

Symmetry and Molecular Chirality

By L. D. Barron

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW G12 8QQ

1 Introduction

The symmetry aspects of optical activity have fascinated scientists ever since the realization by Fresnel and Pasteur in the early years of the last century that the molecules which exhibit optical rotation must have a structure that is essentially helical. A finite cylindrical helix is the archetype for all figures exhibiting what Pasteur¹ called *dissymmetry* to describe objects 'which differ only as an image in a mirror differs from the object which produces it'. Dissymmetric figures are not necessarily *asymmetric*, that is devoid of all symmetry elements, since they may possess one or more proper rotation axes (the finite cylindrical helix has a twofold rotation axis through the mid-point of the coil, perpendicular to the long helix axis). However, dissymmetry excludes improper rotation axes; that is centres of inversion, reflection planes, and rotation–reflection axes. In recent years the word dissymmetry has been replaced by the word *chirality*, meaning handedness, in the literature of stereochemistry. 'Chirality' was first used in this context by Lord Kelvin.²

Pasteur felt that molecular chirality was but one aspect of a general cosmic dissymmetry.^{3,4} Quoting from Mason's book:⁵

During his period at Strasbourg, 1850—54, Pasteur generalized the concept of dissymmetry to the forces of nature and the structure of the physical world as a whole. The earth, Pasteur argued, is inherently dissymmetric, on account of the diurnal rotation and the polarity of terrestrial magnetism. The same holds for the system of planets at large, since on 'placing before a mirror the group of bodies which compose the solar system, with their proper movements, we obtain in the mirror an image not superposable on the reality'. The combination of a rotation with a linear motion is expected to generate dissymmetry, Pasteur held, as appeared to be already exemplified by Faraday's discovery in 1845 of optical activity magnetically-induced in otherwise inactive media by the flow of an electric current through a helically-wound conductor.

This passage illustrates nicely the mixture of truth and misconception in Pasteur's perception of chirality. One of the functions of this article is to sharpen these concepts so as to clearly delineate 'true' chirality from 'false' chirality. We shall see

¹ L. Pasteur, *Ann. Chim.*, 1848, 24, 457.

² Lord Kelvin, 'Baltimore Lectures', C. J. Clay and Sons, London, 1904.

³ L. Pasteur, *Rev. Scientifique*, 1884, 7, 2.

⁴ J. B. S. Haldane, *Nature (London)*, 1960, 185, 87.

⁵ S. F. Mason, 'Molecular Optical Activity and the Chiral Discriminations', Cambridge University Press, Cambridge, 1982.

that the combination of a rotation with a linear motion does indeed generate true chirality, but that magnetically-induced optical activity originates in false chirality (the helically-wound conductor in the passage above is a 'red herring' since its function is to provide a uniform magnetic field rather than a source of rotation plus linear motion). Also, there are physical systems such as stationary rotating cones, and co-linear electric and magnetic fields, that are dissymmetric in the sense of Pasteur's definition in the first paragraph and yet are not truly chiral.

In our own time, the triumph of theoretical physics in unifying the weak and electromagnetic forces into a single 'electroweak' force has provided a new perspective on chirality. Since the weak and electromagnetic forces have turned out to be different aspects of the same, but more fundamental, unified force, the absolute parity violation associated with the weak force is now thought to infiltrate to a tiny extent into all electromagnetic phenomena so that free atoms, for example, show tiny optical rotations. This has given a proper scientific basis to the universal dissymmetry that Pasteur sensed a century before, and has provided a fresh perspective on molecular chirality.

The concept of chirality is inextricably linked to that of enantiomers (from the Greek *enantios morphe*, opposite shape). We shall see that the distinction between true and false chirality hinges on the symmetry operations that interconvert enantiomers, and that parity violation provides a cornerstone for the identification of true chirality. Indeed, the use of fundamental symmetry arguments to pursue analogies between the quantum states of a chiral molecule and those of various elementary particles gives force to remarks of Heisenberg⁶ to the effect that elementary particles are much more akin to molecules than to atoms. This insight might encourage theoretical chemists to keep abreast of developments in elementary particle physics in order to introduce concepts that could form the basis of a new quantum chemistry.⁷

In this article I have attempted to bring together several different fundamental symmetry considerations in order to provide stereochemists with a foundation for their concept of molecular chirality that is rooted in sound principles of basic physics. This should facilitate a proper understanding of the physical and chemical properties of chiral molecules and of the factors involved in their synthesis and transformations. The discussion is kept at a general level and so does not review important work such as that of Ruch⁸ or Mislow and Siegel⁹ that elaborates the stereochemist's view of spatial chirality in terms of structural detail. I have included sufficient mathematical detail to satisfy theoreticians that the new concepts elaborated here are sound, but it is not necessary for stereochemists to follow all the details in order to grasp and apply these concepts. For instance, the central concept is the new definition of chirality given in Section 4; and this can be appreciated sufficiently from the simple pictorial arguments that complement the mathematics.

⁶ W. Heisenberg, 'Introduction to the Unified Field Theory of Elementary Particles', Wiley, New York 1966, p. 2.

⁷ H. Primas, 'Chemistry, Quantum Mechanics and Reductionism', Springer-Verlag, Berlin, 1981.

⁸ E. Ruch, *Acc. Chem. Res.*, 1972, **5**, 49.

⁹ K. Mislow and J. Siegel, *J. Am. Chem. Soc.*, 1984, **106**, 3319.

2 The Basic Symmetry Operations: Parity, Time Reversal, and Charge Conjugation

A. General Aspects.—Most chemists are familiar with the spatial symmetry aspects of molecules. An object is said to possess a particular spatial symmetry if, after subjecting it to a symmetry operation such as inversion, reflection, or rotation with respect to a corresponding geometrical symmetry element within the object, it looks the same as it did before. In particular, symmetry operations constituting the point group of the molecule leave one point invariant.

More remarkable than these spatial symmetries is the existence of symmetries in the laws which determine the operation of the physical world. According to Lee,¹⁰ the root of all symmetry principles lies in the assumption that it is impossible to observe certain basic quantities called *non-observables*. This implies invariance of physical laws under an associated transformation and usually generates a conservation or selection rule. The non-observables of relevance here are absolute chirality (absolute right- or left-handedness), absolute direction of time flow (from past to future or future to past), and absolute sign of electric charge.¹⁰

The transformation associated with absolute chirality is *space inversion*, represented by the parity operator \hat{P} which inverts the system through the origin of the space-fixed axes (so that each constituent particle i at some point r_i is moved to $-r_i$). This is equivalent to a reflection of the system in any plane containing the coordinate origin, followed by a rotation through 180° about an axis perpendicular to the reflection plane. Most physical laws, particularly those of electromagnetism (but not those describing weak processes such as β -decay) are unchanged by space inversion: in other words the equations representing the physical laws are unchanged if the space coordinates (x, y, z) are replaced everywhere by $(-x, -y, -z)$, and the corresponding physical processes are said to conserve parity.

The transformation associated with absolute direction of time flow is *time reversal*, represented by the operator \hat{T} , which reverses the motions of all the constituent particles in the system. For our purpose it is better to think of \hat{T} as motion reversal since this does not have the same mysterious connotations as travelling backwards in time. If replacing the time coordinate (t) by $(-t)$ everywhere in equations describing physical laws leaves those equations unchanged, the physical processes represented by those laws are said to conserve time reversal (or to have *reversality*). This reversality of a process must not be confused with the thermodynamic notion of reversibility: a process will have reversality as long as the process with all motions reversed is in principle possible, however improbable it may be; thermodynamics is concerned with calculating the probability. The mechanical shuffling of a pack of cards is, in principle, a reversible process, although thermodynamics would classify it as an irreversible process.

The transformation associated with absolute sign of electric charge is *charge conjugation*, represented by the operator \hat{C} which interconverts corresponding particles and antiparticles (if an elementary particle carries an electric charge, the corresponding antiparticle carries the opposite charge). Although this exotic

¹⁰ T. D. Lee, 'Particle Physics and Introduction to Field Theory', Harwood Academic Publishers, Chur, 1981.

operation might appear to have no relevance to chemistry, we shall see later that it has conceptual significance in the identification of true enantiomers.

A *scalar* physical quantity such as temperature has magnitude but no directional properties; a *vector* quantity such as velocity has magnitude and an associated direction; and a *tensor* quantity such as electric polarizability has magnitudes associated with two or more directions. Scalars, vectors, and tensors are classified according to their behaviour under operations \hat{P} and \hat{T} . A vector whose sign is changed by \hat{P} is called a *polar* or *true* vector; for example a position vector \mathbf{r} , as shown in Figure 1a. A vector whose sign is not changed by \hat{P} is called an *axial* or

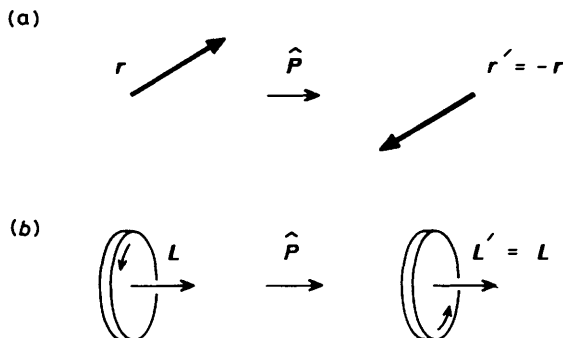


Figure 1 The parity operator \hat{P} changes the sign of the polar position vector \mathbf{r} in (a) but does not change the sign of the axial angular momentum vector \mathbf{L} in (b)

pseudo vector: for example the angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, the vector product of \mathbf{r} and the linear momentum vector \mathbf{p} , and since the polar vectors \mathbf{r} and \mathbf{p} change sign under \hat{P} , the axial vector \mathbf{L} does not. In other words, \mathbf{L} is defined relative to the sense of rotation by a right-hand rule, and \hat{P} does not change the sense of rotation (Figure 1b). A vector whose sign is not changed by \hat{T} is called *time-even*; for example the position vector, which is not a function of time. A vector whose sign is changed by \hat{T} is called *time-odd*; for example, velocity and angular momentum. Figure 2 illustrates the effect of \hat{T} on \mathbf{r} , \mathbf{v} , and \mathbf{L} .

A *pseudoscalar* quantity is a number with no directional properties but which changes sign under \hat{P} . In accordance with the definitions in the previous paragraph, a pseudoscalar is generated by taking the scalar product of a polar and an axial vector. Pseudoscalar quantities are of central importance in *natural* optical activity phenomena because the quantities that are measured, such as optical rotation angle, rotational strength, or Raman circular intensity difference, are pseudoscalars. The fact that natural optical activity is only supported by isotropic bulk samples if the constituent molecules are chiral is a manifestation of Neumann's principle,¹¹⁻¹³ which states that any type of symmetry exhibited by the point

¹¹ F. E. Neumann, 'Vorlesungen über die Theorie Elastizität der festen Körper und des Lichtäthers', Teubner, Leipzig, 1885.

¹² R. R. Birss, 'Symmetry and Magnetism', North-Holland, Amsterdam, 1966.

¹³ A. V. Shubnikov and V. A. Koptsik, 'Symmetry in Science and Art', Plenum Press, New York, 1974.

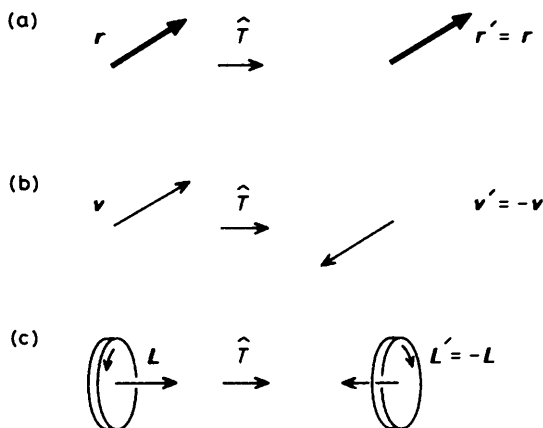


Figure 2 The time reversal operator \hat{T} does not change the sign of the time-even position vector r in (a), but changes the sign of the time-odd velocity vector v in (b) and angular momentum vector L in (c)

group of a system is possessed by every physical property of the system. Curie's re-statement of Neumann's principle is particularly penetrating in this instance:¹⁴ 'C'est la dissymétrie qui crée le phénomène'. Thus no dissymmetry can manifest itself in a physical property which does not already exist in the system: in this instance space inversion interconverts a pair of distinguishable enantiomers, and changes the signs of the associated pseudoscalar observables.

An important consequence of the existence of symmetries in the laws which determine the operation of the physical world is that, if a *complete* experiment is subjected to an associated symmetry operation such as space inversion or time reversal, the resulting experiment should, in principle, be realizable.^{15,16} A detailed consideration of the natural optical rotation experiment shows that it does indeed conserve parity and reversality;^{17,18} and such arguments can also be used to predict or discount possible new effects (such as an electric analogue of the Faraday effect) without recourse to mathematical theories.¹⁷⁻²⁰ Stedman has provided a complementary discussion from the standpoint of photon selection rules.^{21,22}

¹⁴ P. Curie, *J. Phys. (Paris)* (3), 1894, 3, 393.

¹⁵ E. P. Wigner, *Z. Phys.*, 1927, 43, 624.

¹⁶ R. P. Feynman, R. B. Leighton, and M. Sands, 'The Feynman Lectures on Physics', Addison-Wesley, Reading, Massachusetts, 1964.

¹⁷ L. D. Barron, *Nature (London)*, 1972, 238, 17.

¹⁸ L. D. Barron, 'Molecular Light Scattering and Optical Activity', Cambridge University Press, Cambridge, 1982.

¹⁹ I. M. B. de Figueiredo and R. E. Raab, *Proc. R. Soc. London, Ser. A*, 1980, 369, 501.

²⁰ C. Graham, *Proc. R. Soc. London, Ser. A*, 1980, 369, 517.

²¹ G. E. Stedman, *Am. J. Phys.*, 1983, 51, 753.

²² G. E. Stedman, *Adv. Phys.*, 1985, 34, 513.

B. Symmetry in Quantum Mechanics.—(i) *Parity*. The application of the parity operation in quantum mechanics leads to some important new features. The starting point is the invariance of the conventional (that is, parity-conserving) Hamiltonian for a closed system of interacting particles to an inversion of the coordinates of all the particles. \hat{P} is now interpreted as a linear unitary Hermitian operator that changes the sign of the space coordinates in the Hamiltonian and the wavefunction. Consider first the wavefunction:

$$\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}) \quad (1)$$

If $\psi(\mathbf{r})$ happens to be eigenfunction of \hat{P} we can write

$$\hat{P}\psi(\mathbf{r}) = p\psi(\mathbf{r}) \quad (2)$$

The eigenvalues p are found by noticing that a double application amounts to the identity:

$$\hat{P}^2\psi(\mathbf{r}) = p^2\psi(\mathbf{r}) = \psi(\mathbf{r}) \quad (3)$$

so that

$$p^2 = 1, p = \pm 1 \quad (4)$$

Thus for even (+) and odd (−) parity wavefunctions we have

$$\hat{P}\psi(+)=\psi(+), \hat{P}\psi(-)=-\psi(-) \quad (5)$$

Turning now to the Hamiltonian, its invariance under space inversion means we can write

$$\hat{P}\hat{H}\hat{P}^{-1} = \hat{H}, \text{ or } [\hat{P}, \hat{H}] \equiv \hat{P}\hat{H} - \hat{H}\hat{P} = 0 \quad (6)$$

From a consideration of the derivative of an operator with respect to time it follows that the expectation value of \hat{P} is constant in time.²³ Thus equation 6 expresses the *law of conservation of parity*: if the state of a closed system has definite parity, that parity is conserved.

If two eigenfunctions $\psi(+)$ and $\psi(-)$ of opposite parity have energy eigenvalues that are degenerate, or nearly so, the system can exist in states of *mixed* parity with wavefunctions

$$\psi_1 = \frac{1}{\sqrt{2}} [\psi(+) + \psi(-)] \quad (7a)$$

$$\psi_2 = \frac{1}{\sqrt{2}} [\psi(+) - \psi(-)] \quad (7b)$$

²³ L. D. Landau and E. M. Lifshitz, 'Quantum Mechanics', Pergamon Press, Oxford, 1977.

Clearly these two mixed parity states are interconverted by \hat{P} :

$$\hat{P}\psi_1 = \psi_2, \hat{P}\psi_2 = \psi_1 \quad (8)$$

It follows from (6) that a central property of definite parity states is that they are *true* stationary states with constant energy $W(+)$ or $W(-)$, *i.e.*

$$\psi(\pm) = \psi^{(0)}(\pm) e^{-iW(\pm)t/\hbar} \quad (9)$$

but mixed parity states are not. (Mixed parity states can become *quasi*-stationary states when $W(+)$ \approx $W(-)$, and true stationary states if \hat{H} contains a parity-violating term: see Sections 8A and B below.)

All observables can be classified as having even or odd parity depending on whether they are invariant or change sign under space inversion. Even and odd parity operators $\hat{A}(+)$ and $\hat{A}(-)$ associated with these observables are thus defined by

$$\hat{P}\hat{A}(+)\hat{P}^{-1} = \hat{A}(+), \hat{P}\hat{A}(-)\hat{P}^{-1} = -\hat{A}(-) \quad (10)$$

Since integrals taken over all space are only non-zero for totally symmetric integrands, the expectation values of these operators in a state such as (7a) reduce to

$$\langle \psi_1 | \hat{A}(+) | \psi_1 \rangle = \frac{1}{2} [\langle \psi(+) | \hat{A}(+) | \psi(+) \rangle + \langle \psi(-) | \hat{A}(+) | \psi(-) \rangle] \quad (11a)$$

$$\langle \psi_1 | \hat{A}(-) | \psi_1 \rangle = \frac{1}{2} [\langle \psi(+) | \hat{A}(-) | \psi(-) \rangle + \langle \psi(-) | \hat{A}(-) | \psi(+) \rangle] \quad (11b)$$

from which we deduce that the expectation value of any odd parity observable vanishes in any state of definite parity, that is, a state for which either $\psi(+)$ or $\psi(-)$ is zero. Consequently, measurements on a system in a state of *definite* parity can reveal only observables with *even* parity, examples being electric charge, angular momentum, magnetic dipole moment, electric quadrupole moment, *etc.*; whereas measurements on a system in a state of *mixed* parity can reveal, in addition, observables with *odd* parity, examples being magnetic monopole (never observed), linear momentum, electric dipole moment, *etc.*²⁴ The optical rotatory parameter, being a pseudoscalar, has odd parity. Consequently, *resolved chiral molecules exist in mixed parity quantum states*, the detailed nature of which will be elaborated later.

(ii) *Time Reversal*. Although it is possible to classify time-even and time-odd Hermitian operators and their associated observables according to whether they are invariant or change sign under time reversal, a division of quantum states into even and odd reversality, respectively, analogous to the division into even and odd parity, is obscure for several reasons that will not be elaborated here.^{18,24,25} In fact the classical time reversal operator \hat{T} introduced above does not translate directly into a satisfactory quantum-mechanical operator. Instead, the operator^{18,24,25}

²⁴ F. A. Kaempffer, 'Concepts in Quantum Mechanics', Academic Press, New York, 1965.

²⁵ J. J. Sakurai, 'Modern Quantum Mechanics', Benjamin/Cummings, Menlo Park, California, 1985.

$$\hat{\Theta} = \hat{T}\hat{K} \quad (12)$$

where T represents the transformation $t \longrightarrow -t$ and \hat{K} is the operator of complex conjugation, is taken as the time reversal operator in quantum mechanics.

Unlike \hat{P} , $\hat{\Theta}$ does not have eigenvalues so it is not possible to classify a quantum state as being even and odd under time reversal. (On the other hand, the operator $\hat{\Theta}^2$ has eigenvalues, these being $+1$ for an even-electron system and -1 for an odd-electron system). A simple illustration that will prove useful in the subsequent discussion is the effect of $\hat{\Theta}$ on a general atomic state $|JM\rangle$ where both orbital and spin angular momenta can contribute to the total electronic angular momentum characterized by the usual quantum numbers J and M . Using a particular phase convention,¹⁸ we can write

$$\hat{\Theta}|JM\rangle = (-1)^{J-M+q}|J-M\rangle \quad (13)$$

where q is the sum of the individual orbital quantum numbers of all the electrons in the atom. Thus time reversal has generated a new quantum state, orthogonal to the original one, corresponding to a reversal of the sense of the total angular momentum of the atom. Such states can be loosely regarded as having 'mixed reversality', analogous to the mixed parity states (7), and as such can support time-odd observables.^{18,24} It should be emphasized that states $|JM\rangle$ do have definite parity since they are eigenstates of \hat{P} .²³

$$\hat{P}|JM\rangle = (-1)^q|JM\rangle \quad (14)$$

This follows from the behaviour under space inversion of the spherical harmonic functions, which correspond to the orbital angular momentum eigenfunctions, and the standard convention that the 'intrinsic parity' of an electron spin state is $+1$.

(iii) *Charge Conjugation*. A discussion of the effect of the charge conjugation operator \hat{C} in quantum mechanics requires a formulation in terms of relativistic quantum field theory.^{10,26} For the purposes of this article, all we need to appreciate is that a charged particle is not in an eigenstate of \hat{C} .²⁶

3 The Distinction Between Natural and Magnetic Optical Activity

A central theme of this article is the distinction between natural and magnetic optical activity, which is often a source of confusion in the literature of both chemistry and physics. We shall see that optical activity is not necessarily the hallmark of chirality and that a proper symmetry classification of the corresponding observables leads to a more precise definition of a chiral object. This classification is obtained by comparing the results of optical rotation measurements before and after subjecting the sample plus any applied field to space inversion and time reversal (this is a different procedure to that mentioned at the end of Section 2A in which the *complete* experiment, including the probe light beam, is subjected to symmetry operations in order to demonstrate conservation of parity and reversality).

²⁶ V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, 'Quantum Electrodynamics', Pergamon Press, Oxford, 1982.

Consider first the natural optical rotation experiment. Under space inversion, an isotropic collection of chiral molecules is replaced by a collection of enantiomeric molecules, and an observer with a linearly polarized probe light beam will measure equal and opposite optical rotation angles before and after the inversion. This indicates that the observable has odd parity, and it is easy to deduce that it is a pseudoscalar (rather than, say, a polar vector) because it is invariant with respect to any proper rotation in space of the complete sample. Under time reversal, an isotropic collection of chiral molecules is unchanged, so the optical rotation is unchanged. Thus the *natural* optical rotation observable is a *time-even pseudoscalar*.

Now consider the Faraday effect, where optical rotation is induced in an isotropic collection of achiral molecules by a static uniform magnetic field parallel to the light beam. Under space inversion, the molecules and the magnetic field direction are unchanged, so the same magnetic optical rotation will be observed. This indicates that the observable has even parity, and we can further deduce that it is an axial vector (rather than a scalar) by noticing that a proper rotation of the complete sample, including the magnetic field, through π about any axis perpendicular to the field reverses the relative directions of the magnetic field and the probe beam and so changes the sign of the observable. Under time reversal, the collection of molecules (even if they are paramagnetic) can be regarded as unchanged provided it is isotropic in the absence of the field, but again the relative directions of the magnetic field and the probe light beam are reversed and so the optical rotation changes sign. Thus the *magnetic* optical rotation observable is a *time-odd axial vector*.

These conclusions are reinforced by a more fundamental approach in which operators are defined whose expectation values generate the optical activity observables.^{27,18} It is found that the natural optical rotation observable is generated by a time-even odd-parity operator, and the magnetic optical rotation observable is generated by a time-odd even-parity operator. Another viewpoint is to look at the associated molecular property tensors: it is found that all the contributions to natural optical rotation are generated by time-even tensors, and that all the contributions to magnetic optical rotation are generated by time-odd tensors.^{28,29} Indeed, some time ago Zocher and Török³⁰ discussed the space-time symmetry aspects of natural and magnetic optical activity from a general classical viewpoint, and recognized that quite different asymmetries are involved. In order to emphasize the distinction, they suggested that only Faraday optical rotation be described as originating in circular double refraction, enantiomeric double refraction being a better description of natural optical rotation.

Thus the nature of the quantum states of molecules that can support natural optical rotation is quite different from that of the quantum states that can support magnetic optical rotation. From the discussion in Section 2 it is clear that the

²⁷ L. D. Barron, *Mol. Phys.*, 1981, **43**, 1395.

²⁸ A. D. Buckingham, C. Graham, and R. E. Raab, *Chem. Phys. Lett.*, 1971, **8**, 622.

²⁹ A. D. Buckingham, *Philos. Trans. R. Soc. London, Ser. A*, 1979, **293**, 239.

³⁰ H. Zocher and C. Török, *Proc. Natl. Acad. Sci. USA*, 1953, **39**, 681.

former must have, among other things, mixed parity and the latter mixed reversality.³¹ The former is associated with spatial dissymmetry and corresponds to true chirality; whereas the latter originates in a different type of dissymmetry associated with lack of time reversal invariance and corresponds to false chirality. From Pasteur onwards these two types of optical activity have often been confused. Recent examples include the assertion that an achiral molecule in a pure rotational state can be regarded as chiral,^{32,33} and that there exists a chiral discrimination in the intermolecular forces between co- and counter-rotating pairs of such molecules.³⁴ It is certainly correct to call an achiral molecule in a pure rotational quantum state $|JM\rangle$ (or $|JKM\rangle$ for a symmetric top) optically active, since it will induce optical rotation in a light beam travelling parallel to the space-fixed quantization axis. An equal and opposite optical rotation is induced by $|J - M\rangle$. But this is equivalent to magnetic optical activity since a magnetic field, or some other time-odd influence such as a rotation of the bulk sample,³⁵ is required to lift the degeneracy between $|JM\rangle$ and $|J - M\rangle$.

This view is supported by a recent study of Raman optical activity in pure rotational transitions of gas-phase chiral molecules.³⁶ It was shown explicitly that the rotational quantum states by themselves do not introduce any new source of chirality: in the absence of any time-odd influence that discriminates between the rotational states, the optical activity observables originate exclusively in the chiral molecular framework.

4 A New Definition of Chirality

Although Pasteur was mistaken in thinking that the dissymmetry created by magnetic fields is equivalent to purely spatial dissymmetry, he was correct in asserting that the latter is similar to the dissymmetry generated by a rotation coupled with linear motion. In order to distinguish chirality from other types of dissymmetry, I have proposed a new definition^{27,18} that follows directly from the discussion in the previous section of the behaviour of the quantum states of enantiomeric objects under space inversion and time reversal:

True chirality is exhibited by systems that exist in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation.

I suggest that the word 'chiral' be reserved in future for systems that I call here truly chiral (*i.e.* time-invariant dissymmetric or enantiomorphous).

5 Translating Spinning Cones, Spheres, Photons and Electrons

A. Cones and Spheres.—Consider a cone spinning about its symmetry axis. Since the space-inverted version is not superposable on the original (Figure 3a), it might

³¹ L. D. Barron, *Chem. Phys. Lett.*, 1981, **79**, 392.

³² P. W. Atkins and J. A. N. F. Gomes, *Chem. Phys. Lett.*, 1976, **39**, 519.

³³ K. Mislow and P. Bickart, *Isr. J. Chem.*, 1976/77, **15**, 1.

³⁴ P. W. Atkins, *Chem. Phys. Lett.*, 1980, **74**, 358.

³⁵ R. V. Jones, *Proc. R. Soc. London, Ser. A*, 1976, **349**, 423.

³⁶ L. D. Barron and C. J. Johnston, *J. Raman Spectrosc.*, 1985, **16**, 208.

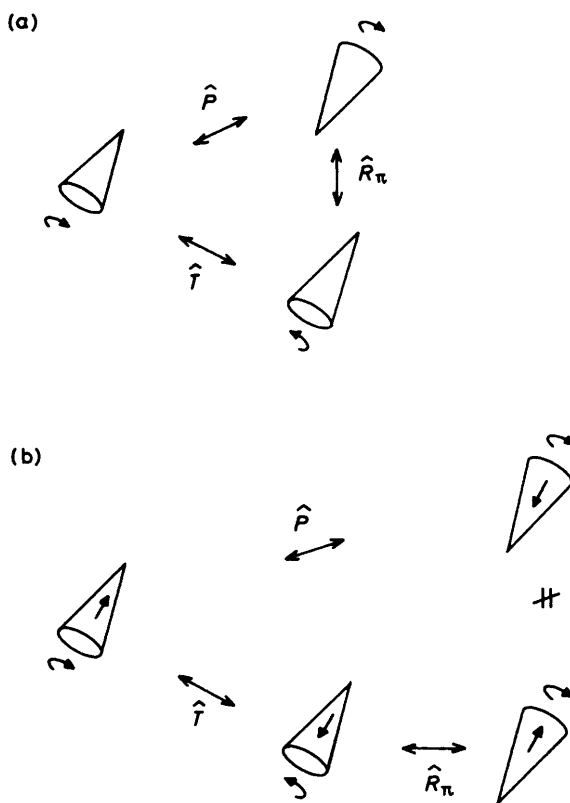


Figure 3 The effect of \hat{P} , \hat{T} , and \hat{R}_π on (a) a stationary spinning cone and (b) a translating spinning cone

be thought that this is a chiral object. However, according to the new definition above, it is false chirality because time reversal followed by a rotation \hat{R}_π through 180° about an axis perpendicular to the symmetry axis generates the same object as space inversion (Figure 3a). The molecular equivalent is a symmetric top in a rotational quantum state $|JKM\rangle$. The parity operator transforms $|JKM\rangle$ into $|J-KM\rangle$, which therefore has mixed parity,³⁷ so that these two states correspond to the two non-superposable cones in Figure 3a. And just as the two cones can be interconverted by time reversal followed by a rotation through 180° about an axis perpendicular to the symmetry axis, so this sequence of operations interconverts $|JKM\rangle$ and $|J-KM\rangle$.

This shows that mixed parity in a particular quantum state is not necessarily sufficient to generate true chirality, despite the fact that it results here in two non-

³⁷ A. Bohm, 'Quantum Mechanics', Springer-Verlag, New York, 1979.

superposable mirror-image objects. The reason is that, although mixed parity is a necessary condition for any odd-parity observable, further attributes are required for different types of odd-parity observable. In this instance the mixed parity attribute of the rotational quantum state $|JKM\rangle$ results in a symmetric top with $K \neq 0$ showing a space-fixed electric dipole moment (an odd-parity observable transforming as a polar vector) and hence a first-order Stark effect provided the top is dipolar to start with; but of course in order for the top to be dipolar there is the additional requirement of mixed parity *internal* (vibrational–electronic) quantum states associated with a molecular framework of C_n or C_{nv} symmetry. On the other hand natural optical rotation in isotropic samples (an odd-parity observable transforming as a pseudoscalar) requires mixed parity vibrational–electronic quantum states associated with a chiral molecular framework (symmetry C_n, D_n, O, T , or I), but there is no requirement for mixed parity rotational states.

However, if the spinning cone is also translating along the axis of spin, time reversal followed by the 180° rotation about an axis perpendicular to the spin axis now generates a different object to that generated by space inversion (Figure 3b). Thus a translating spinning cone exhibits true chirality.

In fact the translating spinning object does not need to be a cone or a symmetric top molecule. A sphere or a spherical top molecule translating along the axis of spin also shows true chirality. This can be appreciated by looking at just the patterns of arrows in Figure 3b and ignoring the cone.

B. Photons, Electrons, and Neutrons.—The photons in a circularly polarized light beam propagating as a plane wave are in spin angular momentum eigenstates characterized by a spin quantum number $s = 1$, with quantum numbers $m_s = +1$ and -1 corresponding to projections of the spin angular momentum vector parallel and antiparallel, respectively, to the propagation direction. The absence of states with $m_s = 0$ is connected with the fact that photons, being massless, have no rest frame and so always move with the velocity of light (the usual $2j + 1$ projections for a general angular momentum vector are defined in the rest frame).²⁶ In the usual convention, the electric vector of a right-circularly polarized light beam rotates in a clockwise sense when viewed towards the source of the beam, so right- and left-circularly polarized photons have spin angular momentum projections $-\hbar$ and $+\hbar$, respectively, along the propagation direction. Considerations analogous to those give above for a translating spinning sphere then show that a circularly polarized photon exhibits true chirality.

The case of a spinning electron ($s = \frac{1}{2}$, $m_s = \pm \frac{1}{2}$) is somewhat different to that of a circularly polarized photon because an electron has rest mass. From the foregoing, it is clear that, whereas a stationary spinning electron is not a chiral object, an electron translating with its spin projection parallel or antiparallel to the propagation direction exhibits true chirality, with opposite spin projections corresponding to opposite handedness. Indeed, experiments have been proposed in which beams of spin-polarized electrons impinging on targets composed of chiral molecules exhibit effects analogous to the polarization effects in the light beams

used as probes in conventional optical activity phenomena.³⁸⁻⁴⁰ A central aspect of such experiments is that, all other things being equal, the magnitudes of the optical activity observables should increase with increasing electron velocity because electron chirality is velocity-dependent. This is emphasized by a mechanism proposed for asymmetric decomposition of enantiomeric chiral molecules by longitudinally spin-polarized electrons that is a function of v/c ,⁴¹ and by the discussion in Section 9B below of the velocity-dependence of the amplitude of parity violation in the weak interaction. As this article was being written, Campbell and Farago⁴² reported observations of an asymmetry in the attenuation of beams of right- and left-handed spin-polarized 5eV electrons on passing through camphor vapour: the fact that a large effect was observed with electron beams of such low energy is probably due to the fact that camphor has a broad resonance associated with $\pi^* \leftarrow n$ carbonyl transitions at about this energy.

Analogous experiments have been proposed for beams of spin-polarized neutrons,⁴³⁻⁴⁶ which are also spin- $\frac{1}{2}$ particles with mass.

6 Absolute Asymmetric Synthesis

The use of an external chiral physical influence to produce an enantiomeric excess in what would otherwise be a racemic product of a prochiral chemical reaction is known as an 'absolute asymmetric synthesis'.^{47,48} Here we apply the symmetry arguments elaborated above in order to distinguish between true and false chirality in the various physical influences that have been proposed.⁴⁹

A. Circularly Polarized Radiation.—It was shown above that a circularly polarized photon exhibits true chirality, and following Le Bel's original suggestion in 1874, many examples of the use of circularly polarized electromagnetic radiation as a chiral physical influence on chemical systems are now known.^{5,48,49} All of these examples use visible or ultraviolet radiation and are usually based on electronic circular dichroism. Although infrared circular dichroism is now well-established,^{50,51} I am unaware of attempts to use circularly polarized infrared radiation as a chiral physical influence by way of vibrational circular dichroism.

³⁸ M. J. M. Beerlage, P. S. Farago, and M. J. Van der Wiel, *J. Phys. B*, 1981, **14**, 3245.

³⁹ P. S. Farago, *J. Phys. B*, 1981, **14**, L743.

⁴⁰ A. Rich, J. Van House, and R. A. Hegstrom, *Phys. Rev. Lett.*, 1982, **48**, 1341.

⁴¹ Ya. B. Zel'dovich and D. B. Saakyan, *Sov. Phys. JETP*, 1980, **51**, 1118.

⁴² D. M. Campbell and P. S. Farago, 1985, *Nature* (London), **318**, 52.

⁴³ P. K. Kabir, G. Karl, and E. Obryk, *Phys. Rev. D*, 1974, **10**, 1471.

⁴⁴ J. N. Cox and F. S. Richardson, *J. Chem. Phys.*, 1977, **67**, 5702.

⁴⁵ R. A. Harris and L. Stodolsky, *J. Chem. Phys.*, 1979, **70**, 2789.

⁴⁶ B. Gazdy and J. Ladik, *Chem. Phys. Lett.*, 1982, **91**, 158.

⁴⁷ J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions', American Chemical Society, Washington, D.C., 1976.

⁴⁸ Y. Izumi and A. Tai, 'Stereo-Differentiating Reactions', Academic Press, New York, 1977.

⁴⁹ S. F. Mason, *Int. Rev. Phys. Chem.*, 1983, **3**, 217.

⁵⁰ S. F. Mason, *Adv. Infrared Raman Spectrosc.*, 1981, **8**, 5.

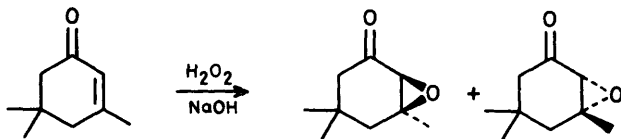
⁵¹ L. A. Nafie, *Adv. Infrared Raman Spectrosc.*, 1984, **11**, 49.

Baranova and Zel'dovich⁵² have suggested the use of circularly polarized radiofrequency radiation partially to resolve racemic fluids by way of the hydrodynamic 'propeller effect'. It is well-known that an arbitrary chiral body rotating about a fixed axis in a viscous medium is affected by a translational force. Since an electric field applied to a fluid will partially orient the constituent molecules, the rotating electric field vector of a circularly polarized radiofrequency field will induce angular velocity in the molecules, thereby inducing equal translational forces in opposite directions for the two enantiomers. However, the radiofrequency field is not in fact acting here as a chiral influence since only the circular component of its motion is involved; the linear component does not act and the bulk sample is racemic overall. It is possible to conceive of an inverse analogue of this experiment: the application of a static electric field to a solution of ionic chiral molecules produces a linear drift of the ions, and the propeller effect gives rise to a rotation, clockwise for one enantiomer and anticlockwise for the other.⁵³ A related suggestion is that an intense circularly polarized laser beam should generate a drift current parallel to the propagation direction in an electron swarm in a gas composed of chiral molecules.⁵⁴

While on the subject of the propeller effect, Evans has used computer simulation methods to show how the correlation between rotational and translational motions of chiral molecules in the liquid phase can be important in explaining the differences in the thermodynamic and spectroscopic properties of a resolved enantiomer and the corresponding racemic mixture.^{55,56}

B. Electric and Magnetic Fields.—Fixed electric and magnetic fields as chiral agents have been more contentious than circularly polarized radiation.

In a paper published in 1975, Gerike⁵⁷ asserted that 'absolute asymmetric syntheses are also possible when reactions are run under the simultaneous influence of electric and magnetic fields'. This was based on his detection of optical rotation in reaction mixtures after the reactions had been allowed to proceed in the presence of simultaneous electric and magnetic fields. A typical reaction was the epoxidation of isophorone (Scheme 1):



Scheme 1

⁵² N. B. Baranova and B. Ya. Zel'dovich, *Chem. Phys. Lett.*, 1978, **57**, 435.

⁵³ N. B. Baranova and B. Ya. Zel'dovich, *Optics Commun.*, 1977, **22**, 246.

⁵⁴ B. Ritchie, *Phys. Rev. A*, 1981, **24**, 950.

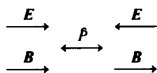
⁵⁵ M. W. Evans, *Phys. Rev. Lett.*, 1983, **50**, 371.

⁵⁶ M. W. Evans, in 'Memory Function Approaches to Stochastic Problems in Condensed Matter', ed. M. W. Evans, P. Grigolini, and G. Pastori Parravicini, Wiley, New York, 1985. (Special issue of *Adv. Chem. Phys.*, **62**.)

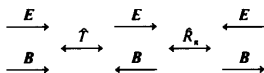
⁵⁷ P. Gerike, *Naturwissenschaften*, 1975, **62**, 38.

Non-zero rotations were reported for both static and time-dependent uniform fields, the fields being sometimes parallel and sometimes orthogonal. Parallel and antiparallel field combinations seemed to cause opposite rotations.

It is clear from the new definition of true chirality given above that, contrary to a suggestion first made by Curie,¹⁴ no combination of a uniform constant electric field \mathbf{E} (a time-even polar vector) and a uniform and constant magnetic field \mathbf{B} (a time-odd axial vector) can constitute a chiral influence. Although parallel and antiparallel arrangements are dissymmetric in that they are interconverted by space inversion and are not superposable,



they are also interconverted by time reversal combined with a rotation through 180°



The apparent chirality here is therefore *false*. Zocher and Török³⁰ also recognized the flaw in Curie's suggestion: they called the combination of electric and magnetic fields with parallel lines of force a time-asymmetric enantiomorphism, and said that it does not permit a time-symmetric optical activity. In fact the basic requirement for two co-linear vectorial influences to generate true chirality is that one transforms as a polar vector and the other as an axial vector, with both either time-even or time-odd (the second case is exemplified by the rotating translating cone or sphere discussed above, and the magneto-chiral effects discussed below).

Several years before Gerike's work, de Gennes⁵⁸ had presented a theorem stating the impossibility of asymmetric synthesis in a static electric and magnetic field that was based on the invariance of the Hamiltonian of a molecule in such fields under space inversion and time reversal. Using similar arguments, Mead *et al.*⁵⁹ concluded that '... a simultaneous application of uniform constant electric and magnetic fields cannot affect the equality of the equilibrium enantiomeric populations in a racemic reaction mixture. Hence, whatever the sources of the reported rotations, they cannot have had their origin in uniform applied fields if the reactions have gone to completion'.

Rhodes and Dougherty⁶⁰ extended the argument by pointing out that the conclusions of deGennes and Mead *et al.* apply only to chemical systems in a state of equilibrium and so are not relevant for reactions that are kinetically, rather than thermodynamically, controlled, since these can go to completion without reaching complete thermodynamic equilibrium. They invoked a current density (or magnetic moment) in the transition states which are precursors to products and claimed to show that, in the presence of \mathbf{E} and \mathbf{B} , this can lead to different rates of

⁵⁸ P. G. de Gennes, *C. R. Hebd. Seances Acad. Sci., Ser. B*, 1970, **270**, 891.

⁵⁹ C. A. Mead, A. Moscowitz, H. Wynberg, and F. Meuwese, *Tetrahedron Lett.*, 1977, 1063.

formation of the two enantiomeric products. However, Mead and Moscowitz⁶¹ found these arguments unconvincing, and claimed to show that such kinetic effects are actually required to be zero by the condition of detailed balancing. De Gennes has returned to the subject⁶² and appears to support Rhodes and Dougherty. See also *ref.* 63.

C. Spinning Vessels and Gravity.—Even more contentious than fixed electric and magnetic fields have been the claims for absolute asymmetric synthesis in a ‘chiral gravitational field’. Dougherty *et al.*^{64–66} reported asymmetric synthesis of isophorone oxide from isophorone in a rapidly rotating vessel, with a positive optical rotation shown when the vessel is spun clockwise (as viewed from above) with the axis of rotation perpendicular to the earth’s surface, and a smaller negative rotation when the vessel is spun counterclockwise; but no optical rotation when the vessel is spun about an axis parallel to the earth’s surface.

This situation is closely analogous to the case of electric and magnetic fields since here we have the time-odd axial angular momentum vector of the spinning vessel either parallel or antiparallel to the earth’s gravitational field, itself a time-even polar vector. The physical influence therefore exhibits *false* chirality. Mead and Moscowitz⁶¹ and Peres⁶⁷ criticized these claims, again using arguments based on the invariance of the Hamiltonian.

A related controversy arose a few years earlier over the use of dissymmetric flow, induced in a conical swirl, to produce a slight enantiomeric excess during the synthesis of a cyanine dye.⁶⁸ Although there is no question here that the physical influence is truly chiral (rotation plus translation), it was suggested that the observed optical rotation was actually an artifact due to linear dichroism from accidentally oriented material.⁶⁹

Experiments have also been reported in which polymerizing amino acid solutions were stirred in a clockwise and an anticlockwise sense and the resulting polymerized material analysed for signs of stereoselectivity.⁷⁰ None was found.

Spinning vessels have also been considered for separating a racemic collection of enantiomeric crystals (in other words, to automate Pasteur’s original technique of sorting the individual crystals by hand).^{71,62} This ‘hydrodynamic resolution’ is the inverse of the radiofrequency propeller effect discussed above: now it is the fluid

⁶⁰ W. Rhodes and R. C. Dougherty, *J. Am. Chem. Soc.*, 1978, **100**, 6247.

⁶¹ C. A. Mead and A. Moscowitz, *J. Am. Chem. Soc.*, 1980, **102**, 7301.

⁶² P. G. de Gennes, in ‘Symmetry and Broken Symmetry’, ed. N. Boccara, Editions IDSET, Paris, 1981.

⁶³ Chr. de Reyff, *J. Chim. Phys. Phys. Chim. Bid.*, 1983, **80**, 563.

⁶⁴ R. C. Dougherty, *J. Am. Chem. Soc.*, 1980, **102**, 380.

⁶⁵ D. Edwards, K. Cooper, and R. C. Dougherty, *J. Am. Chem. Soc.*, 1980, **102**, 381.

⁶⁶ R. C. Dougherty, *Origins Life*, 1981, **11**, 71.

⁶⁷ A. Peres, *J. Am. Chem. Soc.*, 1980, **102**, 7390.

⁶⁸ C. Honda and H. Hada, *Tetrahedron Lett.*, 1976, **3**, 177.

⁶⁹ B. Nordén, *J. Phys. Chem.*, 1978, **82**, 744.

⁷⁰ K. L. Kovacs, L. Kesthelyi, and V. J. Goldanskii, *Origins Life*, 1981, **11**, 93.

⁷¹ D. W. Howard, E. N. Lightfoot, and J. O. Hirschfelder, *A. I. Chem. Eng. J.*, 1976, **22**, 794.

that rotates, and the non-rotating enantiomeric crystals are propelled in opposite directions parallel to the rotation axis of the spinning drum.

D. Magneto-chiral Effects.—An interesting new phenomenon has been discussed recently: a static magnetic field parallel to the direction of propagation of an incident light beam can produce a small shift in the value of the absorption coefficient of a chiral molecule.⁷² This shift is quite independent of the polarization characteristics of the light beam, and changes sign either on replacing the chiral molecule by its mirror-image enantiomer, or on reversing the relative directions of the magnetic field B and propagation vector k (a time-odd polar vector) of the light beam.^{73,74} The name *magneto-chiral dichroism* has been suggested.⁷³ It has been shown that the experiment conserves parity and reversality, and that the magneto-chiral observable transforms as a *time-odd polar vector*⁷³ (cf. the natural optical activity observable which is a time-even pseudoscalar, and the magnetic optical activity observable which is a time-odd axial vector).

Thus a uniform static magnetic field parallel to the propagation direction of a light beam (of arbitrary polarization) constitutes a truly chiral influence, and is a candidate for inducing asymmetric synthesis.⁷⁵ Reversing the relative directions of B and k generates the enantiomeric influence. (Parallel and antiparallel arrangements of B and k are true chiral enantiomers because they cannot be interconverted by time reversal since k , unlike E , is time-odd). The reported attempts to induce photochemical asymmetric synthesis using linearly polarized light in the presence of an intense magnetic field^{76,77} do not now look quite so silly!

E. Further Considerations.—The controversy surrounding the reports of absolute asymmetric synthesis in situations where the external influence exhibits false chirality indicates that caution is required in reaching any definite conclusions based solely on whether or not the external influence is truly chiral. Such arguments are essentially applications of Neumann's principle (Section 2A); and Neumann's principle is only valid in space-time for *static* properties, not for *dynamic* properties such as transport phenomena where a system is permanently in non-equilibrium but has reached a steady state.¹² In general, Neumann's principle cannot be applied to a system in which the entropy is changing,¹² which is certainly the case for a reaction mixture that has not been allowed to reach thermodynamic equilibrium. More mundane reservations are that non-uniform fields or forces could be present, and the reacting species might be partially aligned on the walls of the reaction vessel.

A rather different reservation arises in connection with the application of the principle of detailed balancing to the problem. Lifshitz and Pitaevskii⁷⁸ have

⁷² G. Wagnière and A. Meier, *Chem. Phys. Lett.*, 1982, **93**, 78.

⁷³ L. D. Barron and J. Urbancich, *Mol. Phys.*, 1984, **51**, 715.

⁷⁴ G. Wagnière, *Z. Naturforsch., Teil A*, 1984, **39**, 254.

⁷⁵ G. Wagnière and A. Meier, *Experientia*, 1983, **39**, 1090.

⁷⁶ D. Radulescu and J. Moga, *Bull. Soc. Chim. Romania*, 1939, **1**, 2.

⁷⁷ H. Pracejus, *Top. Curr. Chem.*, 1967, **8**, 54.

⁷⁸ E. M. Lifshitz and L. P. Pitaevskii, 'Physical Kinetics', Pergamon Press, Oxford, 1981.

pointed out that, for a system comprising resolved chiral molecules of just one enantiomer, *strict* detailed balancing does not obtain. This is because the strict detailed balancing result is obtained by applying space inversion as well as time reversal to the system of colliding particles, which means that a completely different system is generated and so cannot be compared with the original. (See Sakurai²⁵ for a quantum-mechanical version of the strict detailed balancing result). However, for a system at equilibrium in which equal numbers of enantiomeric molecules are present, I have suggested that strict detailed balancing *can* be invoked if each microscopic collision process between two molecules is balanced by the reverse process involving the enantiomeric molecules.⁷⁹ Unlike the result of Mead and Moscovitz⁶¹ obtained using the conventional interpretation of the principle of detailed balancing that disregards whether or not chiral molecules are involved, this leads to a less restrictive result that does not rule out the possibility of absolute asymmetric synthesis induced by a falsely chiral influence in a reaction under kinetic control.⁷⁹

In conclusion, it appears that only a truly chiral influence can induce absolute asymmetric synthesis in a reaction mixture which is isotropic in the absence of the influence and which has been allowed to reach thermodynamic equilibrium. But for reactions under kinetic control, false chirality might suffice: the intrinsically preferred direction of time associated with the changing entropy¹² destroys the time reversal symmetry of the bulk reaction system so that the enantiomers of a time-*noninvariant* dissymmetric influence remain distinct.⁷⁹

7 Symmetry Violation

A symmetry violation is manifest when an experiment shows up one of the 'non-observables' discussed in Section 2A above. Although the study of symmetry violation belongs to the realm of physics rather than of chemistry, some consideration of symmetry violation, and its delineation from spontaneous symmetry breaking, provides considerable insight into the phenomenon of molecular chirality.

A. The Fall of Parity.—Prior to 1957, it had been accepted as self-evident that handedness is not built into the world at any level. Thus if two objects exist as non-superposable mirror images of each other, such as the two enantiomers of a chiral molecule, it did not seem reasonable that nature should prefer one over the other. Any difference between enantiomeric objects was thought to be confined to the sign of odd-parity observables: the mirror image of any complete experiment involving one enantiomer should be realizable, with any odd-parity observable (such as optical rotation angle) changing sign but retaining *precisely* the same magnitude. Then in 1956 Lee and Yang⁸⁰ pointed out that, unlike the electromagnetic and strong interactions, there was no evidence whatsoever for parity conservation in processes which involved the weak interaction. Of the experiments they suggested, that executed by Wu *et al.*⁸¹ in 1957 is the most famous.

⁷⁹ L. D. Barron, to be published.

⁸⁰ T. D. Lee and C. N. Yang, *Phys. Rev.*, 1956, **104**, 254.

⁸¹ C. S. Wu, E. Ambler, R. W. Hayward, D. D. Hoppes, and R. P. Hudson, *Phys. Rev.*, 1957, **105**, 1413.



The Wu experiment studied the β -decay process in which, essentially, a neutron n has decayed *via* the weak interaction into a proton p , an electron e^- , and electron antineutrino $\bar{\nu}_e$. The nuclear spin magnetic moment I of the ${}^{60}\text{Co}$ nuclei were aligned with an external magnetic field B , and the angular distribution of the electrons measured. It was found that the electrons are emitted preferentially in the direction *antiparallel* to that of the magnetic field (Figure 4a).

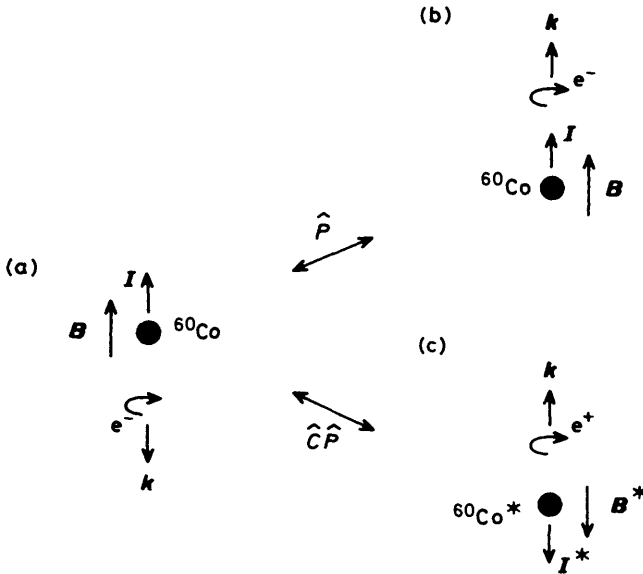


Figure 4 Parity violation in β -decay. Only experiment (a) is found: the space-inverted version (b) cannot be realized. Symmetry is recovered in experiment (c), which obtains from (a) by invoking charge conjugation simultaneously with space inversion (Co^* is anti-Co, and B^* and I^* are reversed relative to B and I because the charges of the moving source particles have reversed)

In accordance with the discussion in Section 2A, B and I are axial vectors and so do not change sign under space inversion, whereas the electron propagation vector k does because it is a polar vector. Thus in the space-inverted experiment the electrons are emitted *parallel* to the magnetic field (Figure 4b). Figures 4a and 4b can only be reconciled with parity conservation if there was no preferred direction for electron emission (an isotropic distribution), or if the electrons were emitted preferentially in the plane perpendicular to B . The observation of (a) alone provides unequivocal evidence for parity violation. Another important aspect of β -decay is that the emitted electrons have a ‘left-handed’ longitudinal spin polarization, being accompanied by ‘right-handed’ antineutrinos. The corresponding antiparticles emitted in β -decays, namely positrons and neutrinos, have the opposite handedness. (The projection of the spin angular momentum s of a particle along its

direction of motion is called the helicity, $\lambda = s \cdot p/|p|$. Spin $-\frac{1}{2}$ particles can have $\lambda = \pm \frac{1}{2}\hbar$, the positive and negative states being termed right- and left-handed; but this corresponds to the opposite sense of circularity to that used in the usual definition of right- and left-circularly polarized light).

In fact symmetry is recovered by invoking charge conjugation simultaneously with space inversion: the missing experiment is to be found in the antiworld! Thus it can be seen from Figure 4c that the combined operation of $\hat{C}\hat{P}$ interconverts two equivalent experiments for which nature appears to have no preference (assuming that T is not violated). This result implies that the \hat{P} -violation is accompanied here by \hat{C} -violation since absolute charge is distinguished: the charge that we call by convention 'negative' is carried by the electrons, which are emitted with a left-handed spin polarization.

Notice that the Wu experiment provides a good example of true chirality, as defined in Section 4. The two experiments (a) and (b) in Figure 4 are enantiomeric with respect to space inversion, but cannot be interconverted by time reversal combined with any proper spatial rotation.

B. Parity Violation in Atoms and Molecules.—(i) *The Weak Neutral Current Interaction.* Since the electromagnetic interaction is formulated in terms of an exchange of virtual photons, it was natural to postulate the existence of a particle, denoted W , that mediated the weak interaction. Like the photon, the W is a boson; but unlike the photon, which is neutral, the W must be charged (W^+ or W^-) since β -decay, for example, involves an exchange of charge between particles. A second difference is that, whereas photons have zero mass, the W s are massive (this follows from the Yukawa–Wick argument that the range of a force is inversely proportional to the mass of the exchanged quantum: the electromagnetic and weak interactions have infinite and very short ranges, respectively).

Following the Wu experiment, the original Fermi theory of the weak interaction⁸² was upgraded in order to take account of parity violation. This was achieved by reformulating the theory in such a way that the interaction takes the form of a left-handed pseudoscalar. However, a number of technical problems remained, which were finally overcome in the celebrated theory of Weinberg⁸³ and Salam⁸⁴ which unified the weak and the electromagnetic interactions into a single 'electroweak' interaction. The conceptual basis of the theory rests on two pillars: gauge invariance and spontaneous symmetry breaking,^{85,86} but the details are beyond the scope of this article. In addition to accommodating the massless photon and the two massive charged W^+ and W^- particles, a new massive *neutral* particle called Z^0 (the neutral intermediate vector boson) was predicted which can generate a whole new range of *neutral current* phenomena, including parity-violating effects in atoms and molecules. The theory provides a simple relation between the weak

⁸² E. Fermi, *Z. Phys.*, 1934, **88**, 161.

⁸³ S. Weinberg, *Phys. Rev. Lett.*, 1967, **19**, 1264.

⁸⁴ A. Salam, in 'Elementary Particle Theory', ed. N. Svartholm, Almquist and Wiksell, Stockholm, 1968, p. 367.

⁸⁵ I. J. R. Aitchison and A. J. Hey, 'Gauge Theories in Particle Physics', Adam Hilger, Bristol, 1982.

⁸⁶ K. Gottfried and V. F. Weisskopf, 'Concepts of Particle Physics', Vol. 1, Clarendon Press, Oxford, 1984.

and electromagnetic coupling constants ($g \sin \theta_w = e$, where g and e are the weak and electromagnetic unit charges, and θ_w is the Weinberg angle), and also gives the masses of the W^+ , W^- , and Z^0 . In one of the most important experiments of all time, these three particles were recently detected from proton-antiproton scattering experiments at CERN.⁸⁶

This weak neutral current generates parity-violating interactions between electrons, and between electrons and nucleons. The latter leads to the following electron-nucleus contact interaction in atoms and molecules (in a.u. where $\hbar = e = m_e = 1$)^{87,88}

$$\hat{V}_{eN}^{PV} = \frac{G\alpha}{4\sqrt{2}} Q_W \{ \sigma_e \cdot p_e, \rho_N(r_e) \}_+ \quad (15a)$$

where G is the Fermi weak coupling constant, α is the fine structure constant, σ_e and p_e are the Pauli spin operator and linear momentum operator of the electron, $\rho_N(r_e)$ is a normalized nuclear density function and

$$Q_W = Z(1 - 4 \sin^2 \theta_w) - N \quad (15b)$$

is an effective weak charge which depends on the proton and neutron numbers Z and N . $\{ \}_+$ denotes an anticommutator. The electron-electron interaction is usually neglected, so (15) is usually taken as the parity-violating term to be added to the Hamiltonian of an atom or molecule. Since σ_e and p_e are axial and polar vectors, respectively, and all other factors are scalars, \hat{V}_{eN}^{PV} transforms as pseudoscalar, as required, and so can mix even and odd parity electronic states at the nucleus.

Manifestations of parity violation in atoms have now been observed in the form of optical activity phenomena such as tiny optical rotations in vapours of heavy metals.⁸⁹⁻⁹¹ The existence of the weak neutral current had previously been confirmed experimentally from observations of parity-violating differential scattering at right- and left-handed spin-polarized high energy electron beams by the nucleons in hydrogen and deuterium targets.⁹² A parity-violating rotation of the spin vector component perpendicular to the propagation direction of a beam of polarized neutrons passing through crystals of ^{117}Sn has also been observed:⁹³ here both the electron-nucleon and nucleon-nucleon weak neutral current interactions make significant contributions.

⁸⁷ M. A. Bouchiat and C. Bouchiat, *J. Phys. (Paris)*, 1974, **35**, 899.

⁸⁸ R. A. Hegstrom, D. W. Rein, and P. G. H. Sandars, *J. Chem. Phys.*, 1980, **73**, 2329.

⁸⁹ P. G. H. Sandars, in 'Fundamental Interactions and Structure of Matter', ed. K. Crowe, J. Duclos, G. Fiorentini, and G. Torelli, Plenum Press, New York, 1980, p. 57.

⁹⁰ E. N. Fortson and L. Wilts, *Adv. At. Mol. Phys.*, 1980, **16**, 319.

⁹¹ M. A. Bouchiat and L. Pottier, *Sci. Am.*, 1984, **250**, No. 6, 76.

⁹² C. Y. Prescott, *et al.*, *Phys. Lett.*, 1978, **77B**, 347.

⁹³ M. Forte, B. R. Heckel, N. F. Ramsey, K. Green, G. L. Greene, J. Byrne, and J. Pendlebury, *Phys. Rev. Lett.*, 1980, **45**, 2088.

(ii) *Enantiomeric Energy Inequivalence.* Chiral molecules support a unique manifestation of parity violation in the form of a lifting of the exact degeneracy of the energy levels of mirror-image enantiomers.^{94–98,88} Being pseudoscalars, the parity-violating weak neutral current terms in the molecular Hamiltonian such as (15), are odd under space inversion:

$$\hat{P}\hat{D}^{PV}\hat{P}^{-1} = -\hat{D}^{PV} \quad (16)$$

As discussed in Section 8A below, the enantiomeric quantum states ψ_L and ψ_R of a chiral molecule are examples of the mixed parity states (7) and so are interconverted by \hat{P} . It then follows that \hat{D}^{PV} shifts the energies of the enantiomeric states in opposite directions:

$$\langle \psi_L | \hat{D}^{PV} | \psi_L \rangle = \langle \hat{P}\psi_R | \hat{D}^{PV} | \hat{P}\psi_R \rangle = \langle \psi_R | \hat{P}^\dagger \hat{D}^{PV} \hat{P} | \psi_R \rangle = -\langle \psi_R | \hat{D}^{PV} | \psi_R \rangle = \varepsilon \quad (17)$$

Attempts to calculate ε are faced with the following difficulty. The electronic coordinate part of \hat{D}_{eN}^{PV} in (15) is linear in p_e and is therefore pure imaginary. Since, in the absence of external magnetic fields, the molecular wavefunction can always be chosen to be real, \hat{D}_{eN}^{PV} has zero expectation values. Also, the presence of σ_e means that only matrix elements between different spin states survive. Consequently, it is necessary to invoke a magnetic perturbation of the wavefunction involving spin, the favourite candidate being spin-orbit coupling.^{96,97,88} This leads to a tractable method for detailed quantum-chemical calculations of parity-violating energy differences between enantiomers, giving values of the order 10^{-20} a.u.^{88,99,100} (the atomic unit of energy, the hartree, is equivalent to 27.2eV or to 4.36×10^{-18} J.)

C. Violation of Time Reversal and the CPT Theorem. Only one example of the violation of time reversal symmetry has been observed, involving decay modes of the neutral K-meson.¹⁰¹ Although unequivocal, the effects are very small; certainly nothing like the parity-violating effects in weak processes, which are absolute. In fact \hat{T} -violation itself was not observed directly: rather, the observation was of $\hat{C}\hat{P}$ violation, from which \hat{T} -violation is implied by the celebrated $\hat{C}\hat{P}\hat{T}$ theorem of Lüders, Pauli, and Villars.^{26,102} This was derived from general considerations using relativistic quantum field theory, and states that the Hamiltonian is invariant to the combined operations of $\hat{C}\hat{P}\hat{T}$ even if it is not invariant to one or more of those operations. One manifestation of $\hat{C}\hat{P}$ violation is the following decay rate asymmetry of the long-lived neutral K-meson, K_L^0 :^{10,86}

⁹⁴ D. W. Rein, *J. Mol. Evol.*, 1974, **4**, 15.

⁹⁵ V. Letokhov, *Phys. Lett.*, 1975, **53A**, 275.

⁹⁶ B. Ya. Zel'dovich, D. B. Saakyan, and I. I. Sobel'man, *Sov. Phys. JETP Lett.*, 1977, **25**, 95.

⁹⁷ R. A. Harris and L. Stodolsky, *Phys. Lett.*, 1978, **78B**, 313.

⁹⁸ R. A. Harris, in 'Quantum Dynamics of Molecules', ed. R. G. Woolley, Plenum Press, New York, 1980, p. 357.

⁹⁹ S. F. Mason and G. E. Tranter, *Mol. Phys.*, 1984, **53**, 1091.

¹⁰⁰ S. F. Mason and G. E. Tranter, *Proc. R. Soc. London, Ser. A*, 1985, **397**, 45.

¹⁰¹ J. H. Christenson, J. W. Cronin, V. L. Fitch, and R. Turlay, *Phys. Rev. Lett.*, 1964, **13**, 138.

¹⁰² D. C. Cheng and G. K. O'Neill, 'Elementary Particle Physics', Addison-Wesley, Reading, Massachusetts, 1979.

$$\frac{\text{Rate}(\text{K}_L^0 \rightarrow \pi^- e_r^+ \nu_l)}{\text{Rate}(\text{K}_L^0 \rightarrow \pi^+ e_l^- \nu_r)} \approx 1.00648 \quad (18)$$

As the formula indicates, K_L^0 can decay either into positive pions π^+ , left helical electrons e_l^- and right helical antineutrinos $\bar{\nu}_r$; or into negative antipions π^- , right helical positrons e_r^+ and left helical neutrinos ν_l . Since these two distinct sets of products are interconverted by $\hat{C}\hat{P}$, this decay rate asymmetry indicates that $\hat{C}\hat{P}$ (and hence \hat{T}) is violated. Further aspects of the neutral K-meson system will be discussed later.

8 The Mixed Parity States of a Chiral Molecule

A. The Double Well Model.—It was demonstrated in Section 2B that, since a chiral molecule can support pseudoscalar observables, which have odd parity, it must exist in mixed parity quantum states. The origin of these mixed parity states can be appreciated by considering the vibrational wavefunctions associated with the 'inversion' coordinate of a molecule such as NH_3 which is said to invert between two equivalent configurations as shown in Figure 5, although this motion does not

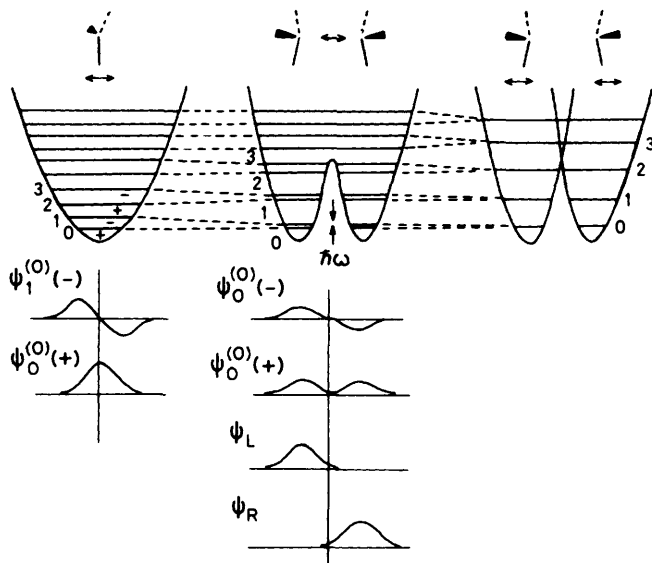


Figure 5 The vibrational states of a molecule that can invert between two equivalent configurations. $\psi^{(0)}(+)$ and $\psi^{(0)}(-)$ are the amplitudes of the definite parity stationary states with energy $W(+)$ and $W(-)$, and ψ_L and ψ_R are the two mixed parity non-stationary states at $t = 0$ and $t = \pi/\omega$, where $\hbar\omega$ is the tunnelling splitting

in fact correspond to inversion through the centre of mass.^{103,104} If the planar configuration were the most stable, the adiabatic potential energy function would

¹⁰³ C. H. Townes and A. L. Schawlow, 'Microwave Spectroscopy', McGraw-Hill, New York, 1955.

¹⁰⁴ G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, New York, 1945.

have the parabolic form shown on the left with simple harmonic vibrational levels equally spaced. If a potential hill is raised gradually in the middle, the two pyramidal configurations become the most stable and the energy levels approach each other in pairs. For an infinitely high potential hill, the pairs of energy levels are exactly degenerate, as shown on the right. The rise of the central potential hill modifies the wavefunctions as shown, but does not destroy their parity. The even and odd parity wavefunctions $\psi(+)$ and $\psi(-)$ describe stationary states in all circumstances. On the other hand, the wavefunctions ψ_L and ψ_R , corresponding to the system in its lowest state of oscillation and localized completely in the left and right wells, respectively, are not true stationary states. They are obtained from the following combinations of the even and odd parity wavefunctions,

$$\psi_L = \frac{1}{\sqrt{2}} [\psi^{(0)}(+)+\psi^{(0)}(-)] \quad (19a)$$

$$\psi_R = \frac{1}{\sqrt{2}} [\psi^{(0)}(+)-\psi^{(0)}(-)] \quad (19b)$$

which are explicit examples of the general mixed parity wavefunctions (7).

The wavefunctions (19) are in fact specializations of the general time-dependent wavefunction for a degenerate two-state system (see Section 8B below). Writing the general wavefunction as a combination of the two definite-parity stationary-state wavefunctions (9) we have ²⁵

$$\begin{aligned} \psi(t) &= \frac{1}{\sqrt{2}} [\psi^{(0)}(+)\ e^{-iW(+)/\hbar} + \psi^{(0)}(-)\ e^{-iW(-)/\hbar}] \\ &= \frac{1}{\sqrt{2}} [\psi^{(0)}(+)+\psi^{(0)}(-)\ e^{-i\omega t}] e^{-iW(+)/\hbar} \quad (20) \end{aligned}$$

where $\hbar\omega = W(-) - W(+)$ is the energy separation of the two opposite parity states, which in this context is interpreted as a tunnelling splitting through the potential energy barrier separating the two wells. Thus at $t = 0$ (20) reduces to (19a) corresponding to the molecule being found in the left well; and at $t = \pi/\omega$ (20) reduces to (19b) corresponding to the right well. The angular frequency ω is interpreted as the frequency of a complete inversion cycle. The tunnelling splitting $\hbar\omega$ is determined by the height and width of the barrier, and is zero if the barrier is infinite.

It is emphasized that a splitting of the energy levels will occur for any normal mode of vibration in which the height of the pyramid changes.¹⁰⁴ In NH_3 , for example, the height of the pyramid changes somewhat in each of the four normal modes, although the non-degenerate 'inversion' mode ν_2 , discussed above, shows by far the greatest change and the corresponding energy levels exhibit the greatest splitting.

One source of confusion in this model is that the parity of the vibrational wavefunctions is defined with respect to a *reflection* σ across the plane of the nuclei,

$$\sigma\psi_v = (-1)^v\psi_v \quad (21)$$

where v is the vibrational quantum number (the associated normal vibrational

coordinate changes sign under σ); whereas the basic definition of the parity operation is an *inversion* with respect to space-fixed axes. In the conventional treatment of inverting non-planar symmetric tops,^{103,105} the rotational wavefunction of a *planar* symmetric top such as BF_3 is multiplied by the wavefunction (20) corresponding to the 'inversion' vibration. The parity operation corresponds to an inversion of all the particle positions (nuclei and electrons), and is achieved by rotating the complete BF_3 molecule through π about the threefold axis, followed by a reflection across the plane containing the nuclei. Since the rotation is an external affair, it affects only the rotational wavefunctions and is used to classify their parity. The reflection is a purely internal affair, and so the parity of the vibrational–electronic parts of the quantum state is determined by their behaviour under reflection across the plane of the nuclei. This sort of consideration has been placed on a more sophisticated footing by the use of permutation–inversion groups to specify the parity of the complete wavefunction of a general non-rigid molecule in the gas phase.^{106,107}

Since an analogous potential energy diagram can be drawn for any chiral molecule with a high barrier separating left and right wells which now correspond to the two enantiomeric states, we now have a model for the source of the mixed parity internal (vibrational–electronic) states of a resolved enantiomer. The horizontal axis might represent the position of an atom above a plane containing three different atoms, the torsion coordinate of a chiral biphenyl, or some more complicated collective coordinate of the molecule. If such a state is prepared, but the tunnelling splitting is finite, its energy will be indefinite because it is a superposition of two opposite parity states of different energy. The splitting of the two definite parity states, and hence the uncertainty in the energy of an enantiomer, is inversely proportional to the left–right conversion time π/ω (this is an explicit example of the general result that the width of an energy level corresponding to a quasi-stationary state with average lifetime T is $\Delta W = \hbar/T$.¹⁰⁸)

A crucial point is therefore the relation between the time scale of the optical activity measurement and the lifetime of the resolved enantiomer. A manifestation of the uncertainty principle appears to arise here, which I have stated loosely as follows:^{109,18} 'If, for the duration of the measurement, there is complete certainty about the enantiomer, there is complete uncertainty about the parity of its quantum state; whereas if there is complete uncertainty about the enantiomer, there is complete certainty about the parity of its quantum state.' Thus experimental resolution of the definite parity states of tartaric acid, say, an enantiomer of which has a lifetime probably greater than the age of the universe, is impossible unless the duration of the experiment is virtually infinite; whereas for a non-resolvable chiral molecule such as H_2O_2 , spectroscopic transitions between states of definite parity are observed routinely.

¹⁰³ H. C. Allen and P. C. Cross, 'Molecular Vib-Rotors', Wiley, New York, 1963.

¹⁰⁶ T. Oka, *J. Mol. Spectrosc.*, 1973, **48**, 503.

¹⁰⁷ P. R. Bunker, 'Molecular Symmetry and Spectroscopy', Academic Press, New York, 1979.

¹⁰⁸ A. S. Davydov, 'Quantum Mechanics', Pergamon Press, Oxford, 1976.

¹⁰⁹ L. D. Barron, *J. Am. Chem. Soc.*, 1979, **101**, 269.

B. Two-state Systems and Parity Violation.—We have just seen how the mixed parity states of a resolved chiral molecule can be pictured in terms of a double well potential. This aspect can be developed further by considering the quantum mechanics of a degenerate two-state system in order to gain insight into the apparent paradox of the stability of optical enantiomers, which was recognized at the beginning of the quantum era since the existence of optical enantiomers was difficult to reconcile with basic quantum mechanics. In the words of Hund,¹¹⁰

If a molecule admits two different nuclear configurations being the mirror images of each other, then the stationary states do not correspond to a motion around one of these two equilibrium configurations. Rather, each stationary state is composed of left-handed and right-handed configurations in equal shares . . . The fact that the right-handed or left-handed configuration of a molecule is not a quantum state (eigenstate of the Hamiltonian) might appear to contradict the existence of optical isomers.

Similarly Rosenfeld:¹¹¹

A system (state) with sharp energy is optically inactive.

And Born and Jordan:¹¹²

Since each molecule consists of point charges interacting *via* Coulomb's law, the energy function (Hamiltonian) is always invariant with respect to space inversion. Consequently there could not exist any optically active molecules, which contradicts experience.

These translated quotations are taken from a critical review by Pfeifer.¹¹³ These points have been emphasized recently by Woolley^{114–117} as part of a re-evaluation of the whole concept of molecular structure.

Hund's resolution of the paradox involves arguments of the type given in the previous section, namely that typical chiral molecules have such large barriers to inversion that the lifetime of a prepared enantiomer is virtually infinite. Recently, Hund's approach has been brought up to date by injecting a small parity-violating term into the Hamiltonian, which can result in the two enantiomeric states becoming the true stationary states.^{97,98,18,63}

For a general two-state system in the orthonormal basis (ψ_1, ψ_2), not necessarily degenerate, the exact energy eigenvalues and eigenfunctions corresponding to the true stationary states are^{16,118}

¹¹⁰ F. Hund, *Z. Phys.*, 1927, **43**, 805.

¹¹¹ L. Rosenfeld, *Z. Phys.*, 1928, **52**, 161.

¹¹² M. Born and P. Jordan, 'Elementare Quantenmechanik', Springer, Berlin, 1930.

¹¹³ P. Pfeifer, 'Chiral Molecules—a Superselection Rule Induced by the Radiation Field', Doctoral Thesis, Swiss Federal Institute of Technology, Zurich (Diss. ETH No. 6551), 1980.

¹¹⁴ R. G. Woolley, *Adv. Phys.*, 1975, **25**, 27.

¹¹⁵ R. G. Woolley, *J. Am. Chem. Soc.*, 1978, **100**, 1073.

¹¹⁶ R. G. Woolley, *Isr. J. Chem.*, 1980, **19**, 30.

¹¹⁷ R. G. Woolley, *Struct. Bonding*, 1982, **52**, 1.

¹¹⁸ C. Cohen-Tannoudji, B. Diu, and F. Laloë, 'Quantum Mechanics', Wiley, New York, 1977.

$$W_{\pm} = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}[(H_{11} - H_{22})^2 + 4|H_{12}|^2]^{\frac{1}{2}} \quad (22a)$$

$$\psi_{+}^{(0)} = \cos\theta e^{-i\phi/2}\psi_1 + \sin\theta e^{i\phi/2}\psi_2 \quad (22b)$$

$$\psi_{-}^{(0)} = -\sin\theta e^{-i\phi/2}\psi_1 + \cos\theta e^{i\phi/2}\psi_2 \quad (22c)$$

where

$$\tan 2\theta = \frac{2|H_{12}|}{(H_{11} - H_{22})} \text{ with } 0 \leq 2\theta < \pi \quad (22d)$$

$$H_{21} = |H_{21}|e^{i\phi} \quad (22e)$$

The superscripts (0) denote the amplitudes of the corresponding time-dependent wavefunctions, and $H_{ab} = \langle \psi_a^{(0)} | \hat{H} | \psi_b^{(0)} \rangle$ are matrix elements of the *total* Hamiltonian of the system. The subscripts \pm here denote higher and lower energy levels, *not* the parity.

Thus ψ_1 and ψ_2 are not the eigenstates (stationary states) of the Hamiltonian of the system and so couple with each other through H_{21} ; whereas the stationary states ψ_{+} and ψ_{-} do not. So if a two-state system is prepared in a non-stationary state ψ_1 or ψ_2 , it might appear falsely to be influenced by a time-dependent perturbation lacking some fundamental symmetry of the internal Hamiltonian of the system. In general, ψ_1 and ψ_2 will be interconverted by a particular symmetry operation of the Hamiltonian, whereas $\psi_{+}^{(0)}$ and $\psi_{-}^{(0)}$ will transform according to one or other of the irreducible representations of the symmetry group comprising the identity and the operation in question.

By restricting attention to the ground and first excited state of the normal mode of vibration that interconverts the enantiomers in Figure 5, we can identify ψ_1 and ψ_2 with ψ_R and ψ_L . If the small parity-violating terms in the Hamiltonian are neglected, the Hamiltonian has inversion symmetry, and since $\hat{P}\psi_R = \psi_L$ and $\hat{P}\psi_L = \psi_R$, the enantiomeric states ψ_R and ψ_L are degenerate. The stationary state amplitudes (22b and c) now specialize to

$$\psi_{+}^{(0)} = \frac{1}{\sqrt{2}} e^{-i\phi/2} (\psi_R + e^{i\phi} \psi_L) \quad (23a)$$

$$\psi_{-}^{(0)} = \frac{1}{\sqrt{2}} e^{-i\phi/2} (-\psi_R + e^{i\phi} \psi_L) \quad (23b)$$

and so transform according to one or other of the irreducible representations of the inversion group comprising \hat{P} plus the identity. Which has even and which has odd parity depends on the choice of ϕ : for example, if $\phi = \pi$ (so that H_{LR} is real and negative), $\psi_{+}^{(0)}$ is odd and $\psi_{-}^{(0)}$ is even. The separation of the two stationary states is simply twice the coupling energy of the two enantiomeric states,

$$W_{+} - W_{-} = 2|\langle \psi_L | \hat{H} | \psi_R \rangle| = 2\delta \quad (24)$$

and is interpreted as a splitting caused by tunnelling through the potential energy barrier separating the two enantiomers (Figure 5).

We now allow the Hamiltonian to contain a small parity-violating term \hat{V}^{PV} such as the electron-nucleus weak neutral current interaction (15). According to (17), this shifts the energies of the two enantiomeric states in opposite directions by an amount ε . The enantiomeric states are now no longer degenerate, so using the general two-state results (22) we have

$$W_+ - W_- = 2(\varepsilon^2 + \delta^2)^{1/2} \quad (25a)$$

$$\tan 2\theta = \delta/\varepsilon \quad (25b)$$

The general time-dependent wavefunction is given by the sum of each stationary state amplitude multiplied by its exponential time factor:

$$\psi(t) = \frac{1}{\sqrt{2}} e^{-iW/2t/\hbar} \{ (\cos\theta \psi_R + \sin\theta e^{i\phi} \psi_L) e^{-iW_+ t/\hbar} + (-\sin\theta \psi_R + \cos\theta e^{i\phi} \psi_L) e^{-iW_- t/\hbar} \} \quad (26)$$

This only has a simple interpretation in the two limits of $\varepsilon = 0$ and $\delta = 0$. When $\varepsilon = 0$ (zero parity violation)

$$\psi(t) = \frac{1}{2} e^{-iW/2t/\hbar} \{ (\psi_R + e^{i\phi} \psi_L) e^{-i\delta t/\hbar} + (-\psi_R + e^{i\phi} \psi_L) e^{i\delta t/\hbar} \} e^{-i(W_+ + W_-)t/2\hbar} \quad (27)$$

which reduces, within a phase factor, to (20) (do not confuse the notation ψ_{\pm} and W_{\pm} for higher- and lower-energy states with $\psi(\pm)$ and $W(\pm)$ for even- and odd-parity states). Thus at $t = 0$ the system is entirely in ψ_L and at $t = \pi\hbar/2\delta$ it is entirely in ψ_R ; the system oscillates between ψ_L and ψ_R with $2\delta/\hbar$ being the frequency of a complete inversion cycle and $\psi_+ = \psi(-)$ and $\psi_- = \psi(+)$ the stationary states. But when $\delta = 0$ (zero tunnelling splitting),

$$\psi(t) = \frac{1}{\sqrt{2}} e^{-iW/2t/\hbar} \{ \psi_R e^{-i\varepsilon t/\hbar} + e^{i\phi} \psi_L e^{i\varepsilon t/\hbar} \} e^{-i(W_+ + W_-)t/2\hbar} \quad (28)$$

so at $t = 0$ the system is entirely in ψ_+ and at $t = \pi\hbar/2\varepsilon$ it is entirely in ψ_- : now the system oscillates between ψ_+ and ψ_- with $2\varepsilon/\hbar$ being the frequency of a complete cycle and ψ_R and ψ_L the stationary states.

The time-dependence of the optical activity observable depends on the nature of the state in which the molecule is prepared initially. Consider first the molecule prepared in a handed state ψ_L or ψ_R , which means that at $t = 0$ the state is given by (19a) or (19b), respectively. At some later time t the corresponding states will be

$$\psi_L(t) = e^{-iW/2t/\hbar} (\sin\theta \psi_+^{(0)} e^{-iW_+ t/\hbar} + \cos\theta \psi_-^{(0)} e^{-iW_- t/\hbar}) \quad (29a)$$

$$\psi_R(t) = e^{-iW/2t/\hbar} (\cos\theta \psi_+^{(0)} e^{-iW_+ t/\hbar} - \sin\theta \psi_-^{(0)} e^{-iW_- t/\hbar}) \quad (29b)$$

which are obtained by inverting (22b and c) and multiplying each stationary state amplitude by its exponential time factor. Thus for a molecule prepared in ψ_L , the time-dependence of the optical rotation angle is given by ^{97,98,18}

$$\alpha(t) = \alpha_L \left\{ \frac{\varepsilon^2 + \delta^2 \cos[2(\delta^2 + \varepsilon^2)^{1/2} t/\hbar]}{\delta^2 + \varepsilon^2} \right\} \quad (30)$$

where α_L is the optical rotation angle of the left-handed enantiomer. So if $\varepsilon \neq 0$, the optical rotation oscillates asymmetrically (but if $\varepsilon = 0$ it oscillates between equal and opposite values associated with the two enantiomers). Taking the time average, we find^{97,98}

$$\frac{\bar{\alpha}}{\alpha_{\max}} = \frac{\varepsilon^2}{\delta^2 + \varepsilon^2} \quad (31)$$

Thus parity violation causes a shift away from zero of $\bar{\alpha}$. This is the basis of an experiment suggested by Harris and Stodolsky⁹⁷ to detect the parity-violating energy shift between enantiomers.

But if the molecule is prepared in one of the stationary states

$$\psi_+(t) = (\cos\theta e^{-i\phi/2}\psi_R + \sin\theta e^{i\phi/2}\psi_L) e^{-iW_+ t/\hbar} \quad (32a)$$

$$\psi_-(t) = (-\sin\theta e^{-i\phi/2}\psi_R + \cos\theta e^{i\phi/2}\psi_L) e^{-iW_- t/\hbar} \quad (32b)$$

the optical rotation will be given by

$$\alpha_+(t) = -\alpha_-(t) = -\alpha_L \frac{\varepsilon}{(\varepsilon^2 + \delta^2)^{1/2}} \quad (33)$$

Thus if $\varepsilon = 0$, the optical rotation will be zero, as required, since the stationary states will have definite parity; but if $\varepsilon \neq 0$, the stationary states will acquire equal and opposite parity-violating optical rotation *that does not change with time*.

It is clear from (26) and (22) that, as $\delta/\varepsilon \rightarrow 0$, ψ_L and ψ_R become the true stationary states. In fact for typical chiral molecules, δ corresponds to tunnelling times of the order of millions of years: Harris and Stodolsky⁹⁷ have estimated ε to correspond to times of the order of seconds to days, so at low temperature and in a vacuum, a prepared enantiomer will retain its handedness essentially for ever. So the ultimate answer to the paradox of the stability of optical enantiomers might lie in the weak interactions.

C. Parity Violation and Spontaneous Parity Breaking in Chiral Molecules.—The existence of parity-violating phenomena is interpreted quantum-mechanically by saying that the Hamiltonian has a lower symmetry than previously thought (since the weak interaction potential is a pseudoscalar). This means that \hat{P} and \hat{H} no longer commute, so the corresponding conservation law no longer holds. Such symmetry violation must be clearly distinguished from *spontaneous symmetry breaking*: current usage in the literature of theoretical physics applies the latter term to describe the situation which arises when a system displays a lower symmetry than expected from its Hamiltonian.^{25,119} As Woolley has stressed, natural optical

¹¹⁹ L. Michel, *Rev. Mod. Phys.*, 1980, **52**, 617.

activity is a phenomenon that arises from spontaneous parity breaking since a resolved chiral molecule displays a lower symmetry than its associated Hamiltonian.¹¹⁴⁻¹¹⁷ If the small parity-violating term in the Hamiltonian is neglected, the symmetry operation that the Hamiltonian possesses but the chiral molecule lacks is inversion, and it is this inversion operation that interconverts the two enantiomeric parity-broken states.

The conventional view, discussed in Section 8A, is that parity violation plays no part in the stabilization of chiral molecules: the optical activity is assumed to remain observable only so long as the observation time is short compared with the interconversion time between enantiomers, which is proportional to the inverse of the tunnelling splitting. Such optical activity is certainly an example of spontaneous parity breaking, and averages to zero over a sufficiently long observation time. Thus Ulbricht's statement¹²⁰ (in an otherwise excellent article) that '... processes involving pseudoscalar quantities will not obey the law of parity' betrays a common misconception: the law of parity is saved in systems exhibiting *spontaneously broken* parity because their pseudoscalar properties average to zero over a sufficiently long observation period, or, equivalently, the space-inverted experiment is realizable. In either interpretation absolute chirality is not observable.

A related misconception has arisen in connection with the correlation of entities that have opposite parities, such as the coupling of rotational and translational motion in collections of chiral molecules, mentioned in Section 6A above. Thus Berne and Pecora¹²¹ have stated that '... in a system such that the Hamiltonian has inversion symmetry, properties of different parity are totally uncorrelated for all time.' Also '... if the system contains optically active molecules, the Hamiltonian does not have even parity and none of these theorems apply.' See also Evans.¹²² Any Hamiltonian involving only electromagnetic interactions *always* has even parity: it is the spontaneous broken parity states of the chiral molecules that mediate the coupling of opposite parity entities, and any associated pseudoscalar properties will therefore average to zero over a sufficiently long period of time.

This brings us to a crucial distinction between spontaneous parity-breaking and parity-violating natural optical activity phenomena: the former are time-dependent and average to zero; the latter are constant in time (*cf.* the stationary states acquiring time-independent optical activity in the previous section when $\epsilon \neq 0$). Hence if a small chiral molecule could be isolated sufficiently from the environment, a parity-violating element is indicated if the optical activity remains observable for longer than the expected interconversion time.¹²³ It is still an open question as to whether the primary source of the apparently constant optical activity of molecules such as tartaric acid is parity violation, spontaneous parity breaking with intrinsically long tunnelling times, or spontaneous parity breaking stabilized by (or induced by) the environment and/or parity violation.^{113-117,123,124}

¹²⁰ T. L. V. Ulbricht, *Q. Rev., Chem. Soc.*, 1959, 13, 48.

¹²¹ B. J. Berne and R. Pecora, 'Dynamic Light Scattering', Wiley, New York, 1976.

¹²² M. W. Evans, *Physica*, 1985, 131B, 273.

¹²³ R. A. Harris and L. Stodolsky, *J. Chem. Phys.*, 1981, 74, 2145.

¹²⁴ M. Simonius, *Phys. Rev. Lett.*, 1978, 40, 980.

9 Some Fundamental Implications

A. Biological Homochirality.—The ubiquity of the L-amino-acids and D-sugars in the biochemistry of living organisms has attracted a great deal of attention.¹²⁵ If living matter evolved in prebiotic times from chiral molecules formed out of simple achiral precursors, how did this resolution appear? There seem to be two options: that it arose by chance, or that it was caused by external chiral influences. These include the cosmic chirality manifest as parity violation in the weak interaction as well as the more mundane possibility of local astronomical dissymmetry producing chirality in electric, magnetic, and gravitational fields at the earth's surface.

Theories that involve parity violation have a sound physical foundation because the influence is truly chiral. Discussion centres on the particular manifestation of parity violation invoked and on the subsequent chemical, thermodynamic, and kinetic details. There are two main lines of thought. One invokes the left-handed spin-polarized electrons (or right-handed positrons) emitted in the β -decay of nucleides: these should give rise to enantio-differentiating radiolysis of racemic mixtures, or to the corresponding photolysis by the circularly polarized electromagnetic radiation arising from the progressive retardation of the spin-polarized electron.^{120,126,127} The other invokes the parity-violating energy difference between chiral enantiomers and claims to show that this provides sufficient bias to produce a spontaneous transition from a racemic reaction process to one or other of the two constituent homochiral reaction sequences.^{128,129,100,125} These two lines of thought have some common ground in that a concentration difference in enantiomeric reactants produced by, say, β -radiolysis has the same effect as a difference in rate-constants for the formation of enantiomeric products.¹³⁰

Theories that involve local astronomical dissymmetry^{70,131,132} are sometimes sound, as when circularly polarized light is invoked, and sometimes controversial, for example when co-linear electric and magnetic fields are involved. However, the new magneto-chiral effects discussed in Section 6D provide a truly chiral influence and, as Wagnière and Meier have emphasized,⁷⁵ are well worth considering as a source of chirality in molecular evolution because all that is required is a source of light of arbitrary polarization and a static magnetic field which is not perpendicular to the propagation direction.

Garay has suggested that violation of time reversal might lead to small differences in 'internal timing' in enantiomeric chiral molecules and hence to

¹²⁵ S. F. Mason, *Nature (London)*, 1984, 311, 1.

¹²⁶ T. L. V. Ulbricht, *Origins Life*, 1981, 11, 35.

¹²⁷ R. A. Hegstrom, *Nature*, 1982, 297, 643.

¹²⁸ D. K. Kondepudi and G. W. Nelson, *Phys. Rev. Lett.*, 1983, 50, 1023.

¹²⁹ D. K. Kondepudi and G. W. Nelson, *Nature*, 1985, 313, 438.

¹³⁰ R. A. Hegstrom, *Nature (London)*, 1985, 315, 749.

¹³¹ L. Mörtberg, in 'Origins of Optical Activity in Nature', ed. D. C. Walker, Elsevier, Amsterdam, 1979, p. 101.

¹³² W. Thiemann, *Origins Life*, 1984, 14, 421.

biological homochirality.^{133,134} This is based on the result (18) which shows that the K_L^0 -meson decays into left-handed electrons at a slower rate than into right-handed positrons, and on the concept of a 'helical electron gas' in chiral molecules.¹³⁵ However, unlike \hat{P} -violation, there is no cogent theory of \hat{T} -violation in atoms and molecules, so such suggestions must be regarded as highly speculative at present, although they cannot be ruled out.

B. Chirality and Relativity.—In Section 5 it was demonstrated that a translating spinning cone or sphere exhibits true chirality. This is an intriguing concept because it exposes a link between chirality and special relativity. Suppose a particle is moving away from an observer with a right-handed helicity. If the observer accelerates to a sufficiently high velocity that he starts to catch up with the particle, it will now appear to be moving towards the observer and so takes on a left-handed helicity. In its rest frame the helicity of the particle is undefined and its chirality vanishes. Only for massless particles such as photons and neutrinos is the chirality conserved since they always move at the velocity of light in any reference frame.

Indeed, this relativistic aspect of chirality is a central feature of modern elementary particle theory, especially in relation to the weak interaction where the parity-violating aspects are velocity-dependent. The interaction of electrons with neutrinos provides a good illustration:¹³⁶ neutrinos are quintessential chiral objects since only left-handed neutrinos and right-handed antineutrinos exist.^{10,26,85,102} Consider first the extreme case of electrons moving close to the velocity of light. Only left-handed relativistic electrons interact with left-handed neutrinos *via* the weak force; right-handed relativistic electrons do not interact at all with neutrinos. But right-handed relativistic *positrons* interact with right-handed *antineutrinos*. For non-relativistic electron momenta, the weak interaction still violates parity, but the amplitude of the violation is reduced to order v/c .⁸⁶ This is used to explain the strange fact that the $\pi^- \longrightarrow e^- \bar{\nu}_e$ decay is a factor of 10^4 rarer than the $\pi^- \longrightarrow \mu^- \bar{\nu}_\mu$ decay, even though the available energy is much larger in the first decay.^{86,102} In the rest frame of the pion, the lepton (electron or muon) and the antineutrino are emitted in opposite directions so that their linear momenta cancel. Also, since the pion is spinless, the lepton must have a right-handed helicity in order to cancel the right-handed helicity of the antineutrino. Thus both decays would be forbidden if e and μ had the velocity c because the associated maximal parity violation dictates that both be pure left-handed. However, on account of its much greater mass, the muon is emitted much more slowly than the electron, so there is a much greater amplitude for it to be emitted with a right-handed helicity.

It should be mentioned that the discussion in the previous paragraph applies

¹³³ A. S. Garay, *Origins Life*, 1978, 9, 1.

¹³⁴ A. S. Garay, in 'Origins of Optical Activity in Nature', ed. D. C. Walker, Elsevier, Amsterdam, 1979, p. 245.

¹³⁵ A. S. Garay and P. Hráskó, *J. Mol. Evol.*, 1975, 6, 77.

¹³⁶ H. Georgi, *Sci. Am.*, 1981, 244, No. 4, 48.

only to *charge-changing* weak processes, mediated by W^+ or W^- particles. Weak *neutral current* processes, mediated by Z^0 particles, are rather different since, even in the relativistic limit, both left- and right-handed electrons participate, but with slightly different amplitudes.^{85,86}

So far in this article, the term 'chirality' has been used in its qualitative chemical sense. In elementary particle physics, 'chirality' is given a precise quantitative meaning: it is the eigenvalue of the Dirac matrix operator $\hat{\gamma}_5$, with values of +1 and -1 corresponding to right- and left-handed leptons. But only massless leptons (such as neutrinos), which always move at the velocity of light, are in eigenstates of $\hat{\gamma}_5$ and so have precise chirality. Leptons with mass (such as electrons) always move more slowly than c and so do not have well-defined chirality. Indeed, the very existence of mass is associated with 'chiral symmetry breaking'.¹³⁷ On the other hand, helicity (defined in Section 7A above) can be defined for both massless and massive particles, but only for the former is it completely invariant to the frame of the observer. For massless particles the helicity is actually equivalent to the chirality (for an antiparticle the helicity and chirality have the opposite sign). The interesting suggestion has been made recently that, if the physical problem singles out a preferred spatial origin, such as the source of an electromagnetic field, then chirality becomes sharply defined even for a particle with mass:¹³⁸ this could have important consequences for the foundations of atomic and molecular physics.

There appears to be another, very different, connection between chirality and relativity. We saw in Section 8C that spontaneous parity-breaking and parity-violating optical activity are distinguished by the fact that the first is time-dependent while the second is independent of time. Because a clock on a moving object slows down relative to a stationary observer, a molecule exhibiting spontaneous parity-breaking optical activity will become increasingly stable with increasing velocity relative to a stationary observer, and as it approaches the speed of light it will become infinitely stable. Thus spontaneous parity-breaking optical activity in a chiral object moving at the speed of light becomes indistinguishable from parity-violating optical activity.

C. True Enantiomers and Parity Violation.—The conceptual value of parity violation in the discussion of molecular chirality now emerges, because *only the space-inverted enantiomers of truly chiral systems show a parity-violating energy difference*.¹³⁹ Space-inverted enantiomers of systems showing false chirality, such as a stationary rotating cone, or co-linear electric and magnetic fields, are strictly degenerate. This follows from the fact that, although the parity-violating weak neutral current Hamiltonian (15) is odd under space inversion, it is invariant under both time reversal and any proper spatial rotation: since the last two operations together interconvert the two space-inverted enantiomers of a system displaying false chirality, it follows from a development analogous to (17) that the energy difference is zero.

¹³⁷ L. B. Okun, 'Particle Physics', Harwood Academic Publishers, Chur, 1985.

¹³⁸ L. C. Biedenharn and L. P. Horwitz, *Found. Phys.*, 1984, 14, 953.

¹³⁹ L. D. Barron, *Chem. Phys. Lett.*, 1986, 123, 423.

Since the space-inverted enantiomers of a truly chiral object are not strictly degenerate, they are not true enantiomers (since the concept of enantiomer implies the *exact* opposite). So where is the true enantiomer of a chiral molecule to be found? In the antiworld of course! The molecule with the opposite absolute configuration but composed of antiparticles will have exactly the same energy as the original.^{27,18} This follows from the $\hat{C}\hat{P}\hat{T}$ theorem and the assumption that \hat{T} is not violated. So true enantiomers are interconverted by $\hat{C}\hat{P}$. Since \hat{P} violation automatically implies \hat{C} violation here, it also follows that there is a small energy difference between a chiral molecule in the real world and the corresponding chiral molecule with the same absolute configuration in the antiworld.

This more general definition of the enantiomers of truly chiral objects is consistent with the chirality that free atoms display on account of parity violation.^{89,90,98} The weak neutral current generates only one type of chiral atom in the real world: the conventional enantiomer of a chiral atom obtained by space inversion alone does not exist. Clearly, the enantiomer of a chiral atom is generated by the combined $\hat{C}\hat{P}$ operation. Thus the corresponding atom composed of antiparticles will of necessity have the opposite 'absolute configuration' and will show an opposite sense of optical rotation.

The space-inverted enantiomers of objects such as translating spinning cones or spheres that only exhibit chirality on account of their motion also show parity-violating differences. One manifestation is that, as mentioned in Section 9B, left- and right-handed particles (or antiparticles) have different weak interactions. Again, true enantiomers are interconverted by $\hat{C}\hat{P}$: for example, a left-handed electron and a right-handed positron are interconverted by $\hat{C}\hat{P}$ (the fact that the left-handed electron and the resulting right-handed positron are moving in opposite directions can be corrected by invoking an operation \hat{P}_* in place of \hat{P} , in which space inversion is followed by an appropriate spatial rotation through 180°).⁸⁶

This is an appropriate point to continue the discussion of the curious behaviour of the neutral K-meson, first mentioned in Section 7C. This particle displays four distinct states: particle and antiparticle states $|k^0\rangle$ and $|\bar{k}^0\rangle$, and two mixed states $|k_1\rangle = (|k^0\rangle + |\bar{k}^0\rangle)/\sqrt{2}$ and $|k_2\rangle = (|k^0\rangle - |\bar{k}^0\rangle)/\sqrt{2}$ which have different energies because of coupling between $|k_0\rangle$ and $|\bar{k}^0\rangle$ via the weak force. The $|k_0\rangle$ and $|\bar{k}^0\rangle$ are interconverted by $\hat{C}\hat{P}$, which means that $|k_1\rangle$ and $|k_2\rangle$ are even and odd eigenstates with respect to $\hat{C}\hat{P}$, and that $|k_0\rangle$ and $|\bar{k}^0\rangle$ are mixed (spontaneously symmetry broken) with respect to $\hat{C}\hat{P}$. Wigner¹⁴⁰ has therefore likened these four distinct states to the four possible states of a chiral molecule in the real world (the two enantiomeric states of mixed parity that are interconverted by \hat{P} and the two definite parity states), although the analogy is best made with a chiral molecule for which $\delta \approx \epsilon$ otherwise only two distinct states will ever be observable (the two definite parity states if $\delta \gg \epsilon$, as in H_2O_2 ; and the two enantiomeric states if $\epsilon \gg \delta$, as in tartaric acid). However, the $\hat{C}\hat{P}$ eigenstates $|k_1\rangle$ and $|k_2\rangle$ are not pure since $|k_2\rangle$, which is *odd* with respect to $\hat{C}\hat{P}$, is occasionally observed to decay into products which are *even* with respect to $\hat{C}\hat{P}$. This implies

¹⁴⁰ E. P. Wigner, *Sci. Am.*, 1965, 213, No. 6, 28.

that the Hamiltonian contains a small $\hat{C}\hat{P}$ violating term which mixes $|k_1\rangle$ and $|k_2\rangle$, like the \hat{P} -violating term which mixes the two definite parity states of a chiral molecule (in fact K_L^0 in Section 7C is the state $|k_2\rangle$ with a small admixture of $|k_1\rangle$). At present all known $\hat{C}\hat{P}$ -violating effects are restricted exclusively to the decays of the K_L^0 mesons. Nature has provided us with just one extraordinarily sensitive system to convey a cryptic message that has still to be deciphered.¹⁴¹

Acknowledgements. I thank Miss C. J. Johnston and Professors A. D. Buckingham, G. Kirby, S. F. Mason, R. G. Moorhouse, and P. G. H. Sandars for helpful discussions.

¹⁴¹ J. W. Cronin, *Rev. Mod. Phys.*, 1981, 53, 373.