Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy
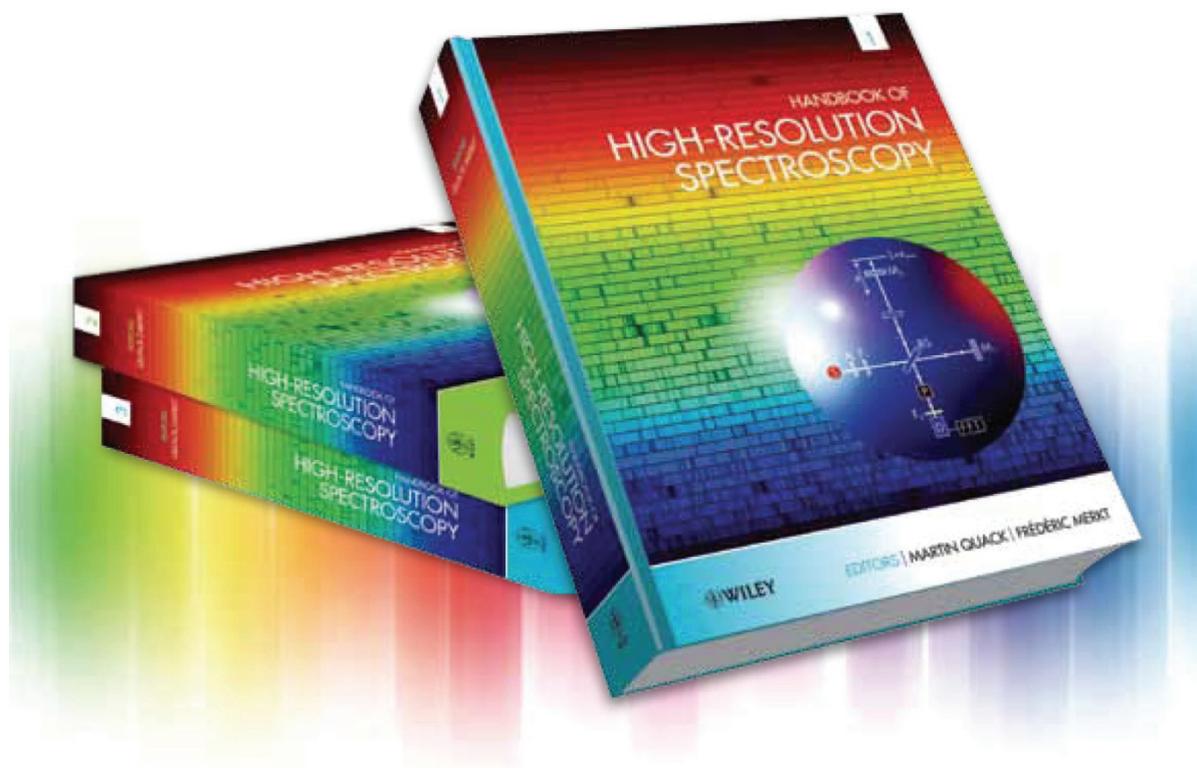
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Abstract

After an introductory survey, we introduce the seven fundamental symmetries of physics in relation to the group of the molecular Hamiltonian and the current standard model of particle physics (SMPP). We discuss the relation of these symmetries to conservation laws and fundamentally nonobservable properties of nature with the example of parity violation. The particular importance of experiments on detecting symmetry breakings is outlined and the three distinct, basic concepts of symmetry breaking (spontaneous, *de facto, de lege*) are illustrated with the example of space inversion symmetry breaking and parity violation in chiral molecules. Similar conceptual situations are found for our understanding of the underlying physics of molecular chirality by various types of symmetry breakings, of the evolution of biomolecular homochirality and of irreversibility as breaking of time reversal symmetry. The current status of the quantitative theory of molecular parity violation in the framework of electroweak quantum chemistry is reviewed, including the change of order of magnitude, which was found in recent years and has since been confirmed repeatedly.

The concepts of high-resolution spectroscopic experiments on parity violation in chiral molecules are discussed and the status of current attempts toward detecting molecular parity violation is summarized with particular emphasis on the possibilities of measuring time-dependent parity violation in the exceptional (still hypothetical) unstable parity isomers of chiral molecules. The concept of successive symmetry breakings in the quantum dynamics of molecules is illustrated with the wide range of time-scales for symmetry-breaking processes ranging from femtoseconds in experiments on very fast intramolecular vibrational redistribution (IVR) to the theoretical times of seconds for molecular parity violation.

The role of approximate symmetries and conservation laws for our understanding of selection rules in spectroscopy and in chemical reaction dynamics is analyzed in some detail with the example of approximate parity and nuclear spin symmetry conservation in radiative and reactive molecular processes. This includes the use of permutation-inversion symmetry groups in applications to spectroscopy and state-selected chemical reactions. Statistical concepts for the description of molecular energy levels are presented for use in high-resolution spectroscopy and chemical reactions in relation to symmetry properties.

We conclude with a summary of the current status of the following symmetries and their violations in spectroscopy and molecular dynamics: nuclear spin symmetry in chemical processes, space inversion symmetry and parity violation in chiral molecules, time reversal symmetry in intramolecular processes, and combined charge conjugation, parity, and time reversal (CPT) symmetry in relation to more fundamental aspects of time reversal and speculations on mass differences in chiral molecules and chiral neutrinos and their antimatter counterparts.

Keywords: fundamental symmetries; symmetry violations; chirality; molecular parity violation; nuclear spin symmetry; densities of states; CPT symmetry; symmetry selection rules; statistical theory of spectra; kinetics; molecular primary processes; intramolecular vibrational redistribution (IVR); chemical reaction dynamics, permutation symmetry; parity and inversion symmetry; time reversal symmetry

Fundamental Symmetries and Symmetry Violations from High-resolution Spectroscopy

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1 INTRODUCTION

Where is the wisdom lost in knowledge,
where is the knowledge, lost in information?
    T. S. Eliot in "The Rock" (as cited in Quack 2010)

Modern high-resolution molecular spectroscopy is often characterized by a large amount of information contained in line positions and intensities, often many thousands of lines in the spectrum of a single molecule. Even though summarized in tables of "spectroscopic constants" of a relevant effective molecular hamiltonian, such tables often have a repelling effect on the reader interested in the fundamental physics of molecules.

However, in the history of spectroscopy, there have been times where it contributed in basic simplicity to our fundamental understanding of chemistry and physics. Relating spectral lines to the chemical elements as done by Bunsen and Kirchhoff (1860) provides one example, leading also to the astrophysical discovery of Helium in the sun by Lockyer and Janssen; the analysis of the spectrum of the blackbody by Planck (1900) and of the spectrum of hydrogen in terms of the "old" quantum theory by Bohr (1913) are further examples. (*see* Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook for some of the history).

More recently, the spectroscopic discovery of the Lamb shift has contributed importantly to the development of quantum electrodynamics after about the 1940s. The

discovery of the spectrum of the cosmic background radiation in the microwave region corresponding to a blackbody emission at 2.7 K has led to an important clue on the origin of the universe in the big bang.

During the last five decades, it would appear, however, that new advances in fundamental physics resulted mostly from work in high-energy physics (with energies MeV and GeV, TeV, and beyond). The knowledge gained has been encoded in the famous "Standard Model of Particle Physics" (SMPP).

Today, "low-energy physics" such as molecular spectroscopy (with energies eV, meV, and below) would mostly help to fill in details into the grand picture or be useful in various applications. As we discuss in this article, however, when the fundamental symmetries of physics and their violations are considered, spectroscopy may take its place in fundamental science again. We argue in Section 2 that the most profound insights and expansion of knowledge arises, indeed, from such symmetry violations, which open a completely new window on the previously fundamentally unknown. In that sense, the study of such symmetry violations contributes to the "wisdom" of physics in concordance with the motto of the article.

We concentrate on the discrete symmetries relating to the fundamental structure of space, time, and matter, and we illustrate many of the fundamental concepts with the example of space inversion symmetry related to parity conservation (parity symmetry P) and its violation, as it is one aspect of these symmetry violations that is easily grasped with the concepts of molecular spectroscopy and where currently great advances are being made in this context (Sections 3 and 4). However, we also discuss other concepts such as time-reversal symmetry (T) and beyond, even CPT symmetry (Sections 2 and 8).

Table 1 Summary of currently known elementary (pointlike) particles with their approximate masses and their charges Q in multiples of the elementary charge (Groom *et al.* 2000, Perkins 2000).

Standard model of particle physics: particles			
Leptons ($S = \hbar/2$, fermions)			
ν_e	ν_μ	ν_τ	$Q = 0$ e
Mass $m/(\text{GeVc}^{-2})$ $<2 \times 10^{-9}$	$<2 \times 10^{-4}$	$<2 \times 10^{-2}$	
e^-	μ^-	τ^-	$Q = -1$ e
Mass $m/(\text{GeVc}^{-2})$ 5×10^{-4}	0.1	1.8	
Quarks ($S = \hbar/2$, fermions)			
u_1, u_2, u_3	c_1, c_2, c_3	t_1, t_2, t_3	$Q = (2/3)$ e
Mass $m/(\text{GeVc}^{-2})$ 5×10^{-3}	1.3	174	
d_1, d_2, d_3	s_1, s_2, s_3	b_1, b_2, b_3	$Q = -(1/3)$ e
Mass $m/(\text{GeVc}^{-2})$ 10^{-2}	0.2	4.3	

The essence of experimental data from high-energy physics can be accounted for by these particles. To each particle, one has an antiparticle of opposite charge (not listed here (Schopper 1999), after Quack and Stohner (2005), see also Quack (2006) and CERN reference cited therein). The recent observations of neutrino oscillations indicate that also $m(\nu_\tau, \nu_\mu)c^2 < 2\text{eV}$.

1.1 General Aspects

This article deals with the fundamental symmetries and symmetry violations as studied by high-resolution spectroscopy, in particular, molecular spectroscopy, with some brief remarks also on atomic and nuclear spectroscopy. Indeed, this may be one of the most fundamental applications of spectroscopy. It is an area of atomic and molecular spectroscopy, where results from high-energy and low-energy physics and molecular spectroscopy meet. We stress, on the one hand, the conceptual foundations and, on the other hand, the current status of the field, which has recently gained much momentum from new developments in theory and experimental spectroscopy.

Our article is largely based on two previous publications, which resulted from lectures, and are not easily accessible

(Quack 1999, 2006). We also draw attention to some earlier reviews (Quack 1983a, 1989b, 1993a,b, 1995d) and three recent reviews of the particular aspect of parity violation in chiral molecules, which is of current interest (Quack 2002, Quack and Stohner 2005, Quack *et al.* 2008).

To start with, it may be useful to consider fundamental forces as they are dealt with in the current "Standard Model" of physics. Tables 1 and 2 summarize the modern view of the elementary particles and the origin of the fundamental interactions (Amsler *et al.* 2008; Quack and Stohner 2005; Quack 2006). According to this, all forces are mediated by certain field particles. For instance, the electromagnetic force, which is included in the "Dirac–Schrödinger-like" ordinary quantum chemistry, leads to the Coulomb repulsion, say, between two electrons in a molecule by exchange of virtual photons. If we do not

Table 2 Summary of interactions and field particles (after Quack and Stohner (2005), see also Quack (2006)).

	Strong	Electromagnetic	Weak	Gravitation
Interactions and field particles				
	SU(3)	SU(2) $\otimes$ U(1)		
Relative Strength	1	1/137	$\approx 10^{-5}$	$\approx 10^{-38}$
Range	0.1–1 fm	(∞)	<0.1 fm	(∞)
Gauge bosons ($S = 1\hbar$) (except graviton)	Gluons $g_1 - g_8$	Photon γ	$W^\pm$, Z^0	(Still hypothetical), (graviton G, $S = 2\hbar$)
Mass $m/(\text{GeVc}^{-2})$	$<10^{-2}$	$<10^{-24}$	≈ 80, ≈ 91	
Acting on particles	Hadrons	Charged	Hadrons, leptons	All
Important in	Atomic nucleus	Atoms and molecules	Radioactive β-decay (neutrons), chiral molecules	Sun, planets, space craft, etc.

"see" the exchange of the field particles, we will observe only the motion of the electrons resulting from the transfer of momentum in "throwing" the field particles, and we could interpret this as resulting from a repulsive "force" between the two electrons (see the graphical representation in Quack (2006), adapted from the CERN Website). The Coulomb force with the $1/r$ potential energy law is of long range. The other forces arise similarly. The strong force with very short range ($0.1–1$ fm) mediated by the gluons is important in nuclear physics but has only indirect influence in chemistry, for which it provides the properties of the nuclei, which enter as parameters in chemistry; otherwise, there is usually no need to retain the strong force explicitly in chemistry. The weak force, on the other hand, is mediated by the $W^{\pm}$ and Z^0 bosons of very high mass ($80–90$ Da, of the order of the mass of a bromine nucleus) and short lifetime (0.26 ys $= 0.26 \times 10^{-24}$ s). This force is thus very weak and of very short range (<0.1 fm) and one might, therefore, think that similar to the even weaker gravitational force (mediated by the still hypothetical graviton of spin 2), it should not contribute significantly to the forces between the particles in molecules (nuclei and electrons). Nevertheless, the weak force, in spite of its short range, becomes effective in molecules, when the electrons penetrate the nucleus, and then it leads only to a very small perturbation on the molecular dynamics, which ordinarily might be neglected completely. However, *symmetry violations* now become important and we illustrate this again with the weak force in molecular physics and spectroscopy.

1.2 The Example of Parity Violation in Molecular Physics

It turns out that because of the different symmetry groups of the electromagnetic and the electroweak hamiltonians, a fundamentally important new aspect arises in the dynamics of chiral molecules, which we, therefore, have added in Table 2 as compared to the similar table from CERN website, where this was not originally included (see Quack 2006). Indeed, the electromagnetic hamiltonian commutes with the space inversion or parity operator $\hat{P}$:

$$\hat{P}\hat{H} = \hat{H}\hat{P} \qquad (1)$$

which leads to the consequence that in chiral molecules the delocalized energy eigenstates χ_+ and χ_- have a well-defined parity and the localized handed states λ and ρ of chiral molecules have exactly the same energy by symmetry (Section 2). Therefore, one can also say that the reaction enthalpy $\Delta_R H_0^{\ominus}$ for the stereomutation reaction (2) between R- and S-enantiomers of a chiral molecule would be exactly zero by symmetry ($\Delta_R H_0^{\ominus} \equiv 0$), a fact already

noted originally by van't Hoff (1887):

$$R \rightleftarrows S$$
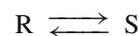
$$\Delta_R H_0^{\ominus} = 0 \text{ (van't Hoff)} \quad \text{or} \quad \Delta_R H_0^{\ominus} = \Delta_{pv} E \cdot N_A \text{ (today)}$$
$$(2)$$

Today, we know that the electroweak hamiltonian does not commute with $\hat{P}$

$$\hat{P}\hat{H}_{ew} \neq \hat{H}_{ew}\hat{P} \qquad (3)$$

and therefore parity is violated, leading to a small, but nonzero, parity-violating energy difference $\Delta_{pv} E$ between enantiomers and thus $\Delta_R H_0^{\ominus} \neq 0$ (for example, about 10^{-11} J mol^{-1} for a molecule like CHFClBr (Quack and Stohner 2000b)). We discuss in Section 2 in more detail, the circumstances under which such small effects lead to observable results dominating the quantum dynamics of chiral molecules.

This symmetry violation in chiral molecules is, indeed, the key concept, which leads to an interesting interaction between high-energy physics and molecular physics and chemistry, and also biochemistry (Quack 1989b, 2002). It results in the following three statements, which may at first perhaps seem surprising:

1. The new physics arising from the discovery of parity violation (Lee and Yang 1956, Wu *et al.* 1957, Garwin *et al.* 1957, Friedman and Telegdi 1957) and the consequent electroweak theory in the SMPP (Glashow 1961, Weinberg 1967, Salam 1968, Veltman 2000, 't Hooft 2000) leads to the prediction of fundamental new effects in the dynamics of chiral molecules and thus in the realm of chemistry and molecular spectroscopy.
2. Molecular parity violation as encoded in equations (2) and (3) has possibly (but not necessarily) important consequences for the evolution of biomolecular homochirality in the evolution of life (Quack 1989b, 2002, 2006, Yamagata 1966, Rein 1974).
3. Possible experiments on molecular parity violation open a new window to look at fundamental aspects of the standard model of high-energy physics, and thus molecular physics might contribute to our understanding of the fundamental laws relevant to high-energy physics. Indeed, going beyond parity violation and the standard model, molecular chirality may provide a new look at time-reversal symmetry and its violation, in fact the nature of time as well as *CPT* symmetry (Quack 1993a, 1994b, 1995b,c,d, 1999, 2002, 2003).

While successful experiments are not yet available, there has been substantial recent progress in theory, which makes experiments promising.

1.3 Recent Developments in Electroweak Quantum Chemistry with Parity Violation

It turns out that new developments in electroweak quantum chemistry have interesting lessons to tell. A brief history of electroweak quantum chemistry is quickly outlined. After the discovery of parity violation in 1956–1957 (Lee and Yang 1956, Wu *et al.* 1957, Garwin *et al.* 1957, Friedman and Telegdi 1957), it took about a decade until the possible consequences for chemistry and biology were pointed out by Yamagata (1966). While his numerical estimates were wrong by many orders of magnitude (as also a later estimate (Garay and Hrasko 1975)) and even some of Yamagata's qualitative reasonings were flawed (see Quack 2002), the relationship between parity violation in high-energy physics and the molecular physics of chirality was thus established and repeatedly discussed qualitatively in the 1970s (Rein 1974, Letokhov 1975, Kompanets *et al.* 1976, Arimondo *et al.* 1977, Keszthelyi 1977a,b, Zeldovich *et al.* 1977, Harris and Stodolsky 1978).

The first quantitative calculations on molecular parity violation were carried out following the work of Hegström, Rein and Sandars (Rein *et al.* 1979, Hegström *et al.* 1980) and Mason and Tranter in the 1980s (Mason and Tranter 1983a,b, 1984, Mason 1984, Tranter 1985a,b,c,d, Barra *et al.* 1986, 1987, 1988, Kondepudi 1987, MacDermott *et al.* 1987, Wiesenfeld 1988, Jungwirth *et al.* 1989, Mac-Dermott and Tranter 1989a,b, Kikuchi and Wang 1990, Kikuchi *et al.* 1990, Chela-Flores 1991, Salam 1991, 1992, Kikuchi and Kiyonaga 1994). Some far reaching conclusions about consequences for biomolecular homochirality were drawn from some of these early calculations, but we know now that none of these early calculations prior to 1995

can be relied on (nor can one retain their conclusions), as they were often incorrect even by orders of magnitude.

Indeed, in 1995 we carefully reinvestigated the calculations of parity-violating energies in molecules and discovered, surprising to many at the time, that an improved theoretical treatment leads to an increase in calculated parity-violating energies by about 2 orders of magnitude in the benchmark molecules H_2O_2 and H_2S_2 (Bakasov *et al.* 1996, 1998a). This discovery triggered substantial further theoretical (Quack and Stohner 2000a,b, Quack 1999, 2002, Bakasov *et al.* 1997, Bakasov and Quack 1999, Berger and Quack 2000a,b, Lazzeretti and Zanasi 1997, Zanasi and Lazzeretti 1998, Laerdahl and Schwerdtfeger 1999, Gottselig *et al.* 2001, Berger *et al.* 2000, 2001, Laerdahl *et al.* 2000a,b, Hennum *et al.* 2002, Quack and Stohner 2001) and experimental activity and suggestions (Beil *et al.* 1994, Bauder *et al.* 1997, Hollenstein *et al.* 1997, Daussy 1999, Daussy *et al.* 1999, Crassous and Collet 2000, Pepper *et al.* 1995, Quack 1994a, Berger 2003, Lahamer *et al.* 2000, Buschmann *et al.* 2000, Frank *et al.* 2001). The new theoretical results from Bakasov *et al.* (1996) were rather quickly confirmed in independent calculations from several research groups as summarized in Table 3. While the earlier overoptimistic conclusions on the selection of biomolecular homochirality had to be revised (Quack 2002), our work has led to a completely new and much more optimistic outlook on the possibility of doing successful spectroscopic experiments, which are now underway in our own group as well as in other groups (Beil *et al.* 1994, Bauder *et al.* 1997, Hollenstein *et al.* 1997, Daussy 1999, Daussy *et al.* 1999, Crassous and Collet 2000, Pepper *et al.* 1995, Quack 1994a, Berger 2003, Lahamer *et al.* 2000). Although no

Table 3 Parity-violating energy differences $\Delta_{pv}H_0^{\ominus} = \Delta_t H_0^{\ominus}(M) - \Delta_t H_0^{\ominus}(P)$ for H_2O_2, H_2S_2, and Cl_2S_2 at the geometries of the P and M enantiomers indicated (close to but not exactly equilibrium geometries, chosen for intercomparison of different results).

Molecule	Method	References	$\Delta_{pv}H_0^{\ominus} / (10^{-12}\,\mathrm{J\,mol^{-1}})$
H_2O_2	SDE-RHF 6-31G	Mason and Tranter (1984)	-0.0036
	CIS-RHF 6-31G	Bakasov *et al.* (1996, 1998a, 1999), Bakasov and Quack (1999)	-0.60
	TDA 6-31G	Lazzeretti and Zanasi (1997), Zanasi and Lazzeretti (1998)	-0.84
	DHF	Laerdahl and Schwerdtfeger (1999)	-0.44
	CASSF-LR/cc-pVTZ	Berger and Quack (2000b)	-0.41
H_2S_2	SDE-RHF 6-31G	Mason (1984)	0.24
	TDA 4.31G	Lazzeretti and Zanasi (1997), Zanasi and Lazzeretti (1998) (scaled 75%, (Bakasov and Quack 1999))	14.4
	CIS-RHF 6-31G	Bakasov *et al.* (1998a, 1999), Bakasov and Quack (1999)	22.5
	MC-LR RPA/aug-cc-pVTZ	Gottselig *et al.* (2001)	22.4
	DHF	Laerdahl and Schwerdtfeger (1999)	33.5
Cl_2S_2	MC-LR RPA/aug-cc-pVTZ	Berger *et al.* (2001)	-15.4

The geometry parameters used were $r_{OO} = 149\,\mathrm{pm}$, $r_{OH} = 97\,\mathrm{pm}$, $\alpha_{OOH} = 100°$, $\tau_{HOOH} = 90°$ for H_2O_2; $r_{SS} = 205{,}5\,\mathrm{pm}$, $r_{SH} = 135.2\,\mathrm{pm}$, $\alpha_{SSH} = 92°$, $\tau_{HSSH} = 92°$ for H_2S_2; and $r_{SS} = 194.7\,\mathrm{pm}$, $r_{SCl} = 205.2\,\mathrm{pm}$, $\alpha_{SSCl} = 107.55°$, $\tau_{ClSSCl} = 85.12°$ for Cl_2S_2 (*see also* Quack and Stohner (2005) and references cited therein).

successful experiment has as yet been reported, one can expect such results in the relatively near future.

1.4 Outline of the Article

The outline of the remainder of this article is as follows. In section 2 fundamental symmetries of physics leading to the conceptual foundations of various types of symmetry breaking are discussed. We discuss the related opinions or "communities of belief" for the physical–chemical dynamics of chirality, for the selection of biomolecular homochirality, and for irreversibility, which are conceptually closely related because of the relationship between parity symmetry P and time-reversal symmetry T. We then introduce the foundations of electroweak quantum chemistry in Section 3, allowing us to calculate $\Delta_{pv}E$ in chiral molecules. This leads to the concepts for current experiments discussed in Section 4. In section 5, we discuss time-dependent processes and the hierarchy of timescales resulting from breaking approximate symmetries. Section 6 deals with approximate conservation and breaking of nuclear spin symmetry in molecules, relating this to densities of states as discussed in Section 7. We conclude in Section 8 with an outlook on time-reversal symmetry breaking and the role of stereochemistry for future experiments on the foundations of CPT symmetry and the ultimate nature of irreversibility. In part of this, we follow an earlier review (in German (Quack 1999), see also Quack (1989b, 1995b, 2002, 2004a,b, 2006). We also draw attention to recent reviews (Quack and Stohner 2005, Berger 2004) as well as to a publication by Bakasov *et al.* (1998a) and an earlier review by Janoschek (1991) with many further references (see Quack 2001, 2003). We do not aim to be encyclopedic here, but rather to provide a conceptual summary.

2 FUNDAMENTAL SYMMETRIES OF PHYSICS AND THE VIOLATION OF PARITY AND TIME-REVERSAL SYMMETRY IN MOLECULES

2.1 Fundamental Symmetries in Molecular Physics

There are thus two types of Cartesian coordinate systems, which are called "right-handed" and "left-handed" systems. The difference between the two is familiar to every physicist and engineer. It is interesting that an absolute geometric definition of the right or left handedness is impossible, only the relationship of opposition between the two can be defined.

(Einstein 1922)[a]

We address here the fundamental symmetries of physics and how they can be investigated by molecular physics, in particular, molecular spectroscopy (Quack 2001, 2003, 2006). The following symmetry operations leave a molecular hamiltonian invariant within the framework of traditional quantum chemical dynamics including only the electromagnetic interaction and considering the isolated system (Quack 1977, 1983a, 1995b, 1999, 2006):

1. translation in space;
2. translation in time;
3. rotation in space;
4. inversion of all particle coordinates at the origin (parity operation P or E^*);
5. "time reversal" or the reversal of all particle momenta and spins (operation T for time reversal);
6. permutation of indices of identical particles (for instance, identical nuclei and electrons); and
7. the replacement of all particles by their corresponding antiparticles (operation C for "charge conjugation", for instance, replacing electrons by positrons, protons by antiprotons, etc.).

These symmetry operations form the symmetry group of the molecular hamiltonian. They are our "seven pillars of wisdom". It is well known following the early work of Noether (1918) and even earlier work of Jacobi (1866) that in connection to an exact symmetry we have a corresponding exact conservation law. For instance, 1. leads to momentum conservation, 2. to energy conservation, 3. to angular momentum conservation (Zare 1988), and 4. to parity conservation, that is, the conservation of the quantum number parity, which describes the symmetry (even or odd; positive or negative) of the wavefunction under reflection at the origin (Wigner 1959). Another interesting observation is that an exact symmetry and conservation law leads to a fundamentally nonobservable property of nature (see the discussion in Lee (1988) and Quack (1989b, 1993a, 1999, 2002)). For example, P corresponds to the fundamentally nonobservable property of the left- or right-handedness of space. This implies that it would be fundamentally impossible to say what is a left- or a right-handed coordinate system or an R or S enantiomeric molecular structure, only the opposition of "left" and "right" would have a meaning.

While the relationship between symmetries and conservation laws is a common textbook subject, the resulting "nonobservability" is less widely appreciated. This consequence of an exact symmetry and conservation law is mentioned in an early citation at beginning of this section (Einstein 1922), when it was believed that the space inversion symmetry was an exact (and unquestioned) property of nature, similar to the other symmetries. It implies that in the presence of such a symmetry, there is a fundamental property of nature that we cannot know for fundamental
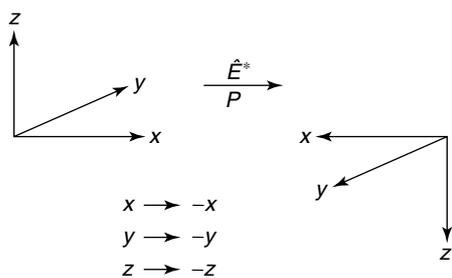
Figure 1 Right-handed (left) and left-handed coordinate systems (right) connected by space inversion symmetry. [Reproduced after Figure 1 of Quack (2002) by permission.]

reasons: it is hidden to us by a veil because of the conservation law. This makes it very important to find an experimental violation of that exact symmetry: The veil is removed and we then find an experimental window to observe this property of nature, which was completely hidden to us before we observed the symmetry violation. In this sense, observations of symmetry violations and violations of conservation laws are among the most fundamental observations in the natural sciences. The basic concepts have a long history and can be traced back to Kant (1783), Einstein (1922), Lee (1988), and our discussion of molecular chirality and the violation of parity conservation and time-reversal symmetries in that context (Quack 1989b, 1993a, 1995d, 1999, 2003). However, it has not become widely appreciated textbook knowledge yet (*see also* Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy**, this handbook). Much historical material can be found in the books by Mainzer (1988, 2005).

Before continuing the basic discussions of the concepts, we illustrate here the simple group operations and corresponding invariances. Figure 1 shows the left- and right-handed coordinate systems as referred to in the citation of Einstein. The symmetry operation (4) of space inversion corresponds to replacing the coordinates $x \to -x$, $y \to -y$, $z \to -z$ for every particle (electrons and nuclei) in the molecule (or other quantum system); this transformation is shown in the figure. The two coordinate systems are also called *left-handed* and *right-handed coordinate systems*, this nomenclature being subject to some criticism, left or right handedness being usually a property attributed to human beings according to their preference of using their left or right hands in their actions, say handwriting, and obviously this is not a property of coordinate systems. We use "handedness" of coordinate systems following common usage without paying attention to such subtleties, but being aware of them. (The original citation from Einstein using German was of "left system" and "right system", avoiding the word "handed".) When one rotates the inverted axis system on the right-hand side of Figure 1 by $180°$ around the x-axis, such that z again points to the top, one gets a

picture of the original "right-handed" coordinate system on the left as it would appear in a mirror. Thus, mirror reflection also transforms the "handedness" of an object and this is the most commonly used representation for enantiomers of chiral molecules as "mirror image isomers". Since the rotation in space by $180°$ is just one of the infinitely many symmetry operations under item (3) at the start of this section, the combined operation obviously also leads to a corresponding invariance. We make use only of operation (4) at present.

The symmetry group S^* of space inversion is extremely simple and has just two operations (E, E^* or E, P) with two irreducible representations A^+ and A^- shown in Table 4 (*see also* Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook).

The conserved quantity under time evolution is the quantum number parity corresponding to the irreducible representation A^+ or A^-, which we label here as $+$ and $-$ as to whether the eigenvalue under the "parity" or space inversion operation $\hat{P}$ (or in different nomenclature $\hat{E}^*$ (*see also* Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**, this handbook)) is $+1$ or -1, i.e.,

$$\hat{P}\Psi_k = (+1)\Psi_k \tag{4}$$

for states of positive parity (A^+) and

$$\hat{P}\Psi_j = (-1)\Psi_j \tag{5}$$

for states of negative parity (A^-). "Parity conservation" implies that a state of initial parity $+1$ (species A^+) will retain this parity under time evolution of the isolated system, even if the system is not in an energy eigenstate (i.e., the time evolution can be nontrivial). Parity is a constant of the motion, if the symmetry is exact.

Yet another way to look at this aspect of an exact symmetry is that it would be impossible to communicate by a coded message (without sending a chiral example) to a distant civilization that we as human beings are made (mostly) of S (or L)-amino acids and not of their R (or D) enantiomers; see Section 2.4 and Quack (1999, 2002). This impossibility of such a communication is removed, if the

Table 4 Character table for the inversion (reflection) group S^*.

Species ($\Gamma(S^*)$)	Class (Q)	
	E	$E^*(P)$
A^+	1	1
A^-	1	-1

exact symmetry is invalid, "broken de lege" as we shall see below.

This again has found discussion, sometimes under the name *Ozma problem* (Gardner and Mackey 1964). With parity violation, this communication problem could, in principle, be solved by simply communicating to the distant extraterrestrials that we are made of the amino acid with the lower ground-state energy, if we have determined a particular L-amino acid to be in fact the more stable enantiomer, experimentally.

Today, we know from nuclear and high-energy physics that P, C, and T are individually all violated, as is also the combination CP. Only the combined operation CPT remains an exact symmetry in the current "standard model" (Quack 1977, 1983a, 1999, 2001, 2003, 2006, Lee 1988, Gabrielse *et al.* 1995, Zimmermann and Hänsch 1993, Amoretti *et al.* 2002, Kobayashi and Maskawa 1973, Abe *et al.* 2001). Parity violation is in fact abundant in a variety of contexts in nuclear and atomic physics (Wu *et al.* 1957, Garwin *et al.* 1957, Friedman and Telegdi 1957, Bouchiat and Bouchiat 1974, Bennett and Wieman 1999). CP violation was originally observed only in the K-meson decays (Christenson *et al.* 1964), but is now also found in the B-Meson system (Abe *et al.* 2001) and direct T-violation has been established in 1995 after it had already been inferred from the earlier CP violation experiments (Adler *et al.* 1995). We have speculated on several occasions that, in principle, all the discrete symmetries might be violated ultimately in molecular physics (see Quack (1993b, 1994b,

1995b, 1999, 2003, 2004a,b), where also some tests for such symmetry violations are cited). We shall, however, now discuss first in more detail the fundamental concepts of symmetry violations and symmetry breakings, starting out with the easy-to-grasp concepts for parity violation. We return to the fundamental CPT symmetry and the remaining fundamentally unknown properties of nature at the end of this article.

2.2 Concepts of Symmetry Breaking—Spontaneous, De facto, De lege—in Relation to Molecular Chirality

Having emphasized the importance of symmetry breaking for our understanding of nature, it is important to define and distinguish different types of such symmetry breaking.

Three basic concepts of symmetry breaking should be distinguished (Quack 1989b) and we illustrate this again with space inversion symmetry and chirality, indeed with a chiral molecular example such as H_2O_2 (Figure 2). This molecule is nonplanar, bent, in its equilibrium geometry, and an accurate full dimensional potential hypersurface has been formulated for its spectroscopy and reaction dynamics (Kuhn *et al.* 1999).

In a simplified manner, the stereomutation reaction (2) interconverting the two enantiomers can be considered as a one-dimensional torsional internal rotation about an angle α indicated in the figure. One has two barriers to this motion,

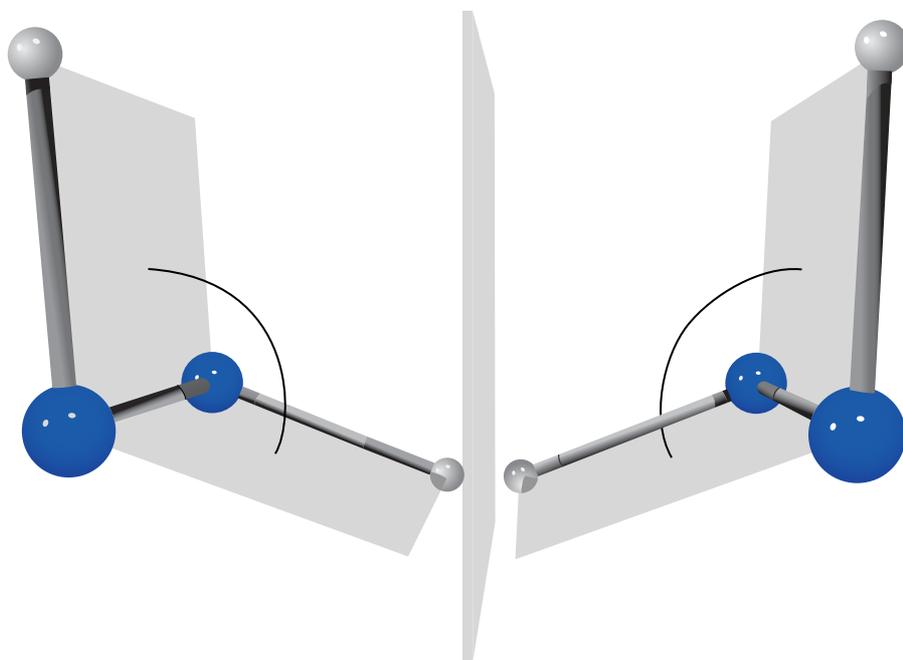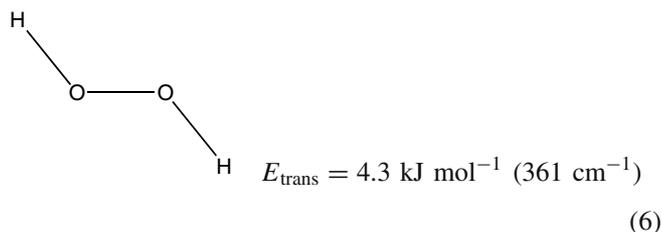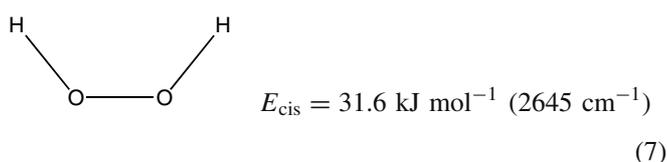**Figure 2** The H_2O_2 molecule in its enantiomeric mirror image forms at the equilibrium geometry. The angle between the two planes indicated is α. [Reproduced from Quack (1999) by permission.]

a low one in the planar trans form

$$E_{\text{trans}} = 4.3 \text{ kJ mol}^{-1} \ (361 \text{ cm}^{-1}) \tag{6}$$

and a much higher one in the planar cis structure

$$E_{\text{cis}} = 31.6 \text{ kJ mol}^{-1} \ (2645 \text{ cm}^{-1}) \tag{7}$$

Thus, we represent the dynamics of stereomutation in a simplified manner as the motion of a reduced mass point in a one-dimensional double-minimum potential considering here only the lower barrier explicitly (Figure 3a), even though the true dynamics correspond to a six-dimensional motion. Indeed, Figure 3(a) corresponds to a standard textbook representation of this type of tunneling stereomutation dynamics. In principle, with parity conservation (equation 1), the eigenstates are delocalized states of positive (χ_+) and negative parity ($-\chi_-$), which show the symmetry of the quantum mechanical problem (Figure 3c). In classical dynamics, there is also a symmetric state at the maximum of the potential in unstable equilibrium (Figure 3a).

In practice, in the chemistry of stable chiral molecules and similar problems in physics, one finds states that are
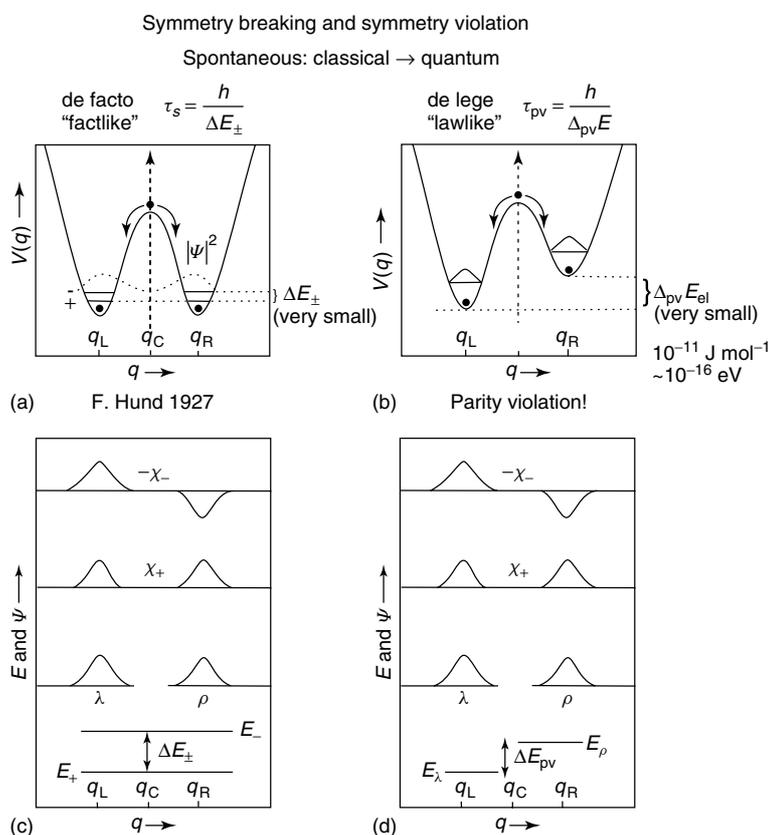

Figure 3 Scheme illustrating de facto and de lege symmetry breaking using the example of potentials $V(q)$ including parity violation in chiral molecules. The eigenstates of positive (*subscript plus signs*) and negative (*subscript minus signs*) parity in the symmetric potential (a) result in a delocalized probability density $|\Psi|^2$ as a function of the inversion coordinate q but with a possibility of de facto localization near the left-hand (q_L) and right-hand (q_R) minima. With parity violation, the potential is asymmetric (b) with localized eigenstates (at L or R). (c, d) Localized wavefunctions λ and ρ and delocalized wavefunctions of well-defined parity χ_+ and $-\chi_-$. In the symmetric case (c), the wavefunctions of well-defined parity χ_+ and $-\chi_-$ are the eigenfunctions for the energies E_+ and E_- (separated by $\Delta E_\pm$). Time-dependent wavefunctions λ and ρ can be generated by superposition of χ_+ and $-\chi_-$. In the asymmetric case (d), the localized wavefunctions λ and ρ are eigenfunctions for the energies E_λ and E_ρ separated by $\Delta_{\text{pv}}E$. Then the time-dependent wavefunctions of well-defined parity can be generated by superposition (see also Hund (1927a,b), Quack (1986, 1993a), Gottselig *et al.* (2001), and Quack (1999, 2006)). [After Quack *et al.* (2008) by permission.]

either left (λ, q_L) or right (ρ, q_R), localized classically or quantum mechanically, which do not show the symmetries of the hamiltonian. The symmetry is said to be broken *spontaneously* in classical dynamics, where at low energy only one (either left or right) solution to the dynamics is possible. The symmetrical state would be impossible at any energy below the barrier maximum. This kind of spontaneous symmetry breaking is essentially a classical concept, which can, however, be extended to quantum mechanical systems with an infinite number of degrees of freedom (Primas 1981, Pfeifer 1983, Amann 1991). At low energies, below the barrier for interconversion, the symmetrical state showing the underlying symmetry of the dynamics is impossible in classical mechanics. This impossibility is the key aspect of spontaneous symmetry breaking as opposed to the other kinds of symmetry breaking.

In molecular quantum mechanics, however, the superposition principle guarantees that we also have the symmetric state of positive parity

$$\chi_+ = \frac{1}{\sqrt{2}}(\lambda + \rho) \tag{8}$$

and the antisymmetric state of negative parity

$$-\chi_- = \frac{1}{\sqrt{2}}(\lambda - \rho) \tag{9}$$

These states are delocalized, right and left structures simultaneously. They correspond to the eigenstates of both the hamiltonian $\hat{H}$ and parity $\hat{P}$ operators in equation (1) for a parity-conserving hamiltonian. According to Hund (1926, 1927a,b), from the eigenstates, one can generate the initial condition of a localized state by superposition, either left

$$\lambda = \frac{1}{\sqrt{2}}(\chi_+ - \chi_-) \tag{10}$$

or right

$$\rho = \frac{1}{\sqrt{2}}(\chi_+ + \chi_-) \tag{11}$$

The symmetry is now broken de facto by the chosen initial condition and these states show a time evolution following the time-dependent Schrödinger equation (Schrödinger 1926)

$$i\frac{h}{2\pi}\frac{\partial \Psi(q,t)}{\partial t} = \hat{H}\Psi(q,t) \tag{12}$$

with the solution

$$\Psi(q,t) = \sum_k c_k \varphi_k(q) \exp(-2\pi i E_k t/h) \tag{13}$$

c_k are complex coefficients, $\varphi_k(q)$ are coordinate-dependent eigenfunctions of $\hat{H}$, if $\hat{H}$ is time independent, and the E_k are the energy eigenvalues in this special case.

For just two levels with energies E_+ and E_- and $\Delta E_\pm = E_- - E_+$ (Figure 3), the evolution reduces to

$$\Psi(q,t) = \frac{1}{\sqrt{2}} \exp(-2\pi i E_+ t)$$
$$\times [\chi_+ + \chi_- \exp(-2\pi i \Delta E_\pm t/h)] \tag{14}$$

The observable probability density

$$P(q,t) = \Psi(q,t)\Psi^*(q,t) = |\Psi|^2$$
$$= \frac{1}{2}|[\chi_+ + \chi_- \exp(-2\pi i \Delta E_\pm t/h)]|^2 \tag{15}$$

shows a period of motion

$$\tau_T = \frac{h}{\Delta E_\pm} \tag{16}$$

and a stereomutation tunneling time from left to right (or the reverse), which is just half of this value:

$$\tau_{\lambda \longrightarrow \rho} = \frac{h}{2\Delta E_\pm} = \frac{1}{2c\Delta\tilde{\nu}} \tag{17}$$

With this kind of de facto *symmetry* breaking, the underlying symmetry of the problem is either visible from the time-averaged motion or in the symmetrical, delocalized, eigenstates, which are possible (even quite natural) states in quantum mechanics, in contrast to classical mechanics, where neither tunneling nor delocalization phenomena exist.

Table 5 shows stereomutation times for H_2O_2 for different degrees of excitation (Fehrensen *et al*. 1999b, 2007) in various modes. It should be made clear that the times shown in Table 5 correspond to the full six-dimensional wave-packet motion, not to the simple one-dimensional textbook model (Fehrensen *et al*. 1999b, 2007, Luckhaus and Quack 2001). Full-dimensional quantum wavepackets have been derived by Fehrensen *et al*. (2007) and are reviewed in relation to the potential hypersurface by Marquardt and Quack 2011: **Global Analytical Potential Energy Surfaces for High-resolution Molecular Spectroscopy and Reaction Dynamics**, this handbook.

The times for stereomutation in H_2O_2 are so short that one would not normally consider H_2O_2 as an ordinary chiral molecule, although for short times it would be chiral.

If we now add to the hamiltonian the electroweak parity-violating part, this will add a small antisymmetric effective potential, as shown in Figure 4, for the cases of H_2O_2 and H_2S_2. While these extra potentials should not naively be considered as Born–Oppenheimer-like potentials, it is true that, without these extra potentials, the molecular

Table 5 Tunneling splittings $\Delta\tilde{\nu}_T$ and stereomutation times $\tau_{\lambda\to\rho}$ in H_2O_2 in the ground state ν_0 and as a function of excitation of different fundamental vibrations $\nu_1 - \nu_6$ (after Quack (1999), Fehrensen *et al.* (1999b, 2007), Luckhaus and Quack (2001)). The experimental result (column Exp.) is uncertain for ν_2 as indicated by the question mark. The column $6D$ gives the full-dimensional quantum result and the column RPH the result from a quasi-adiabatic channel reaction path hamiltonian approximation (Fehrensen *et al.* 1999a,b, 2007).

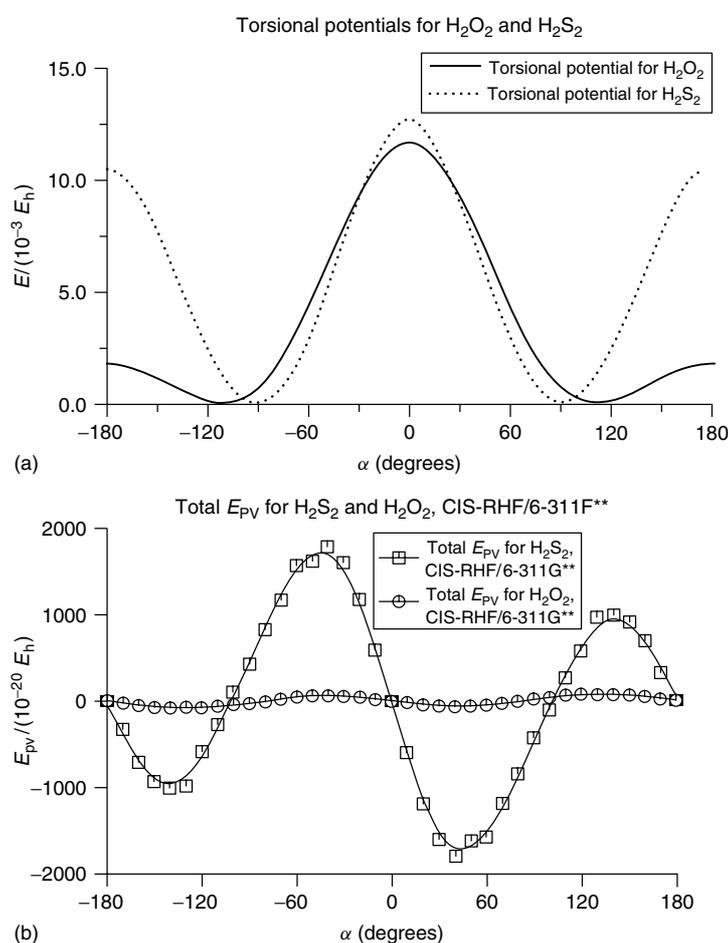| $\tilde{\nu}/(cm^{-1})$	Fundamental mode	Exp.	$6D$ $\Delta\tilde{\nu}_T/(cm^{-1})$	RPH	$\tau_{\lambda\to\rho}(6D)/(ps)$
0	ν_0	11.4	11.0	11.1	1.5
3609	ν_1	8.2	7.4	7.4	2.0
1396	ν_2	(2.4?)	6.1	5.0	2.7
866	ν_3	12.0	11.1	10.8	1.5
255	ν_4	116	118	120.0	0.14
3610	ν_5	8.2	7.6	8.4	2.2
1265	ν_6	20.5	20.8	21.8	0.8

Figure 4 Parity-conserving and parity-violating potentials for H_2O_2 and H_2S_2. [Reproduced after Bakasov and Quack (1999) by permission.]

hamiltonian (beyond the Born–Oppenheimer approximation and exact to all orders) shows exact inversion symmetry (effectively about the planar structures at $180°$ and $0°$ in Figure 4), whereas with the additional potentials the symmetry is broken de lege (from the Latin word "lex", which means law), as in the fundamental natural law now there appears an asymmetry (we prefer de lege in the nomenclature for a law of nature, as the alternative de iure would refer to the man made conventional law, which is "ius" in Latin). Obviously, one of the minima will be

slightly preferred and the explanation of the localized states as arising from a de lege symmetry breaking is fundamentally different from a situation with a de facto symmetry breaking. It turns out that the distinction has a quantitative aspect, related to the relative size of the tunneling splittings $\Delta E_{\pm}$ within the hypothetical symmetrical potential and the parity-violating energy difference $\Delta_{pv}E$, which is about twice the parity-violating potential at the left or right equilibrium geometry (in absolute magnitudes):

$$|\Delta_{pv}E| \simeq |E_{pv}(R) - E_{pv}(L)| = 2|E_{pv}(R)| = 2|E_{pv}(L)| \tag{18}$$

If one has

$$|\Delta E_{\pm}| \gg |\Delta_{pv}E| \tag{19}$$

then the "de facto" symmetry breaking provides the proper explanation for the chiral molecule dynamics, whereas in the case with

$$|\Delta_{pv}E| \gg |\Delta E_{\pm}| \tag{20}$$

the "de lege" symmetry breaking prevails. Comparing the numerical results for H_2O_2 as shown in Table 3 and Figure 4 with the results in Table 5, it is obvious that the de facto symmetry breaking is a proper explanation for H_2O_2 and parity violation is effectively irrelevant for the tunneling dynamics of H_2O_2. However, H_2O_2 is also not a normal chiral molecule that has stable enantiomers. Indeed, the lifetime of enantiomers even at low energy is only about 1 ps, because of the very fast tunneling process.

If we consider the substituted methane derivatives, shown in Figure 5, as typical examples for stable chiral molecules,
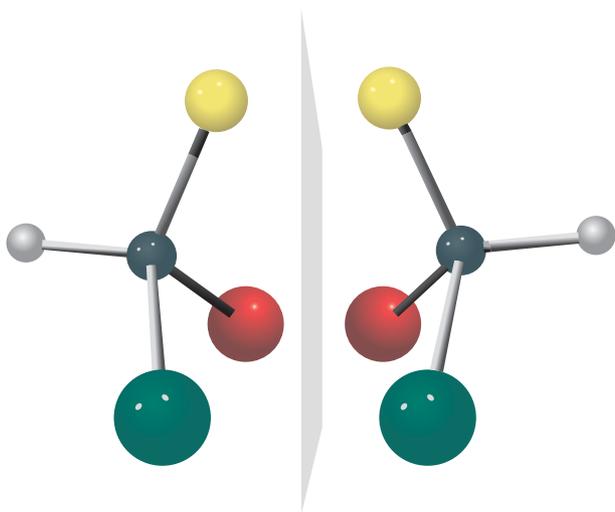

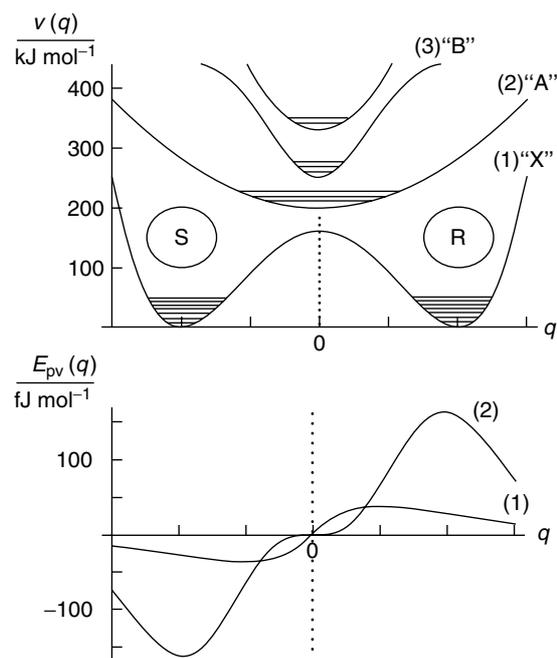**Figure 5** The enantiomeric mirror image isomers of CHFClBr.

Figure 6 Schematic representation of parity-conserving and parity-violating potentials for ground and excited states. [Reproduced after Bakasov *et al.* (1998a) by permission.]

the situation is quite different. The corresponding parity-conserving and parity-violating potentials are shown in Figure 6 schematically for chiral ground and some achiral excited electronic states. It turns out that in molecules such as CHFClBr with barriers to stereomutation of the order of 100–400 kJ mol^{-1}, the tunneling would be completely suppressed by the parity-violating asymmetry and thus the *de lege symmetry breaking* is the correct explanation in this case. This is only an illustration of the conceptual subtleties arising in such a basic chemical question such as to the origin of molecular chirality. Indeed, the three cases of symmetry breaking, spontaneous, de facto, and de lege, are only three examples of several explanations put forward to interpret the physical chemical origin of chirality and summarized in our review of the topic in 1989 (Quack 1989b). Before this critical discussion, there existed essentially noninteracting "communities of belief" for explaining chirality, each of which had a self-consistent set of explanations. We summarize these here in Section 2.3, as very similar situations arise in the discussion of biomolecular homochirality and irreversibility, which we discuss in turn thereafter.

A further subtlety may deserve discussion. Here, we have carefully distinguished the three concepts of symmetry breaking: spontaneous, de facto, and de lege, as was done by us before (Quack 1989b). Frequently, spontaneous symmetry breaking and de facto symmetry breaking are not distinguished, but lumped together under the single concept

of spontaneous symmetry breaking. This is, however, not quite correct as in fact they lead to observable, different consequences. In the classical concept of spontaneous symmetry breaking, it is *impossible* to generate a symmetrical (delocalized) state at energies below the barrier and this consequence has been proposed also with the quantum mechanical extension of spontaneous symmetry breaking (Pfeifer 1983, Amann 1991, Primas 1981). On the other hand, the quantum mechanical concept of de facto symmetry breaking allows for the generation of the symmetrical state even at low energies (below the barrier of the potential (Hund 1927a,b, Quack 1986).

This important difference again is well understood, but does not seem to be widely appreciated. Indeed, the three types of symmetry breaking lead to *three* fundamental hypotheses of the physical–chemical origin of molecular chirality, which are experimentally distinguishable: We discuss these (and others) in the following section.

2.3 Communities of Belief and Hypotheses for Molecular Chirality

As discussed in detail by Quack (1989b), we find in the scientific literature the following fundamental hypotheses for molecular chirality (or dissymmetry):

1. the classical structural hypothesis according to van't Hoff (1887) and Cahn *et al.* (1956, 1966) (a type of spontaneous symmetry breaking);
2. the hypothesis of quantum mechanical de facto symmetry breaking following Hund (1927a,b);
3. the hypothesis of chirality induced by the environment (collisions or other perturbations) (Simonius 1978, Harris and Stodolsky 1981);
4. the hypothesis of a superselection rule (another type of spontaneous symmetry breaking) (Primas 1981, Pfeifer 1983, Amann 1991); and
5. the hypothesis of dominant de lege symmetry breaking because of molecular parity violation (Quack 1989b, 2002, Yamagata 1966, Rein 1974, Letokhov 1975).

We do not discuss details here but refer to Quack (1989b, 1999) for further discussion. The short summary of the current theoretical status would be, that, for molecules such as H_2O_2 in the gas phase, hypothesis (2) is appropriate, whereas for CHFClBr, alanine, and similar stable chiral molecules parity violation according to hypothesis (5) dominates over the tunneling relevant in hypothesis (2) (see the explicit calculations on Cl_2S_2 by Berger *et al.* (2001)). It is still not entirely clear under which circumstances hypotheses (3) and (4) might perhaps provide the most appropriate explanation. We have, however, pointed out that the questions can, in principle, be decided

by carefully designed experiments (Quack 1989b, 1993a, 1995b, 1999, 2004a), although the experiments are nontrivial and predict sometimes striking outcomes depending upon the hypothesis chosen, for instance, when unusual superposition states of enantiomers are considered (Quack 1995b).

Therefore, there remain some open questions, although we think that some of the questions have been resolved by now, at least theoretically, following the quantitative approaches described in Section 3. Today, one can find in larger audiences, almost always, a few proponents of every one of the "communities of belief"; thus, there remains cause for controversy, although the controversies are not usually made the subject of open debate. It is of historical interest that until our critical discussion in 1989 (Quack 1989b), the ambiguities in our understanding of the basis of molecular chirality were hardly appreciated and it remains of scientific interest that fundamental experiments for chiral molecules can be formulated, for which the outcome remains open even until today (Quack 1995b).

We describe this conceptually slightly complex situation, because very similar situations arise for the questions of biomolecular homochirality and irreversibility, which we discuss now.

2.4 Communities of Belief and Hypotheses on the Origin of Biomolecular Homochirality

The origin of biomolecular homochirality is one of the fundamental unsolved problems in the evolution of life, but hardly considered to be a topic of high-resolution spectroscopy. However, high-resolution spectroscopy of chiral molecules may help solving the problem and it is because of this that we discuss homochirality here.

The close relationship between chirality and the biochemistry of life was addressed by Pasteur, who discovered biomolecular homochirality (today expressed as the dominance of L-amino acids and D-sugars in the biopolymers of life). Indeed, Pasteur (1861) considered "dissymmetry" (today called *chirality*) to be the chemical signature of life. Since then, the selection of the actually observed enantiomers (e.g., L-amino acids) in living matter has been the subject of controversy (Frank *et al.* 2001). One has essentially the following main groups, which can be further subdivided in many variants (Quack 1999, 2002, 2006). We briefly mention here the several nomenclature systems that exist for enantiomers (older literature D and L, modern nomenclature R and S or P and M, the latter for axially chiral systems, and in physics often R and L; see Cahn *et al.* (1956, 1966), Mislow (1965), Nicolaou *et al.* (2001) for discussions of nomenclature problems).

1. The first hypothesis is the stochastic "all or nothing" selection of one enantiomer (D or L) in an appropriate nonlinear biochemical selection mechanism (Frank 1953, Eigen 1971, 1982, 1987, Eigen and Winkler 1975, Kuhn 1972, Bolli *et al.* 1997, Siegel 1998) or by an abiotic mechanism (for instance, crystallization) (Calvin 1969, Nicolis and Prigogine 1981, Bonner 1995). According to this (de facto or chance selection) hypothesis, only one enantiomer (either D or L) is selected in a given "evolution experiment", whereas in many different experiments both D and L appear with equal statistical probability.

2. There may be an external chiral influence inducing one type of chirality in a singular initial evolution step, which is later always propagated. There have been numerous different suggestions of this type, starting with the work of Pasteur and many later discussions (for instance, life could have been formed under the influence of circularly polarized light or on the surface of an L-quartz mineral). We refer to Quack (1999), Kavasmaneck and Bonner (1977), Kuhn and Waser (1983), Bonner (1988), Vester *et al.* (1959), Kleindienst and Wagnière (1998) for such hypotheses. These can be not only "de facto" but also "de lege", if one has the external influence, say, of parity-violating β-radioactivity.

3. One might have abiotic selection of an enantiomer de lege in a low-temperature phase transition under the influence of parity violation (Chela-Flores 1991, Salam 1991, 1992, 1995).

4. One might have preferred thermodynamic or kinetic selection in a mechanism that is asymmetric under the influence of parity violation de lege. In such a selection in many separate evolution experiments, one would obtain preferentially one type (say L-amino acids) (Yamagata 1966, Rein 1974, Janoschek 1991, Kondepudi and Nelson 1984a,b, 1985, Mason 1991a,b, MacDermott and Tranter 1989a,b).

Roughly speaking, all these can be classified in the two large classes of de facto ("chance") and de lege ("necessity") selection processes. There have been numerous heated debates, but very little firm evidence—theoretical or experimental. In our opinion, the question is completely open (Quack 1999, 2002) and not likely to be answered definitively in the near future. There have been claims of abiotic de lege selection in crystallization experiments (Szabo-Nagy and Keszthelyi 1999). It is not clear how plausible these are. In our opinion, two necessary conditions would have to be met in order to provide adequate scientific experimental proof for any of these proposals.

1. All possible counter-experiments to disprove the given hypothesis must be made in addition to the "positive" observation of a given outcome.
2. The detailed mechanism of the observed selection must be understood theoretically.

It will be difficult to meet these conditions, but it is true that, in principle, the question of which hypothesis applies could be resolved experimentally—it is not mere convention or "philosophy" (see Quack (1999, 2002) for more discussion on this). It might be, by the way, that under different quantitative conditions, different hypotheses might be applicable, similar to the discussion of molecular chirality in the previous section, but much more complex.

We should draw specific attention to the possible experimental tests of the de facto versus the de lege explanations of homochirality. Provided that some day we can, in a reproducible way, generate life in the test tube, then the de lege hypothesis predicts preferential generation of "L-amino acid life" (perhaps with close to 100% probability), whereas the de facto hypothesis predicts 50% L : 50% D in many separate evolution experiments, apart from statistical fluctuations. This important simple distinction is missed in many discussions of the topic. Short of being able to repeat evolution at present, one can also turn to astrobiological observation: If we were to find simple life forms on Mars (or elsewhere), which were made of D-amino acid proteins, then this would be strong evidence against the "de lege hypothesis". If we were to find L-amino acid life on Mars, this would be weaker evidence, as life could have possibly migrated among the planets, and also ambiguous, because two observations even without migration of life or chiral substances would be hardly significant statistically.

Finally, we also address the separate questions of maintaining L-amino acid life over billions of years in evolution: this could be explained easily by the laws of inheritance and mechanisms of biological "repair", which we know from traditional biology: It is *not* difficult to explain.

The question of the selection of biological homochirality has generated considerable activity (and literature) in the communities of chemists and biologists and we cannot give adequate review of this in this article, which has different goals. Some remarks might be useful to conclude this section.

First, it should be understood that biological homochirality does not imply the absence of the "nonnatural" D-amino acids in living beings. These arise, in fact, abundantly at several levels either by partial racemization (for instance, of aspartic acid in the teeth) or by use in different functions (e.g., D-alanine in cell membranes). "Homochirality" implies preference of L-amino acids (and D-sugars) only concerning their use for a particular function in the biopolymers (for instance, in proteins or in DNA).

As a second remark, we might quote from Vladimir Prelog's Nobel Lecture (12 December 1975):

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.

(Prelog 1975)

We can say today, in contrast to this statement, that an external bias need not be involved, it can be an internal bias (from parity violation) although it need not be.

Finally, we conclude with a slightly less serious observation, which has entered the "newspaper literature", even rather widely (Leopold 1997, Quack 1999). There have been apparently well-confirmed findings that, on the Dutch coast, one finds an excess of left shoes and, on the Scottish coast, more of right shoes, presumably by selection in the streams of the sea. If one assumes following Quack (1999) that a similar selection applies to swimming L-amino acid living (human) beings and to R-amino acid (human) beings, then the clearly better feeding on the French and Dutch coast as compared to the Scottish coast provides a de facto hypothesis for L-amino acids (human beings) selection (of the general class 2 above).

2.5 Communities of Belief or Hypotheses on Irreversibility and the Origin of the Second Law

After our discussion of the comparatively simple concepts of P-symmetry breaking related to molecular chirality, we can now, by analogy, discuss the kind of T-symmetry breaking (of time-reversal symmetry), which ultimately is at the origin of irreversibility and the second law of thermodynamics (Quack 1999, 1995b, 2004a, 2006). Again, we find several hypotheses that might be broadly classified as de facto (1,3) or de lege (2,4,5,6) symmetry breakings.

1. Irreversibility as de facto symmetry breaking is the standard statistical interpretation of the origin of the second law of thermodynamics following Boltzmann (1896a,b, 1897, Lebowitz 1999, Peierls 1979).

There have been a number of detailed illustrations of this hypothesis (Ehrenfest and Ehrenfest 1907, 1911, Kohlrausch and Schrödinger 1926, Orban and Bellemans 1967, Eigen and Winkler 1975, Quack 1981, 1982) and a special variant of this hypothesis uses information theory, which might also be classified as a separate hypothesis ("subjective" interpretation of statistical mechanics).

2. One might rigorously adhere to the second law as an observed empirical, macroscopic law (Clausius 1865, Planck 1910).

3. One can introduce irreversibility through interaction with the environment similar to hypothesis (3) on chirality. In connection with introducing a reduced density matrix description of the dynamics of a subsystem, this is a common textbook trick to get the desired results on irreversibility.

4. One might add irreversible damping terms in the equations for the mechanical laws (Prigogine 1980, Prigogine and Stengers 1981). Sometimes, a connection with the quantum mechanical measurement process (Grigolini 1993) or with gravitation (Hawking and Penrose 1996) is made.

5. One possibility is also to invoke de lege violation of time-reversal symmetry as observed in K-meson decay (Adler 1995).

6. Finally, in a generalized sense, one might speculate about a possible *CPT* symmetry violation as the most fundamental source of irreversibility (Quack 1993b, 1994b, 1995b,c, 1999, 2003, 2004a,b).

Debates between proponents of these various hypotheses have sometimes been rather spiteful (Lebowitz 1999, Pagels 1985, Prigogine 1980, Prigogine and Stengers 1981, 1984), probably because of the metaphysical touch that the "arrow of time" has for all human beings, connected to the inevitable transitoriness of human existence. In this context, Prigogine and Stengers (1981) cite a letter of Einstein as a proponent of hypothesis (1) (Quack 1999). We can summarize again that while various hypotheses can provide self-consistent "explanations" of the observed irreversibility in chemistry and physics, some of the explanations contradict each other and the question which one applies remains open. One key question is whether the second law of thermodynamics finds its origin in a de facto or de lege symmetry breaking (Quack 1995b,c,d, 1999). Similar to the question of molecular chirality, this might be a quantitative question. In molecular chirality, the relative magnitudes of tunneling splittings and electroweak parity-violating potentials were shown to be important (Section 2.2). For irreversibility, the quantitative importance of de lege T-violation (due to the electroweak interaction) in molecules could be considered relative to de facto symmetry-breaking

dynamics. However, unlike in the case of parity violation, there is no quantitative theory of de lege T-violation for molecules yet.

2.6 Violation of the Pauli Principle and the Indistinguishability of Identical Particles

For reasons of completeness, we mention this point here, although it is quite speculative and there is really very little evidence in favor of a possible de lege symmetry breaking in this case (de facto symmetry breakings are common). We refer to Quack (1999) and the references cited there for further discussion and provide just a brief conceptual summary here.

The Pauli principle was originally formulated by Pauli (1925) as an exclusion principle for two electrons not to occupy the same "spin-orbital" in modern quantum chemical language. This was necessary to explain certain properties of atomic spectra. From a more general point of view, it is related to invariance (6) at the beginning of this section concerning the invariance of the hamiltonian under permutation of the indices of "identical" particles.

This invariance results in the corresponding permutation group, the "symmetric group" S_n of permutations of n identical particles in the molecule to be a part of the symmetry group of the hamiltonian (Wigner 1959, Hamermesh 1962, Longuet-Higgins 1963, Quack 1977, 1983a). As there are, in general, more than one kind of identical particles (electrons and nuclei in the case of molecules), the direct product group represents the corresponding group for all kinds of particles:

$$S_{n_1, n_2, n_3 \dots} = \prod_{i=1}^{N} S_{n_i} \qquad (21)$$

Here N is the total number of different particles in the molecule (for instance, $N = 3$ for methane $^{12}CH_4$ or benzene $^{12}C_6H_6$, i.e., electrons, e^-, protons H^+, and carbon nuclei $^{12}_6C^{6+}$) and n_1, n_2, n_3, etc. are the numbers of identical particles in each class (10 electrons, 4 protons, 1 carbon nucleus for CH_4, etc.).

The generalized form of the Pauli principle, which in this form seems to have been formulated by Heisenberg, but is generally also called either simply *Pauli principle* (without "exclusion") or *generalized Pauli principle*, states that the total wavefunction of the system under consideration (the molecule) must transform under the group operations Q_j as the irreducible representation whose characters χ_{Q_j} under Q_j are given by equation (22).

$$\chi_{Q_j} = \prod_{i=1}^{N_F} (-1)^{P_{iQ_j}} \qquad (22)$$

P_{iQ_j} is the parity of the permutation of the ith kind of fermions (particles with half-odd-integer spin, with total number N_F) in the group operation Q_j. Obviously one has $N = N_F + N_B$, where N_B is the total number of bosons (particles with integer spin). If Q_j permutes only bosons, one has $\chi_{Q_j} = +1$. The equation makes use of the "parity of a permutation" (not related to space inversion parity), being uniquely defined for every permutation Q_j. The parity is "even" if Q_j can be written as an even number of "transpositions" (nm) exchanging indices n and m of just two identical particles and "odd" if Q_j is represented by an odd number of such transpositions. Thus, $\chi_{Q_j} = +1$ if the permutation of fermions has even parity and $\chi_{Q_j} = -1$ if the permutation of fermions has odd parity (for one type of particles and similarly generalized to more kinds). For instance for methane $^{12}CH_4$, one has $N_F = 2$ fermion types (electrons and protons) and one boson $N_B = 1(^{12}_6C^{6+})$. Thus, one would have to consider the parity of the permutation of the four protons in CH_4, for instance. One disregards here the individual protons within the carbon nucleus, as the nucleus is considered as "elementary" in this context, not exchanging any subnuclear particles with the external world, because of the high energy needed for such processes (hence "not feasible").

It may be useful to note here the particular nature of the generalized Pauli principle as a fundamental (empirical) natural law beyond the symmetry and conservation law defined by the invariance number (6) of the hamiltonian. This invariance can be stated as

$$\hat{H}\hat{Q}_j = \hat{Q}_j\hat{H} \qquad (23)$$

and the general quantum mechanical result is then that the quantum mechanical states of the system may be assigned, under certain conditions, a good quantum number corresponding to the irreducible representation Γ_k of the group $S_{n_1, n_2, n_3 \dots}$ and, if so, this quantum number is a conserved quantity, a constant of the motion, very similar to parity conservation under space inversion. The conservation law is related to the exchange of two identical particles being fundamentally nonobservable (the state after exchange cannot be distinguished from the state before exchange). The quantum mechanics of identical particles, however, would be perfectly consistent with each of the many irreducible representations Γ_k being allowed for a given state $|\Psi\rangle$, the only constraint being the conservation law for Γ_k in the course of evolution.

The generalized Pauli principle, thus, is a statement that goes beyond this, in that only *one* Γ_k of the many existing for the group $S_{n_1, n_2, n_3 \dots}$ occurs in nature, the "Pauli-allowed" Γ_k defined by the χ_{Q_j} in equation (22). This can

be taken as an additional empirical natural law *beyond* the conservation law resulting from the symmetry. This additional law is consistent with the conservation law: transitions from "Pauli-allowed" states to "Pauli disallowed" states are not observed, i.e., the initial Γ_k is conserved. One says figuratively that the wavefunction always remains "totally antisymmetric under exchange of fermions" and "totally symmetric under exchange of bosons" (this property being defined by equation (22) for $\chi_{Q_j}(\Gamma_k)$ for the Pauli-allowed Γ_k).

After this introductory discussion, we now address the question of the hypothetical violation of the generalized Pauli principle. This would result in the transition to Pauli-forbidden states, in one version of the symmetry breaking. We should stress here that, in contrast to parity violation, there is currently no serious theoretical or empirical basis for such a possibility, which remains purely speculative (and perhaps simply nonsensical).

However, from a purely empirical point of view one might, for instance, assume that some primordial electrons or nuclei either initially or after some time of aging are "distinguishable" from the others. This would result in spectroscopic consequences, for instance, a carbon atom could hold this extra "distinguishable" electron in a 1 s orbital (with corresponding changes for total energy and spectroscopic transitions) or in a ($_6^{12}$C ^{16}O$_2$) molecule, the two oxygen nuclei would be distinguishable, and they would behave as two different isotopes of identical mass, say ^{16A}O and ^{16B}O, with the consequence that the rotational states with odd J would appear in the electronic and vibrational ground state of CO$_2$, where they are normally forbidden by the generalized Pauli principle. Particles would, thus, exist as Pauli-type P particles and non-Pauli-type Q-particles. Actually, there is no evidence for such Q-particles, but, on the other hand, not too many stringent tests have been made. For electrons, observations indicate that the possible number of Q-atoms must be exceedingly small considering the small noise level in many atomic spectra.

For heavier particles, there are fewer stringent tests, but we have reported a limit of ca 10^{-7} for the fraction for "Pauli-contradicting" ^{16}O nuclei in CO$_2$ (Quack 1993b) and there have been a few subsequent reports (Mazzotti *et al.* 2001). This would imply a limit of de lege violation of the Pauli principle for those tests somewhere below 10^{-8}–10^{-11}. It may be noted that one could advance some theoretical arguments against such speculative de lege violations of the Pauli principle, but we do not discuss this rather speculative topic.

We should note that the "de facto" breaking of the exchange symmetry is common. Labeling two molecules with different internal quantum states distinguishes the molecules (even their mass would be slightly different by

$\Delta m = \Delta E_{jk}/c^2$). In the language of particle physics, two such quantum states are different "particles". In a macroscopic sample of larger polyatomic molecules at higher temperatures, the total number of thermally populated quantum states can greatly exceed the total number of particles, which thus could become "distinguishable". The same is true for mesoscopic clusters or macroscopic bodies, which in this sense are all distinguishable. However, this distinguishability disappears for molecular beams at very low T or in the field of very cold samples with "Bose–Einstein" condensation.

We may conclude here that the ideal experiment in molecular spectroscopy would be on molecules in selected, identical quantum states. Such experiments correspond to the ideal quantum mechanical experiment on a sample of "single" identical molecules in the quantum mechanical sense (this is different from the field of "single-molecule spectroscopy" in condensed samples, which should be better called *single chromophores in different environments*).

In summary, while one can formulate the phenomenon of hypothetical de lege violation of Pauli symmetry, there is no experimental or theoretical basis whatsoever for this including, in particular, a large body of spectroscopic evidence. On the other hand, de facto breaking of this symmetry is common.

2.7 Summary

We have shown that the situation of our understanding of molecular chirality, biomolecular homochirality, and irreversibility has close parallels for all three cases, the understanding of molecular chirality being presumably most advanced. There is also the related symmetry C (number (7) of the invariances in Section 2.1) to which we return in Section 8 on *CP* and *CPT* symmetry breakings.

In all cases, one key question concerns the opposition of the hypotheses of de facto symmetry breaking versus de lege symmetry breaking. This question is not simply a qualitative one, but may depend on quantitative aspects of the problem or the relative magnitude of various parameters governing the dynamics. Its investigation is thus open to quantitative theory and experiment. As we have discussed in some detail for the case of molecular chirality and parity violation, the open questions concerning de facto and de lege symmetry breakings can be answered for a given molecule, in principle; in general, it is a *quantitative question* relating to the magnitude of certain molecular properties. We now address the theory of this particularly important example of molecular parity violation in some more quantitative detail.

3 THE QUANTITATIVE THEORY OF PARITY VIOLATION IN ELECTROWEAK QUANTUM CHEMISTRY

Si les principes immédiats de la vie immédiate sont dissymétriques, c'est que, à leur élaboration, président des forces cosmiques dissymétriques, c'est là, suivant moi, un des liens entre la vie à la surface de la terre et le cosmos, c'est-à-dire l'ensemble des forces répandues dans l'univers.
(Pasteur 1861)

Free English translation as cited by Quack (1989b):

If the principles of life are chiral, then because of chiral cosmic forces at their origin; this I think, is one of the links between life on earth and the cosmos or the totality of forces in the universe.

3.1 Introductory Observations and a Change of Order of Magnitude

The theory of molecular parity violation provides an excellent example to illustrate both the conceptual foundations and one of the most active current areas of fundamental symmetry violations in relation to molecular spectroscopy. Early quantitative calculations were carried out by Hegström *et al.* (1980). As we have pointed out in the introduction, there was a significant change in our quantitative understanding of parity-violating potentials calculated from electroweak quantum chemistry in 1995 (Bakasov *et al.* 1996, 1998a). One starting point for this was our observation (Bakasov *et al.* 1996) that there were surprisingly large deviations of the older theoretical calculations from simple estimates following an equation proposed by Zel'dovich and coworkers:

$$\frac{\Delta_{\mathrm{pv}}E}{h} \simeq 10^4 \frac{Z^5}{100^5} \ \mathrm{Hz} \tag{24}$$

This by itself was yet not such a strong argument against the older results, given the complexity of the problem and the many possibilities for the compensation of contributions leading to lower values of parity violation than expected from simple estimates. Indeed, we could rationalize such compensations in part by analyzing the calculated parity-violating potentials in terms of a trace of a tensor (Bakasov *et al.* 1996, 1998a) under certain conditions; thus,

$$E_{\mathrm{pv}} = E_{\mathrm{pv}}^{XX} + E_{\mathrm{pv}}^{YY} + E_{\mathrm{pv}}^{ZZ} \tag{25}$$

As the three components frequently differ in sign, this explains a certain lowering below the maximum possible values that might be realized for the individual components. However, a more serious observation is related to the restricted Hartree–Fock (RHF) wave functions used in the older calculation being really quite inappropriate. Indeed, the simplest improvement of using excited state configuration interaction singles (CIS) wavefunctions already introduced an increase in parity, violating potentials by about 2 orders of magnitude for H_2O_2 and similar prototypical molecules (Bakasov *et al.* 1996, 1998a, 1999), a result later corroborated by our much improved multiconfiguration linear response approach (MC-LR) approach (Berger and Quack 2000b) and further confirmed independently by several other groups as well as in further calculations by our group (Lazzeretti and Zanasi 1997, Zanasi and Lazzeretti 1998, Laerdahl and Schwerdtfeger 1999, Gottselig *et al.* 2001, Berger *et al.* 2001, Quack and Stohner 2000a, Berger and Quack 2000a, Berger *et al.* 2000, Laerdahl *et al.* 2000a,b, Hennum *et al.* 2002, Quack and Stohner 2001).

Here, we provide a brief outline of the new theory following Bakasov *et al.* (1996, 1998a), Bakasov and Quack (1999), and Berger and Quack (2000b), in order to also provide a basic understanding of the limitations and omissions in current approaches (see also Quack and Stohner (2005) and further references cited therein).

3.2 Basic Theory

In the framework of the standard model, the relevant parity-violating interaction is mediated by the electrically neutral Z^0 bosons (Table 2). At molecular energies, which are much lower than the energy corresponding to mc^2 of the Z^0-boson (91.19 GeV), the contribution of Z^0 becomes virtual (Bogoljubov and Shirkov 1983, 1980). This leads at low energies to the hamiltonian density of the fully relativistic parity-violating electron–neutron interaction of the following form (we set $\hbar \equiv c \equiv 1$ to simplify the notation here):

$$\hat{H}^{(e-n)}(x) = \frac{G_{\mathrm{F}}}{2\sqrt{2}} g_A (1 - 4\sin^2\Theta_{\mathrm{w}}) j_\mu[\psi^{(el)}(x)]$$
$$\times j_{(\mathrm{ax})}^\mu[\psi^{(n)}(x)] + \frac{G_{\mathrm{F}}}{2\sqrt{2}} j_\mu[\psi^{(n)}(x)]$$
$$\times j_{(\mathrm{ax})}^\mu[\psi^{(el)}(x)] \tag{26}$$

with $j_{(\mathrm{ax})}^\mu[\psi(x)]$ involving the familiar γ-matrices (Bogoljubov and Shirkov 1980).

$$j_{(\mathrm{ax})}^\mu[\psi(x)] \overset{\mathrm{def}}{=} : \Psi^+(x)\gamma^0\gamma^\mu\gamma^5\Psi(x) \tag{27}$$

The γ^5 matrix converts the four-vector $j^\mu[\psi(x)]$ into the axial vector $j_{(\mathrm{ax})}^\mu[\psi(x)]$. Similar expressions are obtained

for the electron–proton and the electron–electron interaction (Bakasov *et al.* 1998a,b). The electron–neutron and electron–proton interactions could be further derived from the fundamental electron–quark interactions.

In principle, as pointed out by Bakasov *et al.* (1998a) and Bakasov and Quack (1999), one can use these relativistic equations as a starting point for the theory. Relativistic theories of this type have been worked out at different levels of approximation, for instance, by the group of Barra *et al.* (Hückel-type) (Barra *et al.* 1986, 1987, 1988, Wiesenfeld 1988) and four-component relativistic theory by Schwerdtfeger and coworkers (Laerdahl and Schwerdtfeger 1999, Laerdahl *et al.* 2000a,b). Omitting the two small components of the bispinors $\Psi^n(x)$ and $\Psi^{el}(x)$ and thus converting from four-component bispinors to two-component spinors following Bakasov *et al.* (1998a,b) and Bouchiat and Bouchiat (1974, 1975), one obtains

$$
\begin{aligned}
\hat{H}^{(e-n)}(\boldsymbol{x}) = \frac{G_{\mathrm{F}}}{4\sqrt{2}\mu c}[& -\psi^{\dagger(n)}(\boldsymbol{x})\psi^{(n)}(\boldsymbol{x})\{\psi^{\dagger(el)}(\boldsymbol{x}) \\
& \times \boldsymbol{\sigma}(\boldsymbol{P}\psi^{(el)}(\boldsymbol{x})) + (\boldsymbol{P}^*\psi^{\dagger(el)}(\boldsymbol{x}))\boldsymbol{\sigma}\psi^{(el)}(\boldsymbol{x})\} \\
& + \mathrm{i}g_A(1 - 4\sin^2\Theta_w)\boldsymbol{P}\left(\psi^{\dagger(el)}(\boldsymbol{x})\boldsymbol{\sigma}\psi^{(el)}(\boldsymbol{x})\right. \\
& \left.\times \psi^{\dagger(n)}(\boldsymbol{x})\right)\boldsymbol{\sigma}\psi^{(n)}(\boldsymbol{x})]
\end{aligned}
\tag{28}
$$

G_{F} is the Fermi constant, $\boldsymbol{P}$ the momentum operator, $\boldsymbol{\sigma}$ the doubled spin operator that has as components the familiar 2×2 Pauli matrices, $\boldsymbol{x}$ the spatial coordinate set, and μ the reduced mass of the electron. The last term in equation (28) is taken to be small because of the factor $(1 - 4\sin^2\Theta_{\mathrm{w}}) \simeq 0.08$ and because of the dependence on neutron (and similarly proton) spin with the tendency of spin compensation in nuclei. The form factor g_A (from the strong interaction of the neutron) can be taken as 1.25 (Bakasov *et al.* 1998a).

Finally, replacing the neutron density by a delta function because of the contact-like nature of the very short-range weak interaction

$$
\psi^{\dagger(n)}(x)\psi^{(n)}(x) \simeq \delta^3(x - x^{(n)})
\tag{29}
$$

one obtains a Hamilton operator for the electron–neutron interaction

$$
\hat{H}^{(e-n)} = -\frac{G_{\mathrm{F}}}{4\mu c\sqrt{2}}(\boldsymbol{P}\boldsymbol{\sigma}\delta^3(\boldsymbol{x} - \boldsymbol{x}^n) + \delta^3(\boldsymbol{x} - \boldsymbol{x}^n)\boldsymbol{P}\boldsymbol{\sigma})
\tag{30}
$$

For the electron–proton interaction, the hamiltonian is similarly

$$
\begin{aligned}
\hat{H}^{(e-p)} = -\frac{G_{\mathrm{F}}}{4\mu c\sqrt{2}}(1 - 4\sin^2\Theta_{\mathrm{W}}) \cdot (&\boldsymbol{P}\boldsymbol{\sigma}\delta^3(\boldsymbol{x} - \boldsymbol{x}^{(p)}) \\
& + \delta^3(\boldsymbol{x} - \boldsymbol{x}^{(p)})\boldsymbol{P}\boldsymbol{\sigma})
\end{aligned}
\tag{31}
$$

Collecting the terms for neutrons and protons together and defining an electroweak charge Q_a of the nucleus a with charge number Z_a and neutron number N_a

$$
Q_a = Z_a(1 - 4\sin^2\Theta_{\mathrm{W}}) - N_a
\tag{32}
$$

one obtains an effective electron–nucleus interaction:

$$
\begin{aligned}
\hat{H}_a^{(e-\mathrm{nucleus})} = -\frac{G_{\mathrm{F}}}{4\mu c\sqrt{2}}Q_a(&\boldsymbol{P}\boldsymbol{\sigma}\delta^3(\boldsymbol{x} - \boldsymbol{x}^{(\mathrm{nucleus})}) \\
& + \delta^3(\boldsymbol{x} - \boldsymbol{x}^{(\mathrm{nucleus})})\boldsymbol{P}\boldsymbol{\sigma})
\end{aligned}
\tag{33}
$$

This further approximation of representing the whole nucleus as a point particle with position $x^{(\mathrm{nucleus})}$ can be avoided, if one knows and inserts explicitly the proton and neutron positions and distributions in the ground state of the nucleus considered. In addition to the electron–nucleus interaction, one should consider also the electron–electron interaction

$$
\begin{aligned}
\hat{H}^{(e-e)} = -\frac{G_{\mathrm{F}}}{2\mu c\sqrt{2}}(&1 - 4\sin^2\Theta_{\mathrm{W}}) \\
& \cdot \left(\left\{\delta^3(\boldsymbol{x}^{(1)}-\boldsymbol{x}^{(2)}), (\boldsymbol{\sigma}^{(1)}-\boldsymbol{\sigma}^{(2)}) \cdot (\boldsymbol{P}^{(1)}-\boldsymbol{P}^{(2)})\right\}_+ \right. \\
& \left. + \mathrm{i}[\delta^3(\boldsymbol{x}^{(1)}-\boldsymbol{x}^{(2)}), (\boldsymbol{\sigma}^{(1)}\times\boldsymbol{\sigma}^{(2)}) \cdot (\boldsymbol{P}^{(1)}-\boldsymbol{P}^{(2)})]_-\right)
\end{aligned}
\tag{34}
$$

with obvious notation for the two electrons 1 and 2 in a pair and $\{,\}_+$ for the anticommutator and $[,]_-$ for the commutator.

The electron–electron contribution to the effective parity-violating potential is considered to be small (Bakasov *et al.* 1998a), below 1% of the other contributions, because of the small prefactor and the lack of a corresponding enhancement with Q_a. Thus, this term is usually neglected, although one must remember that it really consists of a sum over many electron pairs and not much is known about the actual compensation, which is usually taken for granted. Assembling all terms together and introducing the electron spin $\hat{s}$ (with dimension) together with linear momentum $\hat{p}$, the electron mass m_{e}, and consistent SI units throughout, finally one obtains for the electron–nucleus part of the hamiltonian the approximation:

$$\hat{H}_{\mathrm{pv}}^{(e-\mathrm{nucl})} = \frac{\pi G_{\mathrm{F}}}{m_{\mathrm{e}} h c \sqrt{2}} \sum_{i=1}^{n} \sum_{a=1}^{N} Q_a \{\hat{s}_i \hat{p}_i \delta^3(r_i - r_a)$$
$$+ \delta^3(\boldsymbol{r}_i - r_a) \hat{s}_i \hat{p}_i\} \qquad (35)$$

The sums extend over n electrons and N nuclei. This operator can be evaluated in different ways. The simple perturbative sum-over-states expression in the Breit–Pauli approximation for the spin–orbit interaction reads for the parity-violating potential:

$$E_{\mathrm{pv}} = 2\mathrm{Re} \left\{ \sum_n \frac{\langle \psi_0 | \hat{H}_{\mathrm{pv}}^{e-\mathrm{nucleus}} | \psi_n \rangle \langle \psi_n | \hat{H}_{\mathrm{SO}} | \psi_0 \rangle}{E_0 - E_n} \right\} \quad (36)$$

The Breit–Pauli spin orbit hamiltonian $\hat{H}_{\mathrm{SO}}$ is as usual

$$\hat{H}_{\mathrm{SO}} = \frac{\alpha^2}{2} \left[\sum_{i=1}^{n} \sum_{a=1}^{N} Z_a \frac{\hat{l}_{i,a} \hat{s}_i}{|\boldsymbol{r}_a - \boldsymbol{r}_i|^3} + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{\hat{l}_{i,j}(\hat{s}_i + 2\hat{s}_j)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^3} \right]$$
$$(37)$$

where $\hat{l}_{i,k}$ refers to the orbital angular momentum vector of electron i with respect to particle number k (we omit the vector symbols on top of the corresponding operators to simplify the notation).

The sum-over-states expression (36) essentially mixes the electronic ground-state singlet function with excited-state triplets in order to obtain a parity-violating energy expectation value for the true (mixed singlet–triplet) ground state (for a pure singlet state this would vanish). However, the sum-over-states expression, when used explicitly, converges slowly for larger molecules. It is well known in the framework of propagator methods (Linderberg and Öhrn 1973, Vahtras *et al.* 1992) that the expression in equation (36) is equivalent to the expression from response theory in equation (38) (Berger and Quack 2000b)

$$E_{\mathrm{pv}} = \langle\langle \hat{H}_{\mathrm{pv}}; \hat{H}_{\mathrm{SO}} \rangle\rangle_{\omega=0} = \langle\langle \hat{H}_{\mathrm{SO}}; \hat{H}_{\mathrm{pv}} \rangle\rangle_{\omega=0} \qquad (38)$$

One can say that the parity-violating potential E_{pv} is the response of $\langle \psi_0 | \hat{H}_{\mathrm{pv}} | \psi_0 \rangle$ to the static ($\omega = 0$) perturbation $\hat{H}_{\mathrm{SO}}$ or vice versa. This MC-LR approach to molecular parity violation was derived by Berger and Quack (2000b), to which we refer for details. It shows much better convergence properties than when evaluating equation (36) directly.

We have given this brief summary of the theory developed in more detail in Bakasov *et al.* (1996, 1998a) and Berger and Quack (2000b) in order to show all the steps of the many successive approximations made. Each of these approximations can be removed, when the necessity arises. For instance, if one wishes to describe explicitly hyperfine structure components or NMR experiments, one must not neglect the spin-dependent terms and therefore one has to add to the operator of equation (35) a further operator given by equation (39) (Berger and Quack 2000b):

$$\hat{H}_{\mathrm{pv2}}^{(e-\mathrm{nucl})} = \frac{\pi G_{\mathrm{F}}}{m_{\mathrm{e}} h c \sqrt{2}} \sum_{i=1}^{n} \left[\sum_{a=1}^{N} (-\lambda_a)(1 - 4\sin^2 \Theta_{\mathrm{W}}) \right.$$
$$\times \{\hat{p}_i \hat{I}_a, \delta^3(\boldsymbol{r}_i - \boldsymbol{r}_a)\}_+ + (2\mathrm{i}\lambda_a)(1 - 4\sin^2 \Theta_{\mathrm{W}})$$
$$\left. \times (\hat{s}_i \times \hat{I}_a)[\hat{p}_i, \delta^3(\boldsymbol{r}_i - \boldsymbol{r}_a)] \right] \qquad (39)$$

In addition, sometimes the approximate "theoretical" value of the Weinberg parameter $\sin^2 \Theta_W = 0.25$ is taken, which simplifies the expressions with $(1 - 4\sin^2 \Theta_{\mathrm{W}}) = 0.0$. However, more generally, the accurate experimental parameter will be used with $(1 - 4\sin^2 \Theta_{\mathrm{W}}) = 0.07$, which may further depend on the energy range considered; λ_a is a parameter close to unity. Furthermore, one might use the semirelativistic expressions using the Breit–Pauli spin–orbit operator (37) and the operators for parity violation in equations (35) and (39). This should be an excellent approximation for nuclei with maximum charge number $Z_a = 20$ and acceptable up to $Z_a = 40$. However, for more highly charged nuclei, one must return to the relativistic equation (26) and from there derive various approximate relativistic expressions, for instance, in the four-component Dirac–Fock framework (Laerdahl and Schwerdtfeger 1999) or within two-component relativistic approximations (Berger and van Wüllen 2005). On the other hand, one might also use more approximate treatments such as density functional theory (Schwerdtfeger *et al.* 2005). For general aspects of relativistic quantum chemistry *see* Mastalerz and Reiher 2011: **Relativistic Electronic Structure Theory for Molecular Spectroscopy**, this handbook and Reiher and Wolf (2009).

One might also consider investigating explicit "nonvirtual" couplings going beyond the use of equation (26) as starting point or one might include the electron–electron parity-violating interaction in equation (34) in the calculations. Another obvious improvement would result from replacing the point nucleus approximation of equation (30) by an extended nucleus with nucleon distributions from accurate nuclear structure theory and experiment. Where one wishes to invest effort in removing some of the approximations used depends upon one's intuition whether large improvements are to be expected. At present, it seems unlikely that the order of magnitude improvements will again be found in the future, although only experiment can give a definitive answer. Currently, we feel that the largest chance for improvement resides in appropriate electronic wavefunctions that are highly accurate, in particular, near the nuclei and in further effects from molecular structure and motion to be discussed now.

3.3 Parity-violating Potential Hypersurfaces and Vibrational Effects

Two qualitative aspects of the structure of parity-violating potentials deserve mention. First, similar to the parity-conserving electronic potential, the parity-violating potentials are a function of all $3N - 6$ internal nuclear degrees of freedom in the molecule. Thus, the parity-violating potentials E_{pv} defined by equation (36) or (38) define a parity-violating potential hypersurface:

$$E_{pv} = V_{pv}(q_1, q_2, q_3, \ldots, q_{3N-6}) \tag{40}$$

While isolated distortions or individual coordinate displacements have been considered for some time in such calculations (see Figure 4 for instance), the true multidimensional aspects have been considered only more recently (Quack and Stohner 2000a,b, 2001, 2003, Bakasov *et al.* 2004). The spectroscopically observable parity-violating energy differences $\Delta_{pv}E$ have to be computed as appropriate expectation values of the parity-violating potential in equation (40) for the multidimensional rovibrational state with anharmonically coupled vibrations. This leads to sizable effects as was shown recently (Quack and Stohner 2003). However, we know from our work in rovibrational spectroscopy and dynamics of polyatomic molecules (Quack 1990) that this problem can be handled accurately for not too complex molecules (Beil *et al.* 1994, Bauder *et al.* 1997, Hollenstein *et al.* 1997, Quack 1995b, Kuhn *et al.* 1999, Fehrensen *et al.* 1999b, Luckhaus and Quack 2001) and a similar statement applies to the other important dynamical problem—tunneling (Section 3.4).

The second general aspect of the parity-violating potential arises from the structure of the hamiltonian in equation (35). Because of the contact-like interaction between electrons and nuclei, the parity-violating potential can be written as a sum of contributions from the individual nuclei:

$$V_{pv}(q_1, q_2, q_3 \cdots q_{3N-6}) = \sum_{a=1}^{N} V_{pv}^a(q_1, q_2, q_3 \cdots q_{3N-6}) \tag{41}$$

Because of the approximate Z^5 scaling (Bakasov *et al.* 2004), this allows for an easy analysis of calculations and also some rough estimates. Because the electronic wavefunction generally depends upon the coordinates $(q_1, q_2, q_3 \cdots q_{3N-6})$ in a very complex manner, there are, however, no really simple and generally accurate estimates to be expected. However, one can derive certain sets of rules for special cases (Berger *et al.* 2003b). One can also derive simplified approximate expressions of the scaling,

with an effective nuclear charge Z_{eff} of $\Delta_{pv}E$

$$\frac{\Delta_{pv}E}{h} = f_{geo}(10^4) \left(\frac{Z_{eff}}{100} \right)^5 \text{ Hz} \tag{42}$$

with a geometry dependent of f_{geo} (M. Quack unpublished, cited in Quack *et al.* (2008)).

3.4 The Interplay of Tunneling Dynamics and Parity Violation

From our discussion in Section 2.2, the important role of tunneling dynamics for parity violation is obvious. Indeed, in spite of being a benchmark molecule for calculations on parity violation, H_2O_2 is not a useful molecule for its experimental observation in the electronic ground state because of the very large tunneling splittings, satisfying equation (19). Only if condition (20) is satisfied can, we speak of a directly measurable, observable parity-violating energy difference $\Delta_{pv}E$ between enantiomers. It is, thus, necessary to at least calculate tunneling with sufficient accuracy to guarantee the inequality (20). More generally, accurate calculations for the multidimensional tunneling dynamics are desirable. Methods for this have been developed by our group including light- and heavy-atom tunneling (Fehrensen *et al.* 1999b, Berger *et al.* 2001). Table 6 provides a summary of results for simple H_2O_2-like molecules $X-Y-Y'-X'$. One can clearly see the transition from molecules like H_2O_2, where tunneling dominates over parity violation (equation 19), to molecules such as ClSSCl, where parity violation dominates completely (equation 20) with interesting intermediate cases (Gottselig *et al.* 2001, 2003, 2004) While accurate full dimensional tunneling calculations for larger polyatomic molecules are difficult, approximate treatments exist (Fehrensen *et al.* 1999a), which at least would allow us to verify the validity of equation (20), if applicable.

3.5 Isotopic Chirality and a New Isotope Effect

Recent investigations from our group have dealt with molecules that are chiral only by isotopic substitution, thus "isotopically chiral" (Berger *et al.* 2003a,b, 2005). Examples are the methanol isotopomers CHDTOH and molecules such as $PF^{35}Cl^{37}Cl$. While such molecules have been considered and even synthesized for some time (Quack 1989b, Arigoni and Eliel 1969), our work has provided insight into a fundamentally new isotope effect arising from the weak nuclear interaction.

Molecular isotope effects can arise from the following basic mechanisms (*see also* Hippler *et al.* 2011: **Mass and Isotope-selective Infrared Spectroscopy**, this handbook):

Table 6 Tuning tunneling splittings $|\Delta E_\pm|$ and parity violation (ΔE_{pv}^{el}) in a series of molecules (after Gottselig *et al.* (2004) and Quack *et al.* (2008)).

Molecule	$|\Delta E_{pv}^{el}|(hc)$ (cm^{-1})	$|\Delta E_\pm|(hc)$ (cm^{-1})	Reference
H_2O_2	4×10^{-14}	11	Berger and Quack 2000b[a]−[c]
D_2O_2	4×10^{-14}	2	Berger and Quack 2000b[b]
T_2O_2	4×10^{-14}	0.5	Quack and Willeke 2003
Cl_2O_2	6×10^{-13}	7×10^{-25}	Quack and Willeke 2006
HSOH	4×10^{-13}	2×10^{-3}	Quack and Willeke 2003
DSOD	4×10^{-13}	1×10^{-5}	Quack and Willeke 2003
TSOT	4×10^{-13}	3×10^{-7}	Quack and Willeke 2003
$HClOH^+$	8×10^{-13}	2×10^{-2}	Gottselig *et al.* 2004
$DClOD^+$	—[d]	2×10^{-4}	Gottselig *et al.* 2004
$TClOT^+$	—[d]	7×10^{-6}	Gottselig *et al.* 2004
H_2S_2	1×10^{-12}	2×10^{-6}	Gottselig *et al.* 2001
D_2S_2	1×10^{-12}	5×10^{-10}	Gottselig *et al.* 2001
T_2S_2	1×10^{-12}	1×10^{-12}	Gottselig *et al.* 2001
Cl_2S_2	1×10^{-12}	$\approx 10^{-76[e]}$	Berger *et al.* 2001
H_2Se_2	$2 \times 10^{-10[f]}$	1×10^{-6}	Gottselig *et al.* 2003
D_2Se_2	—[d]	3×10^{-10}	Gottselig *et al.* 2003
T_2Se_2	—[d]	4×10^{-13}	Gottselig *et al.* 2003
H_2Te_2	$3 \times 10^{-9[g]}$	3×10^{-8}	Gottselig *et al.* 2004
D_2Te_2	—[d]	1×10^{-12}	Gottselig *et al.* 2004
T_2Te_2	—[d]	3×10^{-16}	Gottselig *et al.* 2004

[a] Kuhn *et al.* 1999.
[b] Fehrensen *et al.* 1999b.
[c] Olson *et al.* 1988.
[d] Expected to be very similar to the corresponding hydrogen isotopomers.
[e] Extrapolated value.
[f] Calculated in Laerdahl and Schwerdtfeger (1999) for the P-structure ($r_{HSe} = 145$ pm, $\alpha_{HSeSe} = 92°$, and $\tau_{HSeSeH} = 90°$) and the corresponding M-structure.
[g] Calculated in Laerdahl and Schwerdtfeger (1999) 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 very approximate result by Wiesenfeld (1988) should be cited as well, giving $\Delta E_{pv} = 8 \times 10^{-10}$ cm^{-1} for the following structure ($r_{TeTe} = 271.2$ pm, $r_{HTe} = 165.8$ pm, $\alpha_{HTeTe} = 90°$, and $\tau_{HTeTeH} = 90°$).

1. Mass differences of the isotopes generating different rovibrational energy levels and also different translational motion, for instance, in effusion. This is very common (Quack 1990).

2. Different spins of different isotopes again provide a very common origin for isotope effects including isotopic NMR spectra such as in ^{13}C NMR spectroscopy (Ernst 1992).

3. Different symmetry properties of the molecular wave function for different isotopomers lead to different "Pauli principle" selection rules for spectroscopic levels and reaction dynamics (Quack 1977, 1983a). This type of isotope effect would exist without difference of spin and mass, for instance, for certain pairs of nuclear isomers of almost the same mass (or for exactly the same mass with the Pauli-contradicting Q-particles, see Section 2.6). While predicted some time ago (Quack 1977, 1983a), this isotope effect is certainly less commonly studied.

4. A new isotope effect arises from the different electroweak charge Q_a of different isotopes following equation (27). We have discussed that this leads to parity-violating energy difference $\Delta_{pv}E$ in molecules such as PF^{35}Cl^{37}Cl, which are expected to be on the order of about 10% of "normal" values and this is also borne out by quantitative calculations (Berger *et al.* 2005). This opens the route to the use of isotopically chiral molecules for experiments, as clearly the conditions for a measurable $\Delta_{pv}E$ will be frequently met.

Besides the potential application of this isotope effect (4) to measurements of molecular parity violation (Quack 1986, Gottselig and Quack 2005), the addition of a new molecular isotope effect to the ones already known and applied in spectroscopy and reaction dynamics (Hippler and Quack 2005, Hippler *et al.* 2011: **Mass and Isotope-selective Infrared Spectroscopy**, this handbook) is of quite general, fundamental interest (Berger *et al.* 2005). The molecular spectroscopy of this isotope effect follows the

same lines as other spectroscopic experiments on molecular parity violation, which we discuss in the following section.

4   SPECTROSCOPIC EXPERIMENTS ON THE DYNAMICS OF PARITY VIOLATION IN CHIRAL MOLECULES

The greatest inspiration is a challenge to attempt the impossible.

Albert A. Michelson

4.1   Summary of Experimental Schemes

Three basic types of spectroscopic experiments have been proposed in the past as realistic possibilities to detect molecular parity violation. In the first proposal by Letokhov and coworkers in 1975–1976 (Letokhov 1975, Kompanets *et al.* 1976), one tries to measure parity-violating frequency shifts $\Delta \nu_{pv} = \nu_R - \nu_S$ in spectra of R- and S-enantiomers (or in the physicist's notation R- and L-) molecules, as can be seen in Figure 7. Several experimental tests have been made according to this scheme in the infrared (IR) and microwave ranges (Letokhov 1975, Kompanets *et al.* 1976, Arimondo *et al.* 1977, Beil *et al.* 1994, Bauder *et al.* 1997, Daussy *et al.* 1999), but in agreement with theoretical predictions for the relative shifts $\Delta \nu_{pv}/\nu \simeq 10^{-16}$ for the fairly typical case of CHFClBr (Quack and Stohner 2000b),
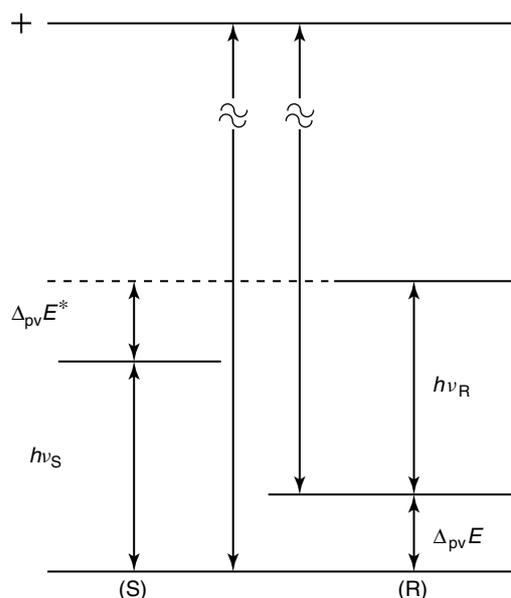

Figure 7   Scheme for energy levels and spectroscopic experiments for parity-violating energy differences $\Delta_{pv} E$. One notes that $\Delta \nu_{pv} = \nu_R - \nu_S = (\Delta_{pv} E^* - \Delta_{pv} E)/h$ in this scheme.

no positive results were obtained so far. In Doppler-limited experiments, one has

$$\frac{\Delta \nu_D}{\nu} \cong 7 \times 10^{-7} \sqrt{\frac{T/K}{m/u}} \qquad (43)$$

which defines the accuracy that can be achieved, if the maximum of the Doppler line is being determined, say, at the level of 1% of the linewidth. Effective temperatures T can be reduced in molecular beam or supersonic jet experiments (Bauder *et al.* 1997), as demonstrated by the Zürich group in IR and microwave spectra of CHFClBr. If one uses a practical lower limit of 1 K and a typical mass of 100 Da, one can achieve about $\Delta \nu/\nu \simeq 10^{-9}$ by this technique. Doppler-free experiments on bulk samples achieved an accuracy of 10^{-8} already decades ago (Arimondo *et al.* 1977), but not much better. Ultraprecise experiments on CHFClBr based on the first high-resolution analysis of the IR spectrum of this molecule by the Zürich group and following our proposal (Bauder *et al.* 1997) were able to do much better today on the order of $\Delta \nu/\nu \simeq 10^{-14}$ (Daussy 1999, Daussy *et al.* 1999, Crassous *et al.* 2003), thus going far beyond the Doppler limit, but it remains true that this approach is unable, even in principle, to provide the value of the ground-state energy difference $\Delta_{pv} E$ (see scheme in Figure 7); rather a difference of such differences $|\Delta_{pv} E^* - \Delta_{pv} E|$ is measured, if successful. Efforts along these lines continue currently in Paris in the IR range and in Zürich in the microwave range. It has been proposed to use NMR spectroscopy with this scheme (Barra *et al.* 1988), but such NMR experiments should be carried out in molecular beams in order to avoid ambiguities arising from environmental effects (Quack 2002).

The second approach proposes measuring time-dependent optical activity in molecules, where $\Delta_{pv} E$ and $\Delta E_\pm$ are of the same order of magnitude (Harris and Stodolsky 1978). Such experiments would provide parity-violating couplings by reference to tunneling splittings $\Delta E_\pm$ and thus would have to rely on a precise analysis of both tunneling and parity violation. In quantitative calculations, we have identified a few candidates for such an approach (see Gottselig *et al.* (2001) and Table 6 and references cited therein), but to our knowledge there exists no current experimental effort along these lines. An extension of the method to excited vibrational levels has been proposed (Quack 1989a,b), which would considerably increase the pool of possible molecules for such experiments, but retaining the difficulty of the insensitive experimental detection of optical activity.

In the third approach, we proposed to measure $\Delta_{pv} E$ directly as shown in Figure 7, by using transitions to achiral excited states with well-defined parity (labeled + in the scheme of Figure 7). This scheme can be realized either as a combination difference measurement in the frequency

domain (Quack 1989b) or as a time-dependent measurement (Quack 1986). We discuss in Section 4.2 in more detail the latter, which is one of the main experimental efforts in Zürich.

To the above mentioned schemes, two of which one can consider as quite realistic possibilities, which are currently actively pursued, one can add two further possibilities which have been mentioned in the literature, but which appear somewhat less realistic for actual experiments.

One of these (scheme number four if we continue the above count) would try to realize methods as they have been successfully used in the atomic spectroscopy of parity violation (Bouchiat and Bouchiat 1975, Bennett and Wieman 1999). In the simplest realization for molecules, one would measure the optical activity of achiral molecules, which arises from parity violation (Quack 2002, Sieben *et al.* 2003, MacDermott and Hegström 2004). The difficulty of such experiments arises from the small magnitude of the effect, which is likely to disappear in the noise from the ubiquitous chiral and thus optically active impurities.

Another scheme (fifth in our count) would try to measure the relevant spectroscopic splittings in level-crossing experiments on T_d-symmetrical molecules (CH_4, CF_4, see Pepper *et al.* (1995)) or also C_{3v} or O_h molecules (Quack *et al.* 2008). We discuss this scheme in a different context in Section 6.7 (Figure 15 therein). It would seem a difficult approach to molecular parity violation.

4.2 The Preparation and Time Evolution of Parity Isomers

Figure 8 shows the basic experimental scheme as originally outlined in Quack (1986, 1989b). A first laser selects an excited state of well-defined parity, for instance, in some electronically excited state (negative parity $(-)$ in the example of Figure 8, see also Figure 7, where a state of positive parity is used as an example).

A second pulse selects a positive parity in the chiral electronic ground state because of the electric dipole selection rule $(-) \rightarrow (+)$ for parity in a one-photon transition. This newly prepared state can be properly called a *special achiral* "parity isomer" of a "chiral" molecule, slightly similar to the common nuclear spin isomers. The two complementary isomers ($+$ and $-$ corresponding to the states χ_+ and $-\chi_-$ in equations 8 and 9) have different optical line spectra at high resolution because of the parity selection rule in electric dipole transitions. These spectra are schematically shown in Figure 9. The parity isomers are, however, neither stable with respect to collisions nor intramolecularly, but show an intramolecular time evolution due to parity violation, the period of motion being
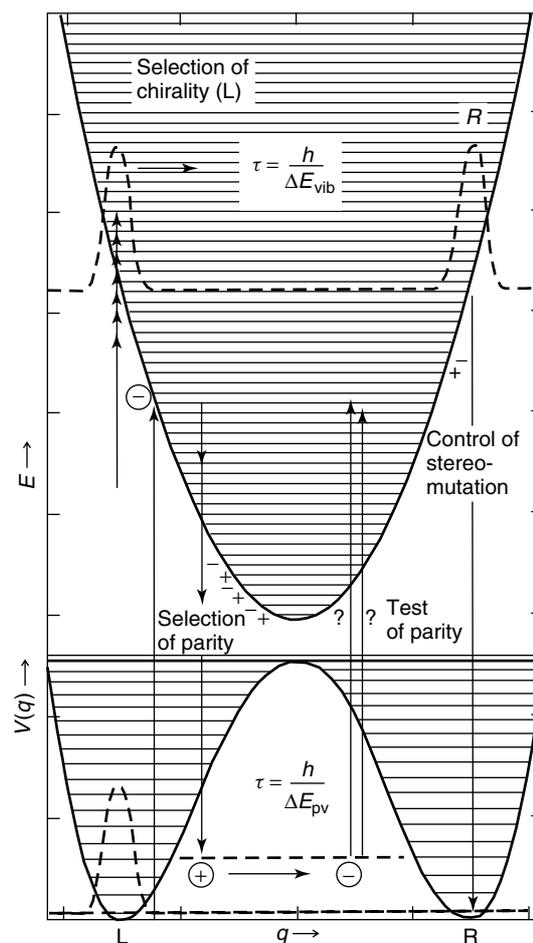
$$\tau_{pv} = h/\Delta_{pv}E \qquad (44)$$

Figure 8 Experimental scheme to measure time-dependent parity violation following the proposal of (Quack 1986). [After Quack (1999) by permission.]

and the initial time evolution for the concentration c_μ of the forbidden (minus) parity isomer would be (with the approximate equality holding for sufficiently small times):

$$c_\mu = \sin^2(\pi t \Delta_{pv} E/h) \simeq (\pi \Delta_{pv} E t/h)^2$$
$$\text{(for small } \pi \Delta_{pv} E t/h) \qquad (45)$$

For the examples in Tables 6 and 7, one can calculate parity-violating times τ_{pv} on the order of seconds. Thus, one has to measure a weak, slowly time-dependent (quadratic) initial signal, for instance, with absorption and subsequent ionization in the detection step, say on the millisecond timescale. One would have to look for growing intensity at the position of the initially absent $(-)$ parity lines in Figure 9. This scheme presents substantial challenges, but candidates for its future realization have been recently studied with the example of 1,3-difluoroallene, (Gottselig and Quack 2005), for example. We have also discussed how this scheme could be realized entirely in the electronic

Table 7 Chiral molecules for which high-resolution spectroscopic analyses of infrared spectra have been achieved.

| Molecule	Spectral range band positions and comment	References
CHFClBr	$1060-1100$ cm^{-1} low-temperature supersonic jet diode laser and FTIR CO$_2$-laser line coincidences identified	Beil *et al.* 1994, Bauder *et al.* 1997
CDFClBr	$600-2300$ cm^{-1} low-temperature supersonic jet diode laser and room-temperature FTIR	Albert and Quack 2007, Quack and Stohner 2001, Albert *et al.* 2003, 2001
Fluorooxirane cyclo-CH$_2$CHFO (and cyclo-CD$_2$CHFO)	$900-1200$ cm^{-1} room-temperature FTIR	Hollenstein *et al.* 1997
D$_{1(2)}$-thiirane-1-oxide (cyclo-CH$_2$CD$_2$SO, cyclo-CH$_2$CHDSO)	$1100-1150$ cm^{-1} (room-temperature FTIR)	Groß *et al.* 1995, 1998
Deuterooxirane (cyclo-CHDCH$_2$O)	$800-1000$ cm^{-1} room-temperature FTIR	Albert *et al.* 2005
1,3-Difluoroallene (CHF=C=CHF)	$800-1200$ cm^{-1} room-temperature FTIR	Gottselig and Quack 2005
CH^{35}Cl^{37}ClF (isotopic chirality)	$800-1250$ cm^{-1}, $2100-2160$ cm^{-1} low-temperature supersonic jet and enclosive He flow cell, FTIR two-photon CO$_2$-laser line coincidences identified	Albert *et al.* 2007, Snels and Quack 1991, Albert *et al.* 2004
PF^{35}Cl^{37}ClF (isotopic chirality)	(510 ± 20) cm^{-1}, (830 ± 20) cm^{-1} room-temperature FTIR	Sieben *et al.* 2003
CHFClI	1100 cm^{-1} supersonic jet FTIR	Soulard *et al.* 2006
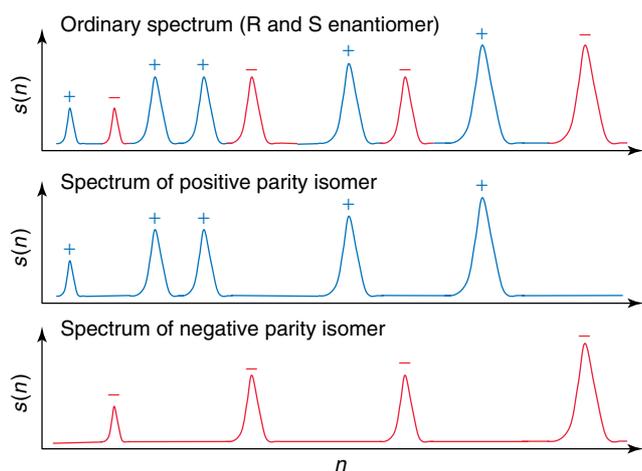
Figure 9 Schematic high-resolution line-resolved spectra of the parity isomers (positive shown in *blue* and negative shown in *red*). The normal line spectrum of a chiral molecule (either enantiomers or racemate) is a combination of two separate spectra from parity isomers. If one pure parity isomer 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 Quack *et al.* (2008) by permission.]

high-resolution spectra in the IR or visible spectra for chiral molecules. It turns out that until recently such analyses were absent and they remain scarce today. Table 7 provides an uptodate summary of currently available high-resolution IR spectroscopic analyses for chiral molecules (from Quack *et al.* (2008)).

5 HIGH-RESOLUTION SPECTROSCOPY AND INTRAMOLECULAR KINETICS: TIME-DEPENDENT PROCESSES AND APPROXIMATE DYNAMICAL SYMMETRIES AND THEIR VIOLATION AS DERIVED FROM HIGH-RESOLUTION SPECTROSCOPY

We measure time by motion and motion by time.
Aristotle cited in (Quack 2004a,b)
Time is what you read from your clock:
(Zeit ist das, was man an der Uhr abliest)
(Einstein 1922, cited in Quack (1999, 2004a,b))

5.1 Time-dependent Quantum Motion, Spectroscopy, and Atomic and Molecular Clocks

We have encountered already two examples of simple periodic quantum motion that can be considered to be

ground state by IR spectroscopy, for molecules such as ClOOCl and the related ones (Quack and Willeke 2006; Quack *et al.* 2008).

A minimum requirement for the realization of this experimental scheme, as for the realization of the alternative schemes discussed, is the availability and analysis of

the basis of atomic and molecular clocks as special cases of general intramolecular dynamics. Indeed, the general quantum dynamics of isolated molecules are described by equations (12) and (13), where the $\varphi_k(q)$ and E_k are obtained from the solution of the stationary Schrödinger equation:

$$\hat{H}\varphi_k(q) = E_k\varphi_k(q) \tag{46}$$

with eigenfunctions $\varphi_k(q)$ depending only on coordinates q (abbreviated in the notation used here for a complete set of space and spin coordinates of the atom or molecule) and energy eigenvalues E_k, which are subject to spectroscopic observation by means of the Bohr condition

$$\Delta E_{jk} = E_k - E_j = h\nu_{jk} \tag{47}$$

with the transition frequency ν_{jk}.

If we consider just two levels as equally populated, one obtains a periodic motion simplified from equations (13)–(15) to some time-dependent probability function:

$$p(t) = |a + b\exp(-2\pi i\Delta E_{jk}t/h)|^2 \tag{48}$$

The time dependence of such an atomic or a molecular clock is fully described by a time-dependent, complex periodic phase factor $\exp(i\alpha)$ represented graphically in Figure 10 in terms of the complex Gaussian plane. The hand of the clock, figuratively speaking, is given by the vector describing $\exp(i\alpha)$ in the plane that moves clockwise for positive time and counter-clockwise for negative time. The period of the clock is given by one energy interval ΔE_{jk}. The modern definition of the second is given by the separation ΔE_{jk} of the two hyperfine levels in ^{133}Cs (total angular momenta $F = 4$ and $F = 3$ resulting from combining nuclear spin $I = 7/2$ and electron spin $s = 1/2$) ($\Delta E_{jk} \simeq hc \cdot 0.3066331899\,\text{cm}^{-1}$) such that $1\,\text{s} = 9\,192\,631\,770\,\tau$ exactly, with $\tau = h/\Delta E_{jk}$ (*see* Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**, this handbook).

Combining equations (12) and (46)–(48), this can be made the basis of a spectroscopic approach to intramolecular kinetics following the scheme in Figure 11.

We have discussed elsewhere how this spectroscopic approach can be used to obtain deep insights into intramolecular processes with time resolution starting from about 200 attoseconds (Quack 1990, 2003, 2004a) (*see also* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra** and Hippler *et al.* 2011: **Mass and Isotope-selective Infrared Spectroscopy**, this handbook). Here, we address the relation to the breaking and violation of symmetries.
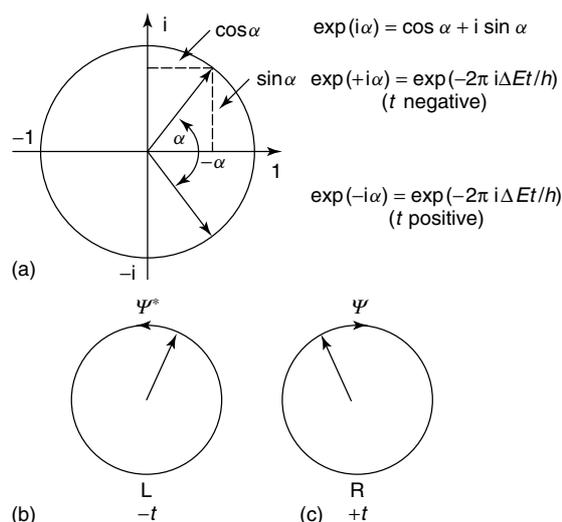

Figure 10 Explanation of the phase factor of the complex, time-dependent wave function for the atomic and molecular clock. (a) The phase factor is graphically depicted as an arrow in the Gaussian plane (α is taken to be positive). For positive times t, one obtains $\exp(-i\alpha)$, the hand of the clocklike phase factor turns in the clockwise direction, in the sense of increasingly negative α. (b) and (c) These illustrate the wavefunction Ψ and its complex conjugate Ψ^*, which both describe a symmetrically equivalent solution of the Schrödinger equation, given time-reversal symmetry. The picture also describes the corresponding orbits of planets around the Sun, symmetric under time reversal. These can move in a clockwise as well as counter-clockwise direction, providing acceptable solutions to the classical equations of motion (after Quack 1999 by permission).

5.2 Hierarchy of Interactions and Hierarchy of Timescales for the Successive Breaking of Approximate Dynamical Symmetries in Intramolecular Primary Processes

The example of intramolecular parity violation can be considered to be a special example in a hierarchy of symmetry breakings in molecules. This hierarchy of symmetry breakings can be related to the size of contributions in the molecular hamiltonian. For instance, one might write the hamiltonian in the following practical order of contributions to a sum, which decrease (roughly) in the following order (Quack 1983a):

$$\begin{aligned}
\hat{H} = {}& \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \\
& + \hat{T}_n \\
& + \hat{H}_{SO} + \hat{H}_{SS} + \hat{H}_{rel} \\
& + \hat{H}_{hfs} \\
& + \hat{H}_{mol,rad} + \hat{H}_{mol,environment} \\
& + \hat{H}_{weak} + \hat{H}_{gravitational} + \cdots
\end{aligned} \tag{49}$$

Molecular spectra

High-resolution molecular spectroscopy
Fourier transform spectroscopy
Laser spectroscopy
(Symmetry selection rules)

Effective Hamilton operators   Ab initio Hamilton operators
(Effective symmetries)   (Theoretical symmetries)

    Rovibronic schrödinger   Electronic Schrödinger
    Equation   equation

Molecular Hamilton operator $\hat{H}$ ← Ab initio potential energy
(Observed symmetries)   Hypersurfaces and Hamilton
                                          operators (symmetries)

Time evolution operator $\hat{U}$ (Matrix)

Molecular kinetics and statistical mechanics
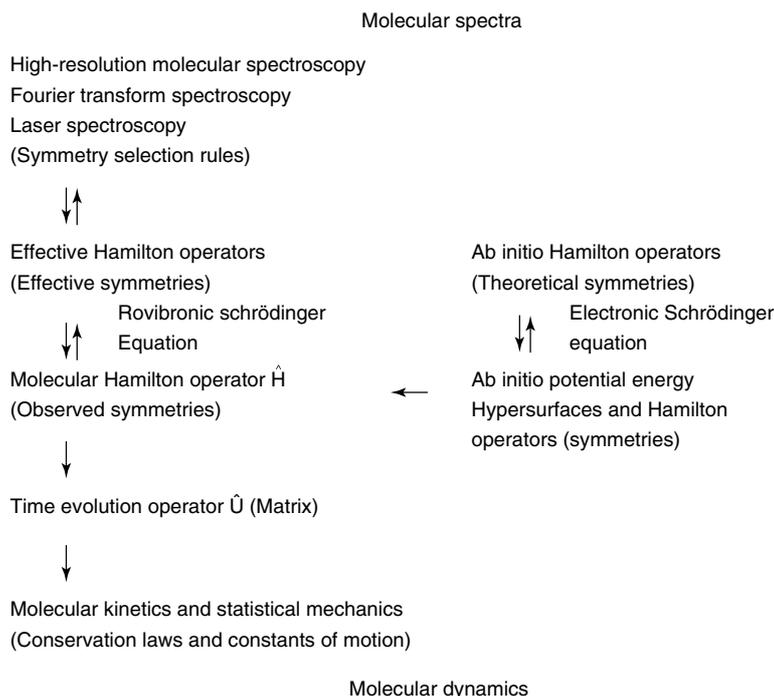(Conservation laws and constants of motion)

Molecular dynamics

Figure 11 Schematic diagram for the determination of molecular dynamics from molecular spectra. The starting point is the experimentally observed infrared spectrum of a molecule, which can then be interpreted in several steps of a complex analysis that will yield, at the end, information about the kinetics and the motion of the molecules. A purely theoretical procedure (ab initio) would also be possible in principle. The precision of such calculations is, however, still insufficient at present. The principal questions (for example, about the basic symmetry in the dynamics) can only be answered experimentally. [After Quack (2001) by permission.]

where $\hat{T}_e$ and $\hat{T}_n$ are the kinetic energy operators for electrons and nuclei and $\hat{V}_{nn}$, $\hat{V}_{ne}$, $\hat{V}_{ee}$ are nucleus–nucleus, nucleus–electron, and electron–electron Coulomb potentials. $\hat{H}_{weak}$ would be, in the example of parity violation, the relevant term contributing to the dynamical symmetry breaking in an intramolecular process as discussed in Section 4, on the timescale of about 1 s. $\hat{H}_{SO}$, $\hat{H}_{SS}$ are spin–orbit, spin–spin, and $\hat{H}_{rel}$ other relativistic contributions to the hamiltonian, with obvious notation for the other terms.

However, one could also separate the molecular hamiltonian into other types of contributions, according to what one considers a practical separation of the hamiltonian, in some abstract manner, say

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4 + \cdots \qquad (50)$$

In such an abstract description, a large $\hat{H}_0$ may show some (very high) symmetry, corresponding to a symmetry group of high order. $\hat{H}_1$ may be smaller (in terms of contributions to total energy), but might have a lower symmetry (smaller subgroup of the symmetry group of $\hat{H}_0$). Thus, considering $\hat{H}_1$, some of the symmetries of $\hat{H}_0$ will be violated or broken, and so forth with $\hat{H}_2$, $\hat{H}_3$, etc.

The formal aspects of the time evolution with more or less symmetry can be summarized by just a few equations.

In general terms, $\Psi(t)$ is obtained from the time evolution operator $\hat{U}$ (*see* Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook)

$$\Psi(t) = \hat{U}(t, t_0)\Psi(t_0) \qquad (51)$$

With $\hat{U}(t, t_0)$ satisfying

$$i\frac{h}{2\pi}\frac{d\hat{U}(t, t_0)}{dt} = \hat{H}\hat{U}(t, t_0) \qquad (52)$$

A dynamical variable represented by the operator $\hat{Q}$ satisfies the Heisenberg equation of motion

$$\hat{Q}(t) = U^{\dagger}(t, t_0)Q(t_0)\hat{U}(t, t_0) \qquad (53)$$

If for a certain dynamical variable corresponding to the operator $\hat{C}$, one has the commutation relation (for an isolated system, $\hat{H}$ being time independent)

$$\hat{C}\hat{H} = \hat{H}\hat{C} \qquad (54)$$

Table 8 Timescales for intramolecular primary processes as successive symmetry breakings (after Quack *et al.* (2008), see also Quack (1990, 1991, 1995b, 2001, 2003, 2007)).

Symmetric state	Coupling and symmetry breaking	Timescale
Conservation of separable vibrational quantum numbers (for harmonic oscillators of normal modes)	Selective vibrational CH-stretch-bend-Fermi-Resonance in R₃CH (Quack 1995c, 1990, Quack and Stohner 1993, Beil *et al.* 1996, 1997, 2000, Pochert *et al.* 2000)	10–200 fs
	Ordinary nonselective anharmonic couplings in CF₃R, Δl coupling in asymmetric R₁R₂R₃CH (Quack 1990, Pochert *et al.* 2000, He *et al.* 2002)	500 fs to 10 ps
Uncoupled oscillators (nearly adiabatically separable)	Adiabatically decoupled dynamics R−C≡C−H (Quack and Stohner 1993, Quack 1995c, von Puttkamer *et al.* 1983, Lehmann *et al.* 1994); (HF)₂ (Quack and Suhm 1998, von Puttkamer and Quack 1989, Quack 2001, 2003); Δl coupling in C₃ᵥ-symmetric R₃CH (Luckhaus and Quack 1993)	10 ps to 1 ns
Separable rotation−vibration−nuclear spin states (conservation of nuclear spin symmetry)	Violation of nuclear spin symmetry (nuclear spin-rotation−vibration coupling) (Quack 1977, 1983a, Chapovsky and Hermans 1999)	1 ns to 1 s (Section 6)
Space inversion symmetry Parity conservation *P*	Parity violation (Quack 1986, Bakasov *et al.* 1996, 1998a, Bakasov and Quack 1999, Berger and Quack 2000b, Quack 2002, 2006, Quack and Stohner 2005)	1 ms to 1 ks (Sections 3 and 4)
Time-reversal symmetry *T*	*T*-violation in chiral and achiral molecules (Quack 1997, Luckhaus *et al.* 1993)	Molecular timescale not known (Section 8)
CPT symmetry	Hypothetical CPT violation (Quack 1994b, 1995b)	∞ (?) (Section 8)

it follows with

$$\hat{U}(t, t_0) = \exp\left[(-2\pi i \hat{H}(t - t_0)/h\right] \qquad (55)$$

that $\hat{U}$, being a function of $\hat{H}$, commutes with $\hat{C}$ as well:

$$\hat{U}\hat{C} = \hat{C}\hat{U} \qquad (56)$$

Thus, one has $\hat{C}(t) = \hat{C}(t_0)$ in the Heisenberg representation from Equation (53). $\hat{C}$ does not depend on time and is a "constant of the motion" or a constant of evolution. Considered as transformations acting on $\hat{H}$ the $\hat{C}$ form a group, the symmetry group of $\hat{H}$ (and $\hat{U}$). One can readily see (Quack 1983a) that with the Liouville−von Neumann equation for the density operator $\hat{P}$ or the corresponding density matrix P

$$\hat{P}(t) = \hat{U}(t, t_0)\hat{P}(t_0)\hat{U}^\dagger(t, t_0) \qquad (57)$$

the expectation value of $\hat{C}$ is constant

$$\langle \hat{C}(t) \rangle = \text{Tr}(\hat{P}\hat{C}) = \langle \hat{C}(t_0) \rangle \qquad (58)$$

and also if $\Psi(t)$ is an eigenfunction ζ_n of $\hat{C}$ with eigenvalue C_n, one has

$$\langle \hat{C}(t) \rangle = \langle \zeta_n(t) | \hat{C} | \zeta_n(t) \rangle = C_n \qquad (59)$$

C_n are "good quantum numbers" in the evolution.

Indeed, we have made this abstract approach a basis for understanding the separation of timescales in intramolecular processes as derived from spectroscopy and Table 8 provides a summary of such results for intramolecular kinetics.

For instance, if $\hat{H}_0$ is taken to correspond to a description of an *N*-atomic nonlinear molecule by $3N - 6$ uncoupled harmonic oscillators and separable rotation, one has a very large symmetry group with all quantum numbers v_k for the individual harmonic oscillators corresponding to conserved "good" quantum numbers or constants of the motion.

As this is not a very good approximation, the anharmonic coupling terms (corresponding then to $\hat{H}_1$) are quite large and will lead to symmetry breaking on a very short timescale (depending on the case ranging from 10 fs to 10 ps as shown in Table 8 in the top group of processes). One can then introduce a number of successive coupling terms $\hat{H}_k$ that lead to further symmetry breakings and specific timescales for primary processes. The case of parity violation appears in group 4 counted from the top of Table 8. This example is also useful for illustrating another related concept. In the case of a very high barrier ($\Delta E_\pm \simeq 0$), the ground state of a chiral molecule is twofold degenerate because of space inversion symmetry, but this degeneracy is lifted by parity violation, resulting in a parity-violating energy difference $\Delta_{pv}E$, which can be interpreted as the "splitting" of the degenerate levels by a symmetry-violating contribution $\hat{H}_{pv}$ arising from H_{weak} to the hamiltonian. The smallness of the symmetry-violating

splitting of the degeneracy is directly related to the long timescale (1 ms to 1 ks, depending on the molecular example) for the dynamical, time-dependent symmetry breaking, simply by the equation for the general period of motion $\Delta\tau$:

$$\Delta\tau = h/\Delta E \qquad (60)$$

which can be called the *elementary timescale for the symmetry breaking*. The ordering of the hamiltonian in Equation (50) by contributions from terms of different magnitude and different symmetry has one further aspect: It allows one to determine small contributions separately from large contributions, like weighing a captain directly and not as a difference of weights of ship with captain and ship without the captain: This is important in experimental and theoretical approaches.

Having introduced these concepts, we now discuss some of the processes of symmetry breaking (the lower parts of Table 8) in relation to some spectroscopic problems of current interest.

6 APPROXIMATE NUCLEAR SPIN SYMMETRY AND PARITY CONSERVATION IN SPECTROSCOPY AND MOLECULAR DYNAMICS AND THEIR VIOLATIONS

Ayant vu combien les idées de Galois se sont peu à peu montrées fécondes dans tant de branches de l'analyse, de la géométrie et même de la mécanique, il est bien permis d'espérer que leur puissance se manifestera également en physique mathématique. Que nous représentent en effet les phénomènes naturels, si ce n'est une succession de transformations infinitésimales, dont les lois de l'univers sont les invariants.[b]

Sophus Lie (1894)

6.1 Approximate Separation of Nuclear Spin from the Other Degrees of Freedom

We have already discussed the role of parity violation on the timescale of seconds in intramolecular dynamics and spectroscopy (so far theoretical). Moving upward in Table 8 toward slightly more approximate symmetries and conservation laws, one finds nuclear spin symmetry conservation and violation. This approximate symmetry results from the nuclear spin part of the molecular wavefunction being only weakly coupled to the other degrees of freedom;

thus, one may write for molecular eigenfunctions of some $\hat{H}_0$ approximately neglecting the coupling hamiltonian

$$\Psi_k \approx \Psi_{0k} = \Psi_{Kk}\Psi_{mk} \qquad (61)$$

with

$$\hat{H}_0\Psi_{0k} = E_{0k}\Psi_{0k} \qquad (62)$$

This results then in approximate constants of the motion or "good quantum numbers" Λ_0, which are connected to the separate irreducible representations Γ_{Kk} of the permutation group for the nuclear spin wave function Ψ_{Kk} and the "motional" (rovibronic) molecular wavefunction Ψ_{mk} corresponding to the state Ψ_{0k} with "motional" species Γ_{mk} in the example, or quite generally, not just the total, Pauli-allowed species discussed in Section 2.6. Furthermore, the total internal nuclear angular momentum ("spin") quantum numbers I and M_I and the total "motional" angular momentum quantum numbers j and M_j are good quantum numbers and constants of the motion in this approximation, not just the total angular momentum quantum numbers F and M_F resulting from the total angular momentum $\boldsymbol{F} = \boldsymbol{j} + \boldsymbol{I}$. This approximation has some interesting and useful consequences for spectroscopy and molecular dynamics, which we discuss here from a general, conceptual point of view with some examples following Quack (1977, 1983b).

6.2 De facto Breaking of Nuclear Spin Symmetry by Chemical Reaction with De lege Nuclear Spin Symmetry Conservation

The well-known and obvious consequence of approximate nuclear spin symmetry is the existence of stable nuclear spin isomers corresponding to the conserved Γ_{mk}. On an appropriate timescale, these do not interconvert, either by radiative transition or by inelastic collisions; indeed, the selection rule both for allowed collisional and radiative transitions is

$$\Gamma_{Kk} = \Gamma_{Kk'} \qquad (63)$$

and

$$\Gamma_{mk} = \Gamma_{mk'} \qquad (64)$$

that is separate conservation of nuclear spin symmetry and "motional" symmetry for two states j and j' connected by the transitions. Furthermore, for radiative electric dipole one-photon transitions, one has

$$+ \longleftrightarrow - \qquad (65)$$

Table 9 Character table for the symmetric group S_2 for the permutation of two identical particles (nuclei).

Species ($\Gamma(S_2)$)	Class (Q)	
	E	(12)
[2] A	1	1
[1^2] B	1	-1

that is change of molecular parity, whereas for one-photon magnetic dipole transitions one has

$$+ \longleftrightarrow + \tag{66}$$

$$- \longleftrightarrow - \tag{67}$$

that is the conservation of molecular parity. There are no firm restrictions on parity change in inelastic collisions, although sometimes there are mild propensities (Oka 1973).

The simplest historical example is the hydrogen molecule H_2, which occurs in two stable modifications, ortho and para, in its $^1\Sigma_g^+$ electronic ground state (see Herzberg (1950), where references to the original literature can also be found, *see also* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook). Table 9 provides the character table for the symmetric group S_2 of the permutation of the two protons in this example. The group elements are the identity E and the permutation of the two identical particles (12) in the usual group theoretical notation (Hamermesh 1962, Longuet-Higgins 1963, Quack 1977). The species of designation uses both the standard group theoretical notation with the partitions [2] and [1^2] and the "spectroscopic notation" A for the symmetric and B for the antisymmetric species. From the Pauli principle in the form of equation (22), it follows that rotational levels of H_2 with even "motional" angular momentum quantum numbers $j = 0, 2, 4, \ldots$ with $\Gamma_{mj} = A$ combine with antisymmetrical nuclear spin wavefunction for the two protons (fermions, thus, $\Gamma_K = B$ and $I = 0$), whereas the odd angular momentum quantum numbers $j = 1, 2, 3, \ldots$ ($\Gamma_{mj'} = B$) combine with symmetrical nuclear spin wave functions (thus $\Gamma_K = A$ and $I = 1$). Because of the higher statistical weight 3 of the latter (I has then $M_I = 0, \pm 1$), this is called the *ortho isomer* and the former the *para isomer* (statistical weight 1 with $I = 0$). The spectroscopic observation of these "spin isomers" in terms of the 3 : 1 line intensity alternation has historically been at the origin of the discovery of the proton spin (1/2), similar to the electron spin (1/2) and is connected with the names of Heisenberg, Hund, and Dennison (the history can be found in Hund (1929)). For a discussion of the historical relevance to our understanding of nuclear structure we refer to Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook.

We simply quote here the well-known results for the combination of quantum numbers for the ortho and para nuclear spin isomers of H_2 in its $^1\Sigma_g^+$ electronic ground state. We refer to (*see* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook) for an elementary, introductory discussion with appropriate derivation of the results, but note here that the symmetry with respect to permutations of nuclei in a homonuclear diatomic molecule depends upon the nuclear spin and rotational quantum numbers as mentioned above. It does not depend on the vibrational quantum number in a diatomic molecule, because the internal vibrational wavefunction of the nuclei is symmetrical upon the permutation of the nuclei (it depends upon the distance of the nuclei, not upon the absolute positions). However, the behavior of the electronic wavefunction under permutation (12) of the nuclei again is nontrivial. For a $^1\Sigma_g^+$ ground-state term, it is symmetric under (12), whereas for the $^3\Sigma_g^-$ ground state of the O_2 molecule, for instance, it is antisymmetric under (12). This fact is sometimes overlooked in elementary textbooks. It has the consequence that the odd j quantum numbers with antisymmetric rotational wavefunctions are allowed for $^{16}O_2$ (giving in combination with the antisymmetric $^3\Sigma_g^-$ electronic wavefunction a totally allowed symmetric wavefunction for the two bosons in $^{16}O_2$). For further discussion, (*see* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook).

It has been shown a long time ago that the ortho and para isomers of H_2 form under certain conditions stable, separable, long-lived modifications of hydrogen in agreement with the selection rules (63) and (64) (Bonhoeffer and Harteck 1929). Thus, one has for an inelastic collision in the electronic ground state

$$A + H_2(v, j) \longrightarrow A + H_2(v', j') \tag{68}$$
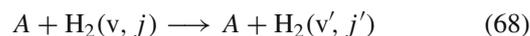
with no transitions connecting even j with odd j' (or odd j with even j'). It has been similarly known that reactive collisions such as (Gerlich 1990)

$$H^+ + H_2(v, j) \longrightarrow H^+ + H_2(v', j') \tag{69}$$
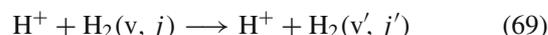
lead to a symmetry breaking in the sense that transitions between even j and odd j' are allowed and therefore concerning the molecule H_2 Γ_{mj} does not appear as a good quantum number in that process, which effectively interconverts ortho and para isomers of hydrogen. We use here a lower case j for the angular momentum quantum number of the individual diatomic molecules H_2 and capital J for the total H_3^+ system. For some time it was believed that reactive collisions of this type will always lead to interconversion of nuclear spin isomers, until it was shown that because of the underlying approximate de

Figure 12 Decomposition of the S-matrix into block diagonal form for collisions of protons H^+ with H_2 at $E \simeq 0.07\,eV$. The rotational quantum number of H_2 is j, and ℓ is the orbital quantum number. The total motional angular momentum is $J = 5$. The nuclear spin angular momentum $I = 3/2$ occurs with motional species A_2 and $I = 1/2$ with E (from Quack (1977)). The exponents $+$ and $-$ indicate the parity, that is, the species in S^*.

lege symmetry conservation, some nuclear spin isomeric selection rules may survive under certain circumstances (Quack 1977). We illustrate the basic concept in Figure 12 for the example shown.

This figure shows schematically the S-matrix for one diagonal block with total angular momentum $J = 5$. The scattering channels are given by the quantum numbers J, M_J, I, M_I, j, l, v, where J is the total motional angular momentum quantum number for the triatomic system ($J = j + l$), l the corresponding angular momentum quantum number for the relative ("orbital") motion of H^+ and H_2 orbiting around each other, I and M_I the total nuclear spin quantum numbers for the triatomic system, and v is the vibrational quantum number of H_2 (v $= 0$ in the example of Figure 12 corresponding to a collision energy

of 0.07 eV). With approximate de lege conservation of parity and nuclear spin symmetry in the collision, one has the block diagonal decomposition shown in Figure 12, which provides many restrictions for transitions ($|S|^2$ is the transition probability, which is zero outside the blocks marked by A_1^+ etc.). Table 10 gives the relevant character table of the symmetry group S_3, implicitly including the direct product group:

$$S_3^* = S_3 \otimes S^* \tag{70}$$

for this reaction of three identical particles in the H_3^+ or $H^+ + H_2$ system. However, although the selection rule results in many restrictions in connecting different scattering channels, it does allow for transitions between even and odd j within the blocks marked E^+ and E^-.

Table 10 Character table for S_3 with the subduced representation $\Gamma(S_3) \downarrow S_2$ and the induced representation $\Gamma(S_3) \uparrow S_4$ (after Quack (1977)).

	E	(132) (123)	(12) (23) (13)	$\Gamma(S_3) \downarrow S_2$	$\Gamma(S_3) \uparrow S_4$
A_1	1	1	1	A	$A_1 + F_2$
A_2	1	1	−1	B	$A_2 + F_1$
E	2	−1	0	A + B	$E + F_1 + F_2$

6.3 Exchange Degeneracy, Induced Representations, and Frobenius Reciprocity Theorem

To understand how the symmetry classifications of scattering channels and the block diagonal structure in Figure 12 arise (following Quack (1977)), one first notes that the overall wavefunction describes now a total of three protons, two of which are bound in H_2 (assumed to be in the electronic ground state) and the third being a free H^+. The parity +1 or −1 of a scattering channel is directly given by $(-1)^{j+l}$ as a consequence of the symmetry properties of the spherical harmonics Y_{lm} and Y_{jm_j} describing rotational motion. In our notation, it is given by the upper index + or − in the species designation. The 2^3 nuclear spin wavefunctions for three protons (each with nuclear spin function α $(m = 1/2)$ and β $(m = -1/2)$) form the basis of a reducible representation D_R of S_3 with (Table 10)

$$D_R = 4A_1 + 2E \tag{71}$$

The four A_1 functions have total nuclear spin $I = 3/2$ $(-3/2 \le M_I \le +3/2)$ and the two E functions have $I = 1/2$ $(M_I = \pm 1/2)$, in this simple example.

The motional (rovibronic) channel wavefunctions for a general scattering system with two molecules containing a total of $k = m + n$ identical nuclei, m in one of the collision partners and n in the other, have an "exchange degeneracy" g_p equal to the number of configurations, which are only distinguished by permutations of identical nuclei between the two collision partners; thus,

$$g_p = \frac{n!}{k! \, m!} \tag{72}$$

Given the species of each state of the collision partners in the individual symmetric groups S_k (hence Γ_k) and S_m (hence Γ_m), the structure of the reducible representation generated from $\Gamma_{k,m}$ of the direct product group $S_{k,m} = S_k \otimes S_m$ in the global symmetric group S_n of permutations of all n nuclei is given by the induced product representation (Löwdin and Goscinski 1969, Coleman 1968)

$$\Gamma_{k,m} \uparrow S_n = (\Gamma_k \otimes \Gamma_m) \uparrow S_n = \sum_{\Gamma_n} f(\Gamma_k, \Gamma_m, \Gamma_n) \Gamma_n \tag{73}$$

with obvious notations. The frequency $f(\Gamma_k, \Gamma_m, \Gamma_n)$ of Γ_n is readily obtained by means of the reciprocity theorem due to Frobenius (1898):

$$\Gamma_n \downarrow S_{k,m} = \sum_{k,m}^{g} f(\Gamma_k, \Gamma_m, \Gamma_n) \Gamma_{k,m} \tag{74}$$

The frequency of Γ_n in the induced representation is the same as the frequency of $\Gamma_{k,m}$ in the subduced representation $\Gamma_n \downarrow S_{k,m}$, the latter being easily computed from the character tables of $S_{k,m}$ and S_n using the standard formula

$$f_i^{D_R} = g^{-1} \sum_{j=1}^{g} (\chi_j^{\Gamma_i})^* (\chi_j^{D_R}) \tag{75}$$

$(\chi_j^{\Gamma_i})^*$ is the complex conjugate of the character of the irreducible representation Γ_i (here $\Gamma_{k,m}$) and $(\chi_i^{D_R})$ is the character of the reducible representation D_R (here $\Gamma_n \downarrow S_{k,m}$). g is the order of the subgroup under consideration.

Other direct ways of obtaining $f(\Gamma_k, \Gamma_m, \Gamma_n)$ include Young tableaux (Hamermesh 1962), but for simple groups the results are obvious just from reading the character tables such as Tables 9 and 10 where the subduced and induced representations are indicated for convenience of the reader and are applicable for $H^+ + H_2$. Using these results in conjunction with the generalized Pauli principle (equation 22), one readily obtains the structure of the S-matrix blocks given in Figure 12:

$$D_R = A_2 + E \text{ for odd } j_{H_2} \tag{76}$$

$$D_R = A_1 + E \text{ for even } j_{H_2} \tag{77}$$

Thus, even with the assumption of (approximate) de lege nuclear spin symmetry conservation in this example, the E symmetry blocks connect scattering channels of even and odd j_{H_2}, because of the induced representation generated by the exchange degeneracy in this case.

Thus, one may call this nonconservation of the ortho or the para character of H_2 in such reactive collisions a "de facto symmetry breaking", because it happens with the underlying symmetry being retained (here by assumption).

6.4 Point Groups and Molecular Symmetry Group

The application of the above concepts to more complex cases would be straightforward, if molecular energy levels were commonly labeled in molecular spectroscopy by the irreducible representations in the appropriate complete group of permutations and inversions. This being not very practical for molecules with semirigid structures, the point groups are the commonly used groups, which are usually defined by the equilibrium geometry of the molecules under consideration (Herzberg 1945, 1950, 1966, Wilson, Decius and Cross 1955). An elementary introduction into molecular point groups can be found in the chapter by Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook. To make use of such results along the lines discussed above, we have to establish a relation of this labeling by point group species to a labeling by an appropriate group consisting of permutations of nuclei and the inversion operation E^* (or P). This can be done following the work of Hougen (1962), Longuet-Higgins (1963), and Watson (1965). We illustrate this here with the simplest examples and refer to Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy** and Schnell 2011: **Group Theory for High-resolution Spectroscopy of Nonrigid Molecules** as well as Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook for more detail. The history, particularly in relation to the molecular symmetry group of nonrigid molecules introduced by Longuet-Higgins, can be found in Mills and Quack (2002). The original discussion by Longuet-Higgins (1963) stressed the qualitative concept of "feasibility" of certain permutation-inversion operations related to tunneling processes connecting minima on the potential hypersurface: If such a permutation, considered as a physical process, has a high activation barrier and therefore leads to nonresolvable tunneling doublets or multiplets, the process is considered not feasible (the tunneling period $\tau = h/\Delta E$ tends to infinity if the splittings ΔE tend to zero). Such a permutation is then not retained in the molecular symmetry group of feasible permutation-inversion operations. The remaining elements form the "molecular symmetry group" M_{sg} of order g, which is the subgroup of feasible permutation-inversion operations of the total permutation-inversion group:

$$S^*_{n_1,n_2,n_3\ldots} = S^* \otimes S_{n_1} \otimes S_{n_2} \otimes S_{n_3} \ldots \tag{78}$$

where n_1, n_2, n_3 are the numbers of identical nuclei in the molecule considered.

The concept of such a tunneling barrier for some process is approximate (a result of the Born–Oppenheimer approximation), and the exchange degeneracy can have reasons other than a high barrier (for instance, spatial separation); it might even persist high above a barrier for the process (Fehrensen *et al.* 2007). Therefore, we take here the more general, albeit perhaps slightly more abstract, point of view following Quack (1977, 1985) *defining* the molecular symmetry group by the structure of the empirically, spectroscopically observed sets of energy levels (or alternatively calculated in an exact calculation):

If in a given molecule in some energy range of the spectrum the rovibronic energy levels labeled by the species in the full permutation inversion group $S^*_{n_1,n_2}$ . . . arise in systematically degenerate level clusters, which are not resolved at the level of resolution of interest and which transform as the induced representations $\Gamma(M_{sg}) \uparrow S^*_{n_1,n_2}$ . . ., then this subgroup M_{sg} will be called the molecular symmetry group (after Longuet-Higgins) at the level of resolution of interest.

Thus, the level structure consists of sets of degenerate states transforming as the reducible representation:

$$D_r = \Gamma_r \uparrow S^*_{n_1,n_2,n_3\ldots} \tag{79}$$

We illustrate the slightly abstract concept with the simple example of the ozone molecule O_3 (Figure 13). Its equilibrium geometry corresponds to the point group C_{2v}, the species A_1, A_2, B_1, B_2 of which can be used to label the rovibronic states (Table 11). Labeling the identical nuclei as shown in Figure 13, exchange of the central nucleus against the outer ones is "not feasible" for a rigid structure, in the sense of Longuet-Higgins, the remaining "feasible" permutation being (12) (by a simple rotation in space).

This is to be combined with the inversion operation E^* resulting in a molecular symmetry group $M_{S4} = S^*_2$ of order 4 isomorphic to C_{2v} as also shown in Table 11. The correlations are straightforward, if one remembers that mirror operations σ in the point groups correspond
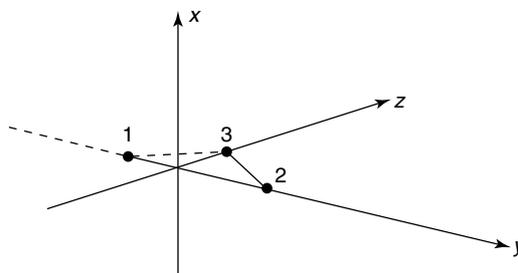

Figure 13 The C_{2v} structure of the ozone molecule O_3 (compare Table 11). There are three equivalent frameworks with nucleus 1, 2, or 3 in the middle, respectively. [After Quack (1977) by permission.]

Table 11 Character table for C_{2v} and S_2^* with the induced representation $\Gamma(S_2^*) \uparrow S_3^*$ (after Quack (1977)).

Species							$\Gamma(S_2^*) \uparrow S_3^*$
				Class			
C_{2v}		E	C_2	σ_{yz}	σ_{xz}		
S_2^*		E	(12)	E^*	$(12)^*$		
C_{2v}	S_2^*						
A_1	A^+	1	1	1	1	T_z	$A_1^+ + E^+$
A_2	A^-	1	1	-1	-1	$R_z(u, v, w)$	$A_1^- + E^-$
B_1	B^-	1	-1	-1	1	T_z, R_y	$A_2^- + E^-$
B_2	B^+	1	-1	1	-1	T_y, R_z	$A_2^+ + E^+$

to inversions (E^* perhaps in combination with some permutations).

The exchange degeneracy corresponding to each of the three nuclei 1, 2, 3 being placed alternately at the center position generates the induced representation $\Gamma(M_{S4}) \uparrow S_3^* = \Gamma(S_2^*) \uparrow S_3^*$ shown in the last column of Table 11, which can be computed using equations (73)–(75).

In practice, this can be read directly from Tables 10 and 11 in such a simple case by "reading the character and correlation tables backward" (following Watson (1965)) and adding parity (+ or −). Of course, one might first write down the character table of S_3^* from the direct product S_3 (Table 10) with S^* (Table 4) explicitly. Our notation for S_2^*

follows the following convention:

$$\Gamma_m(S_n) \uparrow S_n^* = \Gamma_m^+ + \Gamma_m^- \qquad (80)$$

where the exponent indicates parity (see also below). As noted above, the correspondence of the observed level structure with the structure defined by the last column of Table 11 defines the molecular symmetry group M_{sg}.

We note that the subgroup M_{sg} of feasible permutation-inversion operations does not always contain E^* and for clarity we also discuss here one such example, the CH$_3$D molecule.

Figure 14 shows the C_{3v} equilibrium geometry of CH$_3$D with the corresponding axis definitions ($m = 2, n = 1$, if one inverts this to $m = 1, n = 2$ one has equivalently CHD$_3$). In this example, the group of feasible permutation-inversion operations obviously does not contain the inversion E^* and thus is not a direct product group of S^* with some permutation group S_n. Indeed, the point group C_{3v} of order 6 with elements given in the top row of Table 12 is isomorphous to the molecular symmetry group of the same order M_{S6} with elements given by the second row. The three mirror operations σ_v correspond to combined permutation-inversion operations as indicated. Using the same symbols A_1, A_2, E for the irreducible representations of C_{3v} and of M_{S6}, one obtains the character table (Table 12). The last columns of this table provide the induced representations $\Gamma_m(M_{S6}) \uparrow S_3^*$, with the direct product group
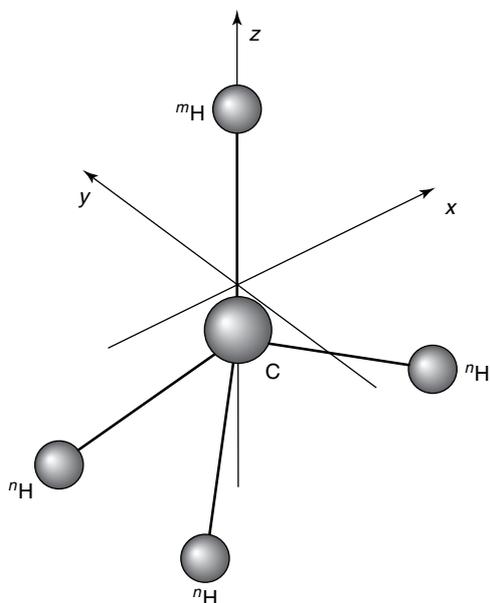

Figure 14 Equilibrium structure of the CH$_3$D molecule and axes definitions ($n = 1$, $m = 2$ for CH$_3$D, a similar definition applies to CHD$_3$ with $n = 2$, $m = 1$, but a shift of the center of mass). [After Ulenikov *et al.* (2010) by permission.]

Table 12 Character table for C_{3v} and the isomorphous group M_{S6} with the induced representation $\Gamma(M_{S6}) \uparrow S_2^*$ (after Quack (1977)).

C_{3v}		E	$2C_3$	$3\sigma_v$	
M_{S6} species	Class	E	$2(123)$	$3(12)^*$	$\Gamma_m \uparrow S_3^*$
A_1		1	1	1	$A_1^+ + A_2^-$
A_2		1	1	-1	$A_2^+ + A_1^-$
E		2	-1	0	$E^+ + E^-$

species notation according to Table 10 and equation (80). These induced representations provide the usually unresolved tunneling substructure of each rovibronic level of CH_3D described by the rigid C_{3v} point group species.

One recognizes that each level has a substructure of sublevels of different parity (+ and −), but in the case of A_1 and A_2 levels in C_{3v} different permutation symmetry in S_3^* ($A_1 \rightarrow A_1^+ + A_2^-$ and $A_2 \rightarrow A_2^+ + A_1^-$) is also present. The motional species Γ_m combine with the nuclear spin species Γ_{ns} resulting from the three identical protons (fermions) in CH_3D to the only Pauli-allowed total species A_2^+ or A_2^-; $\Gamma_m \otimes \Gamma_{ns} = A_2^{\pm}$. The 2^3 nuclear spin functions for the three protons form a reducible representation $D_R = 4A_1^+ + 2E^+$, where the four A_1^+ functions correspond to a total (H_3)-nuclear spin $I = 3/2$ ($-3/2 \leq M_I \leq +3/2$) and the two E^+ functions to total (H_3)-nuclear spin $I = 1/2$ ($M_I = \pm 1/2$). One may write the nuclear spin multiplets as $^4A_1^+$ and $^2E^+$. Therefore, the motional (rovibronic) wavefunctions of species A_2^+ and A_2^+ occur with nuclear spin species A_1^+ and $I = 3/2$ and the motional species E^+ and E^- occur with the nuclear spin species E^+ (and $I = 1/2$). The $A_1^{\pm}$ motional species have no partner among the nuclear spin functions to provide Pauli-allowed total species and thus do not occur. Assigning a symmetry species in S_3^* provides more information on the (sub)level structure of CH_3D than just C_{3v} species. For instance, in reality, the A_1 and A_2 levels (in C_{3v}) have no tunneling substructure and a well-defined parity (− for A_1 in C_{3v} and + for A_2 in C_{3v}). The E levels in C_{3v} have two components of + and − parity. The structure from the nuclear spin ($I_D = 1$) of the deuterium nucleus is to be added, but does not change the symmetry considerations. The situation described here with the example of CH_3D and C_{3v} arises in a qualitatively similar way for all semirigid nonplanar molecules, with details depending on the relevant symmetry groups and their induced representation. We see one further example with groups of higher order below (CH_4). In practice, one first derives in such cases the point group species by conventional methods (Herzberg 1945, 1950, 1966, Wilson *et al.* 1955) and then calculates the sublevel structure from the induced representation. We have discussed here the basic concepts for simple cases. Complex molecules are discussed in Schnell 2011: **Group Theory for High-resolution Spectroscopy of Nonrigid Molecules**, this handbook.

An interesting situation arises in the degenerate electronic ground state of the molecular ion CH_4^+ or the ion CH_3D^+ derived from CH_3D (Wörner and Merkt 2009). Jahn–Teller distortion then results in an equilibrium structure of CH_4^+ with two long and two short bonds, corresponding to the C_s point group in the case of CH_3D^+. However, the tunneling splittings are large, on the order of several cm^{-1}; thus,

one may again use M_{S6} and S_3^* for a full classification of levels, similar to CH_3D. The zero-point energy difference is found to be $\Delta E_0^0 \geq hc\ 100\ cm^{-1}$ for the two isomers with D being positioned either at the "long" or at the "short" bond and thus resulting in different ground-state properties for these and tunneling being suppressed by the asymmetry in the effective potential as in similar cases (see Section 6.8 and Quack and Suhm 1991a,b). This case and further isotopomers of the methane cation have been studied experimentally and theoretically in much detail with numerous important results on Jahn–Teller and tunneling dynamics by Wörner and Merkt (2009).

6.5 De facto Nuclear Spin Symmetry Conservation in Cases with Chemical Reaction

As pointed out by Quack (1977), chemical reactions even with the possibility of scrambling of all the identical nuclei may still show some selection rules on internal levels of the individual reactant and product molecules, thus showing in this sense de facto nuclear spin symmetry conservation with reaction. An example of some general importance ranging from basic reaction dynamics to astrophysics is provided by the following reaction (Quack 1977):

$$H_2^+ + H_2 \longrightarrow H_3^+ + H \quad \Delta_R H_0^0 \simeq -170\ kJ\ mol^{-1}$$
(81)
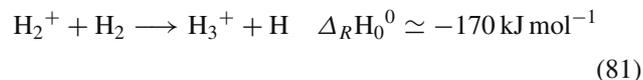
From what we have seen above, selection rules for this reaction can be derived using the groups S_4, S_4^* (Tables 13 and 14) and the induced representations $\Gamma(S_{2,2}) \uparrow S_4$ and $\Gamma(S_3) \uparrow S_4$. The character table for the direct product group $\Gamma(S_{2,2}) = S_2 \otimes S_2$ is readily obtained from Table 9 for S_2 and S_4^* is the direct product $S_4 \otimes S^*$. The reaction has been discussed in detail by Quack (1977) and the readers should be able to derive the relevant results on their own, using the tables and equations reviewed here.

H_3^+ occurs accordingly in the form of two nuclear spin isomers with motional symmetry species A_2 (in S_3, nuclear spin $I = 3/2$, weight 4, "ortho" modification) and E (nuclear spin $I = 1/2$, weight 2, para modification), whereas the motional symmetry A_1 in S_3 is Pauli forbidden ("weight = 0"). One finds (Quack 1977) that from pure para H_2 and H_2^+ ($j =$ even) one cannot produce ortho H_3^+ by reaction (81) (i.e., A_2 species in S_3 or A_2' or A_2'' in the point group D_{3h} of the symmetrical molecular ion H_3^+ in the electronic ground state). This selection rule is of obvious importance for reactions of cold H_2 and H_2^+ to form H_3^+ under astrophysical (interstellar) conditions also including the early universe when only hydrogen and He (with little Li and D) were available for molecule and consequently star

Table 13 Character table for the isomorphous groups S_4, T_d, and M_{S24} with the induced representation $\Gamma(M_{S24}) \uparrow S_4^*$ and the subduced representation $\Gamma(S_4) \downarrow S_3$. $P(S_4)$ is the partition for S_4 (after Quack (1977)).

$P(S_4)$	T_d M_{S24} S_4	E E E	$8C_3$ $8(123)$ $8(123)$	$3C_2$ $3(12)(34)$ $3(12)(34)$	$6S_4$ $6(1234)^*$ $6(1234)$	$6\sigma_d$ $6(12)^*$ $6(12)$	$\Gamma(S_4) \downarrow S_3$	$\Gamma(M_{S24}) \uparrow S_4^*$
[4]	A_1	1	1	1	1	1	A_1	$A_1^+ + A_2^-$
[1^4]	A_2	1	1	1	-1	-1	A_2	$A_2^+ + A_1^-$
[2^2]	E	2	-1	2	0	0	E	$E^+ + E^-$
[2, 1^2]	F_1	3	0	-1	1	-1	$E + A_2$	$F_1^+ + F_2^-$
[3,1]	F_2	3	0	-1	-1	1	$E + A_1$	$F_2^+ + F_1^-$

Table 14 Character table for the permutation inversion group $S_4^* = S_4 \otimes S^*$.

| $\Gamma(S_4^*)$		E	$8(123)$	$3(12)(34)$	$6(1234)$	$6(12)$	E^*	$8(123)^*$	$3(12)(34)^*$	$6(1234)^*$	$6(12)^*$
[4]$^+$	A_1^+	1	1	1	1	1	1	1	1	1	1
[4]$^-$	A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
[1^4]$^+$	A_2^+	1	1	1	-1	-1	1	1	1	-1	-1
[1^4]$^-$	A_2^-	1	1	1	-1	-1	-1	-1	-1	1	1
[2^2]$^+$	E^+	2	-1	2	0	0	$+2$	-1	$+2$	0	0
[2^2]$^-$	E^-	2	-1	2	0	0	-2	1	-2	0	0
[2, 1^2]$^+$	F_1^+	3	0	-1	1	-1	3	0	-1	1	-1
[2, 1^2]$^-$	F_1^-	3	0	-1	1	-1	-3	0	1	-1	1
[3,1]$^+$	F_2^+	3	0	-1	-1	1	3	0	-1	-1	1
[3,1]$^-$	F_2^-	3	0	-1	-1	1	-3	0	1	1	-1

formation. The survival of de facto symmetry even with reactions including exchange, based on the approximate de lege symmetry assumed here, has thus consequences for important "real-life" situations. Brilliant experiments by Uy *et al.* (1997) and Cordonnier *et al.* (2000) were able to establish consequences of these selection rules.

Other simple selection rules of similar type are readily derived as well (Quack 1977).

Another important, more complex reaction, which has been discussed on the basis of the groups S_5^* and S_5 (Table 15), is also of potential astrophysical interest:

$$H_3^+ + H_2 \longrightarrow H_2 + H_3^+ \tag{82}$$
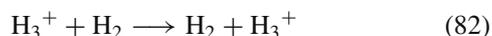
Here, one needs to consider the induced representations $\Gamma(S_{2,3}^*) \uparrow S_5^*$. One finds that certain restrictions on combinations of symmetry species of internal states exist, although repeated reactive collision of the type (82) can lead to scrambling of both ortho and para H_2 and H_3^+ (Quack 1977). Isotopic variants of this reaction such as

$$D_3^+ + H_2 \longrightarrow DH_2^+ + D_2 \tag{83}$$

$$D_3^+ + H_2 \longrightarrow D_2H^+ + HD \tag{84}$$
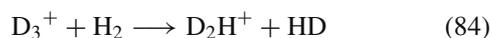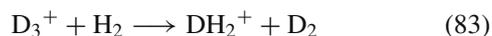
have been discussed theoretically concerning their selection rules using the relevant smaller groups (Quack 1977) and

have also been investigated experimentally in some detail (Gerlich 1993).

Another reaction of some relevance that can be studied on the basis of S_5^* and the relevant subgroups is

$$H^+ + CH_4 \longrightarrow CH_3^+ + H_2 \quad \Delta_R H_0^0 \simeq -375 \text{ kJ mol}^{-1} \tag{85}$$
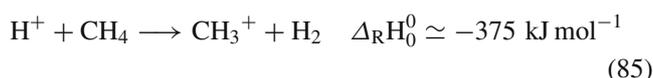
This reaction can proceed through the most interesting highly excited, quasi-bound intermediate CH_5^+ with scrambling of all protons, but still some approximate "de facto" symmetry conservation survives (Quack 1977).

We limit the discussion of details of these reactions and refer to the original literature cited for further information, although the reader should be able to derive all these selection rules on the basis of the tables and equations given here.

Photochemical reactions including radiationless transitions (Jortner *et al.* 1969) have been discussed by Quack (1983b). A special class of photochemical reactions, photoionization, has been treated by Signorell and Merkt (1997). Symmetry corrections for statistical theories including classical trajectory calculations have been discussed (Quack 1977), whereas exact quantum and semiclassical dynamics include symmetry rules implicitly (Miller 1975).

Table 15   Character table for S_5 (and essentially also S_5^*, noting that the Γ_m^- have the signs of the characters changed with all starred operations).

P	Γ_m	E	10 (12)	20 (123)	15 (12)(34)	30 (1234)	20 (123)(45)	24 (12345)	$\Gamma_m \to S_4$	$\Gamma_m \to S_{2,3}$	$\Gamma_m^+ \to M_{S24}$ ($\Gamma_m^- \to M_{S24}$)
[5]	A_1	1	1	1	1	1	1	1	A_1	A_1	A_1 (A_2)
$[1^5]$	A_2	1	−1	1	1	−1	−1	1	A_2	B_2	A_2 (A_1)
[4,1]	G_1	4	2	1	0	0	−1	−1	A_1+F_2	$A_1+B_1+E_1$	A_1+F_2 (A_2+F_1)
$[2,1^3]$	G_2	4	−2	1	0	0	1	−1	A_2+F_1	$A_2+B_2+E_2$	A_2+F_1 (A_1+F_2)
[3,2]	H_1	5	1	−1	1	−1	1	0	$E+F_2$	$A_1+E_1+E_2$	$E+F_1$ ($E+F_2$)
$[2^2,1]$	H_2	5	−1	−1	1	1	−1	0	$E+F_1$	$B_2+E_1+E_2$	$E+F_1$ ($E+F_1$)
$[3,1^2]$	I	6	0	0	−2	0	0	1	F_1+F_2	$A_2+B_1+E_1+E_2$	F_1+F_2 (F_1+F_2)

For the subduced representations $\Gamma_m^\pm(S_5^*) \to S_4^*$ and $\Gamma_m^\pm(S_5^*) \to S_{2,3}^*$, one has $+ \leftrightarrow +$ and $- \leftrightarrow -$. Furthermore, one has the subduced representation $\Gamma_m^+ \to M_{S24}$ (with $\Gamma_m^- \to M_{S24}$ in parentheses) (after Quack (1977)).

6.6 De lege Nuclear Spin Symmetry Violation on Long Timescales

The previous results were all derived on the basis of assuming that de lege violation of nuclear spin symmetry and parity are sufficiently small to be neglected. As already discussed for parity violation, the effects of a violation in some symmetric hamiltonian $\hat{H}_0$ by a symmetry-violating contribution $\hat{H}_1$ become important whenever the separation of close-lying zero-order energies is of the same magnitude or smaller than the symmetry-violating coupling matrix elements $V_{1(n,m)}$:

$$|\Delta E_{0(n,m)}| = |E_{0,m} - E_{0,n}| \lesssim |V_{1(n,m)}| \qquad (86)$$

However, even if one has, in the opposite case,

$$|\Delta E_{0(n,m)}| \gg |V_{1(n,m)}| \qquad (87)$$

there are, of course, slight mixing effects from the symmetry violation, but these are usually without dynamical and spectroscopic consequences, unless investigated by special techniques of extreme sensitivity. The eigenfunctions Ψ_n and Ψ_m then correspond to almost pure symmetry species of the group of the hamiltonian H_0.

Even when the coupling $V_{1(n,m)}$ is small, though, symmetry breaking as implicit in equation (86) can become important, when $\Delta E_{0(n,m)}$ is very small, indeed. Such cases of symmetry-breaking ortho–para mixing have been reported by experiments in the frequency domain for the diatomic molecules $^{127}I_2$, where rotation–vibration levels with different nuclear spin symmetry can become almost degenerate at very high energy near the dissociation limit of I_2, where several electronic states can be mixed (Pique *et al.* 1984). At low energies in a nondegenerate electronic ground state of a homonuclear diatomic molecule, such situations are precluded.

In polyatomic molecules, close degeneracies with $\Delta E_{1(n,m)} \approx 0$ of states with different nuclear spin symmetry are much more abundant due to the much richer spectral structures of $\hat{H}_0$. Close degeneracies are even enforced for certain levels of highly symmetrical molecules. For instance, in the octahedral molecules SF_6, such nuclear spin symmetry-breaking mixings were reported in experiments using saturation spectroscopy on the ν_3 fundamental band of the triply degenerate stretching vibration near $950\,\mathrm{cm}^{-1}$ (Bordé *et al.* 1980).

Nuclear spin symmetry-breaking mixings in polyatomic molecules serve as a catalyzing mechanism in the collisional interconversion of nuclear spin isomers of polyatomic molecules. Such interconversions were studied theoretically and experimentally at an early stage for methane by Curl *et al.* (1967) and a historical review of this research can be found in an article by Pitzer (1987). It is now generally accepted that under ordinary temperature and low-pressure conditions for molecules such as methane, H_2CO, CH_3F, and ethylene, one finds pressure proportional to pseudo-first-order rate constants for interconverting nuclear spin isomers on the order of $k' = (k \cdot p\,\mathrm{mbar}) = 10^{-3}\,\mathrm{s}^{-1}$ corresponding roughly to lifetimes of about an hour or less for pressures in the millibar range, where the collisional transfer occurs via the near degenerate "catalytic" quantum levels. This work is reviewed by Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy**, this handbook and Chapovsky and Hermans (1999). Recently, 10^9 times faster conversion rate constants were reported for the vinyl radical isotopomers H_2CCD, and D_2CCD by Tanaka *et al.* (2004) and Tanaka (2009). There have been claims of the preparation of samples of stable, long-lived para and ortho H_2O, which allegedly could be stored for months at 255 K (Tikhonov and Volkov 2002). However, these results could not be reproduced or confirmed in our experiments in Zurich (Albert *et al.* 2006) nor any other research group, to our knowledge, and thus should be considered questionable. At present, it would be safe to say that no adequate proof exists so far for long-lived (days or months) nuclear spin isomers of any polyatomic molecule under ordinary pressure and temperature conditions (see Section 6.7, however, for results in supersonic jets). Proposals have been made to study nuclear spin symmetry violation in selectively laser excited molecules, which might also be used on H_2O (Quack 1995a).

The order of magnitude estimates by equations (86) and (87) are valid for discrete spectra. Other considerations apply for continuous or quasicontinuous spectra. The selection rules for scattering via intermediate complexes with possibility of scrambling discussed in Section 6.5 apply to continua, where, strictly speaking, $\Delta E_{0(n,m)} = 0$.

Then, the relevant intramolecular interconversion time of nuclear spin isomers τ_{ICns} in relation to the lifetime $\tau_{complex}$ of the intermediate collision complex should be considered. If $\tau_{complex} \ll \tau_{ICns}$, then the selection rule remains valid, with τ_{ICns} falling in the range 1 ns to 1 s, depending on the complex considered, and $\tau_{complex} \ll 1$ ns at higher collision energies, usually, although longer lifetimes do exist at low collision energies or for large polyatomic complexes.

Another special class of systems, which show very close degeneracies leading potentially to nuclear spin symmetry mixing, involves high Rydberg states to be studied in high-resolution photoelectron spectroscopy (*see also* Merkt *et al.* 2011: **High-resolution Photoelectron Spectroscopy**, this handbook). Even effective parity violation might be induced by the very close degeneracies arising in high Rydberg states.

We conclude this section with the observation that near degenerate levels with substantial nuclear spin symmetry

mixing in the eigenstates can be used as intermediates in a radiative transition scheme very similar to Figure 8 to produce superpositions of ortho and para quantum states, for example. This could be used for some interesting studies, but so far such experiments do not exist.

6.7 Nuclear Spin Symmetry and Parity (Conservation and Violation) for Methane and Methanoid Molecules XY₄

In the previous section, we discussed the interconversion of nuclear spin isomers on long timescales. On shorter timescales, methane and other molecules show nuclear spin symmetry conservation when cooled under collisional conditions, for instance, in supersonic jets (Amrein *et al.* 1988). The case of methane and symmetrical methanoid molecules with respect to other spectroscopic properties in relation to symmetry in some detail is also worth discussing. This will allow us to illustrate some aspects of the problem, which are of general importance. Going back to the work of van't Hoff (1887), methane is known to have a tetrahedral equilibrium structure corresponding to the point group T_d. Table 13 shows the character table of this point group together with the molecular symmetry group of feasible permutation-inversion operations M_{S24} and the symmetric group of permutations of four identical particles S_4.

While these groups are all isomorphous and thus have the same character table, *they are not the same groups as the group elements correspond to different physical operations.* S_4 would not be the proper group to describe the species of energy levels of methane when tunneling splittings due to inversion are not resolved, but the group M_{S24} is. M_{S24} does contain permutations with inversion such as $(12)^*$ corresponding to the mirror operation σ_d, but it does not contain E^* and (12). When one includes the description of tunneling sublevels due to inversion of the hydrogen atoms at the central carbon atom, which has a transition state at a very high barrier of about $440\,\text{kJ}\,\text{mol}^{-1}$, very close to the dissociation energy (Pepper *et al.* 1995, Marquardt and Quack 2004), the group S_4^* with character table (Table 14) is the appropriate group to label the species of all levels. Given the extremely small tunneling splittings expected for all spectroscopic states of methane at modest energies well below the dissociation threshold, one might think that S_4^* is not useful for the description of methane spectroscopy at low energy. However, S_4^* does include useful physical information on the symmetry properties of methane wavefunctions even if tunneling splittings are not resolved. To illustrate this, Table 17 shows the lowest rotational levels with their motional species $\Gamma(T_d)$ in T_d and $\Gamma(S_4^*)$ in S_4^* and the corresponding Pauli-allowed total nuclear spin I arising for the four protons of spin 1/2. These assignments are readily obtained by the following

steps. One first assigns the point group species in T_d allowed for each angular momentum quantum number J, with $(2J+1)^2$ nearly (but not exactly) degenerate levels of approximate energy

$$E_J = hcBJ(J+1) \tag{88}$$

This is achieved by calculating the reduction of the positive representations D_+^J or D_g^J of the three-dimensional rotation–reflection group to the subgroup T_d (Wilson 1935, Herzberg 1966, Hougen 1963, 1971).

This reduction is shown in Table 16, which summarizes the result in a convenient form valid in principle for all J, although the energy level structure for very high values of J will deviate substantially from equation (88) (Quack 1975); a similar table has been given by Hougen (1976)). Indeed, even for low J, as seen in Table 17, the degeneracy is

Table 16 Reduction of D_+^J to irreducible representations D_i of T_d (from Quack (1975)).

	$J = 12n + m$		$n = 0, 1, 2, \ldots$		
m		$D_+^J \downarrow (T_d) = \sum_i n^i D_i$			
$D_i =$	A_1	A_2	E	F_1	F_2
			$n_i =$		
0	$n+1$	n	$2n$	$3n$	$3n$
1	n	n	$2n$	$3n+1$	$3n$
2	n	n	$2n+1$	$3n$	$3n+1$
3	n	$n+1$	$2n$	$3n+1$	$3n+1$
4	$n+1$	n	$2n+1$	$3n+1$	$3n+1$
5	n	n	$2n+1$	$3n+2$	$3n+1$
6	$n+1$	$n+1$	$2n+1$	$3n+1$	$3n+2$
7	n	$n+1$	$2n+1$	$3n+2$	$3n+2$
8	$n+1$	n	$2n+2$	$3n+2$	$3n+2$
9	$n+1$	$n+1$	$2n+1$	$3n+3$	$3n+2$
10	$n+1$	$n+1$	$2n+2$	$3n+2$	$3n+3$
11	n	$n+1$	$2n+2$	$3n+3$	$3n+3$

Table 17 The lowest allowed rovibrational energy levels (term values $\tilde{\nu}$) of $^{12}\text{CH}_4$, classified according to T_d and S_4^* symmetry (after Pepper *et al.* (1995)).

J	$\Gamma(T_d)$	$\Gamma(S_4^*)$	Nuclear spin (I)	$\tilde{\nu}$ (cm^{-1})
0	A_1	A_2^-	2	0
1	F_1	F_1^+	1	10.48164867
2	E	E^-	0	31.44212308
	E	E^+	0	31.44212308
	F_2	F_1^-	1	31.44238895
3	F_1	F_1^+	1	62.8757825
	F_2	F_1^-	1	62.8768454
	A_2	A_2^+	2	62.8781733

slightly lifted according to the improved approximate term formula (Jahn 1938a,b, Hecht 1960a,b, Herzberg 1966):

$$E_J = hc\ B_v J(J+1) - D_v J^2(J+1)^2 + D_v^{(t)} f(J, \gamma) \quad (89)$$

where $f(J, \gamma)$ increases roughly with $J^2(J + 1)^2$ and γ stands as an abbreviation for the symmetry species $\Gamma(T_d)$ in T_d. Results for $f(J, \gamma)$ are given by Herzberg (1966) and Hecht (1960a,b), where we note that Hecht (1960a,b) uses a different convention for the symmetry labels (Section 6.9). Our convention is consistent with Herzberg (1966) and with species in M_{S24}. Because of the small term $f(J, \gamma)$, levels of different γ in T_d have different energies, even when they have the same J. A detailed discussion of methane energy levels and spectra can be found in Albert *et al.* (2009) (*see also* Boudon *et al.* 2011: **Spherical Top Theory and Molecular Spectra**, this handbook).

To obtain the column for $\Gamma(S_4^*)$ in Table 17, one then has to compute the induced representation $\Gamma(M_{S24}) \uparrow S_4^*$ generated by the sublevels in T_d and M_{S24}, which, in our convention, carry exactly the same labels. This is given in Table 13. In the next step, one calculates the reduced representation for the $2^4 = 16$ nuclear spin functions of the four protons

$$D_R(CH_4) = 5A_1^+ + E^+ + 3F_2^+ \quad (90)$$

and notes that according to equation (22) the total Pauli-allowed species are $A_2^\pm$ (for four fermions). The $^5A_1^+$ spin function has overall nuclear spin $I = 2$ ($-2 \leq M_I \leq 2$), the $^3F_2^+$ function has $I = 1$ ($-1 \leq M_I \leq 1$), and the $^1E^+$ function has $I = 0$ ($M_I = 0$). The direct products of nuclear spin species and motional species $\Gamma(S_4^*)$ in Table 17 result in the allowed sublevels shown; the other sublevels from the induced representation in Table 13 being forbidden by the Pauli principle. Given these assignments, the last column in Table 17 can then be calculated using equation (89) or more accurate spherical top Hamiltonians (*see also* Albert, Albert and Quack 2011: **High-resolution Fourier Transform Infrared Spectroscopy** and Boudon *et al.* 2011: **Spherical Top Theory and Molecular Spectra**, this handbook). One sees that the sublevels of different $\gamma = \Gamma(T_d)$ have slightly different energies within the accuracy in Table 17, but E^+ and E^- levels have the same energy. This results in the A_1, A_2, F_1, and F_2 sublevels in T_d having a well-defined parity (+ or −), whereas the E levels in T_d have both + and − parity. At higher resolution, these levels will be split in two sublevels. The classification in (S_4^*) thus contains relevant information on total parity. Because the parity of the proton and of the ^{12}C nucleus is positive, Table 17 provides total parity including nuclear parity. Because ^{13}C has negative parity for the nucleus, the parities

in Table 17 must all be reversed to obtain total parity for $^{13}CH_4$ (+ → − and − → +).

We can now draw some interesting conclusions following Amrein *et al.* (1988). The lowest level ($J = 0$) in methane has A_2^- species, negative parity, and nuclear spin $I = 2$. It can be reached by a nuclear spin symmetry conserving collision from a $J = 3$ level of positive parity (A_2^+). The next level at $J = 1$ (F_1^+, $J = 1$) has positive parity and can be reached with nuclear spin symmetry conservation from the $J = 2(F_1^-)$ with a parity changing collision. The following level is a triplet of two E^+ and E^- ($I = 0$) of the same energy within the accuracy of 10 significant digits given, and an F_1^- level that is 2.6587×10^{-4} cm^{-1} higher in energy. The $E^\pm$ sublevels can be reached by nuclear spin symmetry conserving collisions from a higher level with $J = 4$ only ($\Delta J = 2$) and the F_1^- level can be reached from an F_1^- level with $J = 3$. A short conclusion from Amrein *et al.* (1988) was that upon collisional relaxation from a room-temperature sample by a supersonic expansion to about 11 K, one has nuclear spin symmetry conservation, thus generating no thermal equilibrium of the three nuclear spin isomers at 11 K, whereas, within each nuclear spin isomer there is thermal equilibrium of rotational states.

Also there was no evidence of any difference in molecular parity changing and parity-conserving collisions, generating significant effects in the distribution of levels (*overall parity* is, of course, conserved in the collisions). These conclusions were later confirmed by other groups, as reviewed in Quack (1990), Herman *et al.* (2000), and (*see also* Snels *et al.* 2011: **High-resolution FTIR and Diode Laser Spectroscopy of Supersonic Jets**, this handbook).

Thus, on the timescale of the supersonic jet expansion, nuclear spin symmetry conservation in methane holds. These results were recently extended in collisional cooling cell experiments to a timescale of seconds (Niederer *et al.* 2009). Another more fundamental aspect concerns conservation of intramolecular parity in the level structure of methane shown in Table 17 and Figure 15 following Pepper *et al.* (1995). This figure is inspired by the level-crossing experiments of Ozier *et al.* (1970) and the work of Hougen (1971).

Such level crossing experiments in a magnetic field can be used to enforce violation of nuclear spin symmetry as well as molecular parity violation. The latter would be a never previously observed example, although the experiment with present-day technology seems very difficult and less promising than the experiments discussed in Section 4. The experiment outlined in Figure 15 still is of conceptual interest. In principle, the parity-violating potentials calculated for CH_4 by Bakasov *et al.* (1998b) could be a starting point. In practice, if such experiments were to be envisaged, CF_4, CCl_4, or P_4, or even heavier systems with much
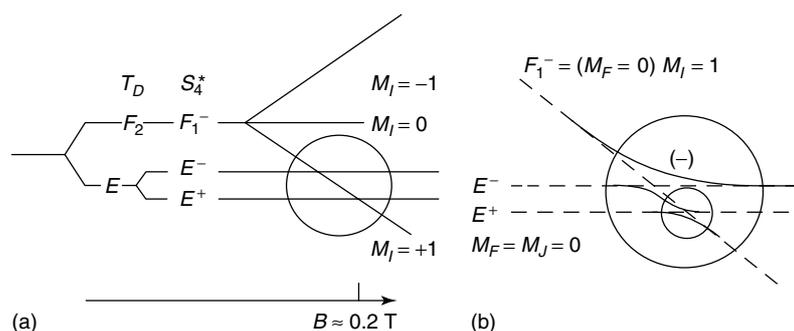
Figure 15 Scheme for crossings and avoided crossings in sublevels of the same rotational angular momentum J in methane CH_4 but different symmetry and nuclear spin ($I = 0$ with E and $I = 1$ with F) in the experiment by Ozier *et al.* (1970). (a) This shows the overall level behavior as a function of magnetic induction. For $J = 2$, the crossing is supposed to occur at 0.2 T (Hougen 1971), and each line would have a further smaller Zeeman splitting into five levels with $M_J = 2, 1, 0, -1, -2$. Furthermore, the crossings in the circle are avoided, as shown in detail in (b). Here, only the sublevels with the same total angular momentum F ($= 2$ for the example with $J = 2$) are shown with $M_F = 0$ (there are similar schemes for the other values of M_F). The crossing in the large circle between the F_1^- and E^- levels is strongly avoided, whereas the crossing between levels of positive and negative parity in the small circle could at most be weakly avoided by the parity-violating weak nuclear force. We assume that the zero-order (dashed lines) E^+ level is below E^- similar to the work of Hougen (1971), where parity violation was not considered, but the opposite ordering is also possible and would result in otherwise equivalent schemes. The parity violation at the crossing would mix levels of different parity, creating potential chirality. It could be observed either by directly mapping the magnetic dipole transition frequencies at extremely high resolution Ozier *et al.* (1970) or by observing magnetic dipole forbidden transitions. [Reproduced from Pepper *et al.* (1995) by permission.]

larger parity-violating potentials would be more promising candidates.

A very interesting case, which can be described by the same symmetry considerations, but with more complex tunneling dynamics, arises for the methane cation CH_4^+. As discussed in much detail by Wörner and Merkt (2009), Jahn–Teller distortion generates 12 equivalent minima of C_{2v} equilibrium geometry, which can be grouped into two sets of six, which are mirror images of each other, when one labels all protons. The barriers separating the minima within each set are about $1000\,\text{cm}^{-1}$ with a large tunneling splitting, whereas the barrier for stereomutation is about $5000\,\text{cm}^{-1}$ with a very small estimated tunneling splitting of less than $10^{-7}\,\text{cm}^{-1}$. If one considers the tunneling sublevels with the large splittings as resolvable, the effective symmetry is similar to that of CH_4. However, the "small" tunneling splitting for stereomutation in CH_4^+ is much larger than in CH_4 and thus would be resolvable at high resolution or when considering vibrationally excited states. Thus, the E^+/E^- splittings would be observable. We might note that there are hyperfine interaction contributions other than stereomutation tunneling to this splitting for molecules such as CH_4 and CH_4^+, which are not truly chiral.

To conclude, we provide Table 18 of nuclear spin statistics for CH_4, CD_4, and $Ru^{16}O_4$, as this may illustrate some further aspects (from Quack (1977) and Snels *et al.* (1991)).

One information that can be read from this table is the statistical weight for A, E, and F levels. This is obtained by adding up all multiplets ($2I + 1$) for each $^{(2I+1)}\Gamma_K$ for the molecule and motional species considered. For instance, for A levels in T and T_d, this results in $g_K = 5$ for CH_4,

Table 18 Pauli-allowed combinations of motional species Γ_m with nuclear spin species $^{2I+1}\Gamma_K$.

Γ_m			$^{2I+1}\Gamma_K(S_4^*)$		
T	$T_d(M_{S24})$	S_4^*	Protons, CH_4	Deuterons, CD_4	$Ru^{16}O_4$
A	A_1	A_1^+	—	$^9A_1^+ + {}^5A_1^+ + {}^1A_1^+$	$^1A_1^+$
		A_2^-	$^5A_1^+$	—	—
	A_2	A_2^+	$^5A_1^+$	—	—
		A_1^-	—	$^9A_1^+ + {}^5A_1^+ + {}^1A_1^+$	$^1A_1^+$
E	E	E^+	$^1E^+$	$^5E^+ + {}^1E^+$	—
		E^-	$^1E^+$	$^5E^+ + {}^1E^+$	—
F	F_1	F_1^+	$^3F_2^+$	$^3F_1^+$	—
		F_2^-	—	$^7F_2^+ + {}^5F_2^+ + {}^3F_2^+$	—
	F_2	F_2^+	—	$^7F_2^+ + {}^5F_2^+ + {}^3F_2^+$	—
		F_1^-	$^3F_2^+$	$^3F_1^+$	—

$g_K = 15$ for CD_4, and $g_K = 1$ for $^{even}Ru^{16}O_4$. These are independent of the sublevel structure and can be easily obtained from the rotational subgroup T in the conventional way (Herzberg 1966, Wilson 1935, Wilson *et al.* 1955) and also by other methods (*see also* Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy**, this handbook).

However, the detailed structure in Table 18 contains much more information. For instance, the statistical weight for E levels (in T and T_d) of CH_4 is 2 from Table 18. However, one can see that this weight is due to a possibly resolvable parity degeneracy ($^1E^+ + {}^1E^-$) and not due to the rigorous M_I degeneracy ($2I + 1$), which can be resolved only in external fields. It would be incorrect to

call the $g = 2$ for the $^1E^{\pm}$ doublet a nuclear spin statistical weight; it is a parity degeneracy weight.

In addition, for CH_4, the F levels all have a weight 3 (in T and T_d) and for CD_4, they have a weight 18. However, for CH_4 this weight arises from a pure M_I degeneracy for $I = 1$, with F_1 in T_d, giving an allowed overall species A_2^+ of positive parity for F_1 in T_d and A_2^- for F_2 in T_d.

On the other hand, for CD_4, the F_1 and F_2 levels in T_d have a complex substructure containing both positive and negative parity and four different types of nuclear spin functions, two of which actually have the same overall spin ($I = 1$), but different permutation symmetry, combining with different motional sublevels in S_4^*. Thus, a full analysis in terms of the sublevel structures in S_4^* contains a large amount of information, which is lost if one just calculates, say, "nuclear spin statistical" weights from the rotational subgroup T.

6.8 Symmetry Breaking by Nuclear Identity and Isotopic Mass Effects in Molecular Isotopomers

In the simplest form of the Born–Oppenheimer approximation, electronic energy is independent of nuclear mass and thus the potential $\hat{V}_0$ in the zero-order hamiltonian $\hat{H}_0$—the potential hypersurface for nuclear motion—would appear to have the same (possibly very high) symmetry for different isotopomers (for instance, the series CH_4, CH_3D, CH_2D_2, CHD_3, CD_4). However, obtaining rotational–vibrational energies even on a perfectly symmetrical potential hypersurface will result in a breaking of that very high symmetry. We mention here briefly two types of such symmetry breakings, which result in particularly interesting effects.

The first type relates to the existence of distinguishable isotope isomers of different ground-state energies due to zero-point effects on an otherwise symmetrical potential energy hypersurface. A good example is the hydrogen-bonded dimer $(HF)_2$, which exists in two interconverting structures distinguished by which hydrogen atom is "free" and which one is involved in the hydrogen bond.

$$(91)$$
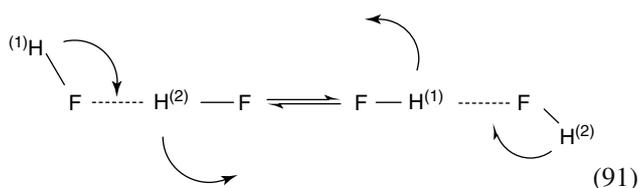
This example was, indeed, the first one, in which the effect to be considered was studied on a full (six-)

dimensional potential hypersurface with full dimensional quantum calculations (by diffusion quantum Monte Carlo, (Quack and Suhm 1991a)).

If the two hydrogen atoms are identical and the labels (1) and (2) serve just to distinguish between identical protons, then one has a symmetrical double-well potential for the process considered with a barrier corresponding to a C_{2h} saddle point of about 350 cm^{-1} and a ground-state tunneling splitting of about 0.66 cm^{-1} (see Quack and Suhm (1991a, 1995), Klopper *et al.* (1998b) for the theory and Howard *et al.* (1984) for experiments). When one substitutes one of the protons by a deuterium nucleus (thus, interprets now the upper index as mass number in equation (91)), then tunneling is suppressed and the two structures in equation (91) correspond to distinguishable isomers with different zero-point energy and different dissociation energies for the processes (in simplified structural notation):

$$HFDF \longrightarrow HF + DF \quad D_0 \simeq 1150 \text{ cm}^{-1} \quad (92)$$

$$DFHF \longrightarrow HF + DF \quad D_0 \simeq 1080 \text{ cm}^{-1} \quad (93)$$

Thus, reaction (91) has a reaction enthalpy $N_A \, \Delta E_0^0 = \Delta_R H_0^0 \cong 70 \text{ cm}^{-1}(hc)N_A$ at 0 K.

Whether these isotope isomers are actually observable separate species and $\Delta_R H_0^0$ has its usual meaning depends on whether one has

$$\Delta E_0^0 \gg \Delta E_T = hc \Delta \tilde{\nu}_T \quad (94)$$

where $\Delta \tilde{\nu}_T$ is the tunneling splitting in the symmetrical case. This situation applies to HFDF with $\Delta \tilde{\nu}_T \leq 0.7 \text{ cm}^{-1}$ and $\Delta E_0^0 / hc \cong 70 \text{ cm}^{-1}$ (Quack and Suhm 1991a,b, 1998, Klopper *et al.* 1998a,b, Oudejans and Miller 1997).

Such situations arise frequently; we have already mentioned above as another example the isotope isomers of CH_3D^+, with $CH_3D_l^+$ and $CH_3D_s^+$ where the index l and s indicate whether the CD bond is "long" or "short" in the distorted structure of the methane cation (Wörner and Merkt 2009). Nevertheless, in related cases, one has to test for inequality (94), in general.

This inequality obviously depends on several factors: not only on the height of the barrier and the reduced mass of the tunneling process but also on the mass difference between the two isotopes involved, which brings us to another interesting symmetry-breaking mass effect.

As pointed out in the conclusion of Quack (1977), the symmetry selection rules are essentially based on the identity of the nuclei and, therefore, introduce a mass-independent isotope effect in molecular reaction dynamics and spectroscopy. From a fundamental point of view, this would be of relevance for nuclear isomers, which are isotopes of essentially the same mass, differing only by the energy corresponding to a γ-quantum or even

more fundamentally the speculative "non-Pauli isotopes" of exactly the same mass. More practically, the symmetry selection rules introduce an extra isotope effect for heavier isotopes of rather similar mass, i.e., with a small *relative* mass difference. In this context, one may speculate whether unusual isotope effects found in some laboratory reactions of ozone and even in atmospheric ozone might include such symmetry-related effects, but the situation is presumably complex, combining several different effects, not necessarily dominated by any one type of effect (Mauersberger *et al.* 2005, Anderson *et al.* 1997). However, every satisfactory treatment of these isotope effects must include the symmetry-related isotope effects pointed out by Quack (1977).

6.9 Remarks on Nomenclature, Notations, and Conventions for Molecular Symmetry in Spectroscopy and Reaction Dynamics

The recommended nomenclature for molecular symmetry is summarized briefly in Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**, this handbook (see also Cohen *et al.* 2007). However, there is such a large variety of notations in common use that a few extra words may be useful. The standard point group symbols are well established and need little comment (Herzberg 1945, 1950, 1966) and (Wilson *et al.* 1955) (Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation**, this handbook). For molecular symmetry groups of the permutation-inversion type following Longuet-Higgins, the situation is less coherent. There are at least three widely used types of notation. One follows essentially Longuet-Higgins (1963) using the symbol M_{Sx} for the molecular symmetry group of feasible permutation-inversion operations of order x. A second notation uses simply G_x for "group of order x". In this handbook, the article by Schnell (*see* Schnell 2011: **Group Theory for High-resolution Spectroscopy of Nonrigid Molecules**, this handbook) uses this latter notation for some groups and it seems to go back to J. T. Hougen as a pioneer of the field. Another widely used notation for groups that are isomorphous to point groups is to use the point group symbol with an (M) added in parentheses, thus emphasizing the group elements being permutation-inversion operations. For instance for M_{S24}, one then uses $T_d(M)$. This notation is used in the textbook by Bunker and Jensen (1998). Finally, in this handbook, Oka uses the symbol $S_4^*/2$ for the same group. Thus, one has for the same group the symbols M_{S24}, G_{24}, $T_d(M)$ and $S_4^*/2$. For the full permutation and permutation-inversion group, Quack (1977)

used the common symbol S_n and introduced $S_n^* = S_n \otimes S^*$ with S_n being the "symmetric group" of permutations of n objects (Hamermesh 1962) and S^* the inversion group of elements (E, E^*) with E^* being the inversion of the coordinates at the origin. In this handbook, Oka (*see* Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy**, this handbook) uses this notation as we did in this article (note that "symmetric group" (of permutations) as defined above following standard mathematical convention is to be distinguished from "symmetry group"). While the multitude of notations for groups may be unfortunate, it can hardly create confusion.

In addition, the notation for group elements is relatively well established, with a few exceptions. Point group geometrical operations are fairly uniquely defined (Herzberg 1966, Wilson *et al.* 1955) with a few exceptions. The identity is most commonly represented by E (from German "Einheit" or "Einselement"). For the inversion of the coordinates at the origin, one frequently uses both P (for parity operation) and E^*. However, sometimes I (identity) is used instead of E (Herzberg 1945, 1950). In molecular spectroscopy, E^* is now most widely used for inversion operations, in order to avoid P, because P is also used for a general permutation. I has been used both for the inversion operation and for the inversion group (Mulliken 1941). Specific permutations are generally represented by the cyclic notation, for instance, (123) operating on the arrangement [1,2,3] generates

$$(123)[1, 2, 3] = [2, 3, 1] \qquad (95)$$

but there exist other notations (Hamermesh 1962), which are, however, less widely used in spectroscopy. Generally, little ambiguity arises in these notations for group elements.

The situation is less favorable for symbols of symmetry species or irreducible representations. One convention uses exactly the point group symbols for species for a molecular symmetry group, which is isomorphous to point groups. For instance for NH_3, one has $D_{3h}(M)$ and A_1', A_1'', A_2', A_2'', E', and E'' in this notation, used by Schnell 2011: **Group Theory for High-resolution Spectroscopy of Nonrigid Molecules**, this handbook. The systematic notation introduced by Quack (1977) uses either a letter symbol for the species of the permutation subgroup or the *partition* following group theoretical nomenclature (Hamermesh 1962). Parity in the permutation-inversion group is then indicated in addition by an exponent $+$ or $-$.

Thus for methane, we have S_4^* with the totally symmetric species A_1^+ or equivalently $[4]^+$ and for the totally antisymmetric species one has $[1^4]^-$ or A_2^- (Table 14). When one uses letter symbols, one can read the order of the representation from the letter: A, B, etc. with various indices are nondegenerate, E is twofold degenerate (originally from

the German "entartet"), F is triply degenerate, G fourfold, H fivefold, etc. (Table 15), simply following the letters of the alphabet as the order increases. For triply degenerate point group species instead of F, the symbol T is also widely used. The systematic nomenclature is used by Oka 2011: **Orders of Magnitude and Symmetry in Molecular Spectroscopy**, this handbook and in our article and it is suggested by Cohen *et al.* (2007) and (Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**, this handbook). It is implicit in the work of Longuet-Higgins (1963).

There is an unfortunate alternative to the systematic nomenclature of molecular symmetry group species by denoting tunneling doublets with the point group symbol and adding $+$ or $-$ depending on the doublet sublevel. In this case, the letter symbol *does not represent* the species in the subgroup of pure permutations. This nomenclature was introduced by Hougen (1962, 1971) for methane. For instance, an A_1 level in T_d generates a tunneling doublet $A_1^+ + A_2^-$ or $[4]^+ + [1^4]^-$ in S_4^* following the systematic nomenclature of Quack (1977), whereas the nomenclature of Hougen describes this as $A_1^+ + A_1^-$. The reason for this notation is that it retains the T_d nomenclature A_1 and just labels the sublevels with $+$ and $-$. This is used quite frequently. However, a severe disadvantage of this nomenclature is that one cannot read the permutation group species directly from the letter symbol. Indeed, the letter symbol then in general depends on the tunneling dynamics and will not be unique, whereas in the notation of Quack (1977) it is uniquely related to the permutation symmetry and the partition. Thus, we would strongly advocate using this notation. However, one must be aware of the multitude of conventions when comparing results in the literature.

The situation of notations and conventions is even more complex when considering other group theoretical approaches to treat nonrigid molecules. The isometric group of Bauder *et al.* (1974) is one example. We refer to the articles by Bauder 2011: **Fundamentals of Rotational Spectroscopy**, this handbook and the short historical summary by Mills and Quack (2002).

With the example of methane, we should also draw attention to the multitude of conventions used to specify symmetry species of eigenstates (Hecht 1960a,b, Herzberg 1966, Hougen 1962, Moret-Bailly 1965, Quack 1977). The conventions of Moret-Bailly (1965) are mostly used by the Dijon school (Berger 1977; *see also* Boudon *et al.* 2011: **Spherical Top Theory and Molecular Spectra**, this handbook).

A further variety of notations is introduced in the book by Harter (1993). It is slightly unfortunate that for a fundamental problem such as the symmetry of methane and tetrahedral molecules, in general, there is such a multitude of

notations. At present, there seems little choice other than to be aware of this situation and to avoid the resulting pitfalls.

7 SYMMETRY, STATISTICS, DENSITIES OF STATES, AND THE DYNAMICS OF SYMMETRY VIOLATIONS

Pauca sed matura.
("Few, but mature", attributed to C. F. Gauss as his favourite motto)

7.1 A Simple Mathematical Analogy

We briefly introduce here some basic statistical concepts of spectra as related to fundamental symmetries and symmetry violations starting out with a mathematical analogy in order to illustrate the origin of the statistical approach (Quack 1981, Quack and Troe 1981, Quack 1982). This approach follows three logical steps.

1. We start out in each case with a well-defined mathematical problem and ask new questions concerning certain average quantities arising in the solutions to the mathematical problem. In spectroscopy, the mathematical problem might be the spectrum of eigenvalues of a hamiltonian.
2. We show that for these average quantities one has new mathematical structures and laws, which were not a priori obvious in the original mathematical problem. One might ask for the average spacing between energy levels in spectroscopy, for instance, as well as for other statistical properties of the level spacings, for instance, the probability density of finding two neighboring levels at some distance.
3. One derives new, possibly simpler mathematical equations for obtaining these average properties directly without solving the complete problem.

Let us consider as an example the infinite sequence of digits in the number e defined by the series expansion in equation (96):

$$e = \sum_{n=0}^{\infty} \frac{1}{n!} = 2.718281828459045235\ldots \qquad (96)$$

The sequence of digits is perfectly well determined and easy to calculate, if one needs only a few digits, but the mathematical problem becomes very difficult, if we need, say, 10^{15} digits and insurmountable if we want 10^{100} digits, still negligibly small compared to infinity. Let us now ask for the probability $f(n, N)$ to find the digit n (i.e., $0, 1, \ldots, 9$) at the Nth position in the series of digit.
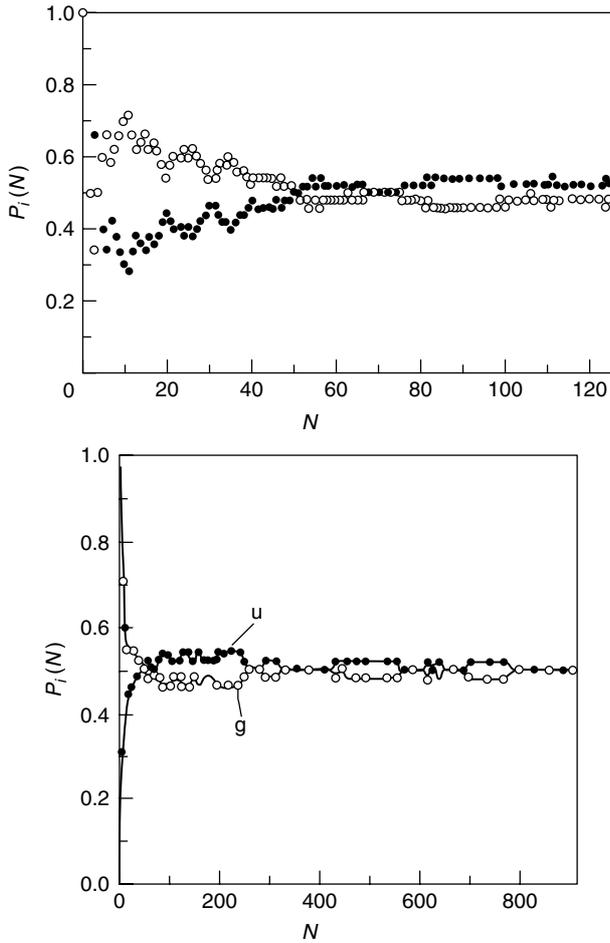
Figure 16 Relative frequency of occurrence ("probability") $P_g(N)$ of even digits (open circles) and $P_u(N)$ of odd digits (filled circles) as a function of the number N of digits in the real number e. [After Quack (1981) by permission.]

Obviously, this is 0 or 1 whether one finds the given digit (say, 2). One can also ask for the probability $f_g(N)$ or $f_u(N)$, whether one has an even or odd digit; again, this is 0 or 1 depending on the case. Let us now ask for a more average question, the relative frequency of even or odd digits up to the position N in the series

$$p_g(N) = \frac{N_g}{N_g + N_u} = \frac{N_g}{N} = 1 - \frac{N_u}{N} = 1 - p_u(N) \quad (97)$$

Figure 16 gives a graphical representation. It becomes obvious that this approaches $p_g(N) \simeq p_u(N) \simeq 1/2$ for large N, a result that one might have expected, but is not so easy to prove. The mathematical proof for e does not seem to exist. However, it is proven that "almost all" real numbers (in the statistical sence) show this behavior (the so-called "absolutely normal" numbers).

One can now also describe this with another concept. One defines functions $W_g(N_r)$ and $W_u(N_r)$, where N_r is
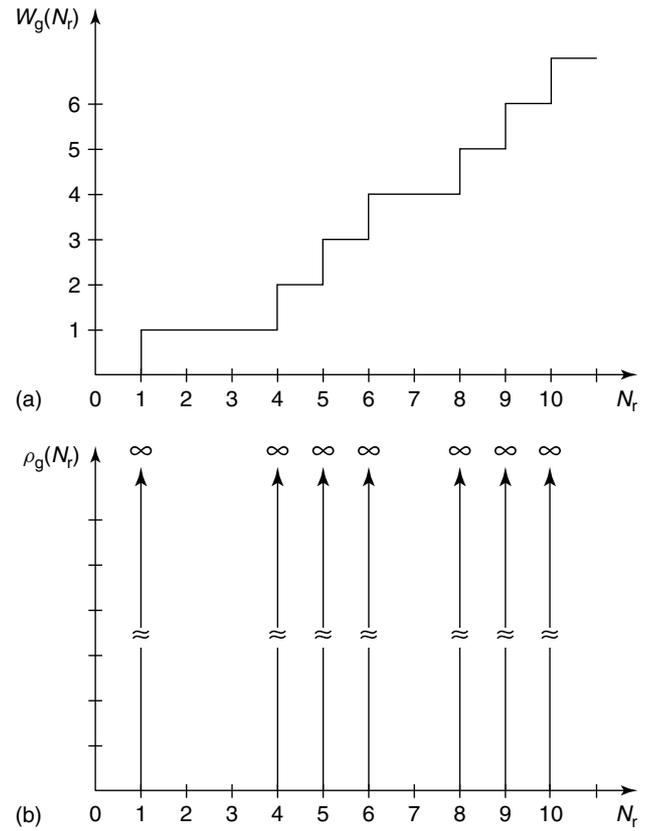
Figure 17 (a) Number $W_g(N_r)$ of even digits as a function of the continuous real number N_r for Euler's number e. (b) Density of even digits $\rho_g(N_r) = dW_g(N_r)/dN_r$.

now the set of continuous real numbers on the real axis. W_g is a staircase function, which increases by 1, when we hit an even number (Figure 17). $W_g(N_r)$ may be called the total number of even digits up to N_r.

The corresponding derivative is a sequence of Dirac δ-distributions and is called the *density* $\rho_g(N_r)$ of even numbers (Figure 17)

$$\rho_g(N_r) = \frac{dW_g(N_r)}{d(N_r)} \quad (98)$$

So far, the mathematical problem is identical to the original one in equation (96).

If we now average over a sufficiently large interval, the empirical finding of Figure 16 results in

$$\langle \rho_g(N_r) \rangle = \frac{\Delta W_g(N_r, \Delta N_r)}{\Delta(N_r)} = \frac{W_g(N_r'') - W_g(N_r'')}{N_r'' - N_r'} \simeq \frac{1}{2} \quad (99)$$

The average slope is just 0.5 in Figure 16. So far, this seems a rather trivial "structure" behind the series of digits, which one might guess anyway, although it is actually not really quite trivial.

Let us now consider a mathematical problem, with an average structure, which is not quite as easily guessed: the sequence and density $\rho_p(N)$ of prime numbers on the real axis (we write now simply N), by analogy

$$\rho_p(N) = \frac{dW_p(N)}{d(N)} \tag{100}$$

with

$$W_p(N) = \sum_{i=0}^{\infty} h(N - P_i) \tag{101}$$

and the Heaviside step function

$$h(x) = 0 \quad \text{for } x < 0 \tag{102}$$

$$h(x) = 1 \quad \text{for } x > 0 \tag{103}$$

and P_i represents the ith prime number calculated by well-known algorithms for small i. Thus, rigorously

$$\rho_p(N) = \sum_{i=1}^{\infty} \delta(N - P_i) \tag{104}$$

Figure 18 gives a graphical representation.

One might again ask for the average slope of the function in Figure 18 and following a conjecture due to Gauss

$$\langle \rho_p(N) \rangle \simeq \frac{1}{\ln N} \tag{105}$$

and

$$\langle W_p(N) \rangle = \int_0^N \rho(x) dx = \int_0^N \frac{dx}{\ln x} = li(N) \tag{106}$$

using the common symbol $li(N)$ for the special function in equation (106). This type of question ultimately leads to a highly nontrivial mathematical problem (Hilbert's eighth problem or Riemann's hypothesis) and one intermediate result proven so far is

$$\lim_{N \to \infty} W_p(N) = \frac{N}{\ln N} \tag{107}$$

The proof for this partial, asymptotic result was given by J. S. Hadamard and C. J. G. N. de la Vallée Poussin in 1896 almost a century after the original conjecture by Gauss. Riemann's hypothesis on the exact structure of the prime number series in terms of the ζ-function remains unproven (Hardy and Wright 1979, Du Sautoy 2003).

The basic formula (105) for the density of primes might not so easily have been guessed, but it is simple enough and certainly an interesting structure. If one interprets the density as proportional to the probability of finding a prime number in a given interval, one might now conjecture further structures, such as the density of pairs of primes (adjacent odd numbers being primes) as

$$\langle \rho_{pp} \rangle \propto \langle \rho_p \rangle^2 \propto \left(\frac{1}{\ln N} \right)^2 \tag{108}$$

Whether this is true is not known.

7.2 Density of Quantum States of Harmonic Oscillators

The concepts of the previous section can be easily extended now for describing the solution of a typical spectroscopic problem, the density of quantum states of one or more
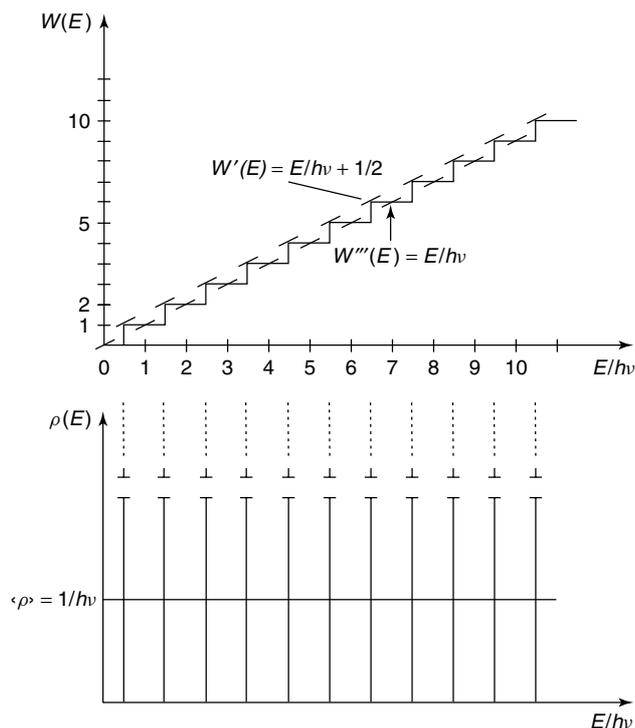

Figure 18 Number $W_p(N)$ of primes with $P_i \leq N$.

Figure 19 Number of states $W(E)$ and density of states $\rho(E)$ for a harmonic oscillator.

harmonic oscillators. This results now from the solution of an eigenvalue problem of a simplified molecular hamiltonian.

Figure 19 again gives a graphical representation for one harmonic oscillator, simple enough as it may seem.

The spectrum is given by

$$E = \left(v + \frac{1}{2}\right) h\nu \tag{109}$$

The exact representation for the number of states W is

$$W(E) = \sum_{v=0}^{\infty} h(E - E_v) \tag{110}$$

$$\rho(E) = \frac{\mathrm{d}W(E)}{\mathrm{d}E} = \sum_{v=0}^{\infty} \delta(E - E_v) \tag{111}$$

The average slope is obviously

$$\langle \rho(E) \rangle \simeq \frac{1}{h\nu} \cong \frac{\Delta W}{\Delta E} \tag{112}$$

and

$$\langle W(E) \rangle \simeq \frac{E}{h\nu} + \frac{1}{2} = \frac{E + E_z}{h\nu} \tag{113}$$

where E_z is the zero-point energy ($h\nu/2$).

If one combines two spectra from a separable system according to equations (114) and (115)

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{114}$$

$$E_m = E_{n_1, n_2} = E_{n_1} + E_{n_2} \tag{115}$$

the combined density of states $\rho_{1,2}$ is obtained from the convolution

$$\rho_{1,2}(E) = \int_{x=0}^{x=E} \rho_2(x)\rho_1(E - x)\mathrm{d}x = \rho_1 \otimes \rho_2 = \rho_2 \otimes \rho_1 \tag{116}$$

This property can be seen very generally through the Laplace transformation (operator $\hat{L}$) of the density of states defining the canonical partition function $q(\beta)$

$$q(\beta) = \int_0^\infty \rho(E) \exp(-\beta E)\mathrm{d}E = \hat{L}\rho(E) \tag{117}$$

Inserting the δ-functions from equation (111), one finds the usual representation of the partition function:

$$q(\beta) = \sum_{j=0}^{\infty} \exp(-\beta E_j) = \sum_{J=0}^{\infty} g_J \exp(-\beta E_J) \tag{118}$$

where the two summations are distinguished by how one sums over degenerate states of the same energy E_J with statistical weight g_J (in statistical thermodynamics, one has $\beta = 1/(kT)$).

From equation (118) one derives the well-known property of a partition function $q_{1,2}$ for a spectrum obtained from combining two separable systems (equation 115), with E_{n_1} and E_{n_2}.

$$
\begin{aligned}
q_{1,2} &= q_1 q_2 \\
&= \left[\sum_{n_1=0}^{\infty} \exp(-\beta E_{n_1})\right]\left[\sum_{n_2=0}^{\infty} \exp(-\beta E_{n_2})\right] \\
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \exp[-\beta(E_{n_1} + E_{n_2})] \\
&= \sum_{m=0}^{\infty} \exp(-\beta E_m)
\end{aligned} \tag{119}
$$

Making use of the general inverse Laplace transformation $\hat{L}^{-1}$ with $\hat{L}\hat{L}^{-1} = \hat{L}^{-1}\hat{L} = 1$ (by definition), thus

$$\rho(E) = \hat{L}^{-1}q(\beta) = \frac{1}{2\pi\mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} q(\beta) \exp(\beta E)\mathrm{d}\beta \tag{120}$$

one has

$$\rho_{1,2} = \hat{L}^{-1}(q_1 \cdot q_2) = \hat{L}^{-1}\hat{L}(\rho_1 \otimes \rho_2) = \rho_1 \otimes \rho_2 \quad (121)$$

where equation (121) makes use of the general property of the Laplace transformation that with $q_1(\beta) = \hat{L}\rho_1$ and $q_2(\beta) = \hat{L}\rho_2$ then $q_{1,2} = q_1 \cdot q_2 = \hat{L}F$ with $F = \rho_1 \otimes \rho_2$, that is, the ordinary product in the space of Laplace transforms q corresponds to the convolution in the space of functions ρ. This is exact if all functions used are exact. If we use, instead, approximate densities of states from the continuous approximation for the harmonic oscillator (equation 112), one finds the total density of states of s harmonic oscillators, each with frequency ν_i, by successive convolutions

$$\rho_{1,2,3\ldots s}(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i} \quad (122)$$

A slightly better approximation is obtained by introducing the total zero-point energy E_Z (cf. equation 113)

$$E_Z = \frac{1}{2}\sum_{i=1}^{s} h\nu_i \quad (123)$$

$$\rho_{1,2,3\ldots s} = \frac{(E + aE_Z)^{s-1}}{(s-1)! \prod_{i=1}^{s}(h\nu_i)} \quad (124)$$

The parameter $0 \le a \le 1$ can be adjusted to provide a best representation.

Figure 20 shows a result for the density of states for fluorobenzene C_6H_5F calculated with $a = 0$, $a = 1$ and obtained from an exact count (Quack 1980).

One sees the limitations of the approximations with $a = 1$ (called *semiclassical density*) and $a = 0$ (*classical density*), but the former is acceptable at the highest energy. There are good algorithms to carry out the convolutions exactly with discrete spectra, i.e., not using the continuous approximations (Beyer and Swinehart 1973) and there is a vast literature available on calculations of densities of states (Quack and Troe 1981, 1998). Figure 20 illustrates the very large values one obtains for $\rho(E)$ at modest excitation energies in C_6H_5F.

Equation (124) gives an estimate for the mathematical "structure" of the average density-of-states function $\rho(E)$ for s harmonic oscillators, just as $\langle\rho_p(N)\rangle$ (equation 105) gives an estimate for the mathematical structure of the density of primes. In both cases, one can replace the approximate functional form by an exact count, in principle.

In a physical situation, of course, even the starting point of using the separable harmonic oscillator model for the hamiltonian is a very rough approximation. Here, we are interested in structures arising from symmetry.
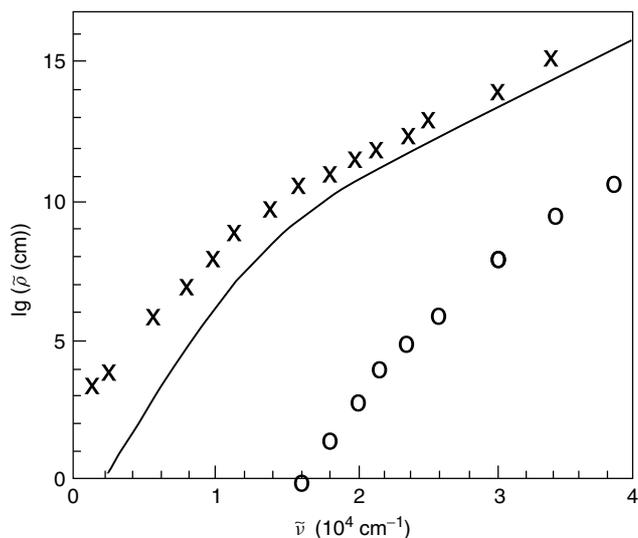

Figure 20 Decadic logarithm lg ($\tilde{\rho}$ (cm)) of densities of states $\tilde{\rho}$ for 30 vibrational degrees of freedom in C_6H_5F, symbol x = "semiclassical" approximation with $a = 1$ in equation (124)), symbol o = "classical" approximation ($a = 0$ in equation 124). The line is from an "exact" count of the step function $W(E)$ (from Quack (1980)). Wavenumbers are used with $E = hc\,\tilde{\nu}$ and for the density $\rho(E) = \tilde{\rho}/(hc)$.

7.3 Densities of Molecular States for a Given Total Angular Momentum and Symmetry Species in the Molecular Symmetry Group

An interesting question concerns the distribution of total numbers $W(E)$ and densities $\rho(E)$ of vibrational and possibly vibrational–rotational states over the different possible symmetry species. The question arises both for applications in spectroscopy and for applications in dynamics (Quack 1977, 1983a, 1985, Quack and Troe 1998). Here, one generally needs densities of states for a given set of good quantum numbers. As a first step, one has then to calculate densities of states for a given total angular momentum quantum number J (Quack and Troe 1974, 1998). For prolate symmetric tops (or near-symmetric tops) with quantum number K, this takes the approximate form, for example,

$$\rho(E, J) = \sum_{K=0}^{J} g_K \rho_{\text{vib}}[E - J(J+1)B$$
$$- (A - B)K^2 - E_Z] \quad (125)$$

where $g_K = 1$ for $K = 0$ and $g_K = 2$ for $K > 0$. E_Z is the total zero-point energy and A and B are the rotational constants (expressed as energies). ρ_{vib} is the vibrational density discussed in the previous section and can be computed either with approximate formulae or by counting algorithms (Beyer and Swinehart 1973, Stein and Rabinovitch 1973, Quack and Troe 1974, 1998).

Similarly, when now considering $\rho(E, J, \Gamma_m^{\pm})$ and $W(E, J, \Gamma_m^{\pm})$ with species in the permutation-inversion group, one can show that in the high-energy limit the following simple limiting equation is approached (Quack 1977, 1985):

$$\frac{\rho(E, J, \Gamma_m^{\pm})}{\rho(E, J, \Gamma_n^{\pm})} = \frac{W(E, J, \Gamma_m^{\pm})}{W(E, J, \Gamma_n^{\pm})} = \frac{[\Gamma_m^{\pm}]}{[\Gamma_n^{\pm}]} \quad (126)$$

$[\Gamma_m^{\pm}]$ stands for the dimension of the irreducible representation $\Gamma_m^{\pm}$. One should note the *additional* motional degeneracy $g_m = [\Gamma_m^{\pm}]$ of a level with symmetry species $\Gamma_m^{\pm}$. If one introduces a count of nondegenerate motional states without considerations from the Pauli principle, one would have

$$\rho_t(E, J, \Gamma_m^{\pm}) = [\Gamma_m^{\pm}]\rho(E, J, \Gamma_m^{\pm}) \quad (127)$$

and

$$W_t(E, J, \Gamma_m^{\pm}) = [\Gamma_m^{\pm}]\rho(E, J, \Gamma_m^{\pm}) \quad (128)$$

In actual fact, of course, each level of motional deneracy $\Gamma_m^{\pm}$ combines with a nuclear spin wavefunction and degeneracy $\Gamma_K^{\pm}$ to give a *nondegenerate* Pauli-allowed symmetry species $\Gamma_{\text{Pauli}}^{\pm}$

$$\Gamma_m^{\pm} \times \Gamma_K^{\pm} = \Gamma_{\text{Pauli}}^{\pm} \quad (129)$$

following equation (22). Degeneracies $(2I + 1)$ arise only from the magnetic quantum numbers M_I with total nuclear spin I. Thus, at high energies, one could calculate densities of states without taking symmetry into account and then use equation (126) in order to derive the densities of states for each symmetry species.

The derivation of equation (126) uses as a starting point the fact that in the high-energy limit of classical mechanics the identical particles would become distinguishable. The appropriate symmetry group is S_1, with only one species $\Gamma_1(S_1)$. One can then show that the induced representation generated from the exchange degeneracy in S_n for n identical particles is a regular representation

$$b\Gamma_1(S_1) \uparrow S_n = bR(S_1) \uparrow S_n = bR(S_n) \quad (130)$$

where the regular representation R of any finite group satisfies

$$R = \sum_m f(\Gamma_m)\Gamma_m \quad (131)$$

$$f(\Gamma_m) = [\Gamma_m] \quad (132)$$

Briefly, this is the basis for equation (126) and we refer to Quack (1985) for a detailed discussion of the derivation.

By further relating the permutation-inversion groups to molecular symmetry groups and point groups, one can show that a similar equation holds quite generally for the species of these groups. Parity needs some special considerations for planar triatomic molecules (Quack 1985). Here, in general, one also has to take the high J limit. For the asymmetric rotor, one has

$$\frac{W(E, J, \text{A}^+)}{W(E, J, \text{A}^-)} = \frac{(J + 1)^{(-1)^J}}{J} \quad (133)$$

For a symmetric rotor such as H_3^+ in a symmetric vibronic state, for the $2J + 1$ functions with even $J = 6m$, one has the reducible representation (as example)

$$D_r = mR + \text{A}_1 \quad (134)$$

$$R = \text{A}_1^+ + \text{A}_1^- + \text{A}_2^+ + \text{A}_2^- + 2\text{E}^+ + 2\text{E}^- \quad (135)$$

which approaches the regular limit for large m also with respect to S^*.

One also easily sees that the reduction in Table 16 approaches a regular representation for high J (and high m) for methane. Equation (126) was given by Quack (1975, 1977) and for special cases of some point groups surmised by Lederman *et al.* (1983) and Pechukas (1984), for a detailed discussion we refer to Quack (1985). This certainly provides insight in the approximate "structure" of densities of states. The results are also of interest in terms of symmetry breakings in the dynamics of polyatomic molecules at high energies and thus high densities of states.

7.4   Symmetry-breaking Dynamics of Polyatomic Molecules at High Densities of States

Equation (124) shows that for large s and large E, very high densities of states are obtained (Figure 20). In combination with equation (126), this guarantees that at some sufficiently high total energy E and angular momentum J, equation (86) will be satisfied for every pair of levels of different symmetry species, because the increase in the density of states (and thus the decrease of $|\Delta E_{0(n,m)}|$) will be faster than a corresponding decrease in the typical couplings $|V_{1(n,m)}|$, at least for tightly bound molecular systems.

Thus, there will always be a point when there will be mixing and symmetry breaking along the lines discussed in Section 6.6. Indeed, for large polyatomic molecules, this is likely to happen at modest energies. Because of the larger $|V_{1(n,m)}|$, this arises for nuclear spin symmetry mixing at lower energies than for parity mixing. However, one must assume that on sufficiently long timescales of seconds or so, such symmetry breakings occur for all larger

polyatomic molecules at energies near the dissociation energy. Symmetry conservation or symmetry breaking will then only be a matter of the timescale considered in Table 8.

Symmetry is also essential when considering the statistical properties of level spacings in quantum systems (Mehta 1967). Characteristic functions are found for such statistical distributions, if one considers levels of a given set of good quantum numbers. The study of such statistical distributions is, thus, an alternative approach both to the analysis of high-resolution spectra and of the underlying fundamental symmetries. This is the motivation for this section. There are also important dynamical consequences (Quack 1978, 1982). Statistical concepts have been also used in studies of parity violation in the compound nucleus (Bowman *et al.* 1993).

8   OUTLOOK ON THE ANALYSIS OF FUTURE POSSIBLE EXPERIMENTS OF VARIOUS POSSIBLE SYMMETRY VIOLATIONS, ON THE QUESTION OF TIME-REVERSAL SYMMETRY, AND ON POSSIBLE TESTS OF CPT SYMMETRY

Dass ich erkenne, was die Welt im Innersten zusammenhält.

Faust (first scene at night), J. W. Goethe

If the particle masses are exclusively due to the Higgs mechanism, then parity **must** *be violated . . .. As it happens, the masses of all particles in the standard model are produced by the Higgs mechanism . . . it appears to be the deus ex machina of the masses of all particles.*

Martinus Veltman (*Veltman 2003*)

We conclude this article with a section summarizing briefly the status of experiments on the various fundamental symmetry violations, in particular also molecular parity violation, and with an outlook on promises of new knowledge from such experiments and their theoretical analysis. We then address the much more speculative question of time-reversal symmetry violation in molecular physics as studied by spectroscopy and on possible spectroscopic tests of *CPT* symmetry.

8.1   Status of Nuclear Spin Symmetry Selection Rules and their Violation

Nuclear spin symmetry violation can be theoretically understood in the framework of the well-formulated electromagnetic interaction used in the traditional analysis of spectra.

It is in this sense a less "fundamental" symmetry violation than the other symmetry violations. Nevertheless, because it gives rise to fairly "exact" good quantum numbers in spectroscopy and reaction dynamics, this symmetry acquires some kind of fundamental status. In addition, as compared to other, even more approximate symmetry rules such as the well-known rules due to Wigner and Witmer (1928) Herzberg (1966), Shuler (1953) and to Woodward and Hoffmann (1970), the detailed state-to-state symmetry rules based on the principles of parity and nuclear spin symmetry conservation (Quack 1977) are much more "exact", neglecting only very small terms in the hamiltonian and in those terms more fundamental.

While there have been some studies of these rules and their violations, as discussed in Section 6, the total number of such studies is still small and there remain many unexplored areas in this field. One expects important consequences in chemical systems at low temperatures, photochemical systems, astrophysics, in particular, also reactions in interstellar clouds, leading to not only star formation but also nuclear spin polarization generated in reactive and photoprocesses under fairly ordinary conditions. We think, therefore, that nuclear spin symmetry and its occasional violation has still great opportunities for future research, even if less fundamental than the symmetries that we discuss now.

8.2   Status of Molecular Parity Violation

We have discussed this symmetry most extensively in this article, because it is just about at that frontier of research where the "impossible" is turned into something "possible". When we started our own investigations a few decades ago, it would have been considered impossible to investigate these effects experimentally. It would also have been considered impossible that the early approximate theories (Hegström *et al.* 1980) might give predictions on such simple systems as H_2O_2, that are incorrect by two orders of magnitude, but this was shown to be possible, indeed (see Section 3 and Bakasov *et al.* (1996, 1998a)). The theory of the field seems now rather well understood (Berger and Quack 2000b, Quack and Stohner 2005).

In the 1980s, even the high-resolution spectroscopic analysis of optical (IR, visible, UV) spectra of chiral molecules—a prerequisite for spectroscopic studies of parity violation in such molecules—appeared "impossible" (and it did not exist). Again, we were able to make such studies possible by the development of appropriate spectroscopic techniques (Quack 1990, Beil *et al.* 1994, Bauder *et al.* 1997, Albert and Quack 2007, 2011; *see also* Albert, Albert, and Quack 2011: **High-resolution Fourier Transform Infrared Spectroscopy**, this handbook). Thus, with

these advances, the high-resolution spectroscopic analysis for not too complex chiral molecules seems now straightforward, even if not quite routine. This is then the essential stepping stone for ongoing spectroscopic investigations of molecular parity violation, as discussed in Section 4. Thus, while there exists still no successful spectroscopic experiment demonstrating molecular parity violation, we think that the outlook is now very bright, indeed, for the ongoing efforts.

We shall also be a little more precise in conclusion of this article in our outlook on possible outcomes of possible theories and experiments of the type discussed here in terms of obtaining fundamental, new knowledge. First, when we shall be able to measure and calculate parity-violating energy differences $\Delta_{pv}E$ for relatively light molecules with very high precision, it should be possible to analyze the results in terms of a fundamental precision experiment on the Standard Model (SMPP, see Quack (2002), and Bakasov and Quack (1999)). In principle, this kind of thinking underlies the already existing experiments on parity violation in atomic spectra (Bouchiat and Bouchiat 1974, Bennett and Wieman 1999). However, these are limited to heavy atoms, which limit the precision of theoretical analyses (Bennett and Wieman 1999). The measurement of parity violation in light chiral molecules might overcome this limitation, thus providing new information beyond the atomic experiments. It may be useful to discuss this point in slightly more detail. It is well known (Schwarzschild 2005, Czarnecki and Marciano 2000) that the effective Weinberg parameter $\sin^2 \Theta_w$ is a function of Q, the four-momentum transfer between the interacting particles or effectively the energy range analyzed by the experiments. At high energy, the effective Weinberg parameter is well determined by the measurement of the properties of the Z-boson ($\sin^2 \Theta_w = 0.231$) (Cohen *et al.* 2007). At lower energy, electron scattering leads to about $\sin^2 \Theta_w = 0.24$ (Anthony *et al.* 2005), whereas the lowest energy range is probed by spectroscopic measurements of atomic optical activity arising from parity violation. Here, $\sin^2 \Theta_w^{\text{eff}} \simeq 0.236$ has been reported with large uncertainty, which is of the same order as the detected change with energy range, making the result, thus, almost useless (Bennett and Wieman 1999, Shabaev *et al.* 2005). In the analysis of the atomic experiments, an important source of uncertainty arises from the theoretical calculations, because experimental results are only available on heavy atoms, such as Cs, for which accurate calculations are difficult (Shabaev *et al.* 2005). Very large effects have recently been reported in experiments for Yb (Tsigutkin *et al.* 2009), but without reducing the theoretical uncertainties. Difficulties arise not only from the complicated electronic structure in heavy atoms but also from poorly known nuclear structure in heavy nuclei.

On the other hand, the close degeneracy of parity sublevels in chiral molecules leads to a maximum perturbation due to parity violation, which should become measurable for molecules involving only light atoms (up to Cl, say). Therefore, very accurate calculations of both electronic structure and knowledge of nuclear structure should be available. The outlook is thus more promising for the analysis of parity violation in chiral molecules, in spite of the additional complications arising from the necessary averaging over the multidimensional vibrational wavefunction (Quack and Stohner 2003).

The sensitivity of molecular parity violation to the effective Weinberg parameter is obvious from equations (26), (28), (31), and (33), where it enters through the weak charge Q_a of the nuclei. The use of isotopic chirality can be of interest here, because of compensations of contributions to the overall uncertainty in such molecules.

This is but one example of such an analysis of future experiments on molecular parity violation. Another possibility is to use the electroweak electron nucleus interaction in molecular parity violation to probe nuclear structure with respect to neutrons, which provide the dominant contribution, whereas the Coulomb interaction would provide a picture of the proton distribution in the nucleus. Of course in such future analyses, calculations would have to take nuclear structure into account explicitly.

Another obvious application of comparison of experiment and theory along those lines would be to test the theory for remaining fallacies.

8.3 Time-reversal Symmetry Violation in Molecular Dynamics and Spectroscopy

As discussed in Section 2.5, the de facto violation of time-reversal symmetry is common and considered to be the "standard interpretation" of the origin of the second law. On the other hand, the de lege violation of time-reversal symmetry has been demonstrated in particle physics for some time in the K-meson system (Adler 1995) and the B-meson system, but in molecular physics it remains a highly speculative topic. The situation here is quite different from parity violation in that we have no secure quantitative theory to predict the magnitude of the effects in molecules. Nevertheless, spectroscopic consequences of de lege time-reversal invariance has been considered for some time in molecular physics (Wigner 1932) and there exist experimental searches for its violation. We discuss here two lines of spectroscopic investigations. The first concerns the searches for permanent electric dipole moments in particles (e.g., electrons, neutrons), atoms, and molecules. It has been discussed that such a dipole moment in an energy eigenstate would be a signature of both de lege

T- and an P-violation (Sandars 1968) and very small effects are even predicted within the Standard Model (SMPP) (Bernreuther and Suzuki 1991). The reason for studying atoms and molecules rather than elementary particles is the so-called enhancement factor for the electron electric dipole moment (Ginges and Flambaum 2004, Pospelov and Ritz 2005). For current experimental searches along these lines we refer to (Gomez *et al.* 2008, Hudson *et al.* 2002). Such experiments have provided various bounds, but no positive demonstration of an electron electric dipole moment, yet.

Quite a different approach would consist in a spectroscopic experiment in the time domain by observing the behavior after an explicit time reversal, that is, the reversal of all momenta and spins in a molecule at some moment of time, say, by means of an appropriately chosen external laser pulse applied to a time-dependent state of an excited polyatomic molecule. One might follow a suitably defined time-dependent coarse grained-quantum entropy S_Q in the complex dynamics of the isolated molecule

$$S_Q = -k \sum_j \langle p_j \rangle \ln \langle p_j \rangle \qquad (136)$$

where $\langle p_j \rangle$ are averaged populations of levels in an appropriate hamiltonian (Luckhaus *et al.* 1993). Figure 21 shows such a result calculated from a spectroscopic time-reversal symmetric hamiltonian of highly excited CHD_2F (Luckhaus *et al.* 1993). One might then speculate that for a very dense, complex spectrum, small time-reversal symmetry-violating terms in the dynamics would lead to a
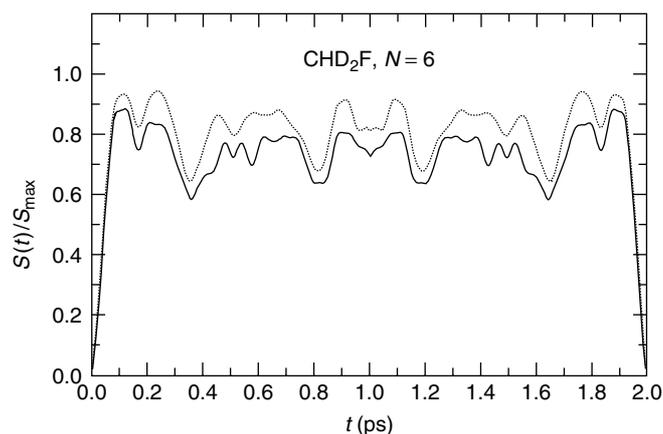
Figure 21 Time-dependent reduced intramolecular entropy for the subset of three coupled oscillators with six quanta of CH stretch initially excited (in the effective hamiltonian basis). Time reversal at $t = 1$ ps. (See discussion in the text.) (——) $S_f(t)/S_{max}$ fine grained; (- - - -) $S_Q(t)/S_{max}$ coarse grained. [After Luckhaus *et al.* (1993) by permission.]

deviation of the time-mirror symmetry in such an experiment (Quack 1997). There are no theoretical predictions on the expected magnitude and thus such proposals for experiments remain conceptual, speculative, and any real sufficiently precise experiment along those lines is expected to be very difficult.

8.4 CPT Symmetry and Fundamental Aspects of Time Reversal

We know from high-energy physics that the individual symmetries C, P, and T (also CP) are violated. After considering time-reversal experiments, one could now consider a similar experiment as depicted in Figure 21, however, much more complex and purely speculative, very far from realization, where at some point of time (momentum) reversal, one reconstructs the quantum state of such a molecule made of antimatter and with the enantiomeric chiral structure, that is, applying the operations CPT at the same time. In the current SMPP and many other fundamental theories in physics, this symmetry is considered exact. This implies the possibility of some form of a "time machine" by generating such a reversed state and by reapplying the same operation after some time repeating exactly the evolution of the system as was observed in past (if one did the experiment on a part of the universe, say, our planetary system, we could go back in history, generating say, a state in the year 1900 and then repeat history). Here, we are not interested in philosophical aspects, but we note that conceptually such experiments could be conceived; in particle physics, they can actually be carried out and show, so far without exception, CPT symmetry. Theoretically, this symmetry has been discussed in the framework of the CPT theorem (sometimes called *Schwinger, Lüders, Pauli theorem*), which can be derived by making some very broad and plausible assumptions (Schwinger 1953, Lüders 1954, 1957, Pauli 1955, Jost 1957).

In the spirit of our discussion in Section 2, exact CPT symmetry again corresponds to a "nonobservable", which could be absolute time direction if space and charge are specified (or a similar "absolute" charge or space direction with appropriate combinations of the other two). As discussed in Quack (1999), it would be impossible to communicate to a distant civilization the sense of rotation ("time direction") of a chiral molecular clock together with the specification of matter/antimatter and enantiomeric structure. However, with a violation of CPT symmetry, the corresponding nonobservable would become observable and the construction of an "absolute" molecular clock (with time direction) possible (Quack 1999).

CPT symmetry has a number of straightforward consequences in particle physics and spectroscopy, which can

be readily tested. For instance, the masses of particles and their antiparticles must be identical. Such tests have been carried out on the proton (antiproton) pair (Gabrielse *et al.* 1995) and the electron/positron pair (Dehmelt *et al.* 1999).

The sensitivity in these tests has reached the level of $\Delta m/m \simeq 10^{-10}$ in the former and $<10^{-14}$ in the latter case. In addition, the high-resolution spectra of the hydrogen atom and the antihydrogen atom are required by *CPT* symmetry to be identical and one might hope that an accuracy corresponding to $\Delta m/m \simeq 10^{-16}$ might be reached in testing the equivalence of such spectra (Charlton *et al.* 1994, Zimmermann and Hänsch 1993, Gabrielse *et al.* 2007, Gabrielse *et al.* 2008). While so far it is difficult to generate and trap neutral antihydrogen atoms in order to do spectroscopy, we have suggested a variant of using a comparison of the H_2^+ ion, i.e., (p^+, p^+, e^-) and its antimatter counterpart $\overline{H}_2^-$, i.e., $(\overline{p}^-, \overline{p}^-, e^+)$ (Quack 2000, 2008). Such ions could be more easily stored in traps and investigated spectroscopically at high accuracy. This would make up for the higher complexity of the spectra.

Finally, at the most fundamental level, we have proposed to use this scheme to test for basic de lege violations of the *CPT* symmetry in chiral molecules (Quack 1993b, 1994b, 2003). This can be done with high precision by finding different $\Delta_{pv}E$ in molecules and their enantiomers made of antimatter (ΔE_{pv}^* refers here to $\Delta_{pv}E$ of a molecule made of antimatter, with a different meaning to the asterisk "*" than that in Figure 7). This is shown in the scheme of Figure 22 (Quack 1994b, 2003). It turns out that this approach might achieve an accuracy $\Delta m/m \simeq 10^{-30}$. One could conceive such experiments using large, chiral clusters of hydrogen vs antihydrogen (possibly ions; see Quack (2003, 2006)).
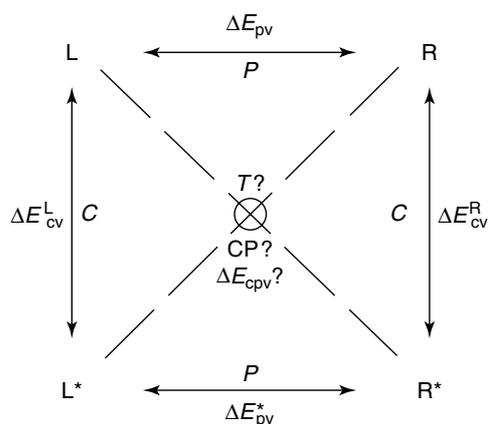

Figure 22 Scheme for a *CPT* test with spectroscopy on chiral molecules. The question marks indicate currently open questions in spectroscopic research. [After Quack (1993b, 1994b) by permission.]

The spectroscopic experiment on *CPT* symmetry violation would involve a measurement of spectra of chiral molecules (say L in Figure 22) and their antimatter enantiomers R* in Figure 22. A difference in spectra of R* and L, say, in the IR, would prove *CPT* violation. The sensitivity of this experiment is expected to be higher than in any other proposed experiment so far (see Quack (1994b) for a discussion).

Future experiments on *CPT* symmetry violation are a highly speculative subject and current wisdom assumes that *CPT* symmetry is valid (Barron 1994). However, again the history of parity violation may teach us a lesson here. About 150 years ago, Pasteur speculated about possible fundamental origins of chirality (called *dissymmetry* by him) in terms of a possible fundamental symmetry violation in "cosmic forces", which today we might call *parity violation* (see the citations in Section 3 and Quack (1989b, 2002)). On the other hand, during the century following Pasteur's discovery of molecular chirality, left–right symmetry was emphasized and even taken for granted, that is, rigorous parity conservation in all aspects of fundamental dynamics. Prominent proponents include van't Hoff, Einstein, Hund, and many others (see Quack 1989b, 2002). The discovery of parity violation in β-decay in 1956–1957 clearly changed our view on the space inversion symmetry or parity. But still, initially parity violation might have been considered as a very special, slightly curious effect important only for some special phenomena such as β-decay (Table 2). However, a further theoretical understanding of the underlying symmetry violation gained over the past half century has led to the view that this symmetry violation is essentially related to even basic theoretical structures of matter in the standard model. Thus, from this point of view, as expressed by Veltman (2003), cited also literally at the start of this section, parity violation is not some curiosity but parity *must* be violated if we want to understand the structure of matter as we do today. It is tempting to make a similarly strong but speculative statement at the other end of the structure of matter, that is, biomolecular homochirality in the evolution of life. However, at this time, such a statement would be premature (Quack 2002). A better understanding of molecular chirality in relation to parity violation may provide some progress in this area as well.

In a final speculation, we might reinterpret the scheme of Figure 22 by calling L the "left-handed" ordinary electron neutrino ν_e and R* its "right-handed" counterpart, the antineutrino $\overline{\nu}_e$ (and similarly for the other types of neutrinos). It is known that the ordinary counterpart, the right-handed "matter neutrino" $\nu_e(R)$, is absent in the Standard Model. If, however, the L/R symmetry violation leads to a very heavy counterpart with a mass equivalent

$m[\nu_e(R)]c^2 \gg 100\,\text{GeV}$, then such particles might not yet have been seen in particle physics, although they might exist as stable particles and even be important in cosmology as contributors to dark matter. As this field is already full of speculations, it might be permissible to add one more.[c]

END NOTES

[a] The original is in German: "Es gibt also zweierlei kartesische Koordinatensysteme, welche man als 'Rechtssysteme' und 'Linkssysteme' bezeichnet. Der Unterschied zwischen beiden ist jedem Physiker und Ingenieur geläufig. Interessant ist, dass man Rechtssysteme bzw. Linkssysteme an sich nicht geometrisch definieren kann, wohl aber die Gegensätzlichkeit beider Systeme." (Einstein 1922). See also Quack (1999) and the translation of the citation in Quack (2002, 2004b).

[b] Having seen how much the ideas of Galois have been fruitful in many branches of analysis, geometry, and even mechanics, one may rightly hope that their power will become evident even in mathematical physics. What else do the effects of natural phenomena represent, if not a succession of infinitesimal transformations, the invariants of which being the laws of the universe (freely translated here from the French original).

[c] Peter Biermann has suggested weakly interacting right handed neutrinos with $2\,\text{keV} \leq m_0^2 \leq 4\,\text{keV}$ ("WIN") providing energetic radiation by a very slow decay, on cosmological grounds (P.L. Biermann 12th Brioni conference, Brijuni 2010).

ABBREVIATIONS AND ACRONYMS

CIS	configuration interaction singles
eV	electron volt
GeV	giga electron volt (10^9 eV)
IR	infrared
IVR	intramolecular vibrational redistribution
MC-LR	multiconfiguration linear response approach
MeV	mega electron volt (10^6 eV)
meV	milli electron volt (10^{-3} eV)
RHF	restricted Hartree–Fock
SMPP	Standard Model of Particle Physics
TeV	tera electron volt (10^{12} eV)

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