Theoretical study of ThF$^+$ in the search for T,P-violation effects: Effective state of a Th atom in ThF$^+$ and ThO compounds

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We report the results of a theoretical investigation of the electronic structure of the ThF$^+$ cation, which is one of the most interesting systems to search for the electron electric dipole moment (eEDM) [H. Loh, K. C. Cossel, M. C. Grau, K.-K. Ni, E. R. Meyer, J. L. Bohn, J. Ye, and E. A. Cornell, Science **342**, 1220 (2013)] and other effects of violation of time reversal (T) and spatial parity (P) symmetries in fundamental interactions. For the working $^3\Delta_1$ state we find a quite high value of the effective electric field acting on unpaired electrons (37.3 GV/cm). The field will be required to interpret the experiment planned on ThF$^+$ in terms of the eEDM. Within the concept of atoms in compounds [A. V. Titov, Y. V. Lomachuk, and L. V. Skripnikov, Phys. Rev. A **90**, 052522 (2014)], we compare the ThF$^+$ electronic structure with that of ThO. Also, we calculate other parameters of T,P-odd interactions: $W_{T,P}$, which is needed for interpretation of the experiment in terms of the dimensionless constant $k_{T,P}$ characterizing the strength of the T,P-odd pseudoscalar-scalar electron-nucleus neutral current interaction (50 kHz); and W_M, which is required to search for the ^{229}Th nuclear magnetic quadrupole moment in ^{229}ThF$^+$ (0.88 $\frac{10^{33} \text{ Hz}}{e \text{ cm}^2}$). A number of properties which can be measured are also calculated: the hyperfine structure constant, molecule-frame dipole moment, and g factor.

I. INTRODUCTION

During the last decade impressive progress in the search for the permanent electric dipole moment (EDM) of the electron (eEDM) has been achieved [1–3]. The great interest in the eEDM is caused by the fact that its nonzero value implies manifestation of interactions which are not symmetric with respect to both time (T) and space (P) inversions (T,P-odd interactions). According to the standard model the eEDM should be less than 10^{-38} e cm [4]. Therefore observation of the eEDM at a notably higher level would indicate the presence of a "new physics" beyond the standard model. Most popular extensions of the standard model predict the magnitude of the eEDM at the level of 10^{-26}–10^{-29} e cm [5] and that range has been almost passed to date by the latest atomic and molecular measurements.

It was found since sixties of the past century [4,6–12] that extremely sensitive experiments in the search for T,P-odd effects can be performed on heavy-atom molecules and solids. The current limit, $|d_e| < 8.7 \times 10^{-29}$ e cm (90% confidence), was set with a molecular beam of thorium monoxide (ThO) molecules in the metastable electronic $H^3\Delta_1$ state [3]. The previous best limit was also established on a molecular beam, but using the YbF radicals [2].

Nowadays, a number of new prospective systems has been suggested, investigated theoretically, and, in part, prepared experimentally (HfF$^+$ [13–17], YbF [2,18–24], ThO [3,25–31], ThF$^+$ [14], WC [32,33], PbF [34–36], RaO [37,38], RaF [39,40], etc.) which promise to achieve a sensitivity to the eEDM up to 10^{-29}–10^{-30} e cm. One promising experiment towards measurement of the eEDM is proposed on the $^3\Delta_1$ state

of the ThF$^+$ cation by Cornell and co-workers [14]. Use of the $^3\Delta_1$ state has a number of advantages from the experimental point of view. Due to the Ω-doublet structure of the $^3\Delta_1$ state the interval between the opposite parity levels is very small. Therefore, the molecule can be polarized by a weak electric field, which leads to cancellation of some systematic errors since the effect on the doublet components has an opposite sign [26,41,42]. Also, the magnetic moment (g factor) of the $^3\Delta_1$ electron state is very small (0 in the nonrelativistic limit), and this is another reason for reducing the systematic errors. The advantage of using such a state has been demonstrated in a recent experiment on the ThO molecule [3].

The working $^3\Delta_1$ state of ThO is a metastable (first excited) one, with a lifetime of about 2 ms [43], whereas the ground state is $^1\Sigma$. In contrast to the ThO case, the energies of the $^3\Delta_1$ and $^1\Sigma$ states in ThF$^+$ are very close [44]. In Ref. [45] the $^3\Delta_1$ state of ThF$^+$ was assigned as the first excited state with transition energy 316 cm^{-1} (versus 5321 cm^{-1} in ThO [46]). However, the most recent experiments by Cornell group show that $^3\Delta_1$ is the ground state of ThF$^+$ [47]. This suggests a very good statistics.

To interpret the results of the ThF$^+$ experiment in terms of the eEDM one should know a parameter usually called "the effective electric field on the electron," E_{eff}, which cannot be measured. E_{eff} is actually relevant only to spin-polarized electrons (the closed shells do not contribute to measured effects in the context of eEDM; see the next section); it can be evaluated as an expectation value of the T,P-odd operator (see Refs. [48–50]),

$$W_d = \frac{1}{\Omega} \langle \Psi | \sum_i \frac{H_d(i)}{d_e} | \Psi \rangle, \qquad (1)$$

where d_e is the value of the eEDM, Ψ is the wave function of the considered state of ThF$^+$, and $\Omega = \langle \Psi | \boldsymbol{J} \cdot \boldsymbol{n} | \Psi \rangle$, where $\boldsymbol{J}$

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is the total electronic momentum, $\boldsymbol{n}$ is the unit vector along the molecular axis ζ directed from Th to F ($\Omega = 1$ for the considered $^3\Delta_1$ state of ThF$^+$),

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma} \boldsymbol{E} \end{pmatrix}, \tag{2}$$

E is the inner molecular electric field, and $\boldsymbol{\sigma}$ are the Pauli matrices. In these designations $E_{\text{eff}} = W_d |\Omega|$.

Besides the interaction given by operator (2) there is a T,P-odd pseudoscalar–scalar electron–nucleus neutral current interaction with the dimensionless constant $k_{T,P}$. Note that it was estimated in Ref. [51] within the standard model that this interaction can induce an even greater T,P-odd effect in ThO simulating the eEDM. The interaction is given by the operator [52]

$$H_{T,P} = i \frac{G_F}{\sqrt{2}} Z k_{T,P} \gamma_0 \gamma_5 \rho_N(\mathbf{r}), \tag{3}$$

where G_F is the Fermi constant, γ_0 and γ_5 are the Dirac matrices, and $\rho_N(\mathbf{r})$ is the nuclear density normalized to unity. To extract the fundamental $k_{T,P}$ constant from an experiment one needs to know the electronic structure factor, $W_{T,P}$, on the nucleus of interest:

$$W_{T,P} = \frac{1}{\Omega} \langle \Psi | \sum_i \frac{H_{T,P}(i)}{k_{T,P}} | \Psi \rangle. \tag{4}$$

Similarly to E_{eff}, the $W_{T,P}$ parameter cannot be measured and must be obtained from a molecular electronic structure calculation.

In Refs. [29] and [53] it was demonstrated that the ^{229}ThO molecule can be used to search for T,P-odd interaction of the ^{229}Th nuclear magnetic quadrupole moment (MQM) with electrons. The T,P-odd electromagnetic interaction is described by the Hamiltonian [11,48,54,55]

$$H^{\text{MQM}} = -\frac{M}{2I(2I-1)} T_{ik} \frac{3}{2} \frac{[\boldsymbol{\alpha} \times \boldsymbol{r}]_i r_k}{r^5}, \tag{5}$$

where Einstein's summation convention is implied, $\boldsymbol{\alpha}$ are the 4×4 Dirac matrices, $\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}$, $\boldsymbol{r}$ is the displacement of the electron from the Th nucleus, $\boldsymbol{I}$ is the nuclear spin, M is the nuclear MQM,

$$M_{i,k} = \frac{3M}{2I(2I-1)} T_{i,k}, \tag{6}$$

$$T_{i,k} = I_i I_k + I_k I_i - \tfrac{2}{3} \delta_{i,k} I(I+1). \tag{7}$$

In the subspace of $\pm\Omega$ states Hamiltonian (5) is reduced to the effective molecular Hamiltonian [9,56]

$$H_{\text{eff}}^{\text{MQM}} = -\frac{W_M M}{2I(2I-1)} S \hat{T} \boldsymbol{n}, \tag{8}$$

where S is the effective electron spin [49], $S = |\Omega| = 1$. The W_M parameter can be evaluated by the following matrix element [53]:

$$W_M = \frac{3}{2\Omega} \langle \Psi | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^5} \right)_\zeta r_\zeta | \Psi \rangle. \tag{9}$$

It was shown in Refs. [29] and [53] that, using the ^{229}Th isotope, one can obtain limits on the strength constants of

T,P-odd nuclear forces, neutron electric dipole moment, QCD vacuum angle θ, quark EDM, and chromo-EDM. This also can be applied to the ^{229}ThF$^+$ cation.

A commonly used way to verify the theoretical E_{eff}, $W_{T,P}$, and W_M values is to calculate "on equal footing" (using the same approximation for the wave function) those molecular characteristics (properties or effective Hamiltonian parameters) which have comparable sensitivity to different variations of the wave function but, in contrast, can be measured. Similarly to E_{eff}, $W_{T,P}$, and W_M, these parameters should be sensitive to a change in the spin-polarized share of the electronic density, etc., in the atomic core region. The hyperfine structure (HFS) constant, $A_{||}$, is traditionally used as such a parameter (e.g., see Ref. [57,58]). To obtain $A_{||}$ on ^{229}Th in the ^{229}ThF$^+$ theoretically, one can evaluate the matrix element

$$A_{||} = \frac{\mu_{\text{Th}}}{I\Omega} \langle \Psi | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3} \right)_\zeta | \Psi \rangle, \tag{10}$$

where μ_{Th} is the magnetic moment of an isotope of the Th nucleus having spin I. In the present paper we do not consider fluorine nuclear spin.

For preparation and conduction of the experiment the value of the g factor of the molecule is of interest. It is defined as

$$G_{||} = \frac{1}{\Omega} \langle \Psi | \hat{L}_{\hat{n}}^e - g_S \hat{S}_{\hat{n}}^e | \Psi \rangle, \tag{11}$$

where $\vec{L}^e$ and $\vec{S}^e$ are the electronic orbital and electronic spin momenta operators, respectively; $g_S = -2.0023$ is a free-electron g factor. Note that the value of $G_{||}$ is close to 0 for the $^3\Delta_1$ state (and equal to 0 when both the scalar-relativistic approximation is applied and the radiation corrections to the free-electron g factor are ignored). Therefore, the parameter is very sensitive to the quality of the wave function, since high-order interference contributions between spin-orbit and electron correlation effects become important.

Recently, ThF$^+$ has been studied both experimentally and theoretically in Refs. [44] and [45]. The measured and calculated values are given there for spectroscopic constants of the lowest-lying states including $^3\Delta_1$. However, up to now there is only one (semiempirical) estimate of E_{eff} in ThF$^+$, published in Ref. [27], $E_{\text{eff}} = 90$ GV/cm. The aim of this paper is to perform an accurate *ab initio* study of the electronic structure of ThF$^+$ and to calculate E_{eff} and other parameters given by Eqs. (1), (4), (9), and (10).

II. TWO-STEP APPROACH

It follows from Eqs. (2)–(10) that the action of operators related to the E_{eff}, $W_{T,P}$, W_M, and $A_{||}$ characteristics is heavily concentrated in the atomic core region. On the other hand, the leading contribution to the corresponding matrix elements (mean values) is due to the valence electrons since contributions from the inert (usually closed and spherically symmetric) inner-core shells compensate each other or are negligible in most cases of practical interest for the operators, in particular, dependent on the total angular momentum and spin. Note, however, that the spin polarization of core (subvalence or outer-core) shells induced by the valence unpaired electrons can provide a comparable contribution

by magnitude to such properties as that from the valence electrons; e.g., see Refs. [18], [38], and [59]. Below we call such properties the "core properties" (or, more generally, "core characteristics," since not only measurable properties but also other effective Hamiltonian parameters which are not always measurable can be considered here), assuming that the main contribution to them comes from the spatially localized core region rather than from core shells. Some well-known examples of such properties are the magnetic dipole hyperfine constants [see Eq. (10)]. In the cases of unpaired s electrons, the leading contribution to the HFS is determined by the Fermi-contact interaction (in the nonrelativistic case), which is proportional to the electronic spin density directly on the nucleus. Other examples of core properties (which have a negligible contribution from inert innermost core shells) are the chemical shifts of x-ray emission spectra [60,61], etc.

One can safely exclude inactive inner-core electrons from correlation calculations due to their negligible contribution to the core properties. In the present consideration, the inner core consists of $1s$-$4f$ electrons of Th. As Th is a very heavy element (atomic number, 90), the interaction of electrons with the Th nucleus should be treated by a fully relativistic manner for a good accuracy. Moreover, for some properties even taking account of the Breit interaction (mainly between valence and core electrons of Th; see [62] and [63]) can be important. With a good accuracy for the properties considered here, the inner-core electrons differ negligibly in the cases of atomic Th and ThF+ cations because their wave functions are mostly defined by the strong Th nucleus potential $\sim \frac{Z}{r}$ screened by inner-most electrons, so that the effective Th core field is much stronger than the energetics of valence (chemically active) electrons. In the correlation calculation they can be frozen without a loss of the accuracy accessible presently. A common way to exclude inner-core electrons is to use the relativistic effective core potential method. Earlier our group developed the generalized relativistic effective core potential (GRECP) version, which permits one to attain a very high accuracy [64–66]. This effective potential emulates the interaction between inner-core electrons (excluded explicitly from GRECP calculations) and valence plus outer-core electrons (treated explicitly with the GRECP).

Performing electronic structure calculations one can evaluate different valence properties such as transition energies between low-lying states and molecule-frame dipole moments. However, since the inner-core parts of the valence one-electron "pseudo–wave functions" are smoothed in GRECP calculations, they have to be recovered with some core-restoration method before using them to evaluate the core characteristics considered above. In a series of papers a nonvariational restoration concept (and its initial implementation; see [50] and references therein), which is based on a proportionality of valence and low-lying virtual spinors in the inner-core region of heavy atoms, was developed (see [61] and the next section). Recently we have developed an implementation of the concept which permits one to use well-developed codes for correlation treatment such as DIRAC [67], MRCC [68], and CFOUR [59,69,70]. Below we give a description of the new implementation; now the code is also extended to characterize effective states (configurations) of atoms in compounds, e.g. Th in ThF+ and ThO.

Using the basic idea of the nonvariational restoration method one generates *equivalent* basis sets of one-center, four-component spinors,

$$\begin{pmatrix} f_{nlj}(r)\theta_{ljm} \\ g_{nlj}(r)\theta_{2j-l,jm} \end{pmatrix},$$

and smoothed two-component pseudospinors,

$$\tilde{f}_{nlj}(r)\theta_{ljm},$$

in all-electron finite-difference Dirac-Fock-Breit and GRECP–self-consistent-field calculations (employing the jj-coupling scheme) of *the same* configurations of a considered atom and its ions [30,71–75]. Here n is the principal quantum number, j is the total electronic momentum, m is its projection, and l is the orbital momentum. In the newly developed procedure a basis set of real spin orbitals (and not complex spin-orbit-mixed spinors) $\tilde{\xi}_p$ is generated additionally. The spin orbitals $\tilde{\xi}_p$ are then expanded in the basis set of one-center, two-component atomic pseudospinors

$$\tilde{\xi}_p \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} T_{nljm}^p \tilde{f}_{nlj}(r)\theta_{ljm}. \tag{12}$$

The atomic two-component pseudospinors are replaced by equivalent four-component spinors, while the expansion coefficients from Eq. (12) are preserved:

$$\xi_p = \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} T_{nljm}^p \begin{pmatrix} f_{nlj}(r)\theta_{ljm} \\ g_{nlj}(r)\theta_{2j-l,jm} \end{pmatrix} \tag{13}$$

and we obtain four-component function ξ_p which is "equivalent" to $\tilde{\xi}_p$. If a one-electron reduced density matrix with elements $\tilde{P}_{\mu\nu}$ in a basis set of multicenter spinors (or spin-orbitals) ψ_μ is evaluated after the (G)RECP calculation of a molecule or some condensed-matter system (see Ref. [70] for details on the condensed-matter case), one can then re-expand it in the basis of one-center $\tilde{\xi}_p$ functions on an atom of interest. This mapping from a multicenter basis $\{\psi_\mu\}$ to a one-center basis $\{\tilde{\xi}_p\}$ corresponds to a similarity transformation of the density matrix,

$$||\tilde{P}_{\mu\nu}|| \longrightarrow ||\tilde{D}_{pq}||, \tag{14}$$

where $\tilde{D}_{pq}$ are elements of the density matrix in the basis of $\tilde{\xi}_p$ functions. Due to "equivalence" of the $\tilde{\xi}_p$ and ξ_p functions [see Eqs. (12) and (13)] based on appropriate properties of the hard-core shape-consistent (G)RECP versions [76], one can write

$$||D_{pq}|| \approx ||\tilde{D}_{pq}||, \tag{15}$$

where D_{pq} are elements of the density matrix in the basis of four-component ξ_p functions, (13). Thus, as an approximation we can equate the D_{pq} elements to $\tilde{D}_{pq}$ and interpret it as a restoration of the "true" four-component structure of the density matrix that is important first of all for the inner-core region.

The mean value of some one-electron operator A corresponding to a core property in a given atom can be evaluated as

$$\langle A \rangle = \sum_{pq} D_{pq} A_{pq}, \tag{16}$$

where A_{pq} are the matrix elements of operator A in the basis of four-component functions ξ_p, (13). In the current implementation of the restoration procedure the functions $\tilde{\xi}_p$ are real spin orbitals with the spatial factor in the form of contracted Gaussians, for which re-expansion (14) is performed analytically. Therefore, significant acceleration is attained, in contrast to the original restoration procedure [50]. Note, however, that the four-component functions used to evaluate matrix elements of operator A are taken in numerical (finite-difference) form. This permits us to exclude some complications in reproducing accurate wave-function behavior in a region near the nucleus which can arise when Gauss-type functions are used there.

III. "ATOMS IN COMPOUNDS" THEORY

In Ref. [61] we introduced the concept of *atoms in compounds* (AIC) and applied it to the problem of chemical shifts of x-ray emission lines. The concept assumes that for the core characteristics one can determine the effective state of a given atom in a chemical compound for which the mean values of operators corresponding to *all* the considered core characteristics have nearly the same magnitudes for the case of an atom bonded in a molecule and for the same atom in the considered effective state. Note that the concept cannot be directly applied to evaluation of the "valence" properties (again, taking in mind spatial localization rather than affiliation with valence shells) such as the molecule-frame dipole moment and g factor.

Let us show how the AIC theory can be formulated in the context of the problems discussed in this paper. Assume that we have obtained a one-electron density matrix from calculation of an atom, molecule, or crystal (in the direct lattice). The density matrix can be formally re-expanded on one center, i.e., on a heavy atom of interest:

$$\rho(\vec{r}|\vec{r}') = \sum_{nljm,n'l'j'm'} \rho_{nljm,n'l'j'm'} \varphi_{nljm}(\vec{r})\varphi_{n'l'j'm'}^{\dagger}(\vec{r}') \quad (17)$$

in a sufficiently complete basis set of orthonormal atomic functions $\{\varphi_{nljm}\}$. Then for the mean value of some one-electron operator A we have

$$\langle A \rangle = \sum_{nljm,n'l'j'm'} \rho_{nljm,n'l'j'm'} \int \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r}. \quad (18)$$

The mean value in Eq. (18) can be rewritten as

$$\int \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r} = \int_{|\vec{r}| \leqslant |\vec{R}_c|} \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r}$$
$$+ \int_{|\vec{r}| > |\vec{R}_c|} \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r}, \quad (19)$$

where R_c is some "core radius" (see also below). Here we consider that the operator A corresponds to a core property. This means that for $r > R_c$ the second term in Eq. (19) has to be negligible compared to the first term. As an extremal case, $R_c = 0$ for the Fermi-contact interactions. Thus, for a core-property operator we have

$$\int \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r} \approx \int_{|\vec{r}| \leqslant |\vec{R}_c|} \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r}. \quad (20)$$

Now we assume that the basis set $\{\varphi_{nljm}\}$ was constructed after calculations of the atom or its low-charged ions. The basis set contains inner core spinors, labeled below with the index C (which are occupied by inert electrons and excluded from molecular calculations with the GRECP as inactive, completely occupied states), and valence, outer core (occupied by explicitly treated core electrons), and low-lying virtual spinors; all together they are labeled with the index W. The remaining spinors, corresponding to high-energy virtual states, are labeled with index R. The core states are only negligibly changed in the low-energy process under consideration (formation of chemical bond, low-energy excitation of atom, etc.). The completeness condition for the $\{\varphi_{nljm}\}$ basis can be formally written as

$$1 = \sum_{nljm} \varphi_{nljm} \varphi_{nljm}^{\dagger} = P_C + P_W + P_R, \quad (21)$$

$$P_C = \sum_{nljm \in C} \varphi_{nljm} \varphi_{nljm}^{\dagger}, \quad (22)$$

$$P_W = \sum_{nljm \in W} \varphi_{nljm} \varphi_{nljm}^{\dagger}, \quad (23)$$

$$P_R = \sum_{nljm \in R} \varphi_{nljm} \varphi_{nljm}^{\dagger}, \quad (24)$$

where P_C is the projector on the inner-core spinors, P_W is the projector on the outer-core, valence, and low-energy virtual spinors, and P_R is the projection on the other (high-energy) states. For low-energy processes, which include chemical bonding, low-lying excitations, and excitations induced by weak external fields, one can usually neglect the high-energy states to study the properties of interest,

$$\rho = (P_C + P_W + P_R)\rho(P_C + P_W + P_R)$$
$$\approx (P_C + P_W)\rho(P_C + P_W)$$
$$\approx P_C \rho P_C + P_W \rho P_W = \rho^C + \rho^W, \quad (25)$$

where $\rho^C = P_C \rho P_C$ and $\rho^W = P_W \rho P_W$. Here we have taken into account that the inner-core electrons usually need not be correlated to preserve a high accuracy for the core properties in general, in contrast to the W states. Therefore, the off-diagonal blocks $P_W \rho P_C$ and $P_C \rho P_W$ can be mostly neglected [77].

Due to Eq. (25), expression (18) for $\langle A \rangle$ reduces to the two terms

$$\langle A \rangle \approx \langle A \rangle^C + \langle A \rangle^W, \quad (26)$$

where

$$\langle A \rangle^C = \sum_{nljm \in C, n'l'j'm' \in C} \rho_{nljm,n'l'j'm'} \int \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r},$$

$$\langle A \rangle^W = \sum_{nljm \in W, n'l'j'm' \in W} \rho_{nljm,n'l'j'm'} \int \varphi_{n'l'j'm'}^{\dagger} A \varphi_{nljm} d\vec{r}.$$

$$(27)$$

For properties such as the HFS constant, etc. considered here, $\langle A \rangle^C \approx 0$; i.e., direct contribution from the closed-shell core electrons can be ignored (and only their spin polarization by open valence shells can be non-negligible; see [59]). In other cases $\langle A \rangle^C$ can be obtained from atomic calculations if one
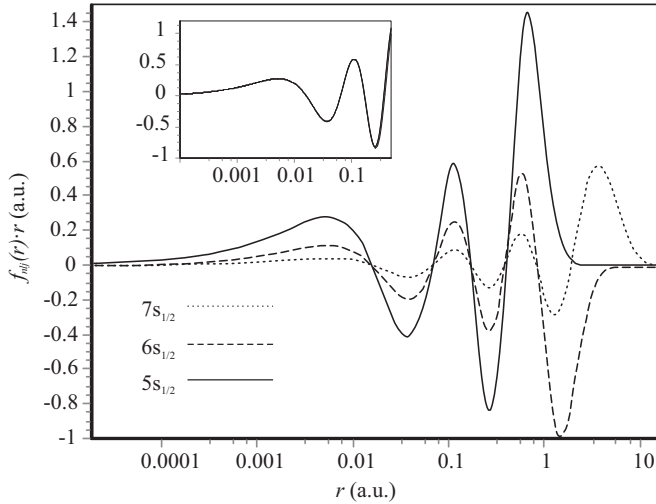
FIG. 1. Large components of the $5s_{1/2}$, $6s_{1/2}$, and $7s_{1/2}$ spinors of Th for the $7s^2 7p^1 6d^1$ configuration. Inset: Large components of $5s_{1/2}$, $6s_{1/2}$, and $7s_{1/2}$ spinors in the core region; the scaling factor is chosen in such a way that the amplitudes of large components of these spinors are equal at $R_c = 0.25$ a.u.

takes into account that the heavy-atom inner-core electrons are inactive in low-energy processes. Thus, for our case we have

$$\langle A \rangle \approx \langle A \rangle^W. \tag{28}$$

It is well known for heavy atoms and their compounds [65,76,78,79] that valence one-electron wave functions and low-lying virtual states are proportional to each other in the vicinity of a nucleus. This is due to the overwhelming contribution of the highly charged (even being shielded) heavy-nucleus potential compared to other potentials from the molecular environment, inter-electron interaction, etc. Figure 1 shows the large components of $5s_{1/2}$, $6s_{1/2}$, and $7s_{1/2}$ of the Th atom taken from a self-consistent field calculation of the $7s^2 7p^1 6d^1$ configuration. Note that the core radius R_c belongs to the region of proportionality for the core properties considered here.

One can introduce some reference functions for each combination of l, j:

$$\mathcal{H}_{ljm}(\vec{r}) \equiv \begin{pmatrix} \eta_{lj}^f(r)\theta_{ljm} \\ \eta_{lj}^g(r)\theta_{2j-l,jm} \end{pmatrix}. \tag{29}$$

The functions $\eta_{lj}^{f,g}(r)$ will be determined such that they are equal to the valence functions $f_{lj}(r)$ and $g_{lj}(r)$ of a given atomic four-component spinor with the same lj for $r < R_c$ and equal to 0 outside the (given core) region. Due to the proportionality property (see Fig. 1) it is not practically important which of the W functions, $\varphi_{nljm}^W(\vec{r})$, is chosen for a given lj or from which configuration it is chosen [80]. For example, for the case of $l = 0$, $j = 1/2$ of Th, one can consider $5s_{1/2}$, or $6s_{1/2}$, or $7s_{1/2}$ as follows from Fig. 1. For all functions from the W diversity (i.e., for all $n \in W$),

$$\varphi_{nljm}(\vec{r}) \approx k_{nljm}\mathcal{H}_{ljm}(\vec{r}), \quad r \leqslant R_c, \tag{30}$$

where k_{nljm} are the proportionality (scaling) factors.

Using Eqs. (20) and (30) we can rewrite Eq. (28) in the form

$$
\begin{aligned}
\langle A \rangle &\approx \sum_{nljm;n'l'j'm' \in W} \rho_{nljm,n'l'j'm'} \int \varphi_{n'l'j'm'}^\dagger A \varphi_{nljm} d\vec{r} \\
&\approx \sum_{nljm;n'l'j'm' \in W} \rho_{nljm,n'l'j'm'} k_{nljm} k_{n'l'j'm'} \int \mathcal{H}_{l'j'm'}^\dagger A \mathcal{H}_{ljm} d\vec{r} \\
&= \sum_{ljm;l'j'm'} \Delta_{ljm,l'j'm'} \int \mathcal{H}_{l'j'm'}^\dagger A \mathcal{H}_{ljm} d\vec{r},
\end{aligned} \tag{31}
$$

where

$$\Delta_{ljm,l'j'm'} = \sum_{nljm;n'l'j'm' \in W} \rho_{nljm,n'l'j'm'} k_{nljm} k_{n'l'j'm'}. \tag{32}$$

Here $||\Delta_{ljm,l'j'm'}||$ is the W-reduced density matrix, in which the terms are summed up on the chosen principal quantum numbers $n \in W$, in contrast to a conventional one-electron density matrix from Eq. (17).

The last expression in Eq. (31) means that for calculation of a core property A it is sufficient to know some W-reduced density matrix $\Delta_{ljm,l'j'm'}$ as well as matrix elements of the operator over the reference functions $\{\mathcal{H}_{ljm}(\vec{r})\}$. One can interpret $||\Delta_{ljm,l'j'm'}||$ as a density matrix of an effective AIC state. The diagonal elements of the matrix are occupancies of the reference functions [81]. The nondiagonal elements between different lj values are "overlap occupancies (populations)." The latter can occur in consideration of a molecule (crystal) due to polarization of atomic orbitals in a molecular (crystalline) environment or in an atom placed in some external field; i.e., they reflect the nonspherical distribution of electron density in the vicinity of the nucleus of the atom under consideration. We should stress that the diagonal and overlap populations have meanings of "observable quantities" (though, in practice, their combination can be, rather, observed experimentally). This means that different parts of the W-reduced density matrix can be obtained from different experiments (or their combinations). In particular, the diagonal matrix elements can be extracted from x-ray emission chemical-shift experiments. The nondiagonal matrix elements predetermine the value of the effective electric field, which, in turn, can formally be extracted from the electron EDM experiments if we know the eEDM value. Finally, one can say that the AIC effective state is in some sense a more general term than the classical effective state term since the AIC effective state can include overlap populations between different harmonics as discussed above.

The AIC concept described here can be applied both in the direct four-component calculation and in the two-step study, in which the four-component density matrix is obtained in the second stage of the procedure discussed in the previous section. Actually, computation of the effective W-reduced density matrix is a special case of the recovery procedure when the equivalent basis sets are constructed only from the reference functions $\{\mathcal{H}_{ljm}(\vec{r})\}$ and some modification of the one-center restoration is applied. In the present paper we report implementation of the procedure and its application to calculation of the W-reduced density matrix for the ThO and ThF$^+$ molecules and a number of core properties: the hyperfine magnetic dipole constant, (10); effective electric field, (2); molecular-structure parameters of the T,P-odd

pseudoscalar-scalar electron-nucleus interaction, (4); and T,P-odd interaction of the nuclear MQM with electrons, (9). The code is interfaced to the DIRAC12 [67] and MRCC [68] codes.

IV. COMPUTATIONAL DETAILS

To evaluate E_{eff}, $W_{T,P}$, W_M, and $A_{\parallel}$ in ThF$^+$ we have applied the two-step method described above. The computational scheme used in the present paper is similar to that employed in [28] and [30] for calculation of ThO, where we have described and analyzed the scheme in detail (possible sources of errors, importance of correlation treatment, importance of multireference approaches, applicability and convergence of multireference configuration interaction approaches, etc.). In all the calculations the $1s$-$4f$ inner-core electrons of Th were excluded from molecular correlation calculations using the valence (semilocal) version of the GRECP [66] method. The main calculation was performed within the 38-electron, two-component, single-reference coupled-cluster method with single, double, and perturbative triple cluster amplitudes, 38e-2c-CCSD(T). The calculation was perform using the MBas basis set, generated in [30] with added h- and i-type functions; i.e., we used the $(30,20,10,11,4,6,5)/[30,8,10,4,4,2,1]$ basis set. For F we have applied the aug-ccpVQZ basis set [82] with two removed g-type basis functions; i.e., the $(13,7,4,3)/[6,5,4,3]$ basis set was used. To consider high-order correlation effects we calculated correlation correction. For this we have frozen 20 outer-core electrons ($5s^25p^65d^{10}$ shells of Th and $1s^2$ shell of F) and performed two-component calculations within the coupled-cluster method with single, double, triple, and perturbative quadruple cluster amplitudes, CCSDT(Q), and within the CCSD(T) method. We utilized the CBasSO atomic natural basis set, which was generated using the same procedure that was used and described in [30] and [83] and can be written as $(35,29,15,10,7)/[6,8,5,3,2]$ for Th and $(13,7)/[4,3]$ for fluorine. The correction was calculated as the difference in the calculated parameters within the CCSDT(Q) versus the CCSD(T) method. 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 main two-component calculation and (ii) scalar-relativistic CCSD(T) calculation utilizing the extended basis set on Th (Lbas basis set $(37,29,15,14,10,10,5)/[22,17,15,14,10,10,5]$ generated in [30]). Corrections were estimated as differences between the values of the corresponding parameters. Finally, we have calculated the vibrational contribution to the considered core properties and molecule-frame dipole moment corresponding to zero vibrational level of the $^3\Delta_1$ electronic state as the difference between the value averaged over zero vibration wave function and the nonaveraged value at the given internuclear distance (3.75 a.u.; see below). The potential energy curve was calculated at the 38-electron one-component CCSD(T) level with the LBas basis set.

V. RESULTS AND DISCUSSION

According to the 38-electron, two-component CCSD(T) calculations the equilibrium internuclear distance in the $^3\Delta_1$ state of ThF$^+$ is 3.75 a.u., which agrees well with the

TABLE I. Equilibrium internuclear distance R_e, harmonic vibrational wave number ω_e, and vibrational anharmonicity $\omega_e x_e$ for the $^3\Delta_1$ state of ThF$^+$.

Method	R_e (a.u.)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
MRCI + Q/SO [44]	3.76	655.6	–
CCSD(T) (this work)	3.75	658.4	1.9
Experiment [44]	3.74(4)	658.3(10)	–

experimental datum [44] (see Table I). In calculations of the parameters under consideration we have set R(Th-F) to 3.75 a.u.

Table II lists the calculated values of the effective electric field along with the parameter of the T,P-odd pseudoscalar–scalar–electron–nucleus interaction, HFS constant, W_M parameter, and G$_{\parallel}$ factor for the $^3\Delta_1$ state of ThF$^+$. It follows from Table II that the calculated value of E_{eff} is stable with respect to the electron correlation improvement and basis set enlargement. Similarly to Ref. [30], using size-extensive coupled-cluster calculations we have found that the outer-core electrons of Th contribute about 3.5 GV/cm to E_{eff} (a similar value was found in Ref. [30] for ThO) and $-161 \frac{\mu_{\text{Th}}}{\mu_{\text{N}}} \cdot$ MHz to A$_{\parallel}$. Thus, if one performs 18-electron rather than 38-electron calculations the outer-core contributions should be taken in mind. According to our calculations the spin-orbit contribution from the valence electrons to E_{eff} (about 1 GV/cm) is almost negligible in the case of ThF$^+$, in contrast to ThO, where it is about 10 GV/cm [30]). According to Table II, in view of the extensive analysis of uncertainties performed in Ref. [30], we suggest that the theoretical uncertainties of E_{eff}, $W_{T,P}$, and A$_{\parallel}$ are within 7%. Unfortunately, A$_{\parallel}$ [Eq. (10)] is yet unknown experimentally for ^{229}ThF$^+$ and it cannot be used currently to check the value of E_{eff} and other considered properties. However, we have shown in Ref. [35] for the ground state of PbF molecule that the computational scheme used is rather accurate: the calculated value of A$_{\parallel}$(PbF) agrees with the experimental datum [84] within 2%. Finally, it should be noted that the estimation made in Ref. [27] for E_{eff} (90 GV/cm) is more than twice overestimated (a similarly large overestimation was also found for E_{eff} in PtH$^+$, see [85]). In a like manner the estimations for the $W_{T,P}$ and W_M parameters made in Refs. [53] and [86], and based on E_{eff} from Ref. [27], are also about twice overestimated.

The effective electric field in the $^3\Delta_1$ state of ThF$^+$ is about two times smaller than the E_{eff} in the $^3\Delta_1$ state of ThO (81.5 GV/cm; see [30]) because of a smaller mixing of s and p orbitals. We can give the following explanation. In the naive ionic model ThO can be considered as Th^{+2} and O^{-2}, ThF$^+$ can be considered as Th^{+2} and F^{-1}. This agrees with the fact that the molecule-frame dipole moment of ThO is about 1.5 times larger than the dipole moment of ThF$^+$ with respect to the Th nucleus (see Table II). This leads to a higher effective negative electric charge on oxygen in ThO than on fluorine in ThF$^+$. Both ThO and ThF$^+$ have two unpaired electrons. They are nonbonding and localized on Th so that Th has the $\sigma^1\delta^1$ configuration in both cases, where σ is mainly the $7s$ atomic orbital of Th and δ is mainly the $6d$ atomic orbital of Th. The unpaired electrons of Th feel a stronger electric field in ThO than in ThF$^+$. This leads to higher polarization of the unpaired electrons in the case of ThO, i.e., stronger s-p mixing of the

TABLE II. Calculated values of the molecule-frame dipole moment (d), effective electric field (E_{eff}), parameter of the T,P-odd pseudoscalar-scalar electron-nucleus neutral current interaction ($W_{T,P}$), parameter of the T,P-odd MQM interaction (W_M), hyperfine structure constant ($A_{\parallel}$), and g factor ($G_{\parallel}$) of the $^3\Delta_1$ state of ThF$^+$ compared to the corresponding values for ThO from Refs. [29,30] using coupled-cluster methods.

Method	d (D)[a]	E_{eff} (GV/cm)	$W_{T,P}$ (kHz)	W_M ($\frac{10^{33}\,\text{Hz}}{e\,\text{cm}^2}$)	$A_{\parallel}$ ($\frac{\mu_{\text{Th}}}{\mu_{\text{N}}}\cdot$ MHz)	$G_{\parallel}$
38e-2c-CCSD	2.69	35.5	48	0.87	−4214	0.039
38e-2c-CCSD(T)	2.66	38.1	51	0.90	−4164	0.033
Correlation correction	0.07	0.0	0	−0.01	13	0.001
Basis set correction	−0.01	−0.6	−1	−0.02	−14	−
Vibr. contribution	0.03	−0.1	0		2	−
Final(ThF$^+$)	2.74	37.3	50	0.88	−4163	0.034
Final(ThO) (see Refs. [29], [30])	4.23	81.5	112	1.66	−2949	0.007

[a]The dipole moment is calculated with respect to the Th nucleus.

σ state (the δ state has no practical interest for E_{eff} here due to the far lower amplitude of $6d$ in the core region than of $7s$). The leading contribution to E_{eff} is roughly proportional to

$$C_{7s}C_{7p}\langle 7s|H_d/d_e|7p\rangle,$$

where Eq. (1) is used. The matrix element is mainly accumulated near the Th nucleus and C_{7s} (≈ 1), C_{7p} are the corresponding MO LCAO coefficients of the atomic Th orbitals in the hybridized molecular one. As a consequence, the effective electric field should be expected to be notably larger in ThO than in ThF$^+$. On the other hand, the smaller polarization of the open-shell σ state leads to a higher s character of the orbital, and the HFS constant in $^3\Delta_1$ of ThF$^+$ is larger than in ThO (see Table II). Note that the HFS constant behaves "inconsistently" with respect to the effective electric field in the present case.

We have applied the AIC theory described in the previous section to the case of ThF$^+$ and ThO. To set the radial reference functions $\{\eta_{lj}^{f,g}\}$ given in Eq. (29) we have used the $7s$, $7p$, and $6d$ functions from calculation of the $7s^27p^16d^1$ configuration of Th and have evaluated the W-reduced density matrix $\Delta_{ljm,l'j'm'}$ defined by Eq. (32) from the molecular density matrices obtained within the CCSD approach. Note that $\{\mathcal{H}_{ljm}\}$, (29), coincide with the $7s$, $7p$, and $6d$ functions within some radius R_c (here we set $R_c = 0.25$ a.u.) and are 0 outside the radius. For brevity we designate the selected reference functions $\widetilde{7s}_{1/2,1/2}$, etc. The operator of the hyperfine interaction mixes states with the same parity and m; the diagonal matrix element of the operator for $|ljm\rangle$ state is opposite by sign to the diagonal matrix element for $|lj-m\rangle$ state. Thus, the diagonal contribution to the mean value of the operator is defined by the difference between the density matrix elements, $\Delta_{ljm,ljm} - \Delta_{lj-m,lj-m}$, and the diagonal hyperfine operator terms for $|ljm\rangle$ states. For the most important elements of the W-reduced density matrix for the ThF$^+$ $^3\Delta_1$ state, we have

$$\Delta_{\widetilde{7s}_{1/2,1/2},\widetilde{7s}_{1/2,1/2}} - \Delta_{\widetilde{7s}_{1/2,-1/2},\widetilde{7s}_{1/2,-1/2}} = -0.99,$$
$$\Delta_{\widetilde{7p}_{1/2,1/2},\widetilde{7p}_{1/2,1/2}} - \Delta_{\widetilde{7p}_{1/2,-1/2},\widetilde{7p}_{1/2,-1/2}} = -0.47,$$
$$\Delta_{\widetilde{6d}_{3/2,3/2},\widetilde{6d}_{3/2,3/2}} - \Delta_{\widetilde{6d}_{3/2,-3/2},\widetilde{6d}_{3/2,-3/2}} = 0.88, \quad (33)$$
$$\Delta_{\widetilde{7s}_{1/2,1/2},\widetilde{7p}_{1/2,1/2}} + \Delta_{\widetilde{7s}_{1/2,-1/2},\widetilde{7p}_{1/2,-1/2}} = 0.105,$$
$$\Delta_{\widetilde{7p}_{1/2,1/2},\widetilde{7s}_{1/2,1/2}} + \Delta_{\widetilde{7p}_{1/2,-1/2},\widetilde{7s}_{1/2,-1/2}} = 0.105.$$

For the most important elements of the W-reduced density matrix for the ThO $^3\Delta_1$ state, we have

$$\Delta_{\widetilde{7s}_{1/2,1/2},\widetilde{7s}_{1/2,1/2}} - \Delta_{\widetilde{7s}_{1/2,-1/2},\widetilde{7s}_{1/2,-1/2}} = -0.72,$$
$$\Delta_{\widetilde{7p}_{1/2,1/2},\widetilde{7p}_{1/2,1/2}} - \Delta_{\widetilde{7p}_{1/2,-1/2},\widetilde{7p}_{1/2,-1/2}} = -0.37,$$
$$\Delta_{\widetilde{6d}_{3/2,3/2},\widetilde{6d}_{3/2,3/2}} - \Delta_{\widetilde{6d}_{3/2,-3/2},\widetilde{6d}_{3/2,-3/2}} = 0.67, \quad (34)$$
$$\Delta_{\widetilde{7s}_{1/2,1/2},\widetilde{7p}_{1/2,1/2}} + \Delta_{\widetilde{7s}_{1/2,-1/2},\widetilde{7p}_{1/2,-1/2}} = 0.238,$$
$$\Delta_{\widetilde{7p}_{1/2,1/2},\widetilde{7s}_{1/2,1/2}} + \Delta_{\widetilde{7p}_{1/2,-1/2},\widetilde{7s}_{1/2,-1/2}} = 0.238.$$

Thus, in terms of the reference functions the effective configuration of unpaired electrons of Th in ThF$^+$ is $\widetilde{7s}^{1.0}\widetilde{7p}^{0.5}\widetilde{6d}^{0.9}$, while in ThO it is $\widetilde{7s}^{0.7}\widetilde{7p}^{0.4}\widetilde{6d}^{0.7}$. The leading matrix element of the HFS operator in the basis of reference functions is between the $\widetilde{7s}$ functions. The ratio of effective occupancies of $\widetilde{7s} \approx 1.4$. This explains the ratio of the HFS constants listed in Table II.

The operator of the effective electric field, (2), mixes states of opposite parity with the same m; the matrix element of the operator between $|ljm\rangle$ and $|l'jm\rangle$ has the same sign as the matrix element between the $|lj-m\rangle$ and the $|l'j-m\rangle$ state. Thus, the mean value of the operator is defined by combination of the types $\Delta_{ljm,l'jm} + \Delta_{lj-m,l'j-m}$ of the W-reduced density matrix $||\Delta_{ljm,l'j'm'}||$ and matrix elements of the E_{eff} operator between the $|ljm\rangle$ and the $|l'jm\rangle$ states. Most important of the combinations of $||\Delta_{ljm,l'j'm'}||$ matrix elements for ThF$^+$ and ThO $^3\Delta_1$ state are given in Eqs. (33) and (34). From the equations one can see that the W-reduced overlap population between the $\widetilde{7s}$ and the $\widetilde{7p}$ functions in ThO is twice as large as that in ThF$^+$. This explains the appropriately larger E_{eff} in ThO (see Table II).

Note that the W-reduced density matrix $||\Delta_{ljm,l'j'm'}||$ (and minimal number of core-property matrix elements over the reference W-reduced functions) can be considered a pretty concise description of the effective AIC state which is appropriate for "almost quantitative" calculation of the mean values of the core properties under consideration.

VI. CONCLUSION

The parameters E_{eff}, $W_{T,P}$, and W_M, which are required to interpret experimental measurements on the $^3\Delta_1$ state of ThF$^+$ in terms of fundamental quantities, are calculated. The value of E_{eff} in ThF$^+$ was found to be notably smaller than that in

ThO. A quantitative explanation is given. On the other hand, $E_{\rm eff}(\text{ThF}^+)$ is 1.6 times larger than the effective electric field in the HfF$^+$ cation [15,16], which is under preparation for eEDM search [13].

In the present paper we have implemented the concept of atoms in compounds and applied it to calculate the W-reduced density matrix for description of the effective state of Th in ThF$^+$ and ThO. This matrix contains "sufficient information" to evaluate such physically observable properties as the HFS constant, etc., whereas the conventional density matrix is excessive here.

According to our preliminary study, the electronic spectrum of ThF$^+$ is more dense than that of the ThO molecule. Its accurate theoretical investigation requires inclusion of quadruple cluster amplitudes as shown in Ref. [44] and is also found in our preliminary study of $^3\Delta_1$–$^1\Sigma$ transition energy. We plan to investigate it in a future study of ThF$^+$.

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