

The Invariance Approach to Structure and Dynamics: Classical Hyperspherical Coordinates

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Abstract. The hyperspherical coordinate systems have been extensively adopted in the study of few-body scattering problems of nuclear and molecular physics, for example in the practical implementation of demanding quantum calculations typical of chemical reactions. Hyperangular momenta are the dynamical quantities used in this representation and the hyperspherical harmonics are the corresponding basis functions. The use of such formalism is limited to the treatment of three- or four-center problems, due to the exceedingly high computational cost of quantum dynamics calculations. To circumvent this restriction, an hyperspherical formulation has been developed in a series of works during the last decades, suitable for the simulation of cluster and large molecular system dynamics. Such a hyperspherical formulation is based on classical definitions of the hyperangular momenta and on the search of invariant dynamical quantities. Exploiting invariance of hyperspherical shape coordinates with respect to rotations and kinematic rotations, we consider the use of the classical hyperspherical representation as a tool for the static analysis of geometry and minimum energy structures of atomic and molecular structures, showing some applications to relatively simple systems.

Keywords: Hyperspherical coordinates · Intermolecular interactions · Atomic clusters · Global minimum · Isomers · Shape coordinates

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

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harmonics basis sets for four-body systems (see e.g [4–9]). These approaches are more suited to represent multi-channel reactive collision processes, due to the invariance of the quantum Hamiltonian with respect to the possible product arrangements. In this sense, the hyperspherical one is largely preferable with respect to other approaches (see e.g. semiclassical [10–17]).

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 [18–45].

So far the practical feasibility of full quantum 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. [46]). 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 [6,47–49]. The hyperangular momenta appearing in the Hamilton function and the other relevant dynamic quantities are given "classical" definitions, so that classical hyperspherical equations of motion could in principle be obtained, although integration in Cartesian coordinates is certainly preferable, provided a specific matrix transformation that permits the evaluation, as a function of time, of the energy terms appearing in the Hyperspherical Hamilton function.

As a last remarkable aspect, it is noticeable that the hyperspherical scheme splits the degrees of freedom into two different sets of rotational coordinates (ordinary rotations and rotations in the kinematic space), so that the remaining three degrees of freedom turn out to be invariant with respect to both kinds of rotation action and solely depend on the global shape of the aggregates of particles. This "invariance‘" approach to structure and dynamics has been validated in a series of applications [47,50–52].

In this paper, we want to review the use of invariant hyperspherical deformation indexes for the study and classification of local and global minimum energy structures of atomic and molecular clusters. In the following Sections, it will be given a description of the hyperspherical coordinates applied to generic N-particle systems and of the related approach to structural aspects of clusters of atoms and molecules. Finally, some applications will be illustrated.

2 Theoretical Background

The representation of N-particle systems in hyperspherical coordinates can be obtained introducing a set of $N-1$ Jacobi vectors $\mathbf{Q}_\alpha$, with $\alpha = 1, \cdots, N-1$, made up by proper combinations of the radial vectors of the particles in the center of mass reference frame, the latter denoted by $\mathbf{r}_\alpha$ [47]. A "canonical" sequence of such vectors can be built by taking the vector which connects particles 1 and

2, then the one connecting the center of mass of the pair to the third particles, 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. The vectors have to be combined being multiplied by proper coefficients which depends on the particle masses, see Sect. 2.1 for details. The next step consists in the definition of an hyperradius ρ as the modulus of a vector of dimension $3N-3$, spanning the configuration space of the system. The Cartesian components of the hyperradial vector, given by the ordered sequence of the Jacobi vector components, can be parametrized by means of the hyperradius and $3N-4$ "hyperangles", which define the hyperspherical coordinate system. The angular parametrization is not unique. Among the various alternatives, for our purposes we select the one corresponding to the so called Symmetric hyperspherical representation, which is a result of a matrix transformation, the *singular value decomposition*, acting on a properly constructed position matrix. In the next sections we will detail the procedure to generate hyperspherical coordinates, outlining some important features.

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* [53], 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:

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

The coordinate frame can be rotated, acting (left-multiplication) on the position matrix by an orthogonal matrix R^t, transpose of a matrix $R \in O(3)$. A rotation of the coordinate frame can also be performed in the so called *kinematic space* [5,48], 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 the 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 $(\mathrm{N}-1)$ 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 [54,55]. Kinematic rotations connect different Jacobi vector sets corresponding 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 $\xi_1 \geq \xi_2 \geq \xi_3 \geq 0$.
The values ξ_i, $(i = 1, 2, 3)$ are called the *singular values* of the matrix Z and are uniquely determined, although the factors R and K in Eq. 3 are not. If $N \leq 3$ and Z is the full $3 \times N$ position matrix, then the smallest singular value ξ_3 is necessarily zero. An important relation can be easily obtained [47,48]:

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

The ξ's are invariant under both ordinary rotations in the physical space and kinematic rotations [5,6,48,56], a remarkable property, with possible applications to molecular dynamics [47,57–60] and properties of the minimum energy structures of N-particle aggregates.

The symmetric case $n = N - 1 = 3$, corresponding to four particles or four center systems, is special, since the two matrices R and K cannot be chosen to be *special orthogonal* ($R \in SO(3)$ and $K \in SO(n)$), but are required to be just orthogonal matrices ($O(3)$). In this case, if the determinant of Z is lower than zero, its sign depends on the sign of the product of the ξ's, and so one has $\xi_3 \leq 0$. This fact is directly connected to the mirror image and chirality sign of the system [50,61,62].

As a result of the matrix transformation described above, we can group the $3N-3$ degrees of freedom of a system of N particles 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, being the only quantities with length units.

2.2 Hyperradius and Invariant Deformation Indexes

The singular values (ξ_1, ξ_2, ξ_3) are considered to be "kinematic invariants" [63], for the reason that they are independent from spatial and kinematic rotations, see Sect. 2.1. They are also directly related to the moments of inertia of the system, through the following relations:

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

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

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

Due to the previous relations, the ξ's can be used to classify the rotational properties of the system, in terms of asymmetric, symmetric and spherical rotors. 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* [47]:

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

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. From the above definitions follows that when both the indexes are zero, the cluster is a spherical top.

2.3 Deformation Indexes of Atomic and Molecular Clusters

To show a perspective use of deformation indexes for the search of trends, symmetries and regularities in the global an local minimum energy structures of

clusters of increasing size, we consider the deformation indexes and the hyperradius of a number of sets of atomic clusters bound by different potentials. 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, for any given configuration, one can construct the Z matrix, using the Cartesian components of the atomic position vectors (see Sect. 2.1), calculate the ZZ^t matrix and diagonalize it, numerically, or by using the well known Cardano's formula for the characteristic equation [47].

Here we consider a series of cluster minima structures, freely available from the Cambridge Cluster Database [64]. In particular, we consider Lennard-Jones (LJ) clusters, with N ranging from 310 to 561 and metal clusters bound by a Sutton-Chen potential 12-6 (see Ref. [65]) In Fig. 1, the deformation indexes of Sect. 2.2 for the LJ clusters are reported for the minimum energy configurations, as a function of the atom number N. The trend shows marked oscillations, interrupted by the occurrence of spherical top configurations. In Fig. 2 the same plot is shown for Sutton-Chen clusters. Such structures are of smaller dimensions, N up to 78, and exhibit strong deviations from the spherical symmetry.

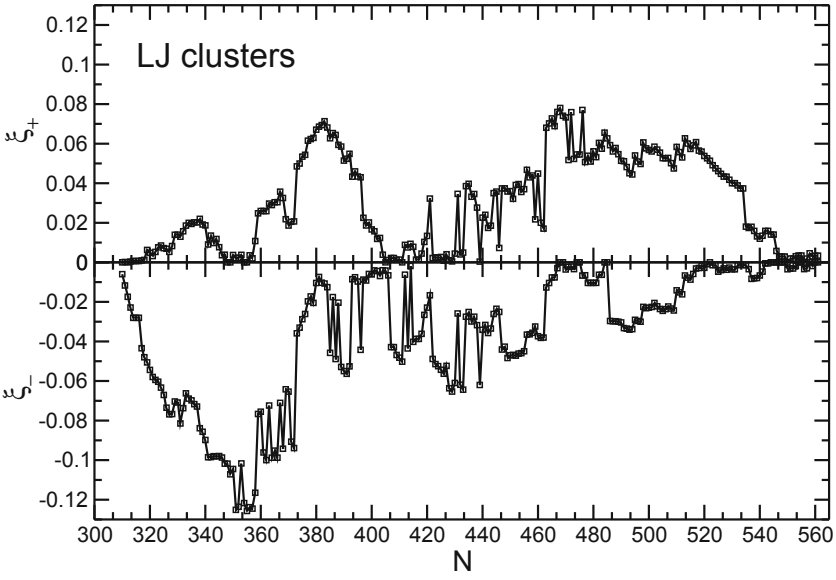

Fig. 1. Plot of the ξ_+ and ξ_+ deformation indexes for the minimum energy structures of Lennard-Jones (LJ) 12-6 clusters for N from 310 to 561. Smaller LJ clusters have been analyzed in Ref. [47]. Structures have been obtained from the database [64]

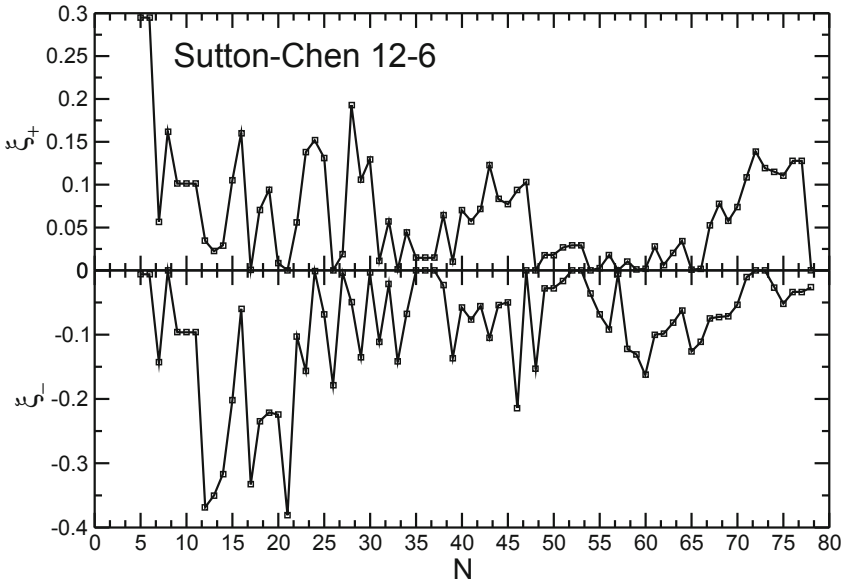

Fig. 2. Plot of the ξ_+ and ξ_+ for the minimum energy structures of atom clusters bound by a Sutton-Chen potential 12-6, for N from 5 to 78.

3 Conclusions

In this paper we reviewed some aspects of the hyperspherical coordinate approach to structure and dynamics of molecules and clusters. Attention has been focused on the use of deformation indexes, obtained combining rotational invariant hyperspherical coordinates, as a tool to systematically study and classify the minimum energy structures of clusters. Regular trends or patterns in the invariant indexes characterizing the structures, wherever found, may help in the search for global minima and in similarity studies.

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