Application of relativistic coupled-cluster theory to the effective electric field in YbF

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An accurate determination of the effective electric field (E_{eff}) in YbF is important as it can be combined with the results of future experiments to give an improved new limit for the electric dipole moment of the electron. We report a relativistic coupled-cluster calculation of this quantity in which all the core electrons were excited. It surpasses the approximations made in the previous reported calculations. We obtain a value of 23.1 GV/cm for E_{eff} in YbF with an estimated error of less than 10%. The crucial roles of the basis sets and the core excitations in our paper are discussed.

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I. INTRODUCTION

The electric dipole moment (EDM) of a nondegenerate system arises from violations of both the parity (P) and the time-reversal (T) symmetries [1]. T violation implies charge parity (CP) violation via the TCP theorem [2]. In general, CP violation is a necessary condition for the existence of the EDMs of physical systems and, in particular, atoms and molecules.

Paramagnetic atoms and molecules are sensitive to the EDM of the electron (eEDM) [3], which is an important probe of the physics beyond the standard model [4]. The eEDM arising from CP violation could also be related to the matter-antimatter asymmetry in the universe [5]. A number of studies using atoms have been performed during the past few decades to extract an upper limit for the eEDM [6]. In general, for heavy polar molecules, the effective electric field experienced by an electron (E_{eff}) obtained from relativistic molecular calculations can be several orders of magnitude larger than that in atoms [7]. Therefore, the experimental observable (i.e., the shift in energy because of the interaction of the electric field with the eEDM) is also several orders of magnitude larger. Owing to the high sensitivity of the eEDM in molecules, there has been a considerable increase in interest in this field during the past decade [8]. Important experimental results have been reported on YbF [9] and ThO [10]. The upper limits of the eEDM are 10.5×10^{-28} e cm in YbF and 8.7×10^{-29} e cm in ThO. Improved results for both these molecules are expected in the next few years [10,11]. The above-mentioned limit for the eEDM from YbF was estimated using the available calculated values of E_{eff}. These calculations were based on semiempirical [12], quasirela-

tivistic [13,14], four-component Dirac-Fock (DF) [15], four-component many-body perturbation theory (MBPT) [16], and four-component relativistic configuration-interaction (CI) methods [17].

The aim of the present paper is to calculate E_{eff} in YbF using a rigorous relativistic many-body method, which is more complete than those used in the previous calculations. The method we have chosen is the four-component relativistic coupled-cluster (RCC) method, which is arguably the current gold standard for calculating the electronic structure of heavy atoms and diatomic molecules [18].

The electron EDM interaction Hamiltonian in a molecule can be written as [19]

$$\hat{H}_{\text{eEDM}} = -d_e \sum_i^{N_e} \beta \boldsymbol{\sigma}_i \cdot \mathbf{E}_{\text{int}}. \tag{1}$$

Here, d_e is the eEDM of an electron, β is one of the Dirac matrices, and $\boldsymbol{\sigma}$ are the Pauli spin matrices. i is the index of summation labeling for electrons, and N_e is the total number of electrons. $\mathbf{E}_{\text{int}}$ is the electric field acting on an electron in a molecule. The quantity that is of experimental interest in the search for the eEDM is an energy shift (ΔE) of a particular state owing to the interaction Hamiltonian given in Eq. (1). This can be expressed as

$$\Delta E = \langle \Psi | \hat{H}_{\text{eEDM}} | \Psi \rangle = -d_e \sum_i^{N_e} \langle \Psi | \beta \boldsymbol{\sigma}_i \cdot \mathbf{E}_{\text{int}} | \Psi \rangle$$
$$\equiv -d_e E_{\text{eff}}. \tag{2}$$

Here $|\Psi\rangle$ represents the wave function of a molecular state built from single-particle four-component Dirac spinors. From

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Eq. (2), it follows that

$$E_{\text{eff}} = \sum_i^{N_e} \langle \Psi | \beta \boldsymbol{\sigma}_i \cdot \mathbf{E}_{\text{int}} | \Psi \rangle$$

$$= \sum_i^{N_e} \langle \Psi | \beta \boldsymbol{\sigma}_i \cdot (\mathbf{E}_A + \mathbf{E}_B + \mathbf{E}_e) | \Psi \rangle. \quad (3)$$

The internal electric field in Eq. (3) consists of contributions from the two nuclei ($\mathbf{E}_A$ and $\mathbf{E}_B$) and the electrons ($\mathbf{E}_e$). It is clear that electronic structure calculations are necessary to obtain E_{eff}. However, the evaluation of the electronic term is complicated. Using the relationship [20],

$$-d_e \sum_{i=1}^{N_{\text{elec}}} \beta \boldsymbol{\sigma} \cdot \mathbf{E}_{\text{int}} = \left[-\frac{d_e}{e} \beta \boldsymbol{\sigma} \cdot \nabla, \hat{H}_0 \right] + 2ic\frac{d_e}{e} \sum_{i=1}^{N_{\text{elec}}} \beta \gamma_5 p^2, \quad (4)$$

Eq. (3) can be rewritten as

$$E_{\text{eff}} = 2i\frac{c}{e} \sum_i^{N_e} \langle \Psi | \sum_i^{N_{\text{elec}}} \beta \gamma_5 p_i^2 | \Psi \rangle, \quad (5)$$

where γ_5 is the product of the four Dirac matrices. Equation (5) represents the expectation value of an effective one-body operator, and it is therefore much simpler to evaluate Eq. (5) than Eq. (3).

To evaluate E_{eff}, we use the ground-state wave function of the Dirac-Coulomb (DC) Hamiltonian,

$$\hat{H}_{\text{DC}} = \sum_i^{N_{\text{elec}}} \left[c\boldsymbol{\alpha} \cdot \mathbf{p}_i + \beta c^2 - \sum_A^{N_{\text{nuc}}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right] + \sum_{i<j}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (6)$$

Here, c is the speed of light, p is the momentum operator, α collectively represents the Dirac matrices, $\mathbf{r}$ and $\mathbf{R}$ refer to the position vectors of the electrons and the nuclei, respectively, and Z is the charge of a nucleus. The capital letters in the summation are the nuclear indices, whereas the lowercase letters are the electronic indices.

We used the RCC method to obtain the ground-state wave function of YbF. The reference state was taken as a single determinant corresponding to an open shell doublet at the Dirac-Fock level. The Dirac-Fock configuration obtained was almost ionic, such as Yb:$(6s)^1$ and F:$(2p)^6$. The coupled-cluster wave function is given by

$$|\psi_{\text{CCSD}}\rangle = \exp(\hat{T}_1 + \hat{T}_2)|\psi_{\text{DF}}\rangle, \quad (7)$$

where $\hat{T}_1$ and $\hat{T}_2$ are single (S) and double (D) excitation operators, respectively. The salient features of our relativistic coupled-cluster singles and doubles (RCCSD) method are as follows: (i) It uses the Dirac-Coulomb approximation. (ii) It treats correlation effects to all orders in the residual Coulomb interaction for one and two hole-particle excitations. (iii) It is size extensive unlike the truncated CI [21].

II. COMPUTATIONAL DETAILS

We used Dyall's four-component valence double-ζ (DZ), triple-ζ (TZ), and quadruple-ζ (QZ) basis sets for ytter-

bium [22]. For fluorine, we used Watanabe's four-component basis sets [23]. In addition, we used some diffuse and polarization functions from the Sapporo basis sets [24]. All of the basis sets were used in the uncontracted form. The exponential parameters that were used in our calculations are summarized in the excel file "SM_basis_YbF_Eeff.xlsx" as Supplemental Material [25]. In the preliminary calculations, we investigated several types of contracted Gaussian-type basis spinors. The results of the contracted basis are close to those of the uncontracted basis at the Dirac-Fock level. However, the contracted basis sets sometimes give rise to large values of the T_1 diagnostic, indicating instability of the coupled-cluster calculations. Hence, we used primitive Gaussian basis sets in the present paper. The sizes of the basis sets are as follows: DZ for Yb: $(24s19p13d8f1g)$, TZ for Yb: $(30s24p18d14f3g2h)$, and QZ for Yb: $(35s30p19d13f5g3h2i)$ and for F: $(13s10i4d3f)$. The total numbers of basis set orbitals for DZ, TZ, and QZ were 270, 423, and 499, respectively. We used a cutoff value of 80 a.u. for the energies of the virtual molecular spinors in our CCSD calculations.

The QZ basis is the most accurate among the ones considered, and its accuracy has been confirmed by Gomes *et al.* [22] The bond length and harmonic frequency they obtained with the QZ basis were 2.0196 Å and 503.2 cm^{-1}, respectively. These results are very close to the experimental values 2.0161 Å and 506.6674 cm^{-1} [26] and are close to the extrapolated values 2.0174 Å and 507.6 cm^{-1}, obtained from the results of DZ, TZ, and QZ basis sets.

We modified and combined two of the most widely used relativistic codes REL4D in UTCHEM [27] and DIRAC08 [28] for our calculations. We used UTCHEM for the generation of the Dirac-Fock orbitals and the molecular orbital (MO) integral transformations [29]. We developed a suitable computational algorithm in UTCHEM to evaluate one-electron integrals of the effective EDM Hamiltonian used in Eq. (5). We used the C$_8$ double group symmetry, which is available in UTCHEM [30] but not in DIRAC08. The adaptation of the C$_8$ point group drastically reduces the computational costs for both the MO transformation and the RCCSD calculations. Using the MO integrals, the DIRAC08 code was used to obtain the RCCSD amplitudes. In the present paper, the expectation value of a normal ordered operator was calculated by considering only the linear terms in the coupled-cluster wave function as they make the most important contributions. We therefore express the expectation value as

$$\langle \psi_{\text{DF}} | (1 + T_1^+ + T_2^+) \hat{O}_N (1 + \hat{T}_1 + \hat{T}_2) | \psi_{\text{DF}} \rangle_C, \quad (8)$$

where the subscript C in Eq. (8) indicates that we calculate all the fully contracted terms. E_{eff} and the molecular electric dipole moment (DM) were calculated using Eq. (8), where $\hat{T}_1$ and $\hat{T}_2$ amplitudes were determined from the CCSD amplitude equations, as mentioned earlier. In the framework of coupled-cluster theory, the normal CC method [31] and its variant the λ-CC method [32] are two of the widely used approaches to calculate expectation values. These methods require substantially more computational time than the CC method used in the present paper. In addition, our approach captures the dominant correlation effects.

We performed three different RCCSD calculations to investigate the importance of core-correlation effects. They

TABLE I. Summary of the calculated results of the present paper.

Basis set type	Method	Total energy (a.u.)	T_1 diagnostic	E_{eff} (GV/cm)	DM[a]	$A_\parallel$ (MHz)
DZ	DF	−14167.289602		17.9	3.21	
TZ	DF	−14167.321791		18.2	3.21	
QZ	DF	−14167.323266		18.2	3.21	6239
DZ	49e-CCSD(197)	−14169.344299	0.0432	21.4	3.37	
TZ	49e-CCSD(255)	−14169.899971	0.0588	21.1	3.46	
QZ	49e-CCSD(293)	−14170.080575	0.0397	22.7	3.59	
QZ	49e-CCSD(303)	−14170.026999	0.0339	22.8	3.59	
QZ	69e-CCSD(293)	−14170.501826	0.0334	23.1	3.60	
QZ	79e-CCSD(293)	−14170.522807	0.0311	23.1	3.60	7913
Expt.					3.91(4)[b]	7424(81)[c]

[a]The direction of the dipole moment is taken as the molecular axis from the fluorine to the ytterbium atom.

[b]Reference [26].

[c]Reference [33].

are referred to as 49e-CCSD, 69e-CCSD, and 79e-CCSD. In the first case, 49 electrons were excited, that is, the $3s$, $3p$, $3d$, $2s$, $2p$, and $1s$ orbitals of Yb and the $1s$ orbital of F were frozen. In the second case, 69 electrons of YbF were excited, that is, the $2s$, $2p$, and $1s$ orbitals of Yb were frozen. In the last case, all 79 electrons of YbF were excited. We performed only a single geometry calculation with the experimental value of a bond length of 2.0161 Å.

III. RESULTS AND DISCUSSION

Table I summarizes our calculated results. At the Dirac-Fock level, the values of E_{eff} and the DM for the three basis sets are very close. However, there is a basis set dependence in the 49e-CCSD calculation. For the TZ basis set, we obtained a relatively large value for the T_1 diagnostic (0.0558), which indicates instability of the single-reference calculations with the TZ basis. Gomes *et al.* also encountered the same problem at the TZ basis and discussed its influence on the spectroscopic constants [22]. In our QZ basis calculation, the T_1 diagnostic is lower (0.0397) than that for the TZ basis. Therefore, it is reasonable to assume that our QZ basis calculations provide reliable results for E_{eff} and the DM. The change in the values of the DM for our three CCSD and QZ (49e-CCSD, 69e-CCSD, and 79e-CCSD) calculations was virtually negligible. However, the corresponding change in the case of E_{eff} was significantly larger, especially in between the 49e-CCSD and the 69e-CCSD levels. The values of E_{eff} and the DM of 69e-CCSD are the same as those of 79e-CCSD to three significant figures, indicating that the results of 69e-CCSD are saturated. We also compared two types of space of the virtual orbitals (293 and 303) in the QZ and 49e-CCSD calculations. The

TABLE II. Contributions of the nine combination terms for E_{eff} at the level of 79e-CCSD.

	DF	S	D
DF	18.16	3.14	0.00
S	3.14	−1.31	0.09
D	0.00	0.09	−0.17

extension of the virtual orbital space produces a very small change in the value of E_{eff}.

In addition, we have calculated the DF and the individual correlation contributions to the E_{eff} for 79e-CCSD. In the calculation of the expectation values shown in Eq. (8), the bra state can be expanded as DF, the singly excited (S) or doubly excited (D) determinants, and the ket state can be similarly expanded as DF, S, or D. We decomposed the value of E_{eff} at the level of 79e-CCSD (23.1 GV/cm) in terms of nine contributions, which are listed in Table II. The dominant contribution comes from the DF-DF term (i.e., the value of E_{eff} at the DF level). The S-DF and DF-S terms are the most important correlation contributions.

To summarize our best result was 23.1 GV/cm for E_{eff} and 3.60 D for the DM obtained from the fully core-correlated calculations with the QZ basis set. The calculated value of the DM was within 8% of the measured value of this quantity [3.91(4) D]. Both the E_{eff} and the DM depend on the mixing of orbitals of opposite parities. Another important property that bears some resemblance to E_{eff} is the hyperfine coupling constant (HFCC). Both these quantities are sensitive to the behavior of the wave function in the region of the nucleus. We calculated the parallel component of the HFCC ($A_\parallel$) based on Quiney's formulation [16]. $A_\parallel$ was obtained as 6239 and 7913 MHz at the DF and QZ and 79e-CCSD and QZ levels, respectively. The corresponding experimental values are 7822(5) MHz by Van Zee *et al.* in 1978 [33] and 7424(81) MHz by Steimle *et al.* in 2007 [34]. Thus, our best calculation of $A_\parallel$ is within 7% of the latest experimental value.

E_{eff} in YbF has been previously calculated by different methods. They are summarized in Table III. The earliest paper by Titov *et al.* in 1996 [13] was based on the RASSCF method with the GRECP. They obtained $E_{\mathrm{eff}} = 18.8$ GV/cm. This result was later improved to 24.9 GV/cm with an effective operator for core polarization by Mosyagin *et al.* in 1998 [14]. Another study by Kozlov in 1997 [12] based on a semiempirical method calculated $E_{\mathrm{eff}} = 26.1$ GV/cm. A comparison with the four-component relativistic methods is necessary to assess the accuracy of the above-mentioned approximations.

In the framework of the four-component Dirac relativistic method, Parpia [15] calculated $E_{\mathrm{eff}} = 19.9$ GV/cm from the

TABLE III. Calculated values of E_{eff}, HFCC ($A_\parallel$), and DM in the previous and present papers.

Method	Reference	E_{eff} (GV/cm)	HFCC ($A_\parallel$) (MHz)	DM (D)
Semiempirical	Kozlov [12]	26.1		
GRECP-RASSCF[a]	Titov *et al.* [13]	18.8	4975	
GRECP-RASSCF effective operator	Mosyagin *et al.* [14]	24.9	8000	
UDF[b] unpaired	Parpia [15]	19.9		
UDF all	Parpia [15]	24.9		4.00
MBPT(DF + core polarization)	Quiney *et al.* [16]	24.8	7985	
DF	Nayak and Chaudhuri [17]	19.9		3.98
RASCI[c]	Nayak and Chaudhuri [17]	22.5		3.90
RASCI	Nayak and Chaudhuri [17]	24.1		
DF and QZ	Present paper	18.2	6239	3.21
79e-CCSD and QZ	Present paper	23.1	7913	3.60
Experiment	[26,33]		7424(81)	3.91(4)

[a]GRECP-RASSCF represents the generalized relativistic effective core potential-restricted-active-space self-consistent field.
[b]Unrestricted Dirac Fock (UDF).
[c]RASCI represents restricted-active-space configuration interaction.

unpaired spinor and 24.9 GV/cm from all the occupied spinors at the unrestricted DF level in 1998. In the same year, Quiney *et al.* [16] calculated E_{eff} = 24.8 GV/cm at the restricted DF level with the first-order core polarization included by MBPT. In 2006 and 2009, Nayak and Chaudhuri [17] accounted for electron correlation in E_{eff} using the RASCI method at the four-component level. Their best result was E_{eff} = 24.1 GV/cm from a 31-electron correlated calculation in a space of 76 active orbitals. This active space is not sufficiently large. Our relativistic CCSD calculation has the following advantages over the relativistic CI approach used by Nayak and Chaudhuri [17]. (i) CCSD is size extensive unlike the approximate CI used in the latter paper. (ii) The size of our QZ basis is substantially larger than that used in Ref. [17]. (iii) We included all the core-correlation effects, while only 31 electrons were excited in the CI calculation. (iv) The number of spinors in our virtual space (293 orbitals) is also much larger than in Ref. [17] (60 orbitals).

Electron correlation increased the value of E_{eff} by about 20% in our paper. This trend is similar to the previous correlation calculations, especially where core-polarization effects were included.

IV. CONCLUSION

In conclusion, our most accurate calculation of the effective field gives E_{eff} = 23.1 GV/cm. This leads to an increase in the value of the upper limit of the electron EDM (11.8×10^{-28} e cm) compared to the earlier result (10.5×10^{-28} e cm) for YbF. Taking into consideration the omitted higher-order correlation effects and the deviations of our DM and HFCC results from their measured values, we estimate an error of 5%–8% in our calculation of E_{eff}. In principle, the method that we used can be applied to any lowest-energy state that can be described by a single-reference determinant in a given irreducible representation. In the future, we will apply the method to some of the molecular candidates that have been proposed in the context of the search for the electron EDM.

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