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# Energetic stabilization of *d*-camphor via weak neutral currents

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It is shown via a series of numerical tests on the camphor molecule, $C_{10}H_{16}O$, that the naturally occurring *d*-enantiomer is energetically stabilized with respect to its mirror image by electroweak force. The calculated energy difference between enantiomers, about $1.5\times10^{-19}$ hartree, is roughly eight orders of magnitude smaller than the upper bound suggested by available spectroscopic investigations on the frequency of a spectroscopic transition. However, such a difference is about ten times larger than previous estimates of parity-violating energy contributions reported in the literature for other chiral molecules, which makes the idea of electroweak stabilization of one enantiomer more reliable than expected before. [S1063-651X(99)13007-1]

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## I. INTRODUCTION

Parity-violation phenomena in atomic physics are well known [1,2], but so far no experimental evidence has been reported for the existence of some observable effects in molecules, although a number of papers have appeared in the literature proposing theoretical models or suggesting experiments aimed at detecting a possible role of weak neutral currents (WNC) carried by the massive $Z^0$ boson [3–11]. The study of narrow resonances of saturated absorption of the chiral molecule CHFClBR has been proposed by Kompanets, Kukudzhanov, and Letokhov [12]. Daussy *et al.* [13] have an experiment underway on the same molecule. Observation of parity nonconservation might be possible by high resolution NMR spectroscopy [14,15]. It might be worth noting that the laser spectroscopy measurements are sensitive to the nuclear-spin-independent part of the parity-nonconserving interaction, while the NMR measurements see the nuclear-spin-dependent part.

Large first-order effects have been predicted for optically inactive molecules possessing a symmetry plane, due to the splitting of excited electronic states induced by parity-violating mechanisms [16].

Several papers have reported theoretical estimates of the parity-violating energy difference in small- and medium-size chiral molecules, including *L*-$\alpha$-amino acids and *D* sugars, using *ab initio* uncoupled Hartree-Fock (UCHF) perturbation theory within the framework of small basis sets [17–25], and relativistic approaches [26,11]. In any event, coupled Hartree-Fock (CHF) predictions adopting extended basis sets [27–29] are more reliable and systematically larger than those provided by UCHF [20,21,30] and by single-excitation configuration interaction CIS-RHF methods [31–33], fully equivalent to a scheme developed by Rebane almost forty years ago [34], and to the Tamm-Dancoff approximation examined in Ref. [27]. Incidentally, it should be noted that the CIS-RHF estimates reported by Bakasov, Ha, and Quack in Refs. [31–33] are to be doubled [35].

Even if the second-order theoretical energy shifts arising from WNC are extremely small, $\approx1\times10^{-20}$ hartree, there is a systematic agreement between higher stability of a given enantiomer predicted by theory and experimental facts, i.e., the dominance of one of the pair of mirror-image biomolecules, for instance, *L*-$\alpha$-amino acids and *D* sugars [21,30,24,28,29].

Kinetic mechanisms have been suggested whereby even a tiny energy difference could be effective to determine the preponderance of only one enantiomeric form [3,5,7,36]. However, this approach has been questioned [37].

Tunneling processes might also have induced second-order phase transition between enantiomers below a critical temperature, as suggested by Salam [38] relying on the WNC hypothesis.

A completely different approach suggests that biomolecular homochirality is related to the influence of strong circular polarization of light of short wavelengths acting on prebiotic material, see Ref. [39], and references therein.

Therefore, further studies in this field seem worth performing, at least to compile a comprehensive inventory of cases that could be examined to asses the reliability of the hypothesis of energy stabilization via parity-violating interactions.

Inverted Lamb dips in separated optical antipods of camphor $C_{10}H_{16}O$ have been investigated to detect any difference arising from WNC [40]: recorded spectra of *d*- and *l*-camphor agree to within an uncertainty of ≈300 kHz, i.e., $\approx4.56\times10^{-11}$ hartree, corresponding to the accuracy $\Delta\nu/\nu=1\times10^{-8}$ [40]. If there is any effect arising from WNC, its magnitude should be smaller than that.

The purpose of this paper is to evaluate the energy differ-

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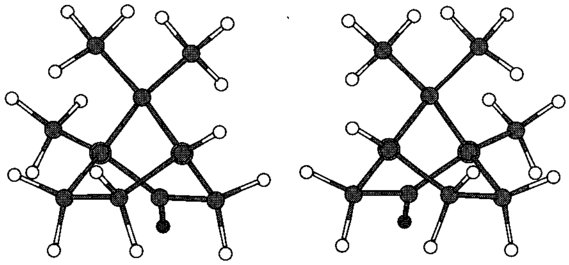

FIG. 1. Chiral structure of the camphor molecule $C_{10}H_{16}O$ the PVED stabilized *d*-enantiomer is on the left, the *l*-enantiomer is on the right. Carbon and hydrogen atoms are represented, respectively, as light gray and white circles; the oxygen atom appears as a dark gray circle. There are two chiral centers, the carbon atoms surrounded by a thin ring.

ence between the two forms of the camphor molecule (see Fig. 1) to check if the theory actually predicts higher stability of the dextrorotatory *d*-enantiomer found in nature, and the magnitude of the effect. In addition, whereas WNC stabilization of *L*-$\alpha$-amino acids seems to take place for zwitterionic species, i.e., solvated molecules in aqueous media, corresponding to a well-defined rotational conformation [21,28,29], the fact that the camphor molecule is rigid seems to make the analysis somewhat easier.

## II. THE PARITY-VIOLATING ENERGY

In the notation of previous papers, the parity-nonconserving Hamiltonian is written [27,28],

$$H_{pv}=-\frac{\Gamma}{2}\sum_{I=1}^{N}\sum_{i=1}^{n} Q_I\{\mathbf{p}_i\cdot\boldsymbol{\sigma}_i,\delta(\mathbf{r}_i-\mathbf{R}_I)\}_+ , \tag{1}$$

(for the sake of simplicity we adopt the theoretical value for the Weinberg angle such that $\sin^2\theta_w=0.25$ [20]: then the effective charges $Q_I$ coincide with the neutron numbers). The experimental value reported in Ref. [41] is $\sin^2\theta_w=0.2325\pm0.0008$.

There are a number of features to note about relationship (1): (i) the magnitude of the interaction is very small, as $\Gamma=5.73416\times10^{-17}$ au, (ii) its range is extremely short; in fact, there is ‘‘contact’’ between $i$th electron and $I$th nucleus, described by the Dirac function $\delta(\mathbf{r}_i-\mathbf{R}_I)$, (iii) its symmetry is that of a time-even parity-odd pseudoscalar, as it contains the scalar product of a polar momentum vector $\mathbf{p}_i$ and an axial spin vector, represented via the Pauli matrix $\sigma_i$, (iv) it is pure imaginary, and has a vanishing expectation value over singlet electronic eigenstates, which can be described by real wave functions for any molecule in the absence of magnetic field; (v) however, it induces spin polarization, i.e., it can couple an electronic singlet reference state to excited triplet states, and (vi) if $H_{pv}$ were a classical function, its minimum would correspond to perfect alignment of $\mathbf{p}_i$ and $\boldsymbol{\sigma}_i$, i.e., an electron experiencing the weak $Z$ force tends to move in the direction of its spin. For this reason, some atomic species are themselves chiral, as electrons, according to a semiclassical visualization, travel up along a right-handed spiral path when they get close to the nucleus, and down along a left-handed helix in the tail regions of the atom. Although the effect of the weak neutral currents is very small, it has been experimentally detected. In the Novosibirsk experiment [1], vapors of bismuth were found to rotate the plane of polarized light by an angle of about $1\times10^{-7}$ rad, i.e., the parallax of a pencil at a distance of one thousand kilometers.

Owing to (v), a second-order parity-violation energy shift (PVES) can be obtained from perturbation theory: it is a cross term with another interaction Hamiltonian, which has got to possess three fundamental requisites; (a) it is also pure imaginary, (b) it can also induce spin polarization, and (c) it is even under parity. From the mathematical point of view, a perfect candidate is the spin-orbit interaction, written in the form [27]

$$H_{so}=\frac{\beta^2}{\hbar}\sum_{I=1}^{N}\sum_{i=1}^{n} Z_I|\mathbf{r}_i-\mathbf{R}_I|^{-3}\boldsymbol{\sigma}_i\cdot(\mathbf{r}_i-\mathbf{R}_I)\times\mathbf{p}_i . \tag{2}$$

This candidate is also quite plausible from the physical standpoint [42–45,17]. In fact, let us model a right-handed molecule as a right-handed helix aligned along the $z$ axis. Electrons traveling up (down) the helix have positive (negative) orbital angular momentum $l_z$, and if the interaction (2) were a classical one, with minimum corresponding to antiparallel $\mathbf{l}_i(\mathbf{R}_I)$ and $\boldsymbol{\sigma}_i$ vectors, they would be left-handed (right-handed), as far as the spin is concerned. For a left-handed molecule, modeled in the shape of a left-handed spiral, the situation would be reversed.

A recent paper [25] has shown that the contribution to PVES arising from one-center two-electron terms of the spin-orbit Hamiltonian is not negligible in small molecules. For the time being we cannot evaluate such a contribution for a molecule of the size of camphor, owing to limitations of our computer program. In fact the two-electron terms are expected to diminish the absolute value of PVES to some extent, without altering the essential conclusions arrived at in the present paper. The estimate of the two-electron spin-orbit contribution for a number of molecules will be the subject of future papers.

Now, since the parity-violating weak force can distinguish between left and right, the cross energy with the spin-orbit interaction will give opposite values for the PVES,

$$E_{pv,so}=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\mathrm{Re}(\langle a|H_{pv}|j\rangle\langle j|H_{so}|a\rangle). \tag{3}$$

Accordingly, the interaction term (3) reverses sign on going from the mixed-parity wave function of an $L$ enantiomer to that of its $D$ enantiomer [17]. The parity-violating energy difference PVED between the mirror-image molecules is then $2|E_{pv,so}|$.

It should be recalled that the second-order perturbation scheme discussed above is a consequence of the use of the nonrelativistic reduction of the parity-violating operator. If four-component Dirac-Hartree-Fock wave functions were used, the parity-violating energy would simply be proportional to the expectation value of $\gamma_5$ Dirac matrix according to procedures developed by Quiney and co-workers [46,11].

TABLE I. The parity-violating energy shift $E_{pv,so}$ ($10^{-20}$ hartree) computed in the CHF approximation and the $E_{scf}$ (hartree) of *d*-camphor as functions of the basis set.

| Basis | $E_{scf}$ (hartree) | $E_{pv,so}$ ($10^{-20}$ hartree) |
|---|---|---|
| 6-31*g* | −462.664 | −6.229 |
| $9s5p1d/5s1p \rightarrow 4s2p1d/2s1p$ | −462.934 | −6.798 |
| $9s5p1d/5s \rightarrow 4s3p1d/2s$ | −462.884 | −6.974 |
| $9s5p/5s1p \rightarrow 4s3p/2s1p$ | −462.775 | −7.578 |
| $9s5p1d/5s1p \rightarrow 4s3p1d/2s1p$ | −462.938 | −7.182 |

## III. RESULTS AND DISCUSSION

In the present paper, the PVES (3) has been evaluated via CHF perturbation theory, fully equivalent to the random-phase approximation adopted in Refs. [27, 28]. Both computational procedures have been implemented in the SYSMO suite of programs [47]. Molecular geometry of *d*-camphor, see Fig. 1, has been optimized at the Hartree-Fock level of theory by means of the GAUSSIAN-94 package [48], adopting the 6-31*G* basis set [49].

Five basis sets have been adopted for the calculations of PVES. The first one is the small 6-31*G* basis set [49], the second basis set is the more extended $(9s5p1d/5s1p)$ contracted to $[4s2p1d/2s1p]$ employed in Ref. [28]. The third basis set does not contain $2p$ polarization functions on hydrogens, but the steepest $2p$ function on carbon and oxygen nuclei has been allowed to vary freely. According to previous studies of magnetic shielding tensors, this procedure is quite effective for improving representation of the spatial part of the spin-orbit operator (2). The fourth basis set does not contain $3d$ polarization functions on heavy atoms, whereas $2p$ functions are added to hydrogen. Their role in increasing the absolute value of $E_{pv,so}$ more than $3d$ functions on C and O is evident. The fifth basis set has been constructed using the same $(s/p)$ substratum, but the exponents of the polarization functions are those corresponding to optimized $E_{scf}$ of smaller molecules [50].

The parity-violating energy shifts evaluated in this work are shown in Table I. We cannot claim that the Hartree-Fock limit for $E_{pv,so}$ in the camphor molecule has been attained in the present paper. Such a limit is difficult to establish *a priori*, as the parity-violating energy (3) is a cross term. A detailed and systematic study would, therefore, be necessary for an empirical assessment of the limit. However, owing to the consistent indications obtained via different basis sets, we are confident that the numerical data we obtained yield reliable information.

From the theoretical estimates it emerges that the natural *d*-enantiomer is more stable than its mirror image owing to WNC: calculated PVEDs are about $1.5 \times 10^{-19}$ hartree, a value that is one order of magnitude larger than those reported previously in several UCHF calculations on a number of molecules [17–22,24].

The importance of this result is hard to overemphasize. In fact, it adds a further important piece of information providing theoretical evidence in favor of the hypothesis that energetically stable enantiomeric species are prevalent in nature [21,19,28].

On the other hand, the present paper does not permit any inference on the existence of a kinetic mechanism, which might have possibly converted the *l*- into the *d*-enantiomer. As a matter of fact, such a route seems somewhat unlikely, owing to the rigid structure of camphor. However, if parity-violating forces are continuously at work during the chemical reaction of synthesis of camphor from achiral reagents, it could be possible that the two enantiomeric transition states are separated by a much larger PVES. Some preliminary calculations on a chemical reaction producing CHFClBr indicate that the PVES in a series of points along the reaction path is approximately two times larger than that of the final product.

It remains to be seen whether such a small difference can be detected via any experimental setup available nowadays. The calculation presented here concerns the PVED for the whole molecule, whereas the experiment [40] set a limit on the frequency of a vibrational transition, which is likely to be very much smaller than the difference in the total energies. To the best of our knowledge an estimate of the relationship between the two is quite difficult to obtain, and would deserve *ad hoc* investigations.

According to the suggestions of some authors [51,12], WNC should remove the degeneracy of energy levels of dextro and levo molecules, making the vibrational and rotational levels to split by a small amount. In the present case of camphor, our findings could spur new experimental studies aimed at detecting any difference between the *d*- and *l*-enantiomers. According to the suggestions of Ref. [40], which dates more than twenty years now, the precision of spectroscopic measurements can be improved by some orders of magnitude by performing the inverted Lamb-dip experiment outside the laser cavity with an expanded laser beam. It should also be recalled that the magnitude of the parity-nonconserving effect can significantly increase in the case of a camphor substratum carrying heavy substituents: an approximate relationship has been, in fact, suggested [44,20], connecting PVES to the fifth power of the atomic number of nucleus $I$, $E_{pv,so} \propto \eta Z_I^5$, with $\eta$ a dissimmetry factor. Accordingly, a crucial experiment [13] could be possibly devised to check the reliability of the WNC energy stabilization in properly substituted camphor enantiomers.

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