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REGULAR ARTICLE

Few-body quantum and many-body classical hyperspherical approaches to reactions and to cluster dynamics

A. Lombardi · F. Palazzetti · L. Peroncelli · G. Grossi · V. Aquilanti · M. B. Sevryuk

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Abstract The hyperspherical method is a widely used and successful approach for the quantum treatment of elementary chemical processes. It has been mostly applied to three-atomic systems, and current progress is here outlined concerning the basic theoretical framework for the extension to four-body bound state and reactive scattering problems. Although most applications only exploit the advantages of the hyperspherical coordinate systems for the formulation of the few-body problem, the full power of the technique implies representations explicitly involving quantum hyperangular momentum operators as dynamical quantities and hyperspherical harmonics as basis functions. In terms of discrete analogues of these harmonics one has a universal representation for the kinetic energy and a diagonal representation for the potential (hyperquantization algorithm). Very recently, advances have been made on the use of the approach in classical dynamics, provided that a hyperspherical formulation is given based on "classical" definitions of the hyperangular momenta and related quantities. The aim of the present paper is to offer a retrospective and prospective view of the hyperspherical methods both in quantum and classical dynamics. Specifically, regarding the general quantum hyperspherical approaches for three- and four-body systems, we first focus on the basis set issue, and then we present developments on the classical formulation that has led to applications involving the implementations of hyperspherical techniques for classical molecular dynamics simulations of simple nanoaggregates.

Keywords Hyperspherical approach · Hyperspherical harmonics · Basis sets · Hyperangular momenta · Kinetic energy partitions · Mode couplings

A. Lombardi (✉) · F. Palazzetti · L. Peroncelli · G. Grossi · V. Aquilanti
Dipartimento di Chimica, Università di Perugia, via Elce di Sotto 8, Perugia 06123, Italy
e-mail: abulafia@dyn.unipg.it

M. B. Sevryuk
Institute of Energy Problems of Chemical Physics, The Russia Academy of Sciences, Leninskiĭ prospect 38, Building 2, Moscow 119334, Russia

1 Introduction

The theoretical study of the internal and reactive dynamics of molecules and of aggregates of atoms and molecules is assisted by models and techniques based upon both quantum and classical mechanics. The rigorous quantum treatment of the dynamics is currently prohibitive for systems involving more than three or possibly four atoms, and the extension of quantum techniques to few-body dynamics, such as the study of elementary reaction and scattering processes involving electrons, atoms, simple molecules, ions, and small clusters, for which a full quantum treatment is yet a considerable challenge, requires the development of proper formulations and perhaps the use of efficient approximations.

The dynamics of larger systems, e.g., that of clusters and polyatomic reactions, is typically tackled by classical mechanics. In these cases, two general classes of methods can be distinguished: a first one based on the numerical integration of the classical equations of motion, leading to constant total energy trajectories for sampling of the phase space of the system (a microcanonical picture), and a second one based on random techniques for statistical sampling of the phase

space enabling to calculate dynamical and thermodynamical quantities. These random walk or Monte Carlo techniques are mainly devoted to constant temperature canonical simulations but their application to constant energy simulations (random walks at constant total energy) is also feasible.

Approximations to the quantum formalism, or introduction of quantum features within a classical framework (the semiclassical approaches) are avenues of intensive current research. We will however not consider them in this paper, where we confine our attention to recent progress in the exact quantum treatment of few-body dynamics through the hyperspherical and related techniques, and to developments that these techniques have obtained when carried over to classical mechanics.

The plan of the paper is as follows. General concepts and formulations are introduced in Sect. 2, where we illustrate the quantum hyperspherical approach for three- and four-body systems, with the emphasis on details of the construction of the symmetric hyperspherical harmonic basis sets. Section 3 discusses the hyperspherical approach to classical mechanics, the central topic here is kinetic energy partitions revealing the relative role of various modes of motion in the evolution of the system. Section 4 concludes the paper.

2 The quantum hyperspherical approach

We will now recall some basic details, which are introductory to the subject of the present paper. Concerning the reactive dynamics of atomic and molecular systems, the time-independent *hyperspherical approach* has been successfully applied to the three-body quantum reactive scattering problem [1–4], and its extension to the challenging four-body case is currently being investigated [5–11]. This approach is widely acknowledged as the one providing the benchmarks for accurate time-independent state-to-state reactive scattering calculations and relies upon the use of the hyperspherical coordinate system, which can be thought of as a generalization of the familiar spherical coordinates for specifying the position of a point in the three-dimensional physical space.

2.1 Radial and angular modes

Within the hyperspherical coordinate framework, the configuration of a system made up of $N \geq 3$ particles is represented as a point in a $(3N-3)$-dimensional hyperspace (after the separation of the center-of-mass motion), and its kinematics is equivalent to that of one body of mass M (the total mass of the system) on the $(3N-4)$-dimensional surface of a sphere embedded in the $(3N-3)$-dimensional space. The size of this hypersphere depends on a *hyperradius*, denoted as ρ (the analogue of the radius of a two-dimensional sphere in the three-dimensional space), while the other key relevant quantity is the so-called *grand angular momentum* [12–14], denoted as Λ. In quantum mechanics, the corresponding grand angular momentum operator $\hat{\Lambda}^2$ appears in the kinetic energy part $\hat{T}$ of the quantum Hamiltonian operator written in terms of hyperspherical coordinates. The operator $\hat{T}$ is split into two parts, a hyperradial operator $\hat{T}_\rho$ and a grand angular momentum operator $\hat{T}_\Lambda$, as follows:

$$\hat{T} = -\frac{1}{2M}\left(\frac{\hbar^2}{\rho^{3N-4}}\frac{\partial}{\partial\rho}\rho^{3N-4}\frac{\partial}{\partial\rho} - \frac{\hat{\Lambda}^2}{\rho^2}\right) = \hat{T}_\rho + \hat{T}_\Lambda. \quad (1)$$

In many other versions of this equation, one uses the reduced mass of the system

$$\mu = \left(\frac{m_1 m_2 \cdots m_N}{m_1 + m_2 + \cdots + m_N}\right)^{1/(N-1)}$$

instead of the total mass

$$M = m_1 + m_2 + \cdots + m_N$$

($m_1, m_2, \ldots, m_N$ being the masses of individual particles); the presence of μ in Eq. (1) requires just another mass scaling of ρ. The expression in Eq. (1) in parentheses is the Laplace operator (multiplied by $\hbar^2$) in terms of hyperspherical coordinates. The simplest separation of variables is thus obtained by virtue of the hyperspherical formulation of the N-body quantum Hamiltonian operator, and is the analogue of the separation into the radial part and the angular momentum part of the Laplacian acting in the three-dimensional Euclidean space. As a consequence of this variable separation, the kinetic energy is partitioned into a radial energy contribution $\hat{T}_\rho$ and an angular energy contribution

$$\hat{T}_\Lambda = \frac{\hat{\Lambda}^2}{2M\rho^2}. \quad (2)$$

The grand angular momentum is an *invariant quantity*, in the sense that it does not change under the action of orthogonal transformations in the configuration and momentum spaces. Indeed, there are many possible explicit expressions for $\hat{\Lambda}^2$, each corresponding to an alternative set of hyperspherical coordinates.

As discussed in detail in many references (see for example our papers [15,16]), the hyperspherical coordinates are introduced as a parametrization on the hypersphere of the $N-1$ Jacobi or related type vectors for the N-particle system. The simplest set of Jacobi vectors

can be constructed by taking as the first vector (with a choice for the vector orientation) the one connecting particles 1 and 2, then the vector connecting the center of mass of particles 1 and 2 to particle 3, and so on. A proper *mass scaling* of the vectors will complete the construction procedure. Note that the choice of these vectors is *not* unique. For example, for a three-body A + BC reactive system three alternative vector pairs can be set up, accounting for the three different rearrangement channels of reactants and products [3,15]. The representation in terms of the Jacobi vectors is particularly convenient for reactive scattering problems of three (and four) bodies in the atom–diatom (and diatom–diatom or atom–triatom) case, where the asymptotic configurations at long distance between the atom and diatom (or the two diatoms, or the atom and triatom) correspond to a separable Hamiltonian which reduces to the situation of one or two independent oscillators (or one free atom plus a triatom). Such a representation is advantageous for the enforcing of the asymptotic conditions. For a review of alternatives, and for recent developments, see Refs. [17,18].

The Schrödinger equation whose solutions contain all the physics of the system is set up by adding to the kinetic energy operator $\hat{T}$ a term representing the interaction potential of the system. To recast the problem in an algebraic fashion, one expands the unknown wave function in terms of a basis function set. The basis set of paramount importance is given by the zero potential eigenvalue problem solutions. The elements of this set are the eigenfunctions of the kinetic energy part $\hat{T}$ of the Hamiltonian operator, which is naturally separated, as already mentioned, into a hyperradial part and a grand angular momentum part, see Eq. (1). It is customary to proceed by fixing the hyperradius ρ in Eq. (1) and looking for the solutions of the grand angular momentum eigenvalue problem. The corresponding eigenfunctions are called *hyperspherical harmonics*, in analogy with the well-known spherical harmonics, and describe the motion of a free particle on the surface of the hypersphere [16]. The general eigenvalue equation is

$$\hat{\Lambda}^2 \mathbf{F}^{\lambda} = (\lambda - 3N - 5)\mathbf{F}^{\lambda}, \tag{3}$$

where $\mathbf{F}^{\lambda}$ indicates the hyperspherical harmonics labeled by the grand angular momentum quantum number λ. The solutions constitute a complete orthonormal set of functions that satisfy the relation

$$\langle \mathbf{F}^{\lambda} \mid \mathbf{F}^{\lambda'} \rangle = \delta_{\lambda\lambda'}.$$

In fact, the labels of the harmonics include, beside the grand angular momentum quantum number λ, quantum numbers related to various hyperangular momenta and their projections along a quantization axis. This is worked out in the given references and sketched below.

The alternative variants of the hyperspherical coordinates correspond to the various choices for the parametrization of the Jacobi vectors on the hypersphere. In this context the natural choice, for explicit definition of the coordinates, is the simple extension of the canonical spherical parametrization for the general $(3N - 3)$-dimensional case, that leads to the so-called *asymmetric* hyperspherical coordinates, whose harmonics are known, under very general conditions, in closed form [16]. This choice, which is of great interest for bound state and elastic or inelastic processes, can be unsatisfactory for reactions, since each rearrangement channel (e.g., A + BC, B + CA, C + AB for the three-body case) corresponds to a different Jacobi coupling scheme. Therefore, the standard asymmetric parametrization would lead to a channel-dependent coordinate system, namely the coordinate system explicitly dependent on the initial Jacobi coupling scheme, typically the one for the reactant entrance channel. The role of the entrance arrangement would then be overemphasized, while in a reactive event all the channels may play a specific role. Mathematically this leads to poor convergence with respect to the product exit channels. Using simultaneously the sets for entrance and exit channels leads to non-orthogonality and overcompleteness problems. There are important examples demonstrating how the latter difficulties can be overcome successfully [19,20].

However, the problem can be tackled adopting a specific alternative to the Jacobi vector parametrization known as the *symmetric* parametrization [5,16] that treats all the channels "democratically" and, even if the corresponding harmonics are not always known in closed form, has very interesting features to be exploited in reaction dynamics. This type of parametrization is considered in this paper. In the following we will sometimes refer to symmetric hyperspherical coordinates as simply hyperspherical.

The choice of the symmetric hyperspherical coordinates leads to a framework in which the $3N - 3$ configuration variables (separating out the motion of the center of mass) are broken up into three ordinary external rotation coordinates, under the form of Euler angles α, β, γ specifying the orientation of the system, and internal coordinates (three in the case of three bodies and six in the case of four bodies) [21,22]. Among the internal coordinates, we have the hyperradius ρ, i.e., the radius of the hypersphere, and two angles Θ and φ which determine the shape and the inertia distribution with respect to the three principal inertia axes [23] (in the three-body case, the angle φ is absent). The remaining angular variables (one for three bodies, three for

four bodies, and $3N-9$ in general for $N \geq 4$) are the so-called internal or kinematic rotation angles $\{\Phi_\iota\}$ [9,22]. These angles parametrize rotations in the $(N-1)$-dimensional *kinematic space* ($N-1$ is the number of the Jacobi vectors) that smoothly connect all the different Jacobi coupling schemes (channels) and make the symmetric hyperspherical coordinates independent of the many possible choices of the arrangements, so to deserve for these coordinates the attribute "democratic". The kinematic angles can be thought of as the minimal variable set performing all the possible permutations of particles and of groups of particles, and correspond therefore to particle exchange. The size and shape coordinates ρ, Θ, and φ are invariant under internal kinematic rotations [7,10] as well as under external rotations and are often referred to simply as *invariants*.

As already pointed out, the choice of a symmetric or democratic parametrization of the hyperspherical coordinates corresponds to *just one* of the many possibilities, which lead to different explicit forms for $\hat{\Lambda}^2$. Different alternatives for parametrizing the Jacobi vectors are associated with distinct sets of hyperspherical harmonics, which are in turn simultaneous eigenfunctions of certain sets of commuting quantum mechanical operators. The operator $\hat{\Lambda}^2$ is common to all the sets, with quantum number λ, see Eq. (3). In what follows we will consider specifically the harmonics corresponding to the symmetric hyperspherical coordinates, which are simultaneous eigenfunctions of the following set of commuting operators:

$$\hat{\Lambda}^2, \quad \hat{J}^2, \quad \hat{K}^2, \quad \hat{J}_z, \quad \hat{K}_{z'},$$

where $\hat{\Lambda}^2$ is again the grand angular momentum operator, $\hat{J}^2$ and $\hat{J}_z$ are the orbital angular momentum of the nuclear motion in the body-fixed frame and its projection along a preferred z-axis, respectively, $\hat{K}^2$ is the *kinematic angular momentum* operator, and $\hat{K}_{z'}$ is its commuting z'-projection within the kinematic space.

Since the commuting operators are not as many as the number of angular variables (for $N \geq 4$), one expects the eigenfunctions of $\hat{\Lambda}^2$ to be degenerate. The desired functions are obtained as the sums of degenerate harmonics over the redundant labels:

$$\mathbf{F}^{\lambda JK}_{M_J M_K} = \sum_{\Omega_J=-J,\ldots,J} \sum_{\{\Omega_K\}} \big|JM_J\Omega_J\big\rangle\big|KM_K\{\Omega_K\}\big\rangle G^{\lambda JK}_{\Omega_J\{\Omega_K\}}, \tag{4}$$

where the J-labeled ket functions are Wigner functions depending on the three Euler rotation angles, while the K-labeled ket functions are, in general, kinematic rotation eigenfunctions depending on the kinematic rotation angles $\{\Phi_\iota\}$ and on a set of quantum numbers $\{\Omega_K\}$. Recall that the number of these angles is equal to $1 = 3N-8$ for $N=3$ and to $3N-9$ for $N \geq 4$. The G functions depend on Θ and φ (on Θ only for $N=3$). The functions $\mathbf{F}^{\lambda JK}_{M_J M_K}$ in Eq. (4) constitute the optimal complete orthonormal basis set for quantum dynamics calculations in hyperspherical coordinates, at a fixed hyperradius ρ. Here and henceforth, one should not confuse the total mass M of the system with the projections M_J, M_K of angular momenta.

Most of the theoretical studies in quantum reaction dynamics adopt the Born–Oppenheimer separation, with only the lowest electronic state taken into account and with the dynamics controlled by a single potential energy surface (PES) [2,3]. In the present paper we are assuming a single PES as well, and thus a scalar potential energy function $\mathbf{V} = V(\rho, \Omega_\lambda)$ of the hyperspherical coordinates. This function depends, in general, on the hyperradius ρ and the complete set of hyperangles, collectively denoted as Ω_λ. In any case, the choice of the basis set of hyperspherical harmonics is the crucial step for successfully implementing the quantum hyperspherical method, and it is important to consider the basis efficiency in reducing the number of functions required to obtain a prescribed numerical convergence as well as the fundamental issue of possible frame singularities [21,22].

2.2 Hyperspherical harmonics for the three-body quantum problem

In the three-body case, one has to solve the eigenvalue problem related to the following total nuclear motion Hamiltonian operator, looking for the total wavefunction $\mathbf{\Psi}^{JM}$ that must be an eigenfunction of the total angular momentum J and its projection along the quantization axis in the space-frame (here and henceforth, we set $\hbar = 1$ and omit the hats over operators of momenta for simplicity):

$$\hat{H} = \hat{T} + \hat{\mathbf{V}} = -\frac{1}{2M}\left(\frac{1}{\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} - \frac{\hat{\Lambda}^2}{\rho^2}\right) + V(\rho, \Omega_\lambda).$$

As before, here $\hat{\Lambda}^2$ is the grand angular momentum operator [12–14] and $V(\rho, \Omega_\lambda)$ is the potential energy function. The explicit expression for $\hat{\Lambda}^2$ is

$$\hat{\Lambda}^2 = \hat{\Lambda}^2_0 + \frac{4J_z^2}{\sin^2 2\Theta} + \frac{J_y^2}{\cos^2 2\Theta} + \frac{J_x^2 - J_z^2}{\cos^2\Theta} - \frac{2\mathrm{i}\sin 2\Theta}{\cos^2 2\Theta} J_y \frac{\partial}{\partial\Phi}, \tag{5}$$

where

$$\hat{\Lambda}_0^2 = -\frac{1}{\sin 4\Theta}\frac{\partial}{\partial\Theta}\sin 4\Theta\frac{\partial}{\partial\Theta} - \frac{1}{\cos^2 2\Theta}\frac{\partial^2}{\partial\Phi^2}$$

and the J_i, $i = x, y, z$, are the total nuclear rotational angular momentum operators in the body-frame. In Eq. (5), one recognizes the Coriolis term

$$-\frac{2\mathrm{i}\sin 2\Theta}{\cos^2 2\Theta}J_y\frac{\partial}{\partial\Phi}$$

that couples external and internal rotations [2,3]. The total wavefunction Ψ^{JM} is expanded as

$$\Psi^{JM} = \sum_{i\Omega K} f_{i\Omega K}(\rho)\Psi_{i\Omega K},$$

where the $f_{i\Omega K}$ are radial functions depending on ρ and the $\Psi_{i\Omega K}$ are nuclear states depending on Θ and Φ and parametrically on ρ, with K the total angular momentum projection on the space-frame and Ω the projection on the body-frame. These in turn are factorized as

$$\Psi_{i\Omega K} = F_\Omega^{JM}\phi_{iK},$$

where the F_Ω^{JM} are eigenfunctions of the total angular momentum and of its projection. The nuclear vibronic states ϕ_{iK} are taken as the solutions of a restricted problem

$$\left[\frac{1}{2M\rho^2}\left(\hat{\Lambda}_0^2 + \frac{4K^2}{\sin^2 2\Theta}\right) + V(\rho,\Omega_\lambda)\right]\phi_{iK} = \epsilon_{iK}(\rho)\phi_{iK},$$

where seeking for the ϕ_{iK} at various fixed ρ values is the core and the most expensive part of the calculations.

To tackle this problem, a basis set is selected given by the exact analytic solutions of the part

$$\hat{\Lambda}_0^2 + \frac{4K^2}{\sin^2 2\Theta},$$

for which the functions are the hyperspherical harmonics

$$Y_{\frac{\lambda}{2}\frac{\sigma}{2}K} = \left(\frac{\lambda+2}{4\pi}\right)^{1/2} d^{\frac{\lambda}{4}}_{\frac{\sigma}{4}-\frac{K}{2}\,\frac{\sigma}{4}+\frac{K}{2}}(4\Theta)\mathrm{e}^{-\mathrm{i}\sigma\Phi}.$$

Here λ is the grand angular momentum quantum number which takes even or odd values according to the parity with respect to the inversion, while σ takes accordingly even or odd values from $-\lambda+2\Omega$ to $\lambda-2\Omega$. What should be provided next is the representation of the Coriolis and the remaining rotational terms in Eq. (5). All these *residual* terms are taken into account in the propagation step [24–27]. We can also record here the recent paper [17], where elliptic types of hyperspherical coordinates, first introduced in [16], provide a general classification of three-body coordinate frames.

2.3 Hyperspherical harmonics for four-body quantum problems

The four-body hyperspherical coordinates involve, compared with the three-body case, one additional shape coordinate φ and two additional kinematic rotation angles Φ_ι [5]. The external rotation part and the internal or kinematic rotation part in the full Hamiltonian operator are formally identical, and we can introduce a kinematic rotation operator K^2 (not to be confused with the total angular momentum projection on the space-frame in Sect. 2.2), with components K_1, K_2, and K_3, which is *dual* to the external angular momentum operator J^2. The kinetic energy operator defining the eigenvalue problem for the four-body basis functions is [5]

$$\hat{T} = -\frac{1}{2M}\left[\frac{1}{\rho^8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} + \frac{\hat{\Lambda}_\xi(\Theta,\varphi)}{\rho^2}\right] + \hat{\Lambda}_{J_i^2,K_\kappa^2}(\rho,\Theta,\{\Phi_\iota\}) + \hat{\Lambda}_{J_i,K_\kappa}(\rho,\Theta,\{\Phi_\iota\})$$

with $i = x, y, z$ and $\kappa, \iota = 1, 2, 3$; for the explicit expression of $\hat{T}$ see Refs. [5,6]. Here $\rho^{-2}\hat{\Lambda}_\xi(\Theta,\varphi)$ is the invariant coordinate part, while $\hat{\Lambda}_{J_i^2,K_\kappa^2}(\rho,\Theta,\{\Phi_\iota\})$ involves the squares of the components of two (the external and internal) angular momenta, whose couplings are in the Coriolis term $\hat{\Lambda}_{J_i,K_\kappa}(\rho,\Theta,\{\Phi_\iota\})$. The total kinetic energy wavefunction (the solution for the zero potential case) can be represented as follows [9,28,29]:

$$\Psi_{nk}^{\lambda JK} = \sum_{n',m}|Jn'n\rangle|Kkm\rangle G_{n'm}^{\lambda JK},$$

where the labels are the total external angular momentum J, the grand angular momentum quantum number λ (see Sect. 2.1), and the total kinematic angular momentum K. The kinematic rotation part is, as remarked above, formally identical to the ordinary rotation part. The $|Kkm\rangle$ kinematic rotation functions are therefore similar to the $|Jn'n\rangle$ external rotation functions, namely symmetrized Wigner d-functions [3,9], with the requirement that the $|Kkm\rangle$ have to be symmetrized with respect to the V_4 group and also with respect to the exchange of identical particles (a full treatment of this issue has been given in Ref. [9]). The hard work in dealing with four-body harmonics is the search for the $G_{n'm}^{\lambda JK}$ functions, which depend on the invariants ρ, Θ, φ. We should solve the eigenvalue problem for the operator

$$-\frac{\hat{\Lambda}_\xi(\Theta,\varphi)}{2M\rho^2} + \hat{\Lambda}_{J_i^2,K_\kappa^2}(\rho,\Theta,\{\Phi_\iota\}) + \hat{\Lambda}_{J_i,K_\kappa}(\rho,\Theta,\{\Phi_\iota\}).$$

What has been achieved so far is obtaining solutions for this problem in the reduced case of zero external and internal angular momenta. We found it convenient

to represent the three-dimensional space (ρ, Θ, φ) of kinematic invariants as a Cartesian space with axes ξ_1, ξ_2, and ξ_3. As a consequence of this choice and of the assumed zero value for the angular momenta, the problem is rewritten as

$$\left(\nabla^2 + \frac{2}{D^{1/2}}\nabla D^{1/2}\nabla\right) G_{00}^{\lambda 00} = E G_{00}^{\lambda 00},$$

where E generically represents the eigenvalue,

$$D = (\xi_2^2 - \xi_1^2)(\xi_3^2 - \xi_1^2)(\xi_3^2 - \xi_2^2)$$

is the volume element, ∇ and ∇^2 are the standard Euclidean gradient and Laplace operators with respect to the ξ's, and G depends on ξ_1, ξ_2, and ξ_3. It can be shown [7,10] that this equation may be solved in the zero energy limit giving the right result for the G's:

$$\left(\nabla^2 + \frac{2}{D^{1/2}}\nabla D^{1/2}\nabla\right) G_{00}^{\lambda 00} = 0.$$

It has been also proven that the solutions G have to enjoy the O_h symmetry and that only symmetry selected values are permitted for λ [7,10]. The G functions are then obtained in the form of harmonic polynomials of degree λ and eigenvalue $E = (\lambda + 3)(\lambda + 4)$ [7] in the (ξ_1, ξ_2, ξ_3) Cartesian space. The angular parametrization of the harmonic polynomials is then found by simply splitting off a factor ρ^λ. The degeneracy of the solutions for a given λ is also known [7,10,30].

In summary, the feasibility of the hyperspherical approach for four-body reactive systems relies upon availability of harmonic sets for the expansion of eigenfunctions. Although these sets can be generated numerically [8], analytic subsets will presumably be of decisive help. As for the case of three bodies of Sect. 2.2, one will have to separate out Coriolis type terms, to be eventually accounted for in the propagation step.

3 Hyperspherical formulation of classical mechanics and energy partitions for cluster dynamics

Present efforts in developing a hyperspherical approach to classical dynamics are motivated by the central role that classical simulations play in the study of large systems, where quantum methods are out of feasibility. The aspect that we exploit to build up a hyperspherical view of the N-body classical motion problem is the geometry of the hyperspherical configuration space spanned by the $3N - 3$ degrees of freedom of the system. Consideration will later be given also to the momentum space, and thus to the full phase space.

As already pointed out in Sect. 2.1, in the symmetric or democratic version of the quantum N-body problem, the hyperspherical coordinates are divided into groups consisting of three ordinary external rotation degrees of freedom, three (or two for $N = 3$) size-shape or inertial degrees of freedom, and $3N - 9$ (or $3N - 8 = 1$ for $N = 3$) kinematic rotations angles. Furthermore, the size-shape coordinates can in turn be divided into the hyperradius ρ and two angles Θ and φ (the latter angle is absent for $N = 3$). The coordinate subgroups span subspaces according to a similar decomposition of the configuration space. During the motion, the system samples its available phase space with a given total energy, while each subgroup of degrees of freedom samples its own subspace.

The classical kinetic energy can be given a similar decomposition, which means to assign the proper energy contribution to each of the subgroups of degrees of freedom. For any given subgroup, the term of the decomposition will be the energy contribution associated with the mode of the motion represented by the corresponding coordinates. The sum of all the contributions, plus eventually couplings among them, will define a *partition* of the kinetic energy. In what follows we will illustrate the practical application of this idea, aiming at giving a precise definition of the meaning of "mode" in this context.

A hyperspherical formulation of classical mechanics would be simply achieved by rewriting the classical Cartesian Hamiltonian function in terms of hyperspherical coordinates. The result would be an analogue of the quantum hyperspherical Hamiltonian operator except for some so-called extra terms [31], not appearing in the classical Hamiltonian, of inherent quantum nature, which arise from non-commuting operators. The obvious further step would be the integration of the classical hyperspherical equations of motion. This could be done by direct integration of the hyperspherical equations. However, the presence of singularities at poles, corresponding to spherical and symmetric top configurations, makes it not really convenient to proceed in that way, and definitely not competitive with established ways of integrating the equations of motion in Cartesian coordinates.

Circumventing direct integration, we obtain expressions for calculating the quantities appearing in the kinetic energy partition (that we know could be found from the hyperspherical view of classical mechanics) from the Cartesian coordinates and velocities. The key point in the hyperspherical formulation of classical mechanics is that, similarly to the quantum case, the classical kinetic energy for a given N-body system is the sum of terms that can be conveniently grouped to represent contributions dependent on clearly identified subgroups of degrees of freedom and corresponding to well-defined

and physically meaningful modes of the motion. The coupling terms (possibly negative) can also be grouped and collectively treated as a *residual* contribution to the total kinetic energy. A small residual energy will then indicate a good separation of the various modes. In the following we will illustrate the partitions starting from some further details about the coordinates. To be definite, we will assume $N \geq 4$, the simplifications for $N = 3$ are straightforward.

3.1 Hyperspherical coordinates from the singular value decomposition

As already pointed out in Sect. 2.1, the symmetric hyperspherical coordinates for an N-body system can be introduced from the Cartesian components of the $n = N - 1$ Jacobi vectors. To operate on these components, a $3 \times n$ matrix Z is introduced, containing column-wise the Jacobi vectors. The suitable mathematical tool here is the so-called *singular value decomposition* of matrices [31–34]. The theorem states that, for any given $3 \times n$ matrix Z, there exists a decomposition into the product of three matrices as follows:

$$Z = D\Xi X^{\mathrm{t}} \tag{6}$$

(the superscript t means matrix transposing), where $D \in O(3)$ is a 3×3 orthogonal matrix, $X \in O(n)$ is an $n \times n$ orthogonal matrix, and Ξ is a $3 \times n$ matrix with all the entries zero except for the diagonal entries ξ_1, ξ_2, ξ_3, which can be (and generically are) non-zero and satisfy the inequalities

$$\xi_1 \geq \xi_2 \geq \xi_3 \geq 0$$

(recall that we assume $N \geq 4$ and hence $n \geq 3$). In fact, the factors D and X in Eq. (6) can be chosen to be special orthogonal: $D \in SO(3)$, $X \in SO(n)$, except for the case where $n = 3$ and $\det Z < 0$. The three ξ's can be thought of as the three components of a Cartesian vector (compare with Sect. 2.3), that can be parametrized in a three-dimensional space by the hyperradius and two angles. The ξ's are called the *singular values* of the matrix Z and are uniquely determined, while the two factors D and X are *not*. In the three-body case ($n = 2$), one has only *two* singular values.

The total kinetic energy T of the system is obtained from the time derivative $\dot{Z}$ of Z as [33,34]

$$T = \frac{M}{2}\,\mathrm{Tr}\big(\dot{Z}\dot{Z}^{\mathrm{t}}\big), \tag{7}$$

where M is as before the total mass of the system (and Tr means the matrix trace). Recall that the quantity $\mathrm{Tr}\big(\dot{Z}\dot{Z}^{\mathrm{t}}\big)$, i.e., the sum of the squares of all the $3n$ entries of $\dot{Z}$, is known as the square of the *Frobenius norm* of the matrix $\dot{Z}$ [32,34]. In our outline of the hyperspherical formulation of classical dynamics, the square of the Frobenius norm of any matrix denoted as $\dot{Z}^{\langle\text{symbols}\rangle}$ or $\dot{Z}_{\langle\text{symbols}\rangle}$ will represent always an energy contribution, see Sect. 3.4.

The 3×3 orthogonal matrix D in Eq. (6) is characterized by three parameters, corresponding to the three Euler angles describing ordinary rotations in the physical space, while the $n \times n$ orthogonal matrix X is to be parametrized by $3n - 6$ angles Φ_ι, corresponding to the kinematic rotation angles (see Sect. 2.1). Of course, matrices in $SO(n)$ are parametrized in general by $n(n-1)/2$ variables, but for $n \geq 4$ only the first three columns of the matrix X are really involved in Eq. (6). The singular values ξ's play the role of size and shape coordinates, and can be shown to be related to the hyperradius as [7,9,23,31,33–35]

$$\rho^2 = \xi_1^2 + \xi_2^2 + \xi_3^2 = \mathrm{Tr}(ZZ^{\mathrm{t}}) \tag{8}$$

and to the principal moments of inertia I_1, I_2, and I_3 of the system with respect to the center of mass as

$$I_1 = M(\xi_1^2 + \xi_2^2), \quad I_2 = M(\xi_1^2 + \xi_3^2), \quad I_3 = M(\xi_2^2 + \xi_3^2).$$

Since the hyperradius is the square root of the sum of the squares of the singular values, it is related to the total inertia $I = I_1 + I_2 + I_3$ of the system through $I = 2M\rho^2$. Two further angles Θ and φ complete a spherical parametrization (as anticipated in the previous exposition) of the three ξ's taking ρ as the radius. This is convenient for separating out the hyperradius whose evolution, along with the angular energy associated with Θ and φ (an appropriate angular momentum L_ξ can be defined), contribute to the ξ variations. For details concerning the singular value decomposition applied to the symmetric hyperspherical coordinates, see Ref. [34].

3.2 The hyperspherical partition: hyperangular momenta

The hyperspherical partition is the simplest way of partitioning the energy of the system, inspired by the hyperspherical coordinate representation. Such a partition results from the integration of the equations of motion in hyperspherical coordinates and involves contributions to the total kinetic energy coming from the various hyperangular momenta. However, we avoid direct integration of the equations of motion and merely define the various kinetic energy terms, according to the grouping of the degrees of freedom that naturally arises while introducing the symmetric hyperspherical coordinates.

Following such a procedure, one can determine contributions to the kinetic energy from the hyperradius variation $\dot{\rho}$ and the hyperangular momenta corresponding to ordinary and kinematic rotations, denoted as J and K, respectively (compare with Sect. 2.1). An energy term accounting for the total angular motion can be calculated from the grand angular momentum Λ. In addition, an angular momentum L_ξ will be defined as a measure of the energy contribution from the angular motion of the three size-shape coordinates, the ξ's, also parametrized in terms of ρ, Θ, and φ.

Let us now give the explicit and rigorous definitions of the above mentioned quantities [33,34]. The key angular characteristic, the *grand angular momentum* Λ, can be thought of as a generalization of the standard three-component angular momentum vector and is defined from the matrices Z and $\dot{Z}$ as follows:

$$\Lambda^2 = M^2 \sum_{\substack{1\le i,j\le 3\\ 1\le \alpha,\beta\le n\\ i<j \text{ or } i=j,\alpha<\beta}} \left(Z_{i\alpha}\dot{Z}_{j\beta} - Z_{j\beta}\dot{Z}_{i\alpha}\right)^2, \tag{9}$$

where M is as before the total mass of the system while $Z_{i\alpha}$ denote the entries of the coordinate matrix Z, with Greek column-indices identifying the Jacobi vectors and row-indices i, j identifying their components. The energy contribution due to the grand angular momentum, the *grand angular energy* T_Λ, will be

$$T_\Lambda = \frac{\Lambda^2}{2M\rho^2},$$

compare with the corresponding quantum mechanical relation of Eq. (2).

From the linear momentum conjugated to the hyperradius

$$P_\rho = M\dot{\rho} = M\rho^{-1}\,\mathrm{Tr}\left(Z\dot{Z}^{\mathrm{t}}\right), \tag{10}$$

the *hyperradial energy* T_ρ accounting for the overall breathing of the system follows as

$$T_\rho = \frac{P_\rho^2}{2M} = \frac{M\dot{\rho}^2}{2}.$$

As in quantum mechanics (see Sect. 2.1), the hyperradial and grand angular energies define the so-called *Smith decomposition* [12,33,34], the simplest partition of the kinetic energy:

$$T = T_\rho + T_\Lambda, \tag{11}$$

compare with Eq. (1).

The three ordinary external rotation variables, with which the total angular momentum J can be associated, support the physical rotation energy term

$$T_J = \frac{J^2}{2M\rho^2}.$$

The quantity dual to the ordinary angular momentum J is the *kinematic hyperangular momentum* K, accounting for kinematic rotations. It is convenient to think of K as the angular momentum of the rows of the matrix Z, instead of the columns. So, while J is the total angular momentum of the n three-dimensional column-vectors of the coordinate matrix, K will be the total angular momentum of the three n-dimensional row-vectors, and its square is obtained as

$$K^2 = \sum_{1\le\alpha<\beta\le n} K_{\alpha\beta}^2, \quad K_{\alpha\beta} = M\sum_{i=1}^{3}\left(Z_{i\alpha}\dot{Z}_{i\beta} - Z_{i\beta}\dot{Z}_{i\alpha}\right), \tag{12}$$

along with the corresponding energy term T_K

$$T_K = \frac{K^2}{2M\rho^2}.$$

Since the kinematic rotations act in the kinematic space (the space of the three n-dimensional row-vectors of Z), the result of their action, as perceived from the three-dimensional physical space, is the mixing of corresponding components of different vectors, an operation that, for definite sets of values of the kinematic angles Φ_ι, should be understood as particle permutations. Indeed the physical interpretation of kinematic rotations is the particle exchange, while in terms of Jacobi vectors, kinematic rotations are transformations that continuously interpolate all the possible Jacobi coupling schemes.

The angular component of the motion associated with variations of the vector (ξ_1, ξ_2, ξ_3), in the three-dimensional Cartesian ξ-space, is measured by the *singular angular momentum* L_ξ as follows:

$$L_\xi^2/M^2 = \left(\xi_1\dot{\xi}_2 - \xi_2\dot{\xi}_1\right)^2 + \left(\xi_1\dot{\xi}_3 - \xi_3\dot{\xi}_1\right)^2 + \left(\xi_2\dot{\xi}_3 - \xi_3\dot{\xi}_2\right)^2, \tag{13}$$

and the corresponding energy term is

$$T_\xi = \frac{L_\xi^2}{2M\rho^2}.$$

The energy terms introduced above represent the contributions to the kinetic energy from distinct groups of degrees of freedom and the corresponding modes of the motion. In other words, this is a proposal of a separation scheme, and we are now proceeding to a brief discussion on the existence and role of coupling terms.

These terms can be included by introducing an *angular coupling energy* $T_{\rm ac}$, accounting collectively for coupling terms contributing to the total kinetic energy T. Since the latter, as well as the terms T_Λ, T_ρ, T_J, T_K, and T_ξ, are explicitly given, $T_{\rm ac}$ is defined as the (possibly negative [34]) difference

$$T_{\rm ac} = T - T_\rho - T_\xi - T_J - T_K = T_\Lambda - T_\xi - T_J - T_K,$$

in such a way that a small value of $|T_{\rm ac}|$ indicates well separated modes. The latter would mean that the description based upon the hyperspherical view is fit to model the system. Finally the sum of the terms giving the total kinetic energy T will be

$$T = T_\rho + T_\xi + T_J + T_K + T_{\rm ac}, \tag{14}$$

representing the so-called *hyperspherical partition*.

3.3 Invariance properties

All the hyperspherical quantities presented by now, the hyperradius ρ, the singular values ξ's of the matrix Z, the grand angular momentum Λ, the "partial" (hyper)angular momenta J, K, L_ξ, and the corresponding energy terms appearing in Eqs. (11) and (14), are instantaneous phase-space invariants, namely they are invariant under orthogonal coordinate transformations in both the physical space and the kinematic space. The details and a rigorous derivation of the invariance properties for all the hyperspherical characteristics are reported in Ref. [34]. Below we sketch some proofs of the invariance features for the various kinetic energy terms.

From Eq. (6) it follows that

$$D^{\rm t} Z Z^{\rm t} D = \Xi \Xi^{\rm t} = {\rm diag}(\xi_1^2, \xi_2^2, \xi_3^2),$$

so that the squares of the ξ's are the eigenvalues of the 3×3 square matrix $ZZ^{\rm t}$. Applying a rotation in the physical space represented by a matrix $R \in SO(3)$ and a rotation in the kinematic space represented by a matrix $Q \in SO(n)$, one arrives at the new coordinate matrix $Z' = R^{\rm t} Z Q$. The matrices $ZZ^{\rm t}$ and

$$Z'(Z')^{\rm t} = R^{\rm t} Z Z^{\rm t} R$$

are similar and possess therefore the same eigenvalues. Obviously, this conclusion will remain true if one considers, more generally, an arbitrary orthogonal transformation in the physical space represented by a matrix $R \in O(3)$ and an arbitrary orthogonal transformation in the kinematic space represented by a matrix $Q \in O(n)$. We have thus proven the invariance of the singular values ξ_1, ξ_2, ξ_3 under orthogonal coordinate transformations of any kind.

This reasoning can be proceeded in a "dual" way. Namely, Eq. (6) implies also that

$$X^{\rm t} Z^{\rm t} Z X = \Xi^{\rm t} \Xi = {\rm diag}\left(\xi_1^2, \xi_2^2, \xi_3^2, \underbrace{0, 0, \ldots, 0}_{n-3 \text{ zeros}}\right),$$

so that the eigenvalues of the $n \times n$ square matrix $Z^{\rm t} Z$ are $\xi_1^2, \xi_2^2, \xi_3^2, 0, 0, \ldots, 0$. Again, the invariance of the ξ's follows immediately from the fact that the matrices $Z^{\rm t} Z$ and

$$(Z')^{\rm t} Z = Q^{\rm t} Z^{\rm t} Z Q$$

are similar, where

$$Z' = R^{\rm t} Z Q, \quad R \in O(3), \quad Q \in O(n). \tag{15}$$

In the sequel, we will always use the notation of Eq. (15) assuming that R and Q are time-independent.

Now Eq. (8) gives the invariance of the hyperradius ρ and consequently of its time derivative $\dot\rho$. Alternatively, the invariance of $\dot\rho$ follows from Eq. (10), because of the similarity of the matrices $Z\dot Z^{\rm t}$ and

$$Z'(\dot Z')^{\rm t} = R^{\rm t} Z \dot Z^{\rm t} R.$$

Hence, the hyperradial energy T_ρ is also invariant under all the orthogonal coordinate transformations in both the physical space and the kinematic space. Besides that, Eq. (13) implies the invariance of the singular angular momentum L_ξ and of the corresponding energy term T_ξ. The invariance of the total kinetic energy T of the system is obvious from Eq. (7), since the matrices $\dot Z \dot Z^{\rm t}$ and

$$\dot Z'(\dot Z')^{\rm t} = R^{\rm t} \dot Z \dot Z^{\rm t} R$$

are similar. Taking into account the Smith decomposition of T, see Eq. (11), one obtains the invariance of the grand angular energy T_Λ and consequently of the grand angular momentum Λ defined by Eq. (9).

The invariance property of the (hyper)angular momenta J and K is a more subtle issue. It is not hard to see that the three components J_x, J_y, J_z of the ordinary angular momentum J are related to the coordinate matrix Z and its time derivative $\dot Z$ as

$$M\left(Z\dot Z^{\rm t} - \dot Z Z^{\rm t}\right) = \begin{pmatrix} 0 & J_z & -J_y \\ -J_z & 0 & J_x \\ J_y & -J_x & 0 \end{pmatrix},$$

so that

$$J^2 = J_x^2 + J_y^2 + J_z^2 = \begin{vmatrix} 0 & J_z \\ -J_z & 0 \end{vmatrix} + \begin{vmatrix} 0 & -J_y \\ J_y & 0 \end{vmatrix} + \begin{vmatrix} 0 & J_x \\ -J_x & 0 \end{vmatrix}$$

is equal to the sum of the three 2×2 principal minors of the matrix $M(Z\dot{Z}^{\mathrm{t}} - \dot{Z}Z^{\mathrm{t}})$. Replacing Z with Z', we will get a similar matrix

$$M(Z'(\dot{Z}')^{\mathrm{t}} - \dot{Z}'(Z')^{\mathrm{t}}) = MR^{\mathrm{t}}(Z\dot{Z}^{\mathrm{t}} - \dot{Z}Z^{\mathrm{t}})R.$$

Similar matrices share the same characteristic polynomial and hence the same sum of the second order principal minors. Indeed, for any $m \times m$ matrix W, the coefficient at χ^{m-k} $(1 \leq k \leq m)$ in the characteristic polynomial $\det(W - \chi\,\mathrm{Id})$ is equal to $(-1)^{m-k}s_k$, where s_k is the sum of all the $k \times k$ principal minors of W. The same can be expressed as follows: the kth elementary symmetric function of the eigenvalues of W is equal to s_k [32]. One concludes that the angular momentum J and consequently the corresponding energy term T_J are invariants.

Analogously, the components $K_{\alpha\beta}$ of the kinematic angular momentum K, see Eq. (12), appear as the entries of the matrix $M(Z^{\mathrm{t}}\dot{Z} - \dot{Z}^{\mathrm{t}}Z)$:

$$M(Z^{\mathrm{t}}\dot{Z} - \dot{Z}^{\mathrm{t}}Z)_{\alpha\beta} = \begin{cases} K_{\alpha\beta} & \text{for } \alpha < \beta, \\ -K_{\beta\alpha} & \text{for } \alpha > \beta, \\ 0 & \text{for } \alpha = \beta, \end{cases}$$

here $1 \leq \alpha, \beta \leq n$. Thus, K^2 is the sum of all the $n(n-1)/2$ second order principal minors of the matrix $M(Z^{\mathrm{t}}\dot{Z} - \dot{Z}^{\mathrm{t}}Z)$. Replacing Z with Z', one obtains a similar matrix

$$M((Z')^{\mathrm{t}}\dot{Z}' - (\dot{Z}')^{\mathrm{t}}Z') = MQ^{\mathrm{t}}(Z^{\mathrm{t}}\dot{Z} - \dot{Z}^{\mathrm{t}}Z)Q.$$

In the same way as in the case of J, this implies the invariance of the kinematic angular momentum K and consequently of the corresponding energy term T_K.

Finally, the invariance of the angular coupling energy T_{ac} follows immediately from its definition and the invariance of the terms T, T_ρ, T_ξ, T_J, T_K, see Eq. (14).

3.4 The projective partition

The projective partition of the total kinetic energy of a system of classical particles has been developed in [33,34] with the aim of improving the separability of the various modes of the motion. To ensure this the mathematical definition of the partition terms, compared with the hyperspherical partition of Eq. (14), has been modified and a geometric projection procedure has been introduced, which is explained below.

The basic idea can be presented as follows. The coordinate matrix Z of the system belongs to the space of $3 \times n$ matrices in which the *Frobenius inner product* [32,34] of any two matrices Z^a and Z^b can be defined as

$$\mathrm{Tr}(Z^a(Z^b)^{\mathrm{t}}) = \sum_{i=1}^{3}\sum_{\alpha=1}^{n} Z^a_{i\alpha}Z^b_{i\alpha}.$$

As we already pointed out, the total kinetic energy T is the square of the Frobenius norm of the matrix $\dot{Z}$ (up to a factor of $M/2$), see Eq. (7). Now imagine the matrix $\dot{Z}$ to be the sum of matrices $\dot{Z}_\iota$:

$$\dot{Z} = \sum_\iota \dot{Z}_\iota, \tag{16}$$

so that

$$\frac{2T}{M} = \mathrm{Tr}\left(\sum_\iota \dot{Z}_\iota \sum_\iota \dot{Z}_\iota^{\mathrm{t}}\right) = \sum_\iota \mathrm{Tr}(\dot{Z}_\iota\dot{Z}_\iota^{\mathrm{t}}) + 2\sum_{\iota<\kappa}\mathrm{Tr}(\dot{Z}_\iota\dot{Z}_\kappa^{\mathrm{t}}). \tag{17}$$

Considering each of the Frobenius products in Eq. (17) as a kinetic energy term, one has an energy partition, where the mixed terms are zero if, and only if, the matrices $\dot{Z}_\iota$ are pairwise orthogonal. The mixed terms are therefore a measure of the separability of the modes corresponding to the various $\dot{Z}_\iota$. Therefore, to find a good partition means, within this scheme, to find a good decomposition of the matrix $\dot{Z}$.

The next step consists in considering the *orbits* of the matrix Z under the action of three orthogonal matrix groups. These are the group $SO(3)$ of ordinary rotations in the physical (or external) space, the group $SO(n)$ of kinematic rotations in the kinematic (or internal) space, and also their direct product, $SO(3) \times SO(n)$. The orbits will be denoted respectively as $\Gamma_e(Z)$, $\Gamma_k(Z)$, and $\Gamma(Z)$. Thus, $\Gamma_e(Z)$ is the manifold of all the $3 \times n$ matrices of the form $R^{\mathrm{t}}Z$ with $R \in SO(3)$ and $\Gamma_k(Z)$ is the manifold of all the matrices ZQ with $Q \in SO(n)$, while $\Gamma(Z)$ contains all the matrices $R^{\mathrm{t}}ZQ$. Note that the "left" action of the group $SO(3)$ and the "right" action of the group $SO(n)$ in the space of $3 \times n$ matrices commute.

We denote as $\Pi_e(Z)$, $\Pi_k(Z)$, and $\Pi(Z)$ the *tangent spaces* to $\Gamma_e(Z)$, $\Gamma_k(Z)$, and $\Gamma(Z)$, respectively, at point Z. The space $\Pi_e(Z)$ is constituted by all the $3 \times n$ matrices $Z + r^{\mathrm{t}}Z$ with skew-symmetric $r \in so(3)$, the space $\Pi_k(Z)$ is constituted by all the matrices $Z + Zq$ with skew-symmetric $q \in so(n)$, and, finally, all the matrices $Z + r^{\mathrm{t}}Z + Zq$ with $r \in so(3)$ and $q \in so(n)$ constitute $\Pi(Z)$.

The key point for us is to find matrices $\dot{Z}_\iota$ in Eq. (16) mutually orthogonal in order to obtain an efficient separation of the modes. Accordingly, the energy terms will have to be given an interpretation as physically motivated motions.

These requirements are best fulfilled if we take as (some of) matrices $\dot{Z}_\iota$ the *projections* (in the sense of the Frobenius product) of $\dot{Z}$ on the tangent spaces we have just defined. Given a tangent space, one can obtain, through a projection procedure, two orthogonal

matrices: the projected component itself plus the orthogonal component. The latter will not have any character of the motion that takes place on the tangent space, and will represent independent modes. Moreover, both the energy terms corresponding to these components will automatically be instantaneous phase-space invariants. This follows from two easy facts. First, for any $R \in SO(3)$ and $Q \in SO(n)$ one has

$$\Upsilon(R^{\mathrm{t}} Z Q) = R^{\mathrm{t}} \Upsilon(Z) Q,$$

where Υ denotes any of the varieties Γ_e, Γ_k, Γ, Π_e, Π_k, Π. Second, orthogonal coordinate transformations in both the physical and kinematic spaces preserve the Frobenius product:

$$\mathrm{Tr}\big(R^{\mathrm{t}} Z^a Q (R^{\mathrm{t}} Z^b Q)^{\mathrm{t}}\big) = \mathrm{Tr}\big(Z^a (Z^b)^{\mathrm{t}}\big)$$

for any matrices Z^a, Z^b.

Using this approach, one can split the matrix $\dot{Z}$ into two parts

$$\dot{Z} = \dot{Z}^{\mathrm{rot}} + \dot{Z}^{\mathrm{I}},$$

where $\dot{Z}^{\mathrm{rot}}$ accounts for all kinds of rotational motions (except for those associated with the ξ's) and $\dot{Z}^{\mathrm{I}}$ accounts for the inertial or size-shape motions. The matrices $\dot{Z}^{\mathrm{rot}}$ and $\dot{Z}^{\mathrm{I}}$ are respectively the projected and the orthogonal components with the tangent space $\Pi(Z)$ used as the projection plane. Taking the squares of the Frobenius norms of these matrices, we get the energy terms

$$T^{\mathrm{rot}} = \frac{M}{2}\,\mathrm{Tr}\big(\dot{Z}^{\mathrm{rot}}(\dot{Z}^{\mathrm{rot}})^{\mathrm{t}}\big), \quad T^{\mathrm{I}} = \frac{M}{2}\,\mathrm{Tr}\big(\dot{Z}^{\mathrm{I}}(\dot{Z}^{\mathrm{I}})^{\mathrm{t}}\big),$$

called the *rotational energy* and the *inertial energy*, respectively. The sum of these terms is equal to the total kinetic energy T. The matrix $\dot{Z}^{\mathrm{I}}$ does not contain the rotational motion contributions, and the term T^{I} must correspond to the energy contribution from the ξ's. Indeed, one can verify [33,34] that

$$T^{\mathrm{I}} = T_\rho + T_\xi, \tag{18}$$

so that

$$T^{\mathrm{rot}} = T_J + T_K + T_{\mathrm{ac}}.$$

By projection on $\Pi_e(Z)$ and $\Pi_k(Z)$, a further decomposition is possible for $\dot{Z}$, giving matrices $\dot{Z}^e$ and $\dot{Z}^k$, respectively, whose Frobenius norms would provide (after squaring and multiplying by $M/2$) the projective analogues of the terms T_J and T_K of the hyperspherical partition of Eq. (14). These new terms are denoted as T^{ext} and T^{int} and called the *external energy* and the *internal energy*, meaning external and internal rotations, respectively:

$$T^{\mathrm{ext}} = \frac{M}{2}\,\mathrm{Tr}\big(\dot{Z}^e(\dot{Z}^e)^{\mathrm{t}}\big), \quad T^{\mathrm{int}} = \frac{M}{2}\,\mathrm{Tr}\big(\dot{Z}^k(\dot{Z}^k)^{\mathrm{t}}\big).$$

As in the case of the hyperspherical partition, we have to take into account couplings, which are cumulatively measured by a (possibly negative [34]) *residual energy* term T^{res}:

$$\begin{aligned} T^{\mathrm{res}} &= T - T_\rho - T_\xi - T^{\mathrm{ext}} - T^{\mathrm{int}} \\ &= T_\Lambda - T_\xi - T^{\mathrm{ext}} - T^{\mathrm{int}} = T^{\mathrm{rot}} - T^{\mathrm{ext}} - T^{\mathrm{int}}. \end{aligned}$$

Finally, the *projective partition* of the total kinetic energy, as a result of the projection procedure that exploits the geometric properties of the hyperspherical phase space, can be written as follows:

$$T = T_\rho + T_\xi + T^{\mathrm{ext}} + T^{\mathrm{int}} + T^{\mathrm{res}}. \tag{19}$$

By construction, the matrix $\dot{Z}^{\mathrm{I}}$ is orthogonal to each of the matrices $\dot{Z}^{\mathrm{rot}}$, $\dot{Z}^e$, and $\dot{Z}^k$:

$$\mathrm{Tr}\big(\dot{Z}^{\mathrm{I}}(\dot{Z}^{\mathrm{rot}})^{\mathrm{t}}\big) = \mathrm{Tr}\big(\dot{Z}^{\mathrm{I}}(\dot{Z}^e)^{\mathrm{t}}\big) = \mathrm{Tr}\big(\dot{Z}^{\mathrm{I}}(\dot{Z}^k)^{\mathrm{t}}\big) = 0. \tag{20}$$

It follows from Eqs. (18) and (20) that there is no couplings between the inertial motion modes (associated with the ξ evolution) and the rotational motion modes (the external and internal rotations), and that the breathing degree of freedom of the system (connected with $\dot{\rho}$) and the two degrees of freedom defined by the rotations of the vector (ξ_1, ξ_2, ξ_3) give no coupling either. The *only* source of couplings in a system of classical particles is the coupling between the ordinary and kinematic rotations.

Between the projective partition terms and the corresponding ones in the hyperspherical partition, there hold the inequalities [33,34]

$$T_J \le T^{\mathrm{ext}}, \quad T_K \le T^{\mathrm{int}},$$

and consequently

$$T^{\mathrm{res}} \le T_{\mathrm{ac}}.$$

In the presumably frequently occurring case where all the terms in Eqs. (14) and (19) are positive, this implies that the couplings in the projective partition do not exceed (and are generically *smaller* than) those in the hyperspherical partition.

4 Summary and outlook

We have confined our presentation to basic issues, leaving out extensive numerical implementations, as well

as the considerable physical insight associated with the hyperspherical approach to the N-body problem. Indeed, one of the characteristic features of this approach is perhaps that the hyperradius ρ, which is also a measure of the total inertia of the system and is independent of the particular choice of the Jacobi scheme, is a physically natural reaction coordinate [2,3]. Its small values correspond to the region of strong interaction, while at large values it describes the asymptotic rearrangement regions corresponding to the reactants and products. In the hyperspherical method, calculations are therefore carried out adiabatically with respect to ρ. The whole range of ρ is conveniently divided into sectors and for each of them, a ρ-fixed Hamiltonian eigenvalue problem is solved, yielding adiabatic curves and nonadiabatic couplings. The ρ dependence is then taken into account on the second step in which the hyperradial functions are propagated from the strong interaction region to the large ρ limit, where the scattering matrix is extracted enforcing the proper boundary conditions. The choice of hyperspherical coordinates, especially for reactive scattering problems, is therefore strongly motivated by the availability of a natural, adiabatic, reaction coordinate, and by the central role that angular momenta and their projections play in all the reactive processes.

For classical dynamics simulations, the approach will prove to be useful in assessing the role of the specific modes of the overall behavior. While in quantum mechanics the geometric properties of the hyperspherical configuration space are made manifest and easily recognized in the *factorization of the harmonics* as products of factors depending on subgroups of variables, correspondingly in classical mechanics a most useful result is the *partitioning of the kinetic energy* as a sum of contributions depending on the distinct groups of degrees of freedom. The basic idea is that of considering the various well-distinct groups of variables—hyperradius, shape invariants, external and internal rotation angles—as representative of physically meaningful modes of the motion. This idea has been fully developed [31,33–35] and illustrated through the construction of an efficient method for calculating the terms in the partitions of the kinetic energy. The hyperspherical formulation of the classical dynamics has been proven to be effective as an interpreting tool for molecular dynamics simulations [31,35–38]. These simulations show that in many cases, one indeed has $0 < T^{\mathrm{res}} \ll T_{\mathrm{ac}}$.

It is worthwhile to mention that some insight in revealing additional features of the dynamics of reactive systems comes from the statistical analysis of the adiabatic ρ-dependent energy levels [39–41]. For the hyperspherical approach, a study can be done of the energy levels of the ρ-fixed problem as functions of the hyperradius ρ. A case study has been performed for the reactive process $\mathrm{F} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{HF}$. We examined spectral properties, such as the level spacings standard deviation σ and the shape of the nearest neighbor spacing distribution (NNSD), evaluating the q parameters of the Brody and Berry–Robnik distributions, which are alternative interpolations between the Poisson and the Wigner distributions. We also applied statistical tools, such as the so-called $\tilde{\Delta}(m)$ test (which is analogous to the $\Delta_3(L)$ test of Dyson and Mehta but less computationally expensive) and the correlation coefficient $C(r)$. This analysis, which is typical of current investigations on the topic of "quantum chaos", gives insight into the nature of the reactive event and may be useful for the development of statistical theories in molecular dynamics, complementary to the purely classical view presented in Sect. 3.

While further developments of the few-body quantum hyperspherical approach to dynamics will probably come from the efforts devoted to build up an efficient time-independent quantum method for four-body interactions, on the classical mechanics side, we expect a more extensive use of the hyperspherical representation (so far largely unexplored in that context) for problems of the dynamics of nanoaggregates usually tackled by a Cartesian representation.

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