Mercury Monohalides: Suitability for Electron Electric Dipole Moment Searches

V.S. Prasannaa, A.C. Vutha2, M. Abe3,4, and B.P. Das1
1Indian Institute of Astrophysics, Koramangala II block, Bangalore-560034, India
2Dept. of Physics and Astronomy, York University, Toronto ON M3J 1P3, Canada
3Tokyo Metropolitan University, 1-1, Minami-Osawa, Hachioji-city, Tokyo 192-0397, Japan and
4JST, CREST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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 \textit{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 interesting candidates for future electric dipole moment search experiments.

Violation of time-reversal ($T$) symmetry is an essential ingredient to explain the matter-antimatter asymmetry of the universe \cite{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 \cite{3,4}, like that of the electron ($d_{e}$). A strong constraint on the electron’s electric dipole moment (eEDM),

$$d_{e} < 10^{-28} \text{e cm},$$

has been set by the experiment with ThO molecules \cite{5}, and improvements of a few orders of magnitude are forecast in the near future \cite{5,6}. The eEDM experiments take advantage of the large effective electric field (often $\gtrsim 10^{10}$ V/cm) experienced by an electron in a polarized heavy polar molecule, which leads to a measurable energy shift, $\Delta E \propto d_{e} \mathcal{E}_{\text{eff}}$. The effective electric field, $\mathcal{E}_{\text{eff}}$, 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.

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. A common heuristic that is used to estimate $\mathcal{E}_{\text{eff}}$ in molecules, motivated from eEDM enhancement scaling in atoms, is that $\mathcal{E}_{\text{eff}} \propto Z_{+}^{3}$, where $Z_{+}$ is the charge of the (usually heavier) cationic atom’s nucleus. But molecules are not atoms. This heuristic ignores the anions which can play an important role. 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 work, we focus on the $\mathcal{E}_{\text{eff}}$ for a class of heavy polar molecules, the mercury monohalides, in order to test their suitability for eEDM searches. The properties of these systems can be evaluated fairly accurately, as they have a single valence electron. The fact that they are sensitive to eEDMs in their ground electronic states (unlike molecules with metastable eEDM-sensitive states which require more complicated descriptions \cite{7}), makes them suitable test cases for high-precision calculations. HgF has one of the largest reported $\mathcal{E}_{\text{eff}}$ \cite{8}, 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 very promising for future eEDM experiments.

The expression for $\mathcal{E}_{\text{eff}}$ in terms of an effective eEDM operator, $H_{\text{eff}}$, is given by \cite{9}

$$\mathcal{E}_{\text{eff}} = \frac{2ic}{e} \sum_{j=1}^{N_{e}} \langle \psi | \beta \gamma_{5} p_{j}^{2} | \psi \rangle,$$

$$= \frac{1}{d_{e}} \langle \psi | H_{\text{eff}} | \psi \rangle \tag{1}$$

Here, $c$ is the speed of light, $e$ is the charge of the electron, $N_{e}$ 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 $p_{j}$ is the momentum of the $j$th electron. $\psi$ is the wavefunction 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 \cite{9}.

To obtain the molecular wavefunction $| \psi \rangle$, we use a relativistic coupled cluster (RCC) method \cite{10,11}. The coupled cluster wavefunction can be written as

$$| \psi \rangle = e^{-T} | \Phi_{0} \rangle \tag{2}$$

Here, $| \Phi_{0} \rangle$ refers to the Dirac-Fock (DF) wavefunction, which is built from single particle four-component spinors. This is the model wavefunction 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 CCSD (Coupled Cluster Singles and Doubles) 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

$$T_1 = \sum_{i,a} t_i^e a_i^+$$

$$T_2 = \sum_{a>b,i>j} t_{ij}^{ab} a_i^+ a_j^+.$$  

Here, $t_i^e$ and $t_{ij}^{ab}$ are called the cluster amplitudes. In our notation, $i, j, k, \ldots$ refer to holes and $a, b, c, \ldots$ refer to particles. When $a_i^+ i$ acts on a state, a hole $i$ is destroyed from that state, and a particle $a_i^+$ is created. The action of $a_i^+ i$ on a model state, $|\Phi_0\rangle$ in a state denoted by $|\Phi_0^e\rangle$.

The CCSD amplitude equations are

$$(\Phi_0^e | e^{-T} H_N e^T | \Phi_0) = 0$$

$$(\Phi_{ij}^e | e^{-T} H_N e^T | \Phi_0) = 0$$

The term $e^{-T} H_N e^T$ can be written as $\{H_N e^T\}_c$, due to the linked cluster theorem [12,13]. $H_N$ is the normal-ordered Hamiltonian [14]. 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 wavefunction, since the dominant contributions come from them. Hence we evaluate

$$\mathcal{E}_{eff} = \langle \Phi_0 | (1 + T_1 + T_2)^{\dagger} (H_{EDM}^{\text{eff}}/\partial e) N (1 + T_1 + T_2) | \Phi_0 \rangle_c$$

$$+ \langle \Phi_0 | H_{EDM}^{\text{eff}}/\partial e | \Phi_0 \rangle_c$$

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

We performed our calculations by combining and modifying the UTCHEM [15–17] and the DIRAC08 [18] codes. We used the $C_3v$ 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, are given in Table I, and the results plotted in Figure 1. We find that the values for $\mathcal{E}_{eff}$ are very large for all of the chosen mercury halides, and are typically about one and a half times that of ThO[7] and about five times that of YbF[9]. This can be attributed to the fact that there is strong mixing between the valence 6s and the virtual 6p orbital.

We chose uncontracted correlation-consistent, polarized valence double zeta (ccpvdz) basis sets for F, Cl and Br [19], and Dyall’s cv2 basis sets for Hg [20]. We use Dyall’s basis for I [20]. We use Gaussian Type Orbitals (GTO), which are kinetically balanced [21]. Our calculations were performed without freezing any of the core orbitals. We used the following bond lengths (in nm) for our calculations: HgF (0.200686) [22], HgCl (0.242), HgBr (0.262), HgI (0.281) [23].

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 the table below, we compare our result for $\mathcal{E}_{eff}$ in HgF with previous calculations. Dmitriev et al. computed the value of $\mathcal{E}_{eff}$ in HgF using relativistic effective core potential calculations. They used the minimal atomic basis set for F, and five relativistic valence orbitals 5$d_{3/2}, 5d_{1/2}, 6s_{1/2}, 6p_{1/2},$ and $6p_{3/2}$ for Hg. Meyer et al. computed $\mathcal{E}_{eff}$ for HgF using

| Molecule | Method | Basis | $T_{1,\text{dia}}$ | $\mathcal{E}_{eff}$ (GV/cm) |
|----------|--------|-------|-----------------|------------------|
| HgF      | DF     | F:9s,4p,1d | -              | 104.25            |
| HgCl     | DF     | Cl:12s,8p,1d | -              | 103.57            |
| HgBr     | DF     | Br:14s,11p,6d | -              | 97.89             |
| HgI      | DF     | I:8s,6p,6d | -              | 96.85             |
| HgF      | CCSD  | F:9s,4p,1d | 0.0268         | 115.42            |
| HgCl     | CCSD  | Cl:12s,8p,1d | 0.0239         | 113.56            |
| HgBr     | CCSD  | Br:14s,11p,6d | 0.0255         | 109.25            |
| HgI      | CCSD  | I:8s,6p,6d | 0.0206         | 109.30            |

$\mathcal{E}_{eff}$ is the effective electron correlation to $\mathcal{E}_{eff}$.
As an illustration of this point, in Table III we show the contributions of the individual terms to the expectation value in (7) for HgF.

| Term            | Contribution (GV/cm) |
|-----------------|----------------------|
| $H_{EDM}^{\text{eff}} T_1$ | 10.08                |
| $H_{EDM}^{\text{eff}} T_2$ | 0                    |
| $T_1^{\text{eff}} H_{EDM}^{\text{eff}} T_1$ | -3.91    |
| $T_2^{\text{eff}} H_{EDM}^{\text{eff}} T_1$ | 0.22             |
| $T_2^{\text{eff}} H_{EDM}^{\text{eff}} T_2$ | 0.22             |
| $T_2^{\text{eff}} H_{EDM}^{\text{eff}} T_3$ | -5.52            |

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

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 (7) for HgF.

In summary, we have performed fully relativistic coupled cluster calculations of the effective electric fields in a family of molecules, the mercury monohalides. We find that these molecules have some of the largest effective electric fields known for polar diatomics, in addition to features that are favourable for experiments. This combination makes the mercury monohalides attractive candidates for the next generation of eEDM experiments.

ACKNOWLEDGMENTS

The computational results reported in this work were performed on the high performance computing facilities.
of IIA, Bangalore, on the Hydra and Kaspar clusters. We acknowledge Anish Parwage for his help with installing codes on the clusters. This research was supported by JST, CREST. M.A. thanks MEXT for financial support. The DiRef database was extremely useful in searching for literature [26].

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