

CHIRALITY*

Lancelot Law Whyte**

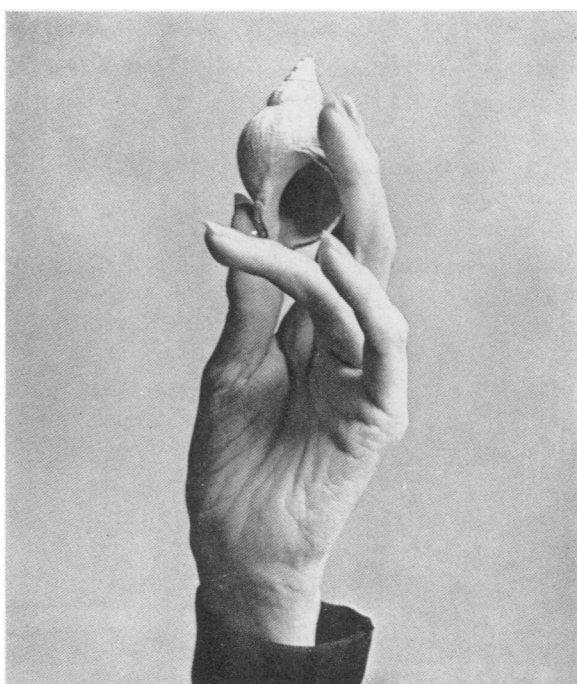
In his Boyle Lecture at Oxford in 1893 on molecular arrangements in crystals, Kelvin introduced the term 'chirality' from (*χειρ*, *hand*). 'I call any geometrical figure or group of points "chiral", and say it has "chirality", if its image in a plane mirror, ideally realized, cannot be brought into coincidence with itself' [1]. He called forms of the same sense (e.g. all L-handed) 'homochiral' and equal forms of opposite sense 'heterochiral'. J. Larmor and A. S. Eddington used 'chiral' and the writer [2] analyzed the concept, listed the main chiral forms and gave a more explicit definition: 'Three-dimensional forms (point arrangements, structures, displacements, and other processes) which possess non-superposable mirror images are called "chiral".' This presupposes that the mirror image of the phenomenon, e.g. of a magnetic vector, is either known from observation or established by an acceptable convention.

'Chirality' is used in preference to similar but ambiguous terms (e.g. asymmetry, dissymetry) with associations which can mislead [2] when it is desired to refer to a general property defined in terms of spatial relations only (e.g. Cahn, 1966 [3]), not of particular physical or chemical effects (e.g. optical rotation, since some non-chiral structures can display optical activity, Wooster, 1946). The property of chirality is dual (L, left, or R, right, laevo or dextro), global, geometrical, three-dimensional, Euclidean and non-relativistic, spatial relations being separated from temporal. Moreover it refers to a structure at some specified level (or set of levels) in the structural hierarchies of the physical universe or of organisms. There is no necessary correlation between chirality at one level and its presence or absence at a neighbouring level. A chiral process is one, successive states of which are chiral. Chiral forms fall into two main classes: screws (conical or helical) ordered with respect to a line, and skews, ordered around a centre. Thus a chiral chemical group or molecule may be skew

(around an asymmetrical centre) or screw (arranged as a helix) and the two chiral forms are called *enantiomers*. A chiral form is (theoretically) converted into its mirror image by a rotation in four-dimensional space.

We cannot consider here the psychological and social connotations that *left* and *right* (or equivalents) possess in different cultures [4, 5] and turn to the history of chirality in physics and biophysics.

Interest in L- or R-handed arrangements of points or atoms and in chiral organic forms long preceded their scientific analysis. Plato considered the properties of mirror images; Aristotle discussed chiral forms; Lucretius devoted 100 lines of *On the Nature of Things* [6] to images in mirrors; Leonardo da Vinci used mirror writing; Kant found in the existence of chiral forms support for his theory of space; Goethe wrote an essay 'On The Spiral Tendency in Vegetation' and many early scientists were interested in the screw forms of plants and shells (cf. Figure).



Edith Sitwell's hand holding a helical shell. (From 1958 Christmas card of Eve and Lance Whyte.)

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The scientific mind looks for symmetry, so it is scarcely surprising that it was not until the 19th and 20th centuries that quantitative science came to grips with the chiral aspects of nature, which we now know to be of great importance. On six occasions from 1810 to 1957, chiral phenomena were unexpectedly discovered that involved a revision of previous theoretical assumptions. The bias in favour of symmetry has meant that the systematic study of skew and screw effects has only been taken up when the experimental facts compelled it.

A primary aim of science is the elimination of arbitrariness by the discovery of intelligible reason for everything being as it is and not otherwise. But no-one has yet conceived a sufficient reason for a fundamental or general chiral bias, say in favour of left-handed forms. So, if a bias has been found in any realm, the natural inference has been that it is due to some contingent local effect and that structures with the opposite bias may exist elsewhere in the universe [7]. Of the six discoveries of new chiral effects, two involved no bias, as both forms were found. We shall consider these first.

Crystal optics. Arago (1810) discovered the rotation of plane-polarized light (optical activity) by quartz crystals and Fresnel (1827) correctly ascribed this to a helical arrangement in the structure of the crystal. No bias was present in this work, as L and R rotations were produced by different specimens.

Crystal mechanics. During the 1950's non-symmetric tensors, representing screw stresses and strains, were discovered in crystals containing helical molecular arrangements. No bias; both forms of crystal exist.

The other four cases are more interesting, as they revealed a bias in nature calling for explanation.

Electromagnetic interaction. Oersted (1820) discovered the anomalous R-handed screw action of an electric current on a magnet. (Mach's 'shock' [8]). This bias was incorporated into classical Electromagnetic Theory but was modified and believed to be substantially explained in *Electron Theory and Quantum Mechanics* (Weyl, 1952).

Living systems and chiral molecules. In 1815, Biot discovered that many materials from organisms (sugar, tartaric acid, oil of turpentine, etc.) in the liquid state or in solution displayed optical activity and conjectured that this might be due to some structural asymmetry of the individual molecules. Pasteur followed this up and, in 1848, separated—by manually sorting out from a mixture the small crystals of the two mirror-image forms, a procedure seldom applicable—two optically active (R and L) forms of tartaric acid. He interpreted this as due to the existence of two mirror image

structures (enantiomers) of otherwise identical molecules, only one of which is present in organisms, though both are present mixed in non-active materials from non-living sources. Pasteur inferred that only in organisms are chiral molecules present unmixed with their enantiomers and at one period he claimed that this capacity of organisms to produce molecules with chirality of one sense only drew a clear boundary between the living and the non-living realms. In 1874 Pasteur suggested that this organic bias was due to a universal cosmic bias (for some reason not appearing in inorganic materials), '*L'Univers est dissymétrique*' [9], though later he stressed the continuity of the two realms.

It was established, from 1920 onwards, that the organic realm is distinguished, as Pasteur had suggested, by the presence of chiral molecules of one sense only in any particular biochemical process. 'In living organisms all syntheses and degradations of dissymmetrical molecules involve one enantiomorph alone' [10]. This must be carefully interpreted; it does not mean one universal bias. While more than 99% of natural amino acids are L, and sugars are R. Moreover, at different levels opposite chiralities may be present; for example, the L amino-acids form R macro helices in proteins. Moreover, as though to prove the capacity of organisms to break what human beings regard as simple rules, a highly active class of enzyme systems (D-amino acid oxidases) contain only R amino acids.

In spite of these complexities, one principle at present appears absolute: where two opposite forms of a molecule are possible, these are never used simultaneously. Mixed enantiomers are never found in cellular organisms. This suggests that the presence of structures of one chirality only in any situation is—at least at the molecular and conformational levels—an indispensable condition of organic stability and coordination. Living controls, it seems, require chirality of one sense only in any one region and at any one level.. 'Life is a linked set of reactions, and therefore their component molecules must depend on fitting their chirality, right- and left-handedness together' [11]. Chirality holds one of the secrets of the dynamic coordination which is 'life'.

But a major problem remains: What caused the almost complete predominance, probably in all cellular organisms, of L amino acids? Several alternative causes have been considered. (1) A predominance of (say) L-handed circularly polarized light reaching the Earth. This is believed to be inadequate. (2) Action by some contingent local factor (such as a chance excess of quartz crystals of one sense in some locality causing a bias in circularly polarized light) producing a slight bias in early forms of life, which then led rapidly to an

effectively complete bias by internal biochemical selection. Some have considered this the most likely cause [10] but it is not wholly satisfactory to ascribe such an important bias, apparently necessary to organic coordination, to some early unknown contingent local factor producing a slight bias. (3) The influence of some pervasive continuing bias in the physical environment. No such bias was known until the discovery (1956, see below) of chiral γ -rays producing an excess of left circularly polarized photons. This entirely unexpected identification of a bias in a widespread radioactive process offered a likely cause of the bias, for example, in natural amino acids. [The author had a question mark beside this statement. Ed.] In 1968, experiments [12] on the stability of L and R enantiomers of amino acids in the presence of radioactive sources showed that the dextro isomer decomposed more than the laevo. If further work confirms this result, the bias in natural amino acids can be regarded as a consequence of a still unexplained bias in the construction of matter (see below).

From 1870 onwards the science of stereochemistry (chemistry in three-dimensional space) and the study of chiral molecules in the inorganic as well as the organic realm has steadily advanced. Important achievements in relation to chirality are: (1) The ascription of optical activity in most cases to an asymmetrical carbon (or other) atom, combined with four different atoms. (2) The determination of the 'absolute configuration' (definite L or R arrangement) of optically active compounds [13]. (3) The development of a comprehensive system of classification of complex compounds using the conception of chirality [3].

Particles and Antiparticles. In 1931 Dirac, using a relativistic wave equation that he had previously proposed for the (negatively charged) electron, predicted the existence of a positively charged anti-particle to the electron and this new antiparticle, called the positron, was discovered in 1932/3. In quantum mechanics such particles in an abstract space (not in ordinary three-dimensional space) and their reflection properties in ordinary space depend on partly arbitrary conventions forming part of the theory. This technical point cannot be discussed here but on certain reasonable assumptions the positron can be regarded as the mirror image of the electron and the general laws show in this respect no chiral bias, both particles corresponding to permissible solutions of the Dirac equation. But quantum mechanics makes no assertion regarding the population statistics of the various particles in any system and here a difficulty arises. For there remains an awkward and fundamental anomaly—in the world as we know it, electricity is not symmetrical with respect to positive and negative charges, since electrons are

present in myriads everywhere, while positrons are very rare and vanish in a flash by fusion with electrons.

Whether this contrast expresses a chiral bias present in all electromagnetic phenomena involving electrons is not clear but it is certainly directly or indirectly connected with mirror image properties. Moreover, it appears to be very deeply rooted in physical theory, as Larmor discussed the possibility of particles of antimatter with opposite electric charges and chirality in 1900 before 20th century physics was born. Indeed, it was Larmor's use of the term 'chirality' that brought it to the attention of 20th-century physicists.

Weak particle interaction. Between 1956 and 1958 it was established that all weak interactions (e.g. in γ -ray radioactive decay) display a marked bias ('failure of parity conservation'). This anomaly in the fundamental constitution of matter, as shown in the processes of atomic nuclei, constitutes a major challenge. What possible reason can there be for a left or right bias in the structure of atomic nuclei?

It could be that this nuclear bias and the electron/positron lack of symmetry are two expressions of one underlying factor, not yet identified, that has to do with the structure of electricity in atoms and nuclei. There appears to exist more asymmetry in the physical universe than is yet understood and it would not be surprising if this required a further revision of fundamental concepts. It has been known since 1956/7 (Time-Charge-Parity T.C.P. Theorem) that reflection symmetry must be regarded as a member of a closely linked triplet of invariances: under (i) reversal of the direction of motion, (ii) reversal of sign of electric charge and (iii) reflection. Any major advance of physical theory beyond this Theorem may be expected to throw light on three basic issues: the reversibility or not of the fundamental physical processes, the nature of electricity and the role of left- and right-handedness in the physical universe.

Thus there are indications that the role of chirality in the universe, or at least on this Earth, may be greater than has yet been understood. This accords with the view often put forward that greater attention should be paid to asymmetries as the necessary initiators of processes. (*'C'est la dissymétrie qui crée le phénomène'* [15].) For this a radical transformation in physical ideas may be necessary. We should probably be much surprised if we could look as long ahead, as Lewis Carroll did when he made Alice wonder: 'Perhaps looking-glass milk isn't good to drink' [16]. Today we know that only an Anti-Alice would be able to assimilate anti-milk but we have no idea why milk, and we ourselves, and perhaps the solar system, share one dominant bias. It is conceivable, perhaps, that this

bias in nature is only apparent and that it arises from a bias in our thinking. But, if so, whence came that bias in thought if we are part of nature?

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