

ON THE MEASUREMENT OF THE PARITY VIOLATING ENERGY DIFFERENCE BETWEEN ENANTIOMERS [☆]

Martin QUACK

Laboratorium für Physikalische Chemie, ETH Zürich (Zentrum), CH-8092 Zurich, Switzerland

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An experiment is outlined for measuring the small energy difference between two enantiomers due to the parity-violating weak neutral current perturbation. The method is based on the violation of the selection rules for the time evolution of states of well defined initial parity in isolated molecules. It could confirm or reject recent quantitative theoretical estimates of parity-violating energy differences.

1. Introduction

Since the early investigations of Pasteur [1] and van 't Hoff [2], molecular chirality has been of interest to chemists, with many important advances even in the last decades [3,4]. The spontaneous occurrence of enantiomeric substances and the prevalence of one type over the other in biology has often led to discussions touching epistemology, natural philosophy (see ref. [2, p. 100] and refs. [5,6]) and, perhaps, "molecular theology" in Prelog's phrasing [4]. The classic discussion in the framework of quantum mechanics has been given by Hund [7], according to whom the fundamental left-right symmetry is broken de facto by the isolation of very slowly varying time-dependent states.

The physical situation has changed drastically with the discovery of parity-violating interactions in elementary particle physics [8] and later in atomic spectroscopy [9,10]. These interactions break the left-right symmetry de lege. This has led to renewed interest and numerous fundamental discussions of the physics of chirality in recent years (see refs. [11-20] and the literature cited therein). An important step forward has been provided by quantitative and apparently reliable estimates of the parity-violating energy

differences between various enantiomers [21-25]. For instance, in the case of α -amino acids the calculated energy differences are of the order of 10^{-14} J mol⁻¹, corresponding to about 10^{-15} cm⁻¹ or 3×10^{-5} Hz in spectroscopic units [25].

Even if one is optimistic concerning present day quantum chemistry and the inclusion of parity-violating weak neutral current perturbations, it seems important to have some direct experimental access to such small quantities. An early attempt from Letokhov's group was published in 1976 [26]. Subsequently [27], an alternative technique was discussed which might be efficient in some molecules if the parity violating energy difference (hereafter ΔE_{PV}) is large enough; at the time this appeared to be uncertain. Because of recent careful estimates of a relatively large ΔE_{PV} [25], it seems suitable to describe the principle of the proposed experiment in more detail.

2. The principle of the experiment

The experiment consists of three steps:

- (i) Preparation of molecular states of well defined parity from optically active molecules of ill defined parity.
- (ii) Free evolution of the isolated molecule with initially well defined parity.
- (iii) Observation of the population of states of the

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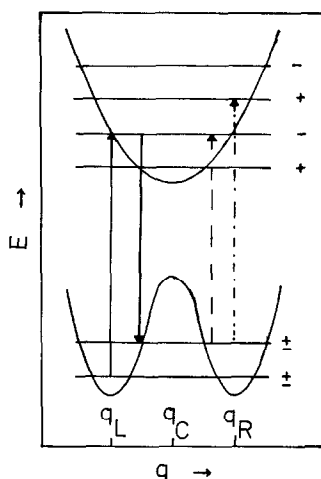


Fig. 1. Schematic drawing of molecular states and electronic potential energy functions with the optical transitions involved in the experiments. The energy is not drawn to scale (the separation of electronic states and the barrier heights are much larger than shown). The \pm labels indicate the parity of the wavefunctions (approximately degenerate in the ground state, non-degenerate in the excited state). In the one-dimensional scheme \hat{E}^* corresponds to reflection at q_C . The full lines indicate the laser pumping in the preparation step (i) and the interrupted lines indicate the spectroscopic probe step (iii). The Born–Oppenheimer potentials have no fundamental significance and are drawn only for visualization in a conventional spectroscopic context.

“forbidden” parity as a function of time. These states are created by the parity violating interactions, which have to be discriminated against a background of parasitic events, that need to be discussed.

Among the possible realizations of this sequence the scheme shown in fig. 1 seems to be promising.

One starts with monochromatic excitation of cold molecules (for example after a supersonic jet expansion [28]) from an electronic ground state with well defined enantiomers, which are separated by a high potential barrier in the Born–Oppenheimer approximation. The electronically excited state has either a small or no barrier for interconversion between the left- and right-handed isomers. Possible candidates which satisfy this condition for the two electronic states are amino compounds with a high barrier for inversion (for example N-substituted azirines) in contrast to ammonia with a low barrier in the ground state, phosphines, arsines, allenes with planar excited

states and perhaps sulfoxides under certain conditions. Whether the initial state is a racemic mixture or one of two enantiomers, the *excited* state will have a well defined parity because of frequency selection for the widely separated spectroscopic states of different parity. Strictly speaking, these spectroscopic states correspond to wavefunctions of the following type (see appendix)

$$\varphi_+ = c_+\chi_+ + c_-\chi_-, \quad (1)$$

$$|c_-|^2/|c_+|^2 \propto |\Delta E_{PV}/\Delta E_{\pm}|^2 \ll 1 \quad (2)$$

and similarly for φ_- . The χ_{\pm} are eigenstates of the space-inversion operator

$$\hat{E}^*\chi_+ = \chi_+, \quad (3a)$$

$$\hat{E}^*\chi_- = -\chi_-. \quad (3b)$$

According to the inequality (2) the φ_{\pm} are very nearly eigenstates of \hat{E}^* with typical values for the separation ΔE_{\pm} of the spectroscopic states of about 1 cm^{-1} or so in the excited electronic state. In a second electronic transition by stimulated emission, one descends to another rovibrational state in the electronic ground state. This state should not have been thermally populated initially and must be metastable with respect to radiative decay in the IR. Because of the strong radiative selection rules with respect to parity change in an electric dipole transition, one will create to within an excellent approximation an eigenstate of E^* , in the example a χ_+ state. This state is not an eigenstate of the molecular Hamiltonian in the high-barrier limit (see appendix), i.e.

$$\Psi(t=0) \approx \chi_+ \approx 2^{-1/2}(\lambda + \rho). \quad (4)$$

λ and ρ are left- and right-handed eigenfunctions with an energy difference $E_{\lambda} - E_{\rho} = \Delta E_{PV}$ as illustrated in fig. 2:

$$\hat{H}\lambda = E_{\lambda}\lambda, \quad (5a)$$

$$\hat{H}\rho = E_{\rho}\rho. \quad (5b)$$

The time evolution of the two-level system is given by

$$\begin{aligned} \Psi(t) = 2^{-1/2} [\lambda \exp(-2\pi i E_{\lambda} t/h) \\ + \rho \exp(-2\pi i E_{\rho} t/h)]. \end{aligned} \quad (6)$$

This can be rewritten using the equations for λ and ρ in

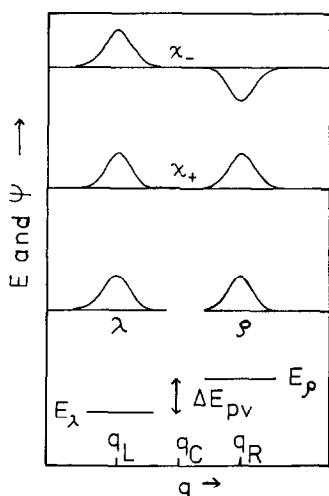


Fig. 2. Schematic drawing of the energies, the eigenfunctions of the molecular Hamiltonian λ and ρ and the eigenfunctions of the inversion operator χ_+ and χ_- for the ground-state level \pm of the system shown in fig. 1. For the higher levels additional nodes appear in λ , ρ , χ on each side of q_C , but the situation is otherwise similar.

the high-barrier limit (see appendix):

$$\lambda = 2^{-1/2}(\chi_+ + \chi_-), \quad (7a)$$

$$\rho = 2^{-1/2}(\chi_+ - \chi_-), \quad (7b)$$

$$\Psi(t) = c_+ \chi_+ + c_- \chi_-. \quad (8)$$

The time-dependent populations of the positive and negative parity states are given by the diagonal matrix elements of the density matrix in the basis χ (equal to the $|c_+|^2$ and $|c_-|^2$ in eq. (8)); therefore from eq. (6) and fig. 2:

$$p_+ = P_{++} = |c_+|^2 = \cos^2(\pi \Delta E_{PV} t / h). \quad (9)$$

$\Psi(t)$ oscillates between χ_+ and χ_- with period

$$\tau_{\pm} = h / \Delta E_{PV}. \quad (10)$$

This period is independent of the barrier height in the high-barrier limit and is about 9 h with the typical values for ΔE_{PV} given in ref. [25].

In the observation phase (iii) of the experiment one uses the electric dipole absorption of the newly created state, which changes as a function of time with the relative populations of the positive and negative parity

states. As is obvious from fig. 1, the absorption lines for the positive and negative parity states in each doublet occur at very different frequencies. The absorption lines arising from the negative parity states grow with time, complementary to the decay according to eq. (9). In the experimental realization in a molecular beam one would observe some indirect signal with high sensitivity, for instance laser-induced fluorescence [29] or multiphoton ionization techniques [30], or – less likely – bolometric detection of the absorbed energy [31]. The sensitivity requirements for the detection can be roughly estimated. For a beam propagating at a speed v over a length l during a flight time $t = l/v$ the signal from the forbidden parity state will grow for small arguments of the \cos^2 function in eq. (9) according to eq. (11):

$$1 - \cos^2 \alpha = \sin^2 \alpha \approx \alpha^2 = (\pi \Delta E_{PV} l / h v)^2. \quad (11)$$

With $\Delta E_{PV} = 2 \times 10^{-14} \text{ J mol}^{-1} = 3.4 \times 10^{-38} \text{ J}$, $l = 10 \text{ m}$ and $v = 100 \text{ m s}^{-1}$ one would have a relative signal of about 2.5×10^{-10} , growing quadratically with the argument on the right-hand side of eq. (11). Thus it would be useful to perform the experiment with molecules involving relatively heavy atoms. This both increases ΔE_{PV} (more neutrons!) and decreases v because of the larger mass. On the other hand, spectroscopy will be more difficult for heavier molecules. For an intense beam one may assume something of the order of 10^{15} to 10^{17} particles per second resulting in up to 1.5×10^7 possible events per second in the above estimate. The total number of events is thus not a serious problem. Rather more serious are background signals, parasitic events and other complicating factors. But our estimate shows that time-dependent parity violation is, at least in principle, observable in realistic experiments [32].

3. Discussion

The realization of the proposed experiment must be considered in relation to complicating factors, alternative techniques and potential consequences of its outcome. We shall discuss some of these, disregarding the special effects investigated by Pfeiffer [20], for which our experiment would provide relevant information as well, if the effects were important.

3.1. Complicating factors

The above discussion has neglected the other degrees of freedom of the molecule. Rotation and vibration can be effectively decoupled from the problem as long as all the states are very well separated spectroscopically, which is true at low energies. This condition will not be satisfied for nuclear spin, if there is any (electronic spin is excluded in our consideration of singlet states only). In general, the hyperfine levels will be widely separated with respect to ΔE_{PV} . Thus they will influence the dynamics only via the nuclear-spin dependence of ΔE_{PV} , which could be modelled and, in principle, also be determined by our experiment for different isotopes.

More serious complications arise from parity changing collisions. Not enough is known about the cross sections of these collisions. The best high-vacuum conditions are essential for the experiment. At 10^{-15} atm, close to the practical limit, with a collision cross section of 100 \AA^2 the probability for a collision during a flight of 10 m is about 2.5×10^{-7} . If each collision has a large probability for parity change, one would have to measure the parity violating signal on a substantial background from collisional events. Even then the situation is not hopeless. The collisional events are incoherent and proportional to the length of flight l , whereas the parity violating changes are coherent and proportional to l^2 . This is one consequence of coherence. One could thus by appropriate difference measurements along the beam distinguish and separate the two contributions. One could also make use of other consequences of coherence (see below). We note that the experiment would allow one to determine cross sections for parity changing collisions in enantiomers, which by itself is a sufficient justification, even in those cases where one cannot determine ΔE_{PV} . Collisions render the χ_{\pm} states chemically unstable (they cannot be bottled, in contrast to the stable λ, ρ states) and rapidly produce a random phase equilibrium system under ordinary chemical conditions.

Other perturbing influences arise from electromagnetic fields. We shall consider (i) static fields, (ii) thermal radiation, and (iii) parasitic transitions due to the laser radiation used in the experiment.

Static electric fields of strength $|E|$ couple the two parity states with a matrix element

$$|V_{\pm}| = |\mu_{\text{P}} \cdot E| 2\pi/\hbar. \quad (12)$$

The transition moment $|\mu_{\pm}| = |\langle \chi_{+} | \hat{\mu} | \chi_{-} \rangle|$ is essentially the permanent dipole moment μ_{P} in a left- or right-handed configuration (see below). With $|\mu_{\text{P}}| = |e_0 a_0|$ and $|E| = 1 \text{ V m}^{-1}$ one would obtain a circular frequency of about 10^5 s^{-1} . It is thus necessary to work with molecules which have a very small dipole moment and to stabilize the electric field to $E < 1 \text{ } \mu\text{V/m}$ in order to avoid all interferences. We may note that the controlled use of finite fields would allow one to carry out a coherent experiment, observing the interference effects from ΔE_{PV} and V_{\pm} . Static electric fields are another cause for the chemical instability of χ_{\pm} states.

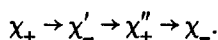
The rate of transitions due to thermal background radiation can be calculated by means of the equation [33]

$$K_{\text{fi}} = A_{\text{fi}} \frac{\text{sign}(E_{\text{f}} - E_{\text{i}})}{\exp[(E_{\text{f}} - E_{\text{i}})/kT] - 1}, \quad (13a)$$

with the Einstein coefficients (cgs system)

$$A_{\text{fi}} = \frac{64\pi^4 |E_{\text{f}} - E_{\text{i}}|^3}{3\hbar^4 c^3} |M_{\text{fi}}|^2. \quad (13b)$$

One has $|M_{\text{fi}}| = |\mu_{\text{P}}|$ for the χ_{\pm} pair. A small $|\Delta E_{\pm}| = |E_{\text{f}} - E_{\text{i}}| \ll kT$ gives rise to absolutely negligible values for the direct transition rates $\chi_{+} \leftrightarrow \chi_{-}$. However a three-step sequence with infrared photons involving vibrational transitions could be important:



Estimating transition rates with medium infrared transition moments one finds that cooling to liquid nitrogen or liquid helium temperatures would remove such transitions totally.

One may question whether the strong lasers used for the experimental observation might induce off-resonant radiative transitions between the parity doublet in the ground state. The time-averaged transition probability to the "wrong" parity state in the doublet is given by [34]

$$\langle p_2 \rangle_{\text{rad}} = \frac{1}{2} |V'_{\text{rad}}|^2 / \omega_{\text{laser}}^2, \quad (14)$$

with $|V'_{\text{rad}}|$ being given by eq. (12) but replacing the field strength E by the laser field amplitude. Although relative populations of the order of 10^{-8} can easily be produced with strong lasers, laser intensity can be controlled to such an extent that the relevant transitions

in fig. 1 are saturated at still negligible values of p_2 ($\ll 10^{-10}$). In any case the laser intensity dependence of the experimental results must be studied. Similarly there will be some background from laser-induced magnetic dipole and electric quadrupole transitions with different parity selection rules. One should thus work with electronic transitions that are strongly allowed according to the electric dipole selection rules in order to improve the discrimination against the background. We stress that the experiment is possible with a very large amount of parasitic signal because of the I^2 dependence, although obviously the noise background must remain below some acceptable level. There is clearly a need to choose a favorable system for which the right-hand side in eq. (11) can be made as large as possible.

3.2. Alternative, direct spectroscopic experiments

Our proposed experiment is based upon a transformation from the energy to the time domain and then to space (the propagation direction of the beam). One might call the technique "high-resolution spectroscopy by time-dependent chemical transformation". In view of the complications discussed in section 3.1 it is questionable whether a direct spectroscopic measurement in the frequency domain would be easier. Note that the direct transition $\lambda \rightarrow \rho$ is forbidden by electric dipole selection rules (schematically):

$$\langle \lambda | \hat{\mu} | \rho \rangle = \frac{1}{2} (\langle \chi_+ | \hat{\mu} | \chi_+ \rangle + \langle \chi_- | \hat{\mu} | \chi_+ \rangle - \langle \chi_- | \hat{\mu} | \chi_- \rangle - \langle \chi_+ | \hat{\mu} | \chi_- \rangle) = 0. \quad (15)$$

One might try magnetic dipole transitions or use molecular systems as shown in fig. 1. There, both left and right isomers give absorption to a common upper level with a frequency difference of 10^{-4} Hz. It is difficult to see how this could be measured directly without stabilizing the visible laser to better than about 10^{-19} , a tremendous task. The proposal of ref. [26] seems to be too optimistic and has not been realized over the last decade. We believe that indirect methods have a higher chance of success although the direct spectroscopic approach should be pursued as well.

3.3. Consequences of molecular parity violation and outlook

The consequences of molecular parity violation in

biochemistry and biology have been amply discussed in the literature and we shall not elaborate upon this further. If a successful experiment confirms the validity of the quantum chemical approach to parity violation [21–25] or suggests perhaps some revisions, then one might with confidence investigate the consequences in chemistry in quantitative detail theoretically.

We shall conclude with two aspects of molecular parity violation that have been given relatively little attention, at least so far. One is a result of the time scale for parity violation, which is found to be short — of the order of a day or less — although the corresponding energy difference is minimal on a molecular level; even without external perturbations the "pure parity isomers" are intrinsically rather unstable compounds in chemical terms. Of course they are even more sensitive to collisions and radiation. This is a good example of the violation of the selection rules for chemical reactions [35]. Nuclear spin symmetry conservation is, of course, violated on even shorter time scales. The effects are sufficiently small that they can all be neglected for short-time collision events. However, for intramolecular processes the very small energy differences result in remarkable time-dependent effects. Parity violation is not only relevant for the very close degeneracy necessarily associated with enantiomers. Whenever the density of coupled states [36] exceeds about 10^{15} states per cm^{-1} we would assume interconversion of parity states to become important. This figure is attained for moderately sized molecules with heavy atoms such as $\text{C}_4\text{F}_9\text{H}$ or $\text{C}_6\text{F}_9\text{H}$ at vibrational energies below the dissociation threshold [37], which are accessible thermally and by laser excitation of vibrational overtones. This is true also for planar molecules, for which parity is a spectroscopic "good quantum number" at low energies. Time-dependent interconversion of states of different parity, mediated by the weak interaction, is thus universal in large polyatomic systems whenever time scales of days are relevant.

It is believed that the dominant parity-violating interactions of interest here conserve time-reversal symmetry. On a more fundamental level one may speculate about the order of magnitude of the effects that are relevant for time reversal asymmetry in chemistry. Through the Schwinger–Lüders–Pauli theorem (*CPT*) there is a close relationship between *P* violation, *CP* violation and *T* violation. The latter two are known in particle physics [38,39]. If time-reversal asymmetry

were of similar importance in molecules as parity violation is expected to be, then this may indeed have consequences on a macroscopic level. I am well aware that current folklore strongly disfavours this possibility. But the experimental and theoretical evidence for the majority point of view is weak. A successful search for molecular parity violation might induce a search for evidence of de lege time asymmetry in chemistry.

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Appendix. Summary of equations for the two-state problem relevant in section 2

The molecular Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (\text{A1})$$

with $[\hat{H}_0, \hat{E}^*] = 0$ and \hat{V} the parity-violating perturbation. Thus:

$$\hat{H}_0 \chi_+ = E_+ \chi_+, \quad (\text{A2})$$

$$\hat{H}_0 \chi_- = E_- \chi_-. \quad (\text{A3})$$

Both the ground-state level separation $|E_+ - E_-|$ and the matrix elements $|V| = |\langle \chi_+ | \hat{V} | \chi_- \rangle|$ are supposed to be much smaller than the separation from other energy levels, which allows us to treat the system as a two-level problem with a matrix representation of \hat{H} (real and symmetric for simplicity):

$$\mathbf{H} = \begin{pmatrix} E_+ & V \\ V & E_- \end{pmatrix}. \quad (\text{A4})$$

Using the abbreviation $D = E_+ - E_-$, the eigenvalues are

$$E_{\lambda'} = \frac{1}{2}(E_+ + E_-) + \frac{1}{2}(4V^2 + D^2)^{1/2}, \quad (\text{A5})$$

$$E_{\rho'} = \frac{1}{2}(E_+ + E_-) - \frac{1}{2}(4V^2 + D^2)^{1/2} \quad (\text{A6})$$

and the eigenfunctions

$$\lambda' = b\chi_+ + a\chi_-, \quad (\text{A7})$$

$$\rho' = a\chi_+ - b\chi_-, \quad (\text{A8})$$

$$a = \left(\frac{(4V^2 + D^2)^{1/2} + D}{2(4V^2 + D^2)^{1/2}} \right)^{1/2}, \quad (\text{A9})$$

$$b = \left(\frac{(4V^2 + D^2)^{1/2} - D}{2(4V^2 + D^2)^{1/2}} \right)^{1/2}. \quad (\text{A10})$$

If $|D| \gg |V|$, then

$$a^2 = 1 - V^2/D^2, \quad (\text{A11})$$

$$b^2 = V^2/D^2. \quad (\text{A12})$$

Therefore $\rho' \rightarrow \varphi_+ \approx \chi_+$ and $\lambda' \rightarrow \varphi_- \approx \chi_-$. This kind of estimate is also valid for other distant pairs. If $|D| \ll |V|$, then

$$a \approx b \approx 2^{-1/2} \quad (\text{A13})$$

and hence eq. (7). According to long-known estimates for D in typical optical isomers [7] and the recent estimates for V [25] it is this case which applies and is discussed in this paper.

One also has

$$\hat{E}^* \lambda = \rho, \quad (\text{A14})$$

$$\langle \chi_+ | \hat{\mu} | \chi_- \rangle = \langle \lambda | \hat{\mu} | \lambda \rangle = -\langle \rho | \hat{\mu} | \rho \rangle = \text{“}\mu_p\text{”} \quad (\text{A15})$$

and

$$\langle \lambda | \hat{\mu} | \rho \rangle = 0. \quad (\text{A16})$$

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