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Mercury monohalides are promising candidates for electron electric dipole moment searches. This is due to their extremely large values of effective electric fields, besides other attractive experimental features. We have elucidated the theoretical reasons of our previous work. We have also presented a detailed analysis of our calculations, by including the most important of the correlation effects' contributions. We have also analyzed the major contributions to the effective electric field, at the Dirac- Fock level, and identified those atomic orbitals' mixings that contribute significantly to it.

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I. INTRODUCTION

The electron electric dipole moment (eEDM) is a consequence of parity and time-reversal violations [1–4]. It is an important non-accelerator probe of physics beyond the Standard Model [5, 6]. Ibrahim et al make a case that the eEDM can be a sensitive probe of PeV physics [7]. There is a large body of work on eEDMs and CP violation in supersymmetric models, for example, see Ref. [8]. A knowledge of eEDM also provides insights into the baryon asymmetry in the Universe (BAU) [9, 10]. One of the Sakharov conditions [11], which gives the necessary prerequisites for BAU, is CP violation. If the CPT theorem [12] is true, then T violation must correspond to CP violation, to preserve CPT symmetry. This correspondence is what connects the two seemingly disparate phenomena, eEDMs and BAU. The importance of this connection is demonstrated in the work by Fuyoto et al [10], who argue that the relationship between the BAU-related CP violations and eEDMs are important for the test of the electroweak baryogenesis (EWBG) scenario. They proceed to show that if BAU-related CP violation does exist, then the EWBG region might be entirely verified by the future eEDM experiments.

Heavy polar diatomic molecules are currently the preferred candidates to look for a shift in the energy of a molecule in a particular state, due to the presence of the eEDM (For example, Ref. [13]). The electric field corresponding to that shift in energy, with the proportionality constant being the eEDM, is called the effective electric field, E_{eff}. It is the electric field that an electron experiences, due to all other electrons and nuclei in the molecule [14]. These calculations warrant a relativistic treatment to compute this quantity, as E_{eff} completely vanishes in the non relativistic limit [15].

We had calculated the effective electric fields of mercury monohalides and identified them as promising candidates for eEDM searches [16]. The main thrust of this work is to elaborate on the theoretical aspects of our previous one [16]. In particular, we analyze and elucidate the contributions to the effective electric fields, at the Dirac-Fock and correlation levels. We employ a relativistic coupled cluster method, for our computations.

II. THEORY

The eEDM Hamiltonian, H_{eEDM}, is given by

$$H_{eEDM} = -d_e \sum_{j=1}^{N_e} \beta \vec{\sigma}_j . \vec{E}_{intl,j} \qquad (1)$$

d_e is the eEDM. The summation is over the number of electrons in the molecule, N_e. β is one of the Dirac matrices, $\vec{\sigma}$ refers to the Pauli matrices, and $\vec{E}_{intl}$ is the internal electric field.

The shift in energy due to eEDM is given by

$$\Delta E = \langle \psi | H_{eEDM} | \psi \rangle \qquad (2)$$
$$= -d_e E_{eff} \qquad (3)$$

Here, $|\psi\rangle$ is the ground state wavefunction of mercury monohalides. Comparing equations (1) and (3), we obtain the following expression for E_{eff}

$$E_{eff} = \langle \psi | \sum_{j=1}^{N_e} \beta \vec{\sigma}_j . \vec{E}_{intl,j} | \psi \rangle \qquad (4)$$

To obtain the wavefunction, we employ a fully relativistic coupled cluster method (RCCM). The wavefunction is given by

$$|\psi\rangle = e^T |\Phi_0\rangle \qquad (5)$$

T is called the cluster operator. $|\Phi_0\rangle$ is the Dirac Fock (DF) wave function. We use the relativistic coupled cluster singles and doubles (CCSD) approximation in our work. More details about the relativistic CCSD method and its salient features can be found in Ref.s [14, 17].

The expectation value of any operator, O, in an RCCM, can be expressesd as [18, 19]:

$$\langle O \rangle = \frac{\langle \psi | O | \psi \rangle}{\langle \psi | \psi \rangle}$$
$$= \langle \Phi_0 | e^{T\dagger} O_N e^T | \Phi_0 \rangle_C + \langle \Phi_0 | O | \Phi_0 \rangle \quad (6)$$

The subscript, 'N' means that the operator is normal ordered [20], and 'C' means that each of the terms are connected [21]. Therefore,

$$E_{eff} = \langle \Phi_0 | e^{T\dagger} H^{eff}_{eEDM,N} e^T | \Phi_0 \rangle_C + \langle \Phi_0 | H^{eff}_{eEDM} | \Phi_0 \rangle \,(7)$$
$$\approx \langle \Phi_0 | (1 + T_1 + T_2)^\dagger H^{eff}_{eEDM,N} (1 + T_1 + T_2) | \Phi_0 \rangle_C$$
$$+ \langle \Phi_0 | H^{eff}_{eEDM} | \Phi_0 \rangle \quad (8)$$

We replace the usual eEDM operator by an effective one [14], H^{eff}_{eEDM}, given by

$$\frac{2ic}{e} \sum_{j=1}^{N_e} \beta \gamma_5 p_j^2 \quad (9)$$

where c is the speed of light, e is the charge of the electron, N_e refers to the number of electrons in the molecule, β is one of the Dirac matrices, γ_5 is the product of the Dirac matrices, and $\mathbf{p}_j$ is the momentum of the jth electron. This is done, so that the Hamiltonian is rewritten in terms of only one-body operators. The term $\vec{E}_{intl}$ (from equation (4)) has a two-body operator in it. Although it can be calculated, in principle, it is very time demanding and complicated. Using an effective one-body operator simplifies the computations by a significant amount. Further details can be found in Ref. [14], and the references therein. We consider only the linear terms in the expansion of e^T, both on the bra and the ket sides, in the first term of equation (6), as shown in equation (8). This is a reasonable approximation, and we can see this from the accuracy of our results from our previous works, where we compare them with experimental values [14, 17, 22, 23]. This approximation, hence, not only saves computational cost by only taking into account only the linear terms, but also provides very accurate results.

Since the dominant contribution to E_{eff} is at the DF level [16], we analyze the terms that constitute it. The contribution, E^{DF}_{eff}, can be rewritten as:

$$E^{DF}_{eff} = \langle \Phi_0 | H^{eff}_{eEDM} | \Phi_0 \rangle$$
$$= \sum_{i}^{MO} \langle \varphi_i | h^{eff}_{eEDM} | \varphi_i \rangle$$
$$= \langle \varphi_v | h^{eff}_{eEDM} | \varphi_v \rangle$$
$$= \frac{4ic}{e} \sum_{k=1}^{NB} \sum_{l=NB+1}^{2NB} C_k^{*S} C_l^L \langle \chi_{v,k}^S | p^2 | \chi_{v,l}^L \rangle \quad (10)$$

Here, φ_v refers to the singly occupied molecular orbital (SOMO). h^{eff}_{eEDM} is the single particle effective eEDM operator. Summation over the number of molecular orbitals (MO) is indicated by i, while summation over the number of large and small components of the basis sets are given by k and l, respectively. NB refers to the number of large component basis funcrtions. C_k and C_l refer to the coefficients, obtained by solving the DF equations, and their superscripts L and S stand for large and small components respectively. The χs refer to the atomic orbitals (basis sets) of the constituent atoms. The mixing between large and small components is due to the fact that the eEDM operator is off-diagonal. Only the SOMO survives in the expression for E^{DF}_{eff}, because the remaining terms cancel out. This can be understood in the following way:

$$\sum_{i}^{MO} \langle \varphi_i | h^{eff}_{eEDM} | \varphi_i \rangle = \sum_{i'}^{(MO-1)/2} [\langle \varphi_{i'} | h^{eff}_{eEDM} | \varphi_{i'} \rangle$$
$$+ \sum_{\bar{i}'}^{(MO-1)/2} \langle \varphi_{\bar{i}'} | h^{eff}_{eEDM} | \varphi_{\bar{i}'} \rangle]$$
$$+ \langle \varphi_v | h^{eff}_{eEDM} | \varphi_v \rangle \quad (11)$$

In the above expression, we have decomposed the left hand side into three terms. The first and the second summation terms on the right hand side denote the contributions from the doubly occupied orbitals in the Kramers pairs, $\varphi_{i'}$ and $\varphi_{\bar{i}'}$. The third term is the contribution from SOMO. The Kramers pair orbitals are related by the time reversal operator (τ) [24]:

$$|\varphi_{\bar{i}'}\rangle = \tau |\varphi_{i'}\rangle \quad (12)$$
$$-|\varphi_{i'}\rangle = \tau |\varphi_{\bar{i}'}\rangle \quad (13)$$

Therefore,

$$\langle \varphi_{\bar{i}'} | h^{eff}_{eEDM} | \varphi_{\bar{i}'} \rangle = \langle \varphi_{i'} | \tau^\dagger h^{eff}_{eEDM} \tau | \varphi_{i'} \rangle$$
$$= -\langle \varphi_{i'} | h^{eff}_{eEDM} | \varphi_{i'} \rangle \quad (14)$$

Hence, the first two terms in equation (11) cancel out pairwise, and only the SOMO remains.

III. RESULTS AND DISCUSSIONS

In this section, we present the method of calculations used in this work, followed by a detailed discussion of the results. We used and modified the UTChem code [25], for the DF and AO (atomic orbital) to MO integral transformations [26]. We performed the CCSD calculations in the Dirac08 program [27].

The details of the basis sets are given in Table I (uncontracted [14], kinetically balanced [24] Gaussian Type Orbitals (GTOs), cc-pV DZ and TZ for F, Cl and Br [28], Dyall's basis for I [29], and Dyall's c2v and c3v basis sets for Hg [29]). We did not freeze any of our occupied orbitals. We chose the following bond lengths (in Angstroms): HgF (2.00686) [30], HgCl (2.42), HgBr (2.62), HgI (2.81) [31].

Atom	Basis (DZ)	Basis(TZ)
Hg	22s,19p,12d,9f,1g	29s,24p,15d,11f,2g
F	9s,4p,1d	10s,5p,2d,1f
Cl	12s,8p,1d	15s,9p,2d,1f
Br	14s,11p,6d	20s,13p,9d,1f
I	21s,15p,11d	28s,21p,15d

TABLE I. Summary of the basis sets employed in our calculations.

Term	HgF	HgCl	HgBr	HgI
DF	104.25	103.57	97.89	96.85
$H_{\mathrm{EDM}}^{\mathrm{eff}}T_1+$ cc	20.16	19.34	22.18	24.78
$T_1^{\dagger}H_{\mathrm{EDM}}^{\mathrm{eff}}T_1$	-3.91	-3.58	-4.07	-4.77
$T_1^{\dagger}H_{\mathrm{EDM}}^{\mathrm{eff}}T_2+$ cc	0.44	0.194	-0.2	-0.30
$T_2^{\dagger}H_{\mathrm{EDM}}^{\mathrm{eff}}T_2$	-5.52	-5.96	-6.5	-7.26
Total	115.42	113.56	109.29	109.30

TABLE II. Contributions, from the individual terms, to the effective electric field of HgX. cc refers to complex conjugate, of the term that it accompanies.

Table II shows the terms from equation (8), and also the total E_{eff}, for HgX. In our previous work, we had performed this analysis for only HgF. Extending it to all HgX enables us to study the trends in E_{eff}, for these molecules. Also, in our previous work, we had identified HgBr as a promising candidate, among the HgX molecules. Hence, theoretical details about HgX other than HgF become important. In the notation used in the Table, $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$, for example, actually refers to $\langle\Phi_0|\{H_{\mathrm{eEDM}}^{\mathrm{eff}}\}T_1|\Phi_0\rangle_C$, where the curly brackets refer to a normal-ordered operator. This is done for the purpose of brevity. Note that the $\langle\Phi_0|\{H_{\mathrm{eEDM}}^{\mathrm{eff}}\}|\Phi_0\rangle_C$ is zero, since the effective eEDM operator is normal ordered [22]. The $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_2$ term, and its complex conjugate, are zero, due to the Slater-Condon rules [20]. Hence, we are left with seven non-zero terms.

The DF term is the largest, and it decreases from HgF to HgI. Correlation effects account for about 9 percent of the total effective field. This indicates that for these molecules, both E_{eff} and the amount of correlation does not significantly vary with Z of the lighter, halide atom. Among the correlation terms, the $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$ term is the largest. The second and the third largest correlation contributions come from the $T_2^{\dagger}H_{\mathrm{eEDM}}^{\mathrm{eff}}T_2$ term, and $T_1^{\dagger}H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$ term. Their effect is to reduce E_{eff}. The overall values of E_{eff} decrease from HgF to HgBr. HgBr and HgI have almost the same values of E_{eff}, although the DF value of HgI is smaller in comparison with HgBr. This can be understood from the fact that the difference between the $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$ term, and the $T_1^{\dagger}H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1 + T_2^{\dagger}H_{\mathrm{eEDM}}^{\mathrm{eff}}T_2$ terms is larger for HgI.

We shall remark briefly about how the correlation trends vary in the E_{eff}s of HgX, as compared to those in our previous and ongoing works. In our previous work on the PDM of SrF [17], and subsequently on the PDMs of the other alkaline earth monofluorides (AEMs) [22], we had performed the same analysis. Although E_{eff} and PDM are different properties, they do share similarities, for example, both the properties depend on the mixing of orbitals of opposite parity. Hence, it is worthwhile to check if there are any similarities in their correlation trends. We first compare the correlation trends between the E_{eff} of HgX and the PDMs of the AEMs. Both of them are systems with one unpaired electron, but we see that in AEMs, while correlation can decrease (for example, BeF, by around 20 percent) or increase (for example, BaF, by around 20 percent) the PDM, the effect of correlation on the E_{eff}s of HgX is almost the same throughout, from HgF to HgI. The PDMs of HgX follow an entirely different trend, where the correlations decrease the PDM drastically [32]. We now compare the correlations in the E_{eff}s of HgX with those in YbF, the candidate that currently sets the second best limit on eEDM, and RaF, a promising candidate for eEDM experiments. In all the HgX molecules, correlations account for about ten percent. In YbF, the correlations account for about twenty percent [14], while in RaF [33], it is close to thirty percent. Again, all of these systems have one unpaired electron, and their heavier atoms have atomic numbers fairly close to one another, but their effective fields and their correlation effects are very different. In HgI, for example, the correlation effects are ten percent, owing to the fact that nearly half of the $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$ term is cancelled out by the other correlation terms. In RaF, this is not so. In fact, the $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$ term adds to about 20 GV/cm, and the rest close to -0.5 GV/cm. The values that we finally obtain are a consequence of several cancellations at work, among the various DF and the correlation terms. We shall attempt to understand further these cancellations for HgX in the rest of this paper. This brief discussion illustrates that further detailed theoretical studies are required to understand better the correlation effects and trends, of these class of polar molecules.

Figure I shows some of the dominant Goldstone diagrams involved in the expectation value expression, given by equation (8), specifically the DF, the $H_{\mathrm{eEDM}}^{\mathrm{eff}}T_1$,

the $T_1^\dagger H_{\text{eEDM}}^{\text{eff}} T_1$ term, the direct counterparts of the $T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_2$, and the $T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_2$ terms. The conjugate diagrams are not given, since they give the same result.
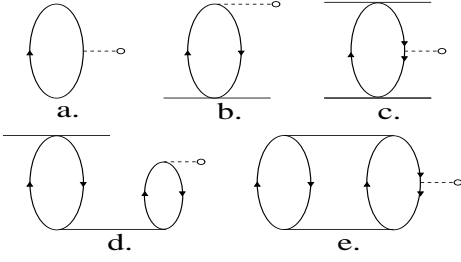

FIG. 1. Goldstone diagrams for E_{eff}: a. DF term, b. $H_{\text{eEDM}}^{\text{eff}} T_1$, c. the $T_1^\dagger H_{\text{eEDM}}^{\text{eff}} T_1$ term, d. Direct diagrams of the $T_1^\dagger H_{\text{eEDM}}^{\text{eff}} T_2$ term and the $T_2^\dagger H_{\text{eEDM}}^{\text{eff}} T_2$ term, respectively.

The physical interpretation of these diagrams are discussed in detail in another work on PDMs [22]. For the sake of completeness, we choose a representative diagram, $H_{\text{eEDM}}^{\text{eff}} T_1$, to explain its physical significance. We choose this diagram, since it contributes the most to the effective electric field. This term can be expanded as

$$\sum_{i,a} [\langle \varphi_i | \{h_{\text{eEDM}}^{\text{eff}}\} | \varphi_a \rangle \langle \varphi_a | t | \varphi_i \rangle]_C \qquad (15)$$

where the summation is over i and a, where i refers to the occupied orbitals (holes), and a to the virtual orbitals (particles). We obtain this expression, if we apply the Slater-Condon rules to the original expression, $\langle \Phi_0 | \{H_{\text{eEDM}}^{\text{eff}}\} T_1 | \Phi_0 \rangle_C$. Mathematically, the $H_{\text{eEDM}}^{\text{eff}} T_1$ term represents an all-order residual Coulomb interaction, resulting in an electron from an occupied orbital, i, being excited to a virtual, a, and then falling back into the same state, i, due to the interaction of the particle with the eEDM. This diagram represents several correlation effects, like the Brueckner pair correlation (BPC) [20], among others, but is not obvious from the coupled cluster diagram, since the T_1 part embodies in it the residual Coulomb interaction, to all orders of perturbation.

Table III presents the various contributions to the DF value of E_{eff}, due to the mixing between various orbitals (or basis sets) (equation (10)), at the TZ level. We have not presented the analysis for the DZ basis sets, since TZ is closer to the actual wave function, and the results from both the basis sets show the same trend. In the second column, $s - p_{1/2}$, for example, is actually a shorthand for $\sum_s \sum_{p_{1/2}} C_s^{*S} C_{p_{1/2}}^L \langle \chi_{v,s}^S | p^2 | \chi_{v,p_{1/2}}^L \rangle$. The first summation is over all the small component basis sets of the s angular momentum function, and the second over the large component basis sets of the $p_{1/2}$ angular momentum function. The mixing between the same parity orbitals is zero, and hence, those terms that contain matrix elements between s and d, for example, are ruled out. Only s, $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, $d_{5/2}$, and $f_{5/2}$ orbitals for

Hg, and s and $p_{1/2}$ for X, have been considered in equation (10), since the terms involving the mixing between other orbitals contribute negligibly to E_{eff}^{DF}. This can also be recognized from the difference between the rows labelled, 'Total', which gives the sum of the mixings associated with the orbitals considered, and 'DF', which gives the total DF contribution. The difference between the two decrease from F to Br.

The combined $s - p_{1/2}$ and $p_{1/2} - s$ contribution is clearly the highest among all others, contributing to over hundred percent of the total DF value of E_{eff} in all cases, except HgI. The 'anomaly' in HgI is due to the halide atom's contribution becoming important.

We observe that the absolute magnitude of all the terms for Hg decreases from F to I. However, in X, we see the opposite trend. In fact, for HgI, the contribution from X increases the effective field by over 2.5 GV/cm.

The angular momentum functions are strictly not atomic orbitals, but the terms from the basis sets that we employ. Hence, we cannot, from our results alone, deduce those principal quantum numbers that contribute significantly. However, we can intuitively guess that the major contribution is from the 6s and the virtual $6p_{1/2}$ orbitals of the Hg atom, since they lie close in energy, and their radial overlap is large. Moreover, we can expect the matrix elements of the eEDM operator between these opposite parity orbitals to be large.

The importance of $s - p_{1/2}$ and $p_{1/2} - s$ mixing of the heavier atom in the E_{eff} of HgF has been understood in the past, for example, Ref.s [34]. We shall compare our results with the previous ones later in this manuscript. In our work, we have taken into account not only the $s - p_{1/2}$ and $p_{1/2} - s$ mixing, but also that of the other orbitals of both the atoms, and then demonstrate that it is the $s - p_{1/2}$ mixing of the heavier atom that dominates. In the Table, we have only shown the $s - p_{1/2}$ and $p_{1/2} - s$ mixing of the lighter atom, but that is because we found the other mixings to be negligibly small. Also, note that our analysis is not only for HgF, but for the heavier mercury monohalides too. For example, in HgI, the 'lighter' atom, iodine, is sufficiently heavy. In spite of that, we see that the $s - p_{1/2}$ and $p_{1/2} - s$ mixing from I is surprisingly small.

Finally, we observe that not only the magnitude of the $s - p_{1/2}$ and the $p_{1/2} - s$ mixings (of the heavier atom) are large, but so is the remainder when these terms cancel each other's contributions. This illustrates the importance of cancellations that occur in ab initio calculations. In the case of iodine (in HgI), the two terms themselves are non-negligible, but they cancel each other out, leaving behind a very small contribution to the DF E_{eff} from the 'lighter' atom.

Atom	Mixing	HgF	HgCl	HgBr	HgI
Hg	$s - p_{1/2}$	-266.29	-262.07	-249.39	-242.34
Hg	$p_{1/2} - s$	373.37	367.74	349.42	339.56
Hg	$p_{3/2} - d_{3/2}$	31.22	25.22	21.84	20.99
Hg	$d_{3/2} - p_{3/2}$	-32.26	-26.35	-22.48	-21.84
Hg	$d_{5/2} - f_{5/2}$	-0.91	-0.51	-0.39	-0.33
Hg	$f_{5/2} - d_{5/2}$	0.92	0.52	0.4	0.33
X	$s - p_{1/2}$	-2.78	-4.85	-10.58	-17.19
X	$p_{1/2} - s$	2.79	4.92	11.17	19.87
Total:		106.06	104.62	99.99	99.05
DF		105.47	104.03	99.55	98.99
	$s-p_{1/2}$ and $p_{1/2}-s$	107.08	105.67	100.03	97.22

TABLE III. Summary of the DF results, of the contributions from various orbitals' mixings, at the TZ level

We shall now attempt to explain why the $H_{\text{eEDM}}^{\text{eff}}T_1$ term is large, among the correlation terms. The DF contribution dominates among the others, due to the significantly high difference between the large values of $s-p_{1/2}$ and $p_{1/2}-s$ of the Hg atom (the notation is same as that in Table III). We wish to reiterate that s is an occupied orbital, while $p_{1/2}$ is a virtual. Now, let us focus only on the matrix elements. Their values are several orders larger than their corresponding coefficients. These large matrix elements, of the form,$\langle o|h_{\text{eEDM}}^{\text{eff}}|v\rangle$ (where we abbreviate occupied orbitals as, 'o', and virtual as 'v'), also occur in the expression for $H_{\text{eEDM}}^{\text{eff}}T_1$ (and hence it also contains matrix elements between s and $p_{1/2}$), except that $H_{\text{eEDM}}^{\text{eff}}T_1$ has accompanying it a t_1 amplitude, which indicates the "weight" associated with a one-hole one-particle excitation. The t amplitudes are like probability amplitudes, and thereby lesser than one always. Hence, we can view the amplitude as having a "reducing" effect on the $H_{\text{eEDM}}^{\text{eff}}T_1$ term, for each i and a. This is probably why the $H_{\text{eEDM}}^{\text{eff}}T_1$ term is not as large as the DF one; the large matrix elements are accompanied by the smaller values of the t_1 amplitudes. Obviously, this is not the only reason why the DF term is substantially larger than the other terms. The term also contains matrix elements of the type $\langle o|h_{\text{eEDM}}^{\text{eff}}|o\rangle$ and $\langle v|h_{\text{eEDM}}^{\text{eff}}|v\rangle$, which cancel each other in a way that results in the final value of the DF term. There are also cancellations between various terms that constitute $H_{\text{eEDM}}^{\text{eff}}T_1$, since not all matrix elements or the t_1 amplitudes are positive.

The matrix elements, of the form $\langle o|h_{\text{eEDM}}^{\text{eff}}|v\rangle$, occur only in $H_{\text{eEDM}}^{\text{eff}}T_1$ and $T_2^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$ (and its complex conjugate term). The latter, however, is not as large as the former, and is, in fact, very small, probably due to two reasons. The first is the cancellations that arise among the four terms that constitute $T_2^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$:

$$\sum_{i>j,a>b} [t_{ij}^{ab*} t_i^a \langle b|h_{\text{eEDM}}^{\text{eff}}|j\rangle + t_{ij}^{ab*} t_j^b \langle a|h_{\text{eEDM}}^{\text{eff}}|i\rangle$$
$$-t_{ij}^{ab*} t_j^a \langle b|h_{\text{eEDM}}^{\text{eff}}|i\rangle - t_{ij}^{ab*} t_i^b \langle a|h_{\text{eEDM}}^{\text{eff}}|j\rangle] \quad (16)$$

We have not explicitly mentioned that the operator is normal ordered, or that each term is connected. The four

terms are 0.72, 0.24, -0.03, and 0.77 respectively, for HgF, which we choose as a representative case (we expect the trends to be similar for the other monohalides). All the four terms have matrix elements of the form, $\langle o|h_{\text{eEDM}}^{\text{eff}}|v\rangle$, of which two are dominant, and they almost cancel each other out. The second reason is that in this term, there is another t amplitude, t_2, which is also less than one, and hence "reduces" the net contribution further.

The $T_1^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$ consists of terms of the type $\langle o|h_{\text{eEDM}}^{\text{eff}}|o\rangle$ and $\langle v|h_{\text{eEDM}}^{\text{eff}}|v\rangle$. To discern how these terms contribute, we expand the $T_1^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$ term:

$$- \sum_{i,j,a} t_i^{a*} t_j^a \langle j|h_{\text{eEDM}}^{\text{eff}}|i\rangle + \sum_{i,a,b} t_i^{a*} t_i^b \langle a|h_{\text{eEDM}}^{\text{eff}}|b\rangle$$
$$- \sum_{i,a} t_i^{a*} t_i^a \langle i|h_{\text{eEDM}}^{\text{eff}}|i\rangle + \sum_{i,a} t_i^{a*} t_i^a \langle a|h_{\text{eEDM}}^{\text{eff}}|a\rangle \quad (17)$$
$$= I + II + III + IV \quad (18)$$

The first term corresponds to Figure 1. c. The second term is similar to the figure, except that the eEDM vertex is between two particles, instead of two holes. The third term is same as the first, except that in its Goldstone diagram, both the holes are the same orbitals, that is, the interaction of the hole with the eEDM leaves it unchanged. The fourth is again, same as the second, but with the two particles being the same orbital. We have expanded $T_1^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$ this way, so that we can understand which type of matrix elements contribute to it dominantly. Table IV summarizes the contributions to this term.

Term	Contribution (GV/cm)
I	10^{-3}
II	2.94
III	-4.44
IV	2.4

TABLE IV. The terms that contribute to $T_1^\dagger H_{\text{eEDM}}^{\text{eff}}T_1$

We observe from the Table that the magnitude-wise, the terms that contain the eEDM operator between the same orbitals (terms II and III) contribute significantly. Note that these matrix elements are non-zero, although $h_{\text{eEDM}}^{\text{eff}}$ is P-odd. This is because the orbitals are MOs, and each MO is expanded as a linear combination of basis functions, of different angular momenta. The major contributions to the $T_2^\dagger H_{\text{eEDM}}^{\text{eff}}T_2$ term is also from matrix elements between the same orbitals (-4.7 GV/cm).

Table V summarizes the results obtained from previous works. Only results for HgF are available, and we proceed to briefly discuss them. The first work on the E_{eff} of HgF was by Kozlov [35]. It was a relativistic, semi-empirical calculation. The focus of the paper was the nuclear anapole moment, and electron-nucleus P and T violating interactions. The table of results gives the final result of E_{eff}. Note that since it is a semi-empirical

calculation, it cannot break the final value of E_{eff} into its constituent DF and correlation parts.

Dmitriev et al [36] computed the E_{eff} of HgF, using their calculated bond length of 2.11 Angstrom. They chose the minimal atomic basis set for F, while for Hg, they used five relativistic valence orbitals, $5d_{3/2}$, $5d_{5/2}$, $6s_{1/2}$. $6p_{1/2}$, and $6p_{3/2}$. They obtained a value of about 100 GV/cm. Their calculation can be described as quasi relativistic, since it requires the addition of the spin-orbit interaction to a non-relativistic Hamiltonian. Our work is fully relativistic (We do not resort to an effective Hamiltonian, but the Dirac-Coulomb one) and has the spin-orbit interaction and other effects built into it. They did not account for mixing between orbitals beyond $d_{5/2}$, the effect of F was ignored, and also only the principal quantum numbers 5 and 6 were chosen. We have made no such restrictions. Finally, they had adopted CI, exciting only three outer electrons. In our CCSD calculation, all the 89 electrons were excited. Hence, the Hilbert space that we considered to capture the correlation effects is larger than that in their work. Our error estimate of 5 percent is better than their estimate of 20 percent. Their estimate of E_{eff} does not contain in it information on the DF or correlation contributions. We have provided a detailed breakdown of E_{eff} in our work. Also, their close agreement with our results for E_{eff} may be a result of fortuitous cancellations. For example, their work computeed the PDM of HgF to be 4.15 D, which is close to our DF value of 3.9 D. But, our relativistic CCSD result is 2.61 D!

Meyer et al [34] calculated E_{eff} for HgF, among several other molecules, using their non-relativistic software, to compare the accuracy of their mehod. Later, in 2008, they improved upon their approach further, to obtain a more accurate value, of 95 GV/cm [37].

In our previous work on HgX [16], we had taken recourse to the relativistic coupled cluster method. We had shown that E_{eff}, for all the HgX molecules, is substantially larger than that for all the current eEDM molecular candidates. However, we had not performed a detailed analysis of the physical effects at the DF and correlation levels, which is what we have done in the present manuscript. We wish to amphasize that besides the fact that we use a fully relativistic coupled cluster approach and extend the results to all HgX, we also break the final value of E_{eff} down into its constituent terms, both at the DF and correlation levels.

Work	$\mathcal{E}_{\text{eff}}$ (GV/cm)
Y Y Dmitriev *et al.* [36]	99.26
Meyer *et al.*[34]	68
Meyer *et al.*[37]	95
This work	115.42

TABLE V. Effective electric field, $\mathcal{E}_{\text{eff}}$, in the HgF molecule, calculated in earlier literature

Since we are elaborating on the theoretical aspects of our previous work, the error estimates are the same (Refer [16]). We recently improved upon our earlier results on HgX E_{eff}s, where we take into account the effect of the neglected non-linear coupled cluster terms in the expectation value [38]. Therefore, the non-linear terms, in fact, contribute far lesser than our earlier estimate of 3.5 percent.
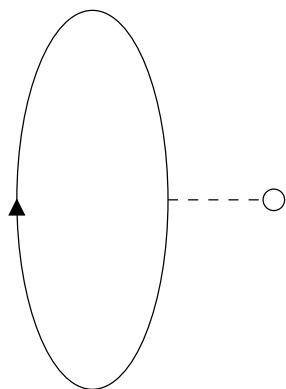
IV. CONCLUSION

We have calculated the effective electric fields of mercury monohalides. We have not frozen any of the core orbitals. We employed Dyall's basis sets for Hg and I, and cc-pV basis sets for the other halides. The DF term contributes the most to E_{eff} (about ninety percent). We have reported the trends in some of the correlation terms for these molecules, at the DZ level. We observe that the dominant contribution to the correlation effects is from a one hole-one particle excitation coupled cluster diagram. We present one example of a physical effect that is included in this diagram. We have also reported on those mixings of atomic orbitals that significantly contribute to the DF value of E_{eff}, and observed their trends, at the TZ level. We recognize that the $s - p_{1/2}$ mixing in Hg contributes dominantly to E_{eff}^{DF}.
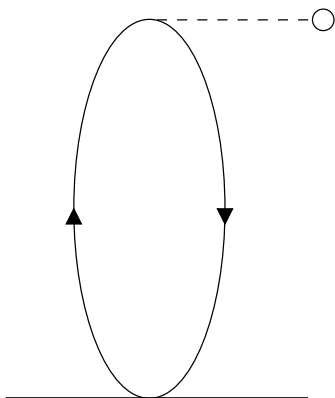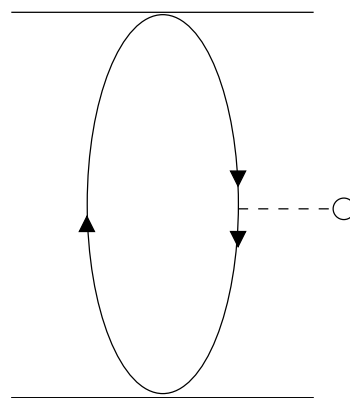
V. ACKNOWLEDGMENT

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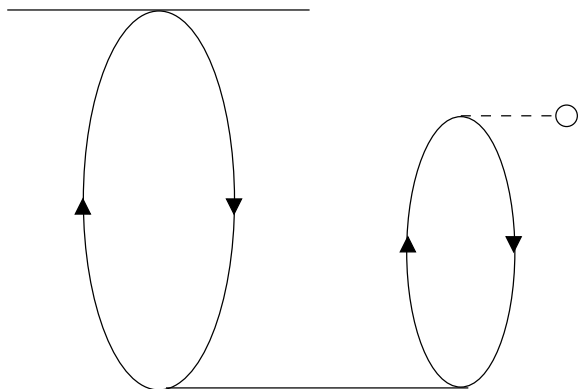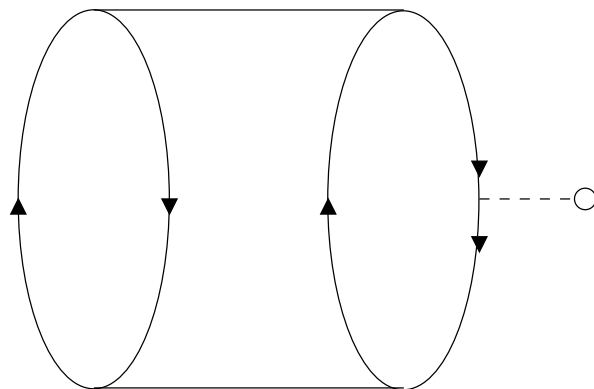
a.   b.   c.

d.   e.

Figure 1   31Mar2017