Numerical generation of hyperspherical harmonics for tetra-atomic systems

Bruno Lepetit[a)]
Laboratoire Collisions, Agrégats, Réactivité, UMR 5589, CNRS, IRSAMC, Université Paul Sabatier Toulouse 3, 31062 Toulouse Cedex 9, France

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

(Received 6 April 2006; accepted 6 June 2006; published online 5 October 2006)

A numerical generation method of hyperspherical harmonics for tetra-atomic systems, in terms of row-orthonormal hyperspherical coordinates—a hyper-radius and eight angles—is presented. The nine-dimensional coordinate space is split into three three-dimensional spaces, the physical rotation, kinematic rotation, and kinematic invariant spaces. The eight-angle principal-axes-of-inertia hyperspherical harmonics are expanded in Wigner rotation matrices for the physical and kinematic rotation angles. The remaining two-angle harmonics defined in kinematic invariant space are expanded in a basis of trigonometric functions, and the diagonalization of the kinetic energy operator in this basis provides highly accurate harmonics. This trigonometric basis is chosen to provide a mathematically exact and finite expansion for the harmonics. Individually, each basis function does not satisfy appropriate boundary conditions at the poles of the kinetic energy operator; however, the numerically generated linear combination of these functions which constitutes the harmonic does. The size of this basis is minimized using the symmetries of the system, in particular, internal symmetries, involving different sets of coordinates in nine-dimensional space corresponding to the same physical configuration.
[DOI: 10.1063/1.2218515]

I. INTRODUCTION

Hyperspherical coordinates are useful tools to perform time-independent quantum reactive scattering calculations. In particular, as compared to the more popular wave packet time-dependent method, they provide, at each energy, the full scattering matrix including all initial and final states. For a general review on quantum scattering calculations, see Ref. 1. The hyperspherical coordinate method has first been used to deal with three-body direct reactions such as $H+H_2$ (Refs. 2 and 3) and $F+H_2$,[4,5] and then extended to indirect reactions, which involve a long lived intermediate complex.[6]

To our knowledge, $OH+H_2 \rightarrow H+H_2O$ at zero total angular momentum is the only four-body reaction for which hyperspherical coordinates have been successfully used.[7,8] In it, different hyperspherical coordinates are used in the different arrangement channels of the reaction. As a result, a non-orthogonal set of rovibrational basis functions is generated, and linear dependence problems in the strong interaction region have to be overcome. The Hamiltonians for triatomic[9] and tetra-atomic[10] systems in row-orthonormal hyperspherical coordinates (ROHCs) were derived previously and display simple properties when kinematic rotations and symmetry operations are performed. The tetra-atomic ones are closely related to the coordinates used by Zickendraht[11] and consist of one hyper-radius, three Euler angles, which specify the orientation of the principal axes of inertia body frame in space, and five internal angles, which specify the shape of the molecular system. The kinetic energy operator expressed in this coordinate system displays singularities at each configuration for which two of the system's principal moments of inertia become identical. A geometrical analysis of these singularities is described in Ref. 12. The corresponding hyperspherical harmonics, which are eigenfunctions of the kinetic energy operator at fixed hyper-radius, provide a complete orthonormal basis which satisfies appropriate boundary conditions at those poles and therefore constitutes an attractive alternative to the arrangement channel hyperspherical coordinate basis on which to expand the wave function of the system. The use of these harmonics for reactive scattering calculations has been described recently.[13]

Progress in the generation of these harmonics has only been achieved recently. In his early work,[11] Zickendraht obtained the four-body harmonics for low values of the hyperangular momentum quantum number, $n=1$ and 2, by a direct coordinate transformation from the arrangement channel hyperspherical coordinate harmonics which are known analytically[14] to the row-orthonormal ones. Littlejohn *et al.*[15] and Aquilanti *et al.*[16,17] obtained analytical expressions for the harmonics, in the special case for which both angular momenta in physical space and in kinematic rotation space are zero, as linear combinations of ordinary spherical harmonics for low values of n. Wang and Kuppermann[18] derived a recursion relation for the harmonics which is general and valid for any value of both angular momenta. Using a

[a)]Electronic mail: bruno.lepetit@irsamc.ups-tlse.fr

MATHEMATICA program, they generated analytical expressions for the harmonics for all values of n up to 30, which represents a set of 43.8×10^6 harmonics. This was an important step forward, but from a practical point of view, this generation method presents several inconveniences. The recursion relation requires the knowledge of all harmonics for a given n, including all values of the total angular momentum quantum number J satisfying $J\leq n$, to generate the harmonics for $n+1$. However, in practice, scattering calculations are performed for fixed values of J which in most cases will be much smaller than the maximum value of n needed for their convergence. The large J hyperspherical harmonics unavoidably generated in the recursion method for large n are not needed for scattering calculations. In addition, this method generates over complete sets of linearly dependent harmonics which have to be culled to reduce them to linearly independent sets. This process involves rank determinations and is also computer-algebra intensive. The amount of CPU time needed to generate the harmonics by the recursion method increases as n^7 for large n and becomes impractical for $n>30$.

In the present paper, we propose an alternate approach to generate harmonics entirely numerically, but very accurately. The method relies on the selection of a suitable finite trigonometric basis in which to expand the harmonics. This basis is chosen so as to satisfy the symmetries of the problem. In some sense, this method extends the spherical harmonic expansion proposed in Ref. 17 to nonzero values of both physical and kinematic rotation space angular momentum quantum numbers, but has little in common with the symmetrized hyperspherical harmonics construction method described in Refs. 19 and 20. Our expansion is mathematically exact so that errors in the final result are due exclusively to round-off errors in finite precision numerical computations and inaccuracies in quadratures. The coefficients of the expansions are obtained numerically by diagonalization of the kinetic energy operator matrix representation in this trigonometric basis. This diagonalization is performed for fixed values of J, and therefore only the harmonics needed for each partial wave scattering calculation are generated at one time. This method is efficient, in particular, for values of n much larger than J. In Sec. II, we summarize the most important properties of row-orthonormal coordinates and of the corresponding kinetic energy operator and harmonics. In Sec. III, we describe the symmetries of the problem and show how to generate harmonics which satisfy the symmetry constraints. The trigonometric basis in which to expand the harmonics is given in Sec. IV, and in Sec. V we describe the calculation of the matrix whose diagonalization provides the expansion coefficients of the harmonics in the chosen trigonometric basis. Some tests of the present approach are described in Sec. VI, and a summary and conclusions are given in Sec. VII.

II. ROW-ORTHONORMAL HYPERSPHERICAL HARMONICS

A. Coordinates

The ROHCs used in this paper, the kinetic energy operator as well as the corresponding harmonics, have been described previously.[10,18] We only summarize here their definitions and properties and refer the reader to these papers for further details. Let us call $(\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3)$ the unit vectors of a reference frame for the three-dimensional physical space. Let $\boldsymbol{\rho}_\lambda^{\rm sf}$ be the Jacobi matrix, whose columns are the three Cartesian coordinates in this frame of the three mass-scaled Jacobi vectors $(\mathbf{r}_\lambda^{(1)},\mathbf{r}_\lambda^{(2)},\mathbf{r}_\lambda^{(3)})$ associated with a given clustering scheme λ. It is given by a matrix of dot products

$$\boldsymbol{\rho}_\lambda^{\rm sf}=\begin{pmatrix}\mathbf{i}_1\mathbf{r}_\lambda^{(1)} & \mathbf{i}_1\mathbf{r}_\lambda^{(2)} & \mathbf{i}_1\mathbf{r}_\lambda^{(3)}\\ \mathbf{i}_2\mathbf{r}_\lambda^{(1)} & \mathbf{i}_2\mathbf{r}_\lambda^{(2)} & \mathbf{i}_2\mathbf{r}_\lambda^{(3)}\\ \mathbf{i}_3\mathbf{r}_\lambda^{(1)} & \mathbf{i}_3\mathbf{r}_\lambda^{(2)} & \mathbf{i}_3\mathbf{r}_\lambda^{(3)}\end{pmatrix}, \tag{1}$$

which can be written in a more compact form

$$\boldsymbol{\rho}_\lambda^{\rm sf}=\begin{pmatrix}\mathbf{i}_1\\ \mathbf{i}_2\\ \mathbf{i}_3\end{pmatrix}(\mathbf{r}_\lambda^{(1)}\ \mathbf{r}_\lambda^{(2)}\ \mathbf{r}_\lambda^{(3)}). \tag{2}$$

This expression is valid if the $\mathbf{i}_i$ and $\mathbf{r}_\lambda^{(j)}$ are considered to be abstract vectors. They are also valid if the $\mathbf{i}_i$ are taken to be row vectors and the $\mathbf{r}_\lambda^{(j)}$ column vectors whose elements are their Cartesian components in the space-fixed frame considered here. Performing a singular value decomposition of this matrix,[21,22] we obtain

$$\boldsymbol{\rho}_\lambda^{\rm sf}=(-1)^\chi\tilde{\mathbf{R}}(\mathbf{a}_\lambda)\rho\mathbf{N}(\theta,\phi)\tilde{\mathbf{R}}(\boldsymbol{\delta}_\lambda), \tag{3}$$

where χ is the chirality variable, $\mathbf{a}_\lambda$ refers collectively to the three Euler angles $(a_\lambda,b_\lambda,c_\lambda)$ of the principal axes of inertia frame with respect to $(\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3)$, and ρ is the usual hyperradius which, together with the angles θ and ϕ, parametrizes the three principal moments of inertia of the system and defines the kinematic invariant space.[15] Three additional angles $(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$ collectively denoted by $\boldsymbol{\delta}_\lambda$ complete the parametrization of the system and define kinematic rotations.[11] The matrix $\tilde{\mathbf{R}}(\mathbf{a}_\lambda)$ is the transpose of the rotation matrix defined by[9]

$$\mathbf{R}(\mathbf{a}_\lambda)=\mathbf{M}_1(c_\lambda)\mathbf{M}_2(b_\lambda)\mathbf{M}_1(a_\lambda), \tag{4}$$

where

$$\mathbf{M}_1(\omega)=\begin{pmatrix}\cos\omega & \sin\omega & 0\\ -\sin\omega & \cos\omega & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{5}$$

and

$$\mathbf{M}_2(\omega)=\begin{pmatrix}\cos\omega & 0 & -\sin\omega\\ 0 & 1 & 0\\ \sin\omega & 0 & \cos\omega\end{pmatrix}. \tag{6}$$

These definitions are also valid for $\tilde{\mathbf{R}}(\boldsymbol{\delta}_\lambda)$. The matrix $\mathbf{N}(\theta,\phi)$ is a diagonal matrix, with diagonal elements

$$N_{11}(\theta,\phi)=\sin\theta\cos\phi,\quad N_{22}(\theta,\phi)=\sin\theta\sin\phi,$$
$$N_{33}(\theta,\phi)=\cos\theta. \tag{7}$$

It was previously shown[10] that a one-to-one correspondence can be achieved between physical configurations and coordinate space by restricting the hyperspherical angles to

$$0 \leqslant a_\lambda, c_\lambda < 2\pi, \quad 0 \leqslant b_\lambda \leqslant \pi, \tag{8}$$

$$0 \leqslant \delta_\lambda^{(1)}, \delta_\lambda^{(3)} < \pi, \quad 0 \leqslant \delta_\lambda^{(2)} \leqslant \pi, \tag{9}$$

$$\begin{aligned} &0 \leqslant \phi \leqslant \pi/4, \\ &0 \leqslant \theta \leqslant \theta_M = \arcsin[1/(1+\cos^2\phi)^{1/2}] \\ &\qquad\qquad \leqslant \arcsin(2/3)^{1/2} \simeq 54.7°, \end{aligned} \tag{10}$$

with $\chi=0$ or 1. An alternative is to restrict the chirality to $\chi=0$ and to extend the range of variation of θ and ϕ to encompass left-handed configurations. Since $\mathbf{N}(\pi-\theta,\pi+\phi) = -\mathbf{N}(\theta,\phi)$, this is achieved by allowing θ to be also in $[\pi - \theta_M, \pi]$ together with ϕ in $[\pi, 5\pi/4]$.

In fact, it is useful to further lift the constraint of having a one-to-one correspondence between configurations and coordinates in order to exhibit the symmetries in the hyperspherical coordinate space. For instance, extending the range of $\boldsymbol{\delta}_\lambda$ in Ref. 18 led to relations (3.25) and (3.26) of that paper. Following Ref. 15, we allow θ and ϕ to span the entire sphere and do not specify bounds for the angles $(a_\lambda, b_\lambda, c_\lambda)$ and $(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$. The chirality coordinate is not necessary in this extended space where several coordinate sets correspond to the same physical configuration. The number of such coordinates is therefore reduced from 10 to 9. In addition to the $(a_\lambda, b_\lambda, c_\lambda)$ coordinate space which is the physical rotation space $\mathcal{S}^{\mathcal{PR}}$, we define the $(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ coordinate space as the kinematic rotation space $\mathcal{S}^{\mathcal{KR}}$ and the (ρ, θ, ϕ) space the kinematic invariant space $\mathcal{S}^{\mathcal{KI}}$.

The body-frame in $\mathcal{S}^{\mathcal{PR}}$ tied to the principal axes of inertia $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$ is defined by

$$\begin{pmatrix} \mathbf{I}_1^\lambda \\ \mathbf{I}_2^\lambda \\ \mathbf{I}_3^\lambda \end{pmatrix} = \mathbf{R}(\mathbf{a}_\lambda) \begin{pmatrix} \mathbf{i}_1 \\ \mathbf{i}_2 \\ \mathbf{i}_3 \end{pmatrix}. \tag{11}$$

Similarly, we define in $\mathcal{S}^{\mathcal{KR}}$ rotated Jacobi vectors $(\mathbf{R}_1^\lambda, \mathbf{R}_2^\lambda, \mathbf{R}_3^\lambda)$ by

$$(\mathbf{R}_1^\lambda \ \mathbf{R}_2^\lambda \ \mathbf{R}_3^\lambda) = (\mathbf{r}_\lambda^{(1)} \ \mathbf{r}_\lambda^{(2)} \ \mathbf{r}_\lambda^{(3)}) \mathbf{R}(\delta_\lambda). \tag{12}$$

Equation (2) can then be rewritten in the form

$$\begin{pmatrix} \mathbf{I}_1^\lambda \\ \mathbf{I}_2^\lambda \\ \mathbf{I}_3^\lambda \end{pmatrix} (\mathbf{R}_1^\lambda \ \mathbf{R}_2^\lambda \ \mathbf{R}_3^\lambda) = \rho \mathbf{N}(\theta, \phi). \tag{13}$$

Since the matrix $\mathbf{N}(\theta,\phi)$ is diagonal, each of the three vectors $\mathbf{R}_i^\lambda$ $(i=1-3)$ is aligned with the corresponding $\mathbf{I}_i^\lambda$.

We define in $\mathcal{S}^{\mathcal{KI}}$ a reference orthonormal frame $(\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3)$ and a fixed vector $\boldsymbol{\rho}=\rho\mathbf{u}_3$. We then consider a (θ,ϕ)-dependent orthonormal frame $(\mathbf{U}_1, \mathbf{U}_2, \mathbf{U}_3)$ such that $\mathbf{U}_i\boldsymbol{\rho}=\rho N_{ii}(\theta,\phi)$. A possible choice is

$$(\mathbf{U}_1 \ \mathbf{U}_2 \ \mathbf{U}_3) = (\mathbf{u}_1 \ \mathbf{u}_2 \ \mathbf{u}_3) \mathbf{R}(\phi, \theta, \varphi), \tag{14}$$

where the value of the angle φ is arbitrary. Using the orthonormality of the frame $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$, the matrix equation (13) becomes equivalent to the three equations:

$$\mathbf{R}_i^\lambda = (\mathbf{U}_i \boldsymbol{\rho}) \mathbf{I}_i^\lambda, \quad i = 1-3. \tag{15}$$

This equation provides a simple geometrical construction of the Jacobi vectors from the set of nine coordinates. A rotation by the Euler angles $(a_\lambda, b_\lambda, c_\lambda)$ is first performed to generate $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$ from $(\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3)$. The length of the vectors $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$ is then adjusted according to Eq. (15) to generate $(\mathbf{R}_1^\lambda, \mathbf{R}_2^\lambda, \mathbf{R}_3^\lambda)$. The rotation through angles $(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ using Eq. (12) finally yields the desired Jacobi vectors. The different sets of coordinates that correspond to the same physical configuration are associated with different sets of the nine vectors $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$, $(\mathbf{U}_1, \mathbf{U}_2, \mathbf{U}_3)$, and $(\mathbf{R}_1^\lambda, \mathbf{R}_2^\lambda, \mathbf{R}_3^\lambda)$ linked by Eq. (15).

We require in the following that the wave function of the system should be the same for all these different sets of coordinates corresponding to the same physical configuration. This requirement is not valid in the presence of conical intersections between electronic potential energy surfaces.[3,23] In this case, the (nuclear) wave function changes sign as the system traverses a closed loop around the conical intersection in nine-dimensional configuration space. Specific harmonics have to be built in these cases, as was done in Ref. 24 for the triatomic case.

B. Hamiltonian

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

$$\hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 = \hat{T}_\rho(\rho) + \frac{\hat{\Lambda}^2}{2\mu\rho^2}, \tag{16}$$

where ∇^2 is the nine-dimensional Laplacian, and $\hat{\Lambda}^2$ is the grand-canonical angular momentum operator,

$$\hat{\Lambda}^2 = \hat{K}^2(\theta,\phi) + \hat{B}(\theta,\phi) + \hat{C}^2(\boldsymbol{\Theta}_\lambda), \tag{17}$$

where Θ_λ denotes the set of eight internal hyperangles $(\mathbf{a}_\lambda, \theta, \phi, \boldsymbol{\delta}_\lambda)$ and $\hat{T}_\rho(\rho)$ is the hyper-radial kinetic energy operator,

$$\hat{T}_\rho(\rho) = -\frac{\hbar^2}{2\mu}\frac{1}{\rho^8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho}. \tag{18}$$

The terms in Eq. (17) are defined by

$$\hat{K}^2(\theta,\phi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{19}$$

$$\hat{B}(\theta,\phi) = -2\hbar^2\left[b_\theta(\theta,\phi)\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}b_\phi(\theta,\phi)\frac{\partial}{\partial\phi}\right], \tag{20}$$

$$\begin{aligned} b_\theta(\theta,\phi) = &\frac{N'_{\theta_{11}}N_{11} - N'_{\theta_{22}}N_{22}}{N_{11}^2 - N_{22}^2} + \frac{N'_{\theta_{11}}N_{11} - N'_{\theta_{33}}N_{33}}{N_{11}^2 - N_{33}^2} \\ &+ \frac{N'_{\theta_{22}}N_{22} - N'_{\theta_{33}}N_{33}}{N_{22}^2 - N_{33}^2}, \end{aligned} \tag{21}$$

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

and

$$\begin{aligned}\hat{C}^2(\mathbf{\Theta}_\lambda)=&\frac{N_{22}^2+N_{33}^2}{(N_{22}^2-N_{33}^2)^2}[\hat{J}_1^{I_\lambda 2}+\hat{L}_{\lambda_1}^2]-\frac{4N_{22}N_{33}}{(N_{22}^2-N_{33}^2)^2}\hat{L}_{\lambda_1}\hat{J}_1^{I_\lambda}\\&+\frac{N_{11}^2+N_{33}^2}{(N_{11}^2-N_{33}^2)^2}[\hat{J}_2^{I_\lambda 2}+\hat{L}_{\lambda_2}^2]-\frac{4N_{11}N_{33}}{(N_{11}^2-N_{33}^2)^2}\hat{L}_{\lambda_2}\hat{J}_2^{I_\lambda}\\&+\frac{N_{11}^2+N_{22}^2}{(N_{11}^2-N_{22}^2)^2}[\hat{J}_3^{I_\lambda 2}+\hat{L}_{\lambda_3}^2]-\frac{4N_{11}N_{22}}{(N_{11}^2-N_{22}^2)^2}\hat{L}_{\lambda_3}\hat{J}_3^{I_\lambda},\end{aligned} \tag{23}$$

where

$$N'_{\theta_{11}}=\cos\theta\cos\phi,\quad N'_{\theta_{22}}=\cos\theta\sin\phi,\quad N'_{\theta_{33}}=-\sin\theta, \tag{24}$$

$$M_{\phi_{11}}=-\sin\phi,\quad M_{\phi_{22}}=\cos\phi. \tag{25}$$

The $\hat{J}_1^{I_\lambda}$, $\hat{J}_2^{I_\lambda}$, and $\hat{J}_3^{I_\lambda}$ operators in Eq. (23) are the components of the nuclear motion angular momentum operator in the body-fixed frame $(\mathbf{I}_1^\lambda,\mathbf{I}_2^\lambda,\mathbf{I}_3^\lambda)$ and $\hat{L}_{\lambda_1}$, $\hat{L}_{\lambda_2}$, and $\hat{L}_{\lambda_3}$ are the components of the $\boldsymbol{\delta}_\lambda$-dependent internal angular momentum operator in a space-fixed-type mathematical frame associated with those $\boldsymbol{\delta}_\lambda$ angles.

C. Harmonics

The five operators $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{J}_z^{\rm sf}$, $\hat{L}^2$, and $\hat{L}_{\lambda_3}^{\rm bf}$ commute with each other. $\hat{J}^2$ is the nuclear motion angular momentum squared, $\hat{J}_z^{\rm sf}$ its component along $\mathbf{i}_3$, $\hat{L}^2$ is the internal angular momentum squared, and $\hat{L}_{\lambda_3}^{\rm bf}$ is the third-body-fixed-type component. Let $F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\chi,\mathbf{\Theta}_\lambda)$ be the simultaneous eigenfunctions of those five operators:

$$\hat{\Lambda}^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=n(n+7)\hbar^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda), \tag{26}$$

$$\hat{J}^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=J(J+1)\hbar^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda), \tag{27}$$

$$\hat{J}_z^{\rm sf}F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=M_J\hbar F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda), \tag{28}$$

$$\hat{L}^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=L(L+1)\hbar^2F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda), \tag{29}$$

$$\hat{L}_{\lambda_3}^{\rm bf}F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=M_{L_\lambda}\hbar F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda). \tag{30}$$

The quantum numbers n, J, M_J, L, and M_{L_λ} appearing in these expressions are all integers, satisfying the constraints

$$n\geq 0,\quad 0\leq J,L\leq n, \tag{31}$$

$$-J\leq M_J\leq J,\quad -L\leq M_{L_\lambda}\leq L. \tag{32}$$

The subscript d and superscript D indicate that the F functions can be degenerate, i.e., for a given set of quantum numbers n, J, M_J, L, and M_{L_λ}, there are D linearly independent F functions. The subscript d indicates which of those degenerate functions is being considered.

These functions can be written as

$$\begin{aligned}F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)=&\sum_{\Omega_{J_\lambda}=-J}^{J}\sum_{\Omega_{L_\lambda}=-L}^{L}D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)\\&\times G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{33}$$

where $D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ and $D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)$ are the Wigner rotation matrices.[25] The F functions given by Eq. (33), which are furthermore required to be regular at the poles of these five operators, are called eight-angle principal-axes-of-inertia hyperspherical harmonics, and the G functions are called two-angle principal-axes-of-inertia hyperspherical harmonics, or simply F hyperspherical harmonics or functions and G hyperspherical harmonics or functions, respectively.

III. SYMMETRIZED HARMONICS

A. Internal and external symmetries

In this section we construct harmonics which are symmetrized with respect to two types of symmetries, internal and external ones. We call internal symmetry operations those in nine dimensional coordinate space $(\mathbf{a}_\lambda,\rho,\theta,\phi,\boldsymbol{\delta}_\lambda)$ which do not modify the physical configuration of the system. The space-fixed Jacobi vectors are invariant under the latter operations, and as a consequence so is the kinetic energy operator, which can be written as a function of the second derivatives with respect to the cartesian coordinates of the mass-scaled space-fixed Jacobi vectors. As stated in Sec. II A, there are several sets of nine coordinates which correspond to a given set of space-fixed Jacobi vectors. As a simple example, it is clear from Eqs. (3) and (7) that keeping the $\mathbf{a}_\lambda$ and $\boldsymbol{\delta}_\lambda$ unchanged, but changing (θ,ϕ) into $(2\pi-\theta,\pi+\phi)$ provides the same physical configuration, i.e., the same set of space-fixed Jacobi vectors. The eight-angle, and thus the two-angle, harmonics should be left unchanged by this transformation, which results in the symmetry relation

$$\textbf{ISYM0}:\ G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(2\pi-\theta,\phi+\pi)=G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \tag{34}$$

Let us call G_S a group of N_S operations $\hat{O}_i$ which transform a set of coordinates into another one, but do not change the physical configuration. As also stated in Sec. II A, we assume that these operations leave the wave function unchanged so that the latter forms a basis for the completely symmetric representation of G_S. Such completely symmetric wave functions can be obtained from the harmonics $F^{nJ\,L\,D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)$ by applying the symmetrization operator $\hat{S}_{G_S}$,

$$\hat{S}_{G_S}=\mathcal{N}\sum_{i=1,N_S}\hat{O}_i, \tag{35}$$

$$^{(G_S)}F^{nJ\ L\ D}_{M_J M_{L_\lambda} d}(\Theta_\lambda) = \hat{\mathcal{S}}_{G_S} F^{nJ\ L\ D}_{M_J M_{L_\lambda} d}(\Theta_\lambda). \quad (36)$$

The superscript before the symmetrized function keeps track of the symmetry group which has been used to symmetrize the harmonic, and $\mathcal{N}$ is a normalization constant.

External symmetry operators change the configuration of the system and thus the corresponding Jacobi vectors, but commute with the kinetic energy operator. One example is the inversion operator $\hat{I}$ which changes the three Jacobi vectors to their opposite. Another are the operations which exchange identical particles and which form a group. The wave function is not necessarily kept unchanged by such operations. However, it is a basis for an irreducible representation of the symmetry group, not necessarily the completely symmetric one, and not necessarily a one-dimensional representation either.

In the following subsections, we show how to construct symmetric harmonics with respect to these two types of operations.

B. Internal symmetries

1. Symmetrization procedure

The internal symmetry group will turn out to be a fairly large group of order $N_S=96$, so that the direct symmetrization procedure suggested by Eq. (36) is difficult to apply in practice. The use of composition series and factor groups transforms this large symmetrization problem into a set of simpler ones.[26] A composition series for G_S is a series of N_Q+1 subgroups H_j starting with the one-element identity group E and ending with G_S: $H_0 = E \subset H_1 \subset \cdots H_j \subset \cdots \subset H_{N_Q} = G_S$. Each H_j is a maximal normal subgroup of H_{j+1}. Let us call Q_j the N_Q quotient groups: $Q_j = H_{j+1}/H_j$, and N_{Q_j} the order of each of these quotient groups. The order of the group G_S is given by $N_S = \Pi_{j=1,N_Q} N_{Q_j}$. In contrast, the number of different elements necessary to generate G_S from its factors is the number of different elements of $\cup_{j=1,N_Q} Q_j$, i.e., $(\Sigma_{j=1,N_Q} N_{Q_j}) - N_Q + 1$ (E being the only element common to all factor groups), which is smaller than the order of G_S. This small number of generating elements, as compared to the total number of elements in the group, is one reason that makes composition series a useful tool to handle large groups. As an example, the full tetrahedral group T_d (including reflection) is of order 24 and has the composition series

$$E \subset C_2 \subset D_2 \subset T \subset T_d, \quad (37)$$

where C_2 is the cyclic group of order 2, D_2 the dihedral group of order 4 (also called Vierergruppe V), and T the tetrahedral group of order 12 (including rotations only). The factor groups are $D_2/C_2 = C_2$, $T/D_2 = C_3$, and $T_d/T = C_s$, where C_3 is the order 3 cyclic group and C_s the order 2 group containing E and a symmetry with respect to a reflection plane. The number of different elements in the factor groups is 6, four times smaller than the order of T_d. More on composition series and factor groups can be found in Ref. 26.

Any element of G_S has a unique factorization as an ordered product: $\hat{O}_i = \Pi_{j=1,N_Q} \hat{O}_{i_j}$, where $\hat{O}_{i_j} \in Q_j$. As a result, the symmetrization operator Eq. (35) can be factored as

$$\hat{\mathcal{S}}_{G_S} = \Pi_{j=1,N_Q} \hat{\mathcal{S}}_{Q_j}, \quad (38)$$

where $\hat{S}_{Q_j}$ is the symmetrization operator for the factor group Q_j. The symmetrization with $\hat{S}_{G_S}$ is thus replaced by a set of successive partial symmetrizations with the $\hat{S}_{Q_j}$, which are usually much simpler to perform. In the next section, we first find the internal symmetry factor groups, and then obtain in Sec. III B 3 the full internal symmetry group G_S by a composition series. In Sec. III B 4, we then perform successive symmetrization of the harmonics using the factor group symmetrization operators to obtain symmetry relations for the harmonics.

2. Internal symmetry factor groups

The symmetry operations are defined simultaneously in three three-dimensional spaces, the physical rotation, kinematic rotation, and kinematic invariant spaces. The usual Schoenflies notations[27,28] have to be adapted to this context. We denote by $C_n^{i(\mathbf{A})}$ $(i=0,\ldots,n-1)$ a rotation by $i(2\pi/n)$ around the axis $\mathbf{A}$ in one of the three spaces. We denote by $C^{\{\mathbf{A},\mathbf{B}\}}$ a reflection through the $\{\mathbf{A},\mathbf{B}\}$ plane. These operations can be combined to occur simultaneously in different spaces. For instance, $C_n^{i(\mathbf{A},\mathbf{B})}$ represents two simultaneous rotations by the same angle $i(2\pi/n)$, performed in the two different spaces containing $\mathbf{A}$ and $\mathbf{B}$, respectively. We call this operation a double rotation. $C_n^{i(\mathbf{A},\mathbf{B},\mathbf{C})}$ is a triple rotation, consisting of three rotations by the same angle $i(2\pi/n)$, performed in the three different spaces containing $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, respectively. $C_n^{i(\mathbf{A},\{\mathbf{B},\mathbf{C}\},\mathbf{D})}$ is a double rotation-single reflection operation, consisting of two rotations by $i(2\pi/n)$ in the two different spaces containing $\mathbf{A}$ and $\mathbf{D}$, and a single reflection through the $\{\mathbf{B},\mathbf{C}\}$ plane in the space which contains this plane. These operations generate cyclic groups which are labeled in a similar fashion. For instance, the order n cyclic groups containing the single, double, and triple rotations by angle $i(2\pi/n)$ are labeled $C_n^{(\mathbf{A})}$, $C_n^{(\mathbf{A},\mathbf{B})}$ and $C_n^{(\mathbf{A},\mathbf{B},\mathbf{C})}$ respectively. The order 2 cyclic group containing the identity and $C_2^{1(\mathbf{A},\{\mathbf{B},\mathbf{C}\},\mathbf{D})}$ is labeled $C_2^{(\mathbf{A},\{\mathbf{B},\mathbf{C}\},\mathbf{D})}$.

We list in Table I a set of internal symmetry factor groups. All these six factor groups are Abelian cyclic groups of order 2 or 3. Only the elements different from identity are given for each group. The effect of the operations in each space can be defined in two equivalent ways.

- Transformation of nine basis vectors from $(\mathbf{I}_1^\lambda, \mathbf{I}_2^\lambda, \mathbf{I}_3^\lambda)$, $(\mathbf{U}_1, \mathbf{U}_2, \mathbf{U}_3)$, and $(\mathbf{R}_1^\lambda, \mathbf{R}_2^\lambda, \mathbf{R}_3^\lambda)$ to $(\mathbf{I}_1^{\lambda'}, \mathbf{I}_2^{\lambda'}, \mathbf{I}_3^{\lambda'})$, $(\mathbf{U}_1', \mathbf{U}_2', \mathbf{U}_3')$, and $(\mathbf{R}_1^{\lambda'}, \mathbf{R}_2^{\lambda'}, \mathbf{R}_3^{\lambda'})$. The primed quantities are defined explicitly for each operation in rows 3, 6, and 9 of Table I.
- Transformation of the eight coordinates from $(a_\lambda, b_\lambda, c_\lambda)$, (θ, ϕ), and $(\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$ to $(a_\lambda', b_\lambda', c_\lambda')$,

TABLE I. Internal symmetry factor groups. The labeling of the groups and operations are defined in the text. $\mathcal{P}$ stands for the plane: $\mathcal{P}=\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\}$. For each group, only the single element (for C_2-type groups) or the two elements (for C_3-type) different from the identity element are given. The basis vectors $(\mathbf{I}_1^\lambda,\mathbf{I}_2^\lambda,\mathbf{I}_3^\lambda)$, $(\mathbf{R}_1^\lambda,\mathbf{R}_2^\lambda,\mathbf{R}_3^\lambda)$, and $(\mathbf{U}_1,\mathbf{U}_2,\mathbf{U}_3)$ are transformed into $(\mathbf{I}_1^{\lambda'},\mathbf{I}_2^{\lambda'},\mathbf{I}_3^{\lambda'})$, $(\mathbf{R}_1^{\lambda'},\mathbf{R}_2^{\lambda'},\mathbf{R}_3^{\lambda'})$, and $(\mathbf{U}_1',\mathbf{U}_2',\mathbf{U}_3')$ by the symmetry operations. Explicit expressions for the transformed vectors are given in rows 3, 6, and 9 of the table. The angles $(a_\lambda,b_\lambda,c_\lambda)$, (θ,ϕ), and $(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$ of the system are transformed by the operation into $(a_\lambda',b_\lambda',c_\lambda')$, (θ',ϕ'), and $(\delta_\lambda^{(1)'},\delta_\lambda^{(2)'},\delta_\lambda^{(3)'})$ as shown in rows 5, 8, and 10 of the table. The row labeled $(a_\lambda^O,b_\lambda^O,c_\lambda^O)$ gives the Euler angles associated with the operations in physical rotation space and are defined by $\mathbf{R}(a_\lambda',b_\lambda',c_\lambda')=\mathbf{R}(a_\lambda^O,b_\lambda^O,c_\lambda^O)\mathbf{R}(a_\lambda,b_\lambda,c_\lambda)$. A similar definition holds for $(\delta_\lambda^{(1)O},\delta_\lambda^{(2)O},\delta_\lambda^{(3)O})$ in kinematic rotation space, except that rotations act in the reverse order: $\mathbf{R}(\delta_\lambda^{(1)'},\delta_\lambda^{(2)'},\delta_\lambda^{(3)'})=\mathbf{R}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})\mathbf{R}(\delta_\lambda^{(1)O},\delta_\lambda^{(2)O},\delta_\lambda^{(3)O})$. The angles θ^1 and ϕ^1 are implicitly defined by the relations $\sin\theta^1\cos\phi^1=\sin\theta\sin\phi$, $\sin\theta^1\sin\phi^1=\cos\theta$, $\cos\theta^1=\sin\theta\cos\phi$. Similarly, $\sin\theta^2\cos\phi^2=\cos\theta$, $\sin\theta^2\sin\phi^2=\sin\theta\cos\phi$, and $\cos\theta^2=\sin\theta\sin\phi$. Implicit expressions for a^1,b^1,c^1 can be obtained from $\mathbf{R}(a^1,b^1,c^1)=\mathbf{R}(0,\pi/2,\pi/2)\mathbf{R}(a,b,c)$. Similarly for (a^2,b^2,c^2) we have $\mathbf{R}(a^2,b^2,c^2)=\mathbf{R}(\pi/2,\pi/2,\pi)\mathbf{R}(a,b,c)$, and in kinematic rotation space $\mathbf{R}(\delta_\lambda^{(1)1},\delta_\lambda^{(2)1},\delta_\lambda^{(3)1})=\mathbf{R}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})\mathbf{R}(\pi/2,\pi/2,\pi)$, and $\mathbf{R}(\delta_\lambda^{(1)2},\delta_\lambda^{(2)2},\delta_\lambda^{(3)2})=\mathbf{R}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})\mathbf{R}(0,\pi/2,\pi/2)$.

Group	$C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$	$C_2^{(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$	$C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$	$C_2^{(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$	$C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\mathcal{P},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$	$C_3^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda,\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3,\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda)}$	
Operation	$C_2^{1(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$	$C_2^{1(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$	$C_2^{1(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$	$C_1^{1(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$	$C_2^{1(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\mathcal{P},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$	$C_3^{1(\Sigma\mathbf{I}_i^\lambda,\Sigma\mathbf{U}_i,\Sigma\mathbf{R}_i^\lambda)}$	$C_3^{2(\Sigma\mathbf{I}_i^\lambda,\Sigma\mathbf{U}_i,\Sigma\mathbf{R}_i^\lambda)}$
$\begin{pmatrix}\mathbf{I}_1^{\lambda'}\\\mathbf{I}_2^{\lambda'}\\\mathbf{I}_3^{\lambda'}\end{pmatrix}$	$\begin{pmatrix}-\mathbf{I}_1^\lambda\\-\mathbf{I}_2^\lambda\\\mathbf{I}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_1^\lambda\\\mathbf{I}_2^\lambda\\\mathbf{I}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_1^\lambda\\-\mathbf{I}_2^\lambda\\-\mathbf{I}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_1^\lambda\\\mathbf{I}_2^\lambda\\\mathbf{I}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_2^\lambda\\\mathbf{I}_1^\lambda\\-\mathbf{I}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_2^\lambda\\\mathbf{I}_3^\lambda\\\mathbf{I}_1^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{I}_3^\lambda\\\mathbf{I}_1^\lambda\\\mathbf{I}_2^\lambda\end{pmatrix}$
$(a_\lambda^O, b_\lambda^O, c_\lambda^O)$	$(0,0,\pi)$	(0,0,0)	$(\pi,\pi,0)$	(0,0,0)	$(0,\pi,\pi/2)$	$(0,\pi/2,\pi/2)$	$(\pi/2,\pi/2,\pi)$
$(a_\lambda',b_\lambda',c_\lambda')$	$(a_\lambda, b_\lambda, \pi+c_\lambda)$	$(a_\lambda,b_\lambda,c_\lambda)$	$(\pi+a_\lambda, \pi-b_\lambda, 2\pi-c_\lambda)$	$(a_\lambda,b_\lambda,c_\lambda)$	$(\pi+a_\lambda, \pi-b_\lambda, 3\pi/2-c_\lambda)$	$(a_\lambda^1,b_\lambda^1,c_\lambda^1)$	$(a_\lambda^2,b_\lambda^2,c_\lambda^2)$
$\begin{pmatrix}\mathbf{R}_1^{\lambda'}\\\mathbf{R}_2^{\lambda'}\\\mathbf{R}_3^{\lambda'}\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_1^\lambda\\\mathbf{R}_2^\lambda\\\mathbf{R}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}-\mathbf{R}_1^\lambda\\-\mathbf{R}_2^\lambda\\\mathbf{R}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_1^\lambda\\\mathbf{R}_2^\lambda\\\mathbf{R}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_1^\lambda\\-\mathbf{R}_2^\lambda\\-\mathbf{R}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_2^\lambda\\\mathbf{R}_1^\lambda\\-\mathbf{R}_3^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_2^\lambda\\\mathbf{R}_3^\lambda\\\mathbf{R}_1^\lambda\end{pmatrix}$	$\begin{pmatrix}\mathbf{R}_3^\lambda\\\mathbf{R}_1^\lambda\\\mathbf{R}_2^\lambda\end{pmatrix}$
$(\delta_\lambda^{(1)O}, \delta_\lambda^{(2)O}, \delta_\lambda^{(3)O})$	(0,0,0)	$(0,0,\pi)$	(0,0,0)	$(\pi,\pi,0)$	$(0,\pi,\pi/2)$	$(\pi/2,\pi/2,\pi)$	$(0,\pi/2,\pi/2)$
$(\delta_\lambda^{(1)'}, \delta_\lambda^{(2)'}, \delta_\lambda^{(3)'})$	$(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$	$(\pi+\delta_\lambda^{(1)}, \delta_\lambda^{(2)}, \delta_\lambda^{(3)})$	$(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$	$(2\pi-\delta_\lambda^{(1)}, \pi-\delta_\lambda^{(2)}, \pi+\delta_\lambda^{(3)})$	$(\pi/2-\delta_\lambda^{(1)}, \pi-\delta_\lambda^{(2)}, \pi+\delta_\lambda^{(3)})$	$(\delta_\lambda^{(1)1}, \delta_\lambda^{(2)1}, \delta_\lambda^{(3)1})$	$(\delta_\lambda^{(1)2}, \delta_\lambda^{(2)2}, \delta_\lambda^{(3)2})$
$\begin{pmatrix}\mathbf{U}_1'\\\mathbf{U}_2'\\\mathbf{U}_3'\end{pmatrix}$	$\begin{pmatrix}-\mathbf{U}_1\\-\mathbf{U}_2\\\mathbf{U}_3\end{pmatrix}$	$\begin{pmatrix}-\mathbf{U}_1\\-\mathbf{U}_2\\\mathbf{U}_3\end{pmatrix}$	$\begin{pmatrix}\mathbf{U}_1\\-\mathbf{U}_2\\-\mathbf{U}_3\end{pmatrix}$	$\begin{pmatrix}\mathbf{U}_1\\-\mathbf{U}_2\\-\mathbf{U}_3\end{pmatrix}$	$\begin{pmatrix}\mathbf{U}_2\\\mathbf{U}_1\\\mathbf{U}_3\end{pmatrix}$	$\begin{pmatrix}\mathbf{U}_2\\\mathbf{U}_3\\\mathbf{U}_1\end{pmatrix}$	$\begin{pmatrix}\mathbf{U}_3\\\mathbf{U}_1\\\mathbf{U}_2\end{pmatrix}$
(θ',ϕ')	$(\theta,\phi+\pi)$	$(\theta,\phi+\pi)$	$(\pi-\theta,2\pi-\phi)$	$(\pi-\theta,2\pi-\phi)$	$(\theta,\pi/2-\phi)$	(θ^1,ϕ^1)	(θ^2,ϕ^2)

(θ',ϕ'), and $(\delta_\lambda^{(1)'},\delta_\lambda^{(2)'},\delta_\lambda^{(3)'})$, as defined in the rows 5, 8, and 10 of Table I. ρ is kept invariant by all operations considered here.

Since these transformations are all rotations in $\mathcal{S}^{\mathcal{PR}}$ and $\mathcal{S}^{\mathcal{KR}}$, we also give in rows 4 and 7 of Table I the Euler angles $(a_\lambda^O,b_\lambda^O,c_\lambda^O)$ and $(\delta_\lambda^{(1)O},\delta_\lambda^{(2)O},\delta_\lambda^{(3)O})$ associated with them.

The operation labeled $C_2^{1(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$ is a rotation by π simultaneously around $\mathbf{I}_3^\lambda$ in $\mathcal{S}^{\mathcal{PR}}$ and $\mathbf{U}_3$ in $\mathcal{S}^{\mathcal{KI}}$. It has no effect on the kinematic rotation space. It changes two of the three basis vectors in physical rotation and kinematic invariant spaces in such a way as to make the three equations (15) still be fulfilled after the transformation. Thus, this transformation is indeed an internal symmetry operation. Together with the identity, this operation forms the order 2 cyclic group $C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$.

The operation $C_2^{1(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$ is the same as $C_2^{1(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$, except that the rotation in physical rotation space is replaced by a similar one in kinematic rotation space (a rotation of π around $\mathbf{R}_3^\lambda$). Looking at Eq. (15), it is straightforward to verify that this is an internal symmetry. Together with the identity, it forms the order 2 internal symmetry group labeled $C_2^{(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$.

The operations $C_2^{1(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ and $C_2^{1(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$ are defined similar to the previous ones, where $\mathbf{I}_3^\lambda$, $\mathbf{U}_3$, and $\mathbf{R}_3^\lambda$ are replaced by

$\mathbf{I}_1^\lambda$, $\mathbf{U}_1$, and $\mathbf{R}_1^\lambda$, respectively. With the identity operation, they define two other order 2 internal symmetry factor groups labeled $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ and $C_2^{(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$.

The operation $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$ induces a permutation of vectors $\mathbf{I}_1^\lambda$ and $\mathbf{I}_2^\lambda$ in $\mathcal{S}^{\mathcal{PR}}$, of vector $\mathbf{U}_1$ with $\mathbf{U}_2$ in $\mathcal{S}^{\mathcal{KI}}$, and $\mathbf{R}_1^\lambda$ with $\mathbf{R}_2^\lambda$ in $\mathcal{S}^{\mathcal{KR}}$. It also changes the sign of $\mathbf{I}_3^\lambda$ and $\mathbf{R}_3^\lambda$; however, in order to satisfy Eq. (15), the vector $\mathbf{U}_3$ must be kept unchanged. As a result, whereas this operation corresponds to rotations by π around $\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda$ in $\mathcal{S}^{\mathcal{PR}}$ and around $\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda$ in $\mathcal{S}^{\mathcal{KR}}$, it is a *reflection* with respect to the plane containing $\mathbf{U}_1+\mathbf{U}_2$ and $\mathbf{U}_3$ in $\mathcal{S}^{\mathcal{KI}}$. Together with the identity operation, it constitutes an order 2 cyclic group designated $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$.

The operations $C_3^{1(\Sigma\mathbf{I}_i^\lambda,\Sigma\mathbf{U}_i,\Sigma\mathbf{R}_i^\lambda)}$ and $C_3^{2(\Sigma\mathbf{I}_i^\lambda,\Sigma\mathbf{U}_i,\Sigma\mathbf{R}_i^\lambda)}$ (where the Σ symbol is a short hand notation for the sum over the three vectors) correspond to cyclic permutations of the three basis vectors simultaneously in the three coordinate spaces. Geometrically, they correspond to rotations by $2\pi/3$ and $4\pi/3$, respectively in each of the three coordinate spaces around the sum of the three basis vectors. Together with the identity operator, they constitute the order 3 cyclic group $C_3^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda,\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3,\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda)}$.

3. Composition of the internal symmetry group

These six factor groups are used in the following length six composition series:

$$E \subset C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)} \subset C_2^2 \subset C_2^3 \subset C_2^4 \subset G_{48} \subset G_{96}, \tag{39}$$

where we have used the short hand notations $C_2^2 = C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)} \times C_2^{(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$, $C_2^3 = C_2^2 \times C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$, and $C_2^4 = C_2^3 \times C_2^{(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$. We can use direct products here because all 16 elements generated by these four factor groups commute. C_2^2 is isomorphic to the dihedral group D_2. C_2^3 and C_2^4 are Abelian groups of order 8 and 16, respectively. The order 48 group G_{48} is defined by $G_{48}/C_2^4 = C_3^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda,\{\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda)}$. We computed eight classes in this group, one containing the single identity element, five containing three elements, and two 16 elements. Since C_2^4 consists of the identity and the five complete three-element classes, we conclude that it is a normal subgroup of G_{48}. Finally, G_{96} is defined by $G_{96}/G_{48} = C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$. G_{96} consists of ten classes, the identity, three classes of three elements, one class of six elements, one class of 32 elements, and four classes of 12 elements. Since G_{48} is identical to the first six classes of G_{96}, it is indeed a normal subgroup.

For the case $J=0$, $L=0$, the harmonics depend only on the three kinematic invariant coordinates (ρ,θ,ϕ). The effect of a symmetry operation $\hat{O}_i$ on the harmonics reduces to the action of the projection $\hat{O}_i^{KI}$ of the symmetry operation in $\mathcal{S}^{\mathcal{KI}}$: $\hat{O}_i F^{nJ\ L\ \ D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) = \hat{O}_i^{KI} F^{nJ\ L\ \ D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda)$. These projected operations generate new groups which can be readily identified from Table I. Both $C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$ and $C_2^{(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$ reduce to $C_2^{(\mathbf{U}_3)}$, and similarly both $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ and $C_2^{(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$ give $C_2^{(\mathbf{U}_1)}$. $C_3^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda,\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3,\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda)}$ gives the order 3 cyclic group $C_3^{(\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3)}$. $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$ yields $C_2^{\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\}}$, which is the C_s group with respect to the plane $\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\}$. One can then build the full symmetry group from these four factor groups $C_2^{(\mathbf{U}_3)}$, $C_2^{(\mathbf{U}_1)}$, $C_3^{(\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3)}$, and $C_2^{\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\}}$. The corresponding composition series has, in fact, already been given by Eq. (37), and the internal symmetry group is T_d for the $J=0$, $L=0$ case. When combined with the inversion, which is an external symmetry, the O_h group, which has been used in Refs. 15 and 17 is obtained.

4. Symmetrization of the harmonics

We now perform a step-by-step symmetrization, by successively using Eq. (36) for each of the six factor groups defined in the previous section. We find the effect of each operation $\hat{O}_i$ of the group on the harmonics defined by Eq. (33) by using Table I. Each operation transforms $(a_\lambda,b_\lambda,c_\lambda)$ into $(a'_\lambda,b'_\lambda,c'_\lambda)$ and $(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$ into $(\delta_\lambda^{(1)'},\delta_\lambda^{(2)'},\delta_\lambda^{(3)'})$. The effect on the Wigner rotation functions can be obtained by using the expressions for $(a'_\lambda,b'_\lambda,c'_\lambda)$ and $(\delta_\lambda^{(1)'},\delta_\lambda^{(2)'},\delta_\lambda^{(3)'})$ given in Table I. An alternative is to use the Euler angles $(a_\lambda^O,b_\lambda^O,c_\lambda^O)$ or $(\delta_\lambda^{(1)O},\delta_\lambda^{(2)O},\delta_\lambda^{(3)O})$, which define the effects of $\hat{O}_i$ in $\mathcal{S}^{\mathcal{PR}}$ and $\mathcal{S}^{\mathcal{KR}}$, and whose values are given also in Table I. The transformed Wigner rotation functions are then given by[25]

$$D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}'_\lambda) = \sum_{\Omega'_{J_\lambda}} D^J_{M_J\Omega'_{J_\lambda}}(\mathbf{a}_\lambda) D^J_{\Omega'_{J_\lambda}\Omega_{J_\lambda}}(a_\lambda^O,b_\lambda^O,c_\lambda^O), \tag{40}$$

$$D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}'_\lambda) = \sum_{\Omega'_{L_\lambda}} D^L_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}(\delta_\lambda^{(1)O},\delta_\lambda^{(2)O},\delta_\lambda^{(3)O}) \times D^L_{\Omega'_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda). \tag{41}$$

The effect on the two-angle principal-axes-of-inertia harmonics $G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ is obtained straightforwardly using the line of Table I designated by (θ',ϕ').

Using this procedure for the group $C_2^{(\mathbf{I}_3^\lambda,\mathbf{U}_3)}$, we obtain the symmetrized harmonic

$$\begin{aligned} {}^{(1)}F^{nJ\ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda) &= \mathcal{N}[1+C_2^{1(\mathbf{I}_3^\lambda,\mathbf{U}_3)}]F^{nJ\ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda) \\ &= \sum_{\Omega_{J_\lambda}=-J}^{J}\sum_{\Omega_{L_\lambda}=-L}^{L} D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad \times {}^{(1)}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi), \end{aligned} \tag{42}$$

with

$$\begin{aligned} {}^{(1)}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) &= \mathcal{N}[G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) \\ &\quad + (-1)^{\Omega_{J_\lambda}}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\pi+\phi)]. \end{aligned} \tag{43}$$

Obviously, ${}^{(1)}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ satisfies the symmetry relation

$$\mathbf{ISYM1}:\ {}^{(1)}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi+\pi) = (-1)^{\Omega_{J_\lambda}}\,{}^{(1)}G^{nJ\ \ L\ \ \ D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \tag{44}$$

For the group $C_2^{(\mathbf{U}_3,\mathbf{R}_3^\lambda)}$, we have

$$\begin{aligned}{}^{(2)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) &= \mathcal{N}[1 + C_2^{1(\mathbf{U}_3,\mathbf{R}_3^\lambda)}][1 + C_2^{1(\mathbf{I}_3^\lambda,\mathbf{U}_3)}]F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) \\ &= \sum_{\Omega_{J_\lambda}=-J}^{J}\sum_{\Omega_{L_\lambda}=-L}^{L} D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad\times {}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{45}$$

with

$$\begin{aligned}{}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) &= \mathcal{N}[{}^{(1)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) + (-1)^{\Omega_{L_\lambda}}\,{}^{(1)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\pi+\phi)],\end{aligned} \tag{46}$$

and with the help of Eq. (44) we obtain

$${}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) = \mathcal{N}\,{}^{(1)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)(1 + (-1)^{\Omega_{J_\lambda}+\Omega_{L_\lambda}}), \tag{47}$$

which proves that internally symmetric harmonics exist for

$$\textbf{ISYM2}:\ (-1)^{\Omega_{J_\lambda}+\Omega_{L_\lambda}} = 1. \tag{48}$$

This condition was already obtained in Ref. 18 and related material is also given in Ref. 16. The ${}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ satisfy the same symmetry relation [Eq. (44)] as ${}^{(1)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$.

For the group $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$, we first introduce symmetrized two-angle harmonics using

$$\begin{aligned}{}^{(3)}\bar{G}^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) &= \mathcal{N}[{}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) \\ &\quad + \epsilon\,{}^{(2)}G^{nJ\,L\,D}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\pi-\theta,2\pi-\phi)].\end{aligned} \tag{49}$$

These functions belong to the symmetric ($\epsilon=1$) or antisymmetric ($\epsilon=-1$) representations of projection $C_2^{(\mathbf{U}_1)}$ of the group $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ in $\mathcal{S}^{\mathcal{KI}}$. The eight-angle harmonics symmetrized with respect to $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ can then be written as

$$\begin{aligned}{}^{(3)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) &= \mathcal{N}[1 + C_2^{1(\mathbf{I}_1^\lambda,\mathbf{U}_1)}]\,{}^{(2)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) \\ &= \sum_{\Omega_{J_\lambda}=-J}^{J}\sum_{\Omega_{L_\lambda}=-L}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad\times {}^{(3)}\bar{G}^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{50}$$

where

$$\epsilon_J = (-1)^J, \tag{51}$$

and where we have introduced symmetrized Wigner functions

$$\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda) = \frac{1}{\sqrt{2(1+\delta_{\Omega_{J_\lambda}0})}}(D^J_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda) + \epsilon_J\epsilon D^J_{M_J-\Omega_{J_\lambda}}(\mathbf{a}_\lambda)). \tag{52}$$

Since $\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J-\Omega_{J_\lambda}}(\mathbf{a}_\lambda) = \epsilon_J\epsilon\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)$ it is easy to restrict the summation over Ω_{J_λ} in Eq. (50) to positive values

$$\begin{aligned}{}^{(3)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) &= \sum_{\Omega_{J_\lambda}=0}^{J}\sum_{\Omega_{L_\lambda}=-L}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad\times {}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{53}$$

with

$$\begin{aligned}{}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) &= {}^{(3)}\bar{G}^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) \\ &\quad + \epsilon_J\epsilon\,{}^{(3)}\bar{G}^{nJ\,L\,D\,\epsilon}_{-\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi).\end{aligned} \tag{54}$$

In addition to Eq. (44), the new symmetrized two-angle harmonics satisfy the symmetry relations

$$\textbf{ISYM3}:\ {}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\pi-\theta,2\pi-\phi) = \epsilon\,{}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \tag{55}$$

These two-angle harmonics also belong to the symmetric ($\epsilon=1$) or antisymmetric ($\epsilon=-1$) representations of the projection of the group $C_2^{(\mathbf{I}_1^\lambda,\mathbf{U}_1)}$ in $\mathcal{S}^{\mathcal{KI}}$. We also have

$$\textbf{ISYM4}:\ {}^{(3)}G^{nJ\,L\,D\,\epsilon}_{-\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) = \epsilon_J\epsilon\,{}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \tag{56}$$

Similarly, the group $C_2^{(\mathbf{U}_1,\mathbf{R}_1^\lambda)}$ yields

$$\begin{aligned}{}^{(4)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) &= \mathcal{N}[1 + C_2^{1(\mathbf{U}_1,\mathbf{R}_1^\lambda)}]\,{}^{(3)}F^{nJ\,L\,D}_{M_J M_{L_\lambda} d}(\mathbf{\Theta}_\lambda) \\ &= \sum_{\Omega_{J_\lambda}=0}^{J}\sum_{\Omega_{L_\lambda}=0}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad\times {}^{(4)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{57}$$

with

$$\epsilon_L = (-1)^L, \tag{58}$$

$$\begin{aligned}\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) &= \frac{1}{\sqrt{2(1+\delta_{\Omega_{L_\lambda}0})}}(D^L_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda) \\ &\quad + \epsilon_L\epsilon D^L_{-\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)),\end{aligned} \tag{59}$$

$$\begin{aligned}{}^{(4)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) &= \mathcal{N}[{}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi) \\ &\quad + \epsilon_L\epsilon\,{}^{(3)}G^{nJ\,L\,D\,\epsilon}_{\Omega_{J_\lambda}-\Omega_{L_\lambda}d}(\theta,\phi)],\end{aligned} \tag{60}$$

where ${}^{(4)}G^{nJ\,L\,D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ satisfy the three symmetry relations, Eqs. (44), (55), and (56) and also

$$\textbf{ISYM5}: {}^{(4)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}-\Omega_{L_\lambda}d}(\theta,\phi)=\epsilon_L\epsilon^{(4)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \tag{61}$$

The relation ${}^{(4)}G^{nJ\ \ L\ \ D\epsilon}_{-\Omega_{J_\lambda}-\Omega_{L_\lambda}d}(\theta,\phi)=(-1)^{J+L}\,{}^{(4)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ derived in Ref. 18 [Eq. (3.26)] is a direct consequence of Eqs. (56) and (61).

The group $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$ yields

$$\begin{aligned}&{}^{(5)}F^{nJ\ \ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\mathcal{N}[1+C_2^{1(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}]^{(4)}F^{nJ\ \ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\sum_{\Omega_{J_\lambda}=0}^{J}\sum_{\Omega_{L_\lambda}=0}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)\\&\quad\times{}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi),\end{aligned} \tag{62}$$

with

$$\begin{aligned}&{}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)\\&=\mathcal{N}[{}^{(4)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)+(-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2}\\&\quad\times{}^{(4)}G^{nJ\ \ L\ \ D\bar{\epsilon}}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\pi/2-\phi)],\end{aligned} \tag{63}$$

$$\bar{\epsilon}=\epsilon(-1)^{\Omega_{J_\lambda}}=\epsilon(-1)^{\Omega_{L_\lambda}}. \tag{64}$$

In addition to Eqs. (44), (55), (56), and (61), the ${}^{(5)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ satisfy

$$\begin{aligned}&\textbf{ISYM6}: {}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\pi/2-\phi)\\&=(-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2(5)}G^{nJ\ \ L\ \ D\ \bar{\epsilon}}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi).\end{aligned} \tag{65}$$

When Ω_{J_λ} and Ω_{L_λ} are even, Eq. (65) is another symmetry relation for ${}^{(5)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$. However, when Ω_{J_λ} and Ω_{L_λ} are odd, Eq. (65) is a relation between ${}^{(5)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ and ${}^{(5)}G^{nJ\ \ L\ \ D-\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$.

Symmetrization with respect to the factor group $C_3^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda,\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3,\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda)}$ is more difficult with the coordinates used in the present paper. Simplifications should be achieved if rotated frames, with Z axes corresponding to $\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda+\mathbf{I}_3^\lambda$, $\mathbf{U}_1+\mathbf{U}_2+\mathbf{U}_3$, and $\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda+\mathbf{R}_3^\lambda$ are used in the three spaces, but this goes beyond the scope of this paper.

C. External symmetries

1. Inversion

We define inversion as the operation $\hat{I}$ which changes the matrix of Jacobi vectors $\boldsymbol{\rho}_\lambda^{\mathrm{sf}}$ in Eq. (1) to their opposites. This operator commutes with $\hat{\Lambda}^2$, $\hat{J}^2$, $\hat{J}_z^{\mathrm{sf}}$, $\hat{L}^2$, and $\hat{L}^{\mathrm{bf}}_{\lambda_3}$. Symmetric $(\Pi=0)$ or antisymmetric $(\Pi=1)$ eight-angle harmonics ${}^{(6)}F^{nJ\ \ L\ \ D}_{\Omega_J\Omega_{L_\lambda}d}(\mathbf{\Theta}_\lambda)$ with respect to inversion are obtained as

$$\begin{aligned}&{}^{(6)}F^{nJ\ \ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\mathcal{N}[1+(-1)^\Pi\hat{I}]^{(5)}F^{nJ\ \ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\sum_{\Omega_{J_\lambda}=0}^{J}\sum_{\Omega_{L_\lambda}=0}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)\\&\quad\times{}^{(6)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi).\end{aligned} \tag{66}$$

From Eq. (3), the effect of $\hat{I}$ on the angles $\mathbf{a}_\lambda$ and $\boldsymbol{\delta}_\lambda$ can leave them unchanged, and to change (θ,ϕ) to $(\pi-\theta,\pi+\phi)$. Therefore

$$\begin{aligned}{}^{(6)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)&=\mathcal{N}[{}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)+(-1)^\Pi\\&\quad\times{}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\pi-\theta,\pi+\phi)],\end{aligned} \tag{67}$$

and we have another symmetry relation

$$\begin{aligned}&\textbf{INV}: {}^{(6)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\pi-\theta,\pi+\phi)\\&=(-1)^{\Pi(6)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi).\end{aligned} \tag{68}$$

We know from Ref. 18 that $(-1)^\Pi=(-1)^n$.

2. Permutations of particles

When the system contains identical particles, it is possible to consider additional external symmetries resulting from the exchange of these particles. As an example, let us assume that we have two identical particles, let us call λ a Jacobi clustering scheme starting from these identical particles, and let us call $\hat{P}_{12}$ the operator which permutes these two particles. $\hat{P}_{12}$ changes the Jacobi vector $\mathbf{r}_\lambda^{(1)}$ to its negative, but leaves the two other Jacobi vectors unchanged. In order to symmetrize the eight-angle harmonics with respect to $\hat{P}_{12}$, we use the known transformations of the coordinates under this symmetry operation[10]

$$\begin{aligned}&a_\lambda'=\pi+a_\lambda,\quad b_\lambda'=\pi-b_\lambda,\quad c_\lambda'=2\pi-c_\lambda,\\&\theta'=\pi-\theta,\quad \phi'=\pi+\phi,\\&\delta_\lambda^{(1)'}=\pi-\delta_\lambda^{(1)},\quad \delta_\lambda^{(2)'}=\delta_\lambda^{(2)},\quad \delta_\lambda^{(3)'}=\pi-\delta_\lambda^{(3)}.\end{aligned} \tag{69}$$

Symmetric $(\epsilon_P=1)$ or antisymmetric $(\epsilon_P=-1)$ harmonics with respect to $\hat{P}_{12}$ are obtained as

$$\begin{aligned}&{}^{(7)}F^{nJ\ \ L\ \ D\ \epsilon_P}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\mathcal{N}[1+\epsilon_P\hat{P}_{12}]^{(6)}F^{nJ\ \ L\ \ D}_{M_JM_{L_\lambda}d}(\mathbf{\Theta}_\lambda)\\&=\mathcal{N}\sum_{\Omega_{J_\lambda}=0}^{J}\sum_{\Omega_{L_\lambda}=0}^{L}\sum_{\epsilon=\pm1}\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)(\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)\\&\quad+\epsilon_P(-1)^{\Pi+L}\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}-M_{L_\lambda}}(\boldsymbol{\delta}_\lambda))^{(6)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi).\end{aligned} \tag{70}$$

IV. BASIS DEFINITION

A. Symmetry-adapted trigonometric basis

It was shown previously[18] that two-angle harmonics $G^{nJ}_{\Omega_{J_\lambda}}{}^{L}_{\Omega_{L_\lambda}}{}^{D}_{d}(\theta,\phi)$ are homogeneous polynomials in $x=\sin\theta(\cos\phi+\sin\phi)$, $y=\sin\theta(\cos\phi-\sin\phi)$, and $z=\cos\theta$ and are thus sums of products of powers of cosines and sines in θ and ϕ. These powers can in turn be written as linear combinations of cosines and sines of $p\theta$ and $q\phi$, where p and q are integers. As a result, the harmonics are exact linear combinations of the following products of trigonometric functions: $\cos(p\theta)\cos(q\phi)$, $\cos(p\theta)\sin(q\phi)$, $\sin(p\theta)\cos(q\phi)$, and $\sin(p\theta)\sin(q\phi)$. Notice that the number of trigonometric functions to be included in the exact expansions of the harmonics is finite; in fact, for two-angle harmonics being of degree n, we have $p,q\leqslant n$.

The symmetry relations derived in the previous section for the harmonics can be used to select the basis functions in which to expand the harmonics. Each symmetry relation imposes constraints on the basis and reduces the number of basis functions needed as follows:

ISYM0:

$(-1)^q=1$: the functions of θ are $\cos p\theta$,

$(-1)^q=-1$: the functions of θ are $\sin p\theta$.

$$\textbf{ISYM1}: (-1)^q=(-1)^{\Omega_{J_\lambda}}. \tag{71}$$

This symmetry requires that the parity of q be the same as that of Ω_{J_λ} or equivalently Ω_{L_λ} according to **ISYM2**. Equation **ISYM3** provides the following relations:

ISYM3:

$(-1)^p=\epsilon$: the functions of θ and ϕ are simultaneously sines or cosines,

$(-1)^p=-\epsilon$: the functions of θ and ϕ are not simultaneously sines and cosines.

Equations **ISYM4** and **ISYM5** provide definitions for negative Ω symmetrized two-angle harmonics, which are not used in the expansions of the eight-angle harmonics [see Eq. (62)].

In the present implementation of the formalism described in the next sections, we have not used symmetries **ISYM6** and **ISYM7** which, although they would lead to significant reductions of the computing times, introduce additional complexity in the computer programs. However, we describe in the Appendix a symmetrized basis with respect to **ISYM6**.

Finally, **INV** provides, assuming **ISYM0** is fulfilled,

$$\textbf{INV}: (-1)^p=(-1)^{\Pi}. \tag{72}$$

We give in Table II a summary of the choice of the symmetry-adapted trigonometric basis. We denote this basis $t^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}_{pq}(\theta,\phi)$ to point out the quantum numbers on which it depends.

TABLE II. Symmetry-adapted trigonometric basis functions $t^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}_{pq}(\theta,\phi)$ to be used in the expansion of the harmonic $G^{nJ}_{\Omega_{J_\lambda}}{}^{L}_{\Omega_{L_\lambda}}{}^{D}_{d}(\theta,\phi)$.

	Ω_{J_λ}, Ω_{L_λ} even (q even)		Ω_{J_λ}, Ω_{L_λ} odd (q odd)	
	$\cos(p\theta)$		$\sin(p\theta)$	
	$\epsilon=1$	$\epsilon=-1$	$\epsilon=1$	$\epsilon=-1$
$\Pi=0$ (p even)	$\cos(q\phi)$	$\sin(q\phi)$	$\sin(q\phi)$	$\cos(q\phi)$
$\Pi=1$ (p odd)	$\sin(q\phi)$	$\cos(q\phi)$	$\cos(q\phi)$	$\sin(q\phi)$

B. Symmetry-adapted spherical harmonics

An alternative to the trigonometric basis described in the previous section is the spherical harmonic basis $Y^q_p(\theta,\phi)$, suggested in Ref. 15. In fact, since spherical harmonics can be written as linear combinations of trigonometric functions, the space spanned by the spherical harmonic basis is the same as the one spanned by the trigonometric basis. **ISYM1** provides the same relation as Eq. (71) whereas **ISYM3** transforms complex harmonics into sine and cosine-type ones, $Y^{q\epsilon}_p(\theta,\phi)=\mathcal{N}[Y^q_p(\theta,\phi)+\epsilon Y^q_p(\pi-\theta,2\pi-\phi)]$ [cf. Eq. (49)], with a slightly different condition,

ISYM3:
$(-1)^p(-1)^q=\epsilon$: functions in ϕ are cosines,
$(-1)^p(-1)^q=-\epsilon$: functions in ϕ are sines.
Finally, **INV** is the same relation as in Eq. (72).

For practical implementations of these symmetries, the spherical harmonic basis does not have specific advantages over the trigonometric one. Orthogonalization and pole problems are equivalent in both bases, as described in Secs. IV C and V. The trigonometric basis is used in the rest of this paper.

C. Orthogonalization

The optimal basis $t^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}_{pq}(\theta,\phi)$ defined in Sec. IV A is not orthogonal with respect to the two-dimensional volume element:[10]

$$w(\theta,\phi)=\sin^3\theta\cos 2\phi(\cos^2\theta-\sin^2\theta\sin^2\phi)\times(\cos^2\theta-\sin^2\theta\cos^2\phi). \tag{73}$$

We perform an orthogonalization of the basis using a singular value decomposition.[21,22] We consider the rectangular matrix

$$\boldsymbol{T}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}_{(ij),(pq)}=\sqrt{w(\theta_i,\phi_j)}\,t^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}_{pq}(\theta_i,\phi_j), \tag{74}$$

where (θ_i,ϕ_j) defines a two-dimensional Gauss-Legendre quadrature grid and where (ij) and (pq) are composite row and column indices, respectively. The singular value decomposition of $\boldsymbol{T}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ can be written as

$$\boldsymbol{T}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}=\boldsymbol{B}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}\boldsymbol{d}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}\boldsymbol{V}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}, \tag{75}$$

where $\boldsymbol{B}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ is a column-orthonormal rectangular matrix, $\boldsymbol{V}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ is a square orthonormal, and $\boldsymbol{d}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ is a diagonal matrix whose elements squared are the eigenvalues of the scalar product matrix $\tilde{\boldsymbol{T}}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}\boldsymbol{T}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$. Due to linear dependences of the nonorthogonal trigonometric basis, some of the diagonal elements of $\boldsymbol{d}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ turn out to be very close to zero. It is crucial for convergence to keep in the matrix $\boldsymbol{B}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ only those columns which correspond to diagonal values of $\boldsymbol{d}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}$ larger than some threshold $t_{\rm svd}$. These columns provide a set of N_b orthonormal basis functions $b_k^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\phi)$, $k=1,N_b$.

V. MATRIX REPRESENTATION OF THE GRAND-CANONICAL ANGULAR MOMENTUM OPERATOR

Let us first give the matrix elements of the grand-canonical angular momentum operator $\hat{\Lambda}^2$ for fixed J, L, M_J, and M_{L_λ} in the symmetrized Wigner basis $|\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon\rangle = \mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(a_\lambda,b_\lambda,c_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$. The first task is to calculate the matrix elements of the operators which involve the angular momenta that appear in the expression for $\hat{C}^2(\boldsymbol{\Theta}_\lambda)$ [Eq. (23)]. These matrix elements are obtained using Eqs. (A13)–(A18) of Ref. 18 [where the sign of the right hand side of (A18) is wrong]. The operators $\hat{J}_i^{I_\lambda 2}+\hat{L}^2_{\lambda_i}$, $i=1-3$ are diagonal in ϵ. We have

$$\langle\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon|\hat{J}_3^{I_\lambda 2}+\hat{L}^2_{\lambda_3}|\Omega'_{J_\lambda},\Omega'_{L_\lambda},\epsilon\rangle = \delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}(\Omega^2_{J_\lambda}+\Omega^2_{L_\lambda}), \tag{76}$$

and

$$\begin{aligned}\langle\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon|\hat{J}_1^{I_\lambda 2}+\hat{L}^2_{\lambda_1}|\Omega'_{J_\lambda},\Omega'_{L_\lambda},\epsilon\rangle &= \delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\left(\frac{J(J+1)-\Omega^2_{J_\lambda}+L(L+1)-\Omega^2_{L_\lambda}}{2}+\epsilon\epsilon_J\delta_{\Omega_{J_\lambda}1}\frac{J(J+1)}{4}+\epsilon\epsilon_L\delta_{\Omega_{L_\lambda}1}\frac{L(L+1)}{4}\right)\\ &+c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}\delta_{\Omega_{J_\lambda}+2\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\frac{\xi_-(J,\Omega'_{J_\lambda})\xi_-(J,\Omega'_{J_\lambda}-1)}{4}+c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}\delta_{\Omega_{J_\lambda}-2\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\frac{\xi_+(J,\Omega'_{J_\lambda})\xi_+(J,\Omega'_{J_\lambda}+1)}{4}\\ &+c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\delta_{\Omega_{L_\lambda}+2\Omega'_{L_\lambda}}\delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\frac{\xi_-(L,\Omega'_{L_\lambda})\xi_-(L,\Omega'_{L_\lambda}-1)}{4}+c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\delta_{\Omega_{L_\lambda}-2\Omega'_{L_\lambda}}\delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\frac{\xi_+(L,\Omega'_{L_\lambda})\xi_+(L,\Omega'_{L_\lambda}+1)}{4},\end{aligned} \tag{77}$$

with $c_{\Omega\Omega'}=((1+\delta_{\Omega 0})(1+\delta_{\Omega' 0}))^{1/2}$, and $\xi_\pm(J,\Omega)=(J(J+1)-\Omega(\Omega\pm 1))^{1/2}$. The terms in $\delta_{\Omega_{J_\lambda}1}$, $\delta_{\Omega_{L_\lambda}1}$, and $c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}$ appear because we use symmetrized Wigner functions. Similarly,

$$\begin{aligned}\langle\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon|\hat{J}_2^{I_\lambda 2}+\hat{L}^2_{\lambda_2}|\Omega'_{J_\lambda},\Omega'_{L_\lambda},\epsilon\rangle &= \delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\left(\frac{J(J+1)-\Omega^2_{J_\lambda}+L(L+1)-\Omega^2_{L_\lambda}}{2}-\epsilon\epsilon_J\delta_{\Omega_{J_\lambda}1}\frac{J(J+1)}{4}-\epsilon\epsilon_L\delta_{\Omega_{L_\lambda}1}\frac{L(L+1)}{4}\right)\\ &-c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}\delta_{\Omega_{J_\lambda}+2\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\frac{\xi_-(J,\Omega'_{J_\lambda})\xi_-(J,\Omega'_{J_\lambda}-1)}{4}-c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}\delta_{\Omega_{J_\lambda}-2\Omega'_{J_\lambda}}\delta_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\frac{\xi_+(J,\Omega'_{J_\lambda})\xi_+(J,\Omega'_{J_\lambda}+1)}{4}\\ &-c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\delta_{\Omega_{L_\lambda}+2\Omega'_{L_\lambda}}\delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\frac{\xi_-(L,\Omega'_{L_\lambda})\xi_-(L,\Omega'_{L_\lambda}-1)}{4}-c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\delta_{\Omega_{L_\lambda}-2\Omega'_{L_\lambda}}\delta_{\Omega_{J_\lambda}\Omega'_{J_\lambda}}\frac{\xi_+(L,\Omega'_{L_\lambda})\xi_+(L,\Omega'_{L_\lambda}+1)}{4}.\end{aligned} \tag{78}$$

The product $\hat{J}_1^{I_\lambda}\hat{L}_{\lambda_1}$ is also diagonal in ϵ. We have

$$\begin{aligned}\langle\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon|\hat{J}_1^{I_\lambda}\hat{L}_{\lambda_1}|\Omega'_{J_\lambda},\Omega'_{L_\lambda},\epsilon\rangle &= \tfrac{1}{4}c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\xi_{\mathrm{sign}(\Omega_{J_\lambda}-\Omega'_{J_\lambda})}(J,\Omega_{J_\lambda},\Omega'_{J_\lambda})\\ &\times\xi_{\mathrm{sign}(\Omega_{L_\lambda}-\Omega'_{L_\lambda})}(L,\Omega_{L_\lambda},\Omega'_{L_\lambda}).\end{aligned} \tag{79}$$

The products $\hat{J}_2^{I_\lambda}\hat{L}_{\lambda_2}$ and $\hat{J}_3^{I_\lambda}\hat{L}_{\lambda_3}$ are the only terms which couple states with opposite ϵ. We have

$$\begin{aligned}\langle\Omega_{J_\lambda},\Omega_{L_\lambda},\epsilon|\hat{J}_2^{I_\lambda}\hat{L}_{\lambda_2}|\Omega'_{J_\lambda},\Omega'_{L_\lambda},-\epsilon\rangle &= \tfrac{1}{4}c_{\Omega_{J_\lambda}\Omega_{J'_\lambda}}c_{\Omega_{L_\lambda}\Omega'_{L_\lambda}}\xi_{\mathrm{sign}(\Omega_{J_\lambda}-\Omega'_{J_\lambda})}(J,\Omega_{J_\lambda},\Omega'_{J_\lambda})\\ &\times\xi_{\mathrm{sign}(\Omega_{L_\lambda}-\Omega'_{L_\lambda})}(L,\Omega_{L_\lambda},\Omega'_{L_\lambda})\mathrm{sign}(\Omega_{J_\lambda}-\Omega'_{J_\lambda})\\ &\times\mathrm{sign}(\Omega_{L_\lambda}-\Omega'_{L_\lambda}),\end{aligned} \tag{80}$$

where $\xi_{\mathrm{sign}(\Omega-\Omega')}(J,\Omega,\Omega')$ is the usual $\xi_\pm(J,\Omega)$ except that it is also defined in the case when $|\Omega-\Omega'|\neq 1$ and is 0 in that case: $\xi_{\mathrm{sign}(\Omega-\Omega')}(J,\Omega,\Omega')=\xi_{\mathrm{sign}(\Omega-\Omega')}(J,\Omega)\delta_{\Omega\Omega'+\mathrm{sign}(\Omega-\Omega')}$. We also have

$$\langle \Omega_{J_\lambda}, \Omega_{L_\lambda}, \epsilon | \hat{J}_3^{l_\lambda} \hat{L}_{\lambda_3} | \Omega'_{J_\lambda}, \Omega'_{L_\lambda}, -\epsilon \rangle = \delta_{\Omega_{J_\lambda} \Omega'_{J_\lambda}} \delta_{\Omega_{L_\lambda} \Omega'_{L_\lambda}} \Omega_{J_\lambda} \Omega_{L_\lambda}. \quad (81)$$

To obtain the matrix representation of $\hat{\Lambda}^2$ in the basis $b_k^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\phi)\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(a_\lambda,b_\lambda,c_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$, one must perform two-dimensional quadratures involving the two dimensional volume element given by Eq. (73), the functions $b_k^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\phi)$ defined in Sec. IV C, and the Hamiltonian matrix elements given above. This is done by two-dimensional Gauss-Legendre integration.

The matrix to be diagonalized has a block structure, each block corresponding to a given ϵ and positive Ω_{J_λ}, Ω_{L_λ}. There are of the order of JL such blocks [due to Eq. (48) which reduces the number of blocks by a factor of 2]. To obtain all harmonics up to $n_{\max}$ for fixed J, L, and parity Π, we need $n_{\max}/2$ functions in θ and ϕ corresponding to even or odd p and q (see Table II) for each Ω_{J_λ} and Ω_{L_λ}. The size of each block is therefore $n_{\max}^2/4$, and the number of rows or columns of $\hat{\Lambda}^2$ matrix representation is $JLn_{\max}^2/4$. In the general case, each ϵ, Ω_{J_λ}, and Ω_{L_λ} block is coupled to 13 others:

- Four blocks corresponding to ϵ and $|\Delta\Omega_{J_\lambda}|=\pm 1$, $|\Delta\Omega_{L_\lambda}|=\pm 1$.
- Four blocks corresponding to ϵ and $|\Delta\Omega_{J_\lambda}|=\pm 2$, $\Delta\Omega_{L_\lambda}=0$ and $\Delta\Omega_{J_\lambda}=0$, $|\Delta\Omega_{L_\lambda}|=\pm 2$.
- One block corresponding to $-\epsilon$, Ω_{J_λ}, and Ω_{L_λ}.
- Four blocks corresponding to $-\epsilon$ and $|\Delta\Omega_{J_\lambda}|=\pm 1$, $|\Delta\Omega_{L_\lambda}|=\pm 1$.

For nuclear configurations for which any two of the three principal moments of inertia are identical, $\hat{\Lambda}^2$ has a pole.[10] In these cases, some of the two-dimensional integrals in θ and ϕ necessary for the computation of the matrix elements of $\hat{\Lambda}^2$ in the basis $b_k^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\phi)\mathcal{D}^{J,\epsilon_J\epsilon}_{M_J\Omega_{J_\lambda}}(a_\lambda,b_\lambda,c_\lambda)\mathcal{D}^{L,\epsilon_L\epsilon}_{\Omega_{L_\lambda}M_{L_\lambda}}(\delta_\lambda^{(1)},\delta_\lambda^{(2)},\delta_\lambda^{(3)})$ diverge. The results of their numerical evaluations can be large, but remain finite because Gauss-Legendre quadratures avoid singular points. The eigenvalues and eigenvectors obtained from the diagonalization of the matrix representation of $\hat{\Lambda}^2$ in this basis are extremely accurate, as described in Sec. VI. We thus perform a numerical removal of singularities instead of an analytical one. $\hat{\Lambda}^2$ applied to each individual basis function diverges at the poles of the kinetic energy operator. However, upon diagonalization of $\hat{\Lambda}^2$, the proper linear combination of basis functions is formed, which cancels these singularities. A similar numerical removal of singularities, in the context of a Jacobi polynomial basis, is also described in Ref. 29.

VI. NUMERICAL TESTS

The first test case involves the computation of all harmonics up to $n_{\max}=30$ for $J=0$ and even parity. The number of trigonometric functions needed for each value of θ and ϕ is 16. In this simple case, Ω_{L_λ} is always even [Eq. (48)], and $\epsilon=1$ [Eq. (52)]. The trigonometric functions are always cosines (see Table II). We use 35 quadrature points each for θ and ϕ. The tolerance parameter for orthogonalization is chosen to be $t_{\text{svd}}=10^{-10}$. With this tolerance, we obtain 205 orthogonal functions from the $16^2=256$ primitives using Eq. (75). For fixed J, M_J, and M_{L_λ}, but varying Ω_{L_λ}, we generate the matrix representation of $\hat{\Lambda}^2$. The total size of the matrix to be diagonalized increases with L from 205 for $L=0$ to 3075 for $L=28$, since the number of coupled Ω_{L_λ} blocks increases accordingly. The $\hat{\Lambda}^2$ eigenvalues which result from the diagonalization of these matrices are equal to $n(n+7)\hbar^2$, where n was found to be an integer to at least nine significant digits, as expected. For fixed J, M_J, and M_{L_λ}, we find often many degenerate harmonics. As M_{L_λ} varies, this degeneracy increases further. For n up to $n_{\max}=30$, we thus generated 738 harmonics, counting all M_{L_λ} degenerate harmonics as a single one. This amounts to 15 504 harmonics if the M_{L_λ} degeneracy is included (still counting M_J degenerate harmonics as a single one).

The second calculation involved $n_{\max}=40$ for $J=0$ and even parity. We used 45 quadrature points each for θ and ϕ. The number of trigonometric functions needed for each value of θ and ϕ is 21. With the same t_{svd} tolerance parameter of 10^{-10}, we obtained 308 orthogonal functions from the $21^2=441$ primitives. The maximum size of the matrix to be diagonalized for $L=40$ is 6468. We again obtained eigenvalues given by $n(n+7)\hbar^2$, n being integer to at least seven significant digits. We thus generated a total of 53 130 harmonics or equivalently 1958 if all M_{L_λ} degenerate harmonics are counted as a single one.

The third test was for $J=2$, $n_{\max}=28$, even parity. We used 33 quadrature points each for θ and ϕ. The number of trigonometric functions needed for each value of θ and ϕ is 15. With the same tolerance parameter, we obtained between 176 and 185 orthogonal functions from the $15^2=225$ primitives, depending on the parity of Ω_{J_λ} and ϵ. The maximum size of the matrix to be diagonalized was 13 054 obtained for $L=28$. The resulting eigenvalues continued to be of the form $n(n+7)\hbar^2$, n being an integer to at least eight significant digits. We thus generated a total of 47 040 harmonics or equivalently 2416, excluding the M_{L_λ} degeneracy.

As a final test, we studied the accuracy of the eigenvectors generated by this numerical method. For simplicity, the test was limited to the nondegenerate case $n=4$, $J=2$, and $L=1$, for which the analytical harmonics given in Table II of Ref. 18 provide a basis for comparison. Numerical and analytical two-angle harmonics are computed on a grid of 100 points in θ and ϕ. For $\Omega_{J_\lambda}=1$, $\Omega_{L_\lambda}=1$, numerical and analytical harmonics agree within nine significant digits at least for all grid points. For $\Omega_{J_\lambda}=2$, $\Omega_{L_\lambda}=0$, the agreement is better than eight significant digits, except near the pole $\theta=0$ where the harmonic becomes very small but where the absolute error remains smaller than 10^{-11}. We therefore conclude that our numerical method provides both highly accurate eigenvalues and eigenvectors.

VII. SUMMARY AND CONCLUSIONS

We have described a numerical method to generate row-orthonormal hyperspherical harmonics for tetra-atomic systems. It relies on the choice of a simple but compact trigonometric basis set in which the two-angle tetra-atomic hyperspherical harmonics can be expanded exactly. This basis set satisfies the symmetries of the problem and is orthogonalized numerically. The singularities associated with the poles of the grand-canonical angular momentum operator are canceled numerically upon diagonalization of the matrix representation of the grand-canonical angular momentum operator in this basis set. This method allows the generation of harmonics for chosen total angular momentum quantum numbers J and L by diagonalization of the kinetic energy operator representation in this basis. Future work will focus on practical applications of this method for scattering and bound state calculations of tetra-atomic systems.

ACKNOWLEDGMENTS

This work has been supported in part by CNRS to one of the authors (B.L.) and NSF (Grant No. CHE981). The authors are also grateful to CNRS and NSF for allocations of computing time at IDRIS and SDSC, respectively.

APPENDIX: SYMMETRIZATION OF THE TRIGONOMETRIC BASIS WITH RESPECT TO $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$

We have shown in Sec. III B 4 that two-angle harmonics symmetrized with respect to $C_2^{(\mathbf{I}_1^\lambda+\mathbf{I}_2^\lambda,\{\mathbf{U}_1+\mathbf{U}_2,\mathbf{U}_3\},\mathbf{R}_1^\lambda+\mathbf{R}_2^\lambda)}$ satisfy

$$\textbf{ISYM6}: {}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\pi/2-\phi) = (-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2}\,{}^{(5)}G^{nJ\ \ L\ \ D\ \bar{\epsilon}}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi). \quad \text{(A1)}$$

- When Ω_{J_λ} is even, q is even (see **ISYM1**), the function of θ is $\cos(p\theta)$ (see **ISYM0**). If $\epsilon(-1)^p=1$, the function of ϕ is $\cos(q\phi)$ and if $\epsilon(-1)^p=-1$, the function of ϕ is $\sin(q\phi)$ (see **ISYM3**). We have [Eq. (64)] $\bar{\epsilon}=\epsilon$ and therefore **ISYM6** gives $(-1)^{q/2}=\epsilon(-1)^p(-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2}$.
- When Ω_{J_λ} is odd, $\bar{\epsilon}=-\epsilon$ and **ISYM6** is a relation between ${}^{(5)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ and ${}^{(5)}G^{nJ\ \ L\ \ D-\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$. Let us assume that ${}^{(5)}G^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)$ is expanded on the trigonometric basis given by Table II,

$$ {}^{(5)}G^{nJ\ \ L\ \ D\ \epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d}(\theta,\phi)=\sum_{p,q} c^{nJ\ \ L\ \ D\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d\,pq}\, t_{pq}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\phi). \quad \text{(A2)}$$

Using $t_{pq}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon}(\theta,\pi/2-\phi)=(-1)^{(q-1)/2}t_{pq}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}-\epsilon}(\theta,\phi)$, **ISYM6** gives $c^{nJ\ \ L\ \ D-\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d\,pq}=(-1)^{(q-1)/2}(-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2}c^{nJ\ \ L\ \ D-\epsilon}_{\Omega_{J_\lambda}\Omega_{L_\lambda}d\,pq}$. In this case, an appropriate basis on which to expand the harmonic ${}^{(5)}F^{nJ\ \ L\ \ D}_{M_J M_{L_\lambda}d}(\Theta_\lambda)$ symmetrized with respect to **ISYM6** is therefore

$$\mathcal{D}^{J,\epsilon_J}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\mathcal{D}^{L,\epsilon_L}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)t_{pq}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon=1}(\theta,\phi) + (-1)^{(q-1)/2}(-1)^{(\Omega_{J_\lambda}-\Omega_{L_\lambda})/2} \times\mathcal{D}^{J,-\epsilon_J}_{M_J\Omega_{J_\lambda}}(\mathbf{a}_\lambda)\mathcal{D}^{L,-\epsilon_L}_{\Omega_{L_\lambda}M_{L_\lambda}}(\boldsymbol{\delta}_\lambda)t_{pq}^{\Pi\Omega_{J_\lambda}\Omega_{L_\lambda}\epsilon=-1}(\theta,\phi).$$

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