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Symmetry and Evolution: Molecules in Motion between less than Yoctoseconds and more than Days*

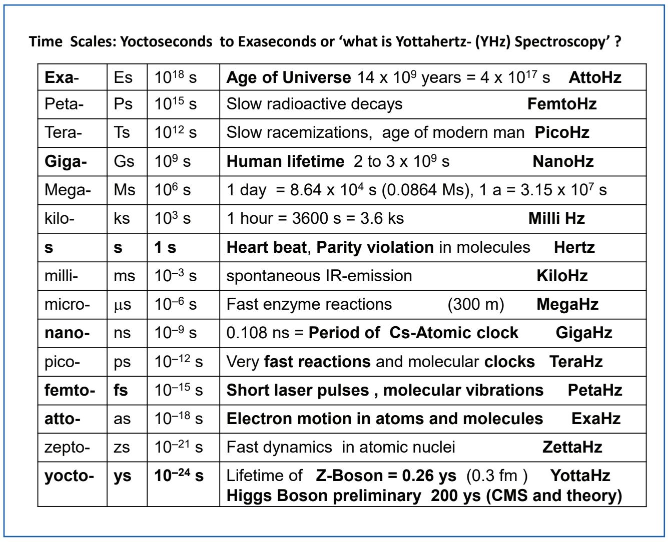
Abstract

We review briefly the role of symmetries in the time evolution of molecular quantum systems as well as of biomolecular systems leading to biological evolution. Emphasis is placed on fundamental concepts and the role of approximate symmetries in defining different time scales for primary processes. We provide a brief summary of a new foundation of tunneling spectra and the current status of our work on parity violation in chiral molecules.

1. Introduction

When we consider the time scales for physical-chemical primary processes in the Universe as we know it today they range over 42 orders of magnitude, from more than 10^{10} years for slow radioactive decays, about the age of the Universe or the time needed for the evolution of 'intelligent life' from the estimated time of the start of life on Earth 3×10^9 years ago (about 0.1 ES) to the time of a heart beat or the change of parity in isolated chiral molecules (about a second, 1 s) and to the period of fast molecular vibrations (about 10 fs), fast electronic processes in atoms and molecules (100 as) and finally the lifetime of less than a yoctosecond (0.26 ys) for the Z-boson, which is at the origin of molecular parity violation (see Fig. 1).

The questions then arise on how to study atomic and molecular primary processes over such wide ranges of time scales experimentally and how to understand these different time scales for primary processes theoretically. We shall provide here a very brief review of our experimental and theoretical approaches towards these questions with an emphasis on the role of symmetry. We shall focus attention on fundamental concepts of molecular primary processes, symmetries and conservation laws as they relate to the very foundations of chemical reaction kinetics, which has obviously a wide range of applications from atmospheric and astrophysical chemistry to combustion, from photochemistry to multiphoton excitation and IR laser chemistry or the fragmentation patterns in mass spectra and finally the kinetics of catalysis, say, by enzymes in biology, to name just the more fundamental aspects. Physical-chemical kinetics is at the core as well of chemical engineering and technology.



Time Scales: Yoctoseconds to Exaseconds or 'what is Yottahertz- (YHz) Spectroscopy' ?

Exa-	Es	10^{18} s	**Age of Universe** 14 x 10^9 years = 4 x 10^{17} s **AttoHz**
Peta-	Ps	10^{15} s	Slow radioactive decays **FemtoHz**
Tera-	Ts	10^{12} s	Slow racemizations, age of modern man **PicoHz**
Giga-	Gs	10^9 s	**Human lifetime** 2 to 3 x 10^9 s **NanoHz**
Mega-	Ms	10^6 s	1 day = 8.64 x 10^4 s (0.0864 Ms), 1 a = 3.15 x 10^7 s
kilo-	ks	10^3 s	1 hour = 3600 s = 3.6 ks **Milli Hz**
s	**s**	**1 s**	**Heart beat**, **Parity violation** in molecules **Hertz**
milli-	ms	10^{-3} s	spontaneous IR-emission **KiloHz**
micro-	µs	10^{-6} s	Fast enzyme reactions (300 m) **MegaHz**
nano-	ns	10^{-9} s	0.108 ns = **Period of Cs-Atomic clock** **GigaHz**
pico-	ps	10^{-12} s	Very **fast reactions** and molecular **clocks** **TeraHz**
femto-	**fs**	10^{-15} s	**Short laser pulses , molecular vibrations** **PetaHz**
atto-	as	10^{-18} s	**Electron motion in atoms and molecules** **ExaHz**
zepto-	zs	10^{-21} s	Fast dynamics in atomic nuclei **ZettaHz**
yocto-	**ys**	**10^{-24} s**	Lifetime of **Z-Boson = 0.26 ys** (0.3 fm) **YottaHz** **Higgs Boson preliminary 200 ys (CMS and theory)**

Fig. 1: Time scales and primary processes, 42 orders of magnitude

Fig. 2 provides a picture of how to understand the wide range of time scales for chemical elementary reactions in two prototypical situations. For chemical reactions that proceed by passing over a potential energy barrier (in a description using the Born-Oppenheimer or related approximations) shown on the left hand side of the figure, statistical theories such as transition state theory (TST) or the statistical adiabatic channel model (SACM) provide a law for the rate coefficient k(T), which depends about exponentially on the barrier height E_0 and the thermodynamic temperature T:

$$k(T) = (kT/h)\,(Q^*/Q)\,\exp(-E_0/RT) \qquad (1)$$

where the partition functions Q (quasi-partition function Q* from adiabatic channel maxima or for the transition state) depend only moderately on temperature and where we use common symbols in our notation throughout [1-5]. The exponential dependence described by Eq. (1) results in an enormous possible range for time scales related to k(T). This is, however, the con-

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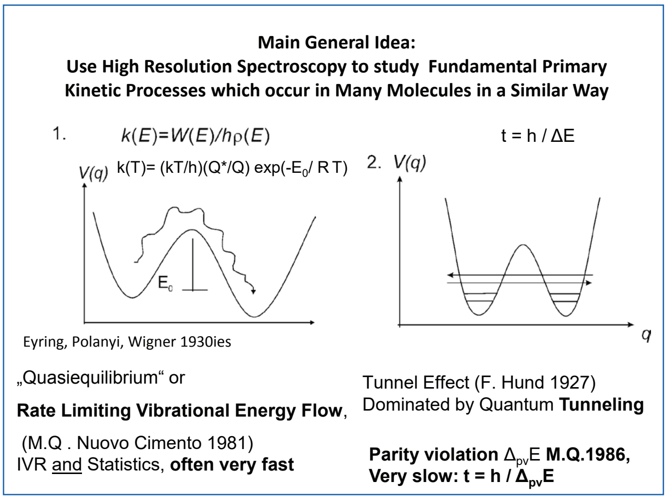
sequence of ‘non-dynamical’, statistical effects arising from the Boltzmann factor for thermal populations as a function of energy and temperature, as in exp($-E_0$ /RT). This point had in fact already been noted by van’t Hoff and notably Svante Arrhenius with the ‘Arrhenius equation’, both honorary members of the Bunsen Society elected in 1895. Also the expression for specific (microcanonical) rate coefficients k(E) as a function of energy E arises in statistical theories in a ‘non-dynamical’ way through counting numbers of reaction channels W(E) in the numerator and densities of molecular states in the denominator (Fig. 2). Some simple dynamical effects are included in the SACM as a generalized state specific form of quasi-adiabatic transition state theory by taking into account explicitly certain constants of the motion such as total angular momentum J in k(E, J), but otherwise statistics dominates [1, 2]. Truly dynamical effects arise, when intramolecular energy flow becomes rate determining, subject to various constraints due to approximate symmetries and conservation laws, and we shall return to this in section 2.


Main General Idea:
Use High Resolution Spectroscopy to study Fundamental Primary Kinetic Processes which occur in Many Molecules in a Similar Way

1. $k(E)=W(E)/h\rho(E)$

$t = h / \Delta E$

$k(T)= (kT/h)(Q^*/Q) \exp(-E_0/ RT)$

2.

Eyring, Polanyi, Wigner 1930ies

„Quasiequilibrium“ or

Rate Limiting Vibrational Energy Flow,

(M.Q . Nuovo Cimento 1981)
IVR and Statistics, **often very fast**

Tunnel Effect (F. Hund 1927)
Dominated by Quantum **Tunneling**

Parity violation $\Delta_{pv}E$ M.Q.1986,
Very slow: $t = h / \Delta_{pv}E$

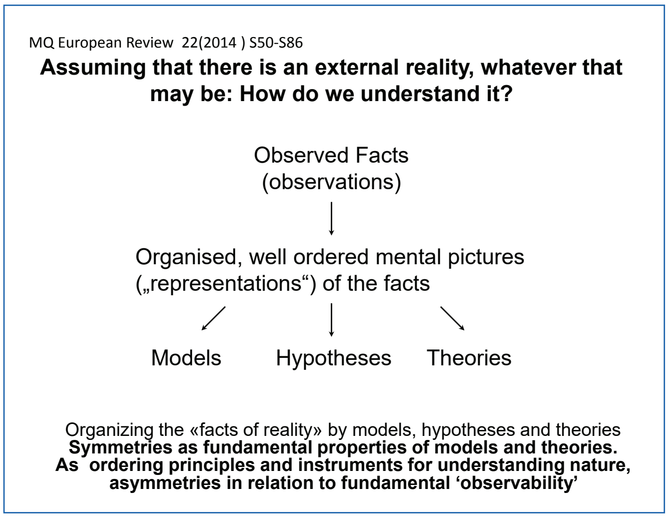
Fig. 2: Schemes for prototypical situations for molecular primary processes and chemical reactions as described by the corresponding potential energy diagrams with V(q) as function of a reaction coordinate q.

Another prototypical primary process leading to reaction arises from the tunnel effect in quantum mechanics discovered by Friedrich Hund in 1927 (elected honorary member of the Bunsen Society in 1970) in the context of his quantum mechanical treatment of chiral molecules (see ref. [6] for the history). The quantum dynamics of the primary process of tunneling leads to an enormous range of time scales because of the strong dependence on the effective tunneling mass and the shape (height and width) of the potential barrier to be penetrated. We shall discuss in section 4 below a new and more fundamental aspect of the spectroscopy and dynamics of tunneling, which results from symmetry considerations beyond the approximate description by Born-Oppenheimer potential barriers.

The main common idea to be introduced here is, how frequency or energy resolved high resolution spectroscopy can be used for the study of these dynamical primary processes of intramolecular energy flow and tunneling over an extremely wide range of time scales, besides and beyond the common time resolved experiments. A further primary process of a very new and different nature arises from parity violation- the violation of space inversion symmetry- in chiral (and also achiral) molecules. We have to restrict our attention here to the basic concepts of the role of symmetry for molecular primary processes and refer to recent reviews and books for a more detailed discussion and more comprehensive citation of the literature on the topic [1-12].

2. Why study abstract conservation laws and symmetry violations for kinetic primary processes?

Fig. 3 illustrates, how science provides an understanding of natural phenomena or external reality quite generally, by starting from observed facts, which are organized as well ordered ‘representations’ by models, hypotheses and theories [13]. Indeed, symmetries provide further, more fundamental ordering principles common to and beyond the various models, hypotheses and theories. Symmetries and asymmetries can further be related to a fundamental concept of ‘observability’, as was already noted by Einstein [14] (see the discussion in ref. [7] with a detailed citation).


MQ European Review 22(2014) S50-S86

Assuming that there is an external reality, whatever that may be: How do we understand it?

Observed Facts
(observations)

Organised, well ordered mental pictures
(„representations“) of the facts

Models Hypotheses Theories

Organizing the «facts of reality» by models, hypotheses and theories
Symmetries as fundamental properties of models and theories.
As ordering principles and instruments for understanding nature,
asymmetries in relation to fundamental ‘observability’

Fig. 3: Understanding the facts of nature and external reality by models hypotheses, theories and, at a fundamental level, symmetries.

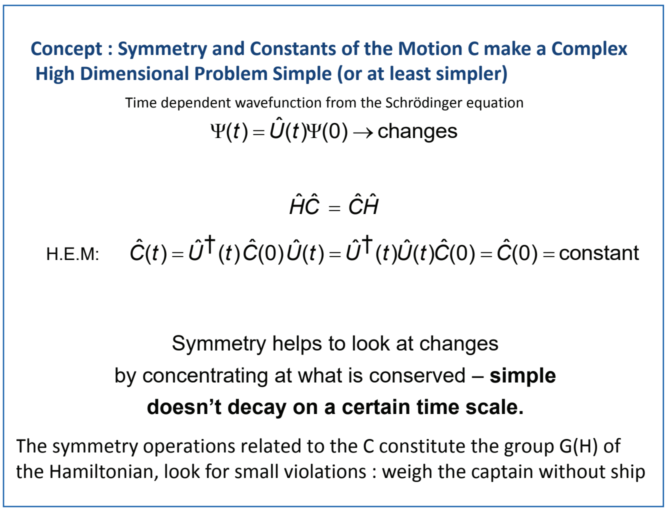
Concentrating here on the quantum dynamics of microscopic systems in general and molecular quantum motion as kinetic primary process in particular this can be described by the time dependent Schrödinger equation for the time dependent wavefunction $\Psi(t)$, the solution of which is given in Fig. 4 by means of the time evolution operator $\hat{U}(t)$, which transforms the wavefunction at time t=0 to the wavefunction at time t. The time evolution operator is obtained by the solution of a Schrödinger-like differential equation in general [4, 5],

$$i\left(\frac{h}{2\pi}\right)\frac{d\hat{U}(t, t_0 = 0)}{dt} = \hat{H}\,\hat{U}(t, t_0 = 0) \qquad (2)$$

but for the case of an isolated quantum system with a time independent Hamiltonian $\hat{H}=\hat{T}+\hat{V}$ as sum of kinetic and potential energy, it can be obtained directly as an exponential function of H:

$$\hat{U}(t\ t_0 = 0)) = \exp(-2\pi i\,\hat{H}\,t/h) \qquad (3)$$

One can now instead of asking for the time dependent observables ask the opposite question : What among the many possible time dependent observables remains constant in time, is a 'constant of the time evolution' or more briefly a 'constant of evolution' or a 'constant of motion' related to an operator $\hat{C}$ (Fig. 4) ?



Concept : Symmetry and Constants of the Motion C make a Complex High Dimensional Problem Simple (or at least simpler)

Time dependent wavefunction from the Schrödinger equation

$$\Psi(t) = \hat{U}(t)\Psi(0) \rightarrow \text{changes}$$

$$\hat{H}\hat{C} = \hat{C}\hat{H}$$

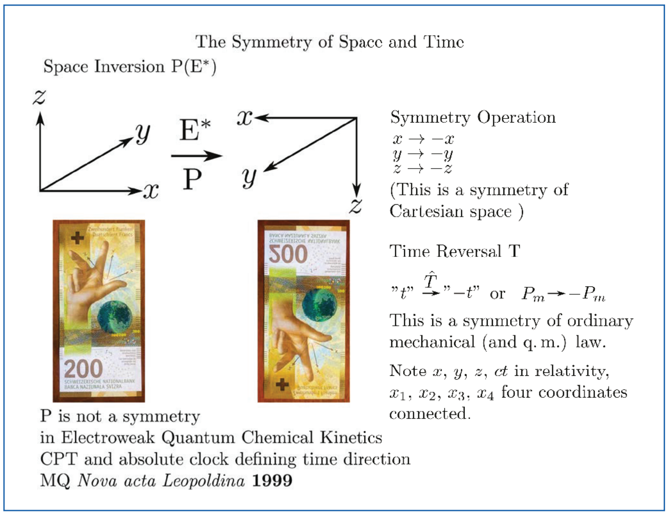
H.E.M: $\hat{C}(t) = \hat{U}^{\dagger}(t)\hat{C}(0)\hat{U}(t) = \hat{U}^{\dagger}(t)\hat{U}(t)\hat{C}(0) = \hat{C}(0) = \text{constant}$

Symmetry helps to look at changes
by concentrating at what is conserved – **simple**
doesn't decay on a certain time scale.

The symmetry operations related to the C constitute the group G(H) of the Hamiltonian, look for small violations : weigh the captain without ship

Fig. 4: Symmetries and constants of time evolution, constants of motion

Indeed, these are related to the symmetry operations, which form the symmetry group of the Hamiltonian G(H), which commute with the Hamiltonian ($\hat{H}\hat{C}=\hat{C}\hat{H}$). Because $\hat{U}$ is a function of $\hat{H}$, Eq. (2), it also commutes with the C (i.e. $\hat{U}\hat{C}=\hat{C}\hat{U}$). Furthermore, $\hat{U}$ is unitary ($\hat{U}\hat{U}^{\dagger}=1$). Therefore as summarized in Fig. 4 in the line H.E.M. for the Heisenberg equations of motion one can prove in one line that the potentially time dependent observables $\hat{C}(t)$ stay in fact constant in time, being at all times t equal to $\hat{C}(t=0)$, they are, indeed, the constants of evolution. In the familiar terms of classical mechanics the symmetry or invariance of H with respect to any rotation in free space leads to the conservation of angular momentum, for example, and the symmetry of the Hamiltonian with respect to space inversion (P for parity in high energy physics or commonly labeled E* in spectroscopy, i.e. the change of all Cartesian coordinates of all particles into their negative values, x—>-x, y—>-y, z—>-z, Fig. 5) leads to parity conservation or the conservation of the 'good quantum number' parity in quantum mechanics. The well known conservation laws were proven by Emmy Noether in the framework of classical mechanics in a rather complex mathematical proof [15] (with some preceding work by Jacobi [16]). They can be proven in the framework of quantum mechanics in 'one line' as shown in Fig. 4, making, however, use of the background knowledge from quantum theory. The notion of 'proof' needs some comment in this context. The mathematical proof starts from the premiss of the existence of the symmetry and then proceeds with mathematical rigor. It is not a proof that the symmetry actually exists for the physical-chemical system under consideration. This latter fact must be established by experiment. The relation between the fundamental symmetries of physics and the conservation laws is common textbook matter [17]. The relation of symmetries to 'observability' or 'non-observables' is less widely known and we have not found a common textbook referring to this (except specialized handbooks etc. [4, 5]), although it was certainly appreciated by some long ago already (see [7, 8, 11, 14, 18, 19] and references cited therein). For instance with respect to space inversion symmetry and parity conservation, the 'absolute handedness' or 'image- mirror image' nature of a chiral object is non-observable, it cannot be defined in an absolute way [14] (or communicated by a coded message without sending a handed object [19]. When we define 'handedness' (left- or right-) in teaching on our Earth we can use the anthropomorphic 'right hand rule' as convention, which is actually illustrated on the Swiss 200 Franc bank note (Fig 5.). This would not work, however, with a distant non- anthropic civilization. When the symmetry is broken, however, such as through parity violation, handedness becomes 'observable' in an absolute sense.



The Symmetry of Space and Time

Space Inversion P(E*)

Symmetry Operation

$x \rightarrow -x$
$y \rightarrow -y$
$z \rightarrow -z$

(This is a symmetry of Cartesian space)

Time Reversal T

$"t" \xrightarrow{\hat{T}} "-t"$ or $P_m \rightarrow -P_m$

This is a symmetry of ordinary mechanical (and q. m.) law.

Note x, y, z, ct in relativity, x_1, x_2, x_3, x_4 four coordinates connected.

P is not a symmetry
in Electroweak Quantum Chemical Kinetics
CPT and absolute clock defining time direction
MQ *Nova acta Leopoldina* **1999**

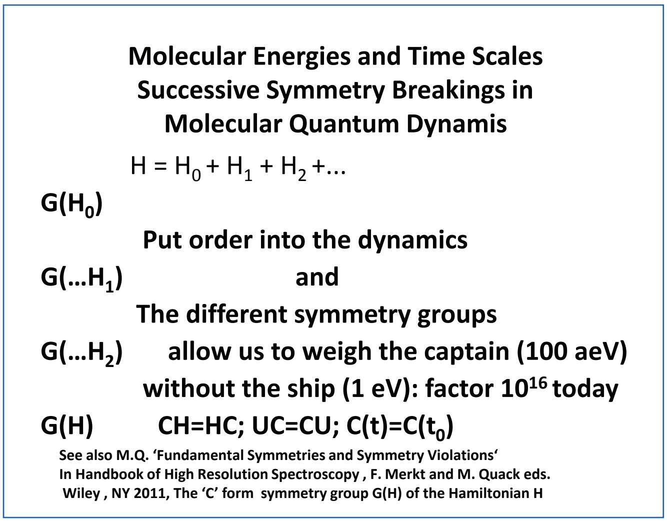
Fig. 5: Space inversion symmetry and parity: 'handed' Cartesian coordinate systems (see text).

This allows us now to make further use of the concept of approximate symmetries and proceed beyond the mere statement that there can be constants of evolution. When we represent some Hamiltonian as a sum of contributions of very different magnitude (Fig. 6), where we switch to a matrix representation now, omitting in the notation the "hat" for the operator symbol:

$$H=H_0 + H_1 + H_2 + H_3 + \ldots. \tag{4}$$

(with $H_0 >> H_1 >> H_2 >> H_3 \ldots$), we can introduce the concept of approximate symmetries and approximate constants of evolution.

The energy levels of a molecule, say, would be described to a good approximation by H_0, and when adding H_1, this would change the energy only a little, being a small 'perturbation'. The symmetry group G of the Hamiltonian may now depend on which terms are retained in Eq. (3), with groups $G_0(H_0)$, $G_1(H_0 + H_1)$, etc.. Then one can have a symmetry or constant of the motion C_0 belonging to $G_0(H_0)$, which may not appear in $G_1(H_0 + H_1)$, etc. Thus, if one observes a change in time for this observable corresponding to C_0, this cannot be due to H_0, as C_0 would be exactly time independent, if only H_0 is considered. The change of C_0 in time must entirely arise from H_1 (or H_2, H_3, ..., if any). At the same time, the different magnitudes of the contributions in H introduce a natural hierarchy of time scales, H_0 leading to some possibly very fast changes for some observables but no change in C_0, the small H_1 introducing a slow change of C_0, and so forth. This allows one to isolate very small contributions in the Hamiltonian arising from H_1 independent of any large uncertainties, which may occur in the very large H_0. To use a common picture: One can weigh the 'captain' directly without having to measure a difference in the weight of 'ship+captain' and 'ship alone', where the uncertainty in the latter measurement would be much larger than any possible weight of a captain. For the example of parity violation we shall have differences on the order of magnitude of typical electronic energies of molecules (say, on the order of 1 eV) compared to parity violating energies on the order of 100 aeV to 1 feV, more than 15 orders of magnitude smaller. One may compare this with the weight of a large ship (for example Queen Elisabeth 2) with about 50'000 tons displacement and a captain with 50 to 100 kg, less than 6 orders of magnitude difference. This concept can be made use of for theory, where the uncertainties in solutions of the Schrödinger equation may be due to theoretical or just numerical uncertainties, typically much larger than a fraction of 10^{-15}: In quantum chemical calculations an uncertainty of 1meV (in H_0) would be considered quite acceptable, but it is huge compared to 1 feV. The concept can also be made use of in the design of experiments, where a relative experimental uncertainty of less than 10^{-15} may be very difficult to achieve otherwise.



Molecular Energies and Time Scales
Successive Symmetry Breakings in
Molecular Quantum Dynamis

$H = H_0 + H_1 + H_2 + \dots$

$G(H_0)$

Put order into the dynamics

$G(\dots H_1)$ and

The different symmetry groups

$G(\dots H_2)$ allow us to weigh the captain (100 aeV)

without the ship (1 eV): factor 10^{16} today

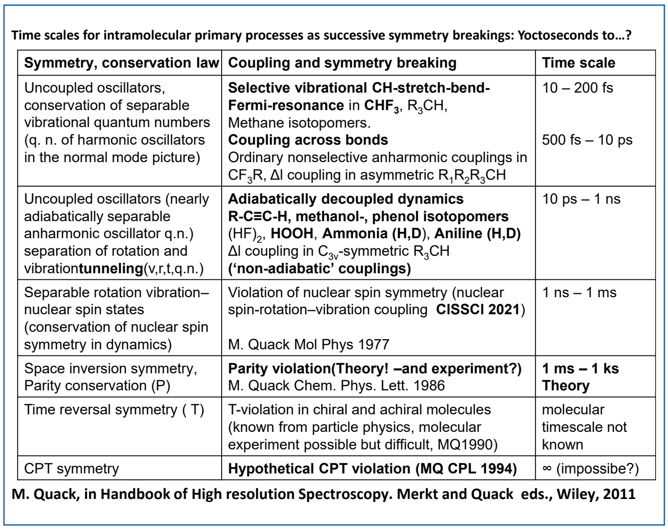
$G(H)$ CH=HC; UC=CU; $C(t)=C(t_0)$

See also M.Q. 'Fundamental Symmetries and Symmetry Violations'
In Handbook of High Resolution Spectroscopy , F. Merkt and M. Quack eds.
Wiley , NY 2011, The 'C' form symmetry group G(H) of the Hamiltonian H

Fig. 6: Symmetry, molecular energies and time scales: Contributions to a Hamiltonian with different symmetry groups

This concept can be made use of in many ways for various primary processes and table 1 summarizes results for primary processes, which we have studied experimentally and theoretically over several decades. As a first example we may mention intramolecular vibrational redistribution (IVR) and energy flow. The dominant part of the Hamiltonian may be described in the harmonic approximation by a set of uncoupled harmonic oscillators. Then, all the quantum numbers of all the oscillators are constants of evolution when the molecule carries out its time dependent harmonic vibrational motion on the time scale of some 10 femtoseconds. Anharmonic contributions break this symmetry, however and remove the conservation of the harmonic quantum numbers, the time scales for this ranging from 10 to 100 fs and to much longer times depending on the nature of the molecules and functional groups considered.

Another example concerns the conservation of nuclear spin symmetry in molecular and physical chemical processes including reactions [7, 20]. As the contribution from nuclear spin symmetry breaking terms in the Hamiltonian are small, there are in fact only few examples, where such violations have been directly observed in isolated molecules. The transformation from the para nuclear spin isomer to the ortho isomer by coherent radiative excitation or in the isolated molecule ClSSCl is a recent example, and this process happens on relatively long time scales from ns to ms (or up to seconds [9, 21]).



Time scales for intramolecular primary processes as successive symmetry breakings: Yoctoseconds to…?

Symmetry, conservation law	Coupling and symmetry breaking	Time scale
Uncoupled oscillators, conservation of separable vibrational quantum numbers (q. n. of harmonic oscillators in the normal mode picture)	**Selective vibrational CH-stretch-bend-Fermi-resonance** in **CHF_3**, R_3CH, Methane isotopomers. **Coupling across bonds** Ordinary nonselective anharmonic couplings in CF_3R, ΔI coupling in asymmetric $R_1R_2R_3CH$	10 – 200 fs 500 fs – 10 ps
Uncoupled oscillators (nearly adiabatically separable anharmonic oscillator q.n.) separation of rotation and vibration**tunneling**(v,r,t,q.n.)	**Adiabatically decoupled dynamics** **R-C≡C-H, methanol-, phenol isotopomers** $(HF)_2$, **HOOH**, **Ammonia (H,D)**, **Aniline (H,D)** ΔI coupling in C_{3v}-symmetric R_3CH **('non-adiabatic' couplings)**	10 ps – 1 ns
Separable rotation vibration–nuclear spin states (conservation of nuclear spin symmetry in dynamics)	Violation of nuclear spin symmetry (nuclear spin-rotation–vibration coupling **ClSSCl 2021**) M. Quack Mol Phys 1977	1 ns – 1 ms
Space inversion symmetry, Parity conservation (P)	**Parity violation(Theory! –and experiment?)** M. Quack Chem. Phys. Lett. 1986	**1 ms – 1 ks Theory**
Time reversal symmetry (T)	T-violation in chiral and achiral molecules (known from particle physics, molecular experiment possible but difficult, MQ1990)	molecular timescale not known
CPT symmetry	**Hypothetical CPT violation (MQ CPL 1994)**	∞ (impossibe?)

M. Quack, in Handbook of High resolution Spectroscopy. Merkt and Quack eds., Wiley, 2011

Table 1: Time scales for intramolecular primary processes, symmetries and approximate constants of evolution (after [7, 9, 23, 26], where references to the original literature can be found).

Further down in table 1 we mention the process of parity violation in molecules. Here we have so far only theoretical results and one predicts time scales from ms to s, depending on the molecule. This process of the time evolution of parity arising from the effect of parity violation by the weak nuclear force found in nuclear and elementary particle physics and described theoretically in the Standard Model of Particle Physics (SMPP) thus constitutes the experimental long time frontier of molecular primary processes [9, 22]. For the molecular primary processes by further symmetry violations further down in table 1, there is so far neither a quantitative molecular theory nor any successful experiment, although some of the effects are known from high energy physics (see discussion in [9]).

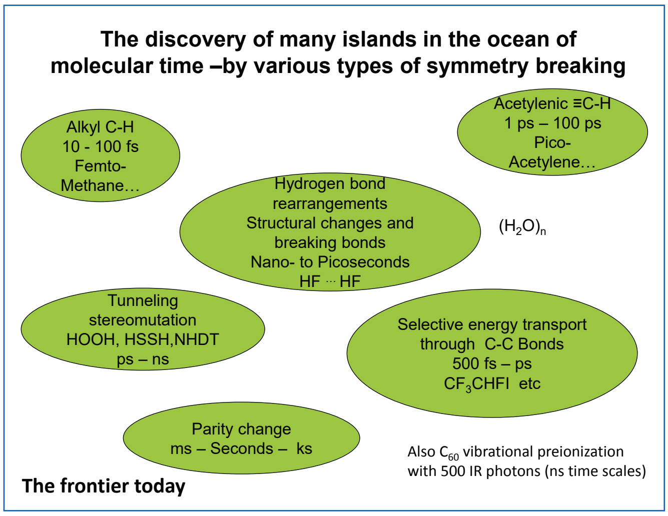


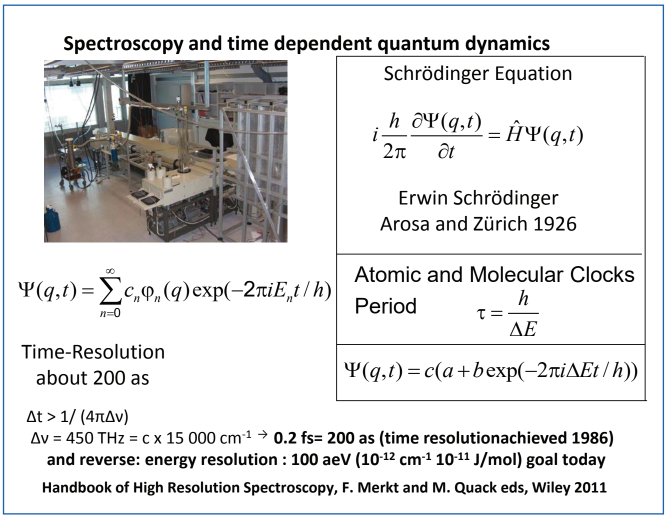
Fig. 7: Islands in the ocean of time

We have seen here how symmetries and asymmetries allow us to identify and understand very different time scales for various processes which can thus be seen as islands in the ocean of time (Figure 7). Before turning attention now to parity violation in molecules, we shall briefly discuss the experimental approaches to time dependent processes by either time resolved or frequency resolved spectroscopy as this gives occasionally rise to debate [23].

3. The experimental study of kinetic primary processes by time resolved and frequency resolved approaches

The most obvious approach to chemical kinetics is the time dependent observation, for example by spectroscopic techniques and there is a huge literature on such experiments starting with the early quantitative investigations by Wilhelmy 1850 leading to the quantitative formulation of a differential equation for a pseudo first order reaction (see [24, 25] for some history). From the 1980s we have developed an alternative approach for quantum dynamical molecular processes over a wide range of time scales using spectroscopy at high frequency resolution but not necessarily high time resolution (see [7, 9, 23-26] for reviews). There has been some debate on how it can be that by spectroscopic observation of 'molecular eigenstates at high energy resolution and long, ideally infinite lifetime', one can derive information on possibly very fast processes.

While we refer to the reviews cited for details we provide here a cursory summary of the approach in Figs. 8 and 9. When one considers the solutions of the time dependent Schrödinger equation for an isolated quantum system such as a molecule, the solution can be given by a sum over an infinite number of contributions of different energies of the eigenstates (Fig. 8). Thus, in principle, spectroscopic knowledge of the energy-eigenstates can provide the relevant information. However, obtaining this knowledge requires the maximum of information to be obtained at high resolution together with all the ingenuity available from spectroscopic analysis with appropriate models, which allows one to construct also the eigenfunctions related to the relevant 'spectroscopic eigenstate' energies, which are derived from the accurate measurement of spectral lines. The frequent statement that "one simply has to Fourier transform the spectrum" is incorrect, even non-sensical, as this would not provide the information obtained by a proper spectroscopic analysis. In fact, often the primary data are a Fourier transform of the spectrum (either in the time domain or by interferometric Fourier transform spectroscopy), from which the frequency spectrum is obtained by a Fourier transformation. The reverse Fourier transformation would simply be a back transformation to the primary data, the two representations of the spectrum being essentially equivalent.


Spectroscopy and time dependent quantum dynamics

Schrödinger Equation

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

Erwin Schrödinger
Arosa and Zürich 1926

$$\Psi(q,t) = \sum_{n=0}^{\infty} c_n \varphi_n(q) \exp(-2\pi i E_n t / h)$$

Atomic and Molecular Clocks
Period $\tau = \frac{h}{\Delta E}$

$$\Psi(q,t) = c(a + b\exp(-2\pi i \Delta E t / h))$$

Time-Resolution
about 200 as

$\Delta t > 1/(4\pi\Delta\nu)$

$\Delta\nu = 450$ THz = c x 15 000 cm^{-1} → **0.2 fs= 200 as (time resolutionachieved 1986)**

and reverse: energy resolution : 100 aeV (10^{-12} cm^{-1} 10^{-11} J/mol) goal today

Handbook of High Resolution Spectroscopy, F. Merkt and M. Quack eds, Wiley 2011

Fig. 8: The spectroscopic approach with high frequency resolution towards the analysis of time dependent primary processes.

Only in the two limiting cases of (i) an isolated resonance decaying into a continuum with an exponential decay giving rise to a Lorentzian line shape providing an accurate lifetime of the resonance state from the width of the line, and (ii) of a single spectroscopic line corresponding to a well defined process, for instance a tunneling transition such as in the well known case of ammonia can one speak of a 'simple' analysis. The former example has provided the sub-ys lifetime of the Z-boson which we have mentioned (with relativistic corrections to the line shape (see [9] and references cited therein). The latter example is at the origin of atomic and molecular clocks, also mentioned in Fig. 8 as the simple two level limit. In real molecules such as ammonia or the chiral NHDT [27] the interpretation is not truly that simple, but the essence remains valid.

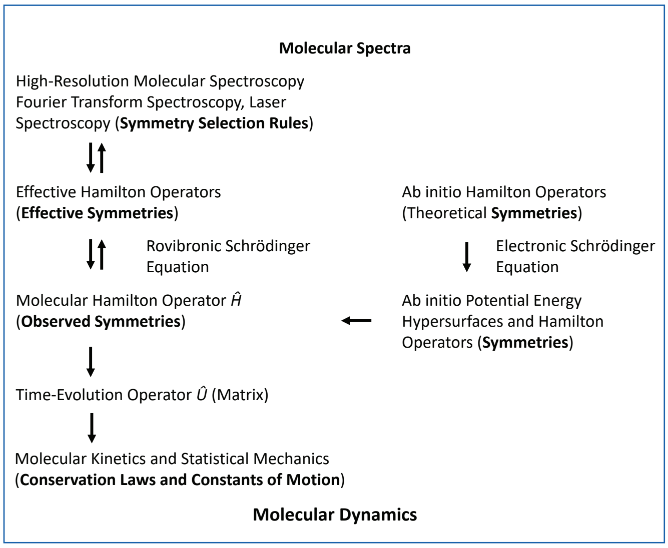


Fig. 9: From high-resolution molecular spectra and symmetries to molecular dynamics and kinetics and their constants of motion.

In practice the realization of the frequency resolved approach towards the quantum dynamics of polyatomic molecules requires a complex analysis of often several ten thousand spectral lines and some ingenuity in assigning patterns [28] (see Fig. 9), for instance also in view of identifying a molecular quantum switch [44]. This is not trivial but leads to highly accurate results, if carried out correctly. An obvious limitation is that the summation for the solution of the Schrödinger equation shown in Fig 8 can be extended only over a finite energy and frequency range, in practice, which then defines the time-resolution Δt obtainable with this approach (Fig. 8). In some examples analyzed by us for IVR in the 1980s a wavenumber range of about 15000 cm^{-1} could be covered by combining several spectra, allowing us to claim a time-resolution, in principle, of about 200 as, even though the fastest relevant IVR processes observed then had time ranges of 30 to 100 fs, typically. It might be of interest that a striking discovery by the frequency resolved approach of these years was the large difference in IVR between alkylic and acetylenic C-H groups attached to a polyatomic frame [29], recently confirmed by time resolved femtosecond pump probe experiments on selected bichromophoric molecules [30].

We mention here also the approach to kinetic spectroscopy with high frequency resolution of hyperfine structures and with uncertainty limited time resolution [31]. Fig. 8 also mentions the possibility of obtaining very high energy resolution by time resolved measurements on long time scales, which we shall address now in the context of parity violation in chiral molecules.

4. Theory and the experimental approach towards parity violation in chiral molecules

The energies arising from parity violation in chiral molecules are exceedingly small and one may justly ask why investigation of these effects might have any interest. The main reasons are twofold. Firstly successful experiments on parity violation in chiral molecules will open a new window to look at aspects of the standard model SMPP and fundamental physics at energies and conditions where there are no successful precision experiments yet and therefore important contributions and even surprises with 'new physics' are possible. Secondly a fundamental understanding of parity violation in chiral molecules may open avenues towards an understanding of the role of parity violation in the evolution of biomolecular homochirality. We have mentioned the possible and ongoing experiments for measuring parity violation in chiral molecules by detecting the new primary process of the change of parity in isolated molecules, although no experiment, so far, has demonstrated successfully the effects from parity violation in molecules.

Parity violation was one of the most striking discoveries in nuclear and elementary particle physics of the 20th century. Shortly after its discovery it was pointed out that one consequence for molecular physics is the prediction of a small parity violating energy difference $\Delta_{pv}E$ between the ground states of enantiomers of chiral molecules and possible consequences also for the interpretation of the long established observation of biomolecular homochirality. Early estimates for $\Delta_{pv}E$ and also quantitative calculations of these extremely small energies up to 1995 were, however, wrong by orders of magnitude. In 1986 I proposed an experimental scheme for measuring $\Delta_{pv}E$ [32] by measuring the time evolution of parity by high resolution spectroscopy. Following our theoretical discovery in 1995 of a new, larger order of magnitude for the predicted $\Delta_{pv}E$ there was considerable theoretical activity by several groups, which confirmed the new orders of magnitude, and there is now also some experimental activity in this field. We have early on and also recently reviewed the status of the research on parity violation in chiral molecules and we refer to these reviews for quite comprehensive information on the topic [7-12, 33, 34]. Here we shall provide just a brief summary.

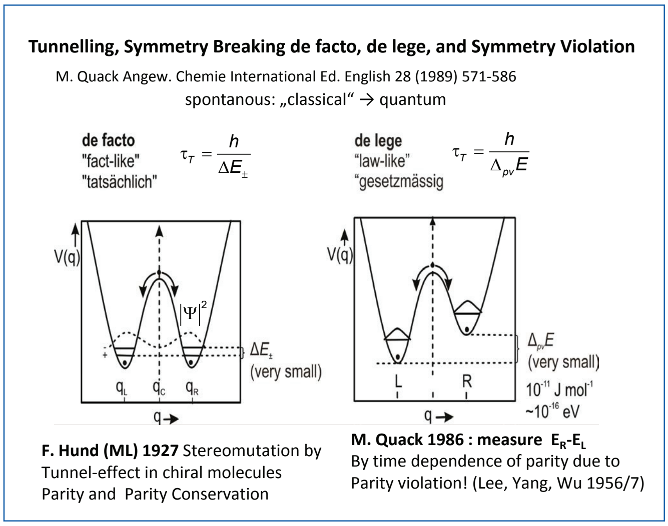


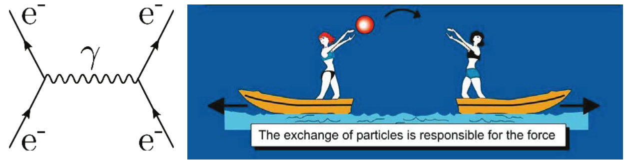
Fig. 10: The potential energy diagram for the stereomutation of chiral molecules with space inversion symmetry and parity conservation (left following Hund 1927) and with parity violation (right) as predicted today (see discussion in the text).

Fig. 10 summarizes simple schemes for the stereomutation of chiral molecules by tunneling. The left hand side shows the situation with a symmetric potential arising from space inversion symmetry as it was assumed by Hund in 1927. As Hund pointed out, because of the then generally accepted symmetry, the energy eigenstates must have well defined parity and thus be delocalized, achiral. In order to explain the existence of stable chiral molecules he suggested that they correspond to a superposition of the ground state with positive parity, with an eigenfunction which is symmetric with respect to inversion (i. e. the central point at the maximum of the potential in the simple model of Fig. 10) and a close lying excited state of negative parity. This superposition is localized and because of the energy difference $\Delta E_\pm$ by what we call now the tunneling splitting there will be a time dependence with a period $t = h/\Delta E_\pm$, the localized wave packet moves from left to right, thus from one enantiomeric structure to the other in half of the period. This stereomutation process is possible in quantum mechanics although both energies of the ground and excited state are far lower than the energy of the barrier, an effect impossible in classical mechanics, discovered by Hund on this occasion and today called tunnel effect (see [6] for the history). Hund explained the existence of stable chiral molecules by the time scales of millions of years or more with rough estimates for typical chiral molecules. This is today still the situation described in textbooks. However, we predict today from theory a completely different situation, depicted on the right hand side of Figure 10: The effective potential is asymmetric and the eigenstates will be localized left or right at low energy whenever $\Delta_{pv}E$ is much larger than $\Delta E_\pm$ in the symmetrical case. We know today from calculations that this is the case for all chiral molecules which are stable for more than days or months. The very small symmetry violation by only 100 aeV in the sketch of Fig. 10 changes the qualitative situation completely, the structure and dynamics of stable chiral molecules are governed by parity violation and not by tunneling.

An interesting question concerns the fundamental mechanism by which parity violation in chiral molecules arises. While we do

The Forces in Nature :Theory of electroweak quantum chemistry
Stereochemistry meets high energy physics

Type	Intensity of Forces (Decreasing Order)	Binding Particle (Field Quantum)	Important in
Strong Nuclear Force	~ 1	Gluons (no mass)	Atomic nucleus
Electro-Magnetic Force	~ 10^{-3}	Photons (no mass)	Atoms and Molecules
Weak Nuclear Force	~ 10^{-5}	Bosons Z, W+, W-, (heavy)	Radioactive β-Decay, Neutrino induced dec. **Chiral Molecules**
Gravitation	~ 10^{-38}	Gravitons (?)	Sun and Planets etc.



Piazza Armerina CERN AC_Z04_V25/B/1992

Fig. 11: The fundamental forces of nature (after [11], where further detailed references can be found).

not intend to present an outline of the theory, which is reviewed in refs 7 and 10 for example. Fig. 11 indicates a qualitative picture, which applies to the known forces of nature. The ladies on two boats throw a ball as a classical analogy which leads to a momentum transfer and a consequent acceleration. This is then interpreted as a fundamental "interaction at a distance" by a force field such as the Coulomb force between the two electrons, the ball being a classical analogon of the 'field particle' mediating the force. For the Coulomb repulsion between two electrons the field particle mediating the interaction is a (virtual) photon. The other forces arise similarly and the quantitative description for the example of the electromagnetic interaction between the two electrons is given in the figure by the corresponding Feynman-Stückelberg diagram, which can be translated into quantitative equations for the interaction. The weak nuclear force leading to parity violating potentials in chiral molecules is mediated by the Z-boson as a field particle of large mass and short lifetime and thus very short range. It is effective when electrons in the molecule penetrate the nucleus the dominant contribution coming from the electron neutron interaction, and this leads to a chiral preference, and thus an asymmetric effective 'extra potential'. In this way one obtains the small asymmetry in the effective potential on the right hand side in the simple representation of Fig 10, where the magnitude of the asymmetry is strongly overemphasized for visibility. This effect from the weak nuclear force can be translated into a small perturbation potential in a quantum chemical context which we have called electroweak quantum chemistry. Like the Born Oppenheimer potential arising from the electromagnetic interaction the weak extra potential is a potential energy hypersurface depending on the 3N-6 degrees of freedom for a molecule with N nuclei (atoms).

This new picture leads also to a completely new understanding of the tunnel effect. Indeed, the Born Oppenheimer potential barriers for tunneling are the result of an approximate description and disappear at a higher level of theory. In our discussions of quasiadiabatic channel above barrier tunneling we had already discussed that the characteristic 'tunneling splittings' arise high above the barriers in a multidimensional space for tunneling when a 'non-reactive' vibrational mode is excited. [6, 10, 39-41, 43]. Thus the characteristic features of tunneling spectra are independent of a one dimensional model with barriers to tunnel through and as we had already pointed out in the context of the symmetry groups for non rigid molecules the small splittings in the tunneling spectra are really signatures of an approximate symmetry and its violation [7, 35]. Figure 12 summarizes this completely new view of tunneling dynamics in molecules.

Levels of Understanding Tunnelling by effective potentials and without potentials as symmetry breaking

1 -dimensional model potential based on Born-Oppenheimer (BO) idea (tunneling through potential barrier-Hund 1927 and today textbook material): Parity conserved. Parity tunneling doublets

2. Tunnelling with full multidimensional BO potential hypersurface (includes quasiadiabatic channel above barrier tunneling implicitly) Parity conserved
3. Non BO treatment with nonadiabatic effects and effective potentials: Parity conserved. Parity tunneling doublets
4. Treatment of all 'particles' (electrons and nuclei) explictly with Coulomb potential in very high dimensional space (no BO, **no tunneling barriers): Parity conserved. Parity tunneling doublets**
5. Most general Standard Model treatment with only electromagnetic force (photon field particles). **No 'Coulomb potential' no barriers: Parity conserved**. **Parity tunnelling doublets** ('electromagnetic quantum chemistry' **including quantum electrodynamics**)
6. Include weak nuclear force (and Z Boson field particle). **Parity violated, doublet with parity violating energy difference, tunneling supressed**.

Electroweak Quantum Chemistry (Bakasov Ha Quack 1995)

Fig. 12: The levels of understanding tunneling spectra

There is still the need for experimental confirmation or rejection of the theory of electroweak parity violation. Much progress has been made towards this goal, and we have built an experiment which is estimated to be able to measure energies as small as 100 aeV, as based on an experiment on the achiral test molecule ammonia [9-12, 38], where parity is effectively conserved. The experiment on chiral molecules remains to be carried out successfully, and requires also the analysis of the high-resolution spectra of carefully selected chiral molecules as an initial step [7-12]. Such experiments are in progress and Fig. 13 summarizes briefly the current status as reviewed again recently in detail [9-12].

Whatever the outcome of the experiments will be they will provide fundamental insights into the stereochemistry and

1986-2022: The long journey towards measuring the parity violating energy difference between enantiomers of chiral molecules following proposals M. Q. 1980-1986

1. **Development of a quantitatively correct theory** for parity violating potentials in chiral molecules (success in Zurich from 1995 onwards, Bakasov, Ha and Quack, 1995-1998, Berger and Quack 2000, followed by many groups, e.g. Schwerdtfeger et.al …, recent Horny and Quack 2015
2. **Development of spectroscopic methods** with rovibrational line analysis in optical spectra of chiral molecules (for parity selection, from 1986, first successes 1995 in the Zürich group, continuing efforts)
3. **Set up of experiments for parity selection by population transfer** and measurement of parity evolution (Zürich from ca. 1995, success for achiral molecules 2010-2015)
4. Theoretical calculation, selection, synthesis, **spectroscopy of suitable molecules (current)**
5. **Experiments on one or more chiral molecules in 2022-???**

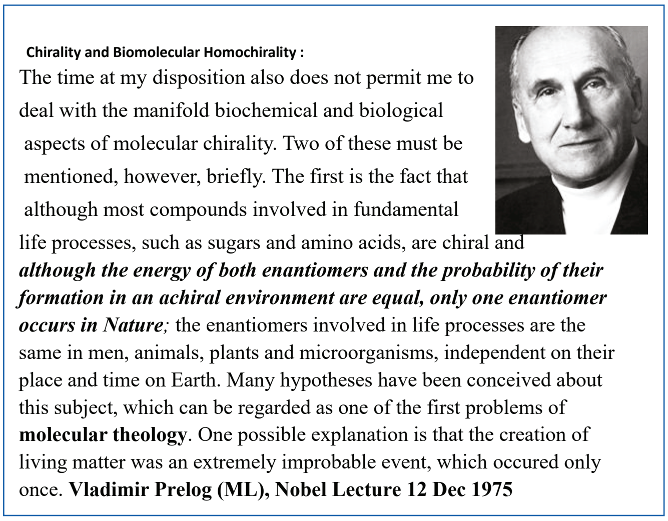
Fig. 13: The long journey towards parity violation in chiral molecules

Zurück zum Inhaltsverzeichnis

quantum dynamics of chiral molecules with the potential even of ‘new physics’ [7-12].

5. Concluding remarks on the role of parity violation in the evolution of biomolecular homochirality.

Biomolecular chirality and homochirality is known to be a constant of evolution in the double sense of the time-dependent quantum dynamics of biomolecules and in the long history of the evolution of life over billions of years until today [36, 37]. The generation of biomolecular homochirality at the origin of life has been an open question for more than a century. There are many plausible proposals for an explanation, but they are contradictory and we do not know which one, if any, is correct. In summary they fall into two large groups, the chance selection de facto or the selection by necessity, de lege, where parity violation is relevant. The question may be fundamentally related to the origin of life, homochirality being a quasi -fossil of early evolution [11, 12, 36, 37]. We can conclude here by citing from Vladimir Prelog’s Nobel lecture 1975 (Fig. 14).



Chirality and Biomolecular Homochirality :

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 occured only once. **Vladimir Prelog (ML), Nobel Lecture 12 Dec 1975**

Fig. 14: The quotation on biomolecular homochirality from the Nobel lecture of Vladimir Prelog 1975 (emphasis added here, see also [11, 12]).

While we have shown that the premiss of his statement on the exact energetic equivalence of enantiomers by symmetry is incorrect, we do not know until today whether parity violation in general and the small asymmetry and energy difference predicted for the enantiomers in particular is at the origin of the preference which we observe today. We should find out.

Acknowledgement

I am grateful to the Bunsen Society, for the honor conferred upon me with the honorary membership, for the hospitality extended to us in Giessen and for half a century of scientific guidance. My early scientific mentors Manfred Stockburger and Albert Weller stimulated my interest in high resolution spectroscopy and tunneling in 1971, while Friedrich Hund, an honorary member of the Bunsen Society reminded us in his lectures in Göttingen of the importance of the historical evolution of science and was gracious in listening to my introductory lecture “Entropie” as Privatdozent in Göttingen in 1977. My academic teacher and mentor Juergen Troe, an honorary member of the Bunsen Society from 2009 provided encouragement and inspiration continuously for 50 years. The (present and former) members of my research group were wonderful companions in our efforts, which would not have achieved much without them. I should name in a representative way those who happened to be in Giessen on the occasion of the 2022 Bunsen-Tagung: Michael Hippler to whom my special thanks are extended for his laudatory speech, Katharina Al-Shamery, née von Puttkamer, Sieghard Albert, Karen Keppler, Frédéric Merkt and Martin Suhm, and special thanks go also to the further current group members Georg Seyfang and Gunther Wichmann. The more complete list of former group-members is too large to be mentioned here but is available in ref. 42. My wife Roswitha deserves my eternal gratitude without limits. Over the decades our work received financial support in particular from ETH Zurich, notably the Laboratory for Physical Chemistry, from the Swiss National Science foundation, from the European Union with an ERC Advanced Grant and COST MOLIM among others. In this brief summary we have refrained from extensive citations of the original literature, retaining only a few key references and reviews. The figures are taken from the author’s lecture, and for simplicity we have not mentioned here the detailed sources from the work of our research group in the captions but these sources can be easily found in the references and reviews cited.

References

[1] M. Quack and J. Troe, *Ber. Bunsenges. Phys.Chem.* **78**, 240-252 (1974).

[2] M. Quack and J.Troe Statistical Adiabatic Channel Models in “Encyclopedia of Computational Chemistry”, Vol. 4, p. 2708-2726, P. von Ragué Schleyer, N. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III, P.R. Schreiner eds., John Wiley and Sons, 1998.

[3] Quantities, Units and Symbols in Physical Chemistry, Third Edition, E. R. Cohen, T. Cvitaš, J. G. Frey, B. Holmström, K. Kuchitsu, R. Marquardt, I. Mills, F. Pavese, M. Quack, J. Stohner, H. L. Strauss, M. Takami, A. Thor, IUPAC and Royal Society of Chemistry, RSC, Cambridge (2007) (Book with 250 pages, ISBN 978-0-85404-433-7).

[4] R. Marquardt and M. Quack eds. Molecular Spectroscopy and Quantum Dynamics, Elsevier, Amsterdam, 2020.

[5] M. Quack and F. Merkt eds. Handbook of High-Resolution Spectroscopy, Preface and chapter 1 by the editors Frédéric Merkt and Martin Quack, Vol. 1, pages XV–XVI and 1-ff Wiley, Chichester (2011), 3 volumes, ISBN-13: 978-0-470-06653-9.

[6] M. Quack and G. Seyfang, Atomic and Molecular Tunneling Processes in Chemistry, Chapter 7, 2020, pp231-282 in R. Marquardt and M. Quack eds. Molecular Spectroscopy and Quantum Dynamics, Elsevier, Amsterdam, 2020.

[7] M. Quack, Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy, in Handbook of High Resolution Spectroscopy, Vol. 1, Chapt. 18, pp. 659-722 (Eds.: M. Quack, F. Merkt), Wiley, Chichester, New York, 2011.

[8] M. Quack, J. Hacker (Eds.), Symmetrie und Asymmetrie in Wissenschaft und Kunst, Nova Acta Leopoldina NF Band 127, Nr. 412, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 2016 (book, 275 pages with contributions in German and English).

[9] M. Quack, G. Seyfang, G. Wichmann, *Adv. Quantum Chem.*, 2020, **81**, 51-99.

[10] M. Quack and G . Seyfang, Tunneling and Parity Violation in Chiral and Achiral Molecules: Theory and High Resolution Spectroscopy, chapter 6, pp192-244 in 'Tunneling in Molecules, Nuclear Quantum Effects from Bio to Physical Chemistry',
J. Kästner and S. Kozuch eds. Royal Society of Chemistry, Cambridge (2020).

[11] M. Quack, G. Seyfang, G. Wichmann, *Chem.Science*, **13**, 10598-10643 (2022).

[12] Proceedings of Nobel Symposium 167 on Chiral Matter, Stockholm 2021 (lecture M. Quack), article by M. Quack, G. Seyfang, G. Wichmann (to be published 2022/23).

[13] M. Quack, European Review, 22 (Supplement S1), pp S50-S86 (2014) doi:10.1017/S106279871300077X.

[14] A. Einstein,Grundzüge der Relativitätstheorie' (Vieweg Wisbaden 1922).

[15] Emmy Noether, Invariante Variationsprobleme, in *Nachr. d. Königl. Gesellschaft der Wiss. zu Göttingen Math.-Phys. Klasse*, 1918, S. 235-257.

[16] C.G.J. Jacobi, Vorlesungen über Dynamik, ed. A. Clebsch, Verlag von Georg Reimer, Berlin, 1866.

[17] K.Mainzer, Symmetrien der Natur, de Gruyter, Berlin 1988.

[18] M. Quack, *Nova Acta Leopoldina*, **127**, 119-166 (2016) in M. Quack, J. Hacker (Eds.), Symmetrie und Asymmetrie in Wissenschaft und Kunst, *Nova Acta Leopoldina NF* Band **127**, Nr. 412, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 2016.

[19] M. Quack, *Nova Acta Leopoldina*, **81**, 137-173 (1999).

[20] M. Quack, *Mol Phys*, **34**, 477-504 (1977).

[21] G. Wichmann, G. Seyfang, and M. Quack *Mol. Phys.* **119**, e1959073 (2021) DOI:10.1080/00268976.2021.1959073 (29 pages) With supplementary material at DOI:10.1080/00268976.2021.1959073 (44 pages).

[22] M. Quack, *Faraday Disc*, **150**, 533–565 (2011).

[23] M. Quack, Molecular femtosecond quantum dynamics between less than yoctoseconds and more than days: Experiment and theory, chapter 27 in: "Femtosecond Chemistry", J. Manz and L. Woeste eds., Proc. Berlin Conf. Femtosecond Chemistry, Berlin (March 1993), Verlag Chemie, Weinheim (1994), p. 781-818.

[24] M. Quack, *Chimia*, **55**, 753–758 (2001).

[25] M. Quack, *Chimia*, **57**, 147–160 (2003).

[26] M. Quack, *J. Mol. Struct.* **292**, 171-195 (1993).

[27] C. Fábri, R. Marquardt, A. Császár, and M. Quack, *J. Chem. Phys.* **150**, 014102 (2019).

[28] S. Albert, K. Keppler Albert, H. Hollenstein, C. Manca Tanner, M. Quack in "Handbook of High-Resolution Spectroscopy", Vol. 1, chapter 3, pages 117–173, M. Quack, and F. Merkt, Eds. Wiley Chichester, 2011, ISBN-13: 978-0-470-06653-9.

[29] K. von Puttkamer, H.R. Dübal and M. Quack, *Faraday Disc. Chem. Soc.* **75**, 197-210 (1983).

[30] A. Kushnarenko, E. Miloglyadov, M. Quack, G. Seyfang, *Phys. Chem. Chem. Phys.*, **20**, 10949-10959 (2018).

[31] Y. He, J. Pochert, M. Quack, R. Ranz and G. Seyfang, *J. Chem. Soc. Faraday Disc.* **102**, 275-300 (1995).

[32] M. Quack, *Chem. Phys. Lett.*, 1986, **132**, 147-153.

[33] M. Quack, J. Stohner, M. Willeke *Annu. Rev. Phys. Chem.* **59**, 741 – 769 (2008).

[34] M. Quack, *Angew. Chem. Int. Ed.* 1989, **28**, 571-586.

[35] M. Quack, *J. Chem. Phys.* **82**, 3277-3283 (1985).

[36] M. Quack, Bunsen-Magazin **24**, 124-125 (2022).

[37] M. Quack, *Adv. Chem. Phys.*, 2014, **157**, 249-290, Chapter 18, *Angew. Chemie Int. Ed.* **41**, 4618-4630 (2002).

[38] P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider, G. Seyfang, *J. Chem. Phys.*, **143**, 244305-1 – 244305-23 (2015).

[39] M. Hippler, L. Oeltjen, M. Quack *J. Phys. Chem. A*, **111**, 12659 – 12668 (2007).

[40] K. von Puttkamer and M. Quack, *Chimia* **39**, 358-360 (1985), *Chem. Phys.,* **139**, 31-53 (1989).

[41] Y. He, H. B. Müller, M. Quack, M. A. Suhm, *Z. Phys. Chem.,* **221**, 1581 - 1645 (2007) (dedicated to Konrad Georg Weil).

[42] R. R Ernst, T. J. Carrington, G. Seyfang, F. Merkt, *Mol. Phys.* **111**, 1939 - 1963 (2013).

[43] B. Fehrensen, D. Luckhaus, M. Quack *Chem. Phys.* **338**, 90 – 105 (2007).

[44] C. Fabri, S. Albert, Z. Chen, R. Prentner, M. Quack, *Phys. Chem. Chem. Phys.* (PCCP) **20**, 7387-7394 (2018); S. Albert, Z. Chen, C. Fabri, Ph. Lerch, R. Prentner, M. Quack, *Mol. Phys.* **114**, 2751-2768 (2016).

Prof. Martin Quack

Martin Quack studied Chemistry and Chemical Physics in Darmstadt, Grenoble, Göttingen and at the École Polytechnique Fédérale de Lausanne, where he received his doctoral degree in 1975. He was 1976/77 Max Kade Fellow at the University of California Berkeley and habilitated in Göttingen in 1978. He was appointed full professor (C4) at the University of Bonn in 1982 and Professor Ordinarius for Physical Chemistry at ETH Zurich in 1983, where he stayed since then. He was also Hinshelwood lecturer and Christensen Fellow of St. Catherine's College at Oxford University (1988) and visiting Miller Research Professor at the University of California Berkeley (2005). In recognition of his research on molecular kinetics and spectroscopy he received numerous prizes and honors, among which is the Paracelsus Prize of the Swiss Chemical Society, and he holds an honorary doctorate from the University of Göttingen. After mandatory retirement from his teaching and administrative functions at age 65 in the fall of 2013 he continued as Professor Emeritus at ETH with research of his group concentrating on some of the most fundamental problems of molecular primary kinetics, in particular also concerning parity violation and tunneling in chiral molecules with support from an ERC advanced grant and grants from the SNFNS and ETH Zurich. He has been elected member of several academies, and also as foreign honorary member of the American Academy of Arts and Sciences, and corresponding member of the Göttingen Academy of Sciences and the Academy of Athens, Greece. In 2014 he was elected as member of the presidium of the Leopoldina (reelected 2019).

Zurück zum Inhaltsverzeichnis