Relativistic coupled-cluster study of BaF in search of CP violation

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Abstract. BaF is one of the potential candidates for the experimental search of the electric dipole moment of the electron (eEDM). The NL-eEDM collaboration is building a new experimental set up to measure the eEDM using the BaF molecule [The NL-eEDM collaboration, Eur. Phys. J. D (2018) 72: 197]. To analyze the results of such an experiment, one would require the accurate value of the molecular $P, T$-odd interaction parameters that cannot be measured from any experiment. In this work, we report the precise value of the $P, T$-odd interaction parameters of the BaF molecule obtained from the four-component relativistic coupled-cluster calculations. We also calculate the hyperfine structure (HFS) constants of the same molecule to assess the reliability of the reported molecular parameters. The calculated HFS constants show good agreement with the available experimental values. Further, the systematic effects of electron-correlation along with the roles of inner-core electrons and the virtual energy functions in the calculation of the studied properties of BaF are investigated.
1. Introduction

BaF, being a heavy polar open-shell molecule, shows excellent potential as a candidate in search of the electric dipole moment (EDM) of an electron. Recently, a new experiment in search of the electric dipole moment of the electron (eEDM) using the BaF molecule is proposed by the NL-eEDM collaboration [1]. (Lifetimes of the molecular states relevant for the experimental search of the eEDM in BaF are recently measured [2].) Observation of the eEDM is a signature of violation of time-reversal (\(T\)) as well as parity \((P)\) invariance. \(T\)-violation is equivalent to charge conjugation \((C)\) and parity violation according to the \(CPT\) theorem that states that the universe remains invariant under the combined operation of \(CPT\). (Thus we shall often use the term “\(P, T\)-odd properties” as a synonym for “\(CP\)-violating properties” throughout this paper.) The \(CP\) violation is one of the several conditions that can explain the matter-antimatter asymmetry of the universe [3]. However, \(CP\) or \(T\) violation in the standard model (SM) of elementary particles miserably fails to justify the observed imbalance between matter and antimatter in the present-day universe. The best upper bound limit of eEDM \((< 1.1 \times 10^{-29} \text{ e.cm})\) to date is obtained from the ThO-experiment [4]. The current experimental sensitivity on the eEDM cannot be explained from the \(CP\)-violating mechanism within the SM. The eEDM is predicted to be almost zero \((\approx 10^{-38} \text{ e.cm})\) in the standard model, up to the three-loop level. That is why new sources of symmetry violation beyond the SM, which is nowadays known as “new physics” is becoming the key interest to the physicists. The eEDM along with the other \(P, T\)-odd violating properties such as the EDM of nucleon [10, 11], the scalar-pseudoscalar (S-PS) nucleon-electron neutral current coupling [9, 12, 13, 14], the nuclear magnetic quadrupole moment (MQM) [15, 16, 17] etc., can contribute to the permanent EDM of an atom or a molecule. In open-shell diatomics, the eEDM and the S-PS nucleon-electron interaction are the major sources of permanent EDM. The open-shell molecules containing heavy deformed nuclei of spin \(I > 1/2\) can also produce additional permanent EDM due to the nuclear MQM effects. However, the EDM due to the MQM effects in molecules with spherical or nearly spherical nuclei is usually insignificant. In the present work, we limit our study only to the eEDM and the S-PS nucleus-electron coupling interactions.

A nonzero EDM of an electron exists if and only if it has an aspherical charge distribution along the spin axis. This is only possible when there is a violation of \(T\) invariance along with \(P\). As mentioned above the eEDM predicted from the SM is much smaller than the current experimental limit, a measurable eEDM is only possible from the \(P, T\)-odd mechanism beyond the SM. The predicted value of the eEDM in many new models lies in the current experimental sensitivity. The S-PS nucleus-electron interaction, on the other hand, arises as a result of coupling between the scalar hadronic current and the pseudoscalar electronic current, which can be mediated via scalar and pseudoscalar components of a neutral Higgs Boson particle [18]. As the known Higgs Boson in the SM is a scalar, it can not explain such interaction. However,
numerous multi-Higgs models (along with the minimal supersymmetric standard model) can predict this type of interaction. These models can also predict the nonconservation of baryon number which is another condition for the large imbalance of matter and antimatter in our universe [19]. That is why the measurement of the eEDM and the S-PS nucleon-electron interaction is very significant. Due to the presence of large effective electric field \((E_{\text{eff}})\) in the heavy polar open-shell diatomic molecular systems, they are suitable candidates for the low energy eEDM experiments. In such an experiment, the energy shift caused by the interaction of the permanent molecular EDM with the applied electric field is measured. However, to interpret the experimental results in terms of the eEDM and the fundamental S-PS nucleus-electron coupling constant, one needs the accurate value of the molecular parameter associated with the respective \(\mathcal{P}, \mathcal{T}\)-odd mechanism. But no experiment can provide the knowledge of those parameters. However, the molecular parameters can be calculated by \textit{ab initio} methods. The \(\mathcal{P}, \mathcal{T}\)-odd interaction parameters are very much dependent on the electron density at the vicinity of the heavy nucleus of the diatomic molecule. The same is also true for the hyperfine structure (HFS) interaction constants. This means that properties like the \(\mathcal{P}, \mathcal{T}\)-odd molecular parameters and the HFS coupling constants are sensitive to the wave function near the heavy nucleus of the molecule. Thus, these properties are also known as the core properties or sometimes as the “atom-in-compound” (AIC) properties [20]. For the accurate calculation of such a property, the effects of the relativistic motion of electrons and the electron-correlation are extremely important. Therefore, an \textit{ab initio} method that can efficiently incorporate both the relativistic and the correlation effects of electrons should be suitable for such a calculation. It is worth mentioning that the accurate calculation of an AIC property is often very difficult because of the strong inter-electronic correlation effects present in the molecules. So, one needs to understand the role of electron-correlation in such molecular calculations to obtain the accurate values of the core properties.

The main objective of this article is to precisely calculate the \(\mathcal{P}, \mathcal{T}\)-odd interaction constants \textit{viz.}, \(E_{\text{eff}}\) and \(W_s\) of BaF in its ground electronic \(^2\Sigma_{\frac{3}{2}}\) state using the Z-vector method within the four-component relativistic coupled-cluster singles and doubles (CCSD) model [21]. Although in recent times, the \(\mathcal{P}, \mathcal{T}\)-odd constants of this molecule have been reported from semi-empirical [22] and various \textit{ab initio} calculations [23, 24, 25, 26, 27, 28, 29, 30], the calculation of the same using a higher level of theory is always important. The accuracy of the \(\mathcal{P}, \mathcal{T}\)-odd molecular parameters can not be directly assessed since they can not be experimentally measured. However, there is an indirect way to do so by calculating the HFS constants and then comparing them with the available experimental values. This is because the accuracy in the calculated HFS constants, similar to the \(\mathcal{P}, \mathcal{T}\)-odd molecular parameters, depends on the accuracy of the wavefunction near the nuclear region. Thus, we report the hyperfine structure constants of the BaF molecule to assess the reliability of the calculated \(\mathcal{P}, \mathcal{T}\)-odd interaction constants. Further, the systematic effects of electron-correlation as well as the roles of inner-core electrons and the virtual spinors in the molecular calculations of BaF are
Relativistic coupled-cluster study of BaF discussed in this article.

The paper is organized as follows: The theory of the calculated properties and the relativistic coupled-cluster method is discussed in Sec. 2. In Sec. 3 computational details are given. The Sec. 4 deals with the discussion of the results. Finally, the concluding remark is given in Sec. 5. Atomic units are used here unless stated.

2. Theory

The Hamiltonian for the interaction of eEDM \((d_e)\) with the internal molecular electric field \[31, 32\] is

\[
H_{d_e} = 2icd_e\gamma^0\gamma^5p^2,
\]

where \(c\) is the speed of light, \(\gamma\) are the usual Dirac matrices and \(p\) is the momentum operator. Now, the \(E_{\text{eff}}\) can be defined as

\[
E_{\text{eff}} = |\langle \Psi_\Omega | \sum_j^n \frac{H_{d_e}(j)}{d_e} | \Psi_\Omega \rangle|.
\]

(1)

Here \(\Psi_\Omega\) is the wavefunction of the state \(\Omega = 1/2\), which is the projection of total electron angular momentum of BaF on the molecular axis \((z-\text{axis})\) and \(n\) is the total number of electrons.

The interaction Hamiltonian for S-PS nucleus-electron coupling \[33\] is defined as

\[
H_{SP} = ig_F/\sqrt{2}Zk_s\gamma^0\gamma^5\rho_N(r),
\]

where \(g_F\) is the Fermi constant, \(Z\) is the number of protons, and \(\rho_N(r)\) is the nuclear charge density normalized to unity. The fundamental S-PS coupling constant \(k_s\) is defined as \(Zk_s=(Zk_{s,p}+Nk_{s,n})\), where \(N\) is the number of neutrons, and \(k_{s,p}\) and \(k_{s,n}\) are the electron-proton and electron-neutron coupling constant, respectively. The parameter \(W_s\) can be evaluated by

\[
W_s = |\frac{1}{\Omega k_s} \langle \Psi_\Omega | \sum_j^n H_{SP}(j) | \Psi_\Omega \rangle|.
\]

(2)

The parallel \((A_\parallel)\) and perpendicular \((A_\perp)\) components of the HFS constant of a diatomic molecule can be defined as

\[
A_\parallel(\perp) = \frac{\mu_k}{I\Omega} \langle \Psi_\Omega | \sum_i^n \left( \frac{\bar{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_{z(\alpha/\gamma)} | \Psi_{\Omega(-\Omega)} \rangle,
\]

(3)

where \(\mu_k\) is the magnetic moment of the nucleus \(k\) and \(\bar{\alpha}_i\) is Dirac matrix for \(i\)th electron.

To calculate the above mentioned properties, we use the relativistic coupled-cluster singles and doubles (CCSD) wavefunction, which is given by \(|\Psi_{\text{cc}}\rangle = e^T|\Phi_0\rangle\). Here \(\Phi_0\) is the four-component Dirac-Hartree-Fock wavefunction and \(T = T_1 + T_2\), is known as excitation operator which is defined as

\[
T_m = \frac{1}{(m!)^2} \sum_{ij...ab...} t_{ij...ab...}^{ab...a^\dagger a^\dagger a_j...},
\]

(4)

where \(i,j(a,b)\) indices refer to the occupied (unoccupied) spinors, and \(a^\dagger_p\) \((a_p)\) refers to the creation (annihilation) operator for spinor \(p\). \(t_{ij...ab...}^{ab...a^\dagger a^\dagger a_j...}\) is the cluster amplitude corresponding to \(T_m\). The unknown amplitudes corresponding to \(T_1\) and \(T_2\) are solved using the following equations:

\[
\langle \Phi_1^a | (H_Ne^T) c | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | (H_Ne^T) c | \Phi_0 \rangle = 0,
\]

(5)
where \( H_N \) is the normal ordered Dirac-Coulomb Hamiltonian, and \( \Phi_0^a \) and \( \Phi_{ij}^{ab} \) are the single and double excited determinants with reference to \( \Phi_0 \), respectively. The subscript \( c \) means that only the connected terms survive in the contraction between \( H_N \) and \( T \).

Recently, Sasmal et al. [21] extended the \( Z \)-vector technique into the four-component relativistic CCSD framework and successfully implemented the method to precisely calculate various AIC properties of molecules [12, 14, 34, 35]. For more detailed knowledge of the \( Z \)-vector method, one can see Refs. [36, 37, 38]. The perturbation independent linear operator used in the \( Z \)-vector method within the CCSD framework is \( \Lambda = \Lambda_1 + \Lambda_2 \), where

\[
\Lambda_m = \frac{1}{(m!)^2} \sum_{ij...ab...} \lambda_{ij...}^{ab...} a_i^{\dagger} a_j^{\dagger} a_a ... a_b a_a,
\]

where \( \lambda_{ij...}^{ab...} \) is the amplitude corresponding to \( \Lambda_m \). The explicit equations for the amplitudes of \( \Lambda_1 \) and \( \Lambda_2 \) are

\[
\langle \Phi_0 | [\Lambda(H_N e^T)_c]_c | \Phi_0^a \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_0^a \rangle = 0,
\]

\[
\langle \Phi_0 | [\Lambda(H_N e^T)_c]_c | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle \langle \Phi_j^a | \Lambda | \Phi_{ij}^{ab} \rangle = 0.
\]

Once the amplitudes are known, the energy derivative (or the desired property) can be obtained by

\[
\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda(O_N e^T)_c]_c | \Phi_0 \rangle,
\]

where, \( O_N \) is known as the derivative of normal ordered perturbed Hamiltonian with respect to external field of perturbation.

3. Computational details

We perform our calculations using a locally modified version of DIRAC17 [39], which is interfaced with the \( Z \)-vector code developed in our group. The default parameters for the nuclei in DIRAC are used as the nuclear parameters in our calculations where the nuclei are modeled by the Gaussian charge distribution [40]. The small basis sets are generated from the large basis using the restricted kinetic balance [41] condition. In our calculation, the negative energy spectrum is projected out using the “no virtual pair approximation” [42]. The bond length of BaF is taken as 2.16 Å [43]. We use the following uncontracted Gaussian basis sets: double-zeta (DZ): dyall.cv2z [44] for Ba, cc-pCVDZ [45] for F, triple-zeta (TZ) basis: dyall.cv3z [44] for Ba and cc-pCVTZ [45] for F; quadruple-zeta (QZ) basis: dyall.cv4z [44] for Ba and cc-pCVQZ [45] for F. We correlate all the electrons in most of the calculations, however, 30 inner-core (1s-3d) electrons are excluded from correlation treatment for the frozen-core calculations (see Table 4). We cut off the virtual spinors having energy more than a certain value. The information about the basis sets and the cutoffs used for virtual spinors are given in Table [4].
4. Results and discussion

The molecular frame dipole moment ($\mu$), and the parallel and perpendicular components of the HFS constant of $^{137}$Ba in BaF calculated with different basis sets are presented in Table 2. Our results are compared with the available experimental values \[46, 47\] as well as other theoretically calculated values \[24, 25, 30\] in the same table. The magnitude of both the dipole moment and the HFS constants increases with the use of a higher quality basis set. This trend is expected as the addition of the higher angular momentum basis functions and the high-energy virtual functions usually improve the correlation space, which in turn, provide some improvement in the calculated results. However, the use of basis C over B does not improve the molecular dipole moment of BaF which is probably due to the fact that both B (TZ, 200 a.u.) and C (TZ, 500 a.u.) basis sets are of triple-zeta quality and the additional high-lying virtual energy functions present in basis C contribute negligibly to the molecular frame dipole moment. The relative deviation ($= \left| \frac{\text{Theory} - \text{Experiment}}{\text{Theory}} \right| \times 100\%$) of the calculated properties from the experimental values are shown in Fig. 1. From Table 2 and Fig. 1, we observe that the values obtained with basis D (QZ, 200 a.u.) show the least relative deviation. Our HFS constants using this basis set are in better agreement with the experimental results than those reported by Kozlov et al. \[24\] using the generalized relativistic effective core potential (GRECP) method with effective operator (EO) based perturbative corrections within the restricted active space self-consistent field (RASSCF) framework and by Fukuda et al. \[30\] employing the restricted active space configuration interaction (RASCI) singles and doubles method. On the other hand, the molecular frame dipole moments calculated by Fukuda et al. (including all the electrons in the RASCI active space) \[30\] and Nayak et al. (including only 17 electrons in the active space) \[25\] using the RASCI method show better agreement with the experiment than that reported by us.

In Table 3, we present the $P, T$-odd interaction constants $E_{\text{eff}}$ and $W_s$ along with their ratio ($R$) for the BaF molecule. The effective electric field in BaF increases from 6.35 to 6.56 and then to 6.59 GV/cm when we go from basis A (DZ, 500 a.u.) to basis B (TZ, 200 a.u.) and then to basis C (TZ, 500 a.u.). On the contrary, as we go from basis C to basis D (QZ, 200 a.u.), $E_{\text{eff}}$ decreases from 6.59 to 6.52 GV/cm. The S-PS nucleon-electron interaction parameter increases from 7.56 to 8.30 and then to 8.34 kHz.

### Table 1. Cutoffs for virtual spinors and basis sets used in our calculations.

| Basis | Virtual | Name | Nature | Ba | F | Cutoff (a.u.) | Spinors |
|-------|---------|------|--------|----|---|---------------|---------|
| A     |         | DZ   | dyall.cv2z | cc-pCVDZ | 500 | 201          |
| B     |         | TZ   | dyall.cv3z | cc-pCVTZ  | 200 | 325          |
| C     |         | TZ   | dyall.cv3z | cc-pCVTZ  | 500 | 361          |
| D     |         | QZ   | dyall.cv4z | cc-pCVQZ  | 200 | 579          |
Table 2. Molecular frame dipole moment $\mu$ (in Debye), and magnetic HFS constants (in MHz) of BaF

| Basis/Method               | $\mu$ | $^{137}$Ba $A_{||}$ | $A_{\perp}$ |
|----------------------------|-------|---------------------|-------------|
| A                          | 2.76  | 2254                | 2165        |
| B                          | 2.91  | 2326                | 2236        |
| C                          | 2.91  | 2338                | 2247        |
| D                          | 3.08  | 2365                | 2274        |
| GRECP/RASSCF/EO [24]       |       | 2272                | 2200        |
| RASCI(17e) [25]            | 3.20  | -                   | -           |
| RASCI(65e) [30]            | 3.11  | 1589                | -           |
| Experiment                 | 3.17(3)[46] | 2453(9)[47] | 2401(6)[47] |

Figure 1. Relative deviation of the calculated molecular frame dipole moment ($\mu$), parallel HFS constant ($A_{||}$) and perpendicular HFS constant ($A_{\perp}$) from the corresponding experimental values for BaF with different basis sets

Table 3. $P, T$-odd interaction constants ($E_{\text{eff}}$ in GV/cm, $W_s$ in kHz, and $R$ in $10^{18}$/e.cm unit) of BaF

| Basis | Nature | $E_{\text{eff}}$ | $W_s$ | $R=E_{\text{eff}}/W_s$ |
|-------|--------|------------------|-------|-------------------------|
| A     | DZ     | 6.35             | 7.56  | 203.1                   |
| B     | TZ     | 6.56             | 8.30  | 191.1                   |
| C     | TZ     | 6.59             | 8.34  | 191.1                   |
| D     | QZ     | 6.52             | 8.35  | 188.8                   |
Relativistic coupled-cluster study of BaF

Figure 2. Convergence of the AIC properties of BaF with the number of virtual spinors

while going from basis A to basis B and then to basis C. However, a very small (0.01 kHz) increment in $W_s$ is observed for the use of basis D over C. On the other hand, the ratio ($R$) of $E_{\text{eff}}$ to $W_s$ decreases from 203.1 to 188.8 in the unit of $10^{18}$/e.cm with the use of basis A to D. It is noteworthy that the virtual functions with energy in-between 200 a.u. and 500 a.u. are absent in basis D unlike basis A and C. We want to reiterate that the use of TZ basis (both B & C) over DZ basis (A) results in an increase in the magnitude of the studied AIC properties, but the use of basis D (QZ, 200 a.u.) over the TZ basis sets does not reflect the similar trend, especially in the case of $E_{\text{eff}}$. Unlike in the cases of the HFS constants and $W_s$, the high angular momentum basis functions probably decrease the magnitude of the effective electric field of BaF, especially when we go from TZ to QZ basis. A similar observation was also inferred in Ref. [48] for the HgF molecule. In such a case, the addition of high-lying virtual spinors into the configuration space may compensate for the effects of the high angular momentum basis functions. Nevertheless, as the accuracy of the HFS results reflects the reliability of the $\mathcal{P}, \mathcal{T}$-odd interaction parameters and the relative deviation of the HFS constant calculated using basis D is the least, we consider the property values calculated using this basis set to be our most reliable results. Thus, our most reliable results for $E_{\text{eff}}$, $W_s$ and $R$ in BaF are 6.52 GV/cm, 8.35 kHz and $188.8 \times 10^{18}$/e.cm, respectively. One should note, since we have cut off the virtual spinors of energy more than 200 a.u. for basis D, it is important to estimate the contribution of the missing high-energy virtual spinors to the calculated properties to achieve more precision. (The contribution of the virtual spinors to the
core properties of BaF is discussed at the end of this section.)

The convergence of the AIC properties of BaF with the number of virtual spinors is shown in Table 4. Two sets of calculations are performed to understand the effect of virtual spinors and that of core-correlation in the study of AIC properties of BaF. Firstly, we correlate all the electrons in the molecular calculation to report $A_{∥}$, $E_{\text{eff}}$ and $W_{s}$ at different cutoffs for virtual spinors using the DZ (dyall.cv2z for Ba and cc-pCVDZ for F) basis set. Secondly, the same calculations are repeated by correlating only 35 outer-electrons (i.e., freezing the 30 inner-core (1s-3d) electrons) to see the correlation trend of the inner-core electrons. The role of core-correlation effects can be understood by comparing the property-value obtained from the all-electron correlation calculation and the frozen-core molecular calculation. We see from Table 4 that the magnitude of AIC properties gradually increases with the increase in the number of virtual energy functions when all the electrons of BaF are correlated. Unlike the all-electron correlation calculation, the magnitude of the properties obtained from the frozen-core calculation increases negligibly with the number of virtual spinors. This means that the trend of the AIC properties of BaF with the number of virtual spinors in a given basis set is not similar for the all-electron and the frozen-core correlation calculations. As observed in Table 4, the inclusion of the high-energy virtual functions in molecular calculation hardly affects the property-value for the frozen-core case. In other words, the high-energy virtual functions are important only for the proper correlation of the inner-core electrons. This inference is consistent with the findings of Refs. [49, 50, 51].

Furthermore, the correlation of the 30 inner-core (1s-3d) electrons contributes 3.88% to $A_{∥}$, 4.35% to the effective electric field and 4.44% to the S-PS interaction parameter when all the virtual spinors are included in the molecular calculation of BaF. Thus, the correlation of the inner-core electrons along with the high-lying virtual spinors play crucial roles in the precise calculations of the AIC properties.

In Table 5, we compare the $\mathcal{P}, \mathcal{T}$-odd molecular parameters of BaF reported in this work with the literature values [23, 24, 25, 26, 27, 28, 29, 22, 30]. Das and coworkers [23] calculated the $\mathcal{P}, \mathcal{T}$-odd constants of BaF using relativistic linear expectation-value coupled cluster (LECCSD) method. The LECCSD method lacks the non-linear terms in the expectation-value expression [23] and misses some of the correlation effects. Their reported values of $E_{\text{eff}}$ and $W_{s}$ are in good agreement with our results though they used the triple zeta basis set with 80 a.u. as the cutoff for virtual spinors in their calculations. Kozlov et al. [23] performed the first $ab\ initio$ calculation for the $\mathcal{P}, \mathcal{T}$-odd constants of BaF employing the GRECP/RASSCF/EO method. Nayak et al. [25, 26] reported $E_{\text{eff}}$ as well as $W_{s}$ using the restricted active space configuration interaction (RASCI) method (including only 17 electrons in the active space) and Fukuda et al. [30] calculated $E_{\text{eff}}$ employing the RASCI method (including 65 active electrons with DZ basis). Nayak et al. [27] also performed relativistic second-order many-body perturbation theory (MBPT) computation in BaF to report the S-PS interaction constant, which shows good agreement with our value. Recently, Gaul and Berger [28] calculated the $\mathcal{P}, \mathcal{T}$-odd parameter related to the eEDM interaction in the BaF molecule employing a quasi-
Table 4. The AIC properties of BaF at various cutoffs for virtual spinors. (Basis used: dyall.cv2z for Ba and cc-pCVDZ for F.)

| Cutoff (a.u.) | Virtual Spinors | Occupied Spinors | $A_\parallel$ (MHz) | $E_{\text{eff}}$ (GV/cm) | $W_s$ (kHz) |
|---------------|----------------|-----------------|---------------------|-----------------|----------|
| 50            | 155            | 65              | 2216.6              | 6.23            | 7.42     |
| 200           | 181            | 65              | 2239.5              | 6.31            | 7.51     |
| 500           | 201            | 65              | 2254.3              | 6.35            | 7.56     |
| 1000          | 217            | 65              | 2254.5              | 6.37            | 7.59     |
| No cutoff     | 301            | 65              | 2277.6              | 6.43            | 7.66     |
| No cutoff (including Gaunt interaction) | 301 | 65 | 2278.3 | 6.33 | 7.68 |

Table 5. Comparison of $P, T$-odd interaction constants ($E_{\text{eff}}$ in GV/cm and $W_s$ in kHz) of BaF calculated by various methods.

| Method                        | $E_{\text{eff}}$ | $W_s$ |
|-------------------------------|------------------|-------|
| Z-vector CCSD (this work)     | 6.52             | 8.35  |
| LECCSD [23]                   | 6.6              | 8.4   |
| GRECP/RASSCF [24]             | 4.63             | 5.9   |
| GRECP/RASSCF/EO [24]          | 7.53             | -     |
| RASCI (17e) [23, 26]          | 7.28             | 9.7   |
| RASCI (65e) [30]              | 4.56             | -     |
| MBPT [27]                     | -                | 8.4   |
| GHF-ZORA [28]                 | 6.82             | -     |
| GKS-ZORA [28]                 | 5.99             | -     |
| NR-MRCI [29]                  | 5.17             | -     |
| Semi-empirical [22]           | 7.24             | 11.0  |

relativistic two-component approach namely, a complex generalized Hartree-Fock (GHF) and a complex generalized Kohn-Sham (GKS) scheme within the zero-order regular approximation (ZORA). The non-relativistic multi-reference configuration interaction (NR-MRCI) result [29] for the effective electric field of BaF is smaller than our value. On the other hand, the semi-empirical values of the $P, T$-odd parameters in BaF reported by Kozlov et al. [22] are larger than those reported in our work. Nevertheless, our results are more reliable than the other theoretical values because we employ energy-derivative
Relativistic coupled-cluster study of BaF

approach within the four-component relativistic CCSD framework with a sufficiently
high-quality relativistic basis sets in the molecular calculation. The good agreement
of the HFS constants with the experimental results (see Table 2) reflects this fact.

As mentioned above, our most reliable results for BaF are calculated at its
equilibrium bond length with basis D (i.e., QZ, 200 a.u. as a cutoff for virtual spinors)
using the DC Hamiltonian in four-component relativistic CCSD method. We thus
neglect the role of high-lying virtual spinors, the vibrational effects, the higher-order
correlation contribution and the Breit/QED effects, etc. in our molecular calculations.
As one would need the values of \( P, T \)-odd molecular parameters of BaF as accurate as
possible to analyze the experimental findings of the eEDM experiment, the inclusion
of the said effects in the molecular calculations could be important. However, in this work,
it is not possible to perform molecular calculations with QZ basis sets incorporating all
those effects. Instead, we estimate the possible errors with a lower quality (DZ) basis
set. We can estimate the error due to restriction of the correlation space (since we cut off
the virtual spinors with energy above 200 a.u. in basis D) from Table 4. Inclusion of the
virtual functions with energy higher than 200 a.u. at double-zeta basis set contributes
around 1.67% into HFS constant, 1.86% to \( E_{\text{eff}} \), and 1.96% to \( W_s \). Therefore, the error
caused by the exclusion of high-lying virtual spinors with energy more than 200 a.u. in
our results with basis D is expected to be within 2%. The error caused by the neglect of
the higher-order relativistic effects can be avoided by adding the higher-order relativistic
terms (for example, Gaunt interaction term) in the Hamiltonian. The mean field Gaunt
correction to our results can be estimated from Table 4 by comparing the values obtained
using the Dirac-Coulomb and the Dirac-Coulomb-Gaunt Hamiltonian. The Gaunt term
contributes around 1.5% to \( E_{\text{eff}} \) and 0.3% to \( W_s \) with DZ basis. The error due to the
missing higher-order correlation effects is reported as about 3.5% for some other but
similar system to BaF in literature \[13, 52\]. We, therefore, expect a similar amount of
error due to missing higher-order correlation effects in the BaF molecule. On the other
hand, vibrational effects are usually important for those molecular properties which
strongly depend on the internuclear distance of the molecule. As the matrix elements
of AIC properties are highly concentrated near the heavy nucleus, we do not expect a
significantly large error due to the neglect of vibrational effects. Furthermore, the error
due to the basis set incompleteness can be estimated from Table 3 by comparing the
values obtained using DZ basis with those obtained with TZ basis or TZ basis with
QZ basis. The change of magnitude is about 3.64% for \( E_{\text{eff}} \) and 9.35% for \( W_s \) when
we improve the quality of basis from DZ (i.e., A) to TZ (i.e., C). Similarly, for the
improvement in basis from TZ (B) to QZ (D), the magnitude of \( E_{\text{eff}} \) and \( W_s \) changes by
around 0.6% and 0.6%, respectively. Thus, we don’t expect that the error due to basis
set incompleteness would exceed 1%. It is worth mentioning that although we correlate
all the electrons to compute our most reliable results, they are not completely free from
the error associated with core correlation effects since we use dyall.cv4z basis sets, which
are designed only to treat core-valence correlation. However, relying on our previous
studies \[35, 51, 53\] we expect this error to be negligible for BaF as well. Nevertheless,
Relativistic coupled-cluster study of BaF

ignoring the mutual cancellations of different possible sources of error and assuming the errors to be independent, we can argue that the uncertainty in our most reliable results for the $\mathcal{P}, \mathcal{T}$-odd molecular parameters of BaF is within 8%.

5. Conclusion

We report the $\mathcal{P}, \mathcal{T}$-odd interaction coefficients and the hyperfine structure constants of BaF along with its molecular frame dipole moment employing the four-component relativistic CCSD method. The good agreement of the calculated HFS constant with available experimental results reflects the accuracy of the wave function near the nuclear region generated by the employed method. The most reliable values of $E_{\text{eff}}$ and $W_s$ in BaF reported by us are 6.52 GV/cm and 8.35 kHz, respectively, within an uncertainty of 8%.

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