Letter

Screening of the electric field and nuclear electric dipole moment in nonstationary states of atoms and molecules

V. V. Flambaum
School of Physics, University of New South Wales, Sydney 2052, Australia

(Received 11 May 2023; accepted 18 August 2023; published 1 September 2023)

According to the Schiff theorem, an external electric field vanishes at atomic nucleus in a neutral atom in a stationary state, i.e., it is completely shielded by electrons. This makes a nuclear electric dipole moment (EDM) unobservable. We show that if atom or molecule is not in a stationary state (e.g., in a superposition of two stationary states), electric field on the nucleus is not zero and interaction with nuclear EDM does not vanish. In molecules this effect is enhanced by the ratio of nuclear mass to electron mass, M_n/m_e, since nuclei in a molecule are slow (compare to electrons) and do not provide efficient screening in a nonstationary environment. Electric field on the nucleus may also affect nuclear reactions.

DOI: 10.1103/PhysRevA.108.L030801

I. INTRODUCTION

Existence of electric dipole moments (EDM) of elementary particles, nuclei, atoms and molecules in a state with a definite angular momentum violates time-reversal invariance (T) and parity (P). EDM also violates CP invariance if the CPT invariance holds. A very extensive experimental and theoretical activity related to EDM is motivated by the need to test unification theories predicting T, P, and CP violation.

However, there is a problem here. A homogeneous static electric field does not accelerate a neutral atom. This means that the total electric field $\mathbf{E}$ acting on the atomic nucleus is zero since otherwise the charged nucleus would be accelerating, i.e., the external field is completely shielded by atomic electrons. The absence of the electric field means that the nuclear EDM d is unobservable, $\mathbf{d}\cdot\mathbf{E}=0$. One may also present this result differently: total atomic EDM is zero even if the nucleus has EDM, i.e., EDM of electron cloud in atom is exactly opposite in sign to nuclear EDM.

A quantum-mechanical derivation of this result for an arbitrary nonrelativistic system of pointlike charged particles with EDMs has been done by Schiff [1]. Schiff also mentioned that his theorem is violated by the finite nuclear size. The effect of the finite nuclear size was implemented as the nuclear Schiff moment, which was introduced in Refs. [2–5]. An electrostatic interaction between the nuclear Schiff moment and electrons produces atomic and molecular EDM. References [2,3] calculated the finite nuclear size effect of the proton EDM. References [4,5] calculated (and named) the nuclear Schiff moment produced by the P,T-odd nuclear forces. It was shown in Ref. [4] that the contribution of the P,T-odd forces to the nuclear EDM and Schiff moment is $\sim$40 times larger than the contribution of the nucleon EDM. An additional 2–3 orders of magnitude enhancement appears in nuclei with the octupole deformation [6].

The suppression factor for the atomic EDM relative to the nuclear EDM, proportional to a very small ratio ($\sim 10^{-9}$) of the squared nuclear radius to the squared atomic radius, is partly compensated by the factor Z^2R_S, where Z is the nuclear charge and R_S is the relativistic factor [4].

The Schiff theorem is also violated by the magnetic interaction [1,7]. Corresponding atomic EDMs produced by the nuclear EDM and electron-nucleus magnetic interaction have been calculated in Ref. [8]. In light atoms this mechanism of atomic EDM dominates but in heavy atoms it is smaller than the effect of the finite nuclear size since the latter very rapidly increases with the nuclear charge, as Z^2R_S, while the magnetic effect increases slower, as ZR_M where R_M is the relativistic factor for the magnetic effect [8].

There is no complete shielding in ions. For example, in a molecular ion the shielding factor for the nuclear EDM is $(Z_i/Z)(M_n/M_m)$, where Z_i is the ion charge, Z is the nuclear charge, M_n is the nuclear mass and M_m is the total molecular mass [9].

Screening of time-dependent electric field is incomplete. External electric field can even be enhanced if the frequency of electric field oscillations is in resonance with atomic or molecular transition. Screening of oscillating field has been investigated in Refs. [10–14].

Penetration of electric field to atomic nucleus may affect nuclear reactions; see, e.g., Refs. [15,16], where neutron capture to a nucleus, enhanced by a laser field, is discussed. For example, electric field may admix large s-wave neutron capture amplitude to a kinematically suppressed p-wave amplitude in a p-wave resonance and produce effects such as asymmetry in the photon distribution correlated with the direction of the electric field. This effect is somewhat similar to the effects of parity-violating interaction, which mixes s-wave and p-wave resonances. Such kinematic enhancement factor (ratio of s-wave and p-wave amplitudes) is $\sim 10^3$ for slow neutrons. Another enhancement factor is due to a very small energy interval between the energy levels in a compound nucleus. These two enhancement factors lead to a 10^6 enhancement of the parity violating effects in neutron reactions predicted in Refs. [17–20] and confirmed in numerous experiments involving 100 of p-wave resonances in many nuclei;

see reviews [21,22]. The same enhancement may appear if the s and p resonances mixing is produced by the electric field.

The aim of this Letter is to show that for atoms and molecules in a nonstationary state the electric field on the nucleus does not vanish and to derive formulas for this electric field. This electric field may interact with nuclear EDM and affect nuclear reactions.

II. SHIELDING THEORY FOR NONSTATIONARY ATOMIC STATES

The Hamiltonian of a neutral atom in an external electric field along the z axis $E^{\rm ext} = E_z^{\rm ext}$ may be presented as

$$H_E = H_0 - E_z^{\rm ext} D_z, \tag{1}$$

$$D_z = -e\sum_{k=1}^{Z} z_k, \tag{2}$$

where H_0 is the Schrödinger or the Dirac Hamiltonian for the atomic electrons in the absence of the external field $E_z^{\rm ext}$, Z is the number of the electrons and protons, $-e$ is the electron charge (i.e., e is the proton charge), z_k is the z-axis projection of the electron position relative to the nucleus. We assume that the nuclear mass is infinite and neglect very small effects of the Breit and magnetic interactions. The total electric field on the nucleus may be presented as $\mathbf{E}^t = \mathbf{E}^{\rm ext} + \langle \mathbf{E}^e \rangle$, where the z component of the electron electric field on the nucleus is

$$E_z^e = e\sum_{k=1}^{Z} \frac{z_k}{r_k^3} = \frac{i}{Ze\hbar}[P_z, H_0], \tag{3}$$

where $P_z = \sum_{k=1}^{Z} p_{z,k}$ is the total momentum of the atomic electrons. The second equality follows from the differentiation of the nuclear Coulomb potential in the Dirac or Schrodinger Hamiltonian H_0 since the total electron momentum P_z commutes with the electron kinetic energy and the electron-electron interaction. Similarly, the z component of the total electric field on the nucleus may be presented as

$$E_z^t = \frac{i}{Ze\hbar}[P_z, H_E]. \tag{4}$$

In agreement with the Schiff theorem, in a stationary state $|n\rangle$ expectation value of the total electric field on the nucleus vanishes, $\langle n|E_z^t|n\rangle = 0$, since $\langle n|[P_z, H_E]|n\rangle = (\epsilon_n - \epsilon_n)\langle n|P_z|n\rangle = 0$.

A nonstationary state may be presented as a sum over stationary states. For brevity, we include two states in the sum:

$$\psi = c_a\psi_a \exp\left(-\frac{i}{\hbar}\epsilon_a t\right) + c_b\psi_b \exp\left(-\frac{i}{\hbar}\epsilon_b t\right). \tag{5}$$

In such state the z component of the total electric field on the nucleus is

$$\left\langle E_z^t \right\rangle = -\frac{i(\epsilon_a - \epsilon_b)}{Ze\hbar}\left\{c_a^* c_b \langle a|P_z|b\rangle \exp\left[\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right] - c_a c_b^* \langle b|P_z|a\rangle \exp\left[-\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right]\right\}. \tag{6}$$

It is also instructive to present $\langle E_z^t \rangle$ using a substitution of the nonrelativistic expression for the momentum, $P_z = -\frac{im}{e\hbar}[H_E, D_z]$:

$$\left\langle E_z^t \right\rangle = -\frac{(\epsilon_a - \epsilon_b)^2 m}{Ze^2\hbar^2} \times \left\{c_a^* c_b \langle a|D_z|b\rangle \exp\left[\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right] + c_a c_b^* \langle b|D_z|a\rangle \exp\left[-\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right]\right\}, \tag{7}$$

where m in this expression is electron mass. Note that $\psi_a = \psi_a^{(0)} + \delta\psi_a$ and $\psi_b = \psi_b^{(0)} + \delta\psi_b$ are eigenfunctions of the Hamiltonian H_E including interaction with the external electric field $E^{\rm ext}$. Here $\psi_a^{(0)}$ and $\psi_b^{(0)}$ are eigenfunctions of the unperturbed Hamiltonian H_0.

We have two different cases here. If the matrix element between unperturbed wave functions satisfies selection rules for the electric dipole matrix element, i.e., $\langle \psi_a^{(0)}|D_z|\psi_b^{(0)}\rangle$ is not equal to zero, we have oscillating electric field on the nucleus even in the absence of external electric field $E^{\rm ext}$. Indeed, atom in such state Eq. (5) has oscillating electric dipole moment $\langle D_z\rangle$, which produces electric field on the nucleus. For real c_a, c_b, and $\langle a|D_z|b\rangle$ we obtain

$$\langle D_z\rangle = 2c_a c_b \langle a|D_z|b\rangle \cos\left[\frac{(\epsilon_a - \epsilon_b)t}{\hbar}\right] \tag{8}$$

and

$$\left\langle E_z^t \right\rangle = -\frac{2(\epsilon_a - \epsilon_b)^2 m}{Ze^2\hbar^2} c_a c_b \langle a|D_z|b\rangle \cos\left[\frac{(\epsilon_a - \epsilon_b)t}{\hbar}\right]. \tag{9}$$

Numerical estimate for the amplitude of this oscillating field is

$$\left|E_z^t\right| \sim \frac{(\epsilon_a - \epsilon_b)^2}{Z(\text{eV})^2} 10^7 \text{V/cm}. \tag{10}$$

We assumed $c_a c_b \sim 1$. For $Z \sim 1$ and $(\epsilon_a - \epsilon_b)$ equal to few eV, this field may exceed by three orders of magnitude electric fields, which have been used to measure neutron and atomic EDM. However, this is a very rapidly oscillating electric field. In the case of a small oscillation frequency, the electric field is strongly suppressed by the factor $(\epsilon_a - \epsilon_b)^2$.

When $\langle \psi_a^{(0)}|D_z|\psi_b^{(0)}\rangle = 0$, we should consider the effect produced by the external electric field $E^{\rm ext}$. Substitution of the perturbation theory expression for $\delta\psi$ gives, for real c_a, c_b and matrix elements of electric dipole moment operator $\langle a|D_z|n\rangle$ and $\langle b|D_z|n\rangle$,

$$\left\langle E_z^t \right\rangle = \frac{2c_a c_b(\epsilon_a - \epsilon_b)^2 m}{Ze^2\hbar^2} \alpha_{a,b} E_z^{\rm ext} \cos\left[\frac{(\epsilon_a - \epsilon_b)t}{\hbar}\right], \tag{11}$$

where

$$\alpha_{a,b} = \sum_n \frac{\langle a|D_z|n\rangle\langle n|D_z|b\rangle}{\epsilon_a - \epsilon_n} + \frac{\langle a|D_z|n\rangle\langle n|D_z|b\rangle}{\epsilon_b - \epsilon_n} \tag{12}$$

is the Stark amplitude between the states a and b, and $|n\rangle$ are intermediate states in the perturbation theory sum for $\delta\psi$. We see that constant external electric field $E_z^{\rm ext}$ is transformed into

oscillating electric field on the nucleus. Numerical estimate for the amplitude of the field on the nucleus for $c_a c_b \sim 1$ is

$$\left|E_z^t\right| \sim \frac{(\epsilon_a - \epsilon_b)^2}{Z(27\ \mathrm{eV})^2} E_z^{\mathrm{ext}}. \tag{13}$$

Thus, for $\epsilon_a - \epsilon_b$ smaller than atomic unit of energy 27 eV, electric field on the nucleus is smaller than external electric field.

III. SHIELDING IN NONSTATIONARY MOLECULAR STATES

In molecules in a stationary rotational state the screening of external electric field is produced by both electrons and nuclei. However, in a nonstationary state electric field on the nucleus is proportional to mass of the particles, which produce this screening; see Eq. (7). Mass of nuclei is from 3–6 orders of magnitude bigger than mass of electron. Therefore, electric field on the nucleus may be significantly bigger in molecules compare to atoms (for equal values of $\epsilon_a - \epsilon_b$). Indeed, nuclei in molecules are slow, they are not as efficient screeners as electrons in the case when (electron) electric field varies. We observed similar enhancement when considered screening of oscillating external electric field in molecules [14].

Let us consider electric field on the nucleus 1 in a diamagnetic diatomic molecule, which is given by the following expression:

$$\mathbf{E^{(1)}} = -\frac{i}{Z_1 e\hbar}[\mathbf{P^{(1)}}, H_E], \tag{14}$$

where $\mathbf{P^{(1)}}$ is the momentum of the nucleus 1, Z_1 is its charge, and the Hamiltonian H_E includes both nuclei and electrons. We may subtract from the momentum $\mathbf{P^{(1)}}$ the contribution of the center-of-mass motion with velocity $\mathbf{v} = \mathbf{P}_t/M_t$, where $\mathbf{P}_t$ is the total momentum and M_t is the total mass of the molecule:

$$\mathbf{\Pi}^1 = \mathbf{P}^{(1)} - M^{(1)}\mathbf{P}_t/M_t. \tag{15}$$

Center-of-mass momentum commutes with the Hamiltonian, therefore, we may rewrite Eq. (14) using commutator with $\mathbf{\Pi}^1$:

$$\mathbf{E^{(1)}} = -\frac{i}{Z_1 e\hbar}[\mathbf{\Pi}^1, H_E], \tag{16}$$

The expectation value of the total electric field on the nucleus 1 in the state (5) is

$$\langle \mathbf{E^{(1)}} \rangle = -\frac{i(\epsilon_a - \epsilon_b)}{Z_1 e\hbar} \times \left\{ c_a^* c_b \langle a|\mathbf{\Pi}^1|b\rangle \exp\left[\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right] - c_a c_b^* \langle b|\mathbf{\Pi}^1|a\rangle \exp\left[-\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right]\right\}. \tag{17}$$

Now we can use the following relation from Ref. [14], where we have neglected terms proportional to electron mass in comparison with the terms proportional to the nuclear masses:

$$\mathbf{\Pi}^1 = i\mu[\mathbf{R}, H_E'], \tag{18}$$

where $\mu = M_1 M_2/(M_1 + M_2)$ is the reduced nuclear mass, $\mathbf{R} = \mathbf{R^{(1)}} - \mathbf{R^{(2)}}$ is the relative coordinate for the first and second nucleus and H_E' is the Hamiltonian with subtracted contribution of the center-of-mass motion. Using this relation we obtain

$$\langle \mathbf{E^{(1)}} \rangle = -\frac{(\epsilon_a - \epsilon_b)^2 \mu}{Z_1 e\hbar^2} \times \left\{ c_a^* c_b \langle a|\mathbf{R}|b\rangle \exp\left[\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right] + c_a c_b^* \langle b|\mathbf{R}|a\rangle \exp\left[-\frac{i(\epsilon_a - \epsilon_b)t}{\hbar}\right]\right\}. \tag{19}$$

We consider rotational molecular states $|a\rangle = Y_{00}(\theta, \phi)\Psi$ and $|b\rangle = Y_{10}(\theta, \phi)\Psi$ in a diamagnetic diatomic polar molecule, where Y_{00} and Y_{10} describe rotational $L = 0$ and $L = 1$ molecular states and Ψ is an internal molecular wave function, describing electron state and nuclear vibrational state, which are the same for $\langle a|$ and $\langle b|$. Assuming real c_a and c_b we obtain

$$\left\langle E_z^{(1)} \right\rangle = -\frac{2(\epsilon_a - \epsilon_b)^2 \mu R}{\sqrt{3} Z_1 e\hbar^2} c_a c_b \cos\left[\frac{(\epsilon_a - \epsilon_b)t}{\hbar}\right], \tag{20}$$

where R is the distance between the nuclei. Note that the second nucleus experiences electric field of opposite sign ($\mathbf{R} \to -\mathbf{R}$). The electric field is inversely proportional to the nuclear charge, therefore, the electric forces are equal in magnitude and have opposite sign, so there is no acceleration of the center of mass.

The oscillation frequency of the electric field on the nucleus may be many orders of magnitude smaller than frequency of optical transitions in atoms. Indeed, the interval between molecular rotational levels is $\sim \mu/m_e$ times smaller than the interval between the electron levels. Moreover, molecules may have doublets of levels with the energy interval much smaller than the rotational energy. Note, however, that in this case there is strong suppression of the field by the small factor $(\epsilon_a - \epsilon_b)^2$.

IV. CONCLUSION

The Schiff's shielding theorem about total screening of electric field on atomic nucleus does not apply to atoms and molecules in a nonstationary state, i.e., electric field on a nucleus in a neutral system in a nonstationary state may be not equal to zero. The field on the nucleus is much bigger in molecules than in atoms (for equal values of $\epsilon_a - \epsilon_b$) since nuclei in molecules are slow and do not produce such efficient screening in a nonstationary case as electrons do. The field enhancement factor is the ratio of nuclear mass to electron mass. In principle, electric field penetrating to the nucleus makes nuclear EDM observable and may also affect nuclear reactions.

Schiff theorem has a simple classical explanation. Application of a homogeneous electric field to a neutral system does not lead to its motion. In this case the nucleus does not move, despite the fact that it has nonzero charge. This means that the total electric field on the nucleus is zero. The case of a neutral system in a nonstationary state is different. Nuclei may move, keeping center of mass of the system at rest.

For brevity, we presented nonstationary state as a sum of two basis stationary states. In general case the number of

terms in the sum may be arbitrarily large and we have to add summation over basis states ($\sum_{b>a}$) to the formulas for electric field on the nucleus.

ACKNOWLEDGMENTS

The work was supported by the Australian Research Council under Grants No. DP230101058 and No. DP200100150.

[1] L. I. Schiff, Measurability of nuclear electric dipole moments, Phys. Rev. **132**, 2194 (1963).
[2] P. G. H. Sandars, Measurability of the Proton Electric Dipole Moment, Phys. Rev. Lett. **19**, 1396 (1967).
[3] E. A. Hinds and P. G. H. Sandars, Electric dipole hyperfine structure of TIF, Phys. Rev. A **21**, 471 (1980).
[4] O. P. Sushkov, V. V. Flambaum, and I. B. Khriplovich, On the possibility of investigation of P- and T-odd nuclear forces in atomic and molecular experiments, Zh. Exp. Teor. Fiz. **87**, 1521 (1984) [Sov. Phys. JETP **60**, 873 (1984)].
[5] V. V. Flambaum, I. B. Khriplovich, and O. P. Sushkov, On the P- and T-nonconserving nuclear moments, Nucl. Phys. A **449**, 750, (1986).
[6] N. Auerbach, V. V. Flambaum, and V. Spevak, Collective T - and P -Odd Electromagnetic Moments in Nuclei with Octupole Deformations, Phys. Rev. Lett. **76**, 4316 (1996).
[7] I. B. Khriplovich, *Parity Nonconservation in Atomic Phenomena* (Gordon and Breach, Amsterdam, 1991).
[8] S. G. Porsev, J. S. M. Ginges, and V. V. Flambaum, Atomic electric dipole moment induced by the nuclear electric dipole moment: the magnetic moment effect, Phys. Rev. A **83**, 042507 (2011).
[9] V. V. Flambaum and A. Kozlov, Extension of the Schiff theorem to ions and molecules, Phys. Rev. A **85**, 022505 (2012).
[10] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, Shielding of external electric field in atoms, Phys. Lett. A **118**, 177, (1986).
[11] V. V. Flambaum, Shielding of an external oscillating electric field inside atoms, Phys. Rev. A **98**, 043408 (2018).
[12] V. A. Dzuba, J. C. Berengut, J. S. M. Ginges, and V. V. Flambaum, Screening of oscillating external electric field in atoms, Phys. Rev. A **98**, 043411 (2018).
[13] V. V. Flambaum and I. B. Samsonov, Resonant enhancement of an oscillating electric field in atom, Phys. Rev. A **98**, 053437 (2018).
[14] H. B. Tran Tan, V. V. Flambaum, and I. B. Samsonov, Screening and enhancement of oscillating electric field in molecules, Phys. Rev. A **99**, 013430 (2019).
[15] Y. K. Ho, F. C. Khanna, and M. A. Lone. Laser-induced neutron radiative capture reaction, Nucl. Phys. A **440**, 189 (1985).
[16] Y.-K. Ho and Z.-Y. Pan, Laser-induced two-step population of nuclear resonances near neutron binding energies, Phys. Rev. C **39**, 94 (1989).
[17] O. P. Sushkov and V. V. Flambaum, On the possibility to observe parity nonconservation in neutron optics, Pis'ma Zh. Exp. Teor. Fiz. **32**, 377 (1980) [JETP Lett. **32**, 352 (1980)].
[18] O. P. Sushkov and V. V. Flambaum, Parity violation in interaction of neutrons with heavy nuclei, Usp. Fiz. Nauk., **136**, 3 (1982) [Sov. Phys. Usp. **25**, 1 (1982)].
[19] V. V. Flambaum and O. P. Sushkov, Theory of neutron reactions and weak interaction in heavy nuclei, Nucl. Phys. A **412**, 13, (1984).
[20] V. V. Flambaum and O. P. Sushkov, Angular and polarizatron correlations in (n, γ) reaction, Nucl. Phys. A **435**, 352, (1985).
[21] V. V. Flambaum and G. F. Gribakin, Enhancement of parity and time invariance violating effects in compound nuclei, Prog. Part. Nucl. Phys. **35**, 423 (1995).
[22] G. E. Mitchell, J. D. Bowman, and H. A. Weidenmuller, Parity violation in the compound nucleus, Rev. Mod. Phys. **71**, 445 (1999).