Hyperspherical Harmonics for Triatomic Systems†

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A recursion procedure for the analytical generation of hyperspherical harmonics for triatomic systems, in terms of row-orthonormal hyperspherical coordinates, is presented. Using this approach and an algebraic *Mathematica* program, these harmonics were obtained for all values of the hyperangular momentum quantum number up to 40 (about 2.3 million of them). Their properties are presented and discussed. Since they 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.

1. Introduction

Substantial progress has been made recently in applying quantum reactive scattering theory to atom−diatom reactions. Several totally ab initio quantum-dynamical calculations of converged state-to-state integral and differential cross sections have been performed using a propagation approach to solve the time-independent Schrödinger equation. Most of these calculations have been done with some form of symmetrized body-fixed hyperspherical coordinates[1−12] which have the desirable property that a single set of such coordinates span the potential energy surface in all arrangement channels "democratically" (i.e., equivalently).[13−15] This property has been instrumental in the success of such an approach.

We consider in this paper the body-fixed row-orthonormal hyperspherical coordinates (ROHC) proposed previously.[16] The Hamilitonian in these coordinates is quite simple, and each of its terms displays useful invariance properties under kinematic rotations and symmetry operations. However, as for angular coordinates in general, the corresponding kinetic energy operator has poles for two special configurations of the system. One pole occurs for collinear geometries and can be dealt with analytically using a simple set of basis functions which behave regularly at that pole.[1] A second pole occurs for bent configurations of the system. For collinearly-dominated triatomic reactions, these bent configurations are usually classically forbidden at the energies of interest and do not require special consideration. However, for higher energies or for noncollinearly-dominated triatomic reactions, this noncollinear pole must be handled appropriately. One possible approach is to expand the three-body wave function in a basis set of hyperspherical harmonics. These harmonics are eigenfunctions of the square of the grand-canonical angular momentum operator, have the same angular poles as the kinetic energy operator, and behave regularly at those poles. Several approaches for their calculation have been used.[17−23] However, their complete analytical determination has not been possible until now. One of the methods[23] comes close to reaching this objective and involves a numerical implementation of an iterative procedure. The present paper describes a somewhat different approach, based on the general theory of harmonic polynomials.[24] To perform converged state-to-state differential reactive scattering calculations for triatomic systems using these hyperspherical harmonics, a sufficiently large and complete set of such functions must be used, involving both the grand-canonical angular momentum quantum number n and the total angular momentum quantum number J. The $J = 0$ and $J = 1$ harmonics are nondegenerate. The first degenerate hyperspherical harmonics appear for $J = 2$ and $n = 4$, and the degeneracy increases with both of theses quantum numbers. For a contributing J and n, all these degenerate functions are needed to obtain such converged results.

Hyperspherical harmonics have been used to calculate energy levels of few-body systems, including nuclei[25,26] and atoms.[27] Their use in scattering problems, especially those involving contributions from high J partial waves, has been more limited. The reason is 2-fold. One is the difficulty in their determination for large values of J, but this is overcome using the approaches described in ref 23 and in the present paper. It should be noticed that hyperspherical harmonics are appropriate for describing the strong interaction regions of configuration space encompassed by the full ranges of definition of the hyperangles. The second reason is that, for the arrangement channel regions involving separated collision partners (the weak interaction regions), they constitute an inefficient basis set, since these parts of configuration space are spanned by a small range of the hyperangles. This difficulty is overcome by using more appropriate coordinates and basis sets in such regions.[1,6]

Recently, we reported a recursion procedure for the analytical generation of hyperspherical harmonics for tetraatomic systems.[28] In the present paper we describe an analogous efficient recursive method to generate, for triatomic systems, analytical hyperspherical harmonics in the principal-axes-of-inertia frame which are simultaneous eigenfunctions of the operator $\hat{O}_{\hat{I}}$ (associated with the inversion I of the system through its center of mass) and of the four angular momentum operators $\hat{\wedge}^2$, $\hat{J}^2$, $\hat{J}_z^{sf}$, and $\hat{L}$. $\hat{\wedge}^2$ is the grand-canonical angular momentum operator, $\hat{J}^2$ is the square of the total angular momentum operator, $\hat{J}_z^{sf}$ is its space-fixed z component, and $\hat{L}$ is an internal hyperangular momentum operator associated with one of the internal hyperangles. In section 2 we describe these

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operators in greater detail and summarize the ROHC used and the corresponding Hamiltonian,[16] and in section 3 we define the associated hyperspherical harmonics. In section 4 we derive the recursion relations used to generate these harmonics, and in section 5 their degeneracies are analyzed. Some representative results are presented in section 6 and discussed in section 7. Finally, a summary and conclusions are given in section 8.

2. Coordinates and Kinetic Energy Operator

The ROHC used in this paper, as well as their properties, have been described previously,[12] and we only summarize them below. We consider a system of three bodies in a space-fixed frame $Ox^{sf}y^{sf}z^{sf}$ whose mass-scaled λ-arrangement channel Jacobi vectors are $\boldsymbol{r}_\lambda^{(i)}$, $i = 1, 2$. The corresponding Jacobi matrix is defined as

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

The six ROHC

$$\gamma_\lambda \equiv (\rho, \Theta_\lambda) \tag{2.2}$$

$$\Theta_\lambda \equiv (\alpha_\lambda, \theta, \delta_\lambda) \tag{2.3}$$

are defined by the relation

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

In this expression, $\mathbf{a}_\lambda \equiv (a_\lambda, b_\lambda, c_\lambda)$ are the Euler angles that rotate the space-fixed frame $Ox_1^{sf}y_1^{sf}z_1^{sf}$ into the principal-axes-of-inertia body-fixed frame $Ox^{I_\lambda}y^{I_\lambda}z^{I_\lambda}$. The quantity ρ is the usual hyperradius which, together with the two internal hyperangles θ, δ_λ, determines the internal configuration of the system. The $\mathbf{R}$ in (2.4) is the proper 3×3 rotation matrix associated with that rotation, and $\mathbf{N}(\theta)$ is a 3×3 diagonal matrix whose diagonal elements are

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

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

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

To get a one-to-one correspondence between ρ_λ^{sf} and the six ROHC (except for some special geometries), we limit the range of the δ_λ to

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

and that 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 system's principal moments of inertia 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 (2.10), they 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 six-dimensional Laplacian, $\hat{\wedge}^2$ is the hyperangular momentum operator

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

$\hat{T}_\rho(\rho)$ 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 momenta 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 $\hat{J}_x^{I_\lambda}$, $\hat{J}_y^{I_\lambda}$, and $\hat{J}_z^{I_\lambda}$ operators in (2.16) are the components of the nuclear motion angular momentum operator $\hat{\boldsymbol{J}}$ in the body-fixed frame $Ox^{I_\lambda}y^{I_\lambda}z^{I_\lambda}$ and are given explicitly by

$$\begin{pmatrix} \hat{J}_x^{I_\lambda} \\ \hat{J}_y^{I_\lambda} \\ \hat{J}_z^{I_\lambda} \end{pmatrix} = \frac{\hbar}{i}\begin{pmatrix} -\csc b_\lambda \cos c_\lambda & \sin c_\lambda & \cot b_\lambda \cos c_\lambda \\ \csc b_\lambda \sin c_\lambda & \cos c_\lambda & -\cot b_\lambda \sin c_\lambda \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} \partial/\partial a_\lambda \\ \partial/\partial b_\lambda \\ \partial/\partial c_\lambda \end{pmatrix} \tag{2.20}$$

Under a λ to ν change of Jacobi coordinates, the Jacobi matrix ρ_λ^{sf} changes according to the kinematic rotation

$$\rho_\nu^{sf} = \rho_\lambda^{sf}\mathbf{N}_{\lambda\nu} \tag{2.21}$$

where $\mathbf{N}_{\lambda\nu}$ is a 2×2 proper orthogonal square matrix[12−14] whose elements depend only on the masses of the atoms. The coordinates ρ and θ are kinematic-rotation-invariant, as are the operators $\hat{T}_\rho(\rho)$, $\hat{\wedge}^2$, $\hat{K}$, and $\hat{L}$. On the other hand, $\mathbf{R}(\mathbf{a}_\lambda)$, $\mathbf{Q}(\delta_\lambda)$, and $\hat{\boldsymbol{J}}^{I_\lambda}$ transform according to

$$\mathbf{R}(\mathbf{a}_\nu) = \mathbf{I}_{n_{\lambda_\nu}} \mathbf{R}(\mathbf{a}_\lambda) \tag{2.22}$$

$$\mathbf{Q}(\delta_\nu) = \tilde{\mathbf{N}}_{\lambda\nu} \mathbf{Q}(\delta_\lambda)\, \mathbf{I}_{n_{\lambda_\nu}} \tag{2.23}$$

$$\hat{\boldsymbol{J}}^{I_\nu} = \mathbf{I}_{n_{\lambda_\nu}} \hat{\boldsymbol{J}}^{I_\lambda} \tag{2.24}$$

where

$$\mathbf{I}_{n_{\lambda_\nu}} = \begin{pmatrix} (-1)^{n_{\lambda_\nu}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (-1)^{n_{\lambda_\nu}} \end{pmatrix} \tag{2.25}$$

The quantity $n_{\lambda\nu}$ is either 0 or 1 and depends on δ_λ. As a result, $\hat{J}_y^{I_\lambda}$ is invariant whereas $\hat{J}_x^{I_\lambda}$ and $\hat{J}_z^{I_\lambda}$ either are invariant or both change signs under kinematic rotations. Furthermore, the axes of the principal-axes-of-inertia frame $Ox^{I_\lambda}y^{I_\lambda}z^{I_\lambda}$ are invariant under such rotations, as is the sense of Oy^{I_λ}, whereas either none or both of the senses of the two other axes change. An important consequence of these properties is that each one of the seven terms in (2.16) as well as the $\hat{T}_\rho(\rho)$ of (2.17) are invariant under kinematic rotations.

The grand-canonical hyperangular momentum operator of (2.16), and therefore the kinetic energy operator of (2.15), has singularities at collinear configurations, 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 is a prolate symmetric top configuration. The collinear configuration pole can be taken care of by a simple choice of θ basis functions.[1] 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 non-collinearly-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, both at low and high energies.

3. Hyperspherical Functions and Principal-Axes-of-Inertia Hyperspherical Harmonics

For triatomic systems, the five operators $\hat{\wedge}^2$, $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, $\hat{L}$, and $\hat{O}_{\hat{I}}$ commute with each other. $\hat{I}$ is the operator which inverts the system through its center of mass

$$\hat{I}\rho_\lambda^{\rm sf} = -\rho_\lambda^{\rm sf} \tag{3.1}$$

and $\hat{O}_{\hat{I}}$ is the associated operator which acts as a function of $\rho_\lambda^{\rm sf}$. As has been shown previously,[7] $\hat{I}$ acts on the ROHC of (2.2) and (2.3) according to

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

Therefore, both ρ and θ are unchanged under inversion. Let $F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta)$ be the simultaneous eigenfunctions of those five operators:

$$\hat{\wedge}^2 F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = n_\Pi(n_\Pi + 4)\hbar^2 F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) \tag{3.3}$$

$$\hat{J}^2 F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = J(J+1)\hbar^2 F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) \tag{3.4}$$

$$\hat{J}_z^{\rm sf} F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = M_J\hbar F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) \tag{3.5}$$

$$\hat{L} F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = L\hbar F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) \tag{3.6}$$

$$O_{\hat{I}} F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = (-1)^\Pi F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) \tag{3.7}$$

These F functions are furthermore required to be regular at the poles of $\hat{\wedge}^2$ (see (2.16)). The quantum numbers n_Π, J, M_J, L_Π, and Π appearing in these expression are all integers, satisfying the constraints

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

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

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

and, as shown Appendix B, n_Π and L_Π have the same parity as Π

$$(-1)^\Pi = (-1)^{n_\Pi} = (-1)^{L_\Pi} \tag{3.11}$$

The five operators being considered are all independent of the choice of arrangement channel coordinates λ,[16] and therefore, so are the corresponding quantum numbers Π, n_Π, J, M_J, and L_Π. The positive integer superscript D is used to label the number of linearly-independent F functions having the same values of these five quantum numbers. This D degeneracy stems from the fact that the system of three free particles in a center of mass frame has five angular degrees of freedom, as indicated by (2.3) (and as a result has five simultaneously knowable angular constants of the motion), but F has been required to be an eigenfunction of only four differential operators in these angular variables. It is shown in section 6.2 that D depends on the quantum numbers n, J, and L (but not on M_J). The positive integer subscript d, which ranges from 1 to D, designates which one of the F functions is being considered.

As a result of (3.3) through (3.7), the general solution of those equations can be written as

$$F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\Theta_\lambda) = N^{\Pi\, n_\Pi\, J\, L_\Pi}\, e^{i\, L_\Pi\, \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, G^{\Pi\, n_\Pi L_\Pi\, J}_{\quad \Omega_{J_\lambda}\, d}{}^{D}(\theta) \tag{3.12}$$

The presence of the Wigner rotation functions $D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$[29] guarantees that (3.12) will satisfy (3.3) through (3.6). As shown in Appendix A, replacement into (3.3) results in a set of partial differential equations for the functions G which do not contain M_J, and therefore, the G are independent of these quantum numbers. This independence is a consequence of the fact that $\hat{\wedge}^2$ is invariant under both space and kinematic rotations. The degeneracy $D(n_\Pi,J,L_\Pi)$ also represents the number of linearly-independent sets of functions $G^{\Pi\, n_\Pi L_\Pi\, J}_{\quad \Omega_{J_\lambda}\, d}{}^{D}$ with each set spanned by the quantum numbers Ω_{J_λ}, as discussed in section 6.2. The N on the rhs of (3.12) is a normalization constant that will be discussed in section 6 and is shown to be independent of M_J.

According to (3.7), the functions $F^{\Pi\, n_\Pi L_\Pi\, J}_{\quad M_J\, d}{}^{D}(\theta)$ for $\Pi = 0$ and $\Pi = 1$ are respectively symmetric and antisymmetric with respect to inversion through the system's center of mass. If we restrict ourselves to single electronically-adiabatic states of the triatomic system being considered, the potential energy function $V(\rho,\theta,\delta_\lambda)$ which describes the interaction between those atoms is invariant (i.e., symmetric) under such inversion, and matrix elements of V between F functions of different parity vanish. The range of the δ_λ angle is given by (2.8). However, the $e^{iL_\Pi \delta_\lambda}$ functions are only orthonormal over the range

$$0 \le \delta_\lambda < 2\pi \tag{3.13}$$

Therefore, it is desirable to permit (3.12) to be valid over this extended range. This can be accomplished by noticing that the two sets of ROHC

$$(\gamma_\lambda)_i = (\rho, \Theta_{\lambda_i}) \qquad i = 0, 1 \tag{3.14}$$

defined by

$$\Theta_{\lambda_0} = (a_\lambda, b_\lambda, c_\lambda, \theta, \delta_\lambda) \tag{3.15}$$

and

$$\Theta_{\lambda_1} = ((\pi + a_\lambda) \bmod 2\pi, \pi - b_\lambda, (\pi - c_\lambda) \bmod 2\pi, \theta, (\pi + \delta_\lambda) \bmod 2\pi) \tag{3.16}$$

with the δ_λ in the ranges defined by (3.13), yield the same Jacobi matrix of (2.1), that is, correspond to the same configuration of the system. As a result, the system's wave function, in the absence of a conical intersection between the electronically-adiabatic potential energy function being considered and a neighboring one (i.e., in the absence of a geometric phase effect[30]), should have the same value at these two sets of ROHC. We therefore impose the same condition on (3.12). Replacement of (3.15) and (3.16) into (3.12) and use of this condition leads to the relation

$$G^{\Pi\, n_\Pi\, L_\Pi\, J}_{-\Omega_{J_\lambda}\ \ d}{}^{D}(\theta) = (-1)^{(J+L+\Omega_{J_\lambda})} G^{\Pi\, n_\Pi\, L_\Pi\, J}_{\Omega_{J_\lambda}\ \ d}{}^{D}(\theta) \tag{3.17}$$

Since the G are independent of δ_λ, this relation should be imposed regardless of whether the ranges defined by (2.8) or (3.13) are being considered, and therefore, (3.12) is valid in either of these two ranges. It should be stressed, however, that (3.17) is valid only in the absence of a geometric phase. If such a phase is present, a different approach is required, and the F and G of this paper are not applicable. The F functions given by (3.12) are called five-angle principal-axes-of-inertia hyperspherical harmonics, and the G functions in those equations are called principal-axes-of-inertia hyperspherical harmonics, or simply F hyperspherical harmonics or functions and G hyperspherical harmonics or functions, respectively. The F functions, which depend on the five hyperangles Θ_λ, constitute an appropriate complete linearly-independent basis set in these variables, in terms of which the local hyperspherical surface functions (LHSF), defined in the first paragraph of section 7, may be expanded. The coefficients of this expansion will depend only on the hyperradius ρ. An important property of the F functions is that they behave regularly at the poles of the kinetic energy operator $\hat{T}$ of (2.15) and therefore of the system's Hamiltonian. They are, in addition, ρ-independent. If they could be obtained analytically, they would constitute a very useful basis set. In the rest of this paper we show how indeed we can obtain an analytical expression for the G functions and therefore for the F functions. It should be noted that the matrix representation of $\hat{T}$ in the F basis set is completely diagonal. All the Coriolis couplings involving Ω_{J_λ} are automatically included in the evaluation of the G functions. The only matrix elements that must be evaluated numerically are those of the potential energy function. It should also be noted that if some of the system's atoms are equal, it is possible to define modified F functions that transform according to the irreducible representations Γ of the permutation group of identical atoms. This will entail a modification of the $e^{iL_\Pi \delta_\lambda}$ functions in (3.12), but not of the associated G functions.

To solve (3.3) through (3.7), an alternative to the expansion of (3.12) is to use, instead of the $D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$, $\mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ parity, Wigner rotation functions defined by

$$\mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) = \mathscr{N}^{J\Omega}[D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) + (-1)^{J+\Pi+\Omega_{J_\lambda}} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)] \tag{3.18}$$

where

$$\mathscr{N}^{J\Omega} = \left[\frac{2J+1}{16\pi^2(1+\delta_{\Omega_{J_\lambda}}0)}\right]^{1/2} \tag{3.19}$$

The $\mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ is orthonormal with respect to all its four indices and transforms under inversion as

$$\hat{O}_{\hat{I}} \mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) = (-1)^\Pi \mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) \tag{3.20}$$

(3.12) is then replaced by

$$F^{\Pi n_\Pi L_\Pi J}_{\ \ M_J\ \ d}{}^{D}(\Theta) = N'^{\Pi\, n_\Pi\, J\, L_\Pi} e^{i L_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=0}^{J} \mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, G'^{\Pi n_\Pi L_\Pi J}_{\ \ \Omega_{J_\lambda}\ \ d}{}^{D}(\theta) \tag{3.21}$$

Using the properties of the $D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ and $\mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ functions, the following relations result:

$$G'^{\Pi\, n_\Pi\, L_\Pi\, J}_{\ \ \Omega_{J_\lambda}\ \ d}{}^{D}(\theta) = (1 + \delta_{\Omega_{J_\lambda}}0)^{-1/2} G^{\Pi\, n_\Pi\, L_\Pi\, J}_{\ \ \Omega_{J_\lambda}\ \ d}{}^{D}(\theta) \quad \text{for} \quad \Omega_{J_\lambda} \ge 0 \tag{3.22}$$

$$N'^{\Pi\, n_\Pi\, J\, L_\Pi} = \left[\frac{2J+1}{16\pi^2}\right]^{1/2} N^{\Pi\, n_\Pi\, J\, L_\Pi} \tag{3.23}$$

Therefore, for $\Omega_{J_\lambda} > 0$, G' and G are equal, but they differ by a factor of $1/\sqrt{2}$ for $\Omega_{J_\lambda} = 0$. In addition, the replacement of $D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ by $\mathscr{D}^{J\Pi}_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ in (3.12) limits the sum over Ω_{J_λ} to non-negative values only and changes the normalization constant.

4. Analytical Derivation of Principal-Axes-of-Inertia Hyperspherical Harmonics *G*

4.1. General Considerations. Since the kinetic energy operator $\hat{T}$ of (2.15) is the Hamiltonain of three noninteracting particles (for which $V = 0$), its eigenfunctions can be obtained analytically, as follows. Let r^i_λ, $\theta^{(i)}_\lambda$, and $\phi^{(i)}_\lambda$ ($i = 1, 2$) be the space-fixed polar coordinates of the mass-scaled λ-arrangement channel Jacobi coordinates $\boldsymbol{r}^{(i)}_\lambda$ introduced in section 2. The eigenfunctions of $\hat{T}$ can be expressed as products of the two ordinary spherical harmonics of $\theta^{(i)}_\lambda$, $\phi^{(i)}_\lambda$ times a function of $r^{(1)}_\lambda$, $r^{(2)}_\lambda$. These latter two variables can be transformed into the hyperradius ρ and the hyperangle η_λ, defined by the relations

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

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

At a constant ρ, the partial differential equation in $r^{(1)}_\lambda$, $r^{(2)}_\lambda$ is transformed into an ordinary differential equation for η_λ whose solutions are known hypergeometric functions of $\cos^2 \eta_\lambda$. In this way the eigenfunctions of $\hat{\wedge}^2$, for a quantum number n, become known functions of the five angles $\theta_\lambda^{(i)}$, $\phi_\lambda^{(i)}$ ($i = 1, 2$), and η_λ. They are, however, not eigenfunctions of the remaining operators of (3.3) through (3.7). One can nevertheless transform them into functions of the five hyperangles Θ_λ and expand them in the basis set F. This procedure will furnish the G functions analytically. For many triatomic reactions, the values of J up to 30 may be required to obtain state-to-state differential cross sections of benchmark quality. Since, from (3.8), $n \geq J$, G functions up to at least $n_\Pi = 40$ may be needed in these calculations. For this range of n_Π, (6.7) furnishes approximately 2.3 million G functions, of which, for symmetry reasons, only 1.2 million have to be evaluated. The manual algebra involved in this kind of approach cannot be used to obtain such a large number of functions. In the rest of this section we derive a recursion relation that is simple enough to be implemented efficiently using the *Mathematica* computer algebra program[31] and which has generated analytically this large number of G functions. This relation is based on the theory of harmonic polynomials[18] and the use of complex coordinates.

4.2. Complex Coordinates and the Corresponding Hamiltonian. Complex coordinates were first used in connection with the four-body problem by Zickendraht.[32] He introduced them, however, in an ad hoc manner. A rationale for their definition was reported in our previous paper.[28] (2.4) describes the defining relation between the ROHC and the Jacobi mass-scaled space-fixed Cartesian coordinates. By expressing the elements of the **R** matrix on its rhs in terms of Wigner rotation functions, an intermediate set of complex coordinates suggests itself naturally, as was the case for the four-body systems. That expression is[19]

$$\mathbf{R} = \begin{pmatrix} \frac{1}{2}(D^1_{11} - D^1_{1-1} - D^1_{-11} + D^1_{-1-1}) & \frac{-i}{2}(D^1_{11} - D^1_{1-1} + D^1_{-11} + D^1_{-1-1}) & \frac{1}{\sqrt{2}}(D^1_{01} - D^1_{0-1}) \\ \frac{i}{2}(D^1_{11} + D^1_{1-1} - D^1_{-11} - D^1_{-1-1}) & \frac{1}{2}(D^1_{11} + D^1_{1-1} + D^1_{-11} + D^1_{-1-1}) & \frac{i}{\sqrt{2}}(D^1_{01} + D^1_{0-1}) \\ \frac{i}{\sqrt{2}}(D^1_{10} - D^1_{-10}) & \frac{i}{\sqrt{2}}(D^1_{10} + D^1_{-10}) & D^1_{00} \end{pmatrix} \quad (4.3)$$

where **R** and the D^1_{kp} values (k, $p = -1, 0, 1$) are evaluated at the same set of Euler angles. Replacement of (4.3) into (2.4) leads to the six relations

$$x_\lambda^{(1)} = \frac{1}{4i}(T_{\lambda 1}^{\ 1} - T_{\lambda 1}^{\ -1} - T_{\lambda -1}^{\ 1} + T_{\lambda -1}^{\ -1}) \quad (4.4)$$

$$y_\lambda^{(1)} = -\frac{1}{4}(T_{\lambda 1}^{\ 1} + T_{\lambda 1}^{\ -1} - T_{\lambda -1}^{\ 1} - T_{\lambda -1}^{\ -1}) \quad (4.5)$$

$$z_\lambda^{(1)} = \frac{1}{i2\sqrt{2}}(T_{\lambda 1}^{\ 0} - T_{\lambda -1}^{\ 0}) \quad (4.6)$$

$$x_\lambda^{(2)} = \frac{1}{4}(T_{\lambda 1}^{\ 1} - T_{\lambda 1}^{\ -1} + T_{\lambda -1}^{\ 1} - T_{\lambda -1}^{\ -1}) \quad (4.7)$$

$$y_\lambda^{(2)} = \frac{1}{4i}(T_{\lambda 1}^{\ 1} + T_{\lambda 1}^{\ -1} + T_{\lambda -1}^{\ 1} + T_{\lambda -1}^{\ -1}) \quad (4.8)$$

$$z_\lambda^{(2)} = \frac{1}{2\sqrt{2}}(T_{\lambda 1}^{\ 0} + T_{\lambda -1}^{\ 0}) \quad (4.9)$$

The complex quantities $T_{\lambda}{}_{j}^{k}(\rho,\Theta_\lambda)$ are defined in view of (4.10) through (4.14); (4.10) can be rewritten as

$$T_{\lambda j}^{\ k} = \rho e^{ij\delta_\lambda} \sum_{p=-1}^{1} D^1_{kp}(\mathbf{a}_\lambda) e^{i(p-1)\pi/2} t_j^{\,p}(\theta) \quad (4.10)$$

where

$$i = (-1)^{1/2} \quad (4.11)$$

$$k = -1, 0, 1 \quad j = -1, 1 \quad (4.12)$$

$$t_j^{\pm 1} = y = \sin\theta \quad (4.13)$$

$$t_j^0 = \sqrt{2} jx = \sqrt{2} j \cos\theta \quad (4.14)$$

$$k = -1, 0, 1 \quad j = -1, 1 \quad (4.15)$$

We can consider the complex $T_{\lambda}{}_{k}^{j}$ as midway variables between the Cartesian coordinates and the ROHC ρ, Θ_λ. With the help of (4.4) through (4.9) we can express the system's Laplacian in terms of these variables as

$$\nabla^2 = -4 \sum_{k=-1}^{1} \sum_{j=-1,1} (-1)^{j+k} \frac{\partial^2}{\partial T_{\lambda k}^{\ j}\, \partial T_{\lambda -j}^{\ -k}} \quad (4.16)$$

where the $\partial/\partial T_{\lambda}{}_{j}^{k}$ partial derivatives with respect to the complex variables $T_{\lambda}{}_{j}^{k}$ are defined as in Appendix C of ref 28. This is a particularly simple expression and will permit us, as seen in section 4.3, to derive a recursion relation between the F and G functions for the hyperangular momentum quantum numbers n and $n + 1$.

4.3. Recursion Relation for Hyperspherical Harmonics. Let us now derive recursion relations for the F and G functions of (3.12) associated with consecutive values of the hyperangular momentum quantum number n. We make use of the properties of harmonic polynomials.[18] These properties, for an m-dimensional space, are summarized in Appendix D. We will now set $m = 6$ (for triatomic systems) and from here on omit this index. Let $f^n(x_\lambda)$ be an arbitrary homogeneous polynomial of degree n in the six real variables $x_\lambda \equiv \{x_\lambda^{(1)}, y_\lambda^{(1)}, z_\lambda^{(1)}, x_\lambda^{(2)}, y_\lambda^{(2)}, z_\lambda^{(2)}\}$. The associated function $h^n(_\lambda)$ defined by (D.5) is therefore a harmonic polynomial satisfying the six-dimensional Laplace equation

$$\nabla^2 h^n(\boldsymbol{x}_\lambda) = 0 \quad (4.17)$$

Let us define a set of functions $f_{jk}^{\,n+1}(\boldsymbol{x}_\lambda)$ by

$$f_{jk}^{\,n+1}(\boldsymbol{x}_\lambda) = T_{\lambda j}^{\ k}(\boldsymbol{x}_\lambda) h^n(\boldsymbol{x}_\lambda) \quad (4.18)$$

where the $\boldsymbol{x}_\lambda(\boldsymbol{T}_\lambda)$ are given by (4.4) through (4.9) with $T_\lambda = (T_{\lambda -1}^{\ -1}, T_{\lambda -1}^{\ 0}, T_{\lambda -1}^{\ 1}, T_{\lambda 1}^{\ -1}, T_{\lambda 1}^{\ 0}, T_{\lambda 1}^{\ 1})$. Since the $T_{\lambda j}^{\ k}$ are also homogeneous polynomials of the first degree in the $\boldsymbol{x}_\lambda$ components, the $f_{jk}^{\,n+1}(\boldsymbol{x}_\lambda)$ are homogeneous polynomials of degree $n + 1$ in those variables. As a result of (4.14) and (4.15), the following property can be easily derived:

$$\nabla^{2s} f_{jk}^{\,n+1}(\boldsymbol{x}_\lambda) = \begin{cases} -8(-1)^{j+k} \partial h^n / \partial T_{\lambda -j}^{\ -k} & \text{for} \quad s = 1 \\ 0 & \text{for} \quad s > 1 \end{cases} \quad (4.19)$$

In this expression, s is a positive integer. It should be noted that the symbol $\partial h^n / \partial T_{\lambda}{}_{-j}^{-k}$ implies that although $h^n(\boldsymbol{x}_\lambda)$ is a harmonic polynomial in the variables $\boldsymbol{x}_\lambda$, it can also be considered, with the help of (D.5) though (D.13), to be a harmonic polynomial in the variables $T_{\lambda}{}_{j}^{k}$.

Replacing (4.17) into the $n+1$ counterpart of (D.5), we get

$$h_{jk}^{n+1} = T_{\lambda j}^{\ k} h^n - \frac{\rho^2}{4(n+2)}\nabla^2(T_{\lambda j}^{\ k} h^n) \qquad (4.20)$$

This is a recursion relation between the harmonic polynomial h^n and each of the six harmonic polynomials h_{jk}^{n+1} ($k = -1$, 0, 1; $j = -1$, 1), all of which are of degree $n+1$. Let us consider the five-angle hyperspherical harmonics $F^{\Pi\, n_\Pi L_\Pi\, J'\ \ D'}_{\qquad\quad M_J\, d'}(\Theta_\lambda)$ given by (3.12) (with J, D, and d replaced by J', D', and d', respectively). Since it satisfies (3.3), we conclude from (D.4) and (D.10) that the function $h^{\Pi\, n_\Pi L_\Pi\, J'\ \ D'}_{\qquad\quad M_J\, d'}(\rho,\Theta_\lambda)$, defined by

$$h^{\Pi\, n_\Pi L_\Pi\, J'\ \ D'}_{\qquad\quad M_J\, d'}(\rho,\Theta_\lambda) = \rho^n F^{\Pi\, n_\Pi L_\Pi\, J'\ \ D'}_{\qquad\quad M_J\, d'}(\rho,\Theta_\lambda) \qquad (4.21)$$

is a solution of the Laplace equation, (4.17), and is therefore a harmonic polynomial of degree n_Π in the variables $\boldsymbol{x}_\lambda$ or, equivalently, the $\boldsymbol{t}_\lambda$ to which the ROHC ρ, Θ_λ are related. Let us use this choice of h^n on the rhs of (4.19). With the help of (4.10), (3.12), and the multiplication properties of the Wigner rotation functions,[20] but dropping the index Π to avoid confusion (since $n_\Pi + 1$ was a different parity than n_Π), we get

$$h_{jk}^{n+1\, L+j\, J'\qquad D'}_{\qquad\qquad M_J+k\, d'}(\rho,\Theta_\lambda) = \rho^{n+1}\sum_{J=|J'-1|}^{J'+1} C(J'\,1\,J;\,M_J\,k\,M_J+k)[\bar{F}^{n+1\, L+k\, J}_{\qquad\qquad M_J+k}]_{J'D'd'} \qquad (4.22)$$

where

$$[\bar{F}^{n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'} = \frac{1}{\rho^{n+1}}\left[1 - \frac{\rho^2}{4(n+2)}\nabla^2\right]\{\rho^{n+1}[\mathscr{F}^{\,n\, L+j\, J}_{\qquad\quad M_J+k}]_{J'D'd'}\} \qquad (4.23)$$

$$|J'-1| \le J \le J'+1 \qquad (4.24)$$

and is independent of ρ, where

$$[\mathscr{F}^{\,n+1\, L+j\, J}_{\qquad\qquad M_J+j}]_{J'D'd'} = e^{i(L+j)\delta_\lambda}\sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J+j\ \Omega_{J_\lambda}}(\mathbf{a}_\lambda)[\mathscr{G}^{\,n+1\, L+k\, J}_{\qquad\qquad \Omega_{J_\lambda}}]_{J'D'd'} \qquad (4.25)$$

$$[\mathscr{G}^{\,n+1\, L+k\, J}_{\qquad\qquad \Omega_{J_\lambda}}(\theta)]_{J'D'd'} = \sum_{p=-1}^{1} C(J'\,1\,J;\,\Omega_{J_\lambda}-p\ p\ \Omega_{J_\lambda})e^{i(p-1)\pi/2}t_p^{\,k}G^{n\, L\, J'\qquad\quad D'}_{\qquad\quad \Omega_{J_\lambda}-p\ d'} \qquad (4.26)$$

The C in the last three equations are the Clebsch–Gordan coefficients defined by Rose.[33] In addition, the J' that appears as subscripts in those equations is related to J by the triangle inequalities. On the lhs of (4.21), let us allow j and k to assume all their possible values, while at the same time varying M_J so as to maintain $M_J + k$ constant. This will generate, for $J' > 0$, three $h_{jk}^{n+1\, L+j\, J'\qquad D'}_{\qquad\qquad M_J+k\, d'}$. Each of them will be a different linear combination of the same set of three functions $[\bar{F}^{n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'}$, in which $J = J'-1$, J', $J'+1$ (The particular case $J' = 0$ can be considered similarly). These relations can be inverted, so as to express each of the $[\bar{F}^{n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'}$ as different linear combinations of the three $h_{jk}^{n+1\, L+j\, J'\qquad D'}_{\qquad\qquad M_J+k\, d'}(\theta)/\rho^{n+1}$. Since the h_{jk}^{n+1} are all harmonic polynomials of degree $n+1$ in the $T_{\lambda\ j}^{\ k}$, we conclude that each of these $\bar{F}^{n+1\, L+j}$ are eigenfunctions of $\hat{\wedge}^2$ with hyperangular momentum quantum number $n+1$. In addition, because of the $e^{i(L+j)\delta_\lambda}$ and $D^J_{M_J+k\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ functions that appear on the rhs of (4.23), the $[\mathscr{F}^{\,n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'}$ are eigenfunctions of $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, and $\hat{L}$. Since ∇^2 commutes with $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, and $\hat{L}$, we conclude, from (4.21), that so are the $[\bar{F}^{n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'}$, with the corresponding quantum numbers being J, $M_J + k$, and $L + j$. As a result of this important property, we can omit the bar on these F, add a parity index $\Pi' = \Pi + 1$ mod 2 associated with $n+1$ (since Π is associated with n and L), and write them simply as $[\bar{F}^{\Pi'\, n+1\, L+j\, J}_{\qquad\qquad\quad M_J+k}]_{J'D'd'}$, where the indices J', D', and d' indicate that they are expressed, through (4.21), in terms of the $\mathscr{F}$ functions defined by (4.23) and (4.24), which contain those indices. A superscript $D(n+1, J, L)$ will be attached to these functions, as well as a modified d subscript, and the subscripts J', D', and d' will be dropped, after the functions are required to be linearly independent, as described in section 5.2. To calculate the $\nabla^2\{\rho^{n+1}[\mathscr{F}^{\,n+1\, L+j\, J}_{\qquad\qquad M_J+k}]_{J'D'd'}\}$ that appears on the rhs of (4.21), we use for ∇^2 the expression

$$\nabla^2 = -\frac{2\mu}{\hbar^2}\hat{T}_\rho(\rho) - \frac{\hat{\wedge}^2}{\hbar^2\rho^2} \qquad (4.27)$$

easily derived from (2.15). It is useful to define the functions $[G^{n+1\, L+j}]_{J'D'd'}$ as the companions of the $[F^{\Pi'\, n+1\, L+j}]_{J'D'd'}$ in the relation

$$[F^{\Pi'\, n+1\, L+j\, J}_{\qquad\qquad\quad M_J+k}]_{J'D'd'}(\Theta_\lambda) = \sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J+k\ \Omega_{J_\lambda}}(\mathbf{a}_\lambda)[G^{n+1\, L+j\, J}_{\qquad\qquad \Omega_{J_\lambda}}]_{J'D'd'}(\theta) \qquad (4.28)$$

It is now desirable to relate the $[G^{n+1}]_{J'D'd'}$ above to the $[\mathscr{G}^{\,n+1}]_{J'D'd'}$ of (4.23), since the latter have already, by (4.26), been expressed in terms of the G^n. This will, as a final result, generate the desired recursion relation between $[G^{n+1}]_{J'D'd'}$ and G^n. To relate the $[G^{n+1}]_{J'D'd'}$ to the $[\mathscr{G}^{\,n+1}]_{J'D'd'}$, it suffices to replace, in (4.25), its lhs by (4.26) and, on its rhs, use (4.28). We then express $\hat{\wedge}^2$ in terms of the differential operators $\hat{J}^2$, $\hat{J}_z^{I_\lambda}$, $\hat{J}_\pm^{I_\lambda}$, and $\hat{L}$, as was done in Appendix A, after (A.6), and use (A.7) through (A.10) together with the orthogonality of the Wigner rotation functions to obtain the expression

$$\begin{aligned}
[G^{n+1\, L+j\, J}_{\qquad\qquad \Omega_{J_\lambda}}(\theta)]_{J'D'd'} = \sum_{p=-1}^{1} C(J'\,1\,J;\,\Omega_{J_\lambda}-p\ p\ \Omega_{J_\lambda}) \times \\
\Bigg\{\Bigg[\Bigg[(n+4)e^{i(p-1)\pi/2}t_j^{\,p} - \frac{Lj}{\cos 2\theta}(e^{-i(p-1)\pi/2}t_j^{\,p}) + \\
\frac{\Omega_{J_\lambda}-p}{\sin\delta}p^2 - \frac{d}{d\theta}(e^{i(p-1)\pi/2}t_j^{\,p})\frac{d}{d\theta}\Bigg]G^{n\, L\, J'\qquad\quad D'}_{\qquad\quad \Omega_{J_\lambda}-p\ d'} + \\
\frac{ij}{2}\xi_-(J',\Omega_{J_\lambda}-p+1)\left(\frac{p^2}{\cos\theta} + \frac{1}{\cos 2\theta}\frac{d}{d\theta}(e^{i(p-1)\pi/2}t_j^{\,p})\right) \times \\
G^{n\, L\, J'\qquad\qquad D'}_{\qquad\quad \Omega_{J_\lambda}-p+1\ d'} + \frac{ij}{2}\xi_+(J',\Omega_{J_\lambda}-p-1) \times \\
\left(\frac{p^2}{\cos\theta} - \frac{1}{\cos 2\theta}\frac{d}{d\theta}(e^{i(p-1)\pi/2}t_j^{\,p})\right)G^{n\, L\, J'\qquad\qquad D'}_{\qquad\quad \Omega_{J_\lambda}-p-1\ d'}\Bigg\} \qquad (4.29)
\end{aligned}$$

(4.29) relates the $[G^{n+1\, L+j\, J}_{\qquad\qquad \Omega_{J_\lambda}}]_{J'D'd}(\theta)$ to the $G^{n\, L\, J\quad D}_{\qquad \Omega_{J_\lambda}\, d}(\theta)$ and therefore permits us to get, from a complete set of G^n hyperspherical harmonics for a fixed n and all possible values of the remaining five indices, a similarly complete set of G^{n+1} hyperspherical harmonics. Therefore, this equation constitutes a recursion relation for G functions in the index n. This recursion relation has been implemented using the *Mathematica* computer algebra program.[31] In utilizing this recursion relation, we employ (3.17) to decrease the *Mathematica* algebraic effort. With the help of (4.10), it is shown in Appendix C that $G^{n\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta)$ can be written as

$$G^{n\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) = e^{i(\Omega_{J_\lambda} - J)\pi/2}\,\bar{g}^{n\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) \qquad (4.30)$$

where $\bar{g}^{n\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta)$ is real. The symbol g (without a bar) is reserved for a normalized version of $\bar{g}$ given by (5.12). As a result of (3.17), the $\bar{g}$ functions for $\Omega_{J_\lambda} < 0$ are related to those for $\Omega_{J_\lambda} > 0$ by

$$\bar{g}^{n\,L\,J}_{-\Omega_{J_\lambda}}{}^{D}_{d}(\theta) = (-1)^{J+L}\,\bar{g}^{n\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) \qquad (4.31)$$

The corresponding recursion relation for $\bar{g}^{n+1\,L+j}$ is given by

$$[\bar{g}^{n+1\,L+j\,J}_{\Omega_{J_\lambda}}(\theta)]_{J'D'} = \sum_{p=-1}^{1} C(J'\,1\,J;\,\Omega_{J_\lambda} - p\;p\;\Omega_{J_\lambda}) \times \Bigg\{\Bigg[(n+4)t_j^p + \frac{Lj}{\cos 2\theta}t_j^p - \frac{\Omega_{J_\lambda} - p}{\sin\delta}p - \frac{\mathrm{d}t_j^p}{\mathrm{d}\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\Bigg]\bar{g}^{n\,L\,J'}_{\Omega_{J_\lambda}-p}{}^{D'}_{d'} + \frac{j}{2}\xi_-(J',\Omega_{J_\lambda} - p + 1)\left(\frac{p}{\cos\theta} - \frac{1}{\cos 2\theta}\frac{\mathrm{d}t_j^p}{\mathrm{d}\theta}\right)\bar{g}^{n\,L\,J'}_{\Omega_{J_\lambda}-p+1}{}^{D'}_{d'} - \frac{j}{2}\xi_+(J',\Omega_{J_\lambda} - p - 1)\left(\frac{p}{\cos\theta} + \frac{1}{\cos 2\theta}\frac{\mathrm{d}t_j^p}{\mathrm{d}\theta}\right)\bar{g}^{n\,L\,J'}_{\Omega_{J_\lambda}-p-1}{}^{D'}_{d'}\Bigg\} \qquad (4.32)$$

It is therefore more convenient to use this real function recursion relation and (4.30) rather than (4.29) to determine the G functions. Equation 4.32 was also programmed in *Mathematica*,[31] with (4.31) taken into account. To initiate the iteration procedure, it suffices to have the $n = J = \Omega_{J_\lambda} = L = 0$ $\bar{g}$ functions. There is only one linearly-independent solution of (A.21) for this case, and it is a constant, which can be set to unity. As a result, $D = 1$ and $d = 1$, and we can write

$$\bar{g}^{0\,0\,0}_{\;0}{}^{1}_{1} = 1 \qquad (4.33)$$

Alternatively, we may start the iterative procedure from the $n = 1$ functions. The $T_{\lambda}{}^{k}_{j}$ ($k = -1, 0, 1$; $j = -1, 1$) form a complete set of hyperspherical harmonics for $n = 1$. With the help of (4.10) and (3.12), we can identify $F^{\Pi=1\,n=1\,L=j\,J=1}_{M_J=k}{}^{D=1}_{d=1}/\rho N^{\Pi=1\,n_\Pi=1\,L_\Pi=j\,J=1}_{M_J=k}{}^{D=1}_{d=1}$ with $T_{\lambda}{}^{k}_{j}$, and as a result, $\bar{g}^{1\,j\,1}_{\;p}{}^{1}_{1}$ with t_j^p. This results in

$$\bar{g}^{1\,\pm1\,1}_{\;1}{}^{1}_{1} = \bar{g}^{1\,\pm1\,1}_{\;-1}{}^{1}_{1} = y \qquad (4.34)$$

$$\bar{g}^{1\,j\,1}_{\;0}{}^{1}_{1} = \sqrt{2}jx \qquad (4.35)$$

In this way, the $\bar{g}^{1\,L\,J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta)$ for all possible J, Ω_{J_λ}, L, D, and d are known, and this start-up procedure gives the same results as the one defined by (4.33). The iterative procedure based on (4.32) is started from either the $n = 0$ or $n = 1$ G functions obtained from (4.33) or (4.34) and (4.35), using (4.29). The indices J' appearing in the $[\bar{g}^{n+1\,L+k\,J}_{\Omega_{J_\lambda}}]_{J'D'd'}(\theta)$ can, for a given J, assume the sets of values given by (4.22) (which for $J > 0$ is three sets). This generates a branching tree making the number of $\bar{g}^{n+1}$ functions grow very rapidly with n. However, not all of the resulting $[G^{n+1\,L+k\,J}_{\Omega_{J_\lambda}}]_{J'D'd'}$ sets (each set scanned by varying the values of Ω_{J_λ}) are linearly-independent, as described in section 5.2. Before proceeding to the calculation of the $\bar{g}^{n+2}$, the $\bar{g}^{n+1}$ must be culled in order to retain only linearly-independent sets. This is accomplished with the help of a separate routine, also written in *Mathematica*.[31] It should also be noticed that since the $\bar{g}^{n}$ functions generate the $\bar{g}^{n+1}$ ones, they are associated with F^n and F^{n+1} functions which have opposite parity. In solving scattering problems, however, matrix elements of the system's potential energy function in the F basis set will appear. For two such F functions of different parity, those matrix elements vanish. As a result, the n even and n odd sets of F functions do not mix in the scattering equations, even though they are generated by the recursion relation in the mixed manner just described.

The recursion relations of (4.29) and (4.32) have been implemented using *Mathematica*.[31] This calculation involves differentiations of trigonometric functions of θ with respect to this angle. Although *Mathematica* can perform such differentiations, it is not very nimble in simplifying the results by grouping appropriately terms interrelated by trigonometric identities. To overcome this difficulty, we used the intermediate variables x and y defined by (4.13) and (4.14). This approach resulted in a very efficient procedure for generating the $\bar{g}$ functions, as discussed in section 6.1.

5. Normalization and Degeneracy of the Principal-Axes-of-Inertia Hyperspherical Harmonics *F* and *g*

In this section we describe how complete sets of normalized linearly-independent hyperspherical harmonics F and g functions are obtained.

5.1. Prenormalization of the $\bar{g}$ Hyperspherical Harmonics. The g functions are homogeneous polynomials in the variables x and y defined in (4.13) and (4.14). The iterative step described by (4.32), as implemented by a *Mathematica* program, generates the functions

$$[\bar{g}^{n+1\,L+j\,J}_{\Omega_{J_\lambda}}]_{J'D'd'}(\theta) = A^{n+1\,L+j\,J}_{J'D'd'\;\Omega_{J_\lambda}} \sum_{\substack{q,r=1\\q+r=n+1}}^{n+1} (a^{n+1\,L+j\,J}_{J'D'd'\;\Omega_{J_\lambda}})_{qr}\,x^q y^r \qquad (5.1)$$

where the a coefficients are all integers and A is the product of a rational number and the square root of another rational number. Those two rational numbers are generated exactly by that program. These characteristics of a and A stem from the properties of the Clesch−Gordan coefficients that appear in (4.32). On purpose, the superscript D and subscript d do not yet appear in (5.1), since those indices refer to the degeneracy and linear independence properties of the F^{n+1} functions, which will only be imposed in section 5.2. As the $\bar{g}$ functions are always used in connection with the associated F functions of (3.12), together with (4.30) any common multiplicative constant for a set of $\bar{g}$ functions for fixed n and J and spanned by Ω_{J_λ} can be factored out of the sum in that equation and incorporated into the associated normalization constant N. As a result, in a prenormalization of the $\bar{g}$ functions, we replace (5.1) by

$$[\bar{g}^{n+1\,L+j\,J}_{\Omega_{J_\lambda}}]_{J'L'd'}(\theta) = B^{n+1\,L+j\,J}_{J'D'd'\;\Omega_{J_\lambda}} \sum_{\substack{q,r=1\\q+r=n+1}}^{n+1} (a^{n+1\,L+j\,J}_{J'D'd'\;\Omega_{J_\lambda}})_{qr}\,x^q y^r \qquad (5.2)$$

where

$$B^{n+1\,L+j\,J}_{J'D'd'\;\;\Omega_{J_\lambda}} = A^{n+1\,L+j\,J}_{J'D'd'\;\;\Omega_{J_\lambda}} / A^{n+1\,L+j\,J}_{J'D'd'\;\;J} \tag{5.3}$$

The B coefficients are smaller than the corresponding A ones and make the elimination of the linearly-dependent sets of $\bar{g}^{n+1}$ functions, performed exactly by a *Mathematica* program[31] and described in section 5.2, more efficient. As n becomes large (of the order of 40), efficiency becomes important and justifies this prenormalization.

5.2. Degeneracy of the *F* Hyperspherical Harmonics. As discussed in the paragraph following (3.11), it is expected that for a fixed set of quantum numbers Π, n_Π, J, M_J, and L_Π there should be more than one F function. We label the latter with the extra degeneracy subscript d, as $F^{\Pi\,n_\Pi\,L_\Pi\,J\;\;D}_{\qquad\qquad M_J\,d}$, where D indicates the total number of these functions and, therefore, represents their degeneracy. A detailed discussion of this degeneracy issue was given previously for the tetraatomic systems.[28]

Let us now consider the functions $[g^{n+1\,L\,J'}_{\qquad\Omega_{J_\lambda}}]_{J'D'd'}(\theta)$ generated by (4.32) (and expressed in the form of (5.2)) with J' and L' assuming all sets of values permitted by (4.24) for a given J. Since these functions do not yet satisfy the linear-independence condition described in the preceding paragraph, the indices D and d on $\bar{g}^{n+1\,L\,J\;\;D}_{\qquad\Omega_{J_\lambda}\,d}$ have been temporarily omitted, as discussed after (5.1). The index d has instead been replaced, in (6.2), by the set of subscripts J', D', and d', where d' refers to the index in the function $g^{n\,L\,J'\;\;D'}_{\quad\Omega_{J'_\lambda}\,d'}(\theta)$ that appears on the rhs of (4.32); this d' differs to the one that will eventually be attached to $\bar{g}^{n+1\,L\,J\;\;D}_{\qquad\Omega_{J_\lambda}\,d}(\theta)$. Let $\boldsymbol{b}^{n+1\,J\,L}_{J'D'\,d'}$ be the column vector whose elements

$$(\boldsymbol{b}^{n+1\,L\;\;J}_{J'D'\,d'\,\Omega_{J_\lambda}})_{qr} = B^{n+1\,L\;\;J}_{J'D'\,d'\,\Omega_{J_\lambda}}(a^{n+1\;\;\;J}_{J'D'd'\,\Omega_{J_\lambda}})_{qr} \tag{5.4}$$

are spanned by the set of five indices Ω_{J_λ}, q, and r such that

$$q + r = n + 1 \tag{5.5}$$

with q and r being non-negative integers. For each such vector we calculate the sum of the absolute values of its elements, and construct the matrix $b^{n+1\,J\,L}$, whose columns are those vectors placed side-by-side in increasing order of that sum. This ordering is important for optimizing the efficiency of the procedure that generates the linearly-independent hyperspherical harmonics. The next step is to contract this matrix to one whose columns are linearly independent. We adopted the following contraction procedure:

1. Consider the matrix $\boldsymbol{b}_1$ formed by the first two columns of $\boldsymbol{b}$ and determine its rank $\mathscr{R}_1$. If $\mathscr{R}_1 = 1$, replace the second column of $\boldsymbol{b}_1$ by the third column of $\boldsymbol{b}$. If $\mathscr{R}_1 = 2$, augment $\boldsymbol{b}_1$ by the third column of $\boldsymbol{b}$. Call the resulting two or three column matrix $\boldsymbol{b}_2$. Its rank $\mathscr{R}_2$ is equal to its number of columns.

2. Augment $\boldsymbol{b}_2$ by the next column of $\boldsymbol{b}$, and proceed as in step 1 to generate a matrix $\boldsymbol{b}_3$ having four or five columns depending on whether $\mathscr{R}_3$ is four or five.

3. Continue the augmentation procedure, one column at a time, until the columns of $\boldsymbol{b}$ are exhausted.

The resulting final matrix $\boldsymbol{b}_D$ will have rank D and be formed by D linearly-independent columns $\boldsymbol{b}_d$ ($d = 1, 2, ..., D$). The number D will depend on $n + 1$, J, and L only. The rank determination of the matrixes $\boldsymbol{b}_i$ is done exactly, with an available *Mathematica* program. The elements of $\boldsymbol{b}_\mathrm{D}$ are now designated by the symbol $(b^{n+1\,L\,J\;\;D}_{\qquad\Omega_{J_\lambda}\,d})_{qr}$. Inserting them into (5.2) (with obvious changes in notation) and using (5.4) we get

$$\bar{g}^{n+1\,L\,J\;\;D}_{\qquad\Omega_{J_\lambda}\,d}(\theta) = \sum_{\substack{q,r=1\\q+r=n+1}}^{n+1} (b^{n+1\,L\,J\;\;D}_{\qquad\Omega_{J_\lambda}\,d})_{qr}\, x^q y^r \tag{5.6}$$

where $D = D(n + 1, J, L)$. This constitutes a complete ensemble of D linearly-independent sets of g functions for $n + 1$ (each set spanned by Ω_{J_λ}) generated starting with a knowledge of a complete ensemble of g functions for n. When used in (4.30) and (3.12) they yield a complete set of linearly-independent F functions for $n + 1$. It should be noticed that, as a consequence of the ordering of the $\boldsymbol{b}$ vectors described in the paragraph following (5.7), the $\boldsymbol{b}_D$ matrix will have elements that are much smaller than would be the case if the ordering were random. This property significantly speeds up the rank-determination code and generates $\bar{g}$ functions whose coefficients are smaller and simpler than they would be otherwise.

A check of the correctness of the degeneracy number $D(n, J, L)$ obtained by the procedure just described was made as follows. Avery[24] derived a general expression for calculating the total number N_n of linearly-independent hyperspherical harmonics F for a given n:

$$N_n = \frac{(2n + 4)(n + 3)!}{n!4!} \tag{5.7}$$

This number is related to $D(n, J, L)$ by

$$N_n = \sum_{J=0}^{n} {\sum_{L=-n}^{n}}{}' \,(2J + 1)D(n, J, L) \tag{5.8}$$

where the prime in the sum over L indicates that L is increased in steps of 2. The largest degeneracy we encountered in our calculations for $n \leq 40$ was $D(40, 20, 0) = 11$. We calculated the values of D for $n \leq 40$ and used (5.8) to obtain the corresponding N_n. Perfect agreement was obtained with (5.7). As an example, a representative set of values of $D(n, J, L)$ (for $n = 40$) is given in Table 1. For example, for $J = 6$ and $L_\Pi = 4m$ with $m = 0$ through 7, $D = 4$. For the entire table, D ranges from 1 through 11. Using these results and (5.8), one gets $N_{40} = 259\,161$. The same value is obtained from (5.7). Taking into account that N_n varies from 1 for $n = 0$ to 259 161 for $n = 40$, such an agreement is strongly suggestive that the recursion relations used and the codes written to implement them are indeed correct. Table 1 is further discussed in section 6.7.

Finally, an ultimate check was performed on the correctness of all the $G^{n\,L\,J\;\;D}_{\quad\Omega_{J_\lambda}\,d}$ generated by the procedure described. For each set of values of n, J, L, D, and d, these functions (for all Ω_{J_λ}) were replaced on both sides of (A.12) and shown to satisfy it with the help of a *Mathematica* program[31] written for this purpose. This test was done for all G with n up to 40, which, as mentioned in section 5.1, amounted to about 2.3 million functions. Thus, with the correctness of the degeneracy parameter $D(n, J, L)$ and of the G hyperspherical harmonics verified

TABLE 1: Degeneracy of the *F* Hyperspherical Harmonics for $n_\Pi = 40$[a]

J[a]	$\lvert L_\Pi \rvert = 4m$[a,b]	$D(40, J, L_\Pi)$	J[a]	$\lvert L_\Pi \rvert = 4m + 2$[a,b]	$D(40, J, L_\Pi)$
even	$\geq 40 - 2J$	$11 - m$	even	$\geq 42 - 2J$	$10 - m$
even	$< 40 - 2J$	$1 + J/2$	even	$< 42 - 2J$	$J/2$
odd	$\geq 42 - 2J$	$10 - m$	odd	$\geq 40 - 2J$	$10 - m$
odd	$< 42 - 2J$	$(J - 1)/2$	odd	$< 40 - 2J$	$(J + 1)/2$

[a] The ranges of J and $\lvert L_\Pi \rvert$ are from 0 to 40. [b] The quantity m is a non-negative integer whose values range from 0 to 10.

independently, it is concluded that they are both free of error. A similar test was performed for $\bar{g}$ functions with the help of (A.14).

5.3. Normalization and Orthogonality of the *F* and *g* Hyperspherical Harmonics. It is desirable to normalize the F functions according to

$$\int |F^{\Pi\, n_\Pi\, L_\Pi\, J}_{M_J}{}^{D}_{d}(\Theta_\lambda)|^2 \, d\Theta_\lambda = 1 \qquad (5.9)$$

where

$$d\Theta_\lambda = \sin b_\lambda \, da_\lambda \, db_\lambda \, dc_\lambda \, \sin(4\theta) \, d\theta \, d\delta_\lambda \qquad (5.10)$$

The ranges of the angles in the integral above are given by (2.7) through (2.9). The $N^{\Pi\, n_\Pi\, J\, L_\Pi}{}^{D}_{d}$ of (3.12), if chosen to be real and positive, should be, taking (4.31) into account,

$$N^{\Pi\, n_\Pi\; J\, L_\Pi}{}^{D}_{d} = \left\{ \frac{8\pi^3}{2J+1} \int_0^{\pi/4} \sum_{\Omega_{J_\lambda}=-J}^{J} [\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta)]^2 \sin(4\theta)\, d\theta \right\}^{-1/2} \qquad (5.11)$$

Since the normalization coefficient $N^{\Pi\, n_\Pi\, J\, L_\Pi}{}^{D}_{d}$ is independent of M_J, we can use it to define the modified function g by

$$g^{\Pi\, n_\Pi L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) = N^{\Pi\, n_\Pi J\, L_\Pi}{}^{D}_{d}\, \bar{g}^{\Pi\, n_\Pi L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) \qquad (5.12)$$

They satisfy a relation analogous to (4.31):

$$g^{\Pi\, n_\Pi L_\Pi\, J}_{-\Omega_{J_\lambda}}{}^{D}_{d}(\theta) = (-1)^{J+L_\Pi}\, g^{\Pi\, n_\Pi L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}(\theta) \qquad (5.13)$$

The magnitudes of these normalized g functions are considerably smaller than those of the corresponding $\bar{g}$ functions, which is a convenient property. It is important to stress that the functions $F^{\Pi\, n_\Pi\, L_\Pi\, J}_{M_J}$, which are orthogonal with respect to Π, n_Π, L_Π, J, and M_J, are not orthogonal with respect to d even after normalized according to (5.9). If desired, they can be orthogonalized with respect to this quantum number by a Gram–Schmidt or some other orthogonalization procedure.

TABLE 2: Principal-Axes-of-Inertia Hyperspherical Harmonics $\bar{g}$ for $n_\Pi = 1, 2, 3$

n_Π	J	L_Π	Ω_{J_λ} [a]	$\bar{g}^{n\, L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}$ [b]	n_Π	J	L_Π	Ω_{J_λ} [a]	$\bar{g}^{n_\Pi\, L_\Pi\, J}_{\Omega_{J_\lambda}}{}^{D}_{d}$ [b]
1	1	1	0	$\sqrt{2}x$	3	1	3	1	$y(x^2 - y^2)$
1	1	1	1	y	3	2	−1	0	0
1	1	−1	0	$-\sqrt{2}x$	3	2	−1	1	x^2y
1	1	−1	1	y	3	2	−1	2	xy^2
2	0	−2	0	$x^2 - y^2$	3	2	1	0	0
2	0	2	0	$x^2 - y^2$	3	2	1	1	$-x^2y$
2	1	0	0	0	3	2	1	2	$-xy^2$
2	1	0	1	xy	3	3	−3	0	$2x(2x^2 + 3y^2)/\sqrt{5}$
2	2	−2	0	$\sqrt{2/3}(2x^2 + y^2)$	3	3	−3	1	$\sqrt{3/5}y(4x^2 + y^2)$
2	2	−2	1	$2xy$	3	3	−3	2	$\sqrt{6}xy^2$
2	2	−2	2	y^2	3	3	−3	3	y^3
2	2	0	0	$-\sqrt{2/3}(2x^2 - y^2)$	3	3	−1	0	$-2x(2x^2 - y^2)/\sqrt{5}$
2	2	0	1	0	3	3	−1	1	$-y(4x^2 - 3y^2)/\sqrt{15}$
2	2	0	2	y^2	3	3	−1	2	$\sqrt{2/3}xy^2$
2	2	2	0	$\sqrt{2/3}(2x^2 + y^2)$	3	3	−1	3	y^3
2	2	2	1	$-2xy$	3	3	1	0	$2x(2x^2 - y^2)/\sqrt{5}$
2	2	2	2	y^2	3	3	1	1	$-y(4x^2 - 3y^2)/\sqrt{15}$
3	1	−3	0	$\sqrt{2}(x^3 - xy^2)$	3	3	1	2	$-\sqrt{2/3}xy^2$
3	1	−3	1	$y(x^2 - y^2)$	3	3	1	3	y^3
3	1	−1	0	$\sqrt{2}(x^3 - 3xy^2)$	3	3	3	0	$-2x(2x^2 + 3y^2)/\sqrt{5}$
3	1	−1	1	$-3x^2y + y^3$	3	3	3	1	$\sqrt{3/5}y(4x^2 + y^2)$
3	1	1	0	$-\sqrt{2}(x^3 - 3xy^2)$	3	3	3	2	$-\sqrt{6}xy^2$
3	1	1	1	$-3x^2y + y^3$	3	3	3	3	y^3
3	1	3	0	$-\sqrt{2}(x^3 - xy^2)$					

[a] The $\Omega_{J_\lambda} < 0$ functions are obtained from the $\Omega_{J_\lambda} > 0$ functions using (5.13). [b] The Π superscript of $\bar{g}$ (0 for n_Π even and 1 for n_Π odd) was omitted for simplicity.

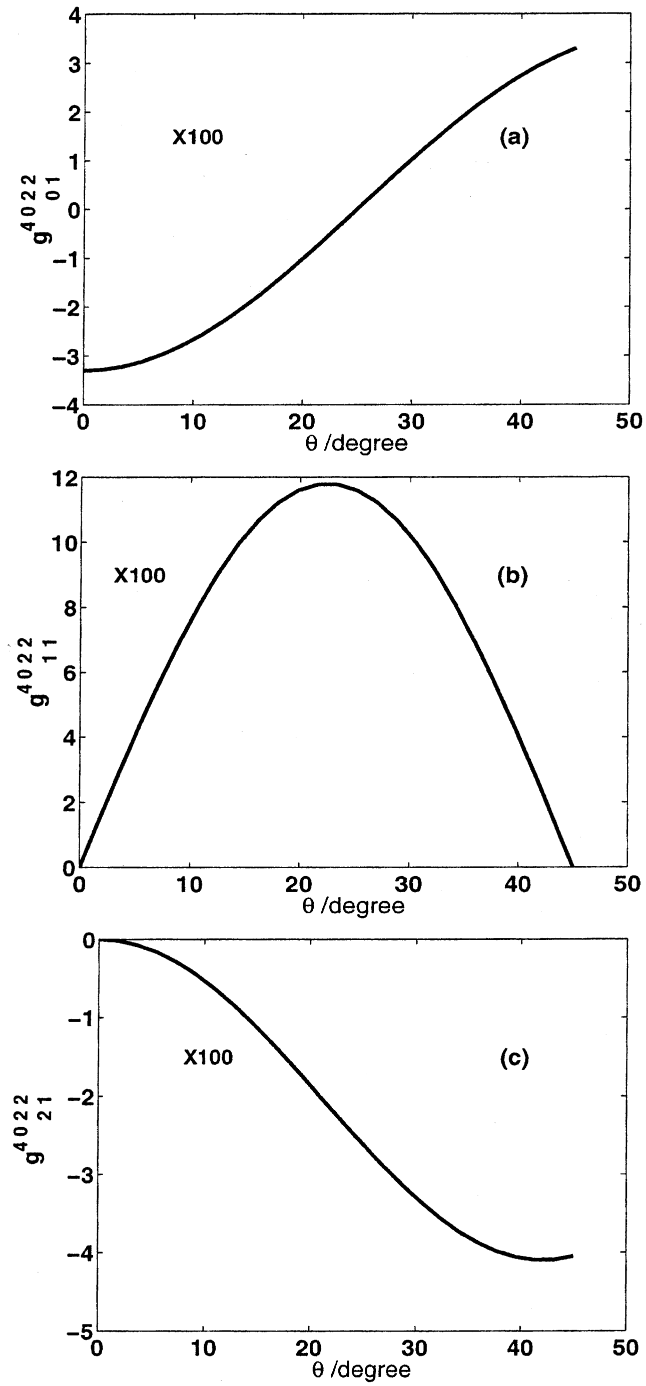

Figure 1. Normalized hyperspherical harmonics $g^{4\,0\,2}_{\Omega_{J_\lambda}}{}^{2}_{d}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 0 through 2. These functions are related to the corresponding $\bar{g}$ functions of Table 3 through (5.12), where $N^{4\,0\,2\,2}_{\;\;\;\;\;\;1} = 0.02022885$. The symbol $X\alpha$ indicates that the values of g were multiplied by α before being plotted. The $\Pi = 0$ superscript was omitted from the g symbol.

6. Representative Results

6.1. General Considerations. We used the procedure described in sections 4 and 5 to generate all the hyperspherical

TABLE 3: Principal-Axes-of-Inertia Hyperspherical Harmonics $\bar{g}$ for $n_\Pi = 4$

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

J	L_Π	Ω_{J_λ}	$\bar{g}^{4\,L_\Pi\,J}_{\;\;\Omega_{J_\lambda}}{}^{2}_{1}$	J	L_Π	Ω_{J_λ}	$\bar{g}^{4\,L_\Pi\,J}_{\;\;\Omega_{J_\lambda}}{}^{2}_{2}$
2	0	0	$\sqrt{2/3}(-2x^4+9x^2y^2+y^4)$	2	0	0	$\sqrt{2/3}(-2x^4+9x^2y^2+y^4)$
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	$y^2(-9x^2+y^2)$

[a,b] See footnotes of Table 2.

TABLE 4: Principal-Axes-of-Inertia Hyperspherical Harmonics $\bar{g}$ for $n_\Pi = 8$, $J = 4$, $L_\Pi = 2$, and $D = 2$

Ω_{J_λ} [a]	$\bar{g}^{8\,2\,4}_{\;\;\Omega_{J_\lambda}}{}^{2}_{1}$ [b]	$\bar{g}^{8\,2\,4}_{\;\;\Omega_{J_\lambda}}{}^{2}_{2}$ [b]
0	$-\sqrt{10/7}x^2y^4(2x^2-y^2)$	$\sqrt{10/7}(112x^6y^2-8x^8-5x^4y^4-74x^2y^6+3y^8)$
1	$xy(4x^6-19x^4y^2+16x^2y^4-3y^6)/\sqrt{14}$	$\sqrt{2/7}xy(743x^4y^2-148x^6-678x^2y^4+111y^6)$
2	$-2x^2y^2(-2x^4+2x^2y^2+y^4)/\sqrt{7}$	$-2y^2(64x^6+5x^4y^2-102x^2y^4+5y^6)/\sqrt{7}$
3	$-xy^3(x^4-4x^2y^2+y^4)/\sqrt{2}$	$\sqrt{2}xy^3(69x^4-134x^2y^2+37y^4)$
4	$x^2y^4(2x^2-y^2)$	$y^4(5x^4-38x^2y^2+5y^4)$

[a,b] See footnotes of Table 2.

TABLE 5: Principal-Axes-of-Inertia Hyperspherical Harmonics $\bar{g}$ for $n_\Pi = 24$, $J = 7$, $L_\Pi = 18$, and $D = 2$

Ω_{J_λ} [a]	$\bar{g}^{24\,18\,7}_{\;\;\Omega_{J_\lambda}}{}^{2}_{1}$ [b]	$\bar{g}^{24\,18\,7}_{\;\;\Omega_{J_\lambda}}{}^{2}_{2}$ [b]
0	0	0
1	$1/\sqrt{3003}xy(x^2-y^2)^6(448x^{10}-8176x^8y^2+35176x^6y^4+22115x^4y^6-1550x^2y^8+35y^{10})$	$1/\sqrt{3003}xy(x^2-y^2)^6(704x^{10}-12848x^8y^2+147848x^6y^4+75895x^4y^6-7450x^2y^8+55y^{10})$
2	$-\sqrt{8/1001}x^2y^2(x^2-y^2)^6(528x^8-1328x^6y^2-14251x^4y^4-1130x^2y^6+165y^8$	$-\sqrt{8/1001}x2y^2(x^2-y^2)^6(2544x^8-12944x^6y^2-55573x^4y^4-2890x^2y^6+795y^8)$
3	$\sqrt{-3/1001}xy^3(x^2-y^2)^6(720x^8-8580x^6y^2-8957x^4y^4+822x^2y^6-21y^8$	$\sqrt{-1/3003}\,xy^3(x^2-y^2)^6(15280x^8-125020x^6y^2-105483x^4y^4+11118x^2y^6-99y^8)$
4	$8x^2y^4(x^2-y^2)^6(130x^6+1211x^4y^2+148x^2y^4-33y^6)/\sqrt{91}$	$-8x^2y^4(x^2-y^2)^6(210x^6-5853x^4y^2-704x^2y^4+159y^6)/\sqrt{91}$
5	$5xy^5(x^2-y^2)^6(660x^6+991x^4y^2-202x^2y^4+7y^6)/\sqrt{91}$	$5xy^5(x^2-y^2)^6(900x^6+6003x^4y^2-726x^2y^4+11y^6)/\sqrt{91}$
6	$6\sqrt{2}/7x^2y^6(x^2-y^2)^6(117x^4+6x^2y^2-11y^4)$	$2\sqrt{2}/7x^2y^6(x^2-y^2)^6(673x^4+914x^2y^2-159y^4)$
7	$xy^7(x^2-y^2)^6(199x^4-94x^2y^2+7y^4)$	$xy^7(x^2-y^2)^6(427x^4+38x^2y^2+11y^4)$

[a,b] See footnotes of Table 2.

harmonic functions $\bar{g}^{n\,L\,J}_{\;\;\Omega_{J_\lambda}}{}^{D}_{d}(\theta)$ for n from 0 to 40. For each n, the number of $\bar{g}$ functions is approximately half the N_n of (6.7). The reason for this decrease is that N_n is the number of linearly-independent $F^{\Pi\,n\,L\,J}_{\;\;\;M_J}{}^{D(n,J,L)}_{d}$ functions. Whereas M_J can assume all values between $-J$ and J, the values of Ω_{J_λ}, although in the same range, can be restricted by (3.22) and (4.30) to the range 0 to J; the total number of $\bar{g}$ functions generated for all those n was about 1.2 million.

The calculation of those 1.2 million functions was performed on a Dell desktop computer operating with a 450 MHz Pentium II processor, and it required about 2 weeks of total running time. Given the independence of these functions on the characteristics

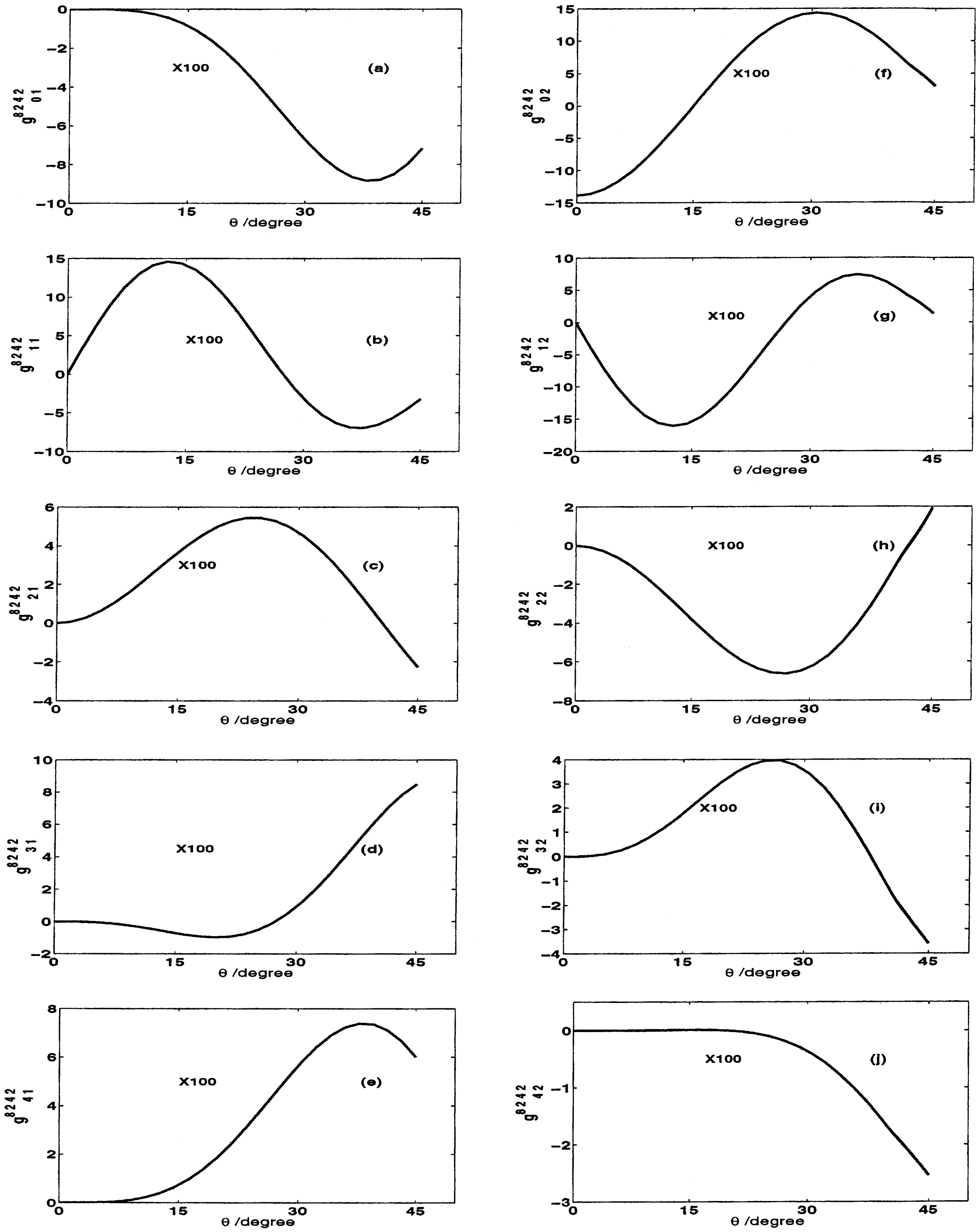

Figure 2. Normalized hyperspherical harmonics $g^{8\,2\,4}_{\Omega_{J_\lambda}}{}^{2}_{d}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 0 through 4 and $d = 1, 2$. $N^{8\,2\,4\,2}_{1} = 0.9610238$, and $N^{8\,2\,4\,2}_{2} = 0.01451439$. See caption of Figure 1 for additional information.

of the triatomic system for which they will be used, they will not have to be calculated again, except for obtaining more of them when needed. They are expressed in the form of (5.6), where the b coefficients have been normalized as described by (5.3). These coefficients are stored as sets of values for fixed n, J, Ω_{J_λ}, L, and d, with the indices q and r scanning each set. It should be noted that these g functions are related to appropriate Jacobi polynomials. We are currently investigating the details of these relations for general values of n, L, and J.

6.2. Comparison with Previous Results. The $\bar{g}^{\,n\,L}{}^{J=0}_{0}{}^{1}_{1}$ functions can be obtained analytically by solving (A.12) for $J = 0$. The result is

$$\bar{g}^{n_\Pi L_\Pi}{}^{J=0}_{0}{}^{1}_{1} = \cos^{|L_\Pi/2|}(2\theta) P_m^{(0,|L_\Pi/2|)}(\cos 4\theta) \qquad (6.1)$$

where $P_m^{(\alpha,\beta)}(\cos 4\theta)$ is the Jacobi polynomial of degree m[34] for $\alpha = 0$ and $\beta = L_\Pi/2$. The quantity m is a non-negative integer, and given m and L_Π, the values of n_Π are given by

$$n_\Pi = 4m + |L_\Pi| \qquad (6.2)$$

Furthermore, L_Π (and therefore n_Π) is constrained to be even;

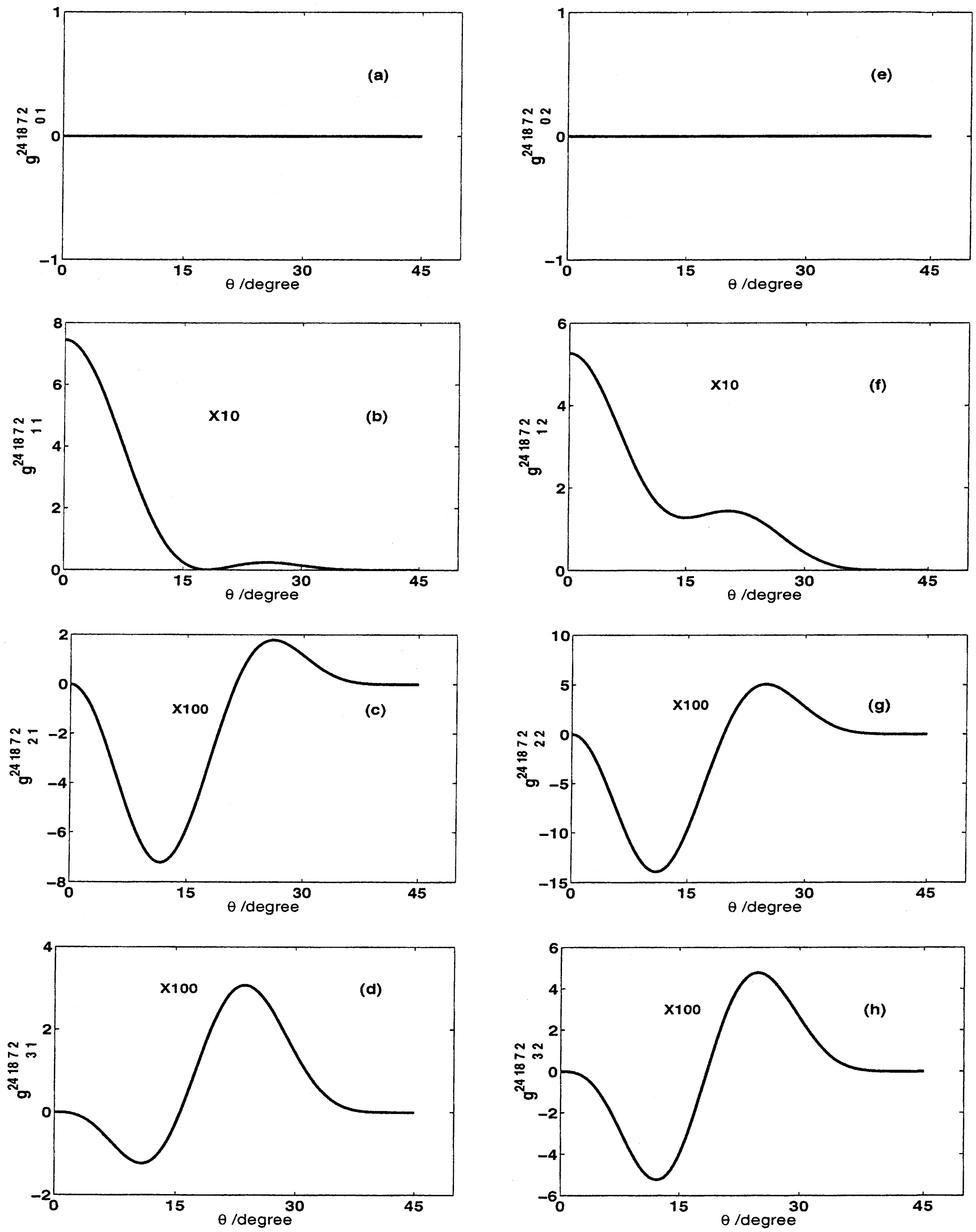

Figure 3. Normalized hyperspherical harmonics $g^{24\,18\,7}{}_{\Omega_{J_\lambda}}{}^{2}_{d}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 0 through 3 and $d = 1$, 2. $N^{24\,18\,7\,2}{}_{1} = 0.0911482$. See caption of Figure 1 for additional information.

that is, the $\Pi = 1$ (odd), $J = 0$ $\bar{g}$ functions vanish. When transformed into the variables x and y defined by (4.13) and (4.14), (6.1) agreed with the present recursion relation results.

6.3. Hyperspherical Harmonics for $n_\Pi = 1, 2, 3$. The principal-axes-of-inertia hyperspherical harmonics $\bar{g}$ for $n_\Pi =$ 1, 2, 3 is given in Table 2 for $\Omega_{J_\lambda} \geq 0$. The $\Omega_{J_\lambda} < 0$ functions can be obtained from the latter with the help of (5.13). None of the associated F functions are degenerate; that is, $D = d = 1$ for all entries of this table. As expectd, they are homogeneous polynomials of order $n_\Pi = 1$, 2, and 3 and n_Π and I_Π have the parity of Π. Furthermore, the coefficients of these polynomials are the products of rational numbers and the sqare roots of rational numbers, as discussed after (5.1).

6.4. Hyperspherical Harmonics for $n_\Pi = 4$. The $\bar{g}$ functions for $n_\Pi = 4$ are presented in Table 3. The value of $D(4, 2, 0)$ is equal to 2; that is, the corresponding F functions are doubly degenerate. This value of n_Π is the smallest one for which we encountered degeneracies in the F functions. In view of the symmetry relation (3.17), only three formulas are given. The corresponding normalization coefficient is calculated using

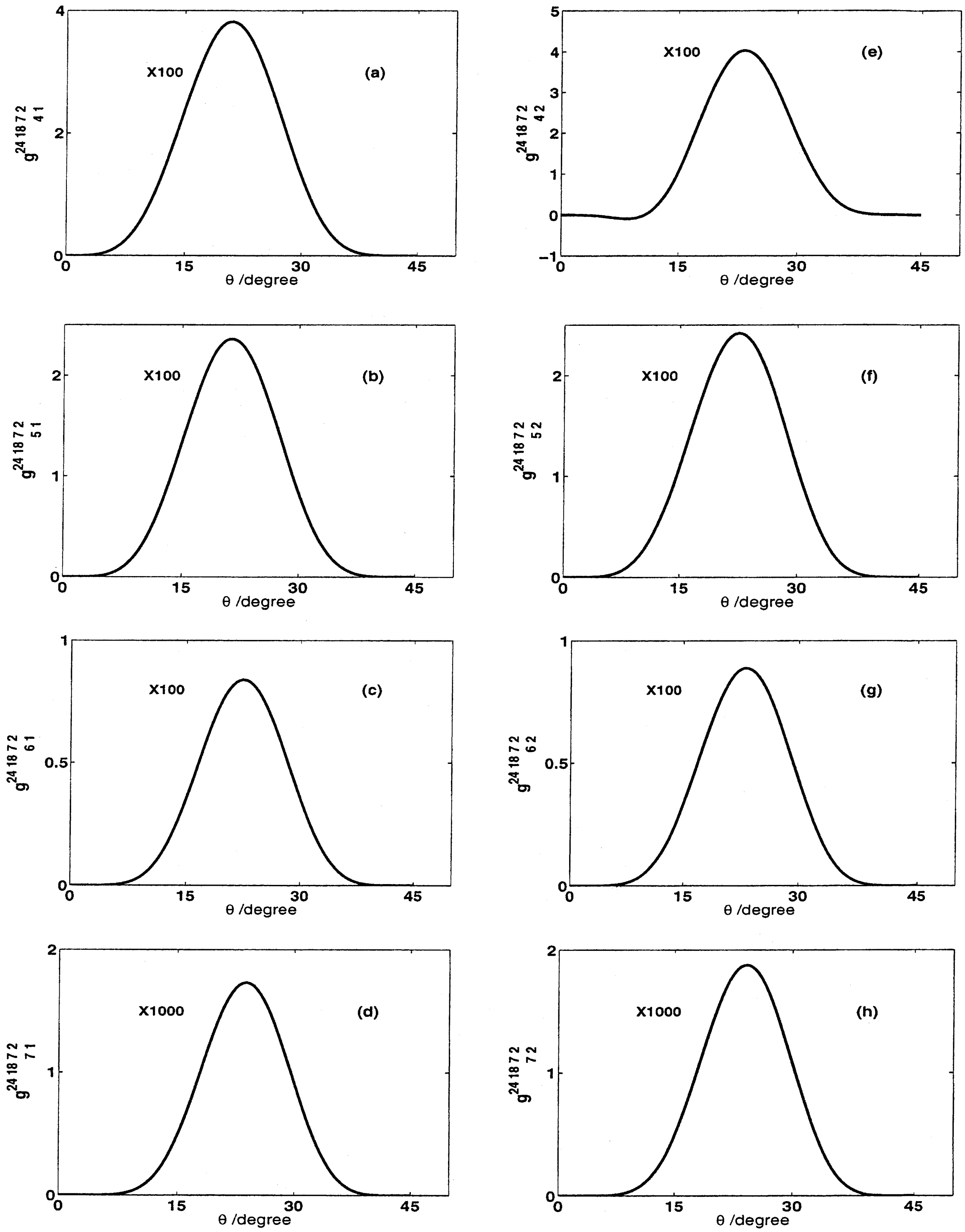

Figure 4. Normalized hyperspherical harmonics $g^{24\ 18\ 7}{}_{\Omega_{J_\lambda}}{}^{2}_{d}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 4 through 7 and $d = 1$, 2. $N^{24\ 18\ 7\ 2}_{\quad\quad\ \ 2} = 0.0410309$. See caption of Figure 1 for additional information.

(5.11). The associated g functions, defined by (5.12), are plotted in Figure 1 as a function of θ. Although these g are quartic polynomials in $x(\theta)$ and $y(\theta)$, the values of $g^{4\,0\,2}{}_{\Omega_{J_\lambda}}{}^{2}_{d}$ only display half an oscillation over the allowed range of θ. In addition, the ranges of variation of these g are rather small. It is interesting to analyze their behavior near the special configurations, namely $\theta = 0$ and $\theta = 45°$, at which the $\hat{\Lambda}^2$ operator has poles. The shape of all of those five curves is, as expected, very smooth and regular, with no unusual behavior, although they sample geometries close to the special configurations considered, confirming the well-behaved nature of the g functions. It is important to notice that although the $D = 2$, $d = 1$ $\bar{g}$ functions of the bottom part of Table 3 differ from the corresponding $D = 2$, $d = 2$ functions at most by a sign, they give rise to linearly-independent F functions as a result of (4.28) and (3.12). This can be seen clearly by noticing that $F^{\Pi=0\ n_\Pi=4\ L=0\ J=2\ D=2}_{\quad\quad\quad\quad\quad\quad\ M_J\ \ d=1} \pm F^{\Pi=0\ n_\Pi=4\ L=0\ J=2\ D=2}_{\quad\quad\quad\quad\quad\quad\ M_J\ \ d=2}$ are two completely different linearly-independent functions.

As noted above, the lowest value of n_Π for which we encountered degeneracy in the F functions was $n_\Pi = 4$. Great

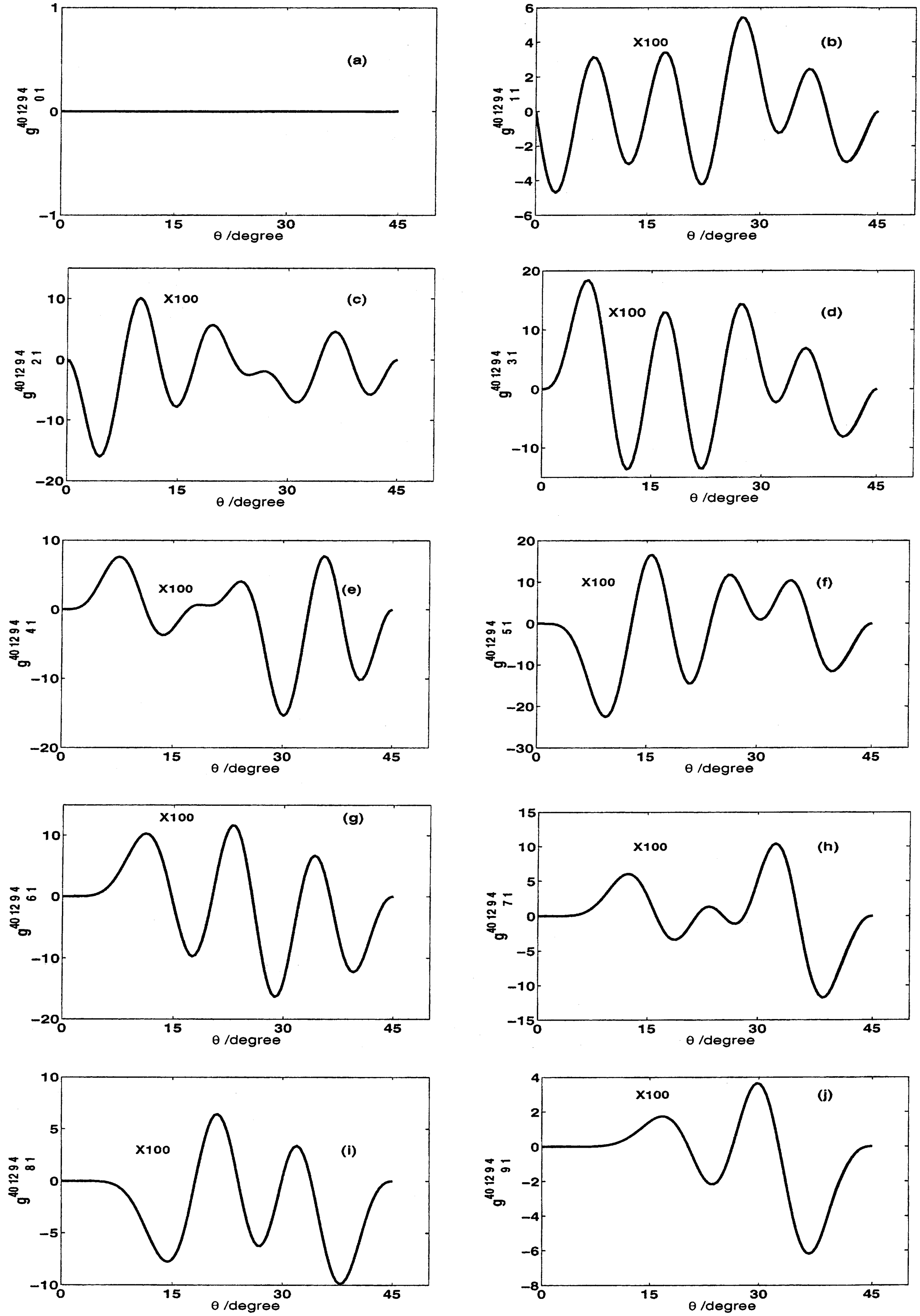

Figure 5. Normalized hyperspherical harmonics $g^{40\ 12\ 9}{}_{\Omega_{J_\lambda}}{}^{1}_{1}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 0 through 9. $N^{40\ 12\ 9\ 4}{}_{1} =$ 0.00901322. See caption of Figure 1 for additional information.

care has to be taken when using other methods,[17−22] as this degeneracy was not explicitly obtained in the corresponding publications. Wolniewicz,[23] however, does carefully discuss this issue.

6.5. Hyperspherical Harmonics for $n_\Pi = 8$. As an example of hyperspherical harmonic g functions for higher n_Π, we give in Table 4 the functions $\bar{g}^{8\ 2\ 4}{}_{\Omega_{J_\lambda}}{}^{2}_{d}$. The corresponding g functions are plotted in Figure 2. The value of $D(8, 4, 2)$ is 2, and

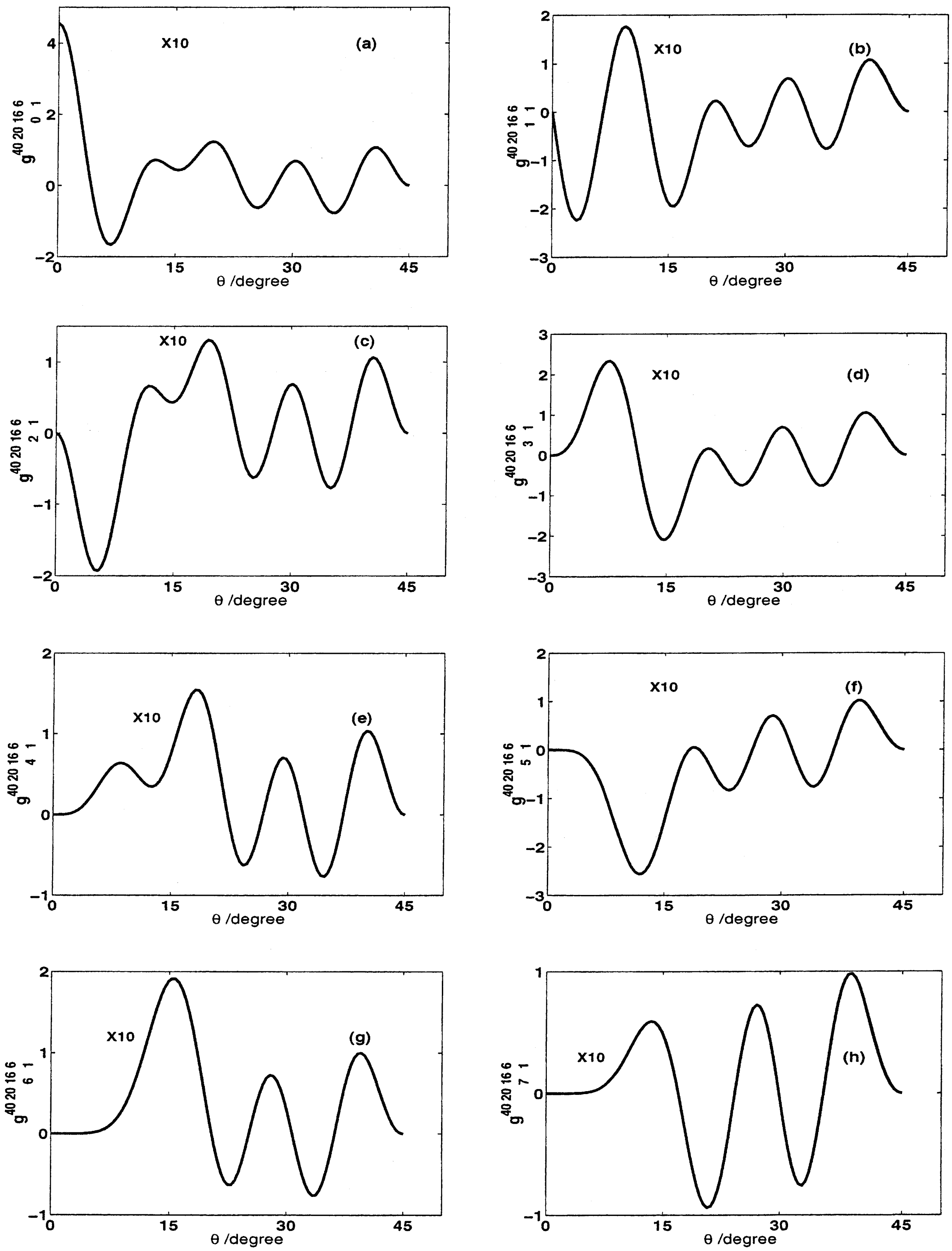

Figure 6. Normalized hyperspherical harmonics $g^{40\,20\,16\,\,\,6}_{\quad\quad\,\Omega_{J_\lambda}\,1}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 0 through 7, where $N^{40\,20\,16\,6}_{\quad\quad\quad\,1} = 1.08303$. See caption of Figure 1 for additional information.

therefore, d can assume the values 1 and 2. Each of these two functions has nine nonvanishing terms that are similar, but their coefficients are different. This is a pattern followed in general by degenerate hyperspherical harmonics. As displayed in Figure 2, a full oscillation over the allowed range of θ is found.

6.6. Hyperspherical Harmonics for $n_\Pi = 24$. Even though the $g^{\Pi\,n_\Pi\,L_\Pi\,J\,\,\,D}_{\quad\quad\quad\,\Omega_{J_\lambda}\,d}$ are homogeneous polynomials of degree n_Π in $x(\theta)$ and $y(\theta)$, as n_Π increases to 24, they do not display pronounced oscillations as a function of θ. This is due to the limited range of this angle, given by (2.9). As an example, the functions $\bar{g}^{24\,18\,7\,\,\,2}_{\quad\quad\Omega_{J_\lambda}\,d}$ (the superscript Π is omitted for simplicity) are given in Table 5 and depicted in Figure 3 for $\Omega_{J_\lambda} = 0{-}3$ and in Figure 4 for $\Omega_{J_\lambda} = 4{-}7$. Since $J + L_\Pi$ is odd, (3.17) and (4.31) predict that $g^{24\,18\,7\,2}_{\quad\quad\,0\,d} = 0$, which is indeed the case, as

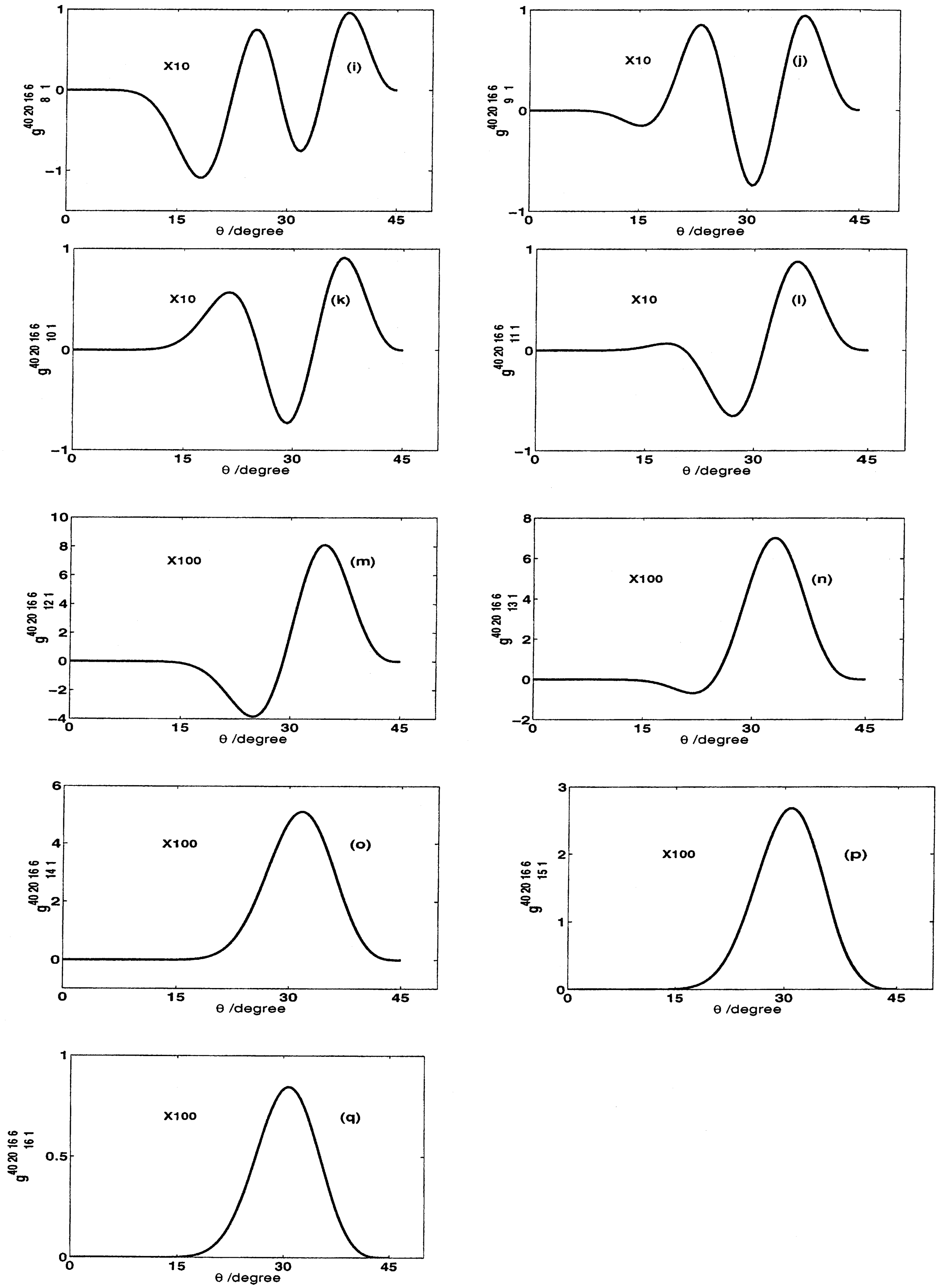

Figure 7. Normalized hyperspherical harmonics $g^{40\ 20\ 16\ \ 6}_{\ \ \ \ \ \ \Omega_{J_\lambda}\ 1}$ as a function of the principal angle of inertia θ, for Ω_{J_λ} from 8 through 16, where $N^{40\ 20\ 16\ 6}_{\ \ \ \ \ \ \ \ \ \ \ 1} = 1.08303$. See caption of Figure 1 for additional information.

seen in panels a and e of Figure 3. Even though we found a full oscillation for one of the $n_\Pi = 8$ cases, only fewer than two full oscillations were found for $n_\Pi = 24$, whereas three full oscillations might have been expected on the basis of the $n_\Pi = 8$ results. This small number of oscillations is a consequence not only of the limited range of θ but also of the nature of the associated homogeneous polynomials in sin θ and cos θ.

6.7. Hyperspherical Harmonics for $n_\Pi = 40$. The degeneracies $D(n_\Pi = 40, J, L_\Pi)$ of the hypershperical harmonics obtained for $n_\Pi = 40$ are given in Table 1 and range, as pointed out after (5.8), from 1 to 11. The g functions for this value of n_Π are displayed in Figure 5 for $L_\Pi = 12$, $J = 9$ and in Figures 6 and 7 for $L_\Pi = 20$, $J = 16$. The corresponding degeneracies are $D(40, 9, 12) = 4$ and $D(40, 16, 20) = 6$. Since it is not practical to display the corresponding g functions for all the values of d from 1 to 4 or from 1 to 6, respectively, only the $d = 1$ harmonics are shown in these figures. Although more oscillations were found than for lower values of n_Π, there are still relatively few such oscillations for a fortieth order polynomial in cos θ and sin θ. The reason for this behavior was discussed in section 6.6. For the $J = 9$, $L_\Pi = 12$ case, $J + L_\Pi$ is odd, and therefore, $g^{40\;12\;9\;4}_{\;0\;\;d} = 0$, as is seen in Figure 5a.

7. Discussion

Once the $\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\, D}_{\Omega_{J_\lambda}\, d}$ hyperspherical harmonics have been obtained, replacement into (4.30) and (3.12) (or equivalently, (A.16), (A.15), and (3.21)) furnishes the corresponding $F^{\Pi\, n_\Pi\, L_\Pi\, J\, D}_{M_J\, d}(\Theta_\lambda)$ hyperspherical harmonics in ROHC. These can then be used as a basis set for expanding the local hyperspherical surface functions (LHSF) Φ, which by definition are the simultaneous eigenfunctions of the surface Hamiltonian

$$\hat{h}(\Theta_\lambda;\rho) = \frac{\hat{\wedge}^2(\Theta_\lambda)}{2\mu\rho^2} + V(\rho,\theta,\delta_\lambda) \tag{7.1}$$

where V is the potential energy function, and of $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, and $\hat{O}_{\hat{\imath}}$. Once that expansion is performed, and the properties of the Wigner rotation functions appearing in (3.12) or (3.21) are taken into account, the corresponding coefficients must satisfy, for each Π and J, a generalized eigenvalue−eigenvector equation involving matrixes that are independent of M_J and whose rows and columns are spanned by the four quantum numbers n_Π, L_Π, D, and d. The calculation of these matrixes involves quadratures over the two variables δ_λ and θ on which $V(\rho,\delta_\lambda,\theta)$, $g^{\Pi\, n_\Pi\, L_\Pi\, J\, D}_{\Omega_{J_\lambda}\, d}$ and $e^{iL_\Pi\delta_\lambda}$ depend. Since all these functions are now known and since the V and g functions do not vary very rapidly with δ_λ and θ, these quadratures can be efficiently performed using relatively few angular integration points and for large blocks of integrals simultaneously, so as to minimize the duplication of numerical operations and thereby optimize the corresponding computer time.

As all Coriolis terms are incorporated in the g functions, all the couplings in the equations satisfied by the coefficients of the LHSF expansion are potential function couplings. Furthermore, the equations for $\Pi = 0$ (i.e., even values of n_Π) are decoupled from those for $\Pi = 1$ (i.e., odd values of n_Π). In addition, as mentioned at the end of the paragraph following (3.17), F hyperspherical harmonics for Γ irreducible representations of the permutation group of identical atoms that the system of interest may contain can easily be generated. Using such parity and irreducible representation F functions decreases the numerical effort required to generate the corresponding LHSF.

Due to the first term on the rhs of (7.1) a hypercentrifugal potential matrix, diagonal in n_Π, will appear as an additive term in the matrix whose generalized eigenvalues and eigenvectors must be evaluated. The diagonal terms of that hypercentrifugal matrix are $n_\Pi(n_\Pi + 4)\hbar^2/2\mu\rho^2$. For a given J, (3.8) requires that $n_\Pi \geq J$. On the other hand, due to the highly repulsive nature of the hypercentrifugal matrix elements, it is expected that the rate of convergence of the calculation with respect to n_Π will be high, that is, that values of n_Π much larger than J will not be needed.

8. Summary and Conclusions

We have described and implemented a recursive procedure for generating analytical hyperspherical harmonics for triatomic systems in row-orthonormal hyperspherical coordinates. These hyperspherical harmonics are regular at the poles of the corresponding kinetic energy operator. The implementation of this procedure was performed with a *Mathematica* algebraic program and used to generate all such functions for values of the grand-canonical hyperangular momentum quantum number up to 40. About 2.3 million such functions were generated. The hyperspherical harmonics obtained were shown to be correct by verifying that they satisfy the appropriate coupled partial differential equations. The degeneracy of these hyperspherical harmonics was also calculated, and it achieved a maximum value of $D = 11$ for $n_\Pi = 40$, $J = 20$, and $L_\Pi = 0$. These functions are attractive candidates for benchmark-quality state-to-state reactive scattering calculations for these systems involving a ground electronically adiabatic potential energy surface, as long as this surface does not display a conical intersection with the neighboring one.

Appendix A. Coupled Partial Differential Equations for the Principal-Axes-of-Inertia Hyperspherical Harmonics *G*

The $G^{\Pi\, n\, L\, J\, D}_{\Omega_{J_\lambda}\, d}(\theta)$ hyperspherical harmonics have been defined by (3.12). The range of the δ_λ angle in these equations can be taken to be those given by (2.8). The results will be the same as long as the $F^{\Pi\, n\, L\, J\, D}_{M_J\, d}(\Theta_\lambda)$ are the same at the two sets of $(\Theta_\lambda)_\lambda$ angles defined by (3.15) and (3.16). We will impose this constraint throughout this paper, and as a result, we are allowed to use the range of the δ_λ given by (3.13) whenever desired. We will do so in this appendix, since then the functions $e^{iL\delta_\lambda}$ that appear in (3.18) are orthogonal. Under these conditions, the coupled partial differential equations satisfied by the $G^{\Pi\, n\, L\, J\, D}_{\Omega_{J_\lambda}\, d}(\theta)$ can be obtained by standard methods. To that effect, we remember that

$$\hat{J}^2 = \hat{J}_x^{I_\lambda^2} + \hat{J}_y^{I_\lambda^2} + \hat{J}_z^{I_\lambda^2} \tag{A.1}$$

and define the operators

$$\hat{J}_\pm^{I_\lambda} = \hat{J}_x^{I_\lambda} \pm i\hat{J}_y^{I_\lambda} \tag{A.2}$$

where the $\hat{J}_x^{I_\lambda}$, $\hat{J}_y^{I_\lambda}$, and $\hat{J}_z^{I_\lambda}$ are given explicitly by (2.20). As a result, we can express $\hat{J}_x^{I_\lambda}$ and $\hat{J}_y^{I_\lambda^2}$ in terms of the $\hat{J}_\pm^{I_\lambda}$ as

$$\hat{J}_x^{I_\lambda} = \frac{1}{2}(\hat{J}_+^{I_\lambda} + \hat{J}_-^{I_\lambda}) \tag{A.3}$$

$$\hat{J}_y^{I_\lambda} = \frac{1}{2i}(\hat{J}_+^{I_\lambda} - \hat{J}_-^{I_\lambda}) \tag{A.4}$$

$$\hat{J}_x^{I_\lambda^2} = \frac{1}{2}(\hat{J}^2 - \hat{J}_z^{I_\lambda^2}) + \frac{1}{4}(\hat{J}_+^{I_\lambda^2} + \hat{J}_-^{I_\lambda^2}) \tag{A.5}$$

$$\hat{J}_y^{I_\lambda^2} = \frac{1}{2}(\hat{J}^2 - \hat{J}_z^{I_\lambda^2}) - \frac{1}{4}(\hat{J}_+^{I_\lambda^2} + \hat{J}_-^{I_\lambda^2}) \tag{A.6}$$

We now use (A.1) through (A.6) to express that operator, and therefore $\hat{\wedge}^2$, in terms of $\hat{J}^2$, $\hat{J}_3^{I_\lambda}$, and $\hat{J}_\pm^{I_\lambda}$. We then replace (3.12) into (3.3), to apply the several angular momentum operators in the resulting expression to the Wigner rotation functions. The effects of these operators on those Wigner rotation functions are[20]

$$\hat{J}^2 D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) = J(J+1)\hbar^2 D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) \tag{A.7}$$

$$\hat{J}_3^{I_\lambda} D^J_{M_J \Omega_{J\lambda}}(\mathbf{a}_\lambda) = \Omega_{J_J}\hbar D^J_{M_J \Omega_{J\lambda}}(\mathbf{a}_\lambda) \tag{A.8}$$

$$\hat{J}_\pm^{I_\lambda} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) = \hbar \xi_\mp(J,\Omega_{J_\lambda}) D^J_{M_J \Omega_{J_\lambda}\mp 1}(\mathbf{a}_\lambda) \tag{A.9}$$

where

$$\xi_\pm(j,\Omega) = [j(j+1) - \Omega(\Omega \pm 1)]^{1/2} = [(j \mp \Omega)(j \pm \Omega + 1)]^{1/2} \tag{A.10}$$

with

$$-j \le \Omega \le j \qquad j \ge 0, \text{ integer} \tag{A.11}$$

Using (A.7) through (A.10) together with the orthogonality of the Wigner rotation functions, we finally get the following system of $2J + 1$ coupled partial differential equations that must be satisfied by the $G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}$

$$\left[\frac{J(J+1) - \Omega_{J_\lambda}{}^2}{2\cos^2\theta} + \frac{J(J+1) + 2L_\Pi{}^2 - \Omega_{J_\lambda}{}^2}{2\cos^2 2\theta} + \frac{\Omega_{J_\lambda}{}^2}{\sin^2\theta} - \frac{d^2}{d\theta^2} - 4\cot 4\theta \frac{d}{d\theta} - n(n+4)\right] G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}\theta + \frac{1}{4}\left(\frac{1}{\cos^2\theta} - \frac{1}{\cos^2 2\theta}\right)[\xi_+(J,\Omega_{J_\lambda} - 2)\xi_+(J,\Omega_{J_\lambda} - 1)G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}-2\ d}(\theta) + \xi_-(J,\Omega_{J_\lambda} + 2)\xi_-(J,\Omega_{J_\lambda} + 1)G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}+2\ d}(\theta)] - iL_\Pi \frac{\sin 2\theta}{\cos^2 2\theta}[\xi_-(J,\Omega_{J_\lambda} + 1)G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}+1\ d}(\theta) - \xi_+(J,\Omega_{J_\lambda} - 1)G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}-1\ d}(\theta)] = 0 \tag{A.12}$$

$$\Omega_{J_\lambda} = -J, -J+1, ..., J \tag{A.13}$$

The corresponding differential equations satisfied by the real $\hat{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}$ functions defined by (4.30) are

$$\left[\frac{J(J+1) - \Omega_{J_\lambda}{}^2}{2\cos^2\theta} + \frac{J(J+1) + 2L_\Pi{}^2 - \Omega_{J_\lambda}{}^2}{2\cos^2 2\theta} + \frac{\Omega_{J_\lambda}{}^2}{\sin^2\theta} - \frac{d^2}{d\theta^2} - 4\cot 4\theta \frac{d}{d\theta} - n(n+4)\right] \bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}\theta - \frac{1}{4}\left(\frac{1}{\cos^2\theta} - \frac{1}{\cos^2 2\theta}\right)[\xi_+(J,\Omega_{J_\lambda} - 2)\xi_+(J,\Omega_{J_\lambda} - 1)\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}-2\ d}(\theta) + \xi_-(J,\Omega_{J_\lambda} + 2)\xi_-(J,\Omega_{J_\lambda} + 1)\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}+2\ d}(\theta)] + L_\Pi \frac{\sin 2\theta}{\cos^2 2\theta}[\xi_-(J,\Omega_{J_\lambda} + 1)\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}+1\ d}(\theta) + \xi_+(J,\Omega_{J_\lambda} - 1)\bar{g}^{n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}-1\ d}(\theta)] = 0 \tag{A.14}$$

where Ω_{J_λ} spans the values given by (A.13). The differential equations satisfied by the G' functions defined by (3.21) can be obtained directly by substituting (3.22) into (A.12). The main difference will be that the range of Ω_{J_λ} is now 0 to J, meaning that the G' satisfy a system of $J + 1$ coupled differential equations instead of the $2J + 1$ equations satisfied by the G. In analogy to (4.30), we define the real functions $\bar{g}'$ by

$$G'^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{-\Omega_{J_\lambda}\ d}(\theta) = (-1)^{i(\Omega_{J_\lambda} - J)\pi/2}\bar{g}'^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}(\theta) \tag{A.15}$$

From (3.22), (4.30), and (A.15) we get

$$\bar{g}'^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{-\Omega_{J_\lambda}\ d}(\theta) = (1 + \delta_{\Omega_{J_\lambda} 0})^{-1/2}\bar{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}(\theta) \tag{A.16}$$

Substitution of this expression into (A.14) leads to a system of $J + 1$ differential equations for the $\bar{g}'$ that bear the same relation to the $2J + 1$ equations [(A.14)] satisfied by the $\bar{g}$ as the one between the G' and G equations.

It should be noticed that, in (A.12) and (A.14), Π, n_Π, and J are fixed, whereas the Ω_{J_λ} span the range indicated in (A.13). The only differential operator appearing in (A.12) and (A.14) acts on the $G^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}(\theta)$ and $\hat{g}^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{\Omega_{J_\lambda}\ d}(\theta)$, respectively. A similar statement is applicable to the G' and $\bar{g}'$ counterparts of these equations. The entire coupling between G functions or their $\bar{g}$ counterparts or between the G' and their $\bar{g}'$ counterparts is completely due to the Coriolis coupling terms associated with the products of ξ coefficients. The $F^{\Pi\, n_\Pi\, L_\Pi\, J\ D}_{M_J\ d}(\Theta_\lambda)$ functions of (3.12) or (3.21) will be used used to expand the local hyperspherical surface functions (LHSF), which are, as mentioned in section 7, the eigenfunctions of the local hyperspherical surface operator $\hat{h}$ defined by (7.1), as well as of $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, and $\hat{O}_{\hat{I}}$. $\hat{h}$ depends on ρ only parametrically; that is, it does not contain differential operators in this variable. The resulting algebraic equations in the coefficients of this expansion will not contain any Coriolis coupling terms. The coupling between these equations is entirely due to the potential energy function.

Finally, we remark that we do not attempt in this paper to solve either (A.12) or (A.14) or their G' or $\bar{g}'$ equivalents. Instead, we derive a recursion relation among the G or $\bar{g}$ functions for consecutive values of n_Π, based on the general properties of harmonic polynomials. We then use this recursion relation to generate analytically the G or $\bar{g}$ functions and then the corresponding G' or $\bar{g}'$ functions. The G or $\bar{g}$ recursion relations are slightly simpler than their G' or $\bar{g}'$ counterparts, which justifies this procedure. (A.12) and (A.14) are however used to check the correctness of the functions thus obtained.

Appendix B. Relation between the Quantum Numbers Π, n_Π, and L_Π

Let us show that the parity quantum number Π, the grand canonical angular momentum quantum quantum number n_Π, and the internal angular momentum quantum number L_Π all have the same parity. The hyperspherical harmonic F of order n is related to the harmonic polynomial of the same order by[18]

$$F^n(\Theta_\lambda) = H_n/\rho^n \tag{B.1}$$

where H_n is expressed in terms of the space-fixed Cartesian coordinates of the mass-scaled Jacobi vectors $\boldsymbol{r}_\lambda^{(1)}$ and $\boldsymbol{r}_\lambda^{(2)}$ as

$$H_{n_\Pi}(\mathbf{x}) = \sum_v a_v x_\lambda^{(1)^{v_1}} y_\lambda^{(1)^{v_2}} z_\lambda^{(1)^{v_3}} x_\lambda^{(2)^{v_4}} y_\lambda^{(2)^{v_5}} z_\lambda^{(2)^{v_6}} \tag{B.2}$$

with $\boldsymbol{v} = (v_1, ..., v_6)$ and where $\sum_v$ indicates a sum over all possible values of the six non-negative integers v_s constrained by the condition

$$\sum_{s=1}^{6} v_s = n_\Pi \tag{B.3}$$

The polynomial coefficients a_v in general are complex numbers. The inversion operator acts on $\mathbf{x}_\lambda$ according to

$$\hat{I}\mathbf{x}_\lambda = (-x_\lambda^{(1)}, -y_\lambda^{(1)}, -z_\lambda^{(1)}, -x_\lambda^{(2)}, -y_\lambda^{(2)}, -z_\lambda^{(2)}) \quad \text{(B.4)}$$

As a result,

$$\hat{O}_{\hat{I}} H_{n_\Pi}(\mathbf{x}_\lambda) = \sum_v a_v (-x_\lambda^{(1)})^{v_1} (-y_\lambda^{(1)})^{v_2} (-z_\lambda^{(1)})^{v_3} (-x_\lambda^{(2)})^{v_4} \times (-y_\lambda^{(2)})^{v_5} (-z_\lambda^{(2)})^{v_6} = (-1)^{n_\Pi} H_{n_\Pi}(\mathbf{x}_\lambda) \quad \text{(B.5)}$$

From (B.1) and (B.5) and the fact that ρ is invariant under the inversion operation, we have

$$\hat{O}_{\hat{I}} F^{n_\Pi}(\Theta_\lambda) = (-1)^{n_\Pi} F^{n_\Pi}(\Theta_\lambda) \quad \text{(B.6)}$$

and, in view of (3.7), we get

$$(-1)^\Pi = (-1)^{n_\Pi} \quad \text{(B.7)}$$

Therefore, n_Π and Π have the same parity.

Let us now relate the parity of Π and L_Π. Applying $\hat{O}_{\hat{I}}$ on both sides of (3.12) and using (3.2), we get

$$\hat{O}_{\hat{I}} F^{\Pi\ n_\Pi\ L_\lambda\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) = N^{\Pi\ n_\Pi\ J\ L_\Pi} e^{iL_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} \times D^J_{M_J \Omega_{J_\lambda}}(\pi + a_\lambda, \pi - b_\lambda, \pi - c_\lambda) G^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta) \quad \text{(B.8)}$$

However,

$$D^J_{M_J \Omega_{J_\lambda}}(\pi + a_\lambda, \pi - b_\lambda, \pi - c_\lambda) = (-1)^{J+\Omega_{J_\lambda}} D^J_{M_J -\Omega_{J_\lambda}}(a_\lambda, b_\lambda, c_\lambda) \quad \text{(B.9)}$$

Replacing this expression into (B.7) and changing the summation index from Ω_{J_λ} to $-\Omega_{J_\lambda}$, we get

$$\hat{O}_{\hat{I}} F^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) = N^{\Pi\ n_\Pi\ J\ L_\Pi} e^{iL_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} \times (-1)^{J-\Omega_{J_\lambda}} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)\, G^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta) \quad \text{(B.10)}$$

With the use of (3.17) this expression becomes

$$\hat{O}_{\hat{I}} F^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) = (-1)^{L_\Pi} F^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) \quad (11)$$

and, in view of (3.7) and (B.6)

$$(-1)^\Pi = (-1)^{n_\Pi} = (-1)^{L_\Pi} \quad \text{(B.12)}$$

that is, Π, n_Π, and L_Π indeed have the same parity, Q.E.D.

Appendix C. *G* Hyperspherical Harmonics as Homogeneous Polynomials

Once the *F* hyperspherical harmonics are explicitly defined by (3.3) through (3.7), the *G* hyperspherical harmonics are implicitly defined by (3.12) and (3.17). We now wish to prove that these *G* functions are homogeneous polynomials of degree *n* in the variables *x* and *y* defined by (4.13) and (4.14). This property will be very useful in obtaining the *G* analytically.

Let us consider the function *h* defined by (4.21). We already know that it is a harmonic polynomial of degree *n* in the variables $T_{\lambda}{}^{k}_{j}$ and can therefore be written (omitting the primes in the indices) as

$$h^{\Pi\ n\ L\ J}_{\qquad M_J\ d}{}^{D}(\rho,\Theta_\lambda) = \sum_{j_1,\ldots,j_n} \sum_{k_1,\ldots,k_n=-1}^{1} C_{j_1k_1\ldots j_nk_n} T_{\lambda}{}^{k_1}_{j_1} \ldots T_{\lambda}{}^{k_n}_{j_n} \quad \text{(C.1)}$$

where the *C* are constant coefficients that may be complex and each of the j_s ($s = 1, ..., n$) in the first sum assumes the value −1 or 1 only. Replacing this relation, as well as (4.10), in (4.21) permits us to write the corresponding $F^{\Pi\ n_\Pi\ L_\Pi}$ as

$$F^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\rho,\Theta_\lambda) = \frac{1}{\rho^n} h^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) = e^{i(j_1+\ldots+j_n)\delta_\lambda} \sum_{j_1,\ldots,j_n} \sum_{k_1,\ldots,k_n=-1}^{1} \times C_{j_1k_1\ldots j_nk_n} \prod_{s=1}^{n} D^1_{k_s p_s}(\mathbf{a}_\lambda) t^{p_s}_{j_s}(\theta) \quad \text{(C.2)}$$

The products of the Wigner rotation functions $D^1_{k_i p_i}(\mathbf{a}_\lambda)$ can be expressed, by successive application of the Clebsch−Gordan series,[29] in terms of the $D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ functions and appropriate Clebsch−Gordan coefficients. As a result, we get

$$F^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad M_J\ d}{}^{D}(\Theta_\lambda) = e^{iL_\Pi \delta_\lambda} \sum_{\Omega_{J_\lambda}=-J}^{J} D^J_{M_J \Omega_{J_\lambda}}(\mathbf{a}_\lambda) \bar{G}^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta) \quad \text{(C.3)}$$

where

$$\Omega_{J_\lambda} = \sum_{s=1}^{n_\Pi} p_s \qquad L = \sum_{s=1}^{n_\Pi} j_s \quad \text{(C.4)}$$

and $\bar{G}^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta)$ is a linear combination of the products of n_Π $t^{p_s}_{j_s}(\theta)$ functions. In other words, this $\bar{G}$ is a homogeneous polynomial of degree n_Π in the six variables $t^p_j(\theta)$ ($p = -1, 0, 1$; $j = -1, 1$) and therefore of the two real variables *x* and *y* defined by (4.13) and (4.15). In view of (3.12) and (C.3), the $G^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta)$ are proportional to $\bar{G}^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta)$ and, as a result, are also homogeneous polynomials of degree n_Π in *x* and *y*, Q.E.D.

Let us now prove that the $\bar{g}^{\Pi\ n_\Pi\ L_\Pi\ J}_{\qquad\quad \Omega_{J_\lambda}\ d}{}^{D}(\theta)$ defined by (4.30) are real. Indeed, we have shown that, for $n = 1$, all six $\bar{g}^{1\,j\,1\,1}_{\quad\ p\,1}$ ($j = -1, 1$; $p = -1, 0, 1$), given by (4.34) and (4.35), are real. Furthermore, all the coefficients on the rhs of (4.32), that relates the $\bar{g}^{n+1}$ to the $\bar{g}^n$, are real. Therefore, by induction from the $n = 1$ case, the $\bar{g}^n$ are real, Q.E.D.

Appendix D. Harmonic Polynomials and Hyperspherical Harmonics

The general theory of harmonic polynomials and hyperspherical harmonics is of central importance for this paper. We summarize here the properties that were used in deriving the basic recursion relations for the principal-axes-of-inertia hyperspherical harmonic *G* functions, defined by (3.18) and given by (4.27) and (4.34).

D.1. Harmonic Polynomials in *m*-Dimensional Space. Consider the $\mathbb{R}^m$ space spanned by $\boldsymbol{x} = (x_1, x_2,..., x_m)$ where the x_i are real variables each spanning the full $-\infty$ to $+\infty$ domain.

A general homogeneous polynomial of non-negative integer degree n in $\mathbb{R}^m$ is defined as

$$f^n_{(m)}(\mathbf{x}) = \sum_{n_i} \mathscr{A}_{n_1 n_2 \ldots n_m} x_1^{n_1} x_2^{n_2} \ldots x_m^{n_m} \qquad \text{(D.1)}$$

where the n_i ($i = 1$ through m) are non-negative integers. The sum extends over all such integers subject to the constraint

$$\sum_{i=1}^{m} n_i = n \qquad \text{(D.2)}$$

and the $\mathscr{A}$ are complex dimensionless constants. A harmonic polynomial $h^n_{(m)}(\mathbf{x})$ in $\mathbb{R}^m$ is a homogeneous polynomial of degree n in that space which, in addition, satisfies the Laplace equation

$$\nabla^2_{(m)} h^n_{(m)}(\mathbf{x}) = 0 \qquad \text{(D.3)}$$

where $\nabla^2_{(m)}$ is the m-dimensional Laplacian defined by

$$\nabla^2_{(m)} = \sum_{i=1}^{m} \frac{\partial^2}{\partial x_i^2} \qquad \text{(D.4)}$$

Given an arbitrary homogeneous polynomial $f^n_{(m)}(\mathbf{x})$, the associated function $h^n_{(m)}(\mathbf{x})$, defined by

$$h^n_{(m)}(\mathbf{x}) = \sum_{k=0}^{[n/2]} \frac{(-1)^k (m + 2n - 2k - 4)!!}{(2k)!!(m + 2n - 4)!!} \rho_m^{(2k)} (\nabla^2_{(m)})^k f^n_{(m)}(\mathbf{x}) \qquad \text{(D.5)}$$

is a harmonic polynomial,[35] where $[n/2]$ denotes the integer part of $n/2$ and ρ_m is the hyperradius, defined by

$$\rho_m^2 = \sum_{i=0}^{m} x_i^2 \qquad \text{(D.6)}$$

D.2. Dimensionless Grand-Canonical Generalized Angular Momentum Operators. This operator is defined by[24]

$$\hat{\lambda}^2_{(m)} = -\sum_{i=1}^{m} \sum_{j=1}^{i-1} \hat{\lambda}^2_{ij} \qquad \text{(D.7)}$$

where

$$\hat{\lambda}^2_{ij} = x_i \frac{\partial}{\partial x_j} - x_j \frac{\partial}{\partial x_i} \qquad \text{(D.8)}$$

From this definition one can easily derive the relation

$$\nabla^2_{(m)} = \frac{1}{\rho_m^{m-1}} \frac{\partial}{\partial \rho_m} \rho_m^{m-1} \frac{\partial}{\partial \rho_m} - \frac{\hat{\lambda}^2_{(m)}}{\rho_m^2} \qquad \text{(D.9)}$$

The dimensionless $\hat{\lambda}^2_{(m)}$ is related to the usual hyperangular momentum operator $\hat{\Lambda}^2_{(m)}$ for a system of particles with m-spatial degrees of freedom by the proportionality constant $\hbar^2$.

Let $F^n_{(m)}$ be the function defined by

$$F^n_{(m)}(\mathbf{y}) = \frac{h^n_{(m)}(\mathbf{x})}{\rho_m^n} \qquad \text{(D.10)}$$

where

$$\mathbf{y} = (y_1, y_2, ..., y_{m-1}) \qquad \text{(D.11)}$$

and

$$y_i = x_i/\rho_m \quad (i = 1, 2, ..., m) \qquad \text{(D.12)}$$

In view of (D.6)

$$\sum_{i=1}^{m} y_i^2 = 1 \qquad \text{(D.13)}$$

and therefore only $m - 1$ of the m dimensionless variables y_i are independent. On the rhs of (D.11) we chose them arbitrarily to be the first $m - 1$ of these quantities, but any set of $m - 1$ of them could have been selected. It can easily be shown[24] that the $F^n_{(m)}$ satisfy the partial differential equation

$$\hat{\lambda}^2_{(m)} F^n_{(m)}(\mathbf{y}) = n(n + m - 2) F^n_{(m)}(\mathbf{y}) \qquad \text{(D.14)}$$

They are eigenfunctions of $\hat{\lambda}^2_{(m)}$ with eigenvalue $n(n + m - 2)$. These functions are called hyperspherical harmonics.

D.3. Generalized Hyperspherical Coordinates. Let $\alpha \equiv (\alpha_1, \alpha_2, ..., \alpha_{m-1})$ be a set of $m - 1$ angles and $g_i(\alpha)$ ($i = 1, 2, ..., m$) be a set of real functions of these angles subject to the constraint

$$\sum_{i=1}^{m} g_i^2(\alpha) = 1 \qquad \text{(D.15)}$$

In addition, let the hyperradius ρ_m and α be related to $\mathbf{x}$ by

$$x_i = \rho_m g_i(\alpha) \quad i = 1, 2, ..., m \qquad \text{(D.16)}$$

The angles α are labeled hyperangles, and the m variables ρ_m and α are called a set of generalized hyperspherical coordinates associated with $\mathbf{x}$. As a result of (D.12) and (D.16), we have

$$y_i = g_i(\alpha) \quad (i = 1, 2, ..., m) \qquad \text{(D.17)}$$

which permits us to change from the independent variables y given by (D.11) to the hyperangles α. Similarly, upon the $\mathbf{x}$ to the ρ_m and y variable transformation, the $\hat{\lambda}^2_{(m)}$ operator defined by (D.7) and (D.8) is seen to be completely independent of ρ_m. As a result, (D.14) can be rewritten (changing from $\hat{\lambda}^2_{(m)}$ to $\hat{\Lambda}^2_{(m)} = \hbar^2 \hat{\lambda}^2_{(m)}$) as

$$\hat{\Lambda}^2_{(m)} F^n_{(m)}(\alpha) = n(n + m - 2)\hbar^2 F^n_{(m)}(\alpha) \qquad \text{(D.18)}$$

and the hyperspherical harmonics $F^n_{(m)}(\alpha)$ are functions of the hyperangles only. The important property they satisfy is that they can be generated from hyperspherical polynomials by multiplication by $(\rho_m)^{-n}$. In the present paper involving tetra-atomic systems we consider the particular case $m = 6$ only.

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