

Molecular CP -violating magnetic momentAndrei Derevianko¹ and M. G. Kozlov²¹Department of Physics, University of Nevada, Reno, Nevada 89557, USA²Petersburg Nuclear Physics Institute, Gatchina 188300, Russia

(Received 26 April 2005; published 6 October 2005)

A concept of CP -violating (T,P -odd) permanent molecular magnetic moments μ^{CP} is introduced. We relate the moments to the electric dipole moment of electron ($eEDM$) and estimate μ^{CP} for several diamagnetic polar molecules. The moments exhibit a steep, Z^5 , scaling with the nuclear charge Z of the heavier molecular constituent. A measurement of the CP -violating magnetization of a polarized sample of heavy molecules may improve the present limit on $eEDM$ by several orders of magnitude.

DOI: 10.1103/PhysRevA.72.040101

PACS number(s): 11.30.Er, 33.15.Kr, 31.30.Jv, 32.10.Dk

It is common knowledge that heteronuclear diatomic molecules possess a static electric dipole moment aligned with the internuclear axis $\hat{\mathbf{n}}$, $\mathbf{D}=D\hat{\mathbf{n}}$. For a diamagnetic molecule, however, there is no similar magnetic moment. As demonstrated below, an existence of such a magnetic moment would violate both parity-transformation (P) and time-reversal (T) discrete symmetries. Because of the compelling CPT theorem, an observation of this magnetic moment would provide an evidence for the CP violation [1,2]. CP violation, although observed in particle physics, still remains a mystery, as much stronger CP -violating mechanisms may be required to explain the matter-antimatter asymmetry of the universe.

Here we introduce the molecular CP -violating magnetic moments, $\boldsymbol{\mu}^{CP}=\mu^{CP}\hat{\mathbf{n}}$. We propose a measurement of μ^{CP} via detection of ultraweak magnetic fields generated by a polarized sample of diamagnetic molecules. For several molecules we evaluate μ^{CP} and express them in terms of the permanent electric dipole moment (EDM) of electron, d_e . A measurement of nonvanishing molecular CP -violating moments would reveal the elusive electron EDM ($eEDM$) ($EDMs$ violate both T and P symmetries). Most supersymmetric extensions of the standard model of elementary particles predict $eEDMs$ that are within a reach of planned and ongoing experimental searches (see, e.g., a popular review [3]). The present limit on d_e comes from an atomic Tl beam experiment [4],

$$d_e(Tl) < 1.6 \times 10^{-27} e \text{ cm}. \quad (1)$$

Here we propose an experimental search for the CP -violating magnetic moments of heavy polar molecules. We argue that the limit on μ^{CP} derived from such experiments would imply constraints on d_e that are several orders of magnitude better than the present limit (1). In principle, the experiments can be carried out with any diamagnetic polar molecules. However, there is no particular advantage in using polyatomics, and we restrict our consideration to polar diatomic molecules.

In the remainder of this paper, unless specified otherwise, we use atomic units $|e|=\hbar=m_e=1$ and the Gaussian system for electromagnetic equations. In these units, the Bohr magneton is $\mu_B=\alpha/2$, where $\alpha\approx 1/137$ is the fine structure con-

stant, and the unit of magnetic field is $me^2e^5/\hbar^4\approx 1.72 \times 10^7$ G.

General considerations. A diatomic molecule is characterized by the projection $\Omega=(\mathbf{J}\cdot\hat{\mathbf{n}})$ of the total electronic angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$ on the internuclear axis $\hat{\mathbf{n}}$. For a molecular state with a definite Ω , the molecular magnetic moment is directed along $\hat{\mathbf{n}}$ and, phenomenologically, we may construct the following combinations of the two vectors

$$\boldsymbol{\mu} = \mu^{CP}\hat{\mathbf{n}} + \mu_B G_{\parallel}(\mathbf{J}\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}, \quad (2)$$

where μ^{CP} and G_{\parallel} are numbers. For the Hund's case (a) the G factor is given by an expression $G_{\parallel}\Omega\approx\Lambda+2\Sigma$, where $\Lambda=(\mathbf{L}\cdot\hat{\mathbf{n}})$ and $\Sigma=(\mathbf{S}\cdot\hat{\mathbf{n}})$ [5]. While the second term in (2) is T , P even, the $\mu^{CP}\hat{\mathbf{n}}$ term violates both time-reversal (and thus CP) and parity. Indeed, under the time reversal the magnetic moment acquires a minus sign, while $\hat{\mathbf{n}}$ is T invariant. Similarly, under parity transformation, $\boldsymbol{\mu}$ is not affected, while $\hat{\mathbf{n}}$ flips direction.

Given a complete set of molecular states $|k\rangle$ (with energies E_k), the magnetic moment μ^{CP} of a state $|0\rangle$ can be computed as

$$\mu^{CP} = 2 \sum_k \frac{\langle 0 | (\mathbf{M}\cdot\hat{\mathbf{n}}) | k \rangle \langle k | V^{CP} | 0 \rangle}{E_0 - E_k}, \quad (3)$$

where \mathbf{M} is the operator of magnetic dipole moment, and the CP violation is due to a T,P -odd interaction V^{CP} . Here we consider $eEDM$ as a source of CP violation, so that $V^{CP}=-d_e(\gamma_0-1)\gamma_0\gamma_5\boldsymbol{\gamma}\cdot\boldsymbol{\mathcal{E}}_{\text{int}}$, where γ_i are the conventional Dirac matrices [1]. The electric field $\boldsymbol{\mathcal{E}}_{\text{int}}$ exerted upon the EDM is the strongest at the nucleus, leading to $\boldsymbol{\mathcal{E}}_{\text{int}}\approx(Z/r^2)\hat{\mathbf{r}}$, where Z is the nuclear charge and \mathbf{r} is the radius vector of the electron with respect to the nucleus. The matrix element of V^{CP} scales as Z^3 , so that the interaction V^{CP} can be considered as localized at the heavier nucleus. Below we will evaluate the molecular sum (3) using an approach similar to the linear combination of atomic orbitals method (LCAO).

Note that Eq. (3) is expressed in the body frame of the molecule. After μ^{CP} is found one has to average Eq. (2) over rotations. In the external electric field $\langle\hat{\mathbf{n}}\rangle\neq 0$ and we get magnetization in the direction of the electric field. The second T,P -even term in Eq. (2) does not contribute to this

magnetization. For diamagnetic molecules $(\mathbf{J} \cdot \hat{\mathbf{n}}) = \Omega = 0$ and this term vanishes. For paramagnetic molecules in the absence of the magnetic the levels with different signs of Ω are equally populated and this term is averaged to zero.

We would like to detect a magnetization of a sample of polarized molecules due to CP violating magnetic moments. In this regard, it is beneficial to work with diamagnetic molecules $\Omega = 0$, so that the traditional T, P -conserving magnetic moment [the last term in Eq. (2)] does not contribute to the magnetization. Some of the molecules may still have non-zero *nuclear* magnetic moments. However, the magnetization due to the nuclear moments in a macroscopic sample will average out to zero, since the nuclear spins have equal probabilities of orienting parallel or antiparallel to the direction of internuclear axis. Another advantage of diamagnetic molecules is that they are also chemically stable allowing for higher sample densities and thus for a larger sample magnetization.

To illustrate our qualitative approach to evaluating CP -violating magnetic moments, consider a polar molecule CsF in its ground $^1\Sigma$ state. Halides exhibit a chemical bond of a strong ionic character, and we model the CsF molecule as the Cs^+ ion perturbed by the electric field \mathcal{E} of negative ion F^- . The perturbing field at the Cs^+ is $\mathcal{E} \approx q/R_e^2$, where R_e is the internuclear separation and $q=1$ is the valency of Cs. The CP violation is enhanced near the heavier atom and we may evaluate the magnetic moment as

$$\mu^{CP}(\text{CsF}) \approx \beta^{CP}(\text{Cs}^+) \frac{q}{R_e^2}, \quad (4)$$

where $\beta^{CP}(\text{Cs}^+)$ is a so-called CP -violating polarizability [6,7] of the Cs^+ ion. Thus the molecular two-center problem is reduced to computing a one-center property— CP -violating polarizability of the heavier constituent. If both constituents of the diatomic molecule AB have comparable nuclear charges, then $\mu^{CP}(AB) \approx [\beta^{CP}(A^{(+q)}) - \beta^{CP}(B^{(-q)})]qR_e^{-2}$, where q is the observed valency of the atoms.

CP-violating polarizabilities. The effect of CP violation on electromagnetic properties of the media has been considered by a number of authors (see, e.g., [6,8–10]). In particular, the atomic CP violating (T, P -odd) polarizability β^{CP} relates induced atomic magnetic moment μ^{CP} to the externally applied electric field \mathcal{E} ,

$$\mu_{\text{at}}^{CP} = \beta^{CP} \mathcal{E}. \quad (5)$$

For a spherically symmetric system, the CP -odd polarizability is a scalar quantity, i.e., the induced magnetic moment is directed along the applied E field.

In Ref. [7] we have computed and explored the atomic CP -violating polarizabilities for rare-gas atoms in their respective 1S_0 ground states. Since the calculation reported here builds upon that work, let us briefly recapitulate our approach and main results. We related β^{CP} to the e EDM through third-order perturbation theory: the CP -odd polarizability of an atomic state Φ_0 can be represented as

TABLE I. Molecular CP -violating magnetic moments, μ^{CP}/d_e , divided by the e EDM for several diamagnetic molecules. The values of μ^{CP}/d_e are dimensionless, d_e and μ^{CP} being expressed in the Gaussian atomic units. The second, third, and the fourth columns list the heavier ion in the molecule, its nuclear charge, and its CP -violating polarizability, β^{CP}/d_e , in units of $\hbar^4/(me^2e^5)$. The notation $x[y]$ stands for $x \times 10^y$.

Molecule	Ion	Z	$\beta^{CP}(\text{Ion})/d_e$	μ^{CP}/d_e
CsF	Cs^+	55	-3.0[-2]	1.5[-3]
BaO	Ba^{2+}	56	-2.3[-2]	3.4[-3]
TlF	Tl^+	81	2.9[-1]	-1.9[-2]
PbO	Pb^{2+}	82	3.2[-1]	-4.9[-2]
BiF	Bi^+	83	4.8	-3.2[-1]

$$\begin{aligned} \beta^{CP} = & -2\langle \Phi_0 | V^{CP} \mathcal{R} M_z \mathcal{R} D_z | \Phi_0 \rangle - 2\langle \Phi_0 | M_z \mathcal{R} V^{CP} \mathcal{R} D_z | \Phi_0 \rangle \\ & - 2\langle \Phi_0 | M_z \mathcal{R} D_z \mathcal{R} V^{CP} | \Phi_0 \rangle, \end{aligned} \quad (6)$$

where the resolvent operator $\mathcal{R} = (\varepsilon_0 - H_{\text{at}})^{-1}$, ε_0 being the energy of the state Φ_0 and H_{at} being the atomic Hamiltonian. We have evaluated Eq. (6) using the Dirac-Hartree-Fock (DHF) approximation. Numerical evaluation has been carried out using a B -spline basis set technique [11].

In Ref. [7], we demonstrated that β^{CP} has a doubly relativistic origin: relativistic effects are essential for nonvanishing matrix elements of V^{CP} (Schiff theorem) and also due to peculiar properties of magnetic-dipole operator M . This doubly relativistic nature leads to a steep, $Z^5 R(Z)$, scaling of β^{CP} with the nuclear charge, where slowly varying $R(Z)$ is a relativistic enhancement factor (see Ref. [7] for details). This result, together with the estimate (4), immediately provides us with the Z scaling of the CP -violating magnetic moments of diamagnetic molecules

$$\mu^{CP} \propto Z^5 R(Z),$$

where Z is the nuclear charge of the heavier constituent. This Z scaling is more substantial than the usual $Z^3 R(Z)$ scaling [12–14] of the effects of e EDM on the energy levels of paramagnetic molecules (radicals). As in the traditional EDM searches, it is beneficial to search for nonvanishing CP -odd magnetic moments with molecules involving heavy atoms. Diamagnetic contribution (6) to CP -odd polarizability is universal. However, for the systems with unpaired electrons this contribution is masked by a larger paramagnetic term that is linked to the electronic angular momentum [8]. The advantage of the diamagnetic systems is the much lower magnetic noise, which may be crucial for the experiment. On the theoretical side, the calculation of μ^{CP} for diamagnetic molecules may be simpler and more reliable than for para- or ferromagnetic crystals.

Results of calculations. In Table I we present the results of our calculations of CP -violating magnetic moments for several diatomics: CsF, BaO, TlF, PbO, and BiF. These diamagnetic molecules possess the $^1\Sigma$ ground state. The heavier atoms of these diatomic pairs are metals, and we assume that the molecules exhibit a pure case of ionic bond, i.e., these

heavier atoms fully lend their valence electrons to their electronegative companions (F and O) and become closed-shelled 1S_0 ions. The second and third columns of Table I list the resulting heavy atomic ions with their nuclear charges, and in the fourth column we present our computed values of CP -violating polarizabilities of these ions. Finally, we combine ionic β^{CP} with the equilibrium internuclear separations [see Eq. (4)] and obtain an estimate for the molecular CP -violating magnetic moments. Our sign convention in expression $\mu^{CP} = \mu^{CP} \hat{\mathbf{n}}$ is such that the unit vector $\hat{\mathbf{n}}$ is directed from the heavier to the lighter nucleus. Notice that we express the μ^{CP} in terms of $eEDM$. Similarly, μ^{CP} can be expressed in terms of the T, P -odd electron-nucleon couplings; a simple prescription of how to relate the present results to the strength of such couplings is given in Ref. [7].

For all the considered molecules, the internuclear separation $R_e \approx 2 \text{ \AA}$, and thus the internal molecular fields are comparable. More significant is the effect of increasing CP -violating polarizabilities (the fourth column of Table I) as one progresses to heavier elements. This trend is largely due to the Z^5 scaling of β^{CP} . Yet, there is an order of magnitude of difference between β^{CP} for Pb^{2+} ($Z=82$) and Bi^+ ($Z=83$). A part of this large enhancement lies in a softer excitation spectrum of Bi^+ and thus smaller energy denominators in Eq. (6). Also, while solving the DHF equations we assumed that the outer shell of Bi^+ ion has the $6p_{1/2}^2$ electronic configuration. In general, however, the ground state of Bi^+ would contain a combination of $6p_{1/2}^2$ and $6p_{3/2}^2$ configurations. Since the $p_{1/2}$ states couple to EDM strongly, while $p_{3/2}$ orbitals contribute at a much smaller level, we expect that our result for β^{CP} of Bi^+ is somewhat overestimated.

The results of Table I should be considered as a qualitative estimate for another reason as well. The expressions (4) and (6) are based on atomic wave functions $|\Phi_i\rangle$, instead of the molecular wave functions of the defining expression (3). An underlying assumption is that the molecular wave functions $|i\rangle$ in the vicinity of the heavier atomic ion can be expressed perturbatively as

$$|i\rangle \approx \left(|\Phi_i\rangle + \sum_k \frac{\langle \Phi_k | -D_z \mathcal{E} | \Phi_i \rangle}{\varepsilon_i - \varepsilon_k} |\Phi_k\rangle \right) |\Psi_0\rangle,$$

where $|\Psi_0\rangle$ is the wave function of the lighter ion (we left out excitations from $|\Psi_0\rangle$ as being nonessential for computing μ^{CP}). Certainly, *ab initio* molecular-structure calculations of CP -violating magnetic moments are desirable to depart from this simple perturbative picture. To motivate more sophisticated calculations, let us evaluate a feasibility of an experimental determination of μ^{CP} based on our qualitative estimates.

Proposed experiments. The molecular CP -odd magnetic moments are tiny. For example, combining the present limit on the $eEDM$ (1) with the computed value of μ^{CP}/d_e , we obtain for BiF,

$$\mu^{CP}(\text{BiF}) < 2.4 \times 10^{-37} \text{ erg/G}. \quad (7)$$

While this is a remarkably small value, only 2.6×10^{-17} of the electron magnetic moment, measuring such small mag-

netic moments seems to be possible with the modern magnetometry.

The CP -violating magnetic moments can be determined by measuring the ultraweak magnetic field generated by a sample of molecules. Because of rotations, the body-fixed μ^{CP} moment averages to zero in the laboratory frame. Experimentally, one needs to apply a polarizing electric field \mathcal{E}_{pol} to orient the molecules along the field. For the efficient polarization, the coupling to the field must be stronger than the rotational spacing, $D\mathcal{E}_{\text{pol}} > 2B$, where B is the rotational constant. For the ground vibrational state of BiF, the rotational constant is $B \approx 0.231 \text{ cm}^{-1}$, requiring the application of the polarizing E field of a few kV/cm. Another consideration comes from thermal averaging over rotational levels [15], and it is beneficial to work at very low temperatures to have the smallest possible number of populated rotational levels.

Suppose we have a spherical cell with polarized diamagnetic molecules; the permanent CP -violating magnetic moments of the molecules produce a macroscopic magnetization of the sample generating an ultraweak magnetic field. The maximum value of the magnetic field at the surface of the cell can be expressed as

$$B_{\text{max}} = \frac{8\pi}{3} n \mu^{CP}, \quad (8)$$

where n is the number density of the sample. One could measure this induced magnetic field and set the limits on the $eEDM$ or other CP -violating mechanisms. Clearly, one should increase the number density to enhance the signal. However, condensing polar molecules with ionic bonds leads to a crystallization of the sample. To maintain the individuality of the molecules, one could employ low-temperature matrices of rare-gas atoms with molecules embedded inside the matrix [16]. The matrix isolation is a well-established technique in chemical physics. For chemically stable molecules, the number of guest molecules per host atom (matrix ratio), could be as high as 1/10 [17], i.e., with the techniques of matrix isolation, one could attain the number densities of molecules in the order of 10^{21} cm^{-3} .

With the sample number density of 10^{21} cm^{-3} and μ^{CP} of BiF (7) derived from the present limit on $eEDM$, from Eq. (8) we obtain a generated B field of $B \approx 2 \times 10^{-15} \text{ G}$. This ultraweak field can be measured within a month of integration time at the present best sensitivity limit [18] of $5 \times 10^{-12} \text{ G}/\sqrt{\text{Hz}}$. A relatively small 0.3-cm^3 -volume sample has been used in that experiment. The projected theoretical limit [18] of this method is $10^{-13} \text{ G}/\sqrt{\text{Hz}}$. More optimistic projected sensitivity of $3 \times 10^{-15} \text{ G}/\sqrt{\text{Hz}}$ is given in Ref. [19]. With this projected sensitivity, we find that the present limit on the $eEDM$ (1) may be improved by three orders of magnitude,

$$d_e(\text{BiF, projected}) \approx 2 \times 10^{-30} e \text{ cm}. \quad (9)$$

In Ref. [7], we have considered a CP -odd magnetization of a sample of liquid Xe caused by an externally applied electric field (5). Here we focused on a similar magnetization due to molecular CP -odd magnetic moments and we find that

the BiF experiment has a substantially better sensitivity to e EDM. This enhancement is due to (i) larger nuclear charge of Bi ($Z=83$) than that of Xe ($Z=54$) and (ii) much larger E field applied to a heavy atom or ion: in case of BiF, the internal molecular field is $\sim 4 \times 10^8$ V/cm, while in liquid Xe the E field is limited by the breakdown strength of 4×10^5 V/cm. This large difference in the maximum attainable laboratory field and the internal molecular field [20] is exploited in more conventional searches for EDMs with molecules [21–24]. It is worth emphasizing that the experiment considered here is based on a bulk magnetization of *diamagnetic* molecules, while the conventional searches for e EDM determine energy splittings in individual *paramagnetic* molecules.

To summarize, we introduced a concept of molecular CP -violating (T,P -odd) magnetic moments, μ^{CP} . We related these magnetic moments to e EDM and we estimated μ^{CP} for

a number of diamagnetic polar molecules. We demonstrated that μ^{CP} exhibit a strong Z^5 dependence on the nuclear charge of the heavier molecular constituent. Finally, we evaluated a feasibility of setting a limit on the e EDM by measuring ultraweak magnetic fields produced by a polarized sample of diamagnetic molecules. We found that such an experiment may improve the present limit on the e EDM by several orders of magnitude.

We would like to thank D. Budker, A. Cronin, M. Romalis, R. Sheridan, S. Lamoreaux, and L. You for discussions. This work was supported in part by NSF Grant No. PHY-0354876, by a NIST precision measurement grant, by RFBR Grant No. 05-02-16914, and by the NSF through a grant to the Institute for Theoretical Atomic, Molecular, and Optical Physics at Harvard University and the Smithsonian Astrophysical Observatory.

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