# Analysis of atomic electric dipole moment in thallium by all-order calculations in many-body perturbation theory

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A procedure is presented for calculations of double-perturbation problems in the coupled-cluster formalism. With use of this method to include to all orders the correlation effects of single and pair excitations, the enhancement factor $R = -585$ is obtained for the electric dipole moment (EDM) in atomic thallium. Equations for EDM perturbed single-excitation amplitudes are solved by diagonalization to take into account mixing between excited core states, and perturbed pair functions are introduced to incorporate correlation effects. Considering contributions from higher-order perturbation terms, we estimate the accuracy of the obtained enhancement factor is approximately at the 5-10% level.

The neutral thallium atom, due to its high $Z$ and high polarizability $a_D$, has been extensively studied to search for a possible electric dipole moment (EDM), which can exist only if parity $(P)$ and time-reversed invariance $(T)$ are violated [1]. According to Sandars [2], the ratio of the atomic to the electron EDM is of order $Z^3 a^2 a_D$, which indicates that the enhancement factor for Tl is expected to be greater than 100. The first experimental limit for the EDM of the $6p_{1/2}$ state in Tl was obtained by Gould [3], $d_{Tl} = (1.3 \pm 2.4) \times 10^{-21}$ $e$ cm. Since then, continuous efforts have been made to lower the upper limit by 3 orders of magnitude. In a recent atomic-beam experiment, Abdullah *et al.* [4] obtained a limit $d_{Tl} = (1.6 \pm 5.0) \times 10^{-24}$ $e$ cm, which, when converted to the electron EDM, is close to the range capable of testing some theoretical models of charge-parity $(CP)$ violation. In fact, the value of $d_e (> 10^{-27}$ $e$ cm$)$ produced by a Higgs-Boson model [5] is already at this level. Motivated by progress in experiments, several atomic calculations have provided the enhancement factor $R$ for Tl. Johnson *et al.* [6] obtained $R = -1041$ by calculating first-order corrections in many-body perturbation theory (MBPT). Further calculations to consider correlation effects, however, gave dramatically reduced results, namely, $R = -301$ by Kraftmakher [7] and $R = -179$ by Hartley, Lindroth, and Mårtensson-Pendrill [8]. All these *ab initio* calculation results were quite different from the semiempirical estimates, e.g., $R = -716$ given by Sandars and Sternheimer [9], $R = -500$ by Flambaum [10], $R = -502 - -607$ by Johnson *et al.* [6]. Therefore it is clearly of great interest to obtain a reliable value of the atomic EDM enhancement factor for Tl, which not only provides an important parameter to set the upper limit of the electron EDM, but also can clarify the discrepancies of different calculations.

The ground state of Tl has one unpaired electron $6p_{1/2}$ outside closed shells, so that it can be treated as an alkali-metal atom. However, the last filled shell $6s^2$ is relatively loosely bound, and can mix strongly with the valence $6p_{1/2}$ state and virtual $6p_{3/2}$, $6d_{3/2}$, $6d_{5/2}$ states. The correlation effects between configurations consisting of these states

play significant roles. Thus the behavior of Tl in MBPT differs from that in alkali-metal atoms, as discussed by several authors [7,8,11]. In particular, Kraftmakher [7] carried out a calculation to treat the mixing between the $6s^2 6p_{1/2}$ and $6s 6p_{1/2}^2$ states which gave $R = -356$, and pointed out that the uncalculated corrections of higher orders might also be large. It is obvious that only when considering all important correlation effects together can one obtain improved results for the accuracy required by the recent EDM measurement.

In this paper we report our implementation of a general two-step procedure to take into account correlation effects due to two perturbation interaction terms, namely, a residual electron-electron Coulomb interaction $H_C$ and an effective $CP$ violating interaction $H_{EDM}$ induced by the electron EDM [12],

$$H_{EDM} = -d_e (\beta - 1) \boldsymbol{\sigma} \cdot \boldsymbol{\nabla} H_{in}, \tag{1}$$

where $\beta$ is a Dirac matrix, $\boldsymbol{\sigma}$ are Pauli matrices, and $H_{in}$ includes the nuclear potential and the electron-electron Coulomb interaction. In this work the exchange part of the interelectron interaction in Eq. (1) is omitted, and $H_{EDM}$ is treated as a one-body interaction. The outline of our procedure is as follows.

The Hamiltonian of the double-perturbation system is taken as

$$H = H_0 + H_C + H_{EDM}, \tag{2}$$

where $H_0$ is a solvable zeroth-order Hamiltonian with $H_0 \Psi_0 = E_0 \Psi_0$, and we use the Dirac-Fock operator for $H_0$.

$$H_C = \sum_{\substack{i,j \\ i>j}} \Lambda_i^+ \Lambda_j^+ \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U_{HF}(r_i) \Lambda_i^+, \tag{3}$$

where $U_{HF}$ is the Hartree-Fock potential in $H_0$, the positive-energy-state projection operators $\Lambda_i^+$ are introduced to avoid the continuum dissolution problem as discussed by Sucher [13]. A wave operator $\hat{\Omega} = [\exp(\hat{T})][\exp(\hat{S})]$ in normal-ordered exponential form [14] is then used to express the exact wave function $\Psi$ as

$$\Psi = \hat{\Omega} \Psi_0. \tag{4}$$

The first step is to solve for the cluster operator $\hat{S}$ associated with $H_C$ from the equation

$$(H_0 + H_C)[\exp(\hat{S})]\Psi_0 = E[\exp(\hat{S})]\Psi_0, \tag{5}$$

which is the open-shell extension of the standard coupled-cluster (CC) approach [14,15]. When $\hat{S}$ is truncated to one- and two-body parts, the single- and pair-excitation amplitudes $S_1$ and $S_2$ can be incorporated to all orders by solving equations

$$D_1 S_1 = V_2(S_1 + S_2) + S_2^+ (V_2 S_2)_3, \tag{6a}$$

$$D_2 S_2 = V_2(1 + S_1 + S_2) + V_2 \tfrac{1}{2} S_1^2, \tag{6b}$$

where $D_i$ ($i = 1,2$) is an energy factor associated with the amplitude $S_i$, given by the difference of the single-particle orbital energies between occupied and virtual states involved in the $i$th-particle excitation. When the occupied orbitals are valence electrons, the correlation correction to the valence removal energy should also be included in the energy factor [14]. We use the $V^{(N-1)}$ Dirac-Fock (DF) potential in $H_0$, so the one-body part in $H_C$ vanishes. The two-body part in $H_C$ is denoted as $V_2$, and its order of magnitude can be denoted as $O(g)$. Therefore $S_2$ and $S_1$ are $O(g)$ and $O(g^2)$, respectively. When one keeps all terms up to $O(g^3)$, Eqs. (6a) and (6b) are obtained. The term $S_2^+ (V_2 S_2)_3$ in Eq. (6a), where the notation of $(V_2 S_2)_3$ represents a triple excitation term coming from the combination of $V_2 S_2$, is added by the Hermitian formulation of the CC approach [16]. Alternatively, this term can be added by considering contributions from triple excitations [17], or in a variational CC approach [18,19]. By using the latter two methods, intermediate normalization can be retained. After solving Eqs. (6a) and (6b) for $S_1$ and $S_2$, which describe a correlated many-electron wave function including relaxation effects, we then solve for the amplitudes $T_1$ and $T_2$ of the EDM perturbed cluster operator $\hat{T}$ from the equations

$$D_1 T_1 = H_{EDM}(1 + S_1 + S_2) + V_2(T_1 + T_2)$$

$$+ V_2 T_1 S_2, \tag{7a}$$

$$D_2 T_2 = H_{EDM} S_2 + V_2(T_1 + T_2) + V_2 T_1 S_2, \tag{7b}$$

where terms up to $O(d_e g^2)$ are kept. We consider the order of magnitude of $T_1$ as $O(d_e)$, so $T_2$ is $O(d_e g)$. The amplitudes of the conventional and EDM perturbed cluster operators can then be used to evaluate the matrix element of the dipole operator. Up to $O(d_e g^2)$, the matrix element can be expressed as

$$M = \langle \Psi | \hat{Z} | \Psi \rangle / \langle \Psi | \Psi \rangle$$

$$= Z(T_1 + T_2) + S_1^+ Z T_1 + S_2^+ Z(T_1 + T_2)$$

$$+ S_2^+ Z T_1 S_2 + c.c. + M^{norm}, \tag{8}$$

where c.c. means complex conjugated terms, and $M^{norm}$ is the contribution from the normalization factor [20].

We next discuss basic processes described by Eq. (8). In the lowest order, there are two major EDM-induced transitions as shown in Fig. 1. One is the valence electron $6p_{1/2}$ excited to a virtual $s_{1/2}$ state. Another is the core electron $6s_{1/2}$ with an opposite spin to the valence electron
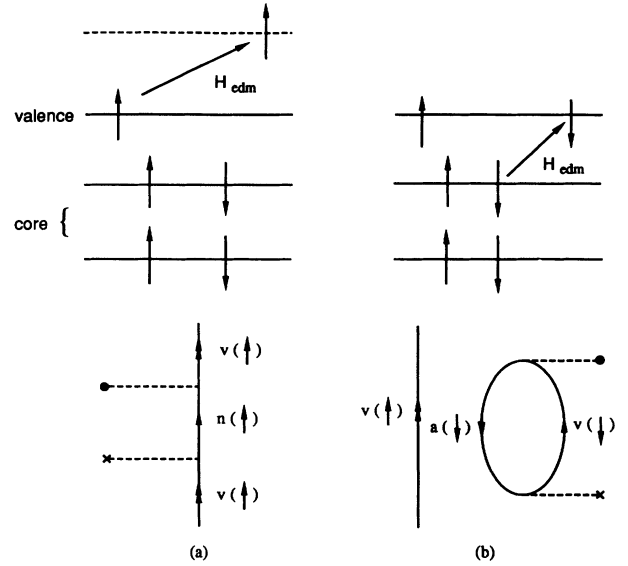


FIG. 1. Two basic processes in the EDM-induced transition: (a) valence excitation, (b) core excitation. Downward lines denote core states or holes; upward, excited states or particles; and double-arrow line, valence state. Lines with a cross represent $H_{EDM}$, and lines with a circle the dipole operator. Graphs with interchange of $H_{EDM}$ and dipole operator lines are not shown.

excited to a vacancy in the $6p_{1/2}$ state. These two processes are evaluated by the lowest order $Z(T_1)_{core} + c.c.$ and $Z(T_1)_{valence} + c.c.$, respectively. Since the $6s_{1/2}$ state has the same principal quantum number as the valence electron $6p_{1/2}$, both the inverse of the energy denominator and the matrix element of $H_{EDM}$ are substantial. Thus the two processes in Figs. 1(a) and 1(b) are both important, which can be seen later in Table III. In order to obtain the all-order energy correction and the correlation of the $6s_{1/2}$ state with other core states, we solve Eq. (7a) as a matrix equation

$$A(T_1)_{core} = B \tag{9}$$

by diagonalizing the matrix

$$A = D_1 - V_2 - V_2 S_2, \tag{10}$$

where the inhomogeneous term

$$B = H_{EDM}(1 + S_1 + S_2) + V_2 T_2. \tag{11}$$

One of the advantages of the method is that eigenvalues and eigenvectors of the matrix $A$ need be calculated only once. After each iteration to calculate the perturbed pair function $T_2$, we can easily update $(T_1)_{core}$. This method offers an efficient way to solve Eq. (7a) to all orders. More details are referred to in Refs. [21] and [22]. Table I shows excitation energies for core electrons excited to their lowest possible virtual state. As far as the energy correction for the excited state $6s \rightarrow 6p_{1/2}$ (i.e., $6s^2 6p_{1/2} \rightarrow 6s 6p_{1/2}^2$) is concerned, the term shown in Fig. 1(b) from the lowest order to all orders gains a factor of about 2. In order to compare with the previous lowest-order result [6], we apply the matrix diagonalization technique to

TABLE I. Energies of excitation states by diagonalizing the matrix $A$ in Eq. (10), and compared with energies obtained from DF orbitals.

| Excited states | Eigenvalues of $A$ | DF energies (a.u.) |
|---|---|---|
| $6s_{1/2} \to 6p_{1/2}$ | 0.2624 | 0.4898 |
| $5d_{5/2} \to 5f_{5/2}$ | 1.0456 | 1.0420 |
| $5d_{3/2} \to 6p_{3/2}$ | 0.7703 | 0.9943 |
| $5p_{3/2} \to 6d_{3/2}$ | 3.3340 | 3.4288 |
| $5p_{1/2} \to 7s_{1/2}$ | 4.0434 | 4.1554 |
| $5s_{1/2} \to 6p_{1/2}$ | 5.3991 | 5.6864 |

$$D_1 T_1 = H_{EDM} + V_2 T_1 + T_1^+ V_2, \tag{12}$$

which one recognizes as the equation in the random-phase approximation (RPA) for the EDM interaction. A full RPA calculation has been performed in Ref. [6] for both the EDM and dipole interaction. However, Eq. (12) is the basic equation to produce perturbed orbitals and plays an important role in the other MBPT calculations [7,8]. In Eq. (12) the excitation energy of $6s \to 6p_{1/2}$ is shifted from 0.4898 to 0.1396 a.u. due to the RPA terms. After diagonalization, which is equivalent to solving Eq. (12) self-consistently for all core orbitals, the energy is shifted further to 0.08565 a.u. This reduced energy factor is responsible for the highly overestimated enhancement factor $R = -1906$ [6]. The overestimation of RPA results was previously analyzed by Kraftmakher [7]. Physically, this overestimation is caused by the exclusion-principle-violation (EPV) diagrams in the RPA which allow for unlimited numbers of $6s \to 6p_{1/2}$ excitations and are unphysical.

In the previous MBPT calculations by Kraftmakher [7] and Hartley, Lindroth, and Mårtensson-Pendrill [8], correlation effects involving the simultaneous excitation of two occupied orbitals were obtained by modifying the valence electron orbital to an approximate Brueckner orbital. In the present work we introduce the EDM-perturbed pair function $T_2$ instead to incorporate the correlation effects. Although this double-perturbation CC approach is computationally demanding, it provides a systematic calculation scheme to obtain high-accuracy results. It avoids contributions from the unphysical EPV terms which cause unstable convergence behavior [7,8]. Introducing pair functions in our calculation ensures the major correlation effects between electrons are taken into account. In Fig. 2 we plot the large component of the reduced part of the EDM-perturbed pair function of a channel from $6p_{1/2}$, $6s_{1/2}$ excited to $p_{1/2}$, $p_{1/2}$ states with coupling angular momentum $L = 1$.

We use the Fock-space CC formalism [23], so that core equations for $N - 1$ electrons are independent of the valence state, and the valence equations have the effect of adding the $N$th electron. The dominant correction term in Eq. (8) attributed to the influence of the valence electron on the process of core electrons excited by $H_{EDM}$ comes from $ZT_2$+c.c. Our calculation is implemented with a relativistic finite basis set generated by $B$ splines [24]. We choose the number of $B$-spline basis functions $n = 32$, and the order of the piecewise polynomial of $B$ splines $k - 1 = 5$. Summation over the last ten states is omitted
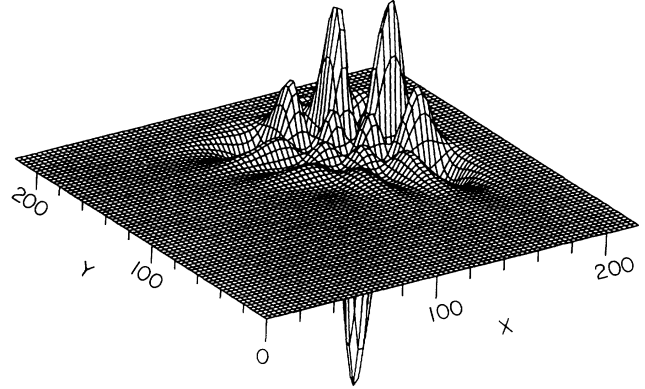


FIG. 2. EDM-perturbed pair function of the channel from $6p_{1/2}$, $6s_{1/2}$ excited to $p_{1/2}$, $p_{1/2}$ states with coupling angular momentum $L = 1$. Radial mesh is logarithmic and denoted by the number of points. Vertical height is relative to the electron EDM $d_e$.

without loss of numerical significance. The upper limit for angular momenta of the intermediate excited states $L_{max} = 6$ for the cluster operator $\hat{S}$ and $L_{max} = 4$ for the perturbed cluster operator $\hat{T}$ have been found to be necessary for proper convergence. The coupled-electron pair approximation scheme [15] is used to simplify the nonlinear term $\frac{1}{2} S_2^2$. A further approximation is to consider only core orbitals $4s$ and higher; and for the iteration solution of pair functions $T_2$ the terms $V_2 T_2$ of Eq. (7b) involving $4s$, $4p$, $4d$ orbitals are omitted. With all the above restrictions, the calculation was able to be carried out on an IBM RISC/6000 workstation.

We present in Table II the ionization energy of the $6p_{1/2}$ valence state, which agrees well with a recent third order plus partial fourth-order MBPT calculations of Blundell, Johnson, and Sapirstein [11]. We summarize in Table III the final result of the enhancement factor for Tl. The first four terms of column $A$ in Table III shows the results from solving Eq. (12), which give a sum of $-1908$. For the whole column $A$, we add $D_2 T_2 = H_{EDM} S_2 + V_2 T_1 + (V_2 T_2)_{ring\ type}$ to be solved together with Eq. (12), where $S_2$ comes from $D_2 S_2 = V_2$, and the enhancement factor is obtained from $M = Z(T_1 + T_2) + (S_2^+ ZT_1)_{RPA\ type}$. This scheme is close but not exactly equivalent to the full RPA result in Ref. [6], because it misses certain higher RPA terms for the dipole operator [20]. Apparently, all higher-order terms in the present

TABLE II. Valence energy for Tl $6p_{1/2}$ state obtained from Eq. (6a).

| Contribution from | Energy (a.u.) |
|---|---|
| DF | $-0.19968$ |
| $V_2 S_1$ | 0.00230 |
| $V_2 S_2$ | $-0.02841$ |
| $S_2^+ (V_2 S_2)_3$ | 0.00192 |
| Total | $-0.22387$ |
| Expt.[a] | $-0.22446$ |
| Other[b] | $-0.2239(7)$ |

[a]Reference [25].                [b]Reference [11].

TABLE III. Contribution of matrix element calculations of Eq. (8) by two different schemes to the enhancement factor $R$ for Tl. In column $A$ Eq. (12) is used as the perturbed orbital to start, and in $B$ Eq. (7a) is used instead. Each term includes its complex conjugate counterpart.

| Contribution from | Enhancement factor $R$ | |
|---|---|---|
| | $A$ | $B$ |
| Lowest order in $Z(T_1)_{valence}$ | $-267.3$ | $-267.3$ |
| Lowest order in $Z(T_1)_{core}$ | $-153.2$ | $-153.2$ |
| Higher order in $Z(T_1)_{valence}$ | $-455.8$ | $-102.5$ |
| Higher order in $Z(T_1)_{core}$ | $-1031.2$ | $-342.1$ |
| $ZT_2$ | $470.1$ | $240.9$ |
| $S_1^+ ZT_1$ | | $22.4$ |
| $S_2^+ ZT_1$ | $336.3$ | $49.3$ |
| $S_2^+ ZT_2$ | | $-36.9$ |
| $S_2^+ ZT_1 S_2$ | | $-2.2$ |
| $M^{norm}$ | | $6.5$ |
| Total | $-1101$ | $-585$ |

work given in column $B$ show more stable behavior. This is because of exclusion of the EPV terms and inclusion of screening, relaxation, and other correlation effects for Coulomb interaction.

The main error in our calculation comes from truncation of the CC expansion. Our calculation is complete through pair excitation contributions in MBPT. A relative error 0.3% for the Tl $6p_{1/2}$ removal energy indicates that the omitted higher excitation terms for the operator $\hat{S}$ are not significant. Other important and more sensitive results, such as hyperfine structure and oscillator strengths, are to be presented elsewhere [19]. The omitted terms in triple and higher excitation for the perturbed operator $\hat{T}$ and matrix-element calculations are partly accounted for by coupled-cluster terms $T_1 S_2$ in Eqs. (7) and (8). It turns out that the terms $T_1 S_2$ account for 2% of the total results. We expect that contributions from omitted terms are at the same order of magnitude. Another possible error source is uncertainty in the numerical procedure. In the present work the size of the $B$-spline basis and the number of partial waves included in the complete set give $\sim 1\%$ accuracy for the correlation corrections. Only if one needs higher accuracy would an increase in the basis set size be required. The third type of error arises from interaction terms neglected in the Hamiltonian of Eq. (2). However, as discussed by Lindroth, Lynn and Sandars [12], the nuclear part and direct electrostatic interaction part in the $(\beta - 1)$ form are dominant over other $\alpha^2$ terms by about 2 orders of magnitude, so that we can neglect the exchange part of electrostatic interaction in Eq. (1), the transverse photon interaction, the virtual-pair effect, and other QED corrections as long as a null result for the EDM has been obtained by measurements. In view of the factors mentioned above, we assign a rough estimate of uncertainty of 5–10% to the final result in Table III. If necessary, including all $O(g^3)$ terms in Eqs. (6)–(8) would be able to improve the accuracy of the enhancement factor of Tl to below the 5% level.

In conclusion, we have presented a general approach to treat a system with two external perturbations. Our calculation of the EDM enhancement factor for Tl, $R = -585$, is complete to second order of Coulomb interaction in MBPT, and includes the most important correlation effects from pair excitations to all orders. Our result has eliminated the discrepancy between the semi-empirical evaluations [6,9,10] and the previous ab initio MBPT calculations [6–8]. The procedure in the present work can also be applied to other double-perturbation problems of interest, such as weak interaction induced electric dipole transitions [6] or atomic polarizabilities.

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