

## Role of electron correlation in the $\mathcal{P}$ , $\mathcal{T}$ -odd effects of CdH: A relativistic coupled-cluster investigation

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We investigate the parity ( $\mathcal{P}$ ) and time-reversal ( $\mathcal{T}$ ) symmetry violating effects in the CdH molecule and perform the relativistic coupled-cluster calculation of the molecular parameters— $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$ —related to the electric dipole moment of electron (eEDM) interaction, the scalar-pseudoscalar (S-PS) nucleus-electron neutral current coupling, and the nuclear magnetic quadrupole moment (MQM) interaction with electrons, respectively. We also compute the molecular dipole moment and the magnetic hyperfine structure coupling constant of CdH. The values of  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  obtained by us in the said molecule are 12.2 GV/cm, 14.0 kHz, and  $0.82 \times 10^{33}$  Hz/e cm<sup>2</sup>, respectively, within an uncertainty of 10%. Furthermore, we study the trend of electron-correlation in the computed properties of CdH and that of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd parameters in the group-12 monohydrides (i.e., ZnH, CdH, and HgH).

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### I. INTRODUCTION

The well-known particles and forces are not able to explain the universe almost entirely composed of matters and thus, there is a strong possibility of the existence of “new particles and forces” (which are unknown to date). The “new physics” beyond the standard model (SM) of elementary particles has emerged as a bright area of research to search the so-called “new particles and forces.” Violations of charge conjugation ( $\mathcal{C}$ ) and parity ( $\mathcal{P}$ ) or time-reversal ( $\mathcal{T}$ ) invariance beyond the standard model can explore this “new physics,” which in turn, helps to unravel the mystery of matter-antimatter asymmetry of our universe. The phenomenon of  $\mathcal{CP}$  violation results in the intrinsic electric dipole moment of the electron [eEDM ( $d_e$ )] [1–5], the scalar-pseudoscalar (S-PS) nucleus-electron neutral current coupling [5–8], and the nuclear magnetic quadrupole moment (MQM) [9–11]. According to the SM, the  $d_e$  is so small ( $<10^{-38}$  e cm [12]) that it cannot be experimentally observed. But many extensions of the SM predict the eEDM to be in the range of  $10^{-29}$ – $10^{-26}$  e cm [13] and interestingly the sensitivity of the modern eEDM experiment is also found to be in the same range. The best upper bound limit of eEDM ( $<1.3 \times 10^{-29}$  e cm) is recently obtained in the ThO-experiment carried out by the ACME collaboration [14]. It is well-known that the eEDM effect is strongly enhanced in heavy polar diatomic paramagnetic molecules due to their high internal effective electric field ( $E_{\text{eff}}$ ). In addition to the

eEDM, the S-PS neutral current coupling and the MQM-electron interaction are the other main possible sources of the permanent electric dipole moment (EDM) in paramagnetic systems. In the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd frequency shift experiment, the permanent EDM of the experimental candidate interacts with the electromagnetic field resulting in a shift in energy (i.e., frequency) that can be measured. To analyze this frequency shift in terms of the eEDM, the fundamental S-PS coupling constant ( $k_s$ ) and the nuclear magnetic quadrupole moment ( $M$ ), the accurate values of  $E_{\text{eff}}$ , scalar-pseudoscalar  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameter ( $W_s$ ), and the MQM interaction constant ( $W_M$ ), respectively, are required. Moreover, a large value of a molecular  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameter implies that the corresponding  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction in that molecule can be significant. But the value of  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  cannot be experimentally measured and can only be calculated using the highly accurate electronic structure theories. The  $\mathcal{P}$ ,  $\mathcal{T}$ -odd molecular parameters are also known as the “atom-in-compound” (AIC) [15] properties because the operators corresponding to these properties are heavily concentrated on nuclei or in atomic cores. Usually, the AIC properties strongly depend on the electronic configuration of a particular atom in a compound rather than on the chemical bond between atoms. The magnetic hyperfine structure (HFS) interaction constant is another important AIC property. These properties are very sensitive to the valence electron density (i.e., the wave function) near the nuclear region of the heavy atom and therefore, can be accurately calculated using an *ab initio* method that can efficiently incorporate both the relativistic and electron-correlation effects.

In the single-reference framework, although the Dirac-Hartree-Fock (DHF) method can treat the relativistic motion of electrons, it misses the correlation effects of electrons in an

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atom or a molecule. Therefore, post-DHF methods are necessary to incorporate the correlation effects of electrons. The many-body methods such as the configuration interaction (CI) [16], the Moller-Plesset perturbation theory (MBPT) [16], the coupled-cluster (CC) [16–19], etc., are widely used in the literature for the treatment of electron-correlation. It is worth mentioning that the multireference many-body theories are used to incorporate the static correlation effects. Nonetheless, for the efficient treatment of the dynamic electron correlation in many-electron systems the single-reference coupled-cluster (SRCC) method has been considered as one of the most suitable tools. Moreover, the properties of atoms and molecules can be calculated using either the energy-derivative method or the expectation-value approach within the SRCC framework. The SRCC method, usually being a nonvariational approach, does not satisfy the generalized Hellman-Feynman theorem. Also, the energy-derivative method and the expectation-value approach are not same in nonvariational framework [20,21]. The energy-derivative in the nonvariational model contains the corresponding expectation-value plus some additional terms, which leads to the fact that the property obtained by the energy-derivative technique is closer to that evaluated by the full CI method than the property value calculated using the expectation-value approach [22]. As stated above, the relativistic effect and the electron-correlation are the keys for the precise calculation of the AIC properties. Thus, for this purpose the relativistic single-reference coupled-cluster method could be a suitable tool as it can deal with both the effects of correlation and relativistic motion of electrons. The  $Z$ -vector method [22,23] is a popular energy-derivative approach to calculate the first-order properties of atoms and molecules. In recent times, Sasmal *et al.* [24] introduced the  $Z$ -vector technique into the four-component relativistic coupled-cluster realm and successfully employed the method to calculate various AIC properties of atoms, ions and molecules.

As mentioned above the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameters in polar heavy molecules are usually large in magnitude and thus, these molecules are always expected to be good candidates for the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd frequency shift experiments. However, the large value of  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameter in a molecule is not sufficient for the success of such an experiment. The experimental molecule must be easily polarizable to fully utilize the applied electric field. Usually, a molecule with small rotational constant and large dipole moment is easily polarizable in a spectroscopic experiment. But recently, Kozlov *et al.* [25] suggested an alternative route to carry out the eEDM experiment using heavy diatomic radicals. They showed that the less polar molecule such as HgH can be polarized easily in the matrix isolated nonspectroscopic solid-state experiment to measure the eEDM. Interestingly, the small dipole moment of the diatomic molecular radical is one of the important conditions to achieve higher sensitivity for the eEDM in the said nonspectroscopic solid-state experiment. It was argued that HgH can be easily trapped in the Ar-matrix of the cell size  $4.5 \text{ \AA}$  since the internuclear distance of the HgH molecule is  $1.7 \text{ \AA}$ . CdH is a molecule having similar characteristics as that of HgH. The dipole moment and internuclear distance of CdH is close to that of HgH. Thus, CdH can also be expected as a possible candidate for the nonspec-

troscopic solid-state experiment and hence, theoretical study of CdH in search of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd effects could be important. Recently, Berger and coworkers [26] performed a systematic study of the relativistic and chemical enhancements of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties in various diatomic radicals including ZnH, CdH, and HgH using a quasirelativistic approach within the framework of complex generalized Hartree-Fock (cGHF) or Kohn-Sham (cGKS). In that work, the periodic trend of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd effects was discussed in detail. However, it is worth mentioning that the calculations of  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties of molecules are often very difficult and challenging due to the strong correlations between the electrons. That is why a systematic study of the role of electron-correlation effects and its trend in the calculations of these properties is extremely important. Use of a more robust method, precisely speaking, a fully relativistic coupled-cluster method would be helpful for a better understanding of the said effects in the molecules. Therefore, in this work, we have calculated the  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  of CdH in its ground electronic ( $^2\Sigma_{1/2}$ ) state and studied the correlation trend in these properties using the  $Z$ -vector method in the domain of four-component relativistic coupled-cluster theory. The magnetic HFS constants of CdH are also calculated to estimate the accuracy of the employed method. We also compute the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd parameters of ZnH and HgH to see the trend of the calculated  $\mathcal{P}$ ,  $\mathcal{T}$ -odd molecular parameters in the group-12 monohydrides.

The structure of the paper is as follows. The important aspects of the theory of the calculated properties and those of 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. Finally, the conclusion of the present study is given in Sec. V. Atomic units are used explicitly in this article unless stated.

## II. THEORY

### A. One-electron property operators

The internal electric field ( $E_{\text{eff}}$ ) experienced by the unpaired electron can be defined by the following matrix element:

$$E_{\text{eff}} = |W_d \Omega| = \left| \langle \Psi_\Omega | \sum_j^n \frac{H_d(j)}{d_e} | \Psi_\Omega \rangle \right|, \quad (1)$$

where  $W_d$  is the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd constant for eEDM interaction,  $\Omega$  is the projection of total angular momentum on the internuclear axis ( $z$  axis) of the molecule,  $\Psi_\Omega$  is the wave function of the  $\Omega$  state, and  $n$  is the total number of electrons. The value of  $\Omega$  is  $1/2$  for the ground electronic ( $^2\Sigma_{1/2}$ ) state of CdH, ZnH, and HgH. And, the  $H_d$  in the above expression is the Hamiltonian for the interaction of the eEDM ( $d_e$ ) with the molecular electric field [27,28], which is given by

$$H_d = 2icd_e \gamma^0 \gamma^5 p^2, \quad (2)$$

where,  $c$  is the speed of light,  $\gamma$  are Dirac matrices, and  $p$  is the momentum operator.

The S-PS interaction constant,  $W_s$  can be evaluated from the following matrix element:

$$W_s = \left| \frac{1}{\Omega k_s} \langle \Psi_\Omega | \sum_j^n H_{\text{SP}}(j) | \Psi_\Omega \rangle \right|, \quad (3)$$

where  $k_s$  is known as the dimensionless nucleus-electron scalar-pseudoscalar coupling constant. This constant is defined as  $Zk_s = (Zk_{s,p} + Nk_{s,n})$ , where  $Z$  and  $N$  are the number of protons and neutrons, respectively. And,  $k_{s,p}$  and  $k_{s,n}$  are known as the electron-proton and electron-neutron coupling constant, respectively.  $H_{\text{SP}}$  is the interaction Hamiltonian for scalar-pseudoscalar(S-PS) nucleus-electron coupling [29], which is defined as follows:

$$H_{\text{SP}} = i \frac{G_F}{\sqrt{2}} Z k_s \gamma^0 \gamma^5 \rho_N(r), \quad (4)$$

where,  $G_F$  is the Fermi constant,  $Z$  is the nuclear charge (i.e., number of protons), and  $\rho_N(r)$  is known as the nuclear charge density normalized to unity.

The ratio of  $E_{\text{eff}}$  to  $W_s$  is known as  $R$  [30], which is very important to set the model independent limit of eEDM and fundamental S-PS nucleus-electron coupling constant. It is worth mentioning here that the  $R$  has a fixed value for a particular nucleus irrespective of the diatom [30]. Using  $R$  we can write the relation of independent  $d_e$  and  $k_s$  with experimentally determined  $d_e^{\text{expt}}$  as follows (for more details see Ref. [8]):

$$d_e + \frac{k_s}{2R} = d_e^{\text{expt}} \Big|_{k_s=0}. \quad (5)$$

Here  $d_e^{\text{expt}} \Big|_{k_s=0}$  is the eEDM limit obtained from the  $\mathcal{P}, \mathcal{T}$ -odd frequency shift experiment at the limit  $k_s = 0$ .

The Hamiltonian for the interaction of nuclear MQM with the magnetic field produced by electrons [10,27] is given by

$$H_{\text{MQM}} = -\frac{M}{2I(2I-1)} T_{ik} \frac{3}{2} \frac{[\vec{\alpha} \times \vec{r}]_i r_k}{r^5}, \quad (6)$$

where  $M$  is known as the nuclear magnetic quadrupole moment with components

$$M_{ik} = \frac{3M}{2I(2I-1)} T_{ik}, \quad (7)$$

$$T_{ik} = I_i I_k + I_k I_i - \frac{2}{3} \delta_{ik} I(I+1). \quad (8)$$

However, as shown in Ref. [31], for the subspace of  $\pm\Omega$ , the Eq. (6) reduces to

$$H_{\text{MQM}} = -\frac{W_M M}{2I(2I-1)} \vec{S}' \hat{T} \vec{n}, \quad (9)$$

where,  $\vec{n}$  and  $\vec{S}'$  are the unit vector along the molecular axis and the effective electron spin, respectively. The  $W_M$  in the above expression is known as the nuclear MQM interaction constant and is defined by the following matrix element:

$$W_M = \left| \frac{3}{2\Omega} \langle \Psi_\Omega | \sum_i^n \left( \frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^5} \right)_z r_z | \Psi_\Omega \rangle \right|. \quad (10)$$

The accuracy of the wave function used for the calculations of Eqs. (1), (3), and (10) can be estimated by comparing the theoretically calculated HFS interaction constant with the

available experimental value, because the HFS constant also depends on a precise wave function near the nuclear region. The parallel ( $A_{\parallel}$ ) and perpendicular ( $A_{\perp}$ ) components of the magnetic hyperfine structure constant of a molecule can be defined by the following matrix element:

$$A_{\parallel(\perp)} = \frac{\vec{\mu}_k}{I\Omega} \cdot \langle \Psi_\Omega | \sum_i^n \left( \frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_{z(x/y)} | \Psi_{\Omega(-\Omega)} \rangle, \quad (11)$$

where,  $\vec{\mu}_k$  is nothing but the magnetic moment of the nucleus  $k$ .

### B. Z-vector method in relativistic coupled-cluster singles and doubles framework

The SRCC wave function has an exponential form and is given as

$$|\Psi_{cc}\rangle = e^T |\Phi_0\rangle, \quad (12)$$

where  $\Phi_0$  is the Dirac-Hartree-Fock (DHF) determinant and  $T$  is known as the coupled-cluster excitation operator.  $T$  is defined as

$$T = T_1 + T_2 + \dots + T_N = \sum_n^n T_n, \quad (13)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} t_{ij\dots}^{ab\dots} a_a^\dagger a_b^\dagger \dots a_j a_i, \quad (14)$$

where  $i, j, (a, b, \dots)$  indices are the occupied (unoccupied) spinors,  $a_p^\dagger (a_p)$  is the creation (annihilation) operator for  $p$ th spinor, and  $t_{ij\dots}^{ab\dots}$  is the cluster amplitude corresponding to  $T_m$ . In coupled-cluster model with single and double excitation (CCSD),  $T = T_1 + T_2$ , and the unknown cluster amplitudes corresponding to  $T_1$  and  $T_2$  can be obtained by solving the following equations:

$$\langle \Phi_i^a | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | (H_N e^T)_c | \Phi_0 \rangle = 0, \quad (15)$$

where  $H_N$  is the normal ordered Dirac-Coulomb (DC) Hamiltonian. The subscript  $c$  represents connectedness that ensures the size-extensivity. Connectedness means that only the connected terms survive in the contraction between  $H_N$  and  $T$ . The DC Hamiltonian is defined as

$$H_{DC} = \sum_j \left[ -ic(\vec{\alpha} \cdot \vec{\nabla})_j + (\beta - \mathbb{1}_4)c^2 + V^{\text{nuc}}(r_j) + \sum_{k>j} \frac{1}{r_{jk}} \mathbb{1}_4 \right]. \quad (16)$$

Here,  $\alpha$  and  $\beta$  are the conventional Dirac matrices. Furthermore,  $\mathbb{1}_4$  is the  $4 \times 4$  identity matrix,  $j$  represents the electron and  $V^{\text{nuc}}(r_j)$  is the potential function for finite size nucleus, defined in terms of a Gaussian charge distribution.

Now, the correlation energy is obtained from the following equation:

$$E_{\text{corr}} = \langle \Phi_0 | (H_N e^T)_c | \Phi_0 \rangle. \quad (17)$$

The properties of many-electron atoms and molecules can be obtained by energy-derivative approach within the

TABLE I. Cutoffs for virtual spinors and basis sets used in our calculations.

Name	Nature	Basis		Virtual	
		Cd	H	Cutoff (a.u.)	Spinors
A	DZ	dyall.ae2z	cc-pCVDZ	500	157
B	TZ	dyall.ae3z	cc-pCVTZ	500	315
C	QZ	dyall.ae4z	cc-pCVQZ	500	513

SRCC framework. The Z-vector method [22] is a widely used energy-derivative approach, which has been recently extended into the relativistic coupled-cluster domain by Sasmal *et al.* [24]. In this approach, the energy derivative can be obtained by the following equation:

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_c | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda (O_N e^T)_c] | \Phi_0 \rangle, \quad (18)$$

where  $O_N$  is known as the derivative of normal ordered perturbed Hamiltonian with respect to external field of perturbation and  $\Lambda$  is an antisymmetrized de-excitation operator. This operator is given as

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots + \Lambda_N = \sum_n \Lambda_n, \quad (19)$$

with

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} \lambda_{ab\dots}^{ij\dots} a_i^\dagger a_j^\dagger \dots a_b a_a, \quad (20)$$

where  $\lambda_{ab\dots}^{ij\dots}$  is the amplitude corresponding to  $\Lambda_m$ . In the CCSD framework,  $\Lambda = \Lambda_1 + \Lambda_2$ . The explicit equations to solve the amplitudes of  $\Lambda_1$  and  $\Lambda_2$  are

$$\langle \Phi_0 | [\Lambda (H_N e^T)_c] | \Phi_i^a \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle = 0, \quad (21)$$

$$\begin{aligned} \langle \Phi_0 | [\Lambda (H_N e^T)_c] | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_c | \Phi_{ij}^{ab} \rangle \\ + \langle \Phi_0 | (H_N e^T)_c | \Phi_i^a \rangle \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle = 0. \end{aligned} \quad (22)$$

Once the amplitudes of  $\Lambda$  are known, the desired property can be obtained from the Eq. (18).

### III. COMPUTATIONAL DETAILS

We use a locally modified version of DIRAC10 [32] to solve the DHF equation and to generate the one- and two-electron integrals along with the necessary property integrals. The finite nucleus described by a Gaussian charge distribution is considered in our calculation [33]. The properties of interest are calculated using the Z-vector code developed in our group. We consider the bond length of CdH as 1.780 Å [34]. We have used the following basis sets: in the double-zeta: dyall.ae2z [35] for Cd, cc-pCVDZ [36] for H, in the triple-zeta (TZ) basis: dyall.ae3z [35] for Cd, and cc-pCVTZ [36] for H; in the quadruple-zeta (QZ) basis: dyall.ae4z for Cd, and cc-pCVQZ [36] basis for H. We correlate all the electrons and exclude the virtual spinors above a certain energy in the molecular calculations unless otherwise stated. The details of the basis sets used for CdH are given in Table I.

TABLE II. Molecular-frame dipole moment,  $\mu$  (in Debye), and the magnetic HFS constants (in MHz) of CdH.

Basis	$\mu$	$^{111}\text{Cd}$	
		$A_{\parallel}$	$A_{\perp}$
A	0.61	4010	3595
B	0.73	4198	3762
C	0.76	4253	3817
Expt. [34]		4358(35)	3966(3)

### IV. RESULTS AND DISCUSSION

We present the molecular dipole moment ( $\mu$ ) and parallel and perpendicular components of the HFS constant of CdH and compare our results with available experimental values [34] in Table II. The magnitude of the dipole moment and the HFS constant increases as we move to a higher basis (i.e., from A to C). This is expected since the inclusion of higher angular momentum basis functions can improve the configuration space. Our results of HFS constants are in good agreement with the available experimental values. However, the lowest deviation of the calculated HFS constants from the experimental values is obtained with the basis C (QZ, 500 a.u.). The  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameters of CdH with different basis sets are presented in Table III. The most reliable values (calculated using basis C) of  $E_{\text{eff}}$ ,  $W_s$ ,  $R$ , and  $W_M$  are 12.2 GV/cm, 14.0 kHz,  $210.7 \times 10^{18}/e$  cm, and  $0.82 \times 10^{33}$  Hz/e cm<sup>2</sup>, respectively. The  $\mathcal{P}$ ,  $\mathcal{T}$ -odd molecular parameters in CdH are significantly large, which means that the eEDM, S-PS nucleus-electron neutral current interaction and the interaction of the nuclear MQM with the magnetic field generated by electrons can contribute to the frequency shift in the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd experiment. One can see from the electronic structure calculation that CdH can be a possible candidate for the experimental search of “new physics” in the lepton-sector of matter. However, it may not be a choice for the MQM search since the isotopes of Cd having  $I > 1/2$  are very unstable.

We have mentioned earlier that the precise calculation of the AIC properties is not a trivial task due to the strong inter-electronic correlations. Therefore, it is important to investigate the systematic effects of the electron correlations and the virtual energy functions in the molecular calculations. To understand the correlation trend in the computed properties, we have performed two sets of calculations for CdH using the DZ basis (i.e., dyall.ae2z for Cd and cc-pCVDZ for H) at various cutoffs for the virtual spinors: first, correlating all the electrons and second, freezing the  $1s$ - $3d$  electrons (i.e., correlating only 19 outer-electrons). We summarize these results in Table IV.

TABLE III.  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction constants ( $W_s$  in kHz,  $E_{\text{eff}}$  in GV/cm,  $R$  in  $10^{18}/e$  cm, and  $W_M$  in  $10^{33}$  Hz/e cm<sup>2</sup> unit) of CdH.

Basis	Nature	$W_s$	$E_{\text{eff}}$	$R = E_{\text{eff}}/W_s$	$W_M$
A	DZ	11.3	10.3	220.4	0.76
B	TZ	13.3	11.9	216.3	0.81
C	QZ	14.0	12.2	210.7	0.82

TABLE IV. The AIC properties of CdH at different cutoffs of virtual spinors (Basis: dyall.ae2z for Cd, cc-pCVDZ for H).

Virtual cutoff (a.u.)	Spinor		$A_{\parallel}$ (MHz)	$W_s$ (kHz)	$E_{\text{eff}}$ (GV/cm)	$W_M$ ( $10^{33}$ Hz/e cm $^2$ )
	Occupied	Virtual				
50	49	121	3916	10.93	10.03	0.74
100	49	139	3976	11.13	10.21	0.75
200	49	145	3979	11.19	10.27	0.76
500	49	157	4010	11.25	10.31	0.76
1000	49	175	4029	11.31	10.36	0.76
No cutoff	49	229	4049	11.40	10.46	0.77
No cutoff <sup>a</sup>	49	229	4050	11.43	10.24	0.77
50	19	121	3676	10.54	9.67	0.71
100	19	139	3681	10.55	9.68	0.71
200	19	145	3681	10.55	9.68	0.71
500	19	157	3682	10.56	9.69	0.71
1000	19	175	3682	10.56	9.69	0.71
No cutoff	19	229	3682	10.56	9.69	0.71

<sup>a</sup>Using Dirac-Coulomb-Gaunt Hamiltonian.

It is seen from this table that the magnitude of the  $A_{\parallel}$ ,  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  increases with the number of virtual spinors in the given basis set for the all-electron correlation case. This is because, as the number of virtual spinors (or the cutoff for virtual spinors) increases, the correlation space expands. In a larger correlation space, the electrons can be correlated more efficiently. However, a different trend is observed in the frozen-core calculations. In this case, the computed properties slightly enhance as we increase the cutoff of virtual spinors from 50 to 500 a.u., but further increase of the virtual cutoff does not enhance the magnitude of the properties anymore. This means that the effect of high-energy virtual functions is more prominent when all the electrons are explicitly correlated in the molecular calculations. From the Table IV, it is also observed that the inner-core ( $1s$ - $3d$ ) electron correlations contribute significantly to the AIC properties in the CdH molecule.

In the calculations of the AIC properties of CdH, we have not incorporated many important effects. As a result, there could be some errors in our calculations. The possible errors in our calculation may be caused by the following reasons: (i) missing of higher-order relativistic effects (the Breit/Gaunt interaction), (ii) absence of higher-order correlation effects, (iii) incompleteness of basis set, and (iv) restriction of correlation space due to cutoff used for the virtual orbitals. The  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties under study usually depend on the electron density of the valence electron near the nuclear region and these properties are not very sensitive to the retardation and magnetic effects [37,38]. However, we have calculated the mean-field Gaunt correction with DZ basis (see Table IV) employing the DIRAC program package which is found to be around 0.3% and 2.2% for  $W_s$  and  $E_{\text{eff}}$ , respectively, and negligible for  $W_M$ . However, the error due to the absence of higher-order electron correlation effects can be evaluated by comparing our values with the CCSD partial triples [CCSD(T)] or the full configuration interaction (FCI) results. But the CCSD(T) or FCI calculation for CdH is too expensive to perform in the present work. However, in literature [7,39], this error was reported as around 3.5% for some other but similar heavy diatomics. Therefore, we

also expect a similar magnitude of the error due to missing higher-order correlation effects in CdH. Similarly, another possible error yielded by basis set incompleteness can be assessed by comparing our results obtained using the A (DZ) and B (TZ) basis sets or the B (TZ) and C (QZ) basis sets. From Tables III and IV, it is observed that while going from the DZ to the TZ basis, the values of  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  are changed by 13.4%, 15.4%, and 6.2%, respectively, and while going from the TZ to the QZ basis, these values are changed by 2.5%, 5.0%, and 1.2%, respectively. Thus, the error due to basis set incompleteness would not exceed 2.5%, 5.0%, and 1.2% for our most reliable results of  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$ , respectively. It is also interesting to observe that the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd S-PS nucleus-electron interaction parameter is more sensitive to the higher angular momentum basis functions than the  $E_{\text{eff}}$  and  $W_M$ . Furthermore, we have restricted the correlation space by excluding the virtual spinors with energy more than 500 a.u. in the calculations of our most reliable results. It may yield some amount of error to our results. To decrease this type of error, we need to consider the higher energy virtual spinors in our calculation which will be very much expensive and is beyond the scope of the present study. However, we have performed the calculations for the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties using the DZ basis (i.e., dyall.ae2z for Cd and cc-pCVDZ for

 TABLE V.  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties of CdH as a function of bond length. (Basis used: dyall.ae2z for Cd and cc-pCVDZ for H; cutoff for virtual spinors = 500 a.u.)

Bond length (Å)	$E_{\text{eff}}$ (GV/cm)	$W_s$ (kHz)	$W_M$ ( $10^{33}$ Hz/e cm $^2$ )
1.580	10.43	11.45	0.760
1.680	10.43	11.41	0.766
1.728	10.39	11.35	0.765
1.780 ( $r_e$ )	10.32	11.25	0.762
1.834	10.21	11.13	0.756
1.880	10.09	10.99	0.749
1.980	9.76	10.61	0.726

TABLE VI. Comparison of  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction constants ( $E_{\text{eff}}$  in GV/cm,  $W_s$  in kHz, and  $W_M$  in  $10^{33}$  Hz/e cm<sup>2</sup> unit) in ZnH, CdH and HgH. (Basis used: dyall.ae3z for Zn, Cd, and Hg; cc-pCVTZ for H. Cutoff for virtual spinors = 500 a.u. Bond lengths for ZnH and HgH are 1.595 Å [34] and 1.766 Å [34], respectively.)

Molecule	$E_{\text{eff}}$		$W_s$		$W_M$	
	DHF	Z vector	DHF	Z vector	DHF	Z vector
ZnH	1.7	2.13	1.4	1.83	0.21	0.27
CdH	9.5	11.91	10.3	13.29	0.65	0.81
HgH	106.8	123.37	241.2	284.34	2.94	3.21 [42]

H) at various cutoffs for the virtual spinors and summarised the results in Table IV from which we can estimate this error. The high-lying virtual spinors with energy more than 500 a.u. contribute 1.3% for S-PS interaction constant, 1.4% for effective electric field and 1.3% for MQM interaction constant. In addition to the above-mentioned sources of error, the neglect of vibrational effects in the molecular calculation may also add some amount of uncertainty to our results. The vibrational effects can be taken into account by doing a vibrational averaging of the calculated properties, but it is beyond the scope of the present study. As per our understanding, the vibrational effects may be important in a case when the molecular properties strongly depend on the internuclear distance of the molecule. In Table V, we summarize the results of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties of CdH at different internuclear distances. From this table, we observe that for a change of around 3% in the internuclear distance from the equilibrium bond length ( $r_e$ ), the change in the values of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd constants is within 1%. This means that the studied properties of CdH do not have a strong dependence on the internuclear distance especially in the vicinity of  $r_e$ . So, we expect that the vibrational correction to the calculated AIC properties of CdH would not be significant. Nevertheless, despite the possible cancellations of errors due to various effects, we assess that the total uncertainty in our most reliable result is within 10%.

We present the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameters of ZnH and HgH and compare them with those of CdH in Table VI to see the trend of the calculated properties in the monohydrides

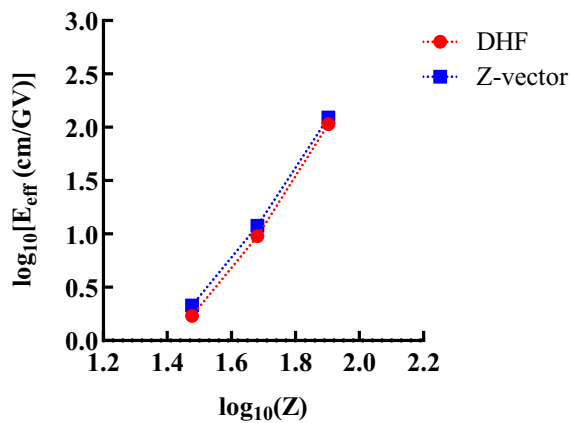


FIG. 1. Effective electric field  $E_{\text{eff}}$  experienced by the unpaired electron in group-12 monohydrides.

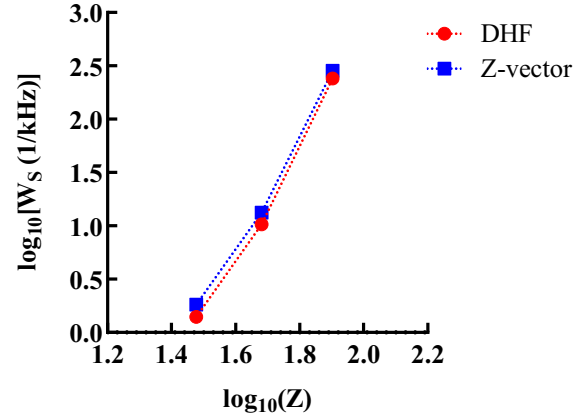


FIG. 2. S-PS nucleus-electron coupling parameter  $W_s$  in group-12 monohydrides.

of group-12 elements. The  $\mathcal{P}$ ,  $\mathcal{T}$ -odd properties usually scale with nuclear charge  $Z$  of the heavy atom, and as shown in the Table VI, there is a monotonic increase in these properties from ZnH to HgH through CdH. We also plot  $\log_{10}[E_{\text{eff}} \text{ (cm/GV)}]$ ,  $\log_{10}[W_s \text{ (1/kHz)}]$ , and  $\log_{10}[W_M \text{ (} 10^{-33} \text{ e cm}^2 \text{/Hz)}]$  against  $\log_{10}(Z)$  in Figures 1–3, respectively. One can see the detailed discussion on the scaling of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd effects with  $Z$  given in Ref. [26]. We see from Table VI that the correlation contributions to  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  in ZnH are around 20%, 23%, and 22%, respectively. In CdH, electron correlation effects contribute around 20%, 22%, and 20% to  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$ , respectively, whereas the said contributions are around 13%, 15%, and 8% to  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$ , respectively, in HgH. The DHF contribution to the total value of each molecular parameter of the group-12 monohydrides is significantly large in comparison to the electron-correlation contribution. One should also note that the said contribution in HgH is much higher than that in ZnH and CdH. The weak screening effects of the  $3d/4d/5d$  electrons in these diatomic molecules can probably result in a significantly large DHF contribution to the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd interaction parameters [40]. Further, in Ref. [41], the reason for the high value of the  $\mathcal{P}$ ,  $\mathcal{T}$ -odd molecular parameter in HgH was discussed using the Mulliken population analysis and the orbital interaction

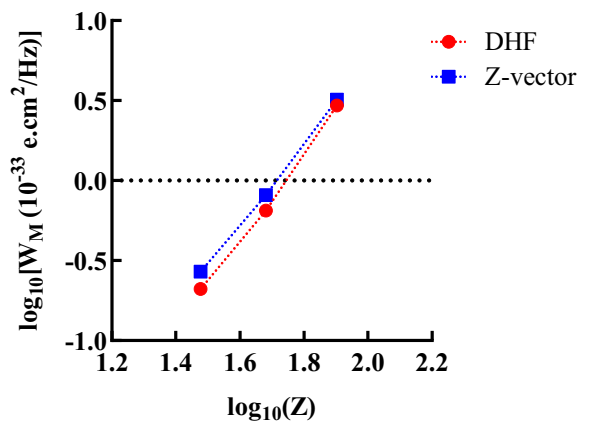


FIG. 3. Nuclear MQM-electron interaction parameter  $W_M$  in group-12 monohydrides.

theory. The authors of the Ref. [41] claimed that the large  $s$ - $p$  mixing in the singly occupied molecular orbital increases the effective electric field in a molecule. Thus, large  $s$ - $p$  mixing may be one of the reasons for the exceptionally high magnitude of the  $\mathcal{P}, \mathcal{T}$ -odd molecular parameters in HgH. It is worth mentioning that explicit study of the  $\mathcal{P}, \mathcal{T}$ -odd effects in the HgH molecule using the relativistic coupled-cluster method has already been done in Refs. [8,42]. Although one would prefer HgH to CdH for the  $\mathcal{P}, \mathcal{T}$ -odd frequency shift experiment due to the much higher values of the  $\mathcal{P}, \mathcal{T}$ -odd constants in HgH than those in CdH, the possibility of CdH as a candidate for the same cannot be ruled out.

## V. CONCLUSION

We have studied the  $\mathcal{PT}$  violating properties in the CdH molecule using the  $Z$ -vector method in the four-component relativistic coupled-cluster framework and reported the corresponding molecular parameters. The value of  $E_{\text{eff}}$ ,  $W_s$ , and  $W_M$  in CdH reported by us are 12.2 GV/cm, 14.0 kHz and 0.82  $\times 10^{33}$  Hz/e cm<sup>2</sup>, respectively, which are sufficiently large to be

a possible candidate for the  $\mathcal{P}, \mathcal{T}$ -odd experiment to reveal new physics beyond the standard model. We also compute the magnetic hyperfine structure constants of CdH and compare them with available experimental results to check the correctness of our calculations. Our reported HFS results are in good agreement with the corresponding experimental values. Our study shows that the correlation of the core-electrons is significantly important for the precise calculation of the AIC properties and the effect of the high-energy virtual spinors is more prominent in all-electron correlation treatment. Moreover, the  $\mathcal{P}, \mathcal{T}$ -odd interaction coefficients monotonically increase with the nuclear charge ( $Z$ ) of the heavy atom in the monohydrides of group-12 elements.

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