Theoretical study of ThO for the electron electric dipole moment search

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An experiment to search for the electron electric dipole moment (eEDM) on the metastable \(H^3Δ_1\) state of ThO molecule was proposed and now in the final stage of preparation by the ACME collaboration [http://www.electronedm.org]. To interpret the experiment in terms of eEDM and dimensionless constant \(k_{T,P}\) characterizing the strength of the scalar T,P-odd electron-nucleus neutral current interaction, an accurate theoretical study of effective electric field on electron, \(E_{\text{eff}}\), and \(W_{T,P}\) constants is required. We report calculation of \(E_{\text{eff}}\) (84 GV/cm) and a parameter of T,P-odd scalar neutral currents interaction, \(W_{T,P}\) (116 kHz), together with the hyperfine structure constant, molecule frame dipole moment and \(H^3Δ_1 \to X^1Σ^+\) transition energy, which can serve as a measure of reliability of the obtained \(E_{\text{eff}}\) and \(W_{T,P}\) values. Besides, our results include a parity assignment and evaluation of the electric-field dependence for the magnetic \(g\) factors for the \(Ω\)-doublets of \(H^3Δ_1\).

One of the most intriguing fundamental problems of modern physics is the search for a permanent electric dipole moment (EDM) of elementary particles. A nonzero value of EDMs implies manifestation of interactions which are not symmetric with respect to both time (T) and spatial (P) inversions (T,P-odd interactions). Particularly, the observation of electron EDM (eEDM) at the level significantly greater than \(10^{-38}\) would indicate the presence of a “new physics” beyond the Standard model. Popular extensions of the Standard model predict the magnitude of the eEDM at the level of \(10^{-26} - 10^{-28}\) \(\text{cm}\). The most rigid upper bound on the eEDM is attained in the experiments on a beam of YbF molecular radicals \(1\) \((1.05 \times 10^{-27}\text{e-cm})\) and in the measurements with atomic Tl beam \(2\) \((1.6 \times 10^{-27}\text{e-cm})\).

Nowadays a number of other prospective experiments are suggested and in part prepared \(3\) \(\textsuperscript{\footnote{3}}\) which promise to achieve a sensitivity to eEDM up to \(10^{-29} - 10^{-30}\text{e-cm}\). One of the most promising experiments towards the measurement of eEDM is proposed and now prepared on the metastable \(3Δ_1\) state of the thorium monoxide (ThO) molecule by ACME collaboration (groups of DeMille, Gabrielse, and Doyle) \(4\) \(\textsuperscript{\footnote{4}}\). A very high sensitivity to eEDM is expected in the nearest future, up to an order of magnitude and more than that attained in the YbF and Tl experiments, due to some unique combination of experimental advantages of the molecule. Even the value for eEDM compatible with zero will lead to serious consequences for the modern theory of fundamental symmetries.

To interpret the measured data in terms of the eEDM one should know a parameter usually called “the effective electric field on electron”, \(E_{\text{eff}}\), which cannot be measured. To obtain \(E_{\text{eff}}\) theoretically one can evaluate an expectation value of some T,P-odd operator (discussed in Refs. \(9\) \(\textsuperscript{\footnote{9}}\) \(\textsuperscript{\footnote{10}}\)):

\[
W_d = \frac{1}{Ω} \langle Ψ | \sum_i \frac{H_d(i)}{d_e} | Ψ \rangle, \tag{1}
\]

where \(Ψ\) is the wave function of the considered state, and \(Ω = ⟨Ψ | J \cdot n | Ψ⟩\), \(J\) is the total electronic momentum, \(n\) is the unit vector along the molecular axis directed from Th to O,

\[
H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & σE \end{pmatrix}, \tag{2}
\]

\(E\) is the inner molecular electric field, and \(σ\) are the Pauli matrices. In these designations \(E_{\text{eff}} = W_d |Ω|\).

In addition to the interaction given by operator \(2\) there is a scalar T,P-odd electron-nucleus neutral currents interaction with the dimensionless constant \(k_{T,P}\). The interaction is given by the following operator (see \(12\)):

\[
H_{T,P} = i \frac{G_F}{\sqrt{2}} Z k_{T,P} γ_0 γ_5 n(r), \tag{3}
\]

where \(G\) is the Fermi constant, \(γ_0\) and \(γ_5\) are the Dirac matrices and \(n(r)\) is the nuclear density normalized tounity. To extract the fundamental \(k_{T,P}\) constant from an experiment one need to know the factor \(W_{T,P}\) that is determined by the electronic structure of a studied molecule on a given nucleus:

\[
W_{T,P} = \frac{1}{Ω} \langle Ψ | \sum_i \frac{H_{T,P}(i)}{k_{T,P}} | Ψ \rangle. \tag{4}
\]

Similarly to \(E_{\text{eff}}\) parameters \(W_{T,P}\) cannot be measured experimentally and have to be obtained from the molecular electronic structure calculations.

A commonly used way of verification the theoretical \(E_{\text{eff}}\) and \(W_{T,P}\) values is to calculate “on equal footing” (the same approximation for the wave function) those molecular characteristics (properties or effective Hamiltonian parameters) which have comparable to \(E_{\text{eff}}\) and \(W_{T,P}\) sensitivity to different variations of wave function
but, in contrast, can be measured. Similar to $E_{\text{eff}}$ and $W_{T,P}$, these parameters should be sensitive to a change of densities of the valence electrons in atomic cores. The hyperfine structure constant, $A_{||}$, is traditionally used as such a parameter (e.g., see [13]) and this is a valid touchstone for the ThO case as well. To obtain $A_{||}$ on Th theoretically, one can evaluate the following matrix element:

$$A_{||} = \frac{\mu_{\text{Th}}}{I \Omega} \langle \Psi | \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) z | \Psi \rangle,$$

where $\mu_{\text{Th}}$ is a magnetic moment of Th nucleus having spin $I$.

To validate our present study of the $E_{\text{eff}}$, $W_{T,P}$ and the hyperfine structure constant $A_{||}$ for the $^3\Delta_1$ state of $^{229}\text{ThO}$, we have also performed calculations of the $H^3\Delta_1 \rightarrow X^3\Sigma$ transition energy and the molecule-frame dipole moment.

**THEORETICAL DETAILS**

The evaluation of $E_{\text{eff}}$, $W_{T,P}$ and $A_{||}$ is usually a challenging problem for modern ab initio methods when studying systems containing heavy transition metals, lanthanides and, particularly, actinides (such as Th in the present consideration). An accurate theoretical investigation of such systems should take account of both the relativistic and correlation effects. The problem of computation of such characteristics can be significantly simplified by splitting the calculation on two steps. The main contribution to the corresponding matrix element is due to the valence electrons since contributions from the closed inner-core shells compensate each other in most cases of practical interest for the operators dependent on the total angular momentum and spin. It was shown by our group (see [11] and references) that the problem of computation of such characteristics is on the level of accuracy early attained by modern ab initio methods when the molecule-frame dipole moment, $E_{\text{eff}}$, $W_{T,P}$ and $A_{||}$ constants for the $^3\Delta_1$ state of ThO were performed using the single reference two-component relativistic coupled clusters with single, double and perturbative treatment of triple cluster amplitudes (CCSD(T)) [29]. In addition, the basis set enlargement corrections to the considered parameters were also calculated. For this we have performed: (i) scalar-relativistic CCSD(T) calculation using the same basis set as used for the two-component calculation; (ii) scalar-relativistic CCSD(T) calculation using extended basis set on Th (with added $f$, $g$, $h$ and $i$ Gaussians). Corrections were estimated as a difference between the values of the corresponding parameters. The results are given in Table I.

The calculated value of transition energy is in a very good agreement with experimental datum, the deviation, 420 cm$^{-1}$, is on the level of accuracy early attained by our group for compounds of transition metals and lanthanides.

It was recently shown in [30] that the magnetic moment of $^{229}\text{Th}$ nucleus determined earlier [31] is inaccurate. Therefore, $A_{||}$ is given in Table I in the units of $\mu_{\text{Th}}/\mu_N$, MHz (where $\mu_N$ is the nuclear magneton) in Table I to exclude the uncertainty of $\mu_{\text{Th}}$ from our result.

One can see from Table I that a good convergence of $E_{\text{eff}}$ with respect to the basis set enlargement and

**RESULTS AND DISCUSSIONS**

The $1s - 4f$ inner-core electrons of Th were excluded from molecular correlation calculations using the valence (semi-local) version of GRECP [14] operator. Thus, the outermost 38 electrons were treated explicitly. Basis set for Th was constructed using the generalized correlated scheme [25]. It consists of 30s, 8p, 6d, 4f, 4g and 1h contracted Gaussians [20]. For oxygen the aug-cc-pvqz basis set was reduced to 6s, 5p, 4d and 3f contracted Gaussians was employed.

According to experimental data [28] the internuclear distances for the ground $^1\Sigma^+$ and excited $^3\Delta_1$ states of ThO are about 3.5 a.u. Therefore, calculations of the states were performed with the given distance. Calculations of the transition energy between these states as well as the molecule-frame dipole moment, $E_{\text{eff}}$, $W_{T,P}$ and $A_{||}$ constants for the $^3\Delta_1$ state of ThO were performed using the single reference two-component relativistic coupled clusters with single, double and perturbative treatment of triple cluster amplitudes (CCSD(T)) [29]. In addition, the basis set enlargement corrections to the considered parameters were also calculated. For this we have performed: (i) scalar-relativistic CCSD(T) calculation using the same basis set as used for the two-component calculation; (ii) scalar-relativistic CCSD(T) calculation using extended basis set on Th (with added $f$, $g$, $h$ and $i$ Gaussians). Corrections were estimated as a difference between the values of the corresponding parameters. The results are given in Table I. The calculated value of transition energy is in a very good agreement with experimental datum, the deviation, 420 cm$^{-1}$, is on the level of accuracy early attained by our group for compounds of transition metals and lanthanides.
TABLE I. The calculated values of transition energy \( (T_e) \), molecule-frame dipole moment \( (\mu^f) \), effective electric field \( (E_{\text{eff}}) \), parameter of the \( T,P \)-odd scalar neutral current interaction \( (W_{T,P}) \) and hyperfine structure constant \( (\Lambda_{\parallel}) \) using the coupled clusters methods.

| Method           | \( T_e \), cm\(^{-1} \) | \( \mu^f \), Debye | \( E_{\text{eff}} \), GV/cm | \( W_{T,P} \), kHz | \( \Lambda_{\parallel} \), \( \mu_B \)-MHz |
|------------------|--------------------------|---------------------|-----------------------------|------------------|--------------------------|
| 2c-CCSD         | 5443                     | 4.22                | 87                          | 118              | -2983                    |
| 2c-CCSD(T)      | 6054                     | 4.17                | 84                          | 116              | -2880                    |
| 2c-CCSD(T) + basis corr. | 5741                     | 4.27                | 84                          | 116              | —                        |
| Experiment      | 5321                     | 4.24 ± 0.1          | —                           | —                | —                        |

correlation level is achieved. Taking into account the results from Table I as well as our earlier studies within the two-step procedure (e.g., see [19]) with calculating the \( E_{\text{eff}}, W_{T,P} \) and \( \Lambda_{\parallel} \), we expect that the theoretical uncertainty for our final values of the constants is smaller than 15%. Unfortunately, there are no experimental data on \( \Lambda_{\parallel} \) up to now. Therefore, the corresponding indirect experimental verification of accuracy of \( E_{\text{eff}} \) (see above) can not be performed to-date and further experimental measurements of \( \Lambda_{\parallel} \) are required.

In the eEDM search experiment on the ThO molecule, the eEDM induced Stark splitting between the \( J = 1 \), \( M = \pm 1 \) states of \( e \) (parity is \( (-1)^J \)) or \( f \) (parity is \( (-1)^J \)) levels of the \( \Omega \)−doublet is measured. The \( H^3\Delta_1 \) state has a very small magnetic moment, \( \mu_{H[\text{ThO}]} = 8.5(5) \times 10^{-3} \mu_B \) [8], where \( \mu_B \) is the Bohr magneton. The latter is a benefit for suppressing systematic effects due to spurious magnetic field. In a polarized molecule the \( e \) and \( f \) levels have opposite signs of \( E_{\text{eff}} \) and almost identical \( g \) factors. Therefore, when taking the difference between the splitting for \( e \) and \( f \) levels further suppression of the systematics is possible [32]. The small difference between \( g \) factors, \( \Delta g \), comes from interactions of \( H^3\Delta_1 \) with \( 0^+ \) and \( 0^- \) electronic states [15]. Our calculations show that being presented in the \( AS \) coupling scheme, the spin-orbit mixed \( H \) state of ThO has the main contribution (more than 95%) from the \( 3\Delta_1 \) configurations. Therefore, due to the identity \( \langle \Psi_1|S_z^e|\Psi_{0^{\pm}} \rangle \equiv 0 \) for pure \( AS \) state, the inequality \( \left| \langle \Psi_1|S_z|\Psi_{0^{\pm}} \rangle \right| \ll 1 \) holds with a good accuracy. This inequality gives sufficient condition for \( \Delta g \) to be determined by the energy splitting between the top and bottom levels of the \( \Omega \)−doublet [15][19]. The rational analysis given in [33] for \( P(\Omega = 0) − H^3\Delta_1 \) and \( O(\Omega = 0) − H^3\Delta_1 \) bands have shown that the \( \Omega \)−doublet spacing \( (\Delta = |E(J = 1^-) − E(J = 1^+)|) \) in \( H^3\Delta_1 \) is \( 350 − 470 \) kHz. At the moment, the parity assignment for electronic states \( P \) and \( O \) is yet unclear. According to [34] \( P \) is \( 0^- \) and \( O \) is \( 0^+ \). The latter, as can be shown, indicate that \( e \) states are the top levels whereas \( f \) states are the bottom levels of the \( \Omega \)-doublets for \( H^3\Delta_1 \). The latter-day microwave spectroscopy confirms our conclusion about the levels ordering and finally gives \( E(J = 1^-) − E(J = 1^+) = 362 ± 10 \) kHz [35]. In Fig. 1 the calculated \( g \) factors for the \( J = 1 \) levels of ThO \( H^3\Delta_1 \) state are given as functions of the laboratory electric field. The lowest value, \( \Delta g = 2.7 \times 10^{-6} \), is attained at the electric field 4.4 V/cm. Note that the molecule is completely polarized at the electric field larger than 3 V/cm.

CONCLUSION

A number of parameters \( (E_{\text{eff}} \) and \( W_{T,P} \)) that are required to interpret experimental measurements on the \( H^3\Delta_1 \) state of ThO molecule in terms of fundamental quantities are calculated. Though the previous estimation of \( E_{\text{eff}} \) made in Ref. [5] is only 25% more than our final value, the good agreement can be rather considered as “fortunate” since the accuracy of the semiempirical estimates for the systems like ThO having a very complicated electronic structure is severely limited, see [16]. In turn, the reliable ab initio calculation of ThO is on the threshold of current possibilities of computational methods and we estimate the accuracy of our calculation of \( E_{\text{eff}} \) by 15% only. Nevertheless, even such accuracy is important to establish a reliable eEDM estimate in the ongoing ThO experiment compared to the measured upper bounds on eEDM in Tl [3] and YbF [2] experiments.

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FIG. 1. (Color online) Calculated g-factor curves for $J = 1$ rotational level of $^{232}$Th$^{16}$O.