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Symmetry and Molecular Chirality

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Symmetry and Molecular Chirality

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1. INTRODUCTION

Scientists have been fascinated by molecular handedness ever since the concept first arose as a result of the discovery of natural optical activity in the early years of the last century. This concept spawned major advances in physics, chemistry and biology and continues to catalyse scientific progress even today.

In 1811 Arago observed colours in sunlight that had passed along the optic axis of a quartz crystal placed between crossed polarizers. Subsequent experiments by Biot established that the colours originated in a rotation of the plane of polarization of linearly polarized light (optical rotation - Fig. 1) with different rotations for light of different wavelengths (optical rotatory dispersion). Biot also discovered a second form of quartz which rotated the plane of polarization in the opposite sense. Then in 1815 Biot discovered that certain organic liquids such as terpentine could also show optical rotation, which indicated that optical activity could reside in individual molecules and may be observed even when the molecules are arranged in random fashion: in contrast, the optical activity of quartz is a property of the crystal structure since molten quartz is not optically active.

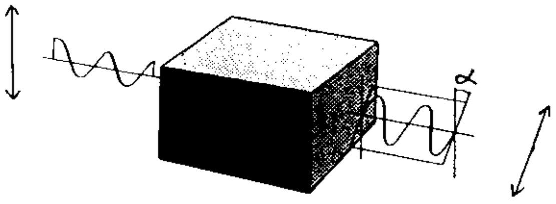


Fig. 1. The plane of polarization of a linearly polarized light beam is rotated on passing through a transparent chiral sample such as a quartz crystal or a solution of chiral molecules.

Fresnel's discovery of circularly polarized light in 1824 enabled him to formulate optical rotation in terms of different refractive indices, and hence velocities, for the coherent right and left circularly polarized components of equal amplitude into which linearly polarized light can be resolved (Fig. 2).

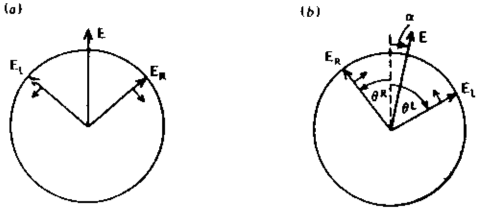


Fig. 2. (a) The electric field vector **E** of a linearly polarized light beam decomposed into coherent right and left circularly polarized components. (b) The rotated electric vector at some further point in the optically active medium.

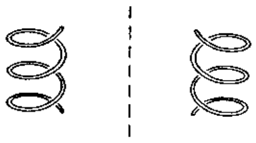
This provided an important insight into the symmetry requirements for an optically active molecule or crystal. Quoting Fresnel:[1]

> "There are certain refracting media, such as quartz in the direction of its axis, turpentine, essence of lemon, etc., which have the property of not transmitting with the same velocity circular vibrations from right to left and those from left to right. This may result from a peculiar constitution of the refracting medium or of its molecules, which produces a difference between the directions right to left and left to right; such, for instance, would be a helicoidal arrangement of the molecules of the medium, which would present inverse properties accordingly as these helices were dextrogyrate or laevogyrate."

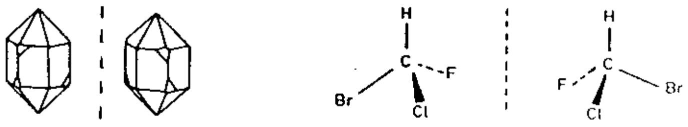
The resolution by Pasteur in 1848 of a sample of the optically inactive (racemic) version of tartaric acid into equal numbers of molecules giving equal and opposite optical rotations in solution provided a dramatic confirmation of Fresnel's insight that optically active molecules must be handed. This discovery emphasised that molecules must be pictured in three dimensions, and led eventually to the concept of tetrahedral valencies for the carbon atom and to the subject of stereochemistry.

In 1846 Faraday discovered that optical activity could be induced in an otherwise inactive sample by a magnetic field. He observed optical rotation in a rod of lead borate glass placed between the poles of an electromagnet with holes bored through the pole pieces to allow a linearly polarized light beam to pass through. This effect is quite general: a Faraday rotation is found when linearly polarized light is transmitted through any crystal or fluid in the direction of a magnetic field, the sense of rotation being reversed on reversing the direction of either the light beam or the magnetic field. At the time, the main significance of this discovery was to demonstrate conclusively the intimate connection between electromagnetism and light; but it also became a source of confusion to some physicists and chemists who failed to appreciate that there is a fundamental distinction between magnetic optical rotation and the natural optical rotation associated with molecular handedness.

In 1848, Pasteur[2] introduced the word *dissymmetric* to describe objects "which differ only as an image in a mirror differs from the object which produces it." A finite cylindrical helix provides a good example since reflection reverses the screw sense and so prevents the superposition of the mirror image on the original (Fig. 3). The two distinguishable mirror-image forms of a dissymmetric system are called enantiomers (from the Greek *enantios morphe* meaning opposite shape). Dissymmetric figures are not necessarily asymmetric, meaning 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 - Fig. 4). Specifically, dissymmetry excludes improper rotation axes (that is, a centre of inversion, reflection planes and rotation-reflection axes) and so corresponds to point groups C_n, D_n, O, T and I. Pasteur attempted to extend the concept of dissymmetry to other aspects of the physical world.[3,4] For example, he thought that a magnetic field, since it can induce optical rotation (the Faraday effect), generates the



Finite helix



Quartz crystal

Asymmetric molecule

Fig. 3. Dissymmetric (chiral) objects and their distinguishable mirror-image forms (enantiomers).

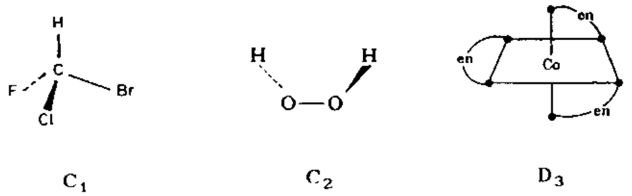


Fig. 4. The point groups of some dissymmetric (chiral) structures.

same type of dissymmetry as that possessed by an optically active molecule. As we shall see, this idea is quite wrong and has been the source of much confusion. However, Pasteur was correct in thinking that the combination of linear motion with a rotation does generate the same type of dissymmetry as an optically active molecule.

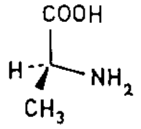
In recent years the word dissymmetry has been replaced by *chirality*, meaning handedness (from the Greek word *chir* for hand) in the literature of stereochemistry. This word was actually first coined by Sir William Thomson, Professor of Natural Philosophy in the University of Glasgow, in his famous Baltimore Lectures delivered as long ago as 1884. These lectures were not published until 1904,[5] by which time Sir William had been elevated to the peerage, taking his title Lord Kelvin from the name of the river which runs through Glasgow University park.

To be specific, the word chiral is introduced in the Baltimore lectures to describe a geometrical figure "if its image in a plane mirror, ideally realized, cannot be brought into coincidence with itself." Although this definition is essentially the same as that used by Pasteur for dissymmetric, the two words *chiral* and *dissymmetric* are not strictly synonymous in the broader context of modern stereochemistry and theoretical physics. Dissymmetry means the absence of certain symmetry elements, these being improper rotation axes in Pasteur's usage. Chirality is a more positive concept in that it refers to the possession of the attribute of handedness which, as shown later, has a physical content: in molecular physics this is the ability to support time-even pseudoscalar observables; whereas in elementary particle physics chirality is defined as the eigenvalue of the Dirac matrix operator γ_5.[6]

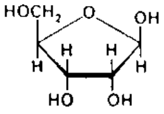
In these lectures, we shall apply some principles of modern physics, especially fundamental symmetry arguments, to develop a deeper description of chirality than that usually encountered in the literature of stereochemistry in order to facilitate a proper understanding of the structure and properties of chiral molecules, and of the factors involved in their synthesis and transformations. *A central result is that, although dissymmetry is sufficient to guarantee chirality in a stationary object such as a finite helix, dissymmetric systems are not necessarily chiral when they involve motion.* I have introduced the concept of 'true' and 'false' chirality to draw attention to this distinction[7-10] and have suggested that the word *chiral* be reserved in future for systems that I call truly chiral. It will be appreciated from what follows that true and false chirality correspond to time-invariant and time-noninvariant enantiomorphism, respectively. We shall see that, as intimated above, the combination of linear motion with a rotation does indeed generate true chirality, but that a magnetic field does not (in fact it is not even false chirality). Examples of dissymmetric systems showing false chirality include a stationary rotating cone, and collinear electric and magnetic fields.

The recent triumph of theoretical physics in unifying the weak and electromagnetic forces into a single 'electroweak' force has provided a new perspective on chirality which has been a source of inspiration for the new synthesis reviewed in these lectures. Since the weak and the 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 known to infiltrate to a tiny extent into all electromagnetic phenomena so that free atoms, for example, show very small optical rotations; and a tiny energy difference exists between the enantiomers of a chiral molecule. 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. It is remarkable that parity violation provides a scientific basis for the general cosmic dissymmetry that Pasteur sensed over a century ago.[11,12]

The importance of all this for biology is that the molecular building blocks of proteins and nucleic acids, the central biological macromolecules, are homochiral. Thus naturally occuring peptides and proteins are almost exclusively constructed from L-amino acids, and nucleic acids from D-sugars, e.g.



L-alanine



D-ribose

The chirality of the amino acids and sugars then predetermines the chirality of the secondary structures of biological polymers such as the polypeptide α-helix and the DNA double helix. The problem of homochirality is central to discussions of chemical evolution and the origin of life; and although this problem is not addressed directly here, nonetheless the physics of molecular chirality developed in these lectures is an important ingredient in the discussion.

2. SYMMETRY PRINCIPLES

The symmetry arguments required for a proper understanding of molecular chirality go beyond the purely spatial aspects employing point group symmetry arguments normally used to deduce qualitative information about molecules. In addition, the fundamental symmetries of space inversion, time reversal and even charge conjugation have something to say about chirality at several levels including the experiments that show up optical activity observables, the objects generating these observables and the quantum states that these objects must be able to support. We therefore start by reviewing these fundamental symmetries.

2.1 Non-observables and Symmetry Operations

According to Lee,[13] symmetry principles can be associated with the impossibility of observing certain basic quantities. Three such non-observables appear to be particularly fundamental: absolute chirality (absolute right- or left-handedness), absolute direction of motion, and absolute sign of electric charge. A non-observable implies invariance of physical laws under an associated transformation and usually generates a conservation law or selection rule that follows from the invariance of the Hamiltonian under the transformation.

The transformation associated with absolute chirality is space inversion, represented by the parity operator P which inverts the system through the origin of the space-fixed axes (Fig. 5). Most physical laws (but not those describing processes which involve the weak force) are unchanged by space inversion. If replacing the space coordinates (x,y,z) by (-x,-y,-z) everywhere in equations describing physical laws (for example in Newton's equations describing the laws of mechanical motion or in Maxwell's equations describing the laws of electromagnetism) leaves those equations unchanged, all physical processes determined by such laws are said to conserve parity. The associated quantum mechanical observable that is conserved is the parity eigenvalue of a state with values +1 or -1 (see later).

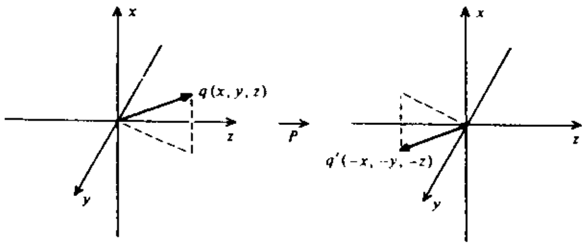


Fig. 5. The operation of space inversion (parity) P changes the coordinates of a point from (x,y,z) to (-x,-y,-z).

The transformation associated with absolute direction of motion is time reversal, represented classically by the operator T which has the effect of reversing the motions of all the particles in the system. If replacing the time coordinate (t) by (-t) everywhere in equations describing physical laws leaves those equations unchanged, all physical processes determined by such laws are said to conserve time reversal invariance (even though the bulk system supporting such processes may not itself be invariant due to thermodynamic irreversibility). As described later, the time reversal operator in quantum mechanics is unusual in that it is antiunitary rather than unitary so that it is not directly related to a Hermitian observable, which means that invariance of the Hamiltonian under time reversal does not lead to a conserved quantity analogous to parity.

The transformation associated with absolute sign of electric charge is charge conjugation, represented by the operator C which interconverts particles and antiparticles. Although this exotic operation might appear to have no relevance to chemistry, we shall see that it has conceptual significance in studies of molecular chirality.

2.2. Physical Quantities

It is important to classify physical quantities according to their behaviour under various symmetry operations. Physical quantities are first classified as *scalars*, *vectors* or *tensors* depending on their directional properties. A scalar such as temperature has magnitude but no associated direction; a vector such as velocity has magnitude and one associated direction; and a tensor such as electric polarizability has magnitudes associated with two or more directions. Scalars, vectors and tensors are then further classified according to their behaviour under P and T.

Vectors such as position **r**, velocity **v** and linear momentum **p** which change sign under the inversion operation P are called *polar* or true vectors (Fig. 6a). A vector such as angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ whose sign is not changed by P is called an *axial* or pseudo vector: **L** is defined relative to the sense of rotation by a right-hand rule, and P does not change the sense of rotation (Fig. 6b). A *pseudoscalar* quantity is a number with no directional

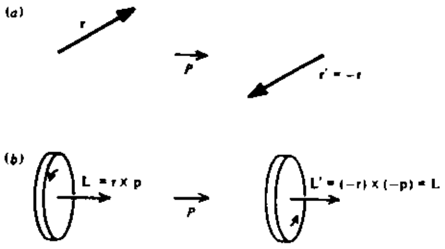


Fig. 6. Space inversion P reverses the polar position vector **r** in (a) but not the axial angular momentum vector **L** in (b).

properties but which changes sign under *P*. A pseudoscalar is generated by taking the scalar product of a polar and an axial vector.

Physical quantities are classified as *time-even* or *time-odd* depending on whether they are invariant or change sign under the time reversal operation *T*. This behaviour is usually immediately obvious (e.g. Fig. 7). Many physical quantities do not involve motion and so of course are time-even, examples being the energy scalar W, position vector **r**, and electric dipole moment vector **μ**. Many other quantities do involve motion and are time-odd: for example the velocity vector **v**, linear momentum vector **p**, angular momentum vector **L**, and magnetic dipole moment vector **m**. The elusive magnetic monopole, which has never been observed, transforms as a time-odd pseudoscalar.

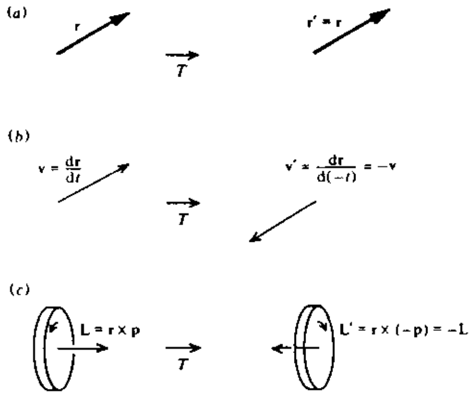


Fig. 7. The time reversal operator *T* does not change the sign of the time-even position vector **r** in (a) but changes the sign of the time-odd velocity vector **v** in (b) and angular momentum vector **L** in (c).

We are particularly interested in the behaviour of the electric and magnetic field vectors **E** and **B** under *P* and *T*, which can be established by examining the physical systems which generate them. Thus a uniform static electric field can be generated by a pair of parallel plates carrying equal and opposite charge densities (Fig. 8a). Under *P*, the two plates exchange positions while retaining their respective charges, so **E** changes sign. Since the charges are stationary, *T* has no effect. Thus **E** is a polar time-even vector. A uniform magnetic field can be generated by a cylindrical current sheet (Fig. 8b). The sense of circulation of the electrons around the current sheet is reversed by *T* but not by *P*. Thus **B** is an axial time-odd vector.

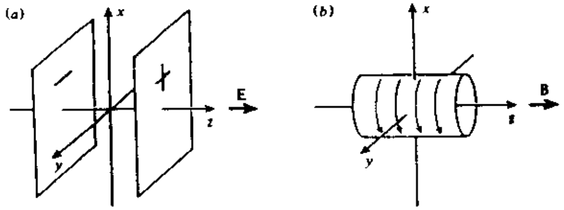


Fig. 8. (a) The generation of an electric field **E** by two plates of opposite charge. (b) The generation of a magnetic field **B** by a cylindrical current sheet.

Pseudoscalar quantities are of central importance in the discussion of molecular chirality because, as shown below, the natural optical activity phenomena supported by chiral molecule are characterized by time-even pseudoscalar observables such as optical rotation angle, rotational strength, Raman circular intensity difference, etc.

2.3. Symmetry in Quantum Mechanics

When symmetry operations are formulated in quantum mechanics, some important new features arise that are not present in the classical discussion.

Parity

The starting point for parity considerations is the invariance of the conventional (*i.e.* parity-conserving) Hamiltonian for a closed system of interacting particles to an inversion of the coordinates of all the particles. *P* is now interpreted as a linear unitary Hermitian operator that changes the sign of the space coordinates in the Hamiltonian and in the wavefunction.

Consider first the wavefunction:

$$P\psi(\mathbf{r}) = \psi(-\mathbf{r}). \qquad (1)$$

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

$$P\psi(\mathbf{r}) = p\psi(\mathbf{r}). \qquad (2)$$

The eigenvalues p are found by realizing that a double application amounts to the identity so that

$$P^2\psi(\mathbf{r}) = p^2\psi(\mathbf{r}) = \psi(\mathbf{r}), \qquad (3)$$

from which we obtain

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

Thus even (+) and odd (-) parity wavefunctions are defined according to whether they are invariant or simply change sign under *P*:

$$P\psi(+) = \psi(+), \quad P\psi(-) = -\psi(-). \qquad (5)$$

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

$$P H P^{-1} = H, \quad \text{or} \quad [P,H] = PH - HP = 0. \tag{6}$$

Since P does not depend explicitly on time and commutes with the Hamiltonian, we can say that, if the state of a closed system has definite parity, that parity is conserved (the law of conservation of parity).[14]

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

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

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

Clearly these two mixed parity states are interconverted by P:

$$P\psi_1 = \psi_2, \quad P\psi_2 = \psi_1. \tag{8}$$

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

$$\psi(\pm) = \psi^{(0)}(\pm)\, e^{-iW(\pm)t/h}, \tag{9}$$

but mixed parity states are not. We shall see in Section 6 below that mixed parity states can become quasi-stationary when $W(+) \approx W(-)$, and true stationary states if H contains a parity-violating term.

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 $A(+)$ and $A(-)$ associated with these observables are therefore defined by

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

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

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

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

from which it follows that the expectation value of any odd-parity observable vanishes in any state of definite parity, i.e. a state for which either $\psi(+)$ or $\psi(-)$ is zero. This means that 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, etc. Measurements on a system in a state of mixed parity can reveal, in addition, observables with odd parity, examples being magnetic monopole, linear momentum, electric dipole moment, etc.[15,16] The optical rotatory parameter, being a pseudoscalar, has odd parity: this leads to the important deduction that *resolved chiral molecules exist in mixed-parity quantum states*. The detailed structure of these mixed-parity states is elaborated in Section 6 below.

Time Reversal

Because of the form of the Schrödinger equation $H\Psi = i\hbar\partial\Psi/\partial t$, the classical time reversal operator T does not translate into a satisfactory quantum-mechanical operator. Instead, the operator

$$\Theta = UK \tag{12}$$

is invoked, where U is a unitary operator and K is the antilinear operator of complex conjugation.[16-18]

It is not possible to classify a quantum state as being even or odd under time reversal because Θ, unlike P, does not have eigenvalues. (However, the operator Θ^2 *does* have eigenvalues, these being +1 for an even-electron system and -1 for an odd-electron system). A simple illustration is the effect of Θ on a general atomic state $|J,M\rangle$ where both orbital and spin angular momenta can contribute to the total electronic angular momentum specified by the usual quantum numbers J and M. Using a particular phase convention, it is found that[15]

$$\Theta|J,M\rangle = (-1)^{J-M+q}|J,-M\rangle, \tag{13}$$

where q is the sum of the individual orbital quantum numbers of all the electrons in the atom. Thus application of the time reversal operator has generated a new quantum state, orthogonal to the original, corresponding to a reversal of the sense of the total angular momentum of the atom. Since they are interconverted by time reversal, such states can be loosely regarded as having 'mixed time parity' analogous to the mixed spatial parity states (7), even though associated states of definite time parity do not exist. Notice, however, that the states $|J,M\rangle$ do have definite spatial parity since they are eigenstates of P:

$$P|J,M\rangle = (-1)^q|J,M\rangle. \tag{14}$$

This follows from the behaviour under space inversion of the spherical harmonics together with the standard convention that the 'intrinsic parity' of an electron spin state is +1.[19]

Unlike states, operators $A(+)$ and $A(-)$ and their associated observables *can* be classified as time-even or time-odd according to whether they are invariant or change sign under time reversal:

$$\Theta A(+)\Theta^{-1} = A(+)^{\dagger}, \qquad \Theta A(-)\Theta^{-1} = -A(-)^{\dagger}. \tag{15}$$

(If A is Hermitian, the Hermitian conjugate symbol † can be omitted.) It can be shown that time-odd observables are only supported by states of 'mixed time parity'.[15,16]

Charge Conjugation

A discussion of the effect of the charge conjugation operator C in quantum mechanics requires a formulation in terms of relativistic quantum field theory[13,20] which is beyond the scope of these lectures. All we need to appreciate here is that a charged particle is not in an eigenstate of C because charge conjugation generates a different quantum state corresponding to the associated antiparticle.

3. TRUE CHIRALITY

It is important to realize that optical activity is not necessarily the hallmark of chirality. In this section it is shown how a proper symmetry classification of the associated observables leads to a more precise definition of a chiral system than that usually encountered. The distinction between natural and magnetic optical activity, which is often a source of confusion in the literature of both chemistry and physics, provides a good example; and a careful analysis leads to the required new definition of chirality.

3.1. Natural and Magnetic Optical Activity

The following statement from Lord Kelvin's Baltimore Lectures[5] shows that it was recognized in the last century that the symmetry aspects of natural and magnetic optical activity are quite different:

> "The magnetic rotation has neither left-handed nor right-handed quality (that is to say, no chirality). This was perfectly understood by Faraday, and made clear in his writings, yet even to the present day we frequently find the chiral rotation and the magnetic rotation of the plane of polarized light classed together in a manner against which Faraday's original description of his discovery of the magnetic polarization contains ample warning."

He probably had Pasteur in mind who, judging from his writings, was a persistent offender.

We obtain the required symmetry classification of the natural and magnetic optical activity observables by comparing the results of optical rotation measurements before and after subjecting the sample plus any applied field to space inversion and time reversal.[15]

Consider first the natural optical rotation experiment. Under space inversion, an isotropic collection of chiral molecules is replaced by a collection of the 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 see 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. Hence *the natural optical rotation observable is a time-even pseudoscalar.*

We now turn to the Faraday effect, where optical rotation is induced in an isotropic collection of achiral molecules by a static uniform magnetic field collinear with 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 individually 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. Hence *the magnetic optical rotation observable is a time-odd axial vector.*

The same conclusions are obtained from a more fundamental approach in which operators are defined whose expectation values generate the optical activity observables.[15,21] It is found that the natural optical rotation observable is generated by a time-even odd-parity operator, and the magnetic optical rotation observable by a time-odd even-parity operator. Another approach 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 all the contributions to magnetic optical rotation are generated by time-odd tensors.[15,22]

This analysis tells us that 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 2.3 above, it is clear that the former must have, among other things, mixed spatial parity and the latter mixed time parity.

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. From Pasteur onwards these two types of optical activity have often been confused, with the magnetic field being thought of as a source of chirality.

3.2 A New Definition of Chirality

By now it should be clear that the hallmark of a chiral system is that it can generate time-even pseudoscalar observables. This leads to the following definition that enables chirality to be distinguished from other types of dissymmetry:[7-10,15,21]

> *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.*

This means that the enantiomorphism shown by truly chiral systems is time-invariant. Enantiomorphism that is time-noninvariant has different characteristics that I call false chirality in order to emphasise the distinction.

It is easy to see that a stationary object such as a finite helix that is chiral according to the traditional stereochemical definition is accommodated by the first part of this definition: space inversion is a more fundamental operation than the mirror reflection traditionally invoked but provides an equivalent result; and the second part of the definition is irrelevant for a stationary object. However, the full definition is required to identify more subtle sources of chirality in which motion is an essential ingredient. The following examples will make this clear.

3.3. Translating spinning Cones, Spheres and Elementary Particles

Consider a cone spinning about its symmetry axis. This system certainly supports enantiomorphism because the space-inverted version is not superposable on the original (Fig. 9a), so it might be thought that a spinning cone is a chiral object. However, according to the definition above, it is false chirality because time reversal followed by a rotation R_π through 180° about an axis perpendicular to the symmetry axis generates the same object as space inversion (Fig. 9a). But if the spinning cone is also translating along the axis of spin, time reversal followed by a 180° rotation now generates a different system to that generated by space inversion (Fig. 9b). Hence a *translating* spinning cone exhibits true chirality.

In fact the translating spinning object does not need to be a cone. A sphere translating along the axis of spin also shows true chirality. This can be appreciated by looking at just the pattern of arrows in Fig. 9b and ignoring the cone.

The molecular equivalent of a stationary spinning cone is a symmetric top in a rotational quantum state $|J,K,M\rangle$. The parity operation transforms $|J,K,M\rangle$ into $|J,-K,M\rangle$, which therefore has mixed parity,[23] so that these two states correspond to the two non-superposable cones in Fig. 9a. 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 $|J,K,M\rangle$ and $|J,-K,M\rangle$.

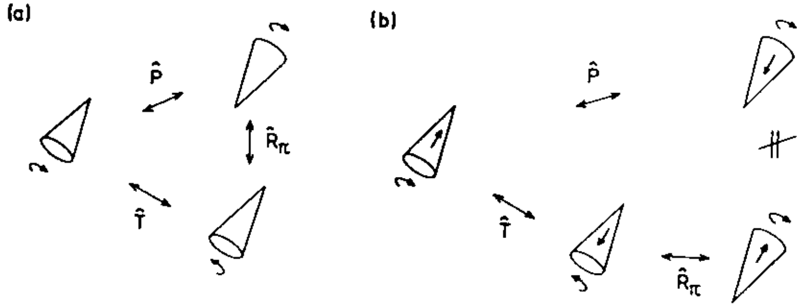


Fig. 9. The effect of P, T and R_π on (a) a stationary spinning cone, and (b) a translating spinning cone.

This shows that mixed parity in a molecular quantum state is not necessarily sufficient to generate chirality, despite the fact that it can result in two enantiomeric objects. Although mixed parity is a necessary condition for any odd-parity observable, further characteristics are required for different types of odd-parity observable. In this instance the mixed parity characteristic of the rotational quantum state $|J,K,M\rangle$ 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 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 is an odd-parity observable transforming as a pseudoscalar and so 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. The origin of these mixed parity internal states is discussed in Section 6 below.

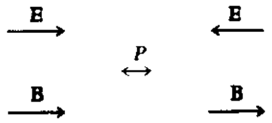
The photons in a circularly polarized light beam propagating as a plane wave are in spin angular momentum eigenstates characterized by a spin quantum number $s = 1$ with quantum numbers $m_s = +1$ and -1 corresponding to projections of the spin angular momentum vector parallel and antiparallel, respectively, 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).[20] 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 above for a translating spinning sphere then show that a circularly polarized photon exhibits true chirality.

The case of a spinning electron ($s = 1/2$, $m_s = \pm 1/2$) is rather 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, beams of spin-polarized electrons impinging on targets composed of chiral molecules are expected to show effects analogous to the polarization effects in the light beams used as probes in conventional optical activity experiments.[24-26] One such effect has recently been observed: an asymmetry in the attenuation of beams of right- and left-handed spin-polarized 5 eV electrons on passing through camphor vapour.[27] 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 suggestion is reinforced by a mechanism proposed for asymmetric decomposition of enantiomeric chiral molecules by longitudinally spin-polarized electrons that is a function of v/c,[28] and by the discussion in Section 7 below of the relativistic aspects of chirality and the associated velocity-dependence of the amplitude of parity violation in the weak interaction. The fact that such a large effect was observed in the experiment just mentioned using electron beams of such low energy is probably due to resonance associated with a temporary negative ion state generated by capture of an electron into the π^* orbital of the carbonyl group.[29]

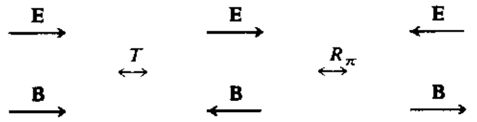
Similar experiments have been proposed for beams of spin-polarized neutrons,[30-33] which are also spin–1/2 particles with rest mass.

3.4. Electric, Magnetic and Gravitational Fields

It is clear that neither a static uniform electric field **E** (a time-even polar vector) nor a static uniform magnetic field **B** (a time-odd axial vector) constitutes a chiral system. Likewise time-dependent uniform electric and magnetic fields. Furthermore, contrary to a suggestion first made by Curie,[34] no combination of a static uniform electric and a static uniform magnetic field can constitute a chiral system. Collinear electric and magnetic fields do indeed generate enantiomorphism, but it is time-noninvariant and so corresponds to false chirality. Thus parallel and antiparallel arrangements are interconverted by space inversion and are not superposable:



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



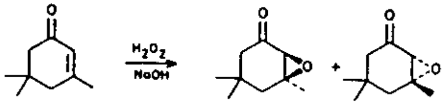
Zocher and Torok[35] also recognized the flaw in Curie's suggestion: they called the collinear arrangement of electric and magnetic fields a time-asymmetric enantiomorphism, and said that it does not permit a time-symmetric optical activity.

In fact the basic requirement for two collinear vectorial influences to generate 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 by *magneto-chiral* phenomena such as a birefringence and a dichroism induced in a chiral sample by a uniform magnetic field collinear with the propagation vector **k** of a light beam of arbitrary polarization.[36-38] Thus 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 magneto-chiral birefringence and dichroism observables transform as time-odd polar vectors.[38]

Analogous to collinear electric and magnetic fields is the case of a rapidly rotating vessel with the axis of rotation perpendicular to the earth's surface.[39] 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 in this case therefore exhibits false chirality.

4. ABSOLUTE ASYMMETRIC SYNTHESIS

In the absence of a chiral influence, a chemical reaction starting from achiral reactants that produces chiral products will always produce equal amounts of the two mirror-image enantiomers (a racemic mixture). A typical example is the epoxidation of isophorone:



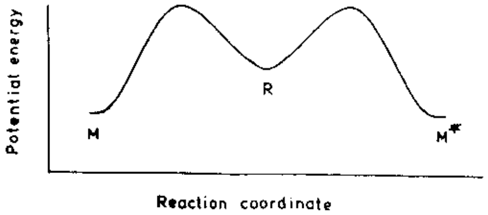
The use of an external physical influence to produce an excess of one or other enantiomer is known as an absolute asymmetric synthesis.[4,40] The subject still attracts much interest and controversy,[8,9,41] not least because it is an important ingredient in considerations of the prebiotic origins of biological molecules.[42-44] As we shall see, the new concepts of true and false chirality have helped to resolve some of the controversies, and have also exposed some rather subtle and unexpected analogies with *CP* violation in elementary particle physics.

4.1. Truly Chiral Influences

If an influence can be classified as truly chiral one can be confident that it has the correct symmetry characteristics to induce absolute asymmetric synthesis, or some associated process such as preferential asymmetric decomposition, in any conceivable situation, although of course the influence might be too weak to produce any observable effect. It is helpful to consider the potential energy barriers over which the reacting system must pass in going from reactants to products. Thus Fig. 10a shows the barriers for production of chiral enantiomers M and M* from the achiral reactant molecule R the absence of a chiral influence: since M and M* have the same energy in this situation, no enantiomeric excess can exist if the reaction is allowed to reach thermodynamic equilibrium. However, as shown in Fig. 10b, in the presence of a truly chiral influence M and M* have different energies so an enantiomeric excess can exist at equilibrium. There are also kinetic effects because the enantiomeric transition states will have different energies.

(a)

$$M \underset{k_b}{\overset{k_f}{\rightleftarrows}} R \underset{k_b^*}{\overset{k_f^*}{\rightleftarrows}} M^*$$



(b)

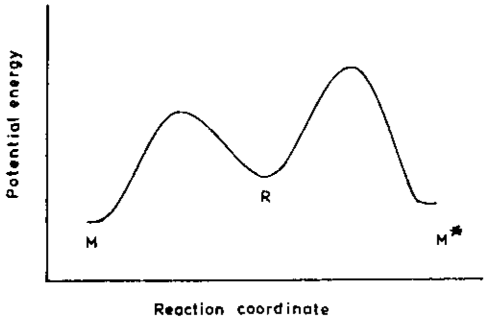


Fig. 10. Potential energy barriers in the absence (a) and presence (b) of a truly chiral influence.

Circularly polarized photons are the obvious choice, and several examples of the use of circularly polarized visible or ultraviolet radiation in asymmetric synthesis or preferential asymmetric photodecomposition are known[4,40-44] and are usually based on electronic circular dichroism.

Much less obvious is the use of an *unpolarized* light beam collinear with a magnetic field. This idea was first mooted by Wagnière and Meier,[45] with a suggested mechanism based on the new phenomenon of magneto-chiral dichroism mentioned in Section 3.4 above. Having seen that this system exhibits true chirality, we can be confident that it can induce absolute asymmetric synthesis regardless of the details of any particular mechanism.[8,9]

4.2. Falsely Chiral Influences

When considering the possibility or otherwise of absolute asymmetric synthesis being induced by a falsely chiral influence, it is important to realize that a fundamental distinction must be made between reactions that have been allowed to reach thermodynamic equilibrium (*thermodynamic control*) and reactions that have not attained equilibrium (*kinetic control*).

The case of thermodynamic control is quite clear. Because a chiral molecule M and its enantiomer M* are isoenergetic in the presence of, say, collinear electric and magnetic fields, or a spinning vessel with its axis perpendicular to the earth's surface (neglecting the very small differences due to parity violation discussed later), such falsely chiral influences cannot 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.[46-48] (The energy equivalence of M and M^* follows from a consideration of the invariance properties of the Hamiltonian in the presence of the influence under the combined operations of space inversion and time reversal).

The situation is less straightforward for reactions under kinetic control since microscopic reversibility and detailed balancing might not hold. This is discussed in the next section.

4.3. The Breakdown of Microscopic Reversibility: Enantiomeric Detailed Balancing

I have suggested that conventional detailed balancing, and the associated kinetic principles, might not be valid for reactions involving chiral molecules in a time-noninvariant enantiomorphous influence.[49,50] This suggestion was inspired by a remark of Lifshitz and Pitaevskii[51] that, for a system comprising chiral molecules of just one enantiomer, detailed balancing in the literal sense does not obtain because space inversion as well as time reversal is applied to each microscopic process, so that a completely different system is generated which cannot be compared with the original in order to deduce new information as to its properties. This is seen most clearly from the following quantum-mechanical description of the microscopic process.[18] The amplitude for a transition from some initial linear momentum state $\mathbf{p}$ to some final state $\mathbf{p}'$ is written $\langle \mathbf{p}'|\mathcal{T}|\mathbf{p}\rangle$, where $\mathcal{T}$ is the operator responsible for the transition. If $\mathcal{T}$ involves purely electromagnetic interactions it will be invariant under both parity and time reversal, which enables us to write

$$\langle \mathbf{p}'|\mathcal{T}|\mathbf{p}\rangle \overset{\text{under } T}{=} \langle -\mathbf{p}|\mathcal{T}|-\mathbf{p}'\rangle \overset{\text{under } P}{=} \langle \mathbf{p}^*|\mathcal{T}|\mathbf{p}^{*\prime}\rangle, \tag{17}$$

where we have allowed the particles to be chiral, the star denoting the P-enantiomer.

The first equality in (17), obtained from time reversal alone, is the basis of the conventional principle of microscopic reversibility and, when averaged over the complete system of reacting particles at equilibrium, of the principle of detailed balancing.[52] The second equality, obtained by applying space inversion to the time-reversed transition amplitude, describes the inverse process involving the *enantiomeric* particles.

Conventional detailed balancing is usually adequate for the kinetic analysis of reactions, even those involving chiral molecules, because conventional microscopic reversibility expressed by the first equality in (17) is usually valid. However, in the presence of a time-noninvariant enantiomorphous influence such as collinear electric and magnetic fields, time reversal alone is not a symmetry operation since a different influence is generated: space inversion must also be applied in order to recover the original relative orientations of **E** and **B**. The first equality in (17) is therefore no longer valid, and we must base any kinetic analysis on the relationship

$$\langle \mathbf{p}'|\mathcal{T}|\mathbf{p}\rangle \overset{TP}{=} \langle \mathbf{p}^*|\mathcal{T}|\mathbf{p}^{*\prime}\rangle. \tag{18}$$

Lifshitz and Pitaevskii considered a system containing just one enantiomer. But if the system contains equal numbers of enantiomeric molecules at equilibrium (a racemic mixture), it does appear to be possible to obtain new information using arguments based on (18). I have suggested that, in this situation, a new *principle of enantiomeric detailed balancing* can be invoked in which the statistical average of all the microscopic processes involving one enantiomer can be balanced by the average of the inverse processes, in the sense of (18), involving the enantiomeric molecules.[8,49] Consider a unimolecular process in which a prochiral molecule R generates a chiral molecule M or its enantiomer M^*:

$$M \underset{k_b}{\overset{k_f}{\leftrightarrows}} R \underset{k_f^*}{\overset{k_b^*}{\leftrightarrows}} M^*. \tag{19}$$

In refs. 8 and 49, enantiomeric detailed balancing was applied to the separate reactions in this scheme (i.e. $[R]k_f = [M^*]k_b^*$ and $[R]k_f^* = [M]k_b$) to show that a time-noninvariant enantiomorphous influence allows a difference in rate constants for enantiomeric processes, i.e $k_f \neq k_f^*$ and $k_b \neq k_b^*$. However, the analysis was incomplete because difficulties arise from the condition that the concentrations $[M]$ and $[M^*]$ of the two enantiomers must be equal at thermodynamic equilibrium. These difficulties were subsequently resolved by realizing that the scheme (19) represents just one racemization pathway: by considering a reaction quadrangle which allows at least one alternative interconversion pathway between the enantiomers, it was shown that the thermodynamic and kinetic requirements can be reconciled.[50] The reason that the conditions $[M] = [M^*]$, $k_f \neq k_f^*$ and $k_b \neq k_b^*$ can hold simultaneously is that, at *true* thermodynamic equilibrium, the different enantiomeric excesses associated with each separate racemization pathway sum to zero.

The conrotatory ring closure of a substituted butadiene to produce a cyclobutene was used as a simple example to show how collinear electric and magnetic fields can bring about a difference in potential energy profiles, and hence rate constants, for enantiomeric reactions.[50] This example exposes the origin of the breakdown of microscopic reversibility in this situation: the transient magnetic dipole moment in the transition state, and hence the interaction with the magnetic field, is velocity-dependent, and reverses in sign for the two directions of motion through the transition state. The function of the electric field is to partially align the molecules in the fluid so that these equal and opposite magnetic interactions for the forward and backward reactions do not average to zero over the bulk sample. In fact the electric field is not required if the molecules are already oriented, which means that a magnetic field alone can induce a breakdown of microscopic reversibility in processes involving chiral molecules aligned in a crystal or on a surface, for example.

In more conventional situations, time reversal invariance and hence microscopic reversibility in the presence of a magnetic field can be recovered by also reversing the moving charged particles that are the source of the magnetic field.[53] This prescription fails in the present situation because the system is only invariant under *TP*, not *T* alone, so microscopic reversibility is only recovered in the time-reversed *enantiomeric* system. In conventional chemical kinetics, the microscopic reversibility which follows from the assumption of *T* invariance is conceptualized in terms of a potential energy profile that is the same in the forward and backward directions for a given reaction (Fig. 11). But for reactions involving chiral molecules in situations where only the combined *TP* invariance holds (as in the presence of collinear electric and magnetic fields, or for oriented molecules in the presence of a magnetic field alone), we must extend this picture to show the same potential energy profiles for the forward and backward *enantiomeric* reactions with the forward and backward profiles for the reaction of a given enantiomer in general different (Fig. 12).

$$\langle p'|\mathcal{T}|p\rangle \overset{\text{under}\ T}{=} \langle -p|\mathcal{T}|-p'\rangle$$

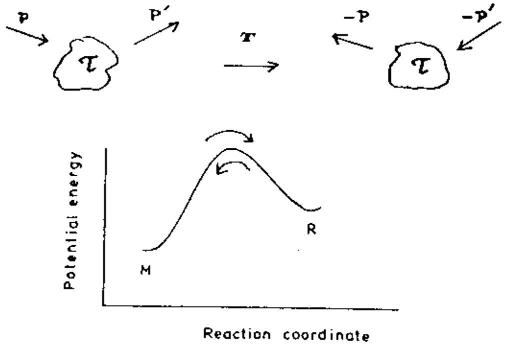


Fig. 11. Microscopic reversibility conceptualized as the same potential energy barrier for the forward and backward processes.

$$\langle p'|\mathcal{T}|p\rangle \overset{TP}{=} \langle p^*|\mathcal{T}|p^{*\prime}\rangle$$

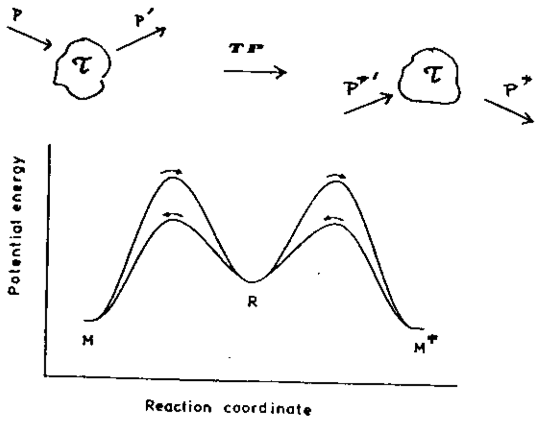


Fig. 12. Potential energy surfaces for enantiomeric reactions in the presence of a time-noninvariant enantiomorphous influence.

4.4. Unitarity and Thermodynamic Equilibrium

The unitarity of the scattering matrix,[20] together with *TP* invariance in the context of a collection of interconverting chiral enantiomers M and M*, can be used to generalize this analysis.[50]

Let $\mathcal{T}_{ij}$ be the amplitude for a transition from a state i to a state j. The requirement of unitarity for the scattering matrix (which corresponds to the fact that the sum of the transition probabilities from a given initial state to all final states is unity) leads to the following relationship for the transition amplitude:[20]

$$\sum_j \mathcal{T}_{ij}\mathcal{T}_{ij}^* = \sum_j \mathcal{T}_{ji}^*\mathcal{T}_{ji} \qquad (20)$$

where the sum over j includes all states j and j* of both enantiomers. It is important to realize that Hermiticity is not invoked in proving this result: $\mathcal{T}_{ij}$ is only Hermitian in a first approximation.[20] If *TP* invariance holds, we can use (18) to write

$$\mathcal{T}_{ji} = \mathcal{T}_{i^*j^*} \qquad (21)$$

and this, together with (20), gives

$$\sum_j |\mathcal{T}_{ji}|^2 = \sum_j |\mathcal{T}_{i^*j}|^2 = \sum_j |\mathcal{T}_{ij}|^2 \qquad (22)$$

If the system is racemic and in thermal equilibrium, equivalent enantiomeric states are equally populated. The second equality in (22) then shows that transitions out of these states must produce molecules in a given state i and the enantiomeric molecules in the equivalent state i^* in equal numbers. Thus no excess of one enantiomer over the other can develop at thermal equilibrium even when the presence of a time-noninvariant enantiomorphous influence destroys the equality between rates for specific enantiomeric transitions, i.e. when

$$|\mathcal{T}_{ji}|^2 \neq |\mathcal{T}_{j^*i^*}|^2. \tag{23}$$

Notice that, had we allowed $\mathcal{T}_{ji}$ to be Hermitian, rates for specific enantiomeric transitions *would* be equal. From (20) and (21) we can also write

$$\sum_j |\mathcal{T}_{ji}|^2 = \sum_j |\mathcal{T}_{ji^*}|^2, \tag{24}$$

which shows that the total transition rates out of equivalent enantiomeric states are equal. Since in thermal equilibrium no excess of i over i^* may develop, this implies that any pre-existing excess tends to be diminished. This argument is similar to that used to demonstrate the existence of equal numbers of particles and antiparticles at thermodynamic equilibrium, despite *CP* violation, in the big bang model of the early universe. [54]

Thus if an absolute asymmetric synthesis starting with a pure prochiral reagent R could indeed be induced by collinear electric and magnetic fields, say, the enantiomeric excess will ultimately disappear if sufficient time is allowed for the establishment of true thermodynamic equilibrium in which all possible racemization pathways have separately equilibrated. Similarly, the influence could not generate an enantiomeric excess in a racemic mixture. Thus no fundamental thermodynamic principles are violated by the suggestion that a time-noninvariant enantiomorphous influence can, *via* a breakdown of microscopic reversibility, generate a difference in rate constants for enantiomeric processes. It should be mentioned that, at first sight, the proposed difference in enantiomeric rate constants appears to lead to the possibility of constructing a perpetual motion machine of the second kind,[50] which conflicts with the conclusion just reached that no fundamental thermodynamic principles are violated. Exactly the same difficulty arises in the analogous discussion of particle–antiparticle processes in the presence of *CP* violation; however, Teller[55] has identified the fallacy present in such schemes for a perpetual motion machine (a violation of unitarity always arises).

There is one last element, not yet demonstrated at the time of writing, required to complete this discussion; namely that the combined influence of collinear electric and magnetic fields on the elementary scattering processes associated with reaction and transport processes involving chiral molecules is able to induce the necessary non-Hermitian contribution to the transition amplitude.

This analysis is important for chemical physics generally because it reinforces the conclusion that it is unitarity, rather than microscopic reversibility, that is necessary for the validity of Boltzmann's H-theorem.[54,56]

5. SYMMETRY VIOLATION

A symmetry violation (often called symmetry nonconservation) arises when one of the 'non-observables' discussed in Section 2.1 above is actually observed. A consideration of symmetry violation, and how it differs from spontaneous symmetry breaking, provides considerable insight into the phenomenon of molecular chirality.

5.1. 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. 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 systems was thought to be confined to the sign of pseudoscalar observables: the mirror image of any complete experiment involving one enantiomer should be realizable, with any pseudoscalar observable (such as optical rotation angle) changing sign but retaining *precisely* the same magnitude. Then in 1956 Lee and Yang[57] pointed out that, unlike the electromagnetic and strong interactions, there was no evidence for parity conservation in processes involving the weak interaction. Of the experiments they suggested, that carried out by Wu et al.[58] is the most famous.

The Wu experiment studied the β-decay process

$$^{60}\mathrm{Co} \rightarrow {}^{60}\mathrm{Ni}^+ + e^- + \tilde{\nu}_e$$

in which, essentially, a neutron n has decayed via the weak interaction into a proton p, an electron e^- and an electron antineutrino $\tilde{\nu}_e$. The nuclear spin magnetic magnetic moment I of each ^{60}Co nucleus in the sample was aligned with an external magnetic field **B**, and the angular distribution of electrons measured. It was found that the electrons are emitted preferentially in the direction *antiparallel* to that of the magnetic field (Fig. 13a). As discussed in Section 2.2, **B** and **I** are axial vectors and so do not change under space inversion, whereas the electron propagation vector **k** does because it is a polar vector. Hence in the corresponding space-inverted experiment the electrons should be emitted *parallel* to the magnetic field (Fig. 13b). It is only possible to reconcile Figs. 13a and 13b with parity conservation if there is no preferred direction for electron emission (an isotropic distribution), or if the

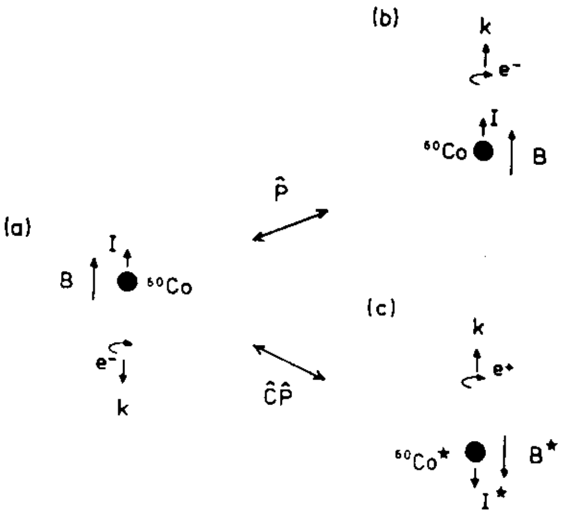


Fig. 13. Parity violation in β-decay. Only experiment (a) is found. The space-inverted version (b) cannot be realized. Symmetry is recovered in experiment (c), which is obtained from (a) by invoking charge conjugation simultaneously with space inversion (Co* is anti-Co, and B* and I* are reversed relative to **B** and **I** because the charges of the moving source particles have reversed).

electrons are emitted preferentially in the plane perpendicular to **B**. The observation of (a) alone provides unequivocal evidence for parity violation. Another important aspect of parity violation in 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 other β-decay processes, 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 $\lambda = \mathbf{s} \cdot \mathbf{p}/|\mathbf{p}|$. Spin–1/2 particles can have $\lambda = \pm \hbar/2$, the positive and negative states being called 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 Fig. 13c that the combined operation of *CP* interconverts the two equivalent experiments for which nature appears to have no preference (assuming *CP* , and hence *T*, is not violated: see Section 5.3 below). This result implies that *P* violation is accompanied here by *C* violation: explicitly, absolute charge is distinguished since the charge that we call negative is carried by the electrons, which are emitted with a left-handed spin polarization.

Notice that the Wu experiment provides a nice example of true chirality, as defined in Section 3.2. The two experiments (a) and (b) in Fig. 13 are enantiomeric with respect to space inversion, but cannot be interconverted by time reversal combined with any proper spatial rotation.

5.2. Parity Violation in Atoms and Molecules: the Weak Neutral Current

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 Ws 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 interaction 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 1960s in the celebrated work of Weinberg,[59] Salam[60] and Glashow,[61] which unified the theory of the weak and electromagnetic interactions into a single electroweak interaction theory. The conceptual basis of the theory rests on two pillars: gauge invariance and spontaneous symmetry breaking,[62,63] but the details are beyond the scope of these lectures. 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 and electromagnetic coupling constants ($g \sin\vartheta_w = e$, 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 particles. In one of the most important experiments of all time, these three particles were detected in 1983 at CERN in proton-antiproton scattering experiments.[64]

This weak neutral current interaction 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 $\hbar = e = m_e = 1$):[65,66]

$$V_{eN}^{PV} = \frac{G\alpha}{4\sqrt{2}} Q_w (\boldsymbol{\sigma}_e \cdot \mathbf{p}_e, \rho_N(\mathbf{r}_e))_+ , \qquad (25)$$

where G is the Fermi weak coupling constant, α is the fine structure constant, $\boldsymbol{\sigma}_e$ and $\mathbf{p}_e$ are the Pauli spin operator and linear momentum operator of the electron, $\rho_N(\mathbf{r}_e)$ is a normalized nuclear density function and

$$Q_w = Z(1 - 4\sin^2\vartheta_w) - N$$

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, in which case (25) is taken as the parity-violating term to be added to the Hamiltonian of an atom or molecule. Since $\boldsymbol{\sigma}_e$ and $\mathbf{p}_e$ are time-odd axial and polar vectors, respectively, and all the other factors are scalars, V_{eN}^{PV} transforms as a time-even pseudoscalar, as required, and so can mix even and odd parity electronic states at the nucleus.

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.[67-69] Being pseudoscalars, the parity-violating weak neutral current terms in the molecular Hamiltonian are odd under space inversion:

$$P V^{PV} P^{-1} = -V^{PV}. \tag{26}$$

As discussed in Section 6 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 P. It then follows that V^{PV} shifts the energies of the enantiomeric states in opposite directions:

$$\begin{aligned} \langle\psi_L| V^{PV} |\psi_L\rangle &= \langle P\psi_R| V^{PV} |P\psi_R\rangle = \langle\psi_R| P^\dagger V^{PV} P |\psi_R\rangle \\ &= -\langle\psi_R| V^{PV} |\psi_R\rangle = \varepsilon. \end{aligned} \tag{27}$$

Attempts to calculate ε are faced with the following difficulty. The electronic coordinate part of V^{PV} in (25) is linear in $\mathbf{p}_e$ and is therefore pure imaginary. Since, in the absence of external magnetic fields, the molecular wavefunction can always be chosen to be real, V^{PV} has zero expectation values. Also, the presence of $\boldsymbol{\sigma}_e$ 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.[66,68] 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.[66,70-72] (The atomic unit of energy, the Hartree, is equivalent to 27.2 eV or to 4.36×10 J). It is intriguing that, in all the cases treated so far, the L-amino acids and the D-sugars, which dominate the biochemistry of living organisms, are found to be the more stable enantiomers.[73,74]

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;[75-79] and Hegstrom *et al.*[80] have provided an appealing pictorial representation of the associated atomic chirality in terms of a helical electron probability current density. Parity violation has not yet been observed in molecules. *Achiral* molecules are expected to show similar manifestations to atoms, such as tiny optical rotations, but enhanced perhaps by several orders of magnitude.[81-83] However, the most important challenge is the measurement of the parity-violating enantiomeric energy difference in chiral molecules. Quack[84] has reviewed the various ideas and attempts to measure this difference, and has made detailed proposals for some new experiments which could enhance the sensitivity of the measurements to the required level. A rather different aspect is the recent claim, on the basis of *ab-initio* calculations, that the observed 1.4% excess of chiral (−)-quartz crystals over (+)-quartz crystals in terrestrial samples is a manifestation of parity violation.[74,85]

5.3. Violation of Time Reversal and the *CPT* Theorem

Violation of time reversal was observed in 1964 in the famous experiment of Cronin, Fitch *et al.* involving measurements of rates for different decay modes of the neutral K-meson.[86-88] Despite intensive efforts since then, no other system has shown the effect. As Cronin has said,[87] nature has provided us with just one extraordinarily sensitive system to convey a cryptic message that has still to be deciphered.

Although unequivocal, the effects are very small; certainly nothing like the parity-violating effects in weak processes, which can sometimes be absolute. in fact T violation itself is not observed directly: rather, the observations show CP violation, from which T violation is implied by the celebrated CPT theorem (this statement is qualified at the end of this section). This theorem is derived from general considerations of relativistic quantum field theory,[13,20] and states that the Hamiltonian is invariant to the combined operation of CPT even if it is not invariant to one or more of these operations.

One manifestation of CP violation is the following decay rate asymmetry of the long-lived neutral K-meson, the K_L:[13,17,63,88]

$$\Delta = \frac{\text{Rate}\,(K_L \rightarrow \pi^- e_r^+ \nu_l)}{\text{Rate}\,(K_L \rightarrow \pi^+ e_l^- \tilde{\nu}_r)} \approx 1.00648. \tag{28}$$

As the formula indicates, K_L can decay into either positive pions π^+ plus left helical electrons e_l^- plus right helical antineutrinos $\tilde{\nu}_r$; or into negative antipions π^- plus right helical positrons e_r^+ plus left helical neutrinos ν_l. Since these two sets of decay products are interconverted by CP, this decay rate asymmetry indicates that *CP* is violated. If we naively represent this decay process in the form of 'chemical equilibria' as in (19),

$$\pi^+ + e_l^- + \tilde{\nu}_r \underset{k_b}{\overset{k_f}{\rightleftarrows}} K_L \underset{k_f^*}{\overset{k_b^*}{\leftrightarrows}} \pi^- + e_r^+ + \nu_l, \qquad (29)$$

a parallel is established with absolute asymmetric synthesis associated with a breakdown in microscopic reversibility discussed in Section 4.2 since in both cases $k_f \neq k_f^*$. Thus the K_L and the two sets of decay products are the equivalents, with respect to *CP*, of R, M and M* with respect to *P*. We can therefore conceptualize the decay rate asymmetry here as arising from a breakdown in microscopic reversibility due to a time-noninvariant *CP* enantiomorphism in the forces of nature[50] (the *CPT* theorem guarantees that the two distinct *CP* enantiomorphous influences are interconverted by *T*). The analogy is completed by the fact that, as mentioned in Section 4.3, the asymmetries cancel out over all possible channels at true thermodynamic equilibrium.

Another manifestation of *CP* violation arises that should be mentioned, but first more needs to be said about the K^0 system. Four distinct states are displayed: particle and antiparticle states $|K^0\rangle$ and $|\tilde{K}^0\rangle$, and two combined states

$$|K_1\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle + |\tilde{K}^0\rangle), \qquad (30a)$$

$$|K_2\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle - |\tilde{K}^0\rangle), \qquad (30b)$$

which have different energies because of coupling between $|K^0\rangle$ and $|\tilde{K}^0\rangle$ via the weak force. Since the particle and antiparticle states are interconverted by *CP*,

$$CP\,|K^0\rangle = |\tilde{K}^0\rangle, \qquad CP\,|\tilde{K}^0\rangle = |K^0\rangle, \qquad (31)$$

we can appreciate that the combined states are even and odd eigenstates of *CP* :

$$CP\,|K_1\rangle = |K_1\rangle, \qquad CP\,|K_2\rangle = -|K_2\rangle. \qquad (32)$$

However, these eigenstates are not pure: for example $|K_2\rangle$, which is odd with respect to *CP*, is occasionally observed to decay into products which are even with respect to *CP*. This implies that the Hamiltonian contains a small *CP*-violating term which mixes $|K_1\rangle$ and $|K_2\rangle$. In fact the long-lived state $|K_L\rangle$ introduced above is actually $|K_2\rangle$ with a small admixture of $|K_1\rangle$; and there is an associated short-lived state $|K_S\rangle$ that is $|K_1\rangle$ with a small admixture of $|K_2\rangle$. One example is the decay into the pair of oppositely charged pions $\pi^+\pi^-$ for which the state of zero angular momentum is even with respect to *CP* so only the decay of $|K_1\rangle$ should yield such a product state. What is found is a very small but significant amplitude for K_L to decay into $\pi^+\pi^-$:

$$\eta_{+-} = \frac{\text{amplitude}\,(K_L \to \pi^+\pi^-)}{\text{amplitude}\,(K_S \to \pi^+\pi^-)} \approx 2.274 \times 10^{-3}. \qquad (33)$$

The *CP* violation parameters Δ and η_{+-} extracted from the two at first sight rather different experiments summarized by (28) and (33), together with a third parameter η_{00} derived from a similar experiment to (33), are in fact all related, and the results of all the experiments involving *CP* violation can be summarized by a single complex number.[17,87] Although it is only *CP* violation that has been observed directly, a detailed but rather complicated analysis of the results of these different experiments does appear to show, without invoking the *CPT* theorem, that *T* itself is violated; however, this analysis does not demonstrate that the *T* violation and the *CP* violation compensate each other to the same degree (in other words, a contribution from *CPT* violation cannot be ruled out).[17]

6. THE MIXED PARITY STATES OF A CHIRAL MOLECULE

It was shown earlier (Sections 2.3 and 3.1) that, since a chiral molecule can support pseudoscalar observables, it must exist in mixed-parity internal quantum states (vibrational-electronic) associated with a chiral molecular framework. We now explore the nature of these quantum states, and investigate the consequences of a small parity-violating term in the Hamiltonian.

6.1. The Double Well Model

The origin of these mixed-parity states is best appreciated by considering vibrational wavefunctions associated with the 'inversion' mode ν_2 of a molecule such as NH_3 which is said to invert between the two equivalent configurations shown in Fig. 14,[89,90] although this motion does not in fact correspond to an inversion through the centre of mass. If the planar configuration were the most stable, the adiabatic potential energy function would 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 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,

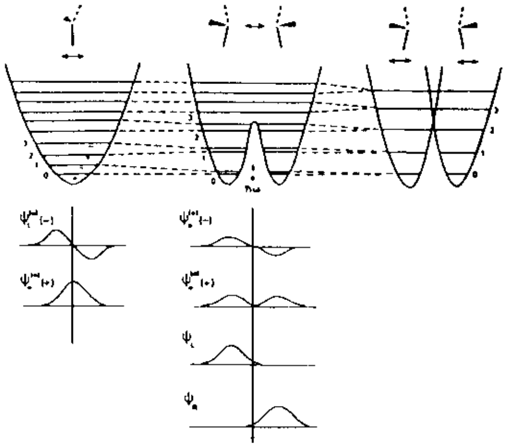


Fig. 14. The vibrational states of a molecule that can invert between two equivalent configurations. $\psi^{(0)}(+)$ and $\psi^{(0)}(-)$ are the amplitudes of the definite parity stationary states with energy $W(+)$ and $W(-)$, and ψ_L and ψ_R are the two mixed-parity non-stationary states at $t = 0$ and $t = \pi/\omega$, where $\hbar\omega$ is the tunnelling splitting.

$$\psi_L = \frac{1}{\sqrt{2}}[\psi^{(O)}(+) + \psi^{(O)}(-)], \tag{34a}$$

$$\psi_R = \frac{1}{\sqrt{2}}[\psi^{(O)}(+) - \psi^{(O)}(-)], \tag{34b}$$

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

The wavefunctions (34) are in fact specializations of the general time-dependent wavefunction of a degenerate two-state system (see Section 6.2 below). To be precise, we assume that the system is in the left well at $t = 0$. Then at a later time t we have[18]

$$\psi(t) = \frac{1}{\sqrt{2}}[\psi^{(O)}(+)e^{-iW(+)t/\hbar} + \psi^{(O)}(-)e^{-iW(-)t/\hbar}]$$

$$= \frac{1}{\sqrt{2}}[\psi^{(O)}(+) + \psi^{(O)}(-)e^{-i\omega t}]e^{-iW(+)t/\hbar}, \tag{35}$$

where $\hbar\omega = W(-) - W(+)$ is the energy separation of the two opposite parity states, which in this context is interpreted as a splitting arising from tunneling through the potential energy barrier separating the two wells. Thus at $t = 0$ (35) reduces to (34a) corresponding to the molecule being found in the left well, as required; and at $t = \pi/\omega$ (35) reduces to (34b) corresponding to the molecule being found in 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.

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,[91]

$$\sigma\psi_v = (-1)^v\psi_v, \tag{36}$$

where v is the vibrational quantum number (the normal vibrational coordinate for ν_2 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 nonplanar symmetric tops,[89,91] the rotational wavefunction of a planar symmetric top such as BF_3 is multiplied by the time-dependent wavefunction (35) corresponding to the 'inversion' vibration. The parity operation corresponds to an inversion of all the particle positions (nuclei plus 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 matter, it affects only the rotational wavefunctions and is used to classify their parity. The reflection is a purely internal matter, 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 type 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 nonrigid molecule in the gas phase.[92-94]

Since an analogous potential energy diagram can be drawn for any chiral molecule with a high barrier separating left and right wells corresponding 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 example of the general result that the width of an energy level corresponding to a quasi-stationary state with average lifetime t is $\Delta W = \hbar/t$.[95]

A central point is therefore the relation between the time scale of the optical activity (or any time-even pseudoscalar observable) measurement and the lifetime of the resolved enantiomer. A new aspect of the uncertainty principle appears to arise here, which I have stated loosely as follows:[15]

> *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 certainty about the parity of its quantum state, there is complete uncertainty about the enantiomer.*

Thus experimental resolution of the definite parity states of tartaric acid, for instance, 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 nonresolvable chiral molecule such as H_2O_2 spectroscopic transitions between definite parity states are observed routinely.

6.2. Two-State Systems and Parity Violation

It was shown in the previous section how the mixed parity states of a resolved chiral molecule can be visualized in terms of a double well potential. We now develop this aspect further by considering the quantum mechanics of a degenerate two-state system. This provides insight into the apparent paradox of the stability of optical enantiomers, which was recognized at the beginning of the quantum era when it was found that the existence of optical enantiomers was difficult to reconcile with basic quantum mechanics.[96–98]

The essence of the 'paradox' is that, because the potential energy term in the Hamiltonian of a molecule originates in Coulomb interactions between point charges, the complete molecular Hamiltonian is always invariant under space inversion and so the energy eigenstates (the stationary states) must be parity eigenstates. However, a resolved chiral molecule cannot be in such an eigenstate because the parity operation generates the mirror image enantiomer, which is a different system. Yet typical chiral molecules, such as alanine, appear to be no less stable than typical achiral molecules. Hund[96] suggested a resolution of the paradox using 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. Hund's approach has been brought up to date by injecting a small parity-violating term into the Hamiltonian which, as demonstrated in the rest of this section, can result in the two enantiomeric states becoming the true stationary states.[68,69]

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[99,100]

$$W_\pm = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\left[(H_{11} - H_{22})^2 + 4|H_{12}|^2\right]^{\frac{1}{2}}, \tag{37a}$$

$$\psi_+^{(0)} = \cos\vartheta\, e^{-i\varphi/2}\psi_1 + \sin\vartheta\, e^{i\varphi/2}\psi_2, \tag{37b}$$

$$\psi_-^{(0)} = -\sin\vartheta\, e^{-i\varphi/2}\psi_1 + \cos\vartheta\, e^{i\varphi/2}\psi_2, \tag{37c}$$

where

$$\tan 2\vartheta = \frac{2|H_{12}|}{(H_{11} - H_{22})} \quad \text{with} \quad 0 \le 2\vartheta < \pi, \tag{37d}$$

$$H_{21} = |H_{21}|e^{i\varphi}. \tag{37e}$$

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

Clearly ψ_1 and ψ_2 are not the stationary states (eigenstates) 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 $\psi_-^{(0)}$ must 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 Fig. 4, we can identify ψ_1 and ψ_2 with ψ_R and ψ_L. If initially we neglect the small parity-violating terms, the Hamiltonian has inversion symmetry so that, since $P\psi_R = \psi_L$ and $P\psi_L = \psi_R$, the enantiomeric states ψ_R and ψ_L are degenerate. The stationary state amplitudes (37b) and (37c) now specialize to

$$\psi_+^{(0)} = \frac{1}{\sqrt{2}} e^{-i\varphi/2}(\psi_R + e^{i\varphi}\psi_L), \tag{38a}$$

$$\psi_-^{(0)} = \frac{1}{\sqrt{2}} e^{-i\varphi/2}(-\psi_R + e^{i\varphi}\psi_L), \tag{38b}$$

and so transform according to one or other of the irreducible representations of the inversion group comprising *P* plus the identity. Which has even and which has odd parity depends on the choice of φ: for example, if $\varphi = \pi$ (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,

$$W_+ - W_- = 2|\langle \psi_L | H | \psi_R \rangle| = 2\delta, \tag{39}$$

and is interpreted as a splitting caused by tunneling through the potential energy barrier separating the two enantiomers (Fig. 4).

We now allow the Hamiltonian to contain a small parity-violating term V^{PV} such as the electron–nucleus weak neutral current interaction (25). According to (27) 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 (37) we have

$$W_+ - W_- = 2(\varepsilon^2 + \delta^2)^{\frac{1}{2}}, \tag{40a}$$

$$\tan 2\vartheta = \delta/\varepsilon. \tag{40b}$$

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

$$\psi(t) = \frac{1}{\sqrt{2}} e^{-i\varphi/2}[(\cos\vartheta\,\psi_R + \sin\vartheta\, e^{i\varphi}\psi_L)e^{-iW_+t/\hbar} + (-\sin\vartheta\,\psi_R + \cos\vartheta\, e^{i\varphi}\psi_L)e^{-iW_-t/\hbar}]. \tag{41}$$

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

$$\psi(t) = \frac{1}{2} e^{-i\varphi/2}[(\psi_R + e^{i\varphi}\psi_L)e^{-i\delta t/\hbar} + (-\psi_R + e^{i\varphi}\psi_L)e^{i\delta t/\hbar}]e^{-i(W_+ + W_-)t/2\hbar} \tag{42}$$

which reduces, within a phase factor, to (35) (do not confuse the notation $\psi_\pm$ 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 the handed states 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 which in this case have definite parity. But when $\delta = 0$ (zero tunnelling splitting)

$$\psi(t) = \frac{1}{\sqrt{2}} e^{-i\varphi/2}(\psi_R e^{-i\varepsilon t/h} + e^{i\varphi}\psi_L e^{i\varepsilon t/h})e^{-i(W_+ + W_-)t/2\hbar}, \tag{43}$$

so at $t = 0$ the system is entirely in $\psi(+)$ and at $t = \pi\hbar/2\varepsilon$ it is entirely in $\psi(-)$: now the system oscillates between the definite parity states $\psi(+)$ and $\psi(-)$ 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 (34a) or (34b), respectively. At some later time t the corresponding states will be

$$\psi_L(t) = e^{-i\varphi/2}(\sin\vartheta\,\psi_+^{(0)}e^{-iW_+t/\hbar} + \cos\vartheta\,\psi_-^{(0)}e^{-iW_-t/\hbar}), \tag{44a}$$

$$\psi_R(t) = e^{i\varphi/2}(\cos\vartheta\,\psi_+^{(0)}e^{-iW_+t/\hbar} - \sin\vartheta\,\psi_-^{(0)}e^{-iW_-t/\hbar}), \tag{44b}$$

which are obtained by inverting (37b) and (37c) 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[15,68,69]

$$\alpha(t) = \alpha_L\{\varepsilon^2 + \delta^2\cos[2(\delta^2 + \varepsilon^2)^{\frac{1}{2}}t/\hbar]\}\Big/(\delta^2 + \varepsilon^2), \tag{45}$$

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

$$\overline{\alpha}/\alpha_{max} = \varepsilon^2/(\delta^2 + \varepsilon^2). \tag{46}$$

Thus parity violation causes a shift away from zero of $\overline{\alpha}$. This is the basis of an experiment suggested by Harris and Stodolsky[68] to detect the parity-violating energy shift between enantiomers.

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

$$\psi_+(t) = (\cos\vartheta\, e^{-i\varphi/2}\psi_R + \sin\vartheta\, e^{i\varphi/2}\psi_L)e^{-iW_+t/\hbar}, \tag{47a}$$

$$\psi_-(t) = (-\sin\vartheta\, e^{-i\varphi/2}\psi_R + \cos\vartheta\, e^{i\varphi/2}\psi_L)e^{-iW_-t/\hbar}, \tag{47b}$$

the optical rotation will be given by

$$\alpha_+(t) = -\alpha_-(t) = -\alpha_L\varepsilon\Big/(\varepsilon^2 + \delta^2)^{\frac{1}{2}}. \tag{48}$$

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 follows from (41) and (37) that, as $\delta/\varepsilon \to 0$, 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 Stodolsky[68] 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 effectively forever. So the ultimate answer to the paradox of the stability of optical enantiomers might lie in the weak interactions.

6.3. Parity Violation and Parity Breaking

The appearance of parity-violating phenomena is interpreted in quantum mechanics by saying that, contrary to what had been previously supposed, the Hamiltonian lacks inversion symmetry (the weak interaction potential being a pseudoscalar). This means that P and H no longer commute, so the associated law of conservation of parity no longer holds. Such *symmetry violation* (non-conservation) must be clearly distinguished from *spontaneous symmetry breaking*: current usage in the physics literature applies the latter term to describe the situation that arises when a system displays a lower symmetry than expected from its Hamiltonian.[101] Natural optical activity is therefore a phenomenon arising from spontaneous parity breaking since, as we have seen, a resolved chiral molecule displays a lower symmetry than its associated Hamiltonian: if the small parity-violating term in the Hamiltonian is neglected, the symmetry operation that the Hamiltonian possesses but the chiral molecule lacks is parity, and it is this parity operation that interconverts the two enantiomeric parity-broken states.

It should be mentioned that the term 'spontaneous symmetry breaking' is often reserved exclusively for quantum mechanical systems with an infinite number of degrees of freedom for which there can be special dynamic instabilities which inevitably generate an unsymmetric state.[102] Quack[84] adheres to this usage, but in order to accommodate the unsymmetric states that occur in finite systems such as molecules and which are so important in the discussion of molecular chirality, he has introduced the term 'symmetry breaking *de facto*' to describe the situation where the unsymmetric states arise through the choice of initial conditions: in this case the existence of symmetric states is still possible. Quack also introduced the term 'symmetry breaking *de lege*' to describe what I have called symmetry violation (non-conservation) above for the case where the asymmetry resides in the Hamiltonian. Although Quack's new terminology has great virtue, in what follows I have used spontaneous symmetry breaking to cover the generation of unsymmetric states in both finite and infinite systems. One reason for this is that, as explained in the next section, there is sometimes no clear distinction between the symmetry breaking in the macroscopic (infinite) system and the symmetry breaking in the microscopic (finite) constituents of that macroscopic system; also the 'inevitability' of an unsymmetric state of an infinite system needs to be qualified since the temperature is a crucial factor.

The conventional view, formulated in terms of the double well model as in Section 6.1, is that parity violation plays no part in the stabilization of chiral molecules. The optical activity remains 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 spontaneous parity-breaking optical activity therefore averages to zero over a sufficiently long observation time. Hence the law of parity is saved in systems displaying spontaneous parity breaking because their pseudoscalar properties average to zero over a sufficiently long observation period on account of tunnelling or, equivalently, the space-inverted experiment is realizable. In either interpretation absolute chirality is not observable.

These considerations lead us to an important criterion for distinguishing 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 (recall the stationary states acquiring time-independent optical activity in the previous section when $\varepsilon \neq 0$). 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 between the enantiomers.[103]

6.4. Spontaneous Symmetry Breaking in Isolated Chiral Molecules and in Condensed Media

Spontaneous symmetry breaking has attracted much attention in recent years in both elementary particle and condensed matter physics, but with rather different emphasis on the various aspects. Anderson has written at length on broken symmetry in condensed matter, with some valuable asides on the molecular aspects.[104,105]

Ferromagnetism provides an important example. The Hamiltonian for an iron crystal is invariant under spatial rotations. However, the ground state of a magnetized sample is not invariant: it distinguishes a specific direction, the direction of magnetization. This non-zero magnetization in zero applied field also breaks time reversal symmetry. When the temperature is raised above the Curie point, the magnetization disappears and the rotational and time reversal symmetries become manifest. In fact the term 'spontaneous symmetry breaking' itself derives from the term 'spontaneous magnetization'. Notice that a vestige of the rotational symmetry still survives in the ferromagnetic phase in that the sense of magnetization is arbitrary; but this would be hidden from an observer living inside the crystal.

Temperature is a central feature here, because behaviour reflecting the full symmetry of the Hamiltonian can be recovered at sufficiently high temperature. Molecules behave rather differently from macroscopic systems in that there are no sharp transitions between symmetric and asymmetric states in molecules.[104] For example, in a molecule described by a double well model, thermal agitation will cause the 'inversion' transition to take place (unless the height and width of the barrier are effectively infinite) so that there is no absolute 'one-sidedness' at any temperature: in other words its spontaneous parity-broken characteristics decrease continuously with increasing temperature. In condensed media, on the other hand, large numbers of particles can cooperate to produce sudden rather than gradual thermal transitions between symmetric and asymmetric states of the complete macroscopic sample. In a ferroelectric crystal below its phase transition temperature, for example, the field associated with each molecular dipole (or the dipole associated with each unit cell) acts to hold the others in the same direction: the reversal of any one will not reverse the others but simply represents a local fluctuation. At the phase transition temperature, however, a sufficient number of dipoles are reversed that the system suddenly transforms into a state where opposite signs for each dipole occur with equal probability. Thus a distinction must be made between spontaneous symmetry breaking in a macroscopic system and in the individual microscopic constituents, although in many cases, including the example of ferroelectricity considered here, broken symmetry in the microscopic constituents (so that they are dipolar) is a prerequisite for the macroscopic spontaneous symmetry breaking associated with ferroelectricity. This distinction between microscopic and macroscopic spontaneous symmetry breaking can sometimes become rather blurred, as in superconductivity.[105]

The relationship between the microscopic and macroscopic aspects of the spontaneous parity-broken states of chiral systems is still an open question with much discussion concerning the rôle of the environment.[10,84,103,106-112] Furthermore, Salam[113] has suggested that there might exist a critical temperature T_c below which a racemic collection of chiral molecules might undergo a second-order phase transition to a chirally pure collection consisting of the enantiomer which is preferentially stabilized by the parity-violating weak neutral current interaction: however, the discussion of the chemical aspects of this interesting idea requires further refinement.

7. CHIRALITY AND RELATIVITY

It was shown in Section 3.3 that a spinning cone or sphere translating along the axis of spin possesses true chirality. This is an interesting concept because it exposes a link between chirality and special relativity. Consider a particle 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 then 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.

This relativistic aspect of chirality is in fact a central feature of modern elementary particle theory, especially in connection with the weak interaction where the parity-violating aspects are velocity-dependent. A good illustration is provided by the interaction of electrons with neutrinos: neutrinos are quintessential chiral objects since only left-handed neutrinos and right-handed antineutrinos exist.[14,20,62,63] 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 nonrelativistic electron momenta, the weak interaction still violates parity, but the amplitude of the violation is reduced to order v/c.[63] This is used to explain the interesting fact that the $\pi^- \to e^- \tilde{\nu}_e$ decay is a factor of 10^4 smaller than the $\pi^- \to \mu^- \tilde{\nu}_\mu$ decay, even though the available energy is much larger in the first decay.[63] Thus 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 anti-neutrino. 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 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.[96,97]

The word *chirality* has been used up to this point in the article in its qualitative chemical sense. But 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 +1 and -1 associated with pure right-handed and pure left-handed leptons.[6] But only massless leptons (such as neutrinos), which always move at the velocity of light, are in eigenstates of γ_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. In fact the very existence of mass is associated with 'chiral symmetry breaking'.[13] On the other hand, helicity (defined in Section 5.1 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).

Another rather different connection between chirality and relativity should be mentioned. It was shown in Section 6.3 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. This means that spontaneous parity-breaking optical activity in a chiral object moving at the speed of light becomes indistinguishable from parity-violating optical activity.

8. MOLECULE-ANTIMOLECULE PAIRS: TRUE ENANTIOMERS

We are now in a position to appreciate that parity violation has great conceptual significance in the discussion of molecular chirality, because only the space-inverted enantiomers of *truly* chiral systems show a parity-violating energy difference.[7] This follows from the fact that, although the parity-violating weak neutral current Hamiltonian (25) 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 (27) that the energy difference is zero.

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 object 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.[15,21,114] This follows from the *CPT* theorem and the assumption that *T* is not violated. So true enantiomers are interconverted by *CP*, which means that a chiral molecule is associated with two distinct pairs of true enantiomers (e.g. L-lactic acid and anti-D-lactic acid; and D-lactic acid and anti-L-lactic acid, illustrated in Fig. 15). Since *P* violation automatically implies *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 (i.e. between *C*—enantiomers), with a magnitude equal to that of the parity-violating energy difference between space-inverted enantiomers in the real world (*P*—enantiomers). Jungwirth et al. have provided a quantum-mechanical development, analogous to (27), that supports this conclusion.[114]

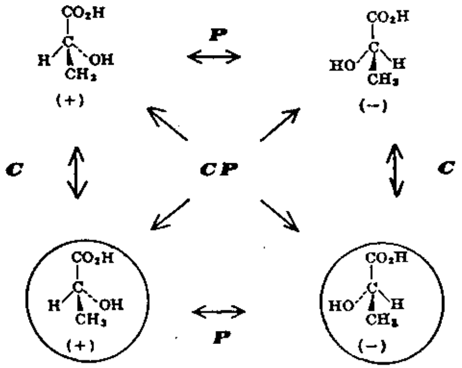


Fig. 15. The two pairs of true enantiomers (i.e. strictly degenerate) of lactic acid that are interconverted by *CP*.

This more general definition of the enantiomers of a truly chiral system is consistent with the chirality that free atoms display on account of parity violation.[15] The weak neutral current interaction 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 *CP* 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 7, left-handed and right-handed particles (or antiparticles) have different weak interactions. Again, *true* enantiomers are interconverted by *CP*: for example, a left-handed electron and a right-handed positron. Notice that right- and left-handed circularly polarized photons are automatically true enantiomers since a photon is its own antiparticle.

9. CONCLUDING REMARKS: LESSONS FOR PHYSICS AND CHEMISTRY

This discussion of the symmetry aspects of molecular chirality has drawn on many concepts from modern physics, especially the physics of elementary particles. It is particularly striking how the pursuit of analogies between the quantum states of a chiral molecule and those of various elementary particles reinforces Heisenberg's perception of a kinship between molecules and elementary particles.[115,116] This insight ought to 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.

Elementary particle physicists can also learn something from chemistry through such analogies. For example, Bohm[117] has reviewed the relationship between the collective motions of a diatomic molecule and the charge-monopole system in order to expose some useful insights into certain aspects of the structure of hadrons (particles which undergo strong interactions-baryons and mesons). Bohm et al.[118] have extended such molecular and also nuclear analogies into the relativistic domain to develop a model of collective motions of extended relativistic objects in order to calculate the mass spectrum and radiative transitions of hadrons.

Also Barut[119] has developed a composite model of elementary particles in which some particles, due to their internal structure, are not in eigenstates of *P* or *CP*, analogous to the spontaneously parity-broken states of chiral molecules. Then, just as a chiral molecule can support pseudoscalar observables, so these broken-symmetry particle states are responsible for the observation of 'symmetry-violating' quantities. The appearance or otherwise of symmetry violation in elementary particle processes then depends on the timescale of the interaction between particles: for example parity violation arises in this model because a left-handed neutrino, say, can escape *via* tunnelling from some long-lived intermediate resonance state of the interacting particles.

Another example is Wigner's comparison[120] of the four distinct states $|K^0\rangle$, $|\tilde{K}^0\rangle$, $|K_1\rangle$ and $|K_2\rangle$ of the neutral K-meson to the four possible states ψ_L, ψ_R, $\psi(+)$ and $\psi(-)$ of a chiral molecule: just as $|K^0\rangle$ and $|\tilde{K}^0\rangle$ are interconverted by *CP* and $|K_1\rangle$ and $|K_2\rangle$ are even and odd eigenstates with respect to *CP*, so ψ_L and ψ_R are interconverted by *P* and $\psi(+)$ and $\psi(-)$ have even and odd parity. However, Wigner's analogy falters when we introduce *CP* violation into the K^0 system and *P* violation into the chiral molecule. Although *CP* violation mixes $|K_1\rangle$ and $|K_2\rangle$ just as *P* violation mixes $\psi(+)$ and $\psi(-)$, there does not appear to be a *CP* analogue of the lifting of the degeneracy of ψ_L and ψ_R through *P* violation because one of the consequences of the *CPT* theorem is that a particle and its associated antiparticle have the same mass and lifetime.[13,17,20] A better molecular analogy would be with the four states of a chiral molecule in a time-noninvariant *P*-enantiomorphous influence such as collinear electric and magnetic fields. Indeed, a detailed quantum-mechanical analysis of a chemical reaction system such as the butadiene–cyclobutene interconversion in collinear electric and magnetic fields, in which expressions for analogues of the *CP*-violating parameters mentioned in Section 5.3 were derived, might help to remove some of the mystery surrounding *CP* violation. Barut's composite particle model[119] could also be useful in this context since it provides an intuitive picture of *CP* violation in the K^0 system involving the breakdown of the perfect symmetry of a double potential well.

Molecular analogies might assist in discussions of the possible characteristics of manifestations of *T* violation that are being sought in atoms and molecules such as permanent electric dipole moments. It is natural to suppose that such *T* violation would be akin to that observed in the K meson system in which direct observation of *CP* violation implies, *via* the *CPT* theorem, *T* violation to the same degree. However, as mentioned in Section 5.3 above, the analogy with absolute asymmetric synthesis induced by collinear electric and magnetic fields leads to the conceptualization of this breakdown in microscopic reversibility as arising from a time-noninvariant *CP*-enantiomorphous influence in the forces of nature: of the two possible influences, only one is found in our world (analogous to, say, parallel rather antiparallel electric and magnetic fields). This implies that manifestations of *T* violation must be associated with a process,[121] not with a state, and can only appear as a breakdown in microscopic reversibility in particle-antiparticle processes (since these involve *CP* enantiomers). *The implication of this interpretation of CP violation is that searches for electric dipole moments, etc., in stationary states of atoms and molecules as manifestations of T violation might be futile!*

Finally, there are tantalizing similarities between the anyon theory of high-temperature superconductivity[122] and the concept of false chirality given in these lectures. A central characteristic of anyons inhabiting the two dimensional world of copper oxide planes is that they break *P* and *T* simultaneously (which parallels the breaking of *P* and *T* by a time-noninvariant enantiomorphous influence such as collinear electric and magnetic fields). The parity operation has a quite different effect in two dimensions than in three since it becomes simply a reflection in only one axis.[123] This has the important consequence that, unlike a spinning system in three dimensions, the sense of a spinning system in two dimensions is reversed under *P*. Since it is still reversed under *T*, the anyon spin in two dimensions is invariant under *PT* together but not under *P* and *T* separately. Hence time-noninvariant enantiomorphism (i.e. false chirality), albeit in two dimensions, is a central feature of the anyon theory of high temperature superconductivity.

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