

Theoretical Analysis of Parity-Violating Energy Differences between the Enantiomers of Chiral Molecules

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Fully relativistic four-component electronic structure *ab initio* calculations including neutral current corrections are reported for a number of small chiral molecules that are of interest in the experimental search for differences in the vibrational spectra of the two enantiomers of handed molecules. The largest vibrational energy differences, of the order 0.2 Hz, are found in chiral methane derivatives which include an iodine substituent. The vibrational energy differences in CHBrClF are 7 and 2 mHz for the carbon-chlorine and carbon-fluorine stretching modes, respectively, which are 3 to 4 orders of magnitude smaller than the precision reported in recent experiments.

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Some of the most fascinating and subtle consequences of electroweak, parity-violating (*P*-odd) processes in nature are to be found in the low-energy properties of atoms and molecules. It was suggested in the early 1970s that the exchange of virtual Z^0 bosons between the electrons and nuclear particles described by the standard model of electroweak theory would give rise to observable *P*-odd effects in atomic and molecular systems. These effects include optical rotation of plane polarized light in monatomic gases [1], and the observation of polarization effects involving parity-violating optical transitions, both of which are strictly forbidden within electromagnetic theory. In combination with highly accurate theoretical calculations, these exquisite and precise experiments place important constraints on the parameters of the standard model at the low momentum transfer limit of the interaction [1].

While the phenomenology of *P*-odd effects in atoms is now well established by experiment, there exist no unambiguous observations of effects which are attributable to electronuclear weak interactions in molecular systems. A number of different experiments have been proposed in the search for *P*-odd effects in molecular physics, and reviews of the activity in this area have been presented in [2–4]. Rein [5] and Letokhov [6] suggested that the *P*-odd character of the electroweak interaction may give rise to observable effects in chiral molecular systems related by parity inversion, breaking the strict degeneracy of the *R* and *S* enantiomers of such systems demanded by the parity-conserving theory of quantum electrodynamics. The class of experiments in which there is the greatest current experimental activity involves the vibrational spectroscopy of separate enantiomers. The recent attempt to measure *P*-odd effects in CHBrClF [7] represents a new generation of experiments whose accuracy approaches the theoretical predictions regarding the order of magnitude of the effect [8,9]. Here we report theoretical *ab initio* calculations of

the parity-violating energy differences in CHBrClF and related chiral molecules. An assessment of the accuracy required to detect these effects and suggestions for suitable experimental candidates are presented as our conclusions of this study.

The nuclear spin-independent electronuclear parity-violating operator which breaks the degeneracy of the *R* and *S* enantiomers of a chiral molecule is

$$H_p = \frac{G_F}{2\sqrt{2}} \sum_{i,n} Q_{w,n} \gamma_i^5 \varrho_n(\mathbf{r}_i), \quad (1)$$

where $G_F = 1.16637 \times 10^{-11} \text{ MeV}^{-2} = 2.22255 \times 10^{-14} \text{ a.u.}$ is the Fermi electroweak coupling constant, γ_5 is the 4×4 pseudoscalar chirality operator, and the summation is over the electrons, i , and nuclei, n . The normalized nucleon density and the weak charge of nucleus n are given by $\varrho_n(\mathbf{r})$ and $Q_{w,n} = -N_n + Z_n(1 - 4 \sin^2 \theta_w)$, respectively, where N_n is the number of neutrons and Z_n the number of protons in the nucleus. In this study we have adopted $\sin^2 \theta_w = 0.2319$ for the Weinberg mixing angle. The effects of the *P*-odd nuclear spin-dependent interactions were neglected as they are strongly suppressed in closed shell atoms and molecules [9].

The parity-violating energy shifts have been calculated as a function of the nuclear geometry, G , within the fully relativistic four-component independent-particle Dirac-Hartree-Fock (DHF) model (Refs. [9–11]) as the matrix elements,

$$E_{PV}^G = \langle \Psi_{\text{DHF}}^G | H_p | \Psi_{\text{DHF}}^G \rangle = \frac{G_F}{2\sqrt{2}} \sum_n Q_{w,n} M_{PV}^{G,n}, \quad (2)$$

where

$$M_{PV}^{G,n} = \sum_i \langle \psi_i^G | \gamma_i^5 \varrho_n(\mathbf{r}_i) | \psi_i^G \rangle. \quad (3)$$

If we denote the geometries of a chiral molecule and its

mirror image by G and \bar{G} , respectively, the electronic energy difference between them is $\Delta E_{\text{PV}}^G = E_{\text{PV}}^G - E_{\text{PV}}^{\bar{G}} = 2E_{\text{PV}}^G$, since H_p is odd with respect to parity inversion. The effect of the geometry dependence of E_{PV}^G is to modify the potential energy surface (PES) of the R and S enantiomers of a chiral molecule, leading to small changes in their vibrational frequencies.

The wave functions and parity-violating energy differences were calculated with the DIRAC program package [12] as described previously [9–11] employing cc-pVDZ + np basis sets for hydrogen and first and second row elements [13], and double zeta quality basis sets [14] for the heavier elements. All halogen basis sets were augmented with diffuse functions [14–16], and all basis sets were used in uncontracted form. The geometry optimizations of the chiral molecules were performed with GAUSSIAN98 [17] at the MBPT2 level applying small core Stuttgart scalar relativistic pseudopotentials and their corresponding basis sets for the period 4 to 6 elements and the cc-pVDZ [15,18] basis set for the lighter elements.

The value of E_{PV}^G in a chiral molecule scales higher than Z^5 , where Z is the largest constituent nuclear charge, and is enhanced by spin-orbit coupling involving two or more heavy centers [8,9]. Therefore, in addition to our studies of the halomethanes presented in Table I, we present an investigation of a series of five-center substituted methane derivatives and their analogs in which the carbon nucleus has been replaced by the group 14 elements from periods 3 to 6 (Table II). It was recently shown that the higher than Z^5 scaling gives reasonable estimates for all of the molecules in the series H_2X_2 ($X = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{and Po}$) [9]. The results of Tables I and II show that this is not the case for the five-atomic chiral molecules of the current study. All of the compounds of the form XHBrCIF ($X = \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$) have very small parity-violating energy differences compared to what one would expect from the Z scaling law applied to CHBrCIF . The reason appears to be that the parity-violating energy shift is localized mostly at the chlorine and bromine nuclei, and the magnitude of the spin-orbit coupling involving these two atomic centers is reduced as the size of the molecule and the distance between the nuclei are increased.

The vibrational modes of a molecule containing five nuclei may be described using a set of nine normal coordinates, $\{Q_r\}$, with vibrational energy levels given by

$$E(\mathbf{n}) = \sum_{r=1}^9 \left(n_r + \frac{1}{2} \right) \omega_r + \sum_{r=1}^9 \sum_{s=1}^r \left(n_r + \frac{1}{2} \right) \times \left(n_s + \frac{1}{2} \right) x_{rs} + \dots, \quad (4)$$

where $\mathbf{n} = \{n_1, n_2, \dots, n_9\}$, ω_r are the harmonic frequencies and x_{rs} the first anharmonicity constants. The fundamental absorption frequencies, ν_j , are obtained from the transition energies between the ground vibrational state and the state which contains a single quantum in mode j .

Consideration of displacements in a single normal mode with $x_{rs} = 0$ ($r \neq s$) reveals important qualitative behavior as reported previously for diatomics [19]. The geometry dependence of E_{PV}^G may be written as an expansion of the form

$$E_{\text{PV}}^G \approx E_{\text{PV}}^G|_{G_0} + \left. \frac{\partial E_{\text{PV}}^G}{\partial Q_r} \right|_{G_0} Q_r + \frac{1}{2} \left. \frac{\partial^2 E_{\text{PV}}^G}{\partial Q_r^2} \right|_{G_0} Q_r^2 + \dots, \quad (5)$$

where G_0 denotes the equilibrium configuration of a given enantiomer. The first term in this expansion has no observable effect on the vibrational energies, while the second term gives a zero contribution if the normal modes are assumed to be harmonic oscillators, but otherwise yields the leading-order anharmonicity corrections. In the harmonic normal mode approximation, the leading-order correction to the vibrational energy of mode $|n_r\rangle$ due to H_p is proportional to the vibrational average, $\langle n_r | Q_r^2 | n_r \rangle$, and the correction to the fundamental transition energy induced by H_p , $h\nu_{\text{PV},r}^H$, is given by

$$h\nu_{\text{PV},r}^H \approx \left. \frac{\partial^2 E_{\text{PV}}^G}{\partial Q_r^2} \right|_{G_0} \frac{\hbar}{2\mu_r \omega_r}, \quad (6)$$

where μ_r is the effective reduced mass. Note that the quantities which determine the magnitudes of the observable shifts in the vibrational energy levels are the derivatives of E_{PV}^G with respect to Q_r , rather than the value of E_{PV}^G itself.

A calculation of the full nine dimensional PES including the P -odd corrections up to energies corresponding to excitations of a few vibrational quanta would be necessary in order to accurately calculate the P -odd differences between the R and S enantiomer spectra. This is beyond what is possible with current codes and computational resources. Consequently, a local mode treatment has been applied in this study, based on a vibrational analysis

TABLE I. Calculated parity-violating matrix elements, M_{PV}^n , and total parity-violating energy shifts, E_{PV} , for the R form of the five chiral halomethanes, CHBrCIF , CHClFI , CHBrFI , CHBrClI , and CBrClFI .

Molecule	M_{PV}^{C} (a.u.)	M_{PV}^{F} (a.u.)	$M_{\text{PV}}^{\text{Cl}}$ (a.u.)	$M_{\text{PV}}^{\text{Br}}$ (a.u.)	M_{PV}^{I} (a.u.)	E_{PV} (a.u.)
CHBrCIF	-1.266×10^{-6}	-1.125×10^{-5}	2.592×10^{-5}	-2.410×10^{-5}	...	5.319×10^{-18}
CHClFI	-4.158×10^{-6}	-3.529×10^{-5}	7.801×10^{-5}	...	-1.165×10^{-4}	5.671×10^{-17}
CHBrFI	-2.386×10^{-6}	-2.651×10^{-5}	...	4.064×10^{-4}	-5.251×10^{-4}	1.591×10^{-16}
CHBrClI	9.488×10^{-7}	...	-6.156×10^{-5}	3.952×10^{-4}	-4.007×10^{-4}	1.002×10^{-16}
CBrClFI	2.270×10^{-7}	2.641×10^{-6}	-7.714×10^{-7}	-3.505×10^{-5}	5.620×10^{-5}	-1.967×10^{-17}

TABLE II. Calculated parity-violating matrix elements, M_{PV}^n , and total parity-violating energy shifts, E_{PV} , for the R form of SiHBrCIF, GeHBrCIF, SnHBrCIF, and PbHBrCIF. X denotes the group 14 element from period 3 to 6 at the chiral center.

Molecule	M_{PV}^{F} (a.u.)	$M_{\text{PV}}^{\text{Cl}}$ (a.u.)	$M_{\text{PV}}^{\text{Br}}$ (a.u.)	M_{PV}^{X} (a.u.)	E_{PV} (a.u.)
SiHBrCIF	-1.496×10^{-6}	3.059×10^{-6}	1.664×10^{-6}	-1.937×10^{-6}	-6.379×10^{-19}
GeHBrCIF	-2.915×10^{-6}	7.789×10^{-6}	5.660×10^{-6}	-1.735×10^{-5}	2.753×10^{-18}
SnHBrCIF	-1.882×10^{-6}	2.961×10^{-6}	1.716×10^{-5}	-3.648×10^{-5}	1.318×10^{-17}
PbHBrCIF	-2.129×10^{-6}	-6.848×10^{-6}	7.851×10^{-5}	-1.937×10^{-4}	1.582×10^{-16}

performed at the scalar relativistic self-consistent field (SCF) level (Table III). The energy shifts induced by H_p in the transition energies corresponding to the normal modes, Q_r , are tabulated in Table III for the harmonic oscillator approximation, $\nu_{\text{PV},r}^H$, and for the more accurate Morse oscillator approximation, $\nu_{\text{PV},r}^M$. We investigated two distinct approximations in order to calculate the parity-violating shifts of the vibrational fundamental transitions, $\nu_{\text{PV},r}$. (i) The harmonic approximation in which cubic and higher-force constants are assumed to be zero and all normal modes are decoupled ($x_{rs} = 0$ for all r, s). The vibrational wave function consists of nine independently vibrating harmonic oscillators. (ii) The local mode anharmonic Morse approximation, involving a local mode treatment of nine independent anharmonic Morse oscillators, with $x_{rs} = 0$ for $r \neq s$. The Morse oscillators provide excellent approximations to the carbon-halogen stretching modes for excitations up to a few vibrational quanta, and were fitted to the calculated total energies at 11 points along the Q_r coordinate on the PES. The diagonal anharmonicity constants x_{rr} of the Morse potentials are given in Table III.

The dependence of E_{PV}^G on variations in the normal coordinates was determined by fitting a high-order polynomial approximation to the calculated values at 11 points along Q_r centered at the equilibrium geometry. The vibra-

tional average of this polynomial in the ground and first excited vibrational state for each carbon-halogen stretching mode was determined in the harmonic and Morse approximations by direct numerical integration. In all cases studied here, the anharmonicity corrections to $\nu_{\text{PV},r}$ are large, and determined mainly by the nonvanishing matrix elements of $\langle n_r | Q_r | n_r \rangle$ in the initial and final Morse oscillator states, and the comparable magnitudes of $\partial E_{\text{PV}} / \partial Q_r$ and $\partial^2 E_{\text{PV}} / \partial Q_r^2$ in the neighborhood of $G = G_0$. While the model defined by Eq. (6) provides adequate quantitative estimates and demonstrates that the anharmonicity corrections may increase or reduce the P -odd shifts depending on the sign of the first and second derivatives, the fully numerical treatments give more accurate results for the vibrational energy shifts in these complex polyatomic systems.

The result of the most immediate experimental importance concerns the carbon-fluorine stretching frequency in CHBrCIF. Our results indicate that $\nu_{\text{PV},r}$ for this mode is 3 to 4 orders of magnitude smaller than that accessible to spectroscopic methods reported recently [7]. The largest values of $\nu_{\text{PV},r}$ are found in the heaviest of the substituted methane derivatives, but these also require an increase in experimental sensitivity in order to be detected.

The conclusions of the current study are as follows. (i) All our theoretical estimates for CHBrCIF are below

TABLE III. Calculated carbon-halogen SCF stretching frequencies, ω_r , and the frequencies scaled according to [20] in parentheses. The parameters ω_r and the diagonal elements of x_{rs} are defined by Eq. (4), and $\partial E_{\text{PV}}^G / \partial Q_r$ and $\partial^2 E_{\text{PV}}^G / \partial Q_r^2$ are defined by Eq. (5), and evaluated at the equilibrium geometry, G_0 . The parity-violating energy shifts in the fundamental vibrational transition are given in mHz for the harmonic and Morse oscillator approximations, $\nu_{\text{PV},r}^H$ and $\nu_{\text{PV},r}^M$, respectively (1 a.u. = 6.5797×10^{18} mHz = 2.1947×10^5 cm $^{-1}$). All parity-violating energy shifts are given for the R form of the molecule; a negative sign indicating that the R form fundamental is at a lower frequency than that of the S form. The magnitude of the frequency difference between the R and S forms is $2|\nu_{\text{PV},r}|$.

Mode	ω_r (cm $^{-1}$)	x_{rr} (cm $^{-1}$)	$\partial E_{\text{PV}}^G / \partial Q_r$ (a.u.)	$\partial^2 E_{\text{PV}}^G / \partial Q_r^2$ (a.u.)	$\nu_{\text{PV},r}^H$ (mHz)	$\nu_{\text{PV},r}^M$ (mHz)
CHBrCIF:						
C-F	1200 (1071)	9.0	-1.66×10^{-17}	2.91×10^{-17}	0.9	-1.0
C-Cl	864 (771)	1.8	-1.26×10^{-17}	-3.80×10^{-17}	-2.4	-3.5
C-Br	716 (639)	1.9	0.44×10^{-17}	0.21×10^{-17}	0.2	0.5
CHBrFI:						
C-F	1178 (1052)	9.5	-2.84×10^{-16}	5.17×10^{-16}	15.7	-17.9
C-Br	761 (679)	0.6	-6.00×10^{-16}	-7.08×10^{-16}	-55.3	-90.0
C-I	612 (546)	0.2	0.74×10^{-16}	0.004×10^{-16}	0.2	3.9
CHBrClI:						
C-Cl	819 (731)	4.0	-2.24×10^{-16}	1.48×10^{-16}	7.6	-19.5
C-Br	719 (642)	0.3	-1.32×10^{-16}	-4.65×10^{-16}	-33.6	-39.5
C-I	558 (498)	0.1	0.14×10^{-16}	-0.16×10^{-16}	-1.6	-0.9

10 mHz and appear to be inaccessible to experimental detection at the current level of sensitivity. (ii) The chiral molecules with a heavier group 14 element replacing carbon at the chiral center in CHBrCIF do not exhibit significantly larger parity-violating energy shifts. The heavier molecules of this type are expected to be chemically labile or unstable and are not good candidates for experiment. (iii) The most promising experimental candidates are the chiral iodomethanes, with the exception of CBrCIF. We expect our values for E_{PV} to be accurate to within 50% at the chosen geometry, but the accuracy of the parity-violating energy differences in the vibrational spectra are less certain. The current study represents what we believe to be at the limit of what is theoretically possible using current algorithms and computational resources. The extreme smallness of the energy differences, however, means that the actual values may be sensitive to dynamic effects, vibrational and rotational couplings neglected in our model, and the details of the nuclear structure. On the basis of our calculations, however, we conclude that only an experimental investigation with a sensitivity of 0.1 Hz or less will be able to detect these vibrational energy differences.

Conclusions similar to ours have been reached by Quack and Stohner [21] for the case of CHBrCIF.

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