

Prospects for an electron electric-dipole moment search in metastable ThO and ThF⁺

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The observation of an electron electric-dipole moment (EEDM) would have major ramifications for the standard model of physics. Polar molecules offer a near-ideal laboratory for such searches due to the large effective electric field (\mathbf{F}_{eff}), on order of tens of GV/cm that can be easily oriented in the laboratory frame. We present an improved method for simply and accurately determining \mathbf{F}_{eff} in a heavy polar molecule, allowing for a quick determination of candidates for an EEDM experiment. We apply this method to ThO and ThF⁺, both of which possess metastable $^3\Delta$ electronic states. The values of \mathbf{F}_{eff} in ThO and ThF⁺ are estimated to be 104 GV/cm and 90 GV/cm, respectively, making them two of the best known candidates for the EEDM search.

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One of the more spectacular goals in the rapidly growing field of ultracold molecules [1] is the search for the electric-dipole moment of the electron (EEDM). If found, the EEDM would be a touchstone against which ideas beyond the standard model (SM), especially supersymmetry, could be checked. On the other hand, if it is not found, but experiments can push the EEDM's value below its current experimental limit of $|d_e| < 1.6 \times 10^{-27} e \text{ cm}$ [2], then key supersymmetric extensions to the SM become much less likely to be true [3]. Thus, table-top experiments at the lowest achievable energies are a direct compliment to collider experiments at the highest.

The current experimental limit on the EEDM originates from a high-resolution spectroscopic experiment on atomic thallium [2]. The ability to make this kind of precise measurement in atoms stems from key insights by Sandars [4] and contributions by Flambaum and Khriplovich [5,6]. These works show that the *apparent* electric field acting on an electron inside an atom can be far larger than the field that is directly applied by a macroscopic laboratory apparatus. A further insight by Sandars [7] pointed out that, for an electron inside a polar molecule, the effective electric field \mathbf{F}_{eff} can be even larger. This field is enhanced by relativistic effects and scales with nuclear charge Z as Z^3 , therefore preferring heavy elements, the same as in the atomic case. Effective electric fields as large as tens of GV/cm have been anticipated in certain heavy molecules, the largest so far being in HgF where $\mathbf{F}_{\text{eff}} \sim 99 \text{ GV/cm}$ [8].

In practice, \mathbf{F}_{eff} is manifested in the molecule by its ability to distort an electron orbital of nominal s symmetry on the heavy atom into a combination of s and p orbitals. For this reason, several candidate molecules are composed of a heavy (ns^2)¹S-state atom with fluorine—which is adept at drawing electrons toward itself—therefore accounting for the needed distortion. Molecules such as BaF [9], YbF [10], HgF, and PbF [8] have all been considered. Departing from this trend, DeMille *et al.* proposed the metastable $a(1)$ state of PbO [11]. More recently, an alternative experimental effort has proposed to trap molecular ions, counting on the long trap

lifetimes to improve the signal [12]. In response, several ions were proposed, including HI⁺ [13], PtH⁺, HfH⁺ [14], and HfF⁺ [14,15].

The molecular ion experiment has stressed the desirability of molecules that are easily polarized in small laboratory electric fields. For ion traps in particular, this attribute is a necessity because strong electric fields would ruin the trap's characteristics. Molecules with this property that also have a reasonable value of \mathbf{F}_{eff} are of $(s\sigma d\delta)^3\Delta$ electronic symmetry. In such a molecule, the overall Δ symmetry guarantees a small Ω doubling, hence easy polarizability, while the electron in the σ orbital may still contribute a large \mathbf{F}_{eff} [14]. In addition, the magnetic g factor of a $^3\Delta_1$ molecule is very small—a tiny fraction of a Bohr magneton because $g_J \sim (g_L\Lambda - g_S\Sigma)$. This is zero, apart from diamagnetic and radiative corrections [16], providing less sensitivity to magnetic field noise.

The ACME Collaboration [17] has seized on the potential utility of $^3\Delta$ molecules in designing a molecular beam EEDM experiment. This experiment will use ThO molecules, which possess a metastable $^3\Delta$ state not far above the ground state. This molecule is also attractive inasmuch as several of its isotopomers have no nuclear spin, eliminating the complexities of hyperfine structure. Similarly, the JILA EDM team is interested in the isoelectronic cation ThF⁺, which is expected to be similar to ThO in its electronic structure, for use in an ion trap experiment [18].

Until now, the most reliable estimates of \mathbf{F}_{eff} were determined using elaborate relativistic many-electron calculations. In this Rapid Communication we instead develop a competitive method based on nonrelativistic molecular structure calculations perturbed by the Hamiltonian arising from the EEDM. The method, based on an initial approximation in Ref. [14], is both fast and accurate. Indeed, we now reproduce, to within 25%, the values \mathbf{F}_{eff} for all species that have been treated by more elaborate relativistic theory. This circumstance opens the door for researchers to perform broad surveys of potential EEDM searches, and to evaluate the expected sensitivity of these experiments. As examples, we present estimates of \mathbf{F}_{eff} for ThO and ThF⁺, finding them both to be excellent candidates.

The simple idea behind the method is that the presence of

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the EEDM causes a perturbation to the molecule's structure due to a relativistic effect [19]. In Dirac notation the perturbation takes the form [5]

$$H_d = \begin{pmatrix} 0 & 0 \\ 0 & 2d_e\sigma \cdot \mathbf{F} \end{pmatrix}. \quad (1)$$

Here σ represents the electron's spin, assumed to point in the same direction as the EEDM; \mathbf{F} is the local electric field experienced by the electron inside the molecule, which is well approximated by the Coulomb field due to the large nucleus; and d_e is the magnitude of the EEDM.

The influence of this interaction on the molecular spectrum is computed in perturbation theory. To do this, Ref. [14] expanded the molecular orbital into atomic orbitals,

$$|\Psi_{\text{mol}}\rangle = \epsilon_s|s\rangle + \epsilon_p|p\rangle + \dots \quad (2)$$

Here the coefficients ϵ_s and ϵ_p represent the contributions to $|\Psi_{\text{mol}}\rangle$ due to the s and p atomic orbitals of the heavy atom. Since the influence of the EEDM relies on relativity, its contribution to the spectrum of the molecule is dominated by motion of the electron near the heavy nucleus. Thus the $|s\rangle$ orbital is essential. Moreover, since the EEDM Hamiltonian (1) has odd symmetry under parity, the matrix element $\langle s|H_d|s\rangle$ vanishes, and we must consider mixing with the heavy atom's $|p\rangle$ orbital. The other atomic orbitals that comprise $|\Psi_{\text{mol}}\rangle$ are far less significant to our purposes.

The energy shift due to the perturbation is therefore

$$\Delta E = \langle \Psi_{\text{mol}} | H_d | \Psi_{\text{mol}} \rangle \approx 2\epsilon_s\epsilon_p \langle s | H_d | p \rangle. \quad (3)$$

To evaluate ΔE , we estimate $\epsilon_{s,p}$ using nonrelativistic molecular structure software. The relativistic effects occur mostly in the matrix element $\langle s | H_d | p \rangle$. To evaluate this, we follow Ref. [19] and use one-electron Dirac-Coulomb wave functions in place of the true orbitals $|s\rangle$ and $|p\rangle$. This allows the integrals to be done analytically. Moreover, they are strikingly accurate provided that the quantum numbers $n_{s,p}$ are replaced in the result by the effective quantum numbers $\nu_{s,p}$, to reflect the fact that these electrons actually exist around a structured ionic core, as opposed to a bare Coulomb potential.

Using this approximation, the energy shift is [14]

$$\Delta E = \mathbf{F}_{\text{eff}} d_e \approx \left[-\frac{4\sigma}{\sqrt{3}} h_0 \chi_0 \epsilon_s \epsilon_p \Gamma_{\text{rel}} \frac{Ze}{a_0^2} \right] d_e, \quad (4)$$

which identifies the item in square brackets as the effective electric field. In this expression, σ is the projection of the s -electron's spin onto the permanent dipole moment of the molecule; e is the electron's charge; and a_0 is the Bohr radius, which means that the factor e/a_0^2 identifies a characteristic electric field strength. The relativistic factor, Γ_{rel} , accounts for the overlap of the Dirac-Coulomb functions:

$$\Gamma_{\text{rel}} = -\frac{4(Z\alpha)^2 Z_{\text{eff}}^2}{\gamma(4\gamma^2 - 1)(\nu_s \nu_p)^{3/2}}, \quad (5)$$

where $\gamma = \sqrt{(j+1/2)^2 - (Z\alpha)^2}$ is a familiar dimensionless quantity, and Z is the atomic number of the heavy nucleus. In contrast, the effective charge Z_{eff} is the charge of the heavy ion that the electron orbits. For example, in YbF, the bond is

very nearly polar, and the valence electron contributed by the Yb^+ orbits about a Yb core with $Z_{\text{eff}}=2$. Further, in Eq. (4), h_0 is a coefficient (usually slightly less than unity) that accounts for the fact that $|\Psi_{\text{mol}}\rangle$ is typically a combination of several different orbital configurations; and χ_0 is a further reduction of order unity that accounts for spin-orbit mixing of $|\Psi_{\text{mol}}\rangle$ with other symmetries. Heavy diatomic molecules are often written in a basis where only the projection of the total angular momentum Ω is a good quantum number. For example, the $^3\Delta_1$ electronic level can have some admixture of a nearby $^3\Pi_1$ electronic level.

The key to the success of the method is that the coefficients $\epsilon_{s,p}$ can be extracted from nonrelativistic molecular structure software (specifically, we have used the MOLPRO suite of codes [20]). This is done via the overlap integrals

$$\epsilon_{s,p} = \langle \Psi_{\text{mol}} | (s,p) \rangle, \quad (6)$$

where in Ref. [14] the wave functions $|\Psi_{\text{mol}}\rangle$ and $|(s,p)\rangle$ were obtained from *separate* calculations, one for the molecule and one for the heavy atom. The atomic calculation moreover identified orbitals with a particular principal quantum number n , associated with the atom's valence shell. In the context of distorting the heavy atom's s orbital, the appropriate p orbital must be the component p_z , i.e., the projection with vanishing angular momentum about the molecular axis.

The true molecular orbital is a combination of many atomic orbitals. Therefore, the s component is not necessarily a state purely composed of a principal quantum number n , though it is likely dominated by one of them. The presence of the light atom will distort the atomic orbitals of the heavy atom and cause mixing of not only s and p but of n and n' , where n' is another atomic energy level of the heavy atom. These other configurations will contribute to a science signal as well, albeit somewhat weakly.

Yet, a basis expansion of $|\Psi_{\text{mol}}\rangle$ can be done into any set of functions; for example, the Gaussian atomic basis set itself can be used. We can read off the contribution of each s and p heavy atom Gaussian to the molecular wave function. These are the functions that are variationally optimized to produce the molecular wave function and therefore utilize all the s and p character that is available to minimize the energy of the molecular state of interest.

Therefore, it is worthwhile (and more direct) to extract the coefficients $\epsilon_{s,p}$ from the molecular orbital calculation itself. A molecular orbital is comprised of a linear combination of Gaussian basis functions with the same projection of λ . In the case of the σ -molecular orbital, we can write out the expansion of the molecular orbital as

$$|\Psi_{\text{mol}}\rangle = \sum_{i_s} c_{i_s}^h |s\sigma_{i_s}^h\rangle + \sum_{i_p} d_{i_p}^h |p\sigma_{i_p}^h\rangle + \dots \\ + \sum_{j_s} c_{j_s}^l |s\sigma_{j_s}^l\rangle + \sum_{j_p} d_{j_p}^l |p\sigma_{j_p}^l\rangle + \dots \quad (7)$$

In this expression each ket represents not an atomic orbital but rather a Gaussian basis function. The coefficients are therefore the direct numerical output of the *ab initio* MOLPRO calculation. The superscripts h (l) identify functions centered

on the heavy (light) atom. Each Gaussian function is moreover identified by whether it has s or p (or d , f , etc.) symmetry with respect to its atom. Viewed in this way, the net s -wave heavy atom character of $|\Psi_{\text{mol}}\rangle$ is given by the sum of all its s -wave contributions, meaning that

$$\epsilon_s = \frac{\sum_{k_s} c_{k_s}^h \langle \Psi_{\text{mol}} | s \sigma_{k_s}^h \rangle}{\sum_{k_s, l_s} c_{k_s}^{h*} c_{l_s}^h \langle s \sigma_{k_s}^h | s \sigma_{l_s}^h \rangle}. \quad (8)$$

Here the denominator is needed because the individual Gaussian orbitals are not necessarily orthogonal to each other. A similar expression holds for ϵ_p .

This method incorporates the influence of several n 's, including those higher than the nominal valence orbital, which may be mixed in virtually. This advantage is also a drawback, however, because the lack of identification of a particular principal quantum number n leads to an uncertainty in identifying the effective quantum numbers $\nu_{s,p}$ in Eq. (5).

This same ambiguity was actually present in the previous form of the calculation [14]. The atomic orbitals $|(s,p)\rangle$ from Eq. (6) merely represent the choice of a basis set. The basis could easily have been the neutral atom or the ion. Each choice of expansion would require a different choice of $\nu_{s,p}$. Because the original Gaussian basis set is optimized for the neutral atom, we extract $\nu_{s,p}$ from the neutral atom spectra. $\nu_{s,p}$ are related to the atomic quantum defect $\mu_{s,p}$ through [21]

$$\nu_l = n - \mu_l = \sqrt{\frac{\text{Ry}}{E_n}}, \quad (9)$$

where Ry is the Rydberg constant, and E_n is the ionization energy of the heavy atom from the $|nl\rangle$ energy level. This method assumes that the spectrum for the atom follows a Rydberg-like series for higher- n levels. We then find the effective quantum number that arises from the structured core of the heavy atom. For example, E_n for Yb in the ground configuration would be given as

$$E_n = E_{6s} = E([\text{Xe}]4f^{14}6s) - E([\text{Xe}]4f^{14}6s^2), \quad (10)$$

with $[\text{Xe}]$ being the Xe core and the configuration $4f^{14}6s$ representing the first ionization level of Yb, the level with one of the $6s$ electrons ripped away. In a similar manner the quantum defect for the p level can be found by finding the difference from the $4f^{14}6s6p$ to the ionization state $4f^{14}6s$. Similarly, for Pb we determine ν_s (ν_p) by considering ionization of the $6s^26p^2$ ground state to the $6s6p^2$ ($6s^26p$) state of Pb^+ , respectively.

Using the molecular orbital calculation directly to find $\epsilon_{s,p}$ also confounds somewhat the determination of Z_{eff} . If we had calculated atomic Yb, we would have $Z_{\text{eff}}=1$, whereas if we had used Yb^+ , we would have had $Z_{\text{eff}}=2$. Since we used neither, the value of Z_{eff} is not specified. However, the molecular calculation does identify the permanent electric-dipole moment of the molecule, as well as the bond length, via the distances r^h (r^l) of the heavy (light) atom from the center of mass. Assuming charges q^h and q^l of the atoms, we can assert

$$d_{\text{mol}} = r^h q^h + r^l q^l, \quad (11)$$

TABLE I. Comparisons of published values of \mathbf{F}_{eff} to old results from Ref. [14] and new results in the present work. All values are given in GV/cm.

Molecule	Published	Old [14]	New
BaF	7.4 [9]	5.1	6.1
YbF	26 [10]	43	32
HgF	99 [8]	68	95
PbF	-29 [8]	-36.6	-31
$\alpha(1)$ PbO	26.2 [11]	3.2 [22]	23
HI^+	0.34 [13]	0.57	0.34
HfF^+	24 [15]	18	30
ThO	N/A	N/A	104
ThF^+	N/A	N/A	90

$$Q_{\text{mol}} = q^h + q^l. \quad (12)$$

For neutral (ionic) molecules, $Q_{\text{mol}}=0$ (1), and we then solve for the individual charges q^h and q^l . Z_{eff} on the heavy atom is then

$$Z_{\text{eff}} = q^h + 1. \quad (13)$$

For ThO (ThF^+) we find $Z_{\text{eff}}=1.6$ (2.3), which we use in evaluating Eq. (5).

In order to check the accuracy of this method, we applied it to several molecules studied previously and present the results in Table I. We used the same *ab initio* calculations as in Ref. [14], but extracted the values of $\epsilon_{s,p}$ as prescribed above. As is evident, this method improves our older method, yielding results within 25% of previously published values, thereby making it useful for estimating experimental feasibility of candidate molecules. The largest deviation in Table I is that of HfF^+ . This deviation can be attributed mainly to the peculiar ionization route of Hf, which goes from $5d^26s^2$ to $5d6s^2$, indicating that the d -electron interloper plays a large role in the low-lying Hf energy levels and our single-channel quantum defect approach is too naive. This deficiency would conceivably be cleared up by a multichannel approach to the quantum defects, which we have not attempted here.

These difficulties are not present for the Th atom. We therefore suspect that the predicted \mathbf{F}_{eff} in Table I probably lie within 25% of the answer that the fully relativistic calculations will ultimately provide. In more detail, to construct the molecular wave function for Th we use the MOLPRO software suite [20]. The augmented correlation-consistent polarization valence quadruple zeta (aug-cc-pVQZ) basis of Dunning [23] is used to describe the O and F atom's s - f orbitals. We use the scalar relativist 78 electron effective core potential (ECP78MWB) of the Stuttgart group [24] to describe the core of Th. In addition, we utilize the ECP78MWB aug-cc-pVQZ basis set to describe the s - f orbitals of Th [24]. We performed the calculation with an occupied (active) space of $\{7,3,3,1\}$ ($\{5,3,3,1\}$). We took several points in R separating Th from O or F between 2.75 and 4.5 a_0 , in order to determine the ground state bond length of $r=3.47$ (3.73) a_0 for ThO (ThF^+), respectively. The value of r for ThO agrees well

with the experimental value of $r=3.48$ [25]. The final calculation included the present electronic state of interest ($^3\Delta$) as well as $X^1\Sigma^+$, $^1\Pi$, $^3\Pi$, $^3\Sigma^+$, and $^1\Delta$ for both ThO and ThF $^+$.

Based on this calculation we find that the effective electric field in ThO (ThF $^+$) is approximately $F_{\text{eff}} \approx 104$ GV/cm (90 GV/cm). This similarity in F_{eff} is perhaps not surprising since the two molecules are isoelectronic. These comparatively large values make the metastable $^3\Delta_1$ states of ThO and ThF $^+$ competitive with even HgF as viable candidates for an EEDM search. There are two more parameters of experimental relevance that need to be estimated along with F_{eff} : the Ω -doublet splitting and the lifetime of the metastable state.

An order of magnitude estimate of the Ω -doublet splitting can be estimated from the molecular parameters determined in the calculation and the use of perturbation theory [26]. We find that the splitting is on the order of 10^{-6} cm $^{-1}$ in both ThO and ThF $^+$ yielding a critical field of a few hundred mV/cm in the metastable states, which is the field required to polarize the molecule.

The lifetime can be estimated by finding the amount of $^1\Pi_1$ that is admixed into the $^3\Delta_1$ state due to the spin-orbit interaction of the molecule. $^1\Pi_1$ can decay to the ground $^1\Sigma_0$

state through electric dipole radiation, whereas the $^3\Delta_1$ state would not decay via this route due to symmetry constraints. From our calculations, we find that the lifetime of the $^3\Delta_1$ state is on the order of 1 ms (100 ms) for ThO (ThF $^+$). This is long enough to make a measurement of this state in a slowed molecular beam experiment [17] or in an ion trap [18].

In summary, we provide a modified and more efficient method of calculating F_{eff} in polar diatomic molecules. Our determination of F_{eff} in several test cases lies within 25% of fully relativistic calculations. We apply this method to the $^3\Delta_1$ states of ThO and ThF $^+$ and find that they are extremely good candidates for an EEDM search yielding effective fields of ≈ 104 GV/cm and 90 GV/cm, respectively. In addition, the Ω -doublet splitting in these molecules is very small, allowing for easy polarization. The lifetimes of the metastable states are long enough to make spectroscopic measurements [17,18].

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