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Anapole moment of a chiral molecule revisited

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Abstract

Parity violation in a chiral, four-atom molecule is discussed. Given the geometrical positions of the four atoms, we calculate the anapole moment of it. This problem was first discussed by Khriplovich and Pospelov [1]. We give a detailed derivation for it so that it can be more accessible to wider range of scientists. We correct errors in their results and generalize their initial state to $|s_{1/2}\rangle$ and $|p_{1/2}\rangle$ states. We also discuss realistic candidates of the chiral molecules to which this approach can be applied.

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1   Introduction

Charge-conjugation (C), parity (P), and time-reversal (T) violations in atoms and molecules are very attractive targets in searching for new physics beyond the standard model (BSM physics) as well as for their own developments of atomic and molecular physics and chemistry. For molecules, we can utilize selectively the precise spectroscopies and special environments of molecules suitable to determine fundamental properties of particles. A typical example is the recent improvement of

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the upper bound on the electron electric dipole moment (EDM) by using a ThO molecule [2]. Also the measurements of energy difference between left- and right-handed molecules are on-going [3]. Such situations conventionally enforce on us complicated numerical calculations based on *ab-initio* molecular orbital (MO) calculation methods. Since there are so many papers on *ab-initio* MO methods, we cite only a textbook [4] and a recent paper [5]. Though they are crucially important, it is rather difficult to elucidate the physical origin of symmetry violations in a given molecular system from molecular orbital calculations. In order to remedy this deficit, analytical treatments of the same objects as those studied by numerical calculations have been awaited even with a cost of less rigor. From this point of view, the work [1] by Khriplovich and Pospelov is methodologically very interesting. Given the geometrical positions of four atoms, they calculated the anapole moment of the chiral molecule which consists of the four atoms. There the P-violating (PV) anapole moment is directly and quantitatively related with geometrical structure of molecules.

In this note we give a more detailed derivation of it than in the original work [1], so that it can be more accessible to many physicists and chemists. Their final result is also corrected.

We note here that in general, there are two possibilities concerning the origin of parity violation in molecules. One of the possibilities is the weak interactions which intrinsically violate parity. This effect is known to work in nuclei in atomic systems, which is discussed, for example, in Refs. [6, 7]. The other possibility is parity violation due to the geometric configuration of atoms in a molecule. When a molecule consists of more than four atoms, the molecule is not necessarily superimposable on its mirror image. Such a non-trivial transformation property under parity is called the chirality, and the chiral molecule and its mirror image are called enantiomers. When we take one of the enantiomers, parity is not a good symmetry to describe the quantum state of the chiral molecule since parity is violated by the configuration of the atoms. It is this latter case of parity violation which is discussed in Ref. [1] and which we consider in this paper.

This paper is organized as follows. In Section 2, we describe our set-up of a four-atom molecule. In Section 3, we discuss the perturbation due to the Coulomb interactions between the valence electron and the light two atoms in the molecule. In Section 4, we calculate the anapole moment by using the results obtained in Section 3. We summarize our results and give discussions in Section 5. In Appendix we discuss realistic candidates of the chiral molecules to which this approach can be applied. We work in the notation of the Landau-Lifshitz textbooks [8, 9] unless noted otherwise. We use the natural units in which $\hbar = c = 1$ throughout this paper.

2   Model Set-up

Chirality in molecules first appears in four-atom molecules. Khriplovich and Pospelov considered a chiral molecule composed of four atoms, A_1, A_2, A_3, A_4, whose geometrical configuration is given in Fig. 1 without specifying its origin [1]. An assumption in this set-up is that A_1 and A_2 (whose electric charges are Z_1 and Z_2 in units of the positron charge e, respectively) are light in comparison with A_4 and A_3. Throughout this paper, we take the position of A_4 as the origin of our coordinate system, and the direction of $\vec{r}_3$ as the z-axis.

We first consider a valence electron which is captured by the diatomic molecule A_3A_4. To specify the position of the valence electron, we define the vector $\vec{r}$ whose initial and final points are

A_4 and the electron, respectively. We assume that the electron is first in one of the $p_{3/2}$ states with $\mu = \pm 3/2$, where μ is the z component of the total angular momentum. We also assume that the degeneracy in the energy levels of the atom A_4 is completely resolved by the presence of the atom A_3, as assumed in Ref. [1]. We treat the effect from the atoms A_1 and A_2 on the valence electron as a perturbation due to the Coulomb potential,

$$V(\vec{r}) = -\frac{Z_1 \alpha}{|\vec{r} - \vec{r}_1|} - \frac{Z_2 \alpha}{|\vec{r} - \vec{r}_2|} \ . \tag{1}$$

Then, the Coulomb interactions between the valence electron depicted as e in Fig. 1 and the atoms A_1 and A_2 can be treated as a perturbation to the electron terms of the diatomic molecule $A_3 A_4$, which induces a PV anapole moment. The unpaired electron is localized in the vicinity of A_4, and hence its orbital can be well described in terms of the atomic orbitals of the atom A_4. To lowest order of the approximation, the angular momentum about the $A_3 A_4$ axis is conserved.
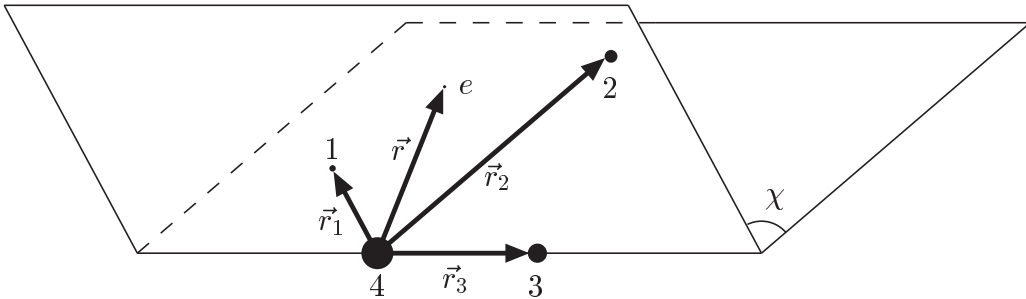

Figure 1: The configuration of the atoms in the four-atom molecule we consider in this paper. The numbers j ($j = 1, \ldots, 4$) in the figure are the labels for the corresponding atoms A_j. e is a valence electron. The two planes are spanned by the atoms $A_1 A_3 A_4$ and the atoms $A_2 A_3 A_4$, respectively. Also shown is the dihedral angle χ of the molecule.

The final result we obtain in this paper is

$$\langle \vec{a} \rangle = \frac{\pi e}{m_e} \frac{4}{45} [r_1(s,p) - 4r(s,p)] \frac{(\mathrm{Ry})^2}{E_s E_p} Z_1 Z_2$$

$$\times (\vec{J} \cdot \vec{n}_3)(\vec{n}_1 \cdot [\vec{n}_2 \times \vec{n}_3])[C_1(r_1)C_2(r_2)\vec{n}_2 - C_1(r_2)C_2(r_1)\vec{n}_1] \ , \tag{2}$$

where $\vec{a}$ is the anapole moment operator and $\langle \vec{a} \rangle$ its expectation value. $\mathrm{Ry} \equiv \alpha^2 m_e/2$ is the Rydberg energy ($\simeq 13.6\mathrm{eV}$) with the electron mass m_e and $\vec{J}$ is the total angular momentum, and the definitions of $\vec{n}_{1,2,3}$, $C_{1,2}$, $r_1(s,p)$, $r(s,p)$, $E_{s,p}$ will be given in the next sections. The result is different from that of Ref. [1] in the factor 4 in front of $r(s,p)$ and also in the overall factor by a factor of $2a_0$, where a_0 is the Bohr radius, $a_0 \equiv 1/(m_e \alpha)$. Thus Eq. (2) explicitly shows the relation between a PV observable and the geometrical structure of the molecule. In the subsequent sections we derive Eq. (2).

3   Perturbation due to Coulomb Interactions

By the perturbation due to $V(\vec{r})$, the states $|p_{3/2}, \mu = \pm 3/2\rangle$ are slightly mixed with the states $|s_{1/2}, \pm 1/2\rangle$ and $|p_{1/2}, \pm 1/2\rangle$. First we write the potential $V(\vec{r})$ as

$$
\begin{aligned}
V(\vec{r}) = -Z_1 \alpha \Bigg\{ & \theta(r - r_1) \left(r_{1m} \frac{\partial}{\partial r_m} \frac{1}{r} + \frac{1}{2} r_{1m} r_{1n} \frac{\partial}{\partial r_m} \frac{\partial}{\partial r_n} \frac{1}{r} + \mathcal{O}(r_1^3/r^3) \right) \\
& + \theta(r_1 - r) \left(r_m \frac{\partial}{\partial r_{1m}} \frac{1}{r_1} + \frac{1}{2} r_m r_n \frac{\partial}{\partial r_{1m}} \frac{\partial}{\partial r_{1n}} \frac{1}{r_1} + \mathcal{O}(r^3/r_1^3) \right) \Bigg\} \\
& - \Big((r_1, Z_1) \to (r_2, Z_2) \Big) \;,
\end{aligned}
\tag{3}
$$

where $r_i \equiv |\vec{r}_i|$ $(i = 1, 2)$ and the indices n and m $(n, m = 1, \ldots, 3)$ run over the three components of the Cartesian coordinates, (x, y, z). For later convenience, we integrate out the dependence of the potential on r $(\equiv |\vec{r}|)$, and rewrite the potential Eq. (3) as

$$
V(\vec{n}) = \mathrm{Ry} \left(2 D_m n_m - 3 Q_{mn} n_m n_n \right) \;,
\tag{4}
$$

where $\vec{n} \equiv \vec{r}/r$. The quantities D_m and Q_{mn} are defined as

$$
D_m \equiv Z_1 C_1(r_1) n_{1m} + Z_2 C_1(r_2) n_{2m} \;,
\tag{5}
$$

$$
Q_{mn} \equiv Z_1 C_2(r_1) n_{1m} n_{1n} + Z_2 C_2(r_2) n_{2m} n_{2n} \;,
\tag{6}
$$

$$
C_k(r_i) \equiv a_0 \int_0^\infty dr \; r^2 R_{1/2}(r) R_{3/2}(r) \left[\frac{r_i^k}{r^{k+1}} \theta(r - r_i) + \frac{r^k}{r_i^{k+1}} \theta(r_i - r) \right] \;,
\tag{7}
$$

where $\vec{n}_i \equiv \vec{r}_i/r_i$ $(i = 1, 2)$. The factors $R_{3/2}(r)$ and $R_{1/2}(r)$ are the radial parts of the $J = 3/2$ and $J = 1/2$ state wave functions for the electron, respectively. With these definitions, the quantity $C_k(r_i)$ becomes dimensionless.

As mentioned above, by the perturbation due to $V(\vec{r})$, the states $|p_{3/2}, \mu = \pm 3/2\rangle$ are slightly mixed with other states ψ_s and ψ_p as:

$$
|p_{3/2}, \mu = \pm 3/2\rangle \to |p_{3/2}, \mu = \pm 3/2\rangle + |\psi_s\rangle + |\psi_p\rangle \;.
\tag{8}
$$

Here

$$
|\psi_s\rangle = -\frac{2}{\sqrt{3}} \frac{\mathrm{Ry}}{E_s} D_i R_s(r) |s_{1/2}, \mu'\rangle \;,
\tag{9}
$$

where $(i, \mu') = (+, 1/2)$ and $(-, -1/2)$ for $\mu = 3/2$ and $-3/2$, respectively, and

$$
|\psi_p\rangle = \frac{2\sqrt{3} i}{5} \frac{\mathrm{Ry}}{E_p} Q_{mi} \sum_{\mu' = \pm 1/2} (\sigma_m)_{\alpha' \beta'} R_p(r) |p_{1/2}, \mu'\rangle \;,
\tag{10}
$$

4

where $(i, \beta') = (+, 1), (-, 2)$ for $\mu = 3/2$ and $-3/2$, respectively, and $\alpha' = 1, 2$ for $\mu' = 1/2$ and $-1/2$, respectively. The definitions of the "$\pm$" symbols which appear in the subscripts in Eqs. (9) and (10) like $D_\pm$ will be given later in this paper at Eq. (16). The factors E_s and E_p are the energy levels of the $|s_{1/2}, \mu'\rangle$ and $|p_{1/2}, \mu'\rangle$ states ($\mu' = \pm 1/2$), measured from the state $|p_{3/2}, \mu\rangle$ ($\mu = \pm 3/2$), respectively, namely,

$$E_s \equiv E(s_{1/2}, \mu') - E(p_{3/2}, \mu) , \qquad E_p \equiv E(p_{1/2}, \mu') - E(p_{3/2}, \mu) . \qquad (11)$$

In Eq. (10), we have neglected the difference between $E(p_{1/2}, 1/2)$ and $E(p_{1/2}, -1/2)$. The functions $R_s(r)$ and $R_p(r)$ are the radial part of the s- and p-wave-state wave functions, respectively. The factor σ_m ($m = 1, \ldots, 3$) denotes the Pauli matrices, and $(\sigma_m)_{\alpha'\beta'}$ ($\alpha', \beta' = 1, 2$) its (α', β') component. Note that our overall phase convention of $|p_{1/2}, \mu'\rangle$ differs from that of Ref. [1] by a factor of i. Since ψ_s in Eq. (8) depends on the value of μ, we denote the ψ_s which mixes with $|p_{3/2}, \mu = +3/2\rangle$, and $|p_{3/2}, \mu = -3/2\rangle$ as ψ_{s+} and ψ_{s-}, respectively. We also define ψ_{p+} and ψ_{p-} similarly, and use the notation $\psi_{s\pm}$ and $\psi_{p\pm}$ instead of ψ_s and ψ_p where the distinction is necessary. In the subsections just below, we prove Eqs. (9) and (10).

3.1 Verification of Eq. (9)

In this subsection we verify Eq. (9). To do so, we need the solutions of the Dirac equation for an electron in the Coulomb potential, $V(r) = -Z\alpha/r$. Since we are interested only in the non-relativistic limit, in this paper we consider only the upper two components of the four-component Dirac spinor.

As a preparation, we first introduce some notations. We define the two-component spinors χ_α ($\alpha = \pm 1/2$) as,

$$\chi_{1/2} = \frac{1}{2\sqrt{\pi}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \qquad \chi_{-1/2} = \frac{1}{2\sqrt{\pi}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \qquad (12)$$

Namely, the angular parts of the states $|s_{1/2}, \alpha\rangle$ ($\alpha = \pm 1/2$) are related to χ_α by

$$|s_{1/2}, \alpha\rangle = \chi_\alpha , \qquad (13)$$

where we have suppressed the radial part of the wave function. Below we suppress the radial part when there may arise no confusion. We also define the vectors $\vec{e}_i$ ($i = \pm, 0$) as

$$\vec{e}_+ \equiv -i(1, i, 0)/\sqrt{2} , \qquad \vec{e}_- \equiv i(1, -i, 0)/\sqrt{2} , \qquad \vec{e}_0 \equiv i(0, 0, 1) . \qquad (14)$$

They satisfy the relations,

$$\vec{e}_+ \cdot \vec{e}_+ = \vec{e}_- \cdot \vec{e}_- = 0 , \qquad \vec{e}_+ \cdot \vec{e}_- = 1 , \qquad \vec{e}_\pm \cdot \vec{e}_0 = 0 , \qquad \vec{e}_0 \cdot \vec{e}_0 = -1 . \qquad (15)$$

We denote the inner product of a general vector $\vec{k}$ and $\vec{e}_{\pm,0}$ as $k_{\pm,0}$:

$$k_i \equiv \vec{k} \cdot \vec{e}_i , \qquad (i = \pm, 0). \qquad (16)$$

With these definitions, the quantities k_i ($i = \pm, 0$) form a spherical tensor of rank 1. Since the vectors $\vec{e}_i$ ($i = \pm, 0$) are linearly independent of each other, any three dimensional vector $\vec{k}$ can be decomposed in terms of $\vec{e}_i$ as

$$\vec{k} = (\vec{k} \cdot \vec{e}_-)\vec{e}_+ + (\vec{k} \cdot \vec{e}_+)\vec{e}_- - (\vec{k} \cdot \vec{e}_0)\vec{e}_0$$
$$= k_-\vec{e}_+ + k_+\vec{e}_- - k_0\vec{e}_0 \ . \tag{17}$$

Now, by using these notations, the angular part of the $|p_{3/2}, \mu\rangle$ ($\mu = \pm 3/2$) states can be written as

$$|p_{3/2}, \mu\rangle = \sqrt{3}n_i\chi_\alpha \ , \tag{18}$$

where $n_i = \vec{n} \cdot \vec{e}_i = (\vec{r} \cdot \vec{e}_i)/r$ with $i = \pm$. The indices i and α in the above equation should be understood as $(i, \alpha) = (+, 1/2)$ for $\mu = 3/2$, and $(i, \alpha) = (-, -1/2)$ for $\mu = -3/2$.

We are now ready to evaluate the angular integral in the factor $\langle s_{1/2}, 1/2|2D_m n_m|p_{3/2}, 3/2\rangle$, where the integral is to be performed only over the angular variables. The integral reads:

$$\langle s_{1/2}, 1/2|2D_m n_m|p_{3/2}, 3/2\rangle = 2Z_1 C_1(r_1) \int d\Omega \frac{1}{2\sqrt{\pi}} \frac{r_{1m}}{r_1} \frac{r_m}{r} (-i)\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$$

$$+ \left((r_1, Z_1) \to (r_2, Z_2) \right) \ , \tag{19}$$

where $d\Omega \equiv \sin\theta d\theta d\phi$. The integral is straightforward, and the result is

$$\langle s_{1/2}, 1/2|2D_m n_m|p_{3/2}, 3/2\rangle = 2Z_1 C_1(r_1) \frac{(-i)(n_{1x} + in_{1y})}{\sqrt{6}} + \left((r_1, Z_1) \to (r_2, Z_2) \right)$$

$$= \frac{2}{\sqrt{3}} \vec{D} \cdot \vec{e}_+ = \frac{2}{\sqrt{3}} D_+ \ . \tag{20}$$

Once the above matrix element is determined, the other matrix elements $\langle s_{1/2}, \mu'|2D_m n_m|p_{3/2}, \mu\rangle$ for $(\mu, \mu') = (-3/2, \pm 1/2), (3/2, -1/2)$ can also be determined by using the Wigner-Eckart theorem. To do so, first by using Eq. (17), we write the quantity $D_m n_m$ as

$$D_m n_m = D_-(\vec{e}_+ \cdot \vec{n}) + D_+(\vec{e}_- \cdot \vec{n}) - D_0(\vec{e}_0 \cdot \vec{n})$$
$$= D_- n_+ + D_+ n_- - D_0 n_0 \ . \tag{21}$$

Then we write the matrix elements as

$\langle s_{1/2}, \mu'|2D_m n_m|p_{3/2}, \mu\rangle$
$= 2D_-\langle s_{1/2}, \mu'|n_+|p_{3/2}, \mu\rangle + 2D_+\langle s_{1/2}, \mu'|n_-|p_{3/2}, \mu\rangle - 2D_0\langle s_{1/2}, \mu'|n_0|p_{3/2}, \mu\rangle$

$= 2i(-1)^{3/2-\mu'}\langle s_{1/2}||n||p_{3/2}\rangle \left\{ D_- \begin{pmatrix} 1/2 & 1 & 3/2 \\ -\mu' & 1 & \mu \end{pmatrix} + D_+ \begin{pmatrix} 1/2 & 1 & 3/2 \\ -\mu' & -1 & \mu \end{pmatrix} - D_0 \begin{pmatrix} 1/2 & 1 & 3/2 \\ -\mu' & 0 & \mu \end{pmatrix} \right\}$

$$\tag{22}$$

where $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are the Wigner $3j$ symbols. In the second equality we have used the Wigner-Eckart theorem,

$$\langle j'm'|f_{kq}|jm\rangle = i^k(-1)^{j_{\max}-m'}\begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix}\langle j'||f_k||j\rangle , \tag{23}$$

where $j_{\max} = \max(j, j')$ and f_{kq} ($q = -k, -k+1, \cdots, k$) are a spherical tensor of rank k. Since we already know the value of $\langle s_{1/2}, 1/2|2D_m n_m|p_{3/2}, 3/2\rangle$ from Eq. (20), we can determine the value of the double-line matrix element $\langle s_{1/2}||n||p_{3/2}\rangle$ by applying Eq. (22) to the case $(\mu, \mu') = (3/2, 1/2)$. This can be done with the help of the numerical values of the Wigner $3j$ symbols as

$$\langle s_{1/2}||n||p_{3/2}\rangle = i\frac{2}{\sqrt{3}} . \tag{24}$$

Then, by using the value of $\langle s_{1/2}||n||p_{3/2}\rangle$, the other relevant matrix elements can be determined from Eq. (22) as

$$\langle s_{1/2}, -1/2|2D_m n_m|p_{3/2}, -3/2\rangle = \frac{2}{\sqrt{3}}D_- , \tag{25}$$

$$\langle s_{1/2}, -1/2|2D_m n_m|p_{3/2}, +3/2\rangle = \langle s_{1/2}, +1/2|2D_m n_m|p_{3/2}, -3/2\rangle = 0 . \tag{26}$$

By combining all the above results, we arrive at

$$\sum_{\mu'=\pm 1/2}|s_{1/2}, \mu'\rangle\langle s_{1/2}, \mu'|2D_m n_m|p_{3/2}, \mu\rangle = \frac{2}{\sqrt{3}}D_i\chi_\alpha , \tag{27}$$

where i and α should be understood as $(i, \alpha) = (+, 1/2)$ for $\mu = 3/2$, and $(i, \alpha) = (-, -1/2)$ for $\mu = -3/2$. From this equation, Eq. (9) immediately follows.

3.2 Verification of Eq. (10)

In this subsection we verify Eq. (10). The matrix element we would like to evaluate is,

$$\langle p_{1/2}, \mu'|(-3)Q_{mn}n_m n_n|p_{3/2}, \pm 3/2\rangle = -3Z_1 C_2(r_1)\langle p_{1/2}, \mu'|(\vec{n}_1 \cdot \vec{n})^2|p_{3/2}, \pm 3/2\rangle$$

$$+ \Big((r_1, Z_1) \to (r_2, Z_2)\Big) . \tag{28}$$

Note that in our notation, which is actually the notation of Landau-Lifshitz, the states $|p_{1/2}, \mu\rangle$ ($\mu = \pm 1/2$) are related to χ_α ($\alpha = \pm 1/2$) by

$$|p_{1/2}, \mu\rangle = -i(\vec{\sigma} \cdot \vec{n})\chi_\alpha , \tag{29}$$

where $\alpha = 1/2$ and $-1/2$ for $\mu = 1/2$ and $-1/2$, respectively. The overall phase convention of $|p_{1/2}, \mu\rangle$ differs from that of Ref. [1] by a factor of i.

We first evaluate the factor $\langle p_{1/2}, \mu' | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, \pm 3/2 \rangle$, where the integral is to be performed only over the angular variables.

To do so, we write the inner product $\vec{n}_1 \cdot \vec{n}$ as

$$\vec{n}_1 \cdot \vec{n} = n_{1x} \frac{x}{r} + n_{1y} \frac{y}{r} + n_{1z} \frac{z}{r}$$

$$= n_{1x} \sin \theta \cos \phi + n_{1y} \sin \theta \sin \phi + n_{1z} \cos \theta$$

$$= \frac{1}{2} \sin \theta \left((n_{1x} + i n_{1y}) e^{-i\phi} + (n_{1x} - i n_{1y}) e^{i\phi} \right) + n_{1z} \cos \theta \ . \tag{30}$$

We now substitute the above expression into the matrix element $\langle p_{1/2}, 1/2 | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, 3/2 \rangle$

$$\langle p_{1/2}, 1/2 | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, 3/2 \rangle = \int d\Omega \frac{i}{2\sqrt{\pi}} \cos \theta \ (\vec{n}_1 \cdot \vec{n})^2 \ (-i) \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$$

$$= \int d\Omega \frac{1}{2\sqrt{\pi}} \cos \theta \left\{ \frac{1}{2} \sin \theta \left((n_{1x} + i n_{1y}) e^{-i\phi} + (n_{1x} - i n_{1y}) e^{i\phi} \right) + n_{1z} \cos \theta \right\}^2$$

$$\times \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \ . \tag{31}$$

The angular integral is straightforward, and we are left with:

$$\langle p_{1/2}, 1/2 | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, 3/2 \rangle = \frac{\sqrt{2}}{5\sqrt{3}} (n_{1x} + i n_{1y}) n_{1z}$$

$$= \frac{2}{5\sqrt{3}} n_{1+} n_{10} \ . \tag{32}$$

We now determine the other relevant matrix elements $\langle p_{1/2}, \pm 1/2 | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, \pm 3/2 \rangle$ by using the Wigner-Eckart theorem. To do so, we have to rewrite $(\vec{n}_1 \cdot \vec{n})^2$ in terms of spherical tensors. We construct a rank-2 spherical tensor $N_{2,q}$ $(q = -2, -1, \cdots, 2)$ by combining two rank-1 spherical tensors n_i $(i = \pm, 0)$. This can be done by using the Clebsch-Gordan coefficients, or equivalently the $3j$ symbols (see Eq. (107.3) of Ref. [9]). The results are:

$$N_{2,\pm 2} = n_{\pm}^2 \ , \qquad N_{2,\pm 1} = \sqrt{2} n_{\pm} n_0 \ , \qquad N_{2,0} = \frac{2}{\sqrt{6}} n_+ n_- + \frac{2}{\sqrt{6}} n_0^2 \ . \tag{33}$$

We also use a spherical tensor of rank 0, $N_{0,0}$, which we construct according to Eq. (107.4) of Ref. [9],

$$N_{0,0} = 2 n_+ n_- - n_0^2 \ . \tag{34}$$

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We now write $(\vec{n}_1 \cdot \vec{n})^2$ in terms of $N_{2,q}$ and $N_{0,0}$:

$$
\begin{aligned}
(\vec{n}_1 \cdot \vec{n})^2 &= (n_{1+}n_- + n_{1-}n_+ - n_{10}n_0)^2 \\
&= (n_{1+})^2 N_{2,-2} - \sqrt{2}n_{1+}n_{10}N_{2,-1} + c_{2,0}N_{2,0} - \sqrt{2}n_{1-}n_{10}N_{2,1} + (n_{1-})^2 N_{2,2} + c_{0,0}N_{0,0} \ ,
\end{aligned}
$$

$$(35)$$

where $c_{2,0}$ and $c_{0,0}$ are linear combinations of $n_{1+}n_{1-}$ and $n_{10}n_{10}$, whose explicit forms we do not need for our purposes here.

We now apply the Wigner-Eckart theorem. First we expand $(\vec{n}_1 \cdot \vec{n})^2$ in terms of the tensors N,

$$
\begin{aligned}
\langle p_{1/2}, \mu' | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, \mu \rangle &= (n_{1+})^2 \langle p_{1/2}, \mu' | N_{2,-2} | p_{3/2}, \mu \rangle - \sqrt{2}n_{1+}n_{10}\langle p_{1/2}, \mu' | N_{2,-1} | p_{3/2}, \mu \rangle \\
&+ c_{2,0}\langle p_{1/2}, \mu' | N_{2,0} | p_{3/2}, \mu \rangle - \sqrt{2}n_{1-}n_{10}\langle p_{1/2}, \mu' | N_{2,1} | p_{3/2}, \mu \rangle \\
&+ (n_{1-})^2 \langle p_{1/2}, \mu' | N_{2,2} | p_{3/2}, \mu \rangle + c_{0,0}\langle p_{1/2}, \mu' | N_{0,0} | p_{3/2}, \mu \rangle \ .
\end{aligned}
$$

$$(36)$$

We use the Wigner-Eckart theorem to rewrite this as

$$
\begin{aligned}
\langle p_{1/2}, \mu' | (\vec{n}_1 \cdot \vec{n})^2 | p_{3/2}, \mu \rangle = i^2 (-1)^{3/2-\mu'} &\left\{ (n_{1+})^2 \begin{pmatrix} 1/2 & 2 & 3/2 \\ -\mu' & -2 & \mu \end{pmatrix} - \sqrt{2}n_{1+}n_{10} \begin{pmatrix} 1/2 & 2 & 3/2 \\ -\mu' & -1 & \mu \end{pmatrix} \right. \\
&+ c_{2,0} \begin{pmatrix} 1/2 & 2 & 3/2 \\ -\mu' & 0 & \mu \end{pmatrix} - \sqrt{2}n_{1-}n_{10} \begin{pmatrix} 1/2 & 2 & 3/2 \\ -\mu' & 1 & \mu \end{pmatrix} \\
&\left. + (n_{1-})^2 \begin{pmatrix} 1/2 & 2 & 3/2 \\ -\mu' & 2 & \mu \end{pmatrix} \right\} \langle p_{1/2} || N_2 || p_{3/2} \rangle \\
&+ (-1)^{3/2-\mu'} c_{0,0} \begin{pmatrix} 1/2 & 0 & 3/2 \\ -\mu' & 0 & \mu \end{pmatrix} \langle p_{1/2} || N_0 || p_{3/2} \rangle \ .
\end{aligned}
$$

$$(37)$$

We can fix the value of $\langle p_{1/2} || N_2 || p_{3/2} \rangle$ from Eq. (32) as

$$
\langle p_{1/2} || N_2 || p_{3/2} \rangle = -\frac{2\sqrt{10}}{5\sqrt{3}} \ .
$$

$$(38)$$

By using this value, we can determine the following matrix elements:

$$\langle p_{1/2}, -1/2|(\vec{n}_1 \cdot \vec{n})^2|p_{3/2}, 3/2\rangle = i^2(-1)^{3/2+1/2}(n_{1+})^2 \begin{pmatrix} 1/2 & 2 & 3/2 \\ 1/2 & -2 & 3/2 \end{pmatrix} \langle p_{1/2}||N_2||p_{3/2}\rangle$$

$$= -\frac{2\sqrt{2}}{5\sqrt{3}}(n_{1+})^2 \ , \tag{39}$$

$$\langle p_{1/2}, 1/2|(\vec{n}_1 \cdot \vec{n})^2|p_{3/2}, -3/2\rangle = i^2(-1)^{3/2-1/2}(n_{1-})^2 \begin{pmatrix} 1/2 & 2 & 3/2 \\ -1/2 & 2 & -3/2 \end{pmatrix} \langle p_{1/2}||N_2||p_{3/2}\rangle$$

$$= \frac{2\sqrt{2}}{5\sqrt{3}}(n_{1-})^2 \ , \tag{40}$$

$$\langle p_{1/2}, -1/2|(\vec{n}_1 \cdot \vec{n})^2|p_{3/2}, -3/2\rangle = i^2(-1)^{3/2+1/2}(-\sqrt{2}n_{1-}n_{10}) \begin{pmatrix} 1/2 & 2 & 3/2 \\ 1/2 & 1 & -3/2 \end{pmatrix} \langle p_{1/2}||N_2||p_{3/2}\rangle$$

$$= -\frac{2}{5\sqrt{3}}n_{1-}n_{10} \ . \tag{41}$$

The results Eqs. (32), (39), (40), (41) can be compactly summarized as

$$\langle p_{1/2}, \mu'|(\vec{n}_1 \cdot \vec{n})^2|p_{3/2}, \mu\rangle = \frac{2i}{5\sqrt{3}}n_{1i}(\vec{\sigma} \cdot \vec{n}_1)_{\alpha'\beta'} \ , \tag{42}$$

where $(i, \beta') = (+, 1), (-, 2)$ for $\mu = 3/2$ and $-3/2$, respectively, and $\alpha' = 1, 2$ for $\mu' = 1/2$ and $-1/2$, respectively. By substituting the above equation into Eq. (28), we obtain

$$\langle p_{1/2}, \mu'|(-3)Q_{mn}n_m n_n|p_{3/2}, \pm 3/2\rangle = -\frac{2\sqrt{3}i}{5}Q_{im}(\sigma_m)_{\alpha'\beta'} \ , \tag{43}$$

where $(i, \beta') = (+, 1), (-, 2)$ for $\mu = 3/2$ and $-3/2$, respectively, and $\alpha' = 1, 2$ for $\mu' = 1/2$ and $-1/2$, respectively. It follows that,

$$\sum_{\mu'=\pm 1/2} |p_{1/2}, \mu'\rangle\langle p_{1/2}, \mu'|(-3)Q_{mn}n_m n_n|p_{3/2}, \pm 3/2\rangle = -\frac{2\sqrt{3}}{5}Q_{im} \sum_{\mu'=\pm 1/2} (\sigma_m)_{\alpha'\beta'}(\vec{\sigma} \cdot \vec{n})\chi_{\mu'} \ , \tag{44}$$

where $(i, \beta') = (+, 1), (-, 2)$ for $\mu = 3/2$ and $-3/2$, respectively, and $\alpha' = 1, 2$ for $\mu' = 1/2$ and $-1/2$, respectively.

4 Evaluation of Anapole Moment

We are now ready to calculate the anapole moment of the four-atom molecule of Fig. 1.

What we are interested in is the expectation value of $\vec{a}$ sandwiched by the state represented by the right-hand side of Eq. (8). The non-trivial lowest-order contribution comes from the terms,

$$\langle \vec{a} \rangle = \langle \psi_{s+} | \vec{a} | \psi_{p+} \rangle + (\text{c. c.}) \tag{45}$$

for $\mu = 3/2$, and

$$\langle \vec{a} \rangle = \langle \psi_{s-} | \vec{a} | \psi_{p-} \rangle + (\text{c. c.}) \ , \tag{46}$$

for $\mu = -3/2$, where (c. c.) stands for the complex conjugate. We need a proof for the above statement (i.e. the statement that the first-order perturbation and the rest of the second-order perturbation both vanish), but at this moment, we admit Eqs. (45) and (46), and calculate the right-hand sides of these equations.

The contribution $\langle \vec{a}_{\text{spin}} \rangle$ from the "spin current" to $\langle \vec{a} \rangle$ is,

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{2m_e} \int d^3\vec{r} \, r^2 \left(\vec{\nabla} \times (\psi_s^\dagger \vec{\sigma} \psi_p) \right) + (\text{c. c.}) \ . \tag{47}$$

We represent the integrand in terms of the spherical coordinates, (r, θ, ϕ):

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{2m_e} \int r^4 dr d\Omega \bigg\{ \mathbf{e}_r \left(\frac{1}{r} \partial_\theta (\psi_s^\dagger \sigma_\phi \psi_p) + \frac{\cos\theta}{r\sin\theta} (\psi_s^\dagger \sigma_\phi \psi_p) - \frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_\theta \psi_p) \right)$$

$$+ \mathbf{e}_\theta \left(-\partial_r (\psi_s^\dagger \sigma_\phi \psi_p) - \frac{1}{r} (\psi_s^\dagger \sigma_\phi \psi_p) + \frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_r \psi_p) \right)$$

$$+ \mathbf{e}_\phi \left(\partial_r (\psi_s^\dagger \sigma_\theta \psi_p) + \frac{1}{r} (\psi_s^\dagger \sigma_\theta \psi_p) - \frac{1}{r} \partial_\theta (\psi_s^\dagger \sigma_r \psi_p) \right) \bigg\} + (\text{c. c.}) \ , \tag{48}$$

where the vectors $\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\phi$ are defined as

$$\begin{pmatrix} \mathbf{e}_r \\ \mathbf{e}_\theta \\ \mathbf{e}_\phi \end{pmatrix} \equiv \begin{pmatrix} \frac{\partial \vec{r}}{\partial r} / \left| \frac{\partial \vec{r}}{\partial r} \right| \\ \frac{\partial \vec{r}}{\partial \theta} / \left| \frac{\partial \vec{r}}{\partial \theta} \right| \\ \frac{\partial \vec{r}}{\partial \phi} / \left| \frac{\partial \vec{r}}{\partial \phi} \right| \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \end{pmatrix} \begin{pmatrix} \mathbf{e}_x \\ \mathbf{e}_y \\ \mathbf{e}_z \end{pmatrix} \ , \tag{49}$$

where $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ are the unit vectors in the x, y, z directions in the Cartesian coordinates, respectively. The matrices $\sigma_r, \sigma_\theta, \sigma_\phi$ are the 2×2 matrices defined in such a way that the identity below holds:

$$\vec{\sigma} \equiv \sigma_x \mathbf{e}_x + \sigma_y \mathbf{e}_y + \sigma_z \mathbf{e}_z = \sigma_r \mathbf{e}_r + \sigma_\theta \mathbf{e}_\theta + \sigma_\phi \mathbf{e}_\phi \ , \tag{50}$$

where $\sigma_{x,y,z}$ are the Pauli matrices. The explicit forms of $\sigma_{r,\theta,\phi}$ are,

$$\sigma_r = \begin{pmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{pmatrix} \ , \qquad \sigma_\theta = \begin{pmatrix} -\sin\theta & e^{-i\phi}\cos\theta \\ e^{i\phi}\cos\theta & \sin\theta \end{pmatrix} \ , \qquad \sigma_\phi = \begin{pmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{pmatrix} \ . \tag{51}$$

We can greatly simplify Eq. (48) by integrating-by-parts those terms which have ∂_r, ∂_θ, or ∂_ϕ. First, integrating-by-parts those terms with ∂_r is equivalent to replacing the operator ∂_r with a factor of $(-4/r)$:

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{2m_e} \int r^4 dr d\Omega \left\{ \mathbf{e}_r \left(\frac{1}{r} \partial_\theta (\psi_s^\dagger \sigma_\phi \psi_p) + \frac{\cos\theta}{r\sin\theta} (\psi_s^\dagger \sigma_\phi \psi_p) - \frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_\theta \psi_p) \right) \right.$$
$$\left. + \mathbf{e}_\theta \left(\frac{3}{r} (\psi_s^\dagger \sigma_\phi \psi_p) + \frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_r \psi_p) \right) + \mathbf{e}_\phi \left(-\frac{3}{r} (\psi_s^\dagger \sigma_\theta \psi_p) - \frac{1}{r} \partial_\theta (\psi_s^\dagger \sigma_r \psi_p) \right) \right\} + \text{(c. c.)} .$$

(52)

We now integrate-by-parts the terms with ∂_θ. By noting that $\partial_\theta \mathbf{e}_r = \mathbf{e}_\theta$ and $\partial_\theta \mathbf{e}_\phi = 0$, we obtain:

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{2m_e} \int r^4 dr d\Omega \left\{ \mathbf{e}_r \left(-\frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_\theta \psi_p) \right) + \mathbf{e}_\theta \left(\frac{2}{r} (\psi_s^\dagger \sigma_\phi \psi_p) + \frac{1}{r\sin\theta} \partial_\phi (\psi_s^\dagger \sigma_r \psi_p) \right) \right.$$
$$\left. + \mathbf{e}_\phi \left(-\frac{3}{r} (\psi_s^\dagger \sigma_\theta \psi_p) + \frac{\cos\theta}{r\sin\theta} (\psi_s^\dagger \sigma_r \psi_p) \right) \right\} + \text{(c. c.)} .$$

(53)

Finally, by integration-by-parts the terms with ∂_ϕ, by noting that $\partial_\phi \mathbf{e}_r = \sin\theta \mathbf{e}_\phi$ and $\partial_\phi \mathbf{e}_\theta = \cos\theta \mathbf{e}_\phi$, we are left with:

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{2m_e} \int r^4 dr d\Omega \left\{ \mathbf{e}_\theta \left(\frac{2}{r} (\psi_s^\dagger \sigma_\phi \psi_p) \right) + \mathbf{e}_\phi \left(-\frac{2}{r} (\psi_s^\dagger \sigma_\theta \psi_p) \right) \right\} + \text{(c. c.)} .$$

(54)

The integral with respect to r is now easy:

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{m_e} r(s,p) \int d\Omega \left\{ \mathbf{e}_\theta (\psi_s^\dagger \sigma_\phi \psi_p)_{\text{angular}} - \mathbf{e}_\phi (\psi_s^\dagger \sigma_\theta \psi_p)_{\text{angular}} \right\} + \text{(c. c.)} ,$$

(55)

where the subscripts "angular" means that only the angular part should be considered, forgetting about the radial part. The factor $r(s,p)$ is defined in the unnumbered equation just above Eq. (15) of Ref. [1],

$$r(s,p) \equiv \int_0^\infty dr \ r^3 R_s(r) R_p(r) ,$$

(56)

where $R_s(r)$ and $R_p(r)$ are the radial parts of ψ_s and ψ_p, respectively.

The contribution $\langle \vec{a}_{\text{orb}} \rangle$ from the usual "orbital current" to $\langle \vec{a} \rangle$ is,

$$\langle \vec{a}_{\text{orb}} \rangle = -\frac{e\pi}{2m_e} \int d^3\vec{r} \ r^2 \left\{ \psi_s^\dagger (-i) \vec{\nabla} \psi_p + i (\vec{\nabla} \psi_s^\dagger) \psi_p \right\} + \text{(c. c.)} .$$

(57)

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The integral can be written in the spherical coordinates as:

$$\langle \vec{a}_{\text{orb}} \rangle = -\frac{e\pi}{2m_e} \int r^4 dr d\Omega \left\{ \psi_s^\dagger (-i) \left(\mathbf{e}_r \partial_r \psi_p + \mathbf{e}_\theta \frac{1}{r} \partial_\theta \psi_p + \mathbf{e}_\phi \frac{1}{r\sin\theta} \partial_\phi \psi_p \right) \right.$$

$$\left. + i \left(\mathbf{e}_r \partial_r \psi_s^\dagger + \mathbf{e}_\theta \frac{1}{r} \partial_\theta \psi_s^\dagger + \mathbf{e}_\phi \frac{1}{r\sin\theta} \partial_\phi \psi_s^\dagger \right) \psi_p \right\} + (\text{c. c.}) . \qquad (58)$$

We can use $\partial_\phi \psi_s = \partial_\theta \psi_s = 0$ to drop two terms in the second line. Upon integrating-by-parts those terms with ∂_θ or ∂_ϕ, we find that such terms cancel with each other. We are then left with:

$$\langle \vec{a}_{\text{orb}} \rangle = i\frac{e\pi}{2m_e} \int r^4 dr d\Omega \; \mathbf{e}_r \left\{ \psi_s^\dagger (\partial_r \psi_p) - (\partial_r \psi_s^\dagger) \psi_p \right\} + (\text{c. c.}) . \qquad (59)$$

The r-integral is now easy:

$$\langle \vec{a}_{\text{orb}} \rangle = i\frac{e\pi}{2m_e} r_1(s,p) \int d\Omega \; \mathbf{e}_r \; (\psi_s^\dagger \psi_p)_{\text{angular}} + (\text{c. c.}) , \qquad (60)$$

where $r_1(s,p)$ is defined as

$$r_1(s,p) \equiv \int_0^\infty dr \; r^4 \left(R_s(r) \frac{dR_p(r)}{dr} - R_p(r) \frac{dR_s(r)}{dr} \right) . \qquad (61)$$

Before going further, it is convenient to calculate the inner products $\langle s_{1/2}, \mu = \pm 1/2 | \mathbf{e}_r | p_{1/2}, \mu' = \pm 1/2 \rangle$, and $\langle s_{1/2}, \mu = \pm 1/2 | (\mathbf{e}_\theta \sigma_\phi - \mathbf{e}_\phi \sigma_\theta) | p_{1/2}, \mu' = \pm 1/2 \rangle$, where the integral is to be performed only over the angular variables, for all the possible combinations of μ and μ'.

$\langle s_{1/2}, \mu = \pm 1/2 | \mathbf{e}_r | p_{1/2}, \mu' = \pm 1/2 \rangle$ are evaluated to be, by using the explicit solutions for the Dirac equation for a particle in the Coulomb potential,

$$\langle s_{1/2}, +1/2 | \mathbf{e}_r | p_{1/2}, +1/2 \rangle = -i \int d\Omega \frac{1}{4\pi} \begin{pmatrix} 1 & 0 \end{pmatrix} \mathbf{e}_r \begin{pmatrix} \cos\theta \\ \sin\theta e^{i\phi} \end{pmatrix}$$

$$= -i \int d\Omega \frac{1}{4\pi} \cos\theta (\sin\theta\cos\phi\, \mathbf{e}_x + \sin\theta\sin\phi\, \mathbf{e}_y + \cos\theta\, \mathbf{e}_z)$$

$$= -\frac{i}{3} \mathbf{e}_z . \qquad (62)$$

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Similarly,

$$\langle s_{1/2}, +1/2|\mathbf{e}_r|p_{1/2}, -1/2\rangle = \int d\Omega \frac{-i}{4\pi} \sin\theta e^{-i\phi}(\sin\theta\cos\phi\mathbf{e}_x + \sin\theta\sin\phi\mathbf{e}_y + \cos\theta\mathbf{e}_z) = -\frac{i}{3}(\mathbf{e}_x - i\mathbf{e}_y) \ , \tag{63}$$

$$\langle s_{1/2}, -1/2|\mathbf{e}_r|p_{1/2}, +1/2\rangle = \int d\Omega \frac{-i}{4\pi} \sin\theta e^{i\phi}(\sin\theta\cos\phi\mathbf{e}_x + \sin\theta\sin\phi\mathbf{e}_y + \cos\theta\mathbf{e}_z) = -\frac{i}{3}(\mathbf{e}_x + i\mathbf{e}_y) \ , \tag{64}$$

$$\langle s_{1/2}, -1/2|\mathbf{e}_r|p_{1/2}, -1/2\rangle = \int d\Omega \frac{i}{4\pi} \cos\theta(\sin\theta\cos\phi\mathbf{e}_x + \sin\theta\sin\phi\mathbf{e}_y + \cos\theta\mathbf{e}_z) = +\frac{i}{3}\mathbf{e}_z \ . \tag{65}$$

Similarly, the other elements $\langle s_{1/2}, \mu = \pm 1/2|(\mathbf{e}_\theta\sigma_\phi - \mathbf{e}_\phi\sigma_\theta)|p_{1/2}, \mu' = \pm 1/2\rangle$ can be computed to be:

$$\langle s_{1/2}, +1/2|(\mathbf{e}_\theta\sigma_\phi - \mathbf{e}_\phi\sigma_\theta)|p_{1/2}, +1/2\rangle = +\frac{2}{3}\mathbf{e}_z \ , \tag{66}$$

$$\langle s_{1/2}, +1/2|(\mathbf{e}_\theta\sigma_\phi - \mathbf{e}_\phi\sigma_\theta)|p_{1/2}, -1/2\rangle = +\frac{2}{3}(\mathbf{e}_x - i\mathbf{e}_y) \ , \tag{67}$$

$$\langle s_{1/2}, -1/2|(\mathbf{e}_\theta\sigma_\phi - \mathbf{e}_\phi\sigma_\theta)|p_{1/2}, +1/2\rangle = +\frac{2}{3}(\mathbf{e}_x + i\mathbf{e}_y) \ , \tag{68}$$

$$\langle s_{1/2}, -1/2|(\mathbf{e}_\theta\sigma_\phi - \mathbf{e}_\phi\sigma_\theta)|p_{1/2}, -1/2\rangle = -\frac{2}{3}\mathbf{e}_z \ . \tag{69}$$

From Eqs. (62–69), the sum of the two contributions $\langle\vec{a}_{\text{spin}}\rangle$ (Eq. (55)) and $\langle\vec{a}_{\text{orb}}\rangle$ (Eq. (60)) can be expressed in a compact form:

$$\langle\vec{a}\rangle = \langle\vec{a}_{\text{spin}}\rangle + \langle\vec{a}_{\text{orb}}\rangle$$

$$= i\frac{e\pi}{2m_e}\left(r_1(s,p) - 4r(s,p)\right)\int d\Omega \ \mathbf{e}_r \ (\psi_s^\dagger\psi_p)_{\text{angular}} + (\text{c. c.}) \ . \tag{70}$$

We now evaluate the matrix element. First, the contribution from $|s_{1/2}, 1/2\rangle$ and $|p_{1/2}, 1/2\rangle$

to $\langle\psi_{s+}|\vec{a}|\psi_{p+}\rangle + \text{(c. c.)}$ is,

$$\left\{ i \int d\Omega (\psi_{s+}^\dagger \psi_{p+})_{\text{angular}} \mathbf{e}_r + \text{(c. c.)} \right\}\bigg|_{|s,1/2\rangle, |p,1/2\rangle}$$

$$= i\frac{-i}{3}\mathbf{e}_z \left\{ \left(-\frac{2}{\sqrt{3}}\frac{\text{Ry}}{E_s}Z_1 C_1(r_1)\frac{i(n_{1x} - in_{1y})}{\sqrt{2}} \right) + \left((r_1, Z_1) \rightarrow (r_2, Z_2) \right) \right\}$$

$$\times \left\{ \left(\frac{2\sqrt{3}i}{5}\frac{\text{Ry}}{E_p}Z_1 C_2(r_1)n_{1z}\frac{-i(n_{1x} + in_{1y})}{\sqrt{2}} \right) + \left((r_1, Z_1) \rightarrow (r_2, Z_2) \right) \right\} + \text{(c. c.)}$$

$$= \mathbf{e}_z \frac{4}{15}\frac{(\text{Ry})^2}{E_s E_p}Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right] \left\{ C_1(r_1)C_2(r_2)n_{2z} - C_2(r_1)C_1(r_2)n_{1z} \right\}, \qquad (71)$$

where we have used $\vec{n}_3 = \mathbf{e}_z$. If we further use $\vec{J} \cdot \vec{n}_3 = 3/2$ which holds for the case $\mu = 3/2$, we get

$$\left\{ i \int d\Omega (\psi_{s+}^\dagger \psi_{p+})_{\text{angular}} \mathbf{e}_r + \text{(c. c.)} \right\}\bigg|_{|s,1/2\rangle, |p,1/2\rangle} = \mathbf{e}_z (\vec{J} \cdot \vec{n}_3)\frac{8}{45}\frac{(\text{Ry})^2}{E_s E_p}Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right]$$

$$\times \left\{ C_1(r_1)C_2(r_2)n_{2z} - C_2(r_1)C_1(r_2)n_{1z} \right\}.$$

$$(72)$$

The contribution from $|s_{1/2}, 1/2\rangle$ and $|p_{1/2}, -1/2\rangle$ to $\langle \psi_{s+}|\vec{a}|\psi_{p+}\rangle + (\text{c. c.})$ is,

$$
\left\{ i \int d\Omega (\psi_{s+}^{\dagger} \psi_{p+})_{\text{angular}} \mathbf{e}_r + (\text{c. c.}) \right\} \Bigg|_{|s,1/2\rangle, |p,-1/2\rangle}
$$

$$
= i \frac{-i}{3} (\mathbf{e}_x - i\mathbf{e}_y) \left\{ \left(-\frac{2}{\sqrt{3}} \frac{\text{Ry}}{E_s} Z_1 C_1(r_1) \frac{i(n_{1x} - i n_{1y})}{\sqrt{2}} \right) + \left((r_1, Z_1) \to (r_2, Z_2) \right) \right\}
$$

$$
\times \left\{ \left(\frac{2\sqrt{3}i}{5} \frac{\text{Ry}}{E_p} Z_1 C_2(r_1)(n_{1x} + i n_{1y}) \frac{-i(n_{1x} + i n_{1y})}{\sqrt{2}} \right) + \left((r_1, Z_1) \to (r_2, Z_2) \right) \right\} + (\text{c. c.})
$$

$$
= \frac{4(\text{Ry})^2}{15 E_s E_p} Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right] \left\{ C_1(r_1) C_2(r_2)(n_{2x}\mathbf{e}_x + n_{2y}\mathbf{e}_y) - C_2(r_1) C_1(r_2)(n_{1x}\mathbf{e}_x + n_{1y}\mathbf{e}_y) \right\}
$$

$$
+ \frac{4(\text{Ry})^2}{15 E_s E_p} \left[Z_1^2 C_1(r_1) C_2(r_1) (\vec{n}_1 \times \vec{n}_3) |\vec{n}_1 \times \vec{n}_3|^2 \right.
$$

$$
+ Z_1 Z_2 C_1(r_1) C_2(r_2) (\vec{n}_2 \times \vec{n}_3) \left((\vec{n}_1 \times \vec{n}_3) \cdot (\vec{n}_2 \times \vec{n}_3) \right)
$$

$$
+ Z_1 Z_2 C_1(r_2) C_2(r_1) (\vec{n}_1 \times \vec{n}_3) \left((\vec{n}_1 \times \vec{n}_3) \cdot (\vec{n}_2 \times \vec{n}_3) \right)
$$

$$
\left. + Z_2^2 C_1(r_2) C_2(r_2) (\vec{n}_2 \times \vec{n}_3) |\vec{n}_2 \times \vec{n}_3|^2 \right]. \tag{73}
$$

By substituting the sum of Eqs. (71) and (73) into Eq. (70), we obtain, for $\mu = 3/2$,

$$
\langle \vec{a} \rangle = \frac{e\pi}{m_e} \left(r_1(s,p) - 4r(s,p) \right) \frac{4(\text{Ry})^2}{45 E_s E_p} Z_1 Z_2 (\vec{J} \cdot \vec{n}_3) \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right] \left\{ C_1(r_1) C_2(r_2) \vec{n}_2 - C_2(r_1) C_1(r_2) \vec{n}_1 \right\}
$$

$$
+ \frac{e\pi}{m_e} \left(r_1(s,p) - 4r(s,p) \right) \frac{4(\text{Ry})^2}{45 E_s E_p} (\vec{J} \cdot \vec{n}_3) \left[Z_1^2 C_1(r_1) C_2(r_1) (\vec{n}_1 \times \vec{n}_3) |\vec{n}_1 \times \vec{n}_3|^2 \right.
$$

$$
+ Z_1 Z_2 C_1(r_1) C_2(r_2) (\vec{n}_2 \times \vec{n}_3) \left((\vec{n}_1 \times \vec{n}_3) \cdot (\vec{n}_2 \times \vec{n}_3) \right)
$$

$$
+ Z_1 Z_2 C_1(r_2) C_2(r_1) (\vec{n}_1 \times \vec{n}_3) \left((\vec{n}_1 \times \vec{n}_3) \cdot (\vec{n}_2 \times \vec{n}_3) \right)
$$

$$
\left. + Z_2^2 C_1(r_2) C_2(r_2) (\vec{n}_2 \times \vec{n}_3) |\vec{n}_2 \times \vec{n}_3|^2 \right], \tag{74}
$$

where we have used $\vec{J} \cdot \vec{n}_3 = 3/2$ which holds for the case $\mu = 3/2$. The terms in the second and the subsequent lines are all perpendicular to the axis of the diatomic molecule $A_3 A_4$ and vanish by averaging the orientation of the molecule with this axis fixed. As long as the rotational

symmetry around the z-axis is a good symmetry, this averaging is legitimate since there is a quantum-mechanical uncertainty relation between J_z and the azimuthal angle ϕ which describes the orientation of the molecule with the A_3A_4 axis fixed at the z-axis. Thus we obtain Eq. (2). The same conclusion can also be obtained for $\mu = -3/2$.

In the above discussion, we have neglected the possible contribution from the terms at first order of perturbation. Below we show that this can be justified. At first order of perturbation, the possible contribution to $\langle \vec{a} \rangle$ comes from

$$\langle \vec{a} \rangle = \langle \psi_{s\pm} | \vec{a} | p_{3/2}, \mu = \pm 3/2 \rangle + \text{(c. c.)} \tag{75}$$

(The matrix element of $\vec{a}$ between $|\psi_{p\pm}\rangle$ and $|p_{3/2}\rangle$ vanishes because of parity). To evaluate Eq. (75), we can use

$$\langle \vec{a} \rangle = \langle \vec{a}_{\text{spin}} \rangle + \langle \vec{a}_{\text{orb}} \rangle \tag{76}$$

$$\langle \vec{a}_{\text{spin}} \rangle = -\frac{e\pi}{m_e} r(s,p) \int d\Omega \left\{ \mathbf{e}_\theta (\psi_s^\dagger \sigma_\phi \psi_p)_{\text{angular}} - \mathbf{e}_\phi (\psi_s^\dagger \sigma_\theta \psi_p)_{\text{angular}} \right\} + \text{(c. c.)} , \tag{77}$$

$$\langle \vec{a}_{\text{orb}} \rangle = i \frac{e\pi}{2m_e} r_1(s,p) \int d\Omega \ \mathbf{e}_r \ (\psi_s^\dagger \psi_p)_{\text{angular}} + \text{(c. c.)} , \tag{78}$$

where ψ_p should be understood as $|p_{3/2}, \mu = \pm 3/2\rangle$. The integrals which can appear in Eqs. (77) and (78) are:

$$\langle s_{1/2}, +1/2 | \mathbf{e}_r | p_{3/2}, +3/2 \rangle = \frac{-i}{\sqrt{6}} (\mathbf{e}_x + i\mathbf{e}_y) , \tag{79}$$

$$\langle s_{1/2}, -1/2 | \mathbf{e}_r | p_{3/2}, -3/2 \rangle = \frac{i}{\sqrt{6}} (\mathbf{e}_x - i\mathbf{e}_y) , \tag{80}$$

$$\langle s_{1/2}, +1/2 | \mathbf{e}_r | p_{3/2}, -3/2 \rangle = \langle s_{1/2}, -1/2 | \mathbf{e}_r | p_{3/2}, +3/2 \rangle = 0 , \tag{81}$$

and

$$\langle s_{1/2}, +1/2 | (\mathbf{e}_\theta \sigma_\phi - \mathbf{e}_\phi \sigma_\theta) | p_{3/2}, +3/2 \rangle = \frac{-1}{\sqrt{6}} (\mathbf{e}_x + i\mathbf{e}_y) , \tag{82}$$

$$\langle s_{1/2}, -1/2 | (\mathbf{e}_\theta \sigma_\phi - \mathbf{e}_\phi \sigma_\theta) | p_{3/2}, -3/2 \rangle = \frac{1}{\sqrt{6}} (\mathbf{e}_x - i\mathbf{e}_y) , \tag{83}$$

$$\langle s_{1/2}, +1/2 | (\mathbf{e}_\theta \sigma_\phi - \mathbf{e}_\phi \sigma_\theta) | p_{3/2}, -3/2 \rangle = \langle s_{1/2}, -1/2 | (\mathbf{e}_\theta \sigma_\phi - \mathbf{e}_\phi \sigma_\theta) | p_{3/2}, +3/2 \rangle = 0 . \tag{84}$$

From Eqs. (79)–(84), we find that the vector $\langle \psi_{s\pm} | \vec{a} | p_{3/2}, \mu = \pm 3/2 \rangle + \text{(c. c.)}$ is zero or perpendicular to $\vec{n}_3$, namely, the axis of the diatomic molecule A_3A_4. In this case, this vector vanishes when averaged over the orientation of the molecule with $\vec{n}_3$ being fixed. Therefore, to first order of perturbation, there is no contribution to the anapole. The same comment also applies to the contribution which comes from second order of perturbation like the term

$$\langle \vec{a} \rangle = \langle \psi'_{s\pm} | \vec{a} | p_{3/2}, \mu = \pm 3/2 \rangle + \text{(c. c.)} , \tag{85}$$

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where $|\psi'_s\rangle$ is the s-wave state which appears as a second-order correction to the initial wave function $|p_{3/2}\rangle$. (Another second-order contribution $\langle\psi'_p|\vec{a}|p_{3/2},\mu=\pm 3/2\rangle + $ (c. c.), where ψ'_p is the p-wave state which appears as a second-order correction to the initial wave function $|p_{3/2}\rangle$, vanishes from parity conservation.) In this case, the angular integrals involved are Eqs. (79), (80), (81), (82), (83), and (84), which all vanish when averaged over the orientation of the molecule with $\vec{n}_3$ being fixed. Therefore there is no other second-order contribution to Eq. (2) which does not vanish after the average over the orientations of the molecule with fixed $\vec{n}_3$ as mentioned above.

5 Discussion

We have analytically derived the direct relation between the anapole moment and the geometrical structure of chiral molecules. A four-atom molecule has been studied as an example since it is the simplest molecule having chirality. We have focused on a valence electron which is captured by the diatomic molecule $A_3 A_4$, and treated effects from the other atoms A_1 and A_2 on the electron as perturbation. We have computed the corrections to the wave function of the electron in the $|p_{3/2},\mu=\pm 3/2\rangle$ state by the Coulomb interactions from the atoms A_1 and A_2, and calculated the anapole moment. Though this method was first developed in Ref. [1], this method has been discussed in much more detail in this paper to be accessible to many scientists over wider regions and their final result has been corrected. The electron terms for n-atom molecules ($n \le 3$) reserve the symmetry of molecules. This is not the case for $n \ge 4$ and needs complicated processes [4, 5]. On the other hand, the procedures developed in this paper have given the direct relation between the PV interactions and the geometrical structure without wandering into complicated *ab-initio* MO calculations. Of course, these two approaches are complementary and we need some bridge between the two approaches. One point which may need improvement in our approach is that our approach might seem to depend on the peculiar initial state $|p_{3/2}\rangle$. We may generalize it to the cases where the initial state is $|p_{1/2}\rangle$ or $|s_{1/2}\rangle$ state. Starting from $|s_{1/2}\rangle$ state in place of $|p_{3/2}\rangle$, we obtain

$$\langle\vec{a}\rangle = \frac{2e\pi}{15m_e}\left(r_1(s,p)-4r(s,p)\right)\left(\frac{1}{E(s_{1/2})-E(p_{3/2},3/2)}-\frac{1}{E(s_{1/2})-E(p_{3/2},-1/2)}\right)\frac{(\mathrm{Ry})^2}{E(s_{1/2})-E(p_{1/2})}$$

$$\times Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2\right)\right]\left\{C_1(r_1)C_2(r_2)\vec{n}_2 - C_2(r_1)C_1(r_2)\vec{n}_1\right\}$$

$$-\frac{4e\pi}{15m_e}\left(\tilde{r}_1(s,p)+2\tilde{r}(s,p)\right)\frac{1}{E(s_{1/2},1/2)-E(p_{1/2},-1/2)}\frac{(\mathrm{Ry})^2}{E(s_{1/2},1/2)-E(p_{3/2},1/2)}$$

$$\times Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2\right)\right]\left\{\tilde{C}_1(r_1)C_2(r_2)\vec{n}_2 - C_2(r_1)\tilde{C}_1(r_2)\vec{n}_1\right\}, \tag{86}$$

where $\tilde{C}_1(r_i) \equiv a_0 \int_0^\infty dr \; r^2 R_{s_{1/2}}(r)R_{p_{1/2}}(r)[(r_i/r^2)\theta(r-r_i)+(r/r_i^2)\theta(r_i-r)]$, where $R_{s_{1/2}}(r)$ and $R_{p_{1/2}}(r)$ are the radial wave functions of the initial $s_{1/2}$ state and the intermediate $p_{1/2}$ state, respectively. $\tilde{r}(s,p)$ and $\tilde{r}_1(s,p)$ are defined as $\tilde{r}(s,p) \equiv \int_0^\infty dr r^3 R_{s_{1/2}}(r)R_{p_{3/2}}(r)$ and $\tilde{r}_1(s,p) \equiv$

$\int_0^\infty dr r^4 (R_{s_{1/2}}(r) R'_{p_{3/2}}(r) - R'_{s_{1/2}}(r) R_{p_{3/2}}(r))$, where $R_{p_{3/2}}(r)$ is the radial wave function of the $p_{3/2}$ state. Instead, if we start from $|p_{1/2}\rangle$ state, we obtain

$$
\begin{aligned}
\langle \vec{a} \rangle = {} & +\frac{2e\pi}{15m_e} \left(r_1(s,p) - 4r(s,p) \right) \left(\frac{1}{E(p_{1/2}) - E(p_{3/2}, 3/2)} - \frac{1}{E(p_{1/2}) - E(p_{3/2}, -1/2)} \right) \frac{(\mathrm{Ry})^2}{E(p_{1/2}) - E(s_{1/2})} \\
& \times Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right] \left\{ C_1(r_1) C_2(r_2) \vec{n}_2 - C_2(r_1) C_1(r_2) \vec{n}_1 \right\} \\
& + \frac{4e\pi}{15m_e} \left(\tilde{r}_1(s,p) + 2\tilde{r}(s,p) \right) \frac{1}{E(p_{1/2}, 1/2) - E(s_{1/2}, -1/2)} \frac{(\mathrm{Ry})^2}{E(p_{1/2}, 1/2) - E(p_{3/2}, -1/2)} \\
& \times Z_1 Z_2 \left[\vec{n}_3 \cdot \left(\vec{n}_1 \times \vec{n}_2 \right) \right] \left\{ \tilde{C}_1(r_1) C_2(r_2) \vec{n}_2 - C_2(r_1) \tilde{C}_1(r_2) \vec{n}_1 \right\} .
\end{aligned}
\tag{87}
$$

This is of a similar form to Eq. (86).

The second point which needs discussions is to apply this approach to realistic molecules. This is discussed in Appendix.

This approach has many applications. One of them is the evaluation of the energy differences between optical isomers. The PV potential due to the weak neutral boson exchange is given by [10, 11, 12]

$$
V^{PV} = \frac{G_F}{4\sqrt{2} m_e} \sum_{\alpha,i} Q_W^\alpha \{ \boldsymbol{\sigma}_i \cdot \mathbf{p}_i, \delta^{(3)}(\mathbf{r}_{i\alpha}) \}_+ ,
\tag{88}
$$

where Q_W^α is the weak charge of the α-th atom in a molecule:

$$
Q_W^\alpha = (1 - 4\sin^2\theta_W) Z^\alpha - N^\alpha ,
\tag{89}
$$

with the atomic number Z^α and the neutron number N^α of the α-th atom, where α runs over the atoms composing of the molecule and i labels the electrons. The precedent analytical methods have not discussed the direct relation between the energy differences and geometrical structures. The model set-up is the same as in the present paper and we may replace the anapole moment by Eq. (88). The detail will be discussed in a separate form [13].

Acknowledgements

A   Candidate molecules

The present paper discusses that chiral molecules having an unpaired electron would be good systems for the measurement of the anapole moment, and the analytical derivation of the expectation value of the anapole moment Hamiltonian (Eqs. (47) and (57)) for four-atom molecules, which are the smallest molecules that have chirality, is given. In order to further simplify the analytical derivation, we assumed that the nature of the unpaired electron is mainly described by atomic orbitals attached to A_4 (Fig.1), and the projection of the angular momentum along the $A_4 - A_3$ axis is a good quantum number. Molecules that satisfy these conditions may be those whose A_4 is a heavy atom, in which most of the unpaired electron distributes on A_4, and whose A_1 and A_2 are lighter atoms than A_3 and A_4.

An example of a four-atom molecule with an unpaired electron is the HNOH radical, in which one hydrogen of an amine group is removed from hydroxylamine (NH_2OH). However, it is not a chiral molecule because this radical has a planer equilibrium structure [14]. We have searched for various four-atom molecules similar to the HNOH radical by the use of *ab-initio* molecular orbital calculations, and found several molecules that have a chiral structure. They include the FAsSH radical, whose dihedral angle, χ, at the equilibrium structure is 61.3 degrees. The potential surface of this molecule along the dihedral angle, χ, based on MP2/6-31G(d) [15] is shown in Fig.2. The potential barrier along χ is 354.6 cm^{-1}, while the vibrational frequency along χ under the harmonic approximation is 136.4 cm^{-1}. The gross orbital population analysis of a simple ROHF molecular orbital calculation indicates that about 82 % of the electron spin locates on the $4p$ orbital of the As atom. Since the ground state of AsS is $^2\Pi_{1/2}$, the anapole moment of this radical may be roughly approximated by Eq. (87).

Another example is the FPOH radical, which has the dihedral angle, χ, of 53.0 degrees. The electron spin of this molecule, however, distributes widely over the radical, and therefore it will be necessary to include higher order terms that we ignored in this paper to estimate the anapole moment of this radical.

So far a spectroscopic study of the HNOH radical has been reported by matrix isolation spectroscopy in solid hydrogen [14]. No spectroscopic information were reported for other molecules.

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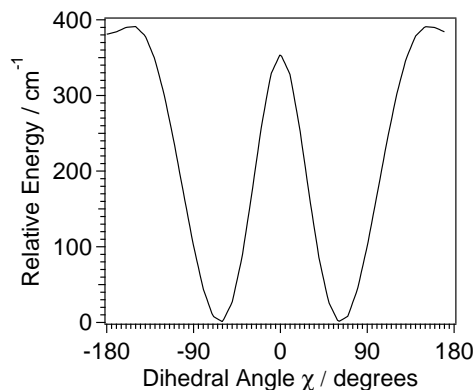[5] C. Thierfelder, G. Rauhut, P. Schwerdtfeger, Phys. Rev. **A 81**, 032513-1-5 (2010)

Figure 2: *The potential curve of FAsSH along the F-As-S-H dihedral angle obtained by an MP2/6-31G(d) ab-initio molecular orbital calculation.*

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