Enhancement of the electron electric dipole moment in Eu²⁺

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(Received 26 March 2011; published 9 August 2011)

Recently, the ferroelectric $Eu_{0.5}Ba_{0.5}TiO_3$ was suggested for experimental searches of the electron electric dipole moment. To analyze results of the experiment and interpret them in terms of fundamental constants, the effective electric field $E_{\rm eff}$ acting on unpaired electrons of the europium cation should be calculated. In the present paper we consider Eu^{2+} cation in the uniform external electric field $E_{\rm ext}$ as the first step and important starting point toward the calculation of $E_{\rm eff}$ in the real solid. We have performed high-level electronic structure correlation calculations using the coupled clusters theory compared to other approaches. The calculated value of the field enhancement coefficient is $K = E_{\rm eff}/E_{\rm ext} = -4.6$.

I. INTRODUCTION

During past decades, significant experimental and theoretical efforts have been undertaken to measure the electric dipole moment of the electron (*e*EDM or d_e below). *e*EDM is of fundamental importance for theories of P,T-odd interactions because its existence violates both space parity (P) and time reversal (T) symmetries [1,2]. The standard model prediction for the *e*EDM is of the order of $10^{-38} e \cdot$ cm or even less, but most other modern theoretical models predict much higher values, at the level of $10^{-27} - 10^{-29} e \cdot$ cm [2]. The latest experimental upper bound on the *e*EDM obtained in measurements with atomic Tl beam [3] is $1.6 \times 10^{-27} e \cdot$ cm. However, recently, the new limit (which is 1.5 times smaller) was obtained in a YbF beam experiment [4]. Therefore, an improvement of experimental sensitivity for *e*EDM by one–two orders of magnitude will dramatically influence a number of models, suggesting "new physics" beyond the standard model; see also Refs. [5,6] and references therein.

Presently, there are several experimental groups that are using molecules with heavy atoms to search for *e*EDM. They include experiments with neutral molecules, e.g., a beam experiment with YbF radicals carried on by Hinds and coworkers [4]. A vapor cell experiment on the metastable $a(1)$ state of PbO is under way by the DeMille group (see Refs. [7,8] and references therein). A Stark-trap experiment with PbF radicals was prepared by Shafer-Ray [9,10]. Beam experiments are prepared on the metastable $^3\Delta_1$ state of ThO* [11] and the ground $^3\Delta_1$ state of WC [12]. In another type of experiment suggested by Cornell and coworkers, trapped cold molecular cations are planned to be used. Up to now, several cations were considered, including HI⁺, HfF⁺, PtH⁺, ThF⁺, etc. (see Ref. [13] and references therein).

The suggestion to use solids for EDM searches was proposed by Shapiro many years ago [14]. However, only during the past decade searches for *e*EDM in solids have become attractive due to the suggestions of Lamoreaux [15] and Hunter [16] to use GdGaO and GdFeO. Recently, a new kind of solid-state experiment was proposed with the

$Eu_{0.5}Ba_{0.5}TiO_3$ (EBTO) crystal [17]. This compound is a ferroelectric, and the idea of the proposal is to utilize the displacement of the paramagnetic Eu atoms with respect to the skeleton of the nearest oxygen atoms. Magnetically, EBTO is similar to GdGaO, Eu ions have seven unpaired spin-aligned $4f$ electrons, and the compound is a paramagnet above 2K. Quantum chemistry calculations [18] confirm that the ferroelectric displacement in EBTO is quite significant and hence the electric field acting on the europium-in-EBTO can be very large. To extract value of d_e from measurements [17], it is necessary to know the value of the effective electric field, acting on the unpaired electrons of Eu in EBTO, though the "conventional *e*EDM semantics" are not quite satisfactory here. It is more correct to talk about the linear Stark effect for the *e*EDM in the EBTO experiment (the effective electric field is then defined as the Stark shift divided by d_e).

In the present paper, we consider a prototype of europium-in-EBTO that is simulated by a solitary Eu^{2+} cation in an external homogeneous electric field $E_{\rm ext}$, which is a good model for the outlined problem according to our preliminary studies of EBTO. So, in essence, we calculate the *permanent* electric dipole moment of Eu^{2+} cation [2] in "*e*EDM units" (since it is induced by *e*EDMs of its electrons) that can be presented as $d_{Eu^{2+}} = K d_e$, where K is the EDM enhancement coefficient. As can see from discussion of the results, a reliable calculation of K in Eu^{2+} is a quite involved many-body problem.

II. METHODS

When an atom (ion) with unpaired electrons is placed in an external electric field $E_{\rm ext}$, the resulting effective field $E_{\rm eff}$ acting on an unpaired electron is proportional to the applied field $E_{\rm ext}$ with the EDM enhancement coefficient K introduced above in the case of weak $E_{\rm ext}$, which is accessible in laboratory conditions:

$$E_{\rm eff} = K E_{\rm ext}.$$

Sandars pointed out a long time ago that P,T-odd effects can be strongly enhanced in heavy atoms due to relativistic effects [20]. A very useful semiempirical expression for $K \sim \alpha^2 Z^3$ was proposed in Ref. [21]. The expression works well for s and p electrons, though it is questionable for f electrons. The

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effective field E_{eff} is defined by the following formula; see, e.g., Refs. [22–24]:

$$E_{\text{eff}} = \langle \Psi | \sum_i H_d(i) | \Psi \rangle, \tag{1}$$

$$H_d(i) = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma_i} \boldsymbol{E}(\mathbf{r_i}) \end{pmatrix}, \tag{2}$$

where Ψ is the wave function of the atom (ion) in the external electric field E_{ext}; $\boldsymbol{E}(\mathbf{r}_i)$ is the total electric field that includes the external field, the field produced by electrons, and the field produced by the nucleus. Since the europium ion is much heavier than the electron we can consider that Schiff theorem still holds. The wavefunction Ψ must take into account the most part of relativistic and relevant correlation effects for valence (and sometimes for outer-core) electrons. The valence electrons are most affected (polarized) by the applied electric field, and hence they dramatically influence E_{eff}. The contribution from the inner-core electrons is usually negligible. These circumstances allow us to use the two-step technique, advanced by our group [24–28] and recently applied for calculation of E_{eff} in molecular systems [29,30].

At the first step, we exclude inactive inner-core orbitals from the correlation calculation using the very accurate generalized relativistic effective core potential method (GRECP) [31–33]. The exclusion reduces the computational work at the first step. In addition, the valence orbitals are smoothed inside the core and this smoothing allows one to reduce the number of primitive Gaussian basis functions required for appropriate description of valence electrons. Moreover, instead of the four-component calculation with Dirac bispinors one can perform two- or one-component GRECP calculation (with or without spin-dependent (spin-orbit and Breit) interactions taken into account, respectively, for the explicitly treated electrons). The described procedures dramatically reduce computational time with minimal loss of accuracy when outercore electrons are treated explicitly. The particular choice of the valence and core electrons' partitioning, first of all, depends on the electronic structure of a particular system and, then, on the accuracy required. We reiterate that having in mind the same level of accuracy, the all-electron four-component calculations are much more time and resources consuming compared to the highly accurate GRECP calculations.

At the second step, when the GRECP calculation is performed (with or without account for the electron correlation), we restore the four-component valence orbitals. Thus, based on the GRECP result we find the corresponding relativistic one-electron density matrix. Using the density matrix one can easily calculate any one-electron property (such as E_{eff}, hyperfine constants, etc.) even if the corresponding operator is localized inside the atomic core. We choose the coupled-cluster (CC) method as the main instrument to account for electron correlation. The CC method has a number of advantages compared to other methods such as restricted active space SCF, configuration interaction, and many-body perturbation theory. It is worth noting that we used all these methods at the preliminary stage of this work. The advantages of the CC method are the rather quick convergence of results with increasing the excitation level and the well suppressed spin

contamination (this is especially important for Eu^{2+} with seven unpaired electrons localized in core region).

Finally, we stress the most important aspect of the present calculation. The operator [Eq. (2)] has nonzero matrix elements only between states of opposite parity, e.g., $s-p, p-d, f-d$, etc. Moreover, the corresponding atomic orbitals should be spin-polarized or singly occupied orbitals; otherwise, the contribution from a "spin-up" matrix element is completely compensated by the corresponding "spin-down" matrix element. The Eu^{2+} cation has the ground state electronic configuration $[..]4s^2 4p^6 4d^{10} 5s^2 5p^6 4f_\uparrow^7$. Therefore, in an external electric field, one should expect direct spatial polarization of unpaired $4f_\uparrow$ electrons into unoccupied low-lying $5d$ states, first of all. This mixing does not lead to a large value of the enhancement coefficient K because $4f$ and $5d$ states have very small amplitudes in the vicinity of the Eu nucleus, where the operator [Eq. (2)] is large due to the electric field of the Eu nucleus. The value of K is significantly larger (few orders of magnitude) in the case of the $s-p$ mixing. The $s-p$ mixing determines the effect in heavy alkali metals, such as cesium with $[Xe]6s^1$ configuration, or in p^1-elements like thallium with $[Hg]6p^1$ configuration. The same $s-p$ mixing determines the effect in a number of molecules such as HfF^+ in the $^3\Delta_1$ state, where the mixing is very large due to the specific internal structure of the polar molecule. The ion Eu^{2+} has no unpaired electrons in s and p states and hence a contribution to K from these states may occur only due to the spin-polarized mixing of these states at least in the first order of perturbation theory [34] by the Coulomb exchange interaction (together with mandatory first-order perturbations on the external field and interaction [Eq. (2)], which are both considered as extremely weak). However, as is shown in the present paper, the higher PT orders by the Coulomb exchange interaction are not less important. Thus, though the $s-p$ matrix elements of the operator [Eq. (2)] are large, the coefficients in front of these elements in the case of Eu^{2+} are small and strongly depend on electron correlation. As a result, the cumulative contribution to K from the $s-p$ matrix elements can be comparable with and even higher than the lowest order $4f-5d$ terms. This is why an accurate account of the correlations is very important; see, e.g., Ref. [35] as an example of strong influence of correlation effects. Due to this reason, the present calculation of K for Eu^{2+} is much more complicated compared to similar calculations for atoms and molecules where the $s-p$ mixing gives the leading effect. Our estimates show that the spin-orbit effects being taken into account at the first step (GRECP stage, see above) only weakly influence contributions of correlations to E_{eff}. In view of this, it is more important to account for higher order correlations without spin-orbit interaction than to account everything but in the lower order. Therefore, considering correlations, we do not account for the spin-orbit interactions in the present study at the GRECP stage for the explicitly treated electrons, whereas, certainly, we take the most important part of the spin-orbit effects into account for all the electrons at the restoration stage (second step) having non-negligible contributions in the vicinity of the Eu nucleus, thus correcting the behavior of one-electron functions in this region.

TABLE I. K values calculated using the CCSD method with different basis sets. ns, np, nd, nf, and ng are the numbers of s-, p-, d-, f-, and g-contracted Gaussian functions included in the corresponding basis set.

ns	np	nd	nf	ng	K(CCSD)
2	2	4	3	0	−0.9
3	3	4	3	0	1.3
4	5	4	3	0	2.3
4	5	5	4	0	2.2
4	5	5	4	2	2.2
5	6	5	4	2	0.1
6	6	5	4	0	−1.3
6	6	4	3	0	−1.2
6	7	4	3	0	−3.0[*]
6	7	5	4	0	−3.1[**]
6	7	5	4	2	−2.8
14	14	5	4	0	−4.1(Lbas)
20	20	5	4	0	−4.1
14	14	12	4	0	−4.4

III. COMPUTATIONAL DETAILS

For Eu^{2+} cation, the 28 core electron GRECP ($1s − 3d$ electrons in the core) was generated and used for subsequent correlation calculations. In order to check if the calculated value for K is reliable, we have performed a detailed analysis of the computation procedure used. This includes a test of the basis set completeness, required level of account of correlation, etc. The tests are described below. To perform correlation calculations we used the MRCC [36,37] and CFOUR [38] codes. To perform density functional theory (DFT) calculations we used the US-GAMESS program package [39].

A. Basis set generation

For the Eu^{2+} cation, the contracted correlation scheme of the basis set generation from Refs. [31–33] was used. The generated basis set includes six s-type, seven p-type, five d-type, four f-type, and two g-type generally contracted Gaussian functions. To check the merit of the generated basis set for evaluating E_{eff} a series of coupled clusters calculations with single and double amplitudes (CCSD) have been performed with increasing step by step the number of basis functions. The results are given in Table I.

One can see from Table I that K in the Eu^{2+} ion strongly depends on the number of basis functions. Even the latest added sixth and seventh contracted correlation functions give significant contributions to K. It is clear from the comparison of (*) and (**) lines that for the d-type and the f-type functions, one can keep only 4 and 3 functions, respectively. The inclusion of the g-type functions in the calculation gives a negligible contribution to K. This is understandable in the context of the $f−d$ mixing discussed above. Therefore, the g functions can be completely excluded from the basis set.

Due to the high sensitivity of K to s and p functions we have performed calculations with uncontracted s and p functions (14 s- and 14 p-primitive Gaussians). To check if the basis set is large enough to evaluate K calculations with 20 s- and 20 p-functions have also been performed. The value of K has

TABLE II. The K values calculated with different correlation methods using UHF and ROHF references. Mean values of the spin-squared operator $\langle S^2 \rangle$ are given in brackets. The "clean" value is $\langle S^2 \rangle = 15.75$.

reference method	K	
	UHF [$\langle S^2 \rangle$]	ROHF [$\langle S^2 \rangle$]
CCSD	−4.1 [15.75033]	−4.6 [15.75026]
CCSDT	−4.6 [15.75000]	−4.6 [15.75000]
MP2	−4.4	−3.6
MP3	−2.5	−2.7
MP4	−5.5	—

not been changed in these calculations. Additional uncontracting d orbitals (12 primitive d-type Gaussian functions) change the value of K by only ∼7%.

The computational time and resources for correlation studies, such as CC with single, double, and triple amplitudes (CCSDT), strongly depend on the number of basis functions. Therefore we choose the basis set, which contains 14 primitive s-Gaussians, 14 primitive p-Gaussians, 5 contracted d-Gaussians, and 4 contracted f-Gaussians. The set gives the "converged" value of K. Below we shall refer to this basis set as to LBas.

B. Optimal external field strength

To compute the enhancement factor K, we naturally limit ourselves by the case of the linear dependence of E_{eff} on the applied field E_{ext}. Hence, the following two circumstances have to be satisfied: (i) the field must be strong enough to reduce influence of computational errors (round-up, etc.) on K; (ii) the field must be weak enough to prevent significant perturbations of the electronic structure (the physical external field is very small in practice and only first-order perturbations of wave functions, linear on E_{ext}, should be taken into account).

We performed a series of the CCSD calculations and found that the linearity is provided in the wide range $E_{ext} = 10^{-6} − 10^{-1}$ a.u. Hence, we have chosen $E_{ext} = 0.001$ a.u. for further calculations.

C. Choosing the correlation method

It is well known that methods based on the unrestricted Hartree-Fock (UHF) reference are not free from the spin contamination problem. To analyze the problem, we performed coupled cluster calculations with the restricted open-shell Hartree-Fock (ROHF) reference. In this case, the spin contamination is excluded at the level of the reference. However, the contamination can arise at the coupled cluster treatment stage due to features of the used codes. Table II gives values of K calculated at different levels of the correlation treatment.

One can see from this table that the account for the iterative triple amplitudes within the UHF-CCSDT method increases the value of K by less than 15% as compared to K, calculated at the UHF-CCSD level. ROHF-based CC methods give

TABLE III. Pair contributions to K calculated at the CCSDT level.

	s	p	d	f
s	0	-3.3	0	0
p		0	$+0.3$	0
d			0	-1.6
f				0

$K = -4.6$ already at the CCSD level and an inclusion of the triples does not change the K value.[1]

From the mean values of the spin-squared operator, one can see that the spin-contamination problem is not dramatic already at the CCSD level and it is negligible at the CCSDT level. All these facts indicate that our ultimate value for K, -4.6, is reliable.

Table II also illustrates why we have chosen the coupled cluster method. The Møller-Plesset (MP) perturbation theory is not converged for K, even at the fourth order. *On the other hand, this demonstrates that the enhancement factor K is determined by high-orders of perturbation theory in the residual Coulomb interaction between electrons.*

From the above analysis, we conclude that the use of the CCSDT method is sufficient for the reliable calculation of K. Our final value of the enhancement coefficient is $K = -4.6$.

IV. ANALYSIS OF CONTRIBUTIONS TO K

It was mentioned above that one of the stages in calculating K is the evaluation of the spin-density matrix at the CCSDT level. Therefore, we can estimate contributions of particular basis functions by considering the corresponding matrix elements of the spin-density matrix and setting all other elements to zero. The contributions estimated in this way are presented in Table III. From this table, one concludes that the main (cumulative) contribution to K comes from the $s-p$ mixing. The next important contribution (which is twice smaller) is due to the $f-d$ mixing. The contribution from the $p-d$ mixing is almost negligible.

It is instructive to estimate contributions to K from the individual (outer-core and valence) ns,np shells. Qualitatively, the spin exchange of a given $ns_{\uparrow}$ and $np_{\uparrow}$ orbital with $(4f_{\uparrow})^7$, leads to the spin-polarization of the ns,np shells, below referred to as the spin-exchange polarization (SEP), and hence leads to a nonzero contribution to K. The contribution roughly depends on the following two factors: (i) their spatial localization relative to the $4f$ shell; (ii) the energy difference between the ns (np) shell and the open $4f$-shell. From Table IV, one can see that $4s$ and $4p$ orbitals are localized essentially in the same region as $4f$ orbitals, at the same time last maxima of $5s$ and $5p$ orbitals are at somewhat larger distances (the factor is 1.5 times larger). On the other hand,

TABLE IV. The average radius, $\langle r \rangle$, the last maximum position, $r_{\max}$, and the energy of the orbital, $\varepsilon_{\mathrm{orb}}$. The values are averaged over the spin-orbit splitting.

orbital	$\langle r \rangle$ (a.u.)	$r_{\max}$ (a.u.)	$\varepsilon_{\mathrm{orb}}$ (a.u.)
$3s$	0.2	0.3	-68.0
$3p$	0.2	0.3	-57.7
$3d$	0.2	0.3	-43.6
$4s$	0.6	0.5	-15.1
$4p$	0.6	0.5	-11.5
$4d$	0.7	0.6	-6.5
$4f$	0.9	0.6	-1.0
$5s$	1.4	1.3	-2.6
$5p$	1.6	1.4	-1.6

$5s,5p$ energy denominators are much smaller than those for $4s$ and $4p$. The spatial $s-p$, $p-d$ polarization, etc., due to the E_{ext}, below referred to as the external field polarization (EFP), should be notably stronger for the $5s$ and $5p$ orbitals, whereas matrix elements of Eq. (2) are smaller for these orbitals. Therefore, both $5s,5p$ and $4s,4p$ shells have to be included in the calculation. Their relative importance can be caught only in the calculation with accurate account of electronic correlations. At the same time, $3s$ and $3p$ orbitals (and those with "lower" n) have essentially different spatial localization and too large energy denominator ~ 60 a.u. Therefore, these shells can be safely neglected (taking into account possible accuracy).

In order to estimate contributions from different shells, we have performed a series of calculations at the CCSDT level with the ROHF reference calculated with zero external electric field. In these calculations we have frozen different orbitals; i.e., we have forbidden their SEP and EFP contributions. For every calculation, we have also decomposed K into contributions coming from the $s-p$ (K_{s-p}), $p-d$ (K_{p-d}), and $f-d$ (K_{f-d}) mixings.

In Ref. [34], Gd^{3+} ion electronically equivalent to Eu^{2+} was studied within the scheme of the $s-p$ mixing with excitations to unoccupied d states. To analyze importance of other possible correlation schemes of the $s-p$ mixing in Eu^{2+}, we have performed calculations in two basis sets: (i) our standard basis set Lbas (which has been used for previous calculations), (ii) the Lbas_nvd basis set, which was derived from Lbas by keeping all s, p, f functions and preserving only one contracted $4d$ function taken from ROHF (all other d functions are excluded). This means that there are no virtual d orbitals in the Hartree-Fock calculation within the Lbas_nvd basis (addition "nvd" means "No Virtual d"). Results of the these calculations are given in Table V.

We shall stress several conclusions that follow from this table:

(i) The K_{s-p} contribution from SEP and EFP of the $5s$ and $5p$ orbitals.

We have frozen the $4s,4p,4d$, and $5p$ orbitals in order to extract some "clean" contribution from polarization of the $5s$ shell. Thus, only the $5s$ and $4f$ occupied shells were included in the correlation CC calculation (see line 3 in the table). The K_{s-p} value for this case in Lbas is $+1.2$. The case with the

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[1]To check the stability of ROHF-CCSD, we have also performed "unrelaxed" ROHF-CCSD calculation, i.e., with the ROHF-reference taken from zero E_{ext} field calculation. This has resulted in 23% divergence of K from the -4.6 value. However, the unrelaxed ROHF-CCSDT calculation (see the next section) gives the same K value as the relaxed UHF-CCSDT and ROHF-CCSDT.

TABLE V. The K values and their different components calculated within the ROHF-CCSDT method (The ROHF-reference is taken from the zero E_{ext} field calculation to prevent the EFP contribution from frozen orbitals).

#	Active orbitals	Frozen orbitals	Lbas				Lbas_nvd			
			K	K_{s-p}	K_{p-d}	K_{f-d}	K	K_{s-p}	K_{p-d}	K_{f-d}
1	all	—	−4.7	−3.4	0.3	−1.7	1.6	1.8	0.0	−0.3
2	$4f$ only	$4s4p4d5s5p$	−1.8	0.0	0.0	−1.8	0.0	0.0	0.0	0.0
3	$5s,4f$	$4s4p4d\_5p$	−0.6	1.2	0.0	−1.8	0.8	0.8	0.0	0.0
4	$5p,4f$	$4s4p4d5s\_$	−1.3	−0.9	0.8	−1.2	2.1	2.1	0.0	0.0
5	$5s\&5p,4f$	$4s4p4d\_\_$	−0.3	0.2	0.8	−1.3	2.0	2.0	0.0	0.0
6	$4d\&5s\&5p,4f$	$4s4p\_\_\_$	−1.9	−0.8	0.6	−1.7	1.3	1.5	0.0	−0.3
7	$4s,4f$	$\_4p4d5s5p$	−3.7	−1.9	0.0	−1.8	0.0	0.0	0.0	0.0
8	$4p,4f$	$4s\_4d5s5p$	−3.2	−1.1	−0.3	−1.8	0.1	0.1	0.0	0.0
9	$4s\&4p,4f$	$\_\_4d5s5p$	−5.4	−3.3	−0.3	−1.8	0.1	0.1	0.0	0.0
10	4s&4p&4d, 4f	$\_\_\_5s5p$	−6.8	−3.8	−0.7	−2.2	−0.1	0.1	0.0	−0.2
11	$4s\&4p\&5s\&5p,4f$	$\_\_4d\_\_$	−2.5	−1.9	0.6	−1.3	2.3	2.3	0.0	0.0
12	$4d,4f$	$4s4p\_5s5p$	−2.7	0.0	−0.4	−2.2	−0.2	0.0	0.0	−0.2

excluded virtual d basis functions (using Lbas_nvd basis) gives $K_{s-p} = +0.8$.

The "clean" SEP contribution of the $5p$ orbitals to K_{s-p} is $−0.9$ (that includes the intermediate virtual s, p, and d functions, see line 4). Note that the nvd mechanism gives $K_{s-p} = +2.1$. Both the SEP contributions of the $5s$ and $5p$ orbitals give significant contributions; however, these terms have opposite signs and the simultaneous correlation of the $5s$ and $5p$ orbitals (see line 5 of the table) results in almost negligible K_{s-p} value, $+0.2$ [note that the sum of the partial 5s ($+1.2$) and 5p ($−0.9$) contributions is $+0.3$, therefore, they are practically additive]. It should be noted that the nvd mechanism gives $K_{s-p} = +2.0$; therefore, it looks as if there is almost exact compensation between the contributions from the intermediate virtual s, p and virtual d states. Additional inclusion of the $4d$ orbitals in the correlation calculation (line 6) leads to a decrease of K_{s-p} by 1.0.

(ii) The SEP contribution to K_{s-p} from the $4s$ and $4p$ electrons.

One can see from lines 7, 8, and 9 that the individual SEP contributions to K_{s-p} from the $4s$ and $4p$ orbitals are slightly higher (by absolute value) than the corresponding $5s$ and $5p$ contributions, and, in turn, they have the same signs, which leads to a large final K_{s-p}; also, both SEP contributions from the $4s$ and $4p$ shells are mainly due to the "virtual d" mechanism and they are also almost additive. Additional inclusion of the $4d$ orbitals in the correlation calculation (line 10) leads to a decrease of K_{s-p} by 0.5. At last, these are the SEP terms from the $4s$ and $4p$ states that give the *leading* contribution to the final K_{s-p} and total K values.

(iii) The simultaneous correlation of the $4s$, $4p$, $5s$, $5p$ (and, of course, $4f$) orbitals (line 11) leads to some decrease of K_{s-p} by absolute value with respect to the sum of the $4s$, $4p$ and $5s$, $5p$ contributions. Here, we have new types of "interfering SEP contributions," e.g., between $4s$ and $5p$, $4p$ and $5s$, etc. Additional inclusion of the $4d$ orbitals into the correlation calculation (line 1) leads to a further decrease of the K_{s-p} value by 1.5.

(iv) K_{f-d} notably depends on the $5p$ orbital (compare lines 2 and 4). One can expect that this is mainly due to the $5p−5d$

EFP terms (together with the SEP terms of the 4f electrons to the intermediate virtual d states) that decrease the direct (lowest order) $4f−5d$ EFP contributions.

(v) The SEP contributions of the $5p$ orbital to the virtual d ones (lines 2, 4) and of the $4d$ orbital to the virtual p ones (lines 2, 12) have the opposite signs (and small magnitudes), which (together with the $4p$ to virtual d SEP term, see lines 2 and 8) result in a negligible final value of K_{p-d} (line 1).

One important note should be made for the K_{f-d} contribution. The amplitude of the f function is very small at the core region of Eu^{2+}. Therefore, it is important to take into account the electric field screening effect from the core shells. We have obtained that neglecting these screening effects leads to 25% overestimation of the K_{f-d} contribution. Also, is should be noted that all the core shells give screening effects, i.e., not only $1s$ but $2s−3d$ shells also give essential contributions to the screening.

It is clear from Table V that mechanisms of forming the final enhancement factor value K are very complicated, and one should consider many orders of the perturbation theory by interelectronic Coulomb interaction (as expected from the qualitative discussion in the "Methods" section). It was stressed above that the coupled cluster method, that we have chosen for our calculation, sums up to (formally) infinite order the most important diagrams of the perturbation theory (in practice, the maximum order of PT corresponds to the number of iterations). This is the only method that allowed us to attain the convergent results for such a complicated problem as evaluating K in Eu^{2+} and, as one can suggest, in other lanthanides.

V. DENSITY FUNCTIONAL AND MØLLER-PLESSET ESTIMATES

As was mentioned above, this paper is the first one in our studies of E_{eff} on Eu^{2+} to describe the effective state of Eu in the crystal $Eu_{0.5}Ba_{0.5}TiO_3$ as our final goal. Since one cannot use such methods as coupled clusters in solid-state calculations, we have calculated K using the Møller-Plesset perturbation theory (see Table II above) and density functional

TABLE VI. The calculated K values using popular exchange-correlation functionals.

Functional	K
PBE [40]	-3.7
TPSS [41]	-3.8
B3LYP [42]	-2.9
PBE0 [43]	-2.7

theory with different popular exchange-correlation functionals including generalized gradient functional by Perdew, Burke and Ernzerhof (PBE) [40], meta-generalized gradient functional by Tao, Perdew, Staroverov and Scuseria (TPSS) [41], hybrid 3-parameter by Becke, Lee, Yang and Parr functional B3LYP [42] and hybrid PBE0 functional by Adamo and Barone [43]. Although the second order Møller-Plesset perturbation theory with the UHF-reference is in a good agreement with our final value of K (and even the individual $s-p$, $p-d$, and $f-d$ contributions are practically the same) for the system under consideration, we cannot consider the UHF-MP2 values as reliable enough because the ROHF-based MP2, as well as the UHF- and ROHF-based MP3 and MP4 values are seriously different from the former, demonstrating divergence of the MP series. Thus, one can try to use the MP2 method (mainly for many-atomic systems) but with great caution.

Unfortunately, there are no reliable theoretical criteria to choose the most appropriate DFT exchange-correlation functional version for a problem of the considered type because it is impossible to perform a series of successive DFT calculations with consistent increase of the level of accuracy of theory to achieve convergence as it can be done, at least formally, in the framework of the explicitly correlated *ab initio* methods (see above). Therefore, the only way to choose a density functional is to "calibrate" it comparing to high-level correlation calculations. We present the calculated K values using different exchange-correlation functionals in Table VI.

One should note that K_{s-p}, K_{p-d}, and K_{f-d} have the same weights as in the case of CCSDT.

VI. CONCLUSION

The Eu^{2+} cation in an external electric field has been considered as the first important model that simulates the effective state of europium in our studies of the EBTO crystal properties. The calculated enhancement factor is $K = -4.6$. The uncertainty of this value in the framework of the used approximations can be estimated from uncertainties of the employed correlation method, basis set incompleteness, and neglecting the spin-orbit interaction between the explicitly treated electrons just at the GRECP calculation stage. It was noted in Section III A (Basis set generation) that increasing the basis set for d functions results in increasing the K value by 7%; at the same time inclusion of g-type basis functions decreases K value by 11% (Table I). According to Table II, we have achieved convergence in the correlation method (ROHF-CCSD and ROHF-CCSDT gives the same K value). Summarizing, we estimate the current K uncertainty as 20%.

It is shown that the K value is not well determined by even the lowest four orders of the many-body perturbation theory by the Coulomb operator, so the coupled-cluster expansion for the wave function is important to attain a convergence for this value. The other exploited methods, including the multiconfigurational SCF and configuration interaction, did not allow us to attain the convergence on K in a reasonable time using the available computer resources. The main SEP and EFP contribution to K originates from the s- and p-occupied orbitals.

[1] I. B. Khriplovich and S. K. Lamoreaux, *CP Violation without Strangeness. The Electric Dipole Moments of Particles, Atoms, and Molecules* (Springer-Verlag, Berlin, 1997).

[2] E. D. Commins, Adv. At. Mol. Opt. Phys. **40**, 1 (1998).

[3] B. C. Regan, E. D. Commins, C. J. Schmidt, and D. DeMille, Phys. Rev. Lett. **88**, 071805 (2002).

[4] J. J. Hudson, D. M. Kara, I. J. Smallman, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Nature (London) **473**, 493 (2011).

[5] J. S. M. Ginges and V. V. Flambaum, Phys. Rep. **397**, 63 (2004).

[6] J. Erler and M. J. Ramsey-Musolf, Prog. Part. Nucl. Phys. **54**, 351 (2005).

[7] D. Kawall, F. Bay, S. Bickman, Y. Jiang, and D. DeMille, Phys. Rev. Lett. **92**, 133007 (2004).

[8] S. Bickman, P. Hamilton, Y. Jiang, and D. DeMille, Phys. Rev. A **80**, 023418 (2009).

[9] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A **78**, 054502(R) (2008).

[10] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A **80**, 029902(E) (2009).

[11] A. C. Vutha *et al.*, J. Phys. B **43**, 074007 (2010), [http://stacks.iop.org/0953-4075/43/i=7/a=074007].

[12] J. Lee, E. R. Meyer, R. Paudel, J. L. Bohn, and A. E. Leanhardt, J. Mod. Opt. **56**, 2005 (2009).

[13] A. E. Leanhardt, J. L. Bohn, H. Loh, P. Maletinsky, E. R. Meyer, L. C. Sinclair, R. P. Stutz, and E. A. Cornell (2010), e-print arXiv:1008.2997 [physics.atom-ph].

[14] F. L. Shapiro, Phys. Usp. **11**, 345 (1968), [http://ufn.ru/en/articles/1968/3/k/].

[15] S. K. Lamoreaux, Phys. Rev. A **66**, 022109 (2002).

[16] L. R. Hunter, talk at the workshop "Tests of Fundamental Symmetries in Atoms and Molecules," (unpublished).

[17] A. O. Sushkov, S. Eckel, and S. K. Lamoreaux, Phys. Rev. A **81**, 022104 (2010).

[18] K. Z. Rushchanskii *et al.*, Nat. Mater. **9**, 648 (2010), [http://www.nature.com/nmat/journal/v9/n8/abs/nmat2799.html].

[19] L. D. Landau, Sov. Phys. JETP **5**, 336 (1957).

[20] P. G. H. Sandars, Phys. Lett. **14**, 194 (1965).
[21] V. V. Flambaum, Yad. Fiz. **24**, 383 (1976) [Sov. J. Nucl. Phys. **24**, 199 (1976)].
[22] M. G. Kozlov, V. I. Fomichev, Yu. Yu. Dmitriev, L. N. Labzovsky, and A. V. Titov, J. Phys. B **20**, 4939 (1987).
[23] M. Kozlov and L. Labzowsky, J. Phys. B **28**, 1933 (1995).
[24] A. V. Titov, N. S. Mosyagin, A. N. Petrov, T. A. Isaev, and D. P. DeMille, Progr. Theor. Chem. Phys. B **15**, 253 (2006).
[25] A. V. Titov, Int. J. Quantum Chem. **57**, 453 (1996).
[26] N. S. Mosyagin, M. G. Kozlov, and A. V. Titov, J. Phys. B **31**, L763 (1998).
[27] A. N. Petrov, N. S. Mosyagin, T. A. Isaev, A. V. Titov, V. F. Ezhov, E. Eliav, and U. Kaldor, Phys. Rev. Lett. **88**, 073001 (2002).
[28] A. N. Petrov, A. V. Titov, T. A. Isaev, N. S. Mosyagin, and D. P. DeMille, Phys. Rev. A **72**, 022505 (2005).
[29] L. V. Skripnikov, A. N. Petrov, A. V. Titov, and N. S. Mosyagin, Phys. Rev. A **80**, 060501(R) (2009).
[30] A. N. Petrov, N. S. Mosyagin, T. A. Isaev, and A. V. Titov, Phys. Rev. A **76**, 030501(R) (2007).
[31] N. S. Mosyagin, E. Eliav, A. V. Titov, and U. Kaldor, J. Phys. B **33**, 667 (2000).
[32] T. A. Isaev, N. S. Mosyagin, M. G. Kozlov, A. V. Titov, E. Eliav, and U. Kaldor, J. Phys. B **33**, 5139 (2000).
[33] N. S. Mosyagin, A. V. Titov, E. Eliav, and U. Kaldor, J. Chem. Phys. **115**, 2007 (2001).
[34] S. Y. Buhmann, V. A. Dzuba, and O. P. Sushkov, Phys. Rev. A **66**, 042109 (2002).
[35] T. A. Isaev, N. S. Mosyagin, A. N. Petrov, and A. V. Titov, Phys. Rev. Lett. **95**, 163004 (2005).
[36] M. Kállay and P. R. Surján, J. Chem. Phys. **115**, 2945 (2001).
[37] M. Kállay, J. Gauss, and P. G. Szalay, J. Chem. Phys. **119**, 2991 (2003).
[38] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, and P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Juselius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vazquez, F. Wang, and J. D. Watts and the integral packages MOLECULE (J. Almlof and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wullen. For the current version, see [http://www.cfour.de].
[39] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).
[40] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[41] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[42] A. Becke, J. Chem. Phys. **98**, 5648 (1993).
[43] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).