

Magnetizabilities of Diatomic and Linear Triatomic Molecules in a Time-Independent Nonuniform Magnetic Field

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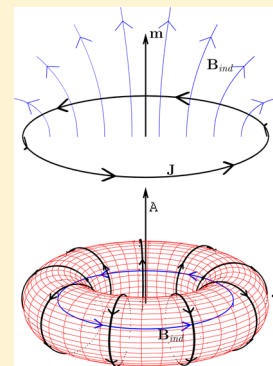
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ABSTRACT: The theory of response of a molecule in the presence of a static nonuniform magnetic field with uniform gradient is reviewed and extended. Induced magnetic dipole, quadrupole, and anapole moments are expressed via multipole magnetic susceptibilities. Dependence of response properties on the origin of the coordinate system with respect to which they are defined is investigated. Relationships describing the change of multipole and anapole susceptibilities in a translation of the reference system are reported. For a single molecule, two quantities are invariant and, in principle, experimentally measurable, that is, the induced magnetic dipole and the interaction energy. The trace of a second-rank anapole susceptibility, related to a pseudoscalar obtained by spatial averaging of the dipole–quadrupole susceptibility, of different sign for *D* and *L* enantiomeric systems, is origin independent. Therefore, in an isotropic chiral medium a homogeneous magnetic field induces an electronic anapole, having the same magnitude but opposite sign for two enantiomorphs. Calculations have been carried out for a set of diatomic and linear triatomic systems characterized by the presence of magnetic-field induced toroidal electron currents.



1. INTRODUCTION

The rationalization of molecular magnetic response of a molecule in the presence of a nonhomogeneous magnetic field, either static or time dependent, is by no means a simple univocal task. Whereas the theory of second rank tensors, for example, magnetic susceptibilities¹ and nuclear magnetic shieldings^{2–4} has been systematized according to a widely accepted scheme if the applied vector field B_α is static and spatially uniform, the definition of higher-rank response tensors (coupled to spatial derivatives

$$B_{\lambda\dots\beta\alpha} = \nabla_\lambda\dots\nabla_\beta B_\alpha \quad (1)$$

in the Taylor series of the molecular interaction energy) depends on the choice of corresponding definitions of total induced magnetic multipoles^{5,6} and on the expression of the vector potential A_α in general a function of position and time. Drawbacks affecting earlier approaches, arising for instance from questionable definitions of magnetic quadrupole, have been pointed out.⁵ An explicit choice of gauge for the electromagnetic potentials is therefore needed as a fundamental preliminary task.

Expressions of magnetizabilities and nuclear magnetic shieldings of a molecule interacting with a spatially nonuniform external magnetic field were reported in previous theoretical

studies,^{7–11} allowing for a magnetic multipole expansion based on the Bloch gauge.^{12–14} The Bloch electromagnetic potentials¹² have been later rediscovered by others.^{15–18} A simple compact expression,^{19–24} defining a gauge usually referred to as Poincaré's,^{19,24,25} yields a power series for the vector potential equivalent to Bloch's.^{26–29}

The present paper is aimed at (i) defining a set of anapole susceptibilities, (ii) determining their properties, (iii) evaluating third- and fourth-rank tensors corresponding respectively to magnetic dipole-magnetic quadrupole and magnetic quadrupole-magnetic quadrupole magnetizabilities in simple diatomics and linear triatomics, allowing for definitions obtained within the Bloch gauge,^{7–11} reported in Section 2. 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,^{10,11,30} which can be related to mixed magnetic

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multipole magnetizabilities. As reported previously,³¹ chiral distortions may give rise to anapolar current density lines, that is, lines spiraling around a topological torus that has been predicted for big molecules with nuclei arranged on a torus surface.³²

Calculations have been carried out at the Hartree–Fock level of accuracy, 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 Section 3, two different origins were considered in preliminary test calculations on the OH[−] anion. The conditions for invariance of the interaction energy and other molecular magnetic properties induced by a nonuniform magnetic field with a uniform gradient, under a translation of the coordinate system, are discussed in the same section. Results are reported in Section 4. Conclusions and outlook are presented in Section 5.

2. MOLECULAR MULTIPOLE AND ANAPOLE MOMENTS

Standard tensor formalism is employed throughout this article, for example, the Einstein convention of implicit summation over two repeated Greek subscripts is in force and $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. The notation adopted in previous references^{7,10,11} is used. The SI system of units has been chosen.

Within the Born–Oppenheimer approximation, for a molecule with n electrons and N clamped nuclei, charge, mass, position, canonical, and angular momentum of the i th electron are indicated in the configuration space by $-e$, m_e , r_i , \hat{p}_i , $\hat{l}_i = r_i \times \hat{p}_i$, $i = 1, 2, \dots, n$. Analogous quantities for nucleus I are $Z_I e$, M_I , R_I , and so forth, for $I = 1, 2, \dots, N$. Capital letters denote total electronic operators, for example

$$\hat{R} = \sum_{i=1}^n r_i, \quad \hat{P} = \sum_{i=1}^n \hat{p}_i, \quad \hat{L} = \sum_{i=1}^n \hat{l}_i$$

etc.

The electric multipole moments of the electron distribution are defined via the Taylor series^{7,10,12}

$$\hat{\mu}_{\alpha_1 \dots \alpha_k} = -\frac{e}{(k+1)!} \sum_{i=1}^n (r_{\alpha_1} \dots r_{\alpha_k})_i \quad (2)$$

then the expressions for the electric dipole and quadrupole operators from eq 2 are

$$\hat{\mu}_{\alpha} = -e \sum_{i=1}^n (r_{\alpha})_i \quad (3)$$

$$\hat{\mu}_{\alpha\beta} = -\frac{e}{2} \sum_{i=1}^n (r_{\alpha} r_{\beta})_i \quad (4)$$

The electronic operators for magnetic multipole moments, omitting contributions from electron spin, are cast in the form^{7,10,12}

$$\hat{m}_{\alpha_1 \dots \alpha_k} = -\frac{k+1}{(k+2)!} \frac{e}{2m_e} \sum_{i=1}^n (\hat{l}_{\alpha_1} r_{\alpha_2} \dots r_{\alpha_k} + r_{\alpha_1} \dots r_{\alpha_{k-1}} \hat{l}_{\alpha_k})_i \quad (5)$$

For instance, the Hermitian magnetic multipole operators up to the hexadecapole are

$$\hat{m}_{\alpha} = -\frac{e}{2m_e} \sum_{i=1}^n \hat{l}_{i\alpha} \quad (6)$$

$$\hat{m}_{\alpha\beta} = -\frac{e}{6m_e} \sum_{i=1}^n \{\hat{l}_{i\alpha}, r_{i\beta}\}_+ \quad (7)$$

$$\hat{m}_{\alpha\beta\gamma} = -\frac{e}{16m_e} \sum_{i=1}^n \{\hat{l}_{i\alpha}, r_{i\beta} r_{i\gamma}\}_+ \quad (8)$$

$$\hat{m}_{\alpha\beta\gamma\delta} = -\frac{e}{60m_e} \sum_{i=1}^n \{\hat{l}_{i\alpha}, r_{i\beta} r_{i\gamma} r_{i\delta}\}_+ \quad (9)$$

using $\{\hat{A}, \hat{B}\}_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$ to denote anticommutators. It is immediately observed that if the initial tensor index is repeated the sum over the Cartesian coordinates of the multipole moment vanishes, giving a null operator, for instance

$$\hat{m}_{\alpha\alpha} = \hat{m}_{\alpha\alpha\beta\dots} = \hat{m}_{\alpha\beta\dots\alpha\dots} = 0 \quad (10)$$

The electronic operators for the permanent (or unperturbed) magnetic multipoles in eq 5 are used to rationalize the response of an isolated molecule. In the presence of a vector potential $\mathbf{A}(\mathbf{r}, t)$, the canonical momentum is replaced by the mechanical momentum, including the electromagnetic interactions via the minimal coupling procedure of Gell-Mann³³

$$\hat{P} = \sum_{i=1}^n \hat{p}_i \rightarrow \hat{\Pi} = \sum_{i=1}^n \hat{\pi}_i, \quad \hat{\pi}_i = \hat{p}_i + e\mathbf{A}_i \quad (11)$$

For the angular momentum the corresponding replacement gives

$$\hat{L} = \sum_{i=1}^n \hat{l}_i \rightarrow \hat{\Lambda} = \hat{L} + e \sum_{i=1}^n r_i \times \mathbf{A}_i \quad (12)$$

Allowing for eqs 5 and 12 within the multipolar Bloch gauge¹² for the vector potential the operators for perturbed magnetic multipole moments become^{7,10}

$$\hat{m}'_{\alpha} = \hat{m}_{\alpha} + \hat{\chi}_{\alpha\beta}^d B_{\beta}(0, t) + \hat{\chi}_{\alpha\beta\gamma}^d B_{\gamma\beta}(0, t) + \hat{\chi}_{\alpha\beta\gamma\delta}^d B_{\delta\gamma\beta}(0, t) + \dots \quad (13)$$

$$\hat{m}'_{\alpha\beta} = \hat{m}_{\alpha\beta} + \hat{\chi}_{\alpha\gamma\beta}^d B_{\gamma}(0, t) + \frac{16}{9} \hat{\chi}_{\alpha\gamma\beta\delta}^d B_{\delta\gamma}(0, t) + \frac{5}{2} \hat{\chi}_{\alpha\gamma\beta\delta\epsilon}^d B_{\epsilon\delta\gamma}(0, t) + \dots \quad (14)$$

$$\hat{m}'_{\alpha\beta\gamma} = \hat{m}_{\alpha\beta\gamma} + \hat{\chi}_{\alpha\delta\beta\gamma}^d B_{\delta}(0, t) + \frac{5}{2} \hat{\chi}_{\alpha\delta\beta\gamma\epsilon}^d B_{\epsilon\delta}(0, t) + \dots \quad (15)$$

and so forth, where the operators for diamagnetic contributions to the multipole magnetizabilities are

$$\hat{\chi}_{\alpha\beta}^d = -\frac{e^2}{4m_e} \sum_{i=1}^n (r_i^2 \delta_{\alpha\beta} - r_{\alpha} r_{\beta})_i \quad (16)$$

$$\hat{\chi}_{\alpha\beta\gamma}^d = -\frac{e^2}{6m_e} \sum_{i=1}^n [(r_i^2 \delta_{\alpha\beta} - r_{\alpha} r_{\beta}) r_{\gamma}]_i \quad (17)$$

$$\hat{\chi}_{\alpha\beta\gamma\delta}^d = -\frac{e^2}{16m_e} \sum_{i=1}^n [(r_i^2 \delta_{\alpha\beta} - r_{\alpha} r_{\beta}) r_{\gamma} r_{\delta}]_i \quad (18)$$

and so forth, denoting by $r_v^2 \equiv r_v r_v$ the squared modulus of the electronic position vector. In these relationships a semicolon

separates sets of symmetric indices, which can be freely permuted within each set.

Tensor operators $\hat{\chi}_{\alpha\beta;\alpha}^d$ and $\hat{\chi}_{\alpha\beta;\alpha\gamma}^d$ vanish identically, therefore an equation analogous to (10) holds also for the perturbed magnetic multipole operators, that is,

$$\hat{m}'_{\alpha\alpha} = \hat{m}'_{\alpha\alpha\beta\dots} = \hat{m}'_{\alpha\beta\dots\alpha\dots} = 0 \quad (19)$$

The expectation values of the multipole operators over the a reference electronic state, $^{34} |\Psi_a\rangle \equiv |a\rangle$ of the perturbed molecule are indicated by, for example

$$\begin{aligned} \mu_{\alpha\beta\dots} &= \langle a | \hat{\mu}_{\alpha\beta\dots} | a \rangle, & m_{\alpha\beta\dots} &= \langle a | \hat{m}_{\alpha\beta\dots} | a \rangle, \\ M_{\alpha\beta\dots} &= \langle a | \hat{m}'_{\alpha\beta\dots} | a \rangle \end{aligned} \quad (20)$$

2.1. Multipole Magnetizabilities in a Static Magnetic Field. Second-order Rayleigh–Schrodinger perturbation theory is applied to obtain the paramagnetic contributions to the multipole magnetic susceptibilities of a molecule in the presence of a nonhomogeneous time-independent magnetic field^{7,10,14}

$$\begin{aligned} \chi_{\alpha,\beta}^p &= \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathcal{R}(\langle a | \hat{m}_{\alpha} | j \rangle \langle j | \hat{m}_{\beta} | a \rangle) \\ &= \chi_{\beta,\alpha}^p \equiv \chi_{\alpha\beta}^p \end{aligned} \quad (21)$$

$$\begin{aligned} \chi_{\alpha,\beta\gamma}^p &= \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathcal{R}(\langle a | \hat{m}_{\alpha} | j \rangle \langle j | \hat{m}_{\beta\gamma} | a \rangle) \\ &= \chi_{\beta\gamma,\alpha}^p \end{aligned} \quad (22)$$

$$\begin{aligned} \chi_{\alpha\beta,\gamma\delta}^p &= \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathcal{R}(\langle a | \hat{m}_{\alpha\beta} | j \rangle \langle j | \hat{m}_{\gamma\delta} | a \rangle) \\ &= \chi_{\gamma\delta,\alpha\beta}^p \end{aligned} \quad (23)$$

etc. Owing to eq 10

$$\chi_{\alpha,\beta\beta}^p = 0 = \chi_{\alpha\beta,\gamma\gamma}^p \quad (24)$$

and so on. In these relationships, a comma is used to separate groups of indices that can be freely permuted, for example, $\chi_{\alpha\beta\dots,\lambda\mu\dots}^p = \chi_{\lambda\mu\dots,\alpha\beta\dots}^p$ since each group refers specifically to a given magnetic multipole of the series, see eq 5.

The diamagnetic contributions to the magnetic susceptibilities in the reference state $|a\rangle$ are arrived at allowing for eqs 16–18

$$\chi_{\alpha\beta}^d = \langle a | \hat{\chi}_{\alpha\beta}^d | a \rangle \quad (25)$$

$$\chi_{\alpha\beta;\gamma}^d = \langle a | \hat{\chi}_{\alpha\beta;\gamma}^d | a \rangle \quad (26)$$

$$\chi_{\alpha\beta;\gamma\delta}^d = \langle a | \hat{\chi}_{\alpha\beta;\gamma\delta}^d | a \rangle \quad (27)$$

and so forth.

Total static susceptibilities are obtained by summing paramagnetic and diamagnetic contributions^{7,10,14}

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^p + \chi_{\alpha\beta}^d \quad (28)$$

$$\chi_{\alpha,\beta\gamma} = \chi_{\alpha,\beta\gamma}^p + \chi_{\alpha,\beta\gamma}^d \quad (29)$$

$$\chi_{\alpha\beta,\gamma\delta} = \chi_{\alpha\beta,\gamma\delta}^p + \frac{16}{9} \chi_{\alpha\gamma;\beta\delta}^d \quad (30)$$

etc.

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

$$\begin{aligned} \bar{\chi} &= \frac{1}{6} \chi_{\alpha\beta,\gamma} \varepsilon_{\alpha\beta\gamma} \\ &= \frac{1}{6} (\chi_{xy,z} - \chi_{xz,y} + \chi_{yz,x} - \chi_{yx,z} + \chi_{zx,y} - \chi_{zy,x}) \end{aligned} \quad (31)$$

is different from zero for a chiral molecule, see Table 1 and eq 46 hereafter.

Table 1. Type and Symmetry of Magnetic Properties under Parity P and Time Reversal T^a

tensor	type	P	T
B_{α}	axial	+	–
$B_{\alpha\beta}$	axial	–	–
$C_{\alpha} = \varepsilon_{\alpha\beta\gamma} B_{\beta\gamma}$	polar	–	–
$B_{\alpha\beta\gamma}$	axial	+	–
M_{α}	axial	+	–
$M_{\alpha\beta}$	axial	–	–
$M_{\alpha\beta\gamma}$	axial	+	–
\mathcal{A}_{α}	polar ^b	–	–
$\chi_{\alpha\beta}$	polar	+	+
$\chi_{\alpha\beta,\gamma}$	polar	–	+
$\chi_{\alpha\beta,\gamma\delta}$	polar	+	+
$a_{\alpha\beta}$	axial	–	+
$\bar{a} = (1/3)a_{\alpha\alpha}$	pseudoscalar ^c	–	+
$b_{\alpha\beta}$	polar	+	+
$c_{\alpha,\beta\gamma}$	axial	+	+
$\bar{c} = (1/6)\varepsilon_{\alpha\beta\gamma} c_{\alpha,\beta\gamma}$	scalar	+	+

^aSee, for instance, the Birss book⁵⁴ and a previous paper.¹¹ ^bReferred to as axio-polar by Schmid.^{11,59} ^c $\bar{\chi} = (1/6)\varepsilon_{\alpha\beta\gamma}\chi_{\alpha,\beta\gamma} = -\bar{a}$.

2.2. Interaction Energy, Induced Magnetic Dipole, Quadrupole, and Anapole for a Molecule in a Magnetic Field with Uniform Gradient. We will now consider a diamagnetic molecule in the presence of a nonuniform magnetic field with flux density \mathbf{B} , assuming for simplicity that the gradient $\nabla\mathbf{B}$ is uniform, and neglecting contributions from higher derivatives. It is also supposed that the molecular response is linear. Accordingly, the interaction energy of the molecule in the field is written in the form

$$W = W^{(0)} - \frac{1}{2} \chi_{\alpha\beta} B_{\alpha} B_{\beta} - \chi_{\alpha,\beta\gamma} B_{\alpha} B_{\beta\gamma} - \frac{1}{2} \chi_{\alpha\beta,\gamma\delta} B_{\beta\alpha} B_{\delta\gamma} \quad (32)$$

with $W^{(0)}$ as the energy of the isolated molecule. The magnetic field is evaluated at the origin of the coordinate system. The induced magnetic dipole moment is obtained by differentiating W

$$-\frac{\partial W}{\partial B_{\alpha}} = M_{\alpha} = \chi_{\alpha\beta} B_{\beta} + \chi_{\alpha,\beta\gamma} B_{\beta\gamma} \quad (33)$$

The induced magnetic quadrupole moment is analogously obtained from

$$-\frac{\partial W}{\partial B_{\beta\alpha}} = M_{\alpha\beta} = \chi_{\alpha\beta,\gamma} B_{\gamma} + \chi_{\alpha\beta,\gamma\delta} B_{\delta\gamma} \quad (34)$$

Alternative expressions of the interaction energy, eq 32, can be obtained by expressing the magnetic field gradient, that is, the nonsymmetric second rank tensor $B_{\beta\alpha}$ in terms of its symmetric and antisymmetric components

$$\begin{aligned} B_{\beta\alpha}^{(S)} &= \frac{1}{2}(B_{\beta\alpha} + B_{\alpha\beta}), \\ B_{\beta\alpha}^{(A)} &= \frac{1}{2}(B_{\beta\alpha} - B_{\alpha\beta}) = \frac{1}{2}\varepsilon_{\beta\alpha\gamma}C_\gamma \end{aligned} \quad (35)$$

introducing the curl $\mathbf{C} = (\nabla \times \mathbf{B})$. The derivative of the energy, eq 32, with respect to the components of \mathbf{C} defines the components of the anapole polar vector^{10,11}

$$\begin{aligned} -\frac{\partial W}{\partial C_\lambda} &= \mathcal{A}_\lambda \\ &= -\frac{1}{2}\varepsilon_{\lambda\alpha\beta}\left\{\chi_{\alpha\beta,\gamma}B_\gamma + \chi_{\alpha\beta,\gamma\delta}\left[B_{\delta\gamma}^{(S)} + \frac{1}{2}\varepsilon_{\mu\delta\gamma}C_\mu\right]\right\} \end{aligned} \quad (36)$$

induced in the electrons of the molecule by a nonuniform magnetic field with uniform gradient.^{10,11}

The electronic anapole of the molecule can alternatively be defined¹⁰ from the magnetic quadrupole, eq 34, induced by the applied nonhomogeneous magnetic field. The latter is not symmetric in the indices α, β , but it can be rewritten as a sum of symmetric and antisymmetric components

$$M_{\alpha\beta} = M_{\alpha\beta}^{(S)} + M_{\alpha\beta}^{(A)} \quad (37)$$

$$M_{\alpha\beta}^{(S)} = \frac{1}{2}(M_{\alpha\beta} + M_{\beta\alpha}) \quad (38)$$

$$M_{\alpha\beta}^{(A)} = \frac{1}{2}(M_{\alpha\beta} - M_{\beta\alpha}) \quad (39)$$

The molecular anapole moment is obtained from the antisymmetric components

$$\mathcal{A}_\gamma = -\frac{1}{2}\varepsilon_{\alpha\beta\gamma}M_{\alpha\beta} \equiv -\frac{1}{2}\varepsilon_{\alpha\beta\gamma}M_{\alpha\beta}^{(A)} \quad (40)$$

This relationship can be inverted to obtain

$$M_{\alpha\beta}^{(A)} = -\varepsilon_{\alpha\beta\gamma}\mathcal{A}_\gamma \quad (41)$$

Allowing for the definition of mixed multipole magnetic susceptibilities, eqs 28–30, the relationship

$$\mathcal{A}_\gamma = -\frac{1}{2}\varepsilon_{\alpha\beta\gamma}(\chi_{\alpha\beta,\delta}B_\delta + \chi_{\alpha\beta,\delta\varepsilon}B_{\varepsilon\delta} + \dots) \quad (42)$$

gives the general perturbation expansion for the electron-orbit contribution to the anapole of a molecule induced by a nonuniform magnetic field. Using eq 35, it can be verified that the definitions for the magnetic-field induced molecular anapole, eqs 36 and 42, are identical for terms up to the first field gradient. It should be recalled that, in accord with eqs 13–15, the magnetic field and its derivatives are evaluated at the origin of the coordinate system within expressions 36 and 42.

The induced magnetic dipole moment, eq 33, is an axial vector, even under parity P and odd under time reversal T , the magnetic quadrupole, eq 34, and the axio-polar¹¹ anapole, eq 36, are P -odd and T -odd, see Table 1. However, there is no parity-violation effect on the interaction energy, see below, eq 49

The tensors

$$a_{\gamma\delta} = -\frac{\partial^2 W}{\partial B_\delta \partial C_\gamma} = \frac{\partial \mathcal{A}_\gamma}{\partial B_\delta} = -\frac{1}{2}\varepsilon_{\alpha\beta\gamma}\chi_{\alpha\beta,\delta} \quad (43)$$

$$b_{\gamma\delta} = -\frac{\partial^2 W}{\partial C_\delta \partial C_\gamma} = \frac{\partial \mathcal{A}_\gamma}{\partial C_\delta} = \frac{1}{4}\varepsilon_{\alpha\beta\gamma}\varepsilon_{\lambda\mu\delta}\chi_{\alpha\beta,\lambda\mu} = b_{\delta\gamma} \quad (44)$$

$$c_{\gamma,\delta\varepsilon} = -\frac{\partial^2 W}{\partial B_{\varepsilon\delta}^{(S)} \partial C_\gamma} = \frac{\partial \mathcal{A}_\gamma}{\partial B_{\varepsilon\delta}^{(S)}} = -\frac{1}{2}\varepsilon_{\alpha\beta\gamma}\chi_{\alpha\beta,\delta\varepsilon} \quad (45)$$

define second- and third-rank anapole susceptibilities.³² The averaged trace of the $a_{\gamma\delta}$ anapole susceptibility, eq 43

$$\bar{a} = \frac{1}{3}a_{\gamma\gamma} = -\frac{1}{6}\varepsilon_{\alpha\beta\gamma}\chi_{\alpha\beta,\gamma} = -\bar{\chi} \quad (46)$$

equals the pseudoscalar defined via eq 31 changed of sign. It 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, eqs 36 and 42.¹¹ In fact, in disordered phase, gas, or solution, the orbital electronic anapole

$$\mathcal{A} = -\bar{\chi}\mathbf{B} \quad (47)$$

induced by an external magnetic field has opposite direction in two enantiomeric molecules. Allowing for the definitions of magnetic dipole, eq 33, magnetic quadrupole, eq 34, anapole, eqs 36 and 42, for eqs 35, 37, and 38, and assuming linear response, the interaction energy, eq 32, can be rewritten in the alternative forms

$$W = W^{(0)} - \frac{1}{2}M_\alpha B_\alpha - \frac{1}{2}M_{\alpha\beta} B_{\beta\alpha} \quad (48)$$

$$= W^{(0)} - \frac{1}{2}M_\alpha B_\alpha - \frac{1}{2}\mathcal{A}_\alpha C_\alpha - \frac{1}{2}M_{\alpha\beta}^{(S)} B_{\beta\alpha}^{(S)} \quad (49)$$

3. CHANGE OF MOLECULAR PROPERTIES IN A TRANSLATION OF THE COORDINATE SYSTEM

In a translation of origin of the coordinate system

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \quad (50)$$

where \mathbf{d} is an arbitrary shift vector, the transformation law for the third-rank magnetic susceptibility, eq 29, reads^{7,10}

$$\chi_{\gamma,\alpha\beta}(\mathbf{r}'') = \chi_{\gamma,\alpha\beta}(\mathbf{r}') - \chi_{\gamma\alpha}d_\beta + \frac{1}{3}\chi_{\gamma\delta}d_\delta\delta_{\alpha\beta} \quad (51)$$

The corresponding equation for the quadrupole–quadrupole susceptibility, eq 30, is¹⁰

$$\begin{aligned} \chi_{\alpha\beta,\gamma\delta}(\mathbf{r}'') &= \chi_{\alpha\beta,\gamma\delta}(\mathbf{r}') - \chi_{\alpha,\gamma\delta}(\mathbf{r}')d_\beta - \chi_{\gamma,\alpha\beta}(\mathbf{r}')d_\delta \\ &+ \frac{1}{3}d_\lambda[\chi_{\lambda,\alpha\beta}(\mathbf{r}')\delta_{\gamma\delta} + \chi_{\lambda,\gamma\delta}(\mathbf{r}')\delta_{\alpha\beta}] + \chi_{\alpha\gamma}d_\beta d_\delta \\ &- \frac{1}{3}d_\nu(\chi_{\nu\gamma}\delta_{\alpha\beta}d_\delta + \chi_{\nu\alpha}\delta_{\gamma\delta}d_\beta) + \frac{1}{9}d_\mu d_\nu \chi_{\mu\nu}\delta_{\alpha\beta}\delta_{\gamma\delta} \end{aligned} \quad (52)$$

The change in the anapole susceptibilities 43 and 45 is obtained by

$$a_{\gamma\delta}(\mathbf{r}'') = a_{\gamma\delta}(\mathbf{r}') + \frac{1}{2}\varepsilon_{\alpha\beta\gamma}\chi_{\delta\alpha}d_\beta \quad (53)$$

and

$$\begin{aligned}
c_{\gamma,\delta\epsilon}(\mathbf{r}') &= c_{\gamma,\delta\epsilon}(\mathbf{r}') + \frac{1}{2}\epsilon_{\alpha\beta\gamma}\chi_{\alpha,\delta\epsilon}(\mathbf{r}')d_{\beta} + \frac{1}{2}\epsilon_{\alpha\beta\gamma}\chi_{\delta,\alpha\beta}(\mathbf{r}')d_{\epsilon} \\
&\quad - \frac{1}{6}\epsilon_{\alpha\beta\gamma}\chi_{\lambda,\alpha\beta}(\mathbf{r}')\delta_{\delta\epsilon}d_{\lambda} - \frac{1}{2}\epsilon_{\alpha\beta\gamma}\chi_{\delta\alpha}d_{\beta}d_{\epsilon} \\
&\quad + \frac{1}{6}\epsilon_{\alpha\beta\gamma}\chi_{\nu\alpha}\delta_{\delta\epsilon}d_{\beta}d_{\nu}
\end{aligned} \quad (54)$$

According to eq 53, the diagonal components (and the trace) of $a_{\gamma\delta}$ are origin independent in the principal axis system of the symmetric $\chi_{\alpha\beta}$ tensor. The pseudoscalar average anapole magnetizability, eq 46, owing to the same relationship, eq 53, is origin independent, that is

$$\bar{a}(\mathbf{r}'') = \bar{a}(\mathbf{r}') \quad (55)$$

in any coordinate system, since the Levi-Civita skew tensor is antisymmetric, whereas the second-rank magnetizability is symmetric. This result is similar to that found for the P -odd and T -even optical rotatory power, rationalized by a tensor having origin-independent trace but origin dependent diagonal and off-diagonal components.^{13,14,35} According to eq 47, the induced anapole, aligned with the applied uniform magnetic field in gas and liquid media, is origin independent.

In an isotropic sample, introducing the scalar

$$\bar{c} = \frac{1}{6}c_{\gamma,\delta\epsilon}\epsilon_{\gamma\delta\epsilon} \quad (56)$$

by spatial averaging, one finds

$$\bar{c} = -\bar{b} \quad (57)$$

where

$$\bar{b} = \frac{1}{3}b_{\gamma\gamma} = \frac{1}{12}(\chi_{\alpha\beta,\alpha\beta} - \chi_{\alpha\beta,\beta\alpha}) \quad (58)$$

is the average trace of the anapole susceptibility, eq 44. These quantities are origin dependent

$$\begin{aligned}
\bar{b}(\mathbf{r}'') &= \bar{b}(\mathbf{r}') + \frac{1}{12}[\chi_{\alpha\alpha}d_{\beta}d_{\beta} - \chi_{\alpha\beta}d_{\alpha}d_{\beta} + \chi_{\alpha,\beta\alpha}(\mathbf{r}')d_{\beta} \\
&\quad + \chi_{\beta,\alpha\beta}(\mathbf{r}')d_{\alpha} - 2\chi_{\alpha,\alpha\beta}(\mathbf{r}')d_{\beta}]
\end{aligned} \quad (59)$$

It should be borne in mind that the origin dependence of mixed multipole magnetizabilities, eqs 51–54 and eq 59, is an intrinsic feature, which cannot be circumvented using gauge-including atomic orbitals (GIAO).^{36,37} In addition, the Hellman-Feynman theorem is not, in principle, satisfied if GIAOs are employed, therefore the anapole susceptibilities calculated via finite perturbation theory as second derivatives of the energy, and/or first derivatives of the anapole moment, see eqs 43–45, are potentially different, according to a general statement by Epstein, see p 90 of his book.³⁸

The invariant electronic properties of a molecule in a magnetic field with uniform gradient are total induced magnetic dipole and interaction energy. In fact, from eq 51, the relation

$$B_{\alpha}(\mathbf{r}'') = B_{\alpha}(\mathbf{r}') + d_{\beta}B_{\beta\alpha} \quad (60)$$

for the magnetic fields at two different origins, and the Maxwell equation $\nabla \cdot \mathbf{B} = 0$, it is readily verified that

$$M_{\alpha}(\mathbf{r}'') = M_{\alpha}(\mathbf{r}') \quad (61)$$

that is, the induced magnetic dipole moment in a nonuniform magnetic field with a uniform magnetic field gradient does not depend on the origin of the coordinate system. In the same

way, it can be proved that the interaction energy, eq 32, is invariant to a translation of the origin, that is,

$$W(\mathbf{r}'') = W(\mathbf{r}') \quad (62)$$

The transformation law for the magnetic quadrupole is¹⁰

$$M_{\alpha\beta}(\mathbf{r}'') = M_{\alpha\beta}(\mathbf{r}') - M_{\alpha}(\mathbf{r}')d_{\beta} + \frac{1}{3}\delta_{\alpha\beta}M_{\gamma}(\mathbf{r}')d_{\gamma} \quad (63)$$

that is, the magnetic quadrupole is invariant to a translation of the coordinate system only if the magnetic dipole vanishes. It can be observed that, according to eqs 19 and 63, the trace of the magnetic quadrupole tensor remains zero in a translation, eq 50.

The variation of the induced anapole defined by eqs 36 and 42 in the shift of origin is¹⁰

$$\mathcal{A}_{\gamma}(\mathbf{r}'') = \mathcal{A}_{\gamma}(\mathbf{r}') + \frac{1}{2}\epsilon_{\alpha\beta\gamma}M_{\alpha}(\mathbf{r}')d_{\beta} \quad (64)$$

then for a single molecule fixed in space and more generally in an ordered medium the anapole is invariant (i) if the induced magnetic dipole vanishes and (ii) if the coordinate system is translated in the direction of either the magnetic dipole or the anapole itself. In the ideal case of a poloidal current density winding on the generatrix circumference of a geometrical torus,^{10,11} $M_{\alpha} = 0$, then $M_{\alpha\beta}$ and \mathcal{A}_{γ} are origin independent.

The important conclusion arrived at in this section is that the observable properties of one molecule responding to a nonuniform static magnetic field are the interaction energy, eq 32, the induced magnetic dipole, eq 33, and the average anapole magnetizability, eq 46, if it does not vanish for symmetry reasons. In an isotropic sample of chiral molecules, the induced anapole vector is parallel to the applied magnetic field. It is origin independent and, in principle, measurable. These findings may open alternative perspectives of chiral discrimination in the presence of a uniform magnetic field.^{39–46}

Both the magnetic quadrupole and the orbital electronic anapole depend, in general, on the origin of the coordinate system. This seems to be the case of diatomics characterized by the presence of distorted tori in the current density vector field.¹¹ Whereas the static second-rank magnetizability, eq 28, is origin independent, the third- and fourth-rank tensors, eqs 29 and 30, are not. They cannot therefore be considered separately measurable properties.

However, the transformation laws, eqs 61–64, for induced magnetic properties and interaction energy are not in general satisfied in approximate calculations, because relations (51) and (52) are only valid either for exact eigenfunctions to a model Hamiltonian, or for optimal variational wave functions, for which off-diagonal hypervirial conditions³⁸ are satisfied.^{7,10,11} Thus the closeness of molecular magnetic properties, calculated by truncated series in the powers of the inducing magnetic field and its derivatives with respect to coordinate systems with different origins, can serve to gauge the quality of the approximations retained in a given calculation. In general, the analysis of the constraints for magnetic properties is as important and informative as the calculation of the properties themselves.

4. CALCULATIONS OF MAGNETIZABILITIES FOR A MOLECULE IN A MAGNETIC FIELD WITH UNIFORM GRADIENT

The multipole magnetizabilities, eqs 28–30, of a set of diatomic and linear triatomic closed-shell molecules in the singlet ground state, LiH, Li₂, OH[−], CO₂, and BeH₂, have been computed at the Hartree–Fock level of accuracy via a computer program interfacing with the DALTON code.⁴⁷ Extended gaugeless basis sets from the Woon–Dunning compilation,⁴⁸ cc-PCVQZ, cc-pVSZ, aug-pc-4, aug-cc-pCVSZ, and the ANO-RCC were adopted. MODENA is an uncontracted (13s10p5d2f/8s4p1d) Gaussian basis set employed to predict near Hartree–Fock magnetic properties.^{49–51} The calculations were carried out for the equilibrium geometry of each system, optimized using the GAUSSIAN code⁵² at the B3LYP/6-31G* level. The *z* axis coincides with the bond direction.

The results are given in Tables 3–6 in SI atomic units (au).^{8,9} The conversion factors from SI-au to SI units per molecule are $e^2 a_0^2/m_e = 7.891\ 036\ 60 \times 10^{-29} \text{ JT}^{-2}$, $e^2 a_0^3/m_e = 4.175\ 756\ 62 \times 10^{-39} \text{ JT}^{-2} \text{ m}$, $e^2 a_0^4/m_e = 2.209\ 715\ 23 \times 10^{-49} \text{ JT}^{-2} \text{ m}^2$, respectively for magnetizabilities eqs 28, 29, and 30, from the CODATA compilation.⁵³ 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 $eE_1 a_0^3/\hbar = 9.815\ 188\ 95 \times 10^{-34} \text{ JT}^{-1} \text{ m} \equiv \text{m}^3 \text{ A}$. The magnitude of these factors, decreasing approximately by 10 orders on each successive differentiation of the electronic energy, eq 32, implies that effects related to higher-order magnetizabilities are possibly hard to detect.

Point group symmetry helps select unique nonvanishing components, which can be obtained from the Birss tabulation.^{54–56} By choosing a subgroup of $C_{\infty v}$ for instance $C_{6v} \equiv 6mm$, the Q₃ set in Birss⁵⁵ Tables 2a and 2e gives $\chi_{x,xz} = \chi_{y,yz}$, $\chi_{z,xx} = \chi_{z,yy}$, $\chi_{z,zz}$ as unique components. The $\chi_{\alpha,\beta\gamma}$ tensor vanishes for molecules with $D_{\infty h}$ symmetry. The unique nonvanishing components of the $\chi_{\alpha,\beta\gamma\delta}$ tensor are analogously obtained via Tables 2a and 2f of Birss,⁵⁵ choosing

Table 2. Character Table of the $2mm$ Magnetic Group, with Elements $\{E\ TC_2\ T\sigma_v\ \sigma'_v\}$ Group for a Few Basis Vectors V^a

	<i>E</i>	<i>TC</i> ₂	<i>Tσ</i> _{<i>v</i>}	<i>σ'</i> _{<i>v</i>}	<i>V</i>
Γ ₁	1	1	1	1	<i>z</i> , \mathcal{A}_y , <i>M</i> _{<i>xz</i>} , <i>M</i> _{<i>zx</i>}
Γ ₂	1	1	−1	−1	<i>R</i> _{<i>z</i>}
Γ ₃	1	−1	1	−1	<i>x</i> , <i>R</i> _{<i>y</i>}
Γ ₄	1	−1	−1	1	<i>y</i> , <i>R</i> _{<i>x</i>}

^aIsomorphic to $2mm \equiv C_{2v}$. The applied magnetic field is parallel to the *x* axis.

the $C_{6v} \equiv 6mm$ subgroup for molecules with $C_{\infty v}$ symmetry, and the $D_{6h} \equiv 6/mmm$ subgroup for molecules with $D_{\infty h}$ symmetry. For both $6mm$ and $6/mmm$ symmetries, the P₄ set of components is obtained from the same tables.⁵⁵ The linear relationship reported by Birss⁵⁵

$$\chi_{xx,xx} = \chi_{xy,yx} + \chi_{yy,xx} + \chi_{yx,yx} \quad (65)$$

can be checked in Tables 4 and 6.

Convergence of calculated third-rank dipole–quadrupole magnetizabilities $\chi_{\alpha,\beta\gamma}$ has preliminarily been investigated in the OH[−] anion. For a given nonvanishing component, results relative to two different origins of the coordinate system, center of mass (CM) and hydrogen nucleus H, are displayed as two

successive rows in Table 3. Values in the third row, for the origin on the H nucleus, have been computed from those of the first one using eq 51. Two complementary pieces of information are obtained from calculated values: (i) convergence arrived at through basis set saturation, compare for the results from cc-PCVQZ, cc-pVSZ, aug-pc-4, aug-cc-pCVSZ, can be observed within each row; (ii) in the limit of a complete basis set, all the required hypervirial theorems³⁸ would be obeyed, so that the second and third rows would be the same for each component. For truncated basis sets like those employed in the present calculations, the increasing agreement between second and third rows gives an indication of basis set quality and closeness to the limit of the theoretical predictions. Therefore, discrepancies of approximately 3% for $\chi_{x,xz}$ between results within second and third rows, calculated via basis sets aug-pc-4 and aug-cc-pCVSZ, absolute values differing by $\approx 1.5\%$, would imply near Hartree–Fock quality, whereas the smallness of $\chi_{x,xz}$ seems to preclude any reasonable assessment. It can also be observed that the second and third rows, for $\chi_{z,xx}$ and $\chi_{z,zz}$ are identical as implied from eq 51, in which the second addendum on the r.h.s. vanishes, since the second-rank magnetizability is diagonal in the coordinate system adopted, whereas the third addendum vanishes due to the off-diagonal Kronecker $\delta_{\alpha\beta}$. At any rate, these sets of data confirm that converged results are obtained from aug-pc-4 and aug-cc-pCVSZ basis sets.

Analogous conclusions are reached by inspection of Table 4, displaying calculated quadrupole–quadrupole magnetizabilities $\chi_{\alpha\beta,\gamma\delta}$. We can reasonably assume that results calculated via basis sets aug-pc-4 and aug-cc-pCVSZ are accurate to a significant extent.

The magnetic symmetry group for LiH, assuming the bond direction along the *z* axis and the perturbing magnetic field $B = B_x \mathbf{e}_x$ along the *x* direction, is determined via the Tavger–Zaitsev algorithm.^{57,58} Denoting time reversal by *T*, it is $2mm$ with elements $\{E\ TC_2\ T\sigma_v\ \sigma'_v\}$, isomorphous to $2mm \equiv C_{2v}$ see Table 2. Nonvanishing basis vectors for this group (transforming as the totally symmetric representation Γ₁) are *M*_{*xz*}, \mathcal{A}_y and *M*_{*zx*} respectively for the induced magnetic dipole and anapole.⁵⁶ For a magnetic field *B_y*, nonvanishing quantities are *M_y* = *M_{xz}*, $\mathcal{A}_x = -\mathcal{A}_y$ and *M_{yz}* = *M_{xz}*.

Theoretical third-rank magnetizabilities, obtained for LiH and OH[−] via basis sets cc-PCVQZ, ANO-RCC, MODENA, cc-pVSZ, aug-pc-4, and aug-cc-pCVSZ assuming the CM origin, are reported in Table 5. They are quite close, possibly of near Hartree–Fock quality, thus providing reliable information on the magnitude of the $\chi_{\alpha,\beta\gamma}$ tensor in diatomics. Fourth-rank magnetizabilities in Table 6 are also expected of Hartree–Fock accuracy. The magnitude of computed values for both tensors is very small. Using $\chi_{x,xz} = 3.66$ au from MODENA basis sets in Table 5, the conversion factor reported above, and assuming a magnetic field gradient $B_{zx} = 10$ T per meter, one finds a contribution $\approx 1.53 \times 10^{-37} \text{ JT}^{-1}$ to the magnetic dipole *M_x* ten orders of magnitude smaller than $\chi_{xx} B_x = \chi_{yy} B_y \approx -1.14 \times 10^{-27} \text{ JT}^{-1}$. Analogously, for the quadrupole *M_{xz}*, with *B_x* = 10 T and *B_{zx}* = 10 T per meter, one finds $\chi_{x,xz} B_x \approx 1.53 \times 10^{-37} \text{ JT}^{-1} \text{ m}$ and $\chi_{x,xz} B_{zx} \approx -8.81 \times 10^{-47} \text{ JT}^{-1} \text{ m}$.

5. CONCLUDING REMARKS AND OUTLOOK

The intrinsic molecular properties which account for manifestation of electronic anapoles induced by a nonuniform magnetic field with uniform gradient are dipole–quadrupole,

Table 3. $\chi_{\alpha,\beta\gamma}$ for the OH⁻ Anion from a Series of Basis Sets in SI Atomic Units.^a

$\chi_{\alpha,\beta\gamma}$	cc-PCVQZ	ANO-RCC	MODENA	cc-pVSZ	aug-pc-4	aug-cc-pCVSZ
$\chi_{xx,xz}$ (CM)	0.99	0.95	1.26	0.91	0.98	0.97
$\chi_{xx,xz}$ (H ₁)	-6.47	-6.05	-5.56	-6.70	-5.74	-5.82
$\chi_{xx,xz}$ (eq 51)	-4.93	-5.68	-5.41	-5.33	-5.67	-5.66
$\chi_{xx,zx}$ (CM)	-0.06	0.03	-0.15	-0.04	-0.02	-0.03
$\chi_{xx,zx}$ (H ₁)	0.63	0.26	0.12	0.60	0.01	0.16
$\chi_{xx,zx}$ (eq 51)	-0.06	-0.03	-0.15	-0.04	-0.02	-0.03
$\chi_{zz,xx}$ (CM)	-0.07	-0.08	-0.20	-0.06	-0.09	-0.08
$\chi_{zz,xx}$ (H ₁)	1.85	2.12	1.99	1.97	2.11	2.11
$\chi_{zz,xx}$ (eq 51)	1.85	2.12	1.99	1.97	2.11	2.11
$\chi_{zz,zz}$ (CM)	0.13	0.16	0.40	0.11	0.18	0.17
$\chi_{zz,zz}$ (H ₁)	-3.71	-4.23	-3.98	-3.95	-4.23	-4.22
$\chi_{zz,zz}$ (eq 51)	-3.71	-4.23	-3.98	-3.95	-4.23	-4.22

^aThe conversion factor to SI units is $e^2 a_0^3 / m_e = 4.175\,756\,62 \times 10^{-39} \text{ JT}^{-2} \text{ m}$ per molecule. The symmetry-unique components can be obtained from the Birss tables,^{54,55} by choosing a subgroup of $C_{\infty v}$, for instance C_{6v} , then selecting Q_3 . For each set of components, the entries between parentheses, in the first two rows, specify the origin of the coordinate system.

Table 4. $\chi_{\alpha\beta,\gamma\delta}$ for the OH⁻ Anion from a Series of Basis Sets in SI Atomic Units^a

$\chi_{\alpha\beta,\gamma\delta}$	cc-PCVQZ	ANO-RCC	MODENA	cc-pVSZ	aug-pc-4	aug-cc-pCVSZ
$\chi_{xx,xx}$ (CM)	-2.24	-4.00	-4.23	-2.71	-4.25	-4.10
$\chi_{xx,xx}$ (H ₁)	-4.86	-7.24	-6.97	-5.61	-7.76	-7.46
$\chi_{xx,xx}$ (eq 52)	-3.29	-5.19	-5.28	-3.83	-5.44	-5.28
$\chi_{xx,yy}$ (CM)	0.97	1.84	1.87	1.21	1.94	1.87
$\chi_{xx,yy}$ (H ₁)	1.50	2.70	2.52	1.87	3.08	2.86
$\chi_{xx,yy}$ (eq 52)	-0.07	0.64	0.83	0.09	0.76	0.68
$\chi_{xx,zz}$ (CM)	1.27	2.16	2.36	1.49	2.31	2.23
$\chi_{xx,zz}$ (H ₁)	3.36	4.54	4.45	3.74	4.68	4.60
$\chi_{xx,zz}$ (eq 52)	3.36	4.54	4.45	3.74	4.68	4.60
$\chi_{xy,xy}$ (CM)	-6.10	-10.41	-10.66	-7.22	-11.14	-10.74
$\chi_{xy,xy}$ (H ₁)	-9.40	-14.69	-14.43	-10.93	-15.81	-15.17
$\chi_{xy,xy}$ (eq 52)	-6.10	-10.41	-10.66	-7.22	-11.14	-10.74
$\chi_{xy,yx}$ (CM)	2.88	4.58	4.55	3.29	4.94	4.77
$\chi_{xy,yx}$ (H ₁)	3.03	4.75	4.94	3.44	4.97	4.86
$\chi_{xy,yx}$ (eq 52)	2.88	4.58	4.55	3.29	4.94	4.77
$\chi_{xz,xz}$ (CM)	-8.75	-13.03	-13.85	-9.91	-13.87	-13.33
$\chi_{xz,xz}$ (H ₁)	-48.14	-55.69	-55.11	-50.46	-57.12	-56.35
$\chi_{xz,xz}$ (eq 52)	-15.68	-21.33	-21.13	-17.66	-22.10	-21.56
$\chi_{xz,zx}$ (CM)	2.51	4.91	5.17	3.13	5.61	5.12
$\chi_{xz,zx}$ (H ₁)	6.05	9.44	9.41	6.97	10.33	9.72
$\chi_{xz,zx}$ (eq 52)	2.40	4.86	4.91	3.06	5.57	5.07
$\chi_{zx,zx}$ (CM)	-5.27	-10.88	-11.24	-6.71	-12.35	-11.31
$\chi_{zx,zx}$ (H ₁)	-5.27	-10.88	-11.24	-6.71	-12.35	-11.31
$\chi_{zx,zx}$ (eq 52)	-5.27	-10.88	-11.24	-6.71	-12.35	-11.31
$\chi_{zz,zz}$ (CM)	-2.53	-4.32	-4.72	-2.99	-4.62	-4.46
$\chi_{zz,zz}$ (H ₁)	-6.72	-9.09	-8.90	-7.47	-9.35	-9.20
$\chi_{zz,zz}$ (eq 52)	-6.72	-9.09	-8.90	-7.47	-9.35	-9.20

^aThe conversion factor from SI au to SI units per molecule is $e^2 a_0^4 / m_e = 2.209\,715\,23 \times 10^{-49} \text{ JT}^{-2} \text{ m}^2$.

Table 5. $\chi_{\alpha,\beta\gamma}$ for Diatomic Systems LiH and OH⁻ in SI Atomic Units^a

molecule	$\alpha,\beta\gamma$	cc-PCVQZ	ANO-RCC	MODENA	cc-pVSZ	aug-pc-4	aug-cc-pCVSZ
LiH	$x,xz = y,yz$	3.66	3.49	3.66	3.57	3.48	3.49
	$x,zx = y,zy$	0.27	0.29	0.27	0.28	0.30	0.30
	$z,xx = z,yy$	-1.27	-1.27	-1.27	-1.27	-1.27	-1.27
	z,zz	2.53	2.54	2.53	2.53	2.53	2.54
OH ⁻	$x,xz = y,yz$	0.99	0.95	1.26	0.91	0.98	0.97
	$x,zx = y,zy$	-0.06	-0.03	-0.15	-0.04	-0.02	-0.03
	$z,xx = z,yy$	-0.07	-0.08	-0.20	-0.06	-0.09	-0.08
	z,zz	0.13	0.16	0.40	0.11	0.18	0.17

^aOrigin in the center of mass. The conversion factor from SI au to SI units per molecule is $e^2 a_0^3 / m_e = 4.175\,756\,62 \times 10^{-39} \text{ JT}^{-2} \text{ m}$.

Table 6. $\chi_{\alpha\beta,\gamma\delta}$ for a Series of Small Molecules in SI Atomic Units^a

molecule	$\alpha\beta, \gamma\delta$	cc-PCVQZ	ANO-RCC	MODENA	cc-pVSZ	aug-pc-4	aug-cc-pCVSZ
LiH	$xx,xx = yy,yy$	-4.91	-5.03	-5.02	-4.97	-5.04	-5.05
	$xx,yy = yy,xx$	1.97	2.07	2.06	2.03	2.09	2.09
	$xx,zz = yy,zz = zz,xx = zz,yy$	2.94	2.96	2.96	2.95	2.95	2.95
	$xy,xy = yx,yx$	-11.72	-11.91	-11.91	-11.80	-11.93	-11.93
	$xy,yx = yx,xy$	4.84	4.81	4.82	4.80	4.79	4.79
	$xz,xz = yz,yz$	-38.69	-39.76	-39.87	-39.22	-39.88	-39.85
	$xz,zx = yz,zy = zx,xz = zy,yz$	8.60	8.78	8.79	8.68	8.79	8.79
	$zx,zx = zy,zy$	-8.41	-8.39	-8.38	-8.38	-8.38	-8.39
CO ₂	$xx,xx = yy,yy$	-10.19	-10.98	-10.52	-10.59	-11.06	-11.06
	$xx,yy = yy,xx$	1.79	2.50	2.04	2.13	2.58	2.58
	$xx,zz = yy,zz = zz,xx = zz,yy$	8.40	8.48	8.47	8.46	8.48	8.48
	$xy,xy = yx,yx$	-17.21	-18.32	-17.84	-17.81	-18.40	-18.40
	$xy,yx = yx,xy$	5.23	4.84	5.28	5.09	4.77	4.76
	$xz,xz = yz,yz$	-134.43	-136.38	-136.78	-134.70	-136.67	-136.88
	$xz,zx = yz,zy = zx,xz = zy,yz$	11.52	12.50	12.50	11.95	12.52	12.51
	$zx,zx = zy,zy$	-7.50	-8.15	-8.14	-7.80	-8.17	-8.16
BeH ₂	$xx,xx = yy,yy$	-4.61	-4.88	-4.98	-4.61	-4.96	-4.75
	$xx,yy = yy,xx$	1.70	1.96	2.04	1.70	2.04	1.83
	$xx,zz = yy,zz = zz,xx = zz,yy$	2.91	2.92	2.94	2.91	2.92	2.92
	$xy,xy = yx,yx$	-10.32	-10.63	-10.75	-10.32	-10.71	-10.48
	$xy,yx = yx,xy$	4.01	3.79	3.73	4.01	3.71	3.90
	$xz,xz = yz,yz$	-41.09	-43.19	-43.40	-41.09	-43.23	-42.03
	$xz,zx = yz,zy = zx,xz = zy,yz$	7.42	7.99	8.02	7.42	7.99	7.67
	$zx,zx = zy,zy$	-6.12	-6.41	-6.44	-6.12	-6.40	-6.24
Li ₂	$xx,xx = yy,yy$	-20.42	-20.57	-21.00	-20.42	-21.00	-20.58
	$xx,yy = yy,xx$	9.06	9.15	9.33	9.06	9.33	9.19
	$xx,zz = yy,zz = zz,xx = zz,yy$	11.37	11.42	11.67	11.37	11.67	11.39
	$xy,xy = yx,yx$	-75.85	-76.20	-77.67	-75.85	-77.67	-76.16
	$xy,yx = yx,xy$	46.37	46.48	47.34	46.37	47.34	46.39
	$xz,xz = yz,yz$	-121.55	-121.85	-127.25	-121.55	-127.25	-121.78
	$xz,zx = yz,zy = zx,xz = zy,yz$	40.75	40.87	41.60	40.75	41.60	40.83
	$zx,zx = zy,zy$	-64.20	-64.65	-65.22	-64.20	-65.22	-64.51
OH-	$xx,xx = yy,yy$	-2.24	-4.00	-4.23	-2.71	-4.25	-4.10
	$xx,yy = yy,xx$	0.97	1.84	1.87	1.21	1.94	1.87
	$xx,zz = yy,zz = zz,xx = zz,yy$	1.27	2.16	2.36	1.49	2.31	2.23
	$xy,xy = yx,yx$	-6.10	-10.41	-10.66	-7.22	-11.14	-10.74
	$xy,yx = yx,xy$	2.88	4.58	4.55	3.29	4.94	4.77
	$xz,xz = yz,yz$	-8.75	-13.03	-13.85	-9.91	-13.87	-13.33
	$xz,zx = yz,zy = zx,xz = zy,yz$	2.51	4.91	5.17	3.13	5.61	5.12
	$zx,zx = zy,zy$	-5.27	-10.88	-11.24	-6.71	-12.35	-11.31
zz,zz	-2.53	-4.32	-4.72	-2.99	-4.62	-4.46	

^aOrigin in the center of mass. The symmetry-unique components can be obtained from the Birss tables.^{54,55} The conversion factor from SI au to SI units per molecule is $e^2 a_0^4 / m_e = 2.209\,715\,23 \times 10^{-49} \text{ JT}^{-2} \text{ m}^2$.

quadrupole–quadrupole, and anapole magnetic susceptibilities. Whereas tensor components depend on the coordinate system which they are referred to, the pseudoscalar $\bar{\chi} = (1/6)\chi_{\alpha\beta,\gamma}\epsilon_{\alpha\beta\gamma}$ obtained by spatial averaging of the third-rank mixed dipole–quadrupole magnetizability $\chi_{\alpha\beta,\gamma}$ is origin independent. It is different from zero for freely tumbling chiral molecules, that is, for an isotropic (gas or liquid) chiral sample. Its magnitude is the same but its sign is opposite for two enantiomers. Analogous properties are predicted for the origin-independent anapole moment $\bar{\mathcal{A}} = -\bar{\chi}\mathbf{B}$, which a spatially uniform magnetic field induces in enantiomeric species in disordered phase. Such a quantity can couple with the curl $\mathbf{C} = \nabla \times \mathbf{B}$,

determining an interaction energy $W = -\bar{\mathcal{A}} \cdot \mathbf{C}$, which in principle may be experimentally measured, although its magnitude is expected to be very small. One can also conceive an experiment in which response is observed via a “kick” given to the anapole by the torque $\mathbf{K} = \bar{\mathcal{A}} \times \mathbf{C}$. These results might pave the way to novel experimental procedures for chiral discrimination.

Calculations aimed at determining magnetic dipole–quadrupole and quadrupole–quadrupole magnetizabilities of very simple systems, that is, diatomic and linear triatomic molecules, have been carried out. The results obtained are of near Hartree–Fock quality, but they should be considered as

preliminary attempts at designing and testing a computer code, as well as estimating orders of magnitude and verifying symmetry properties. Future papers will take into account the general problem of chiral discrimination via the $\bar{\chi}$ pseudoscalar.

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Notes

The authors declare no competing financial interest.

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