Calculations of $\mathcal{P}$ and $\mathcal{T}$-odd interaction constants of alkaline-earth monofluorides using KRCI method

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Abstract

We have reported the results of ab initio calculations of parity- and time-reversal-odd interaction constants for the ground state of alkaline-earth monofluorides. The Kramers-restricted configuration interaction method limited to single and double excitations in conjunction with the quadruple zeta quality basis sets have been employed to perform these four-component relativistic calculations. The results are compared with the existing semi-empirical and other theoretical results, wherever available.

Keywords: parity and time-reversal-odd interaction constants, AEMFs, eEDM

1. Introduction

The parity- and time-reversal ($\mathcal{P}$ and $\mathcal{T}$) symmetry violating effects such as the electric dipole moment of an electron (eEDM) and the scalar-pseudoscalar (S–PS) interactions between nucleons and electrons manifest in giving rise to the intrinsic electric dipole moment (EDM) of atoms and molecules. The effects will be more pronounced in heavier atomic/molecular systems. Numerous atoms and molecules have thoroughly been scrutinized for the observation of such effects [1–11] as they hold answers to some of the fundamental mysteries of our Universe [3, 12–14].

In spite of more than seven decades of laborious efforts by several experimental groups, the conclusive evidence of a non-zero eEDM has mostly been elusive. In this context, the heavy open-shell polar molecules would be considered more suitable than atoms because of the large values of effective intrinsic electric fields ($\varepsilon_{\text{eff}}$) [15] in the former. The high precision measurements carried out using diatomic molecules such as ThO, HFF$^+$ and YbF molecules [4, 6, 7] have yielded best limits on eEDM so far. An accurate knowledge of $\mathcal{P}$ and $\mathcal{T}$-odd interaction constants such as: $W_d$ that characterizes $\varepsilon_{\text{eff}}$ and $W_s$ that characterizes the S–PS interaction between the nucleons and electrons, is required to interpret the results of the experiments. Invocation of accurate quantum chemical methods will be necessary for the calculation of such interaction constants.

Among several diatomic molecules that have been considered, the alkaline-earth monofluorides (AEMFs) have a special place since laser cooling and trapping experiments have been or being performed for MgF [16], CaF [17, 18], SrF [19–22], BaF [23–25] molecules. Heavier members of this series, particularly BaF and RaF, have been studied for the nuclear anapole moment [26–29], another parity-violating effect. The $\mathcal{P}$ and $\mathcal{T}$ odd effects induced by nuclear magnetic quadrupole moments in BaF have also been studied in reference [30]. The theoretical as well as experimental results of spectroscopic constants, valence properties and vibrational parameters for the ground and excited states of AEMFs have also been reported by several research groups [28, 31–48]. Nevertheless, there is a scope to carry out the calculations of $\mathcal{P}$ and $\mathcal{T}$-odd interaction constants of these molecules consistently employing accurate many-body methods as there are only a very few calculations available in the literature. Nayak and Chaudhuri have reported the values of $W_d$ constant for the ground state of BaF system using the Dirac–Fock (DF) and the restricted active space configuration interaction (RASCI) methods [26],...
Kudashov et al have reported the ab initio calculations of $W_d$ and $W_s$ constants for RaF molecule using coupled cluster (CC) method [27]. Kozlov et al have done semi-empirical, and ab initio calculations at self-consistent field (SCF) and restricted active space SCF (RASSCF) levels to report the $P$ and $T$-odd interaction constants of BaF system [49, 50]. Isaev and Berger have computed the $W_d$ and $W_s$ results for BaF and RaF molecules using two-component zeroth order regular approximation (ZORA) together with generalized Hartree–Fock (HF) method [51]. Further, the CC calculations in Z-vector and expectation value approach have been performed by Sasmal et al to report the $\varepsilon_{\text{eff}}$ and $W_s$ constant for the RaF system [52]. Recently, Abe et al have performed the calculations of $\varepsilon_{\text{eff}}$ for AEMF (AE = Be, Mg, Ca, Sr, Ba) molecules using linearized expectation value approach in CC approximation (LECC) and finite-field CC (FFCC) method [53]. The calculations of $W_d$ and $W_s$ constants for AEMFs using two-component ZORA at the generalized HF and generalized Kohn–Sham (KS) level of theories have been reported in references [54, 55].

In the present work, we have performed the calculations of $P$ and $T$-odd interaction constants in AEMFs using Kramers-restricted configuration interaction method limited to single and double excitations (KRCISD) together with the quadruple zeta (QZ) quality basis sets. In reference [35], we have applied this method to compute the valence properties: permanent dipole moments (PDMs) and dipole polarizabilities of AEMFs, and the atomic polarizabilities of AE and fluorine atoms.

This paper is organized in three other sections: the following section 2 discusses theory and method used for the calculations of symmetry violating constants, followed by the detailed discussion on the computed results in section 3 and the summary of the present work in the last section.

2. Theory and method of calculations

2.1. $P$ and $T$-odd interaction constant relevant to eEDM

The $\varepsilon_{\text{eff}}$ arises from the relativistic interactions of the eEDM with the electric fields created due to all other charged particles in a molecular system. The expectation value of the operator describing the interaction of eEDM in a molecular system is given by [56–60],

$$
\Delta U = \left\langle \sum_{j=1}^{n} H_{\text{EDM}}(j) \right\rangle_\Psi \approx -d_e \left\langle \sum_{j=1}^{n} \gamma^0 \gamma_j \hat{S}^j \varepsilon_j \right\rangle_\Psi \approx \frac{2ie\gamma_5}{\hbar} \left\langle \sum_{j=1}^{n} \gamma^0 \gamma_j \hat{S}^j \hat{p}_j \right\rangle_\Psi
$$

where $d_e$ is the electric dipole moment of an electron; $\gamma^0$ and $\gamma^5$ are the four-component Dirac matrices; $\varepsilon_j$ is the electric field at the position of $j$th electron; $p_j$ is the momentum operator; and $\Psi$ is the wavefunction determined from the many-body theory. Finally, the $\varepsilon_{\text{eff}}$ experienced by the unpaired electron in the molecular system is defined as,

$$
\varepsilon_{\text{eff}} = W_d \Omega
$$

Table 1. Details of the basis sets, in uncontracted form, used in this work.

| Atom  | Basis            |
|-------|------------------|
| Be    | cc-pVQZ: 12s, 6p, 3d, 2f, 1g |
| Mg    | cc-pVQZ: 16s, 12p, 3d, 2f, 1g |
| Ca    | dyyall.v4z: 30s, 20p, 6d, 5f, 3g |
| Sr    | dyyall.v4z: 35s, 25p,15d,4f,3g |
| Ba    | dyyall.v4z: 35s, 30p, 19d, 4f, 4g |
| Ra    | dyyall.v4z: 37s, 34p, 23d, 15f, 3g |
| F     | cc-pVQZ: 12s, 6p, 3d, 2f, 1g |

and $\Psi$ is the wavefunction determined from the many-body theory. Finally, the $\varepsilon_{\text{eff}}$ experienced by the unpaired electron in the molecular system is defined as,

$$
\varepsilon_{\text{eff}} = W_d \Omega
$$

where $W_d = (2ie/\hbar)\varepsilon^0(\gamma^0 \gamma^5 \gamma^j \hat{p}_j)$ is the $P$ and $T$-odd interaction constant and $\Omega = \left\langle \gamma^5 \right\rangle_\Psi$ is the $z$-component of the total angular momentum for the ground states of AEMFs. The intrinsic value of eEDM is calculated from the theoretically determined $\varepsilon_{\text{eff}}$ together with the experimentally measured energy shift ($\Delta U$) via equation $\Delta U \propto -d_e \varepsilon_{\text{eff}}$.

2.2. Scalar–pseudoscalar interaction constant

The nucleon–electron interaction that arises due to the coupling between scalar-hadronic current and the pseudoscalar electronic current is known as scalar–pseudoscalar (S–PS) interaction. The S–PS interaction Hamiltonian for any system is given by [27, 59],

$$
H_{S-PS} = \frac{i}{\sqrt{2}} \sum_{j=1}^{n} \sum_{A=1}^{N} k_{A} Z_{A} \gamma^0 \gamma^5 \rho_{A}(r_{A})
$$

where $G_F (= 2.22249 \times 10^{-14} E_{\text{h}} a_0^3)$ is the Fermi coupling constant [27, 61]; $\rho_{A}$ is the nuclear charge density normalized to unity; the summation indices $j$ and $A$ run over the number of electrons and nuclei, respectively. The $k_{A}$ is a dimensionless electron–nucleus S–PS coupling constant of an atom and it is defined as [61],

$$
k_{A} = Z_{A} \frac{N_{A}}{k_{s,p}} \frac{N_{A}}{k_{s,n}}
$$

where $Z_{A}$ and $N_{A}$ represent the number of protons and neutrons, respectively, $k_{s,p}$ and $k_{s,n}$ represent the S–PS coupling constant of an electron and a proton (neutron). Further, the $P$ and $T$-odd interaction constant ($W_s$) arising from the electron–nucleon S–PS interaction can be evaluated as,

$$
W_s = \frac{1}{k_{s,p} \Omega} \left\langle H_{S-PS} \right\rangle_\Psi
$$

In order to compute the $P$ and $T$-odd interaction constants, we have utilized CI method available in the KRCI module.

4 Here, $E_h$ (Hartree) is the atomic unit of energy and $a_0$ (Bohr radius) is the atomic unit of distance.
of DIRAC17 software suite [62]. After generating the reference state using DF Hamiltonian, the generalized active space (GAS) technique is employed to perform KRCISD calculations. The finite nuclear model described by the Gaussian charge distribution is used in these calculations, which is of the form [63],

$$\rho(r) = eZ\left(\frac{\zeta}{\pi}\right)^{3/2}e^{-\zeta r^2}$$  \hspace{1cm} (6)

where \(\zeta = \frac{3}{2r_{\text{rms}}}\); \(r_{\text{rms}}\) is the root mean square value of the Gaussian radial distribution and \(Z\) is the nuclear charge. Further, we have used the uncontracted correlation-consistent polarized valence quadruple zeta (cc-pVQZ) [64] basis sets for low \(Z\) elements: Be, F and Mg, and Dyall basis sets of similar quality (dyall.v4z) [65] for high \(Z\) elements: Ca, Sr, Ba and Ra. These basis sets are significantly large, particularly when used in uncontracted form, as it can be seen from the explicit number of functions shown in table 1.

The DF orbitals having energy less than \(-2E_h\) are considered as frozen core. The alkaline-earth atom is chosen as the coordinate origin of the corresponding diatomic molecule. In the GAS technique, active DF orbitals are divided into three subspaces: paired (GAS1), unpaired (GAS2), and virtual orbitals (GAS3). Further, cutoff energy of \(10E_h\) is set uniformly for all molecules in order to truncate the higher virtual orbitals so as to make the computations manageable. The number of Slater determinants along with the number of active orbitals in different subspaces for all molecules are given in table 2.

The values of equilibrium bond lengths used in the present work are: 1.359 Å for BeF [33], 1.778 Å for MgF [33], 2.015 Å for CaF [33], 2.124 Å for SrF [32], 2.162 Å for BaF [31], and 2.244 Å for RaF [28].

### Results and discussion

#### 3.1 \(P\) and \(T\)-odd interaction constant relevant to \(e\text{EDM}\)

The computed values of \(P\) and \(T\)-odd interaction constants, \(W_d\), calculated at the KRCISD level of theory together with the available results in the literature are tabulated in table 3. The value of \(W_d\) increases as we move from lighter to the heavier system due to increase in the difference between the \(Z\) values of two atoms forming a diatomic molecule. Our results calculated at the KRCISD/QZ level compare well with the existing semi-empirical and \(ab\) initio results reported in references [26, 27, 49–55].

We have also examined the effect of basis set augmentation and core-valence functions on \(W_d\) by performing additional calculations using augmented-pCVQZ basis sets for lighter atoms and augmented-dyall.cv4z basis sets for heavy atoms. We referred these basis sets further as `aug-CV-QZ’. It can be seen from the last column of table 2 that the number of Slater determinants increases significantly with the aug-CV-QZ basis sets. We have observed that the effect of adding extra functions to the QZ basis sets on the values of \(W_d\) are about 1% to all AEMFs, except BeF. The computational cost, on the other hand, increases considerably for the aug-CV-QZ calculations. To quote in this context, the amount of RAM required for the calculation of \(W_d\) for RaF, at KRCISD/aug-CV-QZ level is about 500% times larger than that required for the KRCISD/QZ level calculation, even when the number of filled active orbitals and the virtual energy cutoff are kept intact.

Kozlov and Labzowsky [49] have reported the semi-empirical values of \(W_d\) constant for BaF molecule based on two different experimental values of hyperfine structure constants [66, 67] to be 0.35 \((\times10^{-25} \text{ Hz/e cm})\) and 0.41 \((\times10^{-25} \text{ Hz/e cm})\). Our \(ab\) initio result of \(W_d = 0.27426 \times10^{-25} \text{ Hz/e cm}\) differs from those reported in their work by 0.07574 \((\times10^{-25} \text{ Hz/e cm})\) and 0.13574 \((\times10^{-25} \text{ Hz/e cm})\). Later, in reference [50], Kozlov et al have performed RASSCF calculations by considering 11 electrons in three RASs: RAS1 (2,0,0,0), RAS2 (2,1,1,0) and RAS3 (6,4,4,2). Further, they have used effective operators (EOs) to include the core-polarization effects. Their final value of \(W_d = 0.364 \times10^{-25} \text{ Hz/e cm}\) at RASSCF-EO level, which is larger from that computed in our work at KRCISD/QZ level by 0.08974 \((\times10^{-25} \text{ Hz/e cm})\).

Nayak and Chaudhuri [26] have utilized the RASCI method together with the uncontracted Gaussian basis sets (27s 27p 12d 8f) for Ba and (15s 10p) for F to compute the \(W_d\) constant of BaF. Further, they have considered 17 electrons in 76 active orbitals. We have, on the other hand, considered the same number of electrons in 143 active orbitals, which is very large in comparison to that included in reference [26]. Our computed result using QZ basis sets differs from their result by 0.07774 \((\times10^{-25} \text{ Hz/e cm})\) at the similar level of correlation.

### Table 2. Generalized active space model for the CI wavefunctions of AEMFs with \(10E_h\) virtual cutoff energy.

| Molecule | Frozen core | GAS1 | GAS2 | GAS3 | Number of determinants | Number of determinants |
|----------|-------------|------|------|------|------------------------|------------------------|
| BeF      | 2           | 4    | 1    | 80   | 132                    | 410645                 |
| MgF      | 6           | 4    | 1    | 84   | 146                    | 452681                 |
| CaF      | 7           | 7    | 1    | 139  | 189                    | 3789982                |
| SrF      | 15          | 8    | 1    | 132  | 182                    | 4463853                |
| BaF      | 24          | 8    | 1    | 134  | 212                    | 4600095                |
| RaF      | 40          | 8    | 1    | 133  | 203                    | 4531718                |

*For the case of aug-CV-QZ basis sets.


| Molecule | $\mathcal{W}_d$ ($\times 10^{-25}$) | Ref. |
|----------|----------------------------------|------|
| BeF      | 0.00021\textsuperscript{a}       | This work |
|          | 0.00027\textsuperscript{b}       | This work |
|          | 0.00024\textsuperscript{w}       | [53] |
| MgF      | 0.00269\textsuperscript{a}       | This work |
|          | 0.00272\textsuperscript{b}       | This work |
|          | 0.00339\textsuperscript{w}       | [53] |
|          | 0.00466\textsuperscript{d}       | [55] |
|          | 0.00522\textsuperscript{e}       | [55] |
| CaF      | 0.01161\textsuperscript{a}       | This work |
|          | 0.01165\textsuperscript{b}       | This work |
|          | 0.01354\textsuperscript{w}       | [53] |
|          | 0.0147\textsuperscript{d}        | [55] |
|          | 0.0140\textsuperscript{c}        | [55] |
| SrF      | 0.08979\textsuperscript{a}       | This work |
|          | 0.08964\textsuperscript{b}       | This work |
|          | 0.10446\textsuperscript{w}       | [53] |
|          | 0.105\textsuperscript{f}         | [55] |
|          | 0.101\textsuperscript{e}         | [55] |
| BaF      | 0.27425\textsuperscript{c}       | This work |
|          | 0.27321\textsuperscript{b}       | This work |
|          | 0.293\textsuperscript{f}, 0.352\textsuperscript{f} | [26] |
|          | 0.31240\textsuperscript{w}       | [53] |
|          | 0.26\textsuperscript{w}          | [51] |
|          | 0.230\textsuperscript{e}, 0.224\textsuperscript{e}, 0.375\textsuperscript{e}, 0.364\textsuperscript{e} | [50] |
|          | 0.35\textsuperscript{w}, 0.41\textsuperscript{w} | [49] |
|          | 0.33\textsuperscript{d}          | [54] |
|          | 0.29\textsuperscript{d}          | [54] |
|          | 0.332\textsuperscript{d}         | [55] |
|          | 0.290\textsuperscript{d}         | [55] |
| RaF      | 2.34303\textsuperscript{a}       | This work |
|          | 2.33571\textsuperscript{b}       | This work |
|          | 2.40\textsuperscript{w}, 2.25\textsuperscript{w}, 2.65\textsuperscript{w}, 2.36\textsuperscript{w}, 2.33\textsuperscript{w}, 2.30\textsuperscript{w}, 2.56\textsuperscript{w} | [27] |
|          | 2.20\textsuperscript{w}          | [51] |
|          | 2.54\textsuperscript{w}, 2.55\textsuperscript{w} | [52] |
|          | 2.73\textsuperscript{d}          | [54] |
|          | 2.44\textsuperscript{d}          | [54] |
|          | 2.80\textsuperscript{d}          | [55] |
|          | 2.51\textsuperscript{d}          | [55] |

\textsuperscript{a}These results are calculated using QZ quality basis sets.
\textsuperscript{b}These results are calculated using aug-cc-pVQZ quality basis sets.
\textsuperscript{c}FFCCSD.
\textsuperscript{d}Generalized HF.
\textsuperscript{e}Generalized KS.
\textsuperscript{f}DF.
\textsuperscript{g}Using two-component GHF-ZORA value of $W_s$.
\textsuperscript{h}SCF.
\textsuperscript{i}RASSCF.
\textsuperscript{j}SCF-EO.
\textsuperscript{k}RASSCF-EO.
\textsuperscript{l}Semi-empirical calculations.
\textsuperscript{m}SODCI.
\textsuperscript{n}RASSCF.
\textsuperscript{o}FS-RCCSD.
\textsuperscript{p}CCSD.
\textsuperscript{q}CCSD(T).
\textsuperscript{r}CCSD(T) enlarged.
\textsuperscript{s}CASSCF.
\textsuperscript{t}Z-vector method in CC approach.
\textsuperscript{u}Expectation value in CC approach.
\textsuperscript{v}These results are computed using equation (2) with the values of $\varepsilon_{\text{eff}}$ taken from the corresponding references.
Table 4. $S-PS$ constant, $W_s$ (in kHz) for alkaline-earth atoms in alkaline-earth monofluorides calculated at KRCISD level of theory, compared with the available results in the literature.

| Molecule | Atom | $W_s$ | Ref. |
|----------|------|-------|------|
| BeF      | Be   | 0.00132$^a$ | This work |
|          |      | 0.00142$^b$ | This work |
| F        |      | 0.00301$^a$ | This work |
|          |      | 0.00317$^b$ | This work |
| MgF      | Mg   | 0.04138$^a$ | This work |
|          |      | 0.04116$^b$ | This work |
|          |      | 0.0593$^c$  | [55] |
|          |      | 0.0648$^d$  | [55] |
| F        |      | 0.00408$^a$ | This work |
|          |      | 0.00428$^b$ | This work |
| CaF      | Ca   | 0.17751$^a$ | This work |
|          |      | 0.17699$^b$ | This work |
|          |      | 0.219$^c$   | [55] |
|          |      | 0.209$^d$   | [55] |
| F        |      | 0.00131$^a$ | This work |
|          |      | 0.00137$^b$ | This work |
| SrF      | Sr   | 1.70329$^a$ | This work |
|          |      | 1.70028$^b$ | This work |
|          |      | 2.010$^c$   | [55] |
|          |      | 1.940$^d$   | [55] |
| F        |      | 0.00098$^a$ | This work |
|          |      | 0.00102$^b$ | This work |
| BaF      | Ba   | 7.28604$^a$ | This work |
|          |      | 7.25918$^b$ | This work |
|          |      | 11$^e$, 13$^f$ | [49] |
|          |      | 6.1$^g$, 5.9$^h$ | [50] |
|          |      | 8.670$^i$   | [55] |
|          |      | 7.580$^j$   | [55] |
|          |      | 8.5$^k$     | [51] |
| F        |      | 0.00025$^a$ | This work |
|          |      | 0.00025$^b$ | This work |
| RaF      | Ra   | 130.52357$^a$ | This work |
|          |      | 130.12190$^b$ | This work |
|          |      | 131$^e$, 122$^f$, 144$^g$, 128$^h$, 127$m$, 125$n$, 139$p$ | [27] |
|          |      | 150$p$      | [51] |
|          |      | 141.2$p$, 142$q$ | [52] |
|          |      | 152$q$      | [55] |
|          |      | 136$r$      | [55] |
| F        |      | 0.00066$^a$ | This work |
|          |      | 0.00069$^b$ | This work |

$^a$These results are calculated using QZ quality basis sets.
$^b$These results are calculated using aug-CV-QZ quality basis sets.
$^c$Generalized HF.
$^d$Generalized KS.
$^e$Semi-empirical calculations.
$^f$SCF.
$^g$RASSCF.
$^h$Two-component ZORA generalized Hartree–Fock (GHF).
$^i$SODCI.
$^j$FS-RCCS.
$^k$FS-RCCSD.
$^l$CCSD.
$^m$CCSD(T).
$^n$CCSD enlarged.
$^o$CCfinal.
$^p$Z-vector method in CC approach.
$^q$Expectation value in CC approach.
Isaev and Berger [51] have obtained the $\varepsilon_{\text{eff}}$ for BaF and RaF numerically by using relationship between matrix elements of $P$ and $T$-odd and $P$-odd operators. Our value of $W_d$ parameter is larger by 5.5% (6.5%) for BaF (RaF) from that computed using the results of $\varepsilon_{\text{eff}}$ reported in their work via equation (2).

Kudashov et al [27] have performed spin-orbit direct CI (SODCI) calculations by considering 19 electrons explicitly to report the $W_d$ constant for RaF and our result varies by 2.4% from that estimated in their work. In the same work, those authors have also reported the $W_d$ constant using relativistic two-component Fock-Space CC method by considering single and double excitations (FS-CCSD). Our value of $W_d$ at KRCISD/QZ level differs by 11.9% from that reported at FS-CCSD level in reference [27]. Further, they have corrected FS-CCSD result by including the contributions due to triple excitations as well as basis set enlargement. Their final value $\approx 2.56 \times 10^{-25}$ Hz/e cm of $W_d$ including these corrections is larger by 8.5% from our result $\approx 2.34303 \times 10^{-25}$ Hz/e cm using the relativistic Hamiltonian at the KRCISD/QZ level.

Sasimal et al [52] have applied the expectation value and Z-vector approach in CC framework to compute the $\varepsilon_{\text{eff}}$ of RaF molecule. Further, they have considered single and double excitations together with the dyall.cv3z and dyall.cv4z basis sets for Ra and cc-pCVTZ and cc-pCVQZ basis sets for F atom. Our value of $W_d$ at KRCISD/QZ is smaller by 7.8% and 8.1% than their results using Z-vector method and expectation value approach, respectively, at the similar level of basis sets.

Abe et al [53] have reported the values of $\varepsilon_{\text{eff}}$ for the ground states of AEMFs: BeF, MgF, CaF, SrF and RaF using FFCCSD method. The authors have performed all-electron calculations using cc-pVNZ (N = D, T, Q) basis sets for Be, Mg, Ca and F, and a combination of Dyall and Sapporo basis sets for heavier elements: Sr and Ra. However, we have compared, in table 3, our results with theirs computed at the QZ level only, for a fair comparison. The maximum difference between our results and those reported in their work is 0.038 14 $(\times 10^{-25}$ Hz/e cm) for BaF.

Gaul and Berger [54] have calculated the values of $W_d$ constants for BaF and RaF molecules using quasi-relativistic two-component ZORA at the generalized HF and generalized KS level of theory together with the B3LYP correlation functional. Further, they have used (37s 34p 14d 9f) basis functions for heavy atoms, and atomic natural orbitals basis of triple-zeta quality for the F atom. On the contrary, we have performed fully relativistic four-component calculations using the quadruple-zeta basis sets. In reference [55], the authors have extended their study to several other molecules including the lower members of AEMFs. The mean field methods used in references [54, 55] are not as accurate as compared to post-DF methods. Therefore, the results reported in our work disagree significantly from that reported in their work.

### 3.2. Scalar–pseudoscalar interaction constant

The calculated S–PS $P$ and $T$-odd interaction constants ($W_{T}$) for the ground states of AEMFs at the KRCISD level of correlation along with the available results in the literature are given in table 4. It is clear from equation (3) that the matrix element of $h_{S–PS}$ varies roughly as $A Z^2 \approx Z^2$ [59] and hence, heavy polar molecules are preferred for the study of symmetry violating effects. As can be seen from table 4, the contribution of the lighter atom, viz. fluorine, in a diatomic molecule is negligibly small. On the other hand, as one moves from BeF to RaF, the contribution of AE atom to $W_T$ increases. The value of $W_T$ calculated using aug-CV-QZ basis sets for Be is larger by 7.6% from that computed using QZ basis sets. However, for all other AE atoms, the inclusion of extra functions to the QZ basis sets lower the values of $W_T$ by about 1% or less. The difference between the values of $W_T$ using aug-CV-QZ and QZ basis sets for fluorine is 5.3% in BeF, 4.9% in MgF, 4.6% in CaF, 4.1% in SrF and 4.5% in RaF, whereas for the case of BaF, it does not change at least up to the accuracy reported in our work.

There are not many calculations available in the literature to compare our results for the first four members of the AEMF series. The only existing results reported in reference [55] at KS level differ from the values of our work at KRCISD/QZ level by 36% for MgF, 15% for CaF, and 12% for SrF. However, our values for BaF and RaF lies in between the results reported in references [27, 49–52, 55]. Our result of 130.5236 kHz at KRCISD/QZ level for RaF is very close to 131 kHz reported in reference [27] at SODCI level. The final CC value that includes triple contributions as well as large basis set effects estimated in reference [27], is 6.1% larger than our result. However, the calculated value of $W_T$ using two-component ZORA generalized HF method in reference [51] is larger by 13% than our result. Our result of $W_T$ for RaF system is smaller by 7.6% and 8.1% than computed using Z-vector method and as an expectation value, respectively in reference [52].

### 4. Summary

In summary, we have performed relativistic calculations of $P$ and $T$-odd interaction constants: $W_d$ and $W_T$ in AEMFs using KRCISD method in conjunction with the quadruple-zeta quality basis sets. Further, the effect of adding diffuse as well as core-valence functions to the QZ basis sets on $P$ and $T$-odd interaction constants are studied and we have observed that the results of $W_d$ of AEMFs will not be affected by more than 1% while the results of $W_T$ of AE atoms, the change is also about 1% or less, with an exception of BeF. Our results at KRCISD/QZ level of the theory show reasonably good agreement with most of the existing ab initio calculations in the literature. We thus believe that the results reported in this work would be useful for the future theoretical and experimental studies relevant for the search of electric dipole moment of an electron in these molecules.

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