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Hypersperical harmonics for polyatomic systems: basis set for collective motions

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Abstract. As a continuation of our previous work for the construction of expansion basis sets for the quantum mechanical treatment of N-body problems of interest for intermolecular and intramolecular and reactive dynamics of polyatomic molecules and clusters, we develop here a group-theoretical procedure which allows us to obtain explicitly the hyperspherical harmonics for the description of the collective motions. The coordinates involved are related to the invariants of the N-body system, which are referred to the moments of inertia. Although this work is limited to the case where both external and internal (kinematic) rotations are zero, and the example of $N = 4$ is explicitly worked out, this method, which gives hyperspherical harmonics as linear combinations of ordinary spherical harmonics, can be extended to cover the general N-body case.

Keywords: N-body problem – Hyperspherical coordinates and harmonics – Kinematic invariants – Projection operator

1 Introduction

The dynamical treatment of N-atom systems involves a considerable number of variables ($3N - 3$) whose nature depends on the choice of the coordinate system, which can be crucial for a good representation of all the aspects of the physical problem. We here are concerned with $N \geq 4$. The $N = 3$ case has been studied extensively [1, 2, 3, 4, 5]. After the standard operation of separation of the motion of the center of mass, one has many alternatives for the remaining variables [6]. Among these, however,the symmetric hyperspherical coordinates play a privileged role that we extensively investigated in several preceding papers [4, 7, 8]. In previous papers we have shown that in a symmetric hyperspherical framework the variables are broken up into internal coordinates (six in the case of four bodies) and three rotational coordinates, which specify the orientation of the system under the form of Euler angles. Moreover internal coordinates are subsequently broken up into kinematic invariants [9] (that we call simply "invariant") and kinematic angles [8]. We also considered the kinetic energy operator for a four-particle system in symmetric hyperspherical coordinates [10], and it has been found that the terms depending on invariant coordinates and those depending on the kinematic angles are separated in the expression of the operator. By adding a potential function to the kinetic energy operator, one obtains the Hamiltonian of the system whose eigenfunctions, which have to be found, contain all available information about the system.

Except for the simplest problems, no analytical solution can be obtained for the eigenfunctions of the Hamiltonian operator, and one has to turn to a representation of the desired solution, as a finite series of basis functions. To this aim, it is crucial to make for the basis set an optimal choice, which in general is that of using the eigenfunction of the zero potential Hamiltonian operator, i.e. the kinetic energy operator.

Unfortunately, if coordinates other than Cartesian are adopted to represent the system, the kinetic energy eigenvalue problem itself is not trivial, but in the particularly relevant case of interest to us here, when we concern ourselves with hyperspherical coordinates, the desired basis functions are the hyperspherical harmonics.

We note that the identification of the basis function set can be mandatory because a suitable choice not only may drastically cut down the number of functions required to obtain a prescribed numerical convergence (and then the time and memory needed for the calculation) but also can be crucial from the viewpoint of overcoming problems arising from singularities [11, 12].

The eigenfunctions for the kinematic rotation part of the kinetic energy operator for four-body systems have already been treated in a previous paper [13]. Regarding

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the solution of the invariant part, in Ref.[9] we obtained some relationships for the eigenfunctions. Early work is due to Zickendraht [14], and more recently a very complete treatment has been reported by Wang and Kuppermann [15]. The aim of the present work is to describe relevant features regarding the invariant part of the kinetic energy operator in symmetric hyperspherical coordinates. The proper way to do that is to account in a systematic way for the symmetry properties of the invariant terms in the Laplacian which reflect the symmetry of the space spanned by the invariant coordinates. Indeed having properly defined the invariant space, one can proceed to derive the symmetry properties of the eigenfunctions [9, 11, 12]. Here we give a simple geometrical treatment, by applying it to the four-body case, enforcing the fact that the symmetry of the space is the $SO(3)/O_h$ manifold. This leads to specific restrictions on the expansion basis set. This study of this important aspect can be intended as complementary to other previous approaches to four bodies [16, 17] and in particular to the work of Wang and Kuppermann [15] where the full problem of the invariant eigenfunctions has been tackled.

The treatment applies to systems of any complexity with minor modifications, in spite of the fact that the actual implementation will inevitably be increasingly complicated [18], unless one makes recourse to approximations. Finally we show how to provide a representation of the invariant eigenfunctions in terms of spherical harmonics. Perspective applications of such a basis set would be its use not only for expanding eigenfunctions of the invariant part of the hyperspherical Hamiltonian but also to model elementary collective motions of polyatomic systems as shown in Ref. [19] for the case of the ammonia inversion.

The plan of the paper is as follows. In Sect. 2 we give a brief description of hyperspherical coordinates introducing the *invariants* and the kinematic angles. We show the invariant part of the kinetic energy operator in Sect. 3. Section 4 is dedicated to the general properties of the functions to be found. The symmetry properties of the eigenfunctions are treated in Sect. 5 and two ways to obtain the invariant eigenfunctions in terms of hyperspherical harmonics are given in Sect. 6. We summarize some concluding remarks in Sect. 7.

2 Hyperspherical coordinates

The hyperpsherical coordinates in the symmetric parameterizations are obtained starting from the $(N-1)$ Jacobi vectors of an N-particle system [7, 8, 10, 13, 20].

The Jacobi vectors are proper linear combinations of the N Cartesian position vectors of the particles by coefficients depending only on the masses of the particles [21, 22, 23, 24].

The standard procedure to introduce Jacobi vectors involves the separation of the center-of-mass vector and the next determination of these as follows:

$$\mathbf{x}_j = \left(\frac{\mu_{j-1}}{\mu_N}\right)^{\frac{1}{2}}\left(\frac{\sum_i^j m_i \mathbf{r}_i}{\sum_i^j m_i} - \mathbf{r}_{j+1}\right) , \tag{1}$$

where $\mathbf{x}_j$ is the jth Jacobi vector and the $\mathbf{r}_i$ are the particle position vectors in the center-of-mass reference frame.

The μ's are mass-dependent factors:

$$\begin{aligned}\mu_j &= \left(\frac{m_{j+1}(M_j)}{M_{j+1}}\right) , \\ \mu_N &= \left(\frac{\Pi_{k=i}^N m_i}{M_N}\right)^{\frac{1}{N-1}} ,\end{aligned} \tag{2}$$

where $M_j = \sum_i^j m_i$, and M_N is the total mass of the system.

To switch to the hyperspherical coordinates, we apply the singular value decomposition [25] to a matrix containing columnwise the Jacobi vector components.

If we call that matrix $\mathbf{F}$

$$\mathbf{F} = \mathbf{R}\mathbf{X}\mathbf{K}^{\mathrm{T}} , \tag{3}$$

where $\mathbf{R}$ is a 3×3 orthogonal matrix, $\mathbf{K}$ is an $(N-1)\times(N-1)$ orthogonal matrix [26, 27] and $\mathbf{X}$ is a $3\times(N-1)$ diagonal matrix whose elements ξ_i are such that $\xi_i \neq 0$ for $i \leq 3$ and $\xi_i = 0$ for $i > 3$. The superscript T stands for the transpose of a matrix.

Owing to the nonuniqueness of the singular value decomposition, we assume $0 \leq \xi_1 \leq \xi_2 \leq \xi_3$. In the special case of four bodies, ξ_1 also takes negative values and the previous expression is modified as follows:

$$0 \leq \mid \xi_1 \mid \leq \xi_2 \leq \xi_3 . \tag{4}$$

$\mathbf{R}$ and $\mathbf{K}$ are respectively, $SO(3)$ and $SO(N-1)$ matrices parameterized respectively, by 3 and $3N-9$ angular variables, which are $3N-6$ of the hyperspherical coordinates.

In particular the $3N-9$ angles of $\mathbf{K}$ perform the so-called kinematic rotations [7, 8, 13, 28], describing motions of the system that leave unchanged the three moments of inertia, while the three parameters defining $\mathbf{R}$ describe the rotations of the whole system and are typically taken to be Euler angles [27] specifying the position of the body-fixed reference frame with respect to a space-fixed reference frame.

The three remaining degrees of freedom are the elements ξ of the $\mathbf{X}$ matrix, which are pure shape coordinates [29, 30, 31, 32] and are directly related to the moments of inertia of the system [19]. Since the ξ's are invariant under kinematic rotations, we call them simply invariants [9].

Generally, the three invariants are parameterized as a function of two additional angular variables, which complete the set of the $(3N-4)$ angles spanning the $3N-4$-dimensional hypersphere, plus the hyperradius ρ, whose square corresponds to the sum of the squares of the moduli of the Jacobi vectors.

3 The quantum mechanical Hamiltonian for a four-body system

The kinetic energy operator in the hyperpsherical coordinates assumes the following form:

$$\hat{T} = -\frac{\hbar^2}{2\mu}\left(\rho^{-(3N-4)}\frac{\partial}{\partial\rho}\rho^{(3N-4)}\frac{\partial}{\partial\rho} + \rho^2\hat{T}_\Omega(\Omega_{3N-4})\right) , \quad (5)$$

where $\hat{T}_\Omega(\Omega_{3N-4})$ is the angular part of the operator depending on the $3N-4$ angular variables of the hyperspherical representation and μ is the reduced mass of the system (see Eq. 2).

$\hat{T}_\Omega$ represents the Laplacian on the unit $S^{(3N-4)}$ sphere, and can be interpreted as the operator that gives the quantum analogue of the classical hyperangular momentum tensor [24, 33, 34]. The operator has been determined in previous work [10], and also by Kuppermann [35], for a four-body system.

Four-body systems move on a nine-dimensional hypersphere and the angular part of the kinetic energy operator is the Laplacian on a eight-dimensional hypersphere. The full nine-dimensional hyperpsphere is spanned by three kinematic rotation angles [28, 30], three external rotation Euler angles and by the three invariants ξ [9]. The kinetic energy operator for a four-body system, in which we are interested here, assumes the following form:

$$\hat{T}_4 = \hat{T}_X + \hat{T}_{XK} + \hat{T}_{XR} , \quad (6)$$

where the operator $\hat{T}_X$ depends only on the invariants ξ, the operator $\hat{T}_{XK}$ includes partial derivatives with respect to the kinematic rotation angles multiplied by factors depending on the ξ's and $\hat{T}_{XR}$ contains similarly Euler angle partial derivative terms multiplied by the same ξ factors.

Our work here will be devoted to the eigenvalue problem related to the $\hat{T}_X$ operator with the aim of finding eigenfunctions following a group-theoretical method, while the full problem has already been tackled by Zickendraht [36] and Wang and Kuppermann [15].

4 Hyperspherical harmonics as wavefunctions

Let $\hat{T}$ be the kinetic energy operator for a four-body system and Ψ the eigenfunction corresponding to the eigenvalue λ. The usual separation of variables on the eight-dimensional hypersphere of radius ρ (the hyperradius) leads to the following form for the eigenfunction:

$$\Psi_\lambda = \frac{1}{\rho} j_{\lambda+3}(k\rho) X_\lambda(\Omega_8) , \quad (7)$$

where $\lambda = 1,2,\ldots$ is the grand angular momentum quantum number [8], k is the wavenumber defined by $E = \frac{k^2\hbar^2}{2\mu}$ and X_λ is the harmonic function on the eight-dimensional hyperpsphere spanned by the angular variables collectively denoted by Ω_8. The function $j_{\lambda+3}$ is a spherical Bessel function.

The hyperradial part of the wavefunction is well known, so we need only the "surface" functions X_λ. No matter how the angular variables Ω_8 are defined (in a symmetric or asymmetric way), their eigenvalues are the same as the grand angular momentum operator

$$(\lambda+3)(\lambda+4) \quad (8)$$

and then a calculation is not needed.

As already stated, in the case of N bodies, the hypersphere is $(3N-4)$-dimensional.

We now consider the kinematic invariant wavefunctions. Let us write Ψ_λ as a function of the three Jacobi vectors $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$:

$$\Psi_\lambda = \Psi_\lambda(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \quad (9)$$

and let K and J be, respectively, the internal (kinematic rotations) and external angular momenta in our symmetric hyperpsherical representation.

For $K = 0$ and $J = 0$ the functions Ψ_λ depend uniquely on the kinematic invariants (ξ_1, ξ_2, ξ_3),

$$\Psi_\lambda(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \Psi_\lambda(\xi_1, \xi_2, \xi_3) , \quad (10)$$

and analogously, the kinetic energy operator $\hat{T}_4$ depends uniquely on the ξ's:

$$\hat{T}_X = -\frac{\hbar^2}{2\mu}\left(\nabla^2 + \frac{2}{\sqrt{D}}\nabla\sqrt{D}\nabla\right) , \quad (11)$$

where $D = (\xi_2^2 - \xi_1^2)(\xi_3^2 - \xi_2^2)(\xi_3^2 - \xi_1^2)$ is the volume element and ∇^2 and ∇ are the usual Laplacian and gradient on the three-dimensional Cartesian (ξ_1, ξ_2, ξ_3) space.

The Ψ_λ can be calculated by solving the equation

$$\hat{T}_X\Psi_\lambda = E_\lambda\Psi_\lambda , \quad (12)$$

where E_λ represents the energy of the system.

Note that taking D as the volume element leads to the following normalization condition, for the Ψ_λ:

$$\langle\Psi_\lambda \mid \Psi_\lambda\rangle = \int \mid \Psi_\lambda \mid^2 \sqrt{D}\, \mathrm{d}\xi_1\, \mathrm{d}\xi_2\, \mathrm{d}\xi_3 . \quad (13)$$

We find it convenient to absorb the volume element in Ψ_λ in order to include it into the definition of the function Φ_λ [9],

$$\Phi_\lambda = \sqrt{D}\Psi_\lambda , \quad (14)$$

that we will refer to as the internal wavefunction.

The normalization becomes simply:

$$\langle\Phi_\lambda \mid \Phi_\lambda\rangle = \int \mid \Phi_\lambda \mid^2 \mathrm{d}\xi_1\, \mathrm{d}\xi_2\, \mathrm{d}\xi_3 . \quad (15)$$

The correspondig internal equation has the form of a Schroedinger equation:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V_2\right)\Phi = E\Phi , \quad (16)$$

where ∇^2 is the Euclidean Laplacian and V_2 is a so-called extra potential term arising only for a quantum mechanical picture of the system [37]:

$$V_2 = \frac{\hbar^2}{2\mu}\frac{1}{\sqrt{D}}\nabla^2\sqrt{D}$$
$$= -\frac{\hbar^2}{2\mu}\left(\frac{\xi_1^2+\xi_2^2}{(\xi_2^2-\xi_1^2)} + \frac{\xi_2^2+\xi_3^2}{(\xi_3^2-\xi_2^2)} + \frac{\xi_1^2+\xi_3^2}{(\xi_3^2-\xi_1^2)}\right) . \quad (17)$$

We turn now to the solution of Eq. (12). To this aim, we look at the zero-energy limit of the hyperradial part of the kinematic invariant wavefunction Ψ_λ [9],

$$\lim_{k\to 0}\frac{\Psi(\rho)}{k^{\lambda+3}} = \lim_{k\to 0}\frac{1}{\rho^3}\frac{j_{\lambda+3}(k\rho)}{k^{\lambda+3}} = (\mathrm{const})\rho^{\lambda} \ , \tag{18}$$

which leads to the following expression for the total wavefunction of Eq. (7):

$$\boldsymbol{\Psi}_{\lambda}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3) = \rho^{\lambda}X_{\lambda}(\boldsymbol{\Omega}_8) \ . \tag{19}$$

In the general case ($K \neq 0$, $J \neq 0$) the hyperspherical harmonics X_{λ} (the surface functions) are polynomials in the nine components of the unit vector on the surface of the eight-dimensional hyperpshere. When they are multiplied by a factor ρ_{λ} they become homogeneous polynomials of degree λ in the nine cartesian components of the Jacobi vectors.

Setting $K=0$ (kinematic rotations) and $J=0$ (external rotations) means to require the invariance under kinematic and external rotations of the wavefunction $\boldsymbol{\Psi}_{\lambda}$. The kinematic invariant wavefunctions $\boldsymbol{\Psi}_{\lambda}$ in which we are interested here already exhibit, by definition, the invariance under kinematic rotations, and the rotational invariance can be obtained if the wavefunction involves Jacobi dot product $\mathbf{x}_{\alpha}\cdot\mathbf{x}_{\beta}$ and Jacobi triple product $\mathbf{x}_1\cdot(\mathbf{x}_2\times\mathbf{x}_3)$ only. Thus, in terms of the ξ's, we can write the following form for the kinematic invariant wavefunction with zero angular momentum:

$$\boldsymbol{\Psi}_{\lambda}(\xi_1,\xi_2,\xi_3) = \sum_{(i,j,k,i+j+k=\lambda)}^{\lambda} C^{\lambda}_{ijk}\xi_1^i\xi_2^j\xi_3^k \ , \tag{20}$$

where $i,j,k\ =\ 0,2,4,\ldots$ and where the C's are coefficients which have to be determined by solving Eq. (12) in the zero-energy limit ($E=0$):

$$-\frac{\hbar^2}{2\mu}\left(\nabla^2+\frac{2}{\sqrt{D}}\nabla\sqrt{D}\nabla\right)\boldsymbol{\Psi}_{\lambda}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3) = 0 \ . \tag{21}$$

By inserting Eq. (20) into Eq. (21) we obtain a homogeneous system of linear equations whose solutions are the C's.

5 The symmetry properties of the kinematic invariant wavefunctions

The kinematic invariant wavefunction $\boldsymbol{\Psi}_{\lambda}(\xi_1,\xi_2,\xi_3)$ enjoys the symmetry properties of the operator $\hat{T}_X$

$$\hat{T}_X = -\frac{\hbar^2}{2\mu}\left(\nabla^2+\frac{2}{\sqrt{D}}\nabla\sqrt{D}\nabla\right) \ . \tag{22}$$

The operator $\hat{T}_X$ can be shown to satisfy the symmetry properties of the octahedral group, namely, it is invariant under the action of the 24 operations of the group O [38, 39, 40, 41].

Since the wavefunction is a polynomial of degree λ in the ξ's its behaviour under the inversion operation is directly determined from the parity of the polynomial itself, namely an even λ gives an even wavefunction and an odd λ gives an odd eigenfunction.

Moreover Eq. (20), giving the general form for the kinematic invariant wavefunctions for any λ, can be modified by noticing that only the Jacobi triple product can be odd under the inversion operation. So the form for odd values of the λ quantum number is

$$\boldsymbol{\Psi}_{\lambda}(\xi_1,\xi_2,\xi_3) = \xi_1\xi_2\xi_3 \sum_{(i,j,k,i+j+k=\lambda)}^{\lambda} C^{\lambda-3}_{ijk}\xi_1^i\xi_2^j\xi_3^k, \lambda \text{ odd} \ , \tag{23}$$

where the wavefunction for λ odd is given by wavefunction for (λ-3) multiplied by the factor $\xi_1\xi_2\xi_3$ and where $\lambda\ =\ 0,2,4,\ldots$.

The symmetry group of the kinematic invariant wavefunctions can be extended in order to include the inversion operation. We chose to take into account of this extension in a simple way, obtaining group O plus the inversion, i.e. the O_h group. As a consequence the functions $\boldsymbol{\Psi}_{\lambda}$ must belong to the irreps of the O_h group.

Owing to the constraint $K=0$ it can be demonstrated that only irrep A_1 for even values of λ and irrep A_2' for odd λ's are consistent with the boundary conditions [9].

As a consequence of the symmetry properties of the wavefunction, the following relationships hold for the C coefficients:

$$C_{ijk} = C_{jik} = C_{jki} = C_{kji} = C_{kij} = C_{ikj} \ . \tag{24}$$

In other words the C coefficients are invariant under permutations of their indices (i,j,k).

We can propose as an example the case $\lambda\ =\ 4$,

$$\boldsymbol{\Psi}_{\lambda=4} = C_1(\xi_1^4+\xi_2^4+\xi_3^4) + C_2(\xi_1^2\xi_2^2+\xi_1^2\xi_3^2+\xi_2^2\xi_3^2) \ , \tag{25}$$

where, by virtue of the conditions in Eq. (24), the following holds:

$$C_1 = C_{400} = C_{040} = C_{004}; \;\; C_2 = C_{220} = C_{022} = C_{202} \ . \tag{26}$$

A definitive proof of the invariance of the wavefunctions in Eqs. (20) and (23) under the action of the O_h group can be obtained by examining the symmetry operations of O_h in a matrix form. It can be seen that all operations of the group lead to a permutations of the ξ's plus eventually a change of sign of one, two or three of the ξ's. So, to represent the symmetry operations we deal with 3×3 orthogonal matrices containing three unit vectors.

We will use code symbols for the matrices according to the following examples. For the identity matrix E,

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ , \tag{27}$$

we use the notation (1, 2, 3) and for the matrix $\hat{R}(\xi_1\hat{}\xi_3,\pi)$ corresponding to a rotation of π around the ξ_2-axis,

$$\hat{R}(\xi_1\hat{}\xi_3,\pi) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \ , \tag{28}$$

we use $(3,-2,1)$.

In other words, in this notation the first number of the triplet indicates in what position the 1 is placed in the first row, the second number indicates the position in the second row and so on. The minus sign, where present, stands for -1.

We now report the complete list of the operations of the octahedral group O according to our notation:

$$\begin{bmatrix} (2,3,1) & (3,1,2) & (-2,-3,1) & (-3,-1,2) \\ (-2,3,-1) & (-3,1,-2) & (2,-3,-1) & (3,-2,-1) \end{bmatrix} \quad 8C_3 \text{ class} \ ,$$

$$[(-1,-2,3) \quad (1,-2,-3) \quad (-1,2,-3)] \ 3C_4^2 \text{ class} \ ,$$

$$\begin{bmatrix} (3,-2,1) & (-1,3,2) & (2,1,-3) \\ (-3,-2,-1) & (-1,-3,-2) & (-2,-1,-3) \end{bmatrix} 6C_2 \text{ class} \ ,$$

$$\begin{bmatrix} (2,-1,3) & (1,3,-2) & (-3,2,1) \\ (-2,1,3) & (1,-3,-2) & (3,2,-1) \end{bmatrix} 6C_4 \text{ class} \ .$$

We do not write explicitly the inversion operation [matrix $(-1,-2,-3)$] and the additional 24 symmetry operations of the group O_h since these can be simply obtained by changing the signs of the elements in the matrices.

By using the matrix form of the symmetry operations, it can be verified that the wavefunctions in the form of Eq. (20) and Eq. (23), are O_h-invariant as a consequence of the relationships of Eq. (24).

6 Angular parameterization of the kinematic invariant wavefunctions

We have seen in the previous sections that the kinematic invariant wavefunctions are homogeneous polynomials of degree λ in the ξ_i's. In other words they are a sum of terms of degree λ, which are products of the ξ_i's.

If we introduce an angular parameterization of (ξ_1, ξ_2, ξ_3) involving the hyperradius ρ plus two angular variables, for example, $(\rho \sin\theta\cos\phi, \rho\sin\theta\sin\phi, \rho\cos\theta)$, then the wavefunction Ψ_λ becomes a factor ρ^λ times an angular wavefunctions $X_\lambda(\Omega)$:

$$\Psi_\lambda(\xi_1, \xi_2, \xi_3) = \rho^\lambda X_\lambda(\Omega) \ , \tag{29}$$

where Ω denotes collectively the angular variables.Then to obtain the angular part $X_\lambda(\Omega)$ we need only to factor ρ^λ out of the wavefunction Ψ_λ.

A more direct route to do that is to represent the angular wavefunction $X_\lambda(\Omega)$ as a linear combination of spherical harmonics $Y_{lm}(\theta, \phi)$ [42, 43]. Since the $\Psi_\lambda(\xi_1, \xi_2, \xi_3)$ is a polynomial of degree λ, then only the spherical harmonics with $l \leq \lambda$ contribute to the expansion. So, we have

$$X_\lambda(\Omega) = \sum_{l,m}^{\lambda} a_{lm}^\lambda Y_{lm}(\theta, \phi) \ , \tag{30}$$

where the a_{lm}^λ's are the coefficients of the linear combination. The issue is to determine the a_{lm}^λ's.

In Sect. 4 and 5 we obtained the C coefficients for the wavefunctions in Eqs. (20) and (23) by solving Eq. (21); now we can obtain the a coefficients by solving the angular part of Eq. (21):

$$-\frac{\hbar^2}{2\mu\rho^2}\left(\nabla_\Omega^2 + \frac{2}{\sqrt{D(\Omega)}}\nabla_\Omega\sqrt{D(\Omega)}\nabla_\Omega\right) \ , \tag{31}$$

where ∇_Ω^2 and ∇_Ω are the usual Laplacian and gradient operators in ordinary spherical coordinates. $D(\Omega)$ is the angular part of the volume element D (see Sect. 4):

$$\begin{aligned} D(\Omega) &= (\sin^2\theta\cos 2\phi)(\cos^2\theta - \sin^2\theta\cos^2\phi) \\ &\quad \times (\cos^2\theta - \sin^2\theta\sin^2\phi) \\ D(\xi_1, \xi_2, \xi_3) &= \rho^6 D(\Omega) \ . \end{aligned} \tag{32}$$

Another way to obtain the angular part of the kinematic invariant wavefunction consists in representing the quantities ξ_1^2, ξ_2^2 and ξ_3^2 as a function of spherical harmonics and then substituting them into the wavefunction $\Psi_\lambda(\xi_1, \xi_2, \xi_3)$ obtained as a solution of Eq. (21).

For example, for ξ_1 we have:

$$\xi_1^2 = \rho^2\left[\frac{1}{3}\left(1 - 2\sqrt{\frac{\pi}{5}}Y_{20}\right) - \sqrt{\frac{2\pi}{15}}(Y_{22} + Y_{2-2})\right] \ . \tag{33}$$

Following this procedure, one may calculate, as an example, the angular part of the wavefunction $\Psi_{\lambda=4}(\xi_1, \xi_2, \xi_3)$ as obtained from Eq. (21),

$$\begin{aligned} \Psi_{\lambda=4}(\xi_1, \xi_2, \xi_3) &= 2(\xi_1^2 + \xi_2^2 + \xi_3^2) \\ &\quad - 7(\xi_1^2\xi_2^2 + \xi_1^2\xi_3^2 + \xi_2^2\xi_3^2) \ , \end{aligned} \tag{34}$$

and, after substitutions

$$\Psi_{\lambda=4} = \frac{\rho^4}{15}\left(22\sqrt{\frac{5\pi}{14}}(Y_{44} + Y_{4-4}) + 22\sqrt{\pi}Y_{40} - 3\right) \ . \tag{35}$$

The main difficulty of the substitution procedure is encountered when, especially for the higher values of the quantum number λ, multiple products of the ξ^2's are met, leading to products of spherical harmonics.

Obviously the products of spherical harmonics of whatever order, can be reduced to a sum of simple spherical harmonics by applying to them iteratively the well-known Clebsch–Gordan series [42]. The formula for the product of two spherical harmonics is

$$\begin{aligned} Y_{l_1m_1}Y_{l_2m_2} &= \sum_{LM}\sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} \\ &\quad \times C_{l_10l_20}^{L0}C_{l_1m_1l_2m_2}^{LM}Y_{LM} \ , \end{aligned} \tag{36}$$

where the symbols $C_{l_1m_1l_2m_2}^{LM}$ are Clebsch–Gordan coefficients and the two indices L and M run over all the values permitted by the usual rules for the sum of angular momenta.

Whatever may be the approach to the calculation of the angular part $X_\lambda(\Omega)$ of the kinematic invariant wavefunctions, it is useful to symmetrize the spherical harmonics according to the fact that the wavefunction must belong to the A_1 and A_2' irreps of the O_h symmetry group. Namely, none of the spherical harmonics in the sum representing the wavefunction should contain terms with different symmetry components.So we need to project out the right symmetry components for each of the spherical harmonics by means of the projection operators. It is worth noting that symmetry with respect to the inversion operation is completely determined by the quantum number λ for the wavefunctions and by l for the spherical harmonics. So we can work with the O group instead of the O_h group.

The projection operator $\hat{P}_{A_1}$ for the A_1 irrep of the O group has the following form:

$$\hat{P}_{A_1} = \frac{1}{24}\sum_R \chi^*_{A_1}(R)P_R \ , \tag{37}$$

where the sum runs over the 24 operations of the group, P_R is the operator corresponding to the symmetry operation R and $\chi^{A_1}(R)$ is the character of the operation R in the A_1 irrep of the group O.

Since we reduced our analysis to group O by virtue of the simple behaviour of the Ψ_λ and of the spherical harmonics under the action of the inversion operation, we do not need to use the projection operator for the A'_2 irrep. We simply project out applying the operator in Eq. (37) and in the case of odd values of the quantum number λ (or l for the spherical harmonics), we assume the result to be the A'_2 symmetry component of the function.

6.1 The projection of the spherical harmonics

In the previous section we outlined a general procedure to obtain the angular part $X_\lambda(\Omega)$ of the kinematic invariant wavefunctions Ψ_λ, and suggested the advantages of stressing their symmetry properties. To this aim, the key point is the projection of the right symmetry component of the spherical harmonics, which we use to represent $X_\lambda(\Omega)$ in a finite sum. In the following we illustrate the way to obtain these projections in a systematic manner.

If a given spherical harmonic Y_{lm} has the required symmetry, then

$$\hat{P}_{A_1} Y_{lm} \neq 0 \ , \tag{38}$$

otherwise the projection will vanish.

We have shown in the previous sections that the 24 symmetry operations of group O are rotations. These rotations act, according to a passive representation, by a corresponding rotation of the reference frame to which the harmonics are referred. These rotations can be parameterized, as usual, by means of three Euler angles α, β and γ.

Under the effect of a rotation of the reference frame a spherical harmonic becomes a linear combination of Y_{lm}'s of the same order l. The coefficients of the linear transformation are the Wigner functions $D^l_{m'm}(\alpha\beta\gamma)$ [42]. Therefore, for a symmetry operator $\hat{P}_R$ of group O, we write:

$$\hat{P}_R Y_{lm} = \sum_{m'} D^l_{m'm}(\alpha_R\beta_R\gamma_R) Y_{lm'} \ , \tag{39}$$

where α_R, β_R and γ_R are three Euler angles describing the rotation R according to the symmetry operation.

As a consequence, the explicit form of the projector operator $\hat{P}_{A_1}$ acting on the spherical harmonics is:

$$\hat{P}_{A_1} Y_{lm} = \frac{1}{24}\sum_R \chi^*_{A_1} \sum_{m'} D^l_{m'm}(\alpha_R\beta_R\gamma_R) Y_{lm'} \ . \tag{40}$$

By using the values of the Euler angles for the symmetry operations of group O, the explicit values of the Wigner D functions, and exploiting the simple behaviour of the harmonics under inversion, we find that for a given odd value of l only for $m = \pm 2, \pm 6, \pm 10, \dots$ the function contains symmetry components of the A'_2 irrep of group O_h and for a given even value of l only for $m = 0, \pm 4, \pm 8, \dots$ the function contains symmetry components the of the A_1 irrep of group O_h.

The symmetrized spherical harmonics are found to be

$$\hat{P}_{A_1} Y_{lm} = \frac{1}{6}(Y_{lm} + Y_{l-m}) - \frac{2}{3}\sum_{m'=0,\pm 4,\pm 8,\dots} d^l_{m'm}(\frac{\pi}{2}) Y_{lm'} \tag{41}$$

for even values of l, and

$$\hat{P}_{A'_2} Y_{lm} = \frac{1}{6}(Y_{lm} - Y_{l-m}) - \frac{2}{3}\sum_{m'=\pm 2,\pm 6,\pm 10,\dots} d^l_{m'm}(\frac{\pi}{2}) Y_{lm'} \tag{42}$$

for odd values of l.

6.2 Degeneracy of the kinematic invariant wavefunctions

The degeneracy of the eigenfunctions Ψ_λ depends on the degeneracy of the corresponding angular parts $X_\lambda(\Omega)$. The degeneracy of the $X_\lambda(\Omega)$'s is not zero if and only if it is possible to construct a polynomial (in sines and cosines) of degree λ belonging to the A_1 and A'_2 irreps of the O_h symmetry group, respectively, for even and odd values of the quantum number λ.

However $X_\lambda(\Omega)$ is a linear combination of spherical harmonics Y_{lm} with $l \leq \lambda$. Thus the $X_\lambda(\Omega)$ wavefunction with quantum number λ has nonzero degeneracy if and only if the corresponding spherical harmonic with $l = \lambda$ has nonzero projection under the action of the operators $\hat{P}_{A_1}$ (λ even) or $\hat{P}_{A'_2}$ (λ odd).

Obviously, degeneracies higher than 1 have to be expected since the Y_{lm}'s can generate reducible representations of the O_h group. In this case the number of degenerate wavefunctions for a given λ corresponds to the coefficient of the A_1 (even λ) or A'_2 (odd λ) irreps in the decomposition of the reducible representation in terms of the reducible ones.

For example, if we denote as Γ a given reducible representation of the O_h symmetry group, generated from the $Y_{l=\lambda,m}$ spherical harmonic, and

$$\Gamma = 2A_1 + 2E + \dots$$

then the degeneracy would be equal to 2.

The contribution to the reducible representation of the O_h group can be calculated by standard group theory, and if we denote as N the degeneracy we obtain for the even-λ case (again restricting the analysis to the O group)

$$N(\lambda, A_1) = \frac{1}{24}\sum_R \chi^\lambda(\omega_R)\chi^{A_1}(R) \ , \tag{43}$$

where R runs on the operations of the O symmetry group, ω_R is the angle of the rotation corresponding to the symmetry operation R, in an axis–angle parameterization, and $\chi^\lambda(\omega_R)$ and $\chi^{A_1}(R)$ are the characters of the symmetry operation R in the reducible and irreducible representation, respectively.

For the characters $\chi^(\lambda)(\omega_R)$ of the reducible representation, we have [42]

$$\chi^\lambda(\omega_R) = \frac{\sin\left[(2\lambda+1)\frac{\omega_R}{2}\right]}{\frac{\omega_R}{2}} \ . \tag{44}$$

7 Conclusions

In summary, we have found a group-theoretical procedure to determine the four-body hyperspherical harmonics for zero angular momentum and zero kinematic rotations. The procedure is based on a geometrical approach whose key step is the understanding of the symmetry properties that the harmonics must satisfy.

The extension of this work should be the enlargement of the harmonic basis to comprise the cases with nonzero angular momenta, while the extension to $N > 4$ requires care only regarding the range of a coordinate. For a complete alternative solution of the construction of a harmonic basis set for the four-body problem, see Ref. [15], where a recurrence algorithm is described and exploited.

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