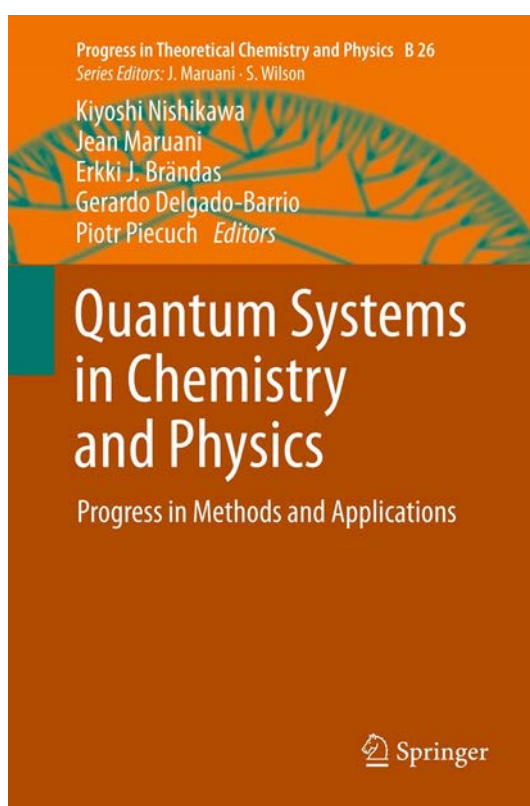# Molecular Parity Violation and Chirality: The Asymmetry of Life and the Symmetry Violations in Physics

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Chapter 3
Molecular Parity Violation and Chirality: The Asymmetry of Life and the Symmetry Violations in Physics

Martin Quack

Abstract After a brief introduction into some basic asymmetries observed in nature, such as the biomolecular homochirality in living species on earth, the dominance of matter over antimatter in the observable universe, and irreversibility in physical-chemical processes providing a preferred arrow of time, we provide a discussion of the concepts of fundamental symmetries in physics and of the three different kinds of symmetry breakings, spontaneous, de facto, and de lege, by means of the example of the dynamics of chiral molecules. We then give a brief review of the current status of the theory and experiments on molecular parity violation. We discuss the various hypotheses on the origin of biomolecular homochirality and conclude with some cosmological speculations related to the fundamental symmetry breakings. These include possibilities of observing CPT violation in future experiments providing a possible fundamental basis for irreversibility, as well as possibilities for observing heavy "right-handed" neutrinos as one possible basis for "dark matter" in the universe.

3.1 Introduction: Strange Asymmetries of Space, Time, and Matter in an Almost Symmetrical Nature

"Naturally there are, and not only when it pertains to the historical framework, still many open questions. For example: on which level is the handedness or chirality of biological macromolecules determined? We know that all proteins, as long as they are produced through the information-guided synthesis apparatus of the cell, exclusively use "left-handed" amino acids and therefore build left turned structures. In the case of the nucleic

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acids it is the "right-handed" monomers which are chosen, which for their part build right-as well as left-turned double spiraled structures.

....

Here we have rather too many than too few answers. We are not confronted here with a paradoxon for which there is no possible explanation. The problem is that physics and chemistry offer an overabundance of choices of alternative explanations. Although research groups throughout the world are working on questions of this kind, until now only few of the possible mechanisms have been experimentally examined in detail." (Manfred Eigen [1]).

"The time at my disposition also does not permit me to deal with the manifold biochemical and biological aspects of molecular chirality. Two of these must be mentioned, however, briefly. The first is the fact that although most compounds involved in fundamental life processes, such as sugars and amino acids, are chiral and although the energy of both enantiomers and the probability of their formation in an achiral environment are equal, only one enantiomer occurs in Nature; the enantiomers involved in life processes are the same in men, animals, plants and microorganisms, independent on their place and time on Earth. Many hypotheses have been conceived about this subject, which can be regarded as one of the first problems of molecular theology. One possible explanation is that the creation of living matter was an extremely improbable event, which occurred only once."

(Vladimir Prelog, Nobel Lecture 12 December 1975 [2])

The present contribution to the special issue of *Progress in Theoretical Chemistry and Physics* resulting from QSCP XVI (Kanazawa, Japan, September 2011) is on one hand related to the lecture presented at this conference [3] but on the other hand and even more closely to an earlier lecture which appeared in print [4] but is available only in German. This chapter is in fact a somewhat adapted translation of the available German text into English in order to make this material more easily accessible to a wider audience. The emphasis of our chapter is thus on the conceptual background of the theory and experiments on molecular chirality and parity violation and its relation to the homochirality of living systems as well as other asymmetries observed in nature. For further more general background, we refer to an extensive recent review [5] in a recent handbook [6, 7].

Both quotations with which we begin this chapter pertain to a remarkable asymmetry in the living nature, the homochirality of biopolymers. With this we describe the fact that in all forms of life which we know on Earth, only one of the two mirror-image enantiomers of chiral amino acids (the L-amino acids) and of chiral sugars (the D-sugars) is important in the assembly of biopolymers (proteins and nucleic acids). The corresponding mirror-image, symmetrically equivalent forms (the D-amino acids and L-sugars) also arise for a few special applications in the biochemistry of nature, but are not involved in the important construction of the biopolymers. The consequences of this were first noticed by the discoverer of molecular chirality, Louis Pasteur, in the nineteenth century, and proposed as a basic characteristic of the chemistry of life [8–10].

In the "usual" organic chemistry of inanimate nature, on the other hand, both mirror-image forms of molecules occur with equal probability. This can be derived from a symmetry of physics [11], which was accepted until the middle of the twentieth century as exact: the exact mirror-image symmetry or parity symmetry of space (see below). This symmetry is referred to in the quote from V. Prelog. This would lead to the two enantiomers of chiral molecules, which relate to each

Fig. 3.1 The energies of enantiomers are different because of a symmetry violation. The energy difference $\Delta_{pv} E_0 = \Delta_{pv} E$ and the reaction enthalpy $\Delta_{pv} H_0^{\sigma} = \left| N_A \Delta_{pv} E_0 \right|$ for the reaction R $=$ S can be described with the spectroscopic schematic diagram shown here. This is estimated to be 10^{-11} J mol^{-1} for CHFClBr [12]. How important is this energy difference for chemistry? What are the consequences for biology? (see also [13])
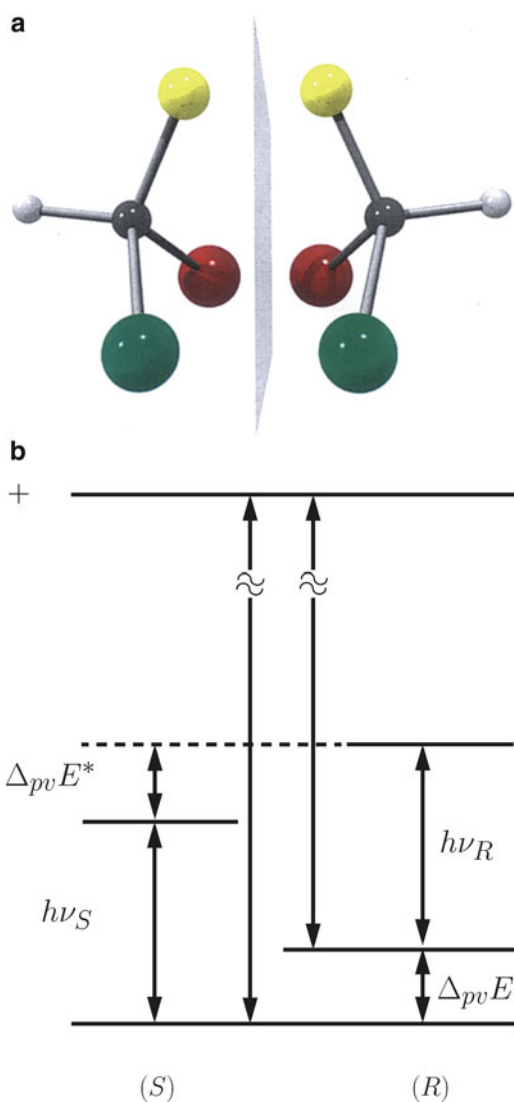
other as image and mirror image or idealized left or right hand, to be energetically exactly equivalent and having therefore the exact same ground state energies, energy level spectra, and enthalpy of combustion. Today, however, we must say that this equivalence is only approximate. Figure 3.1 provides an example for such nearly equivalent enantiomers from the point of view of recent calculations [12, 13].

We take here a prototype molecule, CHFClBr, as an example. If one replaces the three halogen atoms F, Cl, and Br with an amino group –NH$_2$, the –COOH functional groups of organic acids, and a further organic substituent R, one obtains

Table 3.1 Asymmetries in the world as we observe it

Observations: we live in a world	Symmetry
1. Comprised of matter (mainly), not antimatter	C, CP, CPT
2. With biopolymers (proteins, DNA, RNA) out of L-amino acids and D-sugars (not D-amino acids and L-sugars) in usual life forms	P
3. In which the time runs forward, not backward	T

the natural chiral alpha-amino acids, the building blocks of the proteins. With R=CH$_3$, one obtains, for example, the amino acid alanine, and through variations on R, one obtains many other natural amino acids.

Figure 3.1 illustrates that there is actually a very small asymmetry. The enantiomers are not exactly mirror images of each other, and there is a reaction enthalpy for the enantiomerization or stereomutation reaction:

$$R = S; \quad |\Delta_r H_0^\sigma| \approx 10^{-11} \text{J mol}^{-1} \tag{3.1}$$

One speaks of a violation of the symmetry (here parity violation). It should be noted that the modern R, S nomenclature is used in the figure, whereby the R-amino acids normally correspond to the D-amino acids in the old nomenclature and the S-amino acids correspond to the L-amino acids. We shall use both nomenclatures here, because the D, L terminology is widely used in biochemistry. In physics, one tends to use the R, L nomenclature which simply stands for Right/Left. If one takes into account the chemical equilibrium (3.1) at room temperature, the small enthalpy of reaction is reflected in the equilibrium constant:

$$K = \frac{Q_S}{Q_R} \exp\left(\frac{-\Delta_r H_0^\sigma}{RT}\right) \simeq 1 - \frac{\Delta_r H^\sigma}{RT} \simeq \frac{[S]}{[R]} = 1 + \frac{X}{[R]} \simeq 1 \pm 4 \times 10^{-15} \tag{3.2}$$

With the partition functions Q_R, Q_S, and $|\Delta_r H^\sigma| \ll |RT|$, one therefore obtains a relative difference $|X| / [R]$ in the equilibrium concentration of 4×10^{-15} or for a mole R ($N_A = 6.02 \times 10^{23}$ molecules/mol) a difference of approximately 2.4×10^9 molecules. This minimal difference vanishes in the statistical noise (the square root of N_A corresponding to 8×10^{11} molecules for Poisson noise for one mole), and one can ask whether the small value of $|X| / [R]$ or of $\Delta_{pv} E$ in biochemistry can play a role at normal temperatures. We shall return to this point and see that this remains an open question [13].

At first, however, we would like to draw attention to a different notable asymmetry, which has a qualitatively similar consequence (Table 3.1).

If we observe the universe today, we find in the visible matter (stars, planets, interstellar gas clouds, etc.) which consists mainly of the elements of the periodic

table (in fact, quantitatively mainly hydrogen and helium) almost exclusively the normal matter, no antimatter, although for each particle of normal matter, a symmetrically equivalent antiparticle of antimatter with the opposite charge exists. For example, for the electron e^- there exists as antiparticle the positron e^+, which is produced in small quantities by natural radioactive decay, but is then annihilated through reaction with the more common electrons, resulting in the emission of gamma radiation.

Antimatter is also present in cosmic radiation. One can produce the antiproton (with the same mass as the proton but opposite charge) in accelerators, after which it is also quickly annihilated by the more common protons in normal matter. We know of no galaxies comprised of antimatter. Cosmologically, this excess of normal matter is notable, because in the modern big bang theory of the origin of the universe, at the beginning, approximately the same amounts of matter and antimatter were produced. Both disappeared almost completely through annihilation and emission of radiation. A small leftover of matter remained. From the presently observed photon density of the very exactly measured cosmic background radiation, one can estimate that the ratio of the baryon number n_B to the photon number n_γ is approximately [14]

$$\frac{n_B}{n_\gamma} \simeq 6 \times 10^{-10} \tag{3.3}$$

With the assumption that the photon number is approximately the number of particles present initially, one arrives at a very rough estimation of the order of magnitude of the initial surplus:

$$\frac{[\text{Matter}]}{[\text{Antimatter}]} \simeq \frac{10^9 + 1}{10^9} = 1 + 10^{-9} \tag{3.4}$$

Here also, then, a very small initial asymmetry led seemingly to a complete dominance of the normal matter present today. The exact origin of the cosmic asymmetry is not known [14]. However, we know a small fundamental asymmetry in the so-called charge conjugation (C) and also in the combination CP of charge conjugation with parity (P). Hypotheses exist, which make this fundamental asymmetry responsible for the nearly complete asymmetry observed in the cosmos today, but their validity is doubtful. This question, thus, also remains open at the time. We shall address these symmetries in more detail below.

One finds in nature a still more puzzling asymmetry: the asymmetry with respect to time reversal (T). Time runs forward and not backward. The nature of this asymmetry is very subtle, and we shall discuss it below [15].

Of all the observed asymmetries described here, the homochirality of biochemistry is perhaps the most relevant to the everyday life of the chemist, and it also could be the one enigma of the three for which a solution will first be found. An initial step toward solving this problem shall be discussed here in the framework of the theory of molecular parity violation and possible experiments on this phenomenon.

We shall discuss here the basics of the underlying concepts. Our short article is based upon our more detailed earlier discussions [5, 13, 15–22], which we recommend for further reading.

It might seem astonishing that some basic, long recognized phenomena pertaining to asymmetry in the natural sciences have still not been completely explained. These can be phrased as four open questions in the sense of "What is ... ?":

1. The nature of molecular chirality
2. The origin of biomolecular chirality
3. The origin of the abundance of matter as opposed to antimatter and, with it, the origin of the presently observable universe
4. The nature of the irreversibility of physical-chemical processes, which correspond to our observations of a time which possesses a given direction

In a certain sense, one can consider these asymmetries to be quasi-fossils in the evolution of the entire universe. If this is valid, then they contain coded information about the history of the universe from the start of time and matter up to the evolution of life. We shall see here that we are able to answer the first question about the nature of molecular chirality at least theoretically, even though important experimental confirmations are still missing. On the basis of this question, we shall explain also important common concepts of symmetry breaking in the following sections.

The three other questions remain largely open today. The nature of our ignorance, for example, in the question of homochirality, is remarkable. The ignorance is not based upon a shortage of explanations. There are actually many plausible explanations which are also consistent with the presently available information. However, they contradict each other. In such a situation, we simply do not know the truth. The quote which we took from the book of Manfred Eigen and used at the beginning of the chapter indicates this situation of ignorance.

A similar situation is found in the question of the nature of irreversibility which is seen by many to have been answered long ago. This is, however, incorrect. For further discussion, the reader is referred to [5, 15–17, 20].

3.2 Fundamental Symmetries of Physics and Concepts of Symmetry Breaking: spontaneous, de facto, de lege

"Pauca sed matura." (motto as cited in [5], attributed to C. F. Gauss)

A careful explanation of the fundamental terms is important for the later understanding of this topic. We shall follow here for the most part, in part literally, our earlier discussions [5, 15–23].

### 3.2.1 Fundamental Symmetries of Molecular Physics

The following symmetry operations leave a molecular Hamiltonian operator generally invariant ([5, 24–27], for limitations see below):

1. Any translation in space
2. Any translation in time
3. Any rotation in space
4. Reflection of the particle coordinates at the origin (parity operation P or E*)
5. Time reversal or reversing momenta and spins of the particles (T for tempus or time)
6. Every permutation of the indices of identical particles (the atomic nuclei, the nucleons, the electrons)
7. The replacement of all particles by their antiparticles (charge conjugation C)

These symmetry operations form the symmetry group of the Hamiltonian operator. In correspondence with Emmy Noether's theorem, a conserved quantity is associated with a symmetry. Still more interesting is the interpretation that a nonobservable quantity is associated with each exact symmetry [5, 15, 28]. The first three symmetries correspond to continuous operations with symmetry groups of infinite order; the four last discrete operations lead to groups of finite order. We shall concern ourselves here in detail only with these discrete symmetries. The symmetries P, C, and T and the combination CP are not exact; they have been found to be violated in some experiments, whereas their combination CPT is accepted as exact. It serves as a foundation of the entire modern theory of matter as summarized in the so-called standard model of particle physics (SMPP) and has to date not been disproven. The same holds true for the permutation symmetry, point 6 in the list above, with $N!$ symmetry operations for N identical particles, which leads to the generalized Pauli principle [5, 15, 24, 25]. We have, however, already speculated earlier that possibly all discrete symmetries are violated [5, 17–20, 23, 29]. It is important to define the terms symmetry violation and symmetry breaking more carefully, which we can do with the use of the geometrically easily understandable example of molecular chirality, which is connected with the parity operation or the right-left symmetry.

Figure 3.2 illustrates the parity operation P. This is a reflection of the coordinates at the origin of a Cartesian coordinate system. It transforms a right-handed coordinate system into a left-handed coordinate system. If one then rotates the left-handed coordinate system in Fig. 3.2 by an angle of 180º around the x-axis, then the two coordinate systems shown here behave as the image and its mirror image in a normal plane mirror. Because the rotation by 180º is one of the infinitely many symmetry operations of rotation in space (see point 3 of the list above), the reflection in a mirror is in this sense also a symmetry of the molecular Hamilton operator. This type of reflection is mostly used in discussions of enantiomers of chiral molecules, which behave as image and mirror image of a handed system (see Fig. 3.1; the word chiral comes from the Greek χειρ, hand; the Greek word εναντιος means "standing opposite," and μερος is "a part of the whole," meaning that the definition

Fig. 3.2 Reflection $\hat{E}^*$ or
parity operation P (After
[13])

$$x \longrightarrow -x$$
$$y \longrightarrow -y$$
$$z \longrightarrow -z$$
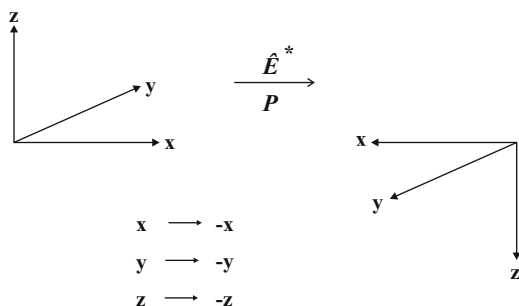
of "enantiomer" is "consisting of parts which are so arranged that they stand opposite to each other as image and mirror image.") The important common aspect of the two symmetries, of reflection from a plane mirror and reflection at the center of coordinates, is the transformation of a "left-handed" into an equivalent "right-handed" system (molecule). The additional rotation, which differentiates the two symmetry operations, is not of importance for the freely moving isolated molecule in this context.

3.2.2 Basic Concepts of Symmetry Breaking: spontaneous, de facto, and de lege, as Related to the Geometric Example of Molecular Chirality

We provide here a short analysis of the three different concepts for symmetry breaking, because often they are not carefully distinguished from each other, and we refer the reader to [5, 15–23] for a more complete discussion. If we consider the example of the chiral hydrogen peroxide molecule H_2O_2 (Fig. 3.3), we can represent the stereomutation as a one-dimensional torsion about the angle τ' ($\simeq q$ below) and represent it with one potential function with two minima corresponding to the two enantiomers and a low potential barrier in the planar trans conformation [30].

The hydrogen peroxide molecule is, in its equilibrium geometry (Fig. 3.3), a very simple example for a molecule with axial chirality. This simplifies the discussion of the stereomutation process. The transition states are planar and achiral, one with trans geometry and a low barrier
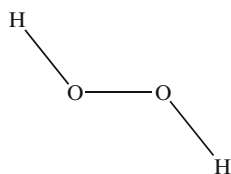

$$E_{trans} \simeq 4.3 \text{ kJmol}^{-1} \tag{3.5}$$
$$(361 \text{ cm}^{-1})$$
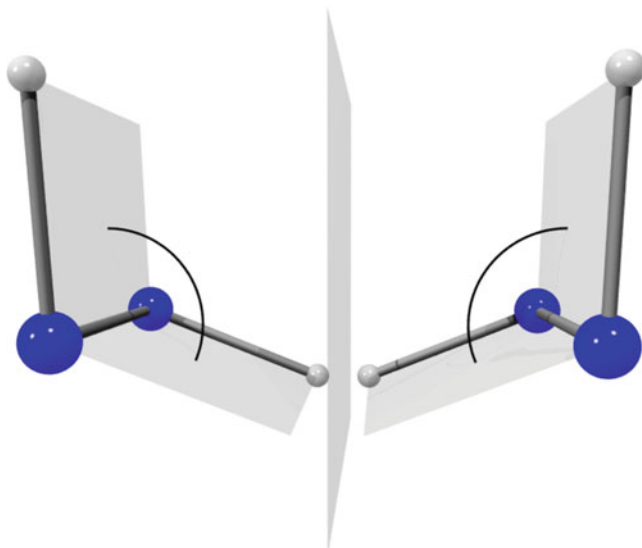
Fig. 3.3 Image and mirror-image form of H_2O_2 (HOOH) in the chiral equilibrium geometry of the PCPSDE-potential hypersurface [30]. Image and mirror image are enantiomers which cannot be converted into each other through a rotation in space but instead through an internal rotation about the OO-axis preferably via the trans geometry [30]. *White*, H; *blue*, O (After [15])

and a substantially higher barrier in the planar cis configuration

$$E_{cis} \simeq 31.6 \text{ kJmol}^{-1}$$
$$(2645 \text{ cm}^{-1}) \tag{3.6}$$
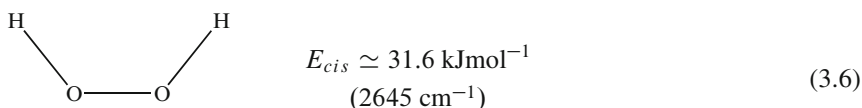
We therefore can illustrate the process of the stereomutation as the movement of a point mass in a one-dimensional double minimum potential with a low barrier (Fig. 3.4). The real stereomutation dynamics take place in a six-dimensional space.

Classically, the point mass reaches both symmetrically equivalent space regions at high energies. The mechanical state shows then on the average the symmetry of the underlying potential. If one reduces the energy, then in principle a symmetric state at the maximum in the middle of the potential function in Fig. 3.4 can be assumed. This corresponds to an unstable mechanical equilibrium. In practice, however, with the reduction of the energy, a state at the minimum energy either left (λ) or right (ρ) is realized. These states do not show the symmetry of the potential, and one speaks of a spontaneous symmetry breaking. Spontaneous symmetry breaking is in essence a classical concept, even though it can be extended to quantum mechanical systems with infinitely many degrees of freedom [31, 32]. In molecular quantum mechanics, the superposition principle demands that superposition states of positive parity (symmetric with respect to the reflection at q_c)
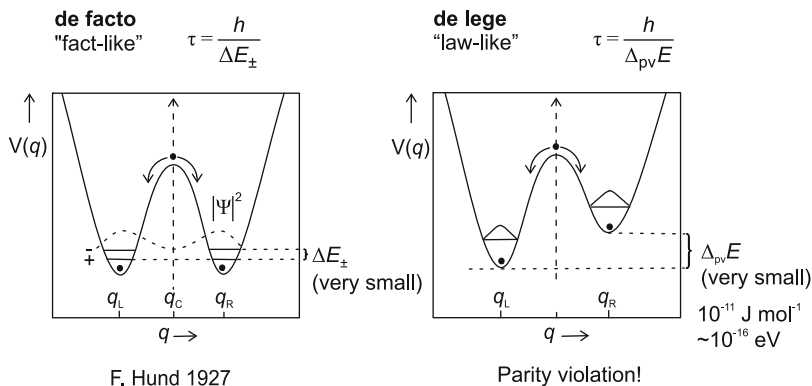
Fig. 3.4 Symmetry breaking and symmetry violation (After [22]). In the classical limit, the *left-hand picture* can also be used for illustrating "spontaneous" symmetry breaking (see text)

$$\chi_+ = \frac{1}{\sqrt{2}} (\lambda + \rho) \tag{3.7}$$

and negative parity (antisymmetric)

$$-\chi_- = \frac{1}{\sqrt{2}} (\lambda - \rho) \tag{3.8}$$

are possible states. These are delocalized at the same time both left and right. In fact, such states are the eigenstates of the Hamilton operator and are differentiated from each other by the small energy difference $\Delta E_\pm$ (Fig. 3.4).

Following Hund [33, 34], one can, however, generate left or right localized states λ and ρ, in which the symmetry is broken de facto:

$$\lambda = \frac{1}{\sqrt{2}} (\chi_+ - \chi_-) \tag{3.9}$$

$$\rho = \frac{1}{\sqrt{2}} (\chi_+ + \chi_-) \tag{3.10}$$

These states are time dependent. The quantum dynamics of the stereomutation as also the quantum dynamics of atoms and molecules in general is described through the time-dependent Schrödinger equation (with $i = \sqrt{-1}$)

$$i \frac{h}{2\pi} \frac{\partial \Psi(q, t)}{\partial t} = \hat{H} \Psi(q, t) \tag{3.11}$$

with the solution

$$\Psi(q, t) = \sum_k c_k \, \varphi_k(q) \exp \left(\frac{-2\pi \, i \, E_k t}{h} \right) \tag{3.12}$$

The c_k are complex coefficients. The functions $\varphi_k(q)$ and the energies E_k are obtained as eigenfunctions and eigenvalues of the solution of the time-independent Schrödinger equation:

$$\hat{H}\varphi_k(q) = E_k\varphi_k(q) \tag{3.13}$$

If one takes into account for purposes of simplification only two quantum states, for example, the two lowest states with the energies $E_1 = E_+$ and $E_2 = E_-$ and the energy difference $\Delta E_\pm = E_- - E_+$, one can represent the time-dependent dynamics of H_2O_2 following Eq. (3.12) in a simplified fashion as two-state dynamics using

$$\Psi(q,t) = \frac{1}{\sqrt{2}}\exp(-2\pi\,\mathrm{i}\,E_+ t)\left[\chi_+ + \chi_-\exp\left(\frac{-2\pi\,\mathrm{i}\,\Delta E_\pm t}{h}\right)\right] \tag{3.14}$$

The observable probability density, which is the quantum mechanical equivalent of the time-dependent molecular structure, can be represented as

$$P(q,t) = \Psi(q,t)\Psi^*(q,t) = |\Psi|^2 = \frac{1}{2}\left|\left[\chi_+ + \chi_-\exp\left(\frac{-2\pi\,\mathrm{i}\,\Delta E_\pm t}{h}\right)\right]\right|^2 \tag{3.15}$$

This follows a periodic motion with the period:

$$\tau = \frac{h}{\Delta E_\pm} \tag{3.16}$$

One can easily recognize from Eq. (3.15) that the probability density changes from a left localized state λ (Eq. 3.9) into a right localized state ρ (Eq. 3.10) in a half period, which we can also relate to the stereomutation time $\tau_{\lambda\to\rho}$:

$$\tau_{\lambda\to\rho} = \frac{h}{2\Delta E_\pm} = \frac{1}{2c\Delta\tilde{\nu}} \tag{3.17}$$

That this transformation takes place at an energy below the potential barrier, which would be forbidden in classical mechanics, permits one to speak of a quantum mechanical tunneling effect (pictorially, as though there were a tunnel through the potential barrier).

If, however, $\Delta E_\pm$ is very small, the chiral states are in effect stable, because $\tau_{\lambda\to\rho}$ in Eq. (3.17) will become very large. As opposed to spontaneous symmetry breaking in classical mechanics, which is *necessary* at small energies, the de facto symmetry breaking of quantum mechanics through the choice of the initial conditions is *possible* but *not necessary*.

In the de lege symmetry breaking, the potential no longer has a symmetric form, and the rules (Latin word lex = law or rule, "de lege" meaning by law) for the dynamics show no symmetry. When the departure from exact symmetry is small,

one can speak of a symmetry being present, which is "broken" or violated through small asymmetric additional terms in the Hamilton operator, in this case "de lege."

By the introduction of this nomenclature, one distinguishes the natural (God-given) law (*lex*) from the arbitrary human law (*ius*) (thus not in this case "*de iure*").

It is in view of this example obvious that the symmetry breakings de facto and de lege are fundamentally different descriptions of an observed asymmetry of a phenomenon. The distinction between the two, which is geometrically very easy to understand in the example of chirality, is analogous to that of other asymmetric phenomena, for example, the asymmetry of time, which is apparent from the observed irreversibility. It is also clear that the distinction between de facto and de lege symmetry breaking is not one of language and "philosophy" but instead rather completely scientific, subject to possible tests by experiment. Through careful investigation of the potential, a possible asymmetry (de lege) could be identified, even when perhaps the potential had appeared to be symmetric in initial experiments of low accuracy. One could, of course, argue that under these conditions, the description of an asymmetrical phenomenon through a de lege symmetry breaking could never be ruled out experimentally. This would be true because one could always have a small asymmetry of the potential, smaller than the capability of current state-of-the-art experiments to prove this. However, the question as to a de lege or de facto symmetry breaking also has quantitative aspects. This has to do with the relative size of the tunneling splitting $\Delta E_{\pm}$ leading to delocalization in the symmetric case, as compared with the symmetry violating potential asymmetry ($\Delta E_{\lambda\rho} \cong \Delta_{pv}E$ being the approximate energy difference between the minima, the index pv representing "parity violation"). Whenever

$$\Delta E_{\pm} \gg \Delta_{pv}E \tag{3.18}$$

is true, one can speak essentially of a symmetry breaking de facto even when $\Delta_{pv}E$ is not zero. Whenever

$$\Delta_{pv}E \gg \Delta E_{\pm} \tag{3.19}$$

is true, the symmetry breaking de lege dominates the phenomenon.

In the case of the stereomutation of H_2O_2, we know today, for example, that $\Delta E_{\pm} \gg \Delta_{pv}E$ is true and the symmetry breaking is here, essentially, de facto. On the other hand, we also know that in the case of the chiral isolated methane derivatives (CHFClBr, Fig. 3.1, amino acids, etc.), the chirality is dominated by a symmetry breaking de lege. However, this theoretically well-founded statement still requires experimental confirmation [22].

When we presented in 1989 a systematic analysis of the hypotheses of the foundations of chirality [16], it was discovered, surprisingly, that there were at least five fundamentally different hypotheses to this seemingly simple, basic question about structures in chemistry. Their supporters barely communicated with each other. An experimental confirmation of one or the other hypothesis, then as now, was

Table 3.2 Communities of belief concerning structural hypotheses for chiral molecules (After [16])

De facto	Spontaneous	De lege
Hypothesis of Hund 1927	*"Classical" hypothesis*	*Electroweak interaction with parity violation*
	- van't Hoff and le Bel 1874	
		- Lee and Yang 1956, Wu et al. 1957
	- Cahn, Ingold, Prelog (1956/1966)	
		- Yamagata 1966
	"External perturbation" or "environmental" hypothesis	
		- Rein, Hegström, and Sandars 1979, 1980
		- Mason, Tranter, McDermott et al. 1983 ff (calculations)
	- Simonius 1978, Harris and Stodolsky 1981, Davies 1978/1979	- Quack 1980/1986 (proposed experiments on $\Delta_{pv}E$, see also [5, 21, 22] for more recent theory)
	Superselection rule hypothesis	
	- Pfeifer, Primas 1980	
	- A. Amann 1989f	

not available. The same situation exists in the area of the analysis and interpretation of biochemical dissymmetry or homochirality, as well as the question of time asymmetry or irreversibility.

Table 3.2 provides an overview of the various communities of belief which hold different views about the hypotheses for the structure of chiral molecules, classified according to the type of symmetry breaking. It should be noted here that the two concepts of de facto symmetry breaking and spontaneous symmetry breaking, in many descriptions, simply get tossed into one pot, which is not exactly correct: in principle and in practice, they can be experimentally differentiated from each other. The original classical mechanical concept of spontaneous symmetry breaking can be extended to the quantum mechanics of systems with (infinitely) many degrees of freedom [31, 32, 35]. For a further discussion with many references, we refer particularly to [15, 16, 23].

It should also be noted here that H_2O_2 was the first example for which the full, six-dimensional quantum mechanical wave packet dynamics of stereomutation was demonstrated, which goes much further than the simple one-dimensional picture which we have used here for the discussion of the concepts (see [36, 37]). Such investigations are of great importance for the present understanding of quantum chemical kinetics of molecules containing many atoms and have led to new results for kinetics through the tunneling processes in "quasiadiabatic channels" far above

the energy barrier for the reaction ("quasiadiabatic above barrier tunneling"). They are, however, less important for the basic concepts discussed here.

The concepts of symmetry breaking discussed here with the example of molecular chirality find its analog in the investigation of time reversal symmetry and irreversibility in chemical processes [15–20, 38].

3.3 The Theory of Molecular Parity Violation in Chiral Molecules

"The underlying physical laws for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of complex atomic systems without too much computation." (Paul Adrien Maurice Dirac (1929) as cited in [39])

In the previous section, we have seen that the relative size of the energy for the splitting $\Delta E_{\pm}$ of the ground state through the tunneling process in the symmetrical potential and the asymmetry $\Delta_{pv} E$ of the potential is important for the understanding of the nature of molecular chirality. The tunneling splitting can be understood with the help of the usual, parity conserving molecular quantum mechanics and also investigated experimentally (spectroscopically). A number of these "traditional" investigations have been conducted during the previous decades (see, e.g., the corresponding chapters in [6]). In contrast to this, one must carry out a new type of theoretical calculations in the framework of the so-called electroweak quantum chemistry [40, 41] in order to obtain the parity violating potentials and asymmetry energies $\Delta_{pv} E_{el}$. Electroweak quantum chemistry including parity violation fundamentally goes beyond the parity conserving "electromagnetic" quantum chemistry implied by the quotation from Dirac at the beginning of this section. As we shall see, parity violation is important for the stereomutation of ordinary chiral molecules and in this sense from our knowledge today, Dirac's statement concerning "the whole of chemistry" is incorrect (he obviously did not know about molecular parity violation at the time).

The discussion of these calculations must be preceded by some more detailed comments about the concept of such potentials. The usual electronic ("adiabatic" or "Born-Oppenheimer") potential function is effectively a hypersurface of potential energies $V(q_1, q_2, q_3 \ldots q_S)$ as a function of $S = 3N - 6$ internal coordinates for an N atom molecule (e.g., $S = 6$ for H_2O_2). It conserves parity and can be calculated using the methods of ordinary quantum chemistry. This means that it is strictly symmetric upon reflection, and that the difference $V_R(q_1, q_2, q_3 \ldots q_S) - V_S(\bar{q}_1, \bar{q}_2, \bar{q}_3 \ldots \bar{q}_S)$ of the potential energies is exactly zero for enantiomeric structures described by the complementary set of coordinates $(q_1, q_2, q_3 \ldots q_S)$ and $\bar{q}_1, \bar{q}_2, \bar{q}_3 \ldots \bar{q}_S$ for enantiomeric structures.

Incidentally, the typical potential energy differences for various chemically relevant structures fall in the range of 1–100 kJ mol^{-1} (as molar energies). As opposed to this, the parity violating contributions to the potential calculated with the methods of electroweak quantum chemistry are antisymmetric relative to the reflection and yield a parity violating energy difference of

$$\Delta_{pv}E_{el}(q_1, q_2, q_3 \ldots q_S) = V_{pvR}(q_1, q_2, q_3 \ldots q_S) - V_{pvS}(\bar{q}_1, \bar{q}_2, \bar{q}_3 \ldots \bar{q}_S)$$
(3.20)

for enantiomeric structures. These energy differences fall typically in the order of magnitude of 100 aeV corresponding to about 10^{-11} J mol^{-1}. Strictly speaking, the ground state energy differences are quantum mechanical average values over the ground states of the enantiomers, which also are often near to the values of $\Delta_{\text{pv}}E_{el}$ for the equilibrium geometries. We distinguish these quantities for this reason only explicitly in our nomenclature where it is particularly important.

Early calculations of parity violation in chiral molecules were already carried out following earlier theories for parity violation in atoms [42]. Work on molecules by Hegström, Rein, and Sandars started about in 1980 [43]. Later, these calculations were continued by Mason, Tranter, and MacDermott [44–46]. Our theoretical work after 1990, however, showed that the earlier calculations for prototype molecules like H_2O_2 and H_2S_2 and others were incorrect by approximately one to two orders of magnitude. Our new calculations yielded much larger values for $\Delta_{\text{pv}}E$ than had been previously estimated (although still quite small) [40, 41, 47–49]. This is important also in the planning of experiments [50]. The results for biochemically important molecules like alanine were also completely revised by our more recent theoretical work [51]. These results have been confirmed in the meantime by independent work by other research groups and can be seen as well accepted, although the experimental confirmation of these theoretical results is still lacking.

We cannot provide a complete overview of the recent theoretical results here, but refer the reader to several articles which provide an overview from various perspectives [5, 13, 15, 21, 22, 39, 41, 52]. Figure 3.5 provides a graphical survey of the big jump in theory provided by our work in the early 1990s and later confirmed with a variety of theoretical methods.

Table 3.3 provides a summary of the parity violating energy differences $\Delta_{\text{pv}}E$ and tunneling splittings $\Delta E_{\pm}$ for a series of simple axially chiral molecules of type XYZX analogous to H_2O_2. This is an important summary table for our discussion. One recognizes that the inequality (3.18) is valid in the case of H_2O_2 and many similar hydrides, for which reason the parity violation de lege hardly plays a role here. It is, however, true that the chirality of these molecules is very short lived, often on the order of ps. For molecules like ClOOCl and ClSSCl, on the other hand, the inequality (3.19) is valid and $\Delta_{\text{pv}}E$ is a measureable ground state energy difference between the enantiomers.

This is the case for all molecules for which one generates enantiomers as stable chiral molecules and can store them for a long time. The transition between the limiting cases is dependent upon the single case under observation, but one must
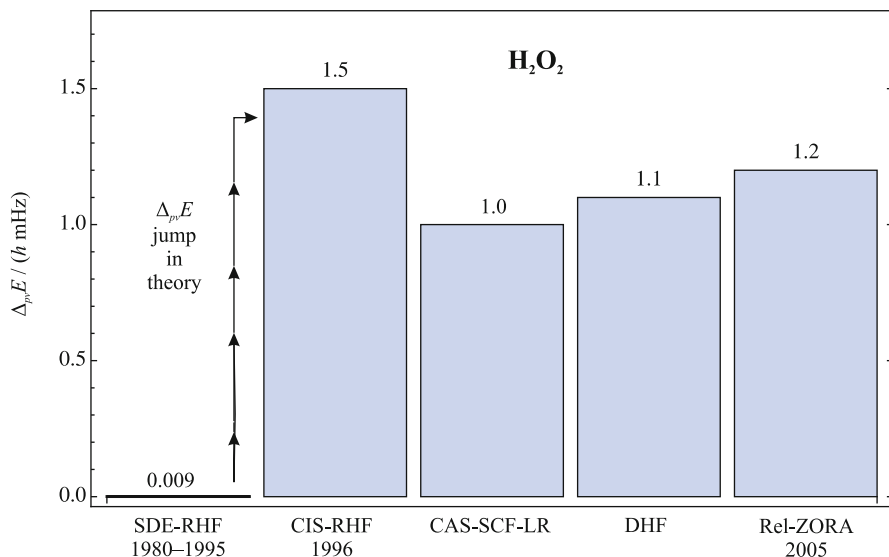
Fig. 3.5 Theoretical results for parity violating energy differences in H_2O_2 near the equilibrium geometry illustrating the order of magnitude change in 1995. The results are taken from the more extensive summary in [21, 22], where further references can be found. The early results with SDE-RHF (1980–1995) are from [43, 44], the CIS-RHF results from [40, 41, 47], the CASSCF(MC)-LR results from [48, 49], the relativistic four-component theory Dirac-Hartree-Fock (DHF) from [53], and Rel-ZORA (two-component theory) from [54]. Recent results with a coupled cluster approach reported at the Faraday Discussion on Frontiers in Spectroscopy 2011 are in agreement with the large values for $\Delta_{pv}E$ as well [55] (After [56])

remember that it occurs when the tunneling period in the hypothetical, symmetric potential is a time significantly longer than a second.

With this, one has obtained a significant semiquantitative statement about question 1 from the introduction, namely, to the question as to the nature of and the quantum dynamical origin of molecular chirality. The parity violation de lege is the dominant effect in the characterization of quantum dynamics of molecular chirality for all long lived ($\tau \gg 1$s), isolated chiral molecules, and is much more important than the symmetry breaking de facto as described in the work of F. Hund. This importance of parity violation for the normal case of chiral molecules is perhaps surprising and provides, at least for the time being, valid theoretical answers to question 1 about the nature of molecular chirality. The experimental confirmation of the theoretical values for $\Delta_{pv}E$ is not yet available, but can be expected in the near future.

As an example for the calculation of parity conserving and parity violating potentials in a molecule, in which in principle a measurement of the parity violating ground state energy difference $\Delta_{pv}E$ is possible, we show the torsional potential $V(\tau)$ for ClSSCl in Fig. 3.6. One recognizes that the normal parity conserving potential for the torsional motion is symmetric with respect to the planar geometry

Table 3.3 Tuning tunneling splittings $|\Delta E_\pm|$ and parity violation $\left(\Delta E_{pv}^{el}\right)$ in a series of molecules (After [57] and [22])

Molecule	$\left|\Delta E_{pv}^{el}\right| (hc\ cm^{-1})$	$|\Delta E_\pm| (hc\ cm^{-1})$	Literature
H_2O_2	$4 \cdot 10^{-14}$	11	[36, 37, 40, 41, 48, 49]
D_2O_2	$4 \cdot 10^{-14}$	2	[36, 37, 40, 41, 48, 49]
T_2O_2	$4 \cdot 10^{-14}$	0.5	[36, 37, 40, 41, 45, 48]
Cl_2O_2	$6 \cdot 10^{-13}$	$7 \cdot 10^{-25}$	[58]
HSOH	$4 \cdot 10^{-13}$	$2 \cdot 10^{-3}$	[59]
DSOD	$4 \cdot 10^{-13}$	$1 \cdot 10^{-5}$	[59]
TSOT	$4 \cdot 10^{-13}$	$3 \cdot 10^{-7}$	[59]
$HClOH^+$	$8 \cdot 10^{-13}$	$2 \cdot 10^{-2}$	[57]
$DClOD^+$	$-^a$	$2 \cdot 10^{-4}$	[57]
$TClOT^+$	$-^a$	$7 \cdot 10^{-6}$	[57]
H_2S_2	$1 \cdot 10^{-12}$	$2 \cdot 10^{-6}$	[60]
D_2S_2	$1 \cdot 10^{-12}$	$5 \cdot 10^{-10}$	[60]
T_2S_2	$1 \cdot 10^{-12}$	$1 \cdot 10^{-12}$	[60]
Cl_2S_2	$1 \cdot 10^{-12}$	$\approx 10^{-76b}$	[61]
H_2Se_2	$2 \cdot 10^{-10c}$	$1 \cdot 10^{-6}$	[62]
D_2Se_2	$-^a$	$3 \cdot 10^{-10}$	[62]
T_2Se_2	$-^a$	$4 \cdot 10^{-13}$	[62]
H_2Te_2	$3 \cdot 10^{-9d}$	$3 \cdot 10^{-8}$	[57]
D_2Te_2	$-^a$	$1 \cdot 10^{-12}$	[57]
T_2Te_2	$-^a$	$3 \cdot 10^{-16}$	[57]

^{a}Approximately the same value as for the H-isotopomer
^{b}Extrapolated value
^{c}Calculated value from [53]
^{d}Calculated by Laerdahl and Schwerdtfeger [53] for the P-structure ($r_{TeTe} = 284$ pm, $r_{HTe} = 164$ pm, $\alpha_{HTeTe} = 92°$, and $\tau_{HTeTeH} = 90°$) and the corresponding M-structure. An earlier calculation from Wiesenfeld [63] resulted in a value of $\Delta_{pv}E = (hc)\ 8 \cdot 10^{-10}\ cm^{-1}$ for the structure ($r_{TeTe} = 271.2$ pm, $r_{HTe} = 165.8$ pm, $\alpha_{HTeTe} = 90°$, and $\tau_{HTeTeH} = 90°$)

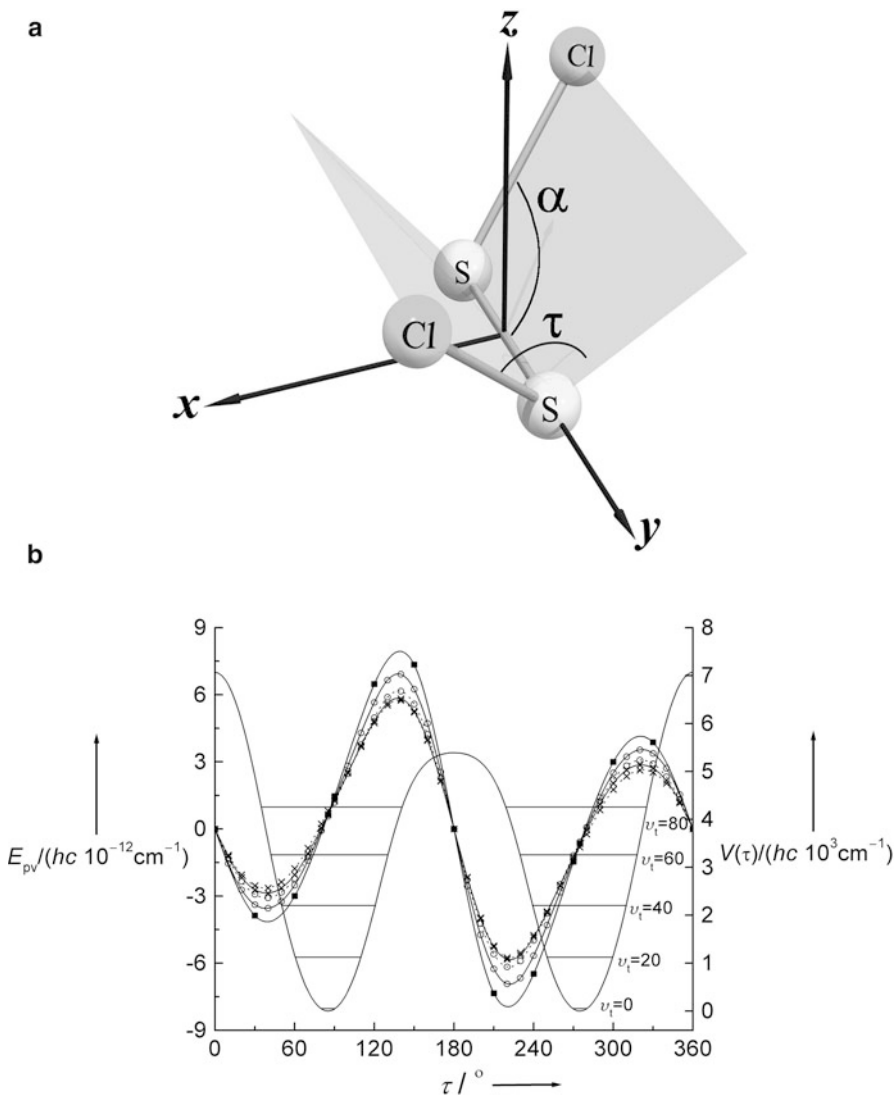at 180°, while the parity violating potential is antisymmetric (and therefore parity violating). The tunneling splitting for small energies is in this example vanishingly small (Table 3.3).

3.4 Experiments on Parity Violation in Chiral Molecules

"The greatest inspiration is a challenge to attempt the impossible."

(Albert A. Michelson [as cited in [5]])

Experiments to detect parity violation in chiral molecules are very difficult because of the very small size of the effects. In our opinion, the experiment we proposed in 1986 for the measurement of parity violation by time evolution after

a

b

Fig. 3.6 In the *upper part* of the figure, we show the chiral equilibrium geometry of dichlorodisulfane Cl–S–S–Cl. In the *lower part*, we show the calculated torsional potential (*full line*, *right ordinate scale*) and the parity violating potential (*left ordinate scale*, lines with various symbols for various approximations). The definition of the torsional angle τ (we use the symbol $\tau' \simeq q$ elsewhere in the text in order to distinguish it from the period τ of motion) is shown in the *upper part* of the figure (After [23, 61])

preparation of a parity isomer [50] is the most promising concept so far. However, experiments based on this have not yet been successful. These experiments were long said (and are thought by many today) to be "impossible" [5]. In addition to the

clear advances in the theory described in the preceding section, during the past few decades we have also been able to make considerable progress in the preparation of such experiments. An important step was the first rotationally resolved analysis of rotation-vibration spectra of chiral molecules, which provided an essential basis for all current approaches to the observation of parity violation in chiral molecules [64–66]. Approximately ten such analyses have been carried out successfully to date on chiral molecules [5, 22].

We would however like to point out a further conceptually interesting aspect of such experiments. According to the diagram in Fig. 3.1, one can, in principle, arrive at the parity violating energy difference by using the combination difference of the spectral lines which correspond to the transitions shown with the broken arrows ($\leftrightarrow$) [16, 50]. To do this, one would also need a resolving power $\nu/\Delta\nu \geq 10^{16}$ [5, 21, 22] or a resolution $\Delta\nu$ of about 1 mHz in the IR region, which is at the moment almost attainable with current experiments, but still not quite possible.

As an alternative, one can carry out a time-dependent kinetics experiment in which one uses an intermediate state of well-defined parity (+) and then creates by means of stimulated emission a superposition state of (well-)defined parity (–) in the ground state (The relevant states are identified by appropriate analysis as discussed above.)

For such an experiment, only the "usual" fully rotationally resolved spectral structure is necessary to obtain the selection, and we can achieve this using lasers with resolution in the range of $\Delta\nu \simeq 1\,\text{MHz}$ (or better). The requirements for the resolution are then about nine orders of magnitude less than for the frequency-resolved combination differences experiment mentioned above.

The preparation of such a "parity isomer" of a stable chiral molecule in the "high barrier" range of molecular quantum dynamics being dominated by parity violation ($\Delta_{\text{pv}}E \gg \Delta E_{\pm}$), Eq. (3.19), remains difficult and has not yet been realized. In the case of molecules with a tunneling-dominated quantum dynamics like H_2O_2 ($\Delta E_{\pm} \gg \Delta_{\text{pv}}E$), Eq. (3.18), the parity isomers are the natural isomers and easy to create.

The kinetic steps of the time-resolved experiment can then be summarized as

$$\text{R (or S)} \xrightarrow{h\nu} \text{X}^*(+) \text{ (or X}^*(-)) \tag{3.21}$$
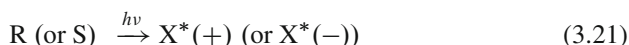
in which $X^*(+)$ corresponds to the highest level in the diagram in Fig. 3.1. One then selects through the electric dipole selection rule ($+ \leftrightarrow -$) a state of negative parity (–).

$$\text{X}^*(+) \xrightarrow{h\nu'} \text{X}'(-) \tag{3.22}$$

This state is a superposition of R and S states and is not an energy eigenstate. It develops with time as

$$\text{X}^*(-) \to \text{X}'(+) \tag{3.23}$$

$$\Psi(t) = \frac{1}{\sqrt{2}} \exp(-iE_\lambda t / \hbar)[\lambda + \rho \exp(-i\Delta_{\mathrm{pv}} E\, t / \hbar)]$$
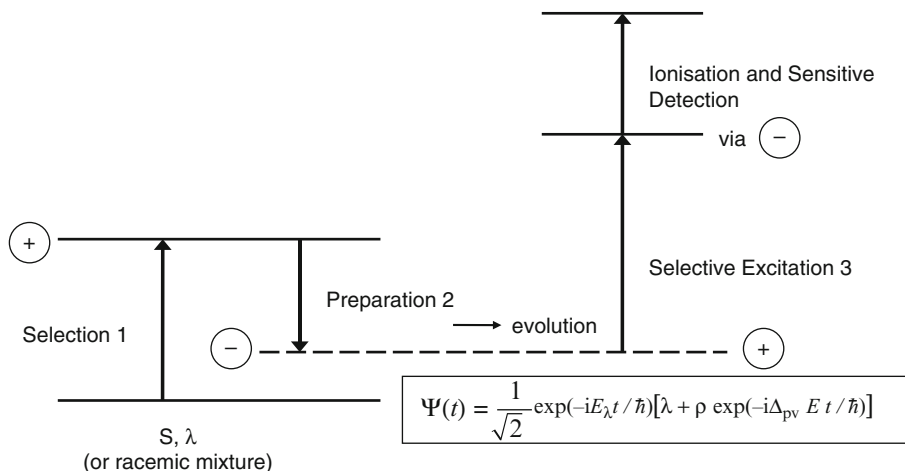
Fig. 3.7 Sequence of steps in the experiment on molecular parity violation (After [56])

This change from a parity isomer of negative parity $(X'(-))$ to a parity isomer of positive parity $(X'(+))$ obeys a rate law for the concentration (or number of particles) of the $X'(+)$ isomer (not present initially), expressed as a mole fraction $y_\pi = c_\pi/(c_\mu + c_\pi)$ as a function of time in Eq. (3.24):

$$y_\pi = \sin^2\left(\frac{\pi t \Delta_{\mathrm{pv}} E}{h}\right) \tag{3.24}$$

From this, one can also obtain the parity violating energy difference $\Delta_{\mathrm{pv}} E$. Because the highly resolved spectra of both parity isomers $X'(+)$ and $X'(-)$ are different because of the electric dipole selection rule, one can obtain the concentration c_π of $X(+)$ through the determination of the increase of the initially "forbidden" spectral lines $(c_\pi(t = 0) = 0)$. For short times with $\sin^2 x \simeq x^2$, the following approximation holds

$$y_\pi(\text{small } t) \simeq \frac{\pi^2 t^2 \Delta_{\mathrm{pv}} E^2}{h^2} \tag{3.25}$$

One has then at the beginning a quadratic time development, which can be used to distinguish the "real" effect from the linear noise effects. Figure 3.7 shows a graphical description of the kinetic scheme discussed here.

For further aspects of such experiments, we refer to [5, 15, 16, 22, 39, 50]. When they work, they make possible, on the one hand, a measurement of $\Delta_{\mathrm{pv}} E$ and with it a test of the various theories discussed above. These theories can then be used for the investigation of mechanisms of biochemical evolution of homochirality. On the other hand, the combination of exact measurements and calculations of $\Delta_{\mathrm{pv}} E$ can also be used to obtain fundamental parameters of the standard model
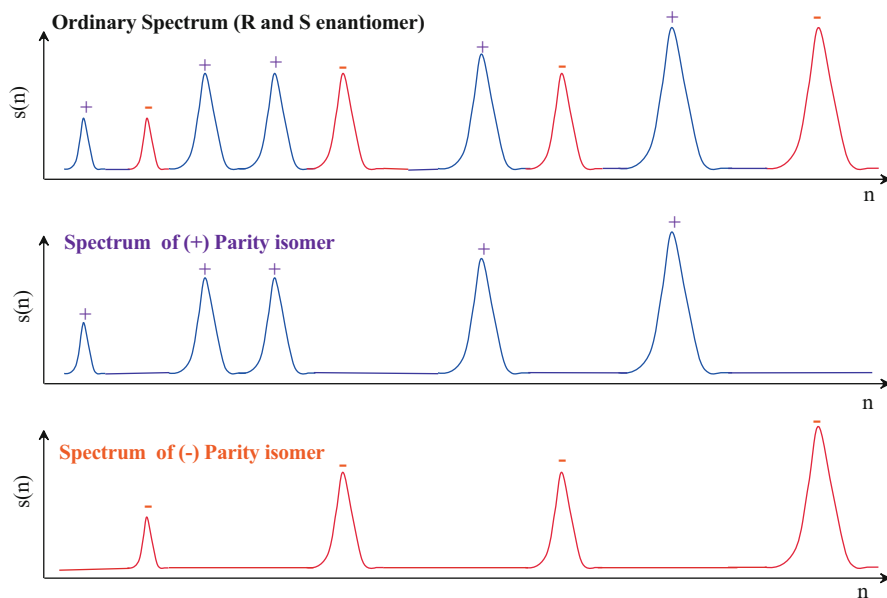
Fig. 3.8 Schematic high-resolution line-resolved spectra of the parity isomers (positive shown in *blue* and negative shown in *red*). The *normal line* spectrum of a chiral molecule (either enantiomers or racemate) is a combination of two separate spectra from parity isomers. If one pure parity isomer is prepared, only its spectrum is observed initially, but as time proceeds, the forbidden lines of the other isomer will appear because of parity violation. $n = \nu/\nu_0$ is the normalized frequency, and $s(n)$ is the spectral signal (After [22])

of physics, which otherwise would only be accessible through experiments of high energy physics and sometimes not even through these. The experiments very briefly and simply described here for molecular parity violation belong to one of the fascinating frontiers of spectroscopy today [5, 56]. Figure 3.8 shows also for illustration a schematic drawing of the high-resolution spectra of the parity isomers discussed here [22]. We have omitted here for brevity a discussion of other types of experiments, which could detect molecular parity violation and we refer to the much more comprehensive review [5] for a critical overview of these.

3.5 Hypotheses About the Evolution of Biochemical Homochirality

"If the foundations of life are dissymmetric, then because of dissymmetric cosmic forces operating at their origin; this, I think, is one of the links between the life on this earth and the cosmos, that is the totality of forces in the universe."

(Louis Pasteur as cited and translated in [16])

In the case of the evolution of homochirality, one can distinguish in principle two steps:

1. The initial generation of a (possibly small) excess of one enantiomer
2. The reinforcement of this excess through various physical-chemical mechanisms, which can be abiotic as well as biotic

Naturally, both steps can be connected with each other. There are many mechanisms known, which in step 2 amplify the excess of one enantiomer, independent of how the original enantiomeric excess arose. Over the past few decades, a multitude of processes have been investigated and more or less well characterized. No limits seem to be set here for the creativity of chemists, and we cannot refer to the very extensive literature here. We refer simply to the most important concepts, which are associated with the various "communities of belief" (see [15] for details).

1. A stochastic "all or nothing" selection of an enantiomer (D or L) can take place as a result of a biochemical selection mechanism [1, 67–73] or also abiotically, for example, through crystallization and adsorption [74, 75]. According to this hypothesis, only one enantiomer is selected with every single evolution, but at the same time in many, separate evolution experiments, D and L molecules are selected with equal probability or equal frequency on the average.
2. An accidental external chiral influence of a one-time evolutionary step selects in a preferred manner one enantiomer. Pasteur and later van't Hoff considered such possibilities, and since that time there have been innumerable different proposals of this type. As an example, we mention the start of an evolution on a random chiral matrix, for example, a "left-quartz" (L-quartz) crystal [75]. When a favored enantiomer is formed, it could propagate itself and then remain dominant [76]. A currently popular possibility is the generation of an excess of one enantiomer in an interstellar gas cloud through polarized light. This excess could be then carried by meteorites to the early Earth and would provide favorable starting conditions for one type of enantiomer. The observation of an excess of enantiomers of chiral biological precursor molecules in meteorites has persuaded many to favor this hypothesis [77].
3. A low-temperature phase transition causes prebiotically (or, more generally, abiotically) a pure enantiomer on the basis of the parity violating weak interaction. Enantiomerically pure or enriched organic starting material provides the foundations for a later biotic selection [78–80].
4. An enantiomer which is slightly favored, by virtue of thermodynamics or kinetics, by the parity violating weak interaction, gains an advantage through nonlinear kinetic mechanisms and in the end is then exclusively selected [46, 81–84] (see also [39]).

These four basic hypotheses can themselves, like the structural hypotheses of chirality, be grouped into de facto selection hypotheses (1) and (2); one could also use here the term "spontaneous," depending on whether one has a quantum or classical picture of the process and the two de lege selection hypotheses (3) and (4).

The hypotheses also can be grouped into the two large categories "by chance" (hasard, Zufall) and "of necessity" (nécessité, Notwendigkeit) [85]. These categories of the evolution of homochirality can in principle be distinguished experimentally. If one repeats evolution following the mechanism of the category "chance," life based on L-amino acids will be generated in approximately 50% of the cases, and life based on D-amino acids will be generated in the other 50% of the cases. When a mechanism of the type "necessity" dominates, one would obtain as a result always (or mostly) our L-amino acid life form.

In principle, in order to distinguish the categories experimentally, one must repeat and understand the mechanisms of the origin of life and of evolution in the laboratory. At the moment we seem to be far removed from this, in any case further removed than we are from a measurement of parity violation in chiral molecules. We have pointed out that we even do not know whether an "enantiomeric life form" would function in the same way as its "normal" mirror image [86]. One could speculate about the total synthesis of mirror-image bacteria from D-amino acid proteins and L-sugars DNA/RNA [86]. We also seem to be still quite far removed from this [13, 87], although in recent times large advances have been made in the experiments pertaining to the "evolution machine" (see [88]).

3.6 Concluding Remarks and Speculations as to the Role of Symmetry in Cosmology and Evolution: The World Game

"L'ingénuité même d'un regard neuf (celui de la science l'est toujours) peut parfois éclairer d'un jour nouveau d'anciens problèmes."

(Jacques Monod [85])

If we return to our four questions from the introduction, we can answer at present only the first one on the basis of theoretical calculations: for normal, stable, isolated chiral molecules, such as the isolated amino acids and sugars as building blocks of the biopolymers, the nature of molecular chirality is dominated by the quantum dynamics of parity violation (de lege) as opposed to the tunneling processes in symmetrical potentials which would lead to a symmetry violation de facto. Further effects are important in dense media, which however do not change this conclusion. These theoretical conclusions must still be examined and confirmed (or refuted) experimentally. The large advances which our group has made on the way to such experiments are expected to yield at least some initial results in the near future. With these, the theoretical results, if confirmed experimentally, will also be provided with a more solid foundation and can serve as a starting point for the investigation of the question of the evolution of biochemical homochirality. Even more fundamentally, the combination of theory and experiments on molecular parity violation can lead to results on the fundamental parameters of the standard model of high energy physics,

for example, the energy dependence of the Weinberg parameter [5]. It must be noted here that only spectroscopic experiments on isolated molecules in the gas phase make this kind of analysis possible. Experiments on the parity violation of molecules in the condensed phase do not allow safe conclusions due to the large (potentially chiral) influence of the surrounding medium. For this reason, we have completely avoided discussion of such experiments in the condensed phases here (see also [13]).

Concerning answers to the other questions of the introduction, one can presently only speculate. There are many hypotheses for the origin of biochemical homochirality which contradict each other: many of them are credible, but none of them has been proven. The question as to the origin of the cosmic excess of matter as opposed to antimatter is also still completely open today. We have not addressed the nature of irreversibility in detail and refer the reader to [5, 15, 17, 20, 23, 25, 38]. Despite contradictory claims in many textbooks and publications, the question remains open in the sense that as well a de facto symmetry breaking could be the root of the observed irreversibility (this would be a standard textbook explanation), as well as a deeper de lege symmetry breaking. Similar to the case of molecular chirality, the question here can be related to the quantitative question about the relative magnitudes and influences of the relevant parameters. Even the theoretical ground work is at present missing to answer this question pertaining to irreversibility [5].

We conclude here with a cosmological speculation, which touches upon the general considerations of symmetry breaking [5, 15, 19, 23, 29].

Figure 3.9 provides an overview of chiral molecules in their four different enantiomeric forms being made of matter and antimatter. As we have discussed in [29], spectroscopic investigations of these four "isomeric" molecules are well suited, in principle, for a very exact test of the underlying CPT symmetry of the combination of C, P, and T. Such experiments are certainly imaginable [23] with sources of antimatter being in principle available today; however, they are not to be expected in the near future.

One can view the diagram in Fig. 3.9 also in another fashion, highly speculative, and interpret it without a "solid" theoretical basis [5]. If one takes L as the normal, left-handed (strictly speaking, left helical) neutrino, then R* would correspond to the right-handed antineutrino (antimatter). The right-handed neutrino (R) made of normal matter has not been observed: the simplest assumption is that it does not exist. One can, however, imagine that it exists as a particle of very large mass; $\Delta_{pv}E = mc^2$ would then be the parity violating energy difference, for which one in complete absence of further information could assume values up to the GeV or TeV region. An interesting aspect of this speculation is the possibility of such primordial heavy neutrinos being the cause of the so-called dark matter, which has been proven by astrophysicists to exist because of its gravitational effects. Its effects dominate over those of the "visible" matter (mainly H and He). The nature of dark matter is unknown. The so-called WIMPs (weakly interacting massive particles) are one possibility. Heavy neutrinos could be one kind of such WIMPs and contribute to the dark matter [89, 90].
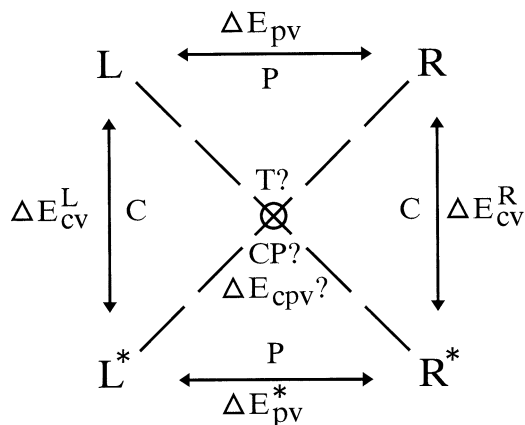
Fig. 3.9 Diagram of enantiomeric molecules (L and R) made of matter and antimatter (L* and R*) with the notation "Left" and "Right," used by physicists for the enantiomers instead of D/L or R/S. With CPT symmetry, the pair L and R* (L* and R) have the same energy. Thus, $\left|\Delta E_{pv}\right| = \left|\Delta E_{pv}^*\right| = \left|\Delta E_{cv}^L\right| = \left|\Delta E_{cv}^R\right|$. The experiment proposed in [29] could observe a departure from this relationship and a CPT symmetry violation with a relative precision of about $\Delta m/m = 10^{-30}$. If one interprets L and R* as neutrino and antineutrino, then R would be a possible heavy enantiomeric neutrino (see text, after [5, 29])

A further cosmological speculation also points to the importance of the symmetry violations. In Refs. [23, 26], we proposed a "world game" which is illustrated in Fig. 3.10.

This was inspired by the book of Eigen and Winkler, which discusses various other types of "games" [68]. In our world game, there is a leader of the game, who draws tetrahedral dice of the type illustrated in Fig. 3.10 out of one of two boxes (shown at the bottom of the figure). The sides of the dice L, L*, R, and R* correspond to the chiral molecules in the diagram in Fig. 3.9. In the de lege box, one finds four different types of dice, in which each individual die shows one symbol on all four sides (e.g., L on all four sides or L* on all four sides) In the de facto box, there are only identical dice, but these have four different sides L, L*, R, and R*. The players (the scientists) are permitted to make one throw of one die which the game leader has drawn and are only permitted to observe one side of this die: the side facing them. They must then guess from which box the die has been drawn (de facto or de lege). Guessing correctly means winning.

If the de lege box has the same number of dice of each type, and the game leader is honest (statistical) when he draws the dice, there is only chance or luck as an overall strategy (therefore, no real strategy). If however a player knows that the distribution in the de lege box is not uniform (symmetry violation, e.g., 40% L and 20% each from the three others), then he will win if he guesses always that the dice are from the de lege box when he sees the L side of a die. Otherwise, he will guess that the dice are from the de facto box. The analogy to the current
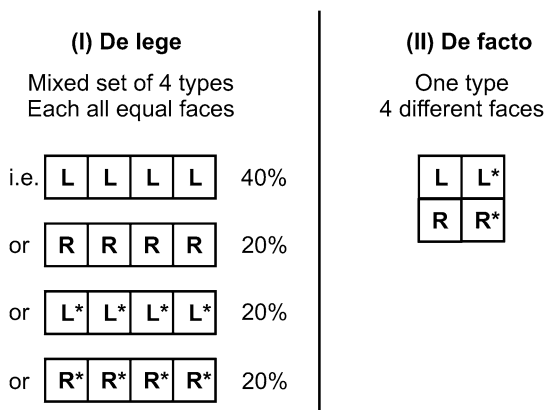
Fig. 3.10 The world game.
The different types of dice
used in the game are shown
schematically with their four
tetrahedral faces and the de
lege box (*bottom left*) and the
de facto box (*bottom right*).
In the middle, we show the
single face allowed for
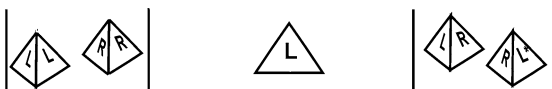observation (After [23, 26])

Origin of Matter and Life

The World Game

M. Q. J. Mol. Struct. <u>347</u>, 245 (1995) section 5, p. 262

Many Players and one **Game Leader** with two boxes
of tetrahedral dice

(I) De lege	(II) De facto
Mixed set of 4 types	One type
Each all equal faces	4 different faces

i.e. | L | L | L | L | 40%

or | R | R | R | R | 20%

or | L* | L* | L* | L* | 20%

or | R* | R* | R* | R* | 20%

| L | L* |
| R | R* |

Game Leader draws from boxes:
Players Observe one Face

situation of scientists, who observe an L-amino acid world, is obvious [23, 26]. If
one understood the mechanisms of symmetry violation and their consequences on
the evolution of matter and life in detail, then "de lege" would have to be at the
moment the correct and best possible answer.

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89. The "dark matter" should be distinguished from the so-called dark energy which is discussed briefly by M. Eigen in [90]. The expression "dark energy" has been introduced as a result of cosmological considerations, the interpretation of which is still subject to large uncertainty. As opposed to this, the existence of "dark matter," through its gravitational effects in the dynamics of galaxies, is confirmed by many astronomical observations, and is thought of as certain. This was concluded by Fritz Zwicky decades ago and has been confirmed many times since then. These conclusions are just as well-founded as for example the earlier conclusions about the existence of the outer planets in our solar system, by observation of their gravitational effects

on the courses of the inner planets which had previously been observed. The existence of the outer planets was then later confirmed through direct observation. The gravitational effect on the observed courses of the galaxies is also confirmed in the case of dark matter. An alternative interpretation would require a modification of the laws of classical mechanics and gravitation and this is thought to be very unlikely. The nature of dark matter is not known however. Speculations range from "difficult to see" normal matter (ionized interstellar hydrogen gas or a multitude of small planets are discussed here) up to new elementary particles, which display few interactions with normal matter, but obey gravitation in a normal fashion (so-called WIMPS). There remain, of course, many fundamental debates about the existence and nature of dark matter.

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