Relativistic coupled-cluster investigation of parity ($P$) and time-reversal ($T$) symmetry violations in HgF

Kaushik Talukdar, 1,* Malaya K. Nayak, 2,† Nayana Vaval, 3,‡ Sourav Pal 4,1,§
1Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
2Theoretical Chemistry Section, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
3Electronic Structure Theory Group, Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, India and
4Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India

We employ the Z-vector method in the four-component relativistic coupled-cluster framework to calculate the parity ($P$) and time-reversal ($T$) symmetry violating scalar-pseudoscalar (S-PS) nucleus-electron interaction constant ($W_s$), the effective electric field ($E_{eff}$) experienced by the unpaired electron and the nuclear magnetic quadrupole moment (NMQM)-electron interaction constant ($W_M$) in the open-shell ground electronic state of HgF. The molecular frame dipole moment and the magnetic hyperfine structure (HFS) constant of the molecule are also calculated at the same level of theory. Our study of HgF has a high value of $E_{eff}$ (115.9 GV/cm), $W_s$ (266.4 kHz) and $W_M$ ($3.59 \times 10^{29}$Hz/e.cm²), which shows that it can be a possible candidate for the search of new physics beyond the Standard model. Our results are in good agreement with the available literature values. Furthermore, we investigate the effect of the basis set and that of the virtual energy functions on the computed properties. The role of the high-energy virtual spinors are found to be significant in the calculation of the HFS constant and the $P, T$-odd interaction coefficients.

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I. INTRODUCTION

The matter-antimatter asymmetry in the universe is one of the biggest mysteries till date. The ongoing accelerator based experiments in the search for physics beyond the standard model (SM) of elementary particle physics can shed some light on the dominance of matter over antimatter. The violation of charge conjugation ($C$) and parity ($P$) is one of the several conditions that can explain the matter-antimatter asymmetry [1]. However, the $CP$ violation in Kobayashi-Maskawa model within the SM is too weak to explain this asymmetry. Therefore, extra symmetry violating interactions that are missing in the Standard model are necessary to explore the physics beyond the SM. Thus, the non-accelerator (i.e., low energy) experiments to study the $P$ and time reversal invariance ($T$) violation in nuclei, atoms and molecules become complementary to the accelerator-based high energy experiments [2–8]. Intrinsic electric dipole moment of electron (eEDM or $d_e$) [9–13] and nucleon (proton or neutron) [8, 14], and $P, T$-odd scalar-pseudoscalar (S-PS) nucleus-electron interaction [13, 15–17] are the two major sources of the permanent electric dipole moment (EDM) of magnetic atomic and molecular systems. In addition, the $P, T$-odd nuclear magnetic quadrupole moment (NMQM) interaction [18–21] can contribute to atomic and molecular EDM. Thus, the NMQM is an alternative way to study the nuclear $P, T$-odd physics in an atom or molecule.

According to the SM, the eEDM is too small ($< 10^{-38}$ e.cm) [22] to be observed experimentally. On the other hand, many extensions of the SM predict the value of eEDM to be in the range of $10^{-26} – 10^{-29}$ e.cm [23]. The sensitivity of the modern eEDM experiment also lies in the same range. Heavy polar diatomic paramagnetic molecules are suitable to be the candidate of modern eEDM experiments due to their high internal effective electric field ($E_{eff}$) [24, 25]. Till date, the best upper bound limit of eEDM ($< 8.7 \times 10^{-29}$ e.cm) is obtained in the experiment carried out by the ACME collaboration [13] using ThO. In addition to the eEDM, the $P, T$-odd S-PS nucleus-electron neutral current interaction, arising from the interaction between pseudo-scalar electronic current and scalar hadronic current can also contribute to the $P, T$-odd frequency shift. So, to interpret the results of experiment in terms of the eEDM and fundamental S-PS coupling constant ($k_s$), we need to know the accurate value of $E_{eff}$ and scalar-pseudoscalar $P, T$-odd interaction constant ($W_s$), respectively. On the other hand, the NMQM, one of the nuclear symmetry violating effects, may arise either due to the nuclear EDM or $P, T$-odd nuclear forces. The nuclear EDM is often screened by the electrons in neutral atoms and molecules and hence, their contribution is negligible to the measurable EDM of the system. However, the interaction of nuclear magnetic moment with electrons is not screened. Also, the NMQM can produce larger EDM in paramagnetic systems than the Schiff moment [26]. However, the NMQM effect only exists for the nuclei having nuclear spin $I > 1/2$ in a paramagnetic system with non-zero electron angular momentum. The effect due to the NMQM increases signif-
icantly in deformed nuclei [27]. Higher nuclear charge ($Z$) is another factor for the enhancement of the said effect. The $\mathcal{P}, \mathcal{T}$-odd interaction between the NMQM and the magnetic field produced by electrons in a paramagnetic system is significantly important as it can help in the investigation of new physics in the hadron sector of matter. Although, in recent times, the $\mathcal{P}, \mathcal{T}$-odd effects caused by the NMQM in various paramagnetic molecules have been studied, further extensive study is important to unravel the new physics. It is worth to mention that the accurate value of the NMQM interaction constant ($W_M$) needs to be known to interpret the experimentally measured $\mathcal{P}, \mathcal{T}$-odd frequency shift due to the NMQM interaction in terms of the magnetic quadrupole moment ($M$) of nuclei. However, the value of $E_{\text{eff}}, W_s$ and $W_M$ cannot be experimentally measured and thus, we need to rely upon the accurate $ab\ initialo$ methods to calculate these quantities. The `Atom in Compound’ (AIC)[28] properties such as $E_{\text{eff}}, W_s$ and $W_M$ are very sensitive to the accuracy of the wavefunction near the nuclear region and thus, an $ab\ initiali$ method which can efficiently incorporate both the relativistic and electron-correlation effects, is necessary to calculate the AIC properties precisely.

The relativistic effects can be most elegantly treated using the four-component Dirac-Hartree-Fock (DHF) method in electronic structure theory. It approximates the electron-electron repulsion in an average way which leads to the missing of correlation between opposite spin electrons. However, this missing dynamic electron correlation can be efficiently incorporated in the single reference coupled-cluster (SRCC) method. Therefore, the relativistic SRCC method is probably the most preferred many-body theory to deal with both the effects of correlation and relativistic motion of electrons. Moreover, the properties of a many-electron system can be accurately calculated by the energy derivative method in the SRCC framework. The $Z$-vector method [29, 30] is a widely used energy derivative technique for the calculation of first order property. Recently, Sasmal et al. [31] extended the $Z$-vector technique into the four-component relativistic coupled-cluster domain and successfully implemented the method to calculate various first order properties of atoms, ions and molecules.

HgF is a highly polar and paramagnetic heavy diatomic molecule. It has high diagonal Franck-Condon matrix element between the ground and first excited electronic state, which is a characteristic of laser coolable molecule and the corresponding transition frequency between these two states lies in the ultra visible region [32]. Recently, Vutha et al. [33] proposed an experiment in which polar molecules such as HgF could be embedded in a solid matrix of inert gas atoms to measure the eEDM. On the other hand, Kozlov [34, 35] studied the $\mathcal{P}, \mathcal{T}$-odd interactions in HgF using the relativistic semiempirical method. Similarly, Dmitriev et al. [35, 36] performed quasirelativistic $ab\ initiali$ calculation of the aforementioned properties using configuration interaction (CI) method. Das and co-workers [37–40] recently computed the $E_{\text{eff}}$ and $W_s$ in the HgF molecule using either the linear expectation-value or the finite field approach within the relativistic coupled-cluster model. It is noteworthy that the calculations of $\mathcal{P}, \mathcal{T}$-odd properties in heavy systems are usually difficult due to the strong interelectron correlations and the relativistic motion of electrons, and the low level theoretical methods often do not produce accurate result. So, the precise calculations of these properties using the higher level of theory are always considered to be important. For the calculation of first order properties, the energy derivative method such as $Z$-vector technique is usually more reliable than the expectation-value approach within the nonvariational SRCC framework. On the other hand, unlike the $Z$-vector method, the coupled-cluster amplitudes in the finite field approach depend on the external field parameters and the error associated with this approach is dependent on the number of data points taken for the numerical differentiation. It is important to compute the aforementioned properties of HgF using a fully relativistic analytical (energy-derivative) method within the SRCC framework. Thus, the study of the AIC properties in HgF using more reliable $ab\ initiali$ method could be interesting. In this work, we have calculated the molecular dipole moment, the hyperfine structure constant, $E_{\text{eff}}, W_s$ and $W_M$ of HgF in its ground electronic ($^3\Sigma$) state using the $Z$-vector method in the domain of four-component relativistic coupled-cluster theory. We also study the effect of the basis sets and that of the virtual spinors on the computed properties. We believe that the present investigation of the effective electric field experienced by the unpaired electron, the S-PS nucleus-electron neutral current coupling and the nuclear magnetic quadrupole moment interaction with electrons in HgF would be important in the search of new physics, and especially to examine the accuracy of the previously reported values in the literature. The manuscript is organized as follows. The important aspects of the theory of the calculated properties and the $Z$-vector approach in the domain of relativistic SRCC method are discussed in Sec. II. Computational details are given in Sec. III. The results of the present work are presented and discussed in Sec. IV and then, the concluding remark is given in Sec. V. Atomic units are used explicitly in the manuscript unless stated.

II. THEORY

A. One-electron property operators

The Hamiltonian for the interaction of the eEDM ($d_e$) with the internal molecular electric field [41, 42] is given as

$$H_d = 2i\alpha d_e \gamma^0 \gamma^5 p^2,$$

(1)
where $\gamma$ are the usual Dirac matrices and $p$ is the momentum operator. Now, the $E_{\text{eff}}$ can be defined as
\begin{equation}
E_{\text{eff}} = |W_{Q}\Omega| = |\langle \Psi_{\Omega} | \sum_{j}^{n} \frac{H_{a}(j)}{d_{e}} |\Psi_{\Omega} \rangle|,
\end{equation}
(2)

Here $\Omega$ is the projection of total electronic angular momentum on the molecular axis ($z$-axis). The value of $\Omega$ is $1/2$ for the ground electronic state ($^2\Sigma$) of HgF. On the other hand, $\Psi_{\Omega}$ is the wavefunction of $\Omega$ state and $n$ is the total number of electrons.

**TABLE I:** Basis and cutoffs for virtual spinors used in our calculations.

| Name | Nature | Hg | F | Virtual Spinors |
|------|--------|----|---|----------------|
| A    | DZ     | 75 | 50| dyall.ae2z cc-pVDZ |
| B    | DZ     | 75 | 50| dyall.ae2z cc-pVDZ |
| C    | TZ     | 75 | 50| dyall.ae3z cc-pVTZ |
| D    | TZ     | 75 | 50| dyall.ae3z cc-pVTZ |
| E    | QZ     | 75 | 50| dyall.ae4z cc-pVQZ |

**TABLE II:** Molecular frame dipole moment, $\mu$ (in Debye) and parallel component of magnetic HFS constant, $A_\parallel$ (in MHz) of HgF in different basis. Expt = Experiment.

| Basis | $\mu$ (D) | $A_\parallel$ (MHz) |
|-------|-----------|---------------------|
| $^{199}$Hg | 2.35 | -6200 |
| $^{201}$Hg | 2.55 | -6370 |
| $^{201}$Hg | 2.94 | -6014 |
| $^{201}$Hg | 2.94 | -7109 |
| $^{201}$Hg | 3.16 | -7267 |
| Expt [52] | 22621 | -8055 |

The interaction Hamiltonian for the S-PS nucleus-electron coupling [43] is defined as
\begin{equation}
H_{SP} = i \frac{G_{F}}{\sqrt{2}} Z k_{s} \gamma_{0} \gamma_{5} \rho_{N}(r),
\end{equation}
(3)

where $G_{F}$ is the Fermi constant, and $\rho_{N}(r)$ is known as the nuclear charge density normalized to unity. The dimensionless constant $k_{s}$ is defined as $Z k_{s} = (Z k_{s,p} + N k_{s,n})$, where $N$ is the number of neutrons, and $k_{s,p}$ and $k_{s,n}$ are known as the electron-proton and electron-neutron coupling constant, respectively. The $W_{S}$ can be evaluated from the following equation:
\begin{equation}
W_{S} = \left| \frac{1}{\Omega k_{s}} \langle \Psi_{\Omega} | \sum_{j}^{n} H_{SP}(j) |\Psi_{\Omega} \rangle \right|.
\end{equation}
(4)

The Hamiltonian for the NMQM-electron interaction [19, 41] is given by
\begin{equation}
H_{\text{MQM}} = -\frac{M}{2I(2I-1)} T_{ik} \frac{3}{2} \frac{[\vec{\alpha} \times \vec{r}]_{ik}}{r^{5}},
\end{equation}
(5)

where $M$ is the NMQM tensor with components
\begin{equation}
M_{ik} = \frac{3M}{2I(2I-1)} T_{ik},
\end{equation}
(6)

\begin{equation}
T_{ik} = I_{i} I_{k} + I_{k} I_{i} - \frac{2}{3} \delta_{ik} I(I + 1)
\end{equation}
(7)

However, for the subspace of $\pm \Omega$, the equation 5 can be written as [26]
\begin{equation}
H_{\text{MQM}} = -\frac{W_{M} M}{2I(2I-1)} \vec{S}^{\prime} \vec{T} \vec{n},
\end{equation}
(8)

where $\vec{n}$ is the unit vector along the $z$-axis, and $\vec{S}^{\prime}$ is the effective electron spin. The $W_{M}$ is defined as
\begin{equation}
W_{M} = \frac{3}{2\Omega} \cdot \langle \Psi_{\Omega} | \sum_{i}^{\infty} \left( \frac{\vec{a}_{i} \times \vec{r}_{i}}{r_{i}^{3}} \right) z \rangle \langle \Psi_{\Omega} \rangle.
\end{equation}
(9)

As the $^{199}$Hg nucleus has $I = 1/2$, it cannot accomodate magnetic quadrupole moment. Thus, we focus on the $^{201}$Hg isotope ($I = 3/2$) in HgF for the NMQM study.

We have mentioned earlier that accurate wave function near the nuclear region is necessary for the precise calculation of the above-mentioned matrix elements. As the accurate calculation of the magnetic hyperfine structure (HFS) constant also depends on the accuracy of the core wave function, the easiest way of testing the accuracy of the electronic wave function of interest is to compare the theoretically calculated magnetic HFS constant with the experimentally measured value.

The matrix element for the magnetic HFS constant of the $J^{th}$ electronic state of an atom can be evaluated by the following expression:
\begin{equation}
A_{J} = \frac{\mu_{J}}{I J} \cdot \langle \Psi_{J} | \sum_{i}^{n} \left( \frac{\vec{\alpha}_{i} \times \vec{r}_{i}}{r_{i}^{3}} \right) z \rangle \langle \Psi_{J} \rangle,
\end{equation}
(10)

where $\Psi_{J}$ is the wave function corresponding to the $J^{th}$ state, $I$ is known as the nuclear spin and $\vec{\mu}_{k}$ is nothing but the magnetic moment of the nucleus $k$. Similarly, the parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) components of the magnetic hyperfine structure constant of a diatomic molecule can be defined as
\begin{equation}
A_{\parallel} = \frac{\mu_{k}}{I \Omega} \cdot \langle \Psi_{\Omega} | \sum_{i}^{n} \left( \frac{\vec{\alpha}_{i} \times \vec{r}_{i}}{r_{i}^{3}} \right) \langle \Psi_{\Omega(-\Omega)} \rangle,
\end{equation}
(11)

**B. Z-vector method**

In a single reference theory, the Dirac-Hartree-Fock (DHF) is the most preferred method to take the relativistic effects into account in an atom or molecule. It
The SRCC wavefunction has exponential ansatz which is defined as

\[ H_{DC} = \sum_i \left[ -c(\vec{\alpha} \cdot \nabla)_{ij} + (\beta - \mathbb{1}_4) c^2 + V^{\text{nuc}}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \mathbb{1}_4 \right]. \]  

Here, \( \alpha \) and \( \beta \) are known to be the Dirac matrices, \( c \) is the speed of light, \( \mathbb{1}_4 \) is the 4\times4 identity matrix and \( i \) denotes the electron. \( V^{\text{nuc}}(r_i) \) is the potential function for finite size nucleus, modelled by the Gaussian charge distribution.

The SRCC wavefunction has exponential ansatz which is given by

\[ |\Psi_{cc}\rangle = c^T |\Phi_0\rangle, \]  

\( T \) in the above equation is known as the coupled-cluster excitation operator, which is defined by

\[ T = T_1 + T_2 + \cdots + T_N = \sum_n T_n, \]  

with

\[ T_m = \frac{1}{(m)!^2} \sum_{i_j \cdots a_{n}} \phi_{i_j \cdots a_{n}} \phi_{a_{n}} \cdots \phi_{a_{n}}. \]  

The occupied (unoccupied) spinors are denoted by \( i_j(a,b) \) indices in the above expression. \( \phi_{i_j(a,b)} \) is the cluster amplitude corresponding to \( T_m \) operator. In coupled-cluster singles and doubles (CCSD) model, \( T = T_1 + T_2 \), and the unknown cluster amplitudes corresponding to \( T_1 \) and \( T_2 \) are solved using the following equations:

\[ \langle \Phi_{i_j}^a | (H_N e^T) | \Phi_0 \rangle = 0, \langle \Phi_{i^a_j b^a} | (H_N e^T) | \Phi_0 \rangle = 0, \]  

where, \( H_N \) is the normal ordered DC Hamiltonian. Connectedness, which is denoted by the subscript \( c \), ensures the size-extensivity. By the term connectedness, we simply mean that only the connected terms survive in the contraction between \( H_N \) and \( T \). Now, the correlated energy can be calculated by the following equation:

\[ E_{\text{corr}} = \langle \Phi_0 | (H_N e^T) c | \Phi_0 \rangle. \]  

\[ \delta \% = \frac{|\text{Theory} - \text{Exp}|}{\text{Theory}} \times 100 \]

**FIG. 1:** Relative deviations of the parallel component of HFS constant of \(^{199}\text{Hg}\) and \(^{201}\text{Hg}\) in HgF at different basis.

**TABLE IV:** \( W_s \) (in kHz), \( E_{\text{eff}} \) (in GV/cm), \( R \) (in 10\(^{18}\) /e.cm), and \( W_M \) (in 10\(^{39}\) /e.cm\(^2\)) of HgF in different basis.

| Basis | Nature | \( W_s \) | \( E_{\text{eff}} \) | \( R = E_{\text{eff}}/W_s \) | \( W_M \) |
|-------|--------|---------|----------------|-----------------|--------|
| A     | DZ     | 251.4   | 111.8          | 107.6           | 3.53   |
| B     | DZ     | 259.3   | 115.5          | 107.6           | 3.64   |
| C     | TZ     | 264.7   | 115.2          | 105.2           | 3.57   |
| D     | TZ     | 273.0   | 118.8          | 105.2           | 3.68   |
| E     | QZ     | 266.4   | 115.9          | 105.2           | 3.59   |
not usually solved variationally and thus the CC energy is not optimized with respect to $C_M$ and $C_D$ for a fixed nuclear geometry [44]. Therefore, to calculate the CC energy derivative with respect to the perturbation, the derivatives of energy with respect to $C_M$ and $C_D$ along with the derivatives of these two coefficients with respect to the external field of perturbation are required. However, the derivative terms associated with $C_D$ can be included introducing a perturbation independent linear vector code. The bond length of HgF is taken as 2.006 Å [48] in all the calculations. We have used the following basis sets: double zeta: dyall.ae2z [49] for Hg, cc-pVDZ [50] for F, triple zeta (TZ) basis: dyall.ae3z [49] for Hg and cc-pVTZ [50] for F; quadruple zeta (QZ) basis: dyall.ae4z [51] basis for Hg and cc-pVQZ [50] basis for F. We consider all the occupied spinors in our calculations. However, we have excluded the virtual spinors having energy more than a cutoff value. DZ basis with 50 and 1000 a.u. as cutoffs for virtual spinors are denoted as A and B, respectively. Similarly, TZ basis with 50 and 1000 a.u., and QZ with 50 a.u. as virtual cutoffs are denoted as C, D, and E, respectively. The details are given in table I.

IV. RESULTS AND DISCUSSION

| Method                      | $W_s$ (in kHz) | $E_{\text{eff}}$ (in GV/cm) | $R = E_{\text{eff}}/W_s$ | $W_M$ (in $10^{33}$Hz/e.cm$^2$) |
|-----------------------------|---------------|-----------------------------|---------------------------|---------------------------------|
| Z-vector CCSD (this work)   | 266.4         | 115.9                       | 105.2                     | 3.59                            |
| LECCSD [37, 38]             |               |                             |                          |                                 |
| FFCCSD [40]                 |               |                             |                          |                                 |
| LECCSD [39]                 | 264.7         | 114.9                       |                           |                                 |
| CI [35, 36]                 | 185.0         | 99.3                        | 4.80                      |                                 |
| non-relativistic MRCI [59]  |               |                             |                          |                                 |
| MRCI [60]                   | 95.0          |                             |                           |                                 |
| Semiepiempirical [34, 35]   | 191.0         | 99.0                        | 4.80                      |                                 |
| analytic [57]               | 204.5         | 112.5                       |                           |                                 |

TABLE V: Comparison of $W_s$ (in kHz), $E_{\text{eff}}$ (in GV/cm), $R = E_{\text{eff}}/W_s$, and $W_M$ (in $10^{33}$Hz/e.cm$^2$) of HgF.

The parallel component of the HFS constant ($A||$) along with the molecular frame dipole moment ($\mu$) of HgF are presented in table II. We have also compared our results with the available experimental values, and the relative deviations of the calculated HFS constants from the experimental values in different basis are shown in figure 1. Magnitude of both the HFS constant and dipole moment increase with the use of a higher basis set. This is due to the fact that the addition of higher angular momentum basis functions improves the configuration space. It is also observed that the HFS value increases with the addition of higher energy virtual spinors. But the same is not true for the molecular dipole moment. The most reliable values of $A||$ of $^{199}$Hg and $^{201}$Hg in HgF are found to be 19687 and -7267 MHz, respectively, which are calculated using basis E (QZ, 50 a.u.). The value of $\mu$ obtained with the same basis is 3.16 Debye. However, it is observed from the table II and figure 1 that our most reliable HFS results deviate from the available experimental values [52] by 10 - 14%. This could be because of two reasons. Firstly, we have not taken into account the Bohr-Weisskopf effect, Breit and QED interactions in our calculations. The Bohr-Weisskopf effect is important for the accurate calculations of the HFS constants of heavy systems [53]. Similarly, the Breit and
QED interactions could be important for the accurate computation of the HFS values. Secondly, there could be some significant uncertainty in the experimental HFS values itself. For better understanding of the second reason, we present the HFS constant of \( ^{199}\text{Hg} \) and that of \( ^{201}\text{Hg} \) nuclei.

The calculated \( P, T \)-odd interaction constants along with the ratio \((R)\) \[57\] of \( E_{\text{eff}} \) to \( W_s \) of HgF are summarized in Table IV. The magnitude of \( E_{\text{eff}} \), \( W_s \) and \( W_M \) increases due to the resultant effect of the addition of higher angular momentum basis functions and that of higher energy virtual spinors. The configuration space improves as we go from A (DZ, 50 a.u.) to C (TZ, 50 a.u.) and then from C (TZ, 50 a.u.) to E (QZ, 50 a.u.) due to the addition of higher angular momentum basis functions and thus, the magnitude of the calculated properties increases. Also, the same trend is observed when we go from A (DZ, 50 a.u.) to B (DZ, 1000 a.u.) or C (TZ, 50 a.u.) to D (TZ, 1000 a.u.) due to the addition of higher virtual energy functions. But unlike the HFS constant, the magnitude of the \( P, T \)-odd constants decreases as we go from D (TZ, 1000 a.u.) to E (QZ, 50 a.u.) basis. This is probably because of the fact that for the \( P, T \)-odd properties, the effect of higher energy virtual spinors is more prominent than that of the higher angular momentum basis functions, especially when we go from TZ to QZ basis. (We discuss the effect of the virtual spinors on the calculated properties at the end of this section.) Nonetheless, as the relative deviation of HFS constants of HgF is lowest in the basis E, we consider the \( P, T \)-odd constants calculated with this basis as the most reliable results. Thus, our most reliable values of \( E_{\text{eff}}, W_s \) and \( W_M \) are found to be 115.9 GV/cm, 266.4 kHz and \( 3.59 \times 10^{33} \text{Hz}/\text{e.cm}^2 \), respectively. Large magnitude of \( E_{\text{eff}} \) and \( W_s \) suggest that the experimental sensitivity of eEDM experiment would be very high for HgF. On the other hand, the value of \( W_M \) in \( ^{201}\text{HgF} \) is probably the largest among all the possible candidates considered till date. Especially, the value is larger than that of ThF\(^+\) \[58\], ThO \[20, 58\], TaN \[18, 58\], HIF\(^+\) \[19, 58\], YbF \[58\] and BaF \[58\]. Although the electronic structure parameter for the NMQM interaction with electrons in \( ^{201}\text{HgF} \) is quite large, the NMQM effect may not be significantly enhanced in this molecule since \( ^{201}\text{Hg} \) is not a highly deformed nucleus. Still, we believe that the nuclear \( P, T \)-odd NMQM effect can enhance the EDM of the said molecule to some extent. On the other hand, we have already mentioned above that Vutha et al. \[33\] proposed a new experiment in which HgF could be embedded in a solid matrix of inert gas atoms to measure the eEDM. Thus, HgF can be an experimental candidate in search of new physics.

In Table V, our results are compared with the other available reported values in literature. Previously, Kozlov \[34, 35\] calculated the \( P, T \)-violating interaction constants of HgF by relativistic semi-empirical method. They reported the value of \( E_{\text{eff}}, W_s \) and \( W_M \) to be 99 GV/cm, 191 kHz and \( 4.8 \times 10^{33} \text{Hz}/\text{e.cm}^2 \), respectively. The first \textit{ab initio} calculation for symmetry violating interaction constants of HgF was performed by Dmitriev et al. \[35, 36\] who reported the value of \( E_{\text{eff}} \), \( W_s \) and \( W_M \) as 99.3 GV/cm, 185 kHz and \( 4.8 \times 10^{33} \text{Hz}/\text{e.cm}^2 \), respectively. We have seen that their \( E_{\text{eff}} \) and \( W_s \) values are smaller than the values reported by our method but for \( W_M \), the trend is reversed. Overall, their re-

### Table VI: Effect of virtual spinors in our calculations. The reported values of \( A_{\parallel} \) are for \(^{199}\text{Hg} \) and those of \( W_M \) are for \(^{201}\text{Hg} \) nuclei.

| Basis          | Virtual        | Cutoff (a.u.) | Spinors | \( A_{\parallel} \) (MHz) | \( W_s \) (kHz) | \( E_{\text{eff}} \) (GV/cm) | \( W_M \) \( \times 10^{33} \text{Hz}/\text{e.cm}^2 \) |
|----------------|----------------|---------------|---------|---------------------------|-----------------|-----------------------------|----------------------------------|
| dyall.ae2z     | cc-pVDZ        | 50            | 153     | 16795                     | 251.4           | 111.8                       | 3.55                             |
| dyall.ae2z     | cc-pVDZ        | 1000          | 249     | 17256                     | 259.3           | 115.4                       | 3.64                             |
| dyall.ae2z     | cc-pVDZ        | 3000          | 281     | 17313                     | 260.2           | 115.8                       | 3.65                             |
| dyall.ae2z     | cc-pVDZ        | No cutoff     | 365     | 17389                     | 261.5           | 116.5                       | 3.67                             |
sults are in good agreement with our values. Dmitriev et al. [35, 36] used relativistic effective core potential (RECP) approach in the molecular SCF calculation part and then treated correlation effects of electrons via configuration interaction (CI) method by exciting only three outer electrons. This means, their calculations are not free from the error associated with the core-polarization effect. Further, minimal atomic basis set for F, and only five relativistic valence orbitals 5d\frac{3}{2}, 5d_{\frac{1}{2}}, 6s_{\frac{1}{2}}, 6p_{\frac{1}{2}}, and 6p_{\frac{3}{2}} for Hg were used in their calculation. In that work, it was claimed that the error in the calculations is around 20%. However, further ab initio study shows that in these calculations a fortuitous cancellation of various effects occurred [42]. On the other hand, we have employed an analytical approach called the Z-vector (energy derivative) method in the four-component relativistic CCSD framework, which incorporates both the relativistic and correlation effects of electrons in an elegant way, to calculate the P,T-odd interaction constants using sufficiently large relativistic basis (QZ) and explicitly correlating all the electrons. Also, Meyer et al. calculated $E_{\text{eff}}$ of HgF to be 68 [59] and 95 [60] GV/cm using the (60 core-electron) effective core potential (ECP)-based nonrelativistic and quasirelativistic multi-reference CI (MRCI) method, respectively. They used nonrelativistic and quasirelativistic pseudopotentials in their calculations. Their non-relativistic value is quite small compared to the results reported by us. This is expected as the relativistic effects are also important for the precise calculation of the AIC properties in heavy systems. With the help of analytic expression, Dzuba et al. [57] reported $W_s$ as 204.5 kHz. Moreover, Das and co-workers recently used linear expectation-value (LECCSD) [37, 39] and finite-field (FFCCSD) [40] relativistic coupled-cluster methodology to study the effective electric field and S-PS coupling constant in HgF. They reported the value of $E_{\text{eff}}$ as 115.4 [37, 38] and 116.4 [40] GV/cm using the double-zeta (DZ) level of basis in the LECCSD and the FFCCSD method, respectively. Further, using the LECCSD method with triple-zeta level of basis, Das and coworkers obtained the value of $E_{\text{eff}}$ to be 114.9 GV/cm and that of $W_s$ to be 264.7 kHz in the HgF molecule [39]. As the LECCSD method does not include the nonlinear terms, it could miss some parts of the electron correlation effects in the molecular calculation. In nonvariational coupled-cluster framework, the expectation-value approach can be thought of as an approximation to the energy-derivative technique since the energy-derivative is the corresponding expectation-value plus some extra terms. On the other hand, the error associated with the numerical method such as the FFCCSD depends on the number of data points considered for the numerical differentiation. However, the same is not true for the analytical method such as Z-vector. Nonetheless, their values fortuitously show good agreement with our results. On the other hand, the most reliable value of $R$ in HgF is found to be 105.2 in the unit of $10^{18}$/e.cm in our study. Dzuba et al. suggested in Ref. [57] that $R$ is very important to achieve the model independent limit of $d_e$ and $k_s$. They also argued that $R$ would have a particular value for a specific heavy nucleus irrespective of the diatom. Previously, Dzuba et al. [57] and Sasmal et al. [17] reported the value of $R$ for Hg as 112.5 in HgF and 104.8 in HgH, respectively in the unit of $10^{18}$/e.cm. So, it is clearly seen that our reported value of $R$ in HgF (i.e., $105.2 \times 10^{18}$/e.cm) is reasonably in good agreement with the previously reported results in the literature.

However, we cannot deny the fact that we have not taken a number of effects (higher order correlation and relativistic effects etc.) into account in our calculations, due to which there could be some errors in our results. The P,T-odd properties described here mainly depend on the valence electron density in the core region of the heavy atom and hence, these properties are not very sensitive to the retardation and magnetic effects [61, 62]. However, the error due to the exclusion of the higher order relativistic effects in the calculation of AIC properties is obtained as 0.5%-1% from the previous study [63-65]. The error associated with the missing higher order correlation effects can be estimated by comparing our values with the full configuration interaction (FCI) results. But FCI calculation for HgF is too much expensive and thus, is not possible to perform in the present work. Nevertheless, we can comment from our experience that the error due to the absence of higher order correlation effects is around 3.5%. Incompleteness of basis set is another source of error in our results. This error can be assessed by comparing our results obtained using TZ and QZ basis. While going from TZ to QZ (i.e. C to E) basis, the values of the P,Todd constants are changed by around 0.6%. So, we can expect that the corresponding error would not exceed 1%. Moreover, to obtain the most reliable results, we have used the sufficiently large Dyall’s relativistic all-electron (dyall.ae4z, QZ) basis, which contains extra core-correlating functions for the proper treatment of core-polarization effect. But we have excluded higher virtual spinors with energy more than 50 a.u. in the calculations and thus, there could be some error due to the restriction of correlation space. Especially, the inner-core (1s-3d) electrons need very high energy virtual spinors for proper correlation [66-68]. To decrease this type of error, we need to consider the higher energy virtual spinors in our calculation which will be too expensive and is beyond the scope of our present study. However, we have calculated the properties of interest using dyall.ae2z basis at various cutoffs for the virtual spinors to estimate the error. The calculated results are summarised in table VI. The contribution of the higher energy virtual spinors above 50 a.u. is found to be 3.4% for the HFS constant, 3.9% for the S-PS interaction coefficient, 4.0% for the effective electric field and 3.8% for the NMQM interaction constant. This means, the high-energy virtual spinors are important for the precise calculation of the AIC properties. Nevertheless, we can comment that the error associated with the restriction of correlation space is about 4%. Considering
all the possible errors, we expect that the uncertainty in our most reliable results is within 10%.

V. CONCLUSION

We have employed the Z-vector method in the four-component relativistic coupled-cluster framework to calculate the symmetry violating interaction constants $E_{\text{eff}}$, $W_s$ and $W_M$ of HgF. We have also calculated the molecular-frame dipole moment of the same molecule and the magnetic HFS constants of $^{199}\text{Hg}$ & $^{201}\text{Hg}$ in HgF. The most reliable value of $E_{\text{eff}}$, $W_s$ and $W_M$ obtained by us are 115.9 GV/cm, 266.4 kHz and $3.59 \times 10^{28}$ Hz/e.cm$^2$, respectively. The estimated error in our reported values is within 10%. However, the previously reported theoretical results are in good agreement with our values. The large values of the $\mathcal{P}$, $\mathcal{T}$-odd interaction constants confirm the candidature of HgF for $\mathcal{P}$, $\mathcal{T}$-odd experiment in search of new physics. Further, it is clearly understood from our study that the high-energy virtual functions play a significant role in the accurate calculation of the AIC properties in the HgF molecule.

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