

## Mercury Monohalides: Suitability for Electron Electric Dipole Moment Searches

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Heavy polar diatomic molecules are the primary tools for searching for the  $T$ -violating permanent electric dipole moment of the electron (eEDM). Valence electrons in some molecules experience extremely large effective electric fields due to relativistic interactions. These large effective electric fields are crucial to the success of polar-molecule-based eEDM search experiments. Here we report on the results of relativistic *ab initio* calculations of the effective electric fields in a series of molecules that are highly sensitive to an eEDM, the mercury monohalides (HgF, HgCl, HgBr, and HgI). We study the influence of the halide anions on  $\mathcal{E}_{\text{eff}}$ , and identify HgBr and HgI as attractive candidates for future electric dipole moment search experiments.

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Violation of time-reversal ( $T$ ) symmetry is an essential ingredient to explain the matter-antimatter asymmetry of the universe [1,2]. As standard model sources of  $T$  violation are inadequate to explain the observed asymmetry, it is imperative to look beyond it. The strongest limits on  $T$  violation arising from new particles and interactions outside the standard model are set by searches for the permanent electric dipole moments of fundamental particles [3–5], like that of the electron ( $d_e$ ). A strong constraint on the electron's electric dipole moment (eEDM),  $|d_e| < 10^{-28} e$  cm, has been set by the experiment with ThO molecules [6], and improvements of a few orders of magnitude are forecast in the near future [6,7]. The eEDM experiments take advantage of the large effective electric field,  $\mathcal{E}_{\text{eff}}$  (often  $\gtrsim 10^{10}$  V/cm) experienced by an electron in a polarized heavy polar molecule. This leads to an energy difference,  $\Delta E \propto d_e \mathcal{E}_{\text{eff}}$ , between states with electron spin oriented parallel versus antiparallel to the molecule's internuclear axis. The effective electric field arises from the relativistic interactions of the eEDM with the electric fields of all the other charged particles in the molecule. This effect, whereby molecules polarized by  $\sim$ kV/cm laboratory fields cause  $> 10$  GV/cm to be applied to a valence electron, is the reason for the high precision achievable in molecule-based eEDM experiments [8]. The value of  $\mathcal{E}_{\text{eff}}$  for a molecule has to be obtained from relativistic many-body calculations in order to convert experimentally measured frequency shifts into eEDM values. An improved understanding of the mechanisms leading to  $\mathcal{E}_{\text{eff}}$  in relativistic polar molecules will lead to better choices of candidate molecules for future eEDM experiments.

In this Letter, we focus on the values of  $\mathcal{E}_{\text{eff}}$  for a class of polar molecules, the mercury monohalides, which have one unpaired valence electron outside a closed shell. Their properties can be accurately evaluated, owing to the

relatively simple description of their molecular bond. The fact that they are sensitive to eEDMs in their ground electronic states, makes them suitable test cases for high-precision calculations. The molecule HgF has been shown to have one of the largest values of  $\mathcal{E}_{\text{eff}}$  [9], making this series of HgX molecules particularly interesting as potential candidates for future eEDM experiments. The heavier Hg monohalides (HgCl, HgBr, HgI) are more electrically polarizable than HgF, which translates to a more effective use of  $\mathcal{E}_{\text{eff}}$  and better control over systematic effects. This, in addition to better prospects for their production and efficient detection, makes the investigation of their  $\mathcal{E}_{\text{eff}}$  values relevant for future eEDM experiments.

The expression for  $\mathcal{E}_{\text{eff}}$  in terms of an effective eEDM operator,  $H_{\text{EDM}}^{\text{eff}}$  is given by

$$\mathcal{E}_{\text{eff}} = -\frac{1}{d_e} \langle \psi | H_{\text{EDM}}^{\text{eff}} | \psi \rangle, \quad (1)$$

where

$$H_{\text{EDM}}^{\text{eff}} = 2icd_e \sum_{j=1}^{N_e} \beta \gamma_5 p_j^2.$$

Here,  $c$  is the speed of light,  $N_e$  refers to the number of electrons in the molecule,  $\beta$  is one of the Dirac matrices,  $\gamma_5$  is the product of the Dirac matrices, and  $\mathbf{p}_j$  is the momentum of the  $j$ th electron.  $\psi$  is the wave function of a molecular state. The above expression casts the eEDM Hamiltonian in terms of one-electron operators, which makes it convenient for computations. Further details of the derivation of this form can be found in Ref. [10].

To obtain the molecular wave function  $|\psi\rangle$ , we use a relativistic coupled cluster method [11,12]. The coupled cluster wave function can be written as

$$|\psi\rangle = e^T |\Phi_0\rangle. \quad (2)$$

Here,  $|\Phi_0\rangle$  refers to the Dirac-Fock (DF) wave function, which is built from single particle four-component spinors. This is the model wave function for the coupled cluster calculations, and is taken to be a single determinant corresponding to an open shell doublet.  $T$  is the cluster operator. In this work, we use the coupled cluster singles and doubles (CCSD) approximation, where  $T = T_1 + T_2$ , where  $T_1$  and  $T_2$  are the single (S) and double (D) excitation operators, respectively. They are given by

$$T_1 = \sum_{ia} t_i^a a^\dagger i, \quad (3)$$

$$T_2 = \sum_{a\neq b, i\neq j} t_{ij}^{ab} a^\dagger b^\dagger ji. \quad (4)$$

Here,  $t_i^a$  and  $t_{ij}^{ab}$  are called the cluster amplitudes. In our notation,  $i, j, k, \dots$  refer to holes and  $a, b, c, \dots$  refer to particles.  $a^\dagger i$  acting on a state means that a hole  $i$  is destroyed from that state, and a particle  $a$  is created. When  $a^\dagger i$  acts on a model state,  $|\Phi_0\rangle$ , the resulting state is denoted by  $|\Phi_i^a\rangle$ .

The CCSD amplitude equations are

$$\langle \Phi_i^a | e^{-T} H_N e^T | \Phi_0 \rangle = 0, \quad (5)$$

$$\langle \Phi_{ij}^{ab} | e^{-T} H_N e^T | \Phi_0 \rangle = 0. \quad (6)$$

The term  $e^{-T} H_N e^T$  can be written as  $\{H_N e^T\}_c$ , using the linked cluster theorem [13,14].  $H_N$  is the normal-ordered Hamiltonian [15]. The subscript  $c$  means that each term in the expression is connected. The effective fields are calculated by using only the linear terms in the coupled cluster wave function, since the dominant contributions come from them. Hence we evaluate

$$\begin{aligned} \mathcal{E}_{\text{eff}} = & \frac{1}{d_e} \langle \Phi_0 | (1 + T_1 + T_2)^\dagger (H_{\text{EDM}}^{\text{eff}})_N (1 + T_1 + T_2) | \Phi_0 \rangle_c \\ & + \frac{1}{d_e} \langle \Phi_0 | H_{\text{EDM}}^{\text{eff}} | \Phi_0 \rangle. \end{aligned} \quad (7)$$

We note that although the expectation value uses the linearized expansion of the coupled cluster wave function, the amplitudes are evaluated at the CCSD level.

We performed our calculations by combining and modifying the UTCHEM [16–18] and the DIRAC08 [19] codes. We used the  $C_8$  point group, which reduces the computational time for the atomic-to-molecular orbital integral transformations. A summary of our calculations, both at the DF and the CCSD level, is given in Table I. We find that the values for  $\mathcal{E}_{\text{eff}}$  are very large for all of the chosen mercury halides.

We chose uncontracted correlation-consistent, polarized valence double- $\zeta$  CCPVDZ for F, Cl and Br [20], and Dyall's c2v for Hg and I [21]. We use Gaussian-type orbitals, which are kinetically balanced [22]. Our

calculations were performed without freezing any of the core orbitals. We used the following bond lengths (in nm) for our calculations: HgF (0.200 686) [23], HgCl (0.242), HgBr (0.262), HgI (0.281) [24].

We have also reported the  $T_1$  diagnostics (denoted as  $T_{1,\text{dia}}$ ), a small value of which indicates the stability of single reference CCSD calculations. In Table II, we compare our result for  $\mathcal{E}_{\text{eff}}$  in HgF with previous calculations. Dmitriev *et al.* computed the value of  $\mathcal{E}_{\text{eff}}$  in HgF using relativistic effective core potential calculations. They used the minimal atomic basis set for F, and five relativistic valence orbitals  $5d_{3/2}$ ,  $5d_{1/2}$ ,  $6s_{1/2}$ ,  $6p_{1/2}$ , and  $6p_{3/2}$  for Hg. Meyer *et al.* computed  $\mathcal{E}_{\text{eff}}$  for HgF using nonrelativistic software to compare their method with results obtained by other methods.

For the first three halides, we observe from the DF and CCSD values of  $\mathcal{E}_{\text{eff}}$  that correlation effects contribute  $\sim 10\%$ . A closer analysis of the eight terms that contribute to the correlation shows that there are cancellations between some of these terms. As an illustration of this point, in Table III we show the contributions of the individual terms to the expectation value in Eq. (7) for HgF.

We see that among the correlation terms, the  $H_{\text{EDM}}^{\text{eff}} T_1$  and the  $T_1^\dagger H_{\text{EDM}}^{\text{eff}}$  terms together contribute 20.16 GV/cm.

TABLE I. Summary of the calculated results ( $\mathcal{E}_{\text{eff}}$ ) of the present work. The difference between DF and CCSD values indicates the contribution of electron correlation to  $\mathcal{E}_{\text{eff}}$ . The CCSD calculations for all four molecules are estimated to have an accuracy of 5%.

Molecule	Method	Basis	$T_{1,\text{dia}}$	$\mathcal{E}_{\text{eff}}$ (GV/cm)
HgF	DF	Hg: 22s, 19p, 12d, 9f, 1g F: 9s, 4p, 1d	...	104.25
HgCl	DF	Hg: 22s, 19p, 12d, 9f, 1g Cl: 12s, 8p, 1d	...	103.57
HgBr	DF	Hg: 22s, 19p, 12d, 9f, 1g Br: 14s, 11p, 6d	...	97.89
HgI	DF	Hg: 22s, 19p, 12d, 9f, 1g I: 8s, 6p, 6d	...	96.85
HgF	CCSD	Hg: 22s, 19p, 12d, 9f, 1g F: 9s, 4p, 1d	0.0268	115.42
HgCl	CCSD	Hg: 22s, 19p, 12d, 9f, 1g Cl: 12s, 8p, 1d	0.0239	113.56
HgBr	CCSD	Hg: 22s, 19p, 12d, 9f, 1g Br: 14s, 11p, 6d	0.0255	109.29
HgI	CCSD	Hg: 22s, 19p, 12d, 9f, 1g I: 8s, 6p, 6d	0.0206	109.30

TABLE II. Effective electric field,  $\mathcal{E}_{\text{eff}}$ , in the HgF molecule.

Work	$\mathcal{E}_{\text{eff}}$ (GV/cm)
Dmitriev <i>et al.</i> [9]	99.26
Meyer <i>et al.</i> [25]	68
This work	115.42

But the  $T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_1$  and the  $T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_2$  terms together contribute  $-9.43$  GV/cm. The 9 correlation terms hence add up to  $11.17$  GV/cm. Note that the  $H_{\text{EDM}}^{\text{eff}} T_2$  term and the  $T_2^\dagger H_{\text{EDM}}^{\text{eff}}$  are zero. This is due to the Slater-Condon rules, and the fact that the  $H_{\text{EDM}}^{\text{eff}}$  operator is a one-body operator. The same reasoning applies, for example, also for the  $H_{\text{EDM}}^{\text{eff}} T_1^2$  term. We find that the  $H_{\text{EDM}}^{\text{eff}} T_1$  and the  $T_1^\dagger H_{\text{EDM}}^{\text{eff}}$  are the largest correlation terms in our calculations—these can be understood as the off-diagonal matrix elements of  $H_{\text{EDM}}^{\text{eff}}$  between the DF reference state, and a state with one electron excited by the electron-electron Coulomb repulsion. As an aside, we note that the relative contribution of correlation effects to the total  $\mathcal{E}_{\text{eff}}$  value in HgX is only about half as large as in YbF [10] (and even smaller compared to ThO [26–28])—this is due to the large values of  $\mathcal{E}_{\text{eff}}$  in HgX molecules already at the DF level.

The largest contribution to  $\mathcal{E}_{\text{eff}}$  is from the DF term, which can be rewritten as

$$\frac{1}{d_e} \langle \Phi_0 | H_{\text{EDM}}^{\text{eff}} | \Phi_0 \rangle = \frac{1}{d_e} \langle \phi_v | h_{\text{EDM}}^{\text{eff}} | \phi_v \rangle \quad (8)$$

$$= \frac{2}{d_e} \sum_{k,l} C_{vk}^* C_{vl} \langle \chi_k | h_{\text{EDM}}^{\text{eff}} | \chi_l \rangle. \quad (9)$$

Here,  $h_{\text{EDM}}^{\text{eff}}$  is the single particle effective eEDM Hamiltonian, and  $\phi_v$  is the valence single particle wave function (the valence molecular orbital). We have expanded

TABLE III. Contributions from the individual terms to the effective electric field of HgF.

Term	Contribution (GV/cm)
DF	104.25
$H_{\text{EDM}}^{\text{eff}} T_1$	10.08
$H_{\text{EDM}}^{\text{eff}} T_2$	0
$T_1^\dagger H_{\text{EDM}}^{\text{eff}}$	10.08
$T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_1$	-3.91
$T_1^\dagger H_{\text{EDM}}^{\text{eff}} T_2$	0.22
$T_2^\dagger H_{\text{EDM}}^{\text{eff}}$	0
$T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_1$	0.22
$T_2^\dagger H_{\text{EDM}}^{\text{eff}} T_2$	-5.52

the valence molecular orbital using some appropriate atomic orbital basis denoted by  $\chi$ . The index  $k$  is over the small components, while  $l$  is over the large components of the wave function. When  $k = 6s$ , and  $l = 6p_{1/2}$ , we expect the  $C_{v6s}^* C_{v6p_{1/2}}$  term (hybridization) to be very large, and hence also the corresponding DF value of  $\mathcal{E}_{\text{eff}}$ . This is because the  $6s$  orbital and the virtual  $6p_{1/2}$  orbital of Hg lie close to each other in energy and have a large radial overlap. Also, the matrix element of  $h_{\text{EDM}}^{\text{eff}}$  between these opposite parity orbitals is large, due to the significant overlap of their wave functions in the nuclear region. This is the reason for the exceptionally large values of  $\mathcal{E}_{\text{eff}}$  in HgX molecules, and it makes them highly interesting candidates for future eEDM experiments.

There are two possible sources of error in our calculations. The first is due to our choice of basis sets. We estimate the error arising from the incompleteness of the single particle basis used in our calculations, by examining the difference between the triple- $\zeta$  (TZ) and double- $\zeta$  (DZ) calculations for HgF. (This method of comparing basis sets has previously been used to estimate the accuracy of calculations on YbF [10] and SrF [29] molecules.) For the TZ calculation, we used Dyalls c3v basis for Hg ( $29s$ ,  $24p$ ,  $15d$ ,  $11f$ ,  $4g$ ) [21] and the CCPVTZ basis sets for F ( $10s$ ,  $5p$ ,  $2d$  and  $1f$ ) [20]. The difference in  $\mathcal{E}_{\text{eff}}$  values calculated with these two basis sets is 1.5%.

The second potential source of error arises from the neglected higher-order correlation terms. Correlation effects contribute to about 10% of the effective fields in HgX, and their relative sizes are half of their counterpart for YbF and even less when compared to ThO. This is the primary reason why we expect that the errors for the mercury halides are less than those of other molecules that are of interest for electron EDM searches. From Table III, we see that the leading contribution comes from the  $H_{\text{EDM}}^{\text{eff}} T_1$  term. The rest of the correlation contributions are less than half the magnitude of this term. Also,  $H_{\text{EDM}}^{\text{eff}} T_2$ ,  $H_{\text{EDM}}^{\text{eff}} T_2^2$ , and the higher order terms of these categories are zero. We estimate that the contribution of the neglected higher order correlation terms cannot exceed 4 GV/cm (half the magnitude of the rest of the correlation) for HgF. This 3.5% error is linearly combined with the basis set error of 1.5% to obtain a conservative estimate of the total error as 5%. Based on the common origin of  $\mathcal{E}_{\text{eff}}$  in HgX molecules as described above, we use this as a representative error estimate for all the mercury monohalides.

In addition to their large effective electric fields, there is the particularly interesting possibility that HgX molecules can be produced in large quantities at ultracold temperatures, e.g., by photoassociation of laser-cooled Hg with magnetically trapped halogen atoms [30]. We anticipate that  $N \gtrsim 10^3$  molecules/s can be feasibly produced with these methods. A slow beam or fountain of HgX molecules (e.g., Refs. [7,31]) could result in long coherence times for

electron spin precession. With a coherence time of 1 s, the eEDM sensitivity of experiments with HgX molecules approaches  $\delta d_e \leq 3 \times 10^{-27} / \sqrt{N} e \text{ cm}$ . These molecules also offer a pathway for efficient detection: above their ground  $X \ ^2\Sigma$  state, they have a repulsive  $A \ ^2\Pi$  state which dissociates into Hg ( $^1S$ ) and X ( $^2P$ ) atoms. State-selective photodissociation of HgX, coupled with laser-induced cycling fluorescence on the product Hg atom, can be used to detect spin precession in these molecules with unit efficiency.

Molecules used in eEDM experiments must be fully polarized by lab electric fields in order to take full advantage of their effective electric fields. The quantity that sets the scale for the required lab electric field is  $\mathcal{E}_{\text{pol}} = 2B_{\text{rot}}/D$ , where  $D$  is the molecular dipole moment and  $B_{\text{rot}}$  is the rotational constant of the molecule. Figure 1 shows the trend in  $\mathcal{E}_{\text{pol}}$  for HgX molecules, and picks out HgBr and HgI as attractive eEDM search candidates due to their combination of large  $\mathcal{E}_{\text{eff}}$  and low  $\mathcal{E}_{\text{pol}}$ .

Finally, we point out that HgX molecules have sets of “internal comagnetometer” states that can be used to suppress systematic effects. We envision that eEDM experiments with these molecules will use a zero spin isotope of Hg (e.g.,  $^{202}\text{Hg}$ )—therefore the manifold of rotational states can be labeled by the quantum numbers  $N$  (rotational angular momentum),  $J = N + S$ , and  $F = J + I$  (total angular momentum), where  $S = 1/2$  is the electron spin and  $I$  is the nuclear spin of the halide anion. We calculated the magnetic moments, and eEDM sensitivity parameter  $\zeta = \langle \vec{S} \cdot \hat{n} \rangle$  (where  $\hat{n}$  is the unit vector along the internuclear axis) for states in the low-lying manifolds of the  $^2\Sigma$  ground electronic state in HgX. The calculations, which included the effect of lab electric fields, are described in the

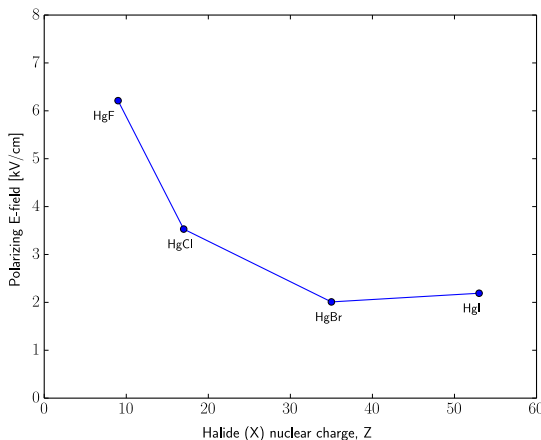


FIG. 1 (color online). Polarizing electric field,  $\mathcal{E}_{\text{pol}} = 2B_{\text{rot}}/D$ , for HgX molecules. The low polarizing field for HgBr and HgI makes them better suited to eEDM experiments, where small lab electric fields to polarize the molecules are desirable for a number of technical reasons (cf. Refs. [6,8]).

Supplemental Material [32,33]. The molecules generically exhibit sets of states that have comparable magnetic field sensitivity, but significantly different eEDM sensitivity (which can, further, be tuned using lab electric fields). The origin of such comagnetometer sets is the fact that the eEDM interaction in the molecule is proportional to  $\zeta$ , and therefore depends on the magnitude and direction of the electric polarization of the molecular state. Examples of comagnetometer sets in  $^{202}\text{Hg}^{79}\text{Br}$  are shown in Fig. 2. States that strongly polarize along the applied lab electric field (e.g.,  $|N=0, J=1/2, F=2, m_F=\pm 2\rangle$ ) have a large eEDM sensitivity, while states that weakly polarize against the applied electric field (e.g.,  $|N=1, J=3/2, F=2, m_F=\pm 2\rangle$ ) have a smaller value (and opposite sign) of eEDM sensitivity—meanwhile, their magnetic moments are quite similar, as they are mostly determined by the spin-rotation and hyperfine interactions.

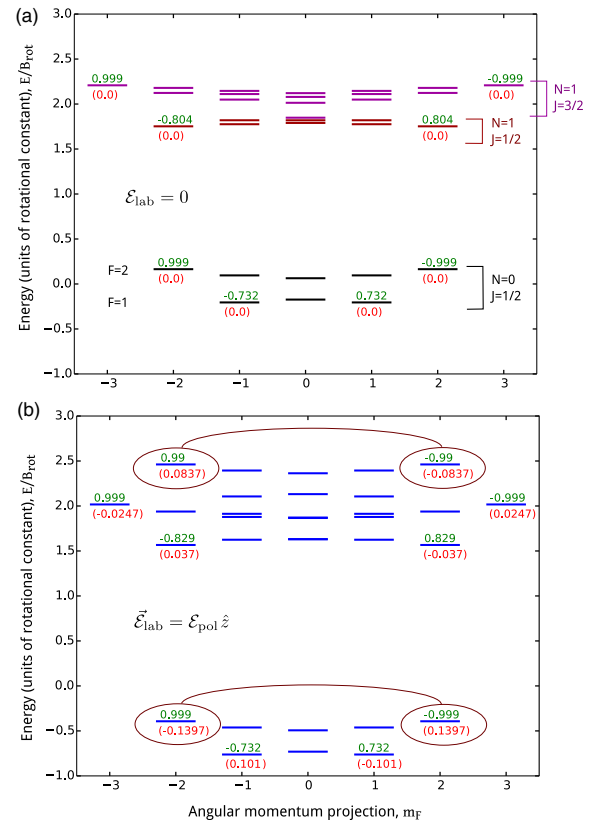


FIG. 2 (color online). Calculated values of the magnetic moment (green) in units of  $\mu_B$ , and eEDM sensitivity parameter  $\zeta = \langle \vec{S} \cdot \hat{n} \rangle$  (red, in brackets) for the lowest-lying energy states in  $^{202}\text{Hg}^{79}\text{Br}$  ( $I = 3/2$ ). Energies are plotted in units of the rotational constant  $B_{\text{rot}} = h \times 1.3 \text{ GHz}$ . The values shown in (a) are calculated in the absence of electric fields, and have  $\zeta = 0$  as expected for an unpolarized molecule. The values shown in (b) are calculated for a lab electric field of  $\approx 2 \text{ kV/cm}$ . One set of comagnetometer states is highlighted in (b), but other combinations can also be used to advantage.



We find that comagnetometer state sets are quite generally available in  $^2\Sigma$  molecules, and are particularly easily accessible in HgBr and HgI due to their small rotational constants and high polarizability. By combining measurements from these comagnetometer sets, and utilizing the characteristic dependence of their eEDM sensitivity on lab electric fields, a true eEDM signal can be cleanly separated from systematics. Taking advantage of such features, systematic effects can be suppressed to a level commensurate with the high statistical precision achievable in eEDM experiments with HgX molecules.

In summary, we have performed precise relativistic coupled cluster calculations of the effective electric fields in a family of molecules, the mercury monohalides. We find that these molecules exhibit some of the largest effective electric fields known for polar diatomics. They also provide features that are useful for precision experiments, including sets of internal comagnetometer states to suppress systematic effects. This combination makes the mercury monohalides very attractive candidates for the next generation of eEDM experiments.

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