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Theoretical estimates of the anapole magnetizabilities of C₄H₄X₂ cyclic molecules for X=O, S, Se, and Te

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Calculations have been carried out for C₄H₄X₂ cyclic molecules, with X=O, S, Se, 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 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 \(-\bar{X}\), the pseudoscalar obtained by spatial averaging of the dipole-quadrupole magnetizability \( x_{a,\beta\gamma} \). 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 \( A_{\alpha} \), having the same magnitude, but opposite sign, for two enantiomorphs. © 2014 AIP Publishing LLC.

I. INTRODUCTION

The existence of a vector \( \mathbf{A} \), 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.¹ Multipole expansions in classical and quantum field theory, including a family of toroidal moments²–⁴ and some peculiar charge-current arrangements,³⁵–⁷ have been considered later on in connection with magnetoelectricity.⁵ More recently, anapole and related moments have been discussed within the context of magnetic multipolar contact fields,⁹ and within the framework of parity violation effects.¹⁰–¹⁵ The nuclei of certain elements are endowed with an anapole¹⁶,¹⁷ and the anapole moment of cesium has been previously calculated¹⁸ and measured.¹⁹ Other measuring procedures have been discussed.²⁰,²¹ Connections between enantiomorphism and electronic anapole moments have been postulated for chiral molecular radicals.²²

The occurrence of an anapole moment has been inferred from a fundamental premise relying on group-theoretical basis,²³–²⁷ and it has been predicted for diatomic molecules,²⁸ chiral molecules,²² and toroidal nanotubes.²⁹ Attestations of nuclear anapole moments in solid-state nuclear magnetic resonance have been discussed.³⁰ A magnetic field can induce toroidal flow in the electrons of molecules.³¹–³³ In the terminology of Schmid,³⁶ 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.³⁴ The orbital anapole moment of a molecule is an intrinsic electronic property which can be rationalized via anapole magnetizabilities,²⁰,²⁵–²⁷ allowing for a magnetic multipole expansion based on the Bloch gauge,³⁴ later rediscovered by others.³⁵–³⁷ A simple compact expression,⁵⁰–⁵⁵ defining a gauge usually referred to as Poincaré’s,⁵⁰,⁵⁵,⁵⁶ yields a power series for the vector potential equivalent to Bloch’s.⁵⁷–⁶⁰

The present paper is aimed at computing translationally invariant diagonal components and average values of anapole magnetizability in cyclic compounds with chemical formula C₄H₄X₂, with X=O, S, Se, 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 papers³⁶,³⁷,⁴⁰,⁴¹ 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,³¹–³³,⁴⁰,⁴¹ which can be related to mixed magnetic multipole magnetizabilities. As reported previously,³⁴ 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.²⁹ 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
supplementary material 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 is used within the multipolar Bloch gauge 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.

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

\[
\chi = \frac{1}{6} \chi_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma}
\]

(1)

is different from zero for a chiral molecule.

Allowing for the Hellmann-Feynman theorem, all the relevant properties, e.g., the induced magnetic dipole and quadrupole moments, second- and third-rank magnetizabilities, are obtained by differentiating either the induced magnetic moments or the electronic interaction energy \( W \) with respect to the components of \( \mathbf{C} \) defines the components of the anapole polar vector

\[
- \frac{\partial W}{\partial C_\gamma} = A_\gamma = - \frac{1}{2} \epsilon_{\alpha\beta\gamma} \chi_{\alpha\beta\delta} B_\delta,
\]

(2)

induced in the electrons of the molecule. In this equation only the contribution arising from the interaction with the nonuniform magnetic field has been included.

The nonsymmetric second-rank tensor

\[
a_{\gamma\delta} = - \frac{\partial^2 W}{\partial B_\delta \partial C_\gamma} = - \frac{\partial A_\gamma}{\partial B_\delta} = - \frac{1}{2} \epsilon_{\alpha\beta\gamma} \chi_{\alpha\beta,\delta}
\]

(3)

is interpreted as anapole magnetizability. It is expedient to split it up into isotropic, symmetric, and antisymmetric parts,
that GIAO’s are indeed leading to a faster basis set convergence and thus remain important.

III. CALCULATIONS OF MAGNETIZABILITIES FOR C₄H₄X₂ 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 C₄H₄X₂ 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. The C₄H₄X₂ 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. Atomic coordinates are reported in the supplementary material. The $z$ axis coincides with the direction of the twofold symmetry axis of the $C_2$ point group, which characterizes the chiral C₄H₄X₂ compounds investigated here. The 1,2-dioxin molecule is unstable and cannot be isolated.

Extended correlation consistent, gaugeless basis sets together with augmented functions, from the compilation by Dunning and co-workers, contracted Sadlej basis sets, and two large basis sets, MODENA I and MODENA II, carrying optimized polarization functions for magnetic properties 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, weighed by the angular momentum $\hat{l}_z$ and by the second moment operator $r_{\alpha}^2$, 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. For these reasons, basis sets containing more diffuse polarizations functions, adopted for accurate calculation of electric dipole polarizabilities, 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 is recommendable to study convergence of calculated magnetizabilities to limit values. In particular, the largest ones are suitable enough for $\chi_{\alpha\beta\gamma}$. A preliminary test was done on the dioxin molecule C₄H₄O₂, using the equations for the change of magnetic properties in a coordinate translation. These relationships are strictly valid only in the ideal case of exact and optimal variational wavefunctions. 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 of increasing size and characteristics, hereafter referred to as DZ, QZ, and 5Z for brevity to designate aug-cc-pCVTZ, 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 $\chi = \chi$ a vector of the convergence test are reported in detail in the supplementary material 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 $d_z = -1$ Å, used on applying Eqs. (51) and (53) of our previous paper, leaves $a_{zz}$ 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 for the other diagonal components, $a_{xx}$ and $a_{yy}$, 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. The average anapole magnetizability is stable, with value $\bar{\chi}(r') = \bar{\chi}(r'') = 0.357$ a.u., calculated via QZ and 5Z basis sets. The results obtained by the 5Z basis set for $a_{zz}(r'')$ 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 $\bar{\chi}$ 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

FIG. 1. The 1,2-$P$ (above) and 1,2-$M$ (below) enantiomers of the C₄H₄X₂ molecules.
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.\textsuperscript{a}

| Basis | \(a_{\alpha\beta}\) | \(\mathcal{M}\) |
|-------|-----------------|--------|
| aug-cc-pVQDZ | 0.065 | 2.040 | 0.000 |
| & -3.492 | 1.226 | 0.000 |
| & 0.000 | 0.000 | -0.183 | 0.369 |
| Sadlej-pVTZ | 0.703 | 2.208 | 0.000 |
| & -4.178 | 0.640 | 0.000 |
| & 0.000 | 0.000 | -0.241 | 0.368 |
| aug-cc-pVTZ/Sadlej-pVTZ | 0.387 | -0.283 | 0.000 |
| & -2.319 | 0.803 | 0.000 |
| & 0.000 | 0.000 | -0.112 | 0.359 |
| aug-cc-pVTZ | 0.377 | 1.964 | 0.000 |
| & -3.761 | 0.709 | 0.000 |
| & 0.000 | 0.000 | -0.013 | 0.357 |
| aug-cc-pVTZ | -0.236 | 1.970 | 0.000 |
| & -3.157 | 1.268 | 0.000 |
| & 0.000 | 0.000 | -0.039 | 0.357 |
| aug-cc-pVTZ | -0.431 | 2.156 | 0.000 |
| & -2.804 | 1.449 | 0.000 |
| & 0.000 | 0.000 | -0.054 | 0.357 |
| MODENA I | 1.522 | 2.467 | 0.000 |
| & -2.333 | -0.527 | 0.000 |
| & 0.000 | 0.000 | 0.078 | 0.358 |

\textsuperscript{a}The diagonal components of the \(a_{\alpha\beta}\) tensor are origin independent within this reference system. The conversion factor to SI units is \(\epsilon^{2}a_{\alpha\beta}/m = 4.175 \times 10^{-30}\text{ JT}^{-1}\text{ m per molecule, from CODATA Recommended Values of the Fundamental Physical Constants}^{[35]}\)

This table shows the basis set convergence of the anapole magnetizability of 1,2-M-dioxin referred to the principal axis system of the second-rank magnetizability, in atomic units (a.u.). The results are given in Tables I–IV in SI atomic units (a.u.). The anapole magnetizabilities of cyclic \(\text{C}_{4}\text{H}_{4}\text{X}_{2}\) compounds do not seem to be biased by the atomic number of the \(X\) atom, for \(X=\text{O, S, Se, and Te}\) (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 \(\mathcal{M}\) 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, so that their accurate theoretical determination would be quite important in view of experimental detection in ordered phase.

TABLE III. 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.\textsuperscript{a}

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

\textsuperscript{a}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 deterministic, 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 on the paramagnetic contributions, Eq. (21) of Ref. 36, to the diagonal components of \(\chi_{\alpha\beta}\), are possibly more reliable.
The predictions for 1,2-M-dithin do not appear to have converged, see the change of sign for the diagonal component passing from SZ to MODENA II basis sets, even if the average \( \bar{\chi} \) 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\(^{35} \) 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 geometrical techniques. 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-dithin, 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 \( \bar{\chi} = 0.230 \) a.u., which is close in magnitude and has the same sign as that of Tellgren and Fliegl.\(^{35} \)

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.\(^{35} \) At any rate, a change of sign for values calculated by different basis sets can be observed in Table XI of Tellgren and Fliegl.\(^{35} \)

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 \( \text{C}_4\text{H}_4\text{Te}_2 \) are not expected to be of Hartree-Fock accuracy. In addition, one can presume that relativistic effects may bias \( a_{ab} \) of this molecule to a significant extent.

A limited attempt has been made at estimating the effects of electron correlation on the \( a_{ab} \) tensor employing Density Functional Theory (DFT). The B3LYP functional approach implemented within the DALTON code\(^{66} \) has been applied, using the aug-cc-pVTZ basis set for dioxin, dithin, 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-dithin the sign of the small \( \bar{\chi} \) 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 \( e^2 a_0^2 / m_e = 7.891 \times 10^{-20} \) JT\(^{-2} \) for second-rank magnetizabilities \( \chi_{ab} \), and \( e^2 a_0^3 / m_e = 4.175 \times 10^{-39} \) JT\(^{-2} \)m for third-rank magnetizabilities \( \chi_{ab,ef} \), and anapole magnetizabilities \( a_{ab} \), from the CODATA compilation.\(^{79} \) The conversion factor for the magnetic dipole moment is \( \mu / m_e = 1.854 \times 10^{-23} \) JT\(^{-1} \), that for the magnetic quadrupole and anapole moment is \( eE_0 a_0^3 / \mu = 9.815 \times 10^{-34} \mu_0 \) m\(^3\) A\(^{-1} \). 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 \( \text{C}_4\text{H}_4\text{X}_2 \), for \( \text{X}=\text{O}, \text{S}, \text{Se}, \text{and Te}, \) studied in this paper are endowed with an orbital electronic anapole having opposite sign in the two enantiomeric forms. The anapole magnetizability \( a_{ab} \) tensor represented in the reference frame of the eigenvectors of the second-rank magnetizability \( \chi_{ab} \) 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\(^{69} \)) is approximately 0.36 a.u., that is, \( \approx 1.5 \times 10^{-39} \) JT\(^{-2} \)m per molecule. The corresponding anapole moment \( \mathcal{A} \) induced by a magnetic field \( B \) of 1 T in isotropic media is, from Eq. (8), \( \approx 1.5 \times 10^{-39} \) JT\(^{-1} \)m per molecule.

The \( M \) enantiomer, in the presence of a curl \( \nabla \times \mathbf{E} = 1 \text{Tm}^{-1} \), in the same direction as \( B = 1 \) T, is more stable than the \( P \)
enantiomer by \(\approx -1.5 \times 10^{-39} \text{ J}\), according to the expression for the interaction energy, Eq. (49), of a previous paper.36 The same order of magnitude has been estimated for the averaged trace of \(\alpha_{\beta\beta}\) in 1,2-M-dietiluluril, in which relativistic effects may possibly determine enhanced response. Since \(\mathcal{A}\) and \(\overline{\mathcal{A}}\) have opposite sign for \(M\) and \(P\) enantiomers, it is theoretically possible that they are meaningful for chiral discrimination.

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52 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).