Relativistic coupled-cluster study of diatomic metal-alkali-metal molecules for electron electric dipole moment searches

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Abstract

Recent improvements in experimental techniques for preparing ultracold molecules that contain alkali atoms (e.g., Li, Na, and K) have been reported. Based on these advances in ultracold molecules, new searches for the electric dipole moment of the electron and the scalar-pseudoscalar interaction can be proposed on such systems. We calculate the effective electric fields ($E_{\text{eff}}$) and the scalar-pseudoscalar coefficients ($W_i$) of SrA and HgA ($A = \text{Li, Na, and K}$) molecules at the Dirac–Fock (DF) and the relativistic coupled cluster (RCC) levels. We elaborate on the following points: (i) basis set dependence of the molecular properties in HgA, (ii) analysis of $E_{\text{eff}}$ and $W_i$ in SrA and HgA, and comparison with their fluoride and hydride counterparts, (iii) ratio of $W_i$ to $E_{\text{eff}} (W_i/E_{\text{eff}})$ at the DF and the correlation RCC levels of theory.

Supplementary material for this article is available online

Keywords: electric dipole moment of the electron (eEDM), relativistic coupled cluster (RCC), ultracold molecule

(Some figures may appear in colour only in the online journal)

1. Introduction

The electric dipole moment of the electron (eEDM) is a physical property of the particle (if detected) that arises from Parity ($P$) and time-reversal ($T$) symmetry violations \cite{1, 2}. Although the existence of the eEDM is predicted in the standard model (SM) of particle physics, its predicted value is extremely small ($|d_e| \approx 10^{-38}$ e cm \cite{3}, $|d_e| \approx 10^{-40}$ e cm \cite{4}) and therefore, measuring its SM value is currently not possible. In contrast, many particle physics theories that are beyond the standard model (BSM) predict values of the eEDMs that are several orders of magnitude greater than their SM counterparts \cite{2–5}, and some are well within reach of current experiments \cite{7, 8, 24}. Therefore, upper bounds on the eEDM placed by experiments, thereby constraining stringently several post-SM theories, are a crucial probe of BSM physics. In particular, eEDM tabletop experiments that use atoms and molecules can probe PeV energy scales, which are well beyond the reach of accelerators \cite{3}. Another $P$, $T$ violating interaction is the scalar-pseudoscalar (S-PS) interaction between the nuclei and the electrons in an atom or a molecule \cite{9–11}. The coupling constant associated with this interaction is the S-PS constant ($k_s$). The S-PS interaction is predicted in, for example, the minimal supersymmetric standard model \cite{12}, where the loop-induced Higgs-gluon–gluon couplings contribute to $k_s$, and the aligned two-Higgs-doublet model \cite{13}. The S-PS interaction is not predicted in all BSM theories, but there is a model which predicts a large contribution of the S-PS interaction to the atomic (and molecular) EDM as compared to the eEDM \cite{14}. More details on the importance of eEDM searches and the S-PS interaction can be found in Chupp’s review \cite{15}.

The values of $d_e$ and $k_s$ are obtained by a combination of experimental energy shifts in atoms or molecules and...
theoretically determined enhancement factors (further details can be found in appendix A of [16]). The latter can be calculated only by using atomic or molecular relativistic many-body theories. The enhancement factor for the eEDM interaction is the effective electric field \( E_{\text{eff}} \), while that for the S-PS interaction is the S-PS coefficient \( W_s \). Since both the eEDM and the S-PS interactions contribute to the measured energy shift in an experiment, we need to perform measurements on two or more systems with different sensitivities to these interactions, in order to obtain their contributions individually (see figure 1 in [17] and figure 1 in [18]). In the subsequent sections, we discuss the sensitivity of a given system in terms of the ratio between its \( W_s \) and \( E_{\text{eff}} \) (\( W_s/E_{\text{eff}} \)).

Molecules that can be cooled to the ultraregime can be attractive as candidate systems for an eEDM experiment because of their large coherence time and the total number of molecules that can be used for that experiment. One such set of molecules that offer promise for future eEDM search experiments are metal-alkali-metal diatomic systems. For instance, several groups have successfully reported on ultracold mixtures of Yb+Li [19, 20], Hg2+Rb [21].

In contrast, the theoretical investigations of metal-alkali-metal molecules for the eEDM searches are limited to the work of Meyer et al. [22], and our recent work on Hg-alkalis (HgA) [23]. In the former, potential energy curves and molecular properties of Yb-alkali and Yb-alkali-earth-metal molecules are calculated at the non-relativistic level [22]. The latter involves calculations of \( E_{\text{eff}} \) and the molecular permanent electric dipole moment (PDM) for HgA systems using Dyall cv3z basis set using a relativistic coupled cluster singles and doubles (CCSD) approach [23]. The work also presents a preliminary estimate of the expected sensitivity in eEDM experiments using HgA molecules.

Metal-alkali-metal systems have weak bonding, which is different from other candidate molecules with ionic bonding (e.g., ThO [6, 8], HFF+ [7], and YbF [24, 25]). Hence, surveys for the basis set dependence and the mechanism of enhancement for \( E_{\text{eff}} \) and \( W_s \) for metal-alkali-metal molecules are important, both from the viewpoint of an accurate determination of these factors, as well as for the search for good candidate molecules for eEDM searches.

In this paper, we focus on the analytical and methodological aspects of the calculations of \( E_{\text{eff}} \) and \( W_s \) of HgA and SrA (A = Li, Na, and K) molecules, which could be relevant for experiments with the aforementioned ultracold molecules. We summarize the three topics that we discuss in this work: (i) we calculated the \( E_{\text{eff}} \) and \( W_s \) and the PDM of HgA (A = Li, Na, and K) molecules at the Dirac–Fock (DF) and CCSD levels of theory, using a series of basis sets from Dyall’s database. We then compare our results and assess the basis sets that would be suitable for proposing eEDM candidates in these class of molecules; (ii) we study the mechanism for enhancement of \( E_{\text{eff}} \) and \( W_s \) in metal-alkali-metal molecules (HgA and SrA), and compare them with that in metal-fluorides (HgF and SrF) and metal-hydrides (HgH and SrH). Our results show that HgA has much smaller values of \( E_{\text{eff}} \) and \( W_s \) compared with HgH and HgF. The values of \( E_{\text{eff}} \) and \( W_s \) for SrLi are comparable with SrH and SrF. We explain the results by invoking the orbital interaction theory, as explained in our previous work [26]; (iii) we observe that the ratio between \( W_s \) and \( E_{\text{eff}} \) of HgX and SrX (X = H, Li, F, Na, and K) are almost constant and are independent of X. The ratio \( W_s/E_{\text{eff}} \) of HgX and SrX are not significantly affected by correlation effects, which was also observed in our previous work [27]. We explain the reason for this trend by expanding \( W_s/E_{\text{eff}} \) using a second quantized formalism.

2. Theory

The expression for the eEDM operator is given by [28]

\[
\hat{H}_{\text{eEDM}} = -d_e \sum_j \beta \Sigma_j \cdot E^{\dagger}_{\text{int}}. \tag{1}
\]

Here, \( d_e \) is the eEDM, \( j \) is the summation index over electronic coordinates, \( \Sigma_j \) is the number of electrons in the molecule, \( \beta \) is the Dirac matrix, and \( \Sigma \) is the four-component Pauli matrix. \( E_{\text{int}} \) is the internal electric field in the molecule. The effective electric field \( E_{\text{eff}} \) is given by

\[
E_{\text{eff}} = -\left\langle \Psi \left| \frac{\hat{H}_{\text{eEDM}}}{d_e} \right| \Psi \right\rangle, \tag{2}
\]

where \( \Psi \) is the four-component electronic wavefunction of the molecule. In this work, we employed a summation over the one-electron operator for the expectation value, as given below [29, 30]

\[
E_{\text{eff}} = -2i c \langle \Psi | \sum_j \beta \gamma_5 p_j | \Psi \rangle, \tag{3}
\]

where \( i \) is the imaginary unit, \( c \) is the speed of light, \( \gamma_5 \) is the product of Dirac matrices, and \( p \) is the momentum operator. The expectation value of equation (3) is equal to that of equation (1) only when \( \Psi \) is the exact eigenfunction of the unperturbed Hamiltonian, which is the Dirac-Coulomb Hamiltonian, in this work.

The S-PS interaction is defined by the following operator [9, 10]

\[
\hat{H}_{\text{S-PS}} = \sum_A \hat{H}_{\text{S-PS}, A} = \sum_A \frac{G_F}{\sqrt{2}} k_{A} Z_{A} \sum_{j} \beta_{j} \rho_{j}(r_{A}), \tag{4}
\]

where \( G_F \) is the Fermi coupling constant, expressed in atomic units \((2.22249 \times 10^{-14} \text{ eV } \cdot \text{a.u.})\). \( N_{A} \) represents the total number of the nuclei in the molecule, and \( A \) labels the nuclei. \( Z \) is the nuclear charge. \( k_{A} \) is the dimensionless S-PS interaction constant of the atom A. We used the same Gaussian-type distribution function, for the nuclear charge density \( \rho \), as in our previous work [31]. The S-PS coefficient \( W_{sA} \) is defined for molecules with \( 2\Sigma \) character as follows:

\[
W_{sA} = 2 \left\langle \Psi \left| \frac{\hat{H}_{\text{S-PS}, A}}{k_{A}} \right| \Psi \right\rangle. \tag{5}
\]
at the CCSD level, we incorporate only at the DF level.

The permanent molecular electric dipole moment (PDM) is defined by

$$\text{PDM} = -\left\langle \psi \left| \sum_{j} r_{j} \right| \psi \right\rangle + \sum_{A} Z_{A} R_{A}. \quad (6)$$

Here, \( r \) and \( R \) are the position vectors of the electrons and nuclei, respectively.

We employed a relativistic CCSD method [32, 33] using the DF wavefunction as the reference state. For the calculation of the expectation value of \( \hat{O} \) at the CCSD level, we incorporate only the linear terms in the CCSD wave function as given below [34]

$$\langle \psi_{0} | (1 + \hat{T}_{1} + \hat{T}_{2}) \hat{O}_{N} (1 + \hat{T}_{1} + \hat{T}_{2}) | \psi_{0} \rangle_{C} + O_{0}, \quad (7)$$

where \( \hat{O}_{N} \) is the normal-ordered version of the operator, the subscript \( C \) refers to connected terms, and \( O_{0} \) is the expectation value of the operator \( \hat{O} \) at the DF level [35, 36].

3. Computational method

We use the UTChem program [37] for generating the DF orbitals and the molecular orbital integral transformation [38]. We use the DIRAC08 program [39] for obtaining the CCSD wave function. We modified the above-mentioned codes to calculate \( E_{\text{eff}} \) and \( W_{s} \) [31]. We employ Dyall 2z, 3z, v3z, cv3z, and 4z basis sets [40–43] with polarization functions added to them in the uncontracted form for all of the elements in our target molecules. Here, v3z and cv3z refer to the basis sets of the same name, as shown in the basis set repository in DIRAC code. Table 1 summarizes the basis sets used in this work. Here, Dyall 2z, 3z, and 4z refer to basis sets without the polarization functions [44], while Dyall 2z_pol and 4z_pol means that we added polarization functions of Dyall v3z basis sets (\( g \) exponents for Hg, \( d \) and \( f \) exponents for Li, Na, and K, respectively) to Dyall 2z and 4z basis sets, respectively. Comparing the results obtained by using these basis sets, we shall discuss the basis set dependence of the molecular properties in HgA. All the electrons in the molecules were correlated, while the virtual orbitals at higher energies were cut-off at the integral transformation and the CCSD level. The threshold energies for the cut-off are summarized in the supplemental material is available online at4 stacks.iop.org/JPB/53/015102/mmmedia.

4. Results

We use the following bond lengths (in Å): HgH: 1.7662 [45], HgF: 2.00686 [46], HgLi: 2.92 [47], HgNa: 3.52 [47] HgK: 3.90 [47], SrH: 2.1456 [45], SrF: 2.07537 [45], SrLi: 3.545 [48], SrNa: 3.889 [49], and SrK: 4.528 [49], respectively. For \( W_{s} \), we provide only the contributions of Sr and Hg atoms, because the contribution of the lighter element for both the molecules is insignificant. We choose the following isotopes, \( ^{202}\text{Hg} \), and \( ^{88}\text{Sr} \), and employ the experimental root-mean-square charge radii [50].

4.1. Basis set dependence

Table 2 shows the results for HgLi, HgNa, and HgK, at the DF level. From the table, we observe that the dependence of \( E_{\text{eff}} \), \( W_{s} \), and PDM on basis sets is very weak at the DF level. We plot the values of \( E_{\text{eff}} \) and \( W_{s} \) versus basis sets for HgLi, HgNa, and HgK at the CCSD level in figure 1. Their values are shown in tables S1–S3 of the supplemental material. From figure 1, we observe three common features in \( E_{\text{eff}} \) and \( W_{s} \) of HgA molecules: (i) the values obtained using the 4z basis set are not close to those obtained from the 4z_pol ones. This indicates that polarization functions play an important role in \( E_{\text{eff}} \) and \( W_{s} \) of HgA molecules. We can also see the contribution of the polarization functions from the large difference between the values at the 2z and 2z_pol; (ii) the values at the v3z, cv3z, and 4z_pol levels broadly agree with each other.

From the comparison between the values at v3z and cv3z, the values of \( E_{\text{eff}} \) and \( W_{s} \) approach convergence at the cv3z level. From the small difference between v3z and 4z_pol results, we conclude that the use of 3z basis set for the occupied orbitals (\( s, p, d, f \) for Hg, and \( s, p \) for alkali) would be reasonably fine. In our previous work [23], we reported the error in \( E_{\text{eff}} \) and \( W_{s} \) due to the basis set at about 15% (using Dyall cv3z basis sets). However, from these figures, the error in the results from cv3z would be much smaller than 15%; (iii) the values at the 2z_pol are clearly far from those at the v3z, cv3z, and 4z_pol. From this, we understand that the 2z basis sets are not sufficient for an accurate calculation, even if we include

Table 1. Basis set information.

|     | Hg  | Li  | Na  | K   | Sr* | H* | F* |
|-----|-----|-----|-----|-----|-----|----|----|
| 2z  | 24s19p12d8f | 10s6p | 12s8p | 15s11p | —  | —  | —  |
| 3z  | 30s24p15d10f | 14s8p | 18s11p | 23s16p | —  | —  | —  |
| 4z  | 34s30p19d12f | 18s10p | 24s14p | 30s21p | —  | —  | —  |
| 2z_pol | 24s19p12d8f2g | 10s6p2d | 12s8p4d2f | 15s11p4d2f | —  | —  | —  |
| v3z | 30s24p15d11f2g | 14s8p2d | 19s12p4d2f | 24s17p4d2f | —  | —  | —  |
| cv3z | 30s24p15d11f4g1h | 14s8p2d | 19s12p5d2f | 24s17p6d3f | 29s20p13d5f1g | 9s2p1d | 14s8p3d1f |
| 4z_pol | 34s30p19d12f2g | 18s10p2d | 25s14p4d2f | —  | —  | —  | —  |

* We employed only cv3z basis set for Sr, H, and F atoms.

* We did not employ 4z_pol basis set for HgK.
polarization functions. However, the trends in $E_{\text{eff}}$ and $W_s$ of HgA systems are the same at any levels of basis (HgLi $>$ HgNa $>$ HgK). This indicates that even the 2z basis sets would be sufficient, for a qualitative analysis of $E_{\text{eff}}$ and $W_s$.

Table 2. Results of our calculations at the DF level.

| Basis set | $E_{\text{eff}}$ (GV cm$^{-1}$) | $W_s$ (kHz) | PDM(D) |
|-----------|---------------------------------|-------------|--------|
|           | HgLi | HgNa | HgK | HgLi | HgNa | HgK | HgLi | HgNa | HgK | HgLi | HgNa | HgK |
| 2z        | 13.39 | 7.45 | 5.70 | 29.51 | 16.41 | 12.56 | -1.58 | -0.94 | -1.59 |
| 3z        | 13.76 | 7.61 | 5.82 | 31.08 | 17.19 | 13.15 | -1.45 | -0.85 | -1.42 |
| 4z        | 13.77 | 7.62 | 5.82 | 31.13 | 17.23 | 13.17 | -1.44 | -0.84 | -1.39 |
| 2z_pol    | 13.44 | 7.46 | 5.61 | 29.63 | 16.44 | 12.34 | -1.58 | -0.96 | -1.60 |
| v3z       | 13.74 | 7.59 | 5.73 | 31.02 | 17.15 | 12.95 | -1.47 | -0.88 | -1.48 |
| cv3z      | 13.74 | 7.59 | 5.73 | 31.02 | 17.15 | 12.95 | -1.47 | -0.88 | -1.48 |
| 4z_pol    | 13.75 | 7.60 | —    | 31.10 | 17.18 | —    | —    | —    | —    |

Figure 1. Calculation results of $E_{\text{eff}}$ and $W_s$ for (a) HgLi, (b) HgNa and (c) HgK at the CCSD level.

Figure 2. Calculation results of PDM for HgLi, HgNa and HgK at the CCSD level.

Finally, we note that the above points (ii) and (iii) are consistent with the work of Hao et al [51]. They calculated the $P$-odd interaction coefficient $W_A$ for BaF by employing the RCC method. In their work, the values they obtained using Dyall v2z are clearly far from those with Dyall v3z basis, while the difference between the values at the Dyall v3z and Dyall v4z is not too significant. The similarities between their results for BaF and our results for HgA indicates that the dependence of these properties using Dyall basis sets would not significantly depend on the electronic structure of molecules.

In figure 2, we plot the values of PDM for HgA at the CCSD level, whose numerical values are shown in tables S1–S3 in the supplemental material stacks.iop.org/JPB/53/015102/mmedia. The direction of the PDM is taken along the molecular axis from the Mercury to the alkali atom. The basis set dependence of PDM is similar qualitatively to that observed in $E_{\text{eff}}$ and $W_s$. Also, the basis set dependence of PDM is stronger than that observed in $E_{\text{eff}}$ and $W_s$; e.g. values at the 2z, 3z, and 2z_pol basis sets do not reproduce the signs of 4z_pol. In contrast to this strong dependence, the values at the v3z, cv3z, and 4z_pol are in broad agreement, similar to $E_{\text{eff}}$ and $W_s$ in figure 1. We, therefore, assess that the results are extremely sensitive to basis sets only for low-quality basis sets (e.g. 2z quality, with and without polarization functions), and hence our previous calculation of PDM at the cv3z [23] are
sufficiently accurate, at least from the point of view of proposing new candidates for eEDM search experiments.

4.2. Analysis of $E_{\text{eff}}$ and $W_s$

In this section, we discuss why HgA has much smaller values of $E_{\text{eff}}$ and $W_s$ than HgH [26, 52] and HgF [26, 53] based on the electronic structure of these molecules. The dependence of molecular enhancement factors of $P$ and $T$, $T$-odd violating properties on the nuclear charge have been investigated thoroughly (e.g. [51, 54–56]). However, the small values of HgA cannot be explained only by invoking nuclear charge. We show the results of the Mulliken population (MP) analysis [57] for the singly occupied molecular orbital (SOMO) in table 3. We employ the Dyall cv3z basis sets for the MP calculations (note that the values of MP for HgH and HgF are not exactly same as our previously reported values [26], where 4z quality basis set was employed). The value of MP indicates the contribution of each atomic orbital (AO) to SOMO in the target molecule. From table 3, we see that the SOMO electrons are localized in the Hg atom for both HgH and HgF. In contrast, the SOMO for HgA is not localized in Hg, but the alkali atom. Since the SOMO is not localized to Hg, HgA molecules do not have an enhanced $E_{\text{eff}}$ and $W_s$ that would have resulted from the large nuclear charge of Hg ($Z = 80$). This shows the reason why HgA has much smaller $E_{\text{eff}}$ and $W_s$ than HgH and HgF, although they contain the Hg atom.

Although the HgA molecules have much smaller $E_{\text{eff}}$ and $W_s$ than HgH and HgF, the trend for $E_{\text{eff}}$ and $W_s$ in the counterparts of Sr molecules is different. We present the results of SrH, SrF, and SrA ($A = \text{Li, Na, and K}$) in table 4. We employ the Dyall cv3z basis sets for all the elements. The virtual orbitals are cut-off at 100 a.u. The trends in $E_{\text{eff}}$ and $W_s$ for Sr molecules is SrH > SrF > SrLi > SrNa > SrK, which are same as those found in Hg-containing molecules. However, the values of $E_{\text{eff}}$ and $W_s$ for SrLi are almost the same as those of SrF, at both the DF and the CCSD levels. SrNa and SrK have $E_{\text{eff}}$ and $W_s$ that are about one order smaller at the DF level, but the values at the CCSD level are about a half and a third of SrH, respectively. It is in stark contrast to HgNa and HgK, $E_{\text{eff}}$ and $W_s$ of HgNa and HgK are one-sixth and one-seventh smaller than HgH at the CCSD level, respectively. Although $E_{\text{eff}}$ and $W_s$ of SrA are smaller than SrH and SrF, the decrease in $E_{\text{eff}}$ and $W_s$ for SrA is clearly lesser than that in HgA. The magnitudes of $E_{\text{eff}}$ and $W_s$ for SrA are smaller than those of conventional polar molecules (such as ThO, HgF$_2$, and YbF), but SrA has an advantage in terms of the ratio $W_s/E_{\text{eff}}$, as discussed later.

When we focus on the electron correlation effects on $E_{\text{eff}}$ in SrA and HgA, their contributions to $E_{\text{eff}}$ are much larger than those at DF. However, the absolute values of the correlation effects are relatively similar among the SrX molecules (0.60–1.07 GV cm$^{-1}$) and HgX molecules (10.41–24.06 GV cm$^{-1}$) regardless of the X atoms. On the other hand, the values of $E_{\text{eff}}$ at the DF level depend on X atoms, and the ordering of the values of $E_{\text{eff}}$ at the CCSD level among our target molecules remains unchanged from that at the DF level. Hence, the values of $E_{\text{eff}}$ among our target molecules can be approximately attributed to the difference in $E_{\text{eff}}$ values at the DF level and consequently, how the SOMOs are constructed in each molecule. The above discussion also holds for $W_s$.

The reason why SrA possess relatively large $E_{\text{eff}}$ and $W_s$ could be explained by invoking the orbital interaction theory [58–60]. Figure 3 shows the energy diagram for the atomic and molecular orbitals of HgLi, HgK, SrLi, and SrK. Here, the AO energies are obtained from atomic DF calculations using the GRASP2K code [61]. We omit HgNa (SrNa), because their electronic structures are in between HgLi (SrLi) and HgK (SrK).

From figure 3, we observe that the 6s electron of Hg hardly transfers to the alkali, because Hg’s 6s orbital is more stable than the valence s orbitals of alkalis, and the transfer would lead to an energetic instability (note that if the electron transfer did not occur at all, $E_{\text{eff}}$ and $W_s$ of HgA would become zero, because Hg is a closed shell system). As a result, in HgLi and HgK, the 2s and 4s orbitals of Li and K mainly contribute to the SOMO, while 6s of Hg mainly contributes to SOMO-1. These electronic structures are in contrast with HgH and HgF molecules, where Hg’s 6s and 6p mainly contributes to SOMO (see figure 1 in [26]).

In contrast, the orbital energy of the valence 5s of Sr is higher than that of 6s of Hg. The valence AOs in Sr and alkali-metal mix more than in the case of Hg and alkali-metal; i.e. the chemical bonds of SrA are more covalent than those of HgA. The difference between the valence s orbitals of Hg and Sr can be explained on account of the stabilization of Hg’s 6s, which is due to the relativistic contraction effect and the weak screening effect of 5d electrons. As a result, the 5s of Sr can contribute to SOMO more than the 6s of Hg in HgA. Especially, in the case of SrLi, the 2s of Li is slightly more stable than 5s of Sr, and the electronic structure of SrLi is similar to that of HgH (figure 1 in [26]), rather than that of HgA. Therefore, $E_{\text{eff}}$ and $W_s$ of SrLi at the DF level are similar to those of SrH and SrF. As an aside, we note that HgA has larger $E_{\text{eff}}$ and $W_s$ than SrA due to the larger Z and relativistic effect of Hg, despite the small contribution of Hg to SOMO.

We show the values of the differences in the energies of AO, as well as the overlap integrals between the 5s and 6s

| $X$ | $E_{\text{eff}}$ (eV) | $W_s$ (eV) |
|-----|-----------------|-----------|
| HgH | 0.42            | 0.74      |
| HgF | 0.38            | 0.16      |
| HgLi| 0.10            | 0.05      |
| HgNa| 0.05            | 0.04      |
| HgK | 0.04            | 0.03      |
| SrH | 0.87            | 0.94      |
| SrF | 0.74            | 0.94      |
| SrLi| 0.90            | 0.95      |
| SrNa| 0.96            | 0.96      |

Table 3. Mulliken population analysis for HgX ($X = H, \text{Li, F, Na and K}$) using Dyall cv3z basis sets.
orbital energies of Sr and Hg atoms and the valence orbitals of the alkalis for HgA and SrA in Table 5. The overlap integrals were obtained by using the contracted Dyall 4z basis sets. We have already discussed the energy differences between the AOs in the previous paragraphs using Figure 3. The values of the overlap integrals of HgA are smaller when compared to SrA with same alkalis. It is consistent with the discussion presented above that the chemical bonds of SrA can be the

Table 4. Results of our calculations for $E_{\text{eff}}$ (GV cm$^{-1}$), $W_{\text{s}}$(kHz) and $W_{\text{s}}/E_{\text{eff}}$(kHz/(GV cm$^{-1}$)) using Dyall cv3z basis set.

| Method | Property | SrH | SrF | SrLi | SrNa | SrK | HgH | HgF | HgLi | HgNa | HgK |
|--------|----------|-----|-----|------|------|-----|-----|-----|------|------|-----|
| DF     | $E_{\text{eff}}$ | 1.76 | 1.50 | 1.41 | 0.41 | 0.24 | 106.79 | 105.32 | 13.74 | 7.59 | 5.73 |
| DF     | $W_{\text{s}}$ | 1.59 | 1.35 | 1.27 | 0.37 | 0.22 | 241.72 | 237.71 | 31.02 | 17.15 | 12.95 |
| DF     | $W_{\text{s}}/E_{\text{eff}}$ | 0.90 | 0.90 | 0.90 | 0.89 | 0.92 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 |
| CCSD   | $E_{\text{eff}}$ | 2.61 | 2.10 | 2.02 | 1.48 | 0.97 | 120.13 | 115.73 | 37.79 | 20.33 | 16.24 |
| CCSD   | $W_{\text{s}}$ | 2.33 | 1.88 | 1.81 | 1.33 | 0.86 | 277.89 | 266.65 | 86.37 | 46.46 | 37.05 |

orbital energetics of the alkalis for HgA and SrA. The overlap integrals were obtained by using the contracted Dyall 4z basis sets. We have already discussed the energy differences between the AOs in the previous paragraphs using Figure 3. The values of the overlap integrals of HgA are smaller when compared to SrA with same alkalis. It is consistent with the discussion presented above that the chemical bonds of SrA can be the

Figure 3. Energy diagrams of HgLi, HgK, SrLi, and SrK molecules. The energies of the valence occupied orbitals of Li, K, Sr and Hg (2s, 4s, 5s, and 6s) were evaluated from the ground states of the atoms. The 5p and 6p orbital energies of Sr and Hg were evaluated from the excited state of the atoms whose valence electron configurations are nsnp ($n = 5, 6$). The atomic calculations were based on GRASP2K [56]. MO energies of the four molecules were evaluated at the DF level and Dyall cv3z basis sets.
mixture of the AOs of Sr and Alkali atoms more than those of HgA, due to the contraction of the 6s orbital of Hg.

Finally, we qualitatively discuss the relationship of the above argument to the equilibrium bond length \( R_e \) and the dissociation energy \( D_e \), both shown in Table 6. From here, the \( R_e \) values of HgA are longer than those of HgH and HgF, which suggests that relatively weak bonding exists in HgA. This weak bonding is consistent with the smaller \( D_e \) and \( W_s \) in HgA, which is due to the localization of the SOMO of HgA and the chemical environment of the heavy nucleus. However, it is weakly dependent on the target molecule: hydrides, nitrides, oxides, and fluorides.

Table 4 shows the values of \( W_s / E_{\text{eff}} \) for HgX and SrX (X = H, Li, F, Na, and K) at the DF and CCSD levels. From this table, we observe that \( W_s / E_{\text{eff}} \) are almost same at both DF and CCSD levels for HgX and SrX, although the \( E_{\text{eff}} \) and \( W_s \) are different between the alkali, the hydrides, and the fluorides.

We can understand the reason for the weaker dependence of the ratio on the molecular electronic structure, by using analytical formulae for \( E_{\text{eff}} \) and \( W_s \). First, we shall discuss this aspect only at the DF level. Here, we use the expression for \( E_{\text{eff}} \) and \( W_s \) based on the molecular orbital representation proposed by Meyer et al. According to their approximation, \( E_{\text{eff}} \) is expressed as follows in atomic units [22, 69]

\[
E_{\text{eff}} = \frac{4\sigma}{\sqrt{3}} c_s c_p Z \Gamma_{\text{rel}},
\]

where

\[
\Gamma_{\text{rel}} = - \frac{4Z^2 \alpha^2 Z_i^2}{\gamma (4\gamma^2 - 1) (\nu_s \nu_p)^{3/2}},
\]

and

\[
\gamma = \sqrt{(j + 1/2)^2 - (Z\alpha)^2}.
\]

Here, \( \sigma = \pm 1/2 \), which is related to the projection of the spin to the molecular axis. \( Z \) is the effective nuclear charge seen by the valence electron; for a neutral atom \( Z_i = 1 \). \( \nu_s \) is the effective quantum number, and \( j \) is the total angular momentum. \( c_s \) and \( c_p \) are the molecular orbital coefficients in SOMO (\( \psi_{\text{SOMO}} \)) and are represented as follows

\[
|\psi_{\text{SOMO}}\rangle = c_s |s\rangle + c_p |p\rangle + \sum_{\text{other}} c_{\text{other}} |\text{other}\rangle,
\]

where

\[
|p\rangle = \frac{2\sigma}{\sqrt{3}} |p_{1/2}\rangle + \sqrt{\frac{2}{3}} |p_{3/2}\rangle.
\]

Here, \( |s\rangle \) and \( |p\rangle \) is the valence \( s \) and \( p \) orbitals of the heavier atom in the molecule, which mainly contributes to \( E_{\text{eff}} \) \( |\text{other}\rangle \) refers to AOs excluding \( |s\rangle \) and \( |p\rangle \).

Equation (8) can be rewritten such that the contributions from the nuclear charge \( Z \) (\( \Gamma'_{\text{rel,edm}} \)) and the electronic structure of the molecule (\( X \)) are separated, as given below

\[
E_{\text{eff}} = X \Gamma'_{\text{rel,edm}},
\]

\[
X = \frac{4\sigma}{\sqrt{3}} c_s c_p (\nu_s \nu_p)^{3/2},
\]

and

\[
\Gamma'_{\text{rel,edm}} = - \frac{4Z^2 \alpha^2 Z_i^2}{\gamma (4\gamma^2 - 1)}.
\]
Next, we give the analogous expression to $E_{\text{eff}}$ in the case of $W_s$ for $\Sigma$ molecule as follows, using the following atomic expression of $W_s$ [2, 9]

$$W_s = 2\Gamma'_{\text{rel,s-PS}},$$

and

$$\Gamma'_{\text{rel,s-ps}} = \frac{G_{\text{rel}} Z^2 \alpha}{\pi \sqrt{2}} \frac{4\gamma^2}{\Gamma^2(2\gamma + 1)} \left( \frac{1}{2Z\text{R}_{\text{nuc}}} \right)^{2-2\gamma}. \quad (17)$$

Here, $R_{\text{nuc}}$ is the nuclear radius. We modify equation (8) in [9] so that it is consistent with the expression for $X$ given in equation (14) for $W_s$. Equations (13) and (16) are based on the first-order perturbation theory and are represented as the expectation values of the unperturbed wavefunction. It is a good approximation because the influence of the eEDM and the S-PS interactions on the wavefunction should be negligible compared with that of the unperturbed Hamiltonian.

To get insights into the ratio $W_s/E_{\text{eff}}$, it is important that the part depending on the electronic structure of the molecules ($X$ in equation (14)) is common for both $E_{\text{eff}}$ and $W_s$ and hence cancel each other out in $W_s/E_{\text{eff}}$. As a result, the remaining part of $W_s/E_{\text{eff}}$ depends on only $Z$, as follows:

$$W_s/E_{\text{eff}} \propto \frac{\gamma^2}{\Gamma^2(2\gamma + 1)} \left( \frac{1}{2Z\text{R}_{\text{nuc}}} \right)^{2-2\gamma} \left/ \frac{1}{\gamma(4\gamma^2 - 1)} \right. \quad (18).$$

Here, we ignore some of the coefficients and physical constants that are not relevant for the analysis, for simplicity. From the expression given above, we can explain the reason why each of the HgX and SrX has similar $W_s/E_{\text{eff}}$. The former is the interaction between nucleons and the electrons inside the nucleus, while the latter is between the nuclear charge and the electrons distributed close to the nucleus.

Another observation from table 4 is that the values of $W_s/E_{\text{eff}}$ at the DF and CCSD levels are almost the same, although each value of $E_{\text{eff}}$ and $W_s$ is different due to correlation effects.

We explain this trend by utilizing the representation of the one-electron operator in the second quantized form. A one-electron operator $\hat{O}$ can be given by [70]

$$\hat{O} = \sum_{q,r} O_{qr} a^\dagger_q a_r, \quad (19)$$

where

$$O_{qr} = \int \psi^*_q \hat{O} \psi_r d\tau. \quad (20)$$

In the above expression, $\psi$ refers to the one-electron molecular spin-orbitals, $q$ and $r$ are arbitrary indices of the spin-orbitals, $a^\dagger_q (a_r)$ is an electron creation operator (annihilation operator) in a spin-orbital $\psi_q (\psi_r)$, respectively. From equation (19), the expectation value of $E_{\text{eff}}$ and $W_s$ can be written as follows:

$$E_{\text{eff}} = \langle \Psi | \hat{E}_{\text{eff}} | \Psi \rangle = \sum_{q,r} (E_{\text{eff}})_{qr} D_{qr}, \quad (21)$$

$$W_s = \langle \Psi | \hat{W}_s | \Psi \rangle = \sum_{q,r} (W_s)_{qr} D_{qr}, \quad (22)$$

where

$$(E_{\text{eff}})_{qr} = \int \psi^*_q \hat{E}_{\text{eff}} \psi_r d\tau, \quad (23)$$

$$(W_s)_{qr} = \int \psi^*_q \hat{W}_s \psi_r d\tau, \quad (24)$$

and

$$D_{qr} = \langle \Psi | a^\dagger_q a_r | \Psi \rangle. \quad (25)$$

Here, $\Psi$ is the electronic wavefunction of the unperturbed Hamiltonian, which includes the correlation effects.

Next, we generalize equation (11) for specifically highlighting the inner $s$ and $p$ orbitals. First, $\psi_q$ may be expressed as follows:

$$|\psi_q\rangle = \sum_{s} c_{s,q}\psi^s_{s'} + \sum_{p'} c_{p,q}\psi^p_{p'} + \sum_{\text{other}} c_{\text{other}}|\text{other}\rangle. \quad (26)$$

Here, $s'$ and $p'$ are the indices of the heavier atomic $s$ and $p$ orbitals in the molecule, respectively. Replacing equation (11) with equation (26), we can express equation (8) as follows:

$$(E_{\text{eff}})_{qr} \approx X_{qr} \Gamma'_{\text{rel,edm}}, \quad (27)$$

and

$$X_{qr} = \frac{2\sigma}{\sqrt{3}^{s'_{qr}}(s'_{qr})^3} \left( c_{s,q}^s c_{p,q}^p + c_{p,q}^p c_{s,q}^s \right) \quad (28)$$

From equation (21), $E_{\text{eff}}$ is expressed as follows

$$E_{\text{eff}} \approx \Gamma'_{\text{rel,edm}} \sum_{q,r} X_{qr} \langle \Psi | a^\dagger_q a_r | \Psi \rangle. \quad (29)$$

The above derivation using equation (26) can also be extended to $W_s$, and one obtains

$$W_s \approx \Gamma'_{\text{rel,s-ps}} \sum_{q,r} X_{qr} D_{qr}. \quad (30)$$

Finally, $W_s/E_{\text{eff}}$ can be expressed as follows

$$W_s/E_{\text{eff}} \approx \frac{\Gamma'_{\text{rel,s-ps}} \sum_{q,r} X_{qr} D_{qr}}{\Gamma'_{\text{rel,edm}} \sum_{q,r} X_{qr} D_{qr}} = \frac{\Gamma'_{\text{rel,s-ps}}}{\Gamma'_{\text{rel,edm}}} \approx \frac{\gamma^2}{\Gamma^2(2\gamma + 1)} \left( \frac{1}{2Z\text{R}_{\text{nuc}}} \right)^{2-2\gamma} \left/ \frac{1}{\gamma(4\gamma^2 - 1)} \right. \quad (31)$$
We see that the parts that depend on the electronic structure $\sum_{\mu} X_{\mu} D_{\mu}$ cancel out. As a result, $W_s/E_{\text{eff}}$ depends only on the nuclear charge $Z$ even at the correlation level.

The points mentioned above can explain the trend in our previously reported results [27]; $E_{\text{eff}}$ and $W_s$ in HgF are each larger than that of RaF (i.e. Z independent), while the ratio $(W_s/E_{\text{eff}})$ is larger for RaF (i.e. monotonically Z dependent). The values of $E_{\text{eff}}$ and $W_s$ themselves depend on the contraction of the core region of the outermost orbitals [27], and reflect the electronic structure of molecular orbitals. In contrast, $W_s/E_{\text{eff}}$ only depends on $Z$ and $R_{\text{soc}}$ as shown in equations (18) and (31), and are independent of the electronic structure of the molecule.

In the above discussion, we ignore the effects of $p_{3/2}$, $d$, $f$, … orbitals. However, their contributions to $E_{\text{eff}}$ and $W_s$ are much smaller than those from the $s$ and $p_{1/2}$ orbitals, because these orbitals are not distributed significantly in the region close to the nucleus. Hence, even though the excitations from (to) $p_{3/2}$, $d$, $f$, … orbitals may exist at the correlation levels, their effects on the total value of $W_s/E_{\text{eff}}$ would be insignificant, as our results for the ratio at the CCSD level indicate. Our analysis can be generalized to any molecules whose $s$ and $p_{1/2}$ orbitals mainly contribute to their open-shell configurations. For example, it is reported that the ratio $W_s/E_{\text{eff}}$ of triatomic molecules are almost the same as that of the corresponding monofluorides [71]. This result can also be understood from our analysis.

5. Conclusion

To conclude, we have discussed three broad aspects of HgA as well as other systems that could be of interest for future eEDM search experiments. In the first part of this work, we calculate molecular properties of HgA, using a series of basis sets from Dyall’s database. We find that double zeta basis sets do not lead to the correct sign for the PDM, even if polarization functions are included. In contrast, the cv3z basis set is of reasonably good quality for the calculation of $E_{\text{eff}}$, $W_s$, and PDM, as are the v3z and 4z_pol ones. This survey will help in the correct choice of basis for calculations that are of interest to fundamental physics, involving molecules with van der Waals-like character, such as HgA.

Next, we analyze the reason for smaller values of $E_{\text{eff}}$ and $W_s$ in HgA systems, where due to the Hg atom, we would normally expect a large $E_{\text{eff}}$ and $W_s$ (for example, Hg halides (HgX) and HgH). We found that in these systems, where van der Waals-like character is present, the SOMO electron localizes in the alkali atom, and leads much smaller $E_{\text{eff}}$ and $W_s$. We also observed that the values of $E_{\text{eff}}$ and $W_s$ for SrLi are comparable with SrH and SrF. The difference between HgA and SrA can be attributed to the stabilization of the valence 6s orbital of Hg. Our idea that SrA has relatively large P, T-odd properties could be extended to molecules containing the same group-2 systems; e.g. BaA and RaA.

Lastly, we found that the ratio $W_s/E_{\text{eff}}$ hardly depends on the electronic structure and the correlation effects, and dominantly depends on Z. We explain the reason for this behavior is due to the cancellation of the electronic structure parts in $W_s/E_{\text{eff}}$. This analysis supports the suggestion of our [27] and Gaul et al’s [56] previous works that performing two different experiments using heavy molecules, and relatively light molecules, is important to separate the contribution from the eEDM and the S-PS interactions. Based on these points, and in view of the successes in ultracold molecules that have been already reported using Sr containing systems (e.g. SrF [72]), in combination with the suitability of SrA for laser cooling as discussed in [66], we propose that the combination of SrA and one of the current leading candidate molecules that are heavier (ThO, HFi+, and YbF) to separate the eEDM and the S-PS interactions.

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