

## THE PARITY NON-CONSERVING ENERGY DIFFERENCE BETWEEN ENANTIOMERS AND A CONSEQUENCE OF THE CPT THEOREM FOR MOLECULE-ANTIMOLECULE PAIRS

P. JUNGWIRTH, L. SKÁLA

*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague 2, Czechoslovakia*

and

R. ZAHRADNÍK

*The J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejskova 3, 182 23 Prague 8, Czechoslovakia*

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The energy difference between a chiral molecule and its antimolecule arising from parity non-conserving weak interactions is discussed. Calculations of this energy difference for methane derivatives are reported and results from the non-empirical Hartree-Fock and extended Hückel method are compared.

### 1. Introduction

Chiral molecules have attracted the attention of chemists and molecular physicists since their discovery by van 't Hoff and Le Bel. It was realized a long time ago that pairs of chiral species, optical antipodes (or enantiomers), differ in their physical characteristics (e.g. melting and boiling points, diffusion, adsorption) and in their chemical reactivity [1]. Quantum-mechanical wavefunctions reflect the handedness of chiral species and, therefore, a theoretical interpretation of, e.g., reactivity differences is possible. Special attention has been paid to association and self-association of chiral species in the sense of dimer formation as well as polycondensation. The former can be illustrated by the formation of hydrogen-bonded dimers, the latter by the formation of peptide or protein chains. Remarkably, proteins and polysaccharides formed under physiological conditions consist almost entirely of *l*-amino acids and *d*-monosaccharides, respectively. Therefore, experimental and theoretical studies of energy differences between *d-d* (or equivalently *l-l*) and *d-l* species offers a useful characteristic, called the discrimina-

tion energy [1]. Discrimination energies have values of a few hundred calories up to kilocalories per mole [2-4].

When considering the differences in the properties and reactivities of optical antipodes, chemists sometimes assert that the energies of both enantiomers are identical. For many years, this remained a real chemical dogma, but it was finally overthrown as a result of the discriminative ability of weak forces. Nonetheless, the majority of chemists still regard this energy "equality" as an unshakable truth.

The left-right asymmetry in nature is manifested by parity non-conservation (PNC). This PNC is connected with weak interactions, which are the only interactions between elementary particles which are discriminative in this sense. More specifically, the weak neutral current is significant for chiral molecules. (For a more detailed description and for the respective references see the Introduction in ref. [5].) The weak neutral current and spin-orbit interactions are responsible for the small energy difference between enantiomers [6-8]. The magnitude of the PNC energy shift can be calculated by a perturbation treatment using MO-LCAO wavefunctions

[5]. In spite of its extremely small magnitude, the energy shift could be responsible for the absolute preference of one enantiomer [9,10]. Although not yet proved, several of the suggested kinetic dissymmetry amplification mechanisms [11,12] indicate that this possibility is plausible. The theory [13-16] and application aspects [17-21] have been investigated by Mason and Tranter. Attention was paid to the parity-violating energy differences (PVED) of amino acids [19] and of chiral conformations of tetrahydrofuran as a model sugar [21]. The origin of biomolecular homochirality was tentatively associated with the chirality of minerals [22] (cf. ref. [23]). From the point of view of this work, the papers by Barron are especially topical [24-28].

The purpose of this work is fourfold. We wish (i) to point out that energy differences do exist between chiral molecules and antimolecules; (ii) to establish the number of terms necessary for a correct perturbation estimation of the PVED; (iii) to ascertain the role of the quality of the wavefunctions in the perturbation treatment, and (iv) to elucidate the influence of heavy atoms on the PVED.

## 2. Theory

The energy difference between optical antipodes is conditioned by weak interactions. It is desirable to realize the consequences of this parity violation from the point of view of the general validity of the *CPT* theorem. In our particular case, the *CP* theorem must be valid too because the time invariance is perturbed only by strange particles. Moreover, we are not interested in the time development, e.g. collisions, but only in stationary states of the systems under study.

We will show now that it follows from the *CP* invariance that the absolute value of the energy difference between the D- and L-forms of a chiral molecule is identical with the absolute value of the energy difference between the chiral molecule and its antimolecule.

Our Hamiltonian has the form

$$H = H_e + H_w, \quad (1)$$

where  $H_e$  is the Hamiltonian for the electromagnetic and  $H_w$  for the weak interaction,

$$H_w = H_{CP}^c + H_{CP}^n. \quad (2)$$

The upper indices c and n correspond to parity conserving and non-conserving interactions.  $H$  can be expressed as a product of "currents"  $J$  ( $J = V + A$ , where  $V$  denotes a vector and  $A$  an axial vector part of the "current";  $V_\mu = k \gamma_\mu \Psi$ ,  $A_\mu = k \gamma_\mu \gamma_5 \Psi$ ,  $\mu = 1, 2, 3, 4$ ):

$$H_w = J \cdot J = V \cdot V + A \cdot A + A \cdot V + V \cdot A \quad (3)$$

and, furthermore

$$H_{CP}^c = V \cdot V + A \cdot A, \quad (4)$$

$$H_{CP}^n = V \cdot A + A \cdot V. \quad (5)$$

Parity eigenstates  $|\psi_R\rangle$  and  $|\psi_L\rangle$  are related to the parity operator  $P$ ,

$$|\psi_R\rangle = e^{i\phi} P |\psi_L\rangle, \quad (6)$$

$$|\psi_L\rangle = e^{-i\phi} P |\psi_R\rangle. \quad (7)$$

The following expressions for the energies of the two forms are valid within the framework of the first-order perturbation treatment:

$$E_L = E_0 + \langle \psi_{L0} | H_{CP}^n | \psi_{L0} \rangle, \quad (8)$$

$$E_R = E_0 + \langle \psi_{R0} | H_{CP}^n | \psi_{R0} \rangle. \quad (9)$$

Here,  $E_L$  and  $E_R$  are energies corresponding to  $\psi_{L0}$  and  $\psi_{R0}$ , and the index 0 denotes zeroth-order eigenfunctions and eigenvalues. It follows that the energy difference between the two forms is

$$E_L - E_R = \langle \psi_{L0} | H_{CP}^n - P^+ H_{CP}^n P | \psi_{L0} \rangle. \quad (10)$$

Since

$$P^+ H_{CP}^n P = -H_{CP}^n \quad (11)$$

(the axial vector  $VA$  changes sign when changing parity), it is possible to write

$$E_L - E_R = 2 \langle \psi_{L0} | H_{CP}^n | \psi_{L0} \rangle = 2 \langle \psi_{R0} | H_{CP}^n | \psi_{R0} \rangle. \quad (12)$$

*CP* invariance yields the wavefunction of the antimolecule  $|\psi'_{L,R}\rangle$

$$C |\psi'_{L,R}\rangle = e^{i\theta} |\psi_{L,R}\rangle. \quad (13)$$

Applying the operator  $P$  to (13), we get

$$e^{i\theta} |\psi'_{L,R}\rangle = e^{i\theta} P |\psi_{L,R}\rangle \quad (14)$$

and, therefore

$$|\psi'_{L,R}\rangle = e^{i\omega} |\psi_{R,L}\rangle, \quad (15)$$

where  $\psi$  and  $\psi'$  correspond to the molecule and antimolecule, respectively.

For a molecule-antimolecule pair the following expressions hold:

$$E = E_0 + \langle \psi_0 | H_{CP}^n | \psi_0 \rangle, \quad (16)$$

$$E' = E_0 + \langle \psi'_0 | H_{CP}^n | \psi'_0 \rangle, \quad (17)$$

where  $E$  and  $E'$  are the energy of the molecule and antimolecule, respectively.

In order to show the equivalence of the absolute value of the energy difference between the left- and right-handed molecule and between the molecule and its antimolecule, let us consider for instance the right-handed molecule,

$$E - E' = \langle \psi_{R0} | H_{CP}^n | \psi_{R0} \rangle - \langle \psi'_{R0} | H_{CP}^n | \psi'_{R0} \rangle. \quad (18)$$

Using eqs. (8), (9) and (18) we get finally

$$E - E' = E_R - E_L. \quad (19)$$

We see that the conversion

(L-molecule)  $\rightarrow$  (R-molecule)

is associated with the energy change

$$\Delta E = E_R - E_L \quad (20)$$

while the transition

(R-molecule)  $\rightarrow$  (R-antimolecule)

gives the opposite energy difference

$$\Delta E' = E' - E = E_L - E_R = -\Delta E. \quad (21)$$

The transformation

(L-molecule)  $\rightarrow$  (R-antimolecule)

does not change the total energy of a molecule.

These results agree completely with those obtained by Barron, who was the first who dealt with the invariance of molecular properties under the combined operation of charge conjugation, space inversion and time reversal [24] (see also refs. [25-28]).

The value of  $\Delta E$  can be calculated by means of perturbation theory in the MO-LCAO approximation ([15], eq. (46)).

$$\Delta E = \frac{G\alpha}{\sqrt{2}} \sum_{\substack{i,n,\alpha,\beta \\ \gamma,\gamma',\gamma'',\gamma'''}} \frac{c_{i\gamma}^\alpha c_{n\gamma'}^\alpha c_{n\gamma''}^\beta c_{n\gamma'''}^\beta Q_w^\alpha}{\epsilon_i - \epsilon_n} \\ \times \langle \chi_\gamma^\alpha | \{p, \delta^3(r_\alpha)\} + | \chi_{\gamma'}^\alpha \rangle \langle \chi_{\gamma''}^\beta | f(r_\beta) l_\beta | \chi_{\gamma'''}^\beta \rangle. \quad (22)$$

Here,  $G = 2.19 \times 10^{-14}$  au is the weak coupling constant,  $\alpha = 1/137$  is the fine structure constant,  $n$  and  $i$  denote occupied and unoccupied MOs,  $c_{i\gamma}^\alpha$  is the LCAO coefficient of the  $i$ th MO, corresponding to the  $\gamma$ th AO of the  $\alpha$ th atom,  $Q_w = (1 - 4 \sin^2 \theta) Z - N$ , and  $\epsilon_i$  is the one-electron energy of  $i$ th MO. The first matrix element in (22) is the parity non-conserving part of the Hamiltonian while the second element represents the spin-orbit interaction (see ref. [5]).

### 3. Calculations

The majority of chiral systems commonly studied (1-8) are trisubstituted methanes (2-7) (see fig. 1). System (1) is a derivative of the methyl anion, system (2) is ionized fluorochloromethanol and (8) is ionized bromofluoromethanol.

In all the investigated cases the energy difference  $\Delta E$  is smaller than  $10^{-16}$  au (see table 1).

Our calculations led to the following answers to items (i)-(iv) in section 1.

(i) We have shown that the energy difference between the chiral molecule and its antimolecule has

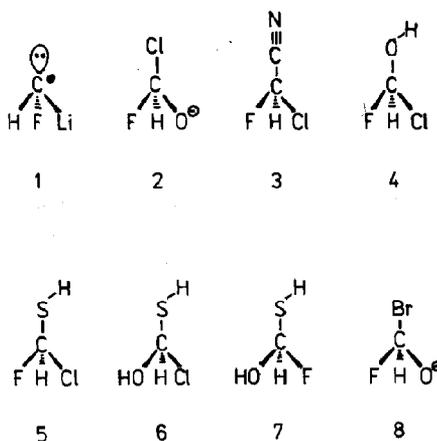


Fig. 1. The chiral molecules investigated.

Table 1

PNC energy shifts  $\Delta E$  (in  $10^{-19}$  au) calculated by means of the non-empirical Hartree-Fock wavefunctions (minimal STO-3G basis set) for systems 1-7 in fig. 1 and extended Hückel theory (EHT) for systems 2, 8

Hartree-Fock wavefunctions							
No. MOs	system						
	1	2	3	4	5	6	7
2	-0.1	-4.6	340	-420	-40	-70	1.1
4	0.2	-3.8	360	-240	-20	-21	7.5
6	-3.1	-2.3	320	-120	-23	-27	10.0
8	-4.2	-99.4	310	40	13	-25	-34.2

EHT wavefunctions			
No. MOs	system		
	2	8	
2	-8.4	-0.01	
4	-4.9	-0.08	
6	-2.4	-5.7	
8	-3.5	-3.4	

the same absolute value as the energy difference between the right- and left-handed isomers of the molecule. The changes of sign in this difference are given in eqs. (19)-(21) and are visualized in fig. 2.

(ii) It follows from table 1 that the number of MOs which must be taken into account to obtain a rea-

sonable estimate of the energy difference  $\Delta E$  (eq. (22)) varies from 2 to 6 for the investigated systems. For a larger number of MOs, when less reliable higher energy levels are taken into account, the  $\Delta E$  value may be incorrect (see molecules No. 2, 4, 5, 7 in table 1).

(iii) The Hartree-Fock and extended Hückel calculations for molecule No. 2 show that the results are comparable within the achieved accuracy of the perturbation theory. To obtain more precise results, a larger basis set yielding better high energy orbitals should be used.

(iv) Table 1 shows that  $|\Delta E|$  increases with increasing atomic number  $Z$  of the substituent (compare species Nos. 1 and 7) (fluorine) with molecules (3-6) (chlorine). The only exception is molecule No. 2, with a relatively small  $\Delta E$  shift, which is however ionic.

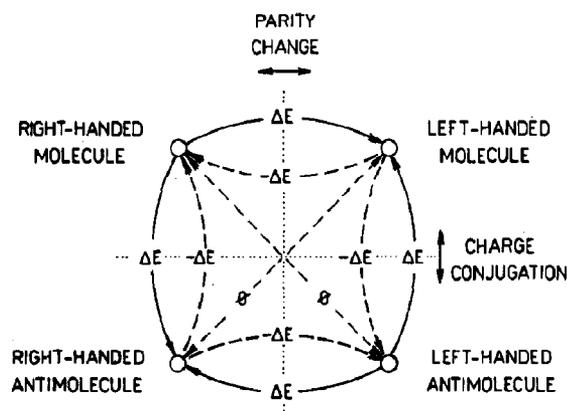


Fig. 2. The relationship between chiral molecules and their antimolecules: the magnitudes and signs of the respective energy changes ( $\pm\Delta E$  or zero) are indicated. Chiral molecules and antimolecules are depicted by circles. (For example the transition from the left-handed antimolecule to the left-handed molecule is associated with the energy change  $\Delta E$ , eq. (20).)

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