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Asymmetry of electron chirality between enantiomeric pair molecules and the origin of homochirality in nature

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We propose the difference of reaction rates of the weak interaction between enantiomers produces the small imbalance of the number density between pairs of enantiomers, which may be the origin of the homochirality in nature. Since left-handed particles have larger reaction rate of the weak interaction than right-handed particles, the nonzero total electron chirality in a chiral molecule, which is the integrated chirality density over the whole molecule, induces different reaction rate of the weak interaction between an enantiomeric pair. Due to this difference of reaction rates, one of the enantiomeric pair is more destroyed than the other by interactions with astronomical particles in space, such as cosmic rays and neutrinos emitted by nuclear fusion in star cores. It is numerically shown that chiral molecules generally have nonzero total electron chirality in addition to parity-violating energy shift, for H_2X_2 ($X = \mathrm{O, S, Se, Te}$) molecules as a typical sample of chiral molecules. This total chirality is shown to be related to the dihedral angle of H_2X_2 molecules and is the result of the cancellation between large contributions from some highest occupied molecular orbitals. It is shown that the value of total chirality in a chiral molecule is drastically enhanced if the molecule is ionized or excited, since this cancellation is broken. The parity-violating energy shift has this property also though the enhancement is smaller for H_2X_2 molecules.

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I. INTRODUCTION

In nature, the amount of one form of an enantiomeric pair of a biological chiral molecule is much larger than the other form, that is, living systems are not parity symmetric. Only (D)-sugar and (L)-amino acid are found in nature on the earth. This bias of biomolecular chirality has remained a mystery for several decades. Some believe that the same number of enantiomers are produced in nature, since the same amount of both of an enantiomeric pair are produced in laboratory without catalysis, and then one form of some enantiomeric pairs is lost or transformed to another of the pair in evolution. Others consider that an unequal number of enantiomers are produced in a parity-violating environment. It is considered that the source of the asymmetry of enantiomeric pairs is born in space, since nonracemic amino acids are found in Murchison meteorite [1]. Even though their enantiomeric excess is not enough to explain the bias in nature on the earth, chiral amplification processes are considered to enhance a small source of the asymmetry to large imbalance between enantiomeric pairs.

The mechanism responsible for the production of the initial small imbalance between enantiomeric pairs remains unclear. Some mechanisms to generate this imbalance are proposed [2]. For example, circularly polarized light originated from astronomical sources, such as pulsars and interstellar medium, are proposed to be the origin of enantiomeric excess. The parity-violating energy shift between enantiomers by the weak interaction is also believed by some people to generate the imbalance of the number of enantiomers. Another example is the Vester-Ulbricht hypothesis [3], where one form of some enantiomeric pairs is preferentially lost by the interaction with left-handed electrons produced by beta decay of nuclei or circularly polarized light emitted from these electrons. In this paper, one contribution of fundamental physics to the generation of this bias is pointed out.

Enantiomers of chiral molecules have nonzero value of integrated chirality density over the whole molecules, which is called total chirality in this paper, and its value for an enantiomer is opposite to that of the enantiomeric partner. This has not been paid attention to after the first report for H_2Te_2 molecule appeared [4], and recently Senami *et al.* have confirmed that chiral molecules have generally nonzero total chirality, numerically for H_2X_2 ($X = \mathrm{O, S, Se, Te}$) molecules [5]. Due to this total chirality, enantiomers of a chiral molecule have different reaction rates of the weak interaction, since the weak interaction is parity-violating interaction and left-handed particles have larger reaction rates of the weak interaction. Hence one of an enantiomeric pair is more destroyed by reactions with particles in space, such as cosmic rays and neutrinos produced by nuclear fusion in stars. This reaction has nonzero contribution to the generation of the difference of the number density of enantiomers. This reaction with particles in space is a different notion from the parity-violating energy shift, where the latter is dependent on only the chirality density at the positions of nuclei. In addition, our mechanism is also different from Vester-Ulbricht hypothesis. Vester-Ulbricht hypothesis requires some chirally polarized sources, while our mechanism does not require any polarized source. An unpolarized source contains both right- and left-handed particles and can interact with molecules by

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the weak interaction. Our mechanism uses the parity-violating source, which is included in molecules.

In our previous work [5], the total chirality was studied for H_2X_2 ($X = \mathrm{O, S, Se, Te}$) molecules. One purpose of this work was to show the direct relation between the total chirality and the parity-violating energy, since we believe that both these two quantities are dependent on the structure of molecules. For parity-violating energy, the relation between molecular structure and the energy has been clarified by the analysis of spin-orbit interaction and parity violation in perturbation theory [6]. For total chirality, theoretical consideration has not been done in viewpoints of the relation with the structure of a chiral molecule. Hence, in our previous work, as the first trial, the relation is studied in numerical computations, and due to the shortage of accuracy we could not show the relation.

In this work, the total chirality of H_2X_2 ($X = \mathrm{O, S, Se, Te}$) molecules is studied with larger basis sets than the work [5] for the confirmation of the relation between the total chirality and the dihedral angle of H_2X_2 molecules. Then we study how the total chirality of this molecule is yielded and show contributions from orbitals to the total chirality separately. We find that the total chirality is derived as the cancellation between large contributions from highest occupied molecular orbitals and excitation or ionization enhances the total chirality due to the disturbance of the cancellation.

This paper is organized as follows. In the next section, the definitions of the chirality density and the total chirality are introduced. As a related quantity to the chirality, parity-violating energy shift is also introduced briefly. This quantity is used for the check of our computation and the comparison with the total chirality. Then, we summarize our mechanism to generate the imbalance between enantiomeric pairs. In Sec. IV, computational detail is explained. In Sec. V, our results are shown. The relation between the total chirality and the dihedral angle of H_2X_2 molecules and contributions from orbitals to the total chirality are shown, and we will see that excitation or ionization enhances the total chirality. The last section is devoted to our summary.

II. THEORY

For the electron, chiral quantities can be defined. This may be surprising, since the electron is a pointlike particle. The electron has spin and momentum, and hence the electron can have a chiral property. One of the simplest chiral quantities is the helicity. If the inner product of spin and momentum is positive (negative), the helicity is defined as positive (negative). This quantity is very intuitive and, however, has a crucial fault; this quantity does not obey Lorentz symmetry. Helicity of an electron may be different in a different inertial frame, if the direction of momentum is inversed by Lorentz transformation. Hence the helicity is not a well-motivated quantity for the electron in spite of its simpleness, and another chiral quantity obeying the Lorentz symmetry should be defined. This is the chirality of the electron [7,8]. Electrons have right- or left-handed chirality. The right- and left-handed electrons are defined as

$$\hat{\psi}_R(\vec{r}) = P_R\hat{\psi}(\vec{r}), \quad \hat{\psi}_L(\vec{r}) = P_L\hat{\psi}(\vec{r}), \tag{1}$$

where $\hat{\psi}$ is the electron field operator and $P_{R,L}$ is the projection operator of the chirality,

$$P_R = \frac{1+\gamma_5}{2}, \quad P_L = \frac{1-\gamma_5}{2}. \tag{2}$$

Here γ_5 is given with gamma matrix γ^μ as $\gamma_5 = i\gamma^0\gamma^1\gamma^2\gamma^3$. Since the parity transformation operator is $P = e^{i\phi}\gamma^0$ [7,8], where ϕ is an arbitrary phase, and hence $\{P, \gamma^5\} = 0$, γ_5 is a parity odd operator. The chirality density operator, $\hat{\psi}^\dagger\gamma_5\hat{\psi}$, is the difference of the density operator between the right-handed and left-handed electrons,

$$\hat{\psi}^\dagger(\vec{r})\gamma_5\hat{\psi}(\vec{r}) = \hat{\psi}_R^\dagger(\vec{r})\hat{\psi}_R(\vec{r}) - \hat{\psi}_L^\dagger(\vec{r})\hat{\psi}_L(\vec{r}). \tag{3}$$

For massless particles, the definition of helicity and chirality is identified. The chirality density $\langle\gamma_5(\vec{r}_e)\rangle$ is derived as the expectation value of this operator,

$$\langle\gamma_5(\vec{r})\rangle \equiv \langle\Psi|\hat{\psi}^\dagger(\vec{r})\gamma_5\hat{\psi}(\vec{r})|\Psi\rangle, \tag{4}$$

where $|\Psi\rangle$ is a state vector. The electron chirality was explained even in textbooks of relativistic quantum theory after the discovery of parity violation in the weak interaction. Then, in the field of computational chemistry, the chirality density was first discussed in Ref. [9] in nonrelativistic formulation. The total electron chirality, which is our main subject, is defined as the integration of the chirality density over a whole molecule,

$$\int d^3\vec{r}\langle\gamma_5(\vec{r})\rangle \equiv \int d^3\vec{r}\langle\Psi|\hat{\psi}^\dagger(\vec{r})\gamma_5\hat{\psi}(\vec{r})|\Psi\rangle. \tag{5}$$

The right- and left-handed electrons are different particles in fundamental physics theory. The left-handed and right-handed electrons have different charge of the weak interaction [8], which is one of the four interactions in particle physics and violates the parity symmetry.

It is known that a molecule generally has internally a nonzero chirality distribution, whose shape is limited by symmetries of molecular structure [10]. Due to the existence of the nonzero electron chirality density at the position of a nucleus, parity-violating energy shift between an enantiomeric pair is given by the weak interaction between electrons and nuclei. Parity-violating energy shift was investigated in a viewpoint of the origin of homochirality [11–13]. However, this energy shift is considered to be too small to generate enough the number asymmetry between enantiomeric pairs [14]. Therefore, in this work, parity-violating energy shift is not seriously considered to be the origin of the homochirality and is taken for two purposes. First, we study the relation between parity-violating energy shift and total electron chirality. We consider that both quantities are dependent on the structure of a molecule and the structure affects the spin-orbit interaction distribution in the molecule. Second, the confirmation of our electronic structure computations. For the purpose of accurate computations for realizing spin quantum state, we adopt four component relativistic quantum chemistry computation. This computation is more difficult than a nonrelativistic one, and hence we should check whether our wave function is accurate enough, though we have speculated that computations of total chirality require higher accuracy than those of parity-violating energy.

The parity-violating energy shift is briefly introduced in this paper, and, for the detail, please see, for example, Ref. [4]. This parity-violating energy shift is given by the vector and axial-vector current interactions of electrons and nucleons in a nucleus. In a molecule, the nonrelativistic limit for a nucleon is a good approximation, and hence the coupling of the timelike components of nucleon vector current and electron axial-vector current gives a dominant contribution. The Hamiltonian of this interaction is given as

$$H_{\mathrm{PV}} = \sum_n \frac{G_F}{2\sqrt{2}} Q_W^n \hat{\psi}_e^\dagger(\vec{r})\gamma_5\hat{\psi}_e(\vec{r})\hat{\psi}_{N_n}^\dagger(\vec{r})\hat{\psi}_{N_n}(\vec{r}), \quad (6)$$

where $\hat{\psi}_e$ and $\hat{\psi}_{N_n}$ are the field operators of electrons and nuclei, respectively, n is the species of nuclei, and $G_F = 1.166378 \times 10^{-5}$ GeV^{-2} is the Fermi coupling constant [15]. Q_W^n is the weak charge of a nucleus, $Q_W^n = Z^n(1 - 4\sin^2\theta_W) - N^n$, where $Z^n(N^n)$ is the number of proton (neutron) in a nucleus n and θ_W is the weak-mixing angle, $\sin^2\theta_W = 0.2313$ [15]. In this approximation, since the virtual exchange of a weak gauge boson is very short range, the weak interaction is given as contact interaction, that is four fermion interaction. The parity-violating energy is derived as the expectation value of this operator,

$$E_{\mathrm{PV}} = \int d^3\vec{r}\langle\Psi|H_{\mathrm{PV}}|\Psi\rangle. \quad (7)$$

The parity-violating energy shift is the energy difference between an enantiomeric pair and given as twice the parity-violating energy,

$$\Delta E_{\mathrm{PV}} = 2|E_{\mathrm{PV}}|. \quad (8)$$

The parity-violating energy is denoted as the sum of contributions from all nuclei,

$$\begin{aligned} E_{\mathrm{PV}} &= \frac{G_F}{2\sqrt{2}} \sum_n Q_W^n \left(\int d^3\vec{r}_e \langle\Psi|\hat{\psi}_e^\dagger\gamma_5\hat{\psi}_e\hat{\psi}_{N_n}^\dagger\hat{\psi}_{N_n}|\Psi\rangle \right) \\ &= \frac{G_F}{2\sqrt{2}} \sum_n Q_W^n M_{\mathrm{PV}}^n, \end{aligned} \quad (9)$$

where M_{PV}^n is the parametrization of the contribution from the nucleus n. Since a nucleus is a very small object compared to electron distribution, a nucleus is considered to be a pointlike particle and its density distribution is given approximately as $\hat{\psi}_{N_n}^\dagger\hat{\psi}_{N_n} = \delta^3(\vec{r} - \vec{r}_n)$, where $\vec{r}_n$ is the position of the nucleus n. Therefore, M_{PV}^n is given by

$$M_{\mathrm{PV}}^n = \langle\Psi|\hat{\psi}_e^\dagger(\vec{r}_n)\gamma_5\hat{\psi}_e(\vec{r}_n)|\Psi\rangle. \quad (10)$$

This is the electron chirality density at the position of N_n. The parity-violating energy is dominantly dependent on the electron chirality density at the positions of nuclei in a molecule.

III. MECHANISM FOR HOMOCHIRALITY

In this section, our mechanism to generate the imbalance between numbers of enantiomers is summarized. It has been confirmed that chiral molecules have generally nonzero total chirality [5]. The value of total chirality for an enantiomer is opposite to that of the enantiomeric partner. Hence both forms of an enantiomeric pair have the same number of electrons (the sum of right- and left-handed electrons), while these have different numbers of left-handed electrons. Due to the difference of the total chirality, one form of an enantiomeric pair has a different reaction rate, from its partner, with other astronomical particles in space, such as protons, electrons, neutrinos, and muons in cosmic rays and neutrinos from nuclear fusion in stars, by the virtual exchange of weak gauge bosons. The weak interaction is the interaction mediated by weak gauge bosons, $W^\pm$ and Z, and one of the four fundamental interactions in particle physics. For this interaction, parity symmetry is violated, and only left-handed particles have charge of this interaction before the electroweak symmetry breaking [8] and, even after the electroweak symmetry breaking, left-handed particles have larger interaction rate with weak gauge bosons than right-handed particles. For the reaction between a molecule and astronomical particles, cosmic rays, neutrinos, and so on, the weak interaction rate is dependent on the total chirality in the molecule, while the reaction rate of electromagnetic interaction is proportional to only the sum of the numbers of right- and left-handed electrons. Hence one of an enantiomeric pair which has more left-handed electrons than the other, that is the negative chirality, is more interacted with astronomical particles in space and gets more energy from the particles. Therefore, one form of an enantiomeric pair is more destroyed by this energy transfer from particles in space.

Our mechanism is different from the Vester-Ulbricht hypothesis in viewpoints of incident particles. In the Vester-Ulbricht hypothesis, polarized source, such as left-handed electrons or circularly polarized light emitted by the electrons, plays an important role, while we do not require any polarized source. Even an unpolarized particle ensemble can react to electrons in molecules by the weak interaction. In our mechanism, the source of the parity violation is the nonzero total chirality in chiral molecules.

We parametrize, by ϵ, the difference of electron chirality between an enantiomeric pair. The cross section of one electron with i particle by the weak interaction is denoted by R_{We}^i, and then the difference of reaction rates between enantiomers with i particles in space are schematically proportional to

$$\int dE\, \epsilon \sum_i R_{We}^i(E) F_L^i(E), \quad (11)$$

where F_L^i is the flux of i particle which has charge of the weak interaction and E is the energy of its astronomical particle. The number difference between enantiomeric pairs is generated by this rate in a space. However, this formula is very complicated, since $R_{We}^i(E)$ and $F_L^i(E)$ are not simple. For example, $F_L^i(E)$ is dependent on the age of the universe and maybe the position. In viewpoints of molecules, by this reaction with particles in space by the weak interaction, what occurs is not simple—excitation of an electron, ionization, deformation of a molecule, excitation of oscillation, destruction, and so on. In addition, the above changes of a molecule are considered to have different effectiveness for the transformation from one form of enantiomeric pair to another and the destruction of enantiomers. There are many things to study to evaluate this quantity, and we do not discuss this expression further in this paper.

Finally, we discuss briefly particles in space. We cannot judge which astronomical particles give dominant contribution to our mechanism, presently. This is because we do not know which energy of these particles and which processes are the most effective for our mechanism. In our future works, we should clarify these points.

Nevertheless, some speculations are discussed in the last part of this section. Cosmic neutrino background, which is one of the remnants of the big-bang process, has the largest particle number in the universe among particles with weak charge. The particle number density is about 0.1 billion particles in cubic meter [16,17]. However, typical energy of these neutrinos is 10^{-4} to 10^{-6} eV and the energy transfer from these neutrinos is considered to be negligible for enantioselection. Neutrino emitted by nuclear fusion in star cores and cosmic rays are considered to be candidates for our mechanism. Typical energy of cosmic rays is often said to be 1 GeV to 10^{20} GeV, while this is 10^{-3} to 1 MeV for solar neutrino [16,17]. In inelastic collision with these high-energy particles, destruction or ionization is speculated to be dominant. Since this collision occurs more frequently for an enantiomer with negative total chirality than the other enantiomer, which has positive total chirality, the destruction process can produce a difference between enantiomers. On the other hand, although ionization does not make the difference, ionization enhances the total chirality of enantiomers.

For lower-energy transfer (1 to 10 eV), the transition from one form of enantiomeric pair to another one is considered to occur, and particles in this energy region are interesting. Flux of interstellar neutrinos, whose energy is eV scale, has not been measured, because of its low energy. Nuclear fusion occurs in all shining stars and inevitably emits neutrinos. Unfortunately, the typical energy of these neutrinos is 10^{-3} to 1 MeV. However, neutrinos emitted by nuclear fusion in the past have lower energy by 1/10 to 1/100. These neutrinos may interact with enantiomers. In addition, there should be interstellar neutrinos produced by scattering of cosmic rays and so on. The flux is unknown and, however, these neutrinos may contribute. Low-energy (eV scale) cosmic ray flux has also not been observed. However, the flux of interstellar cosmic rays is predicted based on a model of a cosmic ray propagation in galaxies [18]. The flux is roughly comparable to cosmic ray flux of 1 GeV, where the cosmic ray flux is almost maximum. This feature was partially confirmed by experiments for the energy region, 0.1 to 1 GeV [19]. Hence we expect that these cosmic rays and neutrinos also contribute to our mechanism.

To evaluate contributions from these candidates, we should do many things, for example, know cross section of reactions and the total chirality of amino acid and estimate flux of these candidates and so on. Hence, in this work as the first trial, we concentrate the estimate of ϵ of H_2X_2. In our future works, we calculate the total chirality of amino acid, study the reaction of electrons in amino acids with cosmic rays and neutrino in space, and the flux and spectrum of these astronomical particles.

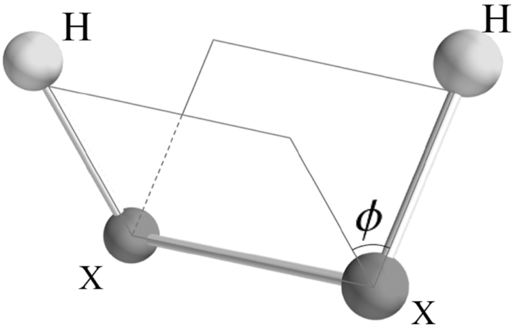


FIG. 1. Structure of H_2X_2 molecules and the definition of the dihedral angle ϕ.

IV. COMPUTATIONAL DETAIL

For the purpose of the study of the electron chirality in a chiral molecule, we choose H_2X_2 ($X = \text{O, S, Se, Te}$) molecules as a reference molecule. The elements, O, S, Se, and Te, are the same group, and we can study the importance of relativistic effects, particularly spin-orbit interaction. Since these molecules have a simple structure, computations are easy to converge and the relation between the structure of the molecules and the electron chirality is also easy to investigate. The structure of the molecules is depicted in Fig. 1. The dihedral angle ϕ is defined in this figure.

Our electronic structure computations are performed by four-component relativistic Hartree-Fock method with the Dirac-Coulomb Hamiltonian. For these computations, we use the DIRAC14 program package [20]. Two basis sets, dyall.ae3z (TZ) [21,22] and dyall.ae4z (QZ) [22,23] are used for all atoms. The geometrical optimization is carried out with the TZ basis. For the study of varying ϕ, only ϕ is varied from this optimized geometry, while the other parameters, such as internuclear lengths, are fixed. Physical quantities, such as chirality density and parity-violating energy, are performed by the QEDynamics program package [24–26]. In the following, we use the atomic unit.

V. RESULTS

For the sake of the check of our computation, the parity-violating energy is studied for $\phi = 45^\circ$, where the parity-violating energy is maximum. In Table I, the values of parity-violating energy and M_{PV} for one X nucleus are shown as well as the reference values [27–29]. Our results are consistent with results by other groups. Our values are slightly smaller than others, while the parity-violating energy is known to easily change even for a slight deformation of molecular structure [30]. The molecular structures are slightly different from others, and hence our results are consistent with other groups in spite of the difference of the value of parity-violating energy. In Table I, slightly larger parity-violating energy is derived for larger basis sets in both our and other group results.

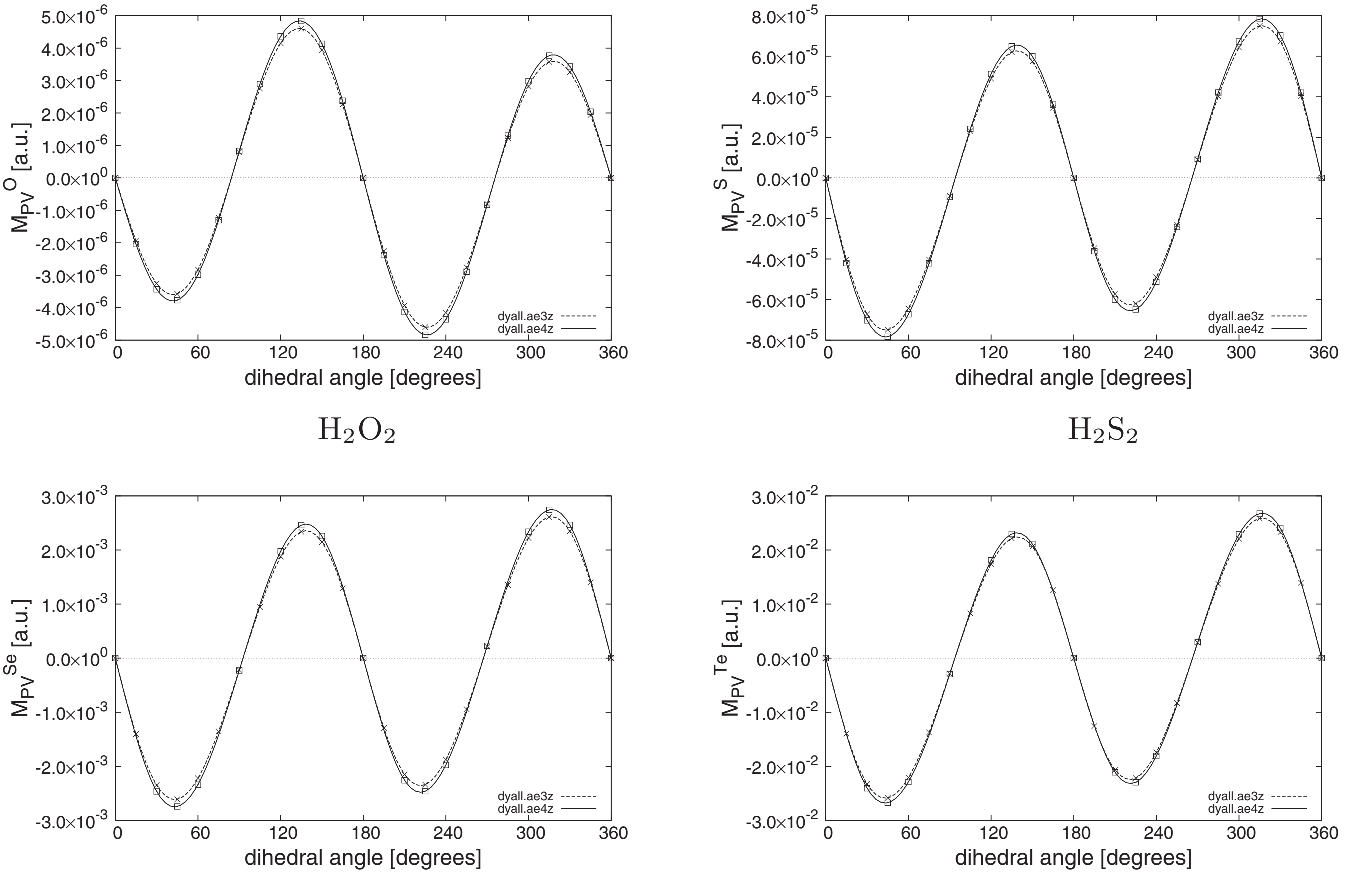
For the further check of our computations, the dependence of M_{PV}^X on the dihedral angle, ϕ, is studied. As mentioned above, only ϕ is changed from the optimized molecular

TABLE I. Parity-violating energy and $M_{\rm PV}^{X}$ of H_2X_2 molecule. $M_{\rm PV}^{X}$ is the electron chirality at one X nucleus. The dihedral angle $\phi = 45^\circ$ for our results. In other works, a definition of the dihedral angle is the same or reversed, and a dihedral angle is chosen to be 45° or −45° so that $M_{\rm PV}^{X}$ has a positive value, since the definition of the dihedral angle is not explicitly shown in Refs. [27,28]. The abbreviations HF, CISD, and CCSD mean Hartree Fock, configuration-interaction single and double, and coupled cluster single and double.

Molecule	Method	Basis set for X	$\lvert M_{\rm PV}^{X}\rvert$ (a.u.)	$\lvert E_{\rm PV}\rvert$ (a.u.)	Ref.
H_2O_2	HF	dyall.ae3z	3.5765×10^{-6}	4.1599×10^{-19}	This study
		dyall.ae4z	3.7713×10^{-6}	4.3865×10^{-19}	This study
		dyall.ae3z		6.051×10^{-19}	[27]
		dyall.ae4z		6.376×10^{-19}	[27]
		cc-pVDZ+3p	5.801×10^{-6}		[28]
		25s25p5d	6.058×10^{-6}		[28]
		aug-cc-pVDZ	3.729×10^{-6}		[29]
		aug-cc-pVTZ	4.239×10^{-6}		[29]
		aug-cc-pVQZ	4.687×10^{-6}		[29]
		25s25p5d	6.057×10^{-6}		[29]
	CISD	cc-pVDZ+3p	5.410×10^{-6}		[28]
	CCSD	dyall.ae3z		5.323×10^{-19}	[27]
		dyall.ae4z		5.583×10^{-19}	[27]
		cc-pVDZ+3p	5.299×10^{-6}		[28]
H_2S_2	HF	dyall.ae3z	7.4955×10^{-5}	1.7508×10^{-17}	This study
		dyall.ae4z	7.8345×10^{-5}	1.8300×10^{-17}	This study
		cc-pCVTZ		1.825826×10^{-17}	[27]
		cc-pVDZ+3p	8.916×10^{-5}		[28]
		25s25p5d	9.581×10^{-5}		[29]
	CCSD	cc-pCVTZ		1.82103×10^{-17}	[27]
		cc-pVDZ+3p	9.283×10^{-5}		[28]
H_2Se_2	HF	dyall.ae3z	2.6107×10^{-3}	1.7408×10^{-15}	This study
		dyall.ae4z	2.7438×10^{-3}	1.8295×10^{-15}	This study
		25s25p5d	3.586×10^{-3}		[29]
	CCSD	dyall.cv3z		2.115×10^{-15}	[27]
H_2Te_2	HF	dyall.ae3z	2.5837×10^{-2}	2.9118×10^{-14}	This study
		dyall.ae4z	2.6737×10^{-2}	3.0132×10^{-14}	This study
		25s25p5d	3.149×10^{-2}		[29]
	CCSD	dyall.cv3z		3.289×10^{-14}	[27]

structure. Our results of $M_{\rm PV}^{X}$ are shown as a function of ϕ in Fig. 2. Due to the limitation of computational resources, data at some dihedral angles are skipped in computations of H_2Se_2 and H_2Te_2 with the QZ basis set. Our results in Fig. 2 are consistent with our previous work [5], which adopts the dyall.ae2z basis set (DZ) [22,23,31]. Our results are also consistent with Ref. [29], where the definition of the dihedral angle is opposite, and inconsistent with Ref. [4], where the definition of the dihedral angle is the same. We speculate that the definition of the dihedral angle in Ref. [4] was the same as Ref. [29]. As seen from Fig. 2, the results are almost independent of the choice of a basis set, and hence our computations are accurate enough for the description of $M_{\rm PV}^{X}$.

In our previous work [5] with the DZ basis set, the total chirality of H_2Te_2 is consistent with the result reported by another group [4], while unfortunately any results have not been reported for other molecules, H_2Se_2, H_2S_2, and H_2O_2, as far as we know. We believe that the structure of molecules governs the total chirality through spin-orbit interaction, and hence the dependence of total chirality on the dihedral angle is considered to have the same tendency for all H_2X_2 molecules. However, results of our previous work [5] showed different dependences for the other molecules, H_2Se_2, H_2S_2, and H_2O_2. Both the total chirality and the parity-violating energy of H_2Te_2 have the same dependence on ϕ, while the other molecules showed different patterns. We speculated that our computations are not sufficiently accurate for the description of the total chirality even if our computation is accurate enough to calculate the parity-violating energy. Therefore, we investigate the total chirality of H_2X_2 with large basis sets in this work. The dependence of the total chirality on the dihedral angle is shown in Fig. 3, for the study of the relation between $M_{\rm PV}^{X}$ and the total chirality. Due to the limitation of computational resources, some computations of H_2Se_2 and H_2Te_2 with the QZ basis set are skipped as in Fig. 2. Nonzero total chirality originates in spin-orbit interaction, since the total chirality is zero if we use a Hamiltonian without spin-orbit interaction [32]. This is consistent with the considera-



H_2O_2 H_2S_2

H_2Se_2 H_2Te_2

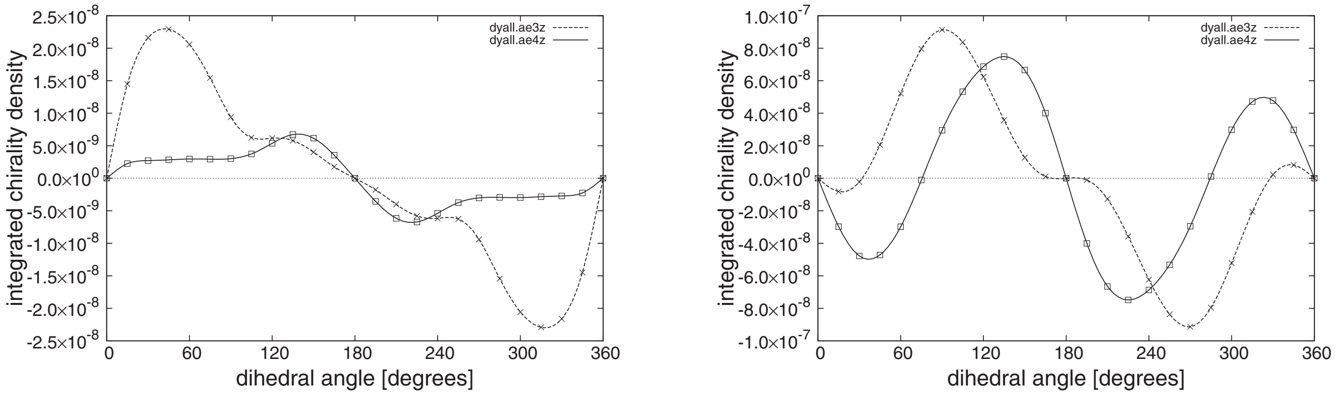
FIG. 2. Value of $M_{\rm PV}^X$ of H_2X_2 as a function of the dihedral angle ϕ. Open square (triangle) is the result by computing with the dyall.ae4z (dyall.ae3z) basis set. Solid (dashed) line is interpolation curve of data with the dyall.ae4z (dyall.ae3z) basis set.

tion of the parity-violating energy based on perturbation in nonrelativistic quantum theory [6]. Our result of H_2Te_2 in Fig. 3 is consistent with our previous result [5] and the result by another group [4]. The result of H_2Se_2 shows the same pattern of curve as the parity-violating energy of H_2Se_2 and the total chirality of H_2Te_2. For the result of H_2S_2, the result with the TZ basis set has a different tendency, while the result with the QZ basis set shows the agreement with the parity-violating energy. Hence our speculation of the shortage of computational accuracy in our previous work is correct. From Figs. 2 and 3, it is confirmed that the total chirality and the parity-violating energy of H_2X_2 have the same dependence on the dihedral angle. This is because the structure of molecules determines the internal distribution of chirality density. In addition, we find that the total chirality is larger for a heavier X atom due to large spin-orbit interaction. In Fig. 3, the result of H_2O_2 has a different pattern from the parity-violating energy of this molecule, even with the QZ basis set. It is speculated that our computation is still not accurate enough. In order to know the correct dependence, better basis set and/or post Hartree-Fock computation is required. For the computation of the total chirality of H_2X_2, lighter elements require more accurate computations.

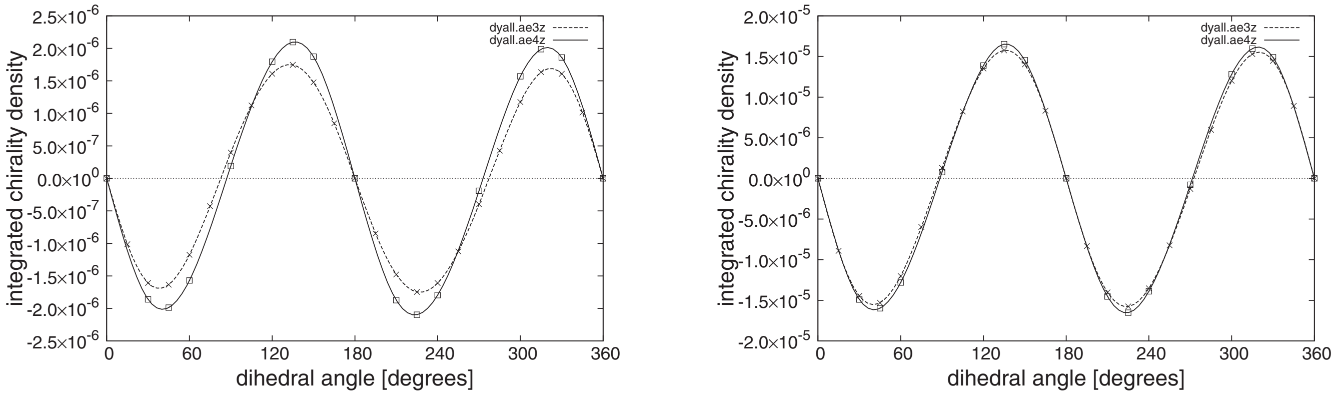
In order to know how this total chirality is generated by spin-orbit interaction, contribution from each orbital to the total chirality is studied. For this study, we take H_2Te_2 with $\phi = 45^\circ$ as an example. Since results of the TZ and QZ basis sets are almost the same, we choose the TZ basis set due to its low cost of computations. In Table II, the orbital energy, the contribution to the chirality density at the position of a Te nucleus, $\langle\gamma_5(\vec{r}_{\rm Te})\rangle_i$, and the contribution to the total chirality, $\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$, as well as the total chirality, $\sum_i\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$, are shown for one of Kramers pair. Both electrons forming Kramers pair have the same value of chirality density. Here $\langle\gamma_5(\vec{r})\rangle_i$ is given as the contribution from the ith orbital to $\langle\gamma_5(\vec{r})\rangle$,

$$\langle\gamma_5(\vec{r})\rangle_i \equiv \langle\Psi|\hat{\psi}_i^\dagger(\vec{r})\gamma_5\hat{\psi}_i(\vec{r})|\Psi\rangle. \qquad (12)$$

The total chirality at $\phi = 45^\circ$ is -1.530×10^{-5}, which is the same as the sum of all contributions from orbitals. The four highest occupied molecular orbitals (HOMOs) and some other molecular orbitals have surprisingly larger contribution to the total chirality than even the total chirality itself. Therefore, the small total chirality of H_2Te_2 is derived as the cancellation between large contributions from HOMOs. Actually, the sum of the contributions from 47th to 53rd orbitals is -1.492×10^{-5}, which includes the contributions from Kramers partners. These orbitals are mainly composed of s orbital of H atoms and s and p orbitals of Te atoms, and distributions



H_2O_2 H_2S_2



H_2Se_2 H_2Te_2

FIG. 3. Total chirality of H_2X_2 as a function of dihedral angle ϕ. Open square (triangle) is the result by computing with the dyall.ae4z (dyall.ae3z) basis set. Solid (dashed) line is interpolation curve of data with the dyall.ae4z (dyall.ae3z) basis set.

of these orbitals spread over the whole molecule. Since such a spreading orbital has largely parity-violating structure only in a single orbital distribution, these parity-violating structure orbitals have large contribution to the total chirality and the parity-violating energy. We have confirmed that an orbital spreading the whole molecule has the large contribution to total chirality for alanine, too [33]. The 47th and 48th orbitals are mainly s orbital of Te atoms and the contribution from other atomic orbitals to these molecular orbitals are smaller than 49th–53rd orbitals. This results in smaller values of contributions to the total chirality than those from 49th to 53rd orbitals. The 49th and 50th orbitals are mainly s orbital of H atoms and p_z orbital of Te atoms, which are responsible for Te-H covalent bonding. The 51st–53rd orbitals are mainly p orbital of Te atoms. Orbitals with lower energy than these orbitals almost consists of only atomic orbitals of Te atoms and contribution from s orbital of H atoms to molecular orbital is less than 10^{-4}, except for the 37th–46th orbitals. The 37th–46th orbitals are mainly d orbital of Te atoms and contributions from s orbital of H atoms to molecular orbitals is about 10^{-4}. These orbitals have larger contributions to total chirality and, however, the sum of them is -4.927×10^{-7}, which is much smaller than that of the 47th–53rd orbitals.

In addition, the chirality density at the position of a Te nucleus, $M_{\mathrm{PV}}^{\mathrm{Te}}$, has also similar property. Particularly, HOMO-1 and HOMO-2 have larger contribution to $M_{\mathrm{PV}}^{\mathrm{Te}}$ than the sum of all contributions. Compared to the total chirality, only two orbitals are larger than the sum of all contributions and the cancellation is not stronger.

Since the contribution from HOMO is larger than the total chirality of H_2Te_2, an excited or ionized state is speculated to have much larger total chirality. We consider that the cancellation may be broken in these states and we study the doubly charged state of H_2Te_2. This state is easier to handle than a singly ionized state or excited state, since singly ionized states or excited states require post-Hartree-Fock computations in the program package we used. For the computation of $H_2Te_2^{2+}$, the geometry of this molecule is chosen to be the same as that of our computation of H_2Te_2 with $\phi = 45^\circ$. In Table III, the orbital energy, the contribution to the chirality density at the position of a Te nucleus, $\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$, and the contribution to the total chirality, $\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$, of $H_2Te_2^{2+}$ with $\phi = 45^\circ$, as well as the total chirality of this molecule, $\sum_i\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$. The total chirality of $H_2Te_2^{2+}$ is 1.891×10^{-4}. It can be seen that the total chirality is much enhanced and the sign is reversed by ionization. The value of the total chirality of $H_2Te_2^{2+}$ is different from the subtraction of the contribution of the HOMO from the total chirality of H_2Te_2, which is 8.957×10^{-5}. This is because other orbitals are deformed into the lowest-energy configuration when an orbital is removed.

TABLE II. Orbital energy E_i, the chirality density at the position of a Te nucleus $\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$, and the contribution to the total chirality $\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$ of H_2Te_2 with $\phi = 45^\circ$. These values shown are for one of Kramers pair. The value of the sum of all the contributions includes contributions from both Kramers pair.

No.	E_i (a.u.)	$\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$	$\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$	No.	E_i (a.u.)	$\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$	$\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$
1	−1175.918	-3.650×10^{-5}	-1.410×10^{-9}	29	−7.108	-3.910×10^{-4}	3.230×10^{-8}
2	−1175.918	-3.650×10^{-5}	-1.410×10^{-9}	30	−7.107	-3.640×10^{-4}	3.200×10^{-8}
3	−183.854	-5.150×10^{-4}	-1.740×10^{-9}	31	−5.304	1.520×10^{-4}	6.280×10^{-9}
4	−183.854	-5.150×10^{-4}	-1.710×10^{-9}	32	−5.304	1.420×10^{-4}	1.250×10^{-8}
5	−171.755	3.980×10^{-4}	-1.520×10^{-9}	33	−4.934	5.710×10^{-6}	-2.000×10^{-7}
6	−171.755	3.980×10^{-4}	-1.520×10^{-9}	34	−4.934	-1.980×10^{-6}	4.610×10^{-7}
7	−161.626	-2.250×10^{-8}	-4.660×10^{-9}	35	−4.929	-1.810×10^{-5}	-1.050×10^{-6}
8	−161.626	-2.200×10^{-8}	-4.510×10^{-9}	36	−4.929	-2.530×10^{-5}	7.540×10^{-7}
9	−161.626	-1.160×10^{-7}	9.280×10^{-9}	37	−1.992	-9.490×10^{-6}	-4.820×10^{-6}
10	−161.626	-1.160×10^{-7}	9.320×10^{-9}	38	−1.991	1.400×10^{-5}	6.590×10^{-6}
11	−38.117	-3.480×10^{-4}	9.080×10^{-10}	39	−1.982	-2.750×10^{-5}	-1.480×10^{-5}
12	−38.117	-3.460×10^{-4}	1.220×10^{-9}	40	−1.981	2.730×10^{-5}	1.260×10^{-5}
13	−33.102	2.180×10^{-4}	-2.720×10^{-9}	41	−1.936	4.150×10^{-6}	-1.440×10^{-5}
14	−33.102	2.170×10^{-4}	-2.650×10^{-9}	42	−1.934	-4.090×10^{-5}	2.410×10^{-5}
15	−31.162	-1.090×10^{-7}	2.930×10^{-9}	43	−1.927	8.520×10^{-5}	-2.230×10^{-5}
16	−31.162	-1.010×10^{-7}	1.520×10^{-9}	44	−1.926	-5.380×10^{-5}	1.180×10^{-5}
17	−31.160	-8.750×10^{-7}	4.640×10^{-9}	45	−1.923	7.100×10^{-5}	-3.590×10^{-6}
18	−31.160	-8.900×10^{-7}	3.070×10^{-9}	46	−1.922	-7.400×10^{-5}	4.600×10^{-6}
19	−22.422	-2.420×10^{-8}	-8.450×10^{-9}	47	−0.866	-8.140×10^{-4}	5.950×10^{-7}
20	−22.422	-2.400×10^{-8}	-8.930×10^{-9}	48	−0.764	-3.350×10^{-4}	6.300×10^{-7}
21	−22.419	1.620×10^{-8}	7.010×10^{-9}	49	−0.513	-2.860×10^{-3}	-1.060×10^{-6}
22	−22.419	1.120×10^{-8}	1.070×10^{-8}	50	−0.461	-1.490×10^{-2}	2.010×10^{-5}
23	−22.022	-4.210×10^{-10}	9.000×10^{-9}	51	−0.396	9.460×10^{-2}	-1.010×10^{-4}
24	−22.022	-4.720×10^{-9}	8.950×10^{-9}	52	−0.358	-8.950×10^{-2}	1.260×10^{-4}
25	−22.020	5.930×10^{-8}	-3.920×10^{-9}	53	−0.301	1.990×10^{-3}	-5.244×10^{-5}
26	−22.020	5.340×10^{-8}	-4.420×10^{-9}				
27	−22.018	-3.410×10^{-8}	-5.280×10^{-9}				
28	−22.018	-4.370×10^{-8}	-5.560×10^{-9}	All		-2.584×10^{-2}	-1.530×10^{-5}

This can be seen from the comparison between Tables II and III. We have confirmed this enhancement of total chirality by ionization for alanine, serine, and valine, too [33].

For the parity-violating energy, this enhancement is not large. The parity-violating energy is proportional to the sum of all contributions, $\sum_i\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$, and this is not enhanced much as seen from the comparison between Tables II and III. This is because the contribution of $\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$ from HOMO is not larger than the total one and the elimination of HOMO does not break the cancellation much. For another reason, the cancellation of $\langle\gamma_5(\vec{r}_{\mathrm{Te}})\rangle_i$ is weaker than the total chirality, and this ionization does not break the cancellation much. In this work, it has not been concluded whether, for other molecules, parity-violating energy is drastically enhanced or not by ionization or excitation. We consider that this topic is also worth studying further.

VI. SUMMARY

It has been numerically confirmed that chiral molecules have nonzero total electron chirality in their molecule, for H_2X_2 (X = O, S, Se, Te) molecules as a typical sample of chiral molecules. It can be said that molecular chirality generates electron chirality as well as parity-violating energy shift. In this paper, we have proposed that this nonzero electron chirality produces a small imbalance between an enantiomeric pair, which may be the origin of the homochirality in nature. Nonzero total chirality of electrons induces different rate of weak interaction between an enantiomeric pair, since the left-handed electron has a larger reaction rate of weak interaction than the right-handed electron. Due to this difference of the reaction rate of weak interaction, one of an enantiomeric pair is more destroyed than the other of the pair. It is shown that the value of the total chirality of H_2X_2 molecules is dependent on the dihedral angle of H_2X_2 molecules, as well as the parity-violating energy shift. In this paper, we have found that the total chirality of a chiral molecule is the result of the cancellation between large contributions from HOMOs. and the value of the total chirality of a chiral molecule is drastically enhanced if the molecule is ionized or excited, since the contribution from the HOMO is larger than the total chirality and ionization or excitation breaks the cancellation.

TABLE III. Orbital energy E_i, the chirality density at the position of a Te nucleus $\langle\gamma_5(\vec{r}_{\rm Te})\rangle_i$, and the contribution to the total chirality $\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$ of H_2Te_2 with $\phi = 45^\circ$. These values shown are for one of Kramers pair. The value of the sum of all the contributions includes contributions from both Kramers pair.

No.	E_i (a.u.)	$\langle\gamma_5(\vec{r}_{\rm Te})\rangle_i$	$\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$	No.	E_i (a.u.)	$\langle\gamma_5(\vec{r}_{\rm Te})\rangle_i$	$\int\langle\gamma_5(\vec{r})\rangle_i d^3\vec{r}$
1	−1176.413	-4.478×10^{-5}	-1.981×10^{-9}	29	−7.598	-6.423×10^{-4}	1.008×10^{-7}
2	−1176.413	-4.478×10^{-5}	-1.980×10^{-9}	30	−7.598	-7.026×10^{-4}	1.160×10^{-7}
3	−184.348	-6.366×10^{-4}	-1.872×10^{-9}	31	−5.795	4.043×10^{-5}	1.497×10^{-8}
4	−184.348	-6.368×10^{-4}	-1.863×10^{-9}	32	−5.795	1.052×10^{-4}	-2.512×10^{-8}
5	−172.249	5.573×10^{-4}	-3.748×10^{-9}	33	−5.422	1.991×10^{-4}	-3.216×10^{-8}
6	−172.249	5.577×10^{-4}	-3.753×10^{-9}	34	−5.422	1.766×10^{-4}	-2.854×10^{-7}
7	−162.120	9.167×10^{-7}	-1.851×10^{-8}	35	−5.420	-1.009×10^{-5}	6.150×10^{-7}
8	−162.120	9.167×10^{-7}	-1.852×10^{-8}	36	−5.420	7.520×10^{-6}	3.281×10^{-7}
9	−162.119	-1.593×10^{-8}	1.282×10^{-8}	37	−2.480	1.673×10^{-5}	-8.947×10^{-6}
10	−162.119	-1.612×10^{-8}	1.279×10^{-8}	38	−2.479	-1.293×10^{-5}	9.098×10^{-6}
11	−38.610	-5.102×10^{-4}	4.388×10^{-9}	39	−2.474	-3.961×10^{-5}	-5.838×10^{-6}
12	−38.610	-5.119×10^{-4}	4.828×10^{-9}	40	−2.474	1.010×10^{-5}	5.882×10^{-6}
13	−33.595	3.435×10^{-4}	-9.589×10^{-9}	41	−2.421	3.788×10^{-6}	-7.559×10^{-6}
14	−33.595	3.435×10^{-4}	-9.645×10^{-9}	42	−2.420	3.754×10^{-5}	1.130×10^{-5}
15	−31.653	1.399×10^{-5}	1.776×10^{-8}	43	−2.418	5.826×10^{-6}	-2.004×10^{-6}
16	−31.653	1.401×10^{-5}	1.895×10^{-8}	44	−2.417	-2.508×10^{-5}	-1.217×10^{-6}
17	−31.653	-1.088×10^{-5}	-4.450×10^{-9}	45	−2.415	3.294×10^{-5}	-6.027×10^{-6}
18	−31.653	-1.089×10^{-5}	-3.430×10^{-9}	46	−2.414	-2.202×10^{-5}	6.300×10^{-6}
19	−22.914	2.817×10^{-8}	1.557×10^{-8}	47	−1.319	1.256×10^{-2}	-1.401×10^{-5}
20	−22.914	2.839×10^{-8}	5.829×10^{-8}	48	−1.206	-1.057×10^{-2}	1.144×10^{-5}
21	−22.912	2.326×10^{-8}	-6.238×10^{-8}	49	−0.948	-7.531×10^{-3}	1.588×10^{-6}
22	−22.912	2.851×10^{-8}	-5.838×10^{-8}	50	−0.889	-6.334×10^{-2}	7.350×10^{-5}
23	−22.514	6.196×10^{-8}	-2.329×10^{-8}	51	−0.840	1.213×10^{-2}	-1.238×10^{-4}
24	−22.514	7.887×10^{-8}	-2.259×10^{-8}	52	−0.761	4.373×10^{-2}	1.441×10^{-4}
25	−22.512	-2.195×10^{-7}	9.048×10^{-9}				
26	−22.512	-2.140×10^{-7}	8.820×10^{-9}				
27	−22.511	1.143×10^{-7}	3.169×10^{-8}				
28	−22.511	1.062×10^{-7}	3.159×10^{-8}	All		-2.884×10^{-2}	1.891×10^{-4}

This property is also seen in the parity-violating energy shift though the enhancement is smaller than the total chirality. The smallness of the enhancement is speculated that the contribution from the HOMO is large but not larger than the total one and the cancellation degree is weaker than the total chirality.

In our future work, we should study many things in order to clarify whether our mechanism can produce enough chiral imbalance or not, quantitatively. First, we confirm numerically that the total chirality of amino acid is nonzero. We have shown that some amino acid molecules have nonzero total chirality as a preliminary result [33]. Second, we should study the reaction of electrons in amino acids with astronomical particles in space. We will study which scale of energy transfer induces what reactions to molecules of amino acids. In addition, the flux and spectrum of astronomical particles should be estimated. For high energy, where the energies of cosmic rays and neutrinos are larger than 0.1 GeV and 1 MeV, the flux has been observed experimentally, while for low energy, eV scale, we will evaluate the flux of these particles by using a galactic propagation model of cosmic rays and so on.

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