

Parity-violating contributions to nuclear magnetic shielding

Alessandro Soncini,* Francesco Faglioni, and Paolo Lazzeretti†
Dipartimento di Chimica, Università degli Studi, Via G. Campi 183, 41100 Modena, Italy
 (Received 10 April 2003; published 10 September 2003)

A gauge-invariant formalism is developed to describe the effect of parity-violating weak-nuclear interactions on nuclear magnetic chemical shift in molecules. Such effect is computed for two molecules with *ab initio* techniques and it is found to be orders of magnitude smaller than experimental resolution for the molecules considered.

DOI: 10.1103/PhysRevA.68.033402

PACS number(s): 33.25.+k, 32.80.Ys, 76.60.Cq, 82.56.-b

I. INTRODUCTION

Electroweak theory predicts two enantiomers, i.e., two molecules which are the nonsuperimposable mirror images of each other to have different energy and response properties due to parity-violating (PV) weak-nuclear interactions between the molecular electrons and nucleons [1–3]. Although this has been known for some time, the differences between a molecule and its specular image are so small that no clear experimental observation of PV for such systems has been reported to date.

Formally, parity violation is due to a few terms in the nonrelativistic reduction of the PV weak-nuclear Hamiltonian for the molecule. These terms contain dot products between a spin vector and a momentum vector, hence, they are pseudoscalars and reverse sign upon inversion of the coordinates, i.e., they violate parity. The leading PV contribution to the total energy arises from a term containing the electronic spin. This term alone was used extensively in recent years to predict PV effects on vibrational spectra [4–7]. In fact, most of the experimental effort towards molecular PV detection was focused on the spectroscopic observation of PV induced vibrational frequency shifts for a few chiral molecules [8–10].

Although the remaining PV terms, which contain the nuclear spin, can usually be neglected in energy computations [11,12], they influence directly nuclear magnetic resonance (NMR) parameters [13,14]. It is thus interesting to estimate the magnitude of such effect and to assess whether experimental PV observation might be possible through NMR spectroscopy. In this regard, we note that ground breaking work was published by Barra and Robert [13]. Among other things, they derived the expression for the paramagnetic PV contribution to the nuclear shielding tensors. Although this may not be the most efficient approach for *ab initio* calculations, these contributions are sufficient to provide quantitative estimates of the PV effect on shielding tensors and hence on the observable chemical shift.

In this paper, we report expressions for both diamagnetic and paramagnetic contributions to the nuclear shielding tensor. Even though both contributions depend on the gauge

choice, their sum is gauge independent for sufficiently large basis sets. This formalism was implemented within the framework of *ab initio* response theory and numerical estimates are reported for two molecules.

Recently, we became aware of work reported previously by Laubender and Berger [15] which is partly reproduced by our present work on hydrogen sulfide. The results obtained here are in good agreement with those of the authors [15].

In the following section we present the formalism, in Sec. III we show that the sum of diamagnetic and paramagnetic terms is independent of the coordinates origin, in Sec. IV we provide technical details needed to reproduce our computations, and in Sec. V we report and discuss the results.

II. FORMALISM

We focus our attention on the PV Hamiltonian term containing the nuclear spin (or magnetic moment) but not the electronic spin. In fact, this term can be used directly to describe the coupling of nuclear spins with each other and with external magnetic fields, i.e., to predict the PV effect on NMR parameters, most notably the chemical shift σ^I and the coupling constants J_{IJ} [13]. For the interaction between n molecular electrons and a nucleus I at position \mathbf{R}_I with intrinsic nuclear magnetic dipole $\boldsymbol{\mu}_I$, this term is [13]

$$H_{PV}^{\mu_I}(\mathbf{R}_I) = -\frac{G_F C_s}{2\sqrt{2}\hbar m_e c} \frac{\lambda_I}{\gamma_I} \boldsymbol{\mu}_I \cdot \sum_{i=1}^n [\mathbf{p}_i, \delta(\mathbf{r}_i - \mathbf{R}_I)]_+, \quad (1)$$

where G_F is the Fermi constant ($G_F = 2.22254 \times 10^{-14}$ a.u.), $C_s = 1 - 4 \sin^2 \theta_W$ is a constant containing the Weinberg angle θ_W ($C_s = -0.0724$), γ_I is the magnetogyric ratio, λ_I is a nuclear factor of the order of one [13], and \mathbf{r}_i and \mathbf{p}_i are the position and canonical momentum of electron i , respectively. Since the electron probability current-density operator at position \mathbf{r} is defined as

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2m_e} \sum_{i=1}^n [\mathbf{p}_i, \delta(\mathbf{r}_i - \mathbf{r})]_+, \quad (2)$$

Hamiltonian (1) may be cast in the form

$$H_{PV}^{\mu_I}(\mathbf{R}_I) = -\frac{G_F C_s}{\sqrt{2}\hbar c} \frac{\lambda_I}{\gamma_I} \boldsymbol{\mu}_I \cdot \hat{\mathbf{j}}_p(\mathbf{R}_I). \quad (3)$$

*Present address: Chemistry Department, Exeter University, United Kingdom.

†Electronic address: lazzeret@unimo.it

In the presence of an external magnetic field \mathbf{B} , which for the sake of simplicity is assumed spatially uniform and time independent, the corresponding vector potential in the Coulomb gauge is $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$. According to Gell-Mann minimal-coupling prescription, the canonical momentum \mathbf{p} is replaced by the mechanical momentum $\boldsymbol{\pi}$ so that

$$\mathbf{p} \rightarrow \boldsymbol{\pi} = \mathbf{p} + \frac{e}{c}\mathbf{A}, \quad (4a)$$

$$\hat{\mathbf{j}}_p \rightarrow \hat{\mathbf{j}} = \hat{\mathbf{j}}_p + \hat{\mathbf{j}}_d, \quad (4b)$$

$$H_{PV}^{\mu_I} \rightarrow \mathcal{H}_{PV}^{\mu_I} = -\frac{G_F C_s \lambda_I}{\sqrt{2}\hbar c} \frac{\lambda_I}{\gamma_I} \boldsymbol{\mu}_I \cdot \hat{\mathbf{j}}(\mathbf{R}_I), \quad (4c)$$

where the diamagnetic contribution to the probability current density is

$$\hat{\mathbf{j}}_d(\mathbf{r}) = \frac{e}{2m_e c} \sum_{i=1}^n [A_i, \delta(\mathbf{r}_i - \mathbf{r})]_+ = \frac{e}{2m_e c} \mathbf{B} \times \sum_{i=1}^n \mathbf{r}_i \delta(\mathbf{r}_i - \mathbf{r}). \quad (5)$$

By virtue of Eqs. (4b) and (4c), the minimal-coupling PV Hamiltonian splits naturally into two terms:

$$\mathcal{H}_{PV}^{\mu_I} = H_{PV}^{\mu_I} + H_{PV}^{\mu_I B}. \quad (6)$$

The diamagnetic term is expressed as

$$H_{PV}^{\mu_I B} = -\frac{G_F C_s \lambda_I}{\sqrt{2}\hbar c} \frac{\lambda_I}{\gamma_I} \boldsymbol{\mu}_I \cdot \hat{\mathbf{j}}_d(\mathbf{R}_I) = \mu_{I\alpha} \hat{\sigma}_{\alpha\beta}^d(\mathbf{R}_I) B_\beta, \quad (7)$$

which defines the electronic operator

$$\hat{\sigma}_{\alpha\beta}^d(\mathbf{r}) = -\frac{G_F C_s e}{2\sqrt{2}\hbar m_e c^2} \frac{\lambda_I}{\gamma_I} \epsilon_{\alpha\beta\gamma} \sum_{i=1}^n r_{i\gamma} \delta(\mathbf{r}_i - \mathbf{r}). \quad (8)$$

Allowing for usual tensor notation, the Einstein summation convention for repeated Greek indices is in force, and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita pseudotensor. For $\mathbf{r} = \mathbf{R}_I$, the position of nucleus I ,

$$\hat{\sigma}_{\alpha\beta}^{dI} \equiv \hat{\sigma}_{\alpha\beta}^d(\mathbf{R}_I), \quad (9)$$

is the diamagnetic contribution to the PV shielding operator at nucleus I .

Within Rayleigh-Schrödinger perturbation theory, the paramagnetic term in Eq. (6), $H_{PV}^{\mu_I}$, couples with Van Vleck Hamiltonian H^B describing the interaction of the orbital magnetic dipole moment \mathbf{m} of the electrons with the external field [16]. Van Vleck Hamiltonian is

$$H^B = -\mathbf{m} \cdot \mathbf{B}, \quad \mathbf{m} = -\frac{e}{2m_e c} \mathbf{L}, \quad (10)$$

where \mathbf{L} is the electronic angular momentum. The second-order PV interaction energy of the molecule in the $|a\rangle$ electron state with the external field is thus

$$W_{PV}^{(2)}(\boldsymbol{\mu}_I, \mathbf{B}) = \langle a | H_{PV}^{\mu_I B}(\mathbf{R}_I) | a \rangle - \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \times \text{Re}(\langle a | H_{PV}^{\mu_I}(\mathbf{R}_I) | j \rangle \langle j | H^B | a \rangle). \quad (11)$$

PV contributions to nuclear shielding constants are obtained as the derivative of this energy with respect to the external field \mathbf{B} and the nuclear magnetic moment $\boldsymbol{\mu}_I$.

The diamagnetic contributions to PV shielding are the expectation values of operator (9):

$$\sigma_{\alpha\beta}^{dI} = \langle a | \hat{\sigma}_{\alpha\beta}^{dI} | a \rangle. \quad (12)$$

Since this tensor is antisymmetric in the indices α and β , it does not contribute to the trace of the total shielding tensor. The off-diagonal diamagnetic PV contributions could only be observed in anisotropic phases.

The paramagnetic contribution to the shielding can be expressed in the form

$$\sigma_{\alpha\beta}^{pI} = \frac{G_F C_s e}{2\sqrt{2}\hbar m_e c^2} \frac{\lambda_I}{\gamma_I} \{ \hat{\mathbf{j}}_{p\alpha}(\mathbf{R}_I), L_\beta \}_{-1}, \quad (13)$$

where we introduced the propagator

$$\{ \hat{\mathbf{j}}_{p\alpha}(\mathbf{r}), L_\beta \}_{-1} = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \text{Re}(\langle a | \hat{\mathbf{j}}_{p\alpha}(\mathbf{r}) | j \rangle \langle j | L_\beta | a \rangle). \quad (14)$$

These equations were implemented in the SYSMO code [17,18] at the coupled Hartree Fock (CHF) level using an iterative density matrix approach [19]. Details on the CHF perturbation theory can be found in the diagrammatic analysis by Caves and Karplus [20].

III. ORIGIN DEPENDENCE OF PV NUCLEAR MAGNETIC SHIELDING

Upon a translation of the coordinate origin $\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}$, the angular momentum operator transforms as

$$L_\beta(\mathbf{r}'') = L_\beta(\mathbf{r}') - \epsilon_{\beta\gamma\delta} d_\gamma P_\delta. \quad (15)$$

Accordingly, the paramagnetic and diamagnetic contributions to PV nuclear magnetic shielding transform as

$$\sigma_{\alpha\beta}^{pI}(\mathbf{r}'') = \sigma_{\alpha\beta}^{pI}(\mathbf{r}') - \frac{G_F C_s e}{2\sqrt{2}\hbar m_e c^2} \frac{\lambda_I}{\gamma_I} \epsilon_{\beta\gamma\delta} d_\gamma \{ \hat{\mathbf{j}}_{p\alpha}(\mathbf{R}_I), P_\delta \}_{-1}, \quad (16)$$

$$\sigma_{\alpha\beta}^{dI}(\mathbf{r}'') = \sigma_{\alpha\beta}^{dI}(\mathbf{r}') + \frac{G_F C_s e}{2\sqrt{2}\hbar m_e c^2} \frac{\lambda_I}{\gamma_I} \epsilon_{\alpha\beta\gamma} d_\gamma \times \left\langle a \left| \sum_{i=1}^n \delta(\mathbf{r}_i - \mathbf{R}_I) \right| a \right\rangle. \quad (17)$$

In the case of optimal electronic wave functions, one can use the off-diagonal hypervirial relation

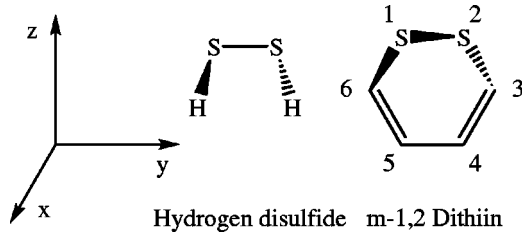


FIG. 1. Molecules studied with orientation and position numbering for 1,2 dithiin.

$$\langle j|P_{\delta}|a\rangle = i m_e \omega_{ja} \langle j|R_{\delta}|a\rangle \quad (18)$$

to transform Eq. (16) and show that the sum of the right-hand side in Eqs. (16) and (17) is independent of the translation vector \mathbf{d} , i.e., the corrections to the paramagnetic and diamagnetic contributions due to a shift in the coordinate system cancel each other. In other words, the total nuclear magnetic shielding

$$\sigma_{\alpha\beta}^I = \sigma_{\alpha\beta}^{pI} + \sigma_{\alpha\beta}^{dI} \quad (19)$$

is origin independent.

The constraint for translational invariance obtained from Eqs. (16) and (17) is

$$\{\hat{j}_{p\alpha}(\mathbf{R}_I), P_{\delta}\}_{-1} = \delta_{\alpha\delta} \left\langle a \left| \sum_{i=1}^n \delta(\mathbf{r}_i - \mathbf{R}_I) \right| a \right\rangle. \quad (20)$$

The degree to which relationship (20) is satisfied in computations relying on the algebraic approximation provides an intrinsic measure of accuracy for the computed PV shifts (19).

We recall that the change in coordinate system $\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}$ amounts to a gauge transformation of the vector potential $\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla f$ with generating function $f(\mathbf{r}) = -\frac{1}{2} \mathbf{B} \times \mathbf{d} \cdot \mathbf{r}$. In the special case when the origin of the gauge is on nucleus I , the corresponding diamagnetic PV contribution (17) vanishes. Therefore, PV contributions can be evaluated for this choice of origin by considering only the paramagnetic contribution. In practice, since one should repeat the calculation moving the origin on each nucleus whose shielding is required, this choice is inconvenient for *ab initio* computations on large molecules. It would generally be preferable to perform only one iterative calculation with a given origin, e.g., the molecular center of mass, and to evaluate both diamagnetic and paramagnetic contributions.

IV. COMPUTATIONAL DETAILS

Two molecules were investigated, namely, m -1,2 dithiin at equilibrium geometry and hydrogen disulfide with various dihedral angles. Schematic geometries for these molecules are reported in Fig. 1 with atomic numbering and Cartesian axes orientation. The geometry for m

rs-1,2 dithiin was optimized at the DFT level [21] with 6-31G* basis set. The geometry for hydrogen disulfide was optimized at the density functional theory (DFT) level [21] with 6-31G** basis set for each preset value of the dihedral angle.

TABLE I. Computed parity-violating contributions to nuclear magnetic shielding tensors in H_2S_2 for various dihedral angles ϕ . Units are in parentheses next to atomic labels.

ϕ	H (10^{-11} ppm)			$1/3(xx+yy+zz)$
	xx	yy	zz	
30°	1.37	-1.28	-3.02	-0.98
60°	3.10	-1.65	-5.21	-1.25
90°	4.80	0.03	-5.52	-0.23
120°	5.14	1.95	-4.21	0.96
150°	3.37	2.14	-1.99	1.17
ϕ	S (10^{-8} ppm)			$1/3(xx+yy+zz)$
	xx	yy	zz	
30°	-35.54	-2.31	20.35	-5.83
60°	-51.23	-1.78	36.28	-5.57
90°	-48.21	-1.71	48.14	-0.59
120°	-35.71	-3.61	51.42	4.03
150°	-18.88	-3.84	34.82	4.03

For the computation of PV contributions to nuclear magnetic shielding, uncontracted Gaussian basis sets were used. These had the form ($12s\ 9p\ 3d\ 1f/8s\ 3p\ 1d$) [22] for hydrogen disulfide and ($12s\ 9p\ 6d/11s\ 7p\ 4d/7\ 1p$) [23] for 1,2 dithiin. Due to the small size of the molecules investigated, only the paramagnetic term was computed with the gauge origin set on each atom unique by symmetry.

V. RESULTS AND DISCUSSION

The computed PV contributions to the nuclear shielding tensors for H_2S_2 and m -1,2 dithiin are reported in Tables I and II.

According to current estimates for optimal nuclear magnetic resonance (NMR) resolution [24], the values we report are several orders of magnitude below detection limit. For instance, the predicted PV effect on sulfur's chemical shift is approximately 5×10^{-8} ppm for 1,2 dithiin. As this effect has opposite signs for two enantiomers, the observable difference is predicted at twice this amount, i.e., 1×10^{-7} ppm. This value corresponds to a difference in resonance frequencies $\Delta\nu$ for ^{33}S , which can be expressed as follows. If the intensity of the applied magnetic field B is expressed in units of Tesla, one ppm corresponds to approximately $B \times 3$ Hz, hence $\Delta\nu \approx B \times 3 \times 10^{-7}$ Hz. In order to reach the maximal theoretical resolution of 6×10^{-3} Hz [24] a magnetic field of the order of 2×10^4 Tesla would be re-

TABLE II. Computed parity-violating contributions to nuclear magnetic shielding tensors in m -1,2 dithiin. All values are in 10^{-10} ppm.

Component	S	C(3)	C(4)	H(3)	H(4)
xx	-2201.8	82.2	-48.2	-0.226	-0.188
yy	-5558.9	-128.7	438.7	0.415	-0.067
zz	6365.8	49.5	-27.4	-0.028	0.067
Average	-465.0	1.0	121.0	0.054	-0.063

quired, which is approximately three orders of magnitude larger than presently used in high-resolution NMR spectrometers.

As pointed out by Schwerdtfeger [25], based on the results from Ref. [15] one can expect the frequency shift to scale with the atomic number Z as approximately $Z^{2.7}$. Hence, systems containing atoms as heavy as polonium ($Z = 84$), with predicted frequency shifts two orders of magnitude larger than those reported in this article, would still be below experimental resolution.

VI. CONCLUSIONS

A gauge-invariant formulation of parity-violation (PV) contributions to nuclear magnetic shielding tensor and chemical shift arising from weak-nuclear interactions was developed. Within this framework, sum rules were derived for potential assessment of computational accuracy. The PV

contributions to chemical shifts for two molecules were then estimated with *ab initio* techniques.

It is found that for the molecules considered PV effects are several orders of magnitude below current experimental accuracy. Although this does not rule out nuclear magnetic resonance (NMR) spectroscopy as a tool for potential PV detection in molecules containing heavy atoms, our results suggest that such detection will prove impossible for atoms as light as sulfur and even in the presence of heavy atoms it may require substantially different molecular systems.

ACKNOWLEDGMENTS

Financial support for the present research from the European research and training network "Molecular Properties and Materials (MOLPROP)," Contract No. HPRN-CT-2000-00013, from the Italian MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), via 60% and 40% funds, is gratefully acknowledged.

-
- [1] T.D. Lee and C.N. Yang, Phys. Rev. **104**, 254 (1956).
 [2] D.W. Rein, J. Mol. Evol. **4**, 15 (1974).
 [3] V.S. Letokhov, Phys. Lett. **53A**, 275 (1975).
 [4] J.K. Laerdahl and P. Schwerdtfeger, Phys. Rev. A **60**, 4439 (1999).
 [5] A.S. Lahamer, S.M. Mahurin, R.N. Compton, D. House, J.K. Laerdahl, M. Lein, and P. Schwerdtfeger, Phys. Rev. Lett. **85**, 4470 (2000).
 [6] M. Quack and J. Stohner, Phys. Rev. Lett. **84**, 3807 (2000).
 [7] F. Faglioni and P. Lazzeretti, Phys. Rev. A **67**, 032101 (2003).
 [8] C. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, C.J. Bordé, and C. Chardonnet, Phys. Rev. Lett. **83**, 1554 (1999).
 [9] P. Schwerdtfeger, J.K. Laerdahl, and C. Chardonnet, Phys. Rev. A **65**, 042508 (2002).
 [10] M. Ziskind, C. Daussy, T. Marrel, and C. Chardonnet, Eur. Phys. J. D **20**, 219 (2002).
 [11] S.A. Blundell, J. Sapirstein, and W.R. Johnson, Phys. Rev. D **45**, 1602 (1992).
 [12] M.G. Kozlov and L.N. Labzowsky, J. Phys. B **28**, 1933 (1995).
 [13] A.L. Barra, J.B. Robert, and L. Wiesenfeld, Europhys. Lett. **5**, 217 (1988).
 [14] A.L. Barra and J.B. Robert, Mol. Phys. **88**, 875 (1996).
 [15] G. Laubender and R. Berger, ChemPhysChem **4**, 395 (2003).
 [16] J.H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).
 [17] P. Lazzeretti, M. Malagoli, and R. Zanasi, CNR Research Report No. 1/67, 1991 (unpublished).
 [18] M. Gnani, P. Lazzeretti, A. Ligabue, U. Pincelli, and A. Soncini, Comput. Phys. Commun. **144**, 130 (2002).
 [19] G. Diercksen and R. McWeeny, J. Chem. Phys. **44**, 3554 (1966).
 [20] T.C. Caves and M. Karplus, J. Chem. Phys. **50**, 3649 (1969).
 [21] Becke3LYP functional as provided in GAUSSIAN98 [26]: exchange functional from Ref. [27], correlation functional from Ref. [28] implemented as described in Ref. [29].
 [22] The basis set used for H₂S₂ is the same used in Ref. [30], i.e., *sp* substratum from Ref. [31] with polarization functions from Ref. [32].
 [23] The basis set used for 1,2 dithiin was based on *sp* substratum from Ref. [31] for S and Ref. [33] for H and C. Polarization function exponents are 14.4, 4.8, 1.6, 0.4, 0.133, and 0.0433 for *d* on sulfur, 1.610, 0.430, 0.150, and 0.062 for *d* on carbon, and 0.540 for *p* on hydrogen.
 [24] J.B. Robert and A.L. Barra, Chirality **13**, 699 (2001).
 [25] P. Schwerdtfeger (private communication).
 [26] M.J. Frisch *et al.*, GAUSSIAN 98, REVISION A.7 (Gaussian, Inc., Pittsburgh, PA, 1998).
 [27] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
 [28] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).
 [29] B. Miehlich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).
 [30] P. Lazzeretti and R. Zanasi, Chem. Phys. Lett. **279**, 349 (1997).
 [31] A.D. McLean and G.S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
 [32] D.E. Woon and T.H. Dunning, J. Chem. Phys. **98**, 1358 (1993).
 [33] F.B. van Duijneveldt, IBM Research Report No. RJ 945, 1971 (unpublished).