Anapole moment of a diatomic polar molecule

Robert R. Lewis

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

We discuss the magnetic toroidal dipole moments (anapole moments) of diatomic molecules by analyzing a calculable "toy model" for a heteronuclear diatomic molecular ion. The model consists of a single unpaired electron with spin σ, in the electrostatic potential of two different point charges; all spin-dependent interactions are neglected. We show that this model predicts a toroidal dipole moment of order $\alpha e a_0^2$ oriented in the direction $\hat{n} \times \sigma$, where $\hat{n}$ is the molecular axis. A simple relation is derived between the three static dipole moments of this model: electric, magnetic, and toroidal. Numerical results are given for a particular choice of model parameters. In addition to the usual magnetic dipole field, there is a toroidal magnetic field inside the molecule, which we evaluate for this model. The two fields are similar in strength but have opposite behavior under spatial inversions, so that the magnetic field, as well as the electric field, fails to have a center of inversion.

INTRODUCTION

In a recent paper by Khriplovich and Pospelov [1], an estimate is given for the toroidal dipole (anapole) moment [2] of a chiral molecule, using

$$t \equiv -(\pi/c)\int d^3r \, r^2 \mathbf{j} \, , \tag{1}$$

where $\mathbf{j}$ is the current density in the molecule. Their model describes a free radical with one unpaired electron in the potentials of four atoms forming a tetrahedral structure. It predicts a toroidal dipole moment (TDM) oriented in the direction

$$t \propto (\hat{n}_1 \cdot \hat{n}_2 \times \hat{n}_3)(\sigma \cdot \hat{n}_3)[f(r_1, r_2)\hat{n}_2 - f(r_2, r_1)\hat{n}_1] \tag{2}$$

in the body-fixed frame; the quantity $f(r_1, r_2)$ is a certain function of the internuclear distances. The indices 1,2,3 refer to the locations of the three atoms, displaced from a heavy atom at the origin. This result is proportional to the factor $(\hat{n}_1 \cdot \hat{n}_2 \times \hat{n}_3)$ giving the handedness of the tetrahedron; the TDM would change sign if the handedness were reversed. The formula shows explicitly that the TDM transforms like a polar vector, odd under space inversion because of the five factors $\hat{n}$, and odd under time inversion because of the factor σ.

Khriplovich and Pospelov estimated the strength of the TDM to be approximately

$$|t| \approx \alpha e a_0^2 \, , \tag{3}$$

which implies a toroidal magnetic field of magnitude

$$|B|_{\text{toroidal}} \approx \alpha e / a_0^2 \tag{4}$$

distributed throughout the interior of the molecule. They also discussed some observable effects of this TDM, coming from the interaction between an external electron current and the internal magnetic field of the molecule. There will be an asymmetry in the scattering of electrons from a sample of polarized molecules. There will also be a molecular polarization proportional to an electric field applied to a conducting solution of chiral radicals.

The central purpose of this paper is to show that toroidal dipole moments exist for a simpler class of molecules, especially heteronuclear diatomic molecules. We construct a "toy model" of a free radical with an unpaired electron, and show that it has a TDM as well as electric and magnetic dipole moments. The model has the advantage of being analytically calculable, removing any concern about approximations or numerical errors. We obtain detailed results for the TDM and its accompanying toroidal magnetic field. The TDM has magnitude similar to the prediction of the model of Khriplovich and Pospelov but with a different direction.

TRANSFORMATION PROPERTIES

If a molecule lacks a center of inversion, then a toroidal dipole moment (t) can exist, in addition to the electric (d) and magnetic dipole moments (μ). These three moments have different transformation properties under space and time inversion, respectively,

$$d \propto (-, +) \, , \quad \mu \propto (+, -) \, , \quad t \propto (-, -) \, .$$

All of these moments are odd under charge conjugation. Elementary considerations of inversion invariance give us unique predictions for the directions of these dipole moments in the body-fixed frame of reference,

$$d \propto \hat{n} \, , \quad \mu \propto \sigma$$

where $\hat{n} \propto (-, +)$ is the direction of the molecular axis and $S \propto (+, -)$ is the direction of the electron spin. In the model of Khriplovich and Pospelov, the TDM has the desired transformation properties, $t \propto (-, -)$, and contains *five* factors of $\hat{n}$ formed from the *three* noncoplanar molecular axes.

Clearly *two* different molecular axes could also be used to define the direction of a TDM,

$$t \propto (f_1 \hat{n}_1 + f_2 \hat{n}_2)(\hat{n}_1 \cdot \hat{n}_2 \times \sigma) \, .$$

This contains *three* factors $\hat{n}$ instead of *five*. This would pertain to a triatomic molecule with noncollinear axes. The number of molecular axes can be further reduced to *one*, with a TDM in the direction

$$\mathbf{t} \propto (\hat{n} \times \sigma)$$

for a diatomic molecule. In all three cases there must be an angular momentum vector to provide a T-odd factor. In all three cases, it is the unpaired electron spin which plays that role although a rotational angular momentum would also satisfy the symmetry requirements.

Khriplovich and Pospelov point out an inherent advantage in studying the TDM of chiral molecules: a sample of *unoriented* molecules will have a net TDM oriented along the electron spin polarization

$$\langle \mathbf{t} \cdot \hat{s} \rangle \propto \langle S \rangle (\hat{n}_1 \cdot \hat{n}_2 \times \hat{n}_3)$$

$$\times \{ [f(r_1, r_2)\hat{n}_2 - f(r_2, r_1)\hat{n}_1] \cdot \hat{n}_3 \} \ ,$$

where $\langle S \rangle$ is the magnitude of the spin polarization and $\hat{s}$ is its direction. The mean TDM will survive the average over molecular orientations, so long as the vector $\hat{n}_3$ has a nonvanishing projection on $[f_{12}\hat{n}_2 - f_{21}\hat{n}_1]$. The disadvantage of using chiral molecules is that calculations of its molecular structure from first principles are difficult.

On the contrary, an advantage in using either a diatomic or triatomic molecule is that the TDM can be more accurately calculated. The disadvantage is that the TDM will vanish on averaging molecular orientations, even for fixed **S**; orientation of both $\hat{n}$ and **S** is required. This might be accomplished by applying both an electric field to orient **d** and a magnetic field to orient **S**. These fields, rather than the chirality and polarization of the chiral molecule, provide a signature which can be reversed to detect the effects of the TDM.

THE MODEL

We consider a "textbook" model of a diatomic molecular ion with an electron moving in the potential of two atoms separated by R. This is a standard model, familiar to every student of molecular quantum mechanics [3]: it has one electron bound to two nuclei with atomic numbers $Z_1 = 1$ and $Z_2 = 2$ separated by distance R. The Hamiltonian is

$$\mathcal{H} = -\nabla^2/2 - 1/r_1 - 2/r_2 + 2/R \ , \tag{5}$$

where $r_1 = |\mathbf{r} + \hat{n}R/2|$ and $r_2 = |\mathbf{r} - \hat{n}R/2|$ are the distances from the two centers; the origin is chosen midway between the two atoms. Atomic units (a.u.'s) are used throughout this section.

We are concerned only with the $^2\Sigma$ ground state, whose (unnormalized) wave function is chosen in linear combination of atomic orbital form

$$\Psi = R\psi_1 + \psi_2 \tag{6}$$

with hydrogenic atomic orbitals

$$\psi_1 = (1/\sqrt{\pi})\exp(-r_1)\chi \ , \quad \psi_2 = (\sqrt{8/\pi})\exp(-2r_2)\chi \ . \tag{7}$$

The weighting factors are chosen so that the electron is predominantly localized on atom 1 for large R, but is on atom 2 for small R. Thus, we are considering a molecular term with the electron in the ground state of atom 1 at large separations.

This model is chosen for its simplicity rather than for its practical importance: the ground-state properties can all be worked out exactly using elliptical coordinates. The term energy is expressed in terms of four matrix elements:

$$A(R) \equiv \langle \psi_1 | 1/r_2 | \psi_1 \rangle \ , \quad B(R) \equiv \langle \psi_2 | 1/r_1 | \psi_2 \rangle \ ,$$

$$C(R) \equiv \langle \psi_1 | 1/r_2 | \psi_2 \rangle \ , \quad N(R) \equiv \langle \psi_2 | \psi_1 \rangle \ .$$

The term energy

$$E(R) = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$$

is given in terms of these quantities by

$$\langle \Psi | \mathcal{H} | \Psi \rangle = \{ -2R^2 A - B - 2RC$$

$$+ 4N - R^2/2 + R - 2 + 2/R \} \ . \tag{8}$$

Explicit formulas for these four integrals have been evaluated and used in the numerical computations. As is well known, this model gives a typical molecular energy curve, shown in Fig. 1, with well depth

$$E_\infty - E(R^*) \cong 0.38 \text{ a.u.}$$

and equilibrium distance

$$R^* \cong 2.58 \text{ a.u.}$$

We can also calculate the electric dipole moment, oriented along the molecular axis,

$$d(R) = -e \langle \Psi | \mathbf{r} \cdot \hat{n} | \Psi \rangle / \langle \Psi | \Psi \rangle \ . \tag{9}$$

This can be expressed in terms of a single new integral

$$d(R) = -eR[2Z(R) - R^2/2 + \tfrac{1}{2}]/\langle \psi | \psi \rangle \ , \tag{10}$$

where

$$Z(R) \equiv \langle \psi_1 | z | \psi_2 \rangle \ .$$

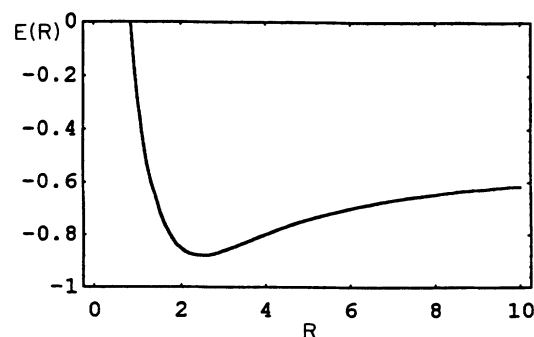

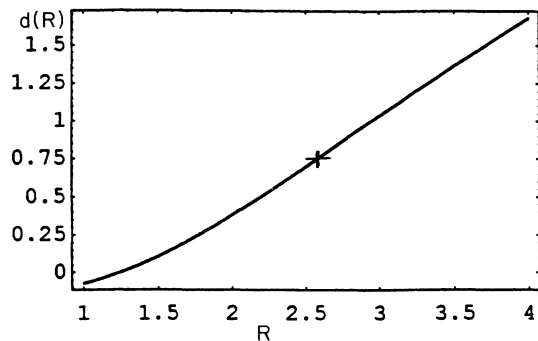FIG. 1. Term energy $E(R)$ vs internuclear distance R, in a.u.

FIG. 2. Dipole moment $d(R)$ vs internuclear separation R, in a.u. The cross marks the value of $d(R^*)$ at the equilibrium separation.

The dipole moment is defined in terms of the charge displacement from an origin midway between the two nuclei; because the molecule has a net charge, the dipole moment is dependent on this choice of origin. The integral $Z(R)$ has also been evaluated analytically, giving positive values at small R with the electron localized predominantly on atom 2. At larger R, the electron is increasingly localized on atom 1 and $Z(R)$ becomes large and negative. The dipole moment $d(R)$ is shown in Fig. 2; at the equilibrium distance, it is

$$d(R^*) \cong +0.756 e a_0 . \tag{11}$$

CALCULATION OF TOROIDAL DIPOLE MOMENT

The "spin" contribution to the TDM is given [4] by

$$\mathbf{t}_s = (\pi e \hbar / mc) \langle \boldsymbol{\sigma} \times \mathbf{r} \rangle . \tag{12}$$

This term comes from the current due to the nonuniform density of the electron spin magnetization in the molecule. If we neglect spin-dependent interactions, the spin is uncoupled from the spatial variables and there is a factorization of the spin and space wave functions. The TDM is given by

$$\mathbf{t}_s = (\pi e \hbar / mc) \langle \boldsymbol{\sigma} \rangle \times \langle \mathbf{r} \rangle . \tag{13}$$

But $-e \langle \mathbf{r} \rangle = \mathbf{d}$ is the electric dipole moment and $-(e \hbar / 2mc) \langle \boldsymbol{\sigma} \rangle = \boldsymbol{\mu}$ is the magnetic dipole moment, so the TDM satisfies the simple relation

$$e \mathbf{t}_s = 2\pi \boldsymbol{\mu} \times \mathbf{d} . \tag{14}$$

This relation is consistent with P, T, and also with C: all three dipole moments are C odd, and so is the electron charge [5]. Without further computation, we get the TDM for our model

$$\mathbf{t}_s \cong (2.38 \alpha e a_0^2) \hat{n} \times \langle \boldsymbol{\sigma} \rangle . \tag{15}$$

There is another contribution to the TDM, due to the flow of electronic charge [4],

$$\mathbf{t}_L = -i (\pi e \hbar / 3mc) \langle [L^2, \mathbf{r}] \rangle , \tag{16}$$

which we will show to vanish for this model. Since the

spin operator does not appear in this expression and the wave function factors into spin and spatial parts, the matrix element is diagonal in both the spin and the spatial variables. The spatial part is the diagonal matrix element of the operator $-i[L^2, \mathbf{r}]$, which is both Hermitian and T odd, in a state with integral orbital angular momentum. But for states with integral spin, Hermitian operators have real diagonal matrix elements and T-odd operators must be imaginary. This result is called "Lloyd's theorem" [6]. Consequently, $\mathbf{t}_L$ must vanish and the TDM must be due entirely to the magnetization current. A formal proof of this is given in the Appendix.

TOROIDAL MAGNETIC FIELD

So far, we have evaluated the TDM treating the molecule as a "point source." In this approximation, the vector potential is proportional to a Dirac δ function,

$$\mathbf{A}_{TDM}(r) = \mathbf{t} \delta^3(r) \tag{17}$$

and the toroidal magnetic field involves derivatives of the δ function. The TDM is related to the first moment of the magnetic field

$$\mathbf{t} = (1/2) \int d^3 r \, \mathbf{r} \times \mathbf{B}_{TDM} . \tag{18}$$

In this approximation, all the internal structure of the potential and field are lost, as well as some physical insight.

We can also treat toroidal moments of a current density of finite size, using the formulas derived directly from the Maxwell equations by Boston and Sandars [7]. They show that the toroidal part of the magnetic field has the form

$$\mathbf{B}_{TDM} = \hat{r} \times \mathbf{g}(r) , \tag{19}$$

which is odd under spatial inversions. Here $\mathbf{g}$ is given by the radial component of the current density

$$\mathbf{g}(r) \equiv -(3/2rc) \int d^3 x' (\hat{r}' \cdot \mathbf{j}) \hat{r}' \delta(r - r') , \tag{20}$$

integrated over a sphere of radius r; note that this is a one-dimensional δ function in the radial variable. This shows that a toroidal magnetic field at radius r is proportional to the current density at r. The magnetic field vanishes unless there is current density somewhere on that sphere; the magnetic field is zero outside of the current distribution. The confined field of a toroidal current on the surface of a torus is the classical example of this.

In quantum mechanics, we can apply this to the radial component of the spin current of a molecule,

$$\mathbf{j}_s = -(e \hbar / 2m) \nabla \times (\Psi^\dagger \boldsymbol{\sigma} \Psi) . \tag{21}$$

Inserting this and integrating by parts, the formula for $\mathbf{g}$ is

$$\mathbf{g} \equiv (3 e \hbar / 4mcr^3) \int d^3 x' \Psi^\dagger [\hat{r}' \times \boldsymbol{\sigma} \delta(r - r')] \Psi . \tag{22}$$

This can be further simplified for a molecule in which spin and space are uncoupled:

$$\mathbf{g} \equiv -(3 e \hbar / 4mcr^3) \mathbf{f}(r) \times \langle \boldsymbol{\sigma} \rangle \tag{23}$$
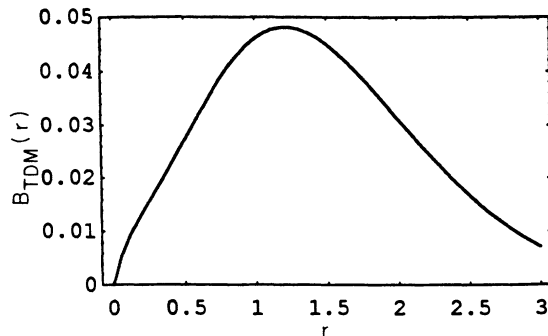
FIG. 3. Toroidal magnetic field $B_{TDM}(r)$ vs radius r, in a.u.

where we have defined the dimensionless integral

$$f(r) \equiv - \int d^3x' \Psi^\dagger r' \delta(r - r') \Psi . \qquad (24)$$

This is proportional to the radial density of the dipole moment of the molecule. In a diatomic molecule, the direction of f is along the molecular axis

$$f(r) = F(r)\hat{n}$$

and so the magnetic field is given by

$$\mathbf{B}_{TDM}(r) = (3e\hbar/4mc)[F(r)/r^3][(\hat{n} \times \sigma) \times \hat{r}] , \qquad (25)$$

which is odd under inversion. This field provides an alternative way to evaluate the TDM: we can either find the second moment of the current density, or the first moment of the toroidal magnetic field. We have used this alternative to check the accuracy of the numerical calculations,

$$e \int dr\, f(r) = \mathbf{d} . \qquad (26)$$

For our model, the integral $F(r)$

$$[F(r)/r^3] \equiv 2\pi \int \sin\theta\, d\theta\, \cos\theta |\psi(r,\theta)|^2 / \langle \psi | \psi \rangle \qquad (27)$$

cannot be done analytically because there is a clash between elliptical and spherical coordinates; it was done numerically. The results are shown in Fig. 3. The magnetic field vanishes like r at the center and decreases exponentially at large distances. Inside the electron density, it reaches its maximum value

$$B_{TDM,max} \cong 0.048(\alpha e/a_0^2)[(\hat{n} \times \sigma) \times \hat{r}] \qquad (28)$$

at $r \cong 1.2a_0$. This can be compared with the magnetic dipole field of the molecule, which is even under inversion. The two fields have similar orders of magnitude inside the molecule, but opposite symmetry under spatial inversions. Thus the internal magnetic field of this molecule, like its electric field, breaks inversion symmetry.

CONCLUSIONS

We can conclude from this model that diatomic polar molecules with unpaired electrons will have toroidal dipole moments of magnitude $|t| \approx \alpha e a_0^2$, pointing in the direction $\hat{n} \times \langle S \rangle$. These molecules have a degenerate ground state and are paramagnetic. In order to prepare an oriented sample of such molecular toroidal dipole moments, it is necessary to orient both the electric and magnetic dipole moments.

Clearly, these computations with an artificial "toy model" should be followed by more detailed calculations for a real molecule. In order to have a TDM, a diatomic molecule must be a polar molecule with an unpaired electron having some angular momentum in the ground state; this is a smaller class of molecules, but it includes some well-known examples such as NO, NO_2, and ClO_2 [8]. At that time, it will be possible to assess experiments to verify the existence of these moments, which have not yet been observed in atoms or molecules.

ACKNOWLEDGMENTS

I gratefully acknowledge stimulating lectures by and conversations with Yulik Khriplovich on the general topic of anapole moments. Finally, I express my appreciation to the positron research group at Michigan for frequent discussions about anapole moments.

APPENDIX

Here is a general proof that the diagonal matrix elements of an operator O which is both Hermitian and T odd, must vanish. The proof is valid only for systems with an even number of electrons having integer spin, for which $T^2 = +1$. The Pauli matrices provide a counterexample for systems with an odd number of electrons having half-integral spin, for which $T^2 = -1$; in the usual choice of these matrices, σ_z has diagonal elements but is T odd and Hermitian. A special case of this general result is given in [9].

We assume that phases of the states are chosen so that the states are self-conjugate under the Wigner time-reversal operator, T. This is a "real basis," satisfying $T\psi = \psi$. This means, for example, choosing angular functions containing $\sin(m\phi)$ or $\cos(m\phi)$ instead of $\exp(im\phi)$. In this basis, the diagonal matrix elements of O satisfy

$$\langle \psi | O | \psi \rangle = + \langle T\psi | TOT^{-1} | T\psi \rangle^* \quad \text{(definition of } T)$$

$$= - \langle T\psi | O | T\psi \rangle^* \quad (T\text{-odd property})$$

$$= - \langle \psi | O | \psi \rangle^* \quad \text{(real basis)}$$

$$= - \langle \psi | O | \psi \rangle \quad \text{(hermiticity) .}$$

It follows that $\langle \psi | O | \psi \rangle = 0$.

[1] I. B. Khriplovich and M. E. Pospelov, Z. Phys. D **17**, 81 (1990).

[2] Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **33**, 1531 (1957) [Sov. Phys. JETP **6**, 1184 (1957)].

[3] F. C. Goodrich, *Primer of Quantum Chemistry* (Wiley, New York, 1972); Chaps. 10 and 11 and references cited therein.

[4] I. B. Khriplovich, *Parity Nonconservation in Atomic Phenomena* (Gordon and Breach, New York, 1991), p. 137*ff* and references cited therein. Note that for a system with a nonzero MDM this definition depends on the choice of origin: if the origin is shifted by $\mathbf{b}$, then the TDM is augmented by $2\pi\mathbf{b}\times\langle\mu\rangle$.

[5] I thank Prof. S. M. Blinder for this remark.

[6] S. P. Lloyd, Phys. Rev. **81**, 161 (1951).

[7] E. R. Boston and P. G. H. Sandars, J. Phys. B **23**, 2663 (1990).

[8] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), Chap. 7.

[9] R. G. Sachs, *The Physics of Time Reversal* (University of Chicago, Chicago, 1987), Sec. 4.2, p. 57.