Atomic and molecular transitions induced by axions via oscillating nuclear moments

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(Dated: October 18, 2019)

The interaction of standard model’s particles with the axionic Dark Matter field may generate oscillating nuclear electric dipole moments (EDMs), oscillating nuclear Schiff moments and oscillating nuclear magnetic quadrupole moments (MQMs) with a frequency corresponding to the axion’s Compton frequency. Within an atom or a molecule an oscillating EDM, Schiff moment or MQM can drive transitions between atomic or molecular states. The excitation events can be detected, for example, via subsequent fluorescence or photoionization. Here we calculate the rates of such transitions. If the nucleus has octupole deformation or quadrupole deformation then the transition rate due to Schiff moment and MQM can be up to $10^{-16}$ transition per molecule per year. In addition, an MQM-induced transition may be of M2-type, which is useful for the elimination of background noise since M2-type transitions are suppressed for photons.

PACS numbers:

I. INTRODUCTION

The nature of dark matter (DM) remains unknown. The axion is a prominent dark matter candidate originally introduced in the 1970s to explain the apparent charge-parity (CP) symmetry of the strong interactions. Most searches for axion and axion-like particles (ALPs)\textsuperscript{1} rely on the conversion between axions and photons. Recently, experiments like the Cosmic Axion Spin Precession experiments (CASPEr) started to look for other types of axion couplings \textsuperscript{1}. Assuming that the dark matter in the Milky Way consists of axions, the dark matter field can be described as a field oscillating at the Compton frequency of the axion. This field induces oscillating electric dipole moments (EDM) of fundamental particles, nuclei, atoms, and molecules \textsuperscript{2,3} and causes precession of particle’s spins due to gradients in the axion field (the axion-wind effect) \textsuperscript{4}. The CASPEr experiments search for spin precession due to axion-induced EDM and axion wind with nuclear magnetic resonance. First results constraining the axion-nucleon couplings have been published by CASPEr \textsuperscript{5,6}, as well as by other experiments re-analysing existing data obtained in the neutron-EDM \textsuperscript{7} and atomic co-magnetometer experiments \textsuperscript{8}.

It is of interest to note that in a nucleus, the interaction with the axion field may give rise to, in addition to an oscillating EDM, an oscillating Schiff moment and an oscillating magnetic quadrupole moment (MQM). In principal, these two moments may be detected in the same way as the nuclear EDM.

In this paper, we analyze the effect of an axion-induced oscillating nuclear EDM, an oscillating nuclear Schiff moment and an oscillating nuclear MQM in atoms and molecules. Such oscillating moments may induce transition in the atom or molecule if the transition frequency matches the axion Compton frequency. We present estimates of the corresponding transition rates, discuss their scaling with the relevant atomic and molecular parameters and comment on the feasibility of experimental observation of the effects.

II. NUCLEAR EDM PRODUCED BY THE AXION DARK MATTER FIELD

As noted in Ref. \textsuperscript{5}, a neutron EDM may be produced by the so-called ‘QCD θ-term’. Numerous references and recent results for the neutron and proton EDMs are summarised in the review \textsuperscript{10}:

\begin{equation}
\begin{aligned}
d_n &= -(2.7 \pm 1.2) \times 10^{-16} \theta \, e \, cm, \\
d_p &= (2.1 \pm 1.2) \times 10^{-16} \theta \, e \, cm.
\end{aligned}
\end{equation}

Calculations of the nuclear EDM produced by the P,T-odd nuclear forces have been performed in Refs. \textsuperscript{11–28}. For a general estimate of the nuclear EDM it is convenient to use a single-valence-nucleon formula from Ref. \textsuperscript{12} and express the result in terms of \(\theta\) following Ref. \textsuperscript{29}:

\begin{equation}
d \approx 7 \times 10^{-16} \left( q - \frac{Z}{A} \right) (1 - 2q) \langle \sigma \rangle \theta \, e \, cm, \end{equation}

where \(q = 1\) for the valence neutron, \(q = 0\) for the valence proton, the nuclear spin matrix element is \(\langle \sigma \rangle = 1\) if \(j = l + 1/2\) and \(\langle \sigma \rangle = -j/j + 1\) if \(j = l - 1/2\). Here, \(j\) and \(l\) are the total and orbital momenta of the valence nucleon.

\textsuperscript{1} ALPs are pseudoscalar particles like the axion that do not, however, solve the strong-CP problem; we refer to both axions and ALPs as ‘axions’ in this paper.
There are many specific results for the $^2$H and $^3$He EDMs, see, e.g., reviews [26, 30]. Within the error bars, the deuterium EDM is consistent with zero due to the cancellation between the proton and neutron contributions. The nucleus $^3$He contains unpaired neutron. Using calculation of the T,P-violating nuclear forces contribution from Refs. [22–25] $(-1.5 \times 10^{-10} \theta e \text{cm})$ and the value of the neutron EDM from Eq. (1), we obtain for the $^3$He EDM

$$d(^3\text{He}) = (-4.2 \pm 1.5) \times 10^{-16} \theta e \text{cm}. \quad (3)$$

This may be compared with an estimate using Eq. (2), which gives $d(^3\text{He}) = -4.7 \times 10^{-16} \theta e \text{cm}$. The Schiff moment of a spherical nucleus with one unpaired nucleon is given by [12]

$$S = -7 \times 10^{-7} q \langle r^2 \rangle \left( \langle \sigma \rangle + \frac{1}{I+1} \right) - \frac{5}{3} \langle \sigma \rangle r^2_q, \quad (4)$$

where $q$ and $\langle \sigma \rangle$ are defined as in Eq. (2). $\langle r^2 \rangle$ is the mean squared radius of the unpaired nucleon and $r^2_q$ is the mean squared charge radius. Approximately, $\langle r^2 \rangle \approx r^2_q \approx (3/5) R^2$ where $R$ is the mean radius of the nucleus.

It is observed from Eq. (4) that the Schiff moment is a result of adding two terms of opposite sign. These two terms are often not known with sufficient accuracy so the result of calculating the Schiff moment becomes unreliable. Also, the Schiff moment is determined by the charge distribution of the protons. However, it is directed along the nuclear spin which, for example in $^{199}$Hg, is carried by the valence neutron, so the Schiff moment is determined by the many-body effects which are harder to calculate. The calculation of nuclear EDMs, on the other hand, does not suffer from these problems (such as the difference of two nearly equal terms) and thus have certain computational advantages.

Despite of these difficulties, numerical calculations of the Schiff moments do exist. Some numerically computed values for the Schiff moments of spherical nuclei with one unpaired nucleon are [12, 14, 31, 32]

$$S(^{205}\text{Tl}) \approx -7.4 \times 10^{-3} \theta e \text{fm}^3,$$
$$S(^{199}\text{Hg}) \approx -4.8 \times 10^{-3} \theta e \text{fm}^3. \quad (5)$$

We note in passing that experimental limits on the static Schiff moments of $^{205}\text{Tl}$ and $^{199}\text{Hg}$ do exist, e.g., $S(^{205}\text{Hg}) \lesssim 3.1 \times 10^{-13} e \text{fm}^3$ corresponding to $\theta \sim 10^{-10}$ [34, 36].

In nuclei with octupole deformation, the nuclear Schiff moments may be enhanced by 100 to 1000 times (thanks to the small energy differences of nuclear levels with opposite parity and collective effects) [37, 42]

$$S(^{153}\text{Eu}) \approx 3.7 \theta e \text{fm}^3,$$
$$S(^{225}\text{Ra}) \approx 7 \theta e \text{fm}^3,$$
$$S(^{227}\text{Ac}) \approx 10 \theta e \text{fm}^3,$$
$$S(^{229}\text{Th}) \approx 2 \theta e \text{fm}^3,$$
$$S(^{235}\text{U}) \approx 3 \theta e \text{fm}^3,$$
$$S(^{237}\text{Np}) \approx 6 \theta e \text{fm}^3, \quad (6)$$

It should also be mentioned that for the Schiff moment of a nucleus with octupole deformation, the aforementioned problem with the cancellation of two nearly equal terms does not persist since the second term in Eq. (1) is practically zero (for similar distribution of protons and neutrons) and the result is stable. The calculation of the Schiff moment is, in this case, reduced to that of the expectation value of the T,P-odd interaction over intrinsic states of the deformed nucleus.

The MQM of a spherical nucleus with one unpaired nucleon is given by [12, 22, 43]

$$M = \left[ d - 6 \times 10^{-16} \theta (\mu - q) (e \text{cm}) \right] \lambda_p (2I - 1) \langle \sigma \rangle. \quad (7)$$

where $d$ is the valence nucleus’s EDM, $\mu$ is its magnetic dipole moment in nuclear magnetons, $q$, $\sigma$, $I$ are as defined in Eqs. (2) and (4) and $\lambda_p = \hbar / m_p c = 2.1 \times 10^{-14} \text{cm} (m_p$ is the proton mass).

Some values for the MQM of spherical nuclei are [12]

$$M(^{131}\text{Xe}) \approx -3 \times 10^{-29} \theta e \text{cm}^2,$$
$$M(^{201}\text{Hg}) \approx 5 \times 10^{-29} \theta e \text{cm}^2. \quad (8)$$

If the nucleus in question has quadrupole deformation, collective effects generally enhance the nuclear MQM by one order of magnitude [24, 42, 45]

$$M(^{173}\text{Yb}) \approx -9 \times 10^{-28} \theta e \text{cm}^2,$$
$$M(^{177}\text{Hf}) \approx -1 \times 10^{-27} \theta e \text{cm}^2,$$
$$M(^{179}\text{Hf}) \approx -2 \times 10^{-27} \theta e \text{cm}^2, \quad (9)$$
$$M(^{181}\text{Ta}) \approx -2 \times 10^{-27} \theta e \text{cm}^2,$$
$$M(^{229}\text{Hf}) \approx -1 \times 10^{-27} \theta e \text{cm}^2.$$

Reference [3] discussed the possibility that the dark matter field is, in fact, an oscillating axion field which generates neutron EDMs. This axion field may also generate oscillating nuclear EDMs, oscillating nuclear Schiff moments and oscillating nuclear MQMs [2]. Relating the value of the axion field to the local dark matter density (Ref. [2]), we may substitute $\theta(t) = \theta_0 \cos(\omega t)$ where $\theta_0 = 4 \times 10^{-18}$, $\omega = m_a c^2 / \hbar$ and $m_a$ is the axion mass$^2$.

$^2$ It is worth mentioning that axions are a stochastic field with a finite coherence times $\tau_c \approx \frac{\hbar}{m_a c^2}$, see, for example Ref. [40]. In this paper, by $\theta_0$ we mean $\sqrt{(\theta_0^2)}$. 

\[\text{References} \]
It is important to keep in mind that ALPs inducing larger dipole moments are also among viable DM candidates, so an experiment with sensitivity less than that necessary to detect axionic DM could already be sensitive to DM composed of such ALPs.

III. ATOMIC TRANSITIONS INDUCED BY OSCILLATING NUCLEAR MOMENTS

We have presented in the last section the possibility of having oscillating nuclear EDMs, Schiff moments and MQMs. The interactions of these moments with the atomic electrons may cause electronic transitions. In what follows, we provide estimates of the transition rates due to the interactions with these moments.

A. Nuclear EDM contribution

The interaction of the atomic electrons with a nuclear EDM $d$ may be presented as

$$V_{\text{atom}}^{\text{EDM}} = e \sum_{k=1}^{N_a} \frac{d \cdot r_k}{r_k^3} = \frac{i}{Z e \hbar} [P \cdot d, H_0],$$

where $H_0$ is the (Schrödinger or Dirac) Hamiltonian for the atomic electrons in the absence of $d$, $N_a$ is the number of the electrons, $Z e$ is the nuclear charge, $-e$ is the electron charge, $r_k$ is the electron position relative to the nucleus and $P = \sum_{k=1}^{N_a} p_k$ is the total momentum of all atomic electrons.

The second equal sign in Eq. (10) holds because we have assumed that the nuclear mass is infinite and neglected the small effects of the Breit and magnetic interactions. The operator $P$ commutes with the electron-electron interaction but does not commute with $U$, the potential energy due to the interaction with the nucleus

$$U = -\sum_{k=1}^{N_a} Z e^2 / r_k,$$

so we have

$$[P, H_0] = [P, U] = -i \hbar Ze^2 \sum_{k=1}^{N_a} \nabla \frac{1}{r_k}$$

$$= i \hbar Ze^2 \sum_{k=1}^{N_a} r_k / r_k^3.$$

Using the nonrelativistic relation

$$P = -\frac{im}{e \hbar} [H_0, D],$$

where $m_e$ is the electron’s mass and $D = -e \sum_{k=1}^{N_a} r_k$ is the atomic electric dipole moment, the matrix element of $V_{\text{atom}}^{\text{EDM}}$ may be written as

$$\langle f | V_{\text{atom}}^{\text{EDM}} | i \rangle = -\frac{\omega^2 m_e}{Z e^2} d \cdot (f | D | i),$$

where $\omega$ is the frequency of the axion field, which must matches the transition frequency $(E_f - E_i) / \hbar$.

The scalar operator $V_{\text{atom}}^{\text{EDM}}$ conserves the total atomic angular momentum $F$. For the electron variables the selection rules are identical to that for E1 amplitudes.

In accordance with the Schiff theorem, which states that the static EDM of a subatomic point particle is unobservable in the nonrelativistic limit, the matrix element is proportional to $\omega^2$ and thus vanishes for $\omega = 0$. This $\omega^2$ suppression should not appear for the transitions induced by oscillating Schiff moments and MQMs which we shall consider below.

The transition probability $W \propto |\langle i | V_{\text{atom}}^{\text{EDM}} | f \rangle|^2$ is inversely proportional to the squared nuclear charge, $W \propto 1/Z^2$, i.e., light atoms like H, He, Li are more advantageous for experiments. The origin of this factor may be related to the extended Schiff theorem for ion: the screening factor for an external electric field scales as $1/Z$.

Note that the transition probability is not suppressed for high electron waves $j, l$. The reason is that the matrix element of $V \sim 1/r^2$ does not converge at small distances. Indeed, an estimate of the contribution of the small distances $\int (\psi_1^+ \psi_2/r^2) r^2 dr = \int \psi_1^+ \psi_2 dr \sim r_1^{1+1/2+1}$ actually converges on the atomic size. This is also the reason why the relativistic corrections are not important (except for in the values of energies $E_{1,2}$).

Note also that the matrix element rapidly decreases with the electron principal quantum number $n$ since $\omega_f \sim (n_f - n_i)/n^3$, $\langle i | D | f \rangle \sim n^2$, i.e., $\langle i | V | f \rangle \sim 1/n^4$ (we assume that $n_f \approx n_i \approx n$).

The probability of the transition on resonance for the stationary case (time $t \gg 1/\Gamma$ with $\Gamma$ being the dominant decoherence mechanism) for the perturbation $V_{\text{atom}}^{\text{EDM}} = V^0 \cos(\omega t)$ is given by the following expression:

$$W_{fi} = \frac{|\langle f | V_{\text{atom}}^{\text{EDM}} | i \rangle|^2 t}{\hbar \Gamma}.$$  (15)

In our case $\Gamma$ may be the width of the axion energy distribution ($\Gamma \sim 10^{-6} m_e c^2 = 10^{-6} \hbar \omega$) if the atomic level width is smaller than the axion energy distribution width (or the atomic energy level width $\Gamma$ in the opposite case).

Inserting Eq. (14) into Eq. (15), we obtain the approximate time for one transition to happen

$$\tau_{\text{atom}}^{\text{EDM}} \approx \frac{2 \times 10^{22}}{N} Z^2 \left( \frac{1 eV}{\omega} \right)^3 \left( \frac{3 e a_B}{|\langle f | D_z | i \rangle|} \right)^2$$

$$\times \left( \frac{4 \times 10^{-16} \theta_0 e \text{ cm}}{d} \right)^2 \text{ years},$$

where $N$ is the number of atoms and $a_B$ is the Bohr radius. We have presented the result for the maximal projection of the atomic angular momentum ($F_z = F = \frac{1}{2}$).
$j + I$, where $j$ is the electron angular momentum and $I$ is the nuclear spin) and normalized the result to an atomic scale energy of 1 eV, a typical value of E1-amplitude $| \langle f | D_z | i \rangle | = 3e\alpha_B$ and a typical value of nuclear EDM $d_0 = 4 \times 10^{-16}$ e fm.

Note that for the hydrogen atom and transitions between highly excited Rydberg states of electron, there are analytical expressions [45] for the transition frequencies (between states with principal quantum numbers $n_i$ and $n_f$) $\omega \sim (n_i-n_f)/n_i^3$ and E1 amplitudes $| \langle f | D_z | i \rangle | \sim n_i^2\alpha$. Altogether we have $t \propto Z^2n_i^5$.

### B. Nuclear Schiff moment contribution

The effective Hamiltonian for the interaction between a nuclear Schiff moment and an atomic electron is given by [12]

$$V_{\text{atom}}^{SCHIFF} = 4\pi S \cdot \nabla \rho,$$

where $S = SI/I$ is the Schiff moment, $I$ is the nuclear spin and $\rho$ is the nuclear density normalized to 1 (a better form for this interaction which takes into account the finite size of the nucleus is available, see, e.g., [31]; for our estimate, the form (17) is sufficient).

The matrix element for this interaction reads

$$\langle f | V_{\text{atom}}^{SCHIFF} | i \rangle = \langle f | 4\pi \frac{\partial\rho}{\partial z} | i \rangle S,$$

where we have assumed maximal projection of the nuclear spin and that the wavefunction of the system factorizes into nuclear and atomic parts.

Inserting Eq. (18) into an analog of Eq. (15), we find the time for detection of one transition

$$t_{\text{atom}}^{SCHIFF} \approx \frac{2 \times 10^{22}}{N} \left( \frac{\omega}{1\text{eV}} \right) \left( \frac{50000a_B^4}{\omega} \right)^2 \frac{\theta_0 e \text{fm}^3}{S}$$

$$\times \left( \frac{\theta_0 e \text{fm}^3}{S} \right)^2 \text{years},$$

where we have normalized the result to the atomic transition energy scale 1 eV, a typical value of the matrix element $\langle f | 4\pi \frac{\partial\rho}{\partial z} | i \rangle \sim 50000a_B^4$ [49] and a typical value of the nuclear Schiff moment of a nucleus with quadrupole deformation $S \sim \theta_0 e \text{fm}^3$. If a maximal value of $S = 10\theta_0 e \text{fm}^3$, then overall result is two to three orders of magnitude smaller than that in Eq. (19).

We observe that unlike $V^{EDM}_{\text{atom}}$, which is proportional to $\omega^{-3}$, $t_{\text{atom}}^{SCHIFF} \propto \omega$. This is because the matrix element [14] is proportional to $\omega^2$ whereas the matrix element [15] does not depend on $\omega$. The factor $\omega$ in Eq. (19) comes from the width $\Gamma$ which is assumed to be $10^{-6}\omega$.

As noted in Sect. II for a typical spherical nucleus with one unpaired nucleon, the Schiff moment is two to three orders of magnitude larger than that in Eq. (19). As a result, the ‘waiting’ time if such nuclei are used is from four to six orders of magnitude larger than that in Eq. (19).

Note also that the matrix element [15] is subjected to E1 selection rules (the matrix element $| \langle f | V^{EDM}_{\text{atom}} | i \rangle |$ contains the factor $\left( \frac{j_f}{m_f} \right) \frac{1}{m_i} \xi (l_f + l_i + 1)$ where $\xi (x) = 1$ if $x$ is even and $\xi (x) = 0$ if $x$ is odd, see, e.g., [49].

### C. Nuclear magnetic quadrupole moment contribution

The interaction of an atomic electron with a nuclear MQM has the form [12]

$$V_{\text{atom}}^{MQM} = -\frac{M}{4I(2I-1)} T_{ij} A_{ij},$$

where we have assumed maximal projection of the nuclear spin) $T_{ij} = I_i I_j + I_j I_i - \frac{2}{3} \delta_{ij} I(I + 1)$, and the tensor $A_{ij}$ by

$$A_{ij} = \epsilon_{nmi} \alpha_n \partial_m \frac{1}{r} \frac{\partial}{\partial r}.$$

Here, $M$ is the magnitude of the MQM, $\alpha_n$ are the Dirac alpha matrices and $r$ the distance from the electron to the nucleus.

The matrix element of this interaction reads (assuming maximal projection of the nuclear spin)

$$\langle f | V_{\text{atom}}^{MQM} | i \rangle = -\frac{I + 1}{6(2I - 1)} (\langle f | A_{zz} | i \rangle) M,$$

so the time for the detection of one transition is

$$t_{\text{atom}}^{MQM} \approx \frac{10^{22}}{N} \left( \frac{2I - 1}{I + 1} \right)^2 \left( \frac{\omega}{1\text{eV}} \right)$$

$$\times \left( \frac{\theta_0 e \text{fm}^3}{S} \right)^2 \text{years},$$

where we have normalized the result to the atomic transition energy scale 1 eV, a typical value of the matrix element $\langle f | A_{zz} | i \rangle \sim 10^{27} \theta_0 e \text{cm}^2$ [40] and a typical value of the nuclear MQM for a nucleus with quadrupole deformation $M \sim 10^{-27} \theta_0 e \text{cm}^2$. If the value $2 \times 10^{-27} \theta_0 e \text{cm}^2$ is used for $M$ (e.g., $^{179}$Hf) then the result is better by a factor of four.

For a nucleus with no deformation, as noted in Sect. II, the MQM is generally an order of magnitude smaller than that presented in Eq. (24). As a result, the ‘waiting’ time in such case is about two orders of magnitude larger than in Eq. (24).
Note that the matrix element \( \langle f | A_{zz} | i \rangle \) is of M2 type (the matrix element \( \langle j_f | A_{zz} | i \rangle \) contains the factor \( \left( j_f \frac{2}{m_f} j_i \right) \xi (l_f + l_i + 1) \)). As a result, an MQM-induced transition, unlike an EDM-induced or a Schiff-moment-induced one, may be strongly suppressed for photons (in cases where E1-type transitions are impossible). This might prove useful for minimizing the effects of background processes.

### IV. MOLECULAR TRANSITIONS INDUCED BY OSCILLATING NUCLEAR MOMENTS IN DIATOMIC MOLECULE

In section III we presented the estimates for the atomic transitions induced by various oscillating nuclear moments. These transitions are suitable for searching for axion with mass in the eV region. For axion mass in the \(10^{-5}\) eV region (the value \(m_a = 26.2 \mu eV \) was recently predicted in Ref. [51]; see also [51]), molecules appear to better suited, with the region \(10^{-5}\) eV coinciding with the typical separation between rotational states. In what follows, we present estimates for low-frequency transitions in diatomic molecules induced by oscillating nuclear moments.

#### A. Nuclear EDM contribution

Let us now consider a diatomic molecule consisting of two nuclei of masses \(M_1\) and \(M_2\), charges \(Z_1\) and nuclear EDMs \(d_1\) (the subscript \(I = 1, 2\) labels the nuclei) and \(N_e\) electrons. As above, the position and momentum operators of the electrons in the laboratory frame are denoted by \(r_e\) and \(p_e\). The position and momentum operators of the nuclei in the laboratory frame will be denoted by \(R_I\) and \(P_I\), respectively.

The interaction between the nuclear EDMs and the nuclei and electrons in the molecule may be presented as

\[
V_{\text{mol}}^{\text{EDM}} = \frac{d_1 \cdot \nabla R_1 V_0}{Z_1 e} + \frac{d_2 \cdot \nabla R_2 V_0}{Z_2 e},
\]

where

\[
V_0 = Z_1 Z_2 e^2 \sum_{k=1}^{N_e} \left( \frac{Z_1 e^2}{R_{1k}} + \frac{Z_2 e^2}{R_{2k}} \right) + \sum_{i \neq j} \frac{e^2}{r_{ij}},
\]

is the Coulomb potential between the constituent particles of the molecule. Here, \(R_{1k} = |R_I - r_k|\), \(r_{hk} = |r_h - r_k|\), and \(R_{1I} = |R_I - R_I|\).

As shown in the Appendix, the matrix element of \(V_{\text{mol}}^{\text{EDM}}\) has the form

\[
\langle f | V_{\text{mol}}^{\text{EDM}} | i \rangle = \frac{\omega^2 \mu N}{e \sqrt{Z_1 Z_2}} \langle f | \delta \cdot X - \Delta \cdot \sum_{i=1}^{N_e} x_i | i \rangle,
\]

where \(X = R_1 - R_2\) is the inter-nuclear distance, \(x_i = r_k - (M_1 R_1 + M_2 R_2) / (M_1 + M_2)\) is the relative position of the electrons with respect to the nuclear center of mass, and \(\mu N = M_1 M_2 / (M_1 + M_2)\) is the reduced nuclear mass. The moments \(\delta\) and \(\Delta\) are defined as

\[
\delta = \sqrt{Z_1 Z_2} \left( \frac{d_1}{Z_1} - \frac{d_2}{Z_2} \right),
\]

and

\[
\Delta \approx \frac{m_e (M_1 Z_2 d_1 + M_2 Z_1 d_2)}{M_1 M_2 \sqrt{Z_1 Z_2}},
\]

where in Eq. (29) we retain only the lowest-order term in the small parameters \(m_e \ll M_{1,2}\). Here, \(\omega\) is again the frequency of the axion field which matches the transition frequency \((E_f - E_i) / h\).

To estimate the matrix element \(\langle f | V_{\text{mol}}^{\text{EDM}} | i \rangle\), it is convenient to use the Born-Oppenheimer approximation, in which the molecular wavefunction can be written as

\[
\psi_n = \sqrt{\frac{2J_n + 1}{8\pi}} \frac{D_{J_n}^{M_n \Omega_n}}{\Omega_n} (\Theta) \phi_n^{\text{vib}}(X) \varphi_n^{\text{eA}}(X, s_i),
\]

where \(\sqrt{(2J + 1) / (8\pi^2)} D_{J\Omega}^{M}(\Theta)\) is the Wigner D matrix depending on the set of Euler angles \(\Theta\) which describes the molecule’s orientation with respect to some laboratory-fixed frame.

As mentioned, an advantage of molecules over atoms is the existence of closely spaced rotational states whose small energy spacing is convenient for searching for sub-eV dark matter. In this paper, we provide estimates for the transitions between such rotational states. Also, in anticipation of the parity selection rules for the EDM, Schiff and MQM operators (see Sect. III), we assume that the states \(f\) and \(i\) have opposite parities, that is, \(f = \left( |J', M, \Omega \rangle - (-1)^J - \Omega |J, M, -\Omega \rangle \right) / \sqrt{2}\) and \(i = \left( |J, M, \Omega \rangle + (-1)^J - \Omega |J, M, -\Omega \rangle \right) / \sqrt{2}\) (here we assume that \(\Omega \neq 0\), the result for the case where \(\Omega = 0\) is similar). We also assume that \(f\) and \(i\) have the same electronic and vibrational states.

Note that due to the small parameters \(m_e / M_{1,2}, |\Delta| \ll |\delta|\). Thus, if \(\langle f | X | i \rangle \neq 0\) then the term \(\Delta \cdot \sum_{i=1}^{N_e} x_i\) may be dropped from Eq. (27) and we are left with

\[
\langle f | V_{\text{mol}}^{\text{EDM}} | i \rangle \approx \frac{\omega^2 \mu N}{e} \langle f | \delta \cdot X | i \rangle = (-1)^{2J' - M - \Omega} B_{J' M' \Omega} \frac{\omega^2 \mu N}{e} \frac{\delta^X}{\sqrt{Z_1 Z_2}},
\]
(assuming maximal projection for $\delta$) where

$$B_{J_{MN}}^{JM} = \sqrt{(2J' + 1)(2J + 1)} \times \left( \begin{array}{cc} J' & 1 & J \\ -M & 0 & M \end{array} \right) \left( \begin{array}{cc} J' & 1 & J \\ -\Omega & 0 & \Omega \end{array} \right),$$

(32)

and

$$\tilde{X} = \int \tilde{\phi}_{J}^{\text{vib}} \chi \tilde{\phi}_{J}^{\text{vib}} dX.$$  

(33)

Thus the time for the detection of one transition due to an oscillating nuclear EDM is (assuming that the dominant contribution to the width is due to the axion frequency distribution $\Gamma \approx 10^{-9} \hbar \omega$; the case where $\Gamma$ is dominated by the collisional width will be considered in Sect. [X])

$$t_{\text{EDM}}^{\text{mol}} \approx \frac{6 \times 10^{30}}{N} \frac{Z_{1} Z_{2}}{(B_{J_{MN}}^{JM})^{2}} \left( \frac{m_p}{m_N} \right)^{2} \left( \frac{\omega \Omega}{\omega} \right)^{3} \times \left( \frac{3a_B}{X} \right)^{2} \left( \frac{4 \times 10^{-16} \theta_0 \ e \times \text{cm}}{\delta} \right)^{2} \text{year},$$

(34)

where we have normalized our result to a typical $\Omega$-doublet separation $\omega \Omega = 10^{-5} \text{eV}$, a typical inter-nuclear distance of $3a_B$ and a typical value for nuclear EDM $4 \times 10^{-16} \theta_0 \ e \times \text{cm}$.

Comparing Eqs. (14) and (31), we see that for the same transition energy the molecular transition probability is enhanced by a factor of $(\mu_{N}/m_e)^{2} \geq 10^{8}$. Note also that the matrix element (31) is subjected to E1 selection rules.

B. Nuclear Schiff moment contribution

The effective Hamiltonian for the interaction between the nuclear Schiff moment and the molecular axis $N = X/X$ of a diatomic molecule is given by

$$V_{\text{mol}}^{\text{SM}} = W_{S} S \cdot N,$$

(35)

where $W_{S}$ is the interaction constant.

Using the Born-Oppenheimer wavefunction (30) and assuming maximal projection of the nuclear spin, we obtain

$$\langle f | V_{\text{mol}}^{\text{SM}} | i \rangle \approx (-1)^{2J' - M - \Omega} B_{J_{MN}}^{JM} W_{S} S,$$

(36)

where $B_{J_{MN}}^{JM}$ is defined as in Eq. (32). The time for the detection of one transition due to an oscillating nuclear Schiff moment is thus

$$t_{\text{mol}}^{\text{SM}} \approx \frac{2 \times 10^{17}}{N} \frac{1}{(B_{J_{MN}}^{JM})^{2}} \frac{\omega}{\omega \Omega} \times \left( \frac{50000 \ a_p}{W_{S}} \right)^{2} \left( \frac{\theta_0 \ e \text{fm}^{3}}{S} \right)^{2} \text{years},$$

(37)

where $W_{S}$ is normalized to a typical value of $50000 \ a_p$ and $S$ to the typical value of $\theta_0 \ e \text{fm}^{3}$ (for a nucleus with octupole deformation). If a maximal value of $S = 10 \theta_0 \ e \text{fm}^{3}$ ($^{227}$Ac) was used then the result is two orders of magnitude better than [37].

We observe that the result (37) is thirteen orders of magnitude better than the result (31). If nuclei with no deformation are used instead, the results are still seven to nine order of magnitude better than that of using EDMs. Hence, for small axion frequency ($\omega \lesssim 10^{-3} \text{eV}$), Schiff moments appear to be more advantageous than EDMs.

C. Nuclear magnetic quadrupole moment contribution

The effective Hamiltonian for the interaction between the nuclear MQM and the molecule is given by

$$V_{\text{mol}}^{\text{MQM}} = -\frac{W_{M} M}{2 T (2I - 1)} S' \cdot T N,$$

(38)

where $S' = (S'_x, S'_y, S'_z)$ is an effective spin defined by the equations:

$$S'_x = S'_x |\Omega \rangle = S'_x |\pm \Omega \rangle = 0, S'_z = S'_z |\pm \Omega \rangle = \pm \Omega$$

and $S'_z = S'_{x} \pm S'_{y}$ where the coordinates $(\xi, \psi, \zeta)$ form the molecular frame of reference with the $\zeta$-axis directed along the vector $N$. [53–55]. The tensor $T$ is defined as in Eq. (21).

The matrix element of this interaction (assuming maximal projection of the nuclear spin) is

$$\langle f | V_{\text{mol}}^{\text{MQM}} | i \rangle \approx (-1)^{2J' - M - \Omega} C_{J_{MN}}^{JM} W_{M} S,$$

(39)

where

$$C_{J_{MN}}^{JM} = -\frac{(2/3) \sqrt{(2J' + 1)(2J + 1)}}{\omega \Omega} \times \left( \begin{array}{cc} J' & 2 & J \\ -M & 0 & M \end{array} \right) \left( \begin{array}{cc} J' & 2 & J \\ -\Omega & 0 & \Omega \end{array} \right).$$

(40)

Thus, the time for the detection of one transition due to an oscillating nuclear magnetic quadrupole moment is

$$t_{\text{mol}}^{\text{MQM}} \approx \frac{8 \times 10^{17}}{N} \frac{1}{(C_{J_{MN}}^{JM})^{2}} \left( \frac{\omega}{\omega \Omega} \right) \times \left( \frac{10^{33} \text{ Hz}}{W_{M}} \right)^{2} \left( \frac{10^{-27} \theta_0 \ e \text{cm}^{2}}{M} \right)^{2} \text{years},$$

(41)

where $W_{M}$ is normalized to a typical value of $10^{33} \text{ Hz}$ and $M$ to the typical value of $10^{-27} \theta_0 \ e \text{cm}^{2}$ (for a nucleus with quadrupole deformation). If the value $2 \times 10^{-27} \theta_0 \ e \text{cm}^{2}$ is used for $M$ (e.g., $^{179}$Hf) then the result is better by a factor of four.

We observe that the result (41) is thirteen orders of magnitude better than (34). If the nucleus in question has no quadrupole deformation, the result is still about eleven orders of magnitude better than using EDMs. Note also that the MQM-induced transition (39) is of M2 type, which is very convenient for suppressing photon backgrounds (if $J' = J \pm 2$).
V. ESTIMATES WITH COLLISIONAL WIDTH

In the previous sections, we assumed that the width $\Gamma$ of the transition comes predominantly from the distribution of axion frequency, $\Gamma_{\text{dis}} \approx 10^{-6}\omega$. Since the Doppler width of the transition is proportional to its frequency, $\Gamma_{\text{dop}} \approx v_0\omega/c$ where $v_0 = \sqrt{k_B T/m}$ is the thermal velocity of the atoms or molecules ($k_B$ is the Boltzmann’s constant, $T$ is the temperature of the atomic or molecular sample and $m$ is the mass of an atom or a molecule), if a sample of heavy particles is used, the Doppler width is not so important.

On the other hand, if the collisional width $\Gamma_{\text{col}}$ does not depend on the frequency of the transition, the condition $\Gamma_{\text{col}} \ll \Gamma_{\text{dis}}$ is not always met. For example, if we assume that the density of the sample is $n = 10^{20}\text{cm}^{-3}$ (e.g., a dilute gas), that the collisional cross section of the particles is $\sigma_{\text{col}} = 10\pi\sigma_B^2 \approx 10^{-15}\text{cm}^2$ and that their velocity is $v_0 \approx 10^{-3}\text{e}$ (reasonably achievable, say, at room temperature $T = 20^\circ\text{C}$ and $m = 4\text{He}$), then the collisional width is $\Gamma_{\text{col}} = n v_0\sigma_{\text{col}} = 10^{-6}\text{eV}$. For $\omega \approx 1\text{eV}$, $\Gamma_{\text{col}} \approx \Gamma_{\text{dis}}$ but for $\omega \lesssim 10^{-6}\text{eV}$ (the region of the most interest), $\Gamma_{\text{col}} \gg \Gamma_{\text{dis}}$. Thus, in addition to the results presented in section IV, it is useful to provide also an estimate for the case where the collisional width dominates. Since MQM-induced transitions appear to be the most advantageous, here we present the estimates for them only.

Inserting Eq. (59) into Eq. (15) and substituting $\Gamma = \Gamma_{\text{col}} = n v_0\sigma_{\text{col}}$, we obtain

$$t_{\text{mol}}^{\text{MQM}} \approx \frac{0.4}{(C J^{\text{MQM}}/M)^2} \left( \frac{1\text{m}^3}{V} \right) \left( \frac{v_0}{10^{-6}} \right) \left( \frac{\sigma_{\text{col}}}{10\pi\sigma_B^2} \right) \times 10^{33} \frac{\text{Hz}}{e\text{cm}^2} \frac{\sqrt{V}}{W_M} 2 \left( 10^{-27} \theta_0 \text{e cm}^2 \right)^2 \frac{\text{M}}{M} \text{ day}, \quad (42)$$

where $V = N/n$ is the volume of the sample, which we have normalized to the value of $1\text{m}^3$. If the value $2 \times 10^{-27} \theta_0 \text{e cm}^2$ is used for $M$ (e.g., $^{179}\text{Hf}$) then the time for one detection to happen is less than three hours. We observe that unlike Eq. (11), Eq. (42) does not depend on the frequency $\omega$ of the transition and density of the sample (provided $\Gamma_{\text{col}} \gg \Gamma_{\text{dis}}$).

VI. DISCUSSION AND CONCLUSION

In this paper, we presented the possibility of searching for axionic dark matter by means of the atomic and molecular transitions induced by the oscillating nuclear EDMs, nuclear Schiff moments and nuclear MQMs. While the search would be limited to axion frequencies closely corresponding to resonant atomic or molecular transitions, the latter can be tuned by using Zeeman and Stark effects. In addition, the transitions are ‘dense’ in the region of Rydberg excitations, so complete coverage of a frequency interval is, in principle, possible. Molecules also have dense spectra and may present additional advantages for this kind of experiments.

From our estimates, it appears that for a transition frequency $\omega \sim 1\text{eV}$, the contribution due to the nuclear Schiff moment (in a nucleus with octupole deformation) and nuclear MQM is comparable to that of the EDM.

On the other hand, in molecular rotational transitions, the contribution due to Schiff moment (in a nucleus with octupole deformation) and MQM is many orders of magnitude larger than that due to EDM. This is because MQM and Schiff moment matrix elements are not suppressed by the factor $\omega^2$ like EDM matrix elements (in this respect, atoms with small-$\omega$ transitions suffer from the same suppression of the EDM matrix elements). Also, an MQM-induced transition, unlike an EDM-induced or a Schiff-moment-induced one, which must be of E1 type and hence susceptible to photon background, can be of M2 type. Since M2-type transitions are strongly suppressed for photons, the effects of background processes may be limited. Thus, overall, MQMs are better suited for the detection of axions using atomic and molecular transition.

We also presented an estimate for the transition rate due the MQM for a realistic sample where the collisional width dominates. We found that for one cubic meter of molecules of reasonable density and temperature, a transition happens every three hours.

Acknowledgment

The authors thank Mikhail G. Kozlov, Derek F. Jackson Kimball, Alexander O. Sushkov and Igor. B. Samsonov for helpful discussions. This work is supported by the Australian Research Council, the Gutenberg Fellowship and the New Zealand Institute for Advanced Study. It has also received support from the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (grant agreement No. 695405), from the DFG Reinhart Koselleck Project and the Heising-Simons Foundation.

Appendix

In this Appendix, we provide the derivation for Eq. (27).

The total Hamiltonian of a diatomic molecule with the
interaction with nuclear EDMs included is given by

\[ H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \sum_{i=1}^{N_e} \frac{p_i^2}{2m_e} + V_0 + V_{\text{atom}}^{\text{EDM}}, \]

where the nuclear positions \( R_{1,2} \), nuclear momenta \( P_{1,2} \), electrons position \( r_i \), and electron momenta \( p_i \) are defined in the laboratory frame.

A change of coordinates to the center-of-mass frame as described in Ref. [57], gives, after discarding the free motion of the molecule

\[ H = H_0 + V_{\text{atom}}^{\text{EDM}}, \]

\[ H_0 = \frac{Q^2}{2\mu_N} + \sum_{i=1}^{N_e} \frac{q_i^2}{2\mu_e} + \sum_{i \neq j}^{N_e} \frac{q_i q_j}{M_N} + V_0, \]  \hspace{1cm} (43)

where \( V_0 \) and \( V_{\text{atom}}^{\text{EDM}} \) are now functions of the new variables \( X = R_1 - R_2 \) and \( x_i = r_i - (M_1 R_1 + M_2 R_2) / M_N \). The momenta \( Q \) and \( q_i \) are conjugate to \( X \) and \( x_i \), respectively. For convenience, we have defined \( M_N = M_1 + M_2, \) \( M_T = M_N + N_e m_e, \) \( \mu_N = M_1 M_2 / M_N \) and \( \mu_e = M_N m_e / (M_N + m_e). \)

We may then write

\[ V_{\text{atom}}^{\text{EDM}} = \frac{d_1 \cdot \nabla R_1 V_0}{Z_1 e} + \frac{d_2 \cdot \nabla R_2 V_0}{Z_2 e}, \]

\[ = \frac{id_1 \cdot [P_1, H_0]}{Z_1 \hbar} + \frac{id_2 \cdot [P_2, H_0]}{Z_2 \hbar}, \]

\[ = \frac{id_1 \cdot \left[ Q - \frac{M_1}{M_N} \sum_{i=1}^{N_e} q_i, H_0 \right]}{Z_1 \hbar}, \]

\[ - \frac{id_2 \cdot \left[ Q + \frac{M_2}{M_N} \sum_{i=1}^{N_e} q_i, H_0 \right]}{Z_2 \hbar}, \]

so

\[ \langle f \vert V_{\text{atom}}^{\text{EDM}} \vert i \rangle = -\frac{i \omega d_1 \cdot \langle f \vert Q - \frac{M_1}{M_N} \sum_{i=1}^{N_e} q_i \vert i \rangle}{Z_1 \hbar}, \]

\[ + \frac{i \omega d_2 \cdot \langle f \vert Q + \frac{M_2}{M_N} \sum_{i=1}^{N_e} q_i \vert i \rangle}{Z_2 \hbar}. \]  \hspace{1cm} (46)

Using the relations

\[ Q + (-1^l) \frac{M_I}{M_N} \sum_{i=1}^{N_e} q_i, \]

\[ = \frac{i}{\hbar} \left[ H_0, \mu_N X + (-1^l) \frac{M_I \mu_e}{M_T} \sum_{i=1}^{N_e} x_i \right], \]  \hspace{1cm} (47)

we obtain

\[ \langle f \vert \delta \cdot X - \Delta \cdot \sum_{i=1}^{N_e} x_i \vert i \rangle \]

[48]

where

\[ \delta = \frac{Z_2 d_1 - Z_1 d_2}{\sqrt{Z_1 Z_2}}, \]  \hspace{1cm} (49)

and

\[ \Delta = \mu_e \left( M_1 Z_2 d_1 + M_2 Z_1 d_2 \right) \]

\[ \approx \frac{M_T \mu_N \sqrt{Z_1 Z_2}}{M_1 M_2 \sqrt{Z_1 Z_2}}. \]  \hspace{1cm} (50)
