# Hyperspherical Harmonics for Tetraatomic Systems. 2. The Weak Interaction Region†

**Aron Kuppermann***

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

*Received: March 13, 2004; In Final Form: May 12, 2004*

Hyperspherical harmonics as functions of hyperspherical coordinates appropriate for describing the weak interaction region of nuclear configuration space of tetraatomic systems are derived. They constitute an efficient basis set for calculating the corresponding local hyperspherical surface functions that avoid overcompleteness problems. Together with the hyperspherical harmonics for the strong interaction region of that space obtained previously, they should permit efficient benchmark-quality calculations of state-to-state differential and integral cross sections for those systems.

## 1. Introduction

We have been developing a method for performing accurate calculations of state-to-state cross sections of tetraatomic chemical reactions by solving the time-independent Schrödinger equation using hyperspherical coordinates. Progress in the calculation of reaction cross sections using time-independent as well as time-dependent methods has been given in a recent review,[1] where a large number of references can be found. In the approach considered in the present paper, nuclear configuration space is divided into two regions: (a) a strong interaction region, in which the system's four atoms are close to each other and in which bonds are broken and made and (b) a weak interaction region, comprising sub-regions in which the system has separated into pairs of molecules, either two diatoms or an atom and a triatom, which interact weakly, and in which the breaking and making of bonds does not take place. In the strong interaction region, row-orthonormal hyperspherical coordinates, consisting of a hyperadius and eight hyperangles, are used.[2,3] These coordinates treat "democratically" all four atoms and describe the system equivalently, regardless of which molecular pairs emerge from that region. In the weak interaction region, Delves hyperspherical coordinates, still comprising a hyperadius and eight hyperangles, are used.[2,4] The hyperangles include appropriately chosen geometrical angles between Jacobi vectors. These coordinates are not "democratic", and different ones are appropriate for and used in different sub-regions, in which different pairs of molecules have become separated. In both the strong and weak interaction regions, local hyperspherical surface functions (LHSF) are defined to be eigenfunctions of the system's Hamiltonian at a frozen hyperradius and of a set of other operators that commute with it. The overall scattering calculation methodology consists of expanding the scattering wave function in those local hyperspherical surface functions and propagating the resulting coupled ordinary differential equations in the hyperadius $\rho$ from very small values of this variable, at which the strong repulsive forces between the atoms cause the wave function to be negligible, to large values, at which the system has separated into noninteracting pairs of molecules.[4,5] This approach or related ones have previously been used for triatomic systems.[6−18]

The calculation of the LHSF can be performed by expanding them in hyperspherical harmonics, which are eigenfunctions of the system's grand-canonical angular momentum operator[3] and of other appropriate operators.[5,19] These harmonics behave regularly at the angular poles of the kinetic energy operator. They have been determined analytically for tetraatomic systems for the strong interaction region[5,19] and form a complete set of basis functions for this region that span "democratically" the entire range of all eight hyperangles. Since a single set of such functions is used, this avoids supercompleteness problems, which result and must be overcome when a union of several overlapping complete sets of basis functions (which are therefore not linearly independent of one another) are used.[20−22]

It is possible to utilize these hyperspherical coordinates and harmonics in the weak interaction region also. Such use would be, however, prohibitively inefficient, since the energetically accessible regions of configuration space constitute a small fraction of that space in the weak interaction region. As the row-orthonormal coordinate hyperspherical harmonics span rather uniformly that entire space, employing them for expanding the highly localized weak interaction region LHSF would require an inordinately large number of basis functions to achieve convergence, making this approach inadequate. An alternative is to use, for each sub-region of the weak interaction region, a different set of Delves hyperspherical coordinates, better suited for describing the geometry of the pair of weakly interacting molecules for that sub-region. This should lead to rapidly converging expansions when appropriate basis set contractions are also introduced. The resulting weak interaction LHSF associated with different sub-regions have a negligible overlap, again avoiding overcompleteness problems.

In the present paper we derive analytical expressions for the hyperspherical harmonics in the weak interaction sub-regions of configuration space, desirable for expanding the corresponding LHSF. Together with the strong interaction region surface functions they are appropriate for reactive scattering calculations of tetraatomic systems. In Section 2 we define the different frames and weak interaction region hyperspherical coordinates used, derive the change of the latter under inversion of the system through its center of mass, and obtain the volume element in these coordinates. In Section 3 we give expressions for the kinetic energy and grand-canonical angular momentum

† Part of the "Gert D. Billing Memorial Issue".

* E-mail address: aron@caltech.edu.

10.1021/jp048874l CCC: $27.50 
Published on Web 09/09/2004

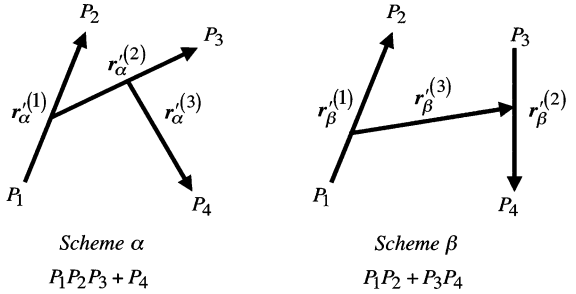


**Figure 1.** Two clustering schemes for a tetraatomic system corresponding to two weak interaction sub-regions of configuration space.

operators. In Section 4 we define and derive explicit analytical expressions for the corresponding hyperspherical harmonics, and in Section 5 we describe the relation between the weak and strong interaction region hyperspherical coordinates. Finally, in Section 6 we give a summary and conclusions.

## 2. Frames and Coordinates

**2.1. Definitions.** Let us consider a tetraatomic system whose nuclei and corresponding masses are $P_i$ and $M_i$ ($i = 1, 2, 3, 4$). Let $\lambda$ denote a clustering scheme of these nuclei that defines the associated Jacobi vectors $\boldsymbol{r}'^{(j)}_\lambda$ ($j = 1, 2, 3$).[2−4] Two such schemes, denoted $\lambda = \alpha$ and $\lambda = \beta$, are depicted in Figure 1. The first is appropriate for describing the atom−triatom weak interaction sub-region of configuration space where the triatomic nuclear system $P_1P_2P_3$ is far from the fourth nucleus $P_4$, whereas the second is well-suited for the diatom−diatom weak interaction sub-region $P_1P_2 + P_3P_4$. Denoting by $\boldsymbol{r}^{(i)}_\lambda$ the corresponding mass-scaled vectors, we define the associated space-fixed Jacobi matrix by

$$\boldsymbol{\rho}^{\mathrm{sf}}_\lambda \equiv (\boldsymbol{r}^{(1)}_\lambda\, \boldsymbol{r}^{(2)}_\lambda\, \boldsymbol{r}^{(3)}_\lambda) = \begin{pmatrix} x^{(1)}_\lambda & x^{(2)}_\lambda & x^{(3)}_\lambda \\ y^{(1)}_\lambda & y^{(2)}_\lambda & y^{(2)}_\lambda \\ z^{(1)}_\lambda & z^{(2)}_\lambda & z^{(3)}_\lambda \end{pmatrix} \tag{2.1}$$

where $x^{(j)}_\lambda$, $y^{(j)}_\lambda$, and $z^{(j)}_\lambda$ are the components of the $\boldsymbol{r}^{(j)}_\lambda$ in either of the two space-fixed Cartesian frames $Ox^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ or $Gx^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ (the latter denoted simply by sf) where $O$ is the space-fixed origin and $G$ is the center of mass of the system. The axes of $Gx^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ are parallel to and have the same senses as the corresponding $Ox^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ axes. Let the polar coordinates of the $\boldsymbol{r}^{(j)}_\lambda$ in either of these frames be $(r^{(j)}_\lambda,\theta^{(j)}_\lambda,\phi^{(j)}_\lambda)$. In terms of these coordinates, the Jacobi matrix $\rho^{\mathrm{sf}}_\lambda$ can be rewritten as

$$\boldsymbol{\rho}^{\mathrm{sf}}_\lambda = \begin{pmatrix} \sin\theta^{(1)}_\lambda \cos\phi^{(1)}_\lambda & \sin\theta^{(2)}_\lambda \cos\phi^{(2)}_\lambda & \sin\theta^{(3)}_\lambda \cos\phi^{(3)}_\lambda \\ \sin\theta^{(1)}_\lambda \sin\phi^{(1)}_\lambda & \sin\theta^{(2)}_\lambda \sin\phi^{(2)}_\lambda & \sin\theta^{(3)}_\lambda \sin\phi^{(3)}_\lambda \\ \cos\theta^{(1)}_\lambda & \cos\theta^{(2)}_\lambda & \cos\theta^{(3)}_\lambda \end{pmatrix} \boldsymbol{r}_\lambda \tag{2.2}$$

where $\boldsymbol{r}_\lambda$ is the diagonal matrix whose diagonal elements are $r^{(1)}_\lambda$, $r^{(2)}_\lambda$, and $r^{(3)}_\lambda$, respectively.

For the purposes of the present paper, it is convenient to define three $\lambda$-arrangement-channel body-fixed frames, labeled $G\, x^{\mathrm{bf}i}_\lambda\, y^{\mathrm{bf}i}_\lambda\, z^{\mathrm{bf}i}_\lambda$ ($i = 1, 2, 3$), or simply bf$i$, by the Euler angle rotations defined in eq 2.3. The angles appearing in this diagram are a subset of the polar angles of the $\boldsymbol{r}^{(j)}_\lambda$ given in Table 1. All of the polar angles in the bf$i$ frames can be expressed in terms

**TABLE 1: Relation between the Cartesian Frames**

| | polar angles | | |
|---|---|---|---|
| frame | $\boldsymbol{r}^{(1)}_\lambda$ | $\boldsymbol{r}^{(2)}_\lambda$ | $\boldsymbol{r}^{(3)}_\lambda$ |
| $Gx^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}}$ | $\theta^{(1)}_\lambda,\phi^{(1)}_\lambda$ | $\theta^{(2)}_\lambda,\phi^{(2)}_\lambda$ | $\theta^{(3)}_\lambda,\phi^{(3)}_\lambda$ |
| $Gx^{\mathrm{bf1}}_\lambda y^{\mathrm{bf1}}z^{\mathrm{bf1}}$ | $\gamma^{(1,3)}_\lambda,\psi^{(1,3)}_\lambda$ | $\gamma^{(2,3)}_\lambda,\psi^{(2,3)}_\lambda$ | 0,0 |
| $Gx^{\mathrm{bf2}}_\lambda y_\lambda{}^{\mathrm{bf2}}z_\lambda{}^{\mathrm{bf2}}$ | $\gamma^{(1,3)}_\lambda,\xi^{(1,3)}_\lambda$ | $\gamma^{(2,3)}_\lambda$,0 | 0,0 |
| $Gx^{\mathrm{bf3}}_\lambda y_\lambda{}^{\mathrm{bf3}}z_\lambda{}^{\mathrm{bf3}}$ | $\gamma^{(1,2)}_\lambda,\psi^{(1,2)}_\lambda$ | 0,0 | $\gamma^{(2,3)}_\lambda$, $\pi$ |

of the $\theta^{(j)}_\lambda$, $\phi^{(j)}_\lambda$ ($j = 1, 2, 3$) with the help of the rotations defined by eq 2.3. For example, the four angles $\gamma^{(j,3)}_\lambda,\psi^{(j,3)}_\lambda$ ($j =$

$$\begin{array}{ccccc} Gx^{\mathrm{sf}}y^{\mathrm{sf}}z^{\mathrm{sf}} & \xrightarrow{\left(\phi^{(3)}_\lambda,\theta^{(3)}_\lambda,0\right)} & Gx^{\mathrm{bf1}}_\lambda y^{\mathrm{bf1}}_\lambda z^{\mathrm{bf1}}_\lambda & \xrightarrow{\left(0,0,\psi^{(2,3)}_\lambda\right)} & Gx^{\mathrm{bf2}}_\lambda y^{\mathrm{bf2}}_\lambda z^{\mathrm{bf2}}_\lambda \\ & & \downarrow \left(\psi^{(2,3)}_\lambda,\gamma^{(2,3)}_\lambda,0\right) & & \swarrow \left(0,\gamma^{(2,3)}_\lambda,0\right) \\ & & Gx^{\mathrm{bf3}}_\lambda y^{\mathrm{bf3}}_\lambda z^{\mathrm{bf3}}_\lambda & & \end{array} \tag{2.3}$$

1, 2) are derived from the transformation of Cartesian coordinates (expressed in terms of polar coordinates) resulting from the sf→bf1 axes rotation:[23]

$$\begin{pmatrix} r^{(j)}_\lambda \sin\gamma^{(j,3)}_\lambda \cos\psi^{(j,3)}_\lambda \\ r^{(j)}_\lambda \sin\gamma^{(j,3)}_\lambda \sin\psi^{(j,3)}_\lambda \\ r^{(j)}_\lambda \cos\gamma^{(j,3)}_\lambda \end{pmatrix} = \mathbf{R}\,(\phi^{(3)}_\lambda,\theta^{(3)}_\lambda,0) \begin{pmatrix} r^{(j)}_\lambda \sin\theta^{(j)}_\lambda \cos\phi^{(j)}_\lambda \\ r^{(j)}_\lambda \sin\theta^{(j)}_\lambda \sin\phi^{(j)}_\lambda \\ r^{(j)}_\lambda \cos\theta^{(j)}_\lambda \end{pmatrix} \tag{2.4}$$

In this expression, $\mathbf{R}(a,b,c)$ is the rotation matrix associated with Euler angles $a,b,c$.

It should be noted that that rotation places $Gz^{\mathrm{bf1}}_\lambda$ along the $\boldsymbol{r}^{(3)}_\lambda$ vector, and therefore $\gamma^{(1,3)}_\lambda$ and $\gamma^{(2,3)}_\lambda$ are respectively the angle between $\boldsymbol{r}^{(1)}_\lambda$ or $\boldsymbol{r}^{(2)}_\lambda$ and $\boldsymbol{r}^{(3)}_\lambda$, in the 0 to $\pi$ range. Similarly, the rotation of bf1 to bf3 by Euler angles ($\psi^{(2,3)}_\lambda$, $\gamma^{(2,3)}_\lambda$, 0) places the $Gz^{\mathrm{bf3}}_\lambda$ axis along $\boldsymbol{r}^{(2)}_\lambda$ and therefore $\gamma^{(1,2)}_\lambda$ is the angle between $\boldsymbol{r}^{(1)}_\lambda$ and $\boldsymbol{r}^{(2)}_\lambda$, also in that range. The polar angles $p^{(3)}_\lambda$ and $q^{(3)}_\lambda$ of $\boldsymbol{r}^{(3)}_\lambda$ in bf3 are easily derived from

$$\begin{pmatrix} \sin p^{(3)}_\lambda \cos q^{(3)}_\lambda \\ \sin p^{(3)}_\lambda \cos q^{(3)}_\lambda \\ \cos p^{(3)}_\lambda \end{pmatrix} = \mathbf{R}\,(\psi^{(2,3)}_\lambda, \gamma^{(2,3)}_\lambda, 0) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{2.5}$$

which results in

$$p^{(3)}_\lambda = \gamma^{(2,3)}_\lambda \qquad q^{(3)}_\lambda = \pi \tag{2.6}$$

as given in Table 1.

It should also be noted that the angles $\phi^{(3)}_\lambda$, $\theta^{(3)}_\lambda$, $\psi^{(2,3)}_\lambda$ of eq 2.3 and Table 1 are Euler angles that rotate sf to bf2. In particular, $\psi^{(2,3)}_\lambda$ is the angle between the $(\boldsymbol{r}^{(3)}_\lambda,Gz^{\mathrm{sf}})$ and $(\boldsymbol{r}^{(3)}_\lambda,\boldsymbol{r}^{2}_\lambda)$ half-planes, having $\boldsymbol{r}^{(3)}_\lambda$ as a common edge, with the first containing the positive $z^{\mathrm{sf}}$ half of the $Gz^{\mathrm{sf}}$ axis. This angle, in the 0 to $2\pi$ range, is measured counter clockwise, as viewed from the tip of $\boldsymbol{r}^{(3)}_\lambda$, from the first to the second of these half-planes, and therefore describes the tumbling of the system around $\boldsymbol{r}^{(3)}_\lambda$. As a result, these Euler angles are external coordinates that orient bf2 with respect to sf. The potential

energy function V, which is a function of internal coordinates only, does not depend on those angles. Such internal coordinates could be chosen to be the six internuclear distances between the four nuclei. However, to obtain simple expressions for the hyperspherical harmonics appropriate for the weak interaction region (as shown in section 4), it is better to use instead the lengths $r_\lambda^{(1)}$, $r_\lambda^{(2)}$, and $r_\lambda^{(3)}$ of the three mass-scaled Jacobi vectors plus the three internal angles $\gamma_\lambda^{(1,2)}$, $\psi_\lambda^{(1,2)}$, and $\gamma_\lambda^{(2,3)}$, in terms of which of those internuclear distances can be expressed. The choice of these angles is justified not only by the simplicity just mentioned but also by how the potential function $V$ depends on them in the weak interaction sub-regions of configuration space. Indeed, let us consider first the sub-regions in which an atom is far away from a triatom. Let $\boldsymbol{r}_\lambda^{(1)}$ and $\boldsymbol{r}_\lambda^{(2)}$ be the mass-scaled Jacobi vectors of the triatom, and $\boldsymbol{r}_\lambda^{(3)}$ the mass-scaled position vector of the atom with respect to the center of mass of the triatom, as depicted in scheme α of Figure 1 for the non-mass-scaled versions of these vectors. Then, as $r_\lambda^{(3)} \sim \infty$, $V$ becomes independent of both $\psi_\lambda^{(1,2)}$ (the tumbling angle of the triatom around $\boldsymbol{r}_\lambda^{(2)}$) and $\gamma_\lambda^{(2,3)}$ while still depending strongly on $\gamma_\lambda^{(1,2)}$. If we consider next the asymptotic sub-regions in which two diatoms are far from each other, we use the Jacobi vectors depicted in scheme $\beta$ of Figure 1, and notice that as $r_\lambda^{(3)} \sim \infty$, $V$ becomes independent not only of $\psi_\lambda^{(1,2)}$ and $\gamma_\lambda^{(2,3)}$ but also of $\gamma_\lambda^{(1,2)}$. In either case, the asymptotic independence of $V$ on $\psi_\lambda^{(1,2)}$ and $\gamma_\lambda^{(2,3)}$ is a very useful property of this function, which justifies the choice of these two angles. The selection of $\gamma_\lambda^{(1,2)}$ as the third angle is justified by its importance in describing the potential function of isolated triatoms.

It is also desirable to replace the three lengths $r_\lambda^{(1)}$, $r_\lambda^{(2)}$, and $r_\lambda^{(3)}$ by a single length, the hyperradius $\rho$, and two hyperangles $\eta_\lambda^{(1)}$ and $\eta_\lambda^{(1)}$, defined by[2,4]

$$r_\lambda^{(1)} = \rho \sin \eta_\lambda^{(2)} \sin \eta_\lambda^{(1)} \tag{2.7}$$

$$r_\lambda^{(2)} = \rho \sin \eta_\lambda^{(2)} \cos \eta_\lambda^{(1)} \tag{2.8}$$

and

$$r_\lambda^{(3)} = \rho \cos \eta_\lambda^{(2)} \tag{2.9}$$

The hyperradius $\rho$, together with the set of eight angles $\boldsymbol{\Phi}_\lambda$ defined by

$$\boldsymbol{\Phi}_\lambda \equiv \{\eta_\lambda^{(1)}, \eta_\lambda^{(2)}, \theta_\lambda^{(3)}, \phi_\lambda^{(3)}, \psi_\lambda^{(2,3)}, \gamma_\lambda^{(2,3)}, \psi_\lambda^{(1,2)}, \gamma_\lambda^{(1,2)}\} \tag{2.10}$$

will hereafter be called the "$\lambda$ weak interaction region hyperspherical coordinates", or $\lambda$ hyperspherical coordinates simply, and we will express the corresponding hyperspherical harmonics in terms of $\boldsymbol{\Phi}_\lambda$. These coordinates are very appropriate for describing the geometry of the pairs of molecules in this $\lambda$ region. It should be noticed that $(\theta_\lambda^{(3)}, \phi_\lambda^{(3)})$, $(\gamma_\lambda^{(2,3)}, \psi_\lambda^{(2,3)})$, and $(\gamma_\lambda^{(1,2)}, \psi_\lambda^{(1,2)})$ are the polar coordinates of $\boldsymbol{r}_\lambda^{(1)}$, $\boldsymbol{r}_\lambda^{(2)}$, and $\boldsymbol{r}_\lambda^{(3)}$ in the sf, bf1, and bf3 frames, respectively.

With the help of eqs 2.3, 2.7 through 2.9, and Table 1, we can express the Jacobi matrix $\boldsymbol{\rho}_\lambda^{\mathrm{sf}}$ defined by eq 2.1 in terms of the body-fixed Jacobi matrices $\rho_\lambda^{\mathrm{bfi}}$ ($i = 1, 2, 3$) by

$$\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = \tilde{\mathbf{R}}(\phi_\lambda^{(3)}, \theta_\lambda^{(3)}, 0)\, \boldsymbol{\rho}_\lambda^{\mathrm{bf1}} \tag{2.11}$$

$$\boldsymbol{\rho}_\lambda^{\mathrm{bf1}} = \rho \begin{pmatrix} \sin\gamma_\lambda^{(1,3)} \cos\psi_\lambda^{(1,3)} & \sin\gamma_\lambda^{(2,3)} \cos\psi_\lambda^{(2,3)} & 0 \\ \sin\gamma_\lambda^{(1,3)} \sin\psi_\lambda^{(1,3)} & \sin\gamma_\lambda^{(2,3)} \sin\psi_\lambda^{(2,3)} & 0 \\ \cos\gamma_\lambda^{(1,3)} & \cos\gamma_\lambda^{(2,3)} & 1 \end{pmatrix} \boldsymbol{n}(\eta_\lambda^{(1)}, \eta_\lambda^{(2)}) \tag{2.12}$$

$$\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = \tilde{\mathbf{R}}(\phi_\lambda^{(3)}, \theta_\lambda^{(3)}, \psi_\lambda^{(2,3)})\, \boldsymbol{\rho}_\lambda^{\mathrm{bf2}} \tag{2.13}$$

$$\boldsymbol{\rho}_\lambda^{\mathrm{bf2}} = \rho \begin{pmatrix} \sin\gamma_\lambda^{(1,3)} \cos\xi_\lambda^{(1,3)} & \sin\gamma_\lambda^{(2,3)} & 0 \\ \sin\gamma_\lambda^{(1,3)} \sin\xi_\lambda^{(1,3)} & 0 & 0 \\ \cos\gamma_\lambda^{(1,3)} & \cos\gamma_\lambda^{(2,3)} & 1 \end{pmatrix} \boldsymbol{n}(\eta_\lambda^{(1)}, \eta_\lambda^{(2)}) \tag{2.14}$$

$$\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = \tilde{\mathbf{R}}(\phi_\lambda^{(3)}, \theta_\lambda^{(3)}, 0)\, \tilde{\mathbf{R}}(\psi_\lambda^{(2,3)}, \gamma_\lambda^{(2,3)}, 0)\, \boldsymbol{\rho}_\lambda^{\mathrm{bf3}} \tag{2.15}$$

and

$$\boldsymbol{\rho}_\lambda^{\mathrm{bf3}} = \rho \begin{pmatrix} \sin\gamma_\lambda^{(1,2)} \cos\psi_\lambda^{(1,2)} & 0 & 0 \\ \sin\gamma_\lambda^{(1,2)} \sin\psi_\lambda^{(1,2)} & 0 & -\sin\gamma_\lambda^{(2,3)} \\ \cos\gamma_\lambda^{(1,2)} & 1 & \cos\gamma_\lambda^{(2,3)} \end{pmatrix} \boldsymbol{n}(\eta_\lambda^{(1)}, \eta_\lambda^{(2)}) \tag{2.16}$$

where

$$\boldsymbol{n}(\eta_\lambda^{(1)}, \eta_\lambda^{(2)}) = \begin{pmatrix} \sin\eta_\lambda^{(2)} \sin\eta_\lambda^{(1)} & 0 & 0 \\ 0 & \sin\eta_\lambda^{(2)} \cos\eta_\lambda^{(1)} & 0 \\ 0 & 0 & \cos\eta_\lambda^{(2)} \end{pmatrix} \tag{2.17}$$

Equations 2.11 through 2.17 are useful not only to interrelate the variables that appear in them but also to determine how they transform under different operations. One such example is given in section 2.2 below.

**2.2. Effect of the Inversion Operator on the $\lambda$ Hyperspherical Coordinates.** Let $\hat{I}$ be the operator that inverts the system through its center of mass. Its effect on the $\boldsymbol{r}_\lambda^{(j)}$ ($j = 1$, 2, 3) is to transform them to $-\boldsymbol{r}_\lambda^{(j)}$, and therefore its effect on the $\boldsymbol{\rho}_\lambda^{\mathrm{sf}}$ of eq 2.1 is

$$\hat{I}\boldsymbol{\rho}_\lambda^{\mathrm{sf}} = -\boldsymbol{\rho}_\lambda^{\mathrm{sf}} \tag{2.18}$$

With the help of this expression we can use eqs 2.2 and 2.11 through 2.17 in a straightforward manner to get the effect of $\hat{I}$ on all the coordinates defined so far. The result is

$$\hat{I}(r_\lambda^{(1)}, r_\lambda^{(2)}, r_\lambda^{(3)}, \rho, \eta_\lambda^{(1)}, \eta_\lambda^{(2)}) = (r_\lambda^{(1)}, r_\lambda^{(2)}, r_\lambda^{(3)}, \rho, \eta_\lambda^{(1)}, \eta_\lambda^{(2)}) \tag{2.19}$$

$$\hat{I}(\theta_\lambda^{(1)}, \theta_\lambda^{(2)}, \theta_\lambda^{(3)}, \gamma_\lambda^{(1,2)}, \gamma_\lambda^{(1,3)}, \gamma_\lambda^{(2,3)}) = (\theta_\lambda^{(1)}, \theta_\lambda^{(2)}, \theta_\lambda^{(3)}, \gamma_\lambda^{(1,2)}, \gamma_\lambda^{(1,3)}, \gamma_\lambda^{(2,3)}) \tag{2.20}$$

$$\hat{I}(\phi_\lambda^{(1)}, \phi_\lambda^{(2)}, \phi_\lambda^{(3)}) = ((\pi + \phi_\lambda^{(1)}) \bmod 2\pi, (\pi + \phi_\lambda^{(2)}) \bmod 2\pi, \pi + \phi_\lambda^{(3)} \bmod 2\pi) \tag{2.21}$$

$$\hat{I}(\psi_\lambda^{(1,2)}, \psi_\lambda^{(1,3)}, \psi_\lambda^{(2,3)}) = (2\pi - \psi_\lambda^{(1,2)}, (\pi - \psi_\lambda^{(1,3)}) \bmod 2\pi, (\pi - \psi_\lambda^{(2,3)}) \bmod 2\pi) \tag{2.22}$$

and

$$\hat{I}\xi_\lambda^{(1,3)} = 2\pi - \xi_\lambda^{(1,3)} \tag{2.23}$$

The effect of $\hat{I}$ on the hyperspherical coordinates for the weak interaction region is therefore:

$$\hat{I}(\rho,\mathbf{\Phi}_\lambda) = (\rho,\eta_\lambda^{(1)},\eta_\lambda^{(2)},\pi - \theta_\lambda^{(3)},(\pi + \phi_\lambda^{(3)})\text{mod } 2\pi, (\pi - \psi_\lambda^{(2,3)})\text{mod } 2\pi, \gamma_\lambda^{(1,2)},2\pi - \psi_\lambda^{(1,2)}, \gamma_\lambda^{(2,3)}) \quad (2.24)$$

**2.3. Volume Element.** The volume element d$V$ associated with the coordinates $\rho,\mathbf{\Phi}_\lambda$ can be derived by starting with the polar coordinates $(r_\lambda^{(j)},\theta_\lambda^{(j)},\phi_\lambda^{(j)})$ $(j = 1, 2, 3)$ in terms of which it is given by

$$dV = r_\lambda^{(1)^2}\, dr_\lambda^{(1)} r_\lambda^{(2)^2}\, dr_\lambda^{(2)} r_\lambda^{(3)^2}\, dr_\lambda^{(3)} \sin\theta_\lambda^{(1)}\, d\theta_\lambda^{(1)}\, d\phi_\lambda^{(1)} \times \sin\theta_\lambda^{(2)}\, d\theta_\lambda^{(2)}\, d\phi_\lambda^{(2)} \sin\theta_\lambda^{(3)}\, d\theta_\lambda^{(3)}\, d\phi_\lambda^{(3)} \quad (2.25)$$

We first introduce the transformation defined by eqs 2.7 through 2.9 which results in

$$dr_\lambda^{(1)}\, dr_\lambda^{(2)}\, dr_\lambda^{(3)} = \rho^2 \sin\eta_\lambda^{(2)}\, d\rho\, d\eta_\lambda^{(2)} \eta_\lambda^{(1)} \quad (2.26)$$

The transformation from $\theta_\lambda^{(2)},\phi_\lambda^{(2)}$ to $\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}$ is achieved, as indicated in eq 2.3 and Table 1, through the rotation of sf to bf1 by Euler angles $(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0)$. Since $\theta_\lambda^{(2)},\phi_\lambda^{(2)}$ are independent of $\theta_\lambda^{(3)},\phi_\lambda^{(3)}$, this is a rigid rotation that does not change the form of the corresponding angular volume element:

$$\sin\theta_\lambda^{(2)}\, d\theta_\lambda^{(2)}\, d\phi_\lambda^{(2)} = \sin\gamma_\lambda^{(2,3)}\, d\gamma_\lambda^{(2,3)}\, d\psi_\lambda^{(2,3)} \quad (2.27)$$

Similarly,

$$\sin\theta_\lambda^{(1)}\, d\theta_\lambda^{(1)}\, d\phi_\lambda^{(1)} = \sin\gamma_\lambda^{(1,3)}\, d\gamma_\lambda^{(1,3)}\, d\psi_\lambda^{(1,3)} \quad (2.28)$$

Finally, the $\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)}$ to $\gamma_\lambda^{(1,2)},\gamma_\lambda^{(1,2)}$ transformation is achieved by rotating bf1 to bf3 by Euler angles $(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)$. Since $\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)}$ are independent of those angles, the corresponding volume element is also unchanged:

$$\sin\gamma_\lambda^{(1,3)}\, d\gamma_\lambda^{(1,3)}\, d\psi_\lambda^{(1,3)} = \sin\gamma_\lambda^{(1,2)}\, d\gamma_\lambda^{(1,2)}\, d\psi_\lambda^{(1,2)} \quad (2.29)$$

Substitution of eqs 2.7 through 2.9 as well as eqs 2.26 through 2.29 into eq 2.25 gives the desired result:

$$dV = \rho^8\, d\rho \sin^2\eta_\lambda^{(1)}\cos^2\eta_\lambda^{(1)}\, d\eta_\lambda^{(1)} \sin^5\eta_\lambda^{(2)}\cos^2\eta_\lambda^{(2)}\, d\eta_\lambda^{(2)} \times \sin\theta_\lambda^{(3)}\, d\theta_\lambda^{(3)}\, d\phi_\lambda^{(3)} \sin\gamma_\lambda^{(2,3)}\, d\gamma_\lambda^{(2,3)}\, d\psi_\lambda^{(2,3)} \times \sin\gamma_\lambda^{(1,2)}\, d\gamma_\lambda^{(1,2)}\, d\psi_\lambda^{(1,2)} \quad (2.30)$$

As a result, the appropriate volume elements for the $\eta_\lambda^{(1)}$ and $\eta_\lambda^{(2)}$ hyperangles are

$$dV_{\eta_\lambda^{(1)}} = \sin^2\eta_\lambda^{(1)} \cos^2\eta_\lambda^{(1)}\, d\eta_\lambda^{(1)} \quad (2.31)$$

and

$$dV_{\eta_\lambda^{(2)}} = \sin^5\eta_\lambda^{(2)} \cos^2\eta_\lambda^{(2)}\, d\eta_\lambda^{(2)} \quad (2.32)$$

## 3. Kinetic Energy and Grand Canonical Angular Momentum Operators

Let us now obtain the kinetic energy operator $\hat{T}$ in terms of the weak interaction region hyperspherical coordinates $\rho,\mathbf{\Phi}_\lambda$. We start with the expression for this operator in the mass-scaled Jacobi vectors $\boldsymbol{r}_\lambda^{(j)}$ $(j = 1, 2, 3)$,

$$\hat{T} = \left(-\frac{\hbar^2}{2\mu}\right)\sum_{j=1}^{3}\nabla^2_{\boldsymbol{r}_\lambda^{(j)}} = \left(-\frac{\hbar^2}{2\mu}\right)\sum_{j=1}^{3}\left[\frac{\partial^2}{\partial r_\lambda^{(j)^2}} + \frac{2}{r_\lambda^{(j)}}\frac{\partial}{\partial r_\lambda^{(j)}} + \frac{\hat{j}_\lambda^{(j)^2}}{2\mu r_\lambda^{(j)^2}}\right] \quad (3.1)$$

where $\mu$ is the reduced mass of the tetraatomic system given by

$$\mu = [M_1M_2M_3M_4/(M_1 + M_2 + M_3 + M_4)]^{1/3} \quad (3.2)$$

and $\hat{j}_\lambda^{(j)^2}$ is the square of the angular momentum operator $\hat{\boldsymbol{j}}_\lambda^{(j)}$ of vector $\boldsymbol{r}_\lambda^{(j)}$ in sf.

The change from $r_\lambda^{(1)},r_\lambda^{(2)},r_\lambda^{(3)}$ to $\rho,\eta_\lambda^{(1)},\eta_\lambda^{(2)}$ is straightforward, because of the orthogonal nature of the transformation defined by eqs 2.7 through 2.9 and results in[4]

$$\hat{T} = -\frac{\hbar^2}{2\mu\rho^8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} + \frac{\hat{\Lambda}^2}{2\mu\rho^2} \quad (3.3)$$

where $\hat{\Lambda}^2$ is the grand canonical angular momentum operator given by

$$\hat{\Lambda}^2 = \frac{\hat{\mathscr{J}}_\lambda^{(1)^2}}{\sin^2\eta_\lambda^{(2)}} + \hat{\mathscr{J}}_\lambda^{(2)^2} + \frac{\hat{j}_\lambda^{(1)^2}}{\sin^2\eta_\lambda^{(1)}\sin^2\eta_\lambda^{(2)}} + \frac{\hat{j}_\lambda^{(2)^2}}{\cos^2\eta_\lambda^{(1)}\sin^2\eta_\lambda^{(2)}} + \frac{\hat{j}_\lambda^{(3)^2}}{\cos^2\eta_\lambda^{(2)}} \quad (3.4)$$

and $\hat{\mathscr{J}}_\lambda^{(1)^2}$ and $\hat{\mathscr{J}}_\lambda^{(2)^2}$ are the hyperangular momentum operators associated with the hyperangles $\eta_\lambda^{(1)}$ and $\eta_\lambda^{(2)}$ and are defined by

$$\hat{\mathscr{J}}_\lambda^{(1)^2}(\eta_\lambda^{(1)}) = -4\hbar^2\frac{1}{(\sin 2\eta_\lambda^{(1)})^2}\frac{\partial}{\partial(2\eta_\lambda^{(1)})}(\sin 2\eta_\lambda^{(1)})^2\frac{\partial}{\partial(2\eta_\lambda^{(1)})} \quad (3.5)$$

and

$$\hat{\mathscr{J}}_\lambda^{(2)^2}(\eta_\lambda^{(2)}) = -\hbar^2\frac{1}{(\sin\eta_\lambda^{(2)})^5(\cos\eta_\lambda^{(2)})^2}\frac{\partial}{\partial\eta_\lambda^{(2)}}(\sin\eta_\lambda^{(2)})^5(\cos\eta_\lambda^{(2)})^2\frac{\partial}{\partial\eta_\lambda^{(2)}} \quad (3.6)$$

Although the $\hat{j}_\lambda^{(j)^2}$ are space-fixed operators, they can be expressed in terms of the angles in eq 2.10. We will choose $(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)})$,$(\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)})$, and $(\theta_\lambda^{(3)},\phi_\lambda^{(3)})$ to express $\hat{j}_\lambda^{(1)^2}$, $\hat{j}_\lambda^{(2)^2}$, and $\hat{j}_\lambda^{(3)^2}$, respectively. These are the polar angles of the $\boldsymbol{r}_\lambda^{(1)}$, $\boldsymbol{r}_\lambda^{(2)}$, and $\boldsymbol{r}_\lambda^{(3)}$ in bf3, bf1, and sf respectively, as indicated in Table 1. The results are

$$\hat{j}_\lambda^{(1)^2} = -\hbar^2\left(\frac{1}{\sin\gamma_\lambda^{(1,2)}}\frac{\partial}{\partial\gamma_\lambda^{(1,2)}}\sin\gamma_\lambda^{(1,2)}\frac{\partial}{\partial\gamma_\lambda^{(1,2)}} + \frac{1}{\sin^2\gamma_\lambda^{(1,2)}}\frac{\partial^2}{\partial\psi_\lambda^{(1,2)^2}}\right) \quad (3.7)$$

$$\hat{j}_\lambda^{(2)^2} = -\hbar^2\left(\frac{1}{\sin\gamma_\lambda^{(2,3)}}\frac{\partial}{\partial\gamma_\lambda^{(2,3)}}\sin\gamma_\lambda^{(2,3)}\frac{\partial}{\partial\gamma_\lambda^{(2,3)}} + \frac{1}{\sin^2\gamma_\lambda^{(2,3)}}\frac{\partial^2}{\partial\psi_\lambda^{(2,3)^2}}\right) \quad (3.8)$$

and

$$\hat{j}_\lambda^{(3)^2} = -\hbar^2\left(\frac{1}{\sin\theta_\lambda^{(3)}}\frac{\partial}{\partial\theta_\lambda^{(3)}}\sin\theta_\lambda^{(3)}\frac{\partial}{\partial\theta_\lambda^{(3)}} + \frac{1}{\sin^2\theta_\lambda^{(3)}}\frac{\partial^2}{\partial\phi_\lambda^{(3)^2}}\right) \tag{3.9}$$

Equation 3.9 is the standard expression for $\hat{j}_\lambda^{(3)^2}$ in the space-fixed coordinates $\theta_\lambda^{(3)},\phi_\lambda^{(3)}$. Equation 3.8 results from the fact that the space-fixed polar angles $\theta_\lambda^{(2)},\phi_\lambda^{(2)}$ of $\boldsymbol{r}_\lambda^{(2)}$ are independent of the Euler angles $(\phi_\lambda^{(3)},\theta_\lambda^{(3)}, 0)$ which, according to eq 2.3, define the sf→bf1 transformation. As a result, $\hat{j}_\lambda^{(2)^2}$ changes as a scalar operator under a rigid rotation, the only difference being that in its explicit expression, $(\theta_\lambda^{(2)},\phi_\lambda^{(2)})$ are replaced by the polar angles of $\boldsymbol{r}_\lambda^{(2)}$ in bf1, namely $(\gamma_\lambda^{(2,3)}, \psi_\lambda^{(2,3)})$. The same is true for $\hat{j}_\lambda^{(1)^2}$, which can, in analogy to eq 3.8, be expressed in terms of $(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)})$. Finally, the polar angles $(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)})$ of $\boldsymbol{r}_\lambda^{(1)}$ in the bf3 frame are independent of the Euler angles $(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)$ which define the bf1→bf3 transformation, permitting $\hat{j}_\lambda^{(1)^2}$ to be written as in eq 3.7. It should be noticed that the partial derivatives in (3.7) through (3.9) are defined with respect to the set of independent variables $(\theta_\lambda^{(3)},\phi_\lambda^{(3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}, \gamma_\lambda^{(1,2)},\psi_\lambda^{(2,3)})$, i.e., for each partial derivative the remaining variables in this set remain constant.

As a result of eqs 3.3−3.9, we have been able to express the kinetic energy operator $\hat{T}$ and the grand canonical angular momentum operator $\hat{\Lambda}^2$ in terms of the $\lambda$-arrangement-channel hyperspherical coordinates, as desired. It should be noticed that these two operators are independent of $\lambda$ (i.e., are kinematic-rotation-invariant),[2] even though they contain individual terms, such as the $\hat{\mathscr{T}}_\lambda^{(i)^2}$ and $\hat{j}_\lambda^{(j)^2}$, that do depend on the chosen arrangement channel $\lambda$.

## 4. Hyperspherical Harmonics in the Weak Interaction Region

**4.1. Definition of the Hyperspherical Harmonics.** In addition to the operators considered in section 3, let us define the angular momentum operators $\hat{\boldsymbol{j}}_\lambda^{(1,2)}$ and $\hat{\boldsymbol{J}}$ by

$$\hat{\boldsymbol{j}}_\lambda^{(1,2)} = \hat{\boldsymbol{j}}_\lambda^{(1)} + \hat{\boldsymbol{j}}_\lambda^{(2)} \tag{4.1}$$

and

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{j}}_\lambda^{(1)} + \hat{\boldsymbol{j}}_\lambda^{(2)} + \hat{\boldsymbol{j}}_\lambda^{(3)} = \hat{\boldsymbol{j}}_\lambda^{(1,2)} + \hat{\boldsymbol{j}}_\lambda^{(3)} \tag{4.2}$$

where the system's total angular momentum $\hat{\boldsymbol{J}}$ is independent of $\lambda$. In addition, let $\hat{J}_{z^{sf}}$ be the component of $\hat{\boldsymbol{J}}$ along the space-fixed axis $Gz^{sf}$.

We now define the weak interaction sub-region $\lambda$ hyperspherical harmonics $F^{\Pi J n j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)} j_\lambda^{(3)}}_{M_J\,\nu}(\boldsymbol{\Phi}_\lambda)$ as the simultaneous eigenfunctions of the operators $\hat{J}^2,\hat{J}_{z^{sf}},\hat{\Lambda}^2,\hat{j}_\lambda^{(1)^2},\hat{j}_\lambda^{(2)^2},\hat{j}_\lambda^{(1,2)^2},\hat{j}_\lambda^{(3)^2}$, $\hat{O}_{\hat{I}}$ and two operators related to $\hat{\mathscr{T}}_\lambda^{(1)^2}$ and $\hat{\mathscr{T}}_\lambda^{(2)^2}$ (see eqs 4.47 and 4.48), where $\hat{O}_{\hat{I}}$ is the function operator associated with $\hat{I}$. Let us denote by $\boldsymbol{p}_\lambda$ the set of quantum numbers

$$\boldsymbol{p}_\lambda \equiv (\Pi, J, M_J, n, \nu, j_\lambda^{(1)}, j_\lambda^{(2)}, j_\lambda^{(1,2)}, j_\lambda^{(3)}) \tag{4.3}$$

The eigenfunction-eigenvalue equations for the first eight operators are

$$\hat{J}^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = J(J+1)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.4}$$

$$\hat{J}_z F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = M_J\hbar F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.5}$$

$$\hat{\Lambda}^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = n(n+7)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.6}$$

$$\hat{j}_\lambda^{(1)^2} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = j_\lambda^{(1)}(j_\lambda^{(1)}+1)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.7}$$

$$\hat{j}_\lambda^{(2)^2} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = j_\lambda^{(2)}(j_\lambda^{(2)}+1)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.8}$$

$$\hat{j}_\lambda^{(1,2)^2} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = j_\lambda^{(1,2)}(j_\lambda^{(1,2)}+1)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.9}$$

$$\hat{j}_\lambda^{(3)^2} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = j_\lambda^{(3)}(j_\lambda^{(3)}+1)\hbar^2 F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.10}$$

and

$$\hat{O}_{\hat{I}} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) = (-1)^{\Pi} F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda) \tag{4.11}$$

Those for the operators related to $\hat{\mathscr{T}}_\lambda^{(1)^2}$ and $\hat{\mathscr{T}}_\lambda^{(2)^2}$ are chosen by the requirement that the dependence of $F^{\boldsymbol{p}_\lambda}(\boldsymbol{\Phi}_\lambda)$ on $\eta_\lambda^{(1)}$ and $\eta_\lambda^{(2)}$ be multiplicative functions of each of these two variables and will be given in section 4.2. All of the quantum numbers included in section 4.3 are integers, and their ranges are also discussed in that section. These hyperspherical harmonics $F^{\boldsymbol{p}_\lambda}$ are required to be regular at all of the poles of these equations. Their usefulness lies in the fact that they constitute, for each weak interaction sub-region, a complete regular basis set in $\boldsymbol{\Phi}_\lambda$ in terms of which the local hyperspherical surface functions of that sub-region can be expanded. These surface functions are defined as the regular eigenfunctions of the operator

$$\hat{h}(\boldsymbol{\Phi}_\lambda;\bar{\rho}) = \frac{\hat{\Lambda}^2(\boldsymbol{\Phi}_\lambda)}{2\mu\bar{\rho}^2} + V(\bar{\rho},\eta_\lambda^{(1)},\eta_\lambda^{(2)},\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)}) \tag{4.12}$$

which are, in addition, eigenfunctions of $\hat{J}^2,\hat{J}_{z^{sf}}$ and $\hat{O}_{\hat{I}}$. They are used, in turn, for expanding, in the weak interaction sub-regions, the scattering wave function for the system.[5]

**4.2. Determination of the Hyperspherical Harmonics.** We start out by determining the simultaneous eigenfunctions of $\hat{j}_\lambda^{(1)^2},\hat{j}_\lambda^{(2)^2},\hat{j}_\lambda^{(1,2)^2},\hat{j}_\lambda^{(3)^2},\hat{J}^2$ and $\hat{J}_{z^{sf}}$, first in the space-fixed polar angles of $\boldsymbol{r}_\lambda^{(1)},\boldsymbol{r}_\lambda^{(2)}$, and $\boldsymbol{r}_\lambda^{(3)}$, then change the sf polar angles of $\boldsymbol{r}_\lambda^{(1)}$ and $\boldsymbol{r}_\lambda^{(2)}$ to their bf1 counterparts, and finally change the bf1 polar angles of $\boldsymbol{r}_\lambda^{(1)}$ to their bf2 counterparts. We then add the condition that these eigenfunctions also be eigenfunctions of the operators related to $\hat{\mathscr{T}}_\lambda^{(1)^2}$ and $\hat{\mathscr{T}}_\lambda^{(2)^2}$ (see eqs 4.47 and 4.48) and of $\hat{\Lambda}^2$. We finally require that they also be eigenfunctions of $\hat{O}_{\hat{I}}$. This will result in explicit expressions for the hyperspherical harmonics $F^{p_\lambda}(\Phi_\lambda)$ defined in the previous section.

*4.2.1. Angular Momentum Eigenfunctions in Space-Fixed Polar Angles.* The simultaneous eigenfunctions of $\hat{j}_\lambda^{(1)^2},\hat{j}_\lambda^{(2)^2}$, $\hat{j}_\lambda^{(1,2)^2}$, and $\hat{j}_{\lambda_{z^{sf}}}^{(1,2)}$ are given by[24]

$$Y^{j_\lambda^{(1,2)} j_\lambda^{(1)} j_\lambda^{(2)}}_{m^{sf}_{j_\lambda^{(1,2)}}}(\phi_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) = \sum_{m^{sf}_{j_\lambda^{(1)}} m^{sf}_{j_\lambda^{(2)}}} C(j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)}; m^{sf}_{j_\lambda^{(1)}} m^{sf}_{j_\lambda^{(2)}} m^{sf}_{j_\lambda^{(1,2)}}) \times Y^{j_\lambda^{(1)}}_{m^{sf}_{j_\lambda^{(1)}}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)})\, Y^{j_\lambda^{(2)}}_{m^{sf}_{j_\lambda^{(2)}}}(\theta_\lambda^{(2)},\phi_\lambda^{(2)}) \tag{4.13}$$

where the C are Clebsch-Gordan coefficients[24] and the $Y^j_m$ are ordinary spherical harmonics.[25] Similarly, the simultaneous

eigenfunctions of $\hat{j}_\lambda^{(1)^2}$, $\hat{j}_\lambda^{(2)^2}$, $\hat{j}_\lambda^{(1,2)^2}$, $\hat{j}_\lambda^{(3)^2}$, $\hat{J}^2$, and $\hat{J}_{z^{sf}}$ are, in the sf polar angles of the $\boldsymbol{r}_\lambda^{(1)}$ ($j = 1, 2, 3$):

$$Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\theta_\lambda^{(1)}, \phi_\lambda^{(1)}, \theta_\lambda^{(2)}, \phi_\lambda^{(2)}, \theta_\lambda^{(3)}, \phi_\lambda^{(3)}) = \sum_{m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf}} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) \times Y_{m_{j_\lambda^{(1,2)}}^{sf}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\theta_\lambda^{(1)}, \phi_\lambda^{(1)}, \theta_\lambda^{(2)}, \phi_\lambda^{(2)}) Y_{m_{j_\lambda^{(3)}}^{sf}}^{j_\lambda^{(3)}}(\theta_\lambda^{(3)}, \phi_\lambda^{(3)}) \quad (4.14)$$

with

$$-J \le M_J \le J \quad (4.15)$$

*4.2.2. Angular Momentum Eigenfunctions in sf Polar Angles of $\boldsymbol{r}_\lambda^{(3)}$ and bf1 Polar Angles of $\boldsymbol{r}_\lambda^{(1)}$, $\boldsymbol{r}_\lambda^{(2)}$.* In view of the relation between the bf1 and sf frames given in eq 2.3 and the definition of the polar angles of $\boldsymbol{r}_\lambda^{(j)}$ ($j = 1, 2, 3$) in those frames given in Table 1, we can re-express the left-hand side of eq 4.13, given in sf angles, in terms of the corresponding bf1 angles by[26]

$$Y_{m_{j_\lambda^{(1,2)}}^{sf}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\theta_\lambda^{(1)},\phi_\lambda^{(1)},\theta_\lambda^{(2)},\phi_\lambda^{(2)}) = \sum_{m_{j_\lambda^{(1,2)}}^{bf1}} D_{m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) \times Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) \quad (4.16)$$

where $D$ is a Wigner rotation function and $Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}$ is related to $Y_{m_{j_\lambda^{(1)}}^{bf1}}^{j_\lambda^{(1)}}$ and $Y_{m_{j_\lambda^{(2)}}^{bf2}}^{j_\lambda^{(2)}}$ by an expression analagous to (4.13) with all the sf quantities replaced by corresponding bf1 quantities:

$$Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) = \sum_{m_{j_\lambda^{(1)}}^{bf1} m_{j_\lambda^{(2)}}^{bf1}} C(j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)}; m_{j_\lambda^{(1)}}^{bf1} m_{j_\lambda^{(2)}}^{bf1} m_{j_\lambda^{(1,2)}}^{bf1}) \times Y_{m_{j_\lambda^{(1)}}^{bf1}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)}) Y_{m_{j_\lambda^{(2)}}^{bf1}}^{j_\lambda^{(2)}}(\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) \quad (4.17)$$

Replacement of eq 4.16 into eq 4.14 gives the eigenfunctions $Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}$ in the desired angles:

$$Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \sum_{m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} m_{j_\lambda^{(1,2)}}^{bf1}} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) \times D_{m_{j_\lambda^{(1,2)}}^{bf1} m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) \times Y_{m_{j_\lambda^{(3)}}^{sf}}^{j_\lambda^{(3)}}(\theta_\lambda^{(3)},\phi_\lambda^{(3)}) \quad (4.18)$$

Since[27]

$$Y_{m_{j_\lambda^{(1,2)}}^{sf}}^{j_\lambda^{(3)}}(\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \left(\frac{2j_\lambda^{(3)}+1}{4\pi}\right)^{1/2} D_{m_{j_\lambda^{(3)}}^{sf} 0}^{j_\lambda^{(3)}}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) \quad (4.19)$$

we see that eq 4.18 contains the product of two Wigner rotation functions of the same Euler angles, $(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0)$. This product can be expressed, with the help of the Clebsch-Gordan series[28] as

$$D_{m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) D_{m_{j_\lambda^{(3)}}^{sf} 0}^{j_\lambda^{(3)}}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) = \sum_{J'=|j_\lambda^{(1,2)}-j_\lambda^{(3)}|}^{j_\lambda^{(1,2)}+j_\lambda^{(3)}} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J'; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) \times D_{M_J m_{j_\lambda^{(1,2)}}^{bf1}}^{J'}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) C(j_\lambda^{(1,2)} j_\lambda^{(3)} J'; m_{j_\lambda^{(1,2)}}^{bf1} 0 m_{j_\lambda^{(1,2)}}^{bf1}) \quad (4.20)$$

With the help of the last two equations, eq 4.18 can be rewritten as

$$Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \sum_{J' m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} m_{j_\lambda^{(1,2)}}^{bf1}} \left(\frac{2j_\lambda^{(3)}+1}{4\pi}\right)^{1/2} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) \times C(j_\lambda^{(1,2)} j_\lambda^{(3)} J'; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) C(j_\lambda^{(1,2)} j_\lambda^{(3)} J'; m_{j_\lambda^{(1,2)}}^{bf1} 0 m_{j_\lambda^{(1,2)}}^{bf1}) \times Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) D_{M_J m_{j_\lambda^{(1,2)}}^{bf1}}^{J'}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) \quad (4.21)$$

We can use the orthogonality of the Clebsch-Gordan coefficients with respect to $J$, namely[29]

$$\sum_{m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf}} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) C(j_\lambda^{(1,2)} j_\lambda^{(3)} J'; m_{j_\lambda^{(1,2)}}^{sf} m_{j_\lambda^{(3)}}^{sf} M_J) = \delta_{JJ'} \quad (4.22)$$

to perform the sum over $m_{j_\lambda^{(1,2)}}^{sf1}$, $m_{j_\lambda^{(3)}}^{bf1}$, and $J'$:

$$Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \left(\frac{2j_\lambda^{(3)}+1}{4\pi}\right)^{1/2} \sum_{m_{j_\lambda^{(1,2)}}^{bf1}} C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; m_{j_\lambda^{(1,2)}}^{bf1} 0 m_{j_\lambda^{(1,2)}}^{bf1}) \times Y_{m_{j_\lambda^{(1,2)}}^{bf1}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) D_{M_J m_{j_\lambda^{(1,2)}}^{bf1}}^{J}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) \quad (4.23)$$

We note that the summation index $m_{j_\lambda^{(1,2)}}^{bf1}$ is not only the quantum number for the bf1 $z$ component of $\hat{\boldsymbol{j}}_\lambda^{(1,2)}$ but also that of $\boldsymbol{J}$. This is due to eq 4.2 and the fact that since $\boldsymbol{r}_\lambda^{(3)}$ lies along $Gz_\lambda^{bf1}$, the bf1 $z$ component of $\hat{\boldsymbol{j}}_\lambda^{(3)}$ vanishes. Let us henceforth replace that index by $\Omega_\lambda$. Using the symmetry relation[30]

$$C(j_\lambda^{(1,2)} j_\lambda^{(3)} J; \Omega_\lambda 0\ \Omega_\lambda) = (-1)^{j_\lambda^{(1,2)}-\Omega_\lambda} \left(\frac{2J+1}{2j_\lambda^{(3)}+1}\right)^{1/2} C(J j_\lambda^{(1,2)} j_\lambda^{(3)}; \Omega_\lambda, -\Omega_\lambda, 0) \quad (4.24)$$

eq 4.23 becomes

$$Y_{M_J^\lambda}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \left(\frac{2J+1}{4\pi}\right)^{1/2}\sum_{\Omega_\lambda}(-1)^{j_\lambda^{(1,2)}-\Omega_\lambda}C(Jj_\lambda^{(1,2)}j_\lambda^{(3)};\Omega_\lambda,-\Omega_\lambda,0)\times Y_{\Omega_\lambda}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)})D_{M_J\Omega_\lambda}^{J}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},0) \quad (4.25)$$

*4.2.3. Angular Momentum Eigenfunctions in sf Polar Angles of $\boldsymbol{r}_\lambda^{(3)}$, bf1 Polar Angles of $\boldsymbol{r}_\lambda^{(2)}$, and bf3 Polar Angles of $\boldsymbol{r}_\lambda^{(1)}$.* We now wish to convert the eigenfunctions of eq 4.25 from the polar angles $\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)}$ of $\boldsymbol{r}_\lambda^{(1)}$ in *bf1* to its polar angles $\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}$ in *bf2*, for the reasons discussed in the paragraph preceding eq 2.7. This can be accomplished with the help of the relation between the bf1 and bf3 frames given in eq 2.3. The corresponding spherical harmonics associated with $\boldsymbol{r}_\lambda^{(1)}$ are related by[26]

$$Y_{m_{j_\lambda^{(1)}}^{\mathrm{bf1}}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)}) = \sum_{m_{j_\lambda^{(1)}}^{\mathrm{bf3}}} D_{m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(1)}}^{\mathrm{bf3}}}^{j_\lambda^{(1)}}(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)\, Y_{m_{j_\lambda^{(1)}}^{\mathrm{bf3}}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.26)$$

We now replace this into eq 4.17:

$$Y_{m_{j_\lambda^{(1,2)}}^{\mathrm{bf1}}}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}}(\gamma_\lambda^{(1,3)},\psi_\lambda^{(1,3)},\gamma_\lambda^{(2,3)}\psi_\lambda^{(2,3)}) = \sum_{m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(2)}}^{\mathrm{bf1}}m_{j_\lambda^{(1)}}^{\mathrm{bf3}}} C(j_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)};m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(2)}}^{\mathrm{bf1}}m_{j_\lambda^{(1,2)}}^{\mathrm{bf1}})\times D_{m_{j_\lambda^{(1)}}^{\mathrm{bf3}}m_{j_\lambda^{(1)}}^{\mathrm{bf1}}}^{j_\lambda^{(1)}}(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)\, Y_{m_{j_\lambda^{(2)}}^{\mathrm{bf1}}}^{j_\lambda^{(2)}}(\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)})\times Y_{m_{j_\lambda^{(1)}}^{\mathrm{bf3}}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.27)$$

We can use expressions analogous to eqs 4.19 and 4.20 to get

$$D_{m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(1)}}^{\mathrm{bf3}}}^{j_\lambda^{(1)}}(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)Y_{m_{j_\lambda^{(2)}}^{\mathrm{bf1}}}^{j_\lambda^{(2)}}(\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)}) = \left(\frac{2j_\lambda^{(2)}+1}{4\pi}\right)^{1/2}\sum_{j'^{(1,2)}_\lambda=|j_\lambda^{(1)}-j_\lambda^{(2)}|}^{j_\lambda^{(1)}+j_\lambda^{(2)}} C(j_\lambda^{(1)}j_\lambda^{(2)}j'^{(1,2)}_\lambda;m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(2)}}^{\mathrm{bf1}}m_{j_\lambda^{(1,2)}}^{\mathrm{bf1}})\times D_{m_{j_\lambda^{(1)}}^{\mathrm{bf1}}m_{j_\lambda^{(1)}}^{\mathrm{bf3}}}^{j'^{(1,2)}_\lambda}(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)\, C(j_\lambda^{(1)}j_\lambda^{(2)}j'^{(1,2)}_\lambda;m_{j_\lambda^{(1)}}^{\mathrm{bf3}}\,0\,m_{j_\lambda^{(1)}}^{\mathrm{bf3}}) \quad (4.28)$$

Substitution into eq 2.47 and the use of an orthogonality relation between the Clebsch−Gordan coefficients similar to eq 4.22 results in, after $m_{j_\lambda^{(1,2)}}^{\mathrm{bf1}}$ is replaced by $\Omega_\lambda$ and $m_{j_\lambda^{(1)}}^{\mathrm{bf3}}$ by $k_{j_\lambda^{(1)}}$,

$$Y_{\Omega_\lambda}^{j_\lambda^{(1,2)}j_\lambda^{(1)}j_\lambda^{(2)}} = \left(\frac{2j_\lambda^{(2)}+1}{4\pi}\right)^{1/2}\sum_{k_{j_\lambda^{(1)}}}C(j_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)};k_{j_\lambda^{(1)}}0\,k_{j_\lambda^{(1)}})\times D_{\Omega_\lambda k_{j_\lambda^{(1)}}}^{j_\lambda^{(1,2)}}(\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},0)\, Y_{k_{j_\lambda^{(1)}}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.29)$$

Finally, replacement of eq 4.29 into eq 4.25 yields

$$Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) = \left(\frac{2J+1}{4\pi}\right)^{1/2}\left(\frac{2j_\lambda^{(2)}+1}{4\pi}\right)^{1/2}\times \sum_{\Omega_\lambda}(-1)^{j_\lambda^{(1,2)}-\Omega_\lambda}C(Jj_\lambda^{(1,2)}j_\lambda^{(3)};\Omega_\lambda,-\Omega_\lambda,0)\times D_{M_J\Omega_\lambda}^{J}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},\psi_\lambda^{(2,3)})\sum_{k_{j_\lambda^{(1)}}}C(j_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)};k_{j_\lambda^{(1)}}0k_{j_\lambda^{(1)}})\times d_{\Omega_\lambda k_{j_\lambda^{(1)}}}^{j_\lambda^{(1,2)}}(\gamma_\lambda^{(2,3)})Y_{k_{j_\lambda^{(1)}}}^{j_\lambda^{(1)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.30)$$

This is the expression for $Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}$ in the desired polar angles $(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)})$ of $\boldsymbol{r}_\lambda^{(1)}$ in bf3, $(\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)})$ of $\boldsymbol{r}_\lambda^{(2)}$ in bf1 and $(\theta_\lambda^{(3)},\phi_\lambda^{(3)})$ of $\boldsymbol{r}_\lambda^{(3)}$ in sf. It should be noted that the ranges of the summation indices $\Omega_\lambda$ and $k_{j_\lambda^{(1)}}$ are implied in the corresponding Clebsch−Gordan coefficients:

$$-J \le \Omega_\lambda \le J \qquad -j_\lambda^{(1,2)} \le \Omega_\lambda \le j_\lambda^{(1,2)} \quad (4.31)$$

and

$$-j_\lambda^{(1)} \le k_{j_\lambda^{(1)}} \le j_\lambda^{(1)} \qquad -j_\lambda^{(1,2)} \le k_{j_\lambda^{(1)}} \le j_\lambda^{(1,2)} \quad (4.32)$$

In addition, the ranges of $j_\lambda^{(1,2)}$ and $j_\lambda^{(3)}$ are determined by the triangle inequalities

$$|j_\lambda^{(1)} - j_\lambda^{(2)}| \le j_\lambda^{(1,2)} \le j_\lambda^{(1)} + j_\lambda^{(2)} \quad (4.33)$$

and

$$|J - j_\lambda^{(1,2)}| \le j_\lambda^{(3)} \le J + j_\lambda^{(1,2)} \quad (4.34)$$

*4.2.4. Eigenfunctions of $\Lambda^2$.* Let us now determine simultaneous solutions $\mathscr{T}$ of eqs 4.4 through 4.10. Because of eqs 4.4, 4.5, and 4.7−4.10, they must have the form

$$\mathscr{T}(\boldsymbol{\Phi}_\lambda) = f(\eta_\lambda^{(1)},\eta_\lambda^{(2)})Y_{M_J}^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) \quad (4.35)$$

Replacement into eq 4.6 with $\hat{\Lambda}^2$ given by eq 3.4 results in

$$\left[\frac{1}{\sin^2\eta_\lambda^{(2)}}\hat{\mathscr{S}}_\lambda^{(1)^2} + \hat{\mathscr{S}}_\lambda^{(2)^2}\right]f + \hbar^2\left[\frac{j_\lambda^{(1)}(j_\lambda^{(1)}+1)}{\sin^2\eta_\lambda^{(1)}\sin^2\eta_\lambda^{(2)}} + \frac{j_\lambda^{(2)}(j_\lambda^{(2)}+1)}{\cos^2\eta_\lambda^{(1)}\sin^2\eta_\lambda^{(2)}} + \frac{j_\lambda^{(3)}(j_\lambda^{(3)}+1)}{\cos^2\eta_\lambda^{(2)}}\right]f = n(n+7)\hbar^2 f(\eta_\lambda^{(1)},\eta_\lambda^{(2)}) \quad (4.36)$$

This is a second-order partial differential equation in the two independent variables $\eta_\lambda^{(1)}$ and $\eta_\lambda^{(2)}$. Let us seek separable solutions of the type

$$f(\eta_\lambda^{(1)},\eta_\lambda^{(2)}) = u(\eta_\lambda^{(1)})v(\eta_\lambda^{(2)}) \quad (4.37)$$

Substitution into eq 4.33 yields the two ordinary differential equations

$$\hat{\mathscr{L}}_\lambda^{(1)^2} u(\eta_\lambda^{(1)}) + \hbar^2\left[\frac{j_\lambda^{(1)}(j_\lambda^{(2)}+1)}{\sin^2\eta_\lambda^{(1)}} + \frac{j_\lambda^{(2)}(j_\lambda^{(2)}+1)}{\cos^2\eta_\lambda^{(1)}}\right] u(\eta_\lambda^{(1)}) = \nu(\nu+4)\hbar^2\, u(\eta_\lambda^{(1)}) \quad (4.38)$$

and

$$\hat{\mathscr{L}}_\lambda^{(2)^2} v(\eta_\lambda^{(2)}) + \hbar^2\left[\frac{\nu(\nu+4)}{\sin^2\eta_\lambda^{(2)}} + \frac{j_\lambda^{(3)}(j_\lambda^{(3)}+1)}{\cos^2\eta_\lambda^{(2)}}\right] v(\eta_\lambda^{(2)}) = n(n+7)\hbar^2 v(\eta_\lambda^{(2)}) \quad (4.39)$$

where $\nu(\nu+4)$ is a separation constant. It is put in this form because it turns out that, for regular solutions, $\nu$ is a nonnegative integer that can be considered to be the quantum number for $\hat{\mathscr{L}}_\lambda^{(1)^2}$. Since $\hat{\mathscr{L}}_\lambda^{(2)^2}$ is related to the eight independent angular momentum operators $\hat{\mathscr{L}}_\lambda^{(1)^2}$, $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{j}_{z^{sf}}$, $\hat{j}_\lambda^{(1)^2}$, $\hat{j}_\lambda^{(2)^2}$, $\hat{j}_\lambda^{(1,2)^2}$ and $\hat{j}_\lambda^{(3)^2}$, with corresponding independent quantum numbers $\nu$, $n$, $J$, $M_J$, $j_\lambda^{(1)}$, $j_\lambda^{(2)}$, $j_\lambda^{(1,2)}$, and $j_\lambda^{(3)}$, eq 4.39 does not involve a new independent quantum number. Equations 4.38 and 4.39 are of the form of eq 22.6.4 of Abramowitz and Stegun,[31] and their regular solutions can be expressed as

$$u_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}(\eta_\lambda^{(1)}) = N_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}} (\sin\eta_\lambda^{(1)})^{j_\lambda^{(1)}} (\cos\eta_\lambda^{(1)})^{j_\lambda^{(2)}} P^{(j_\lambda^{(1)}+1/2,\, j_\lambda^{(2)}+1/2)}_{1/2(\nu-j_\lambda^{(1)}-j_\lambda^{(2)})}(\cos 2\eta_\lambda^{(1)}) \quad (4.40)$$

and

$$v_n^{\nu j_\lambda^{(3)}}(\eta_\lambda^{(2)}) = N_n^{\nu j_\lambda^{(3)}} (\sin\eta_\lambda^{(2)})^{\nu} (\cos\eta_\lambda^{(2)})^{j_\lambda^{(3)}} P^{(\nu+1/2,\, j_\lambda^{(3)}+1/2)}_{1/2(n-\nu-j_\lambda^{(3)})}(\cos 2\eta_\lambda^{(2)}) \quad (4.41)$$

In these expressions, the $P_\gamma^{(\alpha,\beta)}$ are Jacobi polynomials of degree $\gamma$, $\alpha,\beta > -1$ are real numbers, and the $N_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}$ and $N_n^{\nu j_\lambda^{(3)}}$ coefficients are normalization constants determined by the condition that the $u_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}$ and $v_n^{\nu j_\lambda^{(3)}}$ are orthonormal when using the volume elements $dV_{\eta_\lambda^{(1)}}$ and $dV_{\eta_\lambda^{(2)}}$ of eqs 2.31 and 2.32, respectively. They are given by

$$N_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}} = \left\{\frac{(2\nu+4)\left[\frac{1}{2}(n-j_\lambda^{(1)}-j_\lambda^{(2)})\right]!\left[\frac{1}{2}(\nu+j_\lambda^{(1)}+j_\lambda^{(2)}+2)\right]!}{\Gamma\left[\frac{1}{2}(\nu+j_\lambda^{(1)}-j_\lambda^{(2)}+3)\right]\Gamma\left[\frac{1}{2}(\nu-j_\lambda^{(1)}+j_\lambda^{(2)}+3)\right]}\right\}^{1/2} \quad (4.42)$$

and

$$N_n^{\nu j_\lambda^{(3)}} = \left\{\frac{(2n+7)\left[\frac{1}{2}(n-\nu-j_\lambda^{(3)})\right]!\,\Gamma\left[\frac{1}{2}(n+\nu+j_\lambda^{(3)}+7)\right]}{\left[\frac{1}{2}(n+\nu+j_\lambda^{(3)}+4)\right]!\,\Gamma\left[\frac{1}{2}(n+\nu+j_\lambda^{(3)}+3)\right]}\right\}^{1/2} \quad (4.43)$$

The quantum numbers $n$ and $\nu$ are non-negative integers satisfying the conditions

$$\nu - (j_\lambda^{(1)} + j_\lambda^{(2)}) \geq 0 \text{ and even} \quad (4.44)$$

and

$$n - \nu - j_\lambda^{(3)} \geq 0 \text{ and even} \quad (4.45)$$

as a result of which we have

$$n - (j_\lambda^{(1)} + j_\lambda^{(2)} + j_\lambda^{(3)}) \geq 0 \text{ and even} \quad (4.46)$$

We conclude that $\nu$ has the same parity as $j_\lambda^{(1)} + j_\lambda^{(2)}$, $n-\nu$ the same parity as $j_\lambda^{(3)}$, and $n$ the same parity as $j_\lambda^{(1)} + j_\lambda^{(2)} + j_\lambda^{(3)}$. As a result, all the factorials in eqs 4.42 and 4.43 are of nonnegative integers and all the gamma functions are of half odd positive integers, which makes them easy to evaluate.

The $u_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}(\eta_\lambda^{(1)})$ and $v_n^{\nu j_\lambda^{(3)}}(\eta_\lambda^{(2)})$ are eigenfunctions of the operators that appear in the left hand side of eqs 4.38 and 4.39, namely,

$$\hat{\mathscr{L}}_\lambda^{(1) j_\lambda^{(1)} j_\lambda^{(2)^2}}(\eta_\lambda^{(1)}) = \hat{\mathscr{L}}_\lambda^{(1)^2}(\eta_\lambda^{(1)}) + \hbar^2\left[\frac{j_\lambda^{(1)}(j_\lambda^{(1)}+1)}{\sin^2\eta_\lambda^{(1)}} + \frac{j_\lambda^{(2)}(j_\lambda^{(2)}+1)}{\cos^2\eta_\lambda^{(1)}}\right] \quad (4.47)$$

and

$$\hat{\mathscr{L}}_\lambda^{(2) \nu j_\lambda^{(3)^2}}(\eta_\lambda^{(2)}) = \hat{\mathscr{L}}_\lambda^{(2)^2}(\eta_\lambda^{(2)}) + \hbar^2\left[\frac{\nu(\nu+4)}{\sin^2\eta_\lambda^{(2)}} + \frac{j_\lambda^{(3)}(j_\lambda^{(3)}+1)}{\cos^2\eta_\lambda^{(2)}}\right] \quad (4.48)$$

and have eigenvalues $\nu(\nu+4)\hbar^2$ and $n(n+7)\hbar^2$ respectively. These are the $\hat{\mathscr{L}}_\lambda^{(1)^2}$- and $\hat{\mathscr{L}}_\lambda^{(2)^2}$-related operators alluded to in the beginning of sections 4.1 and 4.2. The simultaneous regular solutions of eqs 4.4 through 4.10 can, as a result, be written as

$$\mathscr{T}_{M_J \nu}^{Jn j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)} j_\lambda^{(3)}}(\mathbf{\Phi}_\lambda) = u_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}(\eta_\lambda^{(1)})\, v_n^{\nu j_\lambda^{(3)}}(\eta_\lambda^{(2)}) \times Y_{M_J}^{J j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)} j_\lambda^{(3)}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) \quad (4.49)$$

*4.2.5 Eigenfunctions of $\hat{O}_{\hat{I}}$.* To complete the determination of the hyperspherical harmonics defined in section 4.1, we now require that they satisfy eq 4.11. Let us apply $\hat{O}_{\hat{I}}$ to eq 4.49 and use the fact that $\hat{I}^{-1} = \hat{I}$ as well as eq 2.24 to get

$$\hat{O}_{\hat{I}} \mathscr{T}_{M_J \nu}^{Jn j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)} j_\lambda^{(3)}}(\mathbf{\Phi}_\lambda) = u_\nu^{j_\lambda^{(1)} j_\lambda^{(2)}}(\eta_\lambda^{(1)})\, v_n^{\nu j_\lambda^{(3)}}(\eta_\lambda^{(3)}) \times Y_{M_J}^{J j_\lambda^{(1)} j_\lambda^{(2)} j_\lambda^{(1,2)} j_\lambda^{(3)}}(\gamma_\lambda^{(1,2)}, 2\pi - \psi_\lambda^{(1,2)}, \gamma_\lambda^{(2,3)}, \pi - \psi_\lambda^{(2,3)}, \pi - \theta_\lambda^{(3)}, \pi + \phi_\lambda^{(3)}) \quad (4.50)$$

We now use the relations[32]

$$D^J_{M_J \Omega_\lambda}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},\psi_\lambda^{(2,3)}) = e^{iM_J\phi_\lambda^{(3)}} d^J_{M_J \gamma_\lambda}(\phi_\lambda^{(3)}) e^{i\Omega_\lambda \psi_\lambda^{(2,3)}} \quad (4.51)$$

and

$$d^J_{M_J \Omega_\lambda}(\pi - \theta_\lambda^{(3)}) = (-1)^{J-M_J} d^J_{M_J, -\Omega_\lambda}(\phi_\lambda^{(3)}) \quad (4.52)$$

to obtain

$$D^J_{M_J \Omega_\lambda}(\pi + \phi_\lambda^{(3)}, \pi - \theta_\lambda^{(3)}, \pi - \psi_\lambda^{(2,3)}) = (-1)^{J+\Omega_\lambda} D^J_{M_J, -\Omega_\lambda}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},\psi_\lambda^{(2,3)}) \quad (4.53)$$

In addition, from the definition of spherical harmonics,[25] we have

$$Y^{j_\lambda^{(1)}}_{k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(1,2)},2\pi-\psi_\lambda^{(1,2)}) = (-1)^{k_{j_\lambda^{(1)}}} Y^{j_\lambda^{(1)}}_{k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.54)$$

Use of eqs 4.30, 4.53, and 4.54 results in

$$Y^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J} \times (\gamma_\lambda^{(1,2)},2\pi-\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\pi-\psi_\lambda^{(1,2)},\pi-\theta_\lambda^{(3)},\pi+\phi_\lambda^{(3)}) = \left(\frac{2J+1}{4\pi}\right)^{1/2}\left(\frac{2j_\lambda^{(2)}+1}{4\pi}\right)^{1/2} \times \sum_{\Omega_\lambda}(-1)^{J+j_\lambda^{(1,2)}} Y^{j_\lambda^{(1)}}_{k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) C(Jj_\lambda^{(1,2)}\, j_\lambda^{(1)};\Omega_\lambda,-\Omega_\lambda,0) \times D^J_{M_J,-\Omega_\lambda}(\phi_\lambda^{(3)},\theta_\lambda^{(3)},\psi_\lambda^{(2,3)}) \sum_{k_{j_\lambda^{(1)}}} C(j_\lambda^{(1)}\, j_\lambda^{(2)}\, j_\lambda^{(1,2)};k_{j_\lambda^{(1)}}0\; k_{j_\lambda^{(1)}}) \times d^{j_\lambda^{(1,2)}}_{\Omega_\lambda k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(2,3)})\,(-1)^{k_{j_\lambda^{(1)}}} Y^{j_\lambda^{(1)}}_{k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)}) \quad (4.55)$$

The appearance of $-\Omega_\lambda$ and $-k_{j_\lambda^{(1)}}$ in the subscripts of $D^J_{M_J,-\Omega_\lambda}$ and $Y^{J_\lambda^{(1)}}_{-k_{j_\lambda^{(1)}}}$ suggests that we change summation indices from $\Omega_\lambda$ and $k_{j_\lambda^{(1)}}$ to $-\Omega_\lambda$ and $-k_{j_\lambda^{(1)}}$, respectively. To that effect, the relations[33]

$$C(Jj_\lambda^{(1,2)}\, j_\lambda^{(3)};-\Omega_\lambda,\Omega_\lambda,0) = (-1)^{j_\lambda^{(1,2)}-j_\lambda^{(3)}} C(Jj_\lambda^{(1,2)}\, j_\lambda^{(3)};\,-\Omega_\lambda,\Omega_\lambda,0) \quad (4.56)$$

$$C(j_\lambda^{(1)}\, j_\lambda^{(2)}\, j_\lambda^{(1,2)};\,-k_{j_\lambda^{(1)}},0,\,-k_{j_\lambda^{(1)}}) = (-1)^{j_\lambda^{(1)}+j_\lambda^{(2)}+j_\lambda^{(1,2)}} C(j_\lambda^{(1)}\, j_\lambda^{(2)}\, j_\lambda^{(1,2)};\,-k_{j_\lambda^{(1)}},0,\,-k_{j_\lambda^{(1)}}) \quad (4.57)$$

and [34]

$$d^{j_\lambda^{(1,2)}}_{-\Omega_\lambda,-k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(2,3)}) = (-1)^{k_{j_\lambda^{(1)}}-\Omega_\lambda} d^{j_\lambda^{(1,2)}}_{\Omega_\lambda k_{j_\lambda^{(1)}}}(\gamma_\lambda^{(2,3)}) \quad (4.58)$$

will be employed. Proceeding as indicated, we obtain

$$Y^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J} \times (\gamma_\lambda^{(2,3)},2\pi-\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\pi-\psi_\lambda^{(2,3)},\pi-\theta_\lambda^{(3)},\pi-\phi_\lambda^{(3)}) = (-1)^{j_\lambda^{(1)}+j_\lambda^{(2)}+j_\lambda^{(3)}} Y^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\theta_\lambda^{(3)},\phi_\lambda^{(3)}) \quad (4.59)$$

We now replace eq 4.59 into eq 4.50 and make use of the fact that $j_\lambda^{(1)}+j_\lambda^{(2)}+j_\lambda^{(3)}$ has the same parity as $n$, as remarked after eq 4.46, to get

$$\hat{O}_{\hat{1}}\mathscr{F}^{Jnj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J\nu}(\mathbf{\Phi}_\lambda) = (-1)^n \mathscr{F}^{Jnj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J\nu}(\mathbf{\Phi}_\lambda) \quad (4.60)$$

For a given $\Pi$, in order for eq 4.11 to be satisfied, it suffices to make $n$ have the same parity as $\Pi$:

$$(-1)^n = (-1)^\Pi \quad (4.61)$$

We will designate such an $n$ by $n_\Pi$. As a result, the regular simultaneous solutions of eqs 4.4 through 4.11 are

$$F^{p_\lambda}(\mathbf{\Phi}_\lambda) = u_n^{\nu j_\lambda^{(3)}}(\eta_\lambda^{(1)}) v_\nu^{n_\Pi j_\lambda^{(3)}}(\eta_\lambda^{(2)}) \times Y^{Jj_\lambda^{(1)}j_\lambda^{(2)}j_\lambda^{(1,2)}j_\lambda^{(3)}}_{M_J}(\gamma_\lambda^{(1,2)},\psi_\lambda^{(1,2)},\gamma_\lambda^{(2,3)},\psi_\lambda^{(2,3)},\phi_\lambda^{(3)},\phi_\lambda^{(3)}) \quad (4.62)$$

where $u$, $v$, and $Y$ are given, respectively, by eqs 4.40, 4.4, and 4.30, with $M_J$ being an integer in the usual range given by eq 4.15 and the remaining quantum numbers being non-negative integers subject to the constraints of eqs 4.33, 4.34, 4.44, and 4.45.

## 5. Relation between Weak and Strong Interaction Region Coordinates

The coordinates used in the strong interaction of region of configuration space are the row-orthonormal hyperspherical coordinates developed previously[3] and in terms of which hyperspherical harmonics have been obtained analytically.[19] In performing scattering calculations for tetraatomic systems using those coordinates in that region and the present ones ($\rho$, $\mathbf{\Phi}_\lambda$) in the weak region, it is necessary to obtain the relation between those two sets of coordinates. This can be obtained from the expressions of the Jacobi matrix $\boldsymbol{\rho}_\lambda^{sf}$ of eq 2.1 in terms of such coordinates. To that effect we initially choose the bf2 coordinates together with eqs 2.13 and 2.14 to relate $\boldsymbol{\rho}_\lambda^{sf}$ to $\rho,\eta_\lambda^{(1)},\eta_\lambda^{(2)},\phi_\lambda^{(3)}$, $\theta_\lambda^{(3)},\psi_\lambda^{(2,3)},\gamma_\lambda^{(2,3)},\xi_\lambda^{(1,3)},\gamma_\lambda^{(1,3)}$. The relation of $\boldsymbol{\rho}_\lambda^{sf}$ to the row-orthonormal hyperspherical coordinates $a_\lambda^{\mathscr{I}},b_\lambda^{\mathscr{I}},c_\lambda^{\mathscr{I}},\chi,\rho,\theta,\phi,\delta_\lambda^{(1)}$, $\delta_\lambda^{(2)},\delta_\lambda^{(3)}$ is[3]

$$\boldsymbol{\rho}_\lambda^{sf} = (-1)^\chi \tilde{\mathbf{R}}\,(a_\lambda^{\mathscr{I}},b_\lambda^{\mathscr{I}},c_\lambda^{\mathscr{I}})\,\rho\,\mathbf{N}\,(\theta,\phi)\,\tilde{\mathbf{R}}\,(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)}) \quad (5.1)$$

where $\chi$ is a chirality coordinate, $(a_\lambda^{\mathscr{I}},b_\lambda^{\mathscr{I}},c_\lambda^{\mathscr{I}})$ are the Euler angles which rotate the space-fixed frame to the principal axes of intertia frame $Gx_\lambda^{\mathscr{I}},y_\lambda^{\mathscr{I}},z_\lambda^{\mathscr{I}}$, $\rho$ is the same hyperradius as in the weak interaction region, $(\theta,\phi)$ are principal axes of inertia hyperangles, $(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$ are internal hyperangles, and $\mathrm{N}(\theta,\phi)$ is the matrix

$$\mathbf{N}(\phi,\phi) = \begin{pmatrix} \sin\theta\cos\phi & 0 & 0 \\ 0 & \sin\theta\sin\phi & 0 \\ 0 & 0 & \cos\theta \end{pmatrix} \quad (5.2)$$

The relation between these two sets of coordinates can be obtained by identifying the right hand side of eqs 5.1 and 2.13 and performing some lengthy but straightforward algebra, as described previously.[4] To finally obtain the relation between the row-orthonormal hyperspherical coordinates and the present weak interaction ones ($\rho$,$\mathbf{\Phi}_\lambda$), it suffices to express $\xi^{(1,3)},\gamma_\lambda^{(1,3)}$ in terms of the $\mathbf{\Phi}_\lambda$ angles of eq 2.10. This is easily accomplished using the bf2→bf3 coordinate transformation obtained from eq 2.8 and Table 1:

$$\begin{pmatrix} r_\lambda^{(1)}\sin\gamma_\lambda^{(1,3)}\cos\xi_\lambda^{(1,3)} & r_\lambda^{(2)}\sin\gamma_\lambda^{(2,3)} & 0 \\ r_\lambda^{(1)}\sin\gamma_\lambda^{(1,3)}\sin\xi_\lambda^{(1,3)} & 0 & 0 \\ r_\lambda^{(1)}\cos\gamma_\lambda^{(1,3)} & r_\lambda^{(2)}\cos\gamma_\lambda^{(2,3)} & r_\lambda^{(3)} \end{pmatrix} = \tilde{\mathbf{R}}\,(0,\gamma_\lambda^{(2,3)},0) \begin{pmatrix} r_\lambda^{(1)}\sin\gamma_\lambda^{(1,2)}\cos\psi_\lambda^{(1,2)} & 0 & -r_\lambda^{(3)}\sin\gamma_\lambda^{(2,3)} \\ r_\lambda^{(1)}\sin\gamma_\lambda^{(1,2)}\sin\psi_\lambda^{(1,2)} & 0 & 0 \\ r_\lambda^{(1)}\cos\gamma_\lambda^{(1,2)} & r_\lambda^{(2)} & r_\lambda^{(3)}\cos\gamma_\lambda^{(2,3)} \end{pmatrix} \quad (5.3)$$

From this expression we obtain

$$\cos\gamma_\lambda^{(1,3)} = -\sin\gamma_\lambda^{(2,3)}\sin\gamma_\lambda^{(1,2)}\cos\psi_\lambda^{(1,2)} + \cos\gamma_\lambda^{(2,3)}\cos\psi_\lambda^{(1,2)} \quad (5.4)$$

$$\sin\gamma_\lambda^{(1,3)}\cos\xi_\lambda^{(1,3)} = \cos\gamma_\lambda^{(2,3)}\sin\gamma_\lambda^{(1,2)}\cos\psi_\lambda^{(1,2)} + \sin\gamma_\lambda^{(2,3)}\cos\gamma_\lambda^{(1,2)} \quad (5.5)$$

and

$$\sin\gamma_\lambda^{(1,3)}\sin\xi_\lambda^{(1,3)} = \sin\gamma_\lambda^{(1,2)}\sin\psi_\lambda^{(1,2)} \quad (5.6)$$

Since $\gamma_\lambda^{(1,3)}$ is in the 0 to $\pi$ range, eq 5.3 uniquely furnishes this angle in terms of $\gamma_\lambda^{(1,2)}$, $\psi_\lambda^{(1,2)}$, and $\gamma_\lambda^{(2,3)}$, and eqs 5.4 and 5.5 uniquely determine $\xi^{(1,3)}$ in the 0 to $2\pi$ range, also in terms of those angles. This completes the derivation of the relation between the strong and weak interaction region hyperspherical coordinates.

## 6. Summary and Conclusions

We have derived in this paper explicit analytical expressions for the hyperspherical harmonics of tetraatomic systems in the weak interaction region of configuration space, comprised of sub-regions in which either an atom and a triatom or two diatoms are sufficiently far away from each other for the exchange of atoms between them to be negligible. The nine hyperspherical coordinates chosen are such that in these sub-regions the potential energy function, which depends in general on six of these coordinates, depends strongly on only two (for the two-diatom sub-regions) or three (for the atom−triatom sub-regions) of these coordinates. Each of these sub-region hyperspherical harmonics forms a complete set of functions in the space spanned by the eight hyperangles involved, and behaves regularly at the angular poles of the kinetic energy operator. They constitute an excellent basis set for expanding and, with the help of appropriate contractions, calculating the sub-region local hyperspherical surface functions. Such surface functions are to be used subsequently for expanding and calculating the scattering wave functions for tetraatomic systems.[5] These weak interaction sub-region hyperspherical harmonics involve eight quantum numbers, associated with the eight angular degrees of freedom of the system and are nondegenerate. In addition, they contain a parity quantum number associated with the inversion of the system through its center of mass.

Since the overlap between the different weak interaction sub-regions of configuration space (corresponding to different pairs of weakly interacting molecules) is negligible, supercompleteness problems do not occur in those sub-regions using these surface functions.[20−22] If some of the atoms of the system are identical, the sub-region hyperspherical harmonics can be made to transform according to the associated irreducible representations. For example, for the $H_3O$ system, we consider the two weak interaction sub-regions $H_2 + OH$ and $H + H_2O$. In the first, by using the equivalence of the two atoms in the $H_2$ molecule and appropriate projection operators, we can generate hyperspherical harmonics that belong to the irreducible representations of the permutation group $P_2$ of two identical objects.[35] In the second sub-region, due to the indistinguishability of the two atoms in the $H_2O$ molecule, the same procedure can be followed. In neither sub-region do we need to use the equivalence of the three H atoms, since in the $H_2 + OH$ sub-region we cannot exchange an H atom from $H_2$ with the H atom from OH, and in the $H + H_2O$ sub-region we cannot exchange the isolated H atom with either of the two H atoms of $H_2O$. In the strong interaction region, however, it is useful to consider the indistinguishability of the three H atoms since they can all be permuted with each other, and the hyperspherical harmonics generated for that region can be made to belong to the irreducible representation $P_3$ of three identical objects. These irreducible representation harmonics, both in the weak and strong interaction regions, are useful for decreasing the size of the matrices that must be handled in numerical calculations.

Using the row-orthonormal hyperspherical coordinates (which differ from those employed in the weak interaction sub-regions),[2−4] we had previously developed explicit expressions for tetraatomic system hyperspherical harmonics in the strong interaction region of configuration space,[5,19] in which all four atoms are relatively close to each other. These harmonics form a complete set in the corresponding hyperangles, and since a single such set is used, they do not lead to supercompleteness problems either.[20−22] The relation between the strong and weak interaction region hyperspherical coordinates, which is needed to use the corresponding hyperspherical harmonics in a scattering calculation, was also described.

Since the hyperspherical harmonics, both in the strong and weak interaction regions, incorporate all of the angular momentum couplings, including the Coriolis couplings, the corresponding local hyperspherical surface functions as well as the associated scattering equations involve purely potential couplings,[5,19] even though body-fixed frames are used. This simplifies the scattering equation formalism[5] and the related computer programs. The approach described in this paper should permit efficient benchmark-quality calculations of state-to-state differential and integral cross sections for some tetraatomic systems, using presently available parallel high performance computers.

**Acknowledgment.** Gert D. Billing was a colleague with whom I shared scientific interests and had stimulating interactions for over 20 years. He was also a close friend, whose untimely death is a loss for the scientific community as well as a deeply felt personal loss. This paper is dedicated to his memory. I also thank Dr. Desheng Wang for useful discussions. This work was supported in part by NSF Grant No. CHE-138091.

## References and Notes

(1) Althorpe, S. D.; Clary, D. C. *Annu. Rev. Phys. Chem.* **2003**, *54*, 443−529.
(2) Kuppermann, A. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Ed.; JAI Greenwich Press: Greenwich CT, 1994; Vol. 213, pp 117−186.
(3) Kuppermann, A. *J. Phys. Chem. A* **1997**, *101*, 6368.
(4) Museth, K.; Kuppermann, A. *J. Chem. Phys.* **2001**, *115*, 8285.
(5) Kuppermann, A. *Isr. J. Chem.* **2003**, *43*, 229.
(6) Launay, J. M.; le Dourneuf, M. *Chem. Phys. Lett*. **1989**, *163*, 178; Launay, J. M.; le Dourneuf, M. *Chem. Phys. Lett*. **1990**, *169*, 473.
(7) Launay, J. M.; *Theor. Chim. Acta* **1991**, *79*, 183. Launay, J. M.; Padkjaer, S. B. *Chem. Phys. Lett.* **1991**, *181*, 95.
(8) Branchett, S.; Padkjaer, S. B.; Launay, J. M. *Chem. Phys. Lett*. **1993**, *208*, 523.
(9) Wu, Y. S. M.; Kuppermann, A.; Lepetit, B. *Chem. Phys. Lett*. **1991**, *186*, 319.
(10) Wu, Y. S. M.; Kuppermann, A. *Chem. Phys. Lett*. **1993**, *201*, 175.
(11) Kuppermann, A.; Wu, Y. S. M. *Chem. Phys. Lett*. **1993**, *205*, 577.
(12) Miranda, M. P.; Clary, D. C.; Castillo, J. F.; Manolopoulos, D. E. *J. Chem. Phys*. **1998**, *108*, 3142.
(13) Skouteris, D.; Castillo, J. F.; Manolopoulos, D. E. *Comput. Phys. Commun*. **2000**, *113*, 128.
(14) Chao, S. D.; Skodje, R. T. *J. Chem. Phys*. **2000**, *113*, 3487.
(15) Fernandez-Alonso, F.; Bean, B. D.; Zare, R. N.; Aoiz, F. J.; Banares, L.; Castillo, J. F. *J. Chem. Phys.* **2001**, *114*, 4534.
(16) Kendrick, B. *J. Chem. Phys*. **2001**, *114*, 8796.
(17) Aquilanti, V.; Cavalli, S.; De Fazio, D.; Volpi, A.; Aguilar, A.; Gimenez, X.; Lucas, J. M. *Phys. Chem. Chem. Phys*. **2002**, *4*, 401.
(18) Wang, D.; Kuppermann, A. *J. Phys. Chem. A* **2003**, *107*, 7290.
(19) Wang, D.; Kuppermann, A. *J. Chem. Phys*. **2001**, *115*, 9184.
(20) Cuccaro, S. A. *Ab initio three-dimensional atom−diatom reaction cross sections using hyperspherical coordinates and variational surface functions*, Ph.D. Thesis, California Institute of Technology, Pasadena, CA 1991.

(21) Skouteris, D.; Castillo, J. F.; Manolopoulos, D. E. *Comput. Phys. Commun.* **2000**, *133*, 128.

(22) Pogrebnya, S. K.; Palma, J.; Clary, D. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 693.

(23) Mathews, J.; Walker, R. L. *Mathematical Methods of Physics*; W. A. Benjamin: New York, 1965; p 376.

(24) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons: New York, 1957; section 3.4, p 33.

(25) Merzbacher, E. *Quantum Mechanics*, 2nd ed.; John Wiley & Sons: New York, 1970; sections 9.65 and 9.65a, p 165 with his $Y_j^m$ written as $Y_m^j$ in the present paper.

(26) Davydov, A. S.; Pergamon Press: Oxford, 1976; 2nd ed., section 43.9, p 170.

(27) Davydov, A. S.; Pergamon Press: Oxford, 1976; 2nd ed., section 43.17, p 171.

(28) Davydov, A. S.; Pergamon Press: Oxford, 1976; 2nd ed., section 43.19, p 172.

(29) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons: New York, 1957; section 3.7, p 34.

(30) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons: New York, 1957; section 3.17b, p 39.

(31) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Applied Mathematics Series 55; National Bureau of Standards: Gaithersburg, MD, 1965; p 781.

(32) Davydov, A. S.; Pergamon Press: Oxford, 1976; 2nd ed., section 43.12, p 170.

(33) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons: New York, 1957; section 3.16a, p 38.

(34) Davydov, A. S.; Pergamon Press: Oxford, 1976; 2nd ed., equation preceding section 43.15, p 171.

(35) Hammermesh, M. *Group Theory*; Addison-Wesley: Reading, MA 1962; Chapter 7.