Enhanced sensitivity of the electron electric dipole moment from YbOH: The role of theory

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The prospect of laser cooling of polyatomic molecules has opened a new avenue in the search for the electric dipole moment of the electron (eEDM). An upper bound on the eEDM would probe new physics arising from beyond the standard model of elementary particles. In this work, we report theoretical results for the effective electric field experienced by the electron in YbOH and its molecular electric dipole moment using a relativistic coupled cluster theory. We compare these two properties of YbOH with YbF, which also has a singly unoccupied orbital on the Yb ion. We also present the results of the effective electric field for different bond angles, which sheds light on the sensitivity that can be expected from an eEDM experiment with YbOH.

I. INTRODUCTION

The electric dipole moment of the electron (eEDM) could arise due to simultaneous violations of parity (P) and time reversal (T) symmetries [1–4]. Therefore, if observed, the eEDM would provide a direct proof of T violation. In spite of many ingenious experiments for over five decades, this property has not yet been observed. Currently, heavy polar diatomic molecules provide the best upper bounds on the eEDM [5,6], with the best result coming from ThO [7–9], followed by HfF$^+$ [10] and YbF [11]. The standard model backgrounds for the eEDM are 10 orders of magnitude below the current experimental limit [12]. However, the eEDM values predicted by theories beyond the standard model are much larger [13], and most of them are well within the bounds set by the eEDM experiments to date. These bounds, therefore, constrain theories beyond the standard model [14], as well as offer insights into the baryon asymmetry in the universe [15]. The importance of this approach to furthering our understanding of new physics stems from the fact that one can probe peta electronvolt energy scales without using high-energy accelerators [16] but instead using molecular table-top experiments that measure quantities like the eEDM to very high levels of precision.

A measurement of the shift in energy of a molecule (ΔE) in some state due to an electron's EDM (d_e), in combination with a theoretically determined effective electric field, $\mathcal{E}_{\mathrm{eff}}$ (related by the expression $\Delta E = -d_e \mathcal{E}_{\mathrm{eff}}$), yields an upper bound to the eEDM. However, the choice of a candidate molecule for an experiment depends on various considerations, which include a fairly large $\mathcal{E}_{\mathrm{eff}}$, and a reasonable molecular electric dipole moment (*not P and T violating*, and denoted in this manuscript by d_M). d_M plays a key role in deciding the extent to which one can polarize a molecule in a laboratory frame (quantified by the polarization factor, η). Specifically, η is proportional to $d_M E / \Delta$, where E is the applied electric field, and Δ is the energy difference between opposite parity states in the molecule.

The choice of a candidate molecule for an eEDM experiment also relies upon experimental factors such as the number

of molecules (N) that one can produce, the total integration time (T), coherence times of the molecule (τ), as well as robustness to systematic errors. Of these factors, $\mathcal{E}_{\mathrm{eff}}$ plays a special role, and this can be understood from the expression for the figure of merit for the statistical sensitivity in an eEDM experiment:

$$\mathcal{F} = \sqrt{NT\tau} \, \mathcal{E}_{\mathrm{eff}} \eta \qquad (1)$$

Therefore, a reasonably large value of $\mathcal{E}_{\mathrm{eff}}$ improves the statistical sensitivity substantially. This quantity must be calculated and cannot be measured. However, the challenges in determining $\mathcal{E}_{\mathrm{eff}}$ arise purely due to relativistic effects [3]. This necessitates a relativistic many-body treatment of this quantity.

Not all of the factors mentioned above can be satisfied by a single system. Several diatomic molecules have been proposed in the recent past, including HgX [17], RaF [18], PbF [19], PbO [20], and BaF [21,22], based on a combination of some of the considerations mentioned above. The search for new candidates that can promise better sensitivities than the current best-leading molecules is crucial to future eEDM research.

Polyatomic molecules are currently emerging as promising eEDM candidates. The first fast Sisyphus laser cooling of SrOH opened new avenues for polyatomics to come to the forefront of eEDM search experiments [23]. Subsequently, RaOH was proposed as a suitable candidate [24]. Around the same time, Kozyryev and Hutzler [25] proposed YbOH molecules for eEDM experiments. Unlike most diatomics, YbOH, a triatomic, offers two advantages at the same time, namely, the possibility of laser cooling and possessing a bending mode with closely spaced parity doublets, therefore having internal comagnetometer states and being highly polarizable. Such a comagnetometer state avoids systematics associated with reversing electric fields, while laser-cooling and trapping drastically reduces systematics such as a motional magnetic field. Trapping the molecules in an optical lattice would also offer a tremendous improvement in coherence

time, of the order of seconds, as compared to the usual $\tau \sim$ milliseconds. Lastly, the spectroscopy of the molecule has already been studied reasonably. In conclusion, based on these factors, the authors expect an increase of 4 orders in sensitivity as compared to the current best experiments. However, this would also require that $\mathcal{E}_{\text{eff}}$ be comparable to that of leading eEDM candidates, and a calculation of the quantity has not been performed to date. In this work, we present accurate values of $\mathcal{E}_{\text{eff}}$ and d_M for the ground state of YbOH, in a linear geometry. We also make contact with experiment by presenting a study of $\mathcal{E}_{\text{eff}}$ for bent geometries.

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II. THEORY AND METHODOLOGY

The expectation value expressions for $\mathcal{E}_{\text{eff}}$ and d_M are, respectively,

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

$$d_M = \langle \psi | \left(-\sum_{j=1}^{N_e} r_j + \sum_{A=1}^{N_A} Z_A r_A \right) | \psi \rangle. \tag{3}$$

The summation, j, is over the number of electrons (N_e) in the molecule, while A denotes the summation over the number of nuclei (N_A). β refers to the Dirac beta matrix, and γ_5 is the product of the Dirac matrices. p_j refers to the operator corresponding to the momentum of the jth electron and r_j the position vector from the origin to the site of the jth electron. Z_A is the atomic number of the Ath nucleus, and r_A is the vector from the origin to the Ath nucleus. We work in the Born-Oppenheimer approximation, where the nuclei are "clamped" with respect to the electrons. In order to obtain $\mathcal{E}_{\text{eff}}$ and d_M, we need to take the expectation values of the respective operators. Further details can be found in Refs. [26–28].

In order to evaluate the expressions given in Eqs. (2) and (3), we use a relativistic coupled cluster method (RCCM), where $|\psi\rangle = e^T |\Phi_0\rangle$. Here, T is known as the cluster operator, and Φ_0 is the reference state, which is the Dirac-Fock (DF) wave function in this case. Further details can be found in Refs. [17,26,27]. It is worth noting that at a given level of particle-hole excitation, the evaluation of the electron correlation effects by the coupled cluster method is equivalent to doing so to all orders in perturbation theory [29]. Once we compute the wave function, the property of interest, O, can be obtained by evaluating an expectation value expression [30]

$$\langle O \rangle = \frac{\langle \Phi_0 | e^{T^\dagger} O e^T | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^\dagger} e^T | \Phi_0 \rangle} \tag{4}$$

$$= \langle \Phi_0 | O | \Phi_0 \rangle$$
$$+ \langle \Phi_0 | (1 + T_1 + T_2)^\dagger O_N (1 + T_1 + T_2) | \Phi_0 \rangle_C. \tag{5}$$

The subscripts N and C mean that the creation and annihilation operators are normal ordered and that each term in the expression is fully connected, respectively [29,31,32]. We

work with the coupled cluster singles and doubles (CCSD) approximation, where $T = T_1 + T_2$. Also, although we solve the full CCSD equations to obtain the amplitudes associated with the excitation operators T_1 and T_2, we only use the linear terms in T for solving the expectation value expression in Eq. (5). This approximation is reasonable, since dominant contributions to our properties of interest are mostly from the linear terms. In Eq. (5), the first term is the DF expression. On expanding the second term, we get $\langle \Phi_0 | O_N T_1 | \Phi_0 \rangle_C$, $\langle \Phi_0 | T_1^\dagger O_N T_1 | \Phi_0 \rangle_C$, and so on. Hereafter, we shall write these terms in a more concise manner as OT_1, $T_1^\dagger OT_1$, etc. These terms correspond to different kinds of physical effects arising from electron correlation. One of the principal merits of the above approach is that it makes this connection transparent. We note that in Eq. (5), the bra is a first approximation to the more general relativistic normal RCCM [33], where the bra and the ket are treated on different footings. The first line in the equation below gives the expression for the bra, denoted by $\langle \widetilde{\psi} |$ ($\widetilde{T}$ contains in it deexcitation operators), while the second line corresponds to that from our RCCM approach:

$$\langle \widetilde{\psi} | = \langle \Phi_0 | (1 + \widetilde{T}) e^{-T} \tag{6}$$

$$\approx \langle \Phi_0 | (1 + T^\dagger). \tag{7}$$

For our computations, we used the UTCHEM code [34,35] for DF and atomic orbital (AO) to molecular orbital (MO) integral transformations, while we obtained the t amplitudes, from DIRAC08 [36]. We performed our calculations for a linear geometry (the geometry of YbOH, as demonstrated in Ref. [37]) with the Yb-O bond length being 2.0026 Å [38] and for O-H, 0.922 Å [38]. The DF computations require basis sets, which are single-particle functions, as an input [39]. We employed Gaussian-type orbitals, specifically uncontracted Dyall's double-zeta (DZ), triple-zeta (TZ, which have more elements and are of better quality than the DZ option), and quadruple-zeta (QZ, the largest available in Dyall's database) basis sets for all three atoms [40,41]. We round off all of our calculated values in this work to two decimal places.

III. RESULTS AND DISCUSSIONS

Table I provides the results of our computations for $\mathcal{E}_{\text{eff}}$ and d_M. The results show that $\mathcal{E}_{\text{eff}}$ is comparable to that of YbF. This is not too surprising, since in both systems, the dominant contributions come from the unpaired electron that belongs to the singly occupied MO of the Yb atom. However, we note that d_M is substantially smaller than that for YbF (at 3.91 D [42]). We did not impose any cutoff on the virtuals at the AO-to-MO transformation stage, and therefore subsequently

TABLE I. The calculated values of $\mathcal{E}_{\text{eff}}$ (in GV/cm) and d_M [in Debye (D)]. The Dirac-Fock (DF, in superscript) and the total (no superscript) contributions have been provided. The TZ result is at 800 a.u. virtuals' cut-off value and QZ at 500 a.u.

Basis	d_M^{DF}	d_M	$\mathcal{E}_{\text{eff}}^{DF}$	$\mathcal{E}_{\text{eff}}$
DZ	0.83	0.82	17.78	23.49
TZ	0.90	1.02	18	23.85
QZ	0.94	1.10	18.02	23.80

TABLE II. Contributions from the individual terms of the expectation value expression, at the QZ level of basis (with 200 a.u. cutoff for YbOH), to $\mathcal{E}_{\text{eff}}$ (GV/cm). cc refers to the complex conjugate of the term that it accompanies.

Term	$\mathcal{E}_{\text{eff}}$	$\mathcal{E}_{\text{eff}}^{YbF}$
DF	18.02	18.16
$H_{\text{eEDM}}^{\text{eff}}T_1+$ cc	6.56	6.28
$T_1^{\dagger}H_{\text{eEDM}}^{\text{eff}}T_1$	-0.86	-1.31
$T_1^{\dagger}H_{\text{eEDM}}^{\text{eff}}T_2+$ cc	0.16	0.18
$T_2^{\dagger}H_{\text{eEDM}}^{\text{eff}}T_2$	-0.16	-0.17

in the CCSD level, in the DZ calculations. However, due to the steep computational cost involved in the TZ and QZ calculations, we cut off the high-lying virtuals, specifically those above 800 atomic units (a.u.) for the TZ calculations. We chose this cut-off value not only because it is sufficiently high lying, but also because the energy difference between the cut-off value and the next virtual is 300 a.u. This choice strengthens our case, since the energy of the next orbital is over 1000 a.u. For the QZ basis, we imposed a 200-a.u. cutoff. From previous works, for example, Ref. [43], we know that a cutoff of 200 a.u. is sufficient to obtain accurate results. We still explicitly verify this by examining $\mathcal{E}_{\text{eff}}$ and d_M values for sample cut-off values using the QZ basis. We find that the CCSD value of d_M hardly changes (1.10 D), while $\mathcal{E}_{\text{eff}}$ changes by less than 1% (23.56, 23.72, and 23.80 for 100, 200, and 500 a.u., respectively), which is well within the error bars in our calculations.

We now examine the correlation effects in $\mathcal{E}_{\text{eff}}$ by examining the terms from Eq. (5). The results (for the QZ basis) are presented in Table II. We also give the QZ results for YbF [26] for comparison. This illustrates the similarities not only in the DF values, but also in the correlation trends for the two isoelectronic molecules. These are interesting in their own right from a many-body theoretic point of view and also from the perspective of what one may expect for the $\mathcal{E}_{\text{eff}}$ of YbCH$_3$, which has also been proposed as an interesting eEDM candidate [25]. The similarity in the $\mathcal{E}_{\text{eff}}$ values of YbF, YbOH, and YbOCH$_3$ would not be a surprise, though, since one would expect that the electronic structure of the system would be more important than the number of electrons themselves, particularly the number of electrons, and more importantly, the fact that there is one unpaired electron in the same heavy atom, Yb. Since the expectation value approach and the energy derivative give almost the same result (23.1 and 23 GV/cm, respectively [44]) for YbF, we expect that YbOH's $\mathcal{E}_{\text{eff}}$ would not change if were to be calculated using an energy derivative.

The d_Ms are very different for YbOH and YbF. In the case of YbOH, O can accept electrons from both Yb and H, while in the case of YbF, F can only do so from Yb. There is a cancellation between the dipole moment contributions from "Yb to O" and "O to H," as they are in opposite directions. Therefore, d_M of YbOH is smaller than that of YbF. This is qualitatively confirmed from the values of Mulliken charges of YbOH, 0.684 (Yb), –1.064 (O), and 0.380 (H), obtained
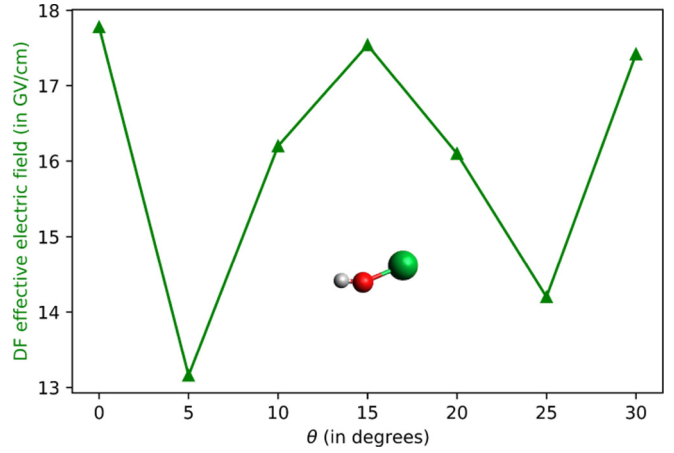

FIG. 1. The calculated values of $\mathcal{E}_{\text{eff}}^{DF}$ (GV/cm) at different bond angles (in degrees). As the inset shows, in the H-O-Yb molecule, θ is the angle formed by O-Yb with respect to H-O.

at the DF level, using the DZ basis set (details of Mulliken analysis can be found in Ref. [45]).

We now present the error estimate in our calculations. The error in the calculated values can be due to exclusion of higher-order correlation effects and choice of basis sets. For $\mathcal{E}_{\text{eff}}$, we look at the contributions from terms involving T_2 (which is negligibly small, since the contributions from $T_1^{\dagger}H_{\text{eEDM}}^{\text{eff}}T_2$ and $T_2^{\dagger}H_{\text{eEDM}}^{\text{eff}}T_2$ almost exactly cancel) and compare the sum with that obtained from terms involving T_1 (5.7 GV/cm). We expect that terms containing T_3 and beyond will contribute less than those that contain T_2 and therefore estimate the error from higher-order excitations to be almost negligible, and conservatively set it at 2%. The finite-field CCSD(T) results for $\mathcal{E}_{\text{eff}}$ of several other molecules, from our previous work [46], indicate that both partial triples and the nonlinear terms in the expectation value will not contribute significantly. Hence, a conservative error estimate by neglecting nonlinear terms is about 2%. The error due to basis-set incompleteness can be estimated as 2% by assuming that the result would not change more than the difference between the TZ and QZ values. The combined error from these sources for $\mathcal{E}_{\text{eff}}$ is about 6%.

We now turn to $\mathcal{E}_{\text{eff}}$ at the DF level ($\mathcal{E}_{\text{eff}}^{DF}$) for bent geometries, as shown in Fig. 1. Although the ground state of the YbOH molecule is linear, results for bent geometries are relevant for eEDM experiments that rely on low-lying vibrational states of the ground electronic states with parity doubling [25]. In the case of YbOH, since the dominant contribution to $\mathcal{E}_{\text{eff}}$ is at the DF level (about 75%), the results do not change significantly from DZ through the QZ basis, and with the assumption that the correlation effects do not drastically change with bond angle, it suffices to compute the quantity at the DF level, with the DZ basis.

The figure shows that $\mathcal{E}_{\text{eff}}^{DF}$ varies from around 13 to 18 GV/cm, which is clearly non-negligible. Results from relativistic many-body theory have proven to be surprising in many cases in that one can never, with certainty, predecide what to expect of a physical quantity. It is indeed true that intuition points to the wave function, and therefore $\mathcal{E}_{\text{eff}}$ should not change significantly in a low-lying mode, especially given

TABLE III. The calculated values of $\mathcal{E}_{\text{eff}}^{DF}$ (in GV/cm) at different bond lengths, $R_{\text{Yb-O}}$ (in Angstroms). A bond length of 2.0026 Å corresponds to the original value.

$R_{\text{Yb-O}}$	$\mathcal{E}_{\text{eff}}^{DF}$
1.5026	12.24
1.7526	15.78
2.0026	17.78
2.2526	18.73
2.5026	18.97

that the energy difference between the ground state and the (010) state is only 10 THz. For example, if the state of interest had been a stretch mode, the change in bond length between the two ends of that vibrational state could not be over 0.1 Å, leading to almost no change in $\mathcal{E}_{\text{eff}}$. However, the state of interest to the YbOH eEDM experiment is a low-lying *bent* mode. As the bond angle for the mode is not known, nor is it currently possible to determine it in a straightforward way, we studied systematically the variation of the effective electric field with θ. We observe, in contrast to expectations based on intuition, a change in θ could change $\mathcal{E}_{\text{eff}}^{DF}$ from 13 to 18 GV/cm—a staggering 38%! Therefore, the quantity is quite different at $0°$ and $5°$ angles. Also, note that the figure shows that $\mathcal{E}_{\text{eff}}^{DF}$ does not change monotonically but in fact oscillates! Therefore, to not perform an explicit bent geometry calculation and to assume that the changes in effective electric field would be extremely small in a low-lying vibrational state could potentially lead to wrong expectations from a very important eEDM experiment on YbOH.

In order to understand the underlying many-body effects that lead to the unexpected change in $\mathcal{E}_{\text{eff}}^{DF}$, we rewrite the DF contribution as

$$\mathcal{E}_{\text{eff}}^{DF} = 2 \sum_{k,l} C_k^{L*} C_l^{S} \langle \chi_k^{L} | h_{\text{eEDM}} | \chi_l^{S} \rangle, \qquad (8)$$

where k and l are summations over the large and small component basis functions, themselves denoted by χ_k^{L} and χ_l^{S}, respectively, Cs are the DF coefficients, and h_{eEDM} is the one-body eEDM operator. We perform this analysis for three bond angles in order to examine the dominant contribution in the equation given above, viz., $s - p_{1/2}$ and $p_{1/2} - s$ mixings of Yb, where the bra and ket in the above equation are s and $p_{1/2}$ for the former, and $p_{1/2}$ and s for the latter [47], for bent geometries. We obtained 13.07, 16.1, and 12.97 GV/cm for them for angles of 5, 10, and 15 deg, respectively, while the effective electric fields at the DF level for these angles are 13.16, 16.20, and 13.06 GV/cm, respectively. The other

TABLE IV. The calculated values of $\mathcal{E}_{\text{eff}}^{DF}$ (in GV/cm) at different bond lengths (absolute values), $R_{\text{O-H}}$ (in Angstroms). We had chosen the O atom as our origin. The original bond length value is 0.922 Å.

$R_{\text{O-H}}$	$\mathcal{E}_{\text{eff}}^{DF}$
−0.422	18.14
−0.922	17.78
−1.422	17.49

TABLE V. The calculated values of $\mathcal{E}_{\text{eff}}$ (in GV/cm) at different bond lengths (absolute values) $R_{\text{Yb-O}}$ (in Angstroms). We had chosen the O atom as our origin. The combination of 2.0026 and 0.922 Å corresponds to the original value.

$R_{\text{Yb-O}}$	$R_{\text{O-H}}$	$\mathcal{E}_{\text{eff}}^{DF}$
1.5026	0.422	12.17
1.7526	0.672	15.87
2.0026	0.922	17.78
2.2526	1.172	18.58
2.5026	1.422	18.58

mixings (such as $p_{3/2}$ and $d_{3/2}$ from Yb, as well as all mixings from the lighter atoms) contribute little to $\mathcal{E}_{\text{eff}}^{DF}$, and we found them to usually be around 0.1 GV/cm or less; therefore we have not presented those results here. The analysis shows that it is a change in the terms involving mixings between s and $p_{1/2}$ that is responsible for the change in $\mathcal{E}_{\text{eff}}^{DF}$.

In Table III we discuss the variation of $\mathcal{E}_{\text{eff}}^{DF}$ with bond length ($R_{\text{Yb-O}}$) around the chosen value. We observe that $\mathcal{E}_{\text{eff}}^{DF}$ increases with $R_{\text{Yb-O}}$. However, we also note that $\mathcal{E}_{\text{eff}}^{DF}$ tends towards saturation, as $R_{\text{Yb-O}}$ increases.

We do not expect $\mathcal{E}_{\text{eff}}^{DF}$ to change significantly with $R_{\text{O-H}}$. However, for the sake of completeness, we present the results in Table IV.

Finally, in Table V we present $\mathcal{E}_{\text{eff}}^{DF}$ with both the lengths varied. The trend remains, with $\mathcal{E}_{\text{eff}}^{DF}$ increasing with the bond lengths and reaching towards a "saturation" point. We expect that the inclusion of correlation effects will not change the trends but only shift each of the values obtained at the DF level.

IV. CONCLUSION

In conclusion, we have calculated $\mathcal{E}_{\text{eff}}$ and d_M of the YbOH molecule in its ground state using a relativistic coupled cluster method. The results show that $\mathcal{E}_{\text{eff}}$ is almost as large as that in YbF, at 23.72 GV/cm. We also examine $\mathcal{E}_{\text{eff}}$ and d_M at different cut-off values for the virtual orbitals. We estimate the errors in our calculations of $\mathcal{E}_{\text{eff}}$ to be about 6% due to various sources such as basis-set incompleteness, exclusion of higher-order excitations, and ignoring the terms that are nonlinear in the cluster operator in the expectation value. We also present relativistic mean-field values for a bent geometry. We tried to understand the dependence of $\mathcal{E}_{\text{eff}}^{DF}$ on bond angle by studying the mixings of orbitals in YbOH. Our analysis shows that the mixing between the heavier atom's s and $p_{1/2}$ orbitals is dominant, and its variation is responsible for the value of $\mathcal{E}_{\text{eff}}^{DF}$ changing with angle. These calculations will provide useful inputs for the feasibility of an eEDM experiment with YbOH.

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