Dipole polarizability calculation of the Cd atom: Inconsistency with experiment

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Three earlier relativistic coupled-cluster (RCC) calculations of dipole polarizability (α_d) of the Cd atom are not in good agreement with the available experimental value of 49.65(1.65) ea_0^3 . Among these two are finite-field approaches in which the relativistic effects have been included approximately, while the other calculation uses a four-component perturbed RCC method. However, another work adopting an approach similar to the latter perturbed RCC method gives a result very close to that of experiment. The major difference between these two perturbed RCC approaches lies in their implementation. To resolve this ambiguity, we have developed and employed the relativistic normal coupled-cluster (RNCC) theory to evaluate the α_d value of Cd. The distinct features of the RNCC method are that the expression for the expectation value in this approach terminates naturally and that it satisfies the Hellmann-Feynman theorem. In addition, we determine this quantity in the finite-field approach in the framework of a four-component relativistic coupled-cluster theory. Considering the results from both approaches, we arrive at a reliable value of $\alpha_d = 46.02(50) ea_0^3$. We also demonstrate that the contribution from the triples excitations in this atom is significant.

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I. INTRODUCTION

Accurate values of the electric dipole polarizabilities (α_d) of atomic states are necessary for high-precision experiments on optical lattices, atomic clocks, quantum information, and many other important areas of atomic and molecular physics [1–5]. Comparisons between the calculated α_d values and experimental results could serve as benchmarks to validate many-body methods [6-10]. Methods that are capable of yielding results in close agreement with high-precision experimental results are considered to be accurate and suitable for the evaluation of properties of atomic systems, and their values can be treated as reliable when experimental results are not available. Many-body calculations are performed using finitesize many-electron and single-electron basis wave functions as approximations have to be made in determining higherorder correlation effects due to limitations of computational resources. A large number of numerical operations are performed; thus it is not possible to estimate uncertainties in the calculations due to numerical truncations. In such a situation, just a comparison of a calculated value with an experimental result cannot reliably validate a method [11]. Therefore, it is imperative to perform calculations using many-body methods that can capture a wide range of physical effects and have the merit of capturing correlation effects to all orders of the residual Coulomb interaction at different levels of approximation and

are size-extensive in order to apply them for high-precision studies. To ascertain the accuracies of the results, it is necessary to check the consistencies in the results by employing a number of theories that are equivalent to all-order many-body perturbation methods.

Many-body perturbation theory (MBPT) was first developed by Brueckner [12–14] and Goldstone [15]. Newer versions of this theory are now widely used to calculate atomic wave functions and properties in many-electron systems. Important steps to determine atomic dipole polarizabilities were taken by Dalgarno and his collaborators [16,17] and Kelly [18]. The approach adopted by Dalgarno and collaborators solves an inhomogeneous differential equation to obtain the first-order wave function using Rayleigh-Schrödinger perturbation theory. This approach, known as the coupled-perturbed Hartree-Fock method or random phase approximation (RPA), can predict α_d values very accurately in some cases, but it does not account for a number of different classes of electron correlation effects. On the other hand, the approach adopted by Kelly using the MBPT method pioneered by Brückner and Goldstone follows a diagrammatic technique in which the contributions from different types of electron correlation effects can be illustrated in a transparent manner. However, it is not simple to include higher-order correlation contributions in this approach as it treats the residual Coulomb interaction Hamiltonian and the dipole operator (D = |D|) as two different perturbations. Another suitable approach to determine α_d for atomic systems is to use a finite-field method, in which the interaction Hamiltonian due to D with an arbitrary external electric field is added to the atomic Hamiltonian to obtain the

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energy eigenvalues [19–21]. Then the α_d values are inferred from the second derivative of the energy with respect to the electric field. The disadvantage of this approach is that it neglects the higher-order corrections to the energies due to the electric field. Hence, there is a loss of numerical accuracy in the results. This approach is suitable for the molecular systems where the electron orbitals, described by the Cartesian coordinate system, are mixed in parities and computations are minimized by utilizing group symmetry identities [22,23]. For determining α_d values of atoms in this approach, one can choose a special group symmetry. However, it cannot still describe atomic orbitals with the same accuracy as in the spherical coordinate system. It is to be noted that it is possible to work with mixed parity orbitals in the spherical coordinate system, but it will be computationally more expensive.

One of the key differences between the spherical and Cartesian coordinate systems for carrying out calculations is that the atomic orbitals are divided into radial and angular factors in the former case. Thus, all the physical operators are expressed using spherical tensors to take care of the angular momentum selection rules. The coupled-cluster (CC) theory is an all-order perturbative method, and it is size-consistent and size-extensive, for which it is referred to as the gold standard for treating correlation effects in many-electron systems [24–26]. For performing CC calculations in a spherical coordinate system using atomic orbitals with definite parities, the twobody interactions and the CC wave operators must be expanded in terms of multipoles [27]. We have developed different methods in the relativistic CC theory framework (RCC method) to calculate α_d values of atomic systems in the spherical coordinate system [8,9,28,29]. Since the atomic orbitals in this case have definite parities, we had perturbed the RCC wave functions by considering D as the external perturbation to first order. This is similar in spirit to the aforementioned approach by Dalgarno [16, 17] in which we obtain the solution to the inhomogeneous differential equation in terms of the first-order perturbed RCC wave function. In addition, our RCC method also gives contributions from various electron correlation effects in terms of Goldstone diagrams, similar to Kelly's approach [18]. We have applied this method to a number of atomic systems to determine α_d values very accurately [8,9,28]. In one of our works, we had obtained $\alpha_d = 45.86(15) ea_0^3$ for the Cd atom [9] using our RCC theory, where the corresponding experimental value has been reported as $49.65 \pm 1.49 \pm 0.16 \ ea_0^3$ [30]; with the net uncertainty this value is $\alpha_d = 49.65(1.65) \ ea_0^3$. In the same study, we had also obtained these values for other atoms belonging to the homologous group of Cd in the periodic table like Zn and Hg, which were in very good agreement with their respective experimental results [9]. In fact, our findings were also in agreement with the previous calculations, which were obtained by applying other variants of CC theories in the finite-field procedure. These calculations, however, were performed using quasirelativistic [6] and scalar two-component Douglas-Kroll [7] Hamiltonians in contrast to our four-component relativistic Hamiltonian to account for the relativistic effects. Following these works, another group has reported the α_d value as 49.24 ea_0^2 [10] employing a perturbative RCC method like ours [9] and has referred to it as the perturbed RCC (PRCC) method in the singles and doubles approximation and perturbed RCC

with partial triples [PRCC(T)] method when triples effects were included. This calculation is very close to the central value of the experimental result and is in disagreement with all the previous calculations. Thus, it is necessary to understand the reasons for the disagreement among these theoretical calculations and find a more reliable value of α_d of the Cd atom. Analysis of these methods reveals that there were no additional physical effects included in the PRCC method which could be responsible for improving the result. This means that the difference in the implementation procedures for both four-component perturbative RCC methods is responsible for the discrepancies between the results.

The RCC theories employed in Refs. [8-10] are sizeextensive. In the framework of these theories, the expression for the energies terminate, but the expectation values corresponding to different properties do not. Recently, we have observed that the inclusion of higher-order nonlinear terms in the nonterminating series in the evaluation of α_d and permanent electric dipole moment (EDM) in the ¹⁹⁹Hg atom influences the results significantly [31]. Therefore, it is imperative to adopt a relativistic CC method in the spherical coordinate system in which the expectation value terminates naturally. This would be particularly relevant in the evaluation of α_d for Cd atom where the results of the calculations from different methods are inconsistent and differ substantially from the measured value. In this context, the normal coupled-cluster (NCC) method [26,32,33] would be more appropriate for the evaluation of α_d . This method satisfies the Hellman-Feynman theorem. Moreover, in the NCC method, the expressions for both energies and expectation values corresponding to different physical properties terminate in a natural way. The normalization factor in this method is equal to unity. The additional effort of implementing this method for determining α_d is that it is necessary to solve the unperturbed and perturbed equations for both the bra and ket states. This amounts to a substantial increase in the computational efforts to perform calculations using the NCC method in comparison with the CC method. Complexities grow further to implement it in the spherical coordinate system along with the angular spherical tensor products. Due to recent demands to perform high-accuracy calculations in the atomic systems, we have developed the NCC method in the four-component relativistic theory (RNCC method) adopting the spherical coordinate system, and it has been applied to calculate EDM and α_d values of the ¹⁹⁹Hg atom [34]. In this work, we apply the RNCC method to find α_d of the Cd atom and compare the result with the other theoretical and experimental values. Furthermore, we also estimate this quantity in the finite-field approach using the four-component Dirac-Coulomb (DC) Hamiltonian in the multireference coupled-cluster (MRCC) program [35]. By assessing various uncertainties and checking consistencies in the results from different methods at various levels of approximations, a precise value of α_d has been given. We also elucidate trends of correlation effects in the determination of this quantity by comparing intermediate results from a number of lower-order many-body methods and from different RCC and RNCC terms. In fact, there exists another CC approach for the determination of polarizabilities by evaluating the second derivative of energies [36]. However, development of such a method using a spherical coordinate system is not straightforward, and it will

require one more order expansion of (R)CC operators. This will give three different perturbed (R)CC operators similar to the approach described in Ref. [37] for studying EDMs, and it will lead to handling complicated tensor products to account for the angular momentum couplings in the calculations of the perturbed wave functions.

The remaining part of the paper is organized as follows: In the next section, we give briefly the theory of the atomic dipole polarizability. In Sec. III we describe the RCC and RNCC theories and then discuss and present the results in Sec. IV. We mention our conclusions in Sec. V. Unless stated otherwise, we use atomic units (a.u.) throughout the paper.

II. THEORY

The energy of the ground state of an atom in the presence of an external weak electric field of strength $\vec{\mathcal{E}}$ can be expressed in the perturbation theory as [1,2]

$$E_0(|\vec{\mathcal{E}}|) = E_0(0) - \frac{\alpha_d}{2} |\vec{\mathcal{E}}|^2 - \cdots, \qquad (1)$$

where $E_0(0)$ is the energy of the state in the absence of the electric field and α_d is known as the dipole polarizability of the state. It is obvious from the above expression that α_d can be determined by evaluating the second-order differentiation of $E_0(|\vec{\mathcal{E}}|)$ with a small magnitude of electric field $\vec{\mathcal{E}}$ as

$$\alpha = -\left(\frac{\partial^2 E_0(|\vec{\mathcal{E}}|)}{\partial |\vec{\mathcal{E}}|\partial |\vec{\mathcal{E}}|}\right)_{|\vec{\mathcal{E}}|=0}.$$
(2)

This procedure is known as finite-field approach for evaluating α_d , which involves calculations of $E_0(|\vec{\mathcal{E}}|)$ after including the interaction Hamiltonian $H_{\text{int}} = -\vec{\mathcal{E}} \cdot \vec{D}$ with the atomic Hamiltonian. For achieving numerical stability in the result, it would be necessary to repeat the calculations by considering a number of $|\vec{\mathcal{E}}|$ values.

To estimate α_d in the spherical coordinate system, we can expand the ground state wave function of the atom in the presence of a weak electric field as

$$|\Psi_0\rangle = \left|\Psi_0^{(0)}\right\rangle + |\vec{\mathcal{E}}| \left|\Psi_0^{(1)}\right\rangle + \cdots$$
(3)

with $|\Psi_0^{(0)}\rangle$, $|\Psi_0^{(1)}\rangle$ etc. as the ground state wave function in the absence of the electric field, its first-order correction in the presence of electric field, and so on. From the second-order perturbation expansion, we get

$$\begin{aligned} \alpha_d &= \frac{2}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle} \sum_{I \neq 0} \frac{\langle \Psi_0^{(0)} | D | \Psi_I^{(0)} \rangle \langle \Psi_I^{(0)} | D | \Psi_0^{(0)} \rangle}{E_0^{(0)}(0) - E_I^{(0)}(0)} \\ &= \frac{2}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle} \sum_{I \neq 0} \frac{\left| \langle \Psi_0^{(0)} | D | \Psi_I^{(0)} \rangle \right|^2}{E_0^{(0)}(0) - E_I^{(0)}(0)}, \end{aligned}$$
(4)

where $|\Psi_I^{(0)}\rangle$ are the excited states of the atom with energies $E_I^{(0)}(0)$. Allowing a mathematical formulation, we can express the first-order perturbed wave function of $|\Psi_0^{(0)}\rangle$ due to *D* as

$$\left|\Psi_{0}^{(1)}\right\rangle = \sum_{I \neq 0} \left|\Psi_{I}^{(0)}\right\rangle \frac{\left\langle\Psi_{I}^{(0)}\right| D \left|\Psi_{0}^{(0)}\right\rangle}{E_{0}^{(0)}(0) - E_{I}^{(0)}(0)}.$$
 (5)

Thus, the expression for α_d can be written as [29]

$$\alpha_d = 2 \frac{\langle \Psi_0^{(0)} | D | \Psi_0^{(1)} \rangle}{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle}.$$
 (6)

In the *ab initio* approach, the above first-order perturbed wave function $|\Psi_0^{(1)}\rangle$ can be obtained as the solution to the following inhomogeneous equation [29]:

$$\left(H - E_0^{(0)}\right) \left| \Psi_0^{(1)} \right\rangle = -D \left| \Psi_0^{(0)} \right\rangle. \tag{7}$$

This is equivalent to Dalgarno's approach [16,17] except the fact that the solution for the above first-order perturbed equation has to be obtained for the dipole operator D in place of the interaction Hamiltonian H_{int} . Though the dimensions of \vec{D} and H_{int} are not same, mathematically the solution of $|\Psi_0^{(1)}\rangle$ in Eq. (7) can give rise to the expression for α_d that is equivalent to Eq. (4). Further, we can express

$$\alpha_d = \frac{1}{|\vec{\mathcal{E}}|} \frac{\langle \Psi_0 | D | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle},\tag{8}$$

when $|\Psi_0\rangle$ is evaluated only up to linear in $|\vec{\mathcal{E}}|$ correction.

III. METHODS FOR CALCULATIONS

The exact wave function in the (R)CC theory is expressed as [38]

$$|\Psi_0\rangle = e^{\hat{T}} \left| \Phi_0^N \right\rangle,\tag{9}$$

where $|\Phi_0^N\rangle$ is the reference determinant, obtained using the V^N potential of the $[4d^{10}5s^2]$ configuration of Cd in the Dirac-Hartree-Fock (DHF) method and \hat{T} is known as the (R)CC excitation operator given by

$$\hat{T} = \sum_{k=1}^{N} \hat{T}_{k} = \sum_{\substack{a_{1} < a_{2} \dots < a_{k} \\ i_{1} < i_{2} \dots < i_{k}}} t_{i_{1}i_{2}\dots i_{k}}^{a_{1}a_{2}\dots a_{k}} a_{1}^{+}i_{1}^{-}a_{2}^{+}i_{2}^{-} \cdots a_{k}^{+}i_{k}^{-}, \quad (10)$$

where + and - superscripts on the second quantization operators represent the creation and annihilation of electrons in the virtual (denoted by *a*) and occupied (denoted by *i*) orbitals, respectively, and *t* are the amplitudes in the excitation process in an *N*-electron system. The (R)CC approaches considering up to T_N operators with N = 2, 3, 4, ..., known as the (R)CC singles and doubles (CCSD), (R)CC singles, doubles, and triples (CCSDT), (R)CC singles, doubles, triples, and quadruples (CCSDTQ), etc., methods, constitute a hierarchy, which converges to the exact solution of the wave function in the given one-particle basis set.

The amplitudes *t* of the (R)CC operators are obtained by projecting bra determinants $\langle \Phi_{i_1i_2...i_k}^{a_1a_2...a_k} | e^{-\hat{T}} = \langle \Phi_0^N | a_1^+ i_1^- a_2^+ i_2^- ... a_k^+ i_k^- e^{-\hat{T}}$ from the left of the Schrödinger equation $\hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$, with the ground state energy E_0 , as [24,25]

$$\left\langle \Phi_{i_1i_2\dots i_k}^{a_1a_2\dots a_k} | \overline{H} | \Phi_0^N \right\rangle = E_0 \delta_{k,0} \quad (k = 1, \dots, N), \quad (11)$$

where $\overline{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} = (\hat{H} e^{\hat{T}})_c$ and the subscript *c* means connected terms with the atomic Hamiltonian \hat{H} .

We also perform calculations starting with the V^{N-2} potential for the [4 d^{10}] configuration of Cd in the DHF wave

function calculation by expressing

$$|\Psi_0\rangle = \hat{W}e^{\hat{T}} |\Phi_0^{N-2}\rangle, \qquad (12)$$

with $\hat{T} = \sum_{k=1}^{N-2} \hat{T}_k$, and the doubly valence electron attachment operator $\hat{W} = \sum_{k=1}^{N-2} \hat{W}_k$ is defined as

$$\hat{W} = \sum_{\substack{a_3 < a_4 \cdots < a_k \\ i_3 < i_4 \cdots < i_k}} w_{i_3 i_4 \dots i_k}^{a_3 a_4 \dots a_k} a_1^+ a_2^+ a_3^+ i_3^- \cdots a_k^+ i_k^-, \qquad (13)$$

for the corresponding amplitude w. In this approach, we evaluate the double attachment energy ΔE_{att}^2 in the equationof-motion framework as

$$[\overline{H}, \hat{W}] |\Phi_0^{N-2}\rangle = \Delta E_{\text{att}}^2 \hat{W} |\Phi_0^{N-2}\rangle.$$
(14)

In the finite-field procedure, we first calculate the total energy by considering the DC Hamiltonian, $H \equiv H^{DC}$, of the atom given by

$$H^{\rm DC} = \sum_{i} \left[c \,\alpha_i \cdot \mathbf{p}_i + \beta_i c^2 + V_{\rm nuc}(r_i) + \sum_{j \ge i} \frac{1}{r_{ij}} \right], \ (15)$$

where α and β are the Dirac matrices, *c* is the speed of light, and $V_{\text{nuc}}(r)$ is the nuclear potential energy in the atom. We use the MRCC program [35] to perform the RCC calculations in the finite-field approach. The one-body and two-body integrals were generated using the DIRAC package [39] for the MRCC program. We evaluate energies $E_0(|\vec{\mathcal{E}}|)$ by considering the total Hamiltonian as $H \equiv H^{\text{DC}} + H_{\text{int}}$ using a number of $|\vec{\mathcal{E}}|$ values as 0.0, 0.0005, 0.001, and 0.002 in a.u. to estimate α_d .

In the finite-field approach it is not required to define separate \hat{T} operators of the RCC method in the absence and presence of the interaction Hamiltonian H_{int} in the atomic Hamiltonian. However, it is necessary to do so in the perturbative approach of the RCC method. For this purpose, we express the RCC wave function in this case as

$$|\Psi_{0}\rangle = e^{\hat{T}^{(0)} + |\vec{\mathcal{E}}|\hat{T}^{(1)}|} |\Phi_{0}^{N}\rangle,$$
(16)

where $\hat{T}^{(0)}$ represents for the RCC operator that accounts for electron correlation effects due to the electromagnetic interactions only and $\hat{T}^{(1)}$ takes care of correlation effects due to both the electromagnetic interactions and the *D* operator, respectively, to all orders. In the perturbative expansion, this corresponds to

$$|\Psi_{0}^{(0)}\rangle = e^{\hat{T}^{(0)}}|\Phi_{0}^{N}\rangle$$
 and $|\Psi_{0}^{(1)}\rangle = e^{\hat{T}^{(0)}}\hat{T}^{(1)}|\Phi_{0}^{N}\rangle$. (17)

Both $|\Psi_0^{(0)}\rangle$ and $|\Psi_0^{(1)}\rangle$ can be determined by obtaining amplitudes of the $\hat{T}^{(0)}$ and $\hat{T}^{(1)}$ RCC operators. The amplitude determining equation for $\hat{T}^{(0)}$ is same as Eq. (11) for the DC Hamiltonian. The $\hat{T}^{(1)}$ amplitude-determining equation is given by [8,9,28,31]

$$\left\langle \Phi_{i_1i_2\ldots i_k}^{a_1a_2\ldots a_k} \left| \overline{H}^{\mathrm{DC}} \widehat{T}^{(1)} + \overline{D} \right| \Phi_0^N \right\rangle = 0.$$
(18)

It to be noted that for solving the amplitudes of $\hat{T}^{(0)}$, the projected $\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} |$ determinants have to be even parity, whereas they are the odd parity for the evaluating the $\hat{T}^{(1)}$

amplitudes. In the CCSD method approximation, we denote the RCC operators as

$$\hat{T}^{(0)} = T_1^{(0)} + T_2^{(0)}$$
 and $\hat{T}^{(1)} = T_1^{(1)} + T_2^{(1)}$, (19)

where subscripts 1 and 2 stand for the singles and doubles excitations, respectively.

After obtaining these solutions, we can evaluate α_d , following Eq. (6), as [9,34]

$$\alpha_{d} = \frac{1}{|\vec{\mathcal{E}}|} \frac{\langle \Phi_{0}^{N} | e^{T^{\dagger}} D e^{T} | \Phi_{0}^{N} \rangle}{\langle \Phi_{0}^{N} | e^{T^{\dagger}} e^{T} | \Phi_{0}^{N} \rangle} = \frac{1}{|\vec{\mathcal{E}}|} \langle \Phi_{0}^{N} | e^{T^{\dagger}} D e^{T} | \Phi_{0}^{N} \rangle_{fc}$$
$$= 2 \langle \Phi_{0}^{N} | e^{T^{(0)\dagger}} D e^{T^{(0)}} T^{(1)} | \Phi_{0}^{N} \rangle_{fc}, \qquad (20)$$

where fc stands for the fully contracted terms. The above expression contains a nonterminating series $e^{T^{\dagger(0)}} D e^{T^{(0)}}$. This is computed self-consistently as discussed in Refs. [9,34].

It is worth mentioning two things here. First, the normalization factor in Eq. (20) appears explicitly in the PRCC method, while, as shown above, it *cancels out* in our approach. Second, partial triple excitation is included in the PRCC(T) method by defining a perturbative operator as

$$T_3^{(1),\text{pert}} = \frac{1}{3!} \sum_{abc, pqr} \frac{\left(H^{\text{DC}} T_2^{(1)}\right)_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r} \quad (21)$$

with *a*, *b*, *c* and *p*, *q*, *r* subscripts denoting the occupied and unoccupied orbitals, respectively, and considering it as a part of $T^{(1)}$ in their property-evaluating expression like Eq. (20). To make a similar analysis, we also include the above operator in Eq. (20) in our method to estimate the partial triples effects to the CCSD method and refer to this approach as the CCSD(T) method in order to be consistent with the notation of Ref. [10]. However, it should be noted that the $T_1^{(1)}$ operator is the dominant over $T_2^{(1)}$ in the perturbative approach owing to the one-body form of the *D* operator. Thus, the above approach cannot estimate triples effects rigorously. On the other hand, $T_2^{(0)}$ dominates over the $T_1^{(0)}$ operator due to the two-body nature of the Coulomb interaction. Therefore, it is necessary to include important triples effects through the $T^{(0)}$ operator. We define another triple excitation operator as

$$T_3^{(0),\text{pert}} = \frac{1}{3!} \sum_{abc, pqr} \frac{\left(H^{\text{DC}} T_2^{(0)}\right)_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r} \quad (22)$$

and consider it as a part of the $T_3^{(0)}$ operator. Moreover, we include both the $T_3^{(0),\text{pert}}$ and $T_3^{(1),\text{pert}}$ operators in the amplitude-determining equations as well as in the property-evaluating expression given by Eq. (20). We refer to this procedure as the CCSDTp method in the present work.

For the calculation of α_d using Eq. (20) in the (R)CC method, the bra state was used as the complex conjugate of the ket state. In the (R)NCC method, however, the ket state is determined in the same way as the (R)CC method, but another bra state is used for the corresponding ket state $|\Psi_0\rangle$ and is expressed by [32,33]

$$\left\langle \tilde{\Psi}_{0} \right| = \left\langle \Phi_{0}^{N} \right| (1 + \hat{\Lambda}) e^{-\hat{T}}, \qquad (23)$$

where $\hat{\Lambda}$ is a de-excitation operator defined as

$$\hat{\Lambda} = \sum_{k=1}^{N} \hat{\Lambda}_{k} = \sum_{\substack{i_{1} < i_{2} \cdots < i_{k} \\ a_{1} < a_{2} \cdots < a_{k}}} \tilde{t}_{a_{1}a_{2}\dots a_{k}}^{i_{1}i_{2}\dots i_{k}} i_{1}^{+}a_{1}^{-}i_{2}^{+}a_{2}^{-}\cdots i_{k}^{+}a_{k}^{-}, \quad (24)$$

where \tilde{t} represents amplitude for the corresponding deexcitation operator. The following biorthogonal condition between these two states is evident:

$$\langle \tilde{\Psi}_0 | \Psi_0 \rangle = \left\langle \Phi_0^N \right| (1 + \hat{\Lambda}) e^{-\hat{T}} e^{\hat{T}} \left| \Phi_0^N \right\rangle = 1.$$
 (25)

If $\langle \tilde{\Psi}_0 |$ has the same eigenvalue E_0 of $|\Psi_0\rangle$, then $\langle \tilde{\Psi}_0 |$ can be used in place of $\langle \Psi_0 |$ in the calculation of an expectation value. This choice of bra in the (R)NCC method also satisfies the Hellmann-Feynman equation [33] in contrast to the ordinary (R)CC method. This is attained with the following prerequisite condition:

$$\left\langle \Phi_0^N \left| \hat{\Lambda} \overline{H} \right| \Phi_0^N \right\rangle = 0.$$
 (26)

Indeed, this is the case as per the amplitude-solving equation Eq. (11) of \hat{T} . Now it is necessary to expand the $\hat{\Lambda}$ operator perturbatively like the \hat{T} operator to obtain the first-order perturbed wave function of the bra state for the evaluation of α_d . Thus, we write

$$\begin{split} \langle \tilde{\Psi}_0 | &= \left\langle \tilde{\Psi}_0^{(0)} \right| + |\vec{\mathcal{E}}| \left\langle \tilde{\Psi}_0^{(1)} \right| + \cdots \\ &= \left\langle \Phi_0^N \right| (1 + \Lambda^{(0)} + \lambda \Lambda^{(1)} + \cdots) e^{-(T^0 + |\vec{\mathcal{E}}| T^{(1)})}. \end{split}$$
(27)

Equating to terms of zeroth and linear in $|\vec{\mathcal{E}}|$, we get

$$\tilde{\Psi}_{0}^{(0)} = \left\langle \Phi_{0}^{N} \right| (1 + \Lambda^{(0)}) e^{-T^{(0)}}$$
(28)

and

$$\left| \tilde{\Psi}_{0}^{(1)} \right| = \left| \Phi_{0}^{N} \right| [(1 + \Lambda^{(0)}) T^{(1)} + \Lambda^{(1)}) e^{-T^{(0)}}], \qquad (29)$$

respectively. In order to determine these wave functions, amplitudes of the $\Lambda^{(0)}$ and $\Lambda^{(1)}$ RNCC operators are obtained by solving the following equations [34]:

$$\left\langle \Phi_0^N \left| \Lambda^{(0)} \overline{H}^{\text{DC}} + \overline{H}^{\text{DC}} \right| \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} \right\rangle = 0 \tag{30}$$

and

$$\left\langle \Phi_0^N \middle| [\Lambda^{(1)} \overline{H}^{\text{DC}} + (1 + \Lambda^{(0)}) \{ \overline{D} + (\overline{H}^{\text{DC}} T^{(1)})_c \} \right],$$
$$\times \left| \Phi_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k} \right\rangle = 0$$
(31)

respectively. It can be noticed that the above equations contain more terms than the $T^{(0/1)}$ amplitude-solving equations. Since it contains more nonlinear terms, it means efforts to code the (R)NCC method are more than twice compared to those of the (R)CC method.

Knowing amplitudes of the RCC and RNCC operators, we can evaluate α_d using the expression as [34]

$$\begin{aligned} \alpha_d &= \frac{1}{|\vec{\mathcal{E}}|} \frac{\langle \Psi_0 | D | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \frac{1}{|\vec{\mathcal{E}}|} \frac{\langle \tilde{\Psi}_0 | D | \Psi_0 \rangle}{\langle \tilde{\Psi}_0 | \Psi_0 \rangle} \\ &= \langle \Phi_0^N | (1 + \Lambda) e^{-T} D e^T | \Phi_0^N \rangle_{fc} \\ &= \lambda \langle \Phi_0^N | (1 + \Lambda^{(0)}) \overline{D} T^{(1)} + \Lambda^{(1)} \overline{D} | \Phi_0^N \rangle_{fc}. \end{aligned}$$
(32)

This expression does not have any nonterminating series in contrast to the expression given by Eq. (20), and the normalization of the wave function does not appear in a natural way.

Since *D* is an one-body operator, the above expression will also have fewer terms for the evaluation of α_d as the compensation to the extra calculations for the amplitudes of the $\hat{\Lambda}$ operator. Nevertheless, it is desirable to obtain consistent values for α_d in the approximated RCC and RNCC methods in order to justify reliability in the theoretical calculation of the α_d value. We define the NCC method with the singles and doubles excitations approximation as the NCCSD method and the NCC method with the singles, doubles, and important perturbative triples excitations approximation as the NCCSD(T) method in this work.

We also perform calculations employing many-body perturbation theory considering n orders, say, of residual Coulomb interactions [designated as the MBPT(n) method] to fathom the propagation of electron correlation effects from lower- to all-order many-body methods. In the finite-field approach, the commonly known MBPT(n) approach has been adopted, while we define the unperturbed and the first-order perturbed wave operators in the wave function expansion approach as [8]

$$\left|\Psi_{0}^{(n,0)}\right\rangle = \sum_{\beta=1}^{n} \Omega^{(\beta,0)} \left|\Phi_{0}^{N}\right\rangle \tag{33}$$

and

$$|\Psi_{0}^{(n,1)}\rangle = \sum_{\beta=1}^{n-1} \Omega^{(\beta,1)} |\Phi_{0}^{N}\rangle,$$
 (34)

respectively, where the first superscript index *n* represents order of residual Coulomb interactions and the second superscript 0/1 indicates presence of number of *D* operator in the evaluation of these wave functions. In this framework, we evaluate α_d by [8]

$$\alpha_{d} = 2 \frac{\sum_{\beta=0}^{n-1} \left\langle \Phi_{0}^{N} \right| \Omega^{(n-\beta,0)^{\dagger}} D \Omega^{(\beta,1)} \left| \Phi_{0}^{N} \right\rangle}{\sum_{\beta=0}^{n-1} \left\langle \Phi_{0}^{N} \right| \Omega^{(n-\beta,0)^{\dagger}} \Omega^{(\beta,0)} \left| \Phi_{0}^{N} \right\rangle}.$$
 (35)

It is worth noting that the MBPT(n) method in the perturbative formulation is equivalent to the MBPT(n-1) method of the finite-field approach as both involve up to the same orders of residual Coulomb interactions.

Also by perturbing the DHF orbitals to first order by the D operator and adopting a self-consistent procedure, we can include the core-polarization effects to all orders in the RPA for the evaluation of α_d [9]. In this approach, we express

$$\alpha_d = 2 \langle \Phi_0^N | D \Omega_{\text{RPA}}^{(1)} | \Phi_0^N \rangle, \qquad (36)$$

where the perturbed $\Omega_{\text{RPA}}^{(1)}$ wave operator is defined in our earlier work [9]. From the differences between the results obtained by the RPA and CCSD methods in the perturbative approach, we can find contributions from the noncore-polarization correlations to all orders.

We have estimated the Breit interaction contribution by adding the following term [40] in the atomic Hamiltonian:

$$V_B(r_{ij}) = -\frac{1}{2r_{ij}} \{ \alpha_i \cdot \alpha_j + (\alpha_i \cdot \mathbf{\hat{r}_{ij}})(\alpha_j \cdot \mathbf{\hat{r}_{ij}}) \}.$$
(37)

We also estimate contributions from the lower order vacuum polarization effects using the Uehling $[V_U(r)]$ and Wichmann-Kroll $[V_{WK}(r)]$ potential energies and self-energy effects by including the corresponding potential energies due to the electric and magnetic form factors that have been described in our earlier work [41].

We use Gaussian-type orbitals (GTOs) to construct the electron orbitals in the DHF method. The *k*th GTO in the basis expansion is defined as [42]

$$\chi_k(r) = r^l e^{-\zeta_k r^2},\tag{38}$$

with the orbital quantum number l and for an arbitrary parameter ζ_k . Similarly, we use Dyall's uncontracted correlated consistent double-, triple-, and quadruple- ζ GTO basis sets [43], which are referred to as $X\zeta$, where X = 2, 3, and 4, respectively, in the DIRAC package [39], to generate the one-body and two-body integrals for the MRCC program [35]. Each shell is augmented by two additional diffuse functions (d-aug), and the exponential coefficient of the augmented function is calculated based on the following formula:

$$\zeta_{N+1} = \left[\frac{\zeta_N}{\zeta_{N-1}}\right] \zeta_N,\tag{39}$$

where ζ_N and ζ_{N-1} are the two most diffuse exponents for the respective atomic shells in the original GTOs. For the spherical coordinate system in the perturbative approach of α_d calculation, we construct ζ_k using the even tempering condition defining as

$$\zeta_k = \zeta_0 \eta^{k-1},\tag{40}$$

with two unknown parameters ζ_0 and η . We have chosen the ζ_0 parameter as 0.00715, 0.0057, 0.0072, 0.0052, 0.0072, and 0.0072, and the η parameter as 1.92, 2.04, 1.97, 2.07, 2.54, and 2.54 for orbitals with l = 0, 1, 2, 3, 4, and 5, respectively, after optimizing the single-particle orbital energies.

IV. RESULTS AND DISCUSSION

In Table I we list the α_d values of the Cd atom obtained using various many-body methods and from the measurements. Though we quote in this table two experimental values [30,44], they are obtained from the same experimental setup. The most precise measurement is reported as 49.65(1.65) ea_0^3 [30], while we have been informed [45] that a value of 45.3 ea_0^3 for the static polarizability can be inferred from the preliminary experimental data of dynamic polarizabilities reported using dispersive Fourier transform spectroscopy analysis [44]. Following these measurements, the α_d value of Cd was theoretically studied by Kellö and Sadlej using the nonrelativistic CC theory and the first-order basis sets in the finite-field approach. They obtained the results as $57.39 ea_0^3$ and 55.36 ea_0^3 in the CCSD and CCSD(T) approximations, respectively. After inclusion of quasirelativistic correction through the mass-velocity and Darwin terms, the final CCSD(T) value was quoted as 46.80 ea_0^3 . In fact, this study had suggested for the first time large contributions from the triples and relativistic effects to α_d of Cd. This result was slightly smaller than the above precise measurement. Later, this trend was confirmed by Seth *et al.* [7] employing the CCSD(T) method. But they had used pseudopotential in the two-component relativistic Hamiltonian in their calculations. After few years of this work, a four-component relativistic theory with the semiempirical core potential in the configuration interaction (CICP) approach

TABLE I. A summary of α_d values in ea_0^3 of the Cd atom from various calculations and measurements is presented. We give results from the finite-field approach and perturbing wave function approach in separate columns. As can be seen trends are different in both approaches. Calculations carried out using (R)CC variant methods are supposed to be more reliable. The CCSD and PRCC methods (and their variants) are equivalent but differ only in the implementation technique. Uncertainties are quoted within the parentheses, and references from other works are cited beside the corresponding results. The recommended value from the present work is quoted at the bottom of the table.

	Finite field	Perturbation					
	α_d values from this work						
DHF	63.657	49.612					
MBPT(2)	37.288	50.746					
MBPT(3)		37.345					
RPA		63.685					
CCSD [★]	47.618						
CCSD	48.073	45.494					
NCCSD		44.804					
CCSD(T)		45.586					
CCSDTp		46.289					
NCCSD(T)		45.603					
CCSDT	45.852						
CCSDTQ	45.927						
ΔBreit		0.105					
ΔQED		0.105					
Final	46.015(203)	46.0(5)					
	α_d values from previous calculations						
DHF	62.78 [6], 63.37 [7]	49.647 [<mark>9</mark>]					
MBPT(2)	39.14 [6], 38.52 [7]						
MBPT(3)	45.97 [6], 45.86 [7]	35.728 [<mark>9</mark>]					
MBPT(4)	45.06 [6], 47.10 [7]						
CICP		44.63 [<mark>46</mark>]					
CCSD	48.43 [6], 48.09 [7]	45.898 [<mark>9</mark>]					
CCSD(T)	46.80 [6], 46.25 [7]						
PRCC		49.15 [<mark>10</mark>]					
PRCC(T)		49.24 [<mark>10</mark>]					
Experiment	$49.65 \pm 1.49 \pm 0.16$ [30]						
	45.3 [44,45]						
Recommended	46.02(50)						

was employed and reported a value of 44.63 ea_0^3 [46]. Apart from this, it uses a sum-over-states approach mentioned by Eq. (4) with the V^{N-2} potential. In the same work, the authors also give calculated values of α_d for the Zn and Hg atoms using the CICP method, and the results were found to be quite off from their respective experimental values. In 2014 we had employed our perturbative RCC theory in the CCSD method approximation to estimate its value using the four-component relativistic DC Hamiltonian and accounting for correction from the Breit interaction [9]. The obtained result, 45.86(15) ea_0^3 , was close to the previous CCSD(T) calculations in the finite-field approach [6,7]. Following our work, Chattopadhyay et al. had applied their PRCC(T) method in the four-component relativistic theory and reported the α_d value as 49.24 ea_0^3 [10]. This theoretical result was very close to the experimental value of 49.65(1.65) ea_0^3 . The difference 1

2

3





FIG. 1. Yearwise progress of the α_d value (in ea_0^3) of the Cd atom from various works.

between both the calculations was attributed to the inexactness in the evaluation of the RCC expression of Eq. (20) in these works. In fact, about 15% contribution of the total value is added due to the normalization of the wave function in Ref. [10], while we had omitted this contribution, arguing its cancellation with the disconnected part of the numerator [9]. In this work, we find values from both the CCSD and NCCSD methods in the perturbative approach are very close to each other. In fact, the results are becoming even closer in the CCSD(T) and NCCSD(T) methods. This certainly demonstrates normalization of the wave function does not contribute to the α_d value of the ground state of a closed-shell atomic system in the RCC theory framework. Moreover, our results from the finite-field approach using the CCSDT and CCSDTQ methods with the four-component relativistic DC Hamiltonian are also close to the results of the perturbative CCSD(T) and NCCSD(T) methods. Even though both the procedures, finite-field and perturbative, adopted here are very different, good agreement between the results obtained from these calculations strongly advocate for their reliability. We recommend its value as 46.02(50) ea_0^3 by taking into account various uncertainties as discussed below. We show gradual progress in the experimental and theoretical results over the years in Fig. 1, which clearly indicates most of the theoretical results agree with each other except the values from the PRCC and PRCC(T) methods.

In the Table I we also give corrections from the Breit (given as \triangle Breit) and QED (given as \triangle QED) interactions explicitly by estimating them from RPA. We found these contributions are negligibly small. Therefore, uncertainties to α_d can come mainly from the finite-size basis used in the calculations and contributions from the neglected higher-level excitations. The results obtained by us earlier in Ref. [9] and in this work by the CCSD method differ slightly due to use of different basis functions. We had also estimated contributions from the partial triples but only through the perturbed $T_{2}^{(1),\text{pert}}$ RCC operator including in the amplitude-determining

TABLE II. Demonstration of convergence of result in the perturbative approach with different set of active orbitals in the CCSD

Basis set	Active orbitals	Result
Set I	1-15s, 2-13p, 3-13d, 4-10f	46.034
Set II	1-15s, 2-15p, 3-15d, 4-15f	45.872
Set III	1-17s, 2-17p, 3-17d, 4-16f	45.758
Set IV	1-17s, 2-17p, 3-17d, 4-16f, 5-14g	45.494
Set V	1-21s, 2-21p, 3-21d, 4-18f, 5-16g	45.494
Set VI	1-21s, 2-21p, 3-21d, 4-18f, 5-16g, 6-10h	45.494
Set VII	1–21s, 2–21p, 3–21d, 4–18f, 5–16g, 6–12h	45.494

equations of the CCSD method, which were referred to as the CCSDpT method [9]. In this work, we have estimated these contributions more rigorously after including triples effects through the unperturbed and perturbed RCC operators as well as estimating contributions from the $T_3^{(1),pert}$ RCC operator in Eq. (20). In Table II we demonstrate convergence of the result obtained using the perturbative approach in the CCSD method. After accounting for uncertainties, we find that $\alpha_d =$ 46.0(5) ea_0^3 in the wave function perturbative approach. To assess uncertainties associated with our result obtained in the finite-field approach, we describe here how these calculations were performed systematically up to the CCSDTQ method. Contributions from different levels of excitations and inner core orbital correlations, which was neglected in the CCSDT and CCSDTQ methods, are listed in Table III. Due to limited available computational resources, it was not possible to consider correlations among all the core electrons in the CCSDT and CCSDTQ methods using the MRCC program [35]. Thus, we perform first the CCSD calculations using the 4ξ basis but considering electrons only from the 3d, 4s, 4p, and 4d shells (given as α_d^{CCSD}). Contributions from the inner core orbitals were estimated using the 2ξ basis in the CCSD method and given as α_d^{Core} . We had, then, performed calculations using the 4s, 4p, and 4d orbitals in the CCSD and CCSDT methods. The difference is quoted as triples contribution (given as $\alpha_d^{\rm T}$), and uncertainty due to exclusion of other orbitals in the CCSDT method is estimated by scaling their contributions in the CCSD method. The quadruples effects are estimated using orbitals from the 4d shell alone again with the 2 ξ basis (given as α_d^Q), and the same value has been taken as the maximum possible uncertainty due to the quadruple excitations arising from the other less active inner orbitals. Details of these contributions along with their uncertainties can be found in Table III. Adding all

TABLE III. Breakdown of various contributions to α_d in ea_0^3 of Cd along with their uncertainties from the finite-field approach calculation in this work. Basis functions used in different steps are also mentioned for clarity.

Source	Contribution	Basis
α_d^{CCSD}	47.678 ± 0.096	4ξ
$\Delta \alpha_d^{\mathrm{T}}$	-1.370 ± 0.040	2ξ
$\Delta lpha_d^{ m Q}$	-0.075 ± 0.075	2ξ
$\Delta \alpha_d^{\text{Core}}$	-0.176 ± 0.023	2ξ

these uncertainties together, we anticipate α_d in the finite-field approach as 46.015(203) ea_0^3 . This is in very good agreement with the value obtained in the perturbative wave function approach. Now taking confidently the estimated uncertainties from both procedures, we can recommend optimistically the final α_d value of the Cd atom as 46.02(50) ea_0^3 .

It can also be noticed from Table I that the trends of our finite-field results at the DHF value is very large, and the MBPT(2) result is lower than the CCSD and CCSD(T) values. The reason for the DHF value being large in this case is understandable as it is obtained using the variational approach. Compared to the finite-field approach, the trends obtained at various levels of approximations in the perturbative approach are completely different. In this formalism, the DHF method does not give the largest value since the procedure to estimate the expectation value in this case is not variational. RPA gives a very large value with respect to the DHF result, implying core-polarization correlations are very strong in this system. The RPA value of the perturbative approach is close to the DHF value of the finite-field approach. The reason is the DHF value in the finite-field approach includes orbital relaxation effect, which is explicitly taken care of by RPA in the perturbative approach. As we had stated before, the MBPT(n) method approximation in the perturbative approach is equivalent to the MBPT(n-1) method approximation in the finite-field approach. This is why the MBPT(2) value of the finite-field approach matches the MBPT(3) value of the perturbative approach. The above agreements between both procedures support correct implementation of the methods. Also, a significant difference between the RPA and CCSD results suggest that there are also large contributions that come from the all-order noncorepolarization effects. The final result is the outcome of the cancellation between these two contributions, and it becomes closer to the DHF value of the perturbative approach. Another point to be realized is that the inclusion of contributions from the triples excitations increase the value in the perturbative formalism in contrast to the finite-field approach.

We also compare contributions from different RCC terms (contributions from the H.c. terms are given separately) given in Ref. [10] and from the present work in Table IV. We quote explicitly the contribution due to normalization of the wave function for the result reported in Ref. [10] by multiplying the factor 1.157 listed in that reference. As can be seen, normalization contribution is about 15% in the PRCC method, which is absent in our result. Moreover, termwise contributions also differ in both works. Therefore, the results between both works differ not only due to the inclusion of the contribution from the normalization of the wave function, but also due to different amplitudes of the RCC operators. In Table IV we also compare contributions from the RCC and RNCC terms to understand how the amplitudes in the RNCC method are changed from the RCC method. As can be seen, contributions from the counterterms that replace H.c. terms of the CCSD method in the NCCSD method are significantly different. However, the final CCSD and NCCSD values are found to be very close. This supports the validity of our results from our RCC methods. In addition, close agreement between the results from the CCSD(T) and CCSDTQ methods in the perturbed RCC theory and finite-field approach, respectively, justifies our claim for the high-accuracy α_d calculations using these methods.

TABLE IV. Comparison of contributions to α_d in ea_0^3 among various RCC terms from our CCSD and NCCSD methods with the PRCC method of Ref. [10]. Contributions from the H.c. terms are given separately in order to make a comparative analysis with the contributions from the bra terms of the NCCSD method. Contribution due to normalization factor of the wave function is given explicitly for the PRCC method. Contributions from the higher-order nonlinear terms that are not mentioned here are given combined as "Others." As can be seen, contributions from various RCC terms in the CCSD and PRCC methods differ significantly. Also, the bra terms of the NCCSD method give quite different values than the CCSD method, but the final results agree with each other.

RCC	RCC results		RNCC	RNCC
term	This work	Ref. [10]	term	result
$DT_{1}^{(1)}$	27.423	30.728	$DT_{1}^{(1)}$	27.423
$T_1^{(1)\dagger}D$	27.423	30.728	$\Lambda_1^{(1)} D$	21.837
$T_1^{(0)\dagger} D T_1^{(1)}$	-1.756	-1.554	$\Lambda_1^{(0)} DT_1^{(1)}$	-0.715
$T_1^{(1)\dagger} D T_1^{(0)}$	-1.756	-1.554	$\Lambda_1^{(1)} DT_1^{(0)}$	-1.377
$T_2^{(0)\dagger} D T_1^{(1)}$	-3.594	-1.564	$\Lambda_{2}^{(0)} DT_{1}^{(1)}$	0.0
$T_1^{(1)\dagger} D T_2^{(0)}$	-3.594	-1.564	$\Lambda_1^{(1)} DT_2^{(0)}$	-2.867
$T_1^{(0)\dagger} D T_2^{(1)}$	0.112	0.121	$\Lambda_1^{(0)} DT_2^{(1)}$	0.036
$T_2^{(1)\dagger} D T_1^{(0)}$	0.112	0.121	$\Lambda_{2}^{(1)} DT_{1}^{(0)}$	0.0
$T_2^{(0)\dagger} D T_2^{(1)}$	1.008	1.030	$\Lambda_2^{(0)} DT_2^{(1)}$	0.950
$T_2^{(1)\dagger} D T_2^{(0)}$	1.008	1.030	$\Lambda_2^{(1)} DT_2^{(0)}$	0.981
Others	-0.892	0.04	Others	-1.464
Normalization		-7.717		

V. SUMMARY

We have carried out calculations of α_d of the Cd atom in the finite-field and perturbed RCC approaches. All-order RCC theory is employed at various levels of approximations to ascertain its accuracy. We find our calculation is in good agreement with the previous theoretical results that are obtained by the quasirelativistic and two-component relativistic calculations, but differ substantially from another calculation reported recently using a perturbed RCC approach similar to ours. Based on our analysis, we recommend the value $46.02(50) ea_0^3$ rather than the the available experimental result $49.65 \pm 1.49 \pm 0.16 ea_0^3$. This calls for performing further measurements of α_d of the Cd atom to verify our claim. We also observe that the correlation trends for the finite-field and the perturbed RCC approaches are different.

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