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On chiral pathways in E^n: a dimensional analysis

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Summary. A dimensional analysis shows that all chiral labeled and unlabeled simplexes in E^2, and all maximally labeled simplexes in higher dimensions, are unique in that they can be partitioned into disjoint heterochiral sets. Such partition is impossible for all other labeled and unlabeled m-point sets ($m \geqslant n + 2$) in E^n, since they and their enantiomorphs are chirally connected.

Key words: Chirality – Chiral pathways – Homochirality

Introduction

With the reference to his models of chiral molecules, Ruch [1] has pointed out that there are two classes of chiral subsets: those in which the path of continuous deformations that connects two enantiomorphs necessarily requires the passage through an achiral form (class a), and those in which this requirement need not to be met (class b). In class a, the set of achiral models forms the boundary between the chiral subsets, and it is therefore meaningful to assign to all models in each subset a common descriptor, indicative of their shared sense of chirality, such as "right-handed" for one subset and "left-handed" for the other. Any two models that belong to a given subset may be termed "homochiral" and any two models that belong to different subsets "heterochiral". In class b, there is no such boundary, and therefore the "homochiral"–"heterochiral" terminology is meaningless for members of class b. Since labeled point sets represent the simplest models for molecular systems, it is important to know, in the context of chirality, if such sets can be separated into homochirality classes.

It had previously been found for *unlabeled* tetrahedra [2], and was later shown for unlabeled (or, equivalently, *uniformly labeled*) simplexes in higher dimensions [3], that chiral simplexes in E^n ($n \geqslant 3$) and their enantiomorphs are chirally connected and therefore cannot be partitioned into heterochiral "left-handed" and "right-handed" subsets. It immediately follows from this result that any unlabeled chiral m-point set ($m \geqslant n + 2$) in E^n is also chirally connected to its enantiomorph.

At the same time, *maximally labeled* (i.e. with all points labeled differently) tetrahedra [4] and, similarly, maximally labeled simplexes in higher dimensions [5] cannot be transformed continuously into their mirror images without passing through achiral intermediates. The present work extends the dimensional analysis of Ref. [3] to a general case, which includes the limiting cases of uniformly and maximally labeled sets, as well as all intermediate cases of sets with at least two identically labeled points.

Dimensional analysis

Consider an m-point set X_m in an n-dimensional space ($m > n$). One needs nm coordinates to describe this set. If we do not distinguish between sets related by isometries, we have to subtract n degrees of freedom for translations and $n(n-1)/2$ degrees of freedom for rotations. The dimension of the resulting space Ω_m^n of sets X_m is

$$\dim(\Omega_m^n) = n(2m - n - 1)/2. \tag{1}$$

If X_m is an achiral set, its points can be subdivided into two subsets: $m - 2k$ independent points lying in an $(n-1)$-dimensional hyperplane of symmetry H, and $2k$ symmetry-related points ($k \leqslant m/2$) lying outside H. We denote such sets $X_{m,k}$. Every pair of symmetry-related points of $X_{m,k}$ is fully described by their common projection on H and their distance from H. Therefore, the achiral set can be represented by its $(m-k)$-point projection on H and k distances from H to symmetry-related points. Accordingly, the dimension of the space $\Sigma_{m,k}^n$ of achiral sets $X_{m,k}$ is

$$\dim(\Sigma_{m,k}^n) = \dim(\Omega_{m-k}^{n-1}) + k$$

or, with Eq. (1) in mind,

$$\dim(\Sigma_{m,k}^n) = (n-1)(2m-n)/2 - (n-2)k. \tag{2}$$

It follows from Eq. (2) that for $n \geqslant 3$ the highest dimension of $\Sigma_{m,k}^n$ is reached when $k = 0$

$$\dim(\Sigma_{m,0}^n) = (n-1)(2m-n)/2.$$

The difference in dimensions of the full space Ω_m^n and its maximum-dimensional achiral subspace $\Sigma_{m,0}^n = \Omega_m^{n-1}$ is thus

$$\dim(\Omega_m^n) - \dim(\Sigma_{m,0}^n) = m - n. \tag{3}$$

For $m \geqslant n + 2$ the difference in the dimensions of Ω_m^n and $\Sigma_{m,0}^n$ exceeds 1, and hence $\Sigma_{m,0}^n$ cannot separate Ω_m^n into two disjoint subsets. Thus, *independently of how the sets X_n are labeled, any two m-point sets, and hence any two m-point enantiomorphs* ($m \geqslant n + 2$), *are chirally connected in E^n.*

If $m = n + 1$, the difference in the dimensions of Ω_m^n and $\Sigma_{m,0}^n$ is 1 and hence $\Sigma_{m,0}^n$ *does* separate Ω_m^n into two disjoint subsets, Ω_m^{n+} and Ω_m^{n-}. Clearly, if a chiral set X_m belongs to Ω_m^{n+}, one can find its enantiomorph $\bar{X}_m$ in Ω_m^{n-}. If a chiral set X_m is maximally labeled, E^n contains no duplicates of it except for those related to X_m by isometries. Therefore, X_m and its enantiomorph $\bar{X}_m$ are *unique* in Ω_m^n and for this reason must belong to different subsets Ω_m^{n+} and Ω_m^{n-}. This means that any path connecting X_m to $\bar{X}_m$ has to pass through some achiral configuration $X_{m,0} \in \Sigma_{m,0}^n$.

The situation is different if a chiral set X_m is uniformly or submaximally labeled. In these cases there are at least two identical points in X_m and their permutation will produce a duplicate of X_m *not related* to the original by an isometry. As a result, Ω_m^n contains more than one copy of X_m. These two copies belong to different subsets, Ω_m^{n+} and Ω_m^{n-}. Indeed, if x^+ and x^- are identical points of X_m and $x_0 = (x^+ + x^-)/2$ is a midpoint on the line connecting x^+ and x^-, one can choose the hyperplane H to pass through the other points of X_m and x_0, and define Ω_m^{n+} as a set of X_m with x^+ on one side of H and Ω_m^{n-} as a set of X_m with x^+ on the other side. Obviously, if x^+ is on one side of H before its permutation with x^-, it ends up on the other side after the permutation.

Since two copies of X_m belong to different subsets Ω_m^{n+} and Ω_m^{n-} and the same is true for $\bar{X}_m$, X_m and $\bar{X}_m$ both belong to the same subset, say, Ω_m^{n+}. By definition, Ω_m^{n+} does not overlap with the maximum-dimensional achiral space $\Sigma_{m,0}^n$, and can therefore have nonempty intersections only with lower-dimensional achiral spaces $\Sigma_{m,k}^n (k \geqslant 1)$. According to Eq. (2), the maximum dimension of such spaces is reached when $k = 1$ and equals

$$\dim(\Sigma_{m,1}^n) = (n-1)(2m-n)/2 - (n-2)$$

which, subtracted from Eq. (1), gives

$$\dim(\Omega_m^n) - \dim(\Sigma_{m,1}^n) = m - 2.$$

For simplexes, $m = n + 1$ and hence the difference in dimensions is

$$\dim(\Omega_{n+1}^n) - \dim(\Sigma_{n+1,1}^n) = n - 1.$$

This difference is equal to unity only when $n = 2$, which means that of all uniformly and submaximally labeled chiral simplexes only triangles, the simplexes in E^2, can be partitioned into heterochiral sets, in agreement with our earlier finding [3].

The overall conclusion is that chiral triangles (no matter how labeled) in E^2 and maximally labeled chiral simplexes in higher dimensions are unique in that they alone allow a partition into heterochiral sets. Such a partition is impossible for all other chiral labeled and unlabeled m-point sets in E^n because they and their enantiomorphs are chirally connected.

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