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LETTER TO THE EDITOR

Chiral coefficient—a measure of the amount of structural chirality

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Abstract. A new concept of quantitative measure of chiral structure is introduced and labelled as chiral coefficient χ . A distinction is made between geometric and physical chiralities and χ is defined for various physical cases. Few general geometrical features are discussed and it is shown that for every chiral body there exists a natural z direction depending on the physical property treated. Possible practical applications of this concept are discussed. A few simple examples of the chiral coefficient of mass χ_m for chiral molecules are treated.

Structural chirality is an old and well known phenomenon. Almost any arbitrary macroscopic object, such as a piece of rock, is chiral or asymmetric. On the microscopic scale there exist a few well known examples of chiral structures such as α quartz or chiral molecules such as amino acids. It is well known that chiral molecular structure gives rise to several effects associated with the rotation of the vector of polarisation of light (for an excellent review of the phenomena of optical activity, see [1]).

Up to now, structural chirality has largely been a qualitative concept associated with left-right asymmetry, although a few early attempts to quantify it have already been made [2-5]. It is the purpose of the present letter to propose a general quantitative definition for structural chirality. The meaning of this concept is that a question of 'how much chirality?' may receive a quantitative answer. The definition for the amount of structural chirality, or chiral coefficient, is based on purely geometrical considerations which can readily be extended to any physical object, macroscopic as well as microscopic. Before presenting the complete new definition, let us first recall that a three-dimensional chiral object cannot be made to completely overlap its mirror image by any continuous, i.e. rotational and/or translational, transformation. A similar definition also exists for 2D chiral objects, such as asymmetric triangles within a plane.

For simplicity, let us look at any 3D chiral object of volume V . Let O be its centre of volume cv . At this stage only purely geometric bodies are considered. Let us pass a plane MP through O which serves also as a double mirror plane that reflects the body upon itself. In figure 1 the situation is illustrated by a 2D asymmetric quadrangle. According to the definition of chiral objects, the volume of the reflected image of the body cannot fully overlap the original body and vice versa. There must exist a certain excess volume v that does not overlap. Let us now regard the two modes of chirality generated by MP as two independent enantiomers of the same object. Let us now apply all possible transformations, such as rotations, translations and reflections on one enantiomer with respect to the other until an absolute maximum volume of overlap V_0 between the two is found (area S_0 in the 2D case). The minimal non-overlap volume

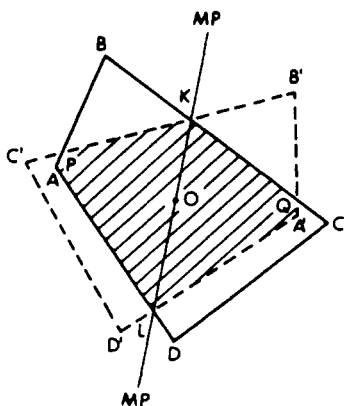


Figure 1. ABCD is a 2D chiral object and O is its centre of area. MP is a double mirror line (plane for a 3D object) passing through O. A'B'C'D' is the mirror reflection of ABCD. The blank areas are the non-overlapping parts of ABCD and its mirror image and their total area is s . S is the area of ABCD and $\chi = s/2S$. Upon varying the orientation θ of MP around O for $0 \leq \theta \leq \pi$, it is possible to find s_{\min} and define $\chi_s = s_{\min}/2S$ as a chiral coefficient of area.

is v_{\min} , (s_{\min} for 2D) where $v_{\min} = 2(V - V_0)$. χ_v , the volume chiral coefficient is defined as

$$\chi_v = v_{\min}/2V. \quad (1)$$

For $\chi_v = 0$, the body is symmetric. In a similar way the area chiral coefficient is

$$\chi_s = s_{\min}/2S \quad (2)$$

and S is the area of the chiral body. It is easy to show that χ_v , or χ_s , must satisfy $0 \leq \chi_v \leq 1$ and χ_v is probably closer to 0 than to 1.

As yet only geometric chiralities have been considered and a natural step forward is to regard physical bodies as well. An obvious next case would be a chiral body with a continuous mass distribution of density ρ . If $\rho = \text{constant}$ then the definition of χ_m , the chiral coefficient of mass, is almost identical to that of χ_v , where $m_{\min} = \rho v_{\min}$ and $M = \rho V$

$$\chi_m = m_{\min}/2M. \quad (3)$$

The case of $\rho \neq \text{constant}$ can readily be treated too. Let $\rho(\mathbf{r})$ be the mass density of one enantiomer so that $\rho^*(\mathbf{r}^*)$ is the mass density of its mirror image, where \mathbf{r} and \mathbf{r}^* are defined with respect to an arbitrary fixed point. Now we apply the same transformations and we search for maximum mass overlap M_0 or, equivalently, for m_{\min} being an absolute minimum of

$$m = \int_{V'} |\rho(\mathbf{r}) - \rho^*(\mathbf{r}^*)| d^3r \quad (4)$$

where V' is the volume for which $\rho \neq \rho^*$. χ_m is given by (3).

A similar, and perhaps physically more significant, definition is that of χ_ψ , the electronic wavefunction distribution over a chiral molecule or unit cell of a crystal.

The procedure here is exactly the same as for m_{\min} and the search is for an absolute minimum of

$$\chi_{\psi} = \frac{1}{2} \int_{V'} \|\psi(\mathbf{r})\|^2 - \|\psi^*(\mathbf{r})\|^2 \, d^3r \quad (5)$$

where it is assumed that the denominator is normalised to 1.

The chiral coefficient χ_{ψ} can be generalised for any Hermitian quantum operator Ω , so that χ_{Ω} is defined as

$$\chi_{\Omega} = \frac{\min(\int_{V'} \|\psi^{\dagger}\Omega(\mathbf{r})\psi\| - \|\psi^{\dagger*}\Omega^*(\mathbf{r})\psi^*\| \, d^3r)}{2|\langle\Omega\rangle|} \quad (6)$$

where $\langle\Omega\rangle$ is the expectation value of Ω and ψ^{\dagger} is the complex conjugate of ψ . Incidentally, it is important to realise that the origin of chirality in the Schrödinger equation is in the possible asymmetry of the potential $V(\mathbf{r})$.

A similar procedure exists also for a discrete mass distribution such as in molecules or in unit cells of a crystal. Let m_i , $i = 1, \dots, n$, be the mass distribution and \mathbf{r}_i the location of m_i with respect to some point O. The mass distribution is confined to some finite volume V' that contains all the point masses. The procedure is very similar to that of continuous and variable mass distribution. m' is given by

$$m' = \sum_{i=1}^n \sum_{j=1}^n \int_{V'} |m_i\delta(\mathbf{r} - \mathbf{r}_i) - m_j^*\delta(\mathbf{r} - \mathbf{r}_j)| \, d^3r \quad (7)$$

where m_i^* located at \mathbf{r}_i is the mirror reflection of m_i located at \mathbf{r} . We now apply the necessary transformations and search for m_{\min} , the minimum of m' . If $M = \sum_i m_i$ then χ_m is given by (3) for a discrete mass distribution. The case of $n = 4$ atoms per molecule can be easily treated. For NHDF we obtain $\chi_m = 0.028$ and for CHFCIBr $\chi_m = 0.088$. Incidentally, it is quite possible to have $\chi_{\alpha} = 0$ whereas $\chi_b \neq 0$ for two different chiral coefficients. For instance, take a symmetric tetrahedron and put four different masses at its corners and then $\chi_v = 0$, $\chi_m \neq 0$.

In addition to χ_m , χ_{ψ} and χ_{Ω} there may exist other coefficients. It is well known that various macroscopic devices, such as windmills, rotating water sprinklers, and the Crookes radiometer, to name a few, are asymmetric. A common feature of all these examples is that they all possess chiral structure that enables them to choose a definite sense of rotation, clockwise or counterclockwise, when interacting with different media [6, 7]. Such an interaction between a chiral device and some medium can be referred to as 'chiral interaction'. A common feature to all these examples is their massive rotation. There is another kind of chiral interaction that does not involve mass rotation, such as in electric cells, which may be referred to as chiral interaction of the second kind. For massive rotation the net result of chiral interaction is the transfer of angular momentum to a rotating mass. The chiral coefficient χ_1 of interest in such cases would be that of the moment of inertia which can be similarly defined. For the case of Crookes' radiometer the physical property of interest is the chiral coefficient χ_{α} of the distribution of α , the light absorption coefficient over the body.

The purpose of these examples is to demonstrate the wide range of physical chiralities that may exist and the possibility of defining a dimensionless chiral coefficient χ_j for each of them that satisfies $0 \leq \chi_j \leq 1$. In many cases it may be possible to analyse the physical nature of the interaction and evaluate it by some appropriate formulae. The amount of power that can be transferred to the device by chiral interaction must be proportional to the appropriate chiral coefficient χ_j associated with the chiral device.

Let us now derive a few general conclusions from the definitions of the various chiral coefficients χ_j , and for simplicity let us consider χ_v although these conclusions are true for any physical χ_j . It is obvious that in order to evaluate χ_v it is necessary to minimise v_{\min} which is equivalent to maximising the overlap volume V_0 . In general, V_0 can be either symmetric or asymmetric. In the case where it is symmetric there exists at least one mirror plane (or line in 2D cases) the normal to which may be regarded as a preferred z axis of the chiral body. For each physical property j there exists a different z axis. In cases when more than one direction exists for a given property j , then we have 'degenerate chirality'. When the maximum overlap volume V_0 is asymmetric, then it is possible to view it in a mirror and obtain a mirror image of the asymmetric volume V_0 . The situation now is that we have on each side of the mirror both enantiomers and let us mark V_0 on each side of the mirror. Now it is possible to take one enantiomer (say L) and overlap it completely with the same L on the other side. There now exist two different domains of maximum asymmetric overlap of equal volume V_0 on each enantiomer. In other words, the case of maximum asymmetric overlap must be at least 'doubly degenerate'. It is easy to show that the transition of one asymmetric overlap to another results from a simple translation of one enantiomer with respect to the other. The direction of such a (linear) translation can also be regarded as a natural z axis for the chiral body. As a conclusion of this discussion, it is possible to state in general that (i) there exist two classes of chiralities, of symmetric and asymmetric maximal overlap, where the second class is doubly degenerate, and (ii) there always exists a preferred direction for any chiral body. These conclusions are also general for any physical chirality.

Let us now look briefly into earlier attempts to quantify chirality. Kitaigorodskii [2]† proposed a parameter ε where

$$\varepsilon = 1 - V_{\text{NO}}/V_0 \quad (8)$$

and $V_{\text{NO}} = v_{\min}$. It is easy to show that

$$\chi_v = (1 - \varepsilon)/(3 - \varepsilon) \quad (9)$$

where $-\infty \leq \varepsilon \leq 1$. Another attempt was made by Rassat [3] but his definition does not correspond to χ_v in a simple manner. The case of 2D chirality was recently treated [5] in the context of computer pattern recognition. To the best of the author's knowledge the extension to physical chiralities is proposed here for the first time.

At this stage it is necessary to emphasise that the main significance of the chiral coefficient χ , geometric or physical, is conceptual. The property of structural chirality, which has been until now a qualitative feature, receives a quantitative meaning via χ_j , which can vary according to the different physical aspects of this asymmetry. The practical aspect of the various chiral coefficients is that it now becomes possible, in principle, to compute chiral coefficients of various physical properties of chiral objects. In particular, it becomes possible to assign a chiral coefficient χ_j to any chiral molecule or unit cell of a crystal. As it now stands, this may involve a considerable amount of mathematical and computational effort [5], but the definition is valid.

Let us look now into possible practical applications of chiral coefficients. In the microscopic realm there exists the problem of chiral recognition [8,9]. Another application is involved in any attempt to transform a symmetric into chiral molecule. The amount of chirality associated with this process can be estimated by the change

† The author is grateful to Professor A Collet for this information.

of χ_ψ , which becomes a natural variable for the amount of energy involved in such symmetry breaking. Another practical aspect of the concept of the chiral coefficient χ_j is the possible calculation of the magnitude of chiral interactions. Hopefully the calculation of this effect can be separated into two independent factors. The first one is the relevant chiral coefficient and the second includes the physical content of the interaction. The present letter, however, is concerned only with chiral coefficients.

Most of the known chiral interactions involve macroscopic chiral devices interacting with various media. The only well known microscopic chiral interaction is the effect of optical activity and associated effects of circular dichroism (CD) and Cotton effects [1, 10]. The physical aspects of the rotation of the vector of polarisation were analysed [11–13] in terms of the induced polarisability of the atoms in a chiral molecule such as CHFCIBr. The relevant chiral coefficient for this case involves the induced polarisability. It may well be the case that the reason why the quantum mechanical treatment [14] of optical activity is less successful [1] has had to do with the lack of an appropriate measure of the amount of chirality involved, i.e. the lack of χ_Ω for the proper operator Ω that deals with this effect. Another effect of chiral interaction between amino acids or proteins and polar solvents was predicted [2, 6, 7] by the same author but is still unobservable. The magnitude of this interaction may be estimated by using an appropriate χ_j .

Another feature associated with this concept is the possibility of assigning an enantiometric title L or D to certain chiral bodies. In general it is impossible to pick up a piece of rock and say whether it is L (left) or D (right). In order to make a meaningful assignment it is necessary to have a direction that refers to the object. This is the case for many pairs of organs in human beings and other species of animals. The direction is from the back to the front of the creature, which enables us to distinguish between a left and right hand, for instance. The assignment of L or D is also relevant to chiral devices that rotate due to some perturbation that advances along a straight line. If the sense of rotation is always right then this is a D-enantiomer. This is the case with chiral molecules or unit cells that are optically active, or with a skew wind propeller. Such devices possess what is regarded here as odd chirality. There exist other chiral devices such as windmills or rotating water sprinklers for which the sense of rotation reverses upon looking at it from opposite directions. Such a device has an even chirality and it is senseless to label it by L or D. Whenever it is possible to define L or D chirality it may be convenient to define $\chi_j^L = -\chi_j^D < 0$.

In conclusion, a new concept of quantitative measure of structural chirality, namely a dimensionless chiral coefficient χ_j , has been introduced and defined for geometric and physical chiralities. This definition contributes quantitative meaning to structural chirality. It is also shown that every chiral body has a natural direction associated with its asymmetry. This definition may have a wide range of applicability in molecular and crystalline physics, chemistry and biology.

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