

Computational Study of Basis Set and Electron Correlation Effects on Anapole Magnetizabilities of Chiral Molecules

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In the presence of a static, nonhomogeneous magnetic field, represented by the axial vector \mathbf{B} at the origin of the coordinate system and by the polar vector $\mathbf{C}=\mathbf{V}\times\mathbf{B}$, assumed to be spatially uniform, the chiral molecules investigated in this paper carry an orbital electronic anapole, described by the polar vector \mathcal{A} . The electronic interaction energy of these molecules in nonordered media is a cross term, coupling \mathbf{B} and \mathbf{C} via \bar{a} , one third of the trace of the anapole magnetizability $a_{\alpha\beta}$ tensor, that is, $W^{\text{BC}}=-\bar{a}\mathbf{B}\cdot\mathbf{C}$. Both \mathcal{A} and W^{BC} have opposite

sign in the two enantiomeric forms, a fact quite remarkable from the conceptual point of view. The magnitude of \bar{a} predicted in the present computational investigation for five chiral molecules is very small and significantly biased by electron correlation contributions, estimated at the density functional level via three different functionals. © 2016 Wiley Periodicals, Inc.

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Introduction

The linear molecular response to a nonuniform magnetic field \mathbf{B} has been rationalized within the framework of Rayleigh–Schrödinger perturbation theory (RSPT).^[1–4] Assuming that the magnetic field gradient $\nabla\mathbf{B}$ is uniform over the molecular dimensions, the relevant response tensors are the magnetic dipole/magnetic quadrupole magnetizability $\chi_{\alpha,\beta\gamma}$ and the magnetic quadrupole/magnetic quadrupole magnetizability $\chi_{\alpha\beta,\gamma\delta}$.

Within standard tensor notation, for example, allowing for the Einstein convention of implicit summation over repeated Greek indices, the anapole magnetizability is defined by contracting the mixed dipole/quadrupole magnetizability with the Levi–Civita third-rank pseudotensor,^[5–7] $a_{\alpha\beta}=-\frac{1}{2}\varepsilon_{\alpha\lambda\mu}\chi_{\beta,\lambda\mu}$. It can be rewritten as a second derivative of the energy W^{BC} , and as the first derivative of either the induced anapole \mathcal{A} or magnetic dipole \mathbf{M} with respect to the components of \mathbf{B} and $\mathbf{C}=\mathbf{V}\times\mathbf{B}$,

$$a_{\alpha\beta}=-\frac{\partial^2 W^{\text{BC}}}{\partial C_\alpha \partial B_\beta}=\frac{\partial \mathcal{A}_\alpha}{\partial B_\beta}=\frac{\partial M_\beta}{\partial C_\alpha}.$$

It is a parity-odd, time-even second-rank tensor. Therefore, the anapolar contribution $W^{\text{BC}}=-a_{\alpha\beta}C_\alpha B_\beta$ to the interaction energy has the same magnitude, but opposite sign, for two enantiomeric molecules.^[5,6] A nonperturbative approach based on these definitions has been recently applied to evaluate the relevant tensors,^[7] employing a powerful computational scheme previously developed to investigate linear and nonlinear atomic and molecular response to strong magnetic fields via basis sets of London orbitals.^[8–10] Calculation efficiency and theoretical generality of such a method, which appears in some instances preferable to RSPT procedures for nonlinear response to very strong magnetic field,^[11–13] are presently being demonstrated.^[14,15]

Nonetheless, some nice features of the RSPT approach can justify its application, for example, possibility of separate definition for diamagnetic and paramagnetic contributions, fulfillment of the Hellmann–Feynman theorem in the case of \mathbf{B} -independent basis sets, definition of auxiliary sum rules for origin independence of calculated magnetizabilities, which can be useful for estimating limit values within a given variational procedure, for example, self consistent field (SCF) approximation to the Hartree–Fock (HF) method,^[1–3] and coupled cluster (CC) response functions.^[16–18]

Previous calculations allowing for SCF approaches^[5–7] have shown that the magnetizabilities $\chi_{\alpha,\beta\gamma}$ and $a_{\alpha\beta}$ are characterized by very small magnitude, which suggests that their experimental determination may be quite difficult. Whereas electron correlation contributions to the second rank magnetizability $\chi_{\alpha\beta}$ are known to be relatively small in general,^[19] somewhat larger correlation contributions seem to affect third-rank magnetic dipole/magnetic quadrupole magnetizabilities and related anapole magnetizability of $\text{C}_4\text{H}_4\text{X}_2$ cyclic molecules for $\text{X}=\text{O}, \text{S}, \text{Se},$ and Te ,^[6] which is expected on inspection of their definitions, eqs. (7) and (8), involving an additional power of the position operator.^[1–3]

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The present article sets out to provide further indications in this direction. It is also aimed at (i) reshaping the definition of anapole magnetizabilities^[5–7] in a simpler and more compact form within the RSPT scheme in view of computational applications, (ii) defining diamagnetic and paramagnetic contributions to the electronic current density vector induced by the curl \mathbf{C} , in terms of which alternative expressions of the interaction energy are written, (iii) applying the theory to evaluate $a_{\alpha\beta}$ anapole magnetizabilities in a series of chiral molecules to investigate the role of basis set quality and the effects of electron correlation on the pseudoscalar $a_{\alpha\alpha}$ characterized by the same magnitude but opposite sign for enantiomeric compounds. Results are reported in Calculations of anapole magnetizabilities for chiral molecules in a magnetic field with uniform curl section. Conclusions are presented in Concluding remarks section.

Anapole Moment and Anapole Magnetizabilities

We consider the linear response of a diamagnetic molecule with n electrons and N nuclei to a time-independent, nonuniform magnetic field with flux density \mathbf{B} (measured at the origin of the coordinate system), supposing that the curl $\mathbf{C}=\nabla\times\mathbf{B}$ is uniform, omitting the symmetric components of $\nabla\mathbf{B}$, and contributions from higher spatial derivatives. The SI system of units has been chosen. From the CODATA compilation,^[20] the conversion factor from SI-a.u. to SI units per molecule for anapole magnetizabilities, eq. (5) is $e^2 a_0^3/m_e=4.175\ 756\ 62\times 10^{-39}$ JT⁻²m. The notation is the same as in previous Ref. [1,3–6].

The electronic wavefunction for the reference singlet state a is written in the form

$$\Psi_a = \Psi_a^{(0)} + \Psi_a^{B_x} B_x + \Psi_a^{C_x} C_x, \quad (1)$$

in which the first-order perturbed wavefunctions, determined by RSPT, are

$$|\Psi_a^{B_x}\rangle = \frac{1}{\hbar} \sum_{j \neq a} \omega_{ja}^{-1} |j\rangle \langle j | \hat{m}_x | a \rangle, \quad (2)$$

$$|\Psi_a^{C_x}\rangle = \frac{1}{\hbar} \sum_{j \neq a} \omega_{ja}^{-1} |j\rangle \langle j | \hat{a}_x | a \rangle, \quad (3)$$

where \hat{m}_x denotes the electronic magnetic dipole operator,^[1,3] and

$$\hat{a}_x = -\frac{1}{2} \varepsilon_{\alpha\beta\gamma} \hat{m}_{\beta\gamma} = \frac{e}{6m_e} \sum_{i=1}^n [(r^2 \delta_{\alpha\beta} - r_\alpha r_\beta) \hat{p}_\beta + i \hbar r_\alpha]_i \quad (4)$$

is the anapole operator, related to the magnetic quadrupole operator $\hat{m}_{\beta\gamma}$.^[1,3] In these relationships, contributions from electron spin are neglected.

The anapole magnetizabilities are second-rank tensors, defined by derivatives of the second-order RSPT energy or derivatives of the induced anapole and dipole moments,^[5,6]

see the introductory section. They are expressed as sums of paramagnetic and diamagnetic contributions,

$$a_{\alpha\beta} = a_{\alpha\beta}^p + a_{\alpha\beta}^d, \quad (5)$$

$$b_{\alpha\beta} = b_{\alpha\beta}^p + b_{\alpha\beta}^d, \quad (6)$$

specified via the formulae

$$a_{\alpha\beta}^p = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re(\langle a | \hat{a}_\alpha | j \rangle \langle j | \hat{m}_\beta | a \rangle), \quad (7)$$

$$a_{\alpha\beta}^d = \frac{e^2}{12m_e} \varepsilon_{\alpha\beta\gamma} \langle a | \sum_{i=1}^n (r^2 r_\gamma)_i | a \rangle, \quad (8)$$

$$b_{\alpha\beta}^p = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re(\langle a | \hat{a}_\alpha | j \rangle \langle j | \hat{a}_\beta | a \rangle), \quad (9)$$

$$b_{\alpha\beta}^d = -\frac{e^2}{36m_e} \langle a | \sum_{i=1}^n [r^2 (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta)]_i | a \rangle, \quad (10)$$

equivalent to, but more terse and crisp than those reported previously.^[5,6] In particular, it is immediately verified from eqs. (7) and (8), that the average anapole susceptibility

$$\bar{a} = (1/3) a_{\alpha\alpha} \equiv (1/3) a_{\alpha\alpha}^p \quad (11)$$

contains only the paramagnetic contribution, since $a_{\alpha\alpha}^d$ vanishes identically.

To first order in \mathbf{B} and \mathbf{C} , the electronic current densities induced by the nonuniform magnetic field are partitioned into paramagnetic and diamagnetic terms,

$$\mathbf{J}_\alpha^{\mathbf{B}}(\mathbf{r}) = \mathbf{J}_{\text{pz}}^{\mathbf{B}}(\mathbf{r}) + \mathbf{J}_{\text{dx}}^{\mathbf{B}}(\mathbf{r}), \quad (12)$$

$$\mathbf{J}_\alpha^{\mathbf{C}}(\mathbf{r}) = \mathbf{J}_{\text{pz}}^{\mathbf{C}}(\mathbf{r}) + \mathbf{J}_{\text{dx}}^{\mathbf{C}}(\mathbf{r}), \quad (13)$$

which are conveniently represented via corresponding second-rank current density tensors,^[21]

$$\begin{aligned} \mathcal{J}_{\text{pz}}^{\mathbf{B}}(\mathbf{r}) &= \frac{\partial \mathbf{J}_{\text{pz}}^{\mathbf{B}}(\mathbf{r})}{\partial \mathbf{B}_\beta} = -\frac{ne}{m_e} \int \left[\Psi_a^{B_\beta*}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \hat{p}_\alpha \Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \right. \\ &\quad \left. + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \hat{p}_\alpha \Psi_a^{B_\beta}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \right] d\mathbf{x}_2 \dots d\mathbf{x}_n, \end{aligned} \quad (14)$$

$$\mathcal{J}_{\text{dx}}^{\mathbf{B}}(\mathbf{r}) = \frac{\partial \mathbf{J}_{\text{dx}}^{\mathbf{B}}(\mathbf{r})}{\partial \mathbf{B}_\beta} = -\frac{e^2}{2m_e} \varepsilon_{\alpha\beta\gamma} r_\gamma \gamma^{(0)}(\mathbf{r}), \quad (15)$$

$$\begin{aligned} \mathcal{J}_{\text{pz}}^{\mathbf{C}}(\mathbf{r}) &= \frac{\partial \mathbf{J}_{\text{pz}}^{\mathbf{C}}(\mathbf{r})}{\partial \mathbf{C}_\beta} = -\frac{ne}{m_e} \int \left[\Psi_a^{C_\beta*}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \hat{p}_\alpha \Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \right. \\ &\quad \left. + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \hat{p}_\alpha \Psi_a^{C_\beta}(\mathbf{r}, \mathbf{x}_2 \dots \mathbf{x}_n) \right] d\mathbf{x}_2 \dots d\mathbf{x}_n, \end{aligned} \quad (16)$$

$$\mathcal{J}_{\text{dx}}^{\mathbf{C}}(\mathbf{r}) = \frac{\partial \mathbf{J}_{\text{dx}}^{\mathbf{C}}(\mathbf{r})}{\partial \mathbf{C}_\beta} = \frac{e^2}{6m_e} (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta) \gamma^{(0)}(\mathbf{r}), \quad (17)$$

so that, for instance, $\mathbf{J}_{\text{pz}}^{\mathbf{B}} = \mathcal{J}_{\text{pz}}^{\mathbf{B}} \mathbf{B}_\beta$. In eqs. (15) and (17), $\gamma^{(0)}(\mathbf{r})$ is the probability density of electrons at point \mathbf{r} . The electronic

interaction energies can be determined by RSPT^[5,6] or by either side of the interchange theorem

$$W^{BC} = - \int \mathbf{J}^B \cdot \mathbf{A}^C d^3r = - \int \mathbf{J}^C \cdot \mathbf{A}^B d^3r, \quad (18)$$

and by

$$W^{CC} = - \frac{1}{2} \int \mathbf{J}^C \cdot \mathbf{A}^C d^3r, \quad (19)$$

where the vector potential in the multipolar Bloch gauge^[22] is given by

$$\mathbf{A}_\alpha^B = \frac{1}{2} \varepsilon_{\alpha\beta\gamma} B_\beta r_\gamma, \quad (20)$$

$$\mathbf{A}_\alpha^C = - \frac{1}{6} (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta) C_\beta. \quad (21)$$

Allowing for eqs. (18) and (19), the anapole magnetizabilities can be redefined via relationships containing the current density tensors, eqs. (14)–17),

$$\begin{aligned} a_{\delta\gamma} &= - \frac{\partial^2 W^{BC}}{\partial C_\delta \partial B_\gamma} = - \frac{1}{6} \int \mathcal{J}_\alpha^{B_\gamma} (r^2 \delta_{\alpha\delta} - r_\alpha r_\delta) d^3r \\ &= - \frac{1}{2} \varepsilon_{\alpha\beta\gamma} \int \mathcal{J}_\alpha^{C_\delta} r_\beta d^3r, \end{aligned} \quad (22)$$

$$b_{\delta\gamma} = - \frac{\partial^2 W^{CC}}{\partial C_\delta \partial C_\gamma} = - \frac{1}{6} \int \mathcal{J}_\alpha^{C_\delta} (r^2 \delta_{\alpha\gamma} - r_\alpha r_\delta) d^3r. \quad (23)$$

Relationship (11) is also obtained via eq. (22), by using the expressions for the diamagnetic contributions to the current densities, eqs. (15) and (17).

The anapole polar vector^[3–5] induced by the magnetic field \mathbf{B} at the origin is

$$\mathcal{A}_\alpha = a_{\alpha\beta} B_\beta, \quad (24)$$

and the contribution to the magnetic dipole, an axial vector, induced by the curl \mathbf{C} , is

$$\mathcal{M}_\alpha = a_{\beta\alpha} C_\beta. \quad (25)$$

Quite remarkably, the symmetry properties of the $a_{\alpha\beta}$ anapole magnetizability under parity P and time reversal T are identical to those of the mixed electric dipole-magnetic dipole polarizability tensor $\kappa'_{\alpha\beta}$, whose trace $\kappa'_{\alpha\alpha}$ is related to the optical rotatory power of chiral species.^[23,24] In addition, whereas $\kappa'_{\alpha\beta}$ and $a_{\alpha\beta}$ depend on the origin of the reference system, the pseudo-scalars $\overline{\kappa'} = (1/3)\kappa'_{\alpha\alpha}$ and \overline{a} , eq. (11), are origin independent.^[5,6] To finish making the comparison between $\kappa'_{\alpha\beta}(-\omega; \omega)$ and $a_{\alpha\beta}$, it is observed that, while the diagonal components of the former are origin independent in the reference frame defined by the eigenvectors of the dynamic electric dipole polarizability $\alpha_{\alpha\beta}(-\omega; \omega)$ at the same angular frequency ω ,^[25] the diagonal components (and the trace) of the latter are origin independent in the principal axis system of the symmetric $\chi_{\alpha\beta}$ magnetizability tensor.^[5]

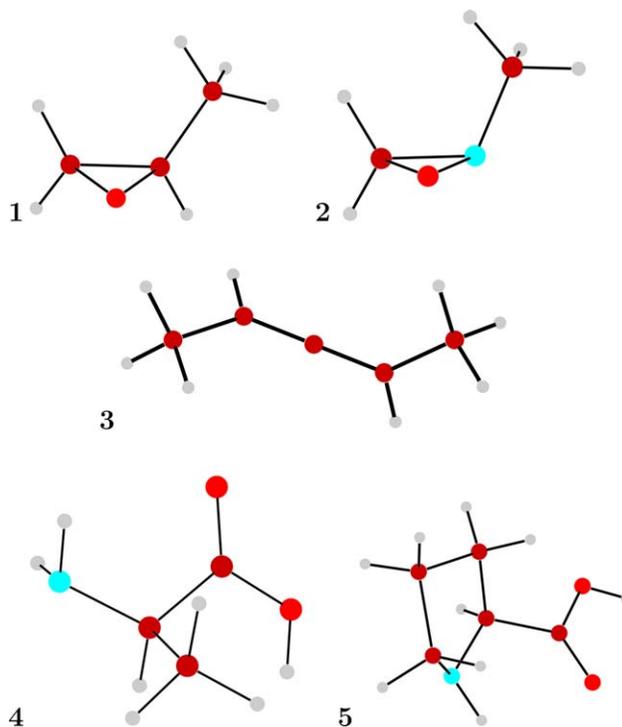


Figure 1. 1) (2R)-2-Methyl-oxirane, 2) (2R)-N-Methyl-oxaziridine, 3) (R_a)-1,3-Dimethyl-allene, 4) L-alanine, and 5) L-proline molecules.

Since $a_{\alpha\beta}$ is odd under parity and even under time reversal, its diagonal components (and trace) vanish in nonchiral molecules. In addition, it has the same magnitude but opposite sign for two enantiomers, and therefore can, in principle, be used for chiral discrimination.^[5,6] In fact, in disordered phase, gas or solution, the orbital electronic anapole and the magnetic dipole

$$\mathcal{A} = \overline{a}\mathbf{B}, \quad \mathcal{M} = \overline{a}\mathbf{C}, \quad (26)$$

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

Calculations of Anapole Magnetizabilities for Chiral Molecules in a Magnetic Field with Uniform Curl

Three of the molecular systems investigated here, displayed in Figure 1, that is, (2R)-2-methyl-oxirane, (2R)-N-methyl-oxaziridine, and (R_a)-1,3-dimethyl-allene had been considered in previous papers as candidates for chiral discriminations via nuclear magnetic resonance spectroscopy (NMRS).^[26,27] Two bigger molecules, the aminoacids L-alanine and L-proline, have been added in consideration of their biological importance. Calculations of the anapole magnetizability, eqs. (7) and (8), have been carried out at the coupled SCF-HF level of accuracy, equivalent to the random-phase approximation (RPA),^[28] using basis set of increasing size and quality to guess limit values.

The effects of electron correlation have been estimated via density functional theory (DFT), taking into account three

Table 1. (2R)-2-methyl-oxirane.^[a]

| Basis set | x | y | z | tr |
|-------------------|---------|---------|---------|---------|
| aug-cc-pVDZ | -0.3649 | -1.2384 | -0.2036 | |
| | 1.2625 | 0.1171 | -1.1465 | |
| | -0.2202 | 0.7890 | 0.2557 | 0.0026 |
| aug-cc-pVTZ | -0.2904 | -0.9380 | -0.4345 | |
| | 1.0954 | 0.1366 | -0.8107 | |
| aug-cc-pVQZ | -0.0131 | 0.5845 | 0.1669 | 0.0044 |
| | -0.1759 | -0.7346 | -0.5508 | |
| | 0.9930 | 0.1069 | -0.4178 | |
| aug-cc-pV5Z | -0.0138 | 0.3224 | 0.0821 | 0.0044 |
| | -0.1128 | -0.6834 | -0.5717 | |
| | 0.9629 | 0.0864 | -0.2839 | |
| MODENA I | -0.0339 | 0.2370 | 0.0395 | 0.0044 |
| | 0.0702 | -0.9515 | 0.1750 | |
| MODENA II | 0.6830 | -0.0474 | -0.5996 | |
| | -0.1913 | -0.0197 | -0.0085 | 0.0048 |
| | 0.0636 | -0.9464 | 0.1738 | |
| KT3/MODENA I | 0.6632 | -0.0419 | -0.5882 | |
| | -0.1721 | -0.0369 | -0.0086 | 0.0044 |
| | 0.1130 | -1.0427 | 0.2411 | |
| B3LYP/MODENA I | 0.7981 | -0.0593 | -0.7440 | |
| | -0.2095 | -0.0939 | -0.0362 | 0.0058 |
| | 0.0966 | -1.0441 | 0.2324 | |
| CAMB3LYP/MODENA I | 0.7822 | -0.0468 | -0.7192 | |
| | -0.2112 | -0.0885 | -0.0339 | 0.0053 |
| | 0.0897 | -1.0545 | 0.2419 | |
| CCSD/aug-cc-pVDZ | 0.7861 | -0.0417 | -0.7104 | |
| | -0.2155 | -0.0891 | -0.0331 | 0.0050 |
| | -0.4485 | -1.3544 | -0.2817 | |
| | 1.3567 | 0.1257 | -1.3745 | |
| | -0.2679 | 1.0046 | 0.3209 | -0.0006 |

[a] In all the Tables the origin of the coordinate system is the centre of mass. The conversion factor from SI-a.u. to SI units per molecule for anapole magnetizabilities, eq. (5), is $\text{Ref. } 20 \text{ } e^2 a_0^3 / m_e = 4.17575662 \times 10^{-39} \text{ JT}^{-2} \text{ m}$. The conversion factor for the magnetic dipole moment is $\hbar / m_e = 1.85480190 \times 10^{-23} \text{ JT}^{-1}$, that for the anapole moment is $e E_h a_0^2 / \hbar = 9.81518895 \times 10^{-34} \text{ JT}^{-1} \text{ m} \equiv \text{m}^3 \text{ A}$.^[20]

functionals, KT3,^[29] B3LYP,^[30] and CAM-B3LYP,^[31] implemented in the DALTON package^[32] used in the computations.

An attempt at sampling the quality of different DFT functionals was made by comparison with coupled cluster singles and doubles (CCSD), limited to the aug-cc-pVDZ basis set.^[33–35]

The equilibrium geometry of compounds **1–3**, see Figure 1, is the same as in previous papers,^[36,37] for alanine and proline, geometrical parameters were optimized at the B3LYP^[30] level of accuracy via the GAUSSIAN code^[38] using aug-cc-pVTZ basis sets.

Extended correlation consistent basis sets of gaugeless Gaussian functions, from the compilation by Dunning and coworkers,^[33–35] were adopted. This choice was motivated by the features of the response properties studied and by the need to describe electron correlation systematically. Within the algebraic approximation, higher quality results are expected by methodically improving the features of the basis set. In fact, it had previously been found that the use of basis sets from Dunning et al.^[33–35] is useful to study convergence of calculated second- and third-rank magnetizabilities to limit values.^[6,7]

Table 2. (2R)-N-methyl-oxaziridine.

| Basis set | x | y | z | tr |
|-------------------|---------|---------|---------|---------|
| aug-cc-pVDZ | -0.2666 | 0.9836 | -0.2671 | |
| | -0.9800 | 0.1822 | -0.5822 | |
| | 0.5745 | 0.5628 | 0.0606 | -0.0079 |
| aug-cc-pVTZ | -0.1849 | 0.7271 | 0.0637 | |
| | -0.9114 | 0.1656 | -0.3524 | |
| aug-cc-pVQZ | 0.2181 | 0.5114 | 0.0017 | -0.0059 |
| | 0.1074 | 0.8523 | -0.0823 | |
| | -0.5470 | -0.0556 | -0.1494 | |
| aug-cc-pV5Z | 0.3402 | -0.0906 | -0.0684 | -0.0055 |
| | 0.0915 | 0.8169 | -0.0122 | |
| | -0.5071 | -0.0089 | -0.1403 | |
| MODENA I | 0.2801 | -0.0825 | -0.0990 | -0.0055 |
| | -0.1235 | 0.0522 | -0.2362 | |
| MODENA II | 0.1509 | 0.0222 | -0.5134 | |
| | -0.0396 | 0.8122 | 0.0879 | -0.0045 |
| | -0.1267 | 0.0684 | -0.2220 | |
| KT3/MODENA I | 0.1410 | 0.0256 | -0.4939 | |
| | -0.0298 | 0.7983 | 0.0837 | -0.0058 |
| | -0.1708 | 0.0307 | -0.1763 | |
| B3LYP/MODENA I | 0.2261 | -0.0217 | -0.7373 | |
| | -0.1519 | 0.9883 | 0.1688 | -0.0079 |
| | -0.1747 | 0.0283 | -0.2242 | |
| CAMB3LYP/MODENA I | 0.2337 | 0.0044 | -0.6894 | |
| | -0.1032 | 0.9630 | 0.1314 | -0.0129 |
| | -0.1717 | 0.0289 | -0.2406 | |
| CCSD/aug-cc-pVDZ | 0.2439 | 0.0142 | -0.6729 | |
| | -0.0716 | 0.9493 | 0.1164 | -0.0137 |
| | -0.2899 | 1.0934 | -0.1719 | |
| | -0.9991 | 0.1395 | -0.7661 | |
| | 0.5696 | 0.7917 | 0.0803 | -0.0234 |

Therefore, we attempted to reach saturation by employing four Dunning basis sets^[33–35] of increasing dimension and characteristics, hereafter referred to as VDZ, VTZ, VQZ, and V5Z for brevity, to designate aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z. They were considered to estimate the degree of convergence of calculated anapole magnetizabilities $a_{\alpha\beta}$, eq. (5), and pseudoscalar \bar{a} . The origin of the coordinate system is the center of mass (CM) in all cases. The result of this preliminary comprehensive test can be judged from the values displayed in Tables (1–5).

Some trends are observed from VDZ to V5Z, for example, decreasing absolute value of a_{xx} and a_{zz} for (2R)-2-methyl-oxirane in Table 1, of a_{yy} and a_{zz} for L-alanine in Table 4, and a_{xx} for L-proline in Table 5, but the overall tendency seems slightly erratic as regards magnitude and sign. Incidentally, a change of sign for values calculated by different basis sets can be observed also in table XI of Tellgren and Fliegl.^[7]

A full assessment of convergence degree is also made difficult by the origin dependence of the $a_{\alpha\beta}$ components. In spite of that, \bar{a} , which is origin independent in the limit of complete basis set,^[6] stabilizes at a nearly converged value with VQZ for **1–3** assuming the coordinate origin at CM. It should also be recalled that the convergence of Dunning basis sets to HF limit values for the second-rank magnetizabilities $\chi_{\alpha\beta}$ is quite slow, as documented by the Supporting Information of our previous paper.^[6]

Now, whereas the $\chi_{\alpha\beta}$ magnetizabilities account for the electron distribution in the intermediate regions of the molecular

Table 3. (R_a)-1,3-dimethyl-allene.

| Basis set | x | y | z | tr |
|-------------------|---------|---------|---------|--------|
| aug-cc-pVDZ | -0.0042 | -2.6390 | 0.0000 | |
| | 3.9610 | 0.0161 | 0.0000 | |
| | 0.0000 | 0.0000 | -0.0055 | 0.0022 |
| aug-cc-pVTZ | -0.2329 | -1.2541 | 0.0000 | |
| | 2.4211 | -0.0321 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.2756 | 0.0035 |
| aug-cc-pVQZ | -0.1568 | -0.1640 | 0.0000 | |
| | 1.3698 | -0.2257 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.3929 | 0.0035 |
| aug-cc-pV5Z | 0.0838 | 0.0628 | 0.0000 | |
| | 0.9941 | -0.4709 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.3975 | 0.0035 |
| MODENA I | -0.8030 | -0.4015 | 0.0000 | |
| | 0.0797 | 0.3452 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.4675 | 0.0032 |
| MODENA II | -0.7982 | -0.3531 | 0.0000 | |
| | 0.0866 | 0.3559 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.4521 | 0.0033 |
| KT3/MODENA I | -0.8925 | -0.4498 | 0.0000 | |
| | 0.1208 | 0.4712 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.4483 | 0.0090 |
| B3LYP/MODENA I | -0.8808 | -0.4652 | 0.0000 | |
| | 0.1435 | 0.4317 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.4700 | 0.0070 |
| CAMB3LYP/MODENA I | -0.8638 | -0.4402 | 0.0000 | |
| | 0.1674 | 0.4293 | 0.0000 | |
| | 0.0000 | 0.0000 | 0.4525 | 0.0060 |
| CCSD/aug-cc-pVDZ | 0.2714 | -2.9316 | 0.0000 | |
| | 4.3655 | 0.0185 | 0.0000 | |
| | 0.0000 | 0.0000 | -0.2502 | 0.0133 |

Table 4. L-alanine.

| Basis set | x | y | z | tr |
|-------------------|---------|---------|---------|---------|
| aug-cc-pVDZ | 0.0035 | -1.0508 | 1.1547 | |
| | 1.4801 | 0.3147 | 0.6732 | |
| | -1.2241 | 0.6543 | -0.3600 | -0.0139 |
| aug-cc-pVTZ | 0.0053 | -0.7422 | 0.8245 | |
| | 1.1212 | 0.2843 | -0.9634 | |
| | -0.8932 | 2.8548 | -0.3234 | -0.0113 |
| aug-cc-pVQZ | 0.0167 | -0.7478 | 0.4201 | |
| | 0.9877 | 0.2152 | -1.6519 | |
| | -0.4040 | 3.8994 | -0.2642 | -0.0107 |
| aug-cc-pV5Z | 0.0133 | -0.8923 | 0.2824 | |
| | 1.0271 | 0.1604 | -1.8383 | |
| | -0.1533 | 4.1754 | -0.2063 | -0.0109 |
| MODENA I | -0.0222 | -1.2997 | -0.2921 | |
| | 1.2483 | 0.1167 | -2.0693 | |
| | 1.0186 | 4.4171 | -0.1229 | -0.0095 |
| MODENA II | -0.0303 | -1.3081 | -0.2548 | |
| | 1.2353 | 0.1195 | -2.0174 | |
| | 0.9738 | 4.3993 | -0.1213 | -0.0107 |
| KT3/MODENA I | 0.0334 | -1.5973 | 0.1866 | |
| | 1.3435 | 0.0256 | -1.9026 | |
| | -0.1336 | 4.5265 | -0.1054 | -0.0155 |
| B3LYP/MODENA I | 0.0212 | -1.5779 | 0.2497 | |
| | 1.3344 | 0.0341 | -1.9596 | |
| | -0.1736 | 4.6420 | -0.0906 | -0.0118 |
| CAMB3LYP/MODENA I | 0.0166 | -1.5533 | 0.2702 | |
| | 1.3319 | 0.0315 | -2.0088 | |
| | -0.1862 | 4.6587 | -0.0785 | -0.0101 |
| CCSD/aug-cc-pVDZ | 0.0219 | -1.1095 | 1.3434 | |
| | 1.5101 | 0.2795 | 0.6046 | |
| | -1.5059 | 0.7849 | -0.3539 | -0.0175 |

Table 5. L-proline.

| Basis set | x | y | z | tr |
|-------------------|---------|---------|---------|---------|
| aug-cc-pVDZ | -1.3511 | -3.0318 | -0.1001 | |
| | 3.4374 | 0.5738 | -3.3772 | |
| | 1.2112 | 3.8300 | 0.7318 | -0.0152 |
| aug-cc-pVTZ | -1.2381 | -1.5736 | 0.0434 | |
| | 2.2077 | 1.0070 | 0.3219 | |
| | 1.1309 | -1.3832 | 0.1969 | -0.0114 |
| aug-cc-pVQZ | -1.0856 | -0.8065 | 0.2222 | |
| | 1.8037 | 1.0866 | 2.1999 | |
| | 0.9019 | -3.6438 | -0.0356 | -0.0116 |
| aug-cc-pV5Z | -0.8185 | -0.6512 | 0.7119 | |
| | 2.0736 | 0.8417 | 2.3413 | |
| | 0.2855 | -4.3241 | -0.0597 | -0.0122 |
| MODENA I | -0.3650 | -2.8497 | -0.9602 | |
| | 1.5071 | 0.7350 | 2.5099 | |
| | 3.3889 | -3.5999 | -0.4066 | -0.0122 |
| MODENA II | -0.3602 | -2.8551 | -0.9279 | |
| | 1.5218 | 0.7441 | 2.5004 | |
| | 3.3756 | -3.6231 | -0.4198 | -0.0120 |
| KT3/MODENA I | -0.5233 | -2.7658 | -0.8546 | |
| | 1.3257 | 1.0150 | 2.3071 | |
| | 3.2648 | -3.0880 | -0.5211 | -0.0098 |
| B3LYP/MODENA I | -0.3989 | -2.9330 | -0.8071 | |
| | 1.4514 | 0.8950 | 2.2905 | |
| | 3.4149 | -3.2837 | -0.5264 | -0.0101 |
| CAMB3LYP/MODENA I | -0.3605 | -3.0143 | -0.8406 | |
| | 1.5047 | 0.8479 | 2.3500 | |
| | 3.4641 | -3.3591 | -0.5166 | -0.0097 |

domain, 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_z factor, eqs. (7) and (8). In any event, the VQZ and V5Z basis sets from Dunning become impractical for big molecules, therefore the basis set MODENA I, an uncontracted (13s10p5d2f/8s4p1d) carrying optimized polarization functions for electric and magnetic properties,^[39] and smaller in size than the largest Dunning basis sets, was also taken into account to further document its quality in view of future applications to larger molecular systems.

Among the basis sets considered in this study, MODENA I gives the best RPA predictions of the second-rank magnetizability $\chi_{\alpha\beta}$ from the point of view of a variational theorem, compare for eq. (21) of Moccia,^[40] since it yields the largest paramagnetic contributions to the diagonal tensor components. Conversely, some additional doubt has been cast on convergence of the results obtained for $a_{\alpha\beta}$ by VDZ-V5Z basis set, since the predictions from MODENA I are in many instances of opposite sign, as can be observed in Tables (1–5), although \bar{a} pseudoscalars computed by VQZ, V5Z, and MODENA I are very close for the systems studied. For these reasons a larger uncontracted (13s10p5d2f/11s7p4d) basis set, previously tested for predicting anapole magnetizabilities of $C_4H_4X_2$ cyclic molecules for $X = O, S, Se,$ and $Te,$ ^[6] hereafter referred to as MODENA II, has also been employed. These basis sets are available as Supporting Information.

The use of a larger basis set for the hydrogen atoms is expected to increase flexibility of the electronic wavefunction in their regions for the molecules studied. Nonetheless, the

theoretical predictions obtained by MODENA I and II are in all cases quite close to one another. Such a result is interpreted as a convincing indication of quite good quality for the smaller MODENA I basis set. Therefore, allowing for the results arrived at in a previous paper^[6] and in the present investigations, we are confident that MODENA I, developed ad hoc for near HF estimates of second-rank magnetizabilities, constitutes a reasonable trade-off between size and accuracy for \bar{a} , and we recommend its use in future computational studies. For that reason it has been employed in the subsequent investigation on the effects of electron correlation via DFT schemes.

The relative quality of the three functionals considered here, B3LYP,^[30] KT3^[29] and CAM-B3LYP,^[31] is difficult to establish, as no regular trend could be observed. For (2R)-2-methyl-oxirane and L-proline, the results displayed in Tables 1 and 5, respectively, are quite close to one another, for (R_a)-1,3-dimethylallene and L-alanine, Tables 3 and 4, KT3 results are larger in magnitude than B3LYP and CAM-B3LYP, but just the opposite was found for (2R)-N-methyl-oxaziridine in Table 2.

A comparison with CCSD, limited to the VDZ basis set because of the dimension of the molecules studied, is not illuminating. For (2R)-2-methyl-oxirane the CCSD value is smaller in magnitude than the corresponding RPA and DFT, but the contrary is observed for (2R)-N-methyl-oxaziridine. In any event, with the possible exception of (2R)-2-methyl-oxirane, correlation effects are sizeable, and the order of magnitude of CCSD and DFT is the same. In some cases the DFT results from MODENA I basis set are one order of magnitude larger than RPA.

Concluding Remarks

The RSPT of the molecular response to a nonuniform magnetic field has been revisited, obtaining relationships more manageable from the computational point of view and showing that the property tensors can also be expressed in terms of the electronic current densities $\mathbf{J}^{\mathbf{B}}$ and $\mathbf{J}^{\mathbf{C}}$, induced by the magnetic field \mathbf{B} and curl $\mathbf{C} = \nabla \times \mathbf{B}$. Approaches based on current densities are expected to be very useful to rationalize the phenomenology of a molecule in the presence of nonuniform magnetic perturbation via streamline and modulus maps of the induced electron flow, by visualizing and quantifying the contributions of different spatial domains.

Five chiral molecules have been investigated in the present paper, (2R)-2-methyl-oxirane, (2R)-N-methyl-oxaziridine, (R_a)-1,3-dimethylallene L-alanine and L-proline, to determine their anapole magnetizability $a_{\alpha\beta}$ via a procedure based on RSPT, outlined in Anapole moment and anapole magnetizabilities and Calculations of anapole magnetizabilities for chiral molecules in a magnetic field with uniform curl sections.

Allowing for the present computational tests, extending those reported in previous papers,^[5,6,41] one can reasonably argue that the approach developed by us to calculate the average value \bar{a} of the $a_{\alpha\beta}$ tensor yields reliable numerical predictions at the RPA and DFT levels of accuracy. Conversely, basis set convergence, investigated via four extended basis sets from Dunning and coworkers,^[33–35] has not been achieved

to a fully satisfactory extent for the individual, diagonal and off-diagonal, components $a_{\alpha\beta}$ shown in Tables (1–5). In fact, results from different basis sets are frequently characterized by opposite sign.

An uncontracted (13s10p5d2f/8s4p1d) MODENA I basis set, smaller in size than the largest Dunning basis sets, constructed ad hoc by employing polarization functions optimized for electric and magnetic properties,^[5] was also taken into account, demonstrating its practicality as an alternative tool for predicting \bar{a} at the RPA level and to study electron correlation effects by DFT via three density functionals.

The $a_{\alpha\beta}$ anapole magnetizability and the pseudoscalar \bar{a} are in principle measurable quantities, even if the tiny magnitude of the values predicted for the compounds studied would seem to make it impractical for experimental detection by laboratory instruments nowadays available. In fact, the largest calculated absolute value of isotropic anapole magnetizability for two aminoacids, alanine and proline, is approximately 0.01 a.u., that is, $\approx 4 \times 10^{-41} \text{ JT}^{-2} \text{ m}$ per molecule. It is hardly possible that this value may be significant in real circumstances for chiral discrimination.

Keywords: magnetic response properties · molecules in a magnetic field with uniform gradient · higher magnetizability tensors · anapole magnetizabilities · electron correlation effects

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 Additional Supporting Information may be found in the online version of this article.

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