

## Theoretical estimates of the anapole magnetizabilities of C<sub>4</sub>H<sub>4</sub>X<sub>2</sub> cyclic molecules for X=O, S, Se, and Te

G. I. Pagola, M. B. Ferraro, P. F. Provasi, S. Pelloni, and P. Lazzeretti

Citation: *The Journal of Chemical Physics* **141**, 094305 (2014); doi: 10.1063/1.4893991

View online: <http://dx.doi.org/10.1063/1.4893991>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/141/9?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

Photodissociation of (SO<sub>2</sub>XH) Van der Waals complexes and clusters (XH = C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) excited at 32 040–32090 cm<sup>-1</sup> with formation of HSO<sub>2</sub> and X

*J. Chem. Phys.* **140**, 054304 (2014); 10.1063/1.4863445

Microwave, infrared-microwave double resonance, and theoretical studies of C<sub>2</sub>H<sub>4</sub>H<sub>2</sub>S complexa)

*J. Chem. Phys.* **139**, 104303 (2013); 10.1063/1.4819787

Experimental and theoretical studies of the O(3P) + C<sub>2</sub>H<sub>4</sub> reaction dynamics: Collision energy dependence of branching ratios and extent of intersystem crossing

*J. Chem. Phys.* **137**, 22A532 (2012); 10.1063/1.4746758

The C<sub>6</sub>H<sub>6</sub>–(H<sub>2</sub>O)<sub>2</sub> complex: Theoretical predictions of the structure, energetics, and tunneling dynamics

*J. Chem. Phys.* **106**, 849 (1997); 10.1063/1.473180

Theoretical analysis of equilibrium geometries and barriers of rotation in molecules H<sub>2</sub>X<sub>2</sub>, with X=O, S, Se, and Te

*J. Chem. Phys.* **82**, 3322 (1985); 10.1063/1.448231

---



**AIP** | Chaos

**CALL FOR APPLICANTS**

Seeking new Editor-in-Chief

# Theoretical estimates of the anapole magnetizabilities of $C_4H_4X_2$ cyclic molecules for $X=O, S, Se, \text{ and } Te$

G. I. Pagola,<sup>1</sup> M. B. Ferraro,<sup>1</sup> P. F. Provasi,<sup>2</sup> S. Pelloni,<sup>3</sup> and P. Lazzeretti<sup>3,a)</sup>

<sup>1</sup>*Departamento de Física, Facultad de Ciencias Exactas y Naturales, and IFIBA, CONICET, Universidad de Buenos Aires, Ciudad Universitaria, Pab. I, (1428) Buenos Aires, Argentina*

<sup>2</sup>*Departamento de Física, Northeastern University, Av. Libertad 5500, W3400 AAS, Corrientes, Argentina*

<sup>3</sup>*Dipartimento di Chimica, Università degli Studi di Modena e Reggio Emilia, via G. Campi 183, 41100 Modena, Italy*

(Received 1 June 2014; accepted 12 August 2014; published online 3 September 2014)

Calculations have been carried out for  $C_4H_4X_2$  cyclic molecules, with  $X=O, S, Se, \text{ and } Te$ , characterized by the presence of magnetic-field induced toroidal electron currents and associated orbital anapole moments. The orbital anapole induced by a static nonuniform magnetic field  $\mathbf{B}$ , with uniform curl  $\mathbf{C} = \nabla \times \mathbf{B}$ , is rationalized via a second-rank anapole magnetizability tensor  $a_{\alpha\beta}$ , defined as minus the second derivative of the second-order interaction energy with respect to the components  $C_\alpha$  and  $B_\beta$ . The average anapole magnetizability  $\bar{a}$  equals  $-\bar{\chi}$ , the pseudoscalar obtained by spatial averaging of the dipole-quadrupole magnetizability  $\chi_{\alpha,\beta\gamma}$ . It has different sign for  $D$  and  $L$  enantiomeric systems and can therefore be used for chiral discrimination. Therefore, in an isotropic chiral medium, a homogeneous magnetic field induces an electronic anapole  $\mathcal{A}_\alpha$ , having the same magnitude, but opposite sign, for two enantiomorphs. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4893991>]

## I. INTRODUCTION

The existence of a vector  $\mathcal{A}$ , associated to an electric current flowing on the surface of a torus, for which Kompaneets proposed the name *anapole*, was first acknowledged by Zel'dovich.<sup>1</sup> Multipole expansions in classical and quantum field theory, including a family of toroidal moments<sup>2-4</sup> and some peculiar charge-current arrangements,<sup>3,5-7</sup> have been considered later on in connection with magnetoelectricity.<sup>8</sup> More recently, anapole and related moments have been discussed within the context of magnetic multipolar contact fields,<sup>9</sup> and within the framework of parity violation effects.<sup>10-15</sup> The nuclei of certain elements are endowed with an anapole<sup>16,17</sup> and the anapole moment of cesium has been calculated<sup>18</sup> and measured.<sup>19</sup> Other measuring procedures have been discussed.<sup>20,21</sup> Connections between enantiomorphism and electronic anapole moments have been postulated for chiral molecular radicals.<sup>22</sup>

The occurrence of an anapole moment has been inferred by a fundamental premise relying on group-theoretical basis,<sup>23-27</sup> and it has been predicted for diatomic molecules,<sup>28</sup> chiral molecules,<sup>22</sup> and toroidal nanotubes.<sup>29</sup> Attestations of nuclear anapole moments in solid-state nuclear magnetic resonance have been discussed.<sup>30</sup> A magnetic field can induce toroidal flow in the electrons of molecules.<sup>31-33</sup> In the terminology of Schmid,<sup>26</sup> the anapole moment is an axio-polar vector, which has opposite sign for the two mirror-images forms of a chiral species, and, in principle, it may be used for chiral discrimination of certain species possessing a magnetic-field induced anapole, e.g., dithiins, associated to toroidal electron flow.<sup>34</sup> The orbital anapole moment of a molecule is an intrinsic

electronic property which can be rationalized via anapole magnetizabilities,<sup>29,35-42</sup> allowing for a magnetic multipole expansion based on the Bloch gauge<sup>43-45</sup> later rediscovered by others.<sup>46-49</sup> A simple compact expression,<sup>50-55</sup> defining a gauge usually referred to as Poincaré's,<sup>50,55,56</sup> yields a power series for the vector potential equivalent to Bloch's.<sup>57-60</sup>

The present paper is aimed at computing translationally invariant diagonal components and average values of anapole magnetizability in cyclic compounds with chemical formula  $C_4H_4X_2$ , with  $X=O, S, Se, \text{ and } Te$ . These molecules are characterized by axial chirality due to the absence of symmetry planes. Therefore, according to the IUPAC nomenclature, the  $M$  and  $P$  letters are used to distinguish two enantiomers. All molecules studied are of  $M$  form. A few essential relationships used in the calculation are reported in Sec. II. An extended theoretical approach outlined in previous papers<sup>36,37,40,41</sup> has been employed.

The molecular systems taken into account have been studied in previous papers, showing that the magnetically induced electronic current density vector field is characterized by the presence of toroidal flow, expected to give rise to orbital anapole moments,<sup>31,40,41</sup> which can be related to mixed magnetic multipole magnetizabilities. As reported previously,<sup>34</sup> chiral distortions may give rise to anapolar current density lines, i.e., lines spiraling around a topological torus that has been predicted for big molecules with nuclei arranged on a torus surface.<sup>29</sup>

Calculations have been carried out at the Hartree-Fock level of theory, using basis set of increasing size and quality to estimate limit values. As the mixed multipole magnetizabilities vary with the origin of the coordinate system, see Sec. II, two different origins were considered in preliminary test calculations on the dioxin molecule. Results are reported as the

<sup>a)</sup>E-mail: lazzeret@unimo.it

supplementary material<sup>80</sup> and discussed in Sec. III. Conclusions and outlook are presented in Sec. IV.

## II. OBSERVABLE ELECTRONIC PROPERTIES OF A MOLECULE IN NONUNIFORM MAGNETIC FIELDS

We consider a diamagnetic molecule in the presence of a nonuniform magnetic field with flux density  $\mathbf{B}$ , assuming for simplicity that the curl  $\mathbf{C} = \nabla \times \mathbf{B}$  is uniform, and neglecting contributions from higher derivatives. The curl  $\mathbf{C}$  describes only the antisymmetric part of the tensor  $B_{\alpha\beta} \equiv \nabla_\alpha B_\beta$ . The trace of  $B_{\alpha\beta}$  vanishes, as it is equivalent to the divergence of  $\mathbf{B}$ ,

$$B_{\alpha\alpha} \equiv \nabla \cdot \mathbf{B} = 0.$$

It is also supposed that the molecular response is linear. Standard tensor formalism is employed throughout this article, e.g., the Einstein convention of implicit summation over two repeated Greek subscripts is in force and  $\epsilon_{\alpha\beta\gamma}$  is the Levi-Civita tensor. The SI system of units has been chosen. The notation adopted in previous references<sup>36,37,40,41</sup> is used within the multipolar Bloch gauge<sup>43</sup> for the vector potential. These papers report the theory in detail.

Assuming that the applied magnetic field is time independent, second-order Rayleigh-Schrödinger perturbation theory (RSPT) is applied to obtain the second-rank magnetizability  $\chi_{\alpha\beta}$  and the third-rank magnetizability  $\chi_{\alpha\beta,\gamma} \equiv \chi_{\gamma,\alpha\beta}$  of a molecule in the presence of a nonhomogeneous time-independent magnetic field.<sup>36,37,40,45</sup>

In disordered media the tensor  $\chi_{\alpha\beta,\gamma}$  has an isotropic part  $\bar{\chi}\epsilon_{\alpha\beta\gamma}$ , and the corresponding pseudoscalar

$$\begin{aligned} \bar{\chi} &= \frac{1}{6}\chi_{\alpha\beta,\gamma}\epsilon_{\alpha\beta\gamma} \\ &= \frac{1}{6}(\chi_{xy,z} - \chi_{xz,y} + \chi_{yz,x} - \chi_{yx,z} + \chi_{zx,y} - \chi_{zy,x}) \end{aligned} \quad (1)$$

is different from zero for a chiral molecule.

Allowing for the Hellmann-Feynman theorem,<sup>61</sup> all the relevant properties, e.g., the induced magnetic dipole and quadrupole moments, second- and third-rank magnetizability, anapole magnetizability, are obtained by differentiating either the induced magnetic moments or the electronic interaction energy  $W$ .<sup>36</sup> In particular, the derivative of  $W$  with respect to the components of  $\mathbf{C}$  defines the components of the anapole polar vector<sup>36,40,41</sup>

$$-\frac{\partial W}{\partial C_\gamma} = \mathcal{A}_\gamma = -\frac{1}{2}\epsilon_{\alpha\beta\gamma}\chi_{\alpha\beta,\delta}B_\delta, \quad (2)$$

induced in the electrons of the molecule.<sup>36,40,41</sup> In this equation only the contribution arising from the interaction with the nonuniform magnetic field has been included.

The nonsymmetric second-rank tensor

$$a_{\gamma\delta} = -\frac{\partial^2 W}{\partial B_\delta \partial C_\gamma} = \frac{\partial \mathcal{A}_\gamma}{\partial B_\delta} = -\frac{1}{2}\epsilon_{\alpha\beta\gamma}\chi_{\alpha\beta,\delta} \quad (3)$$

is interpreted as anapole magnetizability. It is expedient to split it up into isotropic, symmetric, and antisymmetric parts,

$\bar{a}\delta_{\alpha\beta}$ ,  $a_{\alpha\beta}^{(S)}$ , and  $a_{\alpha\beta}^{(A)}$ , respectively,

$$a_{\alpha\beta} = \bar{a}\delta_{\alpha\beta} + (a_{\alpha\beta}^{(S)} - \bar{a}\delta_{\alpha\beta}) + \epsilon_{\alpha\beta\gamma}a_\gamma^{(A)}, \quad (4)$$

$$\bar{a} = \frac{1}{3}a_{\alpha\alpha}, \quad (5)$$

$$a_{\alpha\beta}^{(S)} = \frac{1}{2}(a_{\alpha\beta} + a_{\beta\alpha}), \quad (6)$$

$$a_\gamma^{(A)} = \frac{1}{2}\epsilon_{\alpha\beta\gamma}a_{\alpha\beta}. \quad (7)$$

Thus  $a_{\alpha\beta}^{(S)} - \bar{a}\delta_{\alpha\beta}$  constitutes the symmetric traceless anisotropic part of the  $a_{\alpha\beta}$  tensor.  $\bar{a}$ ,  $a_\gamma^{(A)}$ , and  $a_{\alpha\beta}^{(S)}$  transform as the spherical harmonics  $Y_{00}$ ,  $Y_{1m}$ , and  $Y_{2m}$ .

The averaged trace, Eq. (5) of the  $a_{\alpha\beta}$  anapole magnetizability, Eqs. (3) and (4), is invariant in a translation of coordinate system and satisfies the identity<sup>36</sup>  $\bar{a} = -\bar{\chi}$ . The symmetry properties of the  $a_{\alpha\beta}$  anapole magnetizability under parity  $P$  and time reversal  $T$  are the same as for the mixed electric dipole-magnetic dipole polarizability (MEMDP) tensor  $\kappa'_{\alpha\beta}$ , taken into account to rationalize the optical rotatory power of chiral systems.<sup>44,45,62,63</sup> Therefore,  $\bar{a}$  is odd under parity and even under time reversal, it vanishes in achiral molecules, it has the same magnitude but opposite sign for two enantiomers, and therefore can, in principle, be used for chiral discrimination as the anapole vector, Eq. (2).<sup>41</sup> In fact, in disordered phase, gas or solution, the orbital electronic anapole

$$\mathcal{A} = -\bar{\chi}\mathbf{B} \quad (8)$$

induced by an external magnetic field has opposite direction in two enantiomeric molecules.

To complete the analogy between  $\kappa'_{\alpha\beta}(-\omega; \omega)$  and  $a_{\alpha\beta}$ , whereas the diagonal components of the former are translationally invariant within the reference frame defined by the eigenvectors of the dynamic electric dipole polarizability  $\alpha_{\alpha\beta}(-\omega; \omega)$  at the same angular frequency  $\omega$ ,<sup>63</sup> the diagonal components (and the trace) of the latter are origin independent in the principal axis system of the symmetric  $\chi_{\alpha\beta}$  tensor.<sup>36</sup> The induced anapole, Eq. (8), aligned with the applied uniform magnetic field in gas and liquid media, is origin independent and, in principle, measurable.

It has been emphasized<sup>36</sup> that the origin dependence of mixed dipole-quadrupole magnetizability  $\chi_{\alpha,\beta\gamma}$  and anapole magnetizability  $a_{\alpha\beta}$  is an essential distinctive attribute, which cannot be overcome by using gauge-including atomic orbitals (GIAO).<sup>64,65</sup> This feature has been illustrated in a previous paper,<sup>36</sup> pointing out that anapole moments and anapole magnetizabilities are in general only defined relative to a reference point and that this reference point is not a gauge degree of freedom. Moreover, the Hellman-Feynman theorem is not, in general, satisfied if GIAO's are employed, therefore the anapole magnetizabilities calculated via finite perturbation theory as second derivatives of the energy, and/or first derivatives of the anapole moment, Eq. (3), are potentially different,<sup>36</sup> according to a general statement, see p. 90 of the Epstein book.<sup>61</sup> This has actually been verified in a recent calculation.<sup>35</sup> At any rate, Tellgren and Fliegl<sup>35</sup> have shown

that GIAO's are indeed leading to a faster basis set convergence and thus remain important.

### III. CALCULATIONS OF MAGNETIZABILITIES FOR $C_4H_4X_2$ MOLECULES IN A MAGNETIC FIELD WITH UNIFORM GRADIENT

The dipole magnetizability  $\chi_{\alpha\beta}$ , the mixed dipole-quadrupole magnetizability  $\chi_{\alpha,\beta\gamma}$ , and the anapole magnetizability  $a_{\alpha\beta}$  of the 1,2-*M* enantiomer of cyclic  $C_4H_4X_2$  molecules, with  $X = O, S, Se,$  and  $Te$ , in the singlet ground state, have been computed at the Hartree-Fock level of theory via a computer program interfacing with the DALTON package.<sup>66</sup> The  $C_4H_4X_2$  compounds are endowed with *axial chirality*, a peculiar case of chirality made distinctive by the absence of a stereogenic center, which constitutes the widespread and typical hallmark of most enantiomeric species. Instead, the structure of the C-X-X-C moiety present in these molecules is characterized by a spatial arrangement that is not superimposable on its mirror image, giving rise to *helicity* in connection with screw-shaped geometry. The letter *P* (plus) is used as a stereodescriptor to denote a right-handed helix, whereas *M* (minus) corresponds to a left-handed helix, see Fig. 1.

The equilibrium geometry of each system is the same as in previous papers.<sup>67,68</sup> Atomic coordinates are reported in the supplementary material.<sup>80</sup> The  $z$  axis coincides with the direction of the twofold symmetry axis of the  $C_2$  point group, which characterizes the chiral  $C_4H_4X_2$  compounds investigated here. The 1,2-dioxin molecule is unstable and cannot be isolated.<sup>69</sup>

Extended correlation consistent, gaugeless basis sets together with augmented functions, from the compilation by Dunning and co-workers,<sup>70-72</sup> contracted Sadlej basis sets,<sup>73-77</sup> and two large basis sets, MODENA I and MODENA II, carrying optimized polarization functions for magnetic properties,<sup>67,68</sup> were adopted. This choice was oriented by the characteristics of the response properties studied. Whereas the second-rank magnetizabilities account for the electron distribution in the intermediate regions of the molecular domain,

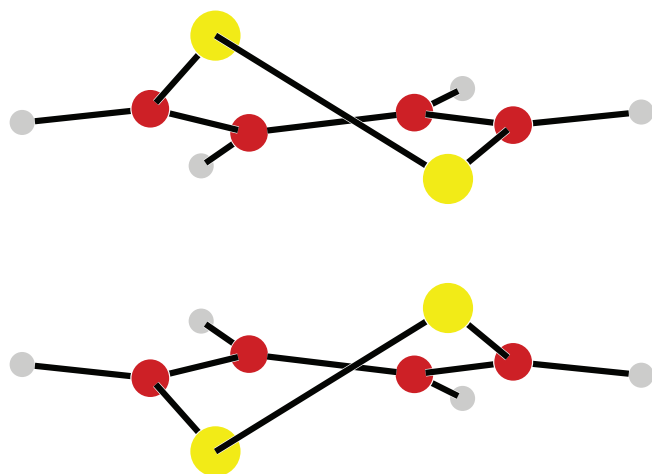


FIG. 1. The 1,2-*P* (above) and 1,2-*M* (below) enantiomers of the  $C_4H_4X_2$  molecules.

weighed by the angular momentum  $\hat{l}_\alpha$  and by the second moment operator  $r_\alpha r_\beta$ , the third-rank and the anapole magnetizabilities are expected to depend also on the boundaries of the charge density, according to the nature of the perturbing operators, which involve an additional  $r_\alpha$  factor, see the definitions, Eqs. (6), (7), (16), and (17) of a previous paper.<sup>36</sup> For these reasons, basis sets containing more diffuse polarization functions, adopted for accurate calculation of electric dipole polarizabilities,<sup>73-77</sup> have been tested to predict  $\chi_{\alpha,\beta\gamma}$  and  $a_{\alpha\beta}$ . Basis sets MODENA I and II, which had been explicitly constructed to compute near Hartree-Fock electric and magnetic response properties, represent a good compromise between size and accuracy for dioxin and dithiin, respectively.

We found that the use of basis sets of increasing quality from Dunning *et al.*<sup>70-72</sup> is recommendable to study convergence of calculated magnetizabilities to limit values. In particular, the largest ones are suitable enough for  $\chi_{\alpha\beta}$ . A preliminary test was done on the dioxin molecule  $C_4H_4O_2$ , using the equations for the change of magnetic properties in a coordinate translation.<sup>36</sup> These relationships are strictly valid only in the ideal case of exact and optimal variational wavefunctions.<sup>36,37,40</sup> Within the algebraic approximation, better and better results are obtained by systematically improving the features of the basis set. Therefore, we attempted at fulfilling these relationships so that basis set saturation could be assessed. Accordingly, three Dunning basis sets<sup>70-72</sup> of increasing size and characteristics, hereafter referred to as DZ, QZ, and 5Z for brevity to designate aug-cc-pCVDZ, aug-cc-pVQZ, and aug-cc-pV5Z, were preliminarily considered to estimate the degree of convergence of calculated magnetizabilities  $\chi_{\alpha\beta}$  and  $\chi_{\alpha,\beta\gamma}$ , anapole magnetizabilities  $a_{\alpha\beta}$ , Eq. (3), and pseudoscalar  $\bar{\chi} = -\bar{a}$ . The results of the convergence test are reported in detail in the supplementary material<sup>80</sup> for interested readers, see, however, Table I for a comprehensive test involving all the other basis sets.

Owing to the antisymmetry of the Levi-Civita unit tensor, a translation of  $d_y = -1 \text{ \AA}$ , used on applying Eqs. (51) and (53) of our previous paper,<sup>36</sup> leaves  $a_{yy}$  unchanged irrespective of basis set size, as can be checked in Tables X and XIII, XI and XIV, XII and XV of the supplementary material,<sup>80</sup> respectively, for  $a_{\alpha\beta}(r')$  and  $a_{\alpha\beta}(r'')$ . Therefore, this component cannot be used to check the convergence degree.

On the other hand, convergence has been achieved to a satisfactory extent for the other diagonal components,  $a_{xx}$  and  $a_{zz}$ , within the series DZ, QZ, and 5Z, see Tables X–XII for  $r'$  origin and Tables XIII–XV for  $r''$  origin in the supplementary material.<sup>80</sup> The average anapole magnetizability is stable, with value  $\bar{a}(r') = \bar{a}(r'') = 0.357$  a.u., calculated via QZ and 5Z basis sets. The results obtained by the 5Z basis set for  $a_{\alpha\beta}(r'')$  by applying Eq. (53) of Ref. 36, see Table XVI, are quite close to those of Table XV, calculated assuming the origin  $r''$ .

The same estimate has been computed for  $\bar{a}$  corresponding to different origins within the reference frame of the eigenvectors of the second-rank magnetizability, see Tables XVIII, XIX, XXI, and XXII. However, the degree of convergence of the individual diagonal components  $a_{xx}$  and  $a_{zz}$  evaluated within this coordinate system is lower than that arrived

TABLE I. Basis set convergence of the anapole magnetizability of 1,2-M-dioxin referred to the principal axis system of the second-rank magnetizability, in a.u.<sup>a</sup>

Basis	$a_{\alpha\beta}$			$\bar{a}$
aug-cc-pCVDZ	0.065	2.040	0.000	0.369
	-3.492	1.226	0.000	
	0.000	0.000	-0.183	
Sadlej-pVTZ	0.703	2.208	0.000	0.368
	-4.178	0.640	0.000	
	0.000	0.000	-0.241	
aug-cc-pVTZ/Sadlej-pVTZ	0.387	-0.283	0.000	0.359
	-2.319	0.803	0.000	
	0.000	0.000	-0.112	
aug-cc-pVQZ/aug-cc-pVTZ	-0.184	0.590	0.000	0.358
	-2.147	1.241	0.000	
	0.000	0.000	0.018	
aug-cc-pVTZ	0.377	1.964	0.000	0.357
	-3.761	0.709	0.000	
	0.000	0.000	-0.013	
aug-cc-pVQZ	-0.236	1.970	0.000	0.357
	-3.157	1.268	0.000	
	0.000	0.000	0.039	
aug-cc-pV5Z	-0.431	2.156	0.000	0.357
	-2.804	1.449	0.000	
	0.000	0.000	0.054	
MODENA I	1.522	2.467	0.000	0.358
	-2.333	-0.527	0.000	
	0.000	0.000	0.078	

<sup>a</sup>The diagonal components of the  $a_{\alpha\beta}$  tensor are origin independent within this reference system. The conversion factor to SI units is  $e^2 a_0^3 / m_e = 4.175\,756\,62 \times 10^{-39}$  JT<sup>-2</sup>m per molecule, from CODATA Recommended Values of the Fundamental Physical Constants.<sup>79</sup>

at for the trace, as can be observed by comparing Tables XIX and XXII (we recall that the predictions would be exactly the same for different origins in the case of complete basis sets).

Allowing for these tests, and for the consistency between computed third-rank  $\chi_{\alpha,\beta\gamma}$  and fourth-rank  $\chi_{\alpha\beta,\gamma\delta}$  magnetizability from a previous test,<sup>36</sup> one can reasonably assume that the approach developed by us to calculate  $\chi_{\alpha\beta}, \chi_{\alpha,\beta\gamma}$ , and  $a_{\alpha\beta}$  magnetizabilities of a molecule via RSPT, gives correct numerical predictions.

The results are given in Tables I–IV in SI atomic units (a.u.). Remarkably, the anapole magnetizabilities of cyclic C<sub>4</sub>H<sub>4</sub>X<sub>2</sub> compounds do not seem to be biased by the atomic number of the X atom, for X=O, S, Se, and Te (see Tables I–IV). As regards the dioxin molecule, Dunning's, Sadlej's, and MODENA I basis sets yield theoretical estimates of average anapole magnetizability  $\bar{a}$  close to 0.36 a.u., which can accordingly be considered a near Hartree-Fock values. On the other hand, convergence has not been obtained for the individual diagonal components  $a_{xx}, a_{yy}$ , and  $a_{zz}$  within the reference frame of the  $\chi_{\alpha\beta}$  eigenvalues, displayed in Table I. Results from different basis sets have opposite sign. Such a result is somewhat disappointing, since these diagonal components are translationally invariant,<sup>36</sup> so that their accurate theoretical determination would be quite important in view of experimental detection in ordered phase.

TABLE II. Basis set convergence of the anapole magnetizability of 1,2-M-dithiin referred to the principal axis system of the second-rank magnetizability, in a.u.<sup>a</sup>

Basis	$a_{\alpha\beta}$			$\bar{a}$
Sadlej-pVTZ	0.980	-7.175	0.000	0.003
	4.127	-0.292	0.000	
	0.000	0.000	-0.680	
aug-cc-pVTZ/Sadlej-pVTZ	1.544	-14.393	0.000	-0.016
	10.150	-1.047	0.000	
	0.000	0.000	-0.544	
aug-cc-pVTZ	1.305	-12.254	0.000	-0.035
	8.444	-0.960	0.000	
	0.000	0.000	-0.448	
aug-cc-pVTQZ/aug-cc-pVTZ	1.768	-16.509	0.000	-0.038
	12.607	-1.438	0.000	
	0.000	0.000	-0.445	
aug-cc-pVQZ	1.528	-14.280	0.000	-0.047
	10.322	-1.296	0.000	
	0.000	0.000	-0.373	
aug-cc-pV5Z	0.135	-4.688	0.000	-0.042
	-0.244	0.204	0.000	
	0.000	0.000	-0.464	
MODENA II	-2.304	2.311	0.000	-0.031
	-2.027	2.731	0.000	
	0.000	0.000	-0.521	

<sup>a</sup>See footnote to Table I.

This failure could depend on a number of factors, the slow convergence of the eigenvectors of  $\chi_{\alpha\beta}$  being probably determinant, see Tables X–XII. Therefore, the diagonal components of  $a_{\alpha\beta}$  from MODENA I, which gives the best predictions of second-rank magnetizability from the point of view of a variational theorem<sup>78</sup> on the paramagnetic contributions, Eq. (21) of Ref. 36, to the diagonal components of  $\chi_{\alpha\beta}$ , are possibly more reliable.

TABLE III. Basis set convergence of the anapole magnetizability of 1,2-M-diselenin referred to the principal axis system of the second-rank magnetizability, in a.u.<sup>a</sup>

Basis	$a_{\alpha\beta}$			$\bar{a}$
Sadlej-pVTZ	0.074	13.060	0.000	-0.133
	-13.040	0.220	0.000	
	0.000	0.000	-0.693	
aug-cc-pVTZ/Sadlej-pVTZ	2.466	-17.553	0.000	-0.157
	14.235	-2.417	0.000	
	0.000	0.000	-0.521	
aug-cc-pVTZ	1.369	-7.595	0.000	-0.159
	5.468	-1.476	0.000	
	0.000	0.000	-0.370	
aug-cc-pVQZ/ aug-cc-pVTZ	1.929	-17.450	0.0000	-0.164
	14.876	-2.042	0.000	
	0.000	0.000	-0.3791	
aug-cc-pVQZ	1.985	-15.231	0.000	-0.169
	12.554	-2.045	0.000	
	0.000	0.000	-0.447	

<sup>a</sup>See footnote to Table I.

TABLE IV. Basis set convergence of the anapole magnetizability of 1,2-*M*-ditellurin referred to the principal axis system of the second-rank magnetizability, in a.u.<sup>a</sup>

Basis	$a$			$\bar{a}$
aug-cc-pVTZ/Sadlej-pVTZ	2.061	11.25	-0.000	
	-14.71	-2.023	0.000	
	0.000	-0.000	-1.140	-0.367
Sadlej-pVTZ	-0.293	35.450	0.000	
	-35.33	0.585	0.000	
	0.000	0.000	-1.325	-0.344

<sup>a</sup>See footnote to Table I.

The predictions for 1,2-*M*-dithiin do not appear to have converged, see the change of sign for the diagonal component passing from 5Z to MODENA II basis sets, even if the average  $\bar{a}$  seems to stabilize at a negative value one order of magnitude smaller than dioxin's.

Anapole magnetizabilities of this molecule have been reported by Tellgren and Fliegl<sup>35</sup> using the nonperturbative method implemented in the LONDON code. For the gaugeless aug-cc-pVTZ basis set, the average trace displayed in Table XI of their paper is 0.164 a.u., to be compared with -0.035 in Table II of the present article. Different magnitude should be attributed to the different theoretical approaches employed, analytical RSPT in the present paper and numerical differentiation allowing for finite perturbation theory by Tellgren and Fliegl,<sup>35</sup> and, in part, to the different geometries. The use of Cartesian polarization functions made by these authors, instead of spherical harmonics employed here, is not expected to introduce significant changes. The opposite sign is related to the choice of the enantiomer, the 1,2-*P*-dithiin, made by these authors, see Fig. 1 displaying the different enantiomers. Actually, a calculation allowing for the RSPT scheme adopted here, using the aug-cc-pVTZ basis set and the geometry from Ref. 35, gives  $\bar{a} = 0.230$  a.u., which is close in magnitude and has the same sign as that of Tellgren and Fliegl.<sup>35</sup>

Other values, from the gaugeless aug-cc-pVDZ basis set and from larger basis sets of GIAO orbitals, lie in the range 0.045–0.175 a.u.<sup>35</sup> At any rate, a change of sign for values calculated by different basis sets can be observed in Table XI of Tellgren and Fliegl.<sup>35</sup>

TABLE V. Anapole magnetizability of 1,2-*M*-C<sub>4</sub>H<sub>4</sub>X<sub>2</sub> referred to the principal axis system of the second-rank magnetizability, in a.u., evaluated employing the B3LYP functional.<sup>a</sup>

	$a_{\alpha\beta}$			$\bar{a}$
C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> aug-cc-pVTZ	0.597	1.782	0.000	
	-3.967	1.197	0.000	
	0.000	0.000	-0.060	0.578
C <sub>4</sub> H <sub>4</sub> S <sub>2</sub> aug-cc-pVTZ	1.705	-11.978	0.000	
	8.395	-1.028	0.000	
	0.000	0.000	-0.516	0.054
C <sub>4</sub> H <sub>4</sub> Se <sub>2</sub> aug-cc-pVTZ	1.354	-7.807	0.000	
	5.955	-1.370	0.000	
	0.000	0.000	-0.414	-0.143

<sup>a</sup>See footnote to Table I.

On the other hand, the results arrived at for diselenin in Table III seem to be quite stable, although we could not afford using larger basis sets. The estimates for the anapole magnetizabilities of C<sub>4</sub>H<sub>4</sub>Te<sub>2</sub> are not expected to be of Hartree-Fock accuracy. In addition, one can presume that relativistic effects may bias  $a_{\alpha\beta}$  of this molecule to a significant extent.

A limited attempt has been made at estimating the effects of electron correlation on the  $a_{\alpha\beta}$  tensor employing Density Functional Theory (DFT). The B3LYP functional approach implemented within the DALTON code<sup>66</sup> has been applied, using the aug-cc-pVTZ basis set for dioxin, dithiin, and diselenin, and the Sadlej-pVTZ basis set for ditellurin. The results are displayed in Table V. A significant increase of magnitude is observed for components and trace of the anapole magnetizability of 1,2-*M*-dioxin, compared to the Hartree-Fock results in Table I. For 1,2-*M*-dithiin the sign of the small  $\bar{a}$  is reversed. Comparatively smaller correlation contributions have been predicted for 1,2-*M*-diselenin. However, we would prefer leaving any conclusive comment to a future paper, after making more extended numerical experience, adopting other DFT functionals and employing also coupled cluster techniques.

The conversion factors from SI-a.u. to SI units per molecule are  $e^2 a_0^2 / m_e = 7.891\,036\,60 \times 10^{-29} \text{ JT}^{-2}$  for second-rank magnetizabilities  $\chi_{\alpha\beta}$ , and  $e^2 a_0^3 / m_e = 4.175\,756\,62 \times 10^{-39} \text{ JT}^{-2} \text{ m}$  for third-rank magnetizabilities  $\chi_{\alpha,\beta\gamma}$ , and anapole magnetizabilities  $a_{\alpha\beta}$ , from the CODATA compilation.<sup>79</sup> The conversion factor for the magnetic dipole moment is  $\hbar/m_e = 1.854\,801\,90 \times 10^{-23} \text{ JT}^{-1}$ , that for the magnetic quadrupole and anapole moment is  $e E_h a_0^3 / \hbar = 9.815\,188\,95 \times 10^{-34} \text{ JT}^{-1} \text{ m} \equiv \text{m}^3 \text{ A}$ . The magnitude of these factors, decreasing approximately by ten orders on each successive differentiation of the electronic interaction energy, implies that the phenomenology associated to third-rank and anapole magnetizabilities may be hard to detect.

#### IV. CONCLUDING REMARKS AND OUTLOOK

In the presence of a static, spatially uniform magnetic field, the chiral cyclic molecules with chemical formula C<sub>4</sub>H<sub>4</sub>X<sub>2</sub>, for X=O, S, Se, and Te, studied in this paper are endowed with an orbital electronic anapole having opposite sign in the two enantiomeric forms. The anapole magnetizability  $a_{\alpha\beta}$  tensor represented in the reference frame of the eigenvectors of the second-rank magnetizability  $\chi_{\alpha\beta}$  is characterized by translationally invariant diagonal tensor components, which are in principle measurable, although their extremely small magnitude would seem to preclude detection via experimental setups available at present. In fact, the largest calculated value of the isotropic anapole magnetizability for the 1,2-*M*-dioxin molecule (which however, is very unstable and could not be isolated<sup>69</sup>) is approximately 0.36 a.u., that is,  $\approx 1.5 \times 10^{-39} \text{ JT}^{-2} \text{ m}$  per molecule. The corresponding anapole moment  $\mathcal{A}$  induced by a magnetic field  $\mathbf{B}$  of 1 T in isotropic media is, from Eq. (8),  $\approx 1.5 \times 10^{-39} \text{ JT}^{-1} \text{ m}$  per molecule.

The *M* enantiomer, in the presence of a curl  $\mathbf{C} = 1 \text{ Tm}^{-1}$ , in the same direction as  $\mathbf{B} = 1 \text{ T}$ , is more stable than the *P*

enantiomer by  $\approx -1.5 \times 10^{-39}$  J, according to the expression for the interaction energy, Eq. (49), of a previous paper.<sup>36</sup> The same order of magnitude has been estimated for the averaged trace  $\bar{a}$  of  $a_{\alpha\beta}$  in 1,2-*M*-ditellurin, in which relativistic effects may possibly determine enhanced response. Since  $\mathcal{A}$  and  $\bar{a}$  have opposite sign for *M* and *P* enantiomers, it is theoretically possible that they are meaningful for chiral discrimination.

## ACKNOWLEDGMENTS

P.L. is grateful to Dr. E. Tellgren for kindly communicating details of calculations reported in Ref. 35. P.F.P. acknowledges financial support from CONICET and UNNE (PI: F002-11 Res.852/11). M.B.F. and G.I.P. acknowledge financial support from Universidad de Buenos Aires, and CONICET. S.P. and P.L. gratefully acknowledge financial support to the present research from the Italian MIUR (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), via PRIN 2009 funds.

- <sup>1</sup>Y. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **33**, 1531 (1957); [J. Exp. Theor. Phys. **6**, 1184 (1958)]. The author acknowledges analogous results obtained by V. G. Vaks.
- <sup>2</sup>V. M. Dubovik and A. A. Cheshkov, Sov. J. Part. Nucl. **5**, 318 (1975).
- <sup>3</sup>V. M. Dubovik, L. A. Tosunyan, and V. V. Tugushev, J. Exp. Theor. Phys. **63**, 344 (1986).
- <sup>4</sup>T. Kaelberer, V. A. Fedotov, N. Papasimakis, D. P. Tsai, and N. I. Zheludev, Science **330**, 1510 (2010).
- <sup>5</sup>G. N. Afanasiev and V. M. Dubovik, Phys. Part. Nucl. **29**, 366 (1998).
- <sup>6</sup>V. M. Dubovik, S. S. Krotov, and V. V. Tugushev, Sov. Phys. Crystallogr. **32**, 314 (1987).
- <sup>7</sup>V. M. Dubovik, M. A. Martsenyuk, and B. Saha, Phys. Rev. E **61**, 7087 (2000).
- <sup>8</sup>A. A. Gorbatsevich *et al.*, Phys.-Usp. **52**, 835 (2009).
- <sup>9</sup>C. G. Gray, G. Karl, and V. A. Novikov, Am. J. Phys. **78**, 936 (2010).
- <sup>10</sup>I. B. Khriplovich, Parity Nonconservation in Atomic Phenomena (Gordon and Breach, Oxford, 1991).
- <sup>11</sup>W. C. Haxton, C.-P. Liu, and M. J. Ramsey-Musolf, Phys. Rev. C **65**, 045502 (2002).
- <sup>12</sup>W. C. Haxton, Science **275**, 1753 (1997).
- <sup>13</sup>A. L. Barra and J. B. Robert, Mol. Phys. **88**, 875 (1996).
- <sup>14</sup>A. L. Barra, J. B. Robert, and L. Wiesenfeld, Europhys. Lett. **5**, 217 (1988).
- <sup>15</sup>J. B. Robert and A. L. Barra, Chirality **13**, 699 (2001).
- <sup>16</sup>V. V. Flambaum, I. B. Y. Khriplovich, and O. P. Sushkov, Phys. Lett. B **146**, 367 (1984).
- <sup>17</sup>R. Hasty *et al.*, Science **290**, 2117 (2000).
- <sup>18</sup>A. Y. Kraftmakher, Phys. Lett. A **132**, 167 (1988).
- <sup>19</sup>C. S. Wood *et al.*, Science **275**, 1759 (1997).
- <sup>20</sup>N. A. Spaldin, M. Fiebig, and M. Mostovoy, J. Phys.: Condens. Matter **20**, 434203 (2008).
- <sup>21</sup>D. Sheng, L. A. Orozco, and E. Gomez, J. Phys. B: At., Mol. Opt. Phys. **43**, 074004 (2010).
- <sup>22</sup>I. B. Khriplovich and M. E. Pospelov, Z. Phys. D **17**, 81 (1990).
- <sup>23</sup>E. Ascher, Helv. Phys. Acta **39**, 40 (1966).
- <sup>24</sup>E. Ascher, Int. J. Magn. **5**, 287 (1974).
- <sup>25</sup>H. Schmid, J. Phys.: Condens. Matter **20**, 434201 (2008).
- <sup>26</sup>H. Schmid, Ferroelectrics **252**, 41 (2001).
- <sup>27</sup>B. V. Aken, J.-P. Rivera, H. Schmid, and M. Fiebig, Nature (London) **449**, 702 (2007).
- <sup>28</sup>R. R. Lewis, Phys. Rev. A **49**, 3376 (1994).
- <sup>29</sup>A. Ceulemans, L. F. Chibotaru, and P. W. Fowler, Phys. Rev. Lett. **80**, 1861 (1998).
- <sup>30</sup>T. N. Mukhamedjanov, O. P. Sushkov, and J. M. Cadogan, Phys. Rev. A **71**, 012107 (2005).
- <sup>31</sup>S. Pelloni and P. Lazzeretti, Chem. Phys. **356**, 153 (2009).
- <sup>32</sup>S. Pelloni, P. Lazzeretti, and R. Zanasi, Theor. Chem. Acc. **123**, 353 (2009).
- <sup>33</sup>R. Berger, Z. Naturforsch. **67b**, 1127 (2012).
- <sup>34</sup>S. Pelloni, F. Faglioni, A. Soncini, A. Ligabue, and P. Lazzeretti, Chem. Phys. Lett. **375**, 583 (2003).
- <sup>35</sup>E. I. Tellgren and H. Fliegl, J. Chem. Phys. **139**, 164118 (2013).
- <sup>36</sup>P. F. Provasi, G. I. Pagola, M. B. Ferraro, S. Pelloni, and P. Lazzeretti, J. Phys. Chem. A **118**, 6333 (2014).
- <sup>37</sup>P. Lazzeretti, Theor. Chim. Acta **87**, 59 (1993).
- <sup>38</sup>M. C. Caputo, M. B. Ferraro, P. Lazzeretti, M. Malagoli, and R. Zanasi, J. Mol. Struct.: THEOCHEM **305**, 89 (1994).
- <sup>39</sup>M. C. Caputo, M. B. Ferraro, P. Lazzeretti, M. Malagoli, and R. Zanasi, Phys. Rev. A **49**, 3445 (1994).
- <sup>40</sup>F. Faglioni, A. Ligabue, S. Pelloni, A. Soncini, and P. Lazzeretti, Chem. Phys. **304**, 289 (2004).
- <sup>41</sup>S. Pelloni, P. Lazzeretti, G. Monaco, and R. Zanasi, Rend. Lincei **22**, 105 (2011).
- <sup>42</sup>P. Lazzeretti, "Invariance of molecular response properties under a coordinate translation," Int. J. Quantum Chem. (published online 2014).
- <sup>43</sup>F. Bloch, "Zur wirkung äußerer elektromagnetischer felder auf kleine systeme," in W. Heisenberg und die Physik Unserer Zeit, edited by F. Bopp (Wievog & Son, Braunschweig, 1961), pp. 93–102.
- <sup>44</sup>P. Lazzeretti, Adv. Chem. Phys. **75**, 507 (1989).
- <sup>45</sup>P. Lazzeretti, "Electric and magnetic properties of molecules," in Handbook of Molecular Physics and Quantum Chemistry (John Wiley & Sons, Ltd., Chichester, 2003), Vol. 3, Part 1, Chapter 3, pp. 53–145.
- <sup>46</sup>A. D. Buckingham and P. J. Stiles, Mol. Phys. **24**, 99 (1972).
- <sup>47</sup>L. D. Barron and C. G. Gray, J. Phys. A: Math., Nucl. Gen. **6**, 59 (1973).
- <sup>48</sup>R. G. Woolley, J. Phys. B: At. Mol. Phys. **6**, L97 (1973).
- <sup>49</sup>D. P. Craig and T. Thirunamachandran, Molecular Quantum Electrodynamics (Academic Press, New York, 1984).
- <sup>50</sup>C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, Photon & Atoms (John Wiley & Sons, New York, 1989).
- <sup>51</sup>J. G. Valatin, Proc. R. Soc. London A **222**, 93 (1954).
- <sup>52</sup>W. E. Brittin, W. R. Smythe, and W. Wyss, Am. J. Phys. **50**, 693 (1982).
- <sup>53</sup>B.-S. K. Skagerstram, Am. J. Phys. **51**, 1148 (1983).
- <sup>54</sup>R. Delbourgo and Triyanta, Int. J. Mod. Phys. A **7**, 5833 (1992).
- <sup>55</sup>T. Saue, "Post Dirac-Hartree-Fock methods - properties," in Relativistic Electronic Structure Theory, Fundamentals Vol. 1, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2002), p. 332.
- <sup>56</sup>The gauge choice referred to as Poincaré's<sup>50</sup> can be made by an ingenious formulation first proposed by Valatin,<sup>51–53</sup> which leads to the same explicit expressions as Bloch's.<sup>37,43,44</sup> A number of different alternative denominations can be found in the literature, see note a, first page of Ref. 54, and Ref. 55.
- <sup>57</sup>A. M. Stewart, J. Phys. A: Math., Nucl. Gen. **32**, 6091 (1999).
- <sup>58</sup>A. M. Stewart, J. Phys. A: Math., Nucl. Gen. **33**, 9165 (2000).
- <sup>59</sup>A. M. Stewart, Aust. J. Phys. **53**, 613 (2000).
- <sup>60</sup>A. M. Stewart, Eur. J. Phys. **24**, 519 (2003).
- <sup>61</sup>S. T. Epstein, The Variation Method in Quantum Chemistry (Academic Press, New York, 1974).
- <sup>62</sup>A. Ligabue, P. Lazzeretti, M. P. B. Varela, and M. B. Ferraro, J. Chem. Phys. **116**, 6427 (2002).
- <sup>63</sup>S. Pelloni and P. Lazzeretti, J. Chem. Phys. **140**, 074105 (2014).
- <sup>64</sup>F. London, J. Phys. Radium **8**, 397 (1937).
- <sup>65</sup>A. E. Hansen and T. D. Bouman, J. Chem. Phys. **82**, 5035 (1985), this is the first reference in which the reinterpretation of the GIAO acronym for gauge-including-atomic-orbitals has been proposed, see footnote 6, p. 5047.
- <sup>66</sup>DALTON, An electronic structure program, Release 2.0, 2005, see <http://www.kjemi.uio.no/software/dalton/>.
- <sup>67</sup>S. Pelloni, F. Faglioni, and P. Lazzeretti, Rend. Lincei **24**, 283 (2013).
- <sup>68</sup>S. Pelloni and P. Lazzeretti, Mol. Phys. **111**, 2387 (2013).
- <sup>69</sup>See <http://en.wikipedia.org/wiki/1,2-Dioxin> for molecular structure, properties and stability.
- <sup>70</sup>T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- <sup>71</sup>R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- <sup>72</sup>D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).
- <sup>73</sup>A. J. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988).
- <sup>74</sup>A. J. Sadlej and M. Urban, J. Mol. Struct.: THEOCHEM **234**, 147 (1991).
- <sup>75</sup>A. Sadlej, Theor. Chim. Acta **79**, 123 (1991).
- <sup>76</sup>A. Sadlej, Theor. Chim. Acta **81**, 45 (1991).
- <sup>77</sup>A. Sadlej, Theor. Chim. Acta **81**, 339 (1992).
- <sup>78</sup>R. Moccia, Chem. Phys. Lett. **5**, 265 (1970).
- <sup>79</sup>P. J. Mohr, B. N. Taylor, and D. B. Newell, Rev. Mod. Phys. **80**, 633 (2008).
- <sup>80</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4893991> for details of the basis set convergence test (second-rank magnetizability, eigenvectors, anapole magnetizabilities for different origins).