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Understanding parity violation in molecular systems

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Parity-violation energy (E_{PV}) due to weak nuclear interactions between nucleons and electrons in chiral molecular systems provides a fundamental tool to verify our understanding of electronic behavior in complex systems. We used both a relativistic and a nonrelativistic approach to study a number of simple molecules and analyze the corresponding E_{PV} in terms of intuitive electrodynamic concepts. We developed a qualitative model to predict the sign of E_{PV} and its behavior against selected geometric distortions. Our model provides a valuable tool to screen large sets of molecules and select interesting candidates for more expensive investigations.

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I. INTRODUCTION

Parity violation energy (E_{PV}) induced by weak nuclear coupling in a number of molecular systems have been studied in recent years (Ref. [1] and references therein and Refs. [2–19]) and references therein due to the possible influence on biochirality [1–7] and to the desire of detecting experimental evidence of parity violation in a chemical environment [8–12]. In all the molecules examined, however, the estimated E_{PV} is several orders of magnitude smaller than current experimental resolution [11,13]. The estimates available for bioorganic molecules are too small to induce significant values of enantiomeric excess under plausible conditions for naturally occurring prebiotic material.

Due mainly to the computational cost, most of the studies focused on restricted sets of small molecules near equilibrium geometry. To our knowledge, there have been no reports of E_{PV} computations for typical catalytic centers involving transition metals and only one report regarding transition state geometries [14]. This is partly because it is not practical to screen many large compounds or reaction pathways. It is thus important to develop an intuitive understanding of which systems might exhibit high values of E_{PV}. To this end, we studied a few simple molecules and developed a qualitative model to predict and understand the behavior of E_{PV} against geometric distortions and group substitutions.

There have been two main approaches to E_{PV} computations in molecular systems. The first and more rigorous approach is based on relativistic (four components) wave functions [17,20,21] whereas the second and more approximate approach uses nonrelativistic (one-component) wave functions [22,23]. Both relativistic and nonrelativistic E_{PV} estimates were published for molecules containing atoms as heavy as bromine and pairs of atoms as heavy as sulfur. In these cases, the two approaches typically yield results of the same sign and magnitude, indicating that even the nonrelativistic treatment contains the essential physical terms responsible for E_{PV}. While we expect the relativistic treatment to be numerically more accurate, the nonrelativistic approach offers the possibility of decomposing E_{PV} into terms due to pairs of atoms and is generally easier to interpret. We hence used the relativistic approach to provide reliable estimates of E_{PV} and the nonrelativistic approach to guide our interpretation of the computed values.

In Sec. II we summarize the methods used for the computations and we focus on the interpretation of various terms. In Sec. III we study a class of molecules for which the computed E_{PV} is particularly easy to interpret and we introduce our model. Finally, in Sec. IV we generalize our model to describe contributions to E_{PV} from individual chiral centers and hence to generic chiral molecules.

II. GENERAL METHOD

A. Relativistic approach

The parity-violation energy is, to first order, the expectation value of the parity-violation operator H_p [17,20],

$$E_{\mathrm{PV}}=\langle\Psi|H_p|\Psi\rangle. \tag{1}$$

Operator H_p describes the weak neutral interaction of the electrons with the nucleons and has the form

$$H_p=\frac{G_F}{2\sqrt{2}}\sum_{i,N} Q_{W,N}\gamma_i^5\rho_N(\mathbf{r}_i), \tag{2}$$

where the sum is over all electrons i and nuclei N. G_F is the Fermi electroweak coupling constant ($2.222\,55\times10^{-14}$ a.u.), γ^5 is the Dirac-γ^5 matrix which is proportional to the chirality operator, $\rho_N(\mathbf{r}_i)$ is the normalized nucleon density, and $Q_{W,N}$ is the weak charge of nucleus N, which is positive for all nuclei except hydrogen and is roughly proportional to the number of neutrons. H_p is the nuclear-spin free operator. Although there are additional parity-odd terms, their contribution is less important and they are usually neglected in molecular computations.

B. Nonrelativistic approach

From a nonrelativistic wave function, E_{PV} is estimated as the second-order perturbative energy due to the coupling of

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spin-orbit (SO) and parity-violation (PV) Hamiltonians [24]. These are given by the expressions[1]

$$H_{\mathrm{SO}}=\frac{\beta^2}{\hbar}\sum_{i,N} Z_N|\mathbf{r}_i-\mathbf{R}_N|^{-3}\boldsymbol{\sigma}_i\cdot(\mathbf{r}_i-\mathbf{R}_N)\times\mathbf{p}_i\,, \qquad (3)$$

$$H_{\mathrm{PV}}=-\frac{G_F}{4\sqrt{2}m_e c}\sum_{i,N} Q_{W,N}\{\mathbf{p}_i\cdot\boldsymbol{\sigma}_i\,,\delta(\mathbf{r}_i-\mathbf{R}_N)\}_+\,, \qquad (4)$$

where β indicates Bohr magneton, Z_N nuclear charge, m_e electron mass, c the speed of light, $\mathbf{r}$ and $\mathbf{p}$ electronic position and momentum, $\boldsymbol{\sigma}$ the vector of Pauli spin matrices, and $\mathbf{R}_N$ is a nuclear coordinate. The explicit form for E_{PV} is

$$E_{\mathrm{PV}}=-\frac{2}{\hbar}\sum_{j\neq a}\frac{\mathrm{Re}(\langle a|H_{\mathrm{PV}}|j\rangle\langle j|H_{\mathrm{SO}}|a\rangle)}{\omega_{ja}}, \qquad (5)$$

where a and j refer to ground and excited state wave function, respectively, and $\hbar\omega_{ja}$ is an energy difference.

1. Interpretation

Both the relativistic and nonrelativistic parity-violation hamiltonians change sign under an improper rotation. In particular, they change sign under (three-dimensional) spatial inversion and under reflection in a mirror plane. E_{PV} is thus nonzero only for chiral systems and it has opposite sign for corresponding enantiomers.

E_{PV} depends on the weak charge $Q_{W,N}$ of the nuclei and hence on the atomic number Z_N. This dependence has been estimated theoretically for atoms as Z_N^3 [24] and for molecules as Z_N^5 [23]. The computed scaling appears to be between these two extremes, depending on the system examined. See Ref. [1] and references therein for a more detailed discussion of scaling. For our discussion it is sufficient to note that heavy nuclei contribute more to E_{PV} than light ones and that hydrogen gives negligible direct contribution.

For each electron and each nucleus, the SO term lowers the total energy when the angular momentum of the electron about the nucleus is antiparallel to the electronic spin. Given a spin orientation $\boldsymbol{\sigma}$, the electron tends to rotate around each nucleus with angular momentum $\boldsymbol{L}$ aligned opposite to $\boldsymbol{\sigma}$ and hence to have canonical momentum $\boldsymbol{p}$ such that $(\mathbf{r}-\mathbf{R})\times\boldsymbol{p}$ has direction antiparallel to $\boldsymbol{\sigma}$. Notice that SO stabilization is maximum when it is possible for the angular momentum to align antiparallel to the spin. When the electron is constrained to move on a fixed path, however, the direction of $\boldsymbol{L}$ may form an angle with $\boldsymbol{\sigma}$. In this case $\boldsymbol{p}$ and $\boldsymbol{\sigma}$ may be not orthogonal and it is possible to couple the SO induced motion with the PV Hamiltonian.

The nonrelativistic PV Hamiltonian gives a negative contribution to the energy when the canonical momentum $\boldsymbol{p}$ of an electron on a nucleus is aligned with the electronic spin.

By estimating the direction of the SO induced momentum for each possible spin orientation it is possible to predict, often without any computation, the sign of E_{PV} for a given molecule. Considering how the induced momentum changes with the geometry we can estimate which configurations or which molecules are likely to have higher values of E_{PV}.

2. Computational details

We report the computational details necessary to reproduce our results.

Geometries were optimized using GAUSSIAN 94 [26] at the MP2 level with Dunning's cc-pVDZ correlation consistent basis set [27,28] on the lighter atoms (aug-cc-pVDZ on halogens and O^-). For atoms heavier than Ar we used Stuttgard [28,29] or Los Alamos [28,30] effective core potentials and corresponding double-ζ quality basis set. In order to simplify the treatment, geometries for the molecules in class A described in Sec. III were optimized imposing local symmetry on each fragment. For instance, in the fragment CH_3 all C-H bonds were constrained to be equivalent. Unless otherwise specified, the bond distances and angles were then assumed to be independent of the dihedral angle and equal to the optimal values. For instance the O-O-H angle in H_2O_2 was held constant at 98.832° even though this value is optimal only for a dihedral angle of 118.382°.

Relativistic E_{PV} were computed using the program DIRAC [31] with Dirac-Coulomb Hamiltonian and Gaussian nuclear-charge distribution. We verified on the molecules H_2O_2 and BiHFBr that neglecting two-electron integrals between small component functions alters the computed E_{PV} by less than 0.3%. We thus chose not to include these integrals for the results reported in this paper. The large component basis set was uncontracted cc-pVDZ (aug-cc-pVDZ on halogens and O^-) [27,28] for the lighter elements and the corresponding uncontracted Dyall basis set [32] for the heavier ones. To this basis we added one set of tight p functions obtained as follows. For hydrogen, no p functions added. For elements in the carbon row (boron to fluorine), three p functions with exponents 8, 64, and 512 times the tighter p exponent in the original cc-pVDZ. For elements in the silicon, germanium, and tin row (sodium to xenon), two p functions with exponents 8, and 64 times the tighter p exponent in the original cc-pVDZ or Dyall basis set. For heavier elements, no p functions added. The small component basis set was obtained from the large component basis by the program DIRAC by restricted kinetic balance.

Nonrelativistic E_{PV} were computed using the internally developed program SYSMO [33] at the random phase approximation (RPA) level based on Hartree Fock (HF) wavefunction. For the molecules in class *A* (Sec. III) we used uncontracted cc-pVDZ (aug-cc-pVDZ on halogens and O^-) [27,28] augmented with tight p functions as described for the large component of the relativistic computations. For the

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[1] Operator 3 does not include the two-electron part of the spin-orbit operator. Based on the results in Ref. [25] and on unpublished work by our group we expect this contribution to reduce the magnitude of nonrelativistic E_{PV} by approximately 30% without changing our qualitative interpretation. In the interest of clarity we decided to neglect such terms in the qualitative analysis. Two-electron spin-orbit interactions are included in full in the relativistic treatment used to obtain quantitative results. Operator 4 was derived from a Foldy-Wouthuysen transformation of operator 2.

TABLE I. Percentage contribution to total E_{PV} due to spin-orbit of atom A coupled with parity-violation on atom B for molecules $A\mathrm{H}_mB\mathrm{H}_n$. In parentheses we report the percentage of each value due to the spin component perpendicular to the A-B bond. The values reported refer to dihedral angles near the maximum value of E_{PV}. The actual angles used are 45° for BH_2BH_2, BH_2NH_2, BH_2OH, and NH_2OH; 30° for CH_3CH_3, CH_3NH_2, and CH_3OH; 135° for NH_2NH_2 and OHOH; 15° for BH_2CH_3.

SO PV	BH_2	CH_3	NH_2	OH
BH_2	48.39(99.5)	0.03(− [a])	49.61(98.9)	46.61(99.8)
CH_3	0.84([a])	48.85(99.7)	55.56(97.7)	51.59(94.6)
NH_2	45.17(99.8)	32.74(95.5)	48.65(85.1)	37.97(88.7)
OH	40.37(99.1)	24.21(86.4)	59.20(95.1)	48.17(96.3)

[a] Data not relevant since not referring to the main contribution to E_{PV}. See the text for details.

molecules in class B (Sec. IV) the basis used was cc-pVDZ (aug-cc-pVDZ on halogens and O^-) [27,28].

III. CLASS A: TWO HEAVY ATOMS AND HYDROGENS

We consider in this section the class of molecules containing two singly bonded heavy atoms and hydrogens: $A\mathrm{H}_n$-$B\mathrm{H}_m$. Examples of molecules in this class are BH_2-CH_3, CH_3-OH, and OH-OH. The symmetry of these molecules depends on the dihedral angle ϕ about the A-B bond. For certain special values of ϕ the molecules contain symmetry planes and hence their E_{PV} must be zero. Upon rotation of the dihedral past one of the special values, the molecules transform from one enantiomeric form to the other, and hence their E_{PV} must change sign. We can thus use symmetry to predict a minimal nodal pattern of E_{PV} as a function of the dihedral angle ϕ.

Furthermore, since the hydrogen atoms have very small values of Q_W, they contribute very little to E_{PV} and the observed behavior will be particularly easy to interpret in terms of the two heavy atoms and the directions of the bonds.

We report in Table I the contributions to the total E_{PV} due to the spin-orbit of one of the heavy atoms coupled with the parity-violation term on the other one, as computed via RPA. For example, the contribution arising from parity-violation on N coupled with spin-orbit on O in NH_2OH is responsible for 37.97% of the total E_{PV}. The parity-violation on O coupled with spin-orbit on N in the same molecule accounts for another 59.20%. These two terms combined account for over 97% of the total E_{PV}. Similarly, in the molecule BH_2BH_2 the coupling between the two B atoms accounts for over 96% of the total E_{PV} (twice 48.39%.) It is apparent that this contribution is by far the most important in determining the total value of E_{PV} for all cases except BH_2CH_3. This molecule, however, has E_{PV} orders of magnitude smaller than the other molecules in this series. We will discuss later why the fragment CH_3 has special behavior toward E_{PV}. These findings are in good agreement with the single-center theorem by Hegstrom, Rein, and Sandars [23], which states that for basis sets containing only s and p atomic-centered functions the E_{PV} contribution from SO and PV terms on the same center is zero.

We conclude that E_{PV} for this class of molecules can be studied focusing only on the coupling between the two heavy atoms.

A. BH_2-BH_2

The simplest molecule we consider is BH_2-BH_2 with geometry reported schematically in Figs. 1(A) and 1(B). The

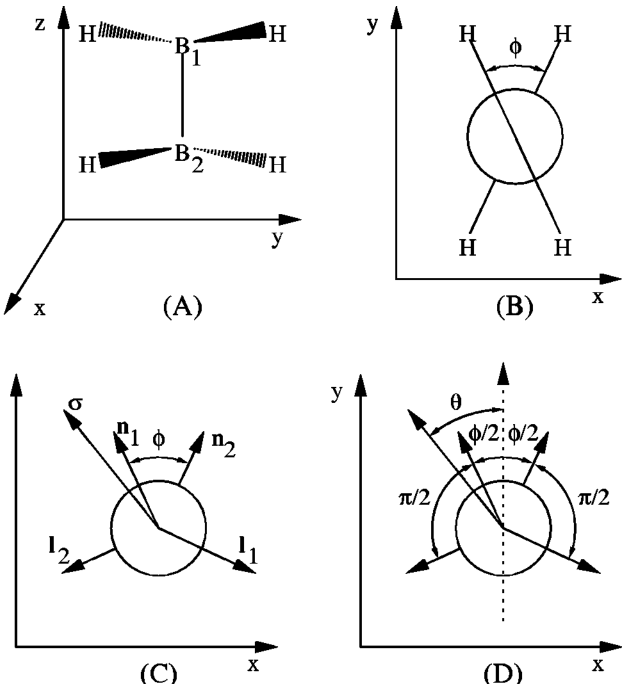

FIG. 1. Geometric description of BH_2–BH_2. (A) Orientation in three dimensions (3D). (B) Newman projection along the z axis. The dihedral angle ϕ is positive for the configuration shown. (C) Directions of the relevant vectors for E_{PV} evaluation. (D) Angles used to estimate E_{PV}. The vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ are eclipsed to the B-H bonds and define the preferential directions for electronic momentum $\boldsymbol{p}$ on nuclei B_1 and B_2, respectively. Vectors $\mathbf{l}_1$ and $\mathbf{l}_2$ are the directions of angular momentum relative to B_1 and B_2 corresponding to motion along $\mathbf{n}_2$ and $\mathbf{n}_1$, respectively. They are given by $\mathbf{l}_1=(\mathbf{R}_{B_2}-\mathbf{R}_{B_1})\times\mathbf{n}_2$ and $\mathbf{l}_2=(\mathbf{R}_{B_1}-\mathbf{R}_{B_2})\times\mathbf{n}_1$. The direction $\boldsymbol{\sigma}$ of the spin component in the xy plane is identified by the arbitrary angle θ.

molecule has symmetry planes for $\phi = 0°,\ 90°,\ 180°$, and $270°$. Since E_{PV} must change sign at each of these special values, we expect it to have periodicity similar to $\sin(2\phi)$.

Consider the effect of PV and SO on one electron at a time. Given an orientation for the electron spin, the PV and SO interactions induce it to move in certain preferential directions. Namely, the PV term pushes the electron on the nuclei in the direction of the spin whereas the SO term moves it in such a way that its angular momentum with respect to each nucleus opposes the spin. Since for a closed-shell molecule all the electrons are singlet paired, for each electron pushed in one direction there must be another electron with opposite spin pushed on the average in the opposite direction, i.e., despite the motion of individual electrons, there is no net (observable) current.

Based on the numerical multiplicative factors in the two Hamiltonians, we expect the SO term to induce most of the motion and the PV term to have a much smaller contribution. The induced canonical momentum $\boldsymbol{p}$ is expected to be larger when the electron is pushed toward regions with high-electron density and high polarizability and smaller when the electron is pushed toward low-electron density regions. Since for this molecule all valence electrons are in bonding orbitals, we assume, in the first approximation, that they can preferentially move in the directions along the bonds of the molecule. The net electronic momentum $\boldsymbol{p}$ contributing to the angular momentum $\boldsymbol{L}$ will thus be mainly along directions $\mathbf{n}_1$ and $\mathbf{n}_2$ in Fig. 1(C). The corresponding angular momenta $\boldsymbol{L}$ must be directed along $\mathbf{l}_2$ and $\mathbf{l}_1$.

For any given spin orientation, we can provide qualitative estimates of the motion induced by spin-orbit coupling and of the quantities $\boldsymbol{p}\cdot\boldsymbol{\sigma}$ and $\boldsymbol{L}\cdot\boldsymbol{\sigma}$. Based on the form of the perturbative expression for E_{PV}, we estimate that the value of E_{PV} for this particular spin orientation will be proportional to the product of these two quantities. Since the PV Hamiltonian includes a nuclear contact term, we only consider the motion of electrons going through the heavy nuclei. The effect of the hydrogens is that of orienting the bonds, and hence the possible directions of electronic motion.

The final value of E_{PV} (independent from spin orientation) will be proportional to the average over all possible spin orientations of the product $(\boldsymbol{p}\cdot\boldsymbol{\sigma})(\boldsymbol{L}\cdot\boldsymbol{\sigma})$.

We consider separately the effects of the components of the spin parallel to the B-B bond and perpendicular to it.

The parallel component of the spin cannot result in any net contribution to E_{PV} because (A) the spin-orbit term leads to no electronic motion since all the bonds are perpendicular to any direction that would produce angular momentum parallel to $\boldsymbol{\sigma}$, and (B) conversely, the PV term leads to motion along the z direction which in turn cannot have any net angular momentum with respect to the two heavy atoms. To support this claim, we computed the RPA contribution to E_{PV} of the components of the spin parallel and perpendicular to the B-B bond. The parallel component accounts for 0.5% of the contribution from the direct coupling of the two boron atoms when the dihedral angle is 45°. Thus, we only need to consider the spin components perpendicular to the B-B bond. We report in parentheses in Table I the percentage contribution of the perpendicular component to the main E_{PV} terms, i.e., to the terms arising from the coupling of PV on one atom with SO on the other one.

The perpendicular component of the spin is treated as follows. Spin-orbit coupling induces canonical momentum that minimize the product $\boldsymbol{L}\cdot\boldsymbol{\sigma}$ at each nucleus. A given orientation of the spin is identified by angle θ in Fig. 1(D). Since the induced angular momentum with respect to each nucleus can only have directions $\mathbf{l}_1$ and $\mathbf{l}_2$, it is expected to be proportional to

$$\begin{aligned} \boldsymbol{L}_1 &\overline{\underline{\propto}} -(\mathbf{l}_1\cdot\boldsymbol{\sigma})\mathbf{l}_1 \overline{\underline{\propto}} -\cos(\pi/2+\phi/2+\theta)\mathbf{l}_1\\ &= \sin(\phi/2+\theta)\mathbf{l}_1,\\ \boldsymbol{L}_2 &\overline{\underline{\propto}} -(\mathbf{l}_2\cdot\boldsymbol{\sigma})\mathbf{l}_2 \overline{\underline{\propto}} -\cos(\pi/2+\phi/2-\theta)\mathbf{l}_2\\ &= \sin(\phi/2-\theta)\mathbf{l}_2, \end{aligned} \tag{6}$$

where the symbol $\overline{\underline{\propto}}$ indicates sign-conserving-proportionality, i.e., with positive proportionality constant. These correspond to canonical momenta on the opposite nuclei with magnitude proportional to the magnitude of $\boldsymbol{L}$:

$$\begin{aligned} \boldsymbol{p}_1 &\overline{\underline{\propto}} (\boldsymbol{L}_2\cdot\mathbf{l}_2)\mathbf{n}_1 \overline{\underline{\propto}} \sin(\phi/2-\theta)\mathbf{n}_1,\\ \boldsymbol{p}_2 &\overline{\underline{\propto}} (\boldsymbol{L}_1\cdot\mathbf{l}_1)\mathbf{n}_2 \overline{\underline{\propto}} \sin(\phi/2+\theta)\mathbf{n}_2, \end{aligned} \tag{7}$$

from which one obtains [see Figs. 1(C) and 1(D) for the orientations of $\mathbf{n}$, $\mathbf{l}$, and $\boldsymbol{\sigma}$ and for the angles used to describe them]

$$\begin{aligned} \boldsymbol{L}_1\cdot\boldsymbol{\sigma} &\overline{\underline{\propto}} -\sin^2(\phi/2+\theta),\\ \boldsymbol{L}_2\cdot\boldsymbol{\sigma} &\overline{\underline{\propto}} -\sin^2(\phi/2-\theta),\\ \boldsymbol{p}_1\cdot\boldsymbol{\sigma} &\overline{\underline{\propto}} \sin(\phi/2-\theta)\cos(\phi/2-\theta),\\ \boldsymbol{p}_2\cdot\boldsymbol{\sigma} &\overline{\underline{\propto}} \sin(\phi/2+\theta)\cos(\phi/2+\theta). \end{aligned} \tag{8}$$

According to Eqs. (3), (4), and (5), the average contribution to the energy is then estimated as the integral over all possible values of θ of the product $-(\boldsymbol{L}\cdot\boldsymbol{\sigma})(-\boldsymbol{p}\cdot\boldsymbol{\sigma})$:

$$\begin{aligned} E_{\mathrm{PV}} &\overline{\underline{\propto}} -\int_0^{2\pi}[(\boldsymbol{L}_1+\boldsymbol{L}_2)\cdot\boldsymbol{\sigma}][-(\boldsymbol{p}_1+\boldsymbol{p}_2)\cdot\boldsymbol{\sigma}]d\theta\\ &\overline{\underline{\propto}} \int_0^{2\pi}[\sin^2(\phi/2+\theta)+\sin^2(\phi/2-\theta)][\sin(\phi/2-\theta)\\ &\quad\times\cos(\phi/2-\theta)+\sin(\phi/2+\theta)\cos(\phi/2+\theta)]d\theta\\ &\overline{\underline{\propto}} -\sin(2\phi), \end{aligned} \tag{9}$$

indicating that E_{PV} should have the functional form of $-\sin(2\phi)$ and that, in particular, it should be negative for $0° < \phi < 90°$ and positive for $90° < \phi < 180°$. This is consistent with the computed values as reported in Fig. 6. We stress the fact that our model predicts only the sign and the general behavior of E_{PV}. It does not predict its amplitude. The values plotted in Fig. 6 are scaled in order to ease the comparison with the computed values.

Although we expect the PV term to give extremely small contribution to the momentum, the same kind of treatment can be applied after reversing the roles of the two Hamiltonians.

The canonical momentum at each nucleus induced by the PV term is proportional to

$$\begin{aligned} \boldsymbol{p}_1 &\mathrel{\overline{\underline{\propto}}} (\mathbf{n}_1\cdot\boldsymbol{\sigma})\mathbf{n}_1 \mathrel{\overline{\underline{\propto}}} \cos(\phi/2-\theta)\mathbf{n}_1, \\ \boldsymbol{p}_2 &\mathrel{\overline{\underline{\propto}}} (\mathbf{n}_2\cdot\boldsymbol{\sigma})\mathbf{n}_2 \mathrel{\overline{\underline{\propto}}} \cos(\phi/2+\theta)\mathbf{n}_2. \end{aligned} \tag{10}$$

It follows that

$$\begin{aligned} \boldsymbol{p}_1\cdot\boldsymbol{\sigma} &\mathrel{\overline{\underline{\propto}}} \cos^2(\phi/2-\theta), \\ \boldsymbol{p}_2\cdot\boldsymbol{\sigma} &\mathrel{\overline{\underline{\propto}}} \cos^2(\phi/2+\theta). \end{aligned} \tag{11}$$

The motion on each nucleus has angular momentum with respect to the other nucleus given by

$$\begin{aligned} \boldsymbol{L}_1 &\mathrel{\overline{\underline{\propto}}} (\boldsymbol{p}_2\cdot\mathbf{n}_2)\mathbf{l}_1 \mathrel{\overline{\underline{\propto}}} \cos(\phi/2+\theta)\mathbf{l}_1, \\ \boldsymbol{L}_2 &\mathrel{\overline{\underline{\propto}}} (\boldsymbol{p}_1\cdot\mathbf{n}_1)\mathbf{l}_2 \mathrel{\overline{\underline{\propto}}} \cos(\phi/2-\theta)\mathbf{l}_2, \end{aligned} \tag{12}$$

hence

$$\begin{aligned} \boldsymbol{L}_1\cdot\boldsymbol{\sigma} &\mathrel{\overline{\underline{\propto}}} -\cos(\phi/2+\theta)\sin(\phi/2+\theta), \\ \boldsymbol{L}_2\cdot\boldsymbol{\sigma} &\mathrel{\overline{\underline{\propto}}} -\cos(\phi/2-\theta)\sin(\phi/2-\theta). \end{aligned} \tag{13}$$

The contribution to the energy is thus estimated as

$$\begin{aligned} E_{\mathrm{PV}} &\mathrel{\overline{\underline{\propto}}} \int_0^{2\pi} (\boldsymbol{p}\cdot\boldsymbol{\sigma})(\boldsymbol{L}\cdot\boldsymbol{\sigma})\,d\theta \\ &\mathrel{\overline{\underline{\propto}}} -\int_0^{2\pi} [\cos^2(\phi/2+\theta)+\cos^2(\phi/2-\theta)][\cos(\phi/2+\theta) \\ &\quad \times\sin(\phi/2+\theta)+\cos(\phi/2-\theta)\sin(\phi/2-\theta)]\,d\theta \\ &\mathrel{\overline{\underline{\propto}}} -\sin(2\phi), \end{aligned} \tag{14}$$

which shows that the two approaches are equivalent.

In conclusion, we find that E_{PV} is proportional to $-\sin(2\phi)$ as predicted based on symmetry requirements. Unlike the symmetry analysis, however, our treatment enables us to make predictions on the sign of E_{PV}.

B. AH_n-CH_3

To a first approximation the fragment CH_3 has three identical C-H bonds with local C_3 symmetry. We are interested in the component of the canonical momentum at the C nucleus which is perpendicular to the A-C axis, i.e., in the component yielding an angular momentum with respect to nucleus A and a PV interaction with the perpendicular component of the spin. We call this component the perpendicular component of $\boldsymbol{p}$, at nucleus C. According to our model, the canonical momentum can have components along all three C-H bonds. Hence, its perpendicular component can assume any direction in the plane perpendicular to A-C without preferential orientations. This being the case, we expect the CH_3 fragment to behave like a fragment which is totally symmetric under rotation about A-C, e.g., hydrogen, fluorine, or bromine. For molecules of the form AH_n-CH_3, E_{PV} must be independent from the dihedral angle and hence must be identically zero, much like for nonchiral molecules.

TABLE II. Maximum values of E_{PV} (in 10^{-20} a.u.) for the class of molecules AH_n-BH_m.

Fragment	BH_2	CH_3	NH_2	OH
BH_2	1.86	0.00	4.19	7.04
CH_3	0.00	0.54	0.66	0.52
NH_2	4.16	0.66	8.95	25.3
OH	7.04	0.52	25.3	66.4

In practice, most of the times the C-H bonds are not identical. As long as they are roughly equivalent, however, E_{PV} should be extremely small. As reported in Table II, the computed values of E_{PV} for these molecules are not zero, but they are at least one order of magnitude smaller than for the corresponding dimers. The maximum value of E_{PV} for molecules containing the fragment CH_3 provides an estimate for the quality of our predictions.

C. NH_2-NH_2

The fragment NH_2 has one lone pair of electrons, so we can no longer assume that the electrons can only move along the chemical bonds. In fact, the motion in the direction of the lone pair is likely to be important for E_{PV} purposes because lone pairs are generally more polarizable than bonds, so the induced momenta are likely to be larger in the regions of lone pairs than in bonding orbitals. This claim is consistent with the trend reported in Table II, although the same trend could also be caused by the change in atomic number and in equilibrium bond distance.

To estimate the sign of E_{PV} we take advantage of the fact that groups with pseudo C_3 symmetry do not contribute to E_{PV} and that lone pair electrons are more polarizable near the nucleus than electrons involved in N-H bonds. As sketched in Fig. 2, we regard the system with electrons allowed to move in the three directions of the N-H bonds and the lone pair as equivalent, for E_{PV} estimation purposes, to a system

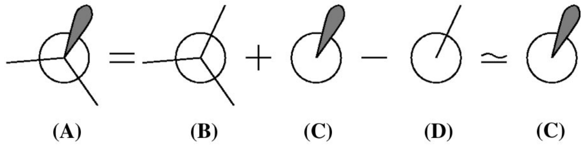

FIG. 2. Geometric description of the NH_2 fragment. The system with electrons moving in the three directions of the lone pair and the two N-H bonds (A) is regarded as a system with three bonds (B), which does not contribute to E_{PV}, plus a system with one lone pair (C), minus a system with one bond (D). The net sum is thus equivalent to the difference between (C) and (D), which is qualitatively equivalent to (C).

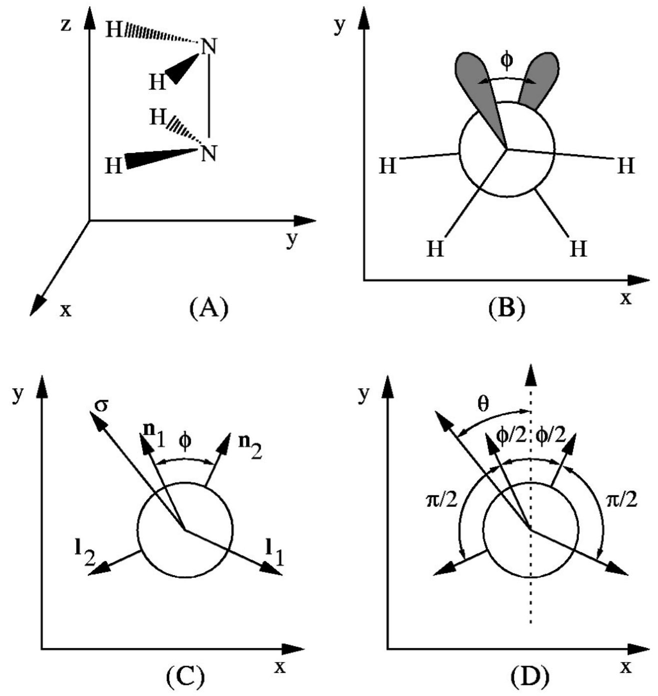

FIG. 3. Geometric description of NH_2-NH_2. (A) Orientation in 3D. (B) Newman projection along the z axis. (C) Direction of relevant vectors for E_{PV} evaluation. (D) Angles used to estimate E_{PV}. Vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ are eclipsed to the nitrogen lone pairs. The vectors $\mathbf{l}_1$ and $\mathbf{l}_2$ are the directions of angular momentum corresponding to motion along $\mathbf{n}_2$ and $\mathbf{n}_1$, respectively. Vector $\boldsymbol{\sigma}$ indicates the direction of the spin. Note that the vectors in (C) and (D) are identical to the ones in Figs. 1(C) and 1(D).

in which the electrons can only move in the direction of the lone pair.

The system can be examined with the geometry depicted in Fig. 3 from which it is apparent that it must behave like the BH_2-BH_2 system already examined. Choosing ϕ as the dihedral angle between the two lone pairs, E_{PV} is expected to behave like $-\sin(2\phi)$. The plot with both computed and expected values of E_{PV} is reported in Fig. 6. Our model captures the correct sign and shape of the curve. Notice that in this case there is no symmetry requirement for E_{PV} to change sign around 90°, so the shape of the curve is not trivial.

D. BH_2-NH_2

The ground state of this molecule is planar with a double bond between B and N and formal charges of $+1$ on the nitrogen and -1 on the boron. The electronic configuration is similar to $CH_2{=}CH_2$. To obtain a suitable structure to investigate E_{PV} we used the singly bonded structure with one lone pair on the nitrogen and one empty p orbital on the boron. To bias the system toward this state, the geometry was optimized with the constraint that one of the B-H bonds be eclipsed to the nitrogen lone pair. The resulting bond distances and angles were then used for all dihedral angles.

Similar to the case of NH_2-NH_2, using the fact that the fragment NH_2 behaves as if the only possible direction of motion was along the lone pair, with a suitable choice of the angle ϕ this case can be reduced to the BH_2-BH_2 already examined. As depicted in Fig. 4, choosing ϕ as the dihedral angle between the nitrogen lone pair and one of the B-H bonds provides the same axis framework used in the previous examples and leads to a functional form proportional to $-\sin(2\phi)$. In this case, symmetry requires that E_{PV} changes sign at 90°. The comparison of calculated and estimated E_{PV} is given in Fig. 6.

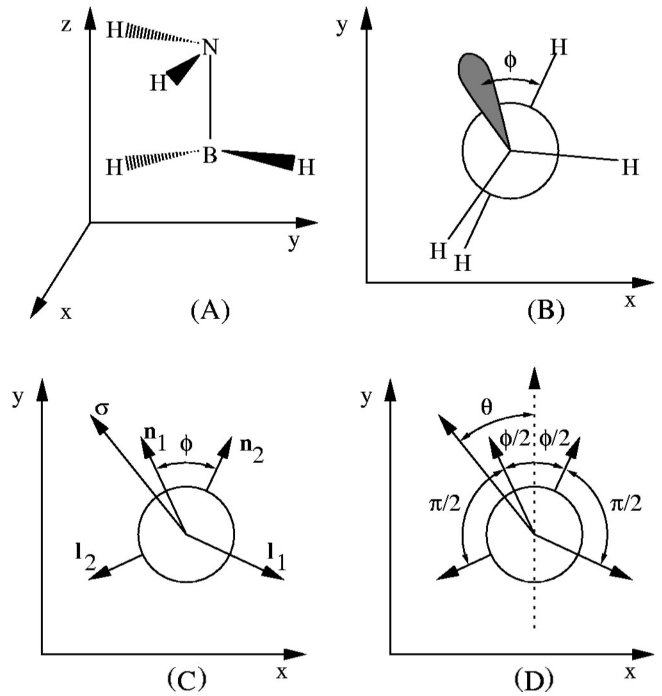

FIG. 4. Geometric description of BH_2–NH_2. (A) Orientation in 3D. (B) Newman projection along the z axis. (C) Direction of relevant vectors for E_{PV} evaluation. (D) Angles used to estimate E_{PV}. Note that the vectors in (C) and (D) are identical to the ones in Figs. 1(C) and 1(D).

E. AH_n-OH

The fragment OH can be regarded as having two equivalent lone pairs and one O-H bond. Once again, we can exploit the fact that these are interchanged upon C_3 rotation so

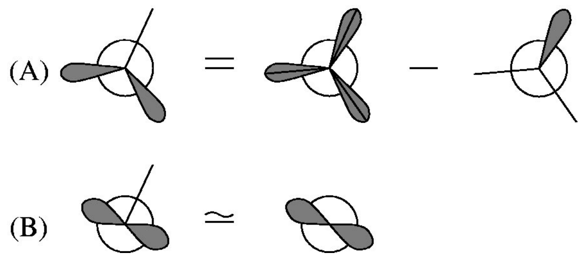

FIG. 5. Geometric description of the OH fragment. (A) The fragment with one O-H bond and two equivalent lone pairs is regarded as the difference between a system with three bonds and three lone pairs and one with two bonds and one lone pair resembling NH_2. (B) The same fragment is regarded as having one s-like (not shown) and one p-like lone pairs.

that we only need to consider the difference between the behavior of lone pairs and bonds.

We formally decompose each OH group into a fragment with three lone pairs and three bonds related by C_3 rotation minus a fragment with only one lone pair in the direction of the OH bond [see Fig. 5(A)] and two bonds. In other words, the spin-orbit induced motion in the two lone pair regions has the same effect toward E_{PV} as the motion that would be induced in a lone pair in the O-H bond region with its sign reversed. Each OH is hence expected to behave as a group with one lone pair (e.g., NH_2), except that the sign of E_{PV} must be reversed.

Alternatively, one can regard the OH fragment as having one *s*-like and one *p*-like lone pairs with the *p*-like pair perpendicular to the O-H bond [see Fig. 5(B)]. In this case the motion should be preferentially in the direction of the *p*-like lone pair and E_{PV} should behave as $-\sin(2\phi)$ when the angle ϕ is measured with respect to the *p*-like lone pair. In agreement with the first approach, this amounts to $-\sin[2(\pi/2+\phi)]=\sin(2\phi)$ when the dihedral angle is mea-

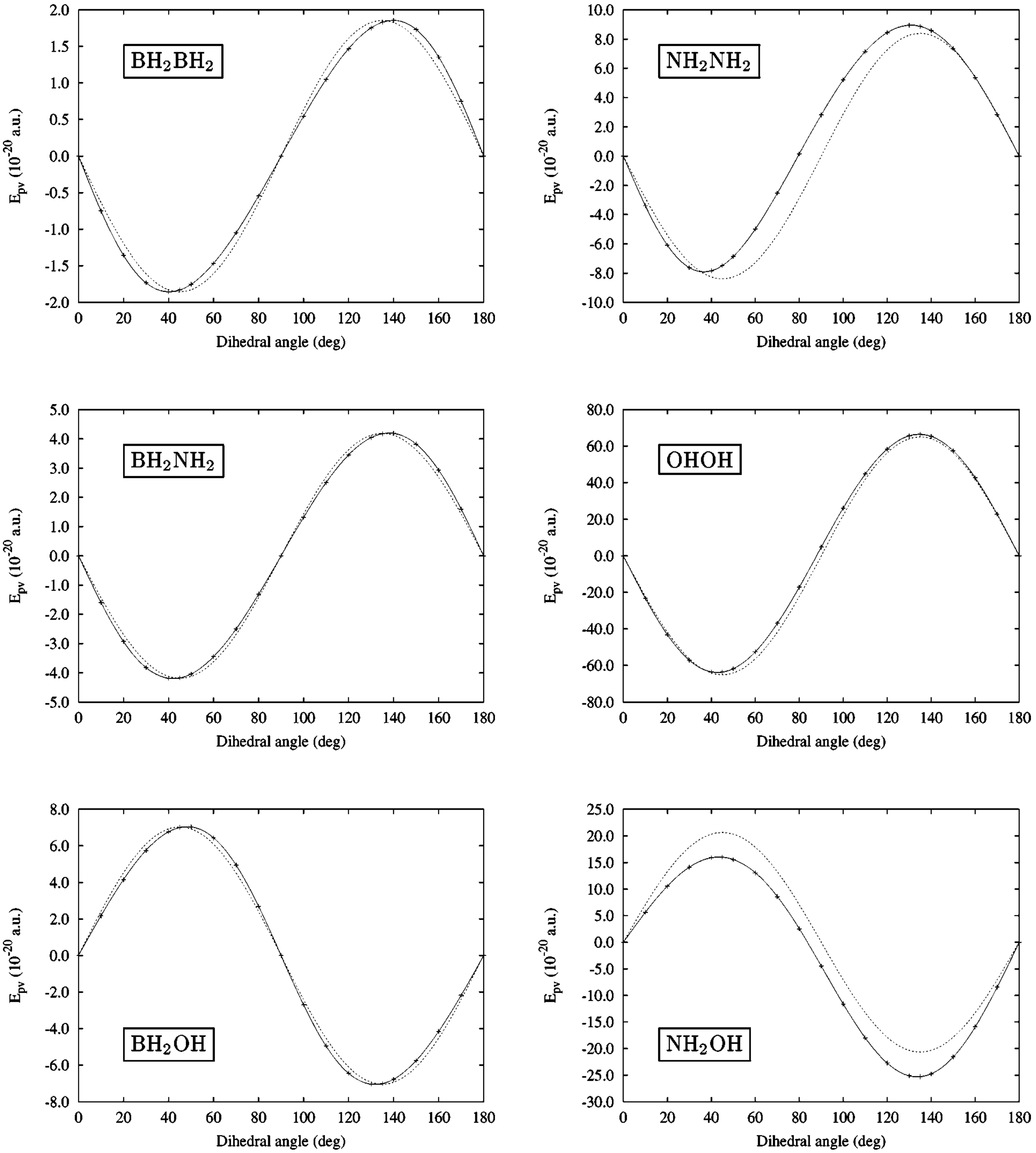

FIG. 6. Computed (solid lines) and estimated (dashed lines) E_{PV} for molecules of the series AH_n-BH_m as a function of the dihedral angle ϕ. The estimates were scaled to ease the comparison with the computed values.

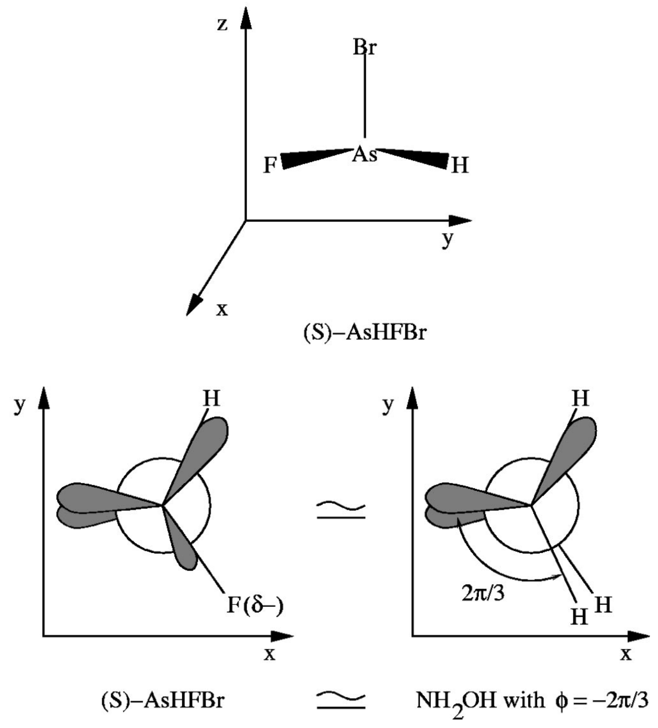

FIG. 7. Schematic view of (S)-AsHFBr. The partial negative charge on fluorine polarizes the electron density on bromine. Our model predicts this molecule to be qualitatively equivalent to NH_2OH with a dihedral angle of $2\pi/3$.

sured with respect to the O-H bond.

In the case of OH-OH, each one of the OH fragments reverses the sign, so the sign does not change and E_{PV} behaves like $-\sin(2\phi)$ when ϕ is taken as the dihedral angle between the O-H bonds.

In conclusion, our model predicts a behavior of E_{PV} like $\sin(2\phi)$ for BH_2-OH and NH_2-OH and like $-\sin(2\phi)$ for OH-OH. For this to hold, the dihedral angle must be measured with respect to the B-H and O-H bonds and the NH_2 lone pair.

The comparison of prediction and computation is reported in Fig. 6.

F. Stretching and bending

In order to validate our model, we investigated the behavior of E_{PV} against simple geometric changes.

Each stretching and bending of chemical bonds is associated with larger changes in electronic configuration than are generally expected for the case of rotation about σ bonds. Nevertheless, our model should indicate the general behavior of E_{PV} at least for the simplest systems. In particular, in the case of BH_2-BH_2 we can control the direction of motion of the electrons $\mathbf{n}$ by changing the hydrogen's positions.

According to the model, for instance, E_{PV} depends on the product of $\mathbf{n}$ with the component of the spin perpendicular to the B-B bond. Therefore, everything else being constant, E_{PV} is expected to increases when the direction of motion of the electrons (vector $\mathbf{n}$) moves away from the direction of the B-B bond. The computed values in a neighborhood of the equilibrium B-B-H value of 122° confirm this behavior. Likewise, for the case of B-B stretching, we expect E_{PV} to be proportional to the electronic momentum induced by spin-orbit coupling due to one nucleus measured on the other nucleus. This momentum should decrease with the distance between the nuclei. E_{PV} should then decrease with the B-B stretching and eventually vanish at infinite distance. This behavior is also consistent with the computed values.

Similar arguments, however, do not hold for systems containing lone pairs. For molecules like OH-OH the stretching of the O-O bond is invariably associated with a change in the direction and polarizability of the lone pairs. In fact, unlike BH_2-BH_2, OH-OH must have null E_{PV} by symmetry for both $R_{\mathrm{O\text{-}O}}=0$ and for $R_{\mathrm{O\text{-}O}}=\infty$. Therefore, E_{PV} cannot be monotonic and we cannot predict its behavior near equilibrium distance.

Similarly, our model does not help in predicting the behavior against stretching of the A-H bonds.

IV. CLASS B: SINGLE CHIRAL CENTERS

We are now in a position to extend the same reasoning used in the previous section to molecules containing a single chiral center. Examples of molecules in this class are CHFClBr, AsHFBr, and PbFClBrI. In this case the chirality of the molecule is defined by a rather stiff bonding configuration so instead of predicting the behavior of E_{PV} against some geometric parameter we can only predict its sign and occasionally determine which of two similar molecules should have larger values.

Consider the molecules in the series XHFBr, with $X=\mathrm{N}$, P, As, Sb, and Bi. We expect most of the E_{PV} to come from the coupling of Br with X. In fact, except for $X=\mathrm{N}$, X and Br are the two heaviest elements in the molecule. The Br-X RPA contributions to E_{PV} for PHFBr and AsHFBr are 84.3% and 91.1%, respectively. In the case of NHFBr, Br is much heavier than any other element in the molecule and is bound directly to N. Although the coupling of Br with itself accounts for 43.5% of the E_{PV}, the coupling with N is the second largest term with 36.8%. It is noteworthy to observe that in this case the single-center theorem [23] does not hold due to the presence of d and higher angular momentum basis functions on the bromine. It is straightforward to generalize our reasoning to the coupling of PV and SO on the same center. We find, however, that this term depends strongly on the polarization of the basis set. For example, the parity violation of Ne in an asymmetric point-charge field was computed to be positive with cc-pVDZ, negative with cc-pVTZ, positive with cc-pVQZ, and negative with cc-pV5Z and cc-pV6Z. We hence focus, for the time being, on the coupling between adjacent nuclei.

The electron density around the bromine atom is roughly symmetric with respect to the X-Br axis. The first-order distortion from the symmetric configuration is due to electrostatic and overlap repulsion interactions with the ligands of X, namely, H and F. Of course, one expects F to have a partial negative charge, so the bromine electrons will polarize to reduce the density eclipsed with the fluorine. As a consequence, the bromine atom should behave like an O-H

TABLE III. Comparison of computed and estimated results.

Molecule	Computed E_{PV} (10^{-18} a.u.)	Prediction
(R)-NHFBr	11.3	$E_{\mathrm{PV}}>0$; $\lvert E_{\mathrm{PV}}\rvert>\lvert E_{\mathrm{PV}}(\mathrm{CHFClBr})\rvert$
(R)-PHFBr	21.2	$E_{\mathrm{PV}}>0$; $\lvert E_{\mathrm{PV}}\rvert<\lvert E_{\mathrm{PV}}(\mathrm{SHOBr})\rvert$; $\lvert E_{\mathrm{PV}}\rvert<\lvert E_{\mathrm{PV}}(\mathrm{PHFSeH}^{a})\rvert$
(R)-AsHFBr	139.4	$E_{\mathrm{PV}}>0$
(R)-SbHFBr	301.5	$E_{\mathrm{PV}}>0$
(R)-BiHFBr	7099.3	$E_{\mathrm{PV}}>0$
(R)-SHOBr	91.7	$E_{\mathrm{PV}}>0$; $\lvert E_{\mathrm{PV}}\rvert>\lvert E_{\mathrm{PV}}(\mathrm{PHFBr})\rvert$
(R)-PHFSeH[a]	49.9	$E_{\mathrm{PV}}>0$; $\lvert E_{\mathrm{PV}}\rvert>\lvert E_{\mathrm{PV}}(\mathrm{PHFBr})\rvert$
(S)-NHClBr	−17.9	$E_{\mathrm{PV}}<0$; $\lvert E_{\mathrm{PV}}\rvert>\lvert E_{\mathrm{PV}}(\mathrm{CHFClBr})\rvert$
(S)-CHFClBr	−4.9	$\lvert E_{\mathrm{PV}}\rvert<\lvert E_{\mathrm{PV}}(\mathrm{NHFBr})\rvert$; $\lvert E_{\mathrm{PV}}\rvert<\lvert E_{\mathrm{PV}}(\mathrm{NHClBr})\rvert$
(S)-$\mathrm{PCH_3FBr}$	−3.5	$E_{\mathrm{PV}}<0$; $\lvert E_{\mathrm{PV}}\rvert<\lvert E_{\mathrm{PV}}(\mathrm{PNH_3FBr^{(+)}})\rvert$
(S)-$\mathrm{PNH_3FBr^{(+)}}$	−7.3	$E_{\mathrm{PV}}<0$; $\lvert E_{\mathrm{PV}}\rvert>\lvert E_{\mathrm{PV}}(\mathrm{PCH_3FBr})\rvert$

[a] Se-H eclipsed to P-F.

fragment with the hydrogen eclipsed to the fluorine, as depicted in Fig. 7 for the case of $X=\mathrm{As}$.

So, (S)-AsHFBr is expected to have E_{PV} of the same sign as $\mathrm{NH_2OH}$ with a dihedral angle between the nitrogen lone pair and the O-H bond of $2\pi/3$. Hence, the model predicts $E_{\mathrm{PV}}<0$. By contrast, (R)-AsHFBr should have $E_{\mathrm{PV}}>0$. These predictions are consistent with the computed values.

Alternatively, one could consider the distortion due to the possibly positive charge on the H. This pulls the electron density on bromine to be eclipsed with the X-H bond. Hence, Br can be regarded as an $\mathrm{NH_2}$ fragment with the lone pair eclipsed to the X-H bond. According to this model, (S)-AsHFBr would then have E_{PV} with the same sign as $\mathrm{NH_2}$-$\mathrm{NH_2}$ with a dihedral angle between the lone pairs of $-2\pi/3$, so we predict $E_{\mathrm{PV}}<0$. Since in this particular case electrostatic interactions with both F and H yield the same sign of E_{PV} it is irrelevant which of the two dominates.

According to our interpretation, the bromine atom in PHFBr is qualitatively equivalent to an OH group with the O-H bond eclipsed to the P-F bond. For a more quantitative comparison, consider the isoelectronic molecules PHFBr and PHFSeH, with the Se-H bond eclipsed with the P-F. The distortion of the electronic distribution should be qualitatively equivalent, resulting in E_{PV} of the same sign. It is reasonable to expect that the presence of the Se-H bond distorts the electronic distribution more than electrostatic effects around the Br. Except for the extra hydrogen, the bond distances and angles in the two molecules are fairly similar, so we expect PHFSeH to have larger E_{PV} than PHFBr.

To further verify our reasoning, we compared the molecules PHFBr and SHOBr. The two molecules have the same electronic configuration. The S-O bond, however, is formally polarized as $\mathrm{S^+}$-$\mathrm{O^-}$, so the oxygen should carry more negative charge than the fluorine. We expect the oxygen atom to induce stronger polarization on the bromine, resulting in a larger magnitude of E_{PV}. In fact, the two molecules have E_{PV} of the same sign [positive for (R) form] with E_{PV} for SHOBr larger that for PHFBr.

A similar effect is observed between the isoelectronic molecules (S)-$\mathrm{PCH_3FBr}$ and (S)-$\mathrm{PNH_3FBr^+}$. Since $\mathrm{NH_3^+}$ induces stronger polarization on the bromine than $\mathrm{CH_3}$, we expect $\lvert E_{\mathrm{PV}}(\mathrm{PNH_3FBr^+})\rvert>\lvert E_{\mathrm{PV}}(\mathrm{PCH_3FBr})\rvert$.

As a further test, we compared NHFBr and CHFClBr. In this case, H is partially positive whereas both F and Cl tend to be partially negative. In the case of CHFClBr, the effects of Cl and F tend to cancel each other, one giving a positive contribution to E_{PV} and the other giving a negative contribution. The final sign of E_{PV} is determined by which of the two dominates and requires quantitative estimates. It is extremely likely, however, that the cancellation will result in absolute values for E_{PV} smaller than for either NHFBr or NHClBr.

We report a summary of the predictions made and the computed values for a number of molecules in Table III. Our model works for all the systems considered.

V. CONCLUSIONS

By analyzing the parity violation energy (E_{PV}) in chiral molecules in terms of an approximate Hamiltonian, we derived a qualitative model to predict its behavior. Our model is shown to be successful for all the molecules we considered, lending credibility to our interpretation of E_{PV}. Our conclusions are the following.

By and large it is qualitatively correct to assume that E_{PV} is due to the coupling of spin-orbit and parity-violation terms, as implicitly assumed by the nonrelativistic approach [Eq. (5)].

For most molecules, the leading terms contributing to E_{PV} are due to spin-orbit and parity-violation interactions with neighboring nuclei, respectively. Exceptions to this rule may be found for systems containing one atom which is much heavier than its neighbors, like NHFBr, and systems with extremely small E_{PV}, like $\mathrm{BH_2}$-$\mathrm{CH_3}$.

Systems containing lone pairs tend to have larger E_{PV} than systems with only bonding orbitals.

E_{PV} is determined by the local environment about each nucleus. This includes bonding configuration and electrostatic interactions with the rest of the molecule.

The approach we propose requires no computations and is based on intuitively simple concepts such as canonical momentum of an electron and charge density. Since it is derived from qualitative considerations, it is intended only to complement the methods already established [17,20,24] by helping in the interpretation of the quantitative results. The approach provides a valuable tool to estimate which complex systems are more likely to have large values of E_{PV}. For example, in the case of larger systems it allows to select the geometric configurations for which the contributions from different functional groups are more likely to reinforce each other.

Work to design molecular systems with observable E_{PV} effects based on our current understanding is currently in progress and will be the subject of future publications.

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