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Rapid Communications

Ultracold mercury–alkali-metal molecules for electron-electric-dipole-moment searches

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Heavy polar diatomic molecules are the leading candidates in searches for the permanent electric-dipole moment of the electron (eEDM). Next-generation eEDM search experiments ideally require extremely large coherence times, in large ensembles of trapped molecules that have a high sensitivity to the eEDM. We consider a family of molecules, mercury–alkali-metal diatomics, that can be feasibly produced from ultracold atoms. We present calculations of the effective electric fields experienced by the electron in these molecules. The combination of reasonably large effective electric fields, and the possibility of obtaining trapped ultracold samples, leads us to identify these molecules as favorable candidates for eEDM search experiments.

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The parity- ($\mathcal{P}$-) and time-reversal ($\mathcal{T}$-) violating electric-dipole moment of the electron (eEDM) is one of the most important tabletop probes of physics beyond the standard model of elementary particles [1–3]. It can provide information on PeV-scale physics, which is well beyond the reach of current accelerators [4]. Also, eEDM could offer insights into the baryon asymmetry in the universe [5]. The leading candidates for eEDM searches are heavy polar diatomic molecules [6–8]. The current best upper bound on the eEDM is provided by ThO [6,8], followed by limits from HfF$^+$ [7] and YbF [9]. A typical experiment measures energy shifts between different electron-spin projections relative to the internuclear axis of a molecule; using the theoretically calculated value of the effective electric field ($\mathcal{E}_{\rm eff}$) experienced by the electrons in the molecule, the measured energy shifts can be related to the fundamental eEDM. There can also be energy shifts due to another $\mathcal{P}$- and T-violating property, the scalar-pseudoscalar (S-PS) interaction between the electrons and the nuclei, parametrized by a theoretically calculated S-PS coefficient (W_s). The observation of a nonzero eEDM or S-PS energy shift could provide model-independent evidence of new physics beyond the standard model.

Out of the plethora of polar molecules that are available for eEDM experiments, mercury-containing diatomics [10–12] are distinguished by their exceptionally large values of $\mathcal{E}_{\rm eff}$ and W_s compared to other analogous systems. For example, HgF [11] has a significantly larger $\mathcal{E}_{\rm eff}$ even compared to molecules with mercury substituted by heavier atoms (e.g., RaF [13]). The enhanced sensitivity of Hg-containing molecules derives from the contraction of the valence $6s_{1/2}$ and $6p_{1/2}$ orbitals due to the weaker screening by the outermost core d electrons in Hg [14].

Beyond just the intrinsic sensitivity of a molecule to $\mathcal{P}$- and $\mathcal{T}$-violating physics determined by its $\mathcal{E}_{\rm eff}$ and W_s values, the sensitivity of an eEDM experiment improves with an increase in the electron spin coherence time and the total number of molecules observed during the experiment. Very long spin coherence times can be obtained with ultracold molecules trapped in optical dipole traps and optical lattices [15,16]. This strongly motivates the use of molecules whose electronic properties are amenable to direct laser cooling (e.g., [17–20]), or which can be assembled out of trapped ultracold atoms [21].

In this Rapid Communication, we identify a set of Hg-containing molecules with high eEDM sensitivities: mercury–alkali-metal diatomic molecules (HgA = HgLi, HgNa, and HgK). Experiments using these molecules have the potential to improve upon the current best eEDM measurements [7,8] by at least one order of magnitude, with a commensurate increase in the energy scale up to which new physics effects can be probed.

Theoretical calculations. The molecular properties of interest, $\mathcal{E}_{\rm eff}$ and W_s, are determined by the expressions [22,23]

$$\mathcal{E}_{\rm eff} = -2ic\sum_{j=1}^{N_e}\langle\psi|\beta\gamma_5\, p_j^2|\psi\rangle, \tag{1}$$

$$W_s = iG_F\sqrt{2}\sum_{j=1}^{N_e}\langle\psi|\beta\gamma_5\rho_A(\boldsymbol{r}_{Aj})|\psi\rangle, \tag{2}$$

where ψ is the ground-state wave function of a molecule, j refers to summation over the electrons in the system, β is the Dirac beta matrix, γ_5 is the product of the gamma matrices, p the momentum operator for electron, ρ_A the nuclear charge density, and G_F is the Fermi coupling constant ($2.222\,49 \times 10^{-14}$ a.u.). We assume that only the ^{202}Hg atom significantly affects W_s, as the contribution of the lighter atom is insignificant (cf. [24]).

We also calculate the molecular dipole moment (MDM), which is useful in determining the external electric field that one needs to apply, in order to polarize the molecule. The expression for the MDM of a molecule is

$$\mathrm{MDM} = \langle\psi|\left(-\sum_i r_i + \sum_A Z_A r_A\right)|\psi\rangle. \tag{3}$$

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In the above expression, the summation over the electronic coordinates is given by i, while that over the nuclear coordinates is indicated by A. Therefore, r_i is the position vector from the origin to the site of the ith electron, while r_A is the position vector from the origin to the coordinate of the Ath nucleus. r_A, in our case, is the equilibrium bond length for the molecule HgA, with A = Li, Na, or K, since we choose the Hg atom as our origin. Z_A is the atomic number of the alkali-metal atom, A.

The properties given by Eqs. (1)–(3) can be obtained once we solve for the wave function, ψ. We employ a relativistic coupled cluster method, where the wave function is given by

$$|\psi\rangle = e^{T}|\Phi_0\rangle. \tag{4}$$

Here, T refers to the cluster operator, and is associated with exciting holes (occupied orbitals) to particles (unoccupied ones). The exponential structure, e^T, takes into account all possible hole-particle excitations in the system, and $|\Phi_0\rangle$ is the Dirac-Fock (DF) reference determinant that it acts on. The DF method is the relativistic version of the Hartree-Fock approach, where each electron in a molecule experiences a mean potential due to all the other electrons. The difference between the two-body Coulomb and the DF interactions is referred to as the residual interaction. The physical processes arising from the residual interaction are known as correlation effects. The coupled cluster method (CCM), which is considered to be the gold standard of many-body theory [25], is a powerful and efficient way of determining electron correlation. The CCM when compared to finite order many-body perturbation theory has the advantage of capturing the effects of the residual interaction to all orders in perturbation, for a given level of hole-particle excitation. It also fares better than the truncated configuration-interaction (CI) method, another well-known approach that goes beyond the DF approximation where the wave function is written as a linear combination of several configuration states, in that for a given level of hole-particle excitation, the CCM includes more physical effects arising due to correlation [25]. Also, unlike truncated CI, the coupled cluster is size extensive, that is, the energy scales with the number of particles. In such a framework, the most straightforward way to express an expectation value of an operator, O, is

$$\langle O\rangle = \frac{\langle\Phi_0|e^{T\dagger}Oe^{T}|\Phi_0\rangle}{\langle\Phi_0|e^{T\dagger}e^{T}|\Phi_0\rangle}. \tag{5}$$

The above equation can be rewritten as follows [26]:

$$\langle O\rangle = \langle\Phi_0|e^{T\dagger}O_N e^{T}|\Phi_0\rangle_C + \langle\Phi_0|O|\Phi_0\rangle. \tag{6}$$

The subscripts N and C refer to normal-ordered arrangement of operators and connected terms, respectively [25,27,28]. In our work, we consider single and double hole-particle excitations (the relativistic coupled-cluster singles and doubles (CCSD) approximation [29,30]) in solving the coupled cluster equations, while for the expectation value, we only consider the terms that are linear in T (the linear expectation value–CCSD or the LE-CCSD approximation). Therefore, the expression for the expectation value becomes

$$\langle O\rangle = \langle\Phi_0|(1+T_1^{\dagger}+T_2^{\dagger})O_N(1+T_1+T_2)|\Phi_0\rangle_C + \langle\Phi_0|O|\Phi_0\rangle. \tag{7}$$

The validity of this approximation in calculating $\mathcal{E}_{\text{eff}}$ has been tested in a previous work [31]. Although the previous work [31] shows that the nonlinear terms may contribute to MDM, the contribution of the higher order correlation would be small for the case of HgA, as shown later.

For DF computations and the atomic to molecular orbital transformations, we employed the UTCHEM code [32,33], while the CCSD amplitudes were obtained from DIRAC08 [34]. We then computed the CCSD expectation values using integrals and amplitudes from UTCHEM and DIRAC08.

For the DF calculation, optimized functions, called basis sets, are employed for each atom in a molecule. Among the simplest options is the Gaussian-type double zeta (DZ) basis [35]. The triple zeta (TZ) basis, an enlarged version of the DZ basis, is a better quality than the latter, followed by quadruple zeta (QZ) basis, and so on. More functions can be included in a basis, to take into account additional physical effects. We used uncontracted Dyall's triple zeta quality basis sets (more specifically the cvTZ basis [36], which includes additional polarizing functions) for all of the atoms in these molecules. In the CCSD calculations, we cut off the virtual spinors with orbital energy above 100 a.u. We used the following bond lengths (in angstroms): HgLi: 2.92; HgNa: 3.52; and HgK: 3.90 [37]. The direction of the MDM and the molecular axis are from the mercury atom to the alkali-metal atom.

The results of our calculations of $\mathcal{E}_{\text{eff}}$, W_s, and the MDM are given in Table I. An interesting feature of these systems is the unusually large effect of electron correlations due to the van der Waals bonding in these molecules, which we have not observed in other eEDM candidates such as YbF or HgX (X = F, Cl, Br, and I) [11,22]. The electron correlations increase $\mathcal{E}_{\text{eff}}$ and W_s to almost thrice their DF values, while substantially affecting the MDM. $\mathcal{E}_{\text{eff}}$ and W_s for all these molecules are comparable to these of YbF ($\mathcal{E}_{\text{eff}} = 23.1$ GV/cm [22], $W_s = -40.5$ kHz [24]).

We provide more detailed results in Tables II–V, where we examine the individual correlation contributions from each term of Eq. (7). In Table II, we present the results for $\mathcal{E}_{\text{eff}}$ and W_s. For brevity, we have used a notation where OT_1, for example, is actually $\langle\Phi_0|O_N T_1|\Phi_0\rangle_C$, $T_1^{\dagger}OT_1$ is actually $\langle\Phi_0|T_1^{\dagger}O_N T_1|\Phi_0\rangle_C$, and so on. The contribution from OT_2 (and its complex conjugate) is zero, due to the Slater-Condon rules. Also, $\langle\Phi_0|O_N|\Phi_0\rangle$ is zero, due to O being in its normal-ordered form.

Table II shows that the correlation effects dominate in these systems, to an extent where the OT_1 term exceeds the DF value. This is in contrast to other eEDM candidates, such as YbF, BaF, or HgF, where correlation effects only slightly change the DF term (within 30%) [22,24,31]. In HgF, for example, each of the terms involving T do not exceed the DF value, and this combined with the fact that there are cancellations between the correlation terms, leaves behind a small correlation contribution (relative to the DF one) [38].

Tables III–V give the individual contributions to the MDM due to the electric term, which is the first term in Eq. (3). The third column is the sum of each electronic term; e.g., the third column for "$T_1^{\dagger}H_{\text{MDM}}T_1$" is the sum of electronic terms: "DF," "$H_{\text{MDM}}T_1$ + cc," and "$T_1^{\dagger}H_{\text{MDM}}T_1$."

TABLE I. The calculated values of $\mathcal{E}_{\text{eff}}$ (in GV/cm), W_s (in kHz), and the MDM (in Debye). The Dirac-Fock (DF, in superscript), the correlation (corr, in superscript), and the total (no superscript) contributions have been provided. The direction of the MDM is taken as the molecular axis from the mercury to the alkali-metal atom.

Molecule	$\mathcal{E}_{\text{eff}}^{\text{DF}}$	W_s^{DF}	MDM$^{\text{DF}}$	$\mathcal{E}_{\text{eff}}^{\text{corr}}$	W_s^{corr}	MDM$^{\text{corr}}$	$\mathcal{E}_{\text{eff}}$	W_s	MDM
HgLi	13.74	31.02	−1.47	24.05	55.35	1.95	37.79	86.37	0.48
HgNa	7.59	17.15	−0.88	12.74	29.31	1.15	20.33	46.46	0.27
HgK	5.73	12.95	−1.48	10.51	24.10	1.72	16.24	37.05	0.24

We observe from Tables III–V that the contribution of the $H_{\text{MDM}}T_1 + \text{cc}$ is much more dominant than the other correlation terms for all of the three molecules. The contributions from the T_2 terms are very small. From the maximum difference between the values including only T_1 (i.e., 0.47, 0.25, and 0.21 for HgLi, HgNa, and HgK, respectively) and the final values (i.e., 0.48, 0.27, and 0.24 for HgLi, HgNa, and HgK, respectively), we expect that the nonlinear terms change the MDM by less than 0.03 D. Therefore the results at the LE-CCSD method are good estimates of the MDM of Hg*A* molecules. Since the dominant correlation contribution to the MDM is from $H_{\text{MDM}}T_1 + \text{cc}$, we observe that low-order correlation effects are important in Hg*A*.

We now estimate the errors in our calculations. The possible sources of the errors in our calculations of $\mathcal{E}_{\text{eff}}$ are due to three effects: (1) the noninclusion of higher excitations in the wave function, for example, triples; (2) ignoring the nonlinear terms in the coupled cluster operators in the expectation value; and (3) incompleteness of the basis functions. To estimate the error due to (1) and (2), we rely on comparisons between LE-CCSD and finite field CCSD(T) [FF-CCSD(T)] in a previous work. In the finite field approach, a property is expressed as an energy derivative, rather than as an expectation value; it therefore takes into account all the nonlinear terms that are neglected in our expectation value approach. In our earlier work on HgF [31], the largest change in $\mathcal{E}_{\text{eff}}$ between LE-CCSD and FF-CCSD(T) was approximately 5%. We assume that the error due to (1) and (2) for Hg*A* is comparable to HgF. For (3), we estimate that the error is ∼15%, by examining the difference between results obtained with double zeta (cvDZ) and triple zeta (cvTZ) basis sets [39]. This estimate assumes that the change from triple zeta (cvTZ) to quadruple zeta (cvQZ) quality basis sets is not larger than 15%; the assumption was tested for Hg*A* using DZ, TZ, and QZ basis functions (but without the polarizing functions) where we observed that the difference between TZ and QZ basis sets was smaller than that between DZ and TZ basis sets [39]. We combine these systematic error estimates linearly, and conservatively estimate a total error of 20% in our calculations of $\mathcal{E}_{\text{eff}}$. Based on similar considerations, we do not expect the error in W_s to be greater than 20% either. From the expansion of the expectation value in Tables III–V, we see that the error in the MDM due to the exclusion of higher-order excitations is as follows: (1) the nonlinear terms may not contribute to more than 0.03 D, and (2) the higher excitations like triples will not alter the MDM noticeably. Calculations of the MDM can be quite sensitive to the choice of basis, especially for molecules with van der Waals bonds such as Hg*A*. Our results for the MDM of Hg*A* molecules are in broad agreement with Cremer *et al.* [40], who used similar equilibrium bond lengths in their calculations but different basis sets and computational methods. Their basis sets were Dyall's DZ for the Hg core, Dyall's TZ for the valence Hg orbitals, aug-ccpVTZ for Li and Na, and 6-311++G(3df) basis for K; in addition, their calculations only considered scalar relativistic effects. Here, in comparison, we use Dyall's cvTZ basis sets and the Dirac-Coulomb Hamiltonian throughout.

TABLE II. Contributions from the individual terms of the LE-CCSD expression, to $\mathcal{E}_{\text{eff}}$ (GV/cm) and W_s (kHz) for HgLi, HgNa, and HgK; cc refers to the complex conjugate of the term that it accompanies. The operator, O, can refer to either the operator of $\mathcal{E}_{\text{eff}}$, or that of W_s, whose expectation value expressions are given in Eqs. (1) and (2), respectively, in the main text.

	$\mathcal{E}_{\text{eff}}$			W_s		
Term	HgLi	HgNa	HgK	HgLi	HgNa	HgK
DF	13.74	7.59	5.73	31.02	17.15	12.95
$OT_1 + \text{cc}$	21.46	11.42	9.24	49.28	26.22	21.15
$T_1^\dagger OT_1$	1.10	0.62	0.56	2.45	1.39	1.25
$T_1^\dagger OT_2 + \text{cc}$	2.96	1.46	1.28	7.03	3.48	3.02
$T_2^\dagger OT_2$	−1.47	−0.76	−0.56	−3.41	−1.78	−1.31

Experimental aspects. In this section, we briefly comment on the possibility of an eEDM experiment, using Hg*A* systems, based on some preliminary considerations. The figure of merit for the statistical sensitivity of an eEDM experiment using molecules is $F = \mathcal{E}_{\text{eff}}\sqrt{N\tau}$, where N is the number of molecules interrogated in the experiment and τ is the coherence time for the electron spin precession. The values of $\mathcal{E}_{\text{eff}}$ for Hg*A* molecules are comparable to, or larger than, those of some other molecules planned for use in next-generation eEDM experiments (cf. [20,41,42]). In a possible optical lattice eEDM experiment with Hg*A*, a fairly large

TABLE III. Contributions from the electronic part of the CCSD linear expectation value, to the MDM of HgLi, in Debye (D). The third column refers to the sum of electronic terms. The term cc refers to the complex conjugate of the term that it accompanies. The nuclear contribution to the MDM is 42.06 D.

Term	Electronic term	Sum	MDM
DF	−43.53	−43.53	−1.47
$H_{\text{MDM}}T_1 + \text{cc}$	1.87	−41.66	0.40
$T_1^\dagger H_{\text{MDM}}T_1$	0.06	−41.60	0.47
$T_1^\dagger H_{\text{MDM}}T_2 + \text{cc}$	−0.04	−41.64	0.42
$T_2^\dagger H_{\text{MDM}}T_2$	0.05	−41.59	0.48

TABLE IV. Contributions from the electronic part of the CCSD linear expectation value, to the MDM of HgNa, in Debye (D). The third column refers to the sum of electronic terms. The term cc refers to the complex conjugate of the term that it accompanies. The nuclear contribution to the MDM is 185.93 D.

Term	Electronic term	Sum	MDM
DF	−186.80	−186.80	−0.88
$H_{\text{MDM}}T_1 + \text{cc}$	1.11	−185.69	0.23
$T_1^\dagger H_{\text{MDM}}T_1$	0.01	−185.68	0.25
$T_1^\dagger H_{\text{MDM}}T_2 + \text{cc}$	−0.01	−185.69	0.23
$T_2^\dagger H_{\text{MDM}}T_2$	0.04	−185.66	0.27

TABLE V. Contributions from the electronic part of the CCSD linear expectation value, to the MDM of HgK, in Debye (D). The third column refers to the sum of electronic terms. The term cc refers to the complex conjugate of the term that it accompanies. The nuclear contribution to the MDM is 355.81 D.

Term	Electronic term	Sum	MDM
DF	−357.30	−357.30	−1.48
$H_{\text{MDM}}T_1 + \text{cc}$	1.68	−355.62	0.19
$T_1^\dagger H_{\text{MDM}}T_1$	0.01	−355.60	0.21
$T_1^\dagger H_{\text{MDM}}T_2 + \text{cc}$	−0.02	−355.63	0.19
$T_2^\dagger H_{\text{MDM}}T_2$	0.05	−355.57	0.24

coherence time can be expected [15]. Using the computed MDM values, we estimated the magnitude of the laboratory electric field required to significantly polarize Hg*A* molecules $\mathcal{E}_{\text{pol}} = 2B_e/D$ (where B_e is the equilibrium rotational constant of the molecule and D is the MDM). The values of $\mathcal{E}_{\text{pol}}$ are (71, 28, 17) kV/cm for (HgLi, HgNa, HgK), implying that one can feasibly polarize a sample of trapped ultracold Hg*A* molecules. It may be possible to apply large external fields without any significant leakage-current-induced spurious magnetic fields [43]. Cooling alkali-metal atoms to microkelvin temperatures and trapping in optical lattices have been implemented for Hg atoms in the context of optical lattice clocks [44,45]. Methods for assembling molecules from ultracold atoms have advanced significantly over the last decade [46–50]. In particular, molecules isoelectronic to Hg*A* have been produced at ultracold temperatures [51,52], and methods for producing other ultracold alkali–alkaline-earth-metal molecules [53] (including a Hg-alkali molecule, HgRb [54,55]) are currently being investigated. It seems within the realm of possibility that these techniques can be extended to the analog molecules HgLi, HgNa, and HgK. We base our estimate for the eEDM sensitivity on the conservative assumption that $N = 10^4$ ultracold Hg*A* molecules can be produced in an optical lattice, using the numbers demonstrated with isoelectronic YbLi molecules [56,57]. Based on the very large coherence times between hyperfine states that have been observed with lattice-trapped ultracold polar molecules [15], we assume that a coherence time $\tau = 1$ s can be realized. From numerical calculations of the Stark effect in the hyperfine and rotational states in Hg*A*, we estimate that an electron-spin orientation factor, $\xi = \langle \vec{S} \cdot \hat{n} \rangle = 0.13$ [58], can be achieved using laboratory electric fields of magnitude $\mathcal{E}_{\text{lab}} = \mathcal{E}_{\text{pol}}$. With these values of N, τ, ξ, and $\mathcal{E}_{\text{eff}}$ and a total integration time of $T = 10^7$ s, we estimate preliminary eEDM sensitivities $\delta d_e = (1.3, 2.5, 3.1) \times 10^{-30}$ *e* cm for (HgLi, HgNa, HgK), offering the prospect of improvements over the current experimental limit ($|d_e| < 1.1 \times 10^{-29}$ *e* cm [8]).

To conclude, we have presented the results of our CCSD calculations of $\mathcal{E}_{\text{eff}}$, W_s, and MDMs of Hg-alkali systems. Also, we present preliminary estimates of the expected sensitivities for Hg-alkali molecules, which suggest that these systems could be promising candidates for eEDM experiments. Further work on the experimental aspects would be necessary in the future to explore the possibilities of performing eEDM experiments using Hg*A* systems.

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