponding to $\theta = 0$, and at configurations for which the two principal moments of inertia I_1 and I_3 are equal, corresponding to $\theta = \pi/4$, which are prolate symmetric top configurations. The collinear configuration poles can be taken care of by a simple choice of θ basis functions.[12] For many collinearly-dominated triatomic systems, the symmetric top singularity corresponds to high-energy regions of the potential energy surface and does not pose special problems at low energies. However, for noncollinearly-dominated triatomic systems, this singularity is, in general, not located in such regions and can result in convergence difficulties for the most common quadrature or basis set expansion methods, including DVR methods, even for low energies. In the present paper, we develop a set of analytical basis functions which overcome these problems, at both low and high energies.

3. Row-Orthonormal (Democratic) Hyperspherical Harmonics

As described previously,[33] the five operators $\hat{\wedge}^2$, $\hat{J}^2$, $\hat{J}_z^{sf}$, $\hat{L}$, and $\hat{O}_{\mathscr{I}}$ commute with each other. $\mathscr{I}$ is the operator which inverts the system through its center of mass,

$$\mathscr{I}\boldsymbol{\rho}_\lambda^{sf} = -\boldsymbol{\rho}_\lambda^{sf} \tag{3.1}$$

and $\hat{O}_{\mathscr{I}}$ the associated operator which acts on functions of $\boldsymbol{\rho}_\lambda^{sf}$. Since $\hat{\mathscr{I}}$ acts on the ROHC of eqs 2.2 and 2.3 according to

$$\hat{\mathscr{I}}(a_\lambda,b_\lambda,c_\lambda,\rho,\theta,\delta_\lambda) = ((\pi + a_\lambda) \bmod 2\pi, \pi - b_\lambda, (\pi - c_\lambda) \bmod 2\pi, \rho, \theta, \delta_\lambda) \tag{3.2}$$

both θ and δ_λ are unchanged under inversion. Let $F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf})$ be the simultaneous normalized eigenfunctions of those five operators:

$$\hat{\wedge}^2 F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) = n_\Pi(n_\Pi + 4)\hbar^2 F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) \tag{3.3}$$

$$\hat{J}^2 F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) = J(J + 1)\hbar^2 F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) \tag{3.4}$$

$$\hat{J}_Z^{sf} F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) = M_J\hbar F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) \tag{3.5}$$

$$\hat{L} F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) = L_\Pi\hbar F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) \tag{3.6}$$

$$\hat{O}_{\mathscr{I}} F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) = (-1)^\Pi F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}_\lambda^{bf}) \tag{3.7}$$

where $d = 1, ..., D$, and D is the number of linearly independent F functions having the same values of the 5 quantum numbers Π, n_Π, L_Π, J, and M_J.[33] This notation differs from that of ref 33 as we have dropped the superscript D from F. Such a modified notation is more convenient for the propose of the present paper. These F functions are orthogonal with respect to Π, n_Π, L_Π, J, and M_J but not necessarily with respect to d. If desired, they can be orthogonalized with respect to that index by a Gram–Schmidt procedure. In either case, they are required to be regular at the poles of $\hat{\wedge}^2$. Those quantum numbers are all integers, satisfying the constraints

$$n_\Pi \geq 0 \quad 0 \leq J \leq n_\Pi \tag{3.8}$$

$$-J \leq M_J \leq J \quad -n_\Pi \leq L_\Pi \leq n_\Pi \tag{3.9}$$

$$\Pi = 0, 1 \tag{3.10}$$

with n_Π and L_Π having the same parity as Π. As has been proven previously[33] and will be proven by a different method in section 4.6, the degeneracy D depends on Π, n_Π, J, and L_Π but is independent of M_J, and an explicit expression for this dependence will be given in eqs 4.81 and 4.82. The five operators being considered are all independent of the choice of arrangement channel coordinates λ and, therefore, so are the corresponding quantum numbers Π, n_Π, J, M_J, and L_Π, as well as D. The solution of eqs 3.3–3.7 can be written as

$$F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda) = N^{\Pi n_\Pi L_\Pi J}_{d}\, e^{iL_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D^{J}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) \quad (3.11)$$

where $N^{\Pi n_\Pi L_\Pi J}_{d}$ is a real positive normalization constant.

Both the F and G functions of eq 3.11 are called row-orthonormal (ROHH) or democratic (DHH) hyperspherical harmonics. The presence of the Wigner rotation functions $D^{J}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$[37] and of $e^{iL_\Pi\delta_\lambda}$ guarantees that eq 3.11 will satisfy eqs 3.4−3.7. Replacement into eq 3.3 results in a set of coupled partial differential equations for the functions G. These equations do not contain M_J,[33] and therefore, the G (and as a result the normalization constants N) are independent of that quantum number. This independence is a consequence of the fact that $\hat{\wedge}^2$ is invariant under both space and kinematic rotations. The degeneracy D also represents the number of linearly independent sets of functions $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}$, each set corresponding to a given Π, n_Π, L_Π, and J and spanned by the quantum number Ω_{J_λ}. Although D depends on the parity quantum number Π, it does not itself have parity Π. Regardless of whether Π is 0 or 1, D can be an even or an odd integer (see section 4.6).

It should be noted that linear combinations the D $F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ ($d = 1, 2, ..., $ D) functions, for a given set of Π, n_Π, L_Π, J, and M_J quantum numbers, are also solutions of eqs 3.3−3.7. If a complete linearly independent set of such linear combinations is used, and the resulting functions are normalized using real positive normalization constants, we obtain a different set $F'^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ ($d' = 1, 2, ..., $ D) of normalized solutions to those equations, and therefore, such equations do not determine the F functions uniquely. Nevertheless, the F and F' functions are equivalent basis for expanding general functions of $\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda$. This matter will be revisited in section 5.4.

We associate to the G functions (which are non-normalized over θ and can be complex), the real functions $\bar{g}$ and g defined by

$$\bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) = e^{i(J-\Omega_{J_\lambda})\pi/2} G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) \quad (3.12)$$

and

$$g^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) = N^{\Pi n_\Pi L_\Pi J}_{d}\, \bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) \quad (3.13)$$

An important property of the G, g, and $\bar{g}$ functions is their parity with respect to the quantum number Ω_{J_λ}, which is given by[33]

$$G^{\Pi n_\Pi L_\Pi J}_{-\Omega_{J_\lambda} d}(\theta) = (-1)^{\Pi+J+\Omega_{J_\lambda}} G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) \quad (3.14)$$

and

$$\bar{g}^{\Pi n_\Pi L_\Pi J}_{-\Omega_{J_\lambda} d}(\theta) = (-1)^{\Pi+J} \bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} d}(\theta) \quad (3.15)$$

with a similar relation holding for the g functions. The volume element associated with the body-fixed angular coordinates $\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda$ is

$$d\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda = \frac{1}{4}\sin 4\theta\, d\theta\, d\delta_\lambda \sin b_\lambda\, da_\lambda\, db_\lambda\, dc_\lambda \quad (3.16)$$

Using a recursion relation approach and a symbolic algebra code, we have previously[33,38] developed a method for obtaining, for a given Π and n_Π, a complete set of linearly independent solutions of eqs 3.3−3.7 for all possible values of J, M_J, and L_Π satisfying eqs 3.8−3.10. In the rest of this paper we will denote this particular set of solutions as F_{rec} and the corresponding G that appear in eq 3.11 by G_{rec}, the subscript standing for recursion. These G_{rec} functions are unique; i.e., $F^{\Pi n_\Pi L_\Pi J}_{M_J d}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ and $N^{\Pi n_\Pi L_\Pi J}_{d}$ were chosen in a specific way.

We will now introduce another particular complete set of F functions having a degeneracy index σ_Π, rather than d. This index is defined in eq 4.23, and the reason for this particular choice will become apparent in section 4.3.

These new $F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ functions also satisfy eqs 3.3−3.7 and can be put in the form of eq 3.11, with d replaced by σ_Π. This new expression defines the $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ functions. We will obtain, in eqs 4.76 and 4.69, an explicit analytical expression for these new G functions in terms of σ_Π. As a result, σ_Π acquires characteristics of a fifth quantum number. The number of allowed values of σ_Π is the same as that of d in eq 3.11 and is equal to D (Π, n_Π, J, L_Π). As will be shown in section 4.6 those allowed values of σ_Π are given by eq 4.83. It is important to notice that the angle θ is invariant under the inversion operator $\hat{\mathscr{I}}$, and therefore, the functions $\hat{O}_{\mathscr{I}} G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, $\hat{O}_{\mathscr{I}} g^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, and $\hat{O}_{\mathscr{I}} \bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ are equal, respectively, to $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, $g^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, and $\bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, However, the superscipt Π in these functions does not mean that $\Pi = 0$, since Π refers to the parity of the associated $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ function under such inversion.

4. Analytical Derivation of the Row-Orthonormal (Democratic) Hyperspherical Harmonics

4.1. Space-Fixed Hyperspherical Coordinates and Harmonics. Let $r^{(i)}_\lambda$, $\theta^{(i)}_\lambda$, $\phi^{(i)}_\lambda$ ($i = 1, 2$) be the space-fixed polar coordinates of the mass-scaled λ-arrangement-channel Jacobi coordinates $\mathbf{r}^{(i)}_\lambda$ introduced in section 2. It is convenient to replace the variables $r^{(1)}_\lambda$ and $r^{(2)}_\lambda$ by the hyperradius ρ and hyperangle η_λ defined by the relations

$$r^{(1)}_\lambda = \rho \sin \eta_\lambda \quad (4.1)$$

$$r^{(2)}_\lambda = \rho \cos \eta_\lambda \quad (4.2)$$

and limited to the ranges

$$\rho \geq 0 \qquad 0 \leq \eta_\lambda \leq \pi/2 \quad (4.3)$$

Let

$$\boldsymbol{\Theta}^{\mathrm{sf}}_\lambda \equiv (\theta^{(1)}_\lambda, \phi^{(1)}_\lambda, \theta^{(2)}_\lambda, \phi^{(2)}_\lambda, \eta_\lambda) \quad (4.4)$$

designate the five space-fixed angles. The 6 coordinates ρ, $\boldsymbol{\Theta}^{\mathrm{sf}}_\lambda$ are called the space-fixed hyperspherical coordinates. The volume element associated with $\boldsymbol{\Theta}^{\mathrm{sf}}_\lambda$ is

$$d\boldsymbol{\Theta}^{\mathrm{sf}}_\lambda = \sin\theta^{(1)}_\lambda\, d\theta^{(1)}_\lambda\, d\phi^{(1)}_\lambda \sin\theta^{(2)}_\lambda\, d\theta^{(2)}_\lambda\, d\phi^{(2)}_\lambda \sin^2\eta_\lambda \cos^2\eta_\lambda\, d\eta_\lambda \quad (4.5)$$

In terms of $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}$, $\hat{\wedge}^2$ is given by

$$\hat{\wedge}^2 = -\frac{\hbar^2}{\sin^2 2\eta_\lambda}\frac{\partial}{\partial\eta_\lambda}\sin^2 2\eta_\lambda\frac{\partial}{\partial\eta_\lambda} + \frac{\hat{l}_\lambda^{(1)^2}}{\sin^2\eta_\lambda} + \frac{\hat{l}_\lambda^{(2)^2}}{\cos^2\eta_\lambda} \tag{4.6}$$

where $\hat{l}_\lambda^{(i)^2}$ $(i = 1, 2)$ is the square of the angular momentum operator associated with $\boldsymbol{r}_\lambda^{(i)}$ and is given by

$$\hat{l}_\lambda^{(i)2} = -\frac{\hbar^2}{\sin\theta_\lambda^{(i)}}\frac{\partial}{\partial\theta_\lambda^{(i)}}\sin\theta_\lambda^{(i)}\frac{\partial}{\partial\theta_\lambda^{(i)}} + \frac{\hat{l}_{z_\lambda}^{(i)^2}}{\sin^2\theta_\lambda^{(i)}}$$
$$\hat{l}_{z_\lambda}^{(i)} = \frac{\hbar}{i}\frac{\partial}{\partial\phi_\lambda^{(i)}} \tag{4.7}$$

The six operators $\hat{\wedge}^2$, $\hat{J}^2$, $\hat{J}_z^{\mathrm{sf}}$, $\hat{l}_\lambda^{(1)^2}$, $\hat{l}_\lambda^{(2)^2}$, and $\hat{O}_{\mathscr{I}}$ commute with each other. Their simultaneous eigenfunctions $\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\Theta_\lambda^{\mathrm{sf}})$are called the space-fixed hyperspherical harmonics. They satisfy

$$\hat{\wedge}^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = n_\Pi(n_\Pi + 4)\hbar^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.8}$$

$$\hat{J}^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = J(J+1)\hbar^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.9}$$

$$\hat{J}_z^{\mathrm{sf}}\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = M_J\hbar^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.10}$$

$$\hat{l}_\lambda^{(1)1}\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = l_\lambda^{(1)}(l_\lambda^{(1)}+1)\hbar^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.11}$$

$$\hat{l}_\lambda^{(2)2}\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = l_\lambda^{(2)}(l_\lambda^{(2)}+1)\hbar^2\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.12}$$

$$\hat{O}_{\mathscr{I}}\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = (-1)^\Pi\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) \tag{4.13}$$

The six quantum numbers Π, n_Π, J, M_J, $l_\lambda^{(1)}$, and $l_\lambda^{(2)}$ are all integers. The first one satisfies eq 3.10, the next three satisfy eq 3.8 and the first of eq 3.9, and the last two are non-negative and satisfy the triangle inequality

$$|l_\lambda^{(1)} - l_\lambda^{(2)}| \le J \le l_\lambda^{(1)} + l_\lambda^{(2)} \tag{4.14}$$

The eigen functions $\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})$ are furthermore required to be regular at the poles of all of those operators.

As is well-known,[39] the simultaneous solution of eqs 4.9−4.12 is

$$Y_{l_\lambda^{(1)}l_\lambda^{(2)}}^{JM_J}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) = \sum_{m_\lambda^{(1)}} C(l_\lambda^{(1)},l_\lambda^{(2)},J;m_\lambda^{(1)},M_J-m_\lambda^{(1)},M_J)\times Y_{m_\lambda^{(1)}}^{l_\lambda^{(1)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\,Y_{M_J-m_\lambda^{(1)}}^{l_\lambda^{(2)}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}) \tag{4.15}$$

where $Y_{m_\lambda^{(i)}}^{l_\lambda^{(i)}}(\theta_\lambda^{(i)},\phi_\lambda^{(i)})$ $(i = 1, 2)$ is the usual spherical harmonics[40] and the C are the Clebsch−Gordan coefficients. Replacing this result into eq 4.8 and using eq 4.13 leads to the expression[41,42]

$$\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = N_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi}\sin^{l_\lambda^{(1)}}\eta_\lambda\cos^{l_\lambda^{(2)}}\eta_\lambda Y_{l_\lambda^{(1)}l_\lambda^{(2)}}^{JM_J}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)})\times P_{\xi_\lambda}^{(l_\lambda^{(1)}+1/2,l_\lambda^{(2)}+1/2)}(\cos 2\eta_\lambda) \tag{4.16}$$

where

$$\xi_\lambda = (n_\Pi - l_\lambda^{(1)} - l_\lambda^{(2)})/2 \tag{4.17}$$

and $P_{\xi_\lambda}^{(\alpha,\beta)}$ is a Jacobi polynomial of order ξ_λ.[43] In addition, n_Π has, as stated after eq 3.10, the same parity as Π. Since ξ_λ must be a non-negative integer, $l_\lambda^{(1)} + l_\lambda^{(2)}$ must also have that parity. The normalization constant $N_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi}$ is given by[41]

$$N_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi} = \left\{\frac{2(n_\Pi+2)[(n_\Pi - l_\lambda^{(1)} - l_\lambda^{(2)})/2]![(n_\Pi + l_\lambda^{(1)} + l_\lambda^{(2)})/2]!}{\Gamma[(n_\Pi + l_\lambda^{(1)} - l_\lambda^{(2)} + 3)/2]\Gamma[(n_\Pi - l_\lambda^{(1)} + l_\lambda^{(2)} + 3)/2]}\right\}^{1/2} \tag{4.18}$$

Since the number of angular degrees of freedom in $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}$ is five and since there are also five independent angular quantum numbers, namely n_Π, J, M_J, $l_\lambda^{(1)}$, and $l_\lambda^{(2)}$, the functions $\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})$ are nondegenerate and constitute a complete orthonormal set of functions that span the $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}$ space.

4.2. Relation between the Space-Fixed and Body-Fixed Hyperspherical Harmonics. Let $\{\Phi^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})\}$ be the set of $\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})$ functions for fixed Π, n_Π, J, and M_J spanned by all distinct pairs of $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ permitted by the triangle inequality eq 4.14. The functions in this set are linearly independent and constitute a set of simultaneous eigenfunctions of $\hat{\wedge}^2$, $\hat{J}^2$, $\hat{J}_z$, and $\hat{O}_{\mathscr{I}}$ corresponding to those four quantum numbers. Similarly, let $\{F^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})\}$ be the set of normalized $F_{M_J\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$ functions, defined at the end of section 3, for fixed values of the same Π, n_Π, J, and M_J quantum numbers and spanned by all distinct L_Π, σ_Π pairs with the L_Π having the values given by the second of eqs 3.9 and σ_Π having the D values given by eq 4.83. They are also linearly independent and constitute a complete orthonormal set of simultaneous eigenfunctions of the same four operators just mentioned with the same values of their four quantum numbers. As a result, these two sets contain the same number of functions and are related by a linear transformation according to

$$\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = \sum_{L_\Pi=-n_\Pi,2}^{n_\Pi}\sum_{\sigma_\Pi}(C^{\Pi n_\Pi J})_{l_\lambda^{(1)}l_\lambda^{(2)}}^{L_\Pi\sigma_\Pi}F_{M_J\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}) \tag{4.19}$$

where the sum over L_Π is in steps of 2 because of parity considerations. In addition, if the $F_{M_J\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$ functions are also required to be orthogonal with respect to the degeneracy σ_Π the transformation eq 4.19 is unitary.[44]

As shown in Appendix A, the C coefficients in the right-hand side (rhs) of eq 4.19 are independent of M_J, in spite of the fact that this quantum number appears in both sides of that equation. The $\Phi_{l_\lambda^{(1)}l_\lambda^{(2)}}^{\Pi n_\Pi JM_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})$ functions are known and are explicitly given by eq 4.16. From this knowledge, and the use of eq 4.19, we wish to determine all of the $F_{M_J\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$. This is equivalent to determining all of the $G_{\Omega_{J_\lambda}\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\theta)$ functions appearing in the

σ_Π counterpart of eq 3.11, and the associated normalization constants. Such a procedure entails two steps. In the first we change the angular variables $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}$ appearing in the left-hand side (lhs) of eq 4.19 to $\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}$. The second involves putting the resulting $\Phi(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})$ in the form given by the rhs of eq 4.19, with F having the form given by the rhs of the σ_Π counterpart of eq 3.11. This approach is appropriate whether or not the F functions are orthogonal with respect to σ_Π. This methodology requires, for given Π, n_Π, J, and M_J, that we consider all $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ pairs simultaneously, and although conceptually correct, it is algebraically laborious. An alternative is to utilize the fact that the F functions in the rhs of eq 4.19 are independent of $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$. Therefore, it may be possible to find a special $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ pair from which the $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$ and $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$ for all allowed L_Π, σ_Π can be determined. It is shown in section 4.3 that such an optimal $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ pair does indeed exist and that, as a result, the necessary algebraic effort to determine these F functions is greatly decreased. In section 4.5 we use this approach to derive an explicit expression for the G functions.

4.3. Selection of an Optimal $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ Quantum Number Pair. Let us first define the σ_Π-independent $\bar{F}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} M_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}})$ functions by

$$\bar{F}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} M_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}) = \sum_{\sigma_\Pi} (C^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}} F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}) \tag{4.20}$$

It is straightforward to verify that the $\bar{F}$ are also hyperspherical harmonics, i.e., are simultaneous eigenfunctions of the five operators involved in eqs 3.3−3.7. Although the F functions are normalized, the $\bar{F}$ are not. The latter can therefore be written in a form similar to eq 3.11,

$$\bar{F}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} M_J}(\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}) = e^{iL_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) \bar{G}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} \Omega_{J_\lambda}}(\theta) \tag{4.21}$$

where the normalization constant has been omitted. With the help of the last two expressions, eq 4.19 can be rewritten as

$$\Phi^{\Pi n_\Pi JM_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}) = \sum_{L_\Pi=-n_\Pi,2}^{n_\Pi} \sum_{\Omega_{J_\lambda}=-J}^{J} e^{iL_\Pi \delta_\lambda} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, \bar{G}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} \Omega_{J_\lambda}}(\theta) \tag{4.22}$$

We now wish to carefully select a particular pair of values of $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$, and the corresponding $\Phi^{\Pi n_\Pi JM_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ and $\bar{G}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)} \Omega_{J_\lambda}}$ so as to obtain from them a complete set of $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}$ functions (which were defined in the last paragraph of section 3). To this effect we define the integer σ_Π by

$$\sigma_\Pi = l_\lambda^{(2)} - l_\lambda^{(1)} \tag{4.23}$$

As stated after eq 4.17, $l_\lambda^{(1)} + l_\lambda^{(2)}$ has parity Π; as a result, σ_Π also has that parity. As will be shown in section 4.4, we may restrict the values of σ_Π to being non-negative. In addition, as demonstrated at the end of section 4.6, these values are independent of the choice of arrangement channel λ.

Since $l_\lambda^{(1)}$, $l_\lambda^{(2)}$, and σ_Π are related by eq 4.23, let us consider $l_\lambda^{(1)}$ and σ_Π to be independent quantities and $l_\lambda^{(2)}$ a function of them. For a given Π and J, replacement of eq 4.23 in eq 4.14 furnishes the following constraints on σ_Π and $l_\lambda^{(1)}$:

$$|\sigma_\Pi| \le J \tag{4.24}$$

$$l_\lambda^{(1)} \ge \frac{J - \sigma_\Pi}{2} \tag{4.25}$$

The equality sign in these two expressions can only hold if J and σ_Π, or equivalently, J and Π, have the same parity. Therefore, the minimum value that $l_\lambda^{(1)}$ can have, for a given J, Π, and σ_Π (regardless of the value of n_Π) is independent of λ and is given by

$$l_{\min}^{(1)}(\Pi,J,\sigma_\Pi) = \frac{J - \sigma_\Pi + b_{J+\Pi}}{2} \tag{4.26}$$

where

$$b_{J+\Pi} = \frac{1-(-1)^{J+\Pi}}{2} = \begin{cases} 0 & \text{for } J+\Pi \text{ even} \\ 1 & \text{for } J+\Pi \text{ odd} \end{cases} \tag{4.27}$$

The corresponding $l_{\min}^{(2)}$ (also for a given J, Π, and σ_Π) is

$$l_{\min}^{(2)}(\Pi,J,\sigma_\Pi) = l_{\min}^{(1)} + \sigma_\Pi = \frac{J + \sigma_\Pi + b_{J+\Pi}}{2} \tag{4.28}$$

and is also independent of λ. For subsequent use we define $L_{\min}$ as

$$L_{\min} = l_{\min}^{(1)} + l_{\min}^{(2)} \tag{4.29}$$

and notice that it is independent of σ_Π, has parity Π, and is given by

$$L_{\min}(\Pi,J) = J + b_{J+\Pi} = \begin{cases} J & \text{for } J+\Pi \text{ even} \\ J+1 & \text{for } J+\Pi \text{ odd} \end{cases} \tag{4.30}$$

In view of eq 4.23 and the fact that the ξ_λ of eq 4.17 is non-negative we must have, for a given Π, $l_\lambda^{(1)}$ and σ_Π,

$$n_\Pi \ge 2l_\lambda^{(1)} + \sigma_\Pi \tag{4.31}$$

Therefore, for a given $l_\lambda^{(1)}$ (and a given Π, J, and σ_Π), the smallest n_Π permitted is $2l_\lambda^{(1)} + \sigma_\Pi$. However, according to eq 3.8, all values of n_Π equal to or greater than $J + b_{J+\Pi}$ are permitted, regardless of the value of $l_\lambda^{(1)}$. As a result, for a choice of $l_\lambda^{(1)}$ not to exclude any permitted values of n_Π, it must satisfy

$$2l_\lambda^{(1)} + \sigma_\Pi \le J + b_{J+\Pi} \tag{4.32}$$

In view of eq 4.26 this relation furnishes

$$l_\lambda^{(1)} \le l_{\min}^{(1)} \tag{4.33}$$

Since $l_{\min}^{(1)}$ is the smallest value that $l_\lambda^{(1)}$ can have (for a given Π, J, and σ_Π), the **only** value of $l_\lambda^{(1)}$ satisfying this condition and eq 4.33 is $l_{\min}^{(1)}$. This means that to obtain the harmonics for all possible n_Π from a single $l_\lambda^{(1)}$ and fixed J, Π, and σ_Π, we must force that $l_\lambda^{(1)}$ to be the $l_{\min}^{(1)}$ of eq 4.26 and therefore the corresponding $l_\lambda^{(2)}$ to be the $l_{\min}^{(2)}$ of eq 4.28. The $\bar{G}$ functions that appear in the version of eqs 4.21 and 4.22 in which $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ is replaced by $l_{\min}^{(1)}$, $l_{\min}^{(2)}$ will depend only on Π, n_Π, L_Π, J, Ω_{J_λ}, and σ_Π. We will label these functions $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$, i.e.,

$$\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = \bar{G}^{\Pi n_\Pi L_\Pi J}_{l_{\min}^{(1)} l_{\min}^{(2)} \Omega_{J_\lambda}}(\theta) \tag{4.34}$$

and use a similar definition for the corresponding $\bar{F}^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\mathbf{\Theta}_\lambda^{\mathrm{bf}})$, which, as those defined by eq 4.21, are non-normalized hyperspherical harmonics. It must be remembered that $l_{\min}^{(1)}$ and $l_{\min}^{(2)}$ depend on Π, J, and σ_Π. We will obtain an explicit expression for these $\bar{G}$ functions in section 4.5.3. In addition, the allowed values of σ_Π (a subset of those satisfying eq 4.24 that lead to a complete set of linearly independent $\bar{F}$ harmonics) are determined in section 4.6 and are given (as stated at the end of section 3) by eq 4.83. The choice $l_\lambda^{(1)} = l_{\min}^{(1)}$ and $l_\lambda^{(2)} = l_{\min}^{(2)}$ is therefore an optimal one.

4.4. Parity of $\bar{G}$ with Respect to Ω_{J_λ} and σ_Π. To simplify the determination of the $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ functions of eq 4.34, it is convenient to restrict the values of Ω_{J_λ} and σ_Π to non-negative integers by relating the $\bar{G}$ for Ω_{J_λ} to that for $-\Omega_{J_\lambda}$ and $\bar{G}$ for σ_Π to that for $-\sigma_\Pi$. The parity of the $\bar{G}$ with respect to Ω_{J_λ} is the same as that of the G functions of eq 3.14, with d replaced by σ_Π. Therefore, the $\bar{G}$ are either symmetric or antisymmetric with respect to Ω_{J_λ} and it suffices to determine these functions for $\Omega_{J_\lambda} \geq 0$.

Let us now consider the $\mathbf{C}^{\Pi n_\Pi J}$ matrix defined by eqs 4.19 and A.1. The parity of $\bar{G}$ with respect to σ_Π stems from the relation between the matrix elements $(\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi\ \sigma_\Pi}_{l_\lambda^{(1)}\ l_\lambda^{(2)}}$ and $(\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi\ \sigma_\Pi}_{l_\lambda^{(2)}\ l_\lambda^{(1)}}$, where $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$ have been interchanged. As shown in Appendix B, that parity is given by

$$\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}-\sigma_\Pi}(\theta) = (-1)^{(n_\Pi - J + b_{J+\Pi})/2}\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{4.35}$$

Therefore, the $\bar{G}$ are also either symmetric or antisymmetric with respect to σ_Π and it suffices to determine them for $\sigma_\Pi \geq 0$. As mentioned at the end of section 4.3, the range of this index is given by eq 4.83.

4.5. Explicit Expression for the Body-Fixed Row-Orthonormal (Democratic) Hyperspherical Harmonics. Replacing $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ by $l_{\min}^{(1)}$, $l_{\min}^{(2)}$ in eq 4.22 and using the same change of notation as in eq 4.34, we obtain

$$\Phi^{\Pi n_\Pi J M_J}_{\sigma_\Pi}(\mathbf{\Theta}_\lambda^{\mathrm{sf}}) = \sum_{L_\Pi=-n_\Pi,2}^{n_\Pi} \sum_{\Omega_{J_\lambda}=-J}^{J} e^{iL_\Pi\delta_\lambda} D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{4.36}$$

Noticing that the $\bar{G}$ in the rhs of this expression is independent of M_J, we are free to set $M_J = J$ to determine that function:

$$\Phi^{\Pi n_\Pi J M_J=J}_{\sigma_\Pi}(\mathbf{\Theta}_\lambda^{\mathrm{sf}}) = \sum_{L_\Pi=-n_\Pi,2}^{n_\Pi} \sum_{\Omega_{J_\lambda}=-J}^{J} e^{iL_\Pi\delta_\lambda} D^J_{J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, \bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{4.37}$$

The lhs of this expression is a known function of $\mathbf{\Theta}_\lambda^{\mathrm{sf}}$ obtained from eq 4.16 by setting in it $M_J = J$, $l_\lambda^{(1)} = l_{\min}^{(1)}(\Pi,J,\sigma_\Pi)$, and $l_\lambda^{(2)} = l_{\min}^{(2)}(\Pi,J,\sigma_\Pi)$:

$$\Phi^{\Pi n_\Pi J M_J=J}_{\sigma_\Pi}(\mathbf{\Theta}_\lambda^{\mathrm{sf}}) = N^{\Pi n_\Pi}_{l_{\min}^{(1)} l_{\min}^{(2)}} \sin^{l_{\min}^{(1)}}\eta_\lambda \cos^{l_{\min}^{(2)}}\eta_\lambda Y^{JM_J=J}_{l_{\min}^{(1)} l_{\min}^{(2)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) \times P_\xi^{(l_{\min}^{(1)}+1/2,\, l_{\min}^{(2)}+1/2)}(\cos 2\eta_\lambda) \tag{4.38}$$

with the corresponding ξ_λ of eq 4.17 being independent of λ and given by

$$\xi = (n_\Pi - L_{\min})/2 \tag{4.39}$$

We now wish to change the variable $\mathbf{\Theta}_\lambda^{\mathrm{sf}}$ in the lhs of eq 4.38 to $\mathbf{\Theta}_\lambda^{\mathrm{bf}}$ and reexpress its rhs as a sum of products of $e^{iL_\Pi\delta_\lambda}$ and $D^J_{J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ functions. Once this is accomplished, identifying the coefficients of these products in both sides of eq 4.37 will give the desired explicit expression for $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$. This in turn will furnish the explicit expression for the $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ defined in the last paragraph of section 3.

4.5.1. Expression for $Y^{JM_J=J}_{l_{\min}^{(1)} l_{\min}^{(2)}}$ in Terms of $\mathbf{\Theta}_\lambda^{bf}$. The $Y^{JM_J=J}_{l_{\min}^{(1)} l_{\min}^{(2)}}$ that appear in the rhs of eq 4.38 can be obtained in terms of the space-fixed polar angles by setting $l_\lambda^{(1)} = l_{\min}^{(1)}$ and $l_\lambda^{(2)} = l_{\min}^{(2)}$ and $M_J = J$ in eq 4.15. The corresponding Clebsch−Gordan coefficients can be obtained explicitly with the help of eqs 4.26 and 4.28. The resulting expressions are

$$Y^{JM_J=J}_{l_{\min}^{(1)} l_{\min}^{(2)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) = Y^{l_{\min}^{(1)}}_{l_{\min}^{(1)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{l_{\min}^{(2)}}_{l_{\min}^{(2)}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}) \qquad \text{for } J + \Pi \text{ even} \tag{4.40}$$

$$Y^{JM_J=J}_{l_{\min}^{(1)} l_{\min}^{(2)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) = -\left(\frac{l_{\min}^{(2)}}{J+1}\right)^{1/2} Y^{l_{\min}^{(1)}}_{l_{\min}^{(1)}-1}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{l_{\min}^{(2)}}_{l_{\min}^{(2)}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}) + \left(\frac{l_{\min}^{(1)}}{J+1}\right)^{1/2} Y^{l_{\min}^{(1)}}_{l_{\min}^{(1)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{l_{\min}^{(2)}}_{l_{\min}^{(2)}-1}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}) \qquad \text{for } J + \Pi \text{ odd} \tag{4.41}$$

where $l_{\min}^{(1)}$ and $l_{\min}^{(2)}$ are functions of J, Π, and σ_Π. We now change from the space-fixed polar angles to the corresponding Cartesian coordinates using the relations obtained from explicit expressions for P_l^l and P_{l-1}^l:[45]

$$Y^{l_\lambda}_{l_\lambda}(\theta_\lambda^{(i)},\phi_\lambda^{(i)}) = N_{l_\lambda}\left(\frac{x_\lambda^{(i)} + iy_\lambda^{(i)}}{r_\lambda^{(i)}}\right)^{l_\lambda} \tag{4.42}$$

and

$$Y^{l_\lambda}_{l_\lambda-1}(\theta^{(i)}_\lambda,\phi^{(i)}_\lambda) = -(2l_\lambda)^{1/2} N_{l_\lambda} \frac{z^{(i)}_\lambda (x^{(i)}_\lambda + \mathrm{i}y^{(i)}_\lambda)^{l_\lambda - 1}}{r^{(i)l_\lambda}_\lambda} \tag{4.43}$$

where

$$N_{l_\lambda} = (-1)^{l_\lambda} \left\{ \frac{(2l_\lambda + 1)!!}{4\pi(2l_\lambda)!!} \right\}^{1/2} \tag{4.44}$$

and

$$n!! = n(n-2)\cdots \begin{cases} 2 & \text{for} \quad n \text{ even} \\ 1 & \text{for} \quad n \text{ odd} \end{cases} \tag{4.45}$$

With the help of the relations between the space-fixed Cartesian coordinates and the complex $T_{\lambda j}^{k}$ functions[33] defined in Appendix E by eqs E.1−E.6 we get

$$Y^{l^{(1)}_\lambda}_{l^{(1)}_\lambda}(\theta^{(1)}_\lambda,\phi^{(1)}_\lambda) = N_{l^{(1)}_\lambda} \left(\frac{T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1}}{2\mathrm{i}\rho \sin \eta_\lambda} \right)^{l^{(1)}_\lambda} \tag{4.46}$$

$$Y^{l^{(2)}_\lambda}_{l^{(2)}_\lambda}(\theta^{(2)}_\lambda,\phi^{(2)}_\lambda) = N_{l^{(2)}_\lambda} \left(\frac{T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1}}{2\rho \cos \eta_\lambda} \right)^{l^{(2)}_\lambda} \tag{4.47}$$

$$Y^{l^{(1)}_\lambda}_{l^{(1)}_\lambda-1}(\theta^{(1)}_\lambda,\phi^{(1)}_\lambda) = -\sqrt{l^{(1)}_\lambda}\, N_{l^{(1)}_\lambda} \frac{(T_{\lambda 1}^{\ 0} - T_{\lambda -1}^{\ \ 0})(T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1})^{l^{(1)}_\lambda - 1}}{(2\mathrm{i}\rho \sin \eta_\lambda)^{l^{(1)}_\lambda}} \tag{4.48}$$

$$Y^{l^{(2)}_\lambda}_{l^{(2)}_\lambda-1}(\theta^{(2)}_\lambda,\phi^{(2)}_\lambda) = -\sqrt{l^{(2)}_\lambda}\, N_{l^{(2)}_\lambda} \frac{(T_{\lambda 1}^{\ 0} + T_{\lambda -1}^{\ \ 0})(T_{\lambda 1}^{\ 1} + T_{\lambda -1}^{\ \ 1})^{l^{(2)}_\lambda - 1}}{(2\rho \cos \eta_\lambda)^{l^{(2)}_\lambda}} \tag{4.49}$$

It should be noticed that the $T_{\lambda j}^{k}$ are expressed in terms of the ROHC by eqs E.7−E.12 and therefore are of central importance for the $\mathbf{\Theta}^{\mathrm{sf}}_\lambda$ to $\mathbf{\Theta}^{\mathrm{bf}}_\lambda$ coordinate transformation. Replacing eqs 4.46−4.49 in eqs 4.40 and 4.41 results in

$$\begin{aligned} Y^{JM_J=J}_{l^{(1)}_{\min} l^{(2)}_{\min}}(\theta^{(1)}_\lambda,\phi^{(1)}_\lambda,\theta^{(2)}_\lambda,\phi^{(2)}_\lambda) &= \frac{N^{\Pi J \sigma_\Pi}}{(\rho \sin \eta_\lambda)^{l^{(1)}_{\min}} (\rho \cos \eta_\lambda)^{l^{(2)}_{\min}}} \times \\ &\begin{cases} (T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1})^{l^{(1)}_{\min}} (T_{\lambda 1}^{\ 1} + T_{\lambda -1}^{\ \ 1})^{l^{(2)}_{\min}} & \text{for} \quad J + \Pi \text{ even} \\ (T_{\lambda 1}^{\ 0} T_{\lambda -1}^{\ \ 1} - T_{\lambda -1}^{\ \ 0} T_{\lambda 1}^{\ 1})(T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1})^{l^{(1)}_{\min}-1} (T_{\lambda 1}^{\ 1} + T_{\lambda -1}^{\ \ 1})^{l^{(2)}_{\min}-1} & \text{for} \quad J + \Pi \text{ odd} \end{cases} \end{aligned} \tag{4.50}$$

where

$$N^{\Pi J \sigma_\Pi} = N_{l^{(1)}_{\min}} N_{l^{(2)}_{\min}} \left(\frac{1}{2i}\right)^{l^{(1)}_{\min}} \left(\frac{1}{2}\right)^{l^{(2)}_{\min}} \begin{cases} 1 & \text{for} \quad J + \Pi \text{ even} \\ \left(\dfrac{4 l^{(1)}_{\min} l^{(2)}_{\min}}{J + 1} \right)^{1/2} & \text{for} \quad J + \Pi \text{ odd} \end{cases} \tag{4.51}$$

An explicit expression for $(T_{\lambda 1}^{\ 1} - T_{\lambda -1}^{\ \ 1})^{l^{(1)}_\lambda} (T_{\lambda 1}^{\ 1} + T_{\lambda -1}^{\ \ 1})^{l^{(2)}_\lambda}$ in terms of the $\mathbf{\Theta}^{\mathrm{bf}}_\lambda$ angular variables is derived in Appendix E (see eq E.45). In addition $(T_{\lambda 1}^{\ 0} T_{\lambda -1}^{\ \ 1} - T_{\lambda -1}^{\ \ 0} T_{\lambda 1}^{\ 1})$ can be expressed in those variables using eq E.7:

$$(T_{\lambda 1}^{\ 0} T_{\lambda -1}^{\ \ 1} - T_{\lambda -1}^{\ \ 0} T_{\lambda 1}^{\ 1}) = -2\sqrt{2}\, \rho^2 \cos \theta \sin \theta \left(D^1_{11}\left(a_\lambda, b_\lambda, c_\lambda + \frac{\pi}{2}\right) - D^1_{1-1}\left(a_\lambda, b_\lambda, c_\lambda + \frac{\pi}{2}\right) \right) \tag{4.52}$$

With the help of eqs E.45 and 4.52, eq 4.50 can be written as

$$Y^{JM_J=J}_{l^{(1)}_{\min}l^{(2)}_{\min}}(\theta^{(1)}_\lambda,\phi^{(1)}_\lambda,\theta^{(2)}_\lambda,\phi^{(2)}_\lambda) = \frac{N^{\Pi J\sigma_\Pi}i^J}{(\sin\eta_\lambda)^{l^{(1)}_{\min}}(\cos\eta_\lambda)^{l^{(2)}_{\min}}}\sum_{L'=-L'_{\min},2}^{L'_{\min}} e^{iL'\delta_\lambda}\sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J=J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, p^{\Pi L_{\min}L'J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{4.53}$$

In eq 4.50, the rhs contains polynomials of degree $l^{(1)}_{\min} + l^{(2)}_{\min} = L_{\min}$ in the T variables for both $J + \Pi$ even and odd. Therefore, for $J + \Pi$ even, $L'_{\min} = L_{\min}$. However, for $J + \Pi$ odd, the factor $(T_{\lambda 1}{}^{0}T_{\lambda -1}{}^{1} - T_{\lambda -1}{}^{0}T_{\lambda 1}{}^{1})$ does not depend on δ_λ, as can be seen from eq 4.52, and as a result, $L'_{\min} = L_{\min} - 2$. Therefore,

$$L'_{\min} = L_{\min} - 2b_{J+\Pi} = J - b_{J+\Pi} \tag{4.54}$$

The summation index L' has the same parity Π as $L'_{\min}$ and as $L_{\min}(\Pi,J)$. The function $p^{\Pi L_{\min}L'J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ is

$$p^{\Pi L_{\min}L'J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = U^{(J-\sigma_\Pi-b_{J+\Pi})/2\ (J+\sigma_\Pi-b_{J+\Pi})/2}_{(L_{\min}-L'-2b_{J+\Pi})/2}\, h^{L_{\min}L'J}_{\Omega_{J_\lambda}}(\theta) \tag{4.55}$$

where

$$h^{L_{\min}L'J}_{\Omega_{J_\lambda}}(\theta) = e^{i(\Omega_{J_\lambda}-J)\pi/2}\begin{cases} A^{(1\ J\ (J-L')/2)}_{|\Omega_{J_\lambda}|}(\theta) & \text{for}\quad J+\Pi \text{ even} \\ \dfrac{\cos\theta\sin\theta}{\sqrt{2J(2J-1)}}\Big[\sqrt{(J+\Omega_{J_\lambda}-1)(J+\Omega_{J_\lambda})}\, A^{(1\ J-1\ (J-1-L')/2)}_{|\Omega_{J_\lambda}-1|}(\theta) + \\ \sqrt{(J-\Omega_{J_\lambda})(J-\Omega_{J_\lambda}-1)}\, A^{(1\ J-1\ (J-1-L')/2)}_{|\Omega_{J_\lambda}+1|}(\theta)\Big] & \text{for}\quad J+\Pi \text{ odd} \end{cases} \tag{4.56}$$

does not depend on σ_Π and the U and $A(\theta)$ are given by eqs E.44 and E.38, respectively. In view of eq E.36 and the remark after eq E.37, if in eq 4.56 $|\Omega_{J_\lambda} - 1|$ or $|\Omega_{J_\lambda} + 1|$ exceed $J - 1$ the corresponding $A(\theta)$ functions are set equal to zero, by convention. For example, for $J = 1$, the functions $A^{(10-L'/2)}_1(\theta)$ and $A^{(10-L'/2)}_2(\theta)$, which result from $\Omega_{J_\lambda} = 0$ and ± 1, respectively, vanish. Equations 4.53, 4.55, and 4.56 furnish $\sin^{l^{(1)}_{\min}}\eta_\lambda \cos^{l^{(2)}_{\min}}\eta_\lambda\, Y^{JM_J=J}_{l^{(1)}_{\min}l^{(2)}_{\min}}$ as a function of the body-fixed angles $\mathbf{\Theta}^{\rm bf}_\lambda$, as desired. A useful particular case is $\Pi = \sigma_\Pi = 0$, for which $L_{\min}$, $L'_{\min}$, and L' are all even. Replacing, in eq E.44, $l^{(1)}_\lambda = l^{(2)}_\lambda$ and m by $(J - \sigma_\Pi - b_{J+\Pi})/2$ and $(L'_{\min} - L')/2$, respectively, and considering the remark made after that equation, we conclude that the corresponding U vanishes if $(L'_{\min} - L')/2$ is odd. As a result, the only nonzero $p^{\Pi L_{\min}L'J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ functions are those for which L' is restricted to the values

$$L' = -L'_{\min}, -L'_{\min} + 4, ..., L'_{\min} - 4, L'_{\min} \tag{4.57}$$

Let us now define L_{σ_Π} by

$$L_{\sigma_\Pi} = \begin{cases} 4 & \text{for}\quad \sigma_\Pi = 0 \\ 2 & \text{for}\quad \sigma_\Pi > 0 \end{cases} \tag{4.58}$$

In terms of it, the step size 2 in eq 4.53 can be replaced by L_{σ_Π}, resulting in

$$Y^{JM_J=J}_{l^{(1)}_{\min}l^{(2)}_{\min}}(\theta^{(1)}_\lambda,\phi^{(1)}_\lambda,\theta^{(2)}_\lambda,\phi^{(2)}_\lambda) = \frac{N^{\Pi J\sigma_\Pi}i^J}{(\sin\ \eta_\lambda)^{l^{(1)}_{\min}}(\cos\ \eta_\lambda)^{l^{(2)}_{\min}}}\sum_{L'=-L'_{\min},L_{\sigma_\Pi}}^{L'_{\min}} e^{iL'\delta_\lambda}\sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J=J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, p^{\Pi L_{\min}L'J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{4.59}$$

4.5.2. Expression for $P_\xi^{(l_{\min}{}^{(1)}+(1/2),l_{\min}{}^{(2)}+(1/2))}(\cos 2\eta_\lambda)$ in Terms of θ and δ_λ. To obtain the dependence of η_λ on θ and δ_λ, we first equate the middle part of eq A.4 with eq 2.4 and use eqs 2.5 and 2.6. The result is

$$\boldsymbol{\rho}^I_\lambda = \begin{pmatrix} x^{I(2)}_\lambda & x^{I(1)}_\lambda \\ y^{I(2)}_\lambda & y^{I(1)}_\lambda \\ z^{I(2)}_\lambda & z^{I(1)}_\lambda \end{pmatrix} = \rho\mathbf{N}(\theta)\,\mathbf{Q}(\delta_\lambda) = \rho\begin{pmatrix} \sin\theta\cos\delta_\lambda & \sin\theta\sin\delta_\lambda \\ 0 & 0 \\ -\sin\theta\sin\delta_\lambda & \cos\theta\cos\delta_\lambda \end{pmatrix} \tag{4.60}$$

We now calculate the quantity $r^{(2)2}_\lambda - r^{(1)2}_\lambda$ obtained first from the second term of this expression and then from its fourth term. Identifying the two results and using eqs 4.1 and 4.2 we obtain

$$\cos 2\eta_\lambda = -\cos 2\theta\cos 2\delta_\lambda \tag{4.61}$$

Using this expression, the Jacobi polynomial in the rhs of eq 4.38 becomes $P_\xi^{(l_{\min}{}^{(1)}+(1/2),l_{\min}{}^{(2)}+(1/2))}(-\cos 2\theta\cos 2\delta_\lambda)$. The δ_λ dependence of this expression does not have a structure convenient for writing the rhs of eq 4.38 in the form of the rhs of eq 4.37. Such a form was, however, obtained in Appendix D by using appropriate Jacobi polynomial properties derived in Appendix C and is given in eqs D.18−D.21. Setting $n = \xi = (n_\Pi - L_{\min})/2$ in those equations results in

$$P_{\xi}^{(l_{\min}^{(1)}+1/2),(l_{\min}^{(2)}+1/2)}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{(-1)^{(n_\Pi-L_{\min})/2}(n_\Pi + \sigma_\Pi + 1)!\,l_{\min}^{(2)}!}{2^{n_\Pi-L_{\min}}(\sigma_\Pi + 1)!\left(\frac{n_\Pi+\sigma_\Pi}{2}\right)!\left(\frac{n_\Pi-\sigma_\Pi}{2} + l_{\min}^{(2)} + 1\right)!} \sum_{L=-n_\Pi+L_{\min},L_{\sigma_\Pi}}^{n_\Pi-L_{\min}} e^{iL\delta_\lambda} S_{n_\Pi|L|}^{(J,\sigma_\Pi)}(\theta) \tag{4.62}$$

where the summation index L is even and

$$S_{n_\Pi|L|}^{(J,\sigma_\Pi)}(\theta) = \cos^{|L/2|}(2\theta) \sum_{v=v_{\min},2}^{v_{\max}} \frac{\binom{\sigma_\Pi}{v}\binom{\frac{n_\Pi - L_{\min} - 2v + |L|}{4} + l_{\min}^{(2)}}{l_{\min}^{(2)}}(n_\Pi - 2v + \sigma_\Pi + 2)}{\binom{n_\Pi - v + \sigma_\Pi + 2}{\sigma_\Pi + 1}} P_{(1/4)(n_\Pi-L_{\min}-2v-|L|)}^{(l_{\min}^{(2)},|L/2|)}(\cos 4\theta) \tag{4.63}$$

The values of $v_{\min}$ and $v_{\max}$ are given by

$$v_{\min} = \frac{1-(-1)^{(n_\Pi-L_{\min}-|L|)/2}}{2} = \begin{cases} 0 & \text{for } (n_\Pi - L_{\min} - |L|)/2 \text{ even} \\ 1 & \text{for } (n_\Pi - L_{\min} - |L|)/2 \text{ odd} \end{cases} \tag{4.64}$$

and

$$v_{\max} = \min\left(\sigma_\Pi - a, \frac{n_\Pi - L_{\min} - |L|}{2}\right) \tag{4.65}$$

where a is zero (one) if σ_Π and $(n_\Pi - L_{\min} - |L|)/2$ have the same (opposite) parity. The summation step size $L_{\sigma\Pi}$ of eq 4.62 was defined in eq 4.58.

4.5.3. Expression for $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$. We now insert eqs 4.53 and 4.62 into eq 4.38 and furthermore define L_Π by

$$L_\Pi = L + L' \tag{4.66}$$

Since, as stated after eqs 4.54 and 4.62, L' has parity Π and L is even, L_Π has parity Π. Changing the summation over L in the resulting expression to a summation over L_Π and changing the order of the summations over L' and L_Π, we get

$$\Phi_{\sigma_\Pi}^{\Pi n_\Pi J M_J=J}(\Theta_\lambda^{\text{sf}}) = \bar{N}_{\sigma_\Pi}^{\Pi n_\Pi J} \sum_{L_\Pi=-n_\Pi^{\max},L_{\sigma_\Pi}}^{n_\Pi^{\max}} e^{iL_\Pi\delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D_{M_J=J\Omega_{J_\lambda}}^{J}(\mathbf{a}_\lambda)\, \mathscr{G}_{\Omega_{J_\lambda}\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\theta) \tag{4.67}$$

where

$$\bar{N}_{\sigma_\Pi}^{\Pi n_\Pi J} = \frac{N^{(l_{\min}^{(1)} l_{\min}^{(2)})}(-1)^{(n_\Pi-L_{\min})/2}(n_\Pi + \sigma_\Pi + 1)!\,l_{\min}^{(2)}!}{2^{n_\Pi-L_{\min}}(\sigma_\Pi + 1)!\left(\frac{n_\Pi+\sigma_\Pi}{2}\right)!\left(\frac{n_\Pi-\sigma_\Pi}{2} + l_{\min}^{(2)} + 1\right)!} \tag{4.68}$$

is independent of L_Π and

$$\mathscr{G}_{\Omega_{J_\lambda}\sigma_\Pi}^{\Pi n_\Pi L_\Pi J}(\theta) = \sum_{L'=\bar{L}'_{\min},L_{\sigma_\Pi}}^{\bar{L}'_{\max}} p_{\Omega_{J_\lambda}\sigma_\Pi}^{\Pi L_{\min} L' J}(\theta)\, S_{n_\Pi|L_\Pi-L'|}^{(J,\sigma_\Pi)}(\theta) \tag{4.69}$$

In analogy to the remarks made at the end of section 3, the superscript Π on the lhs of eq 4.69 does not indicate the parity of the $\mathscr{G}$ functions; it refers instead to the parity of the Φ^Π function of eq 4.67 under inversion of the system through its center of mass. The summation limits $\bar{L}'_{\min}$ and $\bar{L}'_{\max}$ in eq 4.69 are given by

$$\bar{L}'_{\min} = \max(-L'_{\min}, L_\Pi - n_\Pi + L_{\min}) \qquad (4.70)$$

and

$$\bar{L}'_{\max} = \min(L'_{\min}, L_\Pi + n_\Pi - L_{\min}) \qquad (4.71)$$

These limits differ from those of eqs 4.53 and 4.54 because of the change in the order of the summations mentioned after eq 4.66. In view of eqs 4.54, 4.57, and 4.66, the L_Π in eqs 4.67 and 4.69 is restricted to the values

$$L_\Pi = -L_\Pi^{\max}, -L_\Pi^{\max} + L_{\sigma_\Pi}, -L_\Pi^{\max} + 2L_{\sigma_\Pi}, ..., L_\Pi^{\max} - 2L_{\sigma_\Pi}, L_\Pi^{\max} - L_{\sigma_\Pi}, L_\Pi^{\max} \qquad (4.72)$$

where

$$L_\Pi^{\max} = n_\Pi - L_{\min} + L'_{\min} = n_\Pi - 2b_{J+\Pi} \qquad (4.73)$$

If, however, this restriction is ignored, eqs 4.67 (with $L_{\sigma_\Pi} = 2$) and 4.69 are still correct, since the $\mathscr{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ functions for nonallowed values of L_Π vanish. It should be noted that $p^{\Pi L_{\min} L' = L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ differs from $\mathscr{G}^{\Pi L_{\min} L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ only by a proportionality constant that is independent of Ω_{J_λ} but depends on Π, L_Π, J, and σ_Π.

We now identify the rhs of eqs 4.67 and 4.37. In view of the remark after eq 4.73, the summations over L_Π in both those rhs are equivalent. Taking into account the orthonormality relations of the $e^{iL_\Pi\delta_\lambda}$ and $D^J_{M_J=J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ functions, that identification results in

$$\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = \bar{N}^{\Pi n_\Pi J}_{\sigma_\Pi} \mathscr{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \qquad (4.74)$$

Since, as mentioned after eq 4.34, the by $\bar{F}^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ are non-normalized hyperspherical harmonics, the functions obtained from them by replacing $\bar{G}$ by $\mathscr{G}$ are also non-normalized hyperspherical harmonics. The latter can be normalized with the help of a real positive constant,[33] resulting in the desired harmonics:

$$F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda) = N^{\Pi n_\Pi L_\Pi J}_{\sigma_\Pi} e^{iL_\Pi\delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \qquad (4.75)$$

where

$$G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = \mathscr{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \qquad (4.76)$$

These F harmonics are valid for all M_J satisfying the first of eq 3.9, even though they were derived from the Φ functions of eq 4.37 where we set $M_J = J$. In addition, eqs 4.76 and 4.69 give the desired explicit expression for the $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ democratic harmonics for all possible values of the 6 indices that appear in them, in spite of the fact that they were obtained using only a single allowed $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ pair for each value of σ_Π, namely $l_{\min}^{(1)}$, $l_{\min}^{(2)}$. These F harmonics can be orthogonalized with respect to σ_Π by a Gram–Schmidt or some other orthogonalization procedure. The structure of eq 4.69 is relatively simple. In it $\mathscr{G}$ is expressed as a single sum of products of two functions of θ, $p^{\Pi L_{\min} L' J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ and $S^{(J,\sigma_\Pi)}_{n_\Pi |L_\Pi - L'|}(\theta)$. The first, given by eqs 4.55 and 4.56, involves trigonometric functions, and the second, given by eq 4.63, involves Jacobi polynomials. Efficient codes for these functions are available. Associated with the complex $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ functions, we define the $\bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ and $g^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ real functions in analogy with eqs 3.12 and 3.13 but with d replaced by σ_Π.

It is interesting to note that, setting $x = \cos\theta$ and $y = \sin\theta$ and using the identity $x^2 + y^2 = 1$, these G, $\bar{g}$, and g functions can be expressed as homogeneous polynomials of these two variables. This is the form in which their recursion method counterparts were obtained and is useful for comparing the latter with the present results. Such comparisons are made in section 5.

4.6. Allowed Values of the σ_Π Index for the Linearly Independent $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$. As a consequence of eq 4.24, the statement after eq 4.25, and eq 4.27 we conclude that the allowed values of σ_Π, for a given Π and J, are

$$\sigma_\Pi = -(J - b_{J+\Pi}), -(J - b_{J+\Pi}) + 2, ..., J - b_{J+\Pi} - 2, J - b_{J+\Pi} \qquad (4.77)$$

However, not all of these lead to linearly independent $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ functions. Indeed, from eqs 4.35 and 4.74–4.76, $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ and $F^{\Pi n_\Pi L_\Pi J}_{M_J-\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ differ at most by a sign, and therefore, for the $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ set of functions to be linearly independent, it is necessary (but not sufficient) that σ_Π be limited to the range

$$\sigma_\Pi = \Pi, \Pi + 2, ..., J - b_{J+\Pi} \qquad (4.78)$$

We shall now show that only a subset of these σ_Π result in linearly independent $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$. Indeed, from eqs 4.78 and 4.76 and a careful an analysis of the σ_Π dependence of eqs 4.69, 4.55, 4.56, and 4.63 leads to the conclusion that the G are polynomials in σ_Π whose degree q depends only on Π, n_Π, L_Π, and J. Furthermore, the parity of q is given by

$$(-1)^{q(\Pi,n_\Pi,L_\Pi,J)} = (-1)^{(n_\Pi - J + b_{J+\Pi})/2} \qquad (4.79)$$

and all powers of σ_Π that appear in those polynomials have the same parity as q. Therefore, if $q(\Pi,n_\Pi,L_\Pi,J)$ is even (odd), only even (odd) powers of σ_Π occur in G. In addition, the number of terms in these polynomials is $(q/2) + 1$ for q even and $[(q-1)/2] + 1$ for q odd. Since, for a given degree q, the number D of linearly independent polynomials of parity $(-1)^q$ equals the number of their terms, we get, with help of eq 4.78, the important expression

$$D(\Pi,n_\Pi,J,L_\Pi) = \frac{1}{4}[2q(\Pi,n_\Pi,L_\Pi,J) + (-1)^{(n_\Pi - J + b_{J+\Pi})/2} + 3] \qquad (4.80)$$

If $D = 0$, the corresponding set of quantum numbers Π, n_Π, J, L_Π is not allowed; i.e., the associated $F^{\Pi n_\Pi L_\Pi J}_{M_J\sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ harmonic vanishes for all possible M_J and σ_Π. The parity of D is not necessarily that of Π and depends on all four quantum numbers Π, n_Π, L_Π, and J. The values of the degeneracy D that result from eq 4.80 are, with $[a]$ meaning the integer part of a,

(a) for $J + \Pi$ even, i.e., $b_{J+\Pi} = 0$

$$D(\Pi,n_\Pi,J,L_\Pi) = \begin{cases} [(J+2)/2] & \text{for} \quad (n_\Pi - |L_\Pi|)/2 \text{ even and } > J \\ [(J+1)/2] & \text{for} \quad (n_\Pi - |L_\Pi|)/2 \text{ odd and } > J \\ [(n_\Pi - |L_\Pi| + 4)/4] & \text{for} \quad |L_\Pi| \geq |n_\Pi - 2J| \\ [(n_\Pi - J + 2)/2] & \text{for} \quad |L_\Pi| < 2J - n_\Pi \end{cases} \tag{4.81}$$

(b) for $n_\Pi + J$ odd, i.e., $b_{J+\Pi} = 1$

$$D(\Pi,n_\Pi,J,L_\Pi) = \begin{cases} [J/2] & \text{for} \quad (n_\Pi - |L_\Pi|)/2 \text{ even and } > J \\ [(J+1)/2] & \text{for} \quad (n_\Pi - |L_\Pi|)/2 \text{ odd and } > J \\ [(n_\Pi - |L_\Pi| + 2)/4] & \text{for} \quad |L_\Pi| \geq |n_\Pi - 2J| \\ [(n_\Pi - J + 1)/2] & \text{for} \quad |L_\Pi| < 2J - n_\Pi \end{cases} \tag{4.82}$$

As a result, the values of σ_Π that lead to functions $F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\boldsymbol{\Theta}^{bf}_\lambda)$, which are linearly independent are

$$\sigma_\Pi = \begin{cases} 0, 2, ..., 2D(\Pi,n_\Pi,J,L_\Pi) - 2 & \text{for} \quad \Pi = 0 \\ 1, 3, ..., 2D(\Pi,n_\Pi,J,L_\Pi) - 1 & \text{for} \quad \Pi = 1 \end{cases} \tag{4.83}$$

Equations 4.81 and 4.82 agree with the results of Table 1 of Wolniewicz[31] derived by a completely different method based on counting the number of linearly independent solutions of a set of Ω_{J_λ}-coupled ordinary differential equations satisfied by the $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$. As mentioned after eq 3.10, $D(\Pi,n_\Pi,J,L_\Pi)$ is independent of the choice of arrangement channel coordinates λ and, therefore, so are the allowed values of σ_Π given by eq 4.83.

5. Representative Results

5.1. Hyperspherical Harmonics for $J = 0$. The simplest way to obtain the $J = 0$ harmonics is to set $J = 0$ in eq 4.38 and to perform the derivation of eqs 4.69 and 4.76 for this particular case only, following the procedure described in section 4.5. However, to test the correctness of those two equations, it is more appropriate to start with the expression for $\mathscr{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ for general J, and set $J = 0$ in it.

For this particular case, the F function of eq 4.75 is invariant under inversion of the system through its center of mass. As a result, $\Pi = 0$ and eqs 4.81 and 4.83 furnish D = 1 and $\sigma_\Pi = 0$, respectively. In addition, n_Π and L_Π must both be even, and in view of eqs 4.58, 4.72, and 4.73, $(n_\Pi - |L_\Pi|)/4$ must be a non-negative integer. For a given n_Π, $|L_\Pi|$ is limited to the values

$$|L_\Pi| = n_\Pi - 4m \qquad m = 0, 1, ..., \left[\frac{n_\Pi}{4}\right] \tag{5.1}$$

Furthermore, from eqs 4.70 and 4.71 we get $\bar{L}'_{\min} = \bar{L}'_{\max} = 0$, so that the sum in the rhs of eq 4.69 has a single term, yielding, due to eq 4.76,

$$\begin{aligned} G^{\Pi=0 n_\Pi L_\Pi J=0}_{\Omega_{J_\lambda}=0 \sigma_\Pi=0}(\theta) &= \mathscr{G}^{\Pi=0 n_\Pi L_\Pi J=0}_{\Omega_{J_\lambda}=0 \sigma_\Pi=0}(\theta) \\ &= p^{\Pi=0 L_{\min}=0 L'=0 J=0}_{\Omega_{J_\lambda}=0 \sigma_\Pi=0}(\theta)\, S^{(J=0,\sigma_\Pi=0)}_{n_\Pi |L_\Pi|}(\theta) \end{aligned} \tag{5.2}$$

Use of eqs 4.55, 4.56, E.44, E.38, and 4.63 results in

$$G^{\Pi=0 n_\Pi L_\Pi J=0}_{\Omega_{J_\lambda}=0 \sigma_\Pi=0} = \cos^{|L_\Pi/2|} 2\theta P^{(0,|L_\Pi|/2)}_{(n_\Pi - |L_\Pi|)/4}(\cos 4\theta) \tag{5.3}$$

which depends on L_Π through $|L_\Pi|$ only. In view of the definition of $\bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}$ given toward the end of section 4.5.3, this $\bar{g}$ is, in this $J = 0$ case, the same as the G of eq 5.3, and agrees with the corresponding recursion method result.[33] In particular, in Table 2 we present, among others, the $\bar{g}$ for $J = 0$ and $n_\Pi = 4$ (which are the k of that table for these particular J and n_Π). These expressions were obtained from eq 5.3 by introducing variables $x = \cos\theta$ and $y = \sin\theta$ and agree with those of Table 3 of ref 33.

5.2. Hyperspherical Harmonics for $J = 1$. For $J = 1$, eqs 4.81 and 4.82 give D = 1 for both $\Pi = 0$ ($J + \Pi$ odd) and $\Pi = 1$ ($J + \Pi$ even). The corresponding values of σ_Π, obtained from eq 4.83, are $\sigma_\Pi = 0$ for $\Pi = 0$ and $\sigma_\Pi = 1$ for $\Pi = 1$. Since there is only one value of σ_Π for each of these two parities, neither of the corresponding F functions of eq 4.75 is degenerate with respect to the set of indices Π, n_Π, L_Π, J, and M_J. Let us determine the $\bar{g}$ functions for these two parities separately.

(a) $\Pi = 0$, $\sigma_\Pi = 0$

For this case L_Π and n_Π are even, and for a given n_Π the values of L_Π are restricted, due to eqs 4.58, 4.72, and 4.73, to

TABLE 1: Principal-Axes-of-Inertia Hyperspherical Harmonics h for $J = 2$ and $n_\Pi = 2, 3$[a]

n_Π	J	L_Π	Ω_{J_λ}[b]	$h^{n_\Pi L_\Pi J}_{\Omega_{J_\lambda}}$[c]	n_Π	J	L_Π	Ω_{J_λ}[b]	$h^{n_\Pi L_\Pi J}_{\Omega_{J_\lambda}}$[c]
2	2	−2	0	$(2/3)^{1/2}(2x^2 + y^2)$	2	2	2	2	y^2
2	2	−2	1	$2xy$	3	2	1	0	0
2	2	−2	2	y^2	3	2	1	1	$-x^2y$
2	2	0	0	$-(2/3)^{1/2}(2x^2 - y^2)$	3	2	1	2	xy^2 [d]
2	2	0	1	0	3	2	−1	0	0
2	2	0	2	y^2	3	2	−1	1	x^2y
2	2	2	0	$(2/3)^{1/2}(2x^2 + y^2)$	3	2	−1	2	xy^2
2	2	2	1	$-2xy$					

[a] x and y are $\cos\theta$ and $\sin\theta$, respectively. [b] The functions for $\Omega_{J_\lambda} < 0$ can be obtained from the $\Omega_{J_\lambda} > 0$ functions using eq 3.15 with d replaced by σ_Π. [c] h is related to $\bar{\bar{g}}$ and $\bar{g}$ by eqs 5.12, 5.13, 5.18, 5.19, and 5.9, and $\bar{g}$ is related to G by eq 3.12 with d replaced by σ_Π. [d] In Table 2 of ref 33 there was a minus sign in this term due to a typographical error that is corrected here.

TABLE 2: Principal-Axes-of-Inertia Hyperspherical Harmonics k and $\bar{g}$ for $n_\Pi = 4$[a]

J	L_Π	Ω_{J_λ}[b]	$k^{4L_\Pi J}_{\Omega_{J_\lambda}}$[c,d]	J	L_Π	Ω_{J_λ}[b]	$k^{4L_\Pi J}_{\Omega_{J_\lambda}}$[c,d]
0	4	0	$(x^2 - y^2)^2$	3	0	0	0
0	0	0	$x^4 - 6x^2y^2 + y^4$	4	4	4	y^4
1	2	1	$xy(x^2 - y^2)$	4	4	3	$2\cdot 2^{1/2}xy^3$
1	2	0	0	4	4	2	$2y^2(6x^2 + y^2)/7^{1/2}$
2	4	2	$y^2(x^2 - y^2)$	4	4	1	$2(2/7)^{1/2}xy(4x^2 + 3y^2)$
2	4	1	$-2xy(x^2 - y^2)$	4	4	0	$(2/35)^{1/2}(8x^4 + 24x^2y^2 + 3y^4)$
2	4	0	$-(2/3)^{1/2}(-2x^4 + x^2y^2 + y^4)$	4	2	4	y^4
2	2	2	$y^2(-7x^2 + 3y^2)$	4	2	3	$2^{1/2}xy^3$
2	2	1	$-4xy(x^2 + y^2)$	4	2	2	$2y^4/7^{1/2}$
2	2	0	$6^{1/2}(2x^4 - 7x^2y^2 + y^4)$	4	2	1	$-(2/7)^{1/2}xy(4x^2 - 3y^2)$
3	2	3	xy^3	4	2	0	$(2/35)^{1/2}(-8x^4 + 3y^4)$
3	2	2	$2(2/3)^{1/2}x^2y^2$	4	0	4	y^4
3	2	1	$xy(4x^2 + y^2)/15^{1/2}$	4	0	3	0
3	2	0	0	4	0	2	$2y^2(-2x^2 + y^2)$
3	0	3	xy^3	4	0	1	0
3	0	2	0	4	0	0	$(2/35)^{1/2}(8x^4 - 8x^2y^2 + 3y^4)$
3	0	1	$-xy(4x^2 - y^2)15^{1/2}$				

J	L_Π	$\mathcal{M}^{4DJ}_{\sigma_\Pi}$	J	L_Π	$\mathcal{M}^{4DJ}_{\sigma_\Pi}$
0	4	1	3	2	1
0	0	1	3	0	2
1	2	1	4	4	1
2	4	8	4	2	2
2	2	−192	4	0	−2

J	L_Π	Ω_{J_λ}	$\bar{g}^{4L_\Pi J}_{\mathrm{rec}\,\Omega_{J_\lambda} d=1}$	J	L_Π	Ω_{J_λ}	$\bar{g}^{4L_\Pi J}_{\mathrm{rec}\,\Omega_{J_\lambda} d=2}$
2	0	0	$(2/3)^{1/2}(-2x^4 + 9x^2y^2 + y^4)$	2	0	0	$(2/3)^{1/2}(-2x^4 + 9x^2y^2 + y^4)$
2	0	1	$-70/3xy(x^2 - y^2)$	2	0	1	$70/3xy(x^2 - y^2)$
2	0	2	$y^2(-9x^2 + y^2)$	2	0	2	$y^2(-9x^2 + y^2)$

J	L_Π	Ω_{J_λ}	$\bar{g}^{4L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi=0}$	J	L_λ	Ω_{J_λ}	$\bar{g}^{4L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi=2}$
2	0	0	0	2	0	0	$(2/3)^{1/2}(-2x^4 + 9x^2y^2 + y^4)/2$
2	0	1	$-5xy(x^2 - y^2)$	2	0	1	0
2	0	2	0	2	0	2	$y^2(-9x^2 + y^2)/2$

[a] x and y are $\cos\theta$ and $\sin\theta$, respectively. [b] The functions for $\Omega_{J_\lambda} < 0$ can be obtained from the $\Omega_{J_\lambda} > 0$ functions using eq 3.15 with d replaced by σ_Π. [c] The $\Pi = 0$ superscript was omitted from the k for simplicity. [d] $\bar{g}$ is related to k and $\mathcal{M}$ by eqs 5.9 and 5.21 and to G by eq 3.12 with d replaced by σ_Π.

$$|L_\Pi| = (n_\Pi - 2) - 4m \qquad m = 0, 1, ..., \left[\frac{n_\Pi - 2}{4}\right] \tag{5.4}$$

and the corresponding $\bar{g}$ are given by

$$\bar{g}^{\Pi=0 n_\Pi L_\Pi J=1}_{\Omega_{J_\lambda}\sigma_\Pi=0} = \mathcal{N}^{\Pi=0 n_\Pi L_\Pi J=1}_{\sigma_{\Pi=0}} \bar{\bar{g}}^{\Pi=0 n_\Pi L_\Pi J=1}_{\Omega_{J_\lambda}\sigma_\Pi=0} \tag{5.5}$$

where

$$\bar{\bar{g}}^{\Pi=0 n_\Pi L_\Pi J=1}_{\Omega_{J_\lambda}\sigma_\Pi=0} = |\Omega_{J_\lambda}| \sin\theta \cos\theta \cos^{|L_\Pi/2|} 2\theta P^{(1,|L_\Pi/2|)}_{(n_\Pi - 2 - |L_\Pi|)/4}(\cos 4\theta) \tag{5.6}$$

and

$$\mathcal{N}^{\Pi=0n_\Pi L_\Pi J=1}_{\sigma_\Pi=0} = \frac{n_\Pi + 2 + |L_\Pi|}{4} \tag{5.7}$$

In the third and fourth lines of the left column of Table 2 we present the k for $n_\Pi = 4$, $J = 1$, $L_\Pi = 2$, $\Omega_{J_\lambda} = 0, 1$ after introducing variables $x = \cos\theta$ and $y = \sin\theta$. These k are related to $\bar{\bar{g}}$ by eq 5.21 of section 5.4. They agree with their recursion method counterparts $\bar{g}$ of Table 3 of ref 33 as expected.

(b) $\Pi = 1$, $\sigma_\Pi = 1$

The values of L_Π and n_Π are odd, and for a given n_Π, L_Π is restricted, also due to eqs 4.58, 4.72, and 4.73, to the values

$$L_\Pi = n_\Pi - 2m \qquad m = 0, 1, ..., n_\Pi \tag{5.8}$$

In analogy to eq 5.5, let us express the corresponding $\bar{g}$ as

$$\bar{g}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = \mathcal{N}^{\Pi n_\Pi L_\Pi J}_{\sigma_\Pi}\bar{\bar{g}}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) \tag{5.9}$$

where $\mathcal{N}$ is independent of Ω_{J_λ}. This relation is also adopted for arbitrary Π, n_Π, L_Π, J, Ω_{J_λ}, and σ_Π. We get

$$\bar{\bar{g}}^{\Pi=1n_\Pi L_\Pi J=1}_{\Omega_{J_\lambda}\sigma_\Pi=1}(\theta) = \begin{cases} (n_\Pi + 3 + |L_\Pi - 1|)t_1^{\Omega_{J_\lambda}} \cos^{|L_\Pi - 1|/2} 2\theta P^{(1,|L_\Pi-1|/2)}_{(1/4)(n_\Pi-1-|L_\Pi-1|)}(\cos 4\theta) + \\ (n_\Pi + 1 + |L_\Pi + 1|)t_{-1}^{\Omega_{J_\lambda}} \cos^{|L_\Pi+1|/2} 2\theta P^{(1,|L_\Pi+1|/2)}_{(1/4)(n_\Pi-3-|L_\Pi+1|)}(\cos 4\theta) & \text{for} \quad m = 0, 2, ..., n_\Pi - 1 \\ (n_\Pi + 3 + |L_\Pi + 1|)t_{-1}^{\Omega_{J_\lambda}} \cos^{|L_\Pi+1|/2} 2\theta P^{(1,|L_\Pi+1|/2)}_{(1/4)(n_\Pi-1-|L_\Pi+1|)}(\cos 4\theta) + \\ (n_\Pi + 1 + |L_\Pi - 1|)t_1^{\Omega_{J_\lambda}} \cos^{|L_\Pi-1|/2} 2\theta P^{(1,|L_\Pi+1|/2)}_{(1/4)(n_\Pi-3-|L_\Pi-1|)}(\cos 4\theta) & \text{for} \quad m = 1, 3, ..., n_\Pi \end{cases} \tag{5.10}$$

and

$$\mathcal{N}^{\Pi=1n_\Pi L_\Pi J=1}_{\sigma_\Pi=1} = \frac{1}{2n_\Pi + 4} \tag{5.11}$$

The $t_{\pm1}^{\Omega_{J_\lambda}}$ in eq 5.10 are given by eqs E.9−E.12. It should be noted that, in these expressions, and in those of section 5.3, we have adopted the convention that for $n < 0$, $P_n^{(\alpha,\beta)}(x) = 0$. These $J = 1$ $\bar{g}$ functions agree with those obtained previously.[29,30]

5.3. Hyperspherical Harmonics for $J = 2$. For $\Pi = 0$ eqs 4.81 and 4.83 result in $D = 2$ and $\sigma_\Pi = 0, 2$. Therefore, the corresponding F harmonics of eq 4.75 are doubly degenerate with respect to Π, n_Π, L_Π, J, and M_J as long as the corresponding $G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta)$ do not vanish for all Ω_{J_λ} for either of the two values of σ_Π and, in addition, constitute two linearly independent sets of functions scanned by Ω_{J_λ}. For $\Pi = 1$, eqs 4.82 and 4.83 give $D = 1$ and $\sigma_\Pi = 1$, and the corresponding harmonics are nondegenerate. Let us consider these two parities separately.

(a) $\Pi = 0$, $\sigma_\Pi = 0, 2$

The values of n_Π and L_Π are even for both σ_Π.

For $\sigma_\Pi = 0$, the allowed values of L_Π obtained from eqs 4.58, 4.72, and 4.73 are the same as for $J = 0$ and are given by eq 5.1. Equations 4.69 and 4.76 have two terms only, and the corresponding $\bar{\bar{g}}$ and $\mathcal{N}$ defined by eq 5.9 are

$$\begin{aligned} &\bar{\bar{g}}^{\Pi=0n_\Pi L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=0}(\theta) = \\ &h^{222}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 2 + |L_\Pi - 2|) \cos^{|L_\Pi-2|/2} 2\theta P^{(1,|L_\Pi-2|/2)}_{(1/4)(n_\Pi-2-|L_\Pi-2|)}(\cos 4\theta) - \\ &h^{2-22}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 2 + |L_\Pi + 2|) \cos^{|L_\Pi+2|/2} 2\theta P^{(1,|L_\Pi+2|/2)}_{(1/4)(n_\Pi-2-|L_\Pi+2|)}(\cos 4\theta)\} \end{aligned} \tag{5.12}$$

and

$$\mathcal{N}^{\Pi=0n_\Pi L_\Pi J=2}_{\sigma_\Pi=0} = \frac{n_\Pi + 2 + |L_\Pi|}{4} \tag{5.13}$$

where the h were defined in eq 4.56. Some of the h are given in Table 1.

For $\sigma_\Pi = 2$, eqs 4.58, 4.72, and 4.73, furnish the following allowed values of L_Π:

$$L_\Pi = n_\Pi - 2m \qquad m = 0, 1, 2, ..., n_\Pi \tag{5.14}$$

From eqs 4.76, 4.69, and 3.12 (with d replaced by σ_Π) we obtain $\bar{g}$, which together with eq 5.9 furnishes $\bar{\bar{g}}$ and $\mathcal{N}$:

$$\bar{\bar{g}}^{\Pi=1 n_\Pi L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=2}(\theta) = \begin{cases} h^{222}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 2 + |L_\Pi - 2|)\cos^{|L_\Pi-2|/2} 2\theta[(n_\Pi + 1)(n_\Pi + |L_\Pi - 2| + 6)\times \\ P^{(2,|L_\Pi-2|/2)}_{(1/4)(n_\Pi-2-|L_\Pi-2|)}(\cos 4\theta) + (n_\Pi + 3)(n_\Pi + |L_\Pi - 2| - 2)P^{(2,|L_\Pi-2|/2)}_{(1/4)(n_\Pi-6-|L_\Pi-2|)}(\cos 4\theta)] + \\ h^{2-22}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 2 + |L_\Pi + 2|)\cos^{|L_\Pi+2|/2} 2\theta[(n_\Pi + 1)(n_\Pi + |L_\Pi + 2| + 6)\times \\ P^{(2,|L_\Pi+2|/2)}_{(1/4)(n_\Pi-2-|L_\Pi+2|)}(\cos 4\theta) + (n_\Pi + 3)(n_\Pi + |L_\Pi + 2| - 2)P^{(2,|L_\Pi+2|/2)}_{(1/4)(n_\Pi-6-|L_\Pi+2|)}(\cos 4\theta)] \\ \text{for} \quad m = 0, 2, ..., n_\Pi \\ 2h^{202}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 2 + |L_\Pi|)\cos^{|L_\Pi|/2} 2\theta[(n_\Pi + 1)(n_\Pi + |L_\Pi| + 6)P^{(2,|L_\Pi|/2)}_{(1/4)(n_\Pi-2-|L_\Pi|)}(\cos 4\theta) + \\ (n_\Pi + 3)(n_\Pi + |L_\Pi| - 2)P^{(2,|L_\Pi|/2)}_{(1/4)(n_\Pi-6-|L_\Pi|)}(\cos 4\theta)] + (2n_\Pi + 4)[h^{2-22}_{\Omega_{J_\lambda}}(\theta)\times \\ (n_\Pi + 4 + |L_\Pi + 2|)(n_\Pi + |L_\Pi + 2|)\cos^{|L_\Pi+2|/2} 2\theta P^{(2,|L_\Pi+2|/2)}_{(1/4)(n_\Pi-4-|L_\Pi+2|)}(\cos 4\theta) + \\ h^{222}_{\Omega_{J_\lambda}}(\theta)(n_\Pi + 4 + |L_\Pi - 2|)(n_\Pi + |L_\Pi - 2|)\cos^{|L_\Pi-2|/2} 2\theta P^{(2,|L_\Pi-2|/2)}_{(1/4)(n_\Pi-4-|L_\Pi+2|)}(\cos 4\theta)] \\ \text{for} \quad m = 1, 3, ..., n_\Pi - 1 \end{cases} \tag{5.15}$$

$$\mathcal{N}^{\Pi=0 n_\Pi L_\Pi J=2}_{\sigma_\Pi=2} = \frac{3}{16(n_\Pi + 1)(n_\Pi + 2)(n_\Pi + 3)} \tag{5.16}$$

Equations 5.12 and 5.15 agree with expressions obtained previously.[30,32,33] For $n_\Pi > 2$ and $|L_\Pi| \neq n_\Pi$ the $\bar{\bar{g}}^{\Pi=0 n_\Pi L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=0}(\theta)$ and $\bar{\bar{g}}^{\Pi=0 n_\Pi L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=2}(\theta)$ do not vanish for all Ω_{J_λ} and constitute two sets of linearly independent functions scanned by Ω_{J_λ}. Therefore, the corresponding $F^{\Pi=0 n_\Pi L_\Pi J=2}_{M_J \sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda)$ are doubly degenerate. This conclusion agrees with the results of Zickendraht,[30] Wolniewicz,[31] and Mukhtarova, and Efros.[32] Those equations also show that for $n_\Pi = L_\Pi = 2$ the corresponding F harmonics are nondegenerate with respect to Π, n_Π, L_Π, J, and M_J. The reason is that the ratio $\bar{\bar{g}}^{\Pi=0 n_\Pi=2 L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=2}/\bar{\bar{g}}^{\Pi=0 n_\Pi=2 L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=0}$ is a constant independent of Ω_{J_λ} and equal to the ratio of the two quantities $U^{(2-\sigma_\Pi)/2\ (2+\sigma_\Pi)/2}_{(2-L_\Pi)/2}$ (defined by eq E.44) for $\sigma_\Pi = 0$ and 2, respectively. As a result, the corresponding F harmonics are linearly dependent.

(b) $\Pi = 1$, $\sigma_\Pi = 1$

For this case, the values of n_Π, σ_Π, and $J + \Pi$ are odd. Equations 4.58, 4.72, and 4.73 yield the following allowed values of L_Π:

$$L_\Pi = n_\Pi - 2 - 2m \qquad m = 0, 1, 2, ..., n_\Pi - 2 \tag{5.17}$$

The associated $\bar{\bar{g}}$ functions and $\mathcal{N}$ obtained as described for the $\Pi = 0$, $\sigma_\Pi = 2$ case are

$$\bar{\bar{g}}^{\Pi=1 n_\Pi L_\Pi J=2}_{\Omega_{J_\lambda}\sigma_\Pi=1}(\theta) = \begin{cases} (n_\Pi + 5 + |L_\Pi - 1|)(n_\Pi + 1 + |L_\Pi - 1|)h^{312}_{\Omega_{J_\lambda}}(\theta)\cos^{|L_\Pi-1|/2} 2\theta P^{(2,|L_\Pi-1|/2)}_{(1/4)(n_\Pi-3-|L_\Pi-1|)}(\cos 4\theta) + \\ (n_\Pi + 3 + |L_\Pi + 1|)(n_\Pi - 1 + |L_\Pi + 1|)h^{3-12}_{\Omega_{J_\lambda}}(\theta)\cos^{|L_\Pi+1|/2} 2\theta\times \\ P^{(2,|L_\Pi+1|/2)}_{(1/4)(n_\Pi-5-|L_\Pi+1|)}(\cos 4\theta) \quad \text{for} \quad m = 0, 2, ..., (n_\Pi - 3) \\ (n_\Pi + 5 + |L_\Pi + 1|)(n_\Pi + 1 + |L_\Pi + 1|)h^{3-12}_{\Omega_{J_\lambda}}(\theta)\cos^{|L_\Pi+1|/2} 2\theta P^{(2,|L_\Pi+1|/2)}_{(1/4)(n_\Pi-3-|L_\Pi+1|)}(\cos 4\theta) + \\ (n_\Pi + 3 + |L_\Pi - 1|)(n_\Pi - 1 + |L_\Pi - 1|)h^{312}_{\Omega_{J_\lambda}}(\theta)\cos^{|L_\Pi-1|/2} 2\theta\times \\ P^{(2,|L_\Pi-1|/2)}_{(1/4)(n_\Pi-5-|L_\Pi-1|)}(\cos 4\theta) \quad \text{for} \quad m = 1, 3, ..., n_\Pi - 2 \end{cases} \tag{5.18}$$

and

$$\mathcal{N}^{\Pi=1 n_\Pi L_\Pi J=2}_{\sigma_\Pi=1} = \frac{1}{16(n_\Pi + 2)} \tag{5.19}$$

The h values for $J = 2$ and $n_\Pi = 3$ are given in Table 1. Equation 5.18 agrees with the results of Mukhtarova and Efros.[32] Therefore, we are in complete agreement with those authors for all the $J = 2$ cases we tested. It should be noted that their hyperspherical coordinates, principal axes of inertia, and Wigner rotation functions are different from those in the present paper, and this agreement takes this difference into account.[46]

5.4. Hyperspherical Harmonics for $n_\Pi = 4$. For nondegenerate F functions, the results of the present paper and those of the recursion method[33] should be the same, if both are normalized in the same way. However, for the degenerate cases, they should be related by linear combinations, according to

$$F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\boldsymbol{\Theta}^{\rm bf}_\lambda) = \sum_{d=1}^{D} B^{\Pi n_\Pi L_\Pi J d}_{\sigma_\Pi} F^{\Pi n_\Pi L_\Pi J}_{\rm rec\ \ M_J d}(\boldsymbol{\Theta}^{\rm bf}_\lambda) \tag{5.20}$$

We have verified the correctness of these predictions for some $n_\Pi = 4$ harmonics. For the nondegenerate cases, $\bar{g}(\theta)$ is related to $\bar{\bar{g}}$ by eq 5.9. However, when transforming from θ to $x = \cos\theta$, $y = \sin\theta$, additional Ω_{J_λ}-independent factors appear, and it becomes convenient to write $\bar{\bar{g}}$ as

$$\bar{\bar{g}}^{\Pi=0 n_\Pi=4 L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(\theta) = \mathscr{M}^{\Pi=0 n_\Pi=4 L_\Pi J}_{\sigma_\Pi} k^{\Pi=0 n_\Pi=4 L_\Pi J}_{\Omega_{J_\lambda}\sigma_\Pi}(x,y) \tag{5.21}$$

$k(x,y)$ and $\mathscr{M}$ are given, for these nondegenerate cases, in the top two sections of Table 2, and $k(x,y)$ are identical to their recursion relation method counterparts, given in Table 3 of ref 33, where similar Ω_{J_λ}-independent factors also were omitted. The third and fourth sections of that table give the $\bar{g}$ for $J = 2$ and $L_\Pi = 0$ obtained using the recursion and the present paper methods, respectively. The corresponding F harmonics are doubly degenerate and are related by eq 5.20 with the corresponding $B^{402d}_{\sigma_\Pi}$ coefficients given in Table 3 (the $\Pi = 0$ superscript having been omitted for simplicity) for three cases: (a) the F functions are neither normalized (i.e., the normalization coefficients $N^{\Pi n_\Pi L_\Pi J}_{d}$ and $N^{\Pi n_\Pi L_\Pi J}_{\sigma_\Pi}$ in eqs 3.11, for $F_{\rm rec}$, and 4.75, for the present paper F, respectively, were omitted) nor orthogonal with respect to either σ_Π or d; (b) these functions are normalized but still not orthogonal with respect to σ_Π and d; and (c) they are normalized and orthogonal with respect to both σ_Π and d. The fact that a relation of the type of eq 5.20 is valid is an additional check of the equivalence of the G and F functions obtained by both methods and of their correctness. In conclusion, there is complete agreement between the $n_\Pi = 4$ $\bar{g}$ harmonics obtained from the present method and those obtained from the recursion relation method.

6. Discussion

Hyperspherical harmonics in space-fixed hyperspherical coordinates for N-particle systems can be derived analytically in a straightforward manner, as demonstrated for the 4-particle case.[41,42] These harmonics are, however, different for different arrangement channels (i.e., are not "democratic") and are useful mainly in the weak interaction regions of configuration space, where the system has separated into pairs of noninteracting clusters. In the strong interaction region, where any pair of particles can interact with each other, the body-fixed ROHH (i.e., democratic) are much more useful. However, these harmonics, for general N-particle systems, are still unknown.

TABLE 3: $B^{402d}_{\sigma_\Pi}$

d	σ_Π = 0	σ_Π = 2
	(a) For Non-normalized F	
1	3/28	1/8
2	−3/28	1/8
	(b) For Normalized F	
1	$(19/70)^{1/2}$	$(19/6)^{1/2}$
2	$-(19/70)^{1/2}$	$(19/6)^{1/2}$
	(c) For Orthonormalized F	
1	$(35/38)^{1/2}$	$(3/38)^{1/2}$
2	$-(3/38)^{1/2}$	$(35/38)^{1/2}$

In the present paper we reported a new method for the analytical determination of democratic hyperspherical harmonics for 3-particle systems. The expression for the resulting harmonics (eqs 4.75, 4.76, 4.69, 4.63, and 4.55) involve independent single index sums and are significantly simpler than the Mukharova and Efros expression[32] (their eqs 19, 20, 23, and 24) that involve 4-fold sums. We have checked random sets of harmonics, involving nondegenerate and degenerate ones, and verified that our harmonics agree with theirs. We also derived analytically the degeneracy of our harmonics and found them to be in agreement with those of Wolniewicz,[31] which were obtained by a completely independent method. We have written an efficient Fortran program that calculates our harmonics.

In the approach used for the derivation of the 3-particle ROHH, we started with the corresponding space-fixed harmonics given by eq 4.16 and then transformed the space-fixed hyperspherical coordinates to democratic body-fixed coordinates. This approach is applicable to systems of more than 4 particles. The 4-particle version of eq 4.16 is known,[41,42] and a similar method for transforming it from space-fixed to body-fixed coordinates can be used to obtain explicit analytical expressions for the 4-particle ROHH. If this approach is successful, the resulting harmonics could be very useful for reactive scattering calculations of 4-atom systems.

7. Summary and Conclusions

We have developed a new general procedure for deriving hyperspherical harmonics for triatomic systems and used it to obtain explicit analytical expressions for these harmonics in the body-fixed row-orthonomal hyperspherical coordinates (ROHC). These harmonics have been programmed using efficient numerical methods. Their degeneracy was also obtained analytically. These functions are attractive candidates for benchmark-quality state-to-state reactive scattering calculations. The procedure used to obtain them is generalizable to systems of more than three atoms.

Acknowledgment. The present work was strongly influenced by the pioneering research of Vincenzo Aquilanti on hyperspherical coordinates, hyperspherical harmonics, and their use in reactive scattering.

Appendix A. Proof that $\mathbf{C}^{\Pi n_\Pi J}$ is Independent of M_J

Equation 4.19 can be expressed in matrix form as

$$\boldsymbol{\Phi}^{\Pi n_\Pi J M_J}(\boldsymbol{\Theta}^{\rm sf}_\lambda) = \mathbf{C}^{\Pi n_\Pi J}\mathbf{F}^{\Pi n_\Pi J M_J}(\boldsymbol{\Theta}^{\rm bf}_\lambda) \tag{A.1}$$

where $\boldsymbol{\Phi}^{\Pi n_\Pi J M_J}(\Theta^{\rm sf}_\lambda)$ and $F^{\Pi n_\Pi J M_J}(\Theta^{\rm bf}_\lambda)$ are column vectors whose elements are respectively the functions of the sets $\{\boldsymbol{\Phi}^{\Pi n_\Pi J M_J}(\Theta^{\rm sf}_\lambda)\}$ and $\{F^{\Pi n_\Pi J M_J}(\boldsymbol{\Theta}^{\rm bf}_\lambda)\}$, defined in the beging of section 4.2, and $\mathbf{C}^{\Pi n_\Pi J}$ is a square matrix whose rows and columns are spanned by the pairs of indices $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ and L_Π, σ_Π, respectively. This matrix may contain some zeroes, since not all L_Π, dF functions need contribute to a given $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ $\mathbf{\Phi}$ function. However, the determinant of this matrix does not vanish and the square of its absolute values is 1 if the F functions are required to be orthonormal with respect to σ_Π. We wish to show that, in spite of the fact that the quantum number M_J, associated with the space-fixed $\hat{J}_z$ angular momentum operator, appears on both sides of eqs 4.19 and A.1, the $\mathbf{C}^{\Pi n_\Pi J}$ matrix does not depend on M_J. Since the functions $\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\mathbf{\Theta}_\lambda^{\rm sf})$ in the lhs of the first of those equations are orthonormal, but the $F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\mathbf{\Theta}_\lambda^{\rm bf})$ in its rhs need not be, it is more convenient to prove that $\bar{\mathbf{C}}^{\Pi n_\Pi J} = (\mathbf{C}^{\Pi n_\Pi J})^{-1}$ is independent of M_J and, therefore, so is $\mathbf{C}^{\Pi n_\Pi J}$. Indeed, the corresponding elements are given by

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} = (\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\mathbf{\Theta}_\lambda^{\rm sf}), F^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\mathbf{\Theta}_\lambda^{\rm bf})) \tag{A.2}$$

The variables $\mathbf{\Theta}_\lambda^{\rm sf}$ and $\mathbf{\Theta}_\lambda^{\rm bf}$, defined by eqs 4.4 and 2.3 and which appear in the lhs and rhs of eq 4.19, respectively, span the same angular configuration space and therefore are related to each other. The integration variable in the scalar product of eq A.2 can be chosen to be either $\mathbf{\Theta}_\lambda^{\rm sf}$ or $\mathbf{\Theta}_\lambda^{\rm bf}$, whichever is more convenient. Expressing the space-fixed $\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ in terms of its body-fixed counterparts $\Phi^{\Pi n_\Pi J k}_{l_\lambda^{(1)}, l_\lambda^{(2)}}$, we have

$$\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\mathbf{\Theta}_\lambda^{\rm sf}) = \sum_{k=-J}^{J} D^J_{M_J k}(\mathbf{a}_\lambda)\, \Phi^{\Pi n_\Pi J k}_{l_\lambda^{(1)}, l_\lambda^{(2)}}(\bar{\mathbf{\Theta}}_\lambda^{\rm bf}) \tag{A.3}$$

The symbol $\bar{\mathbf{\Theta}}_\lambda^{\rm bf}$ stands for the four body-fixed polar angles $\theta_\lambda^{I(1)}$, $\phi_\lambda^{I(1)}$ and $\theta_\lambda^{I(2)}$, $\phi_\lambda^{I(2)}$ of $\mathbf{r}_\lambda^{(1)}$ and $\mathbf{r}_\lambda^{(2)}$ in the principal axes of inertia frame. This relation permits us to write eq 2.1 in the form

$$\begin{aligned} \rho_\lambda^{\rm sf} &= \tilde{\mathbf{R}}(\mathbf{a}_\lambda) \begin{pmatrix} x_\lambda^{I(2)} & x_\lambda^{I(1)} \\ y_\lambda^{I(2)} & y_\lambda^{I(1)} \\ z_\lambda^{I(2)} & z_\lambda^{I(1)} \end{pmatrix} \\ &= \tilde{\mathbf{R}}(\mathbf{a}_\lambda) \begin{pmatrix} r_\lambda^{(2)} \sin\theta_\lambda^{I(2)} \cos\phi_\lambda^{I(2)} & r_\lambda^{(1)} \sin\theta_\lambda^{I(1)} \cos\phi_\lambda^{I(1)} \\ r_\lambda^{(2)} \sin\theta_\lambda^{I(2)} \sin\phi_\lambda^{I(2)} & r_\lambda^{(1)} \sin\theta_\lambda^{I(1)} \sin\phi_\lambda^{I(1)} \\ r_\lambda^{(2)} \cos\theta_\lambda^{I(2)} & r_\lambda^{(1)} \cos\theta_\lambda^{I(1)} \end{pmatrix} \end{aligned} \tag{A.4}$$

where $x_\lambda^{I(i)}$, $y_\lambda^{I(i)}$ and $z_\lambda^{I(i)}$ ($i = 1, 2$) are the Cartesian coordinates of $\mathbf{r}_\lambda^{(i)}$ in that frame. As a result of eqs A.4, 2.4, 4.1, and 4.2 we conclude that $\bar{\mathbf{\Theta}}_\lambda^{\rm bf}$ depends on θ and δ_λ only. Therefore, substituting eq 3.11 (with d replaced by σ_Π) and eq A.3 into eq A.2 and choosing $\mathbf{\Theta}_\lambda^{\rm bf}$ as the integration variable in its rhs results in

$$\begin{aligned} (\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} = N^{\Pi n_\Pi L_\Pi J}_{\sigma_\Pi} \sum_{\Omega_{J_\lambda}, k=-J}^{J} (D^J_{M_J k}(\mathbf{a}_\lambda), D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda))_{\mathbf{a}_\lambda} \times \\ (\Phi^{\Pi n_\Pi J k}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\theta, \delta_\lambda), \mathrm{e}^{\mathrm{i} L_\Pi \delta_\lambda} G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta))_{\theta, \delta_\lambda} \end{aligned} \tag{A.5}$$

where the two pairs of indices L_Π, σ_Π and $l_\lambda^{(1)}$, $l_\lambda^{(2)}$ span the rows and columns of $\bar{\mathbf{C}}^{\Pi n_\Pi J}$, respectively. The orthonormality property of the D functions,

$$(D^J_{M_J k}(\mathbf{a}_\lambda), D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda))_{\mathbf{a}_\lambda} = \frac{8\pi^2}{2J+1} \delta_{k \Omega_{J_\lambda}} \tag{A.6}$$

is independent of M_J. Replacing eq A.6 into eq A.5 leads to

$$\begin{aligned} (\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} = N^{\Pi n_\Pi L_\Pi J}_{\sigma_\Pi} \frac{8\pi^2}{2J+1} \times \\ \sum_{\Omega_{J_\lambda}=-J}^{J} (\Phi^{\Pi n_\Pi J \Omega_{J_\lambda}}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\theta, \delta_\lambda), \mathrm{e}^{\mathrm{i} L_\Pi \delta_\lambda} G^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta))_{\theta, \delta_\lambda} \end{aligned} \tag{A.7}$$

which is therefore also independent of M_J, QED. This independence is related to the rotational invariance of space.

Appendix B. Parity of the $\bar{G}$ Hyperspherical Harmonics with Respect to σ_Π

The $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta)$ one-dimensonal hyperspherical harmonics and the associated $\bar{F}^{\Pi n_\Pi L_\Pi J}_{M_J \sigma_\Pi}(\mathbf{\Theta}_\lambda^{\rm bf})$ five-dimensional harmonics have been defined in eq 4.34 and the statement immediately following it. To determine the values of σ_Π that lead to a complete set of linearly independent $\bar{F}$ harmonics, it is useful to consider the relation between $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta)$ and $\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} -\sigma_\Pi}(\theta)$, given by eq B.19. This relation, derived in section B.2 of this appendix, is based on the connection between the $l_\lambda^{(1)} l_\lambda^{(2)}$ and $l_\lambda^{(2)}$ $l_\lambda^{(1)}$ elements of the matrix $\mathbf{C}^{\Pi n_\Pi J}$, defined by eqs 4.19 and A.1, derived in section B.1 below.

B.1. Relation between $(\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ and $(\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}$

For the reason given at the beginning of Appendix A, it is more convenient to initially consider the matrix $\bar{\mathbf{C}}^{\Pi n_\Pi J} = (\mathbf{C}^{\Pi n_\Pi J})^{-1}$. Let us, in the rhs of eq A.2, chose $\mathbf{\Theta}_\lambda^{\rm bf}$ as the integration variable and use the corresponding volume element in the scalar product integral. The $\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ function in that expression is a simultaneous eigenfunction of $\hat{J}^2$, $\hat{J}_{z^{\rm sf}}$, $\hat{l}_\lambda^{(1)2}$, and $\hat{l}_\lambda^{(2)2}$ and is related to the simultaneous eigenfunctions $\Phi^{\Pi n_\Pi l_\lambda^{(1)}\ l_\lambda^{(2)}}_{m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}}}$ of $\hat{l}_\lambda^{(1)2}$, $\hat{l}^{(1)}_{\lambda_{z^{\rm sf}}}$, $\hat{l}_\lambda^{(2)2}$, *and* $\hat{l}^{(2)}_{\lambda_{z^{\rm sf}}}$, *by*

$$\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\mathbf{\Theta}_\lambda^{\rm sf}) = \sum_{m_{l_\lambda^{(1)}}, m_{l_\lambda^{(2)}}} C(l_\lambda^{(1)} l_\lambda^{(2)} J; m_{l_\lambda^{(1)}}, m_{l_\lambda^{(2)}} M_J) \Phi^{\Pi n_\Pi l_\lambda^{(1)}\ l_\lambda^{(2)}}_{m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}}}(\mathbf{\Theta}_\lambda^{\rm sf}) \tag{B.1}$$

where the C are Clebsch−Gordan coefficients. The $\Phi^{\Pi n_\Pi l_\lambda^{(1)}\ l_\lambda^{(2)}}_{m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}}}(\mathbf{\Theta}_\lambda^{\rm sf})$ are given explicitly by [41,42]

$$\Phi^{\Pi n_\Pi l_\lambda^{(1)}\ l_\lambda^{(2)}}_{m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}}}(\mathbf{\Theta}_\lambda^{\rm sf}) = Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta_\lambda)\, Y^{l_\lambda^{(1)}}_{m_{l_\lambda^{(1)}}}(\theta_\lambda^{(1)}, \phi_\lambda^{(1)})\, Y^{l_\lambda^{(2)}}_{m_{l_\lambda^{(2)}}}(\theta_\lambda^{(2)}, \phi_\lambda^{(2)}) \tag{B.2}$$

where

$$Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta_\lambda) = N^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}} \sin^{l_\lambda^{(1)}} \eta_\lambda \cos^{l_\lambda^{(2)}} \eta_\lambda P^{(l_\lambda^{(1)}+(1/2), l_\lambda^{(2)}+(1/2))}_{\xi_\lambda}(\cos 2\eta_\lambda) \tag{B.3}$$

with ξ_λ, $N^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}$, and P having been defined by eqs 4.17 and 4.18 and the statement after eq 4.17, respectively. Replacement of eqs B.1 and B.2 in eq A.2 results in

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} = \Big(\sum_{m_{l_\lambda^{(1)}}, m_{l_\lambda^{(2)}}} C(l_\lambda^{(1)} l_\lambda^{(2)} J; m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}} M_J)\, Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta_\lambda)$$
$$Y^{l_\lambda^{(1)}}_{m_{l_\lambda^{(1)}}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{l_\lambda^{(2)}}_{m_{l_\lambda^{(2)}}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}), F^{\Pi n_\Pi L_\Pi J}{}_{M_J \sigma_\Pi}[\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})]\Big) \qquad (B.4)$$

The integration variable in eq B.4 and in all scalar products of Appendix B is chosen to be $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}$. An analogous expression for $(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi}$ (with $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$ interchanged) is valid. Interchanging $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$ in eq A.2 results in

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} = (\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(2)} l_\lambda^{(1)}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}}), F^{\Pi n_\Pi L_\Pi J}{}_{M_J \sigma_\Pi}[\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})]) \qquad (B.5)$$

where $\Phi^{\Pi n_\Pi J M_J}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ is given by expressions analogous to eqs B.2 and B.3 with the pairs of indices $l_\lambda^{(1)}$, $m_{l_\lambda^{(1)}}$, and $l_\lambda^{(2)}$, $m_{l_\lambda^{(2)}}$ switched, but the variables in eq B.2 unchanged. The expression for $Q^{\Pi n_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}(\eta_\lambda)$ is

$$Q^{\Pi n_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}(\eta_\lambda) = N^{\Pi n_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}} \sin^{l_\lambda^{(2)}} \eta_\lambda \cos^{l_\lambda^{(1)}} \eta_\lambda P_{\xi_\lambda}^{(l_\lambda^{(2)}+(1/2), l_\lambda^{(1)}+(1/2))}(\cos 2\eta_\lambda) \qquad (B.6)$$

Using eqs C.4 and 4.18, we get

$$Q^{\Pi n_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}(\eta_\lambda) = (-1)^{\xi_\lambda} N^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}} \sin^{l_\lambda^{(2)}}\Big(\frac{\pi}{2} - \eta_\lambda\Big) \times \cos^{l_\lambda^{(1)}}\Big(\frac{\pi}{2} - \eta_\lambda\Big) P_{\xi_\lambda}^{(l_\lambda^{(1)}+(1/2), l_\lambda^{(2)}+(1/2))}(-\cos 2\eta_\lambda) \qquad (B.7)$$

With the help of the variable

$$\eta'_\lambda = \frac{\pi}{2} - \eta_\lambda \qquad (B.8)$$

we can rewrite eq B.7 as

$$Q^{\Pi n_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}(\eta_\lambda) = (-1)^{\xi_\lambda} Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta'_\lambda) \qquad (B.9)$$

Due to the remarks after eq B.5 and using eqs B.8 and B.9, we can rewrite eq B.5 as

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi} = \sum_{m_{l_\lambda^{(1)}}, m_{l_\lambda^{(1)}}} C(l_\lambda^{(2)} l_\lambda^{(1)} J; m_{l_\lambda^{(2)}} m_{l_\lambda^{(1)}} M_J)(-1)^{\xi_\lambda} \times Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta'_\lambda)\, Y^{l_\lambda^{(2)}}_{m_{l_\lambda^{(2)}}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)}) \times Y^{l_\lambda^{(1)}}_{m_{l_\lambda^{(1)}}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}), F^{\Pi n_\Pi L_\Pi J}{}_{M_J \sigma_\Pi}[\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})]) \qquad (B.10)$$

We now change integration variables $\boldsymbol{\Theta}_\lambda^{\mathrm{sf}} \equiv (\theta_\lambda^{(1)}, \phi_\lambda^{(1)}, \theta_\lambda^{(2)}, \phi_\lambda^{(2)}, \eta_\lambda)$ to integration variables $\boldsymbol{\Theta}_\lambda'^{\mathrm{sf}} \equiv (\theta_\lambda^{(2)}, \phi_\lambda^{(2)}, \theta_\lambda^{(1)}, \phi_\lambda^{(1)}, \eta'_\lambda)$ and then drop the prime in the dummy variable $\boldsymbol{\Theta}_\lambda'^{\mathrm{sf}}$ to get an expression analogous to eq B.10 with $\theta_\lambda^{(2)}$, $\phi_\lambda^{(2)}$ replaced by $\theta_\lambda^{(1)}$, $\phi_\lambda^{(1)}$ and vice versa and η'_λ replaced by η_λ. Use, in the resulting equation, of the symmetry relation between Clebsch−Gordan coefficients[47]

$$C(l_\lambda^{(2)} l_\lambda^{(1)} J; m_{l_\lambda^{(2)}} m_{l_\lambda^{(1)}} M_J) = (-1)^{l_\lambda^{(1)} + l_\lambda^{(2)} - J} C(l_\lambda^{(1)} l_\lambda^{(2)} J; m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}} M_J) \qquad (B.11)$$

yields

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi} = (-1)^{(1/2)(l_\lambda^{(1)} + l_\lambda^{(1)} - J)} \times \sum_{m_{l_\lambda^{(1)}}, m_{l_\lambda^{(1)}}} C(l_\lambda^{(1)} l_\lambda^{(2)} J; m_{l_\lambda^{(1)}} m_{l_\lambda^{(2)}} M_J)(-1)^{\xi_\lambda} Q^{\Pi n_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}(\eta_\lambda) \times Y^{l_\lambda^{(1)}}_{m_{l_\lambda^{(1)}}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{l_\lambda^{(2)}}_{m_{l_\lambda^{(2)}}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}), F_{\mathrm{rec}}^{\Pi n_\Pi L_\Pi J}{}_{M_J \sigma_\Pi}[\boldsymbol{\Theta}_\lambda^{\mathrm{bf}}(\boldsymbol{\Theta}_\lambda^{\mathrm{sf}})]) \qquad (B.12)$$

Comparison of this expression with eq B.4 and use of eq 4.17 results in

$$(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi} = (-1)^{(1/2)(n_\Pi + l_\lambda^{(1)} + l_\lambda^{(2)}) - J} (\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} \qquad (B.13)$$

where the exponent of (-1) is an integer because n_Π and $l_\lambda^{(1)} + l_\lambda^{(2)}$ have the same parity, as pointed out after eq 4.17. Equation B.13 indicates that $(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi}$ and $(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi}$ differ at most by a sign.

From the relation (B.13) between $(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi}$ and $(\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi}$ we wish to obtain an analogous relation between $(\mathbf{C}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi}$ and $(\mathbf{C}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi}$. To that efffect we define the matrix $(\bar{\mathbf{C}}'^{\Pi n_\Pi J})$ as the one whose $L_\Pi d$, $l_\lambda^{(1)} l_\lambda^{(2)}$ element is given by the lhs of eq B.13, i.e.,

$$(\bar{\mathbf{C}}'^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi} = (\bar{\mathbf{C}}^{\Pi n_\Pi J})^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} \qquad (B.14)$$

As a result, eq B.13 can be written in matrix form as

$$(\bar{\mathbf{C}}'^{\Pi n_\Pi J}) = (\bar{\mathbf{C}}^{\Pi n_\Pi J}) \mathbf{q}^{\Pi n_\Pi J} \qquad (B.15)$$

where $\mathbf{q}^{\Pi n_\Pi J}$ is the square diagonal matrix defined by

$$(\mathbf{q}^{\Pi n_\Pi J})^{l_\lambda^{(2)} l_\lambda^{(1)}}_{L_\Pi \sigma_\Pi} = (-1)^{(1/2)(n_\Pi + l_\lambda^{(1)} + l_\lambda^{(2)}) - J} \delta^{l_\lambda^{(1)} l_\lambda^{(2)}}_{L_\Pi \sigma_\Pi} \qquad (B.16)$$

Taking the inverse of eq B.15, utilizing the fact that $\mathbf{q}^{\Pi n_\Pi J}$ equals its inverse and using the definition of $\bar{\mathbf{C}}^{\Pi n_\Pi J}$ given at the beginning of this section results in

$$(\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}} = (-1)^{(1/2)(n_\Pi + l_\lambda^{(1)} + l_\lambda^{(2)}) - J} (\mathbf{C}^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}} \qquad (B.17)$$

This expression will now used to obtain the relation between $\bar{G}^{\Pi n_\Pi L_\Pi J}{}_{\Omega_{J_\lambda} - \sigma_\Pi}(\theta)$ and $\bar{G}^{\Pi n_\Pi L_\Pi J}{}_{\Omega_{J_\lambda} \sigma_\Pi}$.

B.2. Relation between $\bar{G}^{\Pi n_\Pi L_\Pi J}{}_{\Omega_{J_\lambda} - \sigma_\Pi}(\theta)$ and $\bar{G}^{\Pi n_\Pi L_\Pi J}{}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta)$

Interchanging $l_\lambda^{(1)}$ and $l_\lambda^{(2)}$ in eq 4.20 shows that the relation between $\bar{F}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)}}{}_{M_J}(\theta_\lambda^{\mathrm{bf}})$ and $\bar{F}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(2)} l_\lambda^{(1)}}{}_{M_J}(\theta_\lambda^{\mathrm{bf}})$ is the same as between $(C^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(1)} l_\lambda^{(2)}}$ and $(C^{\Pi n_\Pi J})^{L_\Pi \sigma_\Pi}_{l_\lambda^{(2)} l_\lambda^{(1)}}$. Similarly, interchanging those two quantum numbers in eq 4.21 shows that the relation between $\bar{G}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(1)} l_\lambda^{(2)}}{}_{\Omega_{J_\lambda}}(\theta)$ and $\bar{G}^{\Pi n_\Pi L_\Pi J}_{l_\lambda^{(2)} l_\lambda^{(1)}}{}_{\Omega_{J_\lambda}}(\theta)$ is the same as between the corresponding $\bar{F}$ and therefore as between the corresponding $\mathbf{C}^{\Pi n_\Pi J}$ matrix elements. As a result, using eq B.17 we get

$$\bar{G}^{\Pi n_\Pi L_\Pi J}_{l^{(2)}_\lambda l^{(1)}_\lambda \Omega_{J_\lambda}}(\theta) = (-1)^{(1/2)(n_\Pi + l^{(1)}_\lambda + l^{(2)}_\lambda) - J}\, \bar{G}^{\Pi n_\Pi L_\Pi J}_{l^{(1)}_\lambda l^{(2)}_\lambda \Omega_{J_\lambda}}(\theta) \tag{B.18}$$

This expression is valid for any $l^{(1)}_\lambda$, $l^{(2)}_\lambda$ pair, and in particular for the $l^{(1)}_{\min}$ and $l^{(2)}_{\min}$ of eqs 4.26 and 4.28. Interchanging $l^{(1)}_{\min}$ and $l^{(2)}_{\min}$ in eq 4.34 and using eqs 4.26 and 4.28 finally results in

$$\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} - \sigma_\Pi}(\theta) = (-1)^{(1/2)(n_\Pi - J + b_{J+\Pi})}\bar{G}^{\Pi n_\Pi L_\Pi J}_{\Omega_{J_\lambda} \sigma_\Pi}(\theta) \tag{B.19}$$

Appendix C. Some Relevant Properties of Jacobi Polynomials

In this appendix we give some properties of Jacobi polynomials that will be used in Appendices D and E. A formula expressing explicitly Jacobi polynomials of any degree and order in terms of one special kind of Jacobi polynomial having two equal superscripts is given by[48]

$$P_n^{(\beta,\alpha)}(x) = \frac{(1+\beta)_n}{(1+\alpha+\beta)_n}\sum_{k=0}^{n} A_{nk}^{(\beta,\alpha)} P_k^{(\beta,\beta)}(x) \tag{C.1}$$

where

$$(a)_n = a(a+1)\cdots(a+n-1) \tag{C.2}$$

and

$$A_{nk}^{(\beta,\alpha)} = \frac{(-1)^{n-k}(\alpha-\beta)_{n-k}(1+\alpha+\beta)_{n+k}(1+2\beta)_k(1+2\beta+2k)}{(n-k)!(1+2\beta)_{n+k+1}(1+\beta)_k} \tag{C.3}$$

It should be remembered that, whenever n is a non-negative integer, α and β are real numbers greater than -1. Since Jacobi polynomials have the symmetry property:[49]

$$P_n^{(\alpha,\beta)}(x) = (-1)^n P_n^{(\beta,\alpha)}(-x) \tag{C.4}$$

we get, replacing eq C.1 into eq C.4

$$P_n^{(\alpha,\beta)}(x) = \frac{(-1)^n(1+\beta)_n}{(1+\alpha+\beta)_n}\sum_{k=0}^{n} A_{nk}^{(\beta,\alpha)} P_k^{(\beta,\beta)}(-x) \tag{C.5}$$

In addition, eq C.4 furnishes

$$P_k^{(\beta,\beta)}(-x) = (-1)^k P_k^{(\beta,\beta)}(x) \tag{C.6}$$

Inserting eq C.6 into eq C.5 leads to

$$P_n^{(\alpha,\beta)}(x) = \frac{(-1)^n(1+\beta)_n}{(1+\alpha+\beta)_n}\sum_{k=0}^{n} (-1)^k A_{nk}^{(\beta,\alpha)} P_k^{(\beta,\beta)}(x) \tag{C.7}$$

Let us now change from summation index k to $k' = n - k$ and then drop the prime in the k'. We get

$$P_n^{(\alpha,\beta)}(x) = \frac{(1+\beta)_n}{(1+\alpha+\beta)_n}\sum_{k=0}^{n} W_{nk}^{(\alpha,\beta)} P_{n-k}^{(\beta,\beta)}(x) \tag{C.8}$$

where

$$W_{nk}^{(\alpha,\beta)} = \frac{(\alpha-\beta)_k(1+\alpha+\beta)_{2n-k}(1+2\beta)_{n-k}(1+2\beta+2n-2k)}{k!(1+2\beta)_{2n-k+1}(1+\beta)_{n-k}} \tag{C.9}$$

Defining σ by

$$\sigma = \beta - \alpha \tag{C.10}$$

eqs C.8 and C.9 lead to

$$P_n^{(\alpha,\alpha+\sigma)}(x) = \frac{(1+\alpha+\sigma)_n}{(1+2\alpha+\sigma)_n}\sum_{k=0}^{n} W_{nk}^{(\alpha,\alpha+\sigma)}P_{n-k}^{(\alpha+\sigma,\alpha+\sigma)}(x) \tag{C.11}$$

where

$$W_{nk}^{(\alpha,\alpha+\sigma)} = \frac{(-\sigma)_k(1+2\alpha+\sigma)_{2n-k}(1+2\alpha+2\sigma)_{n-k}(1+2\alpha+2\sigma+2n-2k)}{k!(1+2\alpha+2\sigma)_{2n-k+1}(1+\alpha+\sigma)_{n-k}} \tag{C.12}$$

From eq C.2, we know that

$$\frac{(a)_n}{(a)_k} = (a+k)_{n-k} \qquad \text{for } k \le n \tag{C.13}$$

With the help of eqs C.13 and C.12, eq C.11 can be rewritten as

$$P_n^{(\alpha,\alpha+\sigma}(x) = \sum_{k=0}^{n}\frac{(-\sigma)_k(1+2\alpha+\sigma+n)_{n-k}(1+\alpha+\sigma+n-k)_k}{k!(1+2\alpha+2\sigma+n-k)_{n+1}}(1+2\alpha+2\sigma+2n-2k)P_{n-k}^{(\alpha+\sigma,\alpha+\sigma)}(x) \tag{C.14}$$

If σ is a positive integer, $(-\sigma)_k$ has the property

$$(-\sigma)_k = \begin{cases} \dfrac{(-1)^k\sigma!}{(\sigma-k)!} & \text{for} \quad k \le \sigma \\ 0 & \text{for} \quad k > \sigma \end{cases} \tag{C.15}$$

Inserting eq C.15 into eq C.14 leads, for such values of σ, to

$$P_n^{(\alpha,\alpha+\sigma)}(x) = \sum_{k=0}^{\min(n,\sigma)}\binom{\sigma}{k}\frac{(-1)^k(1+2\alpha+\sigma+n)_{n-k}(1+\alpha+\sigma+n-k)_k}{(1+2\alpha+2\sigma+n-k)_{n+1}}(1+2\alpha+2\sigma+2n-2k)P_{n-k}^{(\alpha+\sigma,\alpha+\sigma)}(x) \tag{C.16}$$

This expression is also valid for $\sigma = 0$.

Appendix D. Expansion of $P_k^{(\alpha,\alpha)}(-\cos 2\theta \cos 2\delta_\lambda)$ in Terms of $e^{iL\delta_\lambda}$

We can write $P_k^{(\alpha,\alpha)}(-\cos 2\theta \cos 2\delta_\lambda)$ as[50]

$$P_k^{(\alpha,\alpha)}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{\Gamma(k+\alpha+1)}{k!\Gamma(2\alpha+k+1)}\sum_{m=0}^{k}\binom{k}{m}\frac{\Gamma(2\alpha+k+m+1)(-\cos 2\theta\cos 2\delta_\lambda - 1)^m}{2^m\Gamma(\alpha+m+1)} \tag{D.1}$$

Replacing in eq D.1 $\cos 2\delta_\lambda$ by $(e^{i2\delta_\lambda} + e^{-i2\delta_\lambda})/2$ and grouping the terms with the same power of $e^{i2\delta_\lambda}$ leads to

$$P_k^{(\alpha,\alpha)}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{1}{\Gamma(2\alpha+k+1)}\sum_{q=-k}^{k} e^{i2q\delta_\lambda}f_{kq}^{\alpha}(\theta) \tag{D.2}$$

where

$$f^{\alpha}_{kq}(\theta) = (-1)^{|q|}\sum_{p=|q|,2}^{k}\binom{p}{\frac{p-|q|}{2}}\frac{\Gamma(2\alpha+k+p+1)P^{(\alpha+p,\alpha+p)}_{k-p}(0)\cos^{p}2\theta}{p!4^{p}} \tag{D.3}$$

and[51]

$$P^{(\gamma,\gamma)}_{j}(0) = \begin{cases} 0 & \text{for } j \text{ odd} \\ \dfrac{(-1)^{(j/2)}\Gamma(j+\gamma+1)}{2^{j}(j/2)!\Gamma(j/2+\gamma+1)} & \text{for } j \text{ even} \end{cases} \tag{D.4}$$

As a result, $k - |q|$ must be even for $f^{\alpha}_{kq}(\theta)$ not to vanish. We now define the non-negative integer r by

$$k - |q| = 2r \tag{D.5}$$

Changing, in eq D.3, the summation index from p to $\bar{p} = (p - |q|)/2$ and using eq D.4 with $\gamma = \alpha + 2\bar{p} + |q|$ and $j = 2r - 2\bar{p}$, we get

$$f^{\alpha}_{kq}(\theta) = \left(-\frac{1}{4}\right)^{r}\left(-\frac{\cos 2\theta}{4}\right)^{|q|}\Gamma(2r+\alpha+|q|+1)\frac{1}{r!}\sum_{\bar{p}=0}^{r}\binom{r}{\bar{p}}\frac{\Gamma(2\alpha+2r+2|q|+2\bar{p}+1)}{(\bar{p}+|q|)!\Gamma(r+\bar{p}+\alpha+|q|+1)}\left(-\frac{\cos^{2}2\theta}{4}\right)^{\bar{p}} \tag{D.6}$$

Using the duplication formula of Γ functions[52]

$$\Gamma(2z) = (2\pi)^{-1/2}2^{2z-1/2}\Gamma(z)\Gamma(z+1/2) \tag{D.7}$$

and choosing $z = \alpha + r + |q| + \bar{p} + {}^{1}/_{2}$, we obtain

$$\Gamma(2\alpha+2r+2|q|+2\bar{p}+1) = (\pi)^{-1/2}2^{2\alpha+2r+2|q|+2\bar{p}}\Gamma(\alpha+r+|q|+\bar{p}+1/2)\,\Gamma(\alpha+r+|q|+\bar{p}+1) \tag{D.8}$$

Replacing eq D.8 in eq D.6 results in

$$f^{\alpha}_{2r+|q||q|}(\theta) = \frac{2^{2\alpha}}{\sqrt{\pi}}(-1)^{(r+|q|)}\cos^{|q|}2\theta\frac{\Gamma(2r+\alpha+|q|+1)}{r!}\sum_{\bar{p}=0}^{r}\binom{r}{\bar{p}}\frac{\Gamma(\alpha+r+|q|+\bar{p}+1/2)}{2^{\bar{p}}\Gamma(\bar{p}+|q|+1)}(-\cos 4\theta-1)^{\bar{p}} \tag{D.9}$$

We know, however, that[50]

$$P^{(|q|,\alpha-1/2)}_{r}(-\cos 4\theta) = \frac{\Gamma(r+|q|+1)}{r!\Gamma(r+\alpha+|q|+1/2)}\sum_{\bar{p}=0}^{r}\binom{r}{\bar{p}}\frac{\Gamma(\alpha+r+|q|+\bar{p}+1/2)}{2^{\bar{p}}\Gamma(\bar{p}+|q|+1)}(-\cos 4\theta-1)^{\bar{p}} \tag{D.10}$$

Substitution of eq D.10 in eq D.9 results in

$$f^{\alpha}_{2r+|q||q|}(\theta) = \frac{(-1)^{|q|}2^{2\alpha}\Gamma(2r+\alpha+|q|+1)\,\Gamma(\alpha+r+|q|+1/2)\cos^{|q|}2\theta P^{(\alpha-1/2,|q|)}_{r}(\cos 4\theta)}{\sqrt{\pi}\Gamma(r+|q|+1)} \tag{D.11}$$

It is interesting to notice that the θ dependence in eq D.3 involving a sum of powers of $\cos 2\theta$ has become, in eq D.11, the single product of $\cos^{|q|} 2\theta$ by a Jacobi polynomial of $\cos 4\theta$. This very important property is responsible for the appearance of such polynomials in eqs D.19 below and 4.63 and therefore in the $\mathcal{G}$ harmonics of eq 4.69. Equations D.2 and D.11 now yield

$$P^{(\alpha,\alpha)}_{k}(-\cos 2\theta\cos 2\delta_{\lambda}) = \frac{(-1)^{k}\Gamma(k+\alpha+1)2^{2\alpha}}{\sqrt{\pi}\Gamma(2\alpha+k+1)}\sum_{L=-2k,4}^{2k}\frac{\Gamma((k+|L|/2+1)/2+\alpha)}{\Gamma((k+|L/2|)/2+1)}e^{iL\delta_{\lambda}}\cos^{|L/2|}2\theta P^{(\alpha-1/2,|L/2|)}_{(k-|L/2|)/2}(\cos 4\theta) \tag{D.12}$$

where L is an even integer given by

$$L = 2q \tag{D.13}$$

With the help of eq D.12, eq C.16 can be rewritten as

$$P_n^{(\alpha,\alpha+\sigma)}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{(-1)^n 2^{2\alpha+2\sigma}}{\sqrt{\pi}} \sum_{L=-2n,2}^{2n} e^{iL\delta_\lambda} \bar{s}_{n|L|}^{(\alpha,\sigma)}(\theta) \tag{D.14}$$

where

$$\bar{s}_{n|L|}^{(\alpha,\sigma)}(\theta) = \cos^{|L/2|}(2\theta) \sum_{\bar{v}=\bar{v}_{\min},2}^{\bar{v}_{\max}} \binom{\sigma}{\bar{v}} \frac{(-1)^{\bar{v}}(1+2\alpha+\sigma+n)_{n-\bar{v}}\Gamma(n-\bar{v}+\alpha+\sigma+1)}{\Gamma((n-\bar{v}+|L/2|)/2+1)\,\Gamma(2\alpha+2\sigma+n-\bar{v}+1)} \times \frac{(1+\alpha+\sigma+n-\bar{v})_{\bar{v}}\Gamma((n-\bar{v}+|L/2|+1)/2+\alpha+\sigma)(1+2\alpha+2\sigma+2n-2k)}{(1+2\alpha+2\sigma+n-\bar{v})_{n+1}} P_{(n-\bar{v}-|L/2|)/2}^{(\alpha+\sigma-(1/2),|L/2|)}(\cos 4\theta) \tag{D.15}$$

with $\bar{v}$ having the same parity as $n - |L|/2$ and

$$\bar{v}_{\min} = \frac{1-(-1)^{n-|L|/2}}{2} \tag{D.16}$$

$$\bar{v}_{\max} = \min(n, \sigma, n-|L|/2) = \min\left(n-|L|/2, \sigma - \frac{1-(-1)^{n-|L|/2-\sigma}}{2}\right) \tag{D.17}$$

Since eq C.16 is valid for non-negative integer σ and since σ_Π, as stated after eq 4.23 and proven in section 4.6, can also be restricted to being a non-negative integer, we are free to chose $\sigma = \sigma_\Pi$ in eq D.14. Let us also choose $\alpha = l_{\min}^{(1)} + {}^1/_2$ and $\alpha + \sigma = l_{\min}^{(2)} + {}^1/_2$, where $l_{\min}^{(1)}$ and $l_{\min}^{(2)}$ are defined in eqs 4.26 and 4.28. With these choices, eq D.14 becomes

$$P_n^{(l_{\min}^{(1)}+(1/2),l_{\min}^{(2)}+(1/2))}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{(-1)^n(2n+2l_{\min}^{(2)}+1)!\,l_{\min}^{(2)}!}{2^{2n}(\sigma_\Pi+1)!(n+l_{\min}^{(2)})!(n+2l_{\min}^{(2)}-\sigma_\Pi+1)!} \sum_{L=-2n,2}^{2n} e^{iL\delta_\lambda} s_{n|L|}^{(J,\sigma_\Pi)}(\theta) \tag{D.18}$$

where

$$s_{n|L|}^{(J,\sigma_\Pi)}(\theta) = \cos^{|L/2|}(2\theta) \sum_{\bar{v}=\bar{v}_{\min},2}^{\bar{v}_{\max}} \frac{\binom{\sigma_\Pi}{\bar{v}}\binom{\frac{2n-2\bar{v}+|L|}{4}+l_{\min}^{(2)}}{l_{\min}^{(2)}}}{\binom{2n-\bar{v}+2l_{\min}^{(2)}+2}{\sigma_\Pi+1}}(2n-2\bar{v}+2l_{\min}^{(2)}+2) P_{(1/4)(2n-2\bar{v}-|L|)}^{(l_{\min}^{(2)},|L/2|)}(\cos 4\theta) \tag{D.19}$$

The J dependence of $s_{n|L|}^{(J,\sigma_\Pi)}(\theta)$ stems from the corresponding dependence of $l_{\min}^{(2)}$. For $\sigma_\Pi = 0$, we have $l_{\min}^{(1)} = l_{\min}^{(2)}$, and with the help of eq D.12, eq D.18 can, in this case, be written as

$$P_n^{(l_{\min}^{(2)}+(1/2),l_{\min}^{(2)}+(1/2))}(-\cos 2\theta \cos 2\delta_\lambda) = \frac{(-1)^n(2n+2l_{\min}^{(2)}+1)!\,l_{\min}^{(2)}!}{2^{2n}(n+l_{\min}^{(2)})!(n+2l_{\min}^{(2)}+1)!} \sum_{L=-2n,4}^{2n} e^{iL\delta_\lambda} s_{n|L|}^{(J,\sigma_\Pi=0)}(\theta) \tag{D.20}$$

with

$$s_{n|L|}^{(J,\sigma_\Pi=0)}(\theta) = \cos^{|L/2|}(2\theta) \binom{\frac{2n+|L|}{4}+l_{\min}^{(2)}}{l_{\min}^{(2)}} P_{(1/4)(2n-|L|)}^{(l_{\min}^{(2)},|L/2|)}(\cos 4\theta) \tag{D.21}$$

Therefore, $s_{n|L|}^{(J,\sigma_\Pi=0)}(\theta)$ is reduced to a single term, and the summation index L in eq D.20 varies in steps of 4 instead of the steps of 2 in eq D.18.

Appendix E. Calculation of $(T_{\lambda 1}^{1} - T_{\lambda -1}^{1})^{l_\lambda^{(1)}}(T_{\lambda 1}^{1} - T_{\lambda -1}^{1})^{l_\lambda^{(2)}}$

In the present appendix we express the quantity $(T_{\lambda 1}^{1} - T_{\lambda -1}^{1})^{l_\lambda^{(1)}}(T_{\lambda 1}^{1} - T_{\lambda -1}^{1})^{l_\lambda^{(2)}}$ in the terms of the ROHC of eq 2.2. The resulting relation is needed to transform the $\sin^{l^{(1)}_{\min}} \eta_\lambda \cos^{l^{(2)}_{\min}} \eta_\lambda\, Y^{JM_J=J}_{l^{(1)}_{\min} l^{(2)}_{\min}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)})$ function of the space-fixed angular variables $\mathbf{\Theta}_\lambda^{\mathrm{sf}}$, which appears in eq 4.38, to the body-fixed variables $\mathbf{\Theta}_\lambda^{\mathrm{bf}}$.

The six complex coordinates $T_{\lambda j}^{k}$ ($j = -1, 1$; $k = -1, 0, -1$) are defined in terms of the six space-fixed Cartesian coordinates $x_\lambda^{(i)}$, $y_\lambda^{(i)}$, $z_\lambda^{(i)}$ ($i = 1, 2$) by the inverse of the relations[33]

$$x_\lambda^{(1)} = -\frac{\mathrm{i}}{4}(T_{\lambda 1}^{1} - T_{\lambda -1}^{1} - T_{\lambda 1}^{-1} + T_{\lambda -1}^{-1}) \tag{E.1}$$

$$y_\lambda^{(1)} = \frac{1}{4}(-T_{\lambda 1}^{1} - T_{\lambda 1}^{-1} + T_{\lambda -1}^{1} + T_{\lambda -1}^{-1}) \tag{E.2}$$

$$z_\lambda^{(1)} = \frac{\mathrm{i}\sqrt{2}}{4}(T_{\lambda 1}^{0} - T_{\lambda -1}^{0}) \tag{E.3}$$

$$x_\lambda^{(2)} = \frac{1}{4}(T_{\lambda 1}^{1} - T_{\lambda 1}^{-1} + T_{\lambda -1}^{1} - T_{\lambda -1}^{-1}) \tag{E.4}$$

$$y_\lambda^{(2)} = -\frac{\mathrm{i}}{4}(T_{\lambda 1}^{1} + T_{\lambda 1}^{-1} + T_{\lambda -1}^{1} + T_{\lambda -1}^{-1}) \tag{E.5}$$

$$z_\lambda^{(2)} = -\frac{\sqrt{2}}{4}(T_{\lambda 1}^{0} + T_{\lambda -1}^{0}) \tag{E.6}$$

They can be written in terms of the ROHC as

$$T_{\lambda j}^{k} = \rho \mathrm{e}^{-\mathrm{i}\pi/2} \mathrm{e}^{\mathrm{i}j\delta_\lambda} \tau_{\lambda j}^{k}(\mathbf{\Theta}_\lambda^{\mathrm{bf}}) \tag{E.7}$$

where

$$\tau_{\lambda j}^{k}(\mathbf{\Theta}_\lambda^{\mathrm{bf}}) = \sum_{p=-1}^{1} D_{kp}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2) t_j^{p}(\theta) \tag{E.8}$$

$$t_j^{\pm 1} = \sin\theta \tag{E.9}$$

$$t_j^{0} = j\sqrt{2}\cos\theta \tag{E.10}$$

$$k = -1, 0, 1 \tag{E.11}$$

$$j = -1, 1 \tag{E.12}$$

Equations E.1−E.12 provide a translation dictionary between the 6 space-fixed Cartesian coordinates just mentioned and the 6 ROHC ρ, $\mathbf{\Theta}_\lambda^{\mathrm{bf}}$. To calculate $(T_{\lambda 1}^{1} - T_{\lambda -1}^{1})^{l_\lambda^{(1)}}(T_{\lambda 1}^{1} + T_{\lambda -1}^{1})^{l_\lambda^{(2)}}$ we will need, in view of eq E.7, expressions for $(\tau_{\lambda j}^{1})^{w}$ where w is a non-negative integer. From eq E.8 we have

$$(\tau_{\lambda j}^{1})^{w} = \{D_{10}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\sin\theta + D_{10}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2) j\sqrt{2}\cos\theta + D_{1-1}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\sin\theta\}^{w} \tag{E.13}$$

Using the expression for a power of a trinomial we obtain

$$(\tau_{\lambda j}^{1})^{w} = \sum_{u_1u_2u_3} \begin{pmatrix} & w & \\ u_1 & u_2 & u_3 \end{pmatrix} \{D_{10}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\sin\theta\}^{u_1}\{D_{10}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2) j\sqrt{2}\cos\theta\}^{u_2}\{D_{1-1}^{1}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\sin\theta\}^{u_3} \tag{E.14}$$

where

$$\begin{pmatrix} & w & \\ u_1 & u_2 & u_3 \end{pmatrix} = \frac{w!}{u_1!u_2!u_3!} \tag{E.15}$$

with

$$w = u_1 + u_2 + u_3 \tag{E.16}$$

According to the Clebsch−Gordan series[39]

$$D^{j_1}_{m_1\Omega_1}(a,b,c)\, D^{j_2}_{m_2\Omega_2}(a,b,c) = \sum_{j=|j_1-j_2|}^{j_1+j_2} C(j_1j_2j;m_1m_2m_1+m_2)\, C(j_1j_2j;\Omega_1\Omega_2\Omega_1+\Omega_2)\, D^{j}_{m_1+m_2\Omega_1+\Omega_2}(a,b,c) \tag{E.17}$$

This expression, together with induction over u_1 and u_2, yields

$$\{D^1_{11}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\}^{u_1} = D^{u_1}_{u_1u_1}(a_\lambda,b_\lambda,c_\lambda+\pi/2) \tag{E.18}$$

$$\{D^1_{1-1}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\}^{u_3} = D^{u_3}_{u_3-u_3}(a_\lambda,b_\lambda,c_\lambda+\pi/2) \tag{E.19}$$

and

$$\{\sqrt{2}D^1_{10}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\}^{u_2} = \left(\frac{(2u_2)!!}{(2u_2-1)!!}\right)^{1/2} D^{u_2}_{u_20}(a_\lambda,b_\lambda,c_\lambda+\pi/2) \tag{E.20}$$

Inserting eqs E.17−E.19 into eq E.14, we get

$$(\tau^{\,1}_{\lambda j})^w = \sum_{u_1u_2u_3} \begin{pmatrix} & w & \\ u_1 & u_2 & u_3 \end{pmatrix} \left(\frac{(2u_2)!!}{(2u_2-1)!!}\right)^{1/2} D^{u_1}_{u_1u_1}(a_\lambda,b_\lambda,c_\lambda+\pi/2) D^{u_2}_{u_20}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\, D^{u_3}_{u_3-u_3}(a_\lambda,b_\lambda,c_\lambda+\pi/2)(\sin\theta)^{u_1+u_3}(j\cos\theta)^{u_2} \tag{E.21}$$

Defining the quantity

$$\Omega_\lambda = u_1 - u_3 \tag{E.22}$$

we can, from eq E.16, obtain the relations

$$u_1 = (w + \Omega_\lambda - u_2)/2 \tag{E.23}$$

and

$$u_3 = (w - \Omega_\lambda - u_2)/2 \tag{E.24}$$

With the help of eq E.18, and a change of summation indices from u_1, u_3 to Ω_λ, eq E.21 can be written as

$$(\tau^{\,1}_{\lambda j})^w = \sum_{\Omega_\lambda=-w}^{w} D^{w}_{w\Omega_\lambda}(a_\lambda,b_\lambda,c_\lambda+\pi/2) A^{(jwm=0)}_{|\Omega_\lambda|}(\theta) \tag{E.25}$$

where $0 \le |\Omega_\lambda| \le w$ and

$$A^{(jwm=0)}_{|\Omega_\lambda|}(\theta) = \left[\frac{(w+|\Omega_\lambda|)!(w-|\Omega_\lambda|)!}{(2w)!}\right]^{1/2} \sum_{u_2=u_{2\min},2}^{w-|\Omega_\lambda|} \begin{pmatrix} & w & \\ \frac{w+\Omega_\lambda-u_2}{2} & u_2 & \frac{w-\Omega_\lambda-u_2}{2} \end{pmatrix} (\sin\theta)^{w-u_2}(2j\cos\theta)^{u_2} \tag{E.26}$$

$$u_{2\min} = \frac{1 - (-1)^{w-|\Omega_\lambda|}}{2} \tag{E.27}$$

(A quantity $A^{(jwm)}_{|\Omega_\lambda|}(\theta)$ with $m \geq 0$ and which reduces, for $m = 0$, to eq E.26 will be defined later by eq E.38.) Equation E.26 can be simplified to

$$A^{(jwm=0)}_{|\Omega_\lambda|}(\theta)= \begin{cases} \dfrac{\sin^w \theta (w)!\,{}_2F_1\left(-\dfrac{w + |\Omega_\lambda|}{2}, -\dfrac{w - |\Omega_\lambda|}{2},\dfrac{1}{2};\cot^2 \theta\right)}{\{(w - |\Omega_\lambda|)!(w + |\Omega_\lambda|)!(2w)!\}^{1/2}} & \text{for } w - |\Omega_\lambda| \text{ even} \\ \dfrac{2j \sin^w \theta \cos \theta (w^2 - \Omega_\lambda{}^2)^{1/2}{}_2F_1\left(-\dfrac{w + |\Omega_\lambda| - 1}{2}, -\dfrac{w - |\Omega_\lambda| - 1}{2},\dfrac{3}{2};\cot^2 \theta\right)}{\{(w - |\Omega_\lambda| - 1)!(w + |\Omega_\lambda| - 1)!(2w)!\}^{1/2}} & \text{for } w - |\Omega_\lambda| \text{ odd} \end{cases} \tag{E.28}$$

where ${}_2F_1$ is the hypergeometric function.[53] When evaluating $A^{(jwm=0)}_{|\Omega_\lambda|}(\theta)A^{(jwm=0)}_{|\Omega_\lambda|}(\theta)$ in a computer program, we can use either eq E.26 or, instead, a recursion relation with respect to Ω_λ obtained from it and given by

$$\Omega_\lambda 2jA^{(jwm=0)}_{\Omega_\lambda}(\theta) = \sin \theta[\sqrt{(w + \Omega_\lambda)(w - \Omega_\lambda + 1)}A^{(jwm=0)}_{\Omega_\lambda-1}(\theta) - \sqrt{(w - \Omega_\lambda)(w + \Omega_\lambda + 1)}A^{(jwm=0)}_{\Omega_\lambda+1}(\theta)] \tag{E.29}$$

Using eqs E.7−E.12, $\tau^1_{\lambda-j}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda)$ can be rewritten as

$$\tau^1_{\lambda-j}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda) = \tau^1_{\lambda j}(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda) - D^1_{10}(a_\lambda,b_\lambda,c_\lambda+\pi/2)2j\sqrt{2} \cos \theta \tag{E.30}$$

This expression yields

$$(\tau_{\lambda j}{}^1)^{l_\lambda-m}(\tau_{\lambda-j}{}^1)^m = \sum_{r=0}^{m} \binom{m}{r} (\tau_{\lambda j}{}^1(\boldsymbol{\Theta}^{\mathrm{bf}}_\lambda))^{l_\lambda-r}(-D^1_{10}(a_\lambda,b_\lambda,c_\lambda+\pi/2)2j\sqrt{2} \cos \theta)^r \tag{E.31}$$

Inserting eqs E.25, with $w = l_\lambda - r$, and eq E.20 into eq E.31 results in

$$(\tau_{\lambda j}{}^1)^{l_\lambda-m}(\tau_{\lambda-j}{}^1)^m = \sum_{r=0}^{m} \sum_{\Omega_\lambda=-(l_\lambda-r)}^{l_\lambda-r} \binom{m}{r} D^{l_\lambda-r}_{l_\lambda-r\Omega_\lambda}(a_\lambda,b_\lambda,c_\lambda+\pi/2)A^{(jl_\lambda-rm=0)}_{|\Omega_\lambda|}(\theta)D^r_{r0}(a_\lambda,b_\lambda,c_\lambda+\pi/2)\left(\frac{(2r)!!}{(2r-1)!!}\right)^{1/2}(-2j \cos \theta)^r \tag{E.32}$$

We know that

$$C(l_\lambda-r\ r\ l_\lambda;\Omega_\lambda\ 0\ \Omega_\lambda) = \frac{1}{r!}\left\{\frac{(l_\lambda - \Omega_\lambda)!(l_\lambda + \Omega_\lambda)!(2l_\lambda - 2r)!(2r)!}{(l_\lambda - r - \Omega_\lambda)!(l_\lambda - r + \Omega_\lambda)!(2l_\lambda)!}\right\}^{1/2} \tag{E.33}$$

With the help of this expression and eq E.17, eq E.32 can be written as

$$(\tau_{\lambda j}{}^1)^{l_\lambda-m}(\tau_{\lambda-j}{}^1)^m = \sum_{r=0}^{m} \sum_{\Omega_\lambda=-(l_\lambda-r)}^{l_\lambda-r} \binom{m}{r} D^{l_\lambda}_{l_\lambda\Omega_\lambda}(a_\lambda,b_\lambda,c_\lambda+\pi/2)O^{(jrl_\lambda)}_{|\Omega_\lambda|}(\theta) \tag{E.34}$$

where

$$O^{(jrl_\lambda)}_{|\Omega_\lambda|}(\theta) = A^{(jl_\lambda-rm=0)}_{|\Omega_\lambda|}(\theta)(-4 \cos \theta)^r\left\{\frac{(l_\lambda - \Omega_\lambda)!(l_\lambda + \Omega_\lambda)!(2l_\lambda - 2r)!}{(l_\lambda - r - \Omega_\lambda)!(l_\lambda - r + \Omega_\lambda)!(2l_\lambda)!}\right\}^{1/2} \tag{E.35}$$

Inverting, in eq E.34, the order of the two summations, we obtain

$$(\tau_{\lambda j}^{\;1})^{l_\lambda - m}(\tau_{\lambda -j}^{\;1})^m = \sum_{\Omega_\lambda = -l_\lambda}^{l_\lambda} D^{l_\lambda}_{l_\lambda \Omega_\lambda}(a_\lambda, b_\lambda, c_\lambda + \pi/2) A^{(jl_\lambda m)}_{|\Omega_\lambda|}(\theta) \tag{E.36}$$

where

$$A^{(jl_\lambda m)}_{|\Omega_\lambda|}(\theta) = \sum_{r=0}^{\min(m, l_\lambda - |\Omega_\lambda|)} \binom{m}{r} O^{(jrl_\lambda)}_{|\Omega_\lambda|}(\theta) \tag{E.37}$$

for $|\Omega_\lambda| \le l_\lambda$ and zero othrewise. Inserting eq E.35 into eq E.37 leads to

$$A^{(jl_\lambda m)}_{|\Omega_\lambda|}(\theta) = \left\{\frac{(l_\lambda - \Omega_\lambda)!(l_\lambda + \Omega_\lambda)!}{(2l_\lambda)!}\right\}^{1/2} \sum_{v=u_{2\min},2}^{l_\lambda - |\Omega_\lambda|} C_v^{l_\lambda} \frac{\sin^{l_\lambda - v}\theta(2\cos\theta)^v}{\left(\dfrac{l_\lambda - \Omega_\lambda - v}{2}\right)!\left(\dfrac{l_\lambda + \Omega_\lambda - v}{2}\right)!} \tag{E.38}$$

where

$$C_v^{l_\lambda} = \sum_{r=0}^{r_{\max}} \frac{(l_\lambda - r)!(-2)^r}{(v - r)!} \tag{E.39}$$

$$r_{\max} = \min(v - u_{2\min}, l_\lambda - |\Omega_\lambda|, m) \tag{E.40}$$

with $u_{2\min}$ given by the rhs of eq E.27 with w replaced by l_λ. On the other hand, we know, from the expression for the power of a binomial, that

$$(T_{\lambda 1}^{\;1} - T_{\lambda -1}^{\;1})^{l_\lambda^{(1)}}(T_{\lambda 1}^{\;1} + T_{\lambda -1}^{\;1}))^{l_\lambda^{(2)}} = \sum_{m=0}^{l_\lambda} U_m^{l_\lambda^{(1)} l_\lambda^{(2)}} (T_{\lambda 1}^{\;1})^{l_\lambda - m}(T_{\lambda -1}^{\;1})^m \tag{E.41}$$

where

$$l_\lambda = l_\lambda^{(1)} + l_\lambda^{(2)} \tag{E.42}$$

and

$$U_m^{l_\lambda^{(1)} l_\lambda^{(2)}} = \sum_{r=\max(0, m - l_\lambda^{(2)})}^{\min(m, l_\lambda^{(1)})} (-1)^{l_\lambda^{(1)} - r} \binom{l_\lambda^{(1)}}{r} \binom{l_\lambda^{(2)}}{m - r} \tag{E.43}$$

This quantity can be rewritten, for $l_\lambda^{(1)} \le l_\lambda^{(2)}$, as[54]

$$U_m^{l_\lambda^{(1)} l_\lambda^{(2)}} = \begin{cases} (-1)^{l_\lambda^{(1)}}(-2)^m P_m^{(l_\lambda^{(2)} - m, l_\lambda^{(1)} - m)}(0) & \text{for} \quad m < l_\lambda^{(1)} \\ 2^{l_\lambda^{(1)}} P_{l_\lambda^{(1)}}^{(l_\lambda^{(2)} - l_\lambda^{(1)}, 0)}(0) & \text{for} \quad l_\lambda^{(1)} \le m \le l_\lambda^{(2)} \\ (-2)^{l_\lambda - m} P_{l_\lambda - m}^{(m - l_\lambda^{(2)}, m - l_\lambda^{(1)})}(0) & \text{for} \quad m > l_\lambda^{(2)} \end{cases} \tag{E.44}$$

It can be seen, using eq D.4, that for $l_\lambda^{(1)} = l_\lambda^{(2)}$, $U_m^{l_\lambda^{(1)} l_\lambda^{(2)}}$ vanishes for m odd. With the help of eqs E.7, E.8, and E.36, eq E.41 can be rewritten as

$$(T_{\lambda 1}^{\;1} - T_{\lambda -1}^{\;1})^{l_\lambda^{(1)}}(T_{\lambda 1}^{\;1} + T_{\lambda -1}^{\;1})^{l_\lambda^{(2)}} = (\rho \mathrm{i})^{l_\lambda} \mathrm{e}^{\mathrm{i} l_\lambda \pi/2} \sum_{L' = -l_\lambda, 2}^{l_\lambda} \mathrm{e}^{\mathrm{i} L' \delta_\lambda} \sum_{\Omega_\lambda = -l_\lambda}^{l_\lambda} D^{l_\lambda}_{l_\lambda \Omega_\lambda}(a_\lambda, b_\lambda, c_\lambda)\, U^{l_\lambda^{(1)} l_\lambda^{(2)}}_{(l_\lambda - L')/2} \mathrm{e}^{\mathrm{i}(\Omega_\lambda - l_\lambda)\pi/2} A^{(1 l_\lambda (l_\lambda - L')/2)}_{|\Omega_\lambda|}(\theta) \tag{E.45}$$

This important expression is used in section 4.5.1 to obtain $\sin^{l_{\min}^{(1)}} \eta_\lambda \cos^{l_{\min}^{(2)}} \eta_\lambda\, Y^{JM_J = J}_{l_{\min}^{(1)} l_{\min}^{(2)}}(\theta_\lambda^{(1)}, \phi_\lambda^{(1)}, \theta_\lambda^{(2)}, \phi_\lambda^{(2)})$ in the body-fixed variables $\mathbf{\Theta}_\lambda^{\mathrm{bf}}$ (see eq 4.53).

References and Notes

(1) Hu, W.; Schatz, G. C. *J. Chem. Phys.* **2006**, *125*, 132301.

(2) Zhang, D. H.; Yang, M.; Lee, S.-Y.; Collins, M. A. In *Modern Trends in Chemical Reaction Dynamics*; Yang, X., Liu, K. Eds.; World Scientific: NJ, 2004; pp 409−464.

(3) Althorpe, S. C.; Clary, D. C. *Annu. Rev. Phys. Chem.* **2003**, *54*, 493–529.

(4) Clary, D. C. *Science* **1998**, *279*, 1879.

(5) Bowman, J. M.; Schatz, G. C. *Annu. Rev. Phys. Chem.* **1995**, *46*, 169.

(6) Kuppermann, A. *Isr. J. Chem.* **2003**, *43*, 229.

(7) (a) Kuppermann, A. *J. Phys. Chem.* **1996**, *100*, 2621. (b) Kuppermann, A. *J. Phys. Chem.* **1996**, *100*, 11202.

(8) Kuppermann, A. *J. Phys. Chem.* **1997**, *101*, 6368.

(9) Kuppermann, A. *J. Phys. Chem.* **2009**, *113*, 4518.

(10) Whitten, R. C.; Smith, F. T. *J. Math. Phys.* **1968**, *9*, 1103.

(11) Alacid, M.; Leforestier, C. *J. Chem. Phys.* **2001**, *114*, 1685.

(12) Launay, J. M.; Dourneuf, M. L. *Chem. Phys. Lett.* **1989**, *163*, 178.

(13) Launay, J. M. *Theor. Chim. Acta* **1991**, *79*, 183.

(14) Branchett, S.; Pådkjær, S. B.; Launay, J. M. *Chem. Phys. Lett.* **1993**, *208*, 523.

(15) Wu, Y. S. M.; Kuppermann, A; Lepetit, B. *Chem. Phys. Lett.* **1991**, *186*, 319.

(16) Miranda, M. P.; Clary, D. C.; Castillo, J. F.; Manolopoulos, D. E. *J. Chem. Phys.* **1998**, *108*, 3142.

(17) Skouteris, D.; Castillo, J. F.; Manolopoulos, D. E. *Comput. Phys. Commun.* **2000**, *113*, 128.

(18) Chao, S. D.; Skodje, R. T. *J. Chem. Phys.* **2000**, *113*, 3487.

(19) Fernandez-Alonso, F; Bean, B. D.; Zare, R. N.; Aoiz, F. J.; Bañares, L.; Castillo, J. F. *J. Chem. Phys.* **2001**, *114*, 4534.

(20) Kendrick, B. *J. Chem. Phys.* **2001**, *114*, 8796.

(21) Aquilanti, V.; Cavalli, S.; Fazio, D. De; Volpi, A.; Aguilar, A.; Gimenez, X.; Lucas, J. M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 401.

(22) De Fazio, D.; Aquilanti, V.; Cavalli, S.; Aguilar, A.; Lucas, J. M. *J. Chem. Phys.* **2008**, *129*, 064303.

(23) Parker, G. A.; Pack, R. T. *J. Chem. Phys.* **1993**, *98*, 6883.

(24) Bañares, L.; Aoiz, F. J.; Honvault, B.; Bussery-Honvault, B. *J. Chem. Phys.* **2003**, *118*, 565.

(25) Qiu, M.; Ren, Z.; Che, D.; Harich, S. A.; Wang, X.; Yang, X.; Xu, C.; Xie, D.; Gustafsson, M.; Skodje, R. T.; Sun, Z.; Zhang, D. H. *Science.* **2006**, *311*, 1140.

(26) Lepetit, B.; Peng, Z.; Kuppermann, A. *Chem. Phys. Lett.* **1990**, *166*, 572.

(27) Velilla, L.; Lepetit, B.; Aguado, A.; Beswick, J. A.; Panagua, M. *J. Chem. Phys.* **2008**, *129*, 084307.

(28) Gronwall, T. H. *Phys. Rev.* **1937**, *51*, 655.

(29) Levy-Leblond, J. M.; Levy-Nahas, M. *J. Math Phys.* **1965**, *6*, 1571.

(30) Zickendraht, W. *Ann. Phys.* **1965**, *35*, 18.

(31) Wolniewicz, L. *J. Chem. Phys.* **1989**, *90*, 371.

(32) Mukhtarova, M. I.; Efros, V. D. *J. Phys. A* **1986**, *19*, 1589.

(33) Wang, D.; Kuppermann, A. *J. Phys. Chem. A* **2003**, *107*, 7290 The sign of eqs 4.6 and 4.9 of this reference are wrong. They have been corrected in eqs E.3 and E.6 of the present paper.

(34) Avery, J. S. *Hyperspherical Hamonics*; Kluver: Dordrecht, The Netherlands, 1989.

(35) Lepetit, B.; Wang, D.; Kuppermann, A. *J. Chem. Phys.* **2006**, *125*, 133505.

(36) Kuppermann, A. In *Adavnces in Molecular Vibrations and Collision Dynamics*; Bowman J. M., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 2B, pp 117−186.

(37) Davydov, A. S. *Quantum Mechanics*; Addison-Wesley: Reading, MA, 1965; Chapter VI, section 43. In particular, the Clebsch−Gordan series is given by eq 43.19.

(38) Wang, D.; Kuppermann, A. *Int. J. Quantum Chem.* **2006**, *106*, 152.

(39) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons, Inc.: New York, 1957; p 33.

(40) Merzbacher, E. *Quantum Mechanics*, 2nd ed.; John Wiley: New York, 1970; p 165, sections 9.65 and 9.65a.

(41) Kuppermann, A. *J. Phys. Chem. A* **2004**, *108*, 8894 (eqs 4.40 and 4.42).

(42) Zickendraht, W. *J. Math. Phys.* **1968**, *10*, 30.

(43) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; National Bureau of Standards Applied Mathematics Series 55; NBS: Washington, DC, 1995, Chapter 22.

(44) Reference 39, p 8.

(45) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Ketering, W. T. *Numerical Recipes*: Cambridge Press: New York, 1986; section 6.6.

(46) Kuppermann, A. *J. Phys. Chem. A* **2006**, *110*, 809.

(47) Reference 39, p 38, eq 3.16b.

(48) Rainville, E. D. *Special Functions*; Macmillan: New York, 1960; Chapter 16.

(49) Reference 43, p 777, eq 22.4.1.

(50) Reference 43, p 775, eq 22.3.2.

(51) Reference 43, p 778, eq 22.5.20; p. 777, eq 22.4.2.

(52) Reference 43, p 256, eq 6.1.18.

(53) Reference 43, Chapter 15.

(54) Reference 43, p 775, eq 22.3.1.

JP906473N