Symmetry and Deformations in Shape Space: An Invariant Coordinate Description of Clusters and Biomolecules

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Abstract. Within the hyperspherical formulation of N-body systems, the configuration space can be decomposed into external rotations, kinematic rotations, and kinematic invariants. The latter define the intrinsic geometry of the system and constitute a set of shape coordinates, invariant under both spatial and kinematic rotations. In the work of Littlejohn and co-workers, these invariants are closely related to the principal moments of inertia and provide a natural set of variables for describing the internal structure of clusters and molecules. Building on this framework, hyperspherical shape coordinates can be employed as descriptors of molecular deformation, enabling the classification of equilibrium structures and the analysis of minimum-energy configurations independently of orientation and frame choices.

Keywords: Invariant Shape Coordinates · Molecular clusters · Biomolecular structure · Structural deformation · Minimum-energy configurations Potential energy surfaces

1 Introduction

The hyperspherical approach to molecular dynamics has been widely exploited in the field quantum reactive scattering calculations during the last decades, with significant progress in the theory and implementation of methods based on hyperspherical functions [1–3]. Full dimension calculations for three-body systems are now feasible, while much work has been done on hyperspherical harmonics basis sets for four-body systems (see e.g. [4–9]). The quantum Hamiltonian is actually invariant with respect to the possible product arrangements and therefore the hyperspherical method is useful in the study of multi-channel processes.

Besides their use as quantum scattering basis sets, hyperspherical functions are suitable to be applied to the representation of intermolecular and intramolecular interactions in collision studies [10,11,11–20,20–38]. These representations

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are a practical advantage in the dynamical and kinetic study of reactive processes [39–44].

As a matter of facts, the feasibility, in practice, of full quantum dynamics calculations in hyperspherical coordinates has been limited to three- or at most four-atom systems. This restriction can be in part bypassed, extending the hyperspherical methods to classical dynamics, by which medium size and large molecules and atomic and molecular clusters can be simulated, taking advantage of the lower computational cost of classical trajectories (see e.g. [45]). As a consequence of expressing the classical Hamilton function in terms of hyperspherical coordinates, the degrees of freedom get separated into homogeneous sets of variables corresponding to well defined kinetic energy contributions, accounting for shape deformation, ordinary rotations and kinematic rotations [6,46–48]. The hyperangular momenta appearing in the Hamilton function, as well as the other relevant dynamical quantities, are defined within a classical framework. This, in principle, makes it possible to derive the classical hyperspherical equations of motion. However, time propagation in Cartesian coordinates is certainly more convenient, provided that an appropriate matrix transformation is available to evaluate, at each time step, the energy contributions entering the hyperspherical Hamilton function.

As a final remark, the hyperspherical framework partitions the degrees of freedom into two classes of rotational coordinates-ordinary spatial rotations and kinematic rotations. The remaining three degrees of freedom are thus invariant under both transformations and depend solely on the global shape of the particle aggregate. This invariance-based description of structure and dynamics has been validated in several applications [46,49–51].

We consider here the possible application of the hyperspherical invariants deformation as a tool for the analysis for the classification of the structures associated to local and global minima of clusters of molecules and atoms. The following sections introduce the hyperspherical coordinate framework for general N-particle systems and outline its application to the structural characterization of clusters. Selected applications are presented in the final part of the paper.

2 Methodology

The representation of N-particle systems in hyperspherical coordinates is obtained by introducing a set of $N-1$ Jacobi vectors $\mathbf{Q}_\alpha$, with $\alpha = 1, \cdots, N-1$, defined as linear combinations of the particle position vectors $\mathbf{r}_\alpha$ in the center of mass reference frame [46]. A "canonical" sequence of Jacobi vectors can constructed by first considering the vector connecting particles 1 and 2, then the vector connecting the center of mass of this pair to particle 3, and so on, up to the $(N-1)$-th vector, which connects the center of mass of the first $N-1$ particles to the Nth particle. Each vector is scaled by suitable mass-dependent coefficients, ensuring proper normalization (see Sect. 2.1 for details). The subsequent step is to dedine the hyperradius ρ as the norm of a vector in a $3N-3$-dimensional space, which spans the internal configuration space of the system.

The Cartesian components of the hyperradial vector, given by the ordered set of the Jacobi vector components, can be parametrized in terms of the hyperradius and $3N-4$ "hyperangles", thereby defining the hyperspherical coordinate system. Many choices are possible for the parametrization of the angles. One of the alternatives is the representation knwn as symmetric hyperspherical, which is obtained applying a transformation based on the *singular value decomposition*, applied to the position (Cartesian coordinates) matrix. The procedure for the derivation of the hyperspherical coordinates is presented in the next sections, and some of their remarkable properties are described.

2.1 Hyperspherical Coordinates for Atomic and Molecular Aggregates

An appropriate mathematical tool for the representation of N-center systems is the *singular value decomposition* [52], a matrix decomposition theorem that can be applied to any given set of N atoms, after assigning to them a properly defined position matrix.

Let us suppose we have a collection of $N \geq 2$ particles with masses $m_1, \cdots, m_N$ and positions identified by a set of radii vectores in the center of mass reference frame, $\mathbf{r_1}, \cdots, \mathbf{r_N}$. Mass *scaled* radii vectores $\mathbf{q}_\alpha = (m_\alpha/M)^{1/2}\mathbf{r}_\alpha$ $(1 \leq \alpha \leq N)$, can be obtained, where $M = \sum_\alpha^N m_\alpha$ is the total mass of the system.

A $3 \times N$ position matrix denoted by Z containing column-wise the components of the mass scaled vectors, can be generated, as follows:

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

Left-multiplication of the position matrix by an orthogonal matrix R^t, (transpose of a matrix $R \in O(3)$), rotates the coordinate frame. A rotation of the coordinate frame can also be performed in the so called *kinematic space* [5,47], by action of an orthogonal matrix (right-multiplication) $K \in O(N)$ on the position matrix Z, $Z' = ZK$.

It is possible to identify a subset of K matrices having the following form (see last column):

$$K = \begin{pmatrix} k_{1,1} & k_{1,2} & \cdots & (m_1/M)^{1/2} \\ k_{2,1} & k_{2,2} & \cdots & (m_2/M)^{1/2} \\ \cdots & \cdots & \cdots & \cdots \\ k_{N,1} & k_{N,2} & \cdots & (m_N/M)^{1/2} \end{pmatrix} \tag{2}$$

and its application to the Z matrix generates a subset of all possible Cartesian frames. Note that the elements of the last column of such rotated Z matrices are always zero, due to the relation $\sum_\alpha^N m_\alpha^{1/2}\mathbf{q}_\alpha = 0$, valid for the mass scaled vectors. In such special cases, one only has to deal with a $3 \times (N-1)$ "reduced"

Z matrix. The physical meaning of such a condition is that one separates the motion of the center of mass. This smaller matrix Z is called *reduced position matrix*.

The sets of (N-1) Jacobi and related vectors form reduced matrices. The Jacobi vectors are defined as a linear combinations of the N Cartesian particle position vectors, with coefficients being a function of the particle masses [53,54]. The different Jacobi vector sets are connected by kinematic rotations. These sets correspond to the different coupling schemes and reactive channels of the system.

The *singular value decomposition* theorem applied to the $3\times n$ position matrix Z (where $n = N$ or $n = N - 1$) leads to the following product of three matrices:

$$Z = R\Xi K^t \tag{3}$$

where $R \in O(3)$ and $K \in O(n)$ are 3×3 and $3 \times n$ orthogonal matrices, respectively. The elements of the $3 \times n$ matrix Ξ are zeroes, with the possible exception of the diagonal entries, $\Xi_{11} = \xi_1, \Xi_{22} = \xi_2, \Xi_{33} = \xi_3$, which are subjected to the inequality $\xi_1 \geq \xi_2 \geq \xi_3 \geq 0$.

In the previous equation, we denoted as ξ_i, $(i = 1, 2, 3)$ the *singular values* of the Z matrix. These values are unique, while the factors R and K in Eq. 3 are not. We have to note that the smallest singular value ξ_3 is zero when $N \leq 3$ and Z is the full $3 \times N$ position matrix. An important relation can be easily obtained [46,47]:

$$\xi_1^2 + \xi_2^2 + \xi_3^2 = \rho^2. \tag{4}$$

The ξ's are invariant under both ordinary rotations in the physical space and kinematic rotations [5,6,47,55], a remarkable property, with possible applications to molecular dynamics [46,56–59] and properties of the minimum energy structures of N-particle aggregates.

For $n = N - 1 = 3$, we are accounting for four particle (or equivalently four centers) systems. This case is special, since the two matrices R and K (of same dimension, 3×3) are no longer *special orthogonal* ($R \in SO(3)$ and $K \in SO(n)$), but just orthogonal matrices ($O(3)$). This implies that for a negative determinant of Z, the sign depends on the sign of the ξ's product, meaning $\xi_3 \leq 0$. This fact is directly connected to the mirror image and chirality sign of the four-center system [49,60,61].

The major consequence of the above result is that the $3N - 3$ degrees of freedom of the system can be partitioned into three distinct sets of coordinates: three angles, parametrizing the rotation matrix R and accounting for spatial rotations, $3N - 9$ angles, parametrizing the rotation matrix K, accounting for rotations in the kinematic space, and 3 ξ's, which are related to the hyperradius.

2.2 Hyperradius and Invariant Deformation Indexes

The singular values (ξ_1, ξ_2, ξ_3) are considered to be "kinematic invariants" [62], since they are independent of spatial and kinematic rotations, see Sect. 2.1.

In addition, they are related to the system moments of inertia, as follows:

$$\begin{aligned}\frac{I_1}{M} &= \xi_2^2 + \xi_3^2 \\ \frac{I_2}{M} &= \xi_1^2 + \xi_3^2 \\ \frac{I_3}{M} &= \xi_1^2 + \xi_2^2\end{aligned} \tag{5}$$

where I_1, I_2 and I_3 are the moments of inertia in the principal axis reference frame. From Eq. 4 one obtains:

$$I_1 + I_2 + I_3 = 2M\rho^2. \tag{6}$$

Consequently, the ξ's can be used to define which kind of rotor the system is, in terms asymmetric, symmetric and spherical. One has a spherical top configurations for $\xi_1 = \xi_2 = \xi_3$, a prolate top for $\xi_3 = \xi_2 < \xi_1$ and an oblate top for $\xi_1 = \xi_2 > \xi_3$.

In order to complete the angular parametrization the invariant ξ's can be expressed by a canonical set of spherical coordinates, ρ, θ and ϕ as follows:

$$\begin{aligned}\xi_1 &= \rho \sin\theta \cos\phi \\ \xi_2 &= \rho \sin\theta \sin\phi \\ \xi_2 &= \rho \cos\theta\end{aligned} \tag{7}$$

This connection of the singular values with the distribution of the inertia associated to the N- particle system, has suggested to define a measure of the deviation from the spherical top shape, by two *deformation indexes* [46]:

$$\xi_+ = \frac{\xi_2^2 - \xi_3^2}{\rho^2}, \;\; \xi_+ \geq 0 \tag{8}$$

which is zero for prolate top configurations, and

$$\xi_- = \frac{\xi_2^2 - \xi_1^2}{\rho^2}, \;\; \xi_- \leq 0 \tag{9}$$

which is zero for oblate top configurations. Both the indexes equal to zero, indicate the cluster is a spherical top.

2.3 Deformation Indexes of Atomic and Molecular Clusters

The global and local minimum energy structures of Lennard-Jones (LJ) clusters of increasing size are now analyzed to show the application the ξ's, the hyperradius and the deformation indexes for in the search of trends, symmetries and regularities in the data set.

To determine the value of the indexes, namely of the invariant ξ's of each cluster configuration, one can simply observe that from Eq. 3 the following relation can be obtained:

$$ZZ^t = R\Xi\Xi^t R^t \tag{10}$$

where the product $\Xi\Xi^t$ is 3×3 square diagonal matrix, whose entries are the squares of the ξ's. The diagonal entries are just the eigenvalues of the matrix product ZZ^t involving the position matrix. Therefore, starting from a given configuration, one can construct the Z matrix, using the Cartesian components of the atomic position vectors (see Section 2.1), calculate the ZZ^t matrix and diagonalize it, numerically or analitically, by using the well known Cardano's formula for the characteristic equation [46].

Here we consider a series of cluster minima structures, freely available from the Cambridge Cluster Database [63]. In particular, we consider Lennard-Jones (LJ) clusters, with N, number of atoms, ranging from 310 to 561 (see Ref. [64]). In Fig. 1, the deformation indexes are reported, as a function of the cluster size (N), for the minimum energy configurations. The trend shows marked oscillations, interrupted by the occurrence of spherical top configurations.

3 Trends and Classification of ξ's and Deformation Indexes

In this section, we analyze the relationship between deformation indexes and cluster size, and consider possible classifications, using two well known machine learning classification methods. The trend of the deformation indexes as a function of the cluster size N, number of atoms, is shown in Fig. 1. The trend is suggestive of the fact that, despite the central (isotropic) character of the pairwise Lenard-Jones potential (the potential depends uniquely on the interparticle distance), the global minimum structures often depart from the spherical symmetry (symmetric top), indicating that particle particle packaging hinders the spherical symmetry.

3.1 Clustering Analysis by K-Means and Mean Shift Methods

A preliminary characterization of the ξ's generated from the atom cluster structures in the considered dataset can be obtained by looking for possible classifications. Accordingly, the xi's map was analyzed using two unsupervised clustering methods, namely K-means and mean shift, frequently used to obtain classifications of molecular properties. The methods are briefly described below (see also, e.g. [65,66]). Mean-shift clustering is an iterative nonparametric algorithm used to identify clusters in a data set by locating the peaks (modes) of the underlying data density. Unlike methods such as k-means, it does not require one to specify the number of clusters in advance (a possible advantage and a possible limitation), and it is in this sense complemental to approaches that require the number of clusters. The corresponding algorithm starts by estimating the density of the data using a kernel (usually a Gaussian function). This kernel defines a window (or bandwidth) around each data point. For a given data point, the algorithm computes the weighted mean of all points within its kernel window. The difference between this mean and the original point is called the mean shift vector. Each data point is then moved (shifted) in the direction of the mean

shift vector. This process is repeated iteratively: at each iteration, the point's new location becomes the center of a new window. The algorithm continues to shift until convergence, when any subsequent movement becomes negligible, indicating that the point has reached a local maximum (a mode) of the density. Once all points have converged to their respective modes, points that converge to the same mode are grouped together and considered to be part of the same cluster. The mean shift clustering method is a useful tool for discovering clusters by iteratively shifting data points toward the highest density regions and, in this sense, is what we need to locate the ξ subspace for LJ clusters. Its ability to detect clusters without specifying in advance their number and to handle arbitrarily shaped clusters makes it suitable for us. In our case, the idea is to identify the coordinate clusters of shapes in the population of ξ's generated from the set of structures. The results are illustrated in Fig. 1

To complement and validate the Mean Shift results, the population of ξs was analyzed using the K-means method. Clustering of K-means is a widely used partitioning algorithm that groups data into predefined (k) clusters by minimizing the variance in the cluster. The method is iterative and assigns data points, in this case a triple of ξ s, but in the literature there are applications to protein feature vectors or NMR chemical shifts assigning points to a centroid, the nearest one, based on the simple Euclidean distance, then updating centroids as the mean of assigned points until convergence. K-means excel in tasks such as structural classification, conformational clustering due to their scalability and simplicity, achieving accuracies up to 80% in classifying, for example, structures of proteins from chemical shift data. However, it requires specifying the number of clusters k, but here we have a clue from Mean-Shift results. Weak points are obvious sensitivity to outliers and, reportedly, the risk of convergence to local optima, so requiring careful initialization and a kind of preprocessing od data, for an optimal performance. The combined use with Mean-Shift is meant to minimize such effects. However, to have a clue about the choice of the number of clusters, it was also estimated using the elbow criterion, based on the analysis of the within-cluster sum of squared distances (SSD) as a function of the cluster number [67].

4 Results

The analysis of Lennard–Jones cluster structures in the size range $N = 310$–561 reveals some trends in the invariant hyperspherical quantities. The deformation indexes ξ_+ and ξ_-, reported as a function of cluster size (Fig. 1), exhibit pronounced oscillatory behavior, indicating systematic departures from spherical symmetry despite the isotropic nature of the pairwise potential. Only specific cluster sizes correspond to configurations of spherical-top symmetry, confirming that geometric packing effects dominate over the isotropy of the potential energy.

The distribution of the invariant coordinates (ξ_1, ξ_2, ξ_3) in the shape space shows regions, although not clearly well-defined, corresponding to distinct rotational simmetry (oblate, prolate, ...). The application of unsupervised clustering

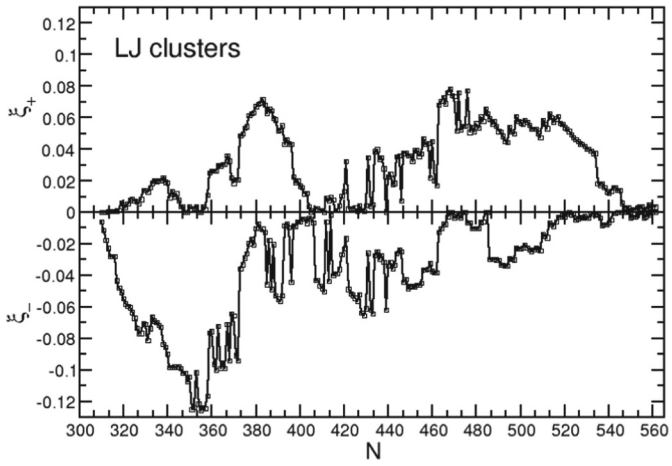

Fig. 1. Cluster deformation indexes as a function of the cluster size (number of atoms) N.

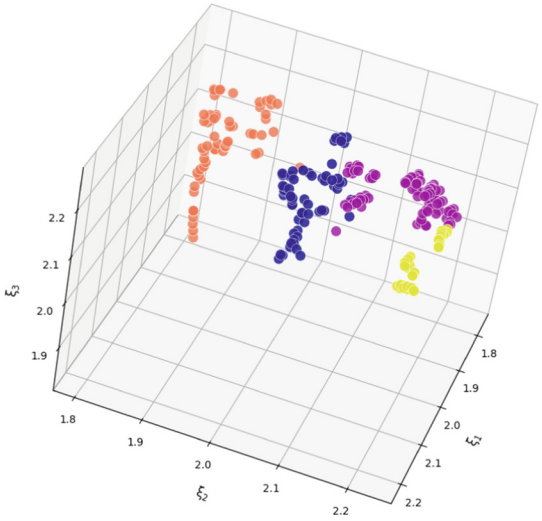

Fig. 2. K-means classification of the ξ's values, based on four different classes (different colors).

techniques provides a quantitative classification of these regions. In particular, K-means clustering identifies four distinct groups in the invariant coordinate space (Fig. 2), suggesting the presence of multiple families of structural packaging. Mean shift clustering, which does not require a predefined number of clusters, detects instead three main maxima of point density (Fig. 3), suggesting the possible existence of underlying structural classes. An estimation of the

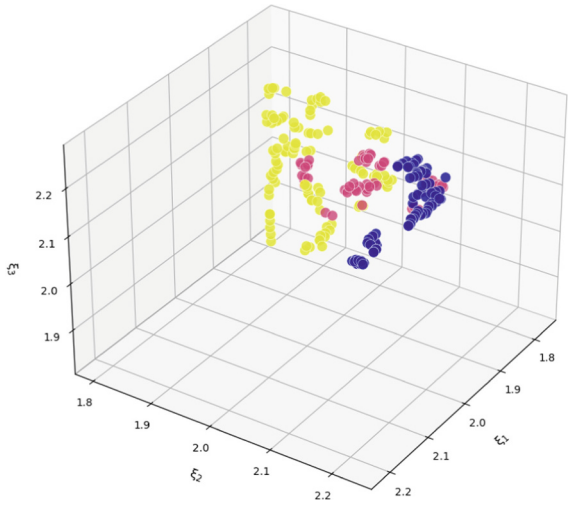

Fig. 3. Mean Shift classification of the values of the ξ's, three classes are identified (different colors).

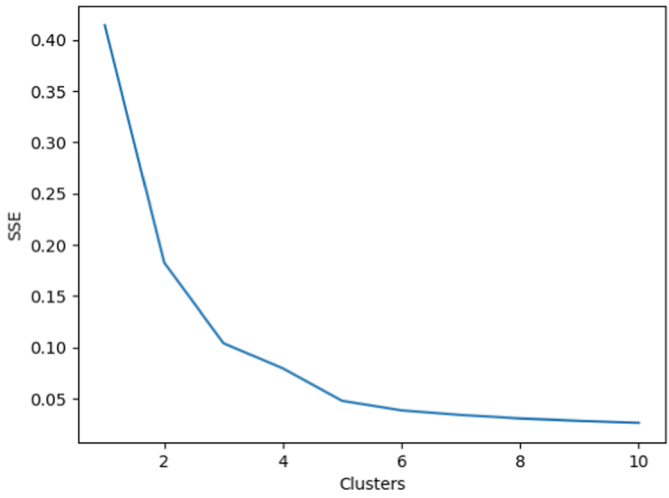

Fig. 4. SSD as a function of the number of clusters.

optimal number of classes was obtained by th so called elbow-method, see Fig. 4, based on the calculation of the SSD.

A similar analysis is performed in the deformation-index space (ξ^+, ξ^-) and shows, similarly, a clear separation of configurations into regions ideally associated with prolate-like, oblate-like, and near-spherical shapes (Figs. 5 and 6). The clustering results, as expected, are consistent with those obtained in the full

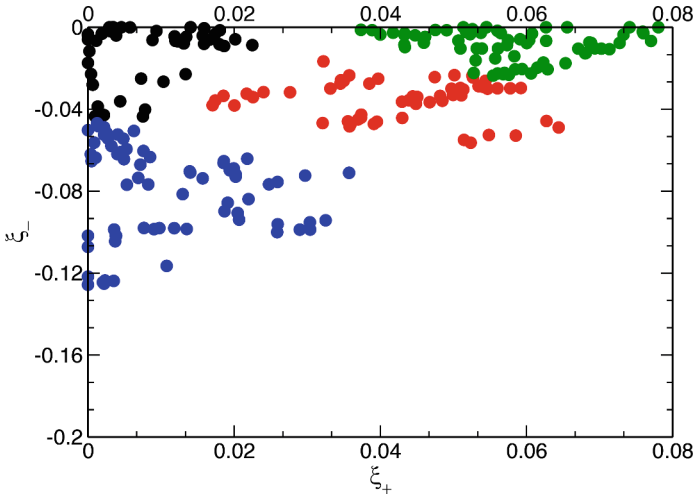

Fig. 5. K means classification of the $\xi_{+/-}$ deformation indexes, for the given structure dataset, $N = 310 - 561$.

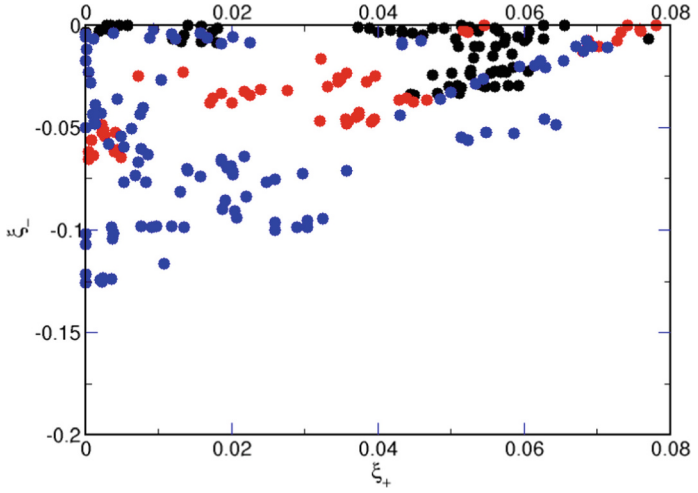

Fig. 6. Mean shift classification of the $\xi_{+/-}$ deformation indexes, for the given structure dataset, $N = 310 - 561$. Three classes are identified.

invariant coordinate space, indicating that the deformation indexes retain the essential information required for structural classification.

The combined use of invariant hyperspherical coordinates and clustering analysis provides a physically meaningful representation of the structural diversity of atomic clusters, enabling the identification of symmetry trends and deformation regimes across a wide range of system sizes.

5 Conclusions and Future Perspectives

In this work, we have analyzed the structure of atomic clusters using invariant descriptors derived from the hyperspherical formulation for general N-body systems. The singular values of the coordinate matrix, interpreted as kinematic invariants, provide a natural and rotation-invariant representation of the cluster shapes, directly connected to the principal moments of inertia and to the classification of rotational tops.

The introduction of deformation indexes based on these invariants allows for a compact quantification of deviations from spherical symmetry and enables the identification of systematic trends in minimum-energy configurations. The results obtained for Lennard–Jones clusters demonstrate that, even in systems governed by isotropic interactions, non-trivial symmetry breaking and deformation patterns emerge as a function of cluster size.

Unsupervised machine learning methods, such as K-means and mean shift clustering, further enhance the classificatory power of the approach. These techniques reveal the existence of distinct families of structures in the invariant shape-space and provide a framework for the classification of molecular configurations.

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