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About second kind continuous chirality measures. 1. Planar sets

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The chirality index of a d-dimensional set of n points is defined as the sum of the n squared distances between the vertices of the set and those of its inverted image, normalized to $4T/d$, T being the inertia of the set. The index is computed after minimization of the sum of the squared distances with respect to all rotations and translations and all permutations between equivalent vertices. The properties of the chiral index are examined for planar sets. The most achiral triangles are obtained analytically for all equivalence situations: one, two, and three equivalent vertices. These triangles are different from those obtained by Weinberg and Mislow with distance functions.

1. Introduction

Continuous chirality measures are being increasingly used in physical organic chemistry [2,6–9,12] and various theoretical studies on continuous chirality have been performed [1,3–5,10,13,15–19]. Two kinds of chirality measures are usually considered: the set is compared to an achiral reference one (first kind), or is compared to its inverted image (second kind). For the latter, it is obvious that any similarity index between two compounds can be used as a chiral index, the second compound being an enantiomer of the first one. Thus, there are potentially many second kind chiral indices [11].

One of the simplest ones is obtained when the optimal superposition of the enantiomers is measured with the minimized sum of the n squared distances between the vertices of the set and its inverted image, the minimization being performed with respect to all rotations and translations. Although this approach is acceptable when all vertices are unequivalent (i.e., each vertex has one color and all the n colors are different), it must be modified if at least two vertices have the same colour. For example, the bromochloromethane $CBrClH_2$ has five atoms, and among them two are chemically equivalent, namely, the hydrogens Ha and Hb. Superimposing the two enantiomers with the trivial correspondence $C \leftrightarrow C'$, $Br \leftrightarrow Br'$, $Cl \leftrightarrow Cl'$, $Ha \leftrightarrow Ha'$ and $Hb \leftrightarrow Hb'$ cannot lead to a null sum of squared distances even if the conformer is perfectly achiral. However, modifying the correspondence such that $Ha \leftrightarrow Hb'$ and

Hb $\leftrightarrow$ Ha$'$ leads indeed to a null sum of squared distances for a perfectly achiral conformer. Thus the sum of the squared distances must be minimized for all rotations and translations and all allowed permutations.

In order to have a chiral index not depending on the size of the system, the minimized sum of the squares is normalized to $4T/d$, T being the inertia of the set and d being the space dimension.

2. Notations and general properties

Let X_0 and X_1 be two n rows and d columns arrays of coordinates. X_0 is the fixed set and X_1 is to move. The quote will denote the transposition operator. All vectors are assumed to be written as one column matrices. The trace and the determinant operators will be denoted Tr and Det, respectively. Let D^2 be the sum of the squared distances and Y_1 be the rotated and translated image of X_1. We have $D^2 = \mathrm{Tr}((X_0 - Y_1)(X_0 - Y_1)')$. As well known, the minimized D^2 for rotation plus translation is obtained when both X_0 and X_1 are centered before computing the optimal rotation, and this remains true when X_1 is an inverted image of X_0. Thus, translations will be no longer considered, and the centering condition will not be assumed unless otherwise mentioned. When needed, this centering condition will be written $1'X_0 = 0$ and $1'X_1 = 0$, 0 being a n rows and d columns matrix, and 1 being the d-dimensional vector containing all elements equal to 1. It will be clear from the context than this vector cannot be confused with the real value 1. The following matrices will be used: $V_{00} = X_0'X_0$, $V_{11} = X_1'X_1$, $V_{10} = X_1'X_0$ and $V_{01} = V_{10}'$. Let $T = (T_0 + T_1)/2$ with $T_0 = \mathrm{Tr}(V_{00})$ and $T_1 = \mathrm{Tr}(V_{11})$ being the respective inertia of X_0 and X_1, reducing to the usual inertia when the arrays are centered. The identity matrix is I, and R is a rotation matrix, such that $Y_1 = X_1R'$.

The correspondence between X_0 and X_1 will be handled via an n-dimensional square permutation matrix P. Let $Z_1 = PY_1$. When X_1 is the inverted image of X_0 and when the centering condition is true, the chiral index is

$$\mathrm{Chi} = D^2/(4T/d) \tag{1}$$

with $D^2 = \mathrm{Tr}((X_0 - PX_1R')(X_0 - PX_1R')')$ being minimized over all rotations R and allowed permutations P.

The number of allowed permutations being finite, the continuity of the chiral index for X_0 is deduced from the continuity properties of the trace operator.

Writing

$$D^2 = \mathrm{Tr}\big(X_0'X_0\big) + \mathrm{Tr}\big(Z_1'Z_1\big) - 2\,\mathrm{Tr}\big(Z_1'X_0\big) = 2T - 2\,\mathrm{Tr}\big(Z_1'X_0\big)$$

and remembering that $\mathrm{Tr}(Z_1'X_0)$ is a scalar product for the (n,d) matrices vector subspace, it comes that $\mathrm{Tr}(Z_1'X_0)$ takes values over $[-T;T]$, then D^2 takes values over $[0;4T]$. But, the trivial permutation $P = I$ is always allowed, and the minimized D^2 cannot exceed the D^2 value obtained for both $P = I$ and $R = I$, which is

$\mathrm{Tr}((X_0 - X_1)(X_0 - X_1)') = 2T - 2\,\mathrm{Tr}(X_1' X_0)$. Assuming now that X_0 is in its principal components axis (i.e., V_{00} is diagonal) and that X_1 is generated from X_0 with replacing one of its column by its opposite, this column being associated to the smallest eigenvalue of V_{00}. Thus, $L(1), L(2), \ldots, L(d)$ being the common eigenvalues of V_{00} and V_{11} arranged in decreasing order, then

$$\mathrm{Tr}\big(X_1' X_0\big) = L(1) + L(2) + \cdots + L(d-1) - L(d) \quad \text{and}$$
$$D^2 = 2T - 2\,\mathrm{Tr}\big(X_1' X_0\big) = 4L(d).$$

D^2/T is a monotonic function of $L(d)$, which is maximized when all eigenvalues are equal to T/d. Thus D^2/T is upper bounded by $4/d$, the minimized D^2 varies over $[0; 4T/d]$ and Chi varies over $[0; 1]$, the zero value corresponding to an achiral compound perfectly superimposed to its inverted image. Monodimensional sets are examined in appendix 1.

All subsequent sections involve planar sets, i.e., $d = 2$ and Chi $= D^2/(2T)$.

3. The optimal rotation for planar sets

In this section, the centering condition is not assumed, and X_1 is not an inverted image of X_0. Although previously established [14], the optimal rotation has to be rewritten in matricial form. The identity permutation $P = I$ is assumed, but the final result will be valid for any P with by replacing X_1 by PX_1.

The base vectors are $e_1' = (1, 0)$ and $e_0' = (0, 1)$, and we define $\Pi = e_2 e_1' - e_1 e_2'$, which is the rotation matrix of angle $+90°$, mapping any vector to its direct orthogonal image. A general rotation R of angle r can be written $R = I\cos(r) + \Pi\sin(r)$. Let be $C = \mathrm{Tr}(V_{10})$, $S = \mathrm{Tr}(\Pi V_{10})$ and E being the square root of $C^2 + S^2$, which means that

$$E^2 = \mathrm{Tr}\big(V_{10} V_{10}'\big) + 2\,\mathrm{Det}(V_{10}). \tag{2}$$

We have

$$D^2 = \mathrm{Tr}\big(\big(X_0 - X_1 R'\big)\big(X_0 - X_1 R'\big)'\big) = \mathrm{Tr}\big(\big(X_0 - X_1 R'\big)'\big(X_0 - X_1 R'\big)\big).$$

Thus, $D^2 = 2T - 2C\cos(r) - 2S\sin(r)$, r being the unknown variable. The first derivative is $\mathrm{grad}(D^2) = 2C\sin(r) - 2S\cos(r)$ and the second derivative is $\mathrm{Hess}(D^2) = 2C\cos(r) + 2S\sin(r)$. The minimum is obtained when $\cos(r) = C/E$ and $\sin(r) = S/E$, with $D^2 = 2(T - E)$ and $\mathrm{Hess}(D^2) = 2E$. The maximum is obtained when $\cos(r) = -C/E$ and $\sin(r) = -S/E$, with $D^2 = 2(T + E)$ and $\mathrm{Hess}(D^2) = -2E$. Both stationary points are reached when $\mathrm{tg}(r) = S/C$. When $C = S = 0$, D^2 is constant for all R.

The minimized sum of squared distances is thus

$$D^2 = 2(T - E). \tag{3}$$

This sum ranges from 0 to $2T$, and $D^2/(2T)$ ranges from 0 to 1.

4. Existence of a symmetry axis

In this section, the centering condition is not assumed, and X_1 is an inverted image of X_0 generated by an orthogonal transformation Q, i.e., $X_1 = X_0Q'$, with Det$(Q) = -1$. The correspondence between X_0 and X_1 is not used, thus $P = I$ is assumed. X_1 is rotated, but the rotation matrix R is not assumed to have any optimality property.

Let us consider the matrix $RQ(e_2e_2' - e_1e_1')$. This a rotation matrix because $e_2e_2' - e_1e_1'$ is an orthogonal matrix with negative determinant. Let r be the angle associated to $RQ(e_2e_2' - e_1e_1')$, and v be the unit vector: $v' = (\cos(r/2), \sin(r/2))$. The matrix $I - 2vv'$ is that of a symmetry operator, v being normal to the symmetry axis. We have

$$X_1R'(I - 2vv')' = X_0\big(e_2e_2' - e_1e_1'\big)\big(e_2e_2' - e_1e_1'\big)'Q'R'(I - 2vv').$$

Expressing the elements of $I - 2vv'$ with $\sin(r)$ and $\cos(r)$, it comes that

$$\big(RQ\big(e_2e_2' - e_1e_1'\big)\big)'(I - 2vv') = \big(e_2e_2' - e_1e_1'\big)'$$

and then $X_1R'(I - 2vv')' = X_0$, meaning that X_0 and X_1R' are symmetrical.

This can be also prooved using Πv instead of v and r being the angle associated to $RQ(e_1e_1' - e_2e_2')$ rather to $RQ(e_2e_2' - e_1e_1')$.

The existence of a symmetry axis is thus a general property, which has nothing to deal with optimality conditions. However, the symmetry can be destroyed if translations are involved, but that does not arise when both X_0 and X_1 are centered.

5. The optimal rotation for enantiomers

In this section, the centering condition is not assumed, and X_1 is an inverted image of X_0 generated by an orthogonal transformation Q: $X_1 = X_0Q'$ and Det$(Q) = -1$. The rotation R is the optimal one established in section 3, and is parametrized by the permutation matrix associated to one correspondence between X_0 and X_1, i.e., $X_1 = PX_0Q'$ and $V_{10} = QX_0'P'X_0$.

For simplification, X_0 is now noted X.

Using equation (2) from section 3, we get the expression of E^2:

$$E^2 = \mathrm{Tr}\big((QX'P'X)(QX'P'X)'\big) + 2\,\mathrm{Det}(QX'P'X),$$

from which

$$E^2 = \mathrm{Tr}(X'P'XX'PX) - 2\,\mathrm{Det}(X'PX). \tag{4}$$

Then, x and y being, respectively, the first and second column of X,

$$E^2 = (x'Px - y'Py)^2 + (x'Py + y'Px)^2. \tag{5}$$

Setting $M = (P + P')/2$, we get

$$E^2 = \big((x + y)'M(x - y)\big)^2 - 4(x'My)^2,$$

and then

$$E^2 = (x'Mx + y'My)^2 - 4\big((x'Mx)(y'My) - (x'My)(y'Mx)\big)^2,$$

which can be written as

$$E^2 = \big(\operatorname{Tr}(X'MX)\big)^2 - 4\operatorname{Det}(X'MX) \tag{6}$$

or, alternatively, $L(1)$ and $L(2)$ being the eigenvalues of the symmetric matrix $X'MX$ arranged in decreasing order:

$$E = L(1) - L(2). \tag{7}$$

As seen in equation (3), the optimal sum of squared distances for a given set X is $D^2 = 2(T - E)$. Equation (7) means that, for a given permutation P, it depends only on the difference of the eigenvalues of $X'MX$. When all allowed permutations are considered, it is needed to keep the one such $L(1) - L(2)$ is the largest. It should be also noted that E depends on $M = (P + P')/2$ rather than P.

6. The extremal values reached for a fixed permutation

All the conditions of the preceding section are assumed to stand. Only one permutation P is considered: P is a parameter and X is the variable.

From equation (3), we know that the extrema of $D^2/(2T)$ are those of E/T, or alternatively, are those $(T - E)/(T + E)$, which is the ratio of the minimized sum of squared distances to the maximized sum of squared distances (see section 3). For simplicity, E^2/T^2 will be considered. Expanding equation (6) gives

$$E^2 = (x'Mx - y'My)^2 + 4(x'My)^2, \tag{8}$$

then

$$E^2/T^2 = \big((x'Mx - y'My)^2 + 4(x'My)^2\big)/(x'x + y'y)^2. \tag{9}$$

This function has all derivatives continuous, except for $T = 0$ which is equivalent to $X = 0$ and has no interest. The extrema can be reached by computing the gradient, which can be splitted in two parts: one related to the derivation for x variable, and the other for y variable. Setting the two parts to zero and dividing by $4T$ leads to

$$T\big((x'Mx - y'My)Mx + 2(x'My)My\big) - E^2x = 0, \tag{10}$$

$$T\big((y'My - x'Mx)My + 2(x'My)Mx\big) - E^2y = 0. \tag{11}$$

Multiplying (10) by $(Mx)'$ and (11) by $(My)'$ and substracting the two resulting equations leads to

$$(x'Mx - y'My)\big(T(x'M'Mx + y'M'My) - E^2\big) = 0. \tag{12}$$

Multiplying (10) by $(My)'$ and (11) by $(Mx)'$ and adding the two resulting equations leads to

$$(x'My)\big(T(x'M'Mx + y'M'My) - E^2\big) = 0. \tag{13}$$

Looking at both equations (12) and (13), either $x'Mx - y'My = 0$ and $x'My = 0$, or $T(x'M'Mx + y'M'My) = E^2$.

The first situation means that $X'MX$ is proportional to the identity matrix, and is such that $E = 0$ and $D^2 = 2T$, corresponding to the absolute maximum of $D^2/(2T)$.

The second situation can be further explicited when P is a symmetric permutation, i.e., $P = P' = M$. The condition $T(x'M'Mx + y'M'My) = E^2$ reduces to $T^2 = E^2$, then $D^2 = 0$, which corresponds to a perfect alignment.

7. The most achiral triangles

The centering condition is now assumed to be satisfied, and the inverted image of X is again generated by an orthogonal transformation with negative determinant. All allowed permutations P are considered. For each permutation, D has been minimized with the optimal rotation established in section 3. For a given set X, the chiral index Chi $= D^2/(2T)$ is then the smallest value of $D^2/(2T)$ among all allowed permutations.

As mentioned in the previous section, $D^2/(2T)$ has all continuous derivatives (except for $X = 0$) when the permutation is fixed, and T does not depend on this permutation.

The set X is now variable. The maxima of Chi are thus located either among those of $D^2/(2T)$ for individual permutations, or are located at singularities occurring when $D^2/(2T)$ takes the same value for at least two permutations.

Only triangles are now considered: $n = 3$. There is only three situations: all vertices are unequivalent, or two vertices are equivalent, or all three vertices are equivalent.

7.1. All vertices are unequivalent

There is only one allowed permutation: $P = I$. We have also $M = P = P' = I$. Using the result of section 6, there is two situations for the extrema: either $E = 0$ and $X'X$ is proportional to the identity matrix, or $T^2 = E^2$ and $D^2 = 0$ which corresponds to a perfect alignment – this is an absolute minimum of Chi, not a maximum.

The absolute maximum is such that $X'X$ is proportional to I, and Chi $= 1$. It is reached only by an equilateral triangle – see appendix 2.

7.2. Two equivalent vertices

We assume that the equivalent vertices are labelled 2 and 3. There is two allowed permutations: I and P, P being a symmetric matrix such that $P(1,1) = P(2,3) = P(3,2) = 1$, all the 6 other elements being zero. The maximum of $D^2/(2T)$ for the identity permutation is, as shown in subsection 7.1, reached by an equilateral triangle, but this latter is perfectly superimposed on itself when the correspondence is P: $D = 0$ and Chi $= 0$. This is an absolute minimum of Chi, not a maximum. The extremum of $D^2/(2T)$ for the symmetric permutation P is, accordingly to the results of section 7, either such that $X'MX$ is proportional to I, or is such that $D = 0$, corresponding to a perfect alignment.

Let us look at the situation where

$$X'MX = (x'Mx)I = (y'My)I.$$

We define the 3 rows and 3 columns square matrix W such that its first column contains the vector 1 and such that the remaining block contains X. We note that $M = P = P'$ and that 1 is an eigenvector of $M = P$: $M1 = 1$. The centering condition $1'X = 0$ shows that $W'MW$ is a diagonal matrix with determinant equal to $(1'M1)(x'Mx)(y'My) = 3(x'Mx)^2$. But this determinant is also equal to $\mathrm{Det}(W')\,\mathrm{Det}(M)\,\mathrm{Det}(W) = -(\mathrm{Det}(W))^2$ because $\mathrm{Det}(P) = -1$. The only possible sign for this determinant is thus zero, which means that $X'MX = 0$ and also that $\mathrm{Det}(W) = 0$. But $\mathrm{Det}(W)$ is twice the signed area of X, then X is not a two-rank matrix: the points are aligned, and they should lead to a perfect superposition when the identity permutation is used.

Thus the maximum of Chi can be located only at singularities occurring when $D^2/(2T)$ takes the same value for the two permutations.

The symmetric matrix P has an orthonormal basis of eigenvectors

$$u_1' = (1,0,0), \quad u_2' = \big(0, 2^{1/2}/2, 2^{1/2}/2\big) \quad \text{and} \quad u_3' = \big(0, 2^{1/2}/2, -2^{1/2}/2\big),$$

associated to the respective eigenvalues $1, 1$ and -1. The two columns of X can be expressed in this orthonormal basis:

$$X = u_1 a_1' + u_2 a_2' + u_3 a_3', \tag{14}$$

a_1, a_2 and a_3 being the unknown bicomponents vectors. Thus, we have

$$X'X = a_1 a_1' + a_2 a_2' + a_3 a_3' \quad \text{and} \quad X'PX = a_1 a_1' + a_2 a_2' - a_3 a_3'.$$

The centering condition is $X'1 = 0$. Thus,

$$a_1 + 2^{1/2} a_2 = 0. \tag{15}$$

Reporting in the expressions of X, $X'X$ and $X'PX$ leads to

$$X'X = 3a_2 a_2' + a_3 a_3', \tag{16}$$

$$X'PX = 3a_2 a_2' - a_3 a_3'. \tag{17}$$

The vector a_2 is not null, because, from (15) we would get $a_1 = 0$, and from the centering condition, $a_3 = 0$ then $X = 0$. Setting the equality of $D^2/(2T)$ for the two permutations is equivalent to set the equality of the two E^2 values. Using equation (6), we have

$$\big(\mathrm{Tr}(X'X)\big)^2 - 4\,\mathrm{Det}(X'X) = \big(\mathrm{Tr}(X'PX)\big)^2 - 4\,\mathrm{Det}(X'PX). \tag{18}$$

Expanding (18) with the expressions get in equations (16) and (17), and after some simplifications, it yields

$$\big(a_3'a_2\big)^2 = \big(a_3'\Pi a_2\big)^2. \tag{19}$$

The sum of the two members of equation (19) is $(a_2'a_2)(a_3'a_3)$. Equation (19) can be understood as the equality between the squared sinus and the squared cosinus of the vectors a_2 and a_3. It can be explicited as follows. The vectors a_2 and Πa_2 are orthogonal and non-null, thus a_3 is expressable as a linear combination of them: $a_3 = ba_2 + c\Pi a_2$. Reporting that in (18) gives $b^2(a_2'a_2)^2 = c^2(a_2'a_2)^2$, and then $c = sb$, with $s = \pm 1$. Then

$$a_3'a_3 = (ba_2 + sb\Pi a_2)'(ba_2 + sb\Pi a_2) = 2b^2 a_2'a_2,$$

i.e., $a_3'a_3 = 2b^2a_2'a_2$. We define k as the ratio of the norm of a_3 to that of a_2:

$$K = \big(a_3'a_3\big)/\big(a_2'a_2\big) \quad \text{and} \quad k = K^{1/2}. \tag{20}$$

Then we have $2b^2 = K$ and $b = \pm k2^{1/2}/2$, and

$$a_3 = \pm k\big(2^{1/2}/2\big)(a_2 + s\Pi a_2). \tag{21}$$

Substituting (21) in (16) and (17),

$$X'X = 3a_2a_2' + (K/2)\big(a_2a_2' + \Pi a_2a_2'\Pi' + s\Pi a_2a_2' + sa_2a_2'\Pi'\big), \tag{22}$$

$$X'PX = 3a_2a_2' - (K/2)\big(a_2a_2' + \Pi a_2a_2'\Pi' + s\Pi a_2a_2' + sa_2a_2'\Pi'\big). \tag{23}$$

The traces are

$$\mathrm{Tr}(X'X) = (3 + K)\big(a_2'a_2\big), \tag{24}$$

$$\mathrm{Tr}(X'PX) = (3 - K)\big(a_2'a_2\big). \tag{25}$$

The determinant is obtained from the square matrix W introduced previously, containing the 1 vector as first column, and X as the remaining block. From the centering condition $1'X = 0$, we see that $W'PW$ is a block-diagonal matrix, one containing the real value 3 as single element, and the other containing $X'PX$. Remembering that $\mathrm{Det}(P) = -1$, we get

$$\mathrm{Det}(W'PW) = -\big(\mathrm{Det}(W)\big)^2 = 3\,\mathrm{Det}(X'PX).$$

Similarly, $\mathrm{Det}(W'IW) = (\mathrm{Det}(W))^2 = 3\,\mathrm{Det}(X'X)$, and thus

$$\mathrm{Det}(X'PX) = -\,\mathrm{Det}(X'X). \tag{26}$$

Substituting (24)–(26) in (18) gives

$$(3+K)\left(a_2' a_2\right)^2 - 4\,\mathrm{Det}(X'X) = (3-K)\left(a_2' a_2\right)^2 + 4\,\mathrm{Det}(X'X),$$

and we get the determinant

$$\mathrm{Det}(X'X) = (3/2)K\left(a_2' a_2\right)^2. \tag{27}$$

The final common E^2 expression is, using (27) with (24) or (25),

$$E^2 = \left(9+K^2\right)\left(a_2' a_2\right)^2. \tag{28}$$

And because $T = \mathrm{Tr}(X'X)$,

$$E^2/T^2 = \left(9+K^2\right)/(3+K)^2, \tag{29}$$

and, from equation (3),

$$D^2/2T = 1 - \left(9+K^2\right)^{1/2}/(3+K). \tag{30}$$

There is no more constraint: k is a free parameter. The coordinates of this family of triangles is obtained by substituting (15) and (21) in (14):

$$X = -2^{1/2}u_1 a_2' + u_2 a_2' \pm k\left(2^{1/2}/2\right)u_3(a_2 + s\Pi a_2)'. \tag{31}$$

The shape of any triangle of this family does not depend on the orientation of X. Applying a rotation R to X, and from the commutativity of the product $\Pi R = R\Pi$, we get

$$X = -2^{1/2}u_1(Ra_2)' + u_2(Ra_2)' \pm k\left(2^{1/2}/2\right)u_3\left((I+s\Pi)(Ra_2)\right)'.$$

The rotation being free, any orientation of the vector Ra_2 can be selected whithout shape modification, and the normalization of a_2 acts as a size parameter. Selecting $Ra_2 = (0,1)$ is thus convenient. The coordinates of the vertices are either

$$x_1 = \left(-2^{1/2}, 0\right), \qquad x_2 = \left(\left(2^{1/2}+k\right)/2, sk/2\right), \qquad x_3 = \left(\left(2^{1/2}-k\right)/2, -sk/2\right)$$

or

$$x_1 = \left(-2^{1/2}, 0\right), \qquad x_2 = \left(\left(2^{1/2}-k\right)/2, -sk/2\right), \qquad x_3 = \left(\left(2^{1/2}+k\right)/2, sk/2\right).$$

Setting s from $+1$ to -1 converts X to its inverted image (ordinates are changed to their opposite), and converting k to $-k$ is just relabelling x_2 to x_3 and x_3 to x_2. Thus, taking $\pm k$ or $s = \pm 1$ is not important.

The final shape of the set is described by

$$\begin{aligned} &x_1 = \left(-2^{1/2}, 0\right), \qquad x_2 = \left(\left(2^{1/2}+k\right)/2, k/2\right), \\ &x_3 = \left(\left(2^{1/2}-k\right)/2, -k/2\right). \end{aligned} \tag{32}$$

The optimum is obtained by derivation of (29) or (30), and is reached for $K = 3$, such that $E^2/T^2 = 1/2$ and $\mathrm{Chi} = D^2/(2T) = 1 - 2^{1/2}/2$. The most achiral triangle

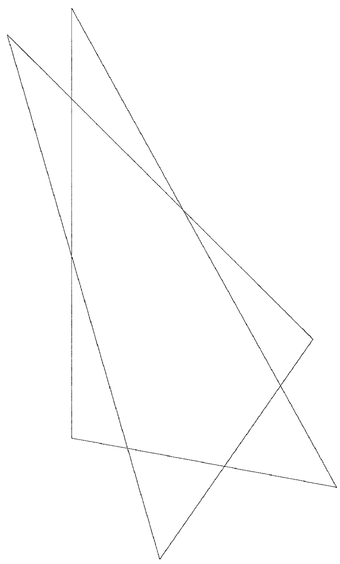

Figure 1. The most achiral triangle and its optimally superposed enantiomer with two equivalent vertices. The latter are lying opposite to the smallest and the largest angles.

has the shape given by equation (32) for $k = 3^{1/2}$. The squared lengths of the edges and the squared norms of the points are

$$\begin{aligned}(x_2 - x_1)'(x_2 - x_1) &= (3/2)\big(4 + 6^{1/2}\big) = 3\big(x_2'x_2\big),\\ (x_3 - x_2)'(x_3 - x_2) &= (3/2)4 = 3\big(x_1'x_1\big),\\ (x_1 - x_3)'(x_1 - x_3) &= (3/2)\big(4 - 6^{1/2}\big) = 3\big(x_3'x_3\big).\end{aligned}$$

The proportionality between the lengths of the edges and the distances vertex–midpoint is remarkable. The squared lengths ratio is near 4.160 : 2.580 : 1, and the angles at the vertices 1, 2 and 3 are, respectively, near 50.768°, 28.833° and 100.398° (see figure 1).

Random triangles were generated following the uniform distribution over a square. The estimated optimal E^2/T^2 ratio was indeed converging to its theoretical value, and the estimated optimal squared length ratio too (see table 1).

7.3. Three quivalent vertices

All the three vertices are equivalent, thus the 3! permutations are allowed. This set of six permutations is partitioned in three subsets. One contains the identity permutation. The second contains the three symmetric permutations, namely P_{12}, P_{23} and P_{31} (P_{ij} being such that the equivalents vertices are i and j). The last contains two permutations, one being the transposed of the other, namely, P and P', and both being such that $P + P' = I - 1 \cdot 1'$.

Table 1
Sampling of E^2/T^2 for two equivalent vertices.

Triangles	$P = I$	E^2/T^2	Squared lengths ratio	
3	yes	0.762391	5.627330	8.639524
12	no	0.586388	4.826188	5.031602
93	yes	0.512625	2.524142	4.186255
218	yes	0.506785	2.034799	3.766179
5373	no	0.501131	2.785811	4.295409
16749	no	0.500653	2.677786	4.223636
44955	yes	0.500241	2.607813	4.180106
525804	yes	0.500072	2.627870	4.192799
1040385	yes	0.500024	2.581866	4.161148
5989420	no	0.500011	2.571022	4.153483
22865206	yes	0.500006	2.584256	4.162699
140327200	yes	0.500003	2.583488	4.162154

Let us look first at these latter. Each of them has the same matrix $M = (P+P')/2$, or equivalently $M = (I-1\cdot 1')/2$. Reporting this in equation (6) and using the centering condition gives

$$E^2 = \big(\operatorname{Tr}(X'MX)\big)^2 - 4\operatorname{Det}(X'MX) = \big(\big(\operatorname{Tr}(X'X)\big)^2 - 4\operatorname{Det}(X'X)\big)/4. \qquad (33)$$

Equation (33) means that the E value obtained for P or P' is always half the E value obtained for the identity permutation. Thus, the best superposition never occurs for the permutations P or P', and these latter are never used to compute the chiral index.

Then we have only the identity permutation and the three symmetric permutations. As shown in subsection 7.2, the maximum of Chi can be located only at singularities occurring when $D^2/(2T)$ takes the same value for at least two permutations.

Let us look first at the situation where the identity permutation is not one of these two permutations. From equation (26), we know that

$$\operatorname{Det}\big(X'P_{12}X\big) = \operatorname{Det}\big(X'P_{23}X\big) = \operatorname{Det}\big(X'P_{31}X\big) = -\operatorname{Det}(X'X).$$

The two permutations leading to the same D^2 value, i.e., to the same E^2 value, are assumed to be P_{12} and P_{23} without loss of generality (the vertices can be relabelled to get that). From equation (6), P_{12} and P_{23} must therefore be such that $|\operatorname{Tr}(X'P_{12}X)| = |\operatorname{Tr}(X'P_{23}X)|$. We have, also, $P_{12} + P_{23} + P_{31} = 1 \cdot 1'$, and from the centering condition,

$$\operatorname{Tr}\big(X'P_{12}X\big) + \operatorname{Tr}\big(X'P_{23}X\big) + \operatorname{Tr}\big(X'P_{31}X\big) = 0.$$

Thus, either

$$\operatorname{Tr}\big(X'P_{12}X\big) + \operatorname{Tr}\big(X'P_{23}X\big) = \operatorname{Tr}\big(X'P_{31}X\big) = 0, \qquad (34)$$

or

$$2\operatorname{Tr}\big(X'P_{12}X\big) = 2\operatorname{Tr}\big(X'P_{23}X\big) = -\operatorname{Tr}\big(X'P_{31}X\big) = 0,$$

which leads to get $|\,\mathrm{Tr}(X'P_{31}X)| > |\,\mathrm{Tr}(X'P_{31}X)|$ unless the three traces are null. This latter inequality cannot occur, because the highest E^2 value cannot be those get with P_{31}. We look now at equation (34), which stands also when the three traces are null. Using the basis of eigenvectors of P_{23} and equations (14) and (15), we have

$$X'P_{12}X = \left(-3a_2a_2' + a_3a_3' - 3a_2a_3' - 3a_3a_2'\right)/2, \tag{35}$$

$$X'P_{31}X = \left(-3a_2a_2' + a_3a_3' + 3a_2a_3' + 3a_3a_2'\right)/2, \tag{36}$$

from which

$$\mathrm{Tr}\left(X'P_{12}X\right) = \left(-3a_2'a_2 + a_3'a_3 - 6a_2'a_3\right)/2, \tag{37}$$

$$\mathrm{Tr}\left(X'P_{31}X\right) = \left(-3a_2'a_2 + a_3'a_3 + 6a_2'a_3\right)/2. \tag{38}$$

From equation (34), $\mathrm{Tr}(X'P_{31}X) = 0$. Substituting it in (38) leads to $6a_2'a_3 = 3a_2'a_2 - a_3'a_3$, which is in turn substituted in (37) to give $\mathrm{Tr}(X'P_{12}X) = -3a_2'a_2 + a_3'a_3$. From (16), we know that $\mathrm{Tr}(X'X) = 3a_2'a_2 + a_3'a_3$, and the highest E^2 value must be that of P_{12}. This is possible only if either $a_2'a_2 = 0$ or $a_3'a_3 = 0$, both meaning that $X'X$ is a one-rank matrix, in which case the three vertices are aligned.

The assumption that the identity is not one of the permutations leading to the most achiral index is therefore false. We return now to the assumptions of section 7.2, and equations (27) to (32) stands (the vertices are labelled such that P_{23} is the permutation having the highest E^2 value). Substituting (20) and (21) in (37) and (38),

$$\mathrm{Tr}\left(X'P_{12}X\right) = \left(a_2'a_2\right)\left(k^2 - 3 - 2^{1/2}ck3\right)/2, \tag{39}$$

$$\mathrm{Tr}\left(X'P_{31}X\right) = \left(a_2'a_2\right)\left(k^2 - 3 + 2^{1/2}ck3\right)/2, \tag{40}$$

where the sign constant c is equal to ± 1.

From equation (29), we know that E^2/T^2 is a function of $K = k^2$ decreasing monotonically from 1 at $K = 0$ to $1/2$ at $K = 3$, then increasing monotonically to 1 when K goes to infinity. The minimum will be obtained for the K value closest to 3, such that $|\,\mathrm{Tr}(X'X)| = |\,\mathrm{Tr}(X'P_{23}X)|$ is greater or equal to $|\,\mathrm{Tr}(X'P_{12}X)|$ and $|\,\mathrm{Tr}(X'P_{31}X)|$. Both these inequalities are such that $|(k^2 - 3 \pm 2k3)/2|$ must not exceed $|K - 3|$. Expanding leads to a quartic polynomial with roots satisfying

$$\left(K^2 - 24K + 9\right)\left(K^2 - 8K + 9\right) = 0. \tag{41}$$

The roots of $K^2 - 8K + 9$ do not satisfy the inequalities, and the associate shape is, according to equation (32), an isocele triangle (which is thus achiral). Both roots of $K^2 - 24K + 9$ are acceptable, and both lead to $E^2/T^2 = 4/5$ and $\mathrm{Chi} = 1 - 2\cdot 5^{1/2}/5$. The final shape of the set described by equation (32) is the same for both K values. From (32), the squared lengths of the edges are

$$(x_2 - x_1)'(x_2 - x_1) = \left(k^2 + 9 + 3k2^{1/2}\right)/2, \tag{42}$$

$$(x_3 - x_2)'(x_3 - x_2) = 2k^2, \tag{43}$$

$$(x_1 - x_3)'(x_1 - x_3) = \left(k^2 + 9 - 3k2^{1/2}\right)/2, \tag{44}$$

where $k = (\pm 3 + 15^{1/2})2^{1/2}/2$. Taking the largest k value, the lengths of the edges and the squared norms of the points are

$$\begin{aligned}
(x_2 - x_1)'(x_2 - x_1) &= 15 + 3 \cdot 15^{1/2} = 3\big(x_3' x_3\big),\\
(x_3 - x_2)'(x_3 - x_2) &= 24 + 6 \cdot 15^{1/2} = 3\big(x_2' x_2\big),\\
(x_1 - x_3)'(x_1 - x_3) &= 6 = 3\big(x_1' x_1\big).
\end{aligned}$$

And for the smallest largest k value,

$$\begin{aligned}
(x_2 - x_1)'(x_2 - x_1) &= 6 = 3\big(x_1' x_1\big),\\
(x_3 - x_2)'(x_3 - x_2) &= 24 - 6 \cdot 15^{1/2} = 3\big(x_3' x_3\big),\\
(x_1 - x_3)'(x_1 - x_3) &= 15 - 3 \cdot 15^{1/2} = 3\big(x_2' x_2\big).
\end{aligned}$$

The remarkable proportionality between the lengths of the edges and the norms of the points stands, as found in subsection 7.2, but with a different labelling. This proportionality stands with any labelling for the equilateral triangle of subsection 7.1. Having two squared distances being three times any of the two squared norms implies that the third squared distance is three times the remaining norm, because the sum of the squared distances is three times the inertia for any triangle.

The squared lengths ratio is, for both k values, $(4 + 15^{1/2}) : (5 + 15^{1/2})/2 : 1$, which is near $7.873 : 4.436 : 1$, and the angles at the vertices are near $16.902°$, $37.761°$ and $125.337°$ (see figure 2). These values are sometimes close, but not equal to those get by Weinberg and Mislow with distance functions [15]. They are also close to the experimental triangle of Zabrodsky and Avnir [16]. One of the reviewer noticed that the most achiral triangle coincides with that of Zimpel [19].

Random triangles were generated as in subsection 7.2. The estimated optimal E^2/T^2 ratio and the estimated optimal squared length ratio were indeed converging to their theoretical value (see table 2).

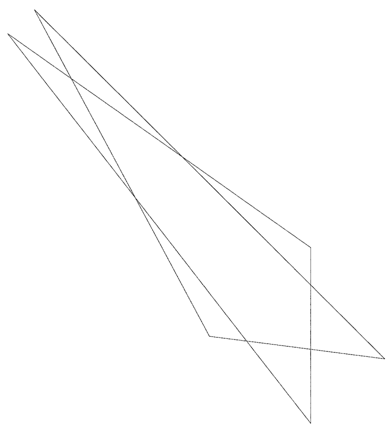

Figure 2. The most achiral triangle and its optimally superposed enantiomer with three equivalent vertices.

Table 2
Sampling of E^2/T^2 for three equivalent vertices.

Triangles	$P = I$	E^2/T^2	Squared lengths ratio	
3	no	0.883215	5.627330	8.639524
5	no	0.832453	5.206245	8.737907
67	no	0.829762	3.792317	6.929571
102	no	0.829266	3.517308	6.034729
123	yes	0.828693	4.304882	7.977873
158	no	0.816909	4.819461	8.310065
528	no	0.806296	4.305131	7.701969
2612	no	0.805984	4.227625	7.464235
2921	no	0.805262	4.319526	7.709475
6857	yes	0.802655	4.444056	7.904681
7242	yes	0.801833	4.459160	7.913541
33927	yes	0.801143	4.450624	7.898254
81025	no	0.801061	4.421007	7.863786
186734	yes	0.800720	4.440413	7.883574
551586	no	0.800572	4.417748	7.838096
648856	no	0.800560	4.422007	7.849967
682287	no	0.800300	4.439599	7.874778
3619635	no	0.800287	4.427296	7.856102
4429230	no	0.800078	4.434256	7.868293
13800935	no	0.800072	4.438385	7.875361
18489622	no	0.800026	4.435565	7.871174
228057215	no	0.800021	4.435795	7.871560

8. Conclusions

The chiral index applies for any d-dimensional finite set of points. Its properties have been examined for planar sets. Spatial sets will be treated in a forthcoming paper. The number of allowed permutations ranges from 1 to $n!$. In this extreme situation, all atoms are equivalent. Using the chemical nature of atoms and bonds should reduce greatly this combinatorial difficulty. Continuous sets are not handled. For these, other techniques should be used, such as those using Hausdorff distances.

Appendix 1. Monodimensional sets

When $d = 1$, $X_1 = -X_0$ and X_0 is a n rows vector denoted by x and which is not assumed to be centered. P is any permutation and P_0 is the optimal one. A is the difference between the two sums of squared distances:

$$A = 2(x'x + x'Px) - 2\big(x'x + x'P_0x\big) = 2\big(x'Px - x'P_0x\big).$$

P_0 being optimal, A is a non-negative quantity.

Lemma 1. P_0 is symmetric.

Proof. A permutation is such that each vertex has exactly one predecessor and one successor. A symmetric permutation contains only 1-cycles (i.e., the vertex is associated to itself) and 2-cycles. We assume that it exists a k-cycle in P_0, where $k > 2$. Let $x(a)$ be the smallest element of the cycle and $x(b)$ be the largest. Their respective predecessors are $x(a_1)$ and $x(c_1)$ and their respective successors are $x(a_2)$ and $x(c_2)$. We consider the alternate permutation P such that $x(a)$ is paired to $x(c)$, $x(c_2)$ succeeds to $x(a_1)$ and $x(a_2)$ succeeds to $x(c_1)$. P is again an allowed permutation and the difference between the sums of squared distances is

$$\begin{aligned}
A &= 2\big(x(a_1)x(c_2) + x(c_1)x(a_2) + 2x(a)x(c) \\
&\quad - x(a_1)x(a) - x(a)x(a_2) - x(c_1)x(c) - x(c)x(c_2)\big), \\
A &= 2\big(\big(x(a_1) - x(c)\big)\big(x(c_2) - x(a)\big) + \big(x(a_2) - x(c)\big)\big(x(c_1) - x(a)\big)\big).
\end{aligned}$$

A cannot be non-negative unless either $x(a_1) = x(a_2) = x(c)$, or $x(c_1) = x(c_2) = x(a)$, or $x(a_1) = x(c)$ and $x(c_1) = x(a)$, or $x(c_2) = x(a)$ and $x(a_2) = x(c)$. Each of these four pairs of equalities means that there are no more two vertices in the cycle. Thus, the optimal permutation has only 1-cycles and 2-cycles: P_0 is symmetric. □

We assume now that all n vertices are equivalent. For simplicity, the set is sorted in increasing order.

Lemma 2. The optimal permutation P_0 associates the vertices $x(i)$ and $x(j)$, with $j = n + 1 - i$ and i varying from 1 to n.

Let $x(a)$ and $x(b)$ be the vertices paired with $x(1)$ and $x(n)$, respectively. We consider the alternate permutation P where $x(1)$ is paired to $x(n)$ and $x(a)$ is paired to $x(b)$. P is again an allowed permutation and the difference between the sums of squared distances is

$$\begin{aligned}
A &= 4\big(x(1)x(n) + x(a)x(b) - x(1)x(a) - x(b)x(n)\big), \\
A &= 4\big(x(1) - x(b)\big)\big(x(n) - x(a)\big).
\end{aligned}$$

A cannot be non-negative unless either $x(1) = x(b)$ or $x(a) = x(n)$, both meaning that $x(1)$ and $x(n)$ are already paired. Iterating for the next smallest and largest elements, we see that the optimal permutation has exactly $n/2$ 2-cycles and one 1-cycle if n is odd. It associates the smallest and the largest values, then the next smallest and the next largest and so on.

When there are non-equivalent vertices, the set is partitioned in subsets such that all vertices associated to a common block are equivalent. Reusing lemma 2 for each subset, we see that the optimal permutation is such that the smallest element of a subset is associated to the greatest one, the second smallest element is associated to the second greatest one and so on. The final optimal permutation is symmetric even when the labelling is modified, and the number of non zero diagonal values of P is equal to the number of subsets with odd cardinality.

When all vertices are unequivalent, $P = I$, $D^2 = 4T$ and Chi $= 1$.

Appendix 2. Isotropy of the regular d-simplex

Let X be a centered d-simplex in the d-dimensional euclidean space, v a real constant and I the identity matrix. The following property stands:

Property. $X'X = vI \;\Leftrightarrow\;$ the simplex is regular.

Proof. X is an array containing d columns and $n = d+1$ rows, and vI is n times its observed variance matrix. Obviously, v cannot be negative because it is the squared norm of each column of X. If $v = 0$, all points are lying at the origin: this is a degenerated regular simplex. We can assume now $v > 0$, and set $v = s^2$ with $s > 0$.

Let m be the square root of n. Let W be the n rows and n columns square matrix such that its first column contains the vector 1 divided by m (i.e., all its n elements takes the real value $1/m$), and such that the remaining block contains X/s (i.e., all elements of X are divided by s).

The centering condition $1'X = 0$ shows that $W'W = I$ and thus W is an orthogonal matrix, which satisfies also to $WW' = I$. This can be written as $(1 \cdot 1')/n + XX'/v = I$, and then $X'X = v(I - 1 \cdot 1'/n)$. Let $x_1, x_2, \ldots, x_n$ be the n points, i.e., the transposed rows of X. We have for any x_i, $x_i'x_i = v(1 - 1/n)$, and for any distincts x_i and x_j, $x_i'x_j = -v/n$. The squared length of an edge is always equal to $(x_i - x_j)'(x_i - x_j) = 2v$, meaning that the d-simplex is regular.

Conversely, prooving that the regular d-simplex has a variance matrix proportional to I is obvious, and of course this is true for any orthogonal transformation of X: $(XQ')'(XQ) = Q'(vI)Q = vI$. □

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