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Electric dipole moment enhancement factor of thallium

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The goal of this work is to resolve the present controversy in the value of the EDM enhancement factor of Tl. We have carried out several calculations by different high-precision methods, studied previously omitted corrections, as well as tested our methodology on other, parity conserving, quantities. We find the EDM enhancement factor of Tl to be equal to $-573(20)$. This value is 20% larger than the recently published result of Nataraj *et al.* [Phys. Rev. Lett. **106**, 200403 (2011)], but agrees very well with several earlier results.

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A number of extensions of the standard model of particle physics predict electric dipole moments (EDM) of particles that may be observable with the present state-of-the art experiments [1] making EDM studies a remarkable tool in search for new physics. The EDMs arise from the violations of both parity and time-reversal invariance. The present constraints on the EDMs are already within bounds predicted by some theories [1]. If the EDMs are not observed in the next generation of the experiments, some of the low-energy supersymmetry and other theories will be ruled out. The standard model predicts tiny electron EDM, $d_e < 10^{-40}\ e$ cm since it can not originate even from three-loop diagrams [2].

The electron EDM is enhanced in certain atomic and molecular systems, and two of the most stringent limits on the electron EDM d_e were obtained from the experiments with ^{205}Tl: $d_e < 1.6 \times 10^{-27} e$ cm [3], and with YbF molecule: $d_e < 1.05 \times 10^{-27} e$ cm [4]. These limits significantly constrain supersymmetric and other extensions of the standard model [1].

Both results crucially depend on the calculated values of the effective electric field on the valence electron. In the case of Tl this effective field is proportional to the applied field E_0, $E_{\rm eff} = KE_0$, and Tl atom EDM is $d_{\rm at}(^{205}{\rm Tl}) = Kd_e$. The quantity K is referred to as the EDM enhancement factor.

Until recently, there was a consensus that the value of K is close to -580 [5, 6], but the latest calculation [7] gave the value $-466(10)$, or more than 20% smaller. All three of these calculations used high-accuracy methods that include some parts of the correlation corrections to all orders. Liu and Kelly [5] used relativistic coupled-cluster approach, but had to make various restrictions in their calculations to make it manageable with the computer power available in 1992. Dzuba and Flambaum [6] used a combination of the configuration interaction (CI) method with many-body perturbation theory (MBPT) starting from the [Xe]$4f^{14}5d^{10}$ Dirac-Fock (DF) potential and considering thallium as a system with three valence electrons. This potential is referred to as $V^{\rm N-3}$, where N is the total number of electrons. Nataraj *et al.* [7] used relativistic coupled-cluster (RCC) method with single, double and perturbative triple excitations of the DF wave functions starting from the [Xe]$4f^{14}5d^{10}6s^2$ potential. In this potential, referred to as $V^{\rm N-1}$, $6s^2$ shell is included in the core and thallium is considered to be a monovalent system, such as an alkali-metal atom. Both relativistic coupled-cluster method, in its various implementations, and CI+MBPT method have been used for a number of years in many other applications, including study of parity violation, calculation of other (P, T-odd) effects, search for variation of fundamental constants, and many others. We note that calculations of the effective field for such a heavy molecule as YbF is more difficult than for atomic Tl, and discrepancy in the theory for atoms may compromise molecular limit [4] as well.

Because of the importance of this issue, we return to the problem of Tl EDM in this letter. We have carried out several calculations by different high-precision methods in different potentials. Below, we briefly summarize the calculations that we have performed and our main findings before providing more details of the methods used in this work.

1. CI+MBPT calculation in $V^{\rm N-3}$ potential. Firstly, we have repeated the calculation of Dzuba and Flambaum [6] and ensured that we agree with their value at the same level of approximation. Then, we have calculated a number of corrections that were omitted in [6], including structure radiation, core-Brueckner, two-particle, selected three-particle, and normalization corrections. We found that some of these corrections are large, $5-7$% percent, but partially canceling, causing lower accuracy of $V^{\rm N-3}$ results than was previously expected.

2. CI+all-order calculation in $V^{\rm N-3}$ potential. Recently, we have developed the relativistic CI+all-order method [8] combining CI with coupled-cluster (CC) approach. This method, first suggested in [9], was success-

fully applied to the calculation of divalent atom properties in Refs. [8, 10]. In this work, we applied it for the first time to calculate properties of system with three valence electrons. This calculation allowed us to evaluate the effect of higher-order core-core and core-valence corrections to the EDM. We found that the effect of these corrections to the enhancement factor is small, 0.7%.

3. CI+MBPT calculation in V^{N-1} potential. We have repeated the entire CI+MBPT calculation described above, including all corrections, in V^{N-1} potential. We note that the CI+MBPT approach still allows us to fully treat all three valence electrons using CI. Therefore, we can accurately treat the contributions of the $6s6p^2$ states to K on the same footing as the $6s^2ns$ terms unlike the approach of [7]. Our final result is based on the V^{N-1} calculation with the higher-order corrections estimated from the V^{N-3} CI+all-order calculation.

4. RCC calculation of the $6s^2ns$ contributions to EDM. In an attempt to compare with RCC calculations of [7], we carried out full relativistic coupled-cluster calculations including single, double, and perturbative triple (RCCSDpT) excitations of the DF functions in V^{N-1} potential. We have also used this calculation to evaluate the effect of the Breit interaction on the EDM and found it to be negligible (0.36%). We have verified that our RCCSDpT value for the $6s^27s$ and $6s^28s$ contributions to the EDM are in excellent (2%) agreement with our final CI+MBPT values confirming the accuracy of our calculations. We have conducted RCC calculations with a truncated basis that we have constructed using parameters of [7]. The truncation of the basis set to the size of the one used in Ref. [7] produced very large reduction (by 18%) in the value of the $6p_{1/2}-7s$ EDM matrix element.

We discuss these four calculations in more details below. We start with solving DF equations $\hat{H}_0\,\psi_c = \varepsilon_c\,\psi_c$, where H_0 is the relativistic DF Hamiltonian [8, 11] and ψ_c and ε_c are single-electron wave functions and energies. The self-consistent calculations were performed for the $[1s,...,5d^{10}]$ closed core and the $6s-8s$, $6p$, $7p$, and $6d$ orbitals were obtained in V^{N-3} approximation. We have constructed the basis set [12, 13] consisting of 166 orbitals, $22s$, $22p$, $21d$, $20f$, $13g$, and $11h$. In order to estimate the accuracy of this basis set, we repeated some of the calculations with significantly larger B-spline basis set consisting of 273 orbitals ($35s$, $34p$, $28d$, $27f$, $21g$, and $20h$) and found that the differences were small and well below our estimated accuracy. Our CI space included orbitals up to $22s$, $22p$, $17d$, and $16f$; higher n orbitals were allowed fewer number of excitations. Such CI space is effectively complete. All MBPT and all-order calculations were carried out with inclusion of all orbitals. In Ref. [6], 40 (out of 50 in the basis set) B-spline states up to $l_{max} = 5$ were used in the MBPT calculations, and the CI space included orbitals up to $16s$, $16p$, and $16d$.

The multiparticle relativistic equation for three valence electrons is solved within the CI framework [14] to find the wave functions and the low-lying energy levels: $H_{\rm eff}(E_n)\Phi_n = E_n\Phi_n$, with the effective Hamiltonian defined as $H_{\rm eff}(E) = H_{\rm FC} + \Sigma(E)$. $H_{\rm FC}$ is the Hamiltonian in the frozen-core approximation and the energy-dependent operator $\Sigma(E)$ takes into account virtual core excitations. The $\Sigma(E)$ part of the effective Hamiltonian is constructed using the second-order perturbation theory in the CI+MBPT approach [11] and linearized coupled-cluster single-double method (LCCSD) in the CI+all-order approach [8]. Since the valence-valence correlations are very large, the CI method provides better description of these correlations than the perturbative approaches such as RCC due to possible large contributions of higher-order (or higher-excitation) corrections. The LCCSD method used here is known to describe the core-core and core-valence correlations very well as demonstrated by its great success in predicting alkali-metal atom properties [15]. Therefore, combination of the CI and all-order LCCSD methods allows to account for all dominant correlations to all orders.

The absolute values of the three-electron binding energy and the energy levels of the low-lying excited states in respect to the ground state obtained in the pure CI, the CI+MBPT, and the CI+all-order approximations are given in Table I of the supplementary material [16]. We find that the CI+all-order improves the accuracy of energies and reduces the error in the ground state three-electron binding energy to 0.2% level.

The atomic EDM $\mathbf{d}_{\rm at}$ of the ground state of Tl is defined as

$$\mathbf{d}_{\rm at} = 2\sum_n \frac{\langle 0|\mathbf{D}|n\rangle\langle n|H_d|0\rangle}{E_0 - E_n}, \qquad (1)$$

where $\mathbf{D}$ is the electric dipole moment operator. The operator H_d is given by [2]:

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma}\mathbf{r} \end{pmatrix} \frac{Z(r)}{r^3}, \qquad (2)$$

where d_e is the EDM of the electron, $Z(r)$ is the charge of the nucleus and core electrons within the sphere of radius r, and $\boldsymbol{\sigma}$ are Pauli matrices. In the CI+MBPT and CI+all-order approaches, we construct effective valence operators for all observables of interest [17, 18]. In this work, we need effective operators for the electric-dipole operator $D_{\rm eff}$, magnetic-dipole hyperfine interaction, and the operator $(H_d)_{\rm eff}$. These effective operators account for the core-valence correlations in analogy with the effective Hamiltonian. We do not perform explicit summation over three-particle states in our approach [17, 18], but use Dalgarno-Lewis-Sternheimer method that involves solution of the inhomogeneous equation with the corresponding effective operators. We include additional corrections beyond random-phase approximation (RPA) in the construction of all effective operators in comparison with [6]. These contributions include the core-Brueckner (σ),

TABLE I: The ground state three-electron binding energy $|E_{\rm v}|$ (in a.u.) and the energy levels of the low-lying excited states in respect to the ground state (in $\rm cm^{-1}$) for $V^{\rm N-1}$ potential. Results of the calculations and the differences with the experimental values [19, 20] (in %) are presented for CI and CI+MBPT approximations.

	CI		CI+MBPT		Expt.[a]
$E_{\rm v}$	1.9809	4%	2.0682	0.2%	2.0722
$6p_{3/2}$	7016	10%	7854	−0.8%	7793
$7s_{1/2}$	24649	7%	26328	0.6%	26478
$7p_{1/2}$	31876	7%	33954	0.6%	34160
$7p_{3/2}$	32834	7%	34974	0.5%	35161
$6d_{3/2}$	33762	7%	36106	0.0%	36118
$6d_{5/2}$	33828	7%	36180	0.1%	36200
$8s_{1/2}$	36549	6%	38693	0.1%	38746

TABLE II: The magnetic-dipole hfs constants (in MHz) and the absolute values of the reduced matrix elements of the electric-dipole operator $|\langle\gamma||D||\gamma'\rangle|$ (in a.u.)

		Theory	Expt.
A (MHz)	$6p_{1/2}$	22041	21310.8 [22]
	$7s_{1/2}$	12395	12297(2) [23]
	$8s_{1/2}$	3900	3871(1) [23]
E1 (a.u.)	$\lvert\langle 7s\rvert\rvert D\rvert\rvert 6p_{1/2}\rangle\rvert$	1.781	1.81(2) [24]
	$\lvert\langle 8s\rvert\rvert D\rvert\rvert 6p_{1/2}\rangle\rvert$	0.521	
	$\lvert\langle 7s\rvert\rvert D\rvert\rvert 6p_{3/2}\rangle\rvert$	3.393	3.28(4) [24]
	$\lvert\langle 8s\rvert\rvert D\rvert\rvert 6p_{3/2}\rangle\rvert$	0.764	

two-particle (2P) corrections, structural radiation (SR), and normalization (norm) corrections. Finally, we calculated selected three-particle (3P) corrections to the effective Hamiltonian [11]. We find that an accurate calculation of different observables in $V^{\rm N-3}$ potential is more complicated due to the poor convergence of the MBPT. We present the contributions to hyperfine structure (hfs) constants A for the 8 low-lying states in Table II of the supplementary material [16]. We find that many corrections beyond CI+MBPT and RPA are large and partially canceling. Partial cancellation of the structural radiation and normalization corrections was discussed in Ref. [21]. Detailed analysis of the structure radiation correction was carried out in the same work [21]. As a result, an agreement between final theoretical values and the experimental results in certain cases is not very good. In particular, the discrepancy between theoretical and experimental values of $A(7s)$ is at the level of 8%. The normalization corrections are unusually large ($\sim 6\%$). We calculated the normalization correction by approximately expressing it in terms of the derivatives of the MBPT corrections in respect to the energy [11]. It appears that accurate treatment of this correction may required development of a different approach in the case of $V^{\rm N-3}$ potential.

We find the same problem when calculating these correction to the EDM enhancement factor in the $V^{\rm N-3}$ approximation. The CI value is −584 and the CI+MBPT, CI+all-order, and RPA corrections contribute only 3, 4, and 3, respectively. Usually these are the most important corrections to the valence CI. At the CI+MBPT+RPA level, our result is −578 and is in a good agreement with the value −582(20) obtained by Dzuba and Flambaum [6] using the same CI+MBPT+RPA approximation in the $V^{\rm N-3}$ potential. Small difference may be due to the use of different basis set and CI space, or treatment of MBPT corrections. The corrections σ, SR, 2P, 3P, and norm are 25, −1, −22, −2, and 36, respectively. The two-particle and normalization corrections are large, +4% and −6%, correspondingly leading to the value $K = -538(46)$. We estimated the uncertainty in K based on the maximum difference of the relevant hyperfine constants with experiment, 8% for $A(7s)$, and the total contribution of all corrections beyond CI (8.6%).

In summary, we find that the corrections beyond CI+all-order+RPA are large; even though they partially cancel each other, their total contribution is significant, almost 7% in $V^{\rm N-3}$ potential. At the same time, the all-order CC corrections due to higher-order core-valence correlations are very small, 0.7%. We conclude that the size of different corrections to the EDM in the $\rm V^{N-3}$ potential is not typical and missing higher-order contributions to the effective operators can be important. Because of that, we repeat calculations in the $\rm V^{N-1}$ approximation. We already used this approximation in the calculation of the parity-nonconserving amplitude for the $6p_{1/2} - 6p_{3/2}$ transition in Tl with 3% accuracy [25]. Comparison of the $V^{\rm N-1}$ and $V^{\rm N-3}$ potentials for Tl calculations has been recently discussed in Ref. [26].

The CI+MBPT calculation in the $\rm V^{N-1}$ potential follows the same procedure as the one in the $\rm V^{N-3}$ approximation, but the self-consistent DF procedure is carried out for the $[1s, ..., 5d^{10},\ 6s^2]$ core. We note that we use the Brillouin-Wigner variant of the MBPT in both cases. In this formalism, the effective Hamiltonian for the valence electrons is energy-dependent. It was shown in our work [27] that the accuracy of the theory can be improved by calculating the Hamiltonian at the optimal valence energy for Tl, which was found to be −1.8 a.u.. In Table I, we present the absolute values of the valence energy of the ground state and the energy levels of the low-lying excited states counted from the ground state obtained in the pure CI and in the CI+MBPT approximations. We note that the CI+all-order formalism is presently limited to the $V^{\rm N-3}$ potential. In $V^{\rm N-1}$, so-called subtraction diagrams have to be included consistently at the all-order level which so far has not been implemented. Since the all-order core-valence corrections contributed only 0.7% in the $V^{\rm N-3}$ approximation, these are small at the present calculation as well. A comparison of the results presented in Tables I shows that the energy levels found in $\rm V^{N-1}$ approximation turn out to be closer to the experimental results than in $\rm V^{N-3}$ approximation,

TABLE III: The breakdown of different contributions to our final value of the EDM enhancement factor K, V^{N-1} potential. First column gives the CI value and the following columns give various corrections described in the text.

CI	CI+MBPT	RPA	Sbt	2P	σ	SR	Norm	Final	Ref. [5]	Ref. [6]	Ref. [7]
-593.6	8.7	-13.0	16.5	-18.8	22.5	0.0	5.2	-573(20)	-585(30-60)	-582(20)	-466(10)

TABLE IV: The contributions to the EDM enhancement factor K in our final V^{N-1} CI+MBPT calculation. Columns D and H_d give reduced matrix elements of the electric-dipole and EDM operators. The results of our RCCSDpT calculation for the $6s^2ns$ contributions are given in the last column labeled K(CC) for comparison.

State	$\Delta E_{\rm th}$	$\Delta E_{\rm expt}$	D	H_d	K	K(CC)
$6s^27s\ ^2S_{1/2}$	26328	26478	-1.798	17.7	-216.6	-212.2
$6s^28s\ ^2S_{1/2}$	38693	38746	-0.526	9.2	-22.4	-22.8
$6s6p^2\ ^4P_{1/2}$	46281	45220	-0.427	45.1	-74.6	
$6s6p^2\ ^2P_{1/2}$	69218	67150	-2.472	28.0	-179.2	
$6s6p^2\ ^4D_{1/2}$?	79830		-0.142	-4.2	1.3	
Other					-81.1	
Total					-572.5	

which is already observed at the stage of pure CI approximation. As a result, the MBPT corrections that give the main contribution to the uncertainty budget are smaller leading to better agreement between the theoretical and experimental energy levels. Our values for the magnetic-dipole hfs constants and E1 transition amplitudes between low-lying levels in V^{N-1} potential are compared with experimental results [22–24] in Table II. The calculation of these properties was discussed in detail in Ref. [25]. The corrections that are taken into account are similar to those for the V^{N-3} potential. The only essential difference is an appearance of the subtraction diagrams (Sbt) in the former case. The differences between the theoretical and experimental results do not exceed 3% for all relevant properties.

In Table III, we present the breakdown of different contributions to the atomic EDM enhancement factor K. The difference between the CI value, -594, and the final value, -573, is only 3.7%. It demonstrates that the interaction between valence electrons is much more important and should be treated as accurately as possible. In Table IV, we list the contributions to K from most significant configurations. These values were calculated using Eq. (1) and results of our V^{N-1} CI+MBPT calculation. We find that contributions from 4 configurations give 85% of the total value. Table IV illustrates that it is very important to accurately account for the contributions of the $6s6p^2$ configurations. Their contribution to the EDM is $\sim 45\%$. In the RCC method of [7], these contributions were treated as excitations of the core electrons which is unlikely to provide required accuracy.

We have also carried out completely different set of calculations using relativistic coupled-cluster method with single, double, and perturbative triple (RCCSDpT) excitations in V^{N-1} potential [15, 28] to evaluate the dominant contributions to the EDM from the $6s^27s$ and $6s^28s$ states by a different approach. All nonlinear terms were included at the SD level. This method is theoretically very close to that of Nataraj *et al.* [7]. While there are differences in the treatment of the triple excitations between ours and Ref. [7] approaches, we find that contributions of the triple excitations to the EDM is small (less than 2%). We have also used this calculation to evaluate the effect of the Breit interaction on EDM and found it to be negligible (0.36% for the $6s^27s$ contribution). Our final values for the $6s^27s$ and $6s^28s$ contributions are given in the last column of Table IV. RCCSDpT values are in excellent (2%) agrement with our final CI+MBPT values. The agreement of the results obtained by two completely different approaches confirms the accuracy of our calculations. However, the value of the $6s^27s$ contribution inferred from Fig. 2 of [7] is 10% lower, about -188. We find that this difference may be due to significant truncation of the basis set used in RCC calculation of [7]. The main part of our RCCSDpT calculation was carried out with very large numerically complete basis set (650 orbitals with $l \leq 6$). Fig. 2 in [7] shows that their $9s$ orbital already belongs to continuum, which is consistent with their restriction of ns orbitals to $n \leq 14$ in the RCC calculation. We have conducted a basis set test truncating our smaller 166 orbital basis to $n = 14$ for all partial waves and using it in the RCC calculations. We find that the value of the $6p_{1/2} - 7s$ EDM matrix element was reduced by 18% due to basis set truncation.

To conclude, we calculated the EDM enhancement factor to be equal to $-573(20)$. The uncertainty is, somewhat conservatively, assigned based on the accuracy of the relevant hyperfine constants (3%) and total size of *all* corrections beyond the CI, which is 3.7%. This value differs by 20% from the recently published result of Nataraj *et al.* [7], but agrees well with the results obtained by Dzuba and Flambaum [6] and Liu and Kelly [5].

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