Molecular Anapole Moments

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A quantum mechanical formalism for molecular anapole moments is developed. London-model calculations show that toroidal carbon frameworks support both permanent and induced anapole moments arising from π-electronic, through-bond currents; dipolar flow in a chiral toroid implies an anapolar component. [S0031-9007(98)05425-8]

The recent observation by Liu *et al.* of circular ropes in scanning force micrographs of carbon nanotube materials [1] heralds the isolation of perfect molecular toroids. Such molecules are expected to exhibit several unusual properties directly related to their special topology. A toroidal network of bonds has two topological flow invariants: a "latitudinal" circulation around the central hole and a "longitudinal" circulation linking the inside and outside of the toroidal ring [2,3]. This second flow has the symmetry of an electric dipole and gives rise to an anapole moment. The existence of nuclear anapole moments, first predicted by Zel'dovich [4], has recently been confirmed by the measurement of parity nonconservation in the $6S \rightarrow 7S$ transition of Cs [5]. These effects may be enhanced by the anisotropy of the molecular environment [6]. The effects of parity nonconservation in atoms and molecules are discussed in the book by Khriplovich [7] and widely reviewed [8,9]. Paramagnetic atoms and molecules also can exhibit an anapole moment of non-parity violating electromagnetic origin in the presence of electric fields [10,11]. However, a genuinely molecular manifestation of the anapole moment has had to await molecular toroids. In the present study we develop the necessary quantum mechanical formalism and perform some model calculations on carbon toroids.

The molecular anapole moment can be derived from the multipole expansion of the electromagnetic interaction Hamiltonian, $\hat{V}$, for a molecule in an external magnetic field, **B**. In Raab's formalism [12] the second-order magnetic moment operators including both spin and orbital contributions are obtained as

$$\hat{M}_{\alpha\beta} = -2 \frac{\partial \hat{V}}{\partial B_{0\beta\alpha}}, \tag{1}$$

in which $B_{0\beta\alpha} = (\nabla_\beta B_\alpha)_0$ at a given origin zero. The antisymmetric combination of these moments with an appropriate multiplication factor yields the anapole moment operator $\hat{\mathbf{a}}$. Hence for the component along the axis of the toroid one has

$$\hat{a}_z = -\tfrac{1}{2}(\hat{M}_{xy} - \hat{M}_{yx}). \tag{2}$$

The anapole moment operator defined in this way describes the interaction of the system with the rotor of the external field. Indeed defining $\mathbf{B}' = \nabla \times \mathbf{B}$, one immediately obtains

$$\hat{\mathbf{a}} = -2\nabla_{\mathbf{B}'}\hat{V}. \tag{3}$$

The expectation value of $\hat{\mathbf{a}}$ is then found by applying the Hellmann-Feynman theorem

$$\langle \hat{\mathbf{a}} \rangle = -2\nabla_{\mathbf{B}'}E, \tag{4}$$

where E is the electronic energy in an external magnetic field. In principle, in order to induce an anapole moment in a toroidal molecule, one would need a circular magnetic field that follows the loop of the torus. However, in toroidal molecules of chiral symmetry, even a uniform magnetic field along the principal axis of revolution may induce an anapole response. Indeed permanent magnetic moments in open-shell molecules of this type also have an anapole component. These points will now be illustrated by model calculations.

Two model toroidal carbon cages were investigated. Each has 120 atoms, 10 pentagonal, 60 hexagonal, and 10 heptagonal faces. The structure shown in Fig. 1(a) has D_{5d} symmetry, while that in 1(b) has only D_5 symmetry. Both were optimized by molecular mechanics, which gave structures with a small ($\leq 3\%$) spread of bond lengths; all
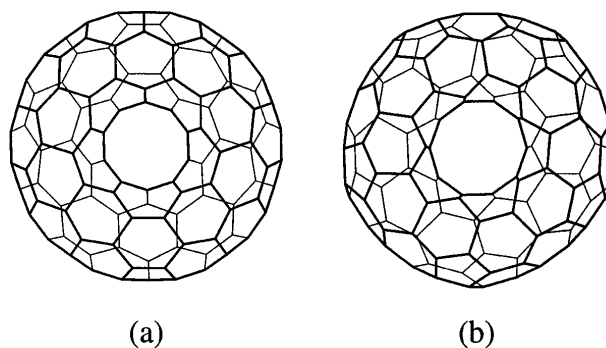

(a)   (b)

FIG. 1. Model 120-atom carbon toroids: (a) an achiral D_{5d}, and (b) a chiral D_5 structure.

coordinates were scaled to a mean bond length of 1.4 Å for comparison with previous magnetic calculations on fullerenes [13]. The D_{5d} structure has been used as a model toroidal fullerene analog in earlier mathematical and computational studies [2,14]. The D_5 isomer is obtained from it by five concerted Stone-Wales rotations [15] of pentagon pairs (see Fig. 2). In the crude Hückel approximation the D_{5d} cage has an e^2 open shell as a neutral, but the D_5 isomer has a properly closed e^4 shell.

Magnetic moments were calculated using the London method [16] in conjunction with the Hückel theory (which considers π electrons only). In this approach the site orbitals are transformed by a gauge factor incorporating a vector potential that generates the external field. The Hückel matrix elements are consequently approximated as [17]

$$h_{kl} = \beta_{kl} \exp(2\pi i f_{kl}),$$

$$\text{with } f_{kl} = \frac{e}{2hc}(\mathbf{A}_k - \mathbf{A}_l) \cdot (\mathbf{R}_k + \mathbf{R}_l). \quad (5)$$

Here β_{kl} is the transfer integral between π orbitals on sites k and l. $\mathbf{A}_k$ denotes the value of the vector potential at the position $\mathbf{R}_k$ of site k. The ground state π energy simply corresponds to the sum of the eigenvalues of this (complex) matrix for occupied levels. For a uniform rotor field $\mathbf{B}'$ the vector potential can be expressed as

$$\mathbf{A}(\mathbf{r}) = \tfrac{1}{6}\, \mathbf{r} \times (\mathbf{r} \times \mathbf{B}'). \quad (6)$$

B' was aligned here along the C_5 axis. The first derivative of E with respect to B' yields the anapole moment, $a_z = -2\partial E/\partial B'$, while the second derivative corresponds
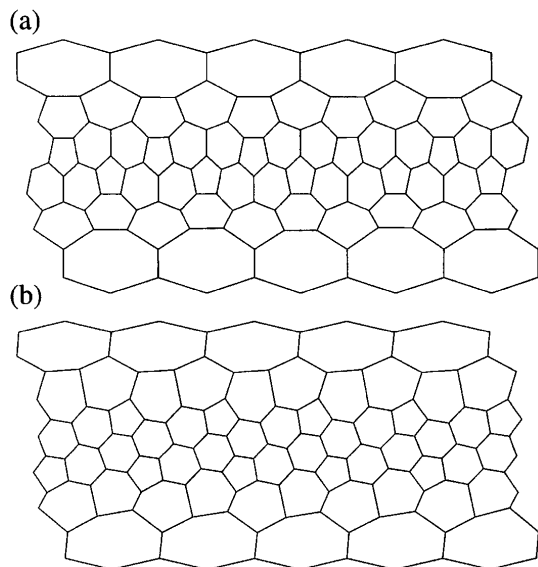
FIG. 2. Projections of the two toroidal polyhedral networks (a) and (b) obtained by unpeeling the toroidal surface. Top and bottom edges of the patch represent the inner equatorial circuit of the torus, the outer equatorial circuit running horizontally across the middle of the patch. Gluing the patch first top to bottom as a tube, then side to side, recovers the 3D torus. Bond lengths are distorted by the equal-angle projection.

to the anapole-type susceptibility, $A_{\parallel} = -2\partial^2/(\partial B')^2$, just as derivatives with respect to a homogeneous field yield the dipole moment, $m_z = -\partial E/\partial B$, and the magnetic susceptibility, $\chi_{\parallel} = -\partial^2 E/\partial B^2$. In the chiral toroid there is additionally a symmetry-allowed cross term of the type $-(\partial^2 E/\partial B'\partial B)$ that will be denoted as $M_{\parallel}$. The results of the calculations are displayed in Table I. In the units used here, Cartesian coordinates are in bohr, energies in units of a single Hückel parameter $|\beta|$ for all bonds, B in $\hbar c/ea_0^2$, and B' in $\hbar c/ea_0^3$. In this convention benzene with a bond length of 1.4 Å has a diamagnetic π-electron susceptibility $\chi_{\parallel} = -73.485$, corresponding to the scaled value of -1.5 given by Elser and Haddon [18].

As already pointed out by Haddon [19], toroids can be expected to have large magnetic dipole susceptibilities. But in the present (spin-free) treatment they are also seen to have large induced anapole moments that may be of either sign. Half-filled open-shell and closed-shell cages carry no orbital moment, in contrast to e^1 and e^3 configurations. For the D_{5d} e^1 cation the anapole moment vanishes because of parity, but in the chiral D_5 e^3 cation an anapole moment is found at zero field (Table I). These symmetry selection rules can easily be generalized. In any system with a principal axis of symmetry, the antisymmetrized square of a degenerate irreducible representation always transforms as the parallel component of the magnetic dipole operator, whereas the anapole moment transforms as an electric dipole operator. The anapole moment will therefore be allowed only in the absence of improper symmetry elements. In contrast, nonzero anapole susceptibilities are compatible with all point groups, but will require toroidal or higher topology for significant through-bond effects. Electron spin will make contributions to permanent magnetic moments in open-shell states.

For a further analysis of these results we now turn to the description of the current densities. For a homogeneous

TABLE I. Calculated dipole and anapole magnetic properties for the two model carbon tori of Fig. 1.[a]

	D_{5d}		D_5	
	neutral e^2	cation e^1	neutral e^4	cation e^3
$\chi_{\parallel}$	-2200	-1890	-1130	-1180
$A_{\parallel}$	5420	8000	$-12\,600$	-9350
m_z	0	2.74	0	4.86
a_z	0	0	0	13.9
$M_{\parallel}$	0	0	-265	-380

[a]All properties are defined as derivatives of the π-electronic energy (see text) and are quoted here in units of $|\beta|\,(e/\hbar c)a_0^n$ where $n = 2$ and 3 for m, a, and of $|\beta|\,(e/\hbar c)^2 a_0^n$ where $n = 4$, 5, and 6 for χ, M, and A, and β is the Hückel bond parameter; χ and m are independent of origin. The origin for A, a, and M is the center of mass. In Hückel theory β is the Hamiltonian integral between basis functions on neighboring atoms, giving the scale of orbital energies, and thus in the purely topological London model used here appears as part of the unit for each response property. An empirical value of 2.66 eV is often used in converting magnetic properties such as χ to SI units [22].

magnetic field, $\mathbf{A} = -\frac{1}{2}\mathbf{r} \times \mathbf{B}$, the phase factor of the Hückel-London parametrization may be written

$$f_{kl} = \frac{e}{hc} \mathbf{B} \cdot \mathbf{S}_{kl}, \qquad (7)$$

where $\mathbf{S}_{kl} = \frac{1}{2}(\mathbf{R}_k \times \mathbf{R}_l)$ is the normal to the triangle spanned by the vectors $\mathbf{R}_k$ and $\mathbf{R}_l$. The quantity f_{kl} thus corresponds to the magnetic flux $\mathbf{B}$ across this triangle. The corresponding through-bond current may then be obtained as in classical magnetism by differentiating the total energy with respect to the magnetic flux

$$J_{kl} = -\frac{e}{h} \frac{\partial E}{\partial f_{kl}}. \qquad (8)$$

This expression is also valid in the case of a nonhomogeneous magnetic field, with f_{kl} defined as in (5). By the Hellmann-Feynman theorem this current contribution may be resolved into a sum over occupied molecular orbitals

$$J_{kl} = \frac{2e\beta_{kl}}{\hbar} \sum_{\mu}^{occ} \text{Im}[c_{\mu k}^* c_{\mu l} \exp(2\pi i f_{kl})]. \qquad (9)$$

Here $c_{\mu k}$ is the coefficient of the orbital on site k in the μth occupied molecular orbital. This result can also be derived from a momentum operator formalism. We start from a standard expression for the nondiagonal matrix element of the current density operator [20]

$$\hat{J}_{kl} = \frac{ie\hbar}{2m_e}[(\nabla\phi_k^*)\phi_l - \phi_k^*\nabla\phi_l], \qquad (10)$$

where ϕ_k and ϕ_l are atomic π orbitals in a given pair of atoms and m_e is the electronic mass. Equation (10) does not contain the contribution from the vector potential, which is in line with approximations made within the London theory [16,17]. To obtain the total current we integrate the current density over a surface cutting the bond. This surface integral can be obtained by taking a volume integral divided by the length of the bond. Thus the bond current operator in second quantization has the form

$$\hat{\mathbf{J}}_{kl} = \frac{e}{m_e} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|}[a_k^\dagger a_l\langle\phi_k|\mathbf{p}|\phi_l\rangle + \text{H.c.}]. \qquad (11)$$

In the tight binding approximation the matrix element for the momentum operator between the real atomic orbitals is given by [21]

$$\langle\phi_k|\mathbf{p}|\phi_l\rangle = \frac{im_e}{\hbar} \beta_{kl}(\mathbf{R}_k - \mathbf{R}_l). \qquad (12)$$

Substituting (12) into (11) and taking the average over the ground state wave function in the external field yields exactly Eq. (9). This derivation completes the bond current formalism introduced by Pasquarello *et al.* [22]. The connection between dipole and anapole moments and the current can easily be obtained by substituting the appropriate vector potential into the classical formulas
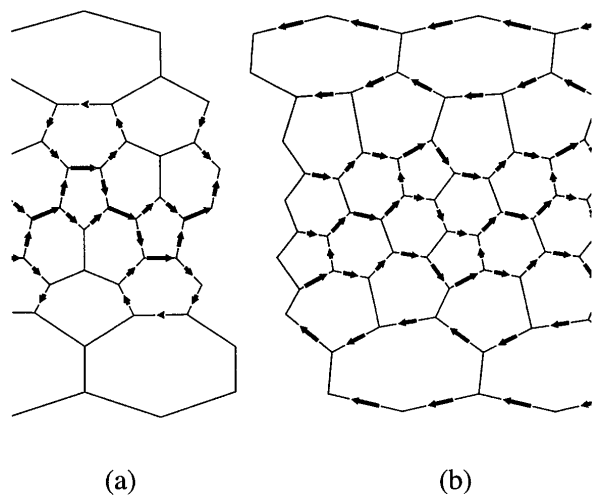

(a)   (b)

FIG. 3.   Induced currents for the tori (a) and (b) under a uniform magnetic field, directed along the central symmetry axis. Only a section of the full toroidal surface is shown. Arrow lengths are proportional to current moduli.

for the energy of currents in the external magnetic field, followed by differentiation with respect to $\mathbf{B}$ or $\mathbf{B}'$

$$\mathbf{m} = \frac{1}{2c} \int \mathbf{r} \times \mathbf{J}\,dv,$$

$$\mathbf{a} = \frac{1}{3c} \int \mathbf{r} \times (\mathbf{r} \times \mathbf{J})\,dv. \qquad (13)$$

These volume integrals may be converted into line integrals along bonds, yielding

$$\mathbf{m} = \frac{1}{2c} \sum_{\langle ij\rangle} J_{ij}\mathbf{S}_{ij},$$

$$\mathbf{a} = \frac{1}{3c} \sum_{\langle ij\rangle} J_{ij}(\mathbf{R}_i + \mathbf{R}_j) \times \mathbf{S}_{ij}, \qquad (14)$$

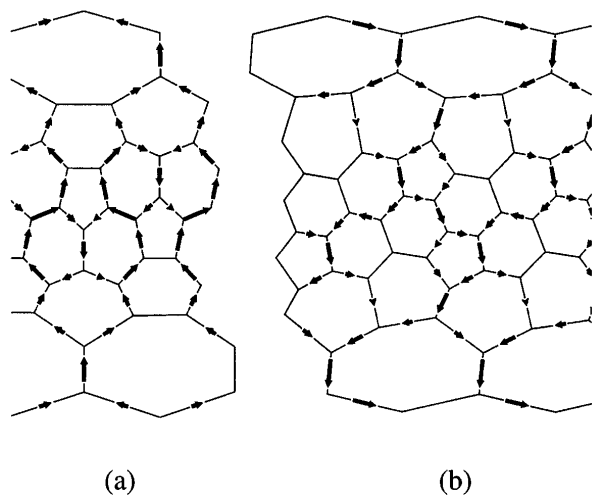where the sums run over distinct bonded pairs. These gauge-invariant current formulas yield exactly the same

(a)   (b)

FIG. 4.   Induced currents for the tori (a) and (b) under a rotor perturbation, directed along the central symmetry axis.
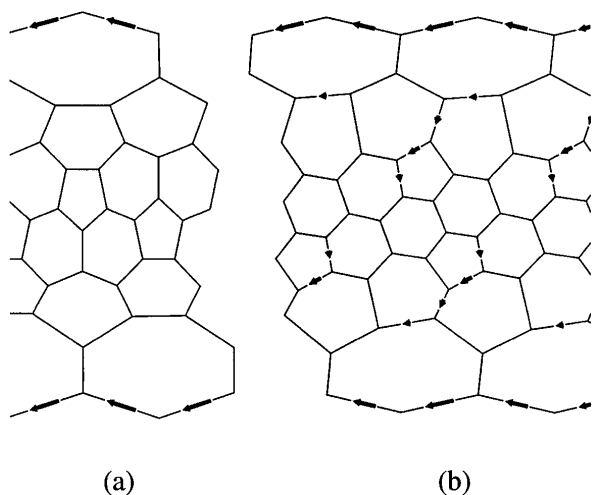
(a)   (b)

FIG. 5. Current states for the open-shell toroidal cations (a) and (b), provoked by application of an infinitesimal uniform field, showing the dominance in the frontier molecular orbital of circulation around the inner equator of the torus i.e., along the line of fusion of the heptagonal rings, and the mixed dipolar/anapolar character of the flow in the chiral torus.

result as the operator formulation. The plots of the currents in Figs. 3–5 illustrate the outcome of the calculations presented in Table I. The induced currents were obtained by performing the calculations with nonzero axial magnetic field (Fig. 3) or rotor perturbation (Fig. 4). Clearly the axial field induces a current that circulates around the central hole of the torus, while the rotor field causes a current that whirls around in a perpendicular direction. For the monocations in degenerate states, permanent moments are found as illustrated in Fig. 5. In the achiral isomer this moment is entirely dipolar, but in the chiral isomer the current has a spiral pattern, consisting of a dipolar flow with an anapolar "leakage."

In conclusion, classical through-bond effects in carbon networks of higher topology can give rise to permanent and induced anapole moments and thereby bring a concept developed in the context of nuclear physics into the realm of molecular physics.

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