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Theoretical results which strengthen the hypothesis of electroweak bioenantioselection

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It is shown via a large series of numerical tests on two fundamental organic molecules, the L-α-amino acid L-valine and the sugar precursor hydrated D-glyceraldheyde, that the *ab initio* calculation of the parity-violating energy shift, at the random-phase approximation level of accuracy, provides results that are about one order of magnitude larger than those obtained by means of less accurate methods employed previously. These findings would make more plausible the hypothesis of electroweak selection of natural enantiomers via the Kondepudi-Nelson scenario, or could imply that Salam phase-transition temperature is higher than previously inferred: accordingly, the hypothesis of terrestrial origin of life would become more realistic.
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Terrestrial biochemistry is characterized by homochirality: living organisms almost exclusively contain L-α-amino acids and D-sugars, whereas their mirror image molecules are apparently not used by nature. Even if no fully satisfactory explanation of this fact has been so far reported, attempts have been made at interpreting chirality manifestation in the macroscopic world in terms of parity nonconserving weak nuclear forces acting at an elementary level [1–8].

In fact, parity violation induced by weak neutral currents (WNC) [9,10] is a well established fact in atomic physics [11–15]. Because of the weak nuclear force, atoms are chiral systems: vapors of bismuth rotate the plane of polarized light, and even if the angle is very small (about 10^{-7} rad, i.e., the parallax of a pencil at a distance of roughly one thousand kilometers), it is large enough to be experimentally detected [16].

On the other hand, proof of the existence of a phenomena, which would arise from weak nuclear force in molecules, has not been reported yet. Although ingenious nonlinear laser spectroscopy experiments have been devised for their detection in molecules [17], infrared spectra of *d*- and *l*-camphor optical antipods agree to within an uncertainty of ≈ 300 kHz, i.e., $\approx 4.56\times10^{-11}$ hartree, which corresponds to the accuracy of 1×10^{-8} [18]. If any effect exists, its magnitude should be smaller than that.

At any rate, the calculations reported so far predict that the energy difference between enantiomeric biomolecules would be of the order of 10^{-20} hartree [1–5,19,7,8,20]. Based on such an estimate, and following the ideas of Frank [21], a kinetic model has been suggested by Kondepudi and Nelson (KN) [22–24] to account for the natural abundance of energetically favored enantiomers, e.g., L-α-amino acids and D-sugars. Supposing that the energy difference of $\approx 10^{-20}$ hartree, which makes natural enantiomers thermodynamically more stable, is comparable with the activation energy of a kinetic process whereby opposite chiral species are formed, KN showed that symmetry can be broken via a catastrophic reaction mechanism [22,23,24]. Autocatalysis of the favored enantiomer should overcome random fluctuations, assuming a series of realistic hypotheses, e.g., reaction volume of 4×10^{9} liter (i.e., a lake of 1 km×1 km×4 m), concentrations of order 10^{-3} M, and reaction rates of $10^{-10}\,\mathrm{M\,sec}^{-1}$. In these conditions 10^{4} yrs would be necessary for an excess of 98% of the favored enantiomer to develop from a primordial racemic mixture [22,23,24].

The KN model has been discounted by Avetisov, Kuz'min, and Anikin, who conclude that the role of WNC in the origination of biomolecular chirality should be regarded irrelevant [25]. In any event, an energy difference of $\approx 10^{-20}$ hartree is too small to make the KN model really effective, which has prompted other scientists to wonder whether the electroweak force could actually play a fundamental role in the appearance of chirality in terrestrial biochemistry. Tunneling mechanisms might instead have caused second-order phase transition between enantiomers below a critical temperature, as suggested by Salam [26] relying on the WNC hypothesis.

However, more recent calculations [27,28] show that accurate estimates of parity violating energies are one order of magnitude larger than those previously reported [1–8].

These results make the KN scenario more plausible, and possibly support the idea that the WNC is responsible for the natural abundance of solvated L-α-amino acids. Nonetheless, further studies are necessary to confirm the findings of Ref. [28] for D-sugars. In addition, the dependence of the parity-violating energy shift (PVES) on molecular conformation needs to be analyzed, as earlier studies examine only one molecular geometry, corresponding to solvated L-α-amino acids [28]. Accordingly, the present paper sets out to investigate the PVES of two archetypal chiral molecules, namely L-valine, in its zwitterionic form, and a sugar precursor, hydrated D-glyceraldheyde, as a function of the intramolecular rotation angle [4,6].

In a molecule with n electrons, with coordinates $\mathbf{r}_i$ and momenta $\mathbf{p}_i$, and N nuclei, with corresponding quantities $\mathbf{R}_I$, charge $Z_I e$, etc, a second-order PVES is obtained from perturbation theory [12,10,13,1,3],

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

The parity nonconserving Hamiltonian is written [12,3]

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

where $\Gamma=G_F/(2\sqrt{2}m_ec)=5.73416\times10^{-17}$ a.u. combines the Fermi weak-coupling constant G_F, the electron mass m_e, and the velocity of light c. The quantities Q_I are model-dependent dimensionless effective weak charges [12,1], defined as

$$Q_I=[\mathcal{N}_I-(1-4\sin^2\theta_w)Z_I], \qquad (3)$$

where $\mathcal{N}_I$ is the number of neutrons of nucleus I, and θ_w is the Weinberg angle. Hereafter, we adopt the theoretical value $\sin^2\theta_w=0.25$ [3], so that the effective charges (3) coincide with the neutron numbers. $\boldsymbol{\sigma}_i$ are Pauli matrices, the exceptionally short range, i.e., ''contact'' interaction between i-th electron and I-th nucleus, is described by the Dirac function $\delta(\mathbf{r}_i-\mathbf{R}_I)$, and $\{\ ,\ \}_+$ indicates the anticommutator of the operators.

Hamiltonian (2) 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. At any rate, as the Pauli operators mix the reference singlet state $|a\rangle$ with the excited triplet states $|j\rangle$, Hamiltonian (2) couples with the electron spin-orbit interaction [29]

$$H_{so}=\frac{\beta^2}{\hbar}\sum_{I=1}^{N}\sum_{i=1}^{n}Z_I|\mathbf{r}_i-\mathbf{R}_I|^{-3}\boldsymbol{\sigma}_i\cdot(\mathbf{r}_i-\mathbf{R}_I)\times\mathbf{p}_i, \qquad (4)$$

(β is the electronic Bohr magneton) yielding the PVES (1) that reverses sign upon going from the mixed-parity wave function of an L-enantiomer to that of its D-enantiomer [1].

It might be worth pointing out that the need for a second-order perturbation expression involving the parity-violating interaction and the spin-orbit interaction is an artifact of the use of the nonrelativistic reduction of the parity-violating operator. If the Dirac form were used, the parity-violating energy would simply be an expectation value over a Dirac based molecular wave function of the type that has been developed by Quiney *et al.* [30] for electric dipole calculations.

In the present paper, the parity-violating energy shift (1) has been calculated via a series of approximations of increasing accuracy to the equation-of-motion method [31], as in Ref. [27]: an uncoupled crude Hartree-Fock (UCHF) approach (for the sake of comparison with Refs. [4,6], where it has been first applied to the study of L-valine and hydrated D-glyceraldheyde), the single-transition approximation (STA), the Tamm-Dancoff approximation (TDA), and the random-phase approximation (RPA), equivalent to coupled Hartree-Fock (CHF) method, using algorithms described previously, implemented in the SYSMO package [32].

It has been shown [3,4] that the magnitude and sign of PVES for chiral molecules strongly depend upon molecular conformation. In the present study we have taken into account several rotational conformers of both L-valine and hydrated D-glyceraldheyde, characterized by different values of the dihedral angle ϕ defined in Figs. 1 and 2. In all cases the species present in aqueous solution have been retained, i.e., the zwitterionic form of L-valine and the hydrated D-glyceraldheyde. The remaining molecular structural parameters have been taken as follows: (i) for L-valine we have assumed the geometry reported by Tranter [4]; (ii) for each fixed value of the dihedral angle ϕ of hydrated D-glyceraldheyde, bond lengths and bond angles have been optimized at the Hartree-Fock level of theory by means of the GAUSSIAN-94 package [33], adopting the 6-31G basis set [34], and fixing the other dihedral angles as shown in Fig. 2.

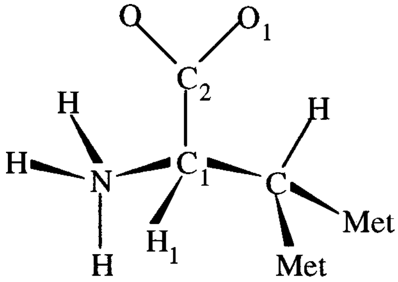

FIG. 1. Structure of L-valine.

As in Ref. [27], two basis sets have been adopted for the calculations of PVES. The former is the small 6-31G basis set [34], which has been used in combination with all the methods, the latter is the more extended $(9s5p1d/5s1p)$ contracted to $[5s4p1d/3s1p]$ basis set [28], hereafter indicated as EXT, which has been used only to obtain CHF estimates. This choice elucidates quite nicely the large improvement, which can be obtained on passing from the combination 6-31G UCHF, adopted in the past [3,4,6], to the combination EXT/CHF, yielding the best results presented here.

The parity-violating energies calculated in this paper as a function of the dihedral angle ϕ in L-valine and hydrated D-glyceraldheyde are reported in Tables I and II. Our UCHF results differ slightly from those of Tranter [4,6]. At all events, for most conformations of both molecules, they are much smaller (in many cases up to an order of magnitude) than corresponding ones yielded by STA, TDA, and RPA schemes. This result confirms previous findings [27,28]. As far as order of magnitude is concerned, there is a general agreement between TDA and RPA small-basis set theoretical

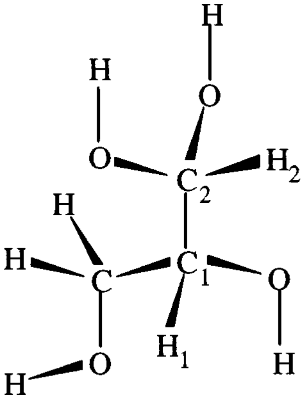

FIG. 2. Structure of hydrated D-glyceraldehyde.

TABLE I. Parity-violating energy shift $E_{\rm pv}/10^{-20}$ hartree of *L*-valine as a function of the dihedral angle ϕ for different approaches, small and extended basis sets.

	6-31G				EXT
ϕ (deg)	UCHF	STA	TDA	RPA	RPA
0	−3.180	−2.936	−11.148	−14.688	−16.525
30	−1.262	−3.335	−6.185	−7.948	−9.107
45	0.442	−1.336	−0.543	−0.407	−0.761
60	2.359	1.210	5.969	8.450	9.364
90	3.946	4.163	12.723	17.243	20.859
120	1.130	2.504	6.146	7.649	10.619
150	−2.497	−1.259	−5.939	−8.450	−9.064

predictions for both molecules, as it can be seen in Tables I and II. It must be recalled that the accuracy of the results is expected to increase from left to right in each row of the tables, according to theoretical arguments and consolidated numerical experience [31,27,28,32], whereby the precision of the different theoretical methods adopted in this study, and the higher accuracy of RPA-CHF estimates for a given basis set, can be safely assessed.

The importance of basis set quality should also be recalled: large discrepancies are observed in Tables I and II between the RPA results provided by 6-31G and extended basis sets: the absolute values systematically increase by using the latter. Therefore, it can be surely stated that the RPA predictions obtained via extended basis set in the present study furnish more reliable indications than corresponding UCHF ones by Tranter [4,6].

The observed trends indicate that parity-violation effects stabilize the zwitterion enantiomeric form of *L*-valine solvated in acqueous media, corresponding to values of the dihedral angle close to 0°. On the other hand, the values for hydrated *D*-glyceraldheyde lie in the range $1-5\times10^{-20}$ hartree, entirely in the region of negative PVES: irrespective of the internal rotational angle, the natural *D* enantiomer is more stable than its unnatural optical antipode owing to WNC. It can be concluded that the RPA-CHF estimates reported in this paper for a series of rotational conformers, support the hypothesis that the excess of the more stable enantiomeric molecules belonging to two major series of chiral biochemistry, e.g., L-α-aminoacids or *D*-sugars, could be explained in terms of electroweak forces by much more convincing arguments than found before, if the KN catastrophic bifurcation route is considered realistic. In fact, in the case of solvated L-α-amino acids (corresponding to their preferred conformation in acqueous medium [4]), a PVES of $\approx 1\times10^{19}$ hartree, i.e., $\approx 3\times10^{-18}$ eV, would imply [26] that 1 out of 10^{16} molecules is stabilized by WNC at room temperature [as $10^{-16}\approx(3\times10^{-18}\,\text{eV})/300\,\text{K}k_B$]. Accordingly, the primordial reaction volume must have contained 10^{32} molecules to overcome random fluctuations. Hence, either the KN lake reduces by two orders of magnitude for the same amplification time, or, for the same lake volume, the amplification time would reduce to one year [8]. These predictions could be in the range of possible verification via a crucial experiment.

TABLE II. Parity-violating energy shift $E_{\rm pv}/10^{-20}$ hartree of hydrated *D*-glyceraldehyde as a function of the dihedral angle ϕ for different approaches, small and extended basis sets.

	6-31G				EXT
ϕ (deg)	UCHF	STA	TDA	RPA	RPA
0	−1.258	−3.190	−1.984	−3.871	−5.024
30	−1.560	1.342	−2.586	−4.156	−5.226
60	−1.641	−0.082	−2.628	−4.621	−6.050
90	−1.017	−2.566	−2.520	−4.157	−4.686
120	−0.672	0.114	−0.951	−2.201	−2.904
150	−0.562	−3.802	−0.058	−0.811	−1.741
180	−0.248	0.340	0.381	−0.196	−0.742
210	−0.145	2.966	−0.292	−1.032	−0.338
240	−1.420	3.499	−2.872	−4.193	−4.961
270	−1.873	4.410	−3.155	−4.874	−6.804
300	−0.854	−2.809	−1.270	−2.609	−3.368
330	−0.491	2.208	−0.712	−2.193	−2.589

If, on the other hand, phase transition between enantiomers [26] occurs, the Salam critical temperature should be somewhat higher than the estimated value of 250–300 K, thus implying that the Earth had the best chance of being the place where prebiotic L-α-amino acids and sugar precursor hydrated *D*-glyceraldheyde might have started to appear [26]. This would also make the hypothesis of extra terrestrial origin of life less likely.

After completion of this paper, theoretical evidence for the importance of the contribution to Eq. (1) arising from one-center two-electron spin-orbit integrals, that should be added to Eq. (4), has been put forward [35]. Although the results of this reference imply that future rigorous calculations of parity-violating energy (1) should include the difficult two-electron terms, the findings of the present papers remain essentially valid.

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[1] R. A. Hegstrom, D. W. Rein, and P. H. G. Sandars, J. Chem. Phys. **73**, 2329 (1980).

[2] D. W. Rein, R. A. Hegstrom, and P. H. G. Sandars, Phys. Lett. **71A**, 499 (1979).

[3] S. F. Mason and G. E. Tranter, Mol. Phys. **53**, 1091 (1984).

[4] G. E. Tranter, Mol. Phys. **56**, 825 (1985).

[5] S. F. Mason and G. E. Tranter, Chem. Phys. Lett. **94**, 34 (1983).

[6] G. E. Tranter, J. Chem. Soc. Chem. Commun. **1986**, 60.

[7] A. J. MacDermott and G. E. Tranter, Chem. Phys. Lett. **163**, 1

(1989).
[8] A. J. MacDermott, G. E. Tranter, and S. J. Trainor, Chem. Phys. Lett. **194**, 152 (1992).
[9] F. C. Michel, Phys. Rev. **138**, B408 (1965).
[10] B. Y. Zel'dovich, D. B. Saakyan, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. Pis'ma Red. **25**, 106 (1977) [JETP Lett. **25**, 94 (1977)].
[11] M. A. Bouchiat and C. C. Bouchiat, Phys. Lett. **48B**, 111 (1974).
[12] M. A. Bouchiat and C. Bouchiat, J. Phys. (Paris) **35**, 899 (1974).
[13] M. A. Bouchiat and C. Bouchiat, J. Phys. (Paris) **36**, 493 (1975).
[14] V. V. Karasev, L. N. Labovsky, and A. V. Nefedov, Phys. Lett. A **172**, 62 (1992).
[15] C. S. Wood *et al.*, Science **125**, 1759 (1997).
[16] I. B. Khriplovich, *Parity Nonconservation in Atomic Phenomena* (Gordon and Breach, Oxford, 1991).
[17] O. N. Kompanets, A. R. Kukudzhanov, and V. S. Letokhov, Opt. Commun. **19**, 414 (1976).
[18] E. Arimondo, P. Glorieux, and T. Oka, Opt. Commun. **23**, 369 (1977).
[19] S. F. Mason and G. E. Tranter, J. Chem. Soc. Chem. Commun. **1983**, 117.
[20] *Chirality from the Werk Bosons to the α-Helix*, edited by R. Jonoshek (Springer-Verlag, Berlin, 1991).
[21] F. C. Frank, Biochem. Biophys. Acta **11**, 459 (1953).
[22] D. K. Kondepudi and G. W. Nelson, Phys. Rev. Lett. **50**, 1023 (1983).
[23] D. K. Kondepudi and G. W. Nelson, Nature (London) **314**, 438 (1985).
[24] D. K. Kondepudi, BioSystems **20**, 75 (1987).
[25] V. A. J. Avetisov, V. V. Kuz'min, and S. A. Anikin, Chem. Phys. **112**, 179 (1987).
[26] A. Salam, J. Mol. Evol. **33**, 105 (1991).
[27] P. Lazzeretti and R. Zanasi, Chem. Phys. Lett. **279**, 349 (1997).
[28] R. Zanasi and P. Lazzeretti, Chem. Phys. Lett. **286**, 240 (1998).
[29] E. Gaizago and G. Marx, Atomki Közleméniek Suppl. **16**, 177 (1974).
[30] H. M. Quiney, J. K. Laerdahl, K. Faegri, and T. Saue, Phys. Rev. A **57**, 920 (1998).
[31] J. T. H. Dunning and V. McKoy, J. Chem. Phys. **48**, 5263 (1968).
[32] P. Lazzeretti, E. Rossi, and R. Zanasi, Phys. Rev. A **27**, 1301 (1983), and references therein.
[33] M. J. Frisch *et al.*, *Gaussian 94, Revision B.3* (Gaussian, Inc., Pittsburgh, PA, 1995).
[34] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).
[35] H. Kiyonaga, K. Morihasi, and O. Kikuchi, J. Chem. Phys. **108**, 2041 (1998).