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Hyperspherical coordinates for molecular dynamics by the method of trees and the mapping of potential energy surfaces for triatomic systems

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Some results on hyperspherical coordinates and harmonics for the representation of the many-body problem are presented, extensive use being made of the method of trees. Properties of these trees are examined: a lemma on the simplification of trees possessing a particular symmetry is proven, and used to discuss the internal coordinates for a system of three particles and the mapping of potential energy surfaces. A framework is provided for relating different couplings of particles by rotations on hyperspheres and alternative hyperangular parametrizations by orthogonal basis transformations. Extensions to nonzero angular momentum or to more than three particles are shown not to be trivial, and the possible role of developments of the tree method, leading to more general hyperspherical coordinates, is briefly considered.

I. INTRODUCTION

The purpose of this paper is to present some results on the hyperspherical coordinates for the representation of the many-body problem. Several reviews are now available,[1–3] and are useful introductions to various aspects of this approach. Although the hyperradius, ρ, the variable which is basic to this method, appears already in Jacobi's investigations on the three-body problem it is in quantum mechanics that its use for the helium problem was first exploited.[4] Since then, the hyperspherical method became one of the main tools in the quantum mechanical treatment of the interaction between few particles. Extensive applications to nuclear, atomic, and molecular processes have been made, and are being made. They involve both studies of bound states, and the treatment of scattering problems.

The basic idea of the hyperspherical approach is the introduction of the ρ variable, which plays the role of a radius of a hypersphere. It arises when the kinetic energy of a system of N particles is written in terms of $N-1$ vectors which allow to factor out the center-of-mass motion. It has the properties of being invariant with respect to particle permutations, and this makes the hyperradius useful for the description of rearrangement problems. Actually, although the results which follow may have relevance for the general many-body problem, the point of view taken in this paper stresses the possible applications to intramolecular dynamics and to chemical kinetics.

Substantial advancements both for the semianalytical, qualitative understanding and for the quantitative treatment of bound states and reactions has been obtained by the introduction of the hyperradius as a nearly separable variable.[5] The other variables, which, besides the hyperradius are needed for the complete formulation of the problem, can be parametrized as (hyper-)angles spanning the surface of hyperspheres. This can be done in many ways,[1,6] many possibilities exist for exploiting harmonic analysis on the surface of hyperspheres, and in general the full power of the theory of representations for the higher rotation groups can be made to enter into play. The assumption of the validity of some of the symmetries which these groups imply (and the variety of choices for hyperangles) will be shown in the following to correspond to the choice of coupling schemes, which suggest approximate decoupling of the dynamic equations: the appearance of approximate quantum numbers labeling the elements of bases may serve as powerful starting points for the numerical approach to the solution of the problem.[7]

The key papers for modern developments were by Smith, who introduced a generalization to hyperspaces of the concept of angular momentum[8] and gave a full treatment of the motion of three particles on a plane.[9]

The early motivation of the work by Smith was to deal with the rearrangement problem which arises in the treatment of chemical reactions[10]: this led him to introduce, in the treatment of several particles constrained to move on a line, the concept of kinematic rotations, which appeared as a generalization of the concept of the reaction skewing angle, already well known in chemical kinetics. The usefulness of this concept in the general case is now apparent, as demonstrated in the previous paper,[11] where the vectors which lead to orthogonal coordinates for the many-body problem were explicitly constructed. This paper proceeds, in the following section, by describing in some detail the hyperspherical parametrization of these vectors, and the concept of kinematic rotation will allow us to reduce within a unified framework several alternatives which are of interest. Section II also provides an introduction to the tree method for the building up of hyperspherical coordinates and harmonics.

In Sec. III, which contains the main results of this paper, we prove a lemma which will serve to simplify the three-body problem for zero total angular momentum. The mapping of the three-body potential energy surfaces is discussed in Sec. IV. Finally, in Appendix A, we have collected working formulas and references for harmonic expansions of interparticle distances and potential energy surfaces, and in Appendix B it is sketched a possible way of generalizing the tree method for obtaining alternative systems of hyperspherical coordinates.

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II. THE HYPERRADIUS AND THE MAPPING OF KINETIC ENERGY ONTO A HYPERSPHERE

In the previous paper[11] we have discussed how to construct vectors for the representation of the motion of N particles in a Euclidean space of dimension D ($D = 1$ for a line, $D = 2$ for a plane, $D = 3$ for the physical space). These vectors, $N - 1$ in number, can be defined in alternative ways depending on the order the particles are considered, their coupling scheme, the possible symmetrization with respect to some particle. The purpose of this section is to introduce the hyperspherical parametrization of these vectors and to exploit some of the advantages one gets in using the properties of the higher rotation groups.

We consider again the matrix formed by taking as columns the Cartesian coordinates of the mass scaled vectors $\mathbf{x}_i$.[11] The resulting $D \times (N-1)$ matrix can be parametrized as

$$\mathbf{x} = \mathbf{e}\ \mathrm{diag}(x_1, x_2, \ldots, x_{N-1}) , \tag{1}$$

where $\mathbf{e}$ is a $D \times (N-1)$ matrix whose normalized columns represent the directions of the vectors in D space, while the lengths x_i of these vectors are arranged in a diagonal $(N-1) \times (N-1)$ matrix. As in the Appendix to Ref. 11, it is also convenient to consider the transpose of the $\mathbf{x}$ matrix, and to parametrize it in a similar way:

$$\tilde{\mathbf{x}} = \mathbf{f}\ \mathrm{diag}(z_1, z_2, \ldots, z_D) , \tag{2}$$

where now the directions and lengths are for vectors in the kinematic $N-1$ dimensional space, and therefore the $(N-1) \times D$ matrix $\mathbf{f}$ specifies the directions, and z_k their lengths.

In the hyperspherical parametrization, a function is introduced, the hyperradius ρ, as [see Eq. (A8) in Ref. 11]:

$$\rho^2 = \sum_{i=1}^{N-1} x_i^2 = \sum_{k=1}^{D} z_k^2 . \tag{3}$$

The remaining $n = (N-1) \times D - 1$ coordinates can now be considered as specifying the coordinates on an S^n hypersphere, and therefore they will typically be n hyperangles Ω_n. The kinetic energy operator in these coordinates can be written

$$\mathbf{T} = -\frac{\hbar^2}{2m}\left[\rho^{-n}\frac{\partial}{\partial\rho}\rho^{n}\frac{\partial}{\partial\rho} + \rho^{-2}\Delta_0(\Omega_n)\right] , \tag{4}$$

where $\Delta_0(\Omega_n)$ is the Laplacian on the unit S^n hypersphere. As in Ref. 11, the mass m (essentially an arbitrary parameter) is here taken as the sum of masses of the particles.

There are very many ways for defining angular parametrizations on hyperspheres. The freedom of choosing between several possibilities is one of the main powers of this approach.

A. Orthogonal coordinates and the tree representation

The method of trees[2,12,13] is very useful to represent in a graphical way the relationships between Cartesian coordinates and angular parametrizations on hyperspheres. It can be illustrated by reference to the examples in Fig. 1 for S^2 and S^3. A n-dimensional sphere will be parametrized either by $n + 1$ Cartesian coordinates or by a (hyper)radius ρ and n (hyper)angles. To the Cartesian coordinates, we will put into correspondence $n + 1$ leaves, which will be connected by branches which join at n nodes, representing the angles. As a convention, we will consider as representing the cosine (sine) of the hyperangle the branch converging to the node from the left-hand side (right-hand side). Starting then from a leaf and descending to the root of the tree, through the various nodes, we have a relationship between coordinates and hyperangles: Fig. 1 shows different ways of doing that by reference to the examples for $S^2 \subset \mathbf{R}^3$ and $S^3 \subset \mathbf{R}^4$. Figure 2 shows the elementary forks which constitute a tree, and gives the ranges span by angles.

When for a hyperspherical parametrization a graphical representation is possible by the tree method, then the coordinates can be shown to form an orthogonal system. This will be demonstrated by showing that the metric tensor is

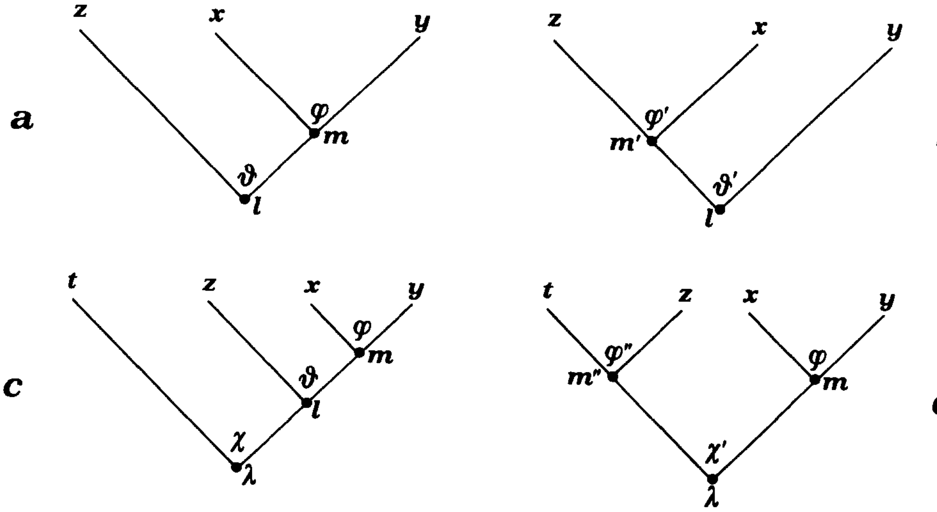

FIG. 1. Trees a and b represent for the three-dimensional sphere, S^2, the correspondence $x = \rho\sin\theta\cos\varphi = \rho\cos\theta'\sin\varphi'$; $y = \rho\sin\theta\sin\varphi = \rho\sin\theta'$; $z = \rho\cos\theta = \rho\cos\theta'\cos\varphi'$. They also represent harmonics of $O(3)$ labeled by l, m, and l, m', respectively. Similarly, trees c and d represent two alternative parametrizations for S^3 and the labels for the corresponding harmonics of $O(4)$: tree c corresponds to the standard subgroup reduction chain $O(4) \supset O(3) \supset O(2)$, and tree d to the chain $O(4) \supset O(2) \times O(2)$.

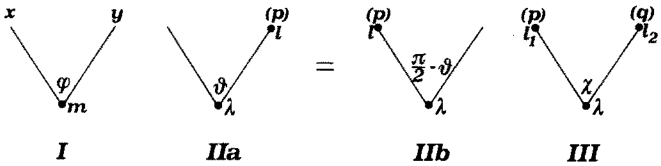

FIG. 2. Elementary binary forks (for ternary forks, see Appendix B). Ranges spanned by angles are $0 \leqslant \varphi < 2\pi$, $0 \leqslant \theta \leqslant \pi$, $0 \leqslant \chi \leqslant \pi/2$. In I, m takes the values 0, $\pm 1, \pm 2, \ldots$. In II and III, λ is zero or a positive integer; l, l_1, l_2 assume the values $0,1,\ldots,\lambda$ (and also the negative values if at the roots of forks of type I). In III, there is the further restriction that $\lambda - l_1 - l_2$ must be even and positive, or zero. The corresponding orthonormal systems are given in Sec. II B.

diagonal: furthermore, since the Laplacian on the hypersphere will not contain cross terms (i.e., products of derivatives corresponding to different hyperangles), the corresponding Laplace equations are separable and the hyperspherical harmonics will be constructed in closed form.

The elements of the metric tensor **g** are defined in terms of the derivatives of the $n+1$ Cartesian coordinates with respect to the n hyperangles ω_i,[14]

$$g_{ij} = \sum_{k=1}^{n+1} \frac{\partial x_k}{\partial \omega_i} \frac{\partial x_k}{\partial \omega_j} = g_{ji} . \tag{5}$$

The Laplace operator on the unit hypersphere is, in these coordinates:

$$\Delta_0(\Omega_n) = g^{-1/2} \sum_{i,j=1}^{n} \frac{\partial}{\partial \omega_i} g^{1/2} g^{ij} \frac{\partial}{\partial \omega_j}, \tag{6}$$

where g^{ij} are the elements of the matrix inverse of **g**,

$$\sum_j g_{ij} g^{jk} = \delta_{ik} \tag{7}$$

and

$$g = \det \mathbf{g} . \tag{8}$$

When x_k and ω_i are related by a tree, it can be verified that the off-diagonal elements of the metric tensor are zero, and therefore the coordinates are orthogonal. Then the diagonal elements can be identified with scale factors, $g_{ii} = h_i^2$, and the Laplace operator simplifies as follows:

$$\Delta_0(\Omega_n) = \left(\prod_{k=1}^{n} h_k\right)^{-1} \sum_{i=1}^{n} \frac{\partial}{\partial \omega_i} \left[\left(\prod_{k=1}^{n} h_k\right) \Big/ h_i^2\right] \frac{\partial}{\partial \omega_i} . \tag{9}$$

This angular Laplacian acts on the $n+1$ space of hyperspherical harmonics:

$$\Delta_0(\Omega_n) Y^{n+1}_{\lambda\{\nu_{n-1}\}}(\Omega_n) = -\lambda(\lambda+n-1) Y^{n+1}_{\lambda\{\nu_{n-1}\}}(\Omega_n) \tag{10}$$

with eigenvalues $-\lambda(\lambda+n-1)$. The number λ labels the root of any tree with $n+1$ leaves. In Eq. (4), it plays the physical role of the hyperangular momentum quantum number.[8] The remaining set of $n-1$ quantum numbers ν_i is associated with the other nodes in the tree (Fig. 1). It can be shown[14] that for a given value of λ, the total number of admissible harmonics is

$$\mathscr{N}(n+1,\lambda) = \frac{(2\lambda+n-1)\Gamma(\lambda+n-1)}{\Gamma(\lambda+1)\Gamma(n)} . \tag{11}$$

For further reference, we also note that the surface of the sphere S^n of unit radius, Σ^{n+1}, is given by[14]

$$\Sigma^{n+1} = \frac{2\pi^{(n+1)/2}}{\Gamma[(n+1)/2]} . \tag{12}$$

Example a in Fig. 1 leads to the usual three-dimensional Laplacian and spherical harmonics for S^2, b being an alternative due to a rotation of the reference frame [see Sec. II C]. For S^3, the two basically different trees c and d lead to the following expressions for the Laplace operator:

$$\begin{aligned}\Delta_0(\Omega_3) &= \frac{1}{\sin^2\chi}\left(\frac{\partial}{\partial\chi}\sin^2\chi\frac{\partial}{\partial\chi} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\frac{\theta\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\ &= \frac{1}{\sin\chi'\cos\chi'}\frac{\partial}{\partial\chi'}\sin\chi'\cos\chi'\frac{\partial}{\partial\chi'} + \frac{1}{\cos^2\chi'}\frac{\partial^2}{\partial\varphi''} + \frac{1}{\sin^2\chi'}\frac{\partial^2}{\partial\varphi'^2},\end{aligned} \tag{13}$$

whose eigenfunctions will be met later. Both hyperangular representations, leading to structurally different harmonics, enter into play for the problem of the motion of three particles in space.

B. Hyperspherical harmonics by the method of trees

Trees not only relate Cartesian coordinates and (hyper) angles: they also can be taken to represent hyperspherical harmonics $Y^{n+1}_{\lambda\{\nu_{n-1}\}}$, i.e., solutions to Eq. (10). Explicitly, when the angular coordinates chosen to parametrize the Cartesian coordinates form an orthogonal system, then the Laplace equation (10) can be solved by the method of separation of angles. The eigenfunctions $Y^{n+1}_{\lambda\{\nu_{n-1}\}}$ are then given by products of orthogonal functions, which are represented by the fundamental forks which form a given tree. The relevant formulas are given in the Russian literature[2,12,15]: here, we collect some of them to establish the notation, correct some misprints and writing down some additional relationships which will be needed later.

These forks can be classified in four types (Fig. 2). The simplest fork is a node with two leaves, its orthonormal system is given by

$$|\varphi;m\rangle = (2\pi)^{-1/2} e^{im\varphi} \tag{14}$$

and the Cartesian coordinates, which span the circle given by $\rho^2 = x^2 + y^2 =$ constant, are

$$x=\rho\cos\varphi;\quad y=\rho\sin\varphi. \tag{15}$$

The fork of the type IIa is given by a leaf on the left-hand side, and a node on the right-hand side. When the node is a root to a tree with p leaves, the corresponding function is

$$|\theta;\lambda;l,p\rangle = A^{p}_{\lambda l}\sin^{l}\theta P^{l+(p-2)/2,\,l+(p-2)/2}_{\lambda-l}(\cos\theta), \tag{16}$$

where the normalization factor is

$$A^{p}_{\lambda l}=\frac{[(2\lambda+p-1)(\lambda-l)!\Gamma(\lambda+l+p-1)]^{1/2}}{2^{l+(p-1)/2}\Gamma(\lambda+p/2)}. \tag{16'}$$

The Jacobi polynomial $P^{l+(p-2)/2,\,l+(p-2)/2}_{\lambda-l}(\cos\theta)$ can be identified with a Gegenbauer, or ultraspherical polynomial,[16] so that we also have[17]

$$|\theta;\lambda;l,p\rangle = B^{p}_{\lambda l}\sin^{l}\theta C^{l+(p-1)/2}_{\lambda-l}(\cos\theta), \tag{17}$$

where

$$B^{p}_{\lambda,l}=\frac{\Gamma(2l+p-1)}{2^{l+(p-1)/2}\Gamma(l+p)}\left[\frac{(2\lambda+p-1)(\lambda-l)!}{\Gamma(\lambda+l+p-1)}\right]^{1/2}. \tag{17'}$$

It has to be noted that the Gegenbauer polynomials can be written as associated Legendre polynomials.[13,16] If the number of leaves is even, the corresponding associated Legendre polynomial will be labeled by integer quantum numbers, if it is odd it will be labeled by half-odd numbers. Forks of type IIb are related to the previous ones (Fig. 2) by a reflection on the root: their functions can be obtained by Eqs. (16) or (17) interchanging sines and cosines.

With these forks, it is possible to build up [see Eq. (10)] the standard hyperspherical harmonics $Y^{n+1}_{\lambda_n,\lambda_{n-1},\ldots,|\lambda_1|}$, which are eigenfunctions of the angular part of the Laplacian, Δ_0, are functions of the n hyperangles Ω_n which parametrize the sphere S^n, and are labeled by n integers

$$\lambda_n \geqslant \lambda_{n-1} \geqslant \cdots \geqslant \lambda_2 \geqslant |\lambda_1|.$$

Such a standard tree is shown in Fig. 3: according to Eq. (17), the corresponding hyperspherical harmonics are given by a product of Gegenbauer polynomials. To exhibit the connection with the familiar eigenfunctions of angular momentum in quantum physics, it is customary to use the symbols l and m for λ_2 and λ_1. For example, in order to obtain the harmonics, corresponding to the tree in Fig. 1a, we have to combine two forks, one of type I, and one of type IIa, obtaining

$$Y^{3}_{l,m}(\theta,\varphi)=|\theta;l;m;2\rangle|\varphi;m\rangle \tag{18}$$

which is recognized as the usual spherical harmonic in $\mathbf{R}^3$. For the example of the sphere S^3 (Fig. 1c) we have

$$Y^{4}_{\lambda lm}(\chi,\theta,\varphi)=|\chi;\lambda;l,3\rangle Y^{3}_{lm}(\theta,\varphi) \tag{19}$$

as the eigenfunction of Eq. (13).

Finally, let us consider now a fork of type III. The corresponding harmonics can be written as a Jacobi polynomial

$$|\chi;\lambda;l_1,p;l_2,q\rangle = N^{p,q}_{\lambda l_1 l_2}\sin^{l_2}\chi\cos^{l_1}\chi P^{l_2+(q-2)/2,\,l_1+(p-2)/2}_{\lambda/2-l_1/2-l_2/2}(\cos 2\chi), \tag{20}$$

$$N^{p,q}_{\lambda l_1 l_2}=\left[\frac{(2\lambda+p+q-2)[(\lambda-l_1-l_2)/2]!\Gamma[(\lambda+l_1+l_2+p+q-2)/2]}{\Gamma[(\lambda+l_1-l_2+p)/2]\Gamma[(\lambda+l_2-l_1+q)/2]}\right]^{1/2}, \tag{20'}$$

where p and q are the number of leaves above l_1 and l_2, respectively. The normalization factor $N^{p,q}_{\lambda l_1 l_2}$ agrees with that given in Ref. 2: the one given by Kil'dyushov[15] has a factor $2^{-(l_1+l_2)/2}$ which appears to be incorrect.

For the particularly important case, $p=q=2$, it is convenient to identify the Jacobi polynomial in Eq. (20) with a reduced Wigner rotation matrix,[18] obtaining

$$|\chi;\lambda;l_1,2;l_2,2\rangle = (-)^{l_1}[2(\lambda+1)]^{1/2} d^{\lambda/2}_{(l_1+l_2)/2,(l_1-l_2)/2}(2\chi). \tag{21}$$

Therefore, the tree in Fig. 1d corresponds to the harmonic

$$\bar{Y}^{4}_{\lambda mm''}(\chi',\varphi,\varphi'') = (-)^{m''}\left(\frac{\lambda+1}{2\pi^2}\right)^{1/2} D^{\lambda/2}_{(m''+m)/2,(m''-m)/2} \times(-\varphi''-\varphi,2\chi',\varphi-\varphi''), \tag{22}$$

where[18]

$$D^{j}_{mm'}(\alpha,\beta,\gamma)=e^{-im\alpha}d^{j}_{mm'}(\beta)e^{-im'\gamma}.$$

The bar over the symbol for the harmonic (22) indicates that we are not dealing with a standard tree of the type d in Fig. 1 (or as in Fig. 3). The harmonic in Eq. (22) is also an eigenfunction of Eq. (13): its connection with Eq. (19) will be established in the next section.

C. Operations on trees

Several types of manipulations of harmonics can be visualized and performed by the aid of the tree method. A basic operation is the multiplication of harmonics, which is exemplified by the well known Clebsch–Gordan series for $O(3)$. The extension to the higher rotation group is straightforward,[2] and, at least in principle, it is possible to expand the product of two harmonics of the same angles in terms of a linear combination of the same harmonics, the coefficients being extensions of the Clebsch–Gordan coefficients.

A more complicated operation on harmonics is addition: addition theorems combine harmonics which are functions of different sets of angles, $\Omega^{(1)}_n$ and $\Omega^{(2)}_n$, say. We will need in Sec. III the following important particular case[14] ($n \geqslant 2$):

$$\sum_{\{\nu_{n-1}\}} Y^{n+1}_{\lambda\{\nu_{n-1}\}}(\Omega_n^{(1)})\, Y^{n+1}_{\lambda\{\nu_{n-1}\}}(\Omega_n^{(2)}) = \frac{(2\lambda+n-1)\Gamma[(n+1)/2]}{2(n-1)\pi^{(n+1)/2}}\, C_\lambda^{(n-1)/2}(\cos\omega)\,. \tag{23}$$

The angle ω measures the angular difference on the surface of S^n between points having coordinates $\Omega_n^{(1)}$ and $\Omega_n^{(2)}$. It is given by the scalar product

$$\omega = \arccos \sum_k \frac{x_k^{(1)} x_k^{(2)}}{|x_k^{(1)}||x_k^{(2)}|}\,.$$

Equation (23) is the extension to higher spaces of the trivial $n = 1$ case:

$$e^{im\varphi_1} e^{im\varphi_2} = e^{im(\varphi_1+\varphi_2)}\,.$$

The case $n = 2$ is also well known:

$$\sum_m Y^3_{lm}(\theta_1,\varphi_1)\, Y^3_{lm}(\theta_2,\varphi_2) = \frac{2l+1}{4\pi} P_l(\cos\theta)\,, \tag{24}$$

where

$$\cos\theta = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)\,.$$

Both multiplication and addition formulas are often given in the literature for the standard tree representation of coordinates and harmonics (Fig. 3). However, it is not difficult to show that the corresponding formulas for nonstandard trees can be obtained through the use of the so-called timber coefficients, first discussed by Kil'dyushov.[15]

The possibility of changes in coupling schemes is described by particular rotations, and can be written as matrix elements (Timber coefficients). These coefficients have been classified and computed in Ref. 15, and the tree method visualizes them as graftings. The simplest ones, which we shall need in the following, are for the trees illustrated in Fig. 1. The relationship between harmonics corresponding to the S^2 trees a and b in Fig. 1, can be established using properties of the familiar $O(3)$ harmonics,

$$Y^3_{lm}(\theta,\varphi) = \sum_{m'=-l}^{l} \overline{Y}^3_{lm'}(\theta',\varphi')\, D^l_{m'm}(0,\pi/2,\pi/2) \tag{25}$$

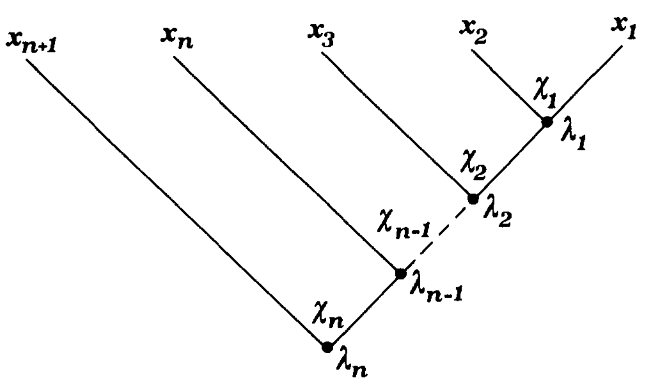

FIG. 3. Tree for the standard hyperspherical parametrization of S^n corresponding to the subgroup reduction chain $O(n+1)\supset O(n)\supset\cdots\supset O(2)$. The tree also represents the standard hyperspherical harmonic $y^{n+1}_{\lambda_n\lambda_{n-1}\ldots|\lambda_1|}(\chi_n,\chi_{n-1},\ldots,\chi_1)$.

(note a misprint in Kil'dyusciov paper) where the bar over the symbol for the harmonics indicates that we are considering the nonstandard tree b in Fig. 1.

The inverse to Eq. (25) is

$$\overline{Y}^3_{lm'}(\theta',\varphi') = \sum_{m=-l}^{+l} Y^3_{lm}(\theta,\varphi)\, D^l_{mm'}(-\pi/2,-\pi/2,0) \tag{26}$$

and it can be verified that

$$\overline{Y}^3_{lm'}(\theta',\varphi') = Y^3_{lm'}(\pi/2-\theta',\varphi') \tag{27}$$

as illustrated by relationships between trees in Fig. 4. The figure also shows that the standard harmonics in Eqs. (26) and (27) may be interpreted by a relabeling of coordinate axes.

For S^3 (trees c and d in Fig. 1), we have an interesting formula from the theory of $O(4)$ group[19]:

$$Y^4_{\lambda lm}(\chi,\theta,\varphi) = \sum_{m''=-l}^{+l} (-)^{(\lambda-m+m'')/2} \times \left\langle \frac{\lambda}{2}\,\frac{m-m''}{2}\,\frac{\lambda}{2}\,\frac{m+m''}{2}\,\middle|\, lm\right\rangle \times \overline{Y}^4_{\lambda mm''}(\chi'\varphi''\varphi)\,, \tag{28}$$

whereby the alternative harmonics given by Eqs. (19) and (22) are related by an orthogonal transformation matrix, whose elements are just the familiar su_2 Clebsch–Gordan coefficients.

III. SIMPLIFICATION OF TREES FOR INTERNAL COORDINATES

Having shown in the previous section how to construct by the tree method systems of hyperspherical coordinates, we return to our main theme, the use of such coordinates for the parametrization of the N-body problem.

In the following, we prove a lemma which will be shown to greatly simplify the problem of representation of potential energy surfaces and the treatment of the three particle motion in the particularly important case of zero total angular momentum.

A. A lemma on the pruning of symmetric trees

Consider a fork of type III, where the number p and q of leaves above each of its nodes is the same, and also $l_1 = l_2 = l$. In this case, the tree possesses a remarkable symmetry, which permits a drastic simplification. Note (Fig. 2) that λ must be even. We will show that the corresponding orthogonal functions [see Eq. (20)]:

$$|\chi;\lambda;l,p;l,p\rangle = N^{p,p}_{\lambda l}\sin^l\chi\cos^l\chi \times P^{l+(p-2)/2,\,l+(p-2)/2}_{(\lambda/2)-l}(\cos 2\chi) \tag{29}$$

are related to simpler ones corresponding to forks of type IIa [see Eq. (17)]:

$$|2\chi;\lambda/2;l,p\rangle = B^p_{(\lambda/2)l}\sin^l 2\chi\, C^{l+(p-1)/2}_{(\lambda/2)-l}(\cos 2\chi)\,. \tag{30}$$

In fact, using a known relationship between Jacobi and Ge-

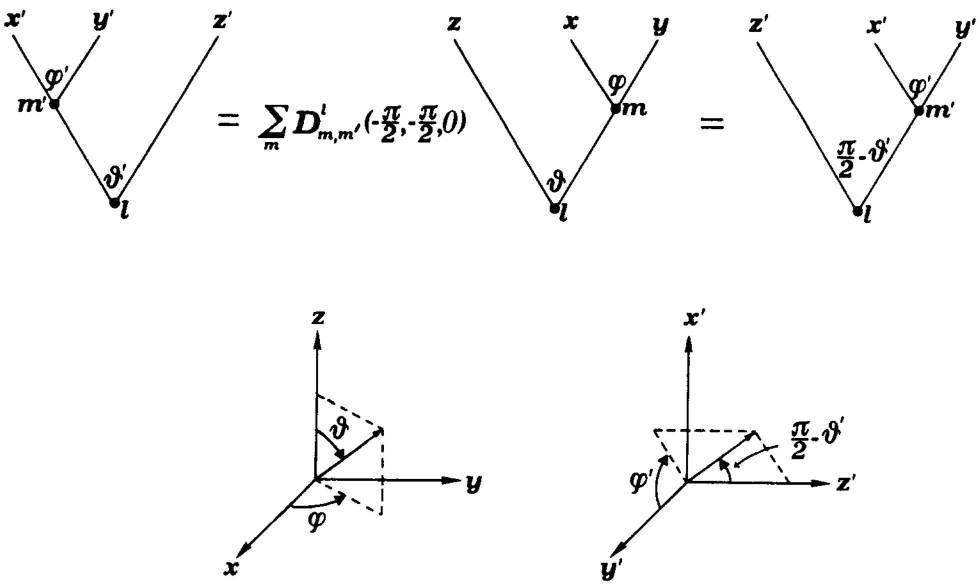

FIG. 4. The relationship between harmonics corresponding to the standard and nonstandard trees a and b in Fig. 1, as given by Eqs. (26) and (27), is illustrated, and seen to correspond to a rotation of the coordinate axes $z \to x', y \to z', x \to y'$.

genbauer polynomials,[16] we have

$$|\chi;\lambda;l,p;l,p\rangle = 2^{p/2}|2\chi;\lambda/2;l,p\rangle . \quad (31)$$

This identity is shown in Fig. 5: forks a and b are at the roots of trees representing harmonics for the group $O(2p)$, and $O(p+1)$, respectively. It can be verified that the factor $2^{p/2}$ accounts for the different contribution of the χ angle to the surfaces of the corresponding unit spheres[14,15] S^{2p-1} and S^p. The identity (31) will therefore be referred to as the *lemma for the pruning of symmetric trees.*

Such a symmetric fork will have grafted in general at its two nodes, two trees representing the product of two harmonics for the group $O(p)$,

$$Y^p_{l,\{\nu_{p-2}\}}(\Omega'_{p-1})\, Y^p_{l,\{\nu_{p-2}\}}(\Omega''_{p-1}) , \quad (32)$$

say, acting on a S^{p-1} sphere for sets of angles Ω'_{p-1} and Ω''_{p-1}, respectively.

Addition theorems (Sec. II C) allow to linearly combine these harmonics, so that the above lemma can be extended to give the possibility of effective simplification of harmonics showing particular symmetry. Explicitly, as a corollary of the above lemma and the addition formula (23), we obtain the following identity between $O(2p)$ harmonics and $O(p+1)$ harmonics,

$$\begin{aligned} |\chi;\lambda;l,p;l,p\rangle \sum_\nu Y^p_{l\{\nu_{p-2}\}}(\Omega'_{p-1})\, Y^p_{l\{\nu_{p-2}\}}(\Omega''_{p-1}) &= [\mathcal{N}(p,l)\Sigma^{p+1}/\Sigma^{2p}]^{1/2}|2\chi;\lambda/2;l,p\rangle\, Y^p_{l\{0_{p-2}\}}(\omega,0,0,...) \\ &= [\mathcal{N}(p,l)\Sigma^{p+1}/\Sigma^{2p}]^{1/2}\, Y^{p+1}_{\lambda/2,l\{0_{p-2}\}}(2\chi,\omega,\{0_{p-2}\}) , \end{aligned} \quad (33)$$

where we have used the identification, holding when the $p-2$ numbers $\nu,\{\nu_{p-2}\}$, are all zero, $\{0_{p-2}\}$:

$$Y^p_{l\{0_{p-2}\}}(\omega,0,0,...) = B^p_{l0}(\Sigma^{p-1})^{-1/2}C_l^{(p-2)/2}(\cos\omega) . \quad (34)$$

The sum over ν in Eq. (33) entails $\mathcal{N}(p,l)$ terms [see Eq. (11)]: this quantity, together with the surfaces Σ of the unit spheres [see Eq. (12)], appears as normalizing factors in Eq. (33).

This corollary allows, in some important cases, to reduce the dimensionality of a problem defined on the surface of a given hypersphere to that defined on a sphere of lower dimensionality. It will be used in the following for the reduction of the space of Jacobi coordinates (or the alternatives obtained by kinematic rotations[11]) to that, of lower dimensionality, of the internal coordinates. It will become apparent therefore that the pruning lemma allows to exploit the invariance of the system with respect to any rotation of the axes of the reference frame.

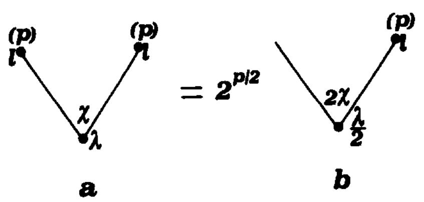

FIG. 5. The lemma for the pruning of the symmetric trees. The figure shows the identity [Eq. (31)] between a symmetric fork of type III and a fork of type II.

B. The pruning lemma for three particles on the plane and in space

The simplest symmetric tree, providing an important application of the pruning lemma, is given in Fig. 1d, where $m'' = \pm m$. In this case, $p = 2$ and identity (31) reads, for $m'' = m$,

$$\bar{Y}^4_{\lambda,m,m}(\chi',\varphi,\varphi'') = (-)^m\left(\frac{\lambda+1}{2\pi^2}\right)^{1/2} d^{\lambda/2}_{m,0}(2\chi')e^{im(\varphi''+\varphi)} = \left(\frac{2}{\pi}\right)^{1/2} Y^3_{\lambda/2,-m}(2\chi',-\varphi''-\varphi) \tag{35}$$

or, for $m'' = -m$,

$$\bar{Y}^4_{\lambda,m,-m}(\chi',\varphi,\varphi'') = (-)^m\left(\frac{\lambda+1}{2\pi^2}\right) d^{\lambda/2}_{0,m}(2\chi')e^{im(\varphi''-\varphi)} = (-)^m\left(\frac{2}{\pi}\right)^{1/2} Y^3_{\lambda/2,-m} \times(2\chi',\varphi-\varphi'') . \tag{36}$$

This reduction of harmonics from $O(4)$ to $O(3)$ is seen to entail a well-known identity between a reduced rotation matrix with zero projection and the associated Legendre polynomial.[18] The multiplicative factor appearing in Eq. (22) is recognized to be simply [see Eq. (33)] the square root of the ratio between the surfaces $\Sigma^3 = 4\pi$ for S^2, and $\Sigma^4 = 2\pi^2$ for S^3 [see Eq. (12)].

This result is useful for the quantum mechanics of three particles on a plane (see also Sec. IV B). It may be recalled[11] (see also Sec. II A) that two vectors are necessary in this case: let their Cartesian components on the plane be denoted (x,y) and (X,Y), respectively. (In the Jacobi parametrization, for example, x and y will be the components of the vector joining any two particles, and X and Y will be those of the vector joining the third particle to the center-of-mass of the other two). The hyperspherical parametrization can be obtained through the tree as shown in Fig. 6, where m_1 and m_2 have the physical meaning of angular momenta: this tree is identical to the one in Fig. 1d, but a new notation has been introduced, to facilitate the identification of symbols with corresponding physical quantities. The total angular momentum M is given in this case by their algebraic sum, $M = m_1 + m_2$.

Consider now $M = 0$, i.e., $m_2 = -m_1$. From Eq. (36) one obtains, by the pruning indicated as an arrow in Fig. 6b, an $O(3)$ tree, which can be taken as defining three new Cartesian coordinates, ξ, η, ζ, which can be parametrized in polar coordinates in alternative ways, two of which are shown in Fig. 6: as discussed previously (Sec. II C), the alternative parametrizations for harmonics are related by a linear combination, in this case the coefficients being rotation matrix elements [see Eq. (25)]. The corresponding relationship between angles is established by comparing trees c and d in Fig. 6:

$$\begin{aligned} \xi &= \rho \sin 2\chi \cos(\varphi_2 - \varphi_1) = \rho \cos 2\Theta \sin 2\Phi , \\ \eta &= \rho \sin 2\chi \sin(\varphi_2 - \varphi_1) = \rho \sin 2\Theta , \\ \zeta &= \rho \cos 2\chi = \rho \cos 2\Theta \cos 2\Phi . \end{aligned} \tag{37}$$

We can identify ξ, η, and ζ with three quantities given by Smith,[9] v/ρ, $4A/\rho$, and u/ρ, respectively; therefore, Eq. (37) provides the two alternative hyperangular parametrizations for the problem of the motion of three particles in a plane. The angles χ and $\varphi_2 - \varphi_1$ are the internal angles for the

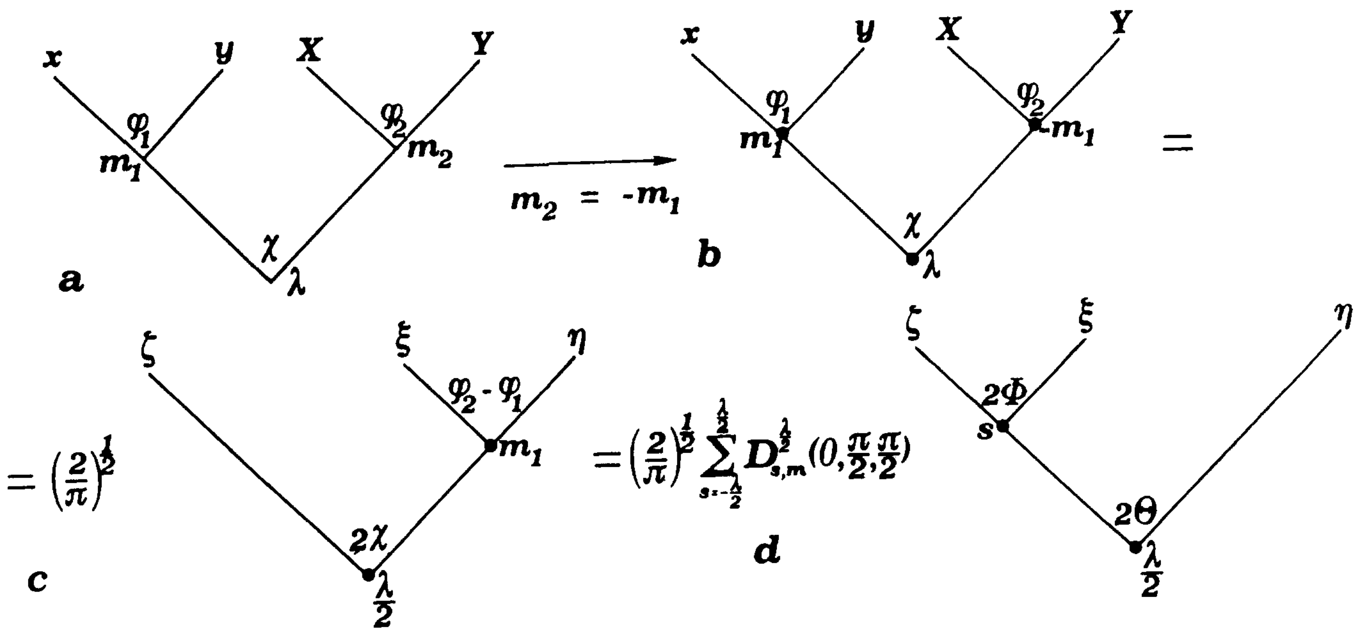

FIG. 6. Tree a represents the hyperspherical parametrization for the components (x,y) and (X,Y) of the two vectors which describe the motion of three particles on a plane. Tree b corresponding to zero total angular momentum ($m_2 = -m_1$), reduces to c by the pruning lemma. Tree d is obtained by c through a linear combination, and corresponds to Smith's parametrization (Ref. 9) for internal coordinates ξ,η,ζ.

asymmetrical representation,[9] and Θ and Φ are the internal angles for the so-called symmetrical representation of Smith.[9] The relationship between the two parametrizations is illustrated by a grafting joining the trees shown in Fig. 6. The "pruned" trees c and d correspond to an S^2 sphere, for which the ranges of angles are well defined: the ranges of $\varphi_2 - \varphi_1$ and 2Φ are between 0 and 2π and the quantum numbers $\lambda/2$, m_1, and s are allowed to assume only integer values. This in order that the space spanned by the internal coordinates ξ, η, ζ be $\mathbb{R}^3$.

In the applications, such a reduction will allow us to represent the interaction between particles by means of harmonics defined on the surface of the three-dimensional sphere S^2, by using coordinates which are invariant with respect to the rotations of the reference frame.

For the motion of three particles in the three-dimensional space, the Cartesian coordinates of the two Jacobi vectors span a Euclidean space $\mathbb{R}_6$ (Fig. 7). Since in this case $p = q = 3$, for the fork of type III (see Fig. 2), we can apply the pruning lemma when the condition $l_1 = l_2 = l$ is verified (tree b in Fig. 7). In such a case, the lemma on the pruning of symmetric trees (31) reduces a fork of type III to one of type IIa. Explicitly, from Eqs. (29)–(31),

$$A^{3}_{(\lambda/2)l} \sin^l\chi \cos^l\chi\, P^{l+1/2,\,l+1/2}_{\lambda/2-l}(\cos 2\chi) = 2^{3/2} B^{3}_{(\lambda/2)l} \sin^l 2\chi\, C^{l+1}_{\lambda/2-l}(\cos 2\chi)\,, \tag{38}$$

which is again recognized as an identity between particular Jacobi polynomials and Gegenbauer polynomials. Furthermore, corollary (33) now reads:

$$|\chi;\lambda;l,3;l,3\rangle \sum_m Y^3_{lm}(\theta_1,\varphi_1) Y^3_{lm}(\theta_2,\varphi_2) = \left[\frac{2(2l+1)}{\pi}\right]^{1/2} |2\chi;\lambda/2;l,3\rangle\, Y^3_{l0}(\theta,0)\,, \tag{39}$$

where use has been made of the addition formula (24). The sequence of trees c and d in Fig. 7 illustrates the reduction (38) and (39) from $O(6)$ to $O(4)$.

As for the previous case, we can obtain the explicit expression for the internal coordinates by considering the leaves of the tree d, the notation being chosen to facilitate the comparison. Moreover, a grafting of branches from a node to another one, illustrated in the figure by the tree e corresponds to a rotation of coordinate axes allows to introduce the angular parametrization of Smith[20,21] for three particles in space: explicity,

$$\begin{aligned} \xi &= \rho \sin 2\chi \cos\theta = \rho \cos 2\Theta \sin 2\Phi\,, \\ \eta &= \rho \sin 2\chi \sin\theta = \rho \sin 2\Theta\,, \\ \zeta &= \rho \cos 2\chi = \rho \cos 2\Theta \cos 2\Phi\,, \\ \tau &= 0\,. \end{aligned} \tag{40}$$

The relationship between the harmonics corresponding to the two angular parametrizations can be obtained by formula (28),

$$\frac{(\lambda+2)^{1/2}}{2\pi} e^{i\sigma\Phi} d^{\lambda/4}_{\sigma/4,\sigma/4}(4\Theta) = (-)^{(\lambda-\sigma)/4} \sum_l \left\langle \frac{\lambda}{4} - \frac{\sigma}{4}\, \frac{\lambda}{4}\, \frac{\sigma}{4} \,\middle|\, l0 \right\rangle \times Y^4_{\lambda/2,l0}(2\chi,\theta,0) \tag{41}$$

using the Timber coefficient described in Sec. II C. In Eq. (41), use has been made of Eq. (22) to write the harmonic for the tree e in terms of reduced rotation matrix elements. This result was first communicated some time ago,[22] and found to be useful for the treatment of three particles interacting through Coulomb forces,[7] and for approximations of the sudden type to elementary chemical reactions.[23]

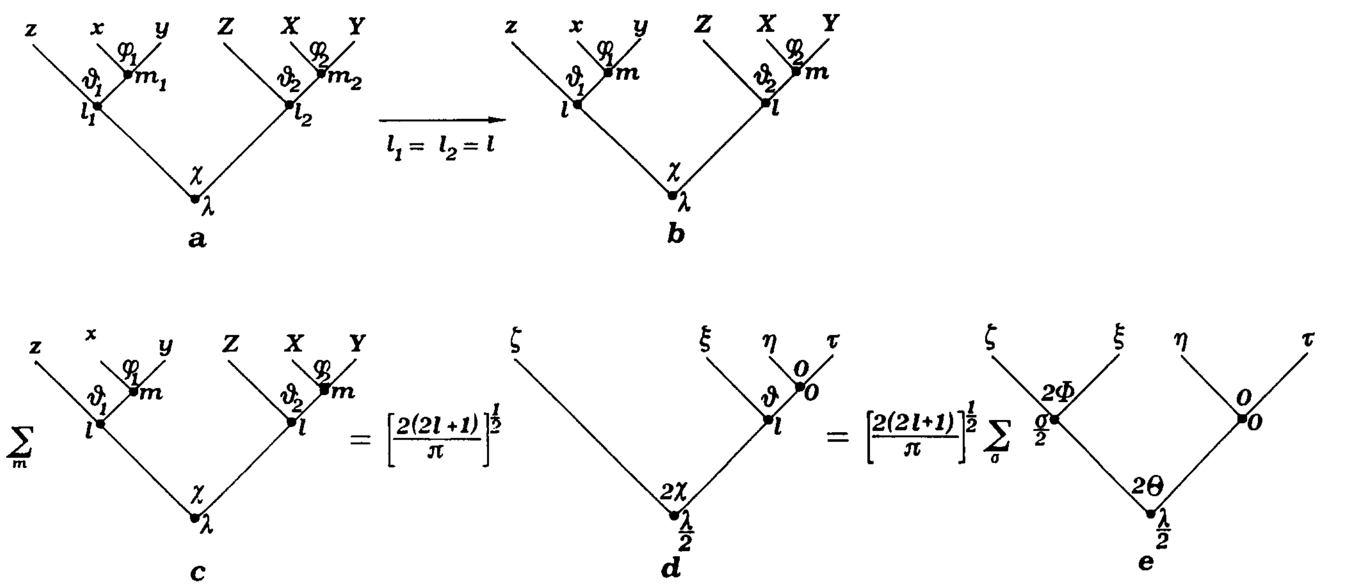

FIG. 7. Tree a represents the hyperspherical (Fock's) parametrization for the components (x,y,z) and (X,Y,Z) of the two vectors needed for describing the motion of three particles in space. The restriction to zero total angular momentum leads to trees of type b, which must be linearly combined as in c, allowing pruning to d and the introduction of the internal coordinates ξ,η,ζ. Tree d is obtained by c through a linear combination, and represents Smith's symmetrical representation (Ref. 20).

C. A theorem on the mapping of potential energy surfaces

From the lemma on the pruning of symmetric trees and its corollary which allows to reduce the dimensionality of spaces when certain conditions are verified, it is possible to draw considerations which are of interest for the quantum mechanical problem. In fact, we can formulate the following *mapping theorem*:

The spherical harmonics on the sphere S^{2D-1}, which are the solutions of the angular part of the Schrödinger equation for the kinetic energy of three particles in a D-dimensional Euclidean space, when the total angular momentum is zero can be linearly combined to give harmonics for the sphere S^{D+1}.

The above result can be interpreted (and given an alternative derivation) by considering directly the Laplacian operator Δ_0 acting on the hypersphere S^{2D-1} [see Eq. (4)]. The tree corresponding to its eigenfunctions is of the type a in Fig. 7, where the leaves above l_1 and l_2 are now in general D in number. The operator corresponding to the lower fork of such a tree is

$$\frac{1}{(\cos\chi\sin\chi)^{D-1}}\frac{\partial}{\partial\chi}(\cos\chi\sin\chi)^{D-1}\times\frac{\partial}{\partial\chi}-\frac{l_1(l_1+D-2)}{\cos^2\chi}-\frac{l_2(l_2+D-2)}{\sin^2\chi} \tag{42}$$

its eigenvalues being $-\lambda(\lambda+2D-2)$, and its eigenfunctions being as in Eq. (20). In turn, l_1 and l_2 will label eigenfunctions of operators acting on D-dimensional spaces. The physical interpretation of these operators is that of angular momenta of D space, and l_1 and l_2 are the corresponding angular momentum quantum numbers. The constraint of zero total angular momentum amounts to requiring $l_1=l_2=l$ (compare tree b in Fig. 7) so that the corresponding fork is as a in Fig. 5: it is easy to manipulate Eq. (42) in order to make it read

$$\frac{1}{(\sin 2\chi)^{D-1}}\frac{\partial}{\partial(2\chi)}(\sin 2\chi)^{D-1}\frac{\partial}{\partial(2\chi)}-\frac{l(l+D-2)}{\sin^2 2\chi} \tag{43}$$

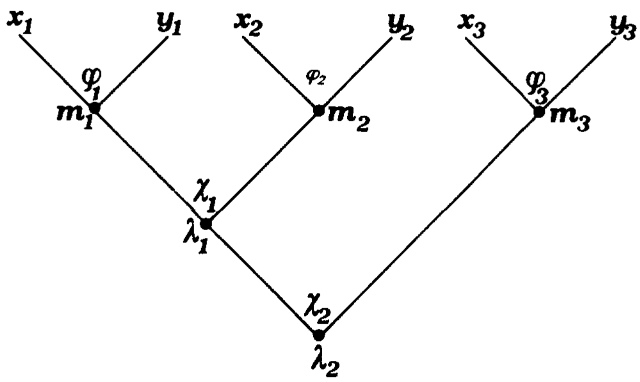

FIG. 8. Hyperangular parametrization of three bidimensional vectors (x_i, y_i) such as needed for describing the motion of four particles in the plane.

and this can be verified to be the operator corresponding to the fork IIa in Fig. 2, with eigenvalues $-(\lambda/2)[(\lambda/2)+D-1]$ and eigenfunctions of the type (15) or (17).

We further remark that a potential energy function which depends on distances between particles and therefore from internal coordinates only, can be expanded in the harmonics which correspond to zero total angular momentum (see next sections and Appendix A). Therefore, we can conclude that the internal motion evolves on a manifold which is the surface of a D-dimensional hypersphere, which has a lower dimensionality than that upon which the full dynamical problem evolves.

It is important to observe that the above results are very hard to be extended to problems involving more than three particles, and in general for nonzero total angular momentum. This can be shown by considering again the problem of four particles on a plane, to which we can associate the tree in Fig. 8. The total angular momentum is now given by $M=m_1+m_2+m_3$. The eigenfunctions of the kinetic energy operator on the unit sphere, S^5, can be obtained from the formulas in Sec. II B,

$$\begin{aligned}\overline{Y}^{6}_{\lambda_1\lambda_2 m_1 m_2 m_3}(\chi_1\chi_2\varphi_1\varphi_2\varphi_3) = {} & N^{4,2}_{\lambda_2\lambda_1 m_3}\left(\frac{\lambda+1}{2\pi^2}\right)^{1/2}\cos^{\lambda_1}\chi_2\sin^{m_3}\chi_2 \\ & \times P^{m_3,\lambda_1+1}_{(\lambda_2-\lambda_1-m_3)/2}(\cos 2\chi_2)\, d^{\lambda_1/2}_{(m_1+m_2)/2,(m_1-m_2)/2}(2\chi_1) \\ & \times e^{i/3(2m_3-m_1-m_2)(\varphi_3-\varphi_2)}e^{i/3(m_3+m_2-2m_1)(\varphi_2-\varphi_1)}e^{iM/3(\varphi_1+\varphi_2+\varphi_3)}.\end{aligned} \tag{44}$$

When the total angular momentum is zero, $m_3=-m_1-m_2$, say, and the eigenfunction (44) reduces to

$$\begin{aligned}& N^{4,2}_{\lambda_2\lambda_1(-m_1-m_2)}\left(\frac{\lambda+1}{2\pi^2}\right)^{1/2}\cos^{\lambda_1}\chi_2\sin^{-m_1-m_2}\chi_2\, P^{-m_1-m_2,\lambda_1+1}_{(\lambda_2-\lambda_1+m_1+m_2)/2}(\cos 2\chi_2) \\ & \times d^{\lambda_1/2}_{(m_1+m_2)/2,(m_1-m_2)/2}(2\chi_1)e^{im_1(\varphi_1-\varphi_3)}e^{im_2(\varphi_2-\varphi_3)}.\end{aligned} \tag{45}$$

It can be verified that Eq. (45) does not correspond to any harmonics on any sphere of lower dimensionality.

In any case, for states of definite angular momentum, the dimensionality of the problem is obviously reduced to evolve on a manifold of lower dimensionality. However, except for the cases seen in this section, it is not easy (nor is obvious that it is even possible) to parametrize such a manifold so as to make it look like the surface of a sphere.

IV. THE MAPPING OF THE INTERACTION BETWEEN THREE PARTICLES

In this section, we consider the coordinate systems and the expansion basis for the interaction between three particles, using the method of trees for setting up orthogonal coordinates which are separable on the hyperspheres. We will focus our attention on the possibility of relating alternative particle coupling schemes by kinematic rotations: this possibility represents one of the main powers of this approach.

A. Three particles on a line

The first case to be treated is the representation of the interaction when the particles lie on a line ($D = 1$).[24,25] The two Jacobi vectors, as seen in the previous paper,[11] can be parametrized in different ways, depending on the particle coupling schemes. The different parametrizations can be related by a kinematic rotation, described by an $O(2)$ matrix. The dependence on the particle coupling scheme will be denoted by the suffix k: the lengths of the two vectors x_k, and X_k, span a two-dimensional Euclidean space and are obviously orthogonal coordinates. The corresponding polar parametrization

$$x_k = \rho \cos \chi_k \; ; \quad X_k = \rho \sin \chi_k \tag{46}$$

can be visualized as for the fork of type I in Fig. 2. Equation (46) defines the range of the angle χ_k,

$$0 \leqslant \chi_k \equiv \arctan(X_k/x_k) < 2\pi \, . \tag{47}$$

The corresponding harmonics are the exponential functions (see Sec. II B):

$$|\chi_k; m\rangle = (2\pi)^{-1/2} e^{im\chi_k} \, . \tag{48}$$

The interaction between the particles $V(x_k, X_k)$ is in this case a function defined on a plane. Such a function, on the sphere S^1 can be expanded in a Fourier series[25]

$$V(\rho, \chi_k) = \sum_{m=-\infty}^{+\infty} v_m^k(\rho) e^{im\chi_k} \, . \tag{49}$$

The qualitative features of the representation on the plane of a potential energy surface for a chemical reaction involving three particles on a line is illustrated in Smith's paper[10] (see also Fig. 9).

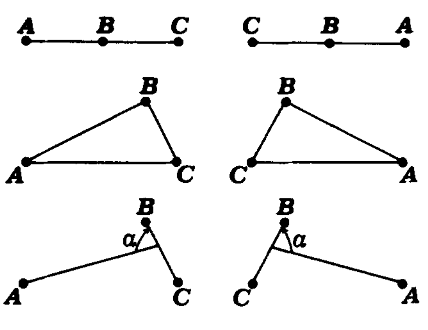

FIG. 9. Showing that ranges for internal coordinates which describe three-particle configurations depend on the dimensionality of space: the collinear configurations on the left- and right-hand side, related by mirror symmetry, are distinguishable in 1D, and indistinguishable (superimposable) in 2D and 3D [this can be related with the difference in ranges for the χ angle, measuring the ratio between Jacobi vectors (see Sec. IV)]; the (nonequilateral) triangles with finite area, impossible in 1D, when related by mirror symmetry as in figure, are distinguishable in 2D but not in 3D [this is the reason for the defferent ranges of η and Θ coordinates in 2D and 3D]; similarly, the angle between two vectors spans a circle on the plane ($0 \leqslant \alpha < 2\pi$) and a hemicircle in space ($0 \leqslant \alpha \leqslant \pi$).

The transformation between the coupling scheme k and an alternative coupling scheme j can be performed through a kinematic rotation by an angle β_{jk}[10,11] and written as a relation between row vectors

$$(x_i, X_j) = (x_k, X_k) \begin{pmatrix} \cos \beta_{jk} & -\sin \beta_{jk} \\ \sin \beta_{jk} & \cos \beta_{jk} \end{pmatrix} . \tag{50}$$

Using the parametrization (46),

$$\chi_j = \chi_k + \beta_{jk} \; ; \tag{51}$$

it is immediate to verify that the transformation of harmonics corresponds to a phase shift

$$e^{im\chi_j} = e^{im\chi_k} e^{im\beta_{jk}} \, , \tag{52}$$

so that in the new coupling scheme the potential expansion (49) becomes

$$V(\rho, \chi_j) = \sum_{m=\infty}^{+\infty} v_m^j(\rho) e^{im\chi_j} \tag{53}$$

the relationship between the coefficients being simply

$$v_m^j(\rho) = e^{i\beta_{jk}} v_m^k(\rho) \, . \tag{54}$$

B. Three particles on a plane

For three particles on a plane, each of the two Jacobi vectors contributes with its two components to setting up a four-dimensional space, which can be parametrized on a hypersphere as shown in Fig. 6. When the total angular momentum $M = m_1 + m_2$ is zero, from the theorem on the mapping of potential energy surfaces (Sec. III B) we find that the kinetic energy operator on S^3 can be reduced to a Laplace operator on S^2, whose eigenfunctions are the usual three-dimensional harmonics.

As before, we here add to the angles introduced in the hyperspherical parametrization (Fig. 6) the suffix k specifying the configuration. Note that the angle χ_k is again defined as in Eq. (47), but its range is now from 0 to $\pi/2$. The interaction potential, which is a function of internal coordinates, can be expanded as follows:

$$V(\rho, \chi_k, \varphi_2^k - \varphi_1^k) = \sum_{\lambda, m_1} v_{\lambda, m_1}^k(\rho) Y_{\lambda/2, m_1}^3 (2\chi_k, \varphi_2^k - \varphi_1^k) \, , \tag{55}$$

where $Y_{\lambda/2, m_1}^3$ are harmonics on $\mathbf{R}^3$ (tree c in Fig. 6) ana proportional (tree b in Fig. 6) to particular harmonics on $\mathbf{R}^4$ (those which are also eigenfunctions of the angular momentum operator for the quantum number $M = 0$). This reduction, which exploits rotational invariance, allows the separation of internal and external coordinates.

The transformation from the configuration k to the configuration j is performed by the same kinematic rotation as before, Eq. (50):

$$\begin{pmatrix} x_j & X_j \\ y_j & Y_j \end{pmatrix} = \begin{pmatrix} x_k & X_k \\ y_k & Y_k \end{pmatrix} \begin{pmatrix} \cos \beta_{jk} & -\sin \beta_{jk} \\ \sin \beta_{jk} & \cos \beta_{jk} \end{pmatrix} . \tag{56}$$

The explicit relationship between internal coordinates ξ_k, η,

ζ_k and the components of Jacobi vectors, can be obtained from a comparison of trees b and c in Fig. 6:

$$\begin{aligned} \xi_k &= 2\rho(x_k X_k + y_k Y_k)\,, \\ \eta &= 2\rho(x_k Y_k - y_k X_k)\,, \\ \zeta_k &= \rho(x_k^2 + y_k^2 - X_k^2 - Y_k^2) \end{aligned} \tag{57}$$

(we recall[9] that ξ_k and η are related to the scalar and vector products of the two Jacobi vectors, respectively, while ζ_k is related to the difference of their squared lengths). In particular, η is related to the area A of the triangle formed by the three particles:

$$\eta = \frac{4A}{\rho} = \rho \sin 2\chi_k \sin(\varphi_2^k - \varphi_1^k) = \rho \sin 2\Theta\,. \tag{58}$$

Therefore η and Θ are independent of the "configuration" and in general are invariant under kinematic rotations. Furthermore, note that since it is necessary to define positive and negative values for the area of a triangle in the plane (Fig. 9), the range of the Θ angle is $-\pi/4, \pi/4$, in agreement with tree d in Fig. 6.

The behavior of the internal coordinates under kinematic rotation can be verified to be

$$\begin{pmatrix} \xi_j \\ \eta \\ \zeta_j \end{pmatrix} = \begin{pmatrix} \cos 2\beta_{jk} & 0 & -\sin 2\beta_{jk} \\ 0 & 1 & 0 \\ \sin 2\beta_{jk} & 0 & \cos 2\beta_{jk} \end{pmatrix} \begin{pmatrix} \xi_k \\ \eta \\ \zeta_k \end{pmatrix}, \tag{59}$$

where the suffix (k or j) denotes the configuration: the so-called symmetric parametrization of angles[9] is therefore seen to be the one for which a change in particle coupling merely amounts to a rotation in the plane $\xi\zeta$, described by a phase shift β_{jk} in the angle Φ_k.

The effect of a kinematic rotation on the spherical harmonics in Eq. (55) corresponding to the configuration k is that of transforming them into harmonics corresponding to the configuration j. The previous discussion suggests that we first consider such a kinematic rotation for the symmetric parametrization (tree d in Fig. 6):

$$\overline{Y}^3_{\lambda/2,s}(2\Theta,2\Phi_k) = \overline{Y}^3_{\lambda/2,s}(2\Theta,2\Phi_j)e^{-2is\beta_{jk}}\,. \tag{60}$$

To obtain the corresponding relationship between harmonics in the asymmetric representation (tree c in Fig. 6) we rewrite Eq. (25) in the present notation,

$$Y^3_{\lambda/2,m_1}(2\chi_k,\varphi_2^k - \varphi_1^k) = \sum_s \overline{Y}^3_{\lambda/2,s}(2\Theta,2\Phi_k)D^{\lambda/2}_{s,m_1}(0,\pi/2,\pi/2)\,. \tag{61}$$

Formula (60) substituted on the right-hand side gives

$$Y^3_{\lambda/2,m_1}(2\chi_k,\varphi_2^k - \varphi_1^k) = \sum_s \overline{Y}^3_{\lambda/2,s}(2\Theta,2\Phi_j)D^{\lambda/2}_{s,m_1}(2\beta_{jk},\pi/2,\pi/2)\,. \tag{62}$$

By inverting Eq. (61) we finally have

$$\begin{aligned} Y^3_{\lambda/2,m_1}(2\chi_k,\varphi_2^k - \varphi_1^k) &= \sum_{\mu s} Y^3_{\lambda/2,\mu}(2\chi_j,\varphi_2^j - \varphi_1^j) \\ &\quad \times D^{\lambda/2}_{\mu s}(-\pi/2,-\pi/2,0)D^{\lambda/2}_{sm_1}(2\beta_{jk},\pi/2,\pi/2) \\ &= \sum_\mu Y^3_{\lambda/2,\mu}(2\chi_j,\varphi_2^j - \varphi_1^j)d^{\lambda/2}_{\mu,m_1}(2\beta_{jk})\,, \end{aligned} \tag{63}$$

where use has been made of a sum rule[18] on the index s.

As for Eqs. (53) and (54), the above formulas can be used to relate the coefficients for the expansion (55) for the potential energy with those for an expansion in alternative angular parametrizations. These formulas are here omitted: the entirely analogous, and more interesting case, of three particles in three dimensions being treated next (see also the Appendix A for the distance formulas).

C. Three particles in space

For the case of three particles in space, the procedure is essentially the same as before, although the algebraic manipulations are more involved: the transformation between configurations k and j is given again by a kinematic rotation similar to the one in Eq. (56):

$$\begin{pmatrix} x_j & X_j \\ y_j & Y_j \\ z_j & Z_j \end{pmatrix} = \begin{pmatrix} x_k & X_k \\ y_k & Y_k \\ z_k & Z_k \end{pmatrix} \begin{pmatrix} \cos\beta_{jk} & -\sin\beta_{jk} \\ \sin\beta_{jk} & \cos\beta_{jk} \end{pmatrix}; \tag{64}$$

The explicit relationship between the internal coordinates and the components of Jacobi vectors is [compare with Eq. (57)]

$$\begin{aligned} \xi_k &= 2\rho(x_k X_k + y_k Y_k + z_k Z_k)\,, \\ \eta &= 2\rho[(x_k Y_k - y_k X_k)^2 + (z_k X_k - x_k Z_k)^2 \\ &\quad + (y_k Z_k - z_k Y_k)^2]^{1/2}\,, \\ \zeta_k &= \rho(x_k^2 + y_k^2 + z_k^2 - X_k^2 - Y_k^2 - Z_k^2)\,. \end{aligned} \tag{65}$$

It is important to remember (see also Fig. 9) that η [Eq. (58)], which spans the whole range from $-\infty$ to $+\infty$ for the 2D case, is now defined only for positive values, $0 \leqslant \eta < \infty$. Again, the effect of kinematic rotations is much simpler for the symmetric parametrization (tree e in Fig. 7): the connection between the corresponding harmonics (41) is similar to Eq. (60) for the planar case:

$$D^{\lambda/4}_{\sigma/4,\sigma/4}(2\Phi_k,4\Theta,2\Phi_k) = D^{\lambda/4}_{\sigma/4,\sigma/4}(2\Phi_j;4\Theta,2\Phi_j)e^{i\sigma\beta_{jk}} \tag{66}$$

[the difference in sign for the phase shift in Eqs. (60) and (66) comes from the different conventions for the spherical harmonics and rotation matrices]. To establish the corresponding relationship between harmonics in the asymmetric (Fock's) representation (tree d in Fig. 7) we have, from inversion of Eq. (41),

$$\begin{aligned} Y^4_{\lambda/2,l,0}(2\chi_k,\theta_k,0) &= \sum_\sigma (-)^{(\lambda-\sigma)/4}(\lambda+2)^{1/2}/2\pi \\ &\quad \times \left\langle \frac{\lambda}{4}\,\frac{\sigma}{4}\,\frac{\lambda}{4} - \frac{\sigma}{4}\right| l0\Big\rangle\, e^{-i\sigma\Phi_k} d^{\lambda/4}_{\sigma/4,\sigma/4}(4\Theta) \end{aligned} \tag{67}$$

which, using Eq. (66) in the right-hand side, gives

$$\begin{aligned} Y^4_{\lambda/2,l,0}(2\chi_k,\theta_k,0) &= \sum_\sigma (-)^{(\lambda-\sigma)/4}\frac{(\lambda+2)^{1/2}}{2\pi}e^{i\sigma\beta_{jk}} \\ &\quad \times \left\langle \frac{\lambda}{4}\,\frac{\sigma}{4}\,\frac{\lambda}{4} - \frac{\sigma}{4}\right| l0\Big\rangle e^{-i\sigma\Phi_j} d^{\lambda/4}_{\sigma/4,\sigma/4}(4\Theta)\,. \end{aligned} \tag{68}$$

Finally, from Eq. (41) (see also Ref. 26),

$$Y^4_{\lambda/2,l,0}(2\chi_k,\theta_k,0) = \sum_{l'} C^{\lambda}_{ll'} Y^4_{\lambda/2,l',0}(2\chi_j,\theta_j,0), \tag{69}$$

where

$$C^{\lambda}_{ll'} = \sum_{\sigma} \left\langle \frac{\lambda}{4}\frac{\sigma}{4}\frac{\lambda}{4} - \frac{\sigma}{4}\middle| l0 \right\rangle e^{i\sigma\beta_{jk}} \left\langle \frac{\lambda}{4}\frac{\sigma}{4}\frac{\lambda}{4} - \frac{\sigma}{4}\middle| l0 \right\rangle. \tag{70}$$

These formulas are of interest for the expansion of any function of internal coordinates, such as the potential energy surface which depends only on distances, or the distances themselves (see also Appendix A).

Specifically,[22] a 3D potential energy surface depending on the distances between three particles will admit an expansion both in the hyperspherical harmonics of Fock's asymmetric parametrization of hyperangles (tree d in Fig. 7)

$$V(\rho,\chi_k,\theta_k) = \sum_{\lambda l} v_{\lambda l}(\rho) Y^4_{\lambda/2,l,0}(2\chi_k,\theta_k,0) \tag{71}$$

and in those of Smith's parametrization (tree e in Fig. 7)

$$V(\rho,\Theta,\Phi_k) = \sum_{\lambda\sigma} v_{\lambda\sigma}(\rho) \frac{(\lambda+2)^{1/2}}{2\pi} e^{-i\sigma\Phi_k} d^{\lambda/4}_{\sigma/4,\sigma/4}(4\Theta). \tag{72}$$

From Eq. (41), we can establish the connection between the coefficients

$$v_{\lambda\sigma}(\rho) = \sum_{l} (-)^{(\lambda-\sigma)/4} \left\langle \frac{\lambda}{4}\frac{\sigma}{4}\frac{\lambda}{4} - \frac{\sigma}{4}\middle| l0 \right\rangle v_{\lambda l}(\rho) \tag{73}$$

or, inversely,

$$v_{\lambda l}(\rho) = \sum_{\sigma} (-)^{(\lambda-\sigma)/4} \left\langle \frac{\lambda}{4}\frac{\sigma}{4}\frac{\lambda}{4} - \frac{\sigma}{4}\middle| l0 \right\rangle v_{\lambda\sigma}(\rho). \tag{74}$$

These results have been reported previously[22]: for the case of H_2^+ (an example of three particles interacting via Coulomb potentials), they have been used to relate different parametrizations of hyperangles.[7] For interactions such as the square well,[27] the Gaussian,[28,29] the harmonic oscillator,[28] for which the expansion in Smith's coordinates is known, the expansion coefficients for the alternative coordinates can be obtained by Eq. (74).

In general, expansion coefficients and matrix elements will have to be generated numerically, and the rate of convergence of expansions will have to be examined. It is likely that these difficulties can be circumvented extending to hyperspherical harmonics the discretization procedure recently introduced[30] for spherical harmonics.

The representation of the potential energy surfaces for three atoms in terms of the internal coordinates ξ, η, ζ provides a mapping equivalent to the one first ingeniously suggested by Kuppermann.[31] As noted elsewhere,[23] its use may effectively simplify the application of approximations of the infinite order sudden type in the theory of chemical reaction dynamics.

V. CONCLUDING REMARKS

By making extensive use of the tree method for representing hyperspherical coordinates and harmonics, we have derived some general results on the mapping of three-particle potential energy surfaces. These results also provide the mapping in terms of the internal coordinates for the kinetic energy, provided the total angular momentum is zero.

For the planar case, fully treated by Smith[9] several years ago, a complete formulation within $O(4)$ is possible for any nonzero angular momentum[32]: such an investigation shows, for example, that the coefficients introduced by Smith,[9] and relating harmonics corresponding to different particle coupling schemes, are actually matrix elements for rotation in ordinary three-dimensional space.

For the 3D case, the extension to nonzero angular momentum leads to complicated algebra and simplifications are not obvious[33]: specifically, the coefficients relating harmonics for different particle coupling schemes, corresponding to Eq. (70) for $J = 0$, are very involved for $J > 0$.[34]

As already noted, simplifications as illuminating as those found for the three-particle system are not obvious also when extension is attempted for a number of particles higher than three. An examination of properties of higher rotation groups, in particular the introduction of alternative hyperspherical parametrizations (see Appendix B) may turn out to be helpful in carrying out such an extension.

APPENDIX A: FORMULAS FOR EXPANSIONS OF INTERATOMIC DISTANCES AND INTERACTIONS IN HYPERSPHERICAL HARMONICS

A list is given of basic formulas relating interparticle distances and hyperspherical harmonics. After numbering particles as 1, 2, and 3, we start by considering a configuration denoted by the suffix $k = 3$: in the standard Jacobi representation, this amounts to defining one of the vectors as joining the first two particles. The distance between these particles, r_{12}, assumes a most simple expression in this case:

$$r_{12} = \rho a \cos \chi_3, \tag{A1}$$

where[11]

$$a = \left[\frac{(m_1+m_2+m_3)(m_1+m_2)}{m_1 m_2}\right]^{1/2} \tag{A2}$$

or, in internal coordinates [Eqs. (37) or (40)]

$$r^2_{12} = \frac{\rho^2 a^2}{2}(1+\cos 2\chi_3) = \frac{\rho^2 a^2}{2}(1+\cos 2\Theta \cos 2\Phi_3). \tag{A1'}$$

The other interparticle distances can now be obtained by identifying Eq. (A1') as appropriate hyperspherical harmonics and using the transformation formulas in Sec. IV.

Let us first note that the cosine function, apart from normalization, can be written as an $\mathbb{R}_3$ harmonic (corresponding to the tree a in Fig. 1):

$$\cos\theta = \left(\frac{4\pi}{3}\right)^{1/2} Y^3_{10}(\theta,\varphi) \tag{A3}$$

suitable for the problem of three particles in the plane.

For the problem in the 3D space, we can establish a relationship with an $\mathbb{R}_4$ harmonic (see the tree c in Fig. 1):

$$\cos\chi = \frac{\pi}{2^{1/2}} Y^4_{1,0,0}(\chi,\theta,\varphi). \tag{A4}$$

From Eq. (A3) into Eq. (A2), we obtain

$$r_{12}^2 = \frac{\rho^2 a^2}{2}\left[1 + \left(\frac{4\pi}{3}\right)^{1/2} Y^3_{10}(2\chi_3,0)\right] \tag{A5}$$

and, expanding Y^3_{10} as in Eq. (25),

$$Y^3_{10}(2\chi_3,0) = \sum_s \overline{Y}^3_{1,s}(2\Theta,2\Phi_3) D^1_{s,0}(0,\pi/2,\pi/2)$$
$$= \frac{1}{2^{1/2}}\left[\overline{Y}^3_{1,-1}(2\Theta,2\Phi_3) - \overline{Y}^3_{1,1}(2\Theta,2\Phi_3)\right] \tag{A6}$$

finally gives r_{12}^2 in Smith's coordinates for three particles on a plane

$$r_{12}^2 = \frac{\rho^2 a^2}{2}\left\{1 + \left(\frac{2\pi}{3}\right)^{1/2}\left[Y^3_{1,-1}\left(\frac{\pi}{2} - 2\Theta,2\Phi_3\right) - Y^3_{1,1}\left(\frac{\pi}{2} - 2\Theta,2\Phi_3\right)\right]\right\} \tag{A7}$$

which can be checked to agree with Eq. (A2).

Similarly, for the 3D case, use of Eq. (A4) into Eq. (A1′) yields

$$r_{12}^2 = \frac{\rho^2 a^2}{2}\left[1 + \frac{\pi}{2^{1/2}} Y^4_{100}(2\chi_3,0,0)\right] \tag{A8}$$

and, expanding Y^4_{100} as in Eq. (28),

$$Y^4_{100}(2\chi_3,0,0) = \sum_{\sigma/4} \frac{(-)^{(2-\sigma)/4}}{\pi}\left\langle \frac{1}{2}\,\frac{\sigma}{4}\,\frac{1}{2} - \frac{\sigma}{4}\middle|00\right\rangle \times D^{1/2}_{\sigma/4,\sigma/4}(2\Phi_3, 4\Theta, 2\Phi_3) \tag{A9}$$

one obtains

$$r_{12}^2 = \frac{\rho^2 a^2}{2}\left\{1 + \frac{1}{2}\left[D^{1/2}_{1/2,1/2}(2\Phi_3,4\Theta,2\Phi_3) + D^{1/2}_{-1/2,-1/2}(2\Phi_3,4\Theta,2\Phi_3)\right]\right\} \tag{A10}$$

again agreeing with Eq. (A2). Note that the particular Gegenbauer polynomials to which the harmonics in Eqs. (A3) and (A8) reduce are easily seen[18] to be essentially Legendre and second kind Chebyshev polynomials, respectively, so that their use as expansion bases is well established. A formula like (A10) for distances was first given by Whitten,[28] which used it as a starting point for finding expansions in harmonics for various interparticle potential forms.

The behavior of these harmonic under kinematic rotations, as described in the text, allows to write down at once expression for the other distances. The well-known group properties of these functions with respect to addition and multiplication are the basic tools for handling matrix elements, including symmetry properties.

APPENDIX B: HYPERSPHERICAL COORDINATES BY TERNARY FORKS

In the main text, we have considered the tree formulation of the usual method for setting up coordinates which parametrize the hypersphere: those coordinates (Sec. II) allow the separation of variables for Laplace equation (and the construction of harmonics) by connecting in sequence the coordinates by couples of branches which join at nodes, the functions corresponding to the branches being sines and cosines of hyperangles (Fig. 1). In this Appendix, we sketch a way of defining more general types of separable coordinates by introducing "forks" where three branches join at a node. Examples of these "ternary" forks are shown in Fig. 10 for the spheres S^2 and S^3.

Although several alternatives are possible, we find it useful, following Refs. 35 and 36, to adopt the following conventions: in the definition of coordinates, a left branch corresponds to $sn(\alpha,k)dn(\beta,k')$, a middle branch corresponds to $cn(\alpha,k)cn(\beta,k')$, and a right branch corresponds to $dn(\alpha,k)sn(\beta,k')$. The arguments α and β of the elliptic functions are the variables: their ranges depend on the number of leaves and nodes which are grafted on the fork. The modulus parameter k [and $k' = (1-k^2)^{1/2}$, with $0 < k,k' < 1$] adds a degree of freedom to these coordinate systems.

A parametrization for the internal coordinates ξ,η, and ζ [Eqs. (37) and (40)], for example is as follows:

$$\begin{aligned}\xi &= \rho cn(\alpha,k)cn(\beta,k'),\\ \eta &= \rho sn(\alpha,k)dn(\beta,k'),\\ \zeta &= \rho dn(\alpha,k)sn(\beta,k'),\end{aligned} \tag{B1}$$

Its use in providing a smooth transition between the representations, and especially the advantages of choosing particular values of k for particular problems is being investigated.

Note that ranges for variables in Eq. (B1) for the 2D and 3D cases must be different. For the 2D case, tree I in Fig. 10 applies; for the 3D case the proper tree is essentially IIb in Fig. 10, one of the leaves (x or y) being set to zero.

Harmonics corresponding to ternary forks can be built in the simpler cases: they involve Lamé polynomials for trees

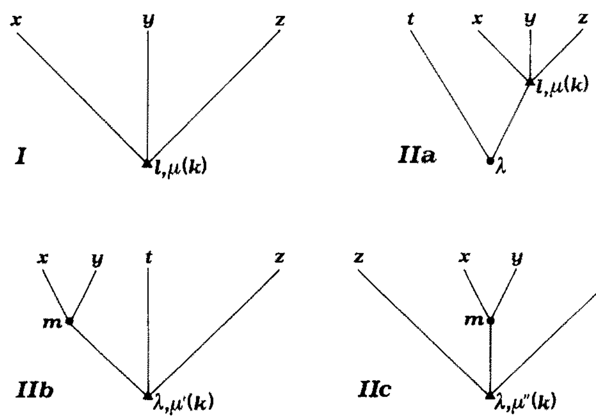

FIG. 10. Use of ternary forks (Appendix B) for setting up coordinate systems for S^2 and S^3. The labels μ, μ', μ'' are separation constants depending on k and in general to be determined as eigenvalues of secular equations (see Refs. 35 and 36). Tree I corresponds to the conical coordinates of Morse and Feshbach (see Ref. 4), for example, and referred to as elliptical in Ref. 35. Trees IIa, IIb, and IIc correspond to the spheroelliptic, elliptic cylindrical of type 1 and elliptic cylindrical of type 2 coordinates, respectively, of Ref. 36.

I[35] and IIa,[36] and associated Lamé polynomials for trees IIb and IIc.[36]

Ternary forks may turn out to be useful for the treatment of more than three particles: it is obvious, for example, looking at Fig. 8, which shows a tree for four particles on a plane, that a ternary fork at the root of the tree would make it look more symmetrical and perhaps, by a proper choice of k, more ready to some effective "pruning." However, it appears that the orthogonal system corresponding to a fork of [A V:such a complexity (depending on three labels besides λ), has not been standardized at the time of writing.

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