Phase-space invariants for aggregates of particles: Hyperangular momenta and partitions of the classical kinetic energy

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Rigorous definitions are presented for the kinematic angular momentum \( K \) of a system of classical particles (a concept dual to the conventional angular momentum \( J \)), the angular momentum \( L_{\xi} \) associated with the moments of inertia, and the contributions to the total kinetic energy of the system from various modes of the motion of the particles. Some key properties of these quantities are described—in particular, their invariance under any orthogonal coordinate transformation and the inequalities they are subject to. The main mathematical tool exploited is the singular value decomposition of rectangular matrices and its differentiation with respect to a parameter. The quantities introduced employ as ingredients particle coordinates and momenta, commonly available in classical trajectory studies of chemical reactions and in molecular dynamics simulations, and thus are of prospective use as sensitive and immediately calculated indicators of phase transitions, isomerizations, onsets of chaotic behavior, and other dynamical critical phenomena in classical microaggregates, such as nanoscale clusters. © 2004 American Institute of Physics.

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I. INTRODUCTION

This paper continues a search for indicators of dynamical features of a system of particles, as arising out of molecular dynamics simulations. The need for such indicators originates from the fact that the exploration of a variety of processes in an aggregate of particles at the nanoscale level usually requires extensive classical trajectory calculations (exact quantum mechanics being currently prohibitive), and it is often very important to be able to characterize the aggregate structure and dynamics by focusing on a few key quantities. More detailed motivations for a search for such quantities and applications to dynamics of classical clusters are presented in our works.\(^\text{1,2}\) Our viewpoint pursued in these works was inspired by progress in the study of few-body systems was inspired in progress in the study of few-body processes in hyperspherical and related coordinates\(^\text{3,4}\) in molecular quantum mechanics, so far mainly developed for three-body bound states and reactions,\(^\text{5–8}\) leading to recent benchmark computational results for trinuclear reactions\(^\text{9,10}\) (first of all, the \( \text{F}+\text{H}_2 \) exchange reaction) via the so called hyperquantization algorithm.\(^\text{11–15}\) Advances for systems of four (or more) particles have to be recorded,\(^\text{6,16–20}\) and although efficient numerical implementations require further study, the role played by hyperspherical harmonics, as eigenfunctions of hyperangular momenta, appears decisive.

The hyperspherical parametrization of the \( N \)-body problem has a long history dating back to the 1930s, but the basic events were the introduction by Smith, at the end of the 1950s and at the beginning of the 1960s, of three interrelated key concepts.

(i) Kinematic rotations, which follow from a generalization of the notion of reaction skewing angle, familiar in chemical kinetics. The skewing angle had been introduced for three-center reactions by Eyring and Polanyi\(^\text{21}\) at the beginning of the 1930s, while Smith generalized the underlying algebraic concept to four- and five-atom systems in 1959.\(^\text{22}\) This extension was subsequently detailed in our paper.\(^\text{3}\) Reference 3 gave explicitly the algorithm for discrete transformations among particle coupling schemes as sequences of “rotations” in the abstract kinematic space and pointed at the use of such transformations for the so-called symmetric or democratic representation of \( N \)-body systems for any \( N \geq 3\). These procedures involve an analysis in terms of continuous group transformations, well classified by now for \( N = 3, 23 \) \( N = 4, 24\) and also for \( N \geq 5.25\)

Also the concepts of the kinematic space and kinematic rotations are crucial for our study, so we recall here very briefly the main idea of these notions. The positions of \( N \) particles are described by \( n \) vectors \( s_1, \ldots, s_n \) where \( n = N \) or \( n = N - 1 \) (one may think of, e.g., \( N \) radii vectors of the particles or \( N - 1 \) Jacobi vectors, or the Radau and the orthogonal local variants).\(^\text{3}\) Each vector \( s_n \) consists of three components \( s_{1,\alpha}, s_{2,\alpha}, s_{3,\alpha} \) (\( 1 \leq \alpha \leq n \)). A rotation of the \( N \)-particle system in the physical space (an “outer motion”) corresponds to replacing \( s_1, \ldots, s_n \) with \( Rs_1, \ldots, Rs_n \), respectively, where \( R \in O(3) \) is a \( 3 \times 3 \) orthogonal matrix. But there is an alternative (in fact, dual) way of describing the system of particles. Instead of considering \( n \) vectors of length 3

\[
\begin{align*}
\mathbf{s}_1 &= (s_{1,1}, s_{2,1}, s_{3,1}), & \ldots, & \mathbf{s}_n &= (s_{1,n}, s_{2,n}, s_{3,n}),
\end{align*}
\]

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In the present paper, we define the angular momentum for kinematic rotations, the so-called kinematic angular momentum, for classical mechanics. This notion is dual to the conventional angular momentum in the same sense as kinematic rotations themselves are dual to conventional rotations in the physical space, see Sec. II B below. Therefore, the kinematic angular momentum generalizes the corresponding quantum mechanical operator whose eigenfunctions constitute a basis set for collective motions of the particles.\(^{30,32}\)

(iii) Symmetric hyperspherical coordinates, which exploit both kinematic rotations and hyperangular momenta and were introduced first for three bodies: in a plane by Smith\(^3^3\) and in the full three-dimensional space by Zickendraht\(^3^4\) (see also Ref. 35) and by Whitten and Smith\(^3^6\) (all variants of symmetric and asymmetric hyperspherical coordinates for three bodies are reviewed in Ref. 5, while Refs. 2 and 37 discuss the elliptic ones, which establish a bridge between symmetric and asymmetric coordinates). Four-body systems were handled by Zickendraht\(^3^8\) and by Ohm and Linderberg.\(^3^9\) The symmetric coordinates can be introduced for a general case of \(N\) particles and any underlying space dimension \(d\) by an approach that uses a singular value decomposition\(^4^0–4^2\) (see Ref. 3, where a generalization was presented of the previous work\(^4^3\) which had treated the case of \(N>4\) and \(d=3\)). By this approach, the singular values are simply related to the principal moments of inertia of the system (accordingly they are often referred to as principal axis coordinates), while the remaining coordinates are related to ordinary rotations in the physical space and kinematic rotations, see Sec. II C below.

Following the techniques justified in Refs. 1 and 2 and general ideas of the hyperspherical parametrization, we present in this paper the precise definitions and basic properties of several new instantaneous phase-space invariants for a classical \(N\)-body system. In fact, some of these invariants have already been described in naive terms and exploited in our note\(^2\) where their usefulness as sensitive and easily calculated indicators of phase transitions and onsets of chaotic behavior in classical nanoaggregates has been shown (for more traditional invariants, see Refs. 2 and 44–48, and references therein). Two of the phase-space invariants defined in the present work are the kinematic angular momentum mentioned above and the angular momentum associated with the moments of inertia, other invariants are terms of various partitions of the kinetic energy. These terms correspond to different modes of the motion of the particles. The word invariant here means that the quantity under consideration is fixed under all the orthogonal coordinate transformations in both the physical space and the kinematic space. The word instantaneous indicates that the quantity in question is by no means an integral of the motion. For instance, there is no conservation law for the kinematic angular momentum, in contrast to the ordinary angular momentum.

The paper is organized as follows. Section II begins with an introduction of fundamental concepts such as position matrices, allowed coordinate frames, and privileged coordinate frames (Sec. II A). The kinematic angular momentum \(K\) of a system of particles is defined in Sec. II B in a way emphasizing the parallelism among \(K\), the conventional angular momentum \(J\), and Smith’s grand angular momentum \(\Lambda\). Section II C is devoted to the main mathematical apparatus for defining and evaluating partitions of the kinetic energy of the system, namely, the singular value decomposition of matrices. In Sec. III, we define three different kinetic energy partitions—the hyperspherical partition (Sec. III A), the projective partition (Sec. III B), and the singular value expansion (Sec. III C)—and point out their basic properties. Section IV summarizes the invariance features of the angular momenta and of the terms of the energy partitions and concludes with remarks on particular cases, extensions, and applications. The Appendix lists the values of all the quantities considered in the simplest two-body problem.

### II. CLASSICAL HYPERANGULAR MOMENTUM THEORY

In this section we discuss some key concepts which serve as a background for the introduction of the energy partitions in Sec. III. We first define the position matrix and the important concepts of allowed coordinate frame and privileged coordinate frame. Then we consider hyperangular momenta \(J\), \(K\), and \(\Lambda\), pointing out their invariance under orthogonal coordinate transformations. The singular value
decomposition is also presented as a mathematical tool for a clearer understanding of the hyperspherical coordinates, of the grouping of coordinates corresponding to different kinds of motion, and as a convenient practical way to calculate various quantities involved in the energy partitions.

A. Position matrices $Z$

Our concern will be systems of $N \geq 2$ classical particles without external forces. Denote by $m_1, \ldots, m_N$ the masses of the particles and by $r_1, \ldots, r_N$, their radii vectors with respect to the center of mass. It is expedient to introduce the mass-scaled radii vectors $q_\alpha = (m_\alpha/M)^{1/2} r_\alpha \ (1 \leq \alpha \leq N)$ where

$$M = \sum_{\alpha=1}^{N} m_\alpha$$

is the total mass of the system. Using the vectors $q_\alpha$ instead of $r_\alpha$ simplifies the expression for the total kinetic energy $T$ of the particles:

$$T = \frac{1}{2} \sum_{\alpha=1}^{N} m_\alpha |q_\alpha|^2 = \frac{M}{2} \sum_{\alpha=1}^{N} |q_\alpha|^2.$$ \hspace{1cm} (1)

Note that

$$\sum_{\alpha=1}^{N} m_\alpha^{1/2} q_\alpha = M^{1/2} \sum_{\alpha=1}^{N} m_\alpha r_\alpha = 0.$$ \hspace{1cm} (2)

Consider any Cartesian coordinate frame whose origin coincides with the center of mass of the system. The $3 \times N$ matrix $Z$ whose $\alpha$th column $(1 \leq \alpha \leq N)$ is constituted by the components $q_{1,\alpha}, q_{2,\alpha}, q_{3,\alpha}$ of the vector $q_\alpha$ in this coordinate frame will be called the position matrix:

$$Z = \begin{pmatrix} q_{1,1} & q_{1,2} & \cdots & q_{1,N} \\ q_{2,1} & q_{2,2} & \cdots & q_{2,N} \\ q_{3,1} & q_{3,2} & \cdots & q_{3,N} \end{pmatrix}.$$  

The choice of another Cartesian coordinate frame corresponds to the coordinate change $Z' = RZ$ where an orthogonal matrix $R \in O(3)$ describes the transformation of the frames and the superscript $t$ designates transposing. On the other hand, one can also consider orthogonal transformations of coordinate frames in the kinematic space. If the orthogonal transformation of the original Cartesian frame is performed in the kinematic space by a matrix $Q \in O(N)$ then the corresponding coordinate change is $Z' = ZQ$.

In the sequel, all the Cartesian coordinate frames will have the origin at the center of mass of the system of particles and all the coordinate frames obtained from these Cartesian frames by orthogonal transformations in the kinematic space will be referred to as **allowed coordinate frames**. The positions of particles in any allowed frame are described by the $3 \times N$ position matrix $Z$, the position matrices in different allowed frames are connected by coordinate changes of the form $Z' = RZQ$ with $R \in O(3), \ Q \in O(N)$.

Among all the allowed coordinate frames, consider those obtained from conventional Cartesian frames by orthogonal transformations $Q$ in the kinematic space of the form

$$Q = \begin{pmatrix} Q_{11} & \cdots & Q_{1,N-1} & (m_1/M)^{1/2} \\ Q_{21} & \cdots & Q_{2,N-1} & (m_2/M)^{1/2} \\ \vdots & \cdots & \vdots & \cdots \\ Q_{N1} & \cdots & Q_{N,N-1} & (m_N/M)^{1/2} \end{pmatrix} \in O(N).$$

We will call such frames **privileged coordinate frames**. The last column of the position matrix $Z$ in a privileged frame is zero due to Eq. (2). While using a privileged coordinate frame, it is therefore more suitable to deal only with the first $N-1$ columns of the position matrix. The $3 \times (N-1)$ matrix constituted by these columns will be referred to as the reduced position matrix. In contrast, the $3 \times N$ position matrices in allowed coordinate frames will be sometimes called the full position matrices.

Thus, we have two alternative descriptions of a system of $N$ particles: by the $3 \times N$ full position matrix in an arbitrary allowed coordinate frame and by the $3 \times (N-1)$ reduced position matrix in a privileged coordinate frame. The prototypes of these two descriptions are, respectively, the collection of $N$ radii vectors of the particles and the collection of $N-1$ Jacobi vectors. The mass-scaled radii vectors constitute the full position matrix in a Cartesian frame; similarly, the Jacobi vectors (for any Jacobi coupling scheme), mass scaled in an appropriate way, constitute the reduced position matrix in a suitable privileged frame. For $N=2$, the $3 \times 1$ reduced position matrix is just

$$(m_1 m_2)^{1/2} r / M,$$

where $r$ is the vector column $r_1 - r_2$ (or $r_2 - r_1$) joining the two particles. For $N=3$, properly mass-scaled Jacobi vectors constituting the $3 \times 2$ reduced position matrix are exemplified by

$$\frac{[(m_1 + m_2) m_3]^{1/2}}{M} \begin{pmatrix} m_1 r_1 + m_2 r_2 - r_3 \\ m_1 + m_2 \\ (m_1 + m_2) M \end{pmatrix}^{1/2} (r_1 - r_3).$$

However, it is not our intention to emphasize the difference between the two descriptions of systems of classical particles outlined above. The reason is that all the important mechanical quantities which will be defined in the sequel (the angular momenta and the terms of various kinetic energy partitions) are independent of the particular choice of an allowed coordinate frame and (in the case of a privileged frame) of whether they are determined on the basis of the full position matrix or the reduced position matrix. Such invariance properties will be summarized in Sec. IV below. So, we will usually utilize the same term “position matrix” and the same notation $Z$ for both cases. For the number of the columns of this matrix, we will adopt the notation $n$, so that $n=N$ in the case of the full position matrix in an allowed coordinate frame and $n=N-1$ in the case of the reduced position matrix in a privileged coordinate frame.

B. The angular momenta $J$, $K$, and $\Lambda$

The total kinetic energy of a system of $N \geq 2$ classical particles described by the $3 \times n$ position matrix $Z$ is
where $\text{Tr}$ denotes the trace of a square matrix. Indeed, this expression is valid for the full position matrices in Cartesian coordinate frames [see Eq. (1)] and is invariant not only under orthogonal coordinate transformations $R \in O(3)$ in the physical space, but also under orthogonal coordinate transformations $Q \in O(n)$ in the kinematic space. The Newtonian equations of motion read

$$ M \ddot{Z}_{ia} = -\partial U / \partial Z_{ia}, \quad 1 \leq i \leq 3, \quad 1 \leq \alpha \leq n, $$

where $U = U(Z)$ is the potential energy of the system.

The quantity

$$ \rho = [\text{Tr}(ZZ^\ell)]^{1/2} = \left( \sum_{a=1}^{n} \sum_{i=1}^{3} Z_{ia}^2 \right)^{1/2} $$

is called the hyperradius of the system of particles under consideration. To hyperradius $\rho$, there is conjugated the linear momentum

$$ P_\rho = M \dot{\rho} = M / \rho \text{Tr}(ZZ^\ell) = M \sum_{a=1}^{n} \sum_{i=1}^{3} Z_{ia} \dot{Z}_{ia}. $$

The total angular momentum $J$ of the system in question is given by the formulas

$$ J^2 = \sum_{1 \leq i < j \leq 3} J_{ij}^2, \quad J_{ij} = M \sum_{a=1}^{n} (Z_{ia} Z_{ja} - Z_{ia} Z_{ja}). \quad (3) $$

One may also call $J$ the physical angular momentum because it accounts for external rotations of the system (rotations in the physical three-dimensional space). It is clear from Eq. (3) that each of the three components $J_{12}, J_{13}, J_{23}$ of $J$ and, consequently, the angular momentum $J$ itself are invariant under orthogonal coordinate transformations $Q \in O(n)$ in the kinematic space. Curiously, the trivial fact that $J$ is also invariant under orthogonal coordinate transformations $R \in O(3)$ in the physical space is not so obvious from Eq. (3). However, this fact follows immediately from another expression for $J$,

$$ J^2 = M^2 \sum_{\alpha, \beta = 1}^{n} \left[ \Gamma_{\alpha \beta}^{(1)} \Gamma_{\alpha \beta}^{(3)} - \Gamma_{\alpha \beta}^{(2)} \Gamma_{\alpha \beta}^{(1)} \right], \quad (4) $$

where

$$ \Gamma_{\alpha \beta}^{(1)} = \sum_{i=1}^{3} Z_{ia} Z_{\beta i}, \quad \Gamma_{\alpha \beta}^{(2)} = \sum_{i=1}^{3} \dot{Z}_{ia} \dot{Z}_{\beta i}, \quad \Gamma_{\alpha \beta}^{(3)} = \sum_{i=1}^{3} \dot{Z}_{ia} \dot{Z}_{\beta i}. $$

The dual concept is the kinematic angular momentum $K$ of the system which accounts for kinematic rotations. We will define it as

$$ K^2 = \sum_{1 \leq \alpha < \beta \leq n} K_{\alpha \beta}^2, \quad K_{\alpha \beta} = M \sum_{i=1}^{3} (Z_{ia} Z_{\beta i} - Z_{ia} Z_{\beta i}), \quad (5) $$

or equivalently as

$$ K^2 = M^2 \sum_{i,j=1}^{3} \left[ \Delta_{ij}^{(1)} \Delta_{ij}^{(3)} - \Delta_{ij}^{(2)} \Delta_{ij}^{(1)} \right], \quad (6) $$

where

$$ \Delta_{ij}^{(1)} = \sum_{a=1}^{n} Z_{ia} Z_{ja}, \quad \Delta_{ij}^{(2)} = \sum_{a=1}^{n} Z_{ia} \dot{Z}_{ja}, \quad \Delta_{ij}^{(3)} = \sum_{a=1}^{n} \dot{Z}_{ia} \dot{Z}_{ja}. $$

It is evident from Eq. (5) that each of the $n(n-1)/2$ components $K_{12}, K_{13}, \ldots, K_{n-1,n}$ of $K$ and, consequently, the kinematic angular momentum $K$ itself are invariant under orthogonal coordinate transformations $R \in O(3)$ in the physical space. Equation (6) implies that $K$ is also invariant under orthogonal coordinate transformations $Q \in O(n)$ in the kinematic space.

The notion of the kinematic angular momentum was first introduced in our paper but with another formula which is not invariant under orthogonal coordinate transformations in the physical space [and not dual to Eqs. (3) and (4) for the physical angular momentum].

The grand angular momentum $\Lambda$ of the system of particles was defined by Smith as

$$ \Lambda^2 = M^2 \sum_{i<j, \alpha<i, \beta<j} \left( Z_{ia} Z_{j\beta} - Z_{ia} Z_{j\beta} \right)^2 $$

$$ = M^2 \sum_{a, \beta=1}^{n} \sum_{i,j=1}^{3} \left( Z_{ia} Z_{j\beta} - Z_{ia} Z_{j\beta} \right)^2 $$

$$ = M^2 \left( \Omega_1 \Omega_1 - \Omega_2^2 \right), \quad (7) $$

where

$$ \Omega_1 = \text{Tr}(ZZ^\ell), \quad \Omega_2 = \text{Tr}(ZZ^\ell) = \rho / M, $$

$$ \Omega_3 = \text{Tr}(ZZ^\ell) = 2T / M. $$

The grand angular momentum $\Lambda$ is also invariant under orthogonal coordinate transformations in both the physical space and the kinematic space. From the relation

$$ \Lambda^2 = 2M \rho^2 T - \rho^2 I^2 $$

it follows immediately that

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

(cf. Ref. 26). We will call $T_\Lambda$ the grand angular energy and $T_\rho$ the hyperradial energy.

Finally, following our previous work, introduce the quantities

$$ T_J = \frac{J^2}{2M \rho^2}, \quad T_K = \frac{K^2}{2M \rho^2}. $$

The term $T_J$ measures the contribution of the external rotations of the system (outer motions) to the total kinetic energy $T$. This term will be therefore called the outer angular energy. Analogously, the term $T_K$ connects with the contribu-
tion of the kinematic rotations (inner motions) to the total kinetic energy $T$ and will be called the inner angular energy.

C. Singular value decomposition of the position matrix

As a matter of fact, the outer angular energy $T_j$ underestimates the kinetic energy associated with external rotations of the system. For instance, suppose that the pairwise distances between the particles are kept fixed, i.e., the system rotates around its center of mass as a rigid body. Then $T_{\rho} = 0$ and $T = T_{\Lambda}$, but $J$ is generically still smaller than $\Lambda$ in this case (as the simplest examples show) and, consequently, $T_j$ is generically smaller than $T_{\Lambda}$, the opposite of what one would probably expect. Similarly, the inner angular energy $T_K$ underestimates the kinetic energy associated with kinematic rotations. Besides, the hyperradial energy $T_{\rho}$ is sensitive to changes in the hyperradius $\rho$, i.e., the “overall size” of the system, but the three principal moments of inertia of the system may well vary in such a way that $p$ will be fixed and $T_{\rho}$ will therefore vanish. For a more precise account of the energy contributions from different kinds of motion in the system, an adequate mathematical apparatus is the singular value decomposition (SVD) of matrices.  

Introduce the notation $m = \min(n,3)$, i.e., let $m = 3$ for $n \geq 3$ and $m = n$ for $n = 1$ or $n = 2$. Any $3 \times n$ matrix $Z$ can be decomposed as the product of three matrices

$$Z = D Y X^t,$$

where $D \in O(3)$ is a $3 \times 3$ orthogonal matrix, $X \in O(n)$ is an $n \times n$ orthogonal matrix, and all the entries of the $3 \times n$ matrix $X$ are zeroes, with the possible exception of the diagonal entries

$$Y_{11} = \xi_1, \quad Y_{22} = \xi_2, \quad \ldots, \quad Y_{mm} = \xi_m, \quad \xi_1 \gg \xi_2 \gg \cdots \gg \xi_m \geq 0.$$

It is the representation of Eq. (8) which is called the SVD of matrix $Z$. The numbers $\xi_1, \xi_2, \ldots, \xi_m$ are called the singular values of matrix $Z$ and are determined uniquely although the factors $D$ and $X$ in Eq. (8) are not. If $n \geq 3$ then the singular values of $Z$ are the square roots of the eigenvalues of the $3 \times 3$ symmetric matrix $Z Z^t$. If $n \leq 3$ then the singular values of $Z$ are the square roots of the eigenvalues of the $n \times n$ symmetric matrix $Z T Z^t$.

The principal moments of inertia $I_1 \geq I_2 \geq I_3$ of the system in question with respect to its center of mass can be expressed in terms of the singular values of the position matrix $Z$ in a remarkably simple way. Namely, if $n \geq 3$ then

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

if $n = 2$ then

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

and if $n = 1$ then

$$I_1 = I_2 = M\xi_1^2, \quad I_3 = 0.$$

These formulas imply, in particular, that for systems of two or three particles, the largest principal moment of inertia is the sum of the two other moments. This relation is in fact valid for any flat body.

If the number $N$ of particles is no greater than 3 and $Z$ is the full $3 \times N$ position matrix then the last singular value $\xi_N$ of $Z$ is necessarily zero. All the preceding singular values $\xi_1, \ldots, \xi_{N-1}$ of $Z$ are generically positive, and in the sequel, we will assume for simplicity that they are positive indeed. In all the other cases, all the singular values of the position matrix $Z$ are generically positive, and we will assume them to be positive.

In all the cases except for reduced position matrices for systems of four particles ($N=4$, $n=3$), the factors $D$ and $X$ in the SVD of Eq. (8) can be chosen to be special orthogonal: $D \in SO(3)$, $X \in SO(n)$. In the case $N=n+1=4$, a SVD of the $3 \times 3$ matrix $Z$ with special orthogonal factors $D$ and $X$ exists if and only if det $Z > 0$. This fact is closely related to the chirality issues, two configurations of four particles with different signs of det $Z$ are of different chiralities.

For $n > 3$, the last $n-3$ columns of matrix $X$ in Eq. (8) are irrelevant ($Z$ does not depend on them), and the so-called thin SVD of $Z$ is more suitable. To be more precise, the $3 \times n$ position matrix $Z$ with $n \geq 3$ can be decomposed as

$$Z = D \Xi B^t, \quad (9)$$

where $D \in O(3)$, $\Xi = \text{diag}(\xi_1, \xi_2, \xi_3)$ is the diagonal $3 \times 3$ matrix with the diagonal entries $\xi_1$, $\xi_2$, $\xi_3$, and $B$ is an $n \times 3$ matrix with orthonormal columns (i.e., the three columns of $B$ are pairwise orthogonal and have unit length as vectors in the $n$-dimensional Euclidean space). One says that the matrix $B$ belongs to the Stiefel manifold $V_{n,3}$.

The representation of Eq. (9) is called the thin SVD (Ref. 42) of $Z$. The practical recipe for obtaining this decomposition is as follows. An orthogonal matrix $D \in O(3)$ is chosen to diagonalize the $3 \times 3$ symmetric matrix $Z Z^t$:

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

The rows $u_1$, $u_2$, $u_3$ of the $3 \times n$ matrix $D^t Z$ are pairwise orthogonal (as vectors in the $n$-dimensional Euclidean space) and their lengths are $\xi_1$, $\xi_2$, $\xi_3$, respectively. If $\xi_1 \gg \xi_2 \gg \xi_3 > 0$ then $B$ is the $n \times 3$ matrix with columns $u_1/\xi_1$, $u_2/\xi_2$, $u_3/\xi_3$. The situation where $\xi_1 \gg \xi_2 > 0$ and $\xi_3 = 0$ corresponds to the case $n = N = 3$. In this case, the first two columns of a $3 \times 3$ matrix $B$ are $u_1/\xi_1$ and $u_2/\xi_2$, while the third column is chosen to ensure the orthogonality of $B$.

For $n < 3$, the last $3-n$ columns of matrix $D$ in Eq. (8) are irrelevant, and it is again better to use the thin SVD of $Z$. Namely, the $3 \times n$ position matrix $Z$ with $n \leq 3$ can be decomposed as

$$Z = A \Xi X^t, \quad (10)$$

where $X \in O(n)$, $\Xi = \text{diag}(\xi_1, \ldots, \xi_n)$ is the diagonal $n \times n$ matrix with the diagonal entries $\xi_1, \ldots, \xi_n$, and $A$ is a $3 \times n$ matrix with orthonormal columns (so that $A$ belongs to the Stiefel manifold $V_{3,n}$, see Refs. 51–53). The representation of Eq. (10) is also called the thin SVD (Ref. 42) of $Z$ and can be computed as follows. An orthogonal matrix $X \in O(n)$ is to be chosen to diagonalize the $n \times n$ symmetric matrix $Z^t Z$:

$$X^t Z Z^t X = \text{diag}(\xi_1^2, \ldots, \xi_n^2).$$

The columns $u_1, \ldots, u_n$ of the $3 \times n$ matrix $Z X$ are pairwise orthogonal (as vectors in the three-dimensional Euclidean space).
space) and their lengths are \( \xi_1, \ldots, \xi_n \), respectively. If \( \xi_1 \geq \cdots \geq \xi_n > 0 \) then \( A \) is the \( 3 \times n \) matrix with columns \( u_1/\xi_1, \ldots, u_n/\xi_n \). The situation where \( \xi_1 \geq \cdots \geq \xi_{n-1} > 0 \) and \( \xi_n = 0 \) corresponds to the cases \( n = N = 2 \) and \( n = N = 3 \). In these cases, the first \( n - 1 \) columns of a \( 3 \times n \) matrix \( A \) are \( u_1/\xi_1, \ldots, u_{n-1}/\xi_{n-1} \), while the last column is to be chosen to be orthogonal to \( u_1, \ldots, u_{n-1} \) and to have unit length.

For square matrices, the thin SVD and the SVD are the same, so that for \( n = 3 \), Eqs. (8), (9), and (10) represent the same decomposition of \( Z \).

### III. PARTITIONS OF THE KINETIC ENERGY

In this section, we show how to obtain energy partitions, following a representation of the \( N \)-particle system based on the hyperangular momenta introduced in Sec. II. Partitions of the kinetic energy are particularly important towards a complete understanding of the different kinds of motion from both a qualitative and a quantitative point of view. Our partitions come from the separation of degrees of freedom induced by the symmetric hyperspherical coordinate representation.3,5,33–36,38,39,43 Such a separation is expected to be more physically motivated, in distinguishing different kinds of motions, than the usual separation of molecular vibrations and rotations, when dynamics is considered for clusters or reactions.

#### A. The hyperspherical partition of the kinetic energy

The hyperspherical partition, to be proposed in the following, is strictly related to the grouping of hyperspherical coordinates, each of them rigorously describing a particular kind of motion. So we will have the hyperradial motion, accounting for the “overall system size” variations, \textit{external rotations} (or outer angular motions), and \textit{kinematic rotations} (or \textit{inner angular motions}), see Sec. II B. On the other hand, as mentioned in Sec. II C, the three principal moments of inertia may well vary in such a way that \( \rho = 0 \), while the inertia is redistributing with respect to the three principal axes. In order to be complete in our description, we will also introduce a term of the partition measuring the total variations of the inertia obtained as the sum of two contributions, the hyperradial term for the total inertia, and a term accounting for the redistribution.

The hyperradius \( \rho \) of the system is expressed in terms of the singular values \( \xi_1, \ldots, \xi_m \) of its \( 3 \times n \) position matrix as

\[
\rho = \xi_1 + \cdots + \xi_m = \frac{1}{2M} (I_1 + I_2 + I_3),
\]

where \( I_1, I_2, I_3 \) are the principal moments of inertia. The linear momentum \( P_\rho \) conjugated to \( \rho \) is therefore

\[
P_\rho = \frac{M}{\rho} (\xi_1 \dot{\xi}_1 + \cdots + \xi_m \dot{\xi}_m)
\]

and the hyperradial energy \( T_\rho \) is

\[
T_\rho = \frac{M}{2\rho^2} (\xi_1 \dot{\xi}_1 + \cdots + \xi_m \dot{\xi}_m)^2.
\]

This quantity accounts for variations of \( \rho \). If the singular values of the position matrix of the system are changing in such a way that \( \rho = 0 \), i.e., \( \xi_1 \dot{\xi}_1 + \cdots + \xi_m \dot{\xi}_m = 0 \), then \( T_\rho = 0 \). The energy measuring arbitrary variations of the singular values, i.e., arbitrary variations of the principal moments of inertia, is

\[
T^I = \frac{M}{2} (\xi_1^2 + \cdots + \xi_m^2).
\]

We will call \( T^I \) the \textit{inertial energy}. The difference

\[
T^{rot} = T - T^I
\]

corresponds to the kinetic energy associated with all the kinds of rotation (both external and kinematic) in the system and will be called the \textit{rotational energy}. There hold the inequalities

\[
0 \leq T^{rot} \leq T < T, \quad 0 \leq T_\rho \leq T^I \leq T.
\]

In addition to the angular momenta \( J, K \), and \( \Lambda \), define the \textit{angular momentum} \( L_\xi \) associated with the singular values (or associated with the moments of inertia) as

\[
L_\xi^2 = \sum_{1 \leq \kappa < \sigma \leq m} L_{\xi,\kappa \sigma}^2, \quad L_{\xi,\kappa \sigma} = M (\xi_{\kappa}^* \delta_{\sigma \kappa} - \xi_{\sigma}^* \delta_{\kappa \sigma}). \quad (11)
\]

This quantity is also invariant under orthogonal coordinate transformations in both the physical space and the kinematic space. Let the \textit{shape energy} corresponding to \( L_\xi \) be

\[
T_\xi = \frac{L_\xi^2}{2M \rho^2}
\]

(cf. Ref. 1). The shape energy measures the redistribution of the inertia around the three principal axes. It is easy to see that

\[
T_\xi = T^I - T_\rho = T - T^{rot}.
\]

Introduce also the difference

\[
T_{ac} = T_\Lambda - T_J - T_K = T^{rot} - T^{I}_J - T^{I}_K.
\]

We will call \( T_{ac} \) the \textit{angular coupling energy}. Finally, we will say that

\[
T = T_\Lambda + T_\rho + T_J + T_K + T_{ac} + T^I
\]

is the \textit{hyperspherical partition} of the kinetic energy \( T \) (see Fig. 1).

The inequalities

\[
J^2 + L_\xi^2 \leq \Lambda^2, \quad K^2 + L_\xi^2 \leq \Lambda^2
\]

hold, so that

\[
T_J + T_{ac} \leq T_\Lambda, \quad T_K + T_{ac} \leq T_\Lambda.
\]

On the other hand, it is not hard to construct examples (for \( N \geq 3 \)) where

\[
J^2 + L_\xi^2 = \Lambda^2 \quad \text{and} \quad K > 0
\]

or

\[
K^2 + L_\xi^2 = \Lambda^2 \quad \text{and} \quad J > 0.
\]

Both situations may occur for \( L_\xi = 0 \). Consequently, the angular coupling energy \( T_{ac} \) (and even the sum \( T_{ac} + T_{\xi} \)) can be negative.
The space $\mathbb{S}^n$ of all the matrices of the form $R Z$ for a given position matrix $Z$ (i.e., the manifold of all the matrices of the form $R Z$ under the action of the first group, i.e., the manifold of all the matrices of the form $R Z$, there act two orthogonal groups: the external rotation group $SO(3)$ which acts as $(R Z) \mapsto R Z$ for any $R \in SO(3)$, and the kinematic rotation group $SO(n)$ which acts as $(Q Z) \mapsto Q Z^*$. Let $S_1(Z)$ be the orbit of $Z$ under the action of the first group, i.e., the manifold of all the matrices of the form $R Z$, $R \in SO(3)$. Let also $S_2(Z)$ be the orbit of $Z$ under the action of the second group, i.e., the manifold of all the matrices of the form $R Z$, $R \in SO(n)$. Denote by $\Pi_1(Z)$ the tangent space to $S_1(Z)$ at point $Z$ and by $\Pi_2(Z)$, the tangent space to $S_2(Z)$ at point $Z$. The space $\Pi_1(Z)$ is constituted by all the matrices of the form $Z + R Z$ with skew-symmetric $R \in so(3)$. The space $\Pi_2(Z)$ is constituted by all the matrices of the form $Z + Z^*$ with skew-symmetric $Q \in so(n)$.

Equip the space of all the $3 \times n$ matrices with the scalar product according to the formula

$$\langle Z^a, Z^b \rangle = Tr[Z^a(Z^b)^*] = \sum_{a=1}^{n} \sum_{i=1}^{3} Z_{i a}^a Z_{i a}^b.$$ 

For a given position matrix $Z$, consider the orthogonal projections $Z^*$ and $Z^k$ (in the sense of this scalar product) of its time derivative $\dot{Z}$ on $\Pi_1(Z)$ and $\Pi_2(Z)$, respectively. Then

$$T_\text{ext} = \frac{M}{2} \left[ \dot{Z}^a(Z^a)^* \right] = \frac{M}{2} \sum_{a=1}^{n} \sum_{i=1}^{3} (\dot{Z}_{i a}^a)^2$$

is the energy of the external rotation of the system at the given moment of time and will be called the external energy. Similarly,

$$T_\text{int} = \frac{M}{2} \left[ \dot{Z}^k(Z^k)^* \right] = \frac{M}{2} \sum_{a=1}^{n} \sum_{i=1}^{3} (\dot{Z}_{i a}^k)^2$$

is the energy of the kinematic rotation of the system and will be called the internal energy. The difference

$$T_\text{res} = T_\text{rot} - T_\text{ext} - T_\text{int}$$

will be called the residual energy. Finally, we will call

$$T = T_\text{rot} + T^I = T_\text{ext} + T_\text{int} + T_\text{res} + T^I$$

the projective partition of the kinetic energy $T$ (see Fig. 1) because the terms $T_\text{ext}$ and $T_\text{int}$ are defined via orthogonal projections in the space of $3 \times n$ matrices.

If the system rotates around its center of mass as a rigid body, then $T^I = 0$ and

$$T_\text{ext} = T_\text{rot} - T_\text{int} = T,$n$$

as expected. The external energy $T_\text{ext}$ vanishes if and only if $J = 0$, and one can prove the inequalities

$$T_2 \leq T_\text{ext} \leq T_\text{rot}.$$n

Moreover, let $\xi_n$ denote the minimal positive singular value of the position matrix $Z$ ($\xi_3 = \xi_3$ in the case of $N \geq 4$ particles and $\xi_2 = \xi_2$ for systems of $N = 2$ or $N = 3$ particles). Then

$$T_\text{ext} = \frac{J^2}{2M \xi_n^n}$$

for $N = 2$,

$$T_\text{ext} = \frac{J^2}{2M \xi_2^n}$$

for $N = 3$, and

$$T_\text{ext} = \frac{J^2}{4M \xi_3^n}$$

for $N \geq 4$.

Analogously, the internal energy $T_\text{int}$ vanishes if and only if $K = 0$, and the inequalities

$$T_2 \leq T_\text{int} \leq T_\text{rot}$$

hold. Moreover,

$$T_2 = 0$$

for $N = 2$,

$$T_\text{int} = \frac{K^2}{4M \xi_2^n}$$

for $N = 3$ or $N = 4$, and

$$T_\text{int} = \frac{K^2}{2M \xi_3^n}$$

for $N \geq 4$.
for \( N \geq 5 \).

Finally, since \( T^\text{ext} \geq T_J \) and \( T^\text{int} \geq T_K \), one has

\[
T^\text{rot} - T^\text{ext} - T^\text{int} = T^\text{res} \leq T_{ac} = T^\text{rot} - T_J - T_K.
\]

In particular, the residual energy \( T^\text{res} \) can be negative. For instance, if the system rotates around its center of mass as a rigid body, then \( T^\text{rot} = - T^\text{int} \), and generically \( T^\text{res} < 0 \).

The time derivatives of the singular values of \( Z \) needed for the computation of the hyperradial energy \( T_\rho \) and the inertial energy \( T^\text{r} \) can be found very easily. In terms of the thin SVD of Eq. (9) for \( n \geq 3 \), the derivatives of the singular values of \( Z \) are just the diagonal entries of the \( 3 \times 3 \) matrix

\[
W = D^T \hat{Z} B; \quad \xi_i = W_{ii}, \quad 1 \leq i \leq 3.
\]

In terms of the thin SVD of Eq. (10) for \( n \leq 3 \), the derivatives of the singular values of \( Z \) are the diagonal entries of the \( n \times n \) matrix

\[
V = A^T \hat{X} Z; \quad \xi_\alpha = V_{\alpha \alpha}, \quad 1 \leq \alpha \leq n.
\]

The works\(^{41,55,56}\) contain also formulas for the \textit{second} derivatives of the singular values of a matrix depending on several parameters. The second derivatives of the smallest singular value were also found in the earlier paper.\(^{61}\)

The external energy \( T^\text{ext} \) and the internal energy \( T^\text{int} \), in spite of their rather complicated definition, are very easy to be calculated as well.

Let first \( n \geq 3 \) and the \( 3 \times n \) position matrix \( Z \) be decomposed as in Eq. (9). Then

\[
T^\text{ext} = \frac{M}{2} \sum_{1 \leq i < j \leq 3} \frac{(\xi_i W_{ji} - \xi_j W_{ij})^2}{\xi_i^2 + \xi_j^2},
\]

\[
T^\text{int} = \frac{M}{2} \sum_{1 \leq i \leq 3} \left( \frac{\xi_i W_{ii} - \xi_j W_{ij}}{\xi_i^2 + \xi_j^2} \right) + T - \frac{M}{2} \sum_{i,j=1}^{3} W_{ij}^2
\]

(recall that \( W = D^T \hat{Z} B \)). The term

\[
T - \frac{M}{2} \sum_{i,j=1}^{3} W_{ij}^2
\]

in the expression for \( T^\text{int} \) vanishes for \( n = 3 \).

Suppose now that we are studying a system of \( N = 3 \) particles in a privileged coordinate frame, and the corresponding \( 3 \times 2 \) reduced position matrix \( Z \) is decomposed as in Eq. (10). Then

\[
T^\text{ext} = \frac{M}{2} \frac{(\xi_1 V_{12} - \xi_2 V_{12})^2}{\xi_1^2 + \xi_2^2} + T - \frac{M}{2} (V_{11}^2 + V_{12}^2 + V_{21}^2 + V_{22}^2),
\]

\[
T^\text{int} = \frac{M}{2} \frac{(\xi_1 V_{12} - \xi_2 V_{21})^2}{\xi_1^2 + \xi_2^2}
\]

(recall that \( V = A^T \hat{X} Z \)).

Finally, for \( N = 2 \) one has

\[
T^\text{ext} = T^\text{rot} = T_J = \frac{J^2}{2 M \rho^2}
\]

and

\[
T^\text{int} = T_K = 0
\]

(the complete summary of the kinetic energy partitions for \( N = 2 \) is given in the Appendix). It is interesting that the relation \( T^\text{int} = T_K \) is valid also for \( N = 3 \), although, of course, the internal and inner angular energies are generically positive in this case.

C. The singular value expansion of the kinetic energy

Finally, we propose an expansion of the kinetic energy obtained directly from the SVD of the position matrix \( Z \). Assume that the singular values of the position matrix \( Z \) are \textit{pairwise distinct}. For generic trajectories \( Z(t) \) this condition is met for every moment of time (an analogue of the von Neumann–Wigner noncrossing rule for diatomic molecule terms of the same symmetry type).\(^{62}\) Then the factors \( D \) and \( X \) in the SVD of Eq. (8) of \( Z \) can be chosen to depend smoothly on time \( t \), and it becomes possible to define a one more partition of the kinetic energy of the system. Namely, set

\[
\dot{Z}^\text{out} = D Y X^t, \quad \dot{Z}^\text{in} = D Y X^t.
\]

It is not hard to prove that the matrix-valued functions \( \dot{Z}^\text{out} \) and \( \dot{Z}^\text{in} \) are independent of the particular choice of the factors \( D(t) \) and \( X(t) \), provided that the singular values of \( Z \) are pairwise distinct. Let

\[
E^\text{out} = \frac{M}{2} \text{Tr}(\dot{Z}^\text{out} \dot{Z}^\text{out}^t) = \frac{M}{2} \sum_{\alpha=1}^{n} \sum_{\alpha=1}^{3} (\dot{Z}^\text{out}_{i\alpha})^2,
\]

\[
E^\text{in} = \frac{M}{2} \text{Tr}(\dot{Z}^\text{in} \dot{Z}^\text{in}^t) = \frac{M}{2} \sum_{\alpha=1}^{n} \sum_{\alpha=1}^{3} (\dot{Z}^\text{in}_{i\alpha})^2,
\]

\[
E^\text{coupl} = M \text{Tr}(\dot{Z}^\text{out} \dot{Z}^\text{in}) = M \sum_{\alpha=1}^{n} \sum_{\alpha=1}^{3} \dot{Z}^\text{out}_{i\alpha} \dot{Z}^\text{in}_{i\alpha}.
\]

We will call \( E^\text{out} \), \( E^\text{in} \), and \( E^\text{coupl} \) the \textit{outer term}, the \textit{inner term}, and the \textit{coupling}, respectively. One can prove that the sum \( E^\text{out} + E^\text{in} + E^\text{coupl} \) is equal to the rotational energy \( T^\text{rot} \).

The relation

\[
T = T^\text{rot} + T^I = E^\text{out} + E^\text{in} + E^\text{coupl} + T^I
\]

will be referred to as the \textit{singular value expansion} of the kinetic energy \( T \) (see Fig. 1) because the terms \( E^\text{out} \), \( E^\text{in} \), and \( E^\text{coupl} \) are obtained directly from the SVD of the position matrix.

If the system rotates around its center of mass as a rigid body, then

\[
E^\text{out} = T^\text{rot} = T_A = T,
\]

as expected. Moreover, \( Z^\text{in} = 0 \) and hence \( E^\text{in} = E^\text{coupl} = 0 \) in this case (note that generically \( T_K > 0 \), \( T_{ac} \neq 0 \), \( T^\text{int} > 0 \), and \( T^\text{res} < 0 \) for rotations of a rigid body!). On the other hand, the equality \( J = 0 \) does \textit{not} imply \( E^\text{out} = 0 \). However, the relations

\[
E^\text{in} - E^\text{out} = T^\text{rot}, \quad E^\text{coupl} = -2 E^\text{out}
\]

hold whenever \( J = 0 \), so that \( E^\text{in} \approx E^\text{out} \), \( E^\text{in} \approx T^\text{rot} \), and \( E^\text{coupl} \approx 0 \) for \( J = 0 \). In the case of an arbitrary value of \( J \), the inequality
\[ |E_{in} - E_{out} - T^{rot}| \leq \frac{J}{\xi_x} \left( \frac{E_{out}}{M} \right)^{1/2} \]

holds for \( N \geq 4 \) (recall that \( \xi_x \) denotes the minimal positive singular value of the position matrix \( Z \), i.e., \( \xi_x = \xi_3 \) for \( N \geq 4 \)).

Similarly, the equality \( K = 0 \) does not imply \( E_{in} = 0 \), but it implies the relations
\[ E_{out} - E_{in} = T^{rot}, \quad E^{coup} = -2E_{in}, \]
so that \( E_{out} \geq E_{in} \), \( E_{out} \geq T^{rot} \), and \( E^{coup} \leq 0 \) for \( K = 0 \). In the case of an arbitrary value of \( K \), the inequality
\[ |E_{out} - E_{in} - T^{rot}| \leq \frac{K}{\xi_x} \left( \frac{E_{out}}{M} \right)^{1/2} \]
is valid for \( N \leq 4 \) (note that the minimal positive singular value \( \xi_x \) of the position matrix \( Z \) is \( \xi_{N-1} \) for \( N \leq 4 \)).

Typically in molecular simulations, \( E_{out} \geq T^{rot} \), \( E_{in} \geq T^{rot} \), and, accordingly, \( E^{coup} \leq 0 \) and \( -E^{coup} \geq T^{rot} \). That is why we call Eq. (16) an expansion rather than a partition.

The terms \( E_{out} \), \( E_{in} \), and \( E^{coup} \) can be calculated as follows. Let first \( n = 3 \). Consider the thin SVD of Eq. (9) of the position matrix \( Z \) and introduce the \( 3 \times 3 \) matrix
\[ G = D^{\dagger} (ZZ^t + ZZ^t) D = D^{\dagger} Z B \Xi + \Xi B^t Z^t D. \]
Then
\[ (D^{\dagger} D)_{ij} = \frac{G_{ij}}{\xi_j - \xi_i}, \quad 1 \leq i,j \leq 3, \quad i \neq j, \quad (17) \]
and
\[ 2 \xi_i \xi_j = G_{i,j}, \quad 1 \leq i,j \leq 3. \quad (18) \]

In fact, Eqs. (17) and (18) are just a particular case of the so-called abstract Hellmann–Feynman theorem.\(^{53}\) Equation (18) provides an alternative expression for the time derivatives of the singular values of \( Z \), cf. Eq. (14). What is important for computing the terms of the singular value expansion of \( T \) is the relations of Eq. (17). Since \( D \in O(3) \) is orthogonal at every moment of time, \( D^{\dagger} D \in \text{so}(3) \) is skew-symmetric. Consequently, Eq. (17) determines the \( 3 \times 3 \) matrix \( D^{\dagger} D \) completely. Now one can successively find
\[ D = D(D^{\dagger} D), \quad Z^{out} = D \Xi B^t, \quad Z^{in} = Z - Z^{out} - D \Xi B^t \]
and, finally, \( E_{out} \), \( E_{in} \), and \( E^{coup} \).

Let now \( n = 3 \). Consider the thin SVD of Eq. (10) of the position matrix \( Z \) and define the \( n \times n \) matrix
\[ F = X'(Z^t Z + Z^t Z) X = X^t Z^t \Xi A^t + \Xi A^t Z X. \]
Then
\[ (X'X)_{\alpha \beta} = \frac{F_{\alpha \beta}}{\xi_{\beta} - \xi_{\alpha}}, \quad 1 \leq \alpha, \beta \leq n, \quad \alpha \neq \beta, \quad (19) \]
and
\[ 2 \xi_{\alpha} \xi_{\beta} = F_{\alpha \alpha}, \quad 1 \leq \alpha \leq n. \quad (20) \]

Equations (19) and (20) are again a particular case of the abstract Hellmann–Feynman theorem.\(^{53}\) and Eq. (20) provides an alternative expression for the time derivatives of the singular values of \( Z \) as compared with Eq. (15). Now, since \( X \in O(n) \) is orthogonal at every moment of time, \( X' X \in \text{so}(n) \) is skew symmetric. Therefore, Eq. (19) determines the \( n \times n \) matrix \( X' X \) completely, so that one can successively find
\[ \dot{X} = X(X'X), \quad \dot{Z}^{in} = A \Xi X, \quad \dot{Z}^{out} = Z - Z^{in} - A \Xi X. \]
and, finally, \( E_{out} \), \( E_{in} \), and \( E^{coup} \).

For alternative expressions for the derivatives of the left and right factors in the SVD of matrices depending on parameters, see Refs. 41, 55, 57, 58, and 64. The formulas presented in Ref. 57 essentially coincide with those given in Ref. 60 and used here in Eqs. (17) and (19). Various subtle mathematical issues on the SVD of parameter-dependent matrices are discussed in Refs. 60 and 64–67.

### IV. CONCLUDING REMARKS

**Summary of the paper.** The main goal of this paper has been the rigorous introduction of several new instantaneous invariant quantities describing the motion of classical particles in a (nano)aggregate. Two of these quantities are the kinematic angular momentum [Eqs. (5) and (6)], dual to the ordinary physical angular momentum [Eqs. (3) and (4)], and the angular momentum of Eq. (11) associated with the singular values. The other quantities are energy characteristics of the motion, they constitute three partitions of the total kinetic energy of the system and are summarized in Fig. 1. All the invariants defined in the paper depend only on the positions and velocities of the particles (and not on the potential energy). All our study agrees with (and is in fact inspired by) the general lines of the hyperspherical parametrization of the multibody problem.

We have also given straightforward computational formulas for all the invariants introduced and presented some identities and inequalities these invariants satisfy (the corresponding proofs will be given elsewhere). Being based on these formulas, we have developed and implemented efficient FORTRAN codes\(^{68}\) which calculate all the terms of the partitions for a given trajectory of an \( N \)-body system.

All the analysis of the present paper can be easily carried over to the case where the dimension \( d \) of the physical space is other than 3. Such a generalization will be also developed elsewhere.

**Summary of the invariance properties of the angular momenta and of the energy partitions.** All the characteristics of a classical system of particles we have considered in the present paper are “instantaneous invariants” of the system in the sense explained in Sec. I. To be more precise, the following statement holds.

The angular momenta \( J, K, \Lambda, \) and \( L_\xi \) given by Eqs. (3)–(7) and (11), the singular values \( \xi_x \), the total kinetic energy \( T \) of the system, the terms \( T^\Lambda, T^\rho, T_J, T_K, T_\xi, T_{\xi c} \) of the hyperspherical partition [Eq. (12)] of the kinetic energy \( T \), the terms \( T^{in}, T^{out}, T^{ext}, T^{rot} \) of the projective partition [Eq. (13)] of the kinetic energy \( T \), and the terms \( E_{out}, E_{in}, E^{coup} \) of the singular value expansion [Eq. (16)] of the kinetic energy \( T \) are invariant under orthogonal coordinate transformations in both the physical space and the kine-
The invariance properties of the singular values require some comment. If the number $N$ of particles is less than 4 then the corresponding $3 \times N$ full position matrices possess $N$ singular values while the $3 \times (N - 1)$ reduced position matrices have $N - 1$ singular values. In this case, the fact that the singular values are independent of the type of the position matrix is to be understood as follows: if $\xi_1, \ldots, \xi_{N-1}$ are the singular values of any reduced position matrix describing the system at a given moment of time then the singular values of any full position matrix are $\xi_1, \ldots, \xi_{N-1}, \xi_N$ with $\xi_N = 0$.

Applications. So far, FORTRAN codes$^{66}$ calculating the energy partitions have been used for various systems and the results are encouraging. As was emphasized in Sec. I, some of the phase-space invariants introduced in this paper can be used as indicators of critical phenomena in classical (nano)aggregates (in the sense that these invariants undergo sharp changes during various critical events—such as phase transitions—in the evolution of the system) and of different dynamical regimes. This has been precisely the concern of our more recent works, where examples of energy partitions for trajectories for rare gas clusters, $\text{Ar}_3$, $\text{Ar}_{13}$, $\text{Ar}_{38}$, and about 66 have been discussed with the aim of finding correlations between the features of the partitions and signatures of phase transitions and chaotic behavior. As a further explanatory application of our theory, we also recently considered classical trajectory simulations of the prototypical reaction $\text{F} + \text{H}_2$.$^{68}$ the results obtained regarding the terms of the partitions allow us to provide a picture of the reactive and inelastic processes in the collision of a fluorine atom with the hydrogen molecule.

In conclusion, we believe that the sphere of applicability of the invariants is wider. Indeed these new invariants are introduced from a phase-space approach to the dynamics, a subject which has persistently been given careful attention as a valid perspective in the general field of many-body dynamics,$^{70,71}$ and in chemical reaction theory in particular.$^{72,74}$ Hopefully, they can help us to describe energy transfer processes in aggregates of particles and to understand the energy partition among various degrees of freedom. Since this theory provides a measure of the energy contributions from various kinds of motion, making feasible a search for approximate conservation laws for the new invariants, we are also encouraged to consider their quantum mechanical analogs, as well as the corresponding energy levels and eigenstates, in order to simplify the task of the quantum extension of the theory.

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APPENDIX: THE CASE OF TWO PARTICLES

It is instructive to list the values of all the quantities considered in the present paper in the simplest case of two particles ($N = 2$). Let $\mathbf{r}$ be the vector joining the particles and $r$ its length (the distance between the particles). Then

$$\rho = \xi_1 = (m_1 m_2)^{1/2} \frac{r}{M} = (\mu / M)^{1/2} r,$$

where $\mu = m_1 m_2 / M$ is the reduced mass of the particles,

$$P_\rho = (m_1 m_2)^{1/2} \frac{\dot{r}}{\mu M} = (\mu / M)^{1/2},$$

$$J = \Lambda = \mu [\mathbf{r} \cdot \dot{\mathbf{r}}],$$

where $[\mathbf{r} \cdot \dot{\mathbf{r}}]$ is the standard vector product of the two vectors,

$$K = L \xi_0 = 0,$$

$$T' = T_\rho = \frac{\mu r^2}{2},$$

$$E_{\text{out}} = E_{\text{ext}} = T_\rho = T_\Lambda = \frac{\mu [\mathbf{r} \cdot \dot{\mathbf{r}}]^2}{2r^2},$$

$$E_{\text{in}} = E_{\text{coupl}} = T_{\text{int}} = T_{\text{res}} = T_K = T_\xi = T_{\omega} = 0,$$

and

$$T = \frac{\mu r^2}{2}.$$
Suppose that a rigid body with the principal moments of inertia $I_1 \geq I_2 \geq I_3$ (with respect to its center of mass) rotates around its principle axis corresponding to say, $I_1$, with angular velocity $\omega > 0$. Then $J = I_1 \omega$ and $T = I_1 \omega^2 / 2$, i.e., $J = 2I_1 T$. On the other hand, $\Lambda^2 = 2M \rho^2 T_k = (I_1 + I_2 + I_3)T$ in this particular case, since $2M \rho^2 = I_1 + I_2 + I_3$ (see Sec. III A). Generically $I_2 + I_3 > I_1$ and $\Lambda > J$. 
