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A geometrical approach to the degree of chirality and asymmetry

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A new measure of the degree of chirality and asymmetry of a finite number of particles is proposed. To this end a space of configurations of identical particles is defined as the orbit space of the group of all permutations of particles embedded in an Euclidean space. This space is shown to be a metric space and the action of the translation and orthogonal groups is also defined. The results are applied to the study of an algebra of polynomials on the configuration space and its equivalence to the algebra of symmetric Cartesian tensors is demonstrated. An illustrative example is presented. Some general features of chirality are also briefly discussed.

1. Introduction

There is an evident *renaissance* of interest in the theory of chirality and related topics, now attracting scientists from different fields ranging from particle physics to biology. On one hand, this is a result of the recent progress in topological stereochemistry which has led to the synthesis of topologically non-trivial molecules (molecular Möbius ladder, knotted molecules) [1]; on the other hand, it is stimulated by a profound penetration of modern mathematical ideas into natural science. These methods have proved successful in the qualitative interpretation of various topological aspects of the problem [2]. However, for the quantitative analysis, the development of classic geometrical methods is still greatly desired [3–8]. To this end, two types of measures of chirality have been proposed and these will be referred to as the degree of chirality of the first and of the second kind according to the nomenclature developed in ref. [9]. The first kind of measure is a function which maps the domain containing a class of objects into the set of real numbers in such a way that for two objects related by a reflection this function gives opposite

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numbers. An example of such a function – the chirality product – was discussed in ref. [5a] and was applied to triangles. However, in this paper we use the chirality measures of the second kind, where the degree of chirality is defined via a distance between an object and its mirror image. Several distance functions have proved successful to quantify the chirality of simple objects. These are based on the common (overlap) area [6], which uses the Boolean distance function on a set algebra of a measurable space with a positive bounded measure [7], the Hausdorff distance function [8], and the construction by Kuz'min [10]. The above methods were critically discussed in a recent up-to-date review article by Buda et al. [9].

The present paper is primarily devoted to the quantification of chirality and asymmetry of configurations of a finite number of particles, although the topological nature of the problem is also briefly discussed. We propose another distance function, which has some similarities to that proposed by Mezey [11] for the reduced nuclear configuration space. A comparison of both distance functions is available [12].

The main objective of this contribution is to propose a method for an analysis of chirality and asymmetry. The particular goals are:

1. To propose a description of a configuration space of a finite number of particles (e.g., atomic nuclei) including its metric properties.
2. To use the above distance function to define the *degree of chirality* and *asymmetry* in a rigorous way suitable for a computer algorithm encompassing numerous cases of practical interest.
3. To classify functions defined on a configuration space in terms of their power series.

Basically, the notion of chirality we use is exactly the same as the classical one introduced more than a hundred years ago [13]. It addresses the question of whether a geometrical object and its image, obtained via reflections, can be superimposed using translations and rotations. Another way to say it is that one can find a rotation–reflection plane transforming a geometrical object onto itself, i.e., being a symmetry element of this particular object. (Let us note that this is not necessarily true in the case of unbounded objects like crystal lattices, where not only rotations and reflections but also their combinations with translations can be symmetry elements). In section 2 an analysis of the configuration space of a finite number of particles is presented. The metric structure defined on this space is then used in section 3 to define the *degree of chirality* and the *degree of asymmetry*. In section 4, a global approach to *chiral* and *asymmetric functions* and *polynomials* is developed using the tensor formalism, to some extent parallel with the *chirality algebra* approach of King [4]. Section 6, the last one, deals with the three particle configurations, which can be identified with a triangular object. The two reasons for this particular choice are the simplicity and the possibility of a comparison with other results. This comparison shows a similarity of our measure of the degree of

chirality based on the Euclidean distance to that based on the Hausdorff distance: for both measures the most chiral triangle is a non-degenerate triangle [9]. The topological aspect of chirality and a generalization of this notion are also briefly discussed.

We do not restrict ourselves to configurations in the three-dimensional Euclidean space because it may happen that some real structures could be considered as projections of highly symmetric configurations embedded in n-dimensional Euclidean spaces on a three-dimensional space. For this reason our approach can eventually be applied to those structures. On the other hand, consideration of multidimensional spaces does not lead to any algebraic problem and the results are still clear. One should remember that for even dimension n of the Euclidean space the inversion coincides with a proper rotation as it is the case in the two-dimensional plane. For this reason we always refer to a reflection $(n\text{-}1)$-dimensional hyperplane in an n-dimensional space as a transformation verifying whether a configuration is chiral or not.

In a sense the problem of chirality can be treated as a particular case of the asymmetry problem. A bounded object is said to be chiral if it is asymmetric with respect to every rotation–reflection and it is achiral otherwise. What makes the chirality problem unique is the relationship between reflections and the group of rotations and translations, as discussed in the last section of this article.

2. Configuration space for N identical particles

Consider a configuration of N identical particles in n-dimensional Euclidean space R^n. Since the particles are assumed to be identical the configuration can be fully described by $N(N-1)/2$ coordinates if $N \leqslant n$ or by $n(n-1)/2 + (N-n)n$ if $N \geqslant n$. These are known as the coordinates of a system in the reduced configuration space [11]. However, to decide whether such a configuration has some postulated symmetry properties we must determine the relationship between the considered configuration of particles and the symmetry reference system. Hence we need some additional coordinates: n coordinates for the determination of the origin and $n(n-1)/2$ coordinates to fix the axes of the symmetry reference system. We shall see shortly that n is the dimension of the translation group $\mathrm{T}(n)$, and $n(n-1)/2$ coincides with the dimension of the orthogonal group $\mathrm{O}(n)$. These two groups contain all transformations of configurations which are necessary to formulate the problem. Thus for $N > n$ (as we shall always assume since the case of $N \leqslant n$ is trivial), the total number of coordinates to be considered is nN. Thus the natural way to define the configuration of N particles is to use their n Cartesian coordinates $\boldsymbol{r}_i$ $(i = 1, 2, \ldots, N)$ in the symmetry reference system to form a vector

$$\boldsymbol{v} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \tag{1}$$

in R^{nN}. However, according to our previous assumption the particles are identical. Therefore the vectors

$$\sigma \boldsymbol{v} = (\boldsymbol{r}_{\sigma(1)}, \boldsymbol{r}_{\sigma(2)}, \ldots, \boldsymbol{r}_{\sigma(N)}) \tag{2}$$

will represent the same configuration as vector (1), for any permutation σ of N particles. Consequently, the configuration of N identical particles can be represented by the collection of vectors $\sigma \boldsymbol{v}$ defined as

$$\bar{v} = \{\sigma \boldsymbol{v} : \sigma \in S^N\}, \tag{3a}$$

where S^N denotes the symmetric group of all permutations of N elements. The configurations $\bar{v}$ are orbits of the action of S^N in R^{nN} as defined in (2). Thus, eq. (3a) can also be written as

$$\bar{v} = S^N \boldsymbol{v}. \tag{3b}$$

The space of configurations is then the space of orbits of S^N in R^{nN} and we shall denote it as $\mathrm{E} = \mathrm{R}^{nN}/S^N$.

On the other hand, for a given symmetry reference frame in R^n we can define the action of every element of the orthogonal group $\mathrm{O}(n)$ on every configuration $\bar{v}$ in a natural way as

$$U\bar{v} = \overline{U\boldsymbol{v}} = S^N(U\boldsymbol{v}), \tag{4a}$$

where

$$U\boldsymbol{v} = (U\boldsymbol{r}_1, U\boldsymbol{r}_2, \ldots, U\boldsymbol{r}_N) \tag{5a}$$

and $U\boldsymbol{r}_i$ $(i = 1, 2, \ldots, N)$ are the transformed coordinates of the ith particle in R^n under action of $U \in \mathrm{O}(n)$ on this particle (and not on the coordinate reference system). In the same way we can define the action of the translation group $\mathrm{T}(n)$ on the configuration space E. In this case one can simply substitute the translation operators T for the orthogonal transformations U in formulas (4) and (5):

$$T\bar{v} = \overline{T\boldsymbol{v}} = S^N(T\boldsymbol{v}) \tag{4b}$$

and

$$T\boldsymbol{v} = (T\boldsymbol{r}_1, T\boldsymbol{r}_2, \ldots, T\boldsymbol{r}_N). \tag{5b}$$

Here $T\boldsymbol{r}_i$ $(i = 1, 2, \ldots, N)$ are the transformed coordinates of the ith particle in R^n under action of $T \in \mathrm{T}(n)$ on this particle (and not on the coordinate reference system).

Finally, we can define a distance d on E to make it a metric space, as follows:

$$d(\bar{v}, \bar{w}) = \inf_{\sigma \in S^N} \|\sigma \boldsymbol{v} - \boldsymbol{w}\|, \tag{6}$$

where

$$\|\boldsymbol{v}\|^2 = \|\boldsymbol{r}_1\|^2 + \|\boldsymbol{r}_2\|^2 + \ldots + \|\boldsymbol{r}_N\|^2 \tag{7}$$

and for every $i = 1, 2, \ldots, N$ the entities

$$\|\bar{r}_i\|^2 = \|r_i^1\|^2 + \|r_i^2\|^2 + \ldots + \|r_i^n\|^2 \tag{8}$$

are the standard Euclidean norms of vector $\boldsymbol{r}_i$ with n coordinates $r_i^1, r_i^2, \ldots, r_i^n$. It is worth mentioning that the transformations defined in eqs. (4) and (5) are isometries for the above distance function d. This means that the equation

$$d(TU\bar{v}, TU\bar{w}) = d(\bar{v}, \bar{w}) \tag{9}$$

holds for every $U \in \mathrm{O}(n)$, $T \in \mathrm{T}(n)$ and $\bar{v}, \bar{w} \in E$, which is also equivalent to saying that d is invariant with respect to the action of $\mathrm{O}(n)$ and $\mathrm{T}(n)$ on E. However, although the distance functions defined in this work and that introduced by Mezey [11] can be related to each other, they are two different functions on two different spaces (both referred to as configuration spaces) the first one being the space of orbits of S^N and the second being the space of orbits of the group generated by all translations and rotations, where all particles, even identical, are distinguished. In this sense, the Hausdorff distance used earlier [8,9] to construct an adequate chirality measure is closer to our function d (eq. (6)) since it acts on the same space E and satisfies eq. (9). As shown below, the most chiral triangles for these functions are closely similar.

In this way we have arrived at a very nice structure on the configuration space E, representing any arrangement of N identical particles. Although the points corresponding to the appearance of the same coordinates for two or more particles have no practical meaning, the existence of such "non-real" configurations does not lead to any trouble since these configurations cannot appear just by transforming the "real" configurations via orthogonal transformations or translations.

3. Symmetry analysis of configurations of N identical particles

The symmetries we are going to consider are always assumed to be composed of orthogonal transformations of $\mathrm{O}(n)$. Let U be an arbitrary element of $\mathrm{O}(n)$. U will be said to be a symmetry element of a configuration $\bar{v} \in \mathrm{E}$ if the distance

$$d(U\bar{v}, \bar{v}) \tag{10}$$

is equal to 0. This is equivalent to saying that $U\bar{v} = \bar{v}$, or that U restricted to the orbit $\bar{v}$ corresponds itself to a permutation σ of S^N. In general, the distance (10) contains the information about how far the transformation U is from being a symmetry element of $\bar{v}$.

A group $G \subset \mathrm{O}(n)$ will be said to be a symmetry group of $\bar{v}$ if every element of G is a symmetry element of $\bar{v}$. The largest symmetry group of a given configuration $\bar{v}$ is the stabilizer of $\bar{v}$ defined as

$$G_{\bar{v}} = \{U \in O(n) : U\bar{v} = \bar{v}\}. \tag{11}$$

Let β be an invariant (Haar) measure on G [14]. The number

$$\left(\int_G (d(U\bar{v}, \bar{v}))^2 \, d\beta(U)\right)^{1/2} \tag{12}$$

contains the information giving how far the group G is from being the symmetry group of the configuration $\bar{v}$. Hence G is a symmetry group of $\bar{v}$ if and only if the number defined by expression (12) is equal to 0.

Until now all the definitions were dependent on the orientation of the considered transformations with respect to the configuration of particles. In other words, they were dependent on the definition of the symmetry reference coordinates. However, most often one tries to make a statement about the symmetry of the configuration which will not depend on one's arbitrary choice of these coordinates. This means that an attempt to find the best reference system is made by minimizing the distances between non-transformed and transformed configurations using translations and rotations. It can be expressed in a rigorous way that we are looking for the global minima of functions

$$T \to d\big((TUT^{-1})\bar{v}, \bar{v}\big) = d\big(U(T^{-1}\bar{v}), T^{-1}\bar{v}\big) \tag{13}$$

and

$$R \to d\big((RUR^{-1})\bar{v}, \bar{v}\big) = d\big(U(R^{-1}\bar{v}), R^{-1}\bar{v}\big) \tag{14}$$

for a fixed symmetry transformation U, where the variable T belongs to $T(n)$, the translation group in R^n, and the variable R belongs to the subgroup of $O(n)$, the special orthogonal group $SO(n)$ consisting of proper rotations. Because the action of both the translations and rotations was defined as a transformation of configurations (eqs. (4) and (5)) we must apply the inverse transformations T^{-1} and R^{-1} to $\bar{v}$ to transform the reference system respectively by T and R. It is obvious from the definition of d as well as from the compactness of $SO(n)$ that both functions attain their minimal values. While the first function (eq. (13)) corresponds to fixed directions of coordinate axes and to movable origin, the second one (eq. (14)) corresponds to a fixed origin and to rotated directions of the coordinate axes. Happily we can find the minimum of the first function quite easily. The graph of the square of this function is an n-dimensional paraboloid centered at a translation T_0 defined by the vector

$$\boldsymbol{r} = \frac{1}{N}(\boldsymbol{r}_1 + \boldsymbol{r}_2 + \ldots + \boldsymbol{r}_N) \tag{15}$$

pointing from the origin of the reference system to the center of mass of the configuration of N identical particles. This translation T_0 is, in fact, the shift of the whole configuration by $-\boldsymbol{r}$, which is equivalent to the shift of the reference system by $\boldsymbol{r}$,

in order to superimpose the origin and the center of mass. Because T_0 does not depend on U we can conclude that the minima of the distance d with respect to both the translations and rotations coincide with the minima of function (14) with the origin of the reference system taken to be the center of mass of the configuration. Thus, from now on we shall always assume that the origin of the symmetry-related reference frame is chosen to be the center of mass of the configuration unless something else is explicitly stated. We are now ready to formulate a few other results.

Let us write the minimum of the function (14) as

$$\inf_{R\in \mathrm{SO}(n)} d(RUR^{-1}\bar{v}, \bar{v}) . \tag{16}$$

Obviously this number does not depend on the class $[U]$ of conjugate elements (in $\mathrm{SO}(n)$) and the configuration $\bar{v}$. The configuration $\bar{v}$ will be called essentially U-symmetric if the number defined by expression (16) is equal to 0. This is equivalent to saying that there is an element $\hat{U}\in[U]$ such that $\hat{U}$ is a symmetry element of $\bar{v}$. In general this number states how far the configuration $\bar{v}$ is from being essentially U-symmetric.

Analogously, a configuration $\bar{v}$ will be called essentially G-symmetric for a certain group $G \subset \mathrm{O}(n)$ if there is an element $R\in\mathrm{SO}(n)$ such that the isomorphism $U \to RUR^{-1}$ transforms G onto another subgroup $\hat{\mathrm{G}} \subset \mathrm{O}(n)$ which is the symmetry group of $\bar{v}$. Then the number

$$\inf_{R\in \mathrm{SO}(n)} \left(\int_{\mathrm{G}} \left(d\left(RUR^{-1}\bar{v}, \bar{v}\right)\right)^2 \mathrm{d}\beta(U) \right)^{1/2} \tag{17}$$

is equal to 0. In general, it defines how far the configuration $\bar{v}$ is from being essentially G-symmetric.

The search for the minimum of function (14) is the toughest non-trivial part of our approach to symmetry. However, since the group $\mathrm{SO}(n)$ is compact, this minimum always exists. Moreover, the group can be easily parametrized, for example, by three Euler rotation angles in the case of a configuration in the 3-dimensional space. In addition, if we are dealing with the degree of chirality, i.e. the deviation from the symmetry generated by a reflection plane, we can neglect the rotations about the axis perpendicular to the reflection plane. This decreases the number of independent variables by one. Consequently, one can use standard routines searching for the minima of a function of several variables.

As was mentioned in the introduction, the measure of the second kind of the degree of chirality is defined as the shortest distance from an initial configuration to its mirror image, which is subsequently rotated and translated in order to minimize this distance. For our particular choice of the origin at the mass center of the configuration, it can be written as

$$\inf_{R\in \mathrm{SO}(n)} d(RU\bar{v}, \bar{v}) . \tag{18}$$

This is identical to the minimum (16) of function (14) for an appropriate choice of the rotation–reflection element U, for which the minimum (18) is obtained for $R = E$, the identity transformation.

It seems natural to choose translations and rotations when U is an $(n-1)$-dimensional rotation–reflection hyperplane. However, one can imagine another kind of chirality similar to this defined by the orthogonal group $O(n)$ and the special orthogonal group $SO(n)$. In this case the problem of a proper definition of the "*superimposition operations*" is still open for discussion. In section 5 we present a general approach to this problem.

4. Functions defined on the configuration space and their power series

Let f be a function assigning a measurable property to every configuration of N identical particles. We can consider f to be a function from R^{nN} into R assuming that it is invariant under permutation of particles, i.e., that the following condition is satisfied:

$$f(v) = f(\sigma v) . \tag{19}$$

The Taylor expansion of f at an arbitrary point $v = (r_1, r_2, \ldots, r_N)$ of R^{nN} can be written as

$$\begin{aligned} f(r'_1, r'_2, \ldots, r'_N) = & f(r_1, r_2, \ldots, r_N) \\ & + \frac{1}{1!} D^{(1)} f(r_1, r_2, \ldots, r_N)\Big(T^{(1)}(r'_1 - r_1, r'_2 - r_2, \ldots, r'_N - r_N)\Big) \\ & + \frac{1}{2!} D^{(2)} f(r_1, r_2, \ldots, r_N)\Big(T^{(2)}(r'_1 - r_1, r'_2 - r_2, \ldots, r'_N - r_N)\Big) + \ldots \\ & + \frac{1}{k!} D^{(k)} f(r_1, r_2, \ldots, r_N)\Big(T^{(k)}(r'_1 - r_1, r'_2 - r_2, \ldots, r'_N - r_N)\Big) + \ldots , \end{aligned} \tag{20}$$

where $D^{(k)} f(r_1, r_2, \ldots, r_N)$ can be interpreted as a linear form on the tensor product space $\otimes_{i=1}^{k} R^n$ of kth rank tensors in R^n given by

$$D^{(K)}_{i_{\alpha_1} i_{\alpha_2} \ldots i_{\alpha_k}} f(r_1, r_2, \ldots, r_N) = \frac{\partial^k f}{\partial r_{\alpha_1}^{i_{\alpha_1}} \partial r_{\alpha_2}^{i_{\alpha_2}} \ldots \partial r_{\alpha_k}^{i_{\alpha_k}}} \tag{21}$$

and $T^{(k)}(r_1, r_2, \ldots, r_N)$ are tensors with components defined as product of coordinates

$$T^{(k)}_{\alpha_1 \alpha_2 \ldots \alpha_k}(r_1, r_2, \ldots, r_N) = r_{\alpha_1}^{i_{\alpha_1}} r_{\alpha_2}^{i_{\alpha_2}} \ldots r_{\alpha_k}^{i_\alpha k} \tag{22}$$

with $\alpha_1, \alpha_2, \ldots, \alpha_k$ running over the indices of particles $1, 2, \ldots, N$, and with $i_\alpha = 1, 2, \ldots, n$ labeling the coordinates of the vector r_α. These coordinates can be also interpreted as monomials of kth order of no more than k of nN variables.

Because of the permutation symmetry of f (eq. (19)), the summation of (20) over all permutations $\sigma \in S^N$ and division by $N!$ allows one to write

$$
\begin{aligned}
f(\boldsymbol{r}'_1, \boldsymbol{r}'_2, \ldots, \boldsymbol{r}'_N) = & f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \\
& + \frac{1}{1!} D^{(1)} f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \left(S^{(1)}(\boldsymbol{r}'_1 - \boldsymbol{r}_1, \boldsymbol{r}'_2 - \boldsymbol{r}_2, \ldots, \boldsymbol{r}'_N - \boldsymbol{r}_N) \right) \\
& + \frac{1}{2!} D^{(2)} f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \left(S^{(2)}(\boldsymbol{r}'_1 - \boldsymbol{r}_1, \boldsymbol{r}'_2 - \boldsymbol{r}_2, \ldots, \boldsymbol{r}'_N - \boldsymbol{r}_N) \right) + \ldots \\
& + \frac{1}{k!} D^{(k)} f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \left(S^{(k)}(\boldsymbol{r}'_1 - \boldsymbol{r}_1, \boldsymbol{r}'_2 - \boldsymbol{r}_2, \ldots, \boldsymbol{r}'_N - \boldsymbol{r}_N) \right) + \ldots ,
\end{aligned} \tag{23}
$$

where $S^{(k)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ are now symmetrized tensors defined by

$$
S^{(k)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \frac{1}{N!} \sum_{\sigma \in S^N} T^{(k)}(\boldsymbol{r}_{\sigma(1)}, \boldsymbol{r}_{\sigma(2)}, \ldots, \boldsymbol{r}_{\sigma(N)}) . \tag{24}
$$

Looking carefully at the expression (23) one can recognize the more common form of polynomial series. Each term of this expansion corresponds to a polynomial, i.e. a linear combination of monomials (22), which is symmetric with respect to permutations $\sigma \in S^N$ of variables $\boldsymbol{v} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$. From a functional point of view, when one limits oneself to the study of functions defined on the configuration space $\mathrm{E} = \mathrm{R}^{nN}/S^N$ (which is equivalent to consider functions on R^{nN} satisfying (19)), then this is equivalent to the study of the algebra of symmetric tensors in R^n. The transformation rules of configurations (eqs. (4) and (5)) canonically define an action of the orthogonal group $\mathrm{O}(n)$ on this algebra. Consequently, for any subgroup G of $\mathrm{O}(n)$ one can define irreducible tensorial sets transforming with the irreducible representations of G [15]. These tensorial sets can be alternatively seen as polynomials which transform according to the irreducible representations of G. In particular, the tensorial sets (polynomials) corresponding to the identity representation are those which do not change under any transformation of G. They are called symmetric with respect to G. Those which change under some transformations are known as asymmetric components (polynomials). When the power series (23) contains exclusively polynomials corresponding to the identity representation, the function f is invariant under transformations of G. Otherwise f is called asymmetric. In particular, the behavior of any function f under rotation–reflections allows to classify these functions either as achiral or as chiral. (It should be noticed that the transformation properties of f usually depend on a particular choice of a symmetry-related reference frame.) In a small neighborhood of $\boldsymbol{v} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ the function f can be approximated by the first order (linear) term. This situation has been considered by Murray-Rust et al. [16], and recently by Auf der Heyde et al. [5b]. These authors' symmetry coordinates are simply the first-order polynomials (i.e., linear combinations) of coordinates of $\boldsymbol{v} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$.

One can also point out that the so-called degree of chirality of the first kind can be treated within the above framework. According to the definition given in ref. [9] the chirality function is a function which (1) to every configuration assigns a real number, and (2) is antisymmetric, meaning that for certain reflection plane the values assigned to every configuration and its mirror image have opposite signs. As a consequence the value assigned to every achiral configuration must be equal to zero. Hence, every polynomial satisfying the above conditions can be a chirality function. To obey the third requirement of the definition, the boundedness of the chirality function, one can simply restrict oneself to normalized configurations, i.e. configurations that correspond to vectors of a constant length in the Euclidean space R^{nN}. In general, the chirality function cannot be defined as a polynomial. However, according to the approximation theorem of Weierstrass [17] such a function can be treated as a limiting case of a sequence of polynomials defined on a compact sphere in R^{nN} or the corresponding set of orbits of S^N in R^{nN}.

5. Example and discussion

In this section we discuss some features of the degree of chirality defined in the preceding sections. We choose two ways of doing it. First, we examine a concrete configuration. Next, we make some comments concerning the problem in general.

To begin with, we choose the best examined configuration space – the configuration space of three identical particles in a plane ($N = 3, n = 2$). These three particles will be treated as vertices of a triangle. According to our definition of the degree of chirality, we are looking for a reflection line for which the distance between the initial and final (i.e. transformed via reflection about this line) configurations attains an absolute minimum. Such a line must obviously pass through the center of mass of our configuration.

Let us denote the vertices of our triangle as A_1, A_2, A_3 and let A'_1, A'_2, A'_3 be their images via reflection about a reflection line $\boldsymbol{m}$. The distance between the triangles $\Delta = \Delta(A_1A_2A_3)$ and $\Delta' = \Delta(A'_1A'_2A'_3)$ is given by

$$d(\Delta, \Delta') = \min_{\sigma \in S^3} d(\sigma)\,, \tag{25}$$

where

$$d(\sigma) = \left[|A_1A'_{\sigma(1)}|^2 + |A_2A'_{\sigma(2)}|^2 + |A_3A'_{\sigma(3)}|^2\right]^{1/2}. \tag{26}$$

Here σ runs over all permutation of indices 1, 2, 3, and $|A_iA'_j|$ stands for the distance between points A_i and A_j. The coordinates of vertices A'_i depend on the angle ϑ which determines the slope of the reflection line $\boldsymbol{m}$ in our arbitrary coordinates system with the origin coinciding with the center of mass of the configuration. Hence, the problem of finding the minimum of (25) reduces to the analysis of a periodic function depending on one variable. In order to make the results independent

of the size of the triangle, we can limit our considerations to configurations satisfying the following normalization condition:

$$|OA_1|^2 + |OA_2|^2 + |OA_3|^2 = 1\,, \tag{27}$$

where O is the center of mass of the configuration, i.e. the centroid of the triangle.

A similar normalization procedure can be applied to every configurations by replacing an arbitrary configuration $\bar{v} = S^N v$ of N particles with $\hat{\bar{v}} = S^N \hat{v}$, where $\hat{v} = v/\|v\|$. In this case the degree of chirality does not depend on the size of a particular configuration. One can also compute the degree of chirality per particle by dividing the final result by the number of particles.

The normalized triangles can be described by two independent variables defined as $p = |A_1A_2|/\sqrt{2}$ and ϕ (fig. 1). The range of the first variable, the length of the base over $\sqrt{2}$, is the interval [0, 1] with 0 and 1 corresponding to the limiting cases where $A_1 = A_2$ for $p = 0$ and A_3 lies in the middle of the interval A_1A_2 for $p = 1$. The range of the angle ϕ is $[0, \pi/2]$. This angle determines the position of A_3 with $\phi = 0$ corresponding to A_3 collinear with A_1 and A_2, and with $\phi = \pi/2$ corresponding to an isosceles triangle with $|A_1A_3| = |A_2A_3|$. The distance r between A_3 and the middle of the interval A_1A_2 is constant for a given p and can be expressed as

$$r = (3/2)(1 - p^2/2)\,. \tag{28}$$

By minimizing the expression (25) with respect to variable ϑ for every pair of parameters (p, ϕ) we can find the degree of chirality as a function of the shape of the triangle. In fig. 2 we show how the domain of this function is divided into several

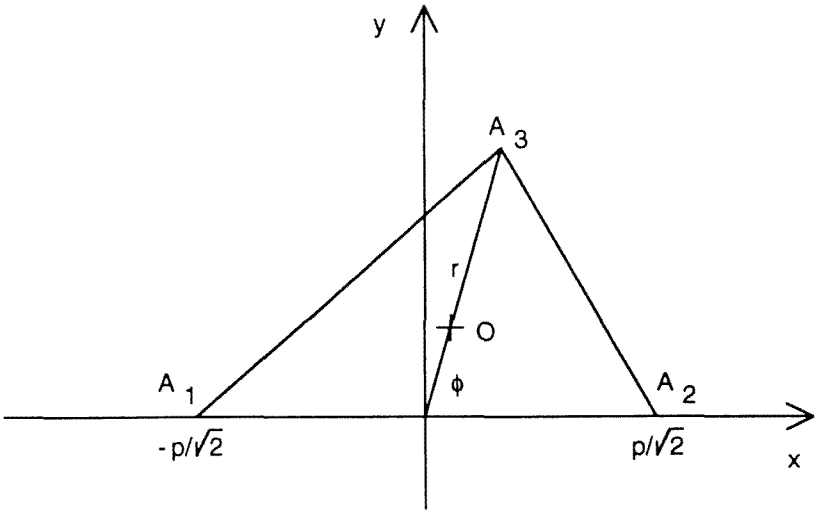

Fig. 1. Parametrization (p, ϕ) of a triangle $A_1A_2A_3$. The third parameter r can be computed from p and ϕ using eq. (28).

areas, where the minimum corresponds to one of four different permutations $\sigma = (123), (132), (321)$ or (213). It is quite clear that if the vertices A_1, A_2, and A_3 are collinear ($\phi = 0$), then the degree of chirality coincides with the minimum of $d(123)$. Only in the case of a triangle with A_2 lying in the middle of the interval A_1A_3 ($x = 1/2$) or with $A_2 = A_3$ ($x = \sqrt{3}/2$), we find that $d(123)$ is identical to $d(321)$ or to $d(132)$, respectively. At the other edge of the domain of ϕ ($\phi = \pi/2$), which corresponds to an isosceles triangle with equal lengths of A_1A_3 and A_2A_3, we find that the minimum of the degree of chirality is the minimum of $d(213)$. The only situation when $d(213)$ is equal to $d(132)$ and to $d(321)$ occurs for the equilateral triangle with ($x = 1/\sqrt{2}$).

The most chiral triangle with $d(\Delta, \Delta') = d(123) = d(213) = d(321) \approx 0.459$ is obtained for $\phi = \pi/4$ and $x = 1/3$. This result corresponds to the triangle with angles 37.8°, 125.4°, and 16.8°. Thus, our most chiral triangle differs from that defined by the chirality product [5a] or the overlap measure [6], which lead to the conclusion that the most chiral triangle is flat. On the other hand, our result is parallel to that obtained using the Hausdorff chirality measure. As was shown in [9], the most chiral triangle for that measure is defined by the angles 44.2°, 114.3°, and 21.5°. Hence, in both cases the most chiral triangles are non-degenerate triangles.

The fact that the most chiral triangle is not flat results from that the distance $d(123)$ was taken into account in the definition of $d(\Delta, \Delta')$ (eq. (25)). This distance

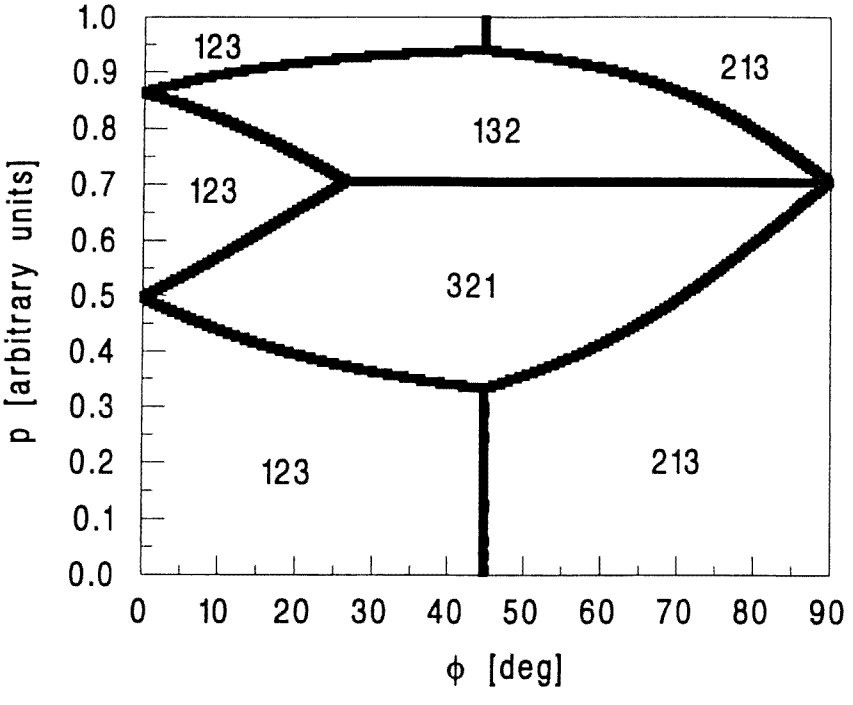

Fig. 2. The partition of the domain of parametrization (p, ϕ) of triangles into areas where the degree of chirality corresponds to the minimum of the indicated function $d(\sigma)$.

tends to zero for every configuration approaching collinear arrangement of vertices. This fact is in agreement with our intuition, since we are used to considering every k-dimensional configuration embodied in an n-dimensional space (the dimension of the space is defined by the rotations) with $n > k$ as achiral. It is an interesting observation that the minimizing of $d(123)$ itself is equivalent to the least-squares problem as applied to a linear regression analysis. This observation can be generalized to other configuration as well as to every distance $d(\sigma)$ with $\sigma \in S^N$.

The degree of chirality obviously depends on the definition of the distance in the configuration space (see ref. [9] for a review). On the other hand, every distance function classifies the configurations as chiral or achiral exactly in the same way because by its definition [18a], this distance is zero if and only if the initial and transformed configurations are identical (superimposed). This implies that chirality is not a metric property. But it also does not depend on the particular topology of the configuration space unless we shall consider some non-metrizable topologies which do not satisfy the Hausdorff separability axiom. (A topological space is said to satisfy the Hausdorff separability axiom if and only if to every pair of distinct points there are two disjoint neighborhoods of each point [18b].) We are not going to consider these herein. Nevertheless, the distance function and the induced topology of the configuration space are vital for the determination of the degree of chirality of chiral objects.

However, let us point out that this is not only the topology of the configuration space E which is relevant to the problem. Here the most important role is played by the topological properties of the orthogonal group $O(n)$, namely by the fact that this group can be defined as a direct product [19] of two compact groups – the special orthogonal group $\mathrm{SO}(n)$ and a group $\boldsymbol{\Sigma}$ consisting of two elements: the identity transformation E and a reflection plane Σ. Consequently, the direct product $\mathrm{SO}(n) \times \boldsymbol{\Sigma}$ consists of two connected components [18b]; the special orthogonal group $\mathrm{SO}(n)$ and its coset $\Sigma\ \mathrm{SO}(n) = \mathrm{SO}(n)\Sigma$.

The topological background of the notion of chirality lies in that the objects are called chiral if their initial and reflected configurations are always isolated points of the configuration space. In metric spaces such points are always separated by a non-zero distance. Because proper and improper rotations belong to different connected components of $\mathrm{O}(n)$, it is not surprising that some objects are chiral, i.e., it is not surprising that if they are transformed by reflections, they cannot by superimposed using only proper rotations.

As was shown in section 3, symmetry transformations other than the mirror reflection or rotation–reflection can also be studied, although the information we can retrieve in this case differs in the topological character from that discussed above. Sometimes we can ask questions of the type: how far a triangle is from having a fourfold symmetry axis, or from being isotropic. The answer to this kind of problem can be important, since certain measurable properties of a system of particles can exhibit symmetry much higher than that resulting from the symmetry of the configuration.

To summarize the present study, we shall formulate an abstract version of the chirality as we see it in the context of our present work.

(1) Take a Hausdorff topological space E to be a configuration space.
(2) Take a connected group O and a finite group **F**, with no common element besides the identity transformation, both acting continuously on E.
(3) Take the direct product $O \times \mathbf{F}$ and choose **F** (or any other subset of $O \times \mathbf{F}$) to be the considered set of symmetry transformations.
(4) Transform configurations of E using the transformations chosen in (3) and check which can be superimposed with its images, using transformations of O.

In order to consider configurations of many different types of particles, the easiest way is to deal with each subconfiguration, composed only of identical particles, separately as outlined in the preceding section, and in the next step to combine the results obtained for each configuration. This procedure is quite simple if the symmetry reference systems are the same for every configuration. However, such situations are rather rare. They are possible for complexes with the central metal ion placed at the mass center of identical ligands of high symmetry, where the origin of the symmetry reference system is always assumed to coincide with the position of this ion, as discussed by King [4]. His method also applies to different ligands and is equivalent to the proposed decomposition of the entire configuration into fully symmetric subconfigurations. One major problem to be reconsidered in the general case is the choice of appropriate coordinate axes of the symmetry reference system so that the sum of contributing distances will be minimal. The choice optimized for one subconfiguration may not be suitable for another one. Therefore, one has to decide which contribution to the degree of chirality should be minimized more efficiently than others. In other words, one has to assign weighting factors to the degree of chirality of every subconfiguration. Finally, the last aspect we are going to point out is that there is another possibility of interpreting the configurations of identical particles. These can be efficiently described as sums of atomic measures (or δ-distributions) which can be treated as elements of the Banach space of bounded measures (or Fréchet space of distributions). From this point of view, one can take into account a much more general situation including continual configurations described by continuous measures (or distributions). However, the study of these advanced generalizations is out of the range and intention of this paper and will be continued in the future.

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