

Perspective

False Chirality, Absolute Enantioselection and *CP* Violation: Pierre Curie's Legacy

Laurence D. Barron

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK; laurence.barron@glasgow.ac.uk

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Abstract: The 1884 suggestion of Pierre Curie (1859–1906) that the type of dissymmetry shown by collinear electric and magnetic fields may induce an enantiomeric excess, in a chemical reaction that would otherwise produce a racemic mixture, is explored in the context of fundamental symmetry arguments. Curie's arrangement exhibits false chirality (time-noninvariant enantiomorphism), and so it may not induce absolute enantioselection (ae) in a process that has reached thermodynamic equilibrium, since it does not lift the degeneracy of chiral enantiomers. However, it may do so in far-from-equilibrium processes via a breakdown in microscopic reversibility analogous to that observed in elementary particle processes under the influence of *CP* violation, the associated force possessing false chirality with respect to *CP* enantiomorphism. In contrast, an influence like circularly polarized light exhibiting true chirality (time-invariant enantiomorphism) lifts the degeneracy of enantiomers, and so may induce ae in all circumstances. Although to date, ae has not been observed under the influence of Curie's arrangement of collinear electric and magnetic fields, it is argued that two different experiments have now demonstrated ae under a falsely chiral influence in systems far from equilibrium, namely in a spinning sample under a gravitational field, and in the separation of enantiomers at a ferromagnetic surface.

Keywords: symmetry in physical laws; optical activity; true and false chirality; absolute enantioselection; parity violation; *CP* violation; biomolecular homochirality

1. Introduction

The term “chirality”, meaning handedness, was first introduced into science in the late nineteenth century by Lord Kelvin (William Thomson, 1st Baron Kelvin, 1824–1907) to describe a figure “if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself” [1]. He called the two distinguishable mirror-image forms “chiroids”; but today we use the term “enantiomers” in the case of chiral molecules. Chirality has become a central and unifying theme in modern science [2,3]. It links the properties of the universe and its constituent elementary particles through organic stereochemistry, to the structure and behavior of the molecules of life with much else besides (nonlinear optics, nanotechnology, planar plasmonic metamaterials, spintronics, materials, electrical engineering, pharmaceuticals, astrobiology, the origin of life, etc.). An especially interesting and fruitful development in recent years is how the interplay of chirality and magnetism can generate new phenomena with implications for, inter alia, new optical and electronic devices and technologies and the production of single enantiomers.

Pierre Curie's pioneering work in the late nineteenth century on the electric and magnetic properties of matter led to many important discoveries and also to the ideas of symmetry in physical laws, which culminated in the enunciation of an essential principle relating the symmetry of ‘effects’ to the symmetry of ‘causes’ [4,5].

This article contributes to the evolving theme of the interplay of chirality and magnetism by showing how one of Curie's ideas still resonates today by providing a remarkable fundamental link

between current problems in stereochemistry and particle physics, and that throws new light on some controversial recent experiments in chiral molecular science.

The use of an external physical influence to produce an enantiomeric excess (ee) in what would otherwise be a racemic product in a chemical reaction is known as an absolute asymmetric synthesis [6]. The production of an ee in more general situations is often referred to as absolute enantioselection (ae). The subject still attracts much interest and controversy, and is central to the problem of the origin of optical activity in nature (see for example [7–15]). One source of confusion is that there are physical systems that can exist in two distinct mirror-image states, and yet are not truly chiral in a fundamental sense. The application of discrete symmetry arguments to the problem, especially motion reversal (time reversal T) in addition to space inversion (parity P), provides a rigorous foundation for the critical assessment of the ability of a physical influence to induce ae. Furthermore, inclusion of charge conjugation C (particle–antiparticle exchange) enables productive analogies to be established between the physics of chiral molecules and elementary particles.

2. Pasteur's Conjecture

In the years following his separation in 1848 of the enantiomers of sodium ammonium tartrate, Louis Pasteur (1822–1895) conjectured that molecular chirality (which he called “dissymmetry”) in the living world is induced by some universal chiral force or influence in nature, since at the time, all substances found to show a natural optical rotation in solution were natural products. As described by Mason [16], he attempted to extend the concept of chirality (dissymmetry) to other aspects of the physical world. For example, he thought that the combination of a translational with a rotational motion generates chirality; likewise, a magnetic field. In 1894 Pierre Curie entered the discussion by suggesting that collinear arrangements of electric and magnetic fields \mathbf{E} and \mathbf{B} might induce asymmetric synthesis [17]. However, of these influences only a translating–rotating system possesses ‘true chirality’ (vide infra). Pasteur's incorrect belief that a static magnetic field alone is also a source of chirality has been shared by many other scientists and led to many futile attempts to induce asymmetric synthesis. This misconception is based on the fact that a static magnetic field can induce optical rotation, discovered by Michael Faraday (1791–1867) in 1846. But from early on Lord Kelvin (then William Thomson) appreciated that there is a fundamental difference between the two types of optical rotation: he suggested that natural rotation is probably due to a spiral heterogeneousness in the optically active substance over distances comparable to the optical wavelengths; whereas Faraday rotation originates in particles set in circular motion by the magnetic field [18]. As he stresses in the Baltimore Lectures [1], “the magnetic rotation has neither a right-handed nor left-handed quality (that is to say, no chirality)”. More formally, chiral phenomena such as natural optical rotation are characterized by time-even pseudoscalar observables; whereas magnetic optical rotation is not a chiral phenomenon, the observable being a time-odd axial vector [2,19–21].

3. Curie's Idea Has False Chirality

A controversy raged throughout the 1970s concerning the nature of physical fields and forces that are able to induce absolute asymmetric synthesis [9,21,22]. Curie's collinear electric and magnetic fields do indeed generate a type of dissymmetry, because the distinguishable parallel and antiparallel arrangements are interconverted by parity P (equivalent to mirror reflection), since \mathbf{E} , being a polar vector, is reversed by P , but \mathbf{B} , being an axial vector, is not. De Gennes made an important contribution by applying time reversal T in addition to space inversion to Curie's idea, which demonstrated that chiral enantiomers remain degenerate in the presence of collinear electric and magnetic fields. His abstract (translated from the original French) summarizes his conclusions [23]: “We show that, even in the presence of two parallel fields (electric \mathbf{E} and magnetic \mathbf{H}), a racemic system of chemical reagents cannot evolve towards an optically active final equilibrium state. On the other hand, if the final state is out of balance, a dissymmetry remains possible”. The last sentence stating that, if the final state is out of equilibrium, dissymmetry remains possible, is sometimes overlooked leading to

the erroneous assertion that de Gennes demonstrated the impossibility of ae in combined electric and magnetic fields. De Gennes revisited this problem a few years later [5]. After emphasizing “no equilibrium effect”, he states “On the other hand, the kinetics may differ. The speed of ‘right’ and ‘left’ reactions are not exactly identical.” He went on to estimate the different rates of attachment of achiral monomers to form a right- or left-handed helix segment of a growing helical polymer aligned in an electric field in the presence of a parallel magnetic field.

Zocher and Török had previously anticipated De Gennes’ introduction of time reversal into the problem by calling Curie’s arrangement of electric and magnetic fields a time-asymmetric enantiomorphism [24]. This, together with De Gennes’ insight, stimulated a series of papers in the early 1980s by the present author, who introduced the concept of ‘true’ and ‘false’ chirality to emphasize the distinction between time-invariant and time-noninvariant enantiomorphism, respectively [21,22,25–28]. Chirality in a stationary system such as a helix or a chiral molecule is easy to recognize. But when motion is an essential ingredient, Lord Kelvin’s original definition of chirality must be extended with the following definitions:

True chirality is exhibited by systems that exist in two distinct enantiomeric states that are interconverted by space inversion (parity P), but not by motion reversal (time reversal T) combined with any proper spatial rotation. It supports time-even pseudoscalar observables, breaking P but not T . Since it lifts the degeneracy of truly chiral enantiomers, a truly chiral influence can induce ae in all circumstances. Circularly polarized light is an important example: P reverses the direction of propagation, but not the sense of circularity, thereby interconverting right- and left-handed systems; T reverses both, thereby preserving the handedness; i.e., time-invariant enantiomorphism.

False chirality is exhibited by systems that exist in two distinct enantiomeric states that are interconverted by time reversal as well as space inversion combined with a proper spatial rotation. It supports time-odd pseudoscalar observables, breaking P and T separately, but being PT invariant overall. Falsely and truly chiral systems have quite different physical properties. A falsely chiral system cannot induce ae in systems at equilibrium since it does not lift the degeneracy of truly chiral enantiomers; but it might in processes under kinetic control and far from equilibrium [21,22,26–28]. Curie’s collinear electric and magnetic fields provide the archetype. A static uniform electric field \mathbf{E} is a time-even, polar vector, whereas a static uniform magnetic field \mathbf{B} is a time-odd, axial vector, so the distinct parallel and antiparallel arrangements are interconverted by P ; but they are also interconverted by T combined with a rotation R_π through 180° about an axis perpendicular to the field direction; i.e., time-noninvariant enantiomorphism (Figure 1).

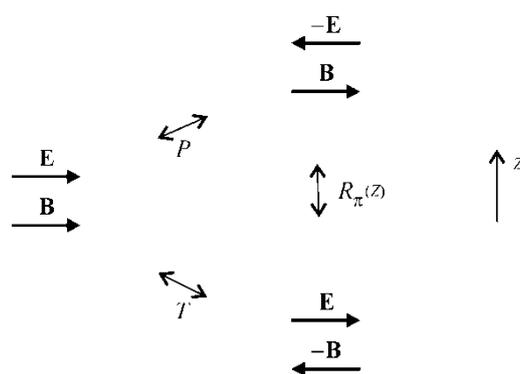


Figure 1. The effect of P and T on Curie’s falsely chiral arrangement of parallel electric and magnetic fields. The antiparallel arrangements generated by P and T separately may be interconverted by a rotation $R_\pi(z)$ about an axis z perpendicular to the field directions. Adapted from [15].

In 1948 Bernard Tellegen (1900–1990) conceived of a medium with novel electromagnetic properties comprising microscopic electric and magnetic dipoles tied together with their moments either parallel or antiparallel [29,30]. Such media, which are of potential interest to nanotechnology, would clearly

exhibit enantiomorphism corresponding to false chirality, and would provide a material realization of Curie's idea. The fabrication of Tellegen media proved elusive and controversial until the construction of particles with coupled electric and magnetic moments was reported in 2008 [31].

Since magnetic charge is odd under both parity and time reversal, it is a time-odd pseudoscalar [32], something also noted by Zocher and Török [24]. Consequently, if it were ever to be discovered, a magnetic monopole would constitute the quintessential falsely chiral object!

In fact, the basic requirement for two collinear vectorial influences to generate true chirality is that one transforms as a polar vector and the other as an axial vector, with both being either time-even or time-odd. The second case is exemplified by birefringence and dichroism phenomena induced in an isotropic chiral sample by a uniform magnetic field \mathbf{B} collinear with the propagation vector \mathbf{k} of a light beam of arbitrary polarization, including unpolarized [2,3,33]. These were christened 'magneto-chiral birefringence and dichroism' in a paper that developed a molecular theory of these phenomena [34]. The parallel and antiparallel arrangements of \mathbf{B} and \mathbf{k} , which are interconverted by P , are true chiral enantiomers, because they cannot be interconverted by T , since both \mathbf{B} and \mathbf{k} are time odd. Magneto-chiral dichroism was first observed in 1997, via luminescence anisotropy in a chiral lanthanide complex in an organic solution, by Rikken and Raupach [35].

4. Parity Violation and the CP Operation

It used to be taken as self-evident that, if two objects exist as non-superposable mirror images, like the two enantiomers of a chiral molecule, nature would not prefer one over the other. The mirror image of any complete experiment should be realizable, with any pseudoscalar observables (such as the optical rotation angle) changing their sign, but retaining precisely the same magnitude. Then in 1957, following a suggestion by Lee and Yang, that parity is violated in the weak interactions, parity violation was demonstrated experimentally in a β -decay process in which the emitted β -electrons were found to have a left-handed spin polarization, thus showing that nature has a preference for one of two possible mirror-image experiments, and makes an absolute distinction between right- and left-handed spin-polarized particles involved in weak interaction processes [36,37]. Hence parity P is not a true symmetry of the world.

It was subsequently realized that symmetry could be recovered by invoking invariance under the combined CP operation in which charge conjugation C (particle-antiparticle exchange) and space inversion P are applied together [36,37]. Hence symmetry is recovered in the space-inverted antiworld made of antimatter!

Parity violation can infiltrate to a tiny extent into the world of atoms and molecules. This realization followed from the discovery in the 1960s that the weak and electromagnetic interactions could be unified into a single, more fundamental, 'electroweak' force [38]. Among other things, there exists a parity-violating electron-nucleus contact potential V_{eN}^{PV} in the atomic or molecular Hamiltonian [39]. The source of parity violation within this potential is a factor $\boldsymbol{\sigma} \cdot \mathbf{p}$, the scalar product of the Pauli spin operator $\boldsymbol{\sigma}$ and linear momentum operator \mathbf{p} of the electron. Since $\boldsymbol{\sigma}$ and \mathbf{p} are axial and polar vectors, respectively, and both are time-odd, their scalar product transforms as a time-even pseudoscalar, and so V_{eN}^{PV} constitutes a truly chiral influence.

One manifestation of parity violation in atomic physics is a tiny natural optical rotation in the vapors of free atoms [40]. CP invariance means that the equal and opposite sense of optical rotation should be shown by the corresponding atoms composed of antiparticles. Chiral molecules support a remarkable manifestation of parity violation in the form of a lifting of the exact degeneracy of the energy levels of mirror-image enantiomers, known as the parity-violating energy difference (PVED).

Although this PVED may be calculated [41–43], it has not yet been observed experimentally. Since, on account of the PVED, the P -enantiomers of a truly chiral object are not exactly degenerate, they are not strict enantiomers. The strict enantiomer of a chiral object is to be found in the antiworld: strict enantiomers are interconverted by CP . In other words, the molecule with the opposite absolute configuration, but composed of antiparticles, should have identical energy to the original [19,20].

5. Violation of CP

Violation of CP was first observed in 1964 in weak interaction decay modes of the neutral K -meson, the K^0 . One manifestation is the following decay rate asymmetry of the long-lived neutral K -meson, the K_L [36,37]:

$$\Delta = \frac{\text{rate}(K_L \rightarrow \pi^- e_r^+ \nu_l)}{\text{rate}(K_L \rightarrow \pi^+ e_l^- \bar{\nu}_r)} = 1.00648. \quad (1)$$

As the formula indicates, K_L can decay into either positive pions π^+ plus left-helical electrons e_l^- plus right-helical antineutrinos $\bar{\nu}_r$; or into negative antipions π^- plus right-helical positrons e_r^+ plus left-helical neutrinos ν_l . Because these two sets of decay products are interconverted by CP ,

$$\pi^- e_r^+ \nu_l \xleftrightarrow{CP} \pi^+ e_l^- \bar{\nu}_r, \quad (2)$$

the decay-rate asymmetry demonstrates that CP is violated.

This manifestation of CP violation implies a breakdown in microscopic reversibility in the corresponding particle–antiparticle processes associated with the accompanying T violation that follows from the CPT theorem of relativistic quantum field theory. This states that, even if one or more of CP or T are violated, invariance under the combined operation CPT will always hold [36,37]. The force responsible for CP violation is therefore characterized by a lack of CP and T invariance separately, but possessing CPT invariance overall. This is analogous to a falsely chiral influence in the molecular case, which is characterized by the lack of P and T invariance separately but possessing PT invariance overall. Hence the force responsible for CP violation may be conceptualized within the framework of false chirality. This perception is reinforced by a remark of Lev Okun (1929–2015) [44] that a CP -violating term, the so-called θ -term, which may be added to the standard quantum electrodynamics (QED) Lagrangian and which is CP -odd, is similar to $\mathbf{E} \cdot \mathbf{B}$, the scalar product of an electric and magnetic field, which corresponds to our archetypal falsely chiral influence, namely Curie's collinear arrangement of electric and magnetic fields!

The CPT theorem has three important consequences: the rest masses of a particle and its antiparticle are equal; the particle and antiparticle lifetimes are the same; and the electromagnetic properties such as the charge and magnetic moment of particles and antiparticles are equal in magnitude but opposite in sign. Using the rest mass (and hence energy) identity of particles and their antiparticles from CPT invariance, it is possible to prove that the CP -enantiomers of a chiral molecule remain strictly degenerate even in the presence of CP violation, provided CPT itself holds [45]. In other words, being falsely chiral, the force responsible for CP violation does not lift the degeneracy of CP enantiomers.

Axions are as yet undetected low-mass, spin-zero particles that are candidates for the cold dark matter thought to comprise most of the mass of the universe [46]. Microwave cavity experiments to detect axions depend on their proposed coupling to two photons via an interaction that again contains our archetypal falsely chiral factor $\mathbf{E} \cdot \mathbf{B}$ [46]. Moody and Wilczek suggested that a long-range axion-mediated spin-dependent force $V_{eN}^{(PT)V}$ between a nucleon and an electron may permit the infiltration of CP violation into macroscopic systems via a P - and T -violating interaction [47]. Since this force depends on the scalar product $\boldsymbol{\sigma} \cdot \mathbf{r}$ of the Pauli spin operator $\boldsymbol{\sigma}$ of the electron and the nucleon–electron separation vector \mathbf{r} , and the first is a time-odd axial vector and the second a time-even polar vector, $\boldsymbol{\sigma} \cdot \mathbf{r}$ is a time-odd pseudoscalar, and so $V_{eN}^{(PT)V}$ constitutes a falsely chiral influence. However, any manifestations in atomic and molecular physics are expected to be very tiny indeed.

6. Absolute Enantioselection

6.1. Truly Chiral Influences

If an influence is classified as truly chiral, it has the correct symmetry characteristics to induce ae in any conceivable situation, although of course it might be too weak to produce an observable effect. The ability of a truly chiral influence to induce ae in the form of absolute asymmetric synthesis may be illustrated by a simple symmetry argument applied to the unimolecular process,



in which an achiral molecule R generates a chiral molecule M or its enantiomer M*, and the k s are corresponding rate constants. In the absence of a truly chiral influence, M and M* have the same energy, so no ee can exist if the reaction reaches thermodynamic equilibrium. As illustrated in Figure 2a, the associated potential energy profiles (barriers) are identical. Now consider a collection of single enantiomers M in the presence of a right-handed truly chiral influence (Ch)_R, say. Under parity P , the collection of enantiomers M becomes an equivalent collection of the mirror-image enantiomers M* and the right-handed influence (Ch)_R becomes the equivalent left-handed influence (Ch)_L. Assuming parity is conserved, this indicates that the energy of M in the presence of (Ch)_R is equal to that of M* in the presence of (Ch)_L. But because P (or any other symmetry operation) does not provide a relation between M and M* in the same influence, be it (Ch)_R or (Ch)_L, as illustrated in Figure 2b they will in general have different energies (along with different potential energy barriers associated with their production from R). Hence an ee can now exist at equilibrium (due to different Boltzmann populations of M and M*). There will also be kinetic effects because the enantiomeric transition states will also have different energies.

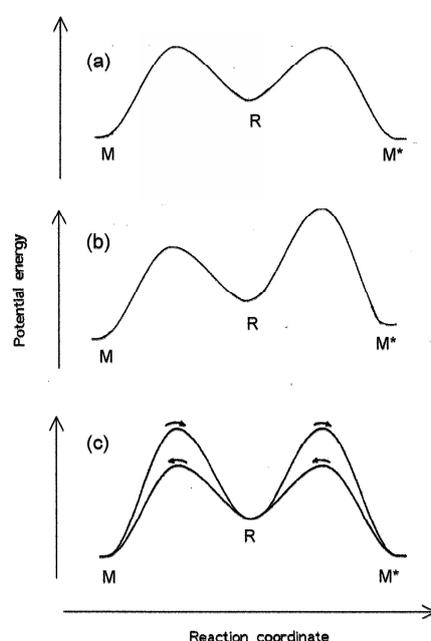


Figure 2. Potential energy profiles for the formation of a chiral molecule M or its enantiomer M* starting from an achiral precursor R. (a) In the absence of any chiral influence. (b) In the presence of a truly chiral influence. (c) In the presence of a falsely chiral influence and illustrating the principle of enantiomeric microscopic reversibility. Adapted from [15].

Circularly polarized photons, or longitudinal spin-polarized electrons associated with radioactive β -decay, are obvious examples of truly chiral influences, and their ability to induce ae has been demonstrated many times (see for example [7,9–12]).

Although a magnetic field alone has no chirality, and so cannot induce ae in a system at equilibrium, as described above a static magnetic field collinear with a light beam of arbitrary polarization is a truly chiral system, and can therefore induce ae in all circumstances. This was first demonstrated experimentally in 2000 by Rikken and Raupach [48], who generated a small but significant ee at photochemical equilibrium in an initially racemic mixture of a chiral organometallic complex in aqueous solution. This was the first unequivocal example of the use of a magnetic field, albeit not in isolation, to induce ae [49]. Although much weaker than circularly polarized light in this respect, magnetic fields and unpolarized light are more ubiquitous in the cosmos than circularly polarized light, and should be considered along with circularly polarized light in discussions of the origins of prebiotic homochirality.

Being a time-even pseudoscalar, the weak neutral current interaction responsible for the PVED lifts the degeneracy of the space-inverted (P -) enantiomers of a truly chiral system. It has attracted much discussion as a possible source of biomolecular homochirality (see for example [8,11,12,41–43]). Parity violation has also been invoked in this context in the interaction of molecular electrons with neutrinos and gravitational fields [50].

6.2. Falsely Chiral Influences

Unlike the case of a truly chiral influence, enantiomers M and M^* remain strictly degenerate in the presence of a falsely chiral influence such as collinear electric and magnetic fields. Again, this can be seen from a simple symmetry argument applied to the unimolecular reaction (3). Under P , the collection of enantiomers M becomes the collection M^* and a parallel arrangement, say, of \mathbf{E} and \mathbf{B} , becomes antiparallel. The antiparallel arrangement of \mathbf{E} and \mathbf{B} , however, becomes parallel again under T ; but this last operation will not affect an isotropic collection of chiral molecules, even if paramagnetic. Hence the energy of the collection M is the same as that of the collection M^* in parallel (or antiparallel) electric and magnetic fields.

When considering the possibility or otherwise of ae being induced by a falsely chiral influence, a distinction must be made between reactions that have been left to reach thermodynamic equilibrium (thermodynamic control) and reactions that have not attained equilibrium (kinetic control). The case of thermodynamic control is quite clear: because M and M^* remain strictly degenerate in the presence of a falsely chiral influence, it cannot induce ae in a reaction which has been allowed to reach thermodynamic equilibrium. The case of kinetic control is more subtle. It has been suggested that, for processes involving chiral molecules under a falsely chiral influence, a breakdown of conventional microscopic reversibility based on T invariance may occur, with symmetry recovered via a new and deeper principle of *enantiomeric* microscopic reversibility (and the corresponding principle of *enantiomeric* detailed balancing) associated with the breaking of P and T separately but with PT invariance maintained overall [21,22,26–28]. This may be visualized in terms of the same potential energy profiles for the forward and backward enantiomeric reactions, but with different forward and backward profiles for the production of a given enantiomer (Figure 2c). The apparently contradictory kinetic and thermodynamic aspects of this breakdown in microscopic reversibility are reconciled by considering all possible interconversion pathways, and invoking the unitarity of the scattering matrix together with PT invariance, which proves that excesses of one product enantiomer over the other cancel at true thermodynamic equilibrium (i.e., when all possible interconversion pathways have equilibrated) [26,27]. This is directly analogous to the procedure adopted in the case of CP violation in the K^0 system, which demonstrated that Boltzmann's H -theorem, and hence the second law of thermodynamics, depends upon unitarity, and not upon microscopic reversibility, as is often used in textbook derivations, and so still holds even when microscopic reversibility breaks down [51,52].

The use of a falsely chiral influence to induce ae was demonstrated by Micali et al. [53], who were able to control at will the handedness of chiral supramolecular aggregates by rotational and gravitational forces applied only during the nucleation phase of an essentially irreversible process. They made clever use of the magnetic levitation of their samples, contained within cylindrical vessels inside a powerful electromagnet and rotated at a fixed frequency. Depending on the positions of the sample vessels within the magnet, the solutions experienced different magnetic levitation forces corresponding to enhanced, normal and inverted gravity. Parallel and antiparallel arrangements of the angular momentum vector L associated with the spinning sample, and the effective gravitational field G_{eff} , consistently generated aggregates of an achiral phenylporphyrin with opposite helicities (Figure 3). Since L and G_{eff} are time-odd axial and time-even polar vectors, respectively, the parallel and antiparallel arrangements are interconverted by P and T separately, and so the system has false chirality [54], just like Curie's arrangement of electric and magnetic fields. The study was careful to show that the magnetic field itself was not involved in the enantioselection. It should be mentioned that in 1980 a similar experiment was reported [55] in which isophorone oxide was synthesized from isophorone in a rapidly spinning vessel, with very small ees of opposite handedness being generated when the vessel was spun clockwise and anticlockwise about an axis perpendicular to the earth's surface, but with zero ees when the vessel was spun parallel to the earth's surface. This attracted much controversy at the time [9,21,22], but we can now appreciate that the observations may have been genuine.

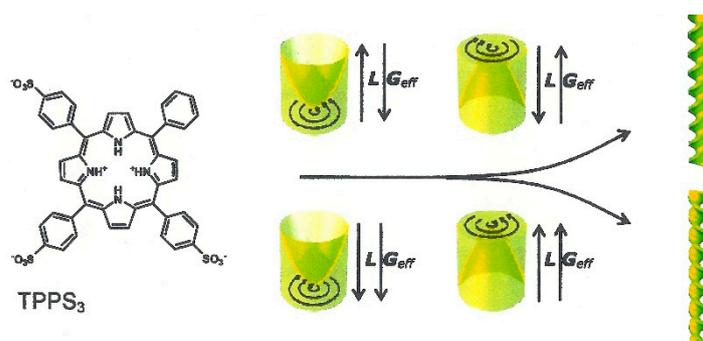


Figure 3. A spinning sample of tris-(4-sulfonatophenyl)phenylporphyrin (TPPS₃) in a gravitational field generates aggregates with opposite helicities depending on whether the falsely chiral arrangement of angular momentum and effective gravity vectors L and G_{eff} are parallel or antiparallel. Adapted from [53] with permission from the publisher.

Since one effect of E in a falsely chiral influence based on collinear E and B is to partially align dipolar molecules [26], as in de Genne's model mentioned earlier of the attachment of achiral monomers to form a right- or left-handed helix segment of a growing polymer aligned in an electric field [5], a magnetic field alone might induce ae if the molecules are pre-aligned, as in a crystal or on a surface, and the process is far from equilibrium [56].

This scenario of ae induced in aligned molecules in a magnetic field brings us to a remarkable experiment by Banerjee-Ghosh et al. [57], which demonstrated that the interaction of chiral molecules (like helical oligopeptides) with a perpendicularly magnetized substrate is enantiospecific. One enantiomer adsorbs preferentially to a ferromagnetic surface when the magnetization points up, whereas the other adsorbs faster for the opposite alignment of the magnetization. They ascribed this to a chirality-induced spin selectivity (CISS) effect [58]: when chiral molecules are polarized by an electric field, the electric polarization is accompanied by an electron spin polarization with spin up or down at each end of the induced dipole, depending on the specific enantiomer (Figure 4, left). Here a charge polarization develops as the molecule approaches the surface, which induces the electron spin polarization responsible for the enantioselection (Figure 4, right). The proposed detailed mechanism involves an exchange interaction between the molecular electron spins and the spins of the ferromagnetic substrate, with the substrate–molecule interaction stabilized if the two spins

are antiparallel (low-spin arrangement) and destabilized if they are parallel (high-spin arrangement). The phenomenon appears to fit within the realm of false chirality, with the polar time-even alignment vectors of the chiral molecule collinear with the axial time-odd spin vectors of the ferromagnetic surface. This perception is reinforced by the fact that for long adsorption times enantioselection is lost, meaning the effect disappears at equilibrium (i.e., a kinetic effect), which is a sine qua non for ae under a falsely chiral influence. This experiment was extended to demonstrate enantioseparation by crystallization on a ferromagnetic surface [59].

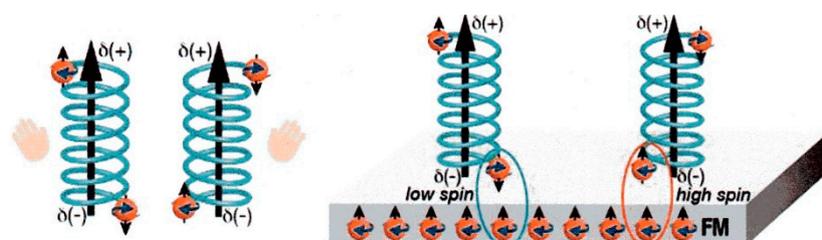
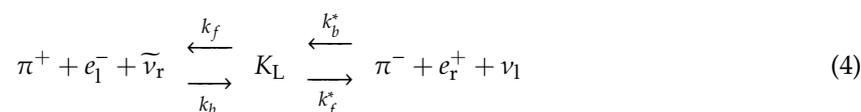


Figure 4. Left: Illustration of the chirality-induced spin selectivity (CISS) effect where the electrical polarization of a chiral molecule is accompanied by an electron spin polarization, with the spin alignment at each pole depending on the specific enantiomer. Right: The interaction between the ferromagnetic surface and the molecule is either low spin or high spin, depending on the specific enantiomer, which depends in turn on the whether the falsely chiral arrangement of molecular alignment vectors (large arrows) are parallel or antiparallel to the ferromagnetic spin vectors (small arrows within the FM surface). Adapted from [57] with permission from the publisher.

If we naively represent the K_L decay process from (2) in a similar form to that of the chemical equilibrium (3),



a parallel is established with absolute asymmetric synthesis associated with a breakdown in microscopic reversibility induced by a falsely chiral influence because in both cases $k_f \neq k_f^*$ and $k_b \neq k_b^*$, yet the corresponding enantiomeric products M and M^* in the molecule case and $\pi^+ e_1^- \tilde{\nu}_r$ and $\pi^- e_r^+ \nu_l$ in the particle case remain degenerate [15,26–28,45]. Thus, K_L and the two sets of decay products in (4) are the equivalents with respect to CP of R , M and M^* in (3). Because the CPT theorem guarantees that the two distinct CP -enantiomorphous influences (of which only one is found in our world, hence CP violation) are interconverted by T , we can conceptualize the decay rate asymmetry here as arising from a breakdown in microscopic reversibility because of a time-noninvariant CP -enantiomorphous influence in the forces of nature. As outlined above, the analogy is completed by the fact that excesses of one set of CP -enantiomeric particle products over the other cancel when summed over all possible interconversion channels at true thermodynamic equilibrium [51,52].

Although, unlike P violation, the infiltration of CP violation into molecular physics via the axion-mediated P - and T -violating interaction $V_{eN}^{(PT)V}$ mentioned earlier would not lift the degeneracy of mirror-image chiral molecules, it could still conceivably induce ae in non-equilibrium processes involving chiral molecules. The cosmos is replete with processes that are subject to a flow of matter and energy, and hence are far from equilibrium. Since axions may be components of the cold dark matter believed to comprise most of the mass of the universe [46], it has been suggested [15,60] that, although it may be incredibly tiny, if it exists, this mechanism might nonetheless be ubiquitous and inexorable, and could be supplying a tiny 'enantioselective push' throughout the cosmos in all far-from-equilibrium processes involving chiral molecules, including life itself.

6.3. A Falsely Chiral Influence Acts Like a Catalyst

In chemistry, a catalyst is defined as a substance that is not consumed in a chemical reaction, and which increases the reaction rate at a given temperature by reducing the activation energy, but without affecting the free energy change. It follows that a falsely chiral influence acts like a special type of catalyst because it modifies potential energy barriers to change the relative rates of formation of enantiomeric products without affecting their relative energies (since it does not lift the degeneracy of *P*-enantiomeric chiral molecules). Because the *CP*-violating interaction responsible for the decay rate asymmetry of the K_L does not lift the degeneracy of the two sets of *CP*-enantiomeric products (a particle and its antiparticle have identical rest mass if *CPT* invariance holds), its action is analogous to that of a special type of catalyst, because it affects the kinetics, but not the thermodynamics, of the particle reaction [45].

7. Concluding Remarks

This perspective has explained how, by extending Lord Kelvin's original definition of chirality to include motion, a distinction between true and false chirality emerges, with Curie's arrangement of collinear electric and magnetic fields providing the archetype of the latter. Although many examples of ae induced by a truly chiral influence are known, it is only recently that the first two examples of ae under a falsely chiral influence have been observed, namely in a spinning sample under a gravitational field and in the separation of enantiomers by a ferromagnetic surface. It was further demonstrated how parity violation and *CP* violation correspond to influences within the fabric of the universe, possessing, respectively, the symmetry characteristics of true and false chirality. Finally, the action both of false chirality on molecular processes, and of *CP* violation on elementary particle processes (perhaps the most enigmatic phenomenon in modern science), may be conceptualized within the framework of chemical catalysis. All this provides an exquisite illustration of Curie's dictum (translated) [4]: "It is the dissymmetry which creates the phenomenon".

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