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Correlation trends in the polarizabilities of atoms and ions in the boron, carbon, and zinc homologous sequences of elements

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We investigate the role of electron-correlation effects in calculations of the electric-dipole polarizabilities α of elements belonging to three different groups (12–14) of the periodic table. To understand the propagation of the electron-correlation effects at different levels of approximations, we employ the relativistic many-body methods developed, based on first principles, at mean-field Dirac–Fock (DF), third-order many-body perturbation theory [MBPT(3)], random-phase approximation (RPA), and singly and doubly approximated coupled-cluster methods at the linearized (LCCSD) and nonlinearized (CCSD) levels. We observe a variance in the trends of the contributions of the correlation effects in a particular group of elements through the many-body method used; however, they resemble a similar tendency among the iso-electronic systems. Our CCSD results are within sub-1% agreement with the experimental values which are further ameliorated by including the contributions from the important triple excitations (CCSD$_p$T method).

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I. INTRODUCTION

The static electric-dipole polarizability α of an atomic system is the measure of distortion of the electron cloud when the system is subjected to a stray electric field. Some of the notable applications with the accurate knowledge of α are in studies of new-generation frequency standards, atomic interactions in optical lattices, and quantum information along with many applications in the areas of atomic and molecular physics [1–8]. Various sophisticated experimental techniques have been used to measure α in different atomic systems having their own merits and disadvantages [9–15]. Despite the technological advancements, we have yet to attain high-precision measurements of α in the ground states of many atomic systems. In fact, there are also some systems where no experimental results are yet available. Nevertheless, accurate evaluation of α can serve as a good test of the potential of any many-body method and can be used to peruse the underlying interplay of the electron-correlation effects in their determination.

A seminal work on the calculations of polarizabilities of the many-electron systems in the *ab initio* framework was first introduced by Dalgarno and his collaborators more than about five decades ago [16,17]. Since then, variants of advanced many-body methods have been developed and applied successfully in the same philosophical stratagem to meticulously evaluate this atomic property. Examples of few well-known many-body methods that are often employed in studies of α are the the random-phase approximation (RPA), the coupled-cluster method in linear response theory (CCLRT), the configuration-interaction (CI) method, etc. [18–25]; however, many of these methods are developed by using nonrelativistic mechanics. Lim and coworkers have used the coupled-cluster (CC) methods developed by using Cartesian coordinates for molecular calculations to demonstrate that the relativistic contributions to determine α values are significant, especially in the heavier atomic systems [26,27]. In their CC method, the relativistic effects are accounted for by using a two-component Douglas–Kroll Hamiltonian.

To encompass both the correlation and relativistic effects in determining α for closed-shell atomic systems, we have developed a CC method by considering the Dirac–Coulomb (DC) Hamiltonian described by the four-component atomic wave functions in the spherical coordinate system [28,29]. The ground state α of a number of closed-shell systems have been successfully evaluated by using such a methodology in the last couple of years [30–32]. Moreover, we have set up methods that use third-order many-body perturbation theory [MBPT(3)] and RPA in the relativistic formalism with the intention of including correlation effects through first-principles calculations as was employed in Refs. [16,17]. The focus of the present work is to apprehend the role of the electron-correlation effects by using the above many-body methods that are restricted at different levels of approximations and to demonstrate more precise results by carrying out the large-scale computations involved in some of these methods. We apply these methods to determine the polarizability of B^+, C^{+2}, Al^+, Si^{+2}, Zn, Ga^+, Ge^{+2}, Cd, In^+, and Sn^{+2}, which belong to the transition and post-transition metallic groups of the periodic table. We also explicitly investigate the contributions arising through the nonlinear mathematical expressions constituting the higher-order excitations by setting up intermediate maneuvers to curtail the computational time at the expense of large memory requirements to achieve more accurate results.

The rest 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 many-body methods that are employed in the present work. Before the conclusion, we give our results in Sec. IV and compare them with the other available calculations and measurements. Unless stated otherwise, atomic units (au) are used throughout the paper.

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II. THEORY OF DIPOLE POLARIZABILITY

The leading second-order change in energy of the ground state in an atomic system due to the application of an external electric field $\vec{\mathcal{E}}$ is given by

$$\Delta E = -\tfrac{1}{2}\alpha|\vec{\mathcal{E}}|^2, \tag{1}$$

where α is known as the dipole polarizability of the state. In the mathematical expression, we can write

$$\alpha = -2\frac{\langle\Psi_0^{(0)}|D|\Psi_0^{(1)}\rangle}{\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle}, \tag{2}$$

with $|\Psi_0^{(0)}\rangle$ and $|\Psi_0^{(1)}\rangle$ are the unperturbed and first-order perturbed ground-state wave functions due to the interaction Hamiltonian $\vec{D}\cdot\vec{\mathcal{E}}$ for the dipole operator D. The arduous part of calculating α by using the above expression lies in the evaluation of $|\Psi_0^{(1)}\rangle$ which entails mixing of different parity states. On the other hand, it is sometimes easy to use a sum-over-states approach given by

$$\alpha = -\frac{2}{\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle}\sum_{I\neq 0}\frac{|\langle\Psi_0^{(0)}|D|\Psi_I^{(0)}\rangle|^2}{E_0^{(0)}-E_I^{(0)}}, \tag{3}$$

where I represents summation over all the allowed intermediate states $|\Psi_I^{(0)}\rangle$, and $E_0^{(0)}$ and $E_I^{(0)}$ are the energies of the ground and the corresponding intermediate states, respectively. The above approach is convenient to use if the electric-dipole ($E1$) matrix elements between the ground state and a sufficient number of intermediate states are known or can be calculated to reasonable accuracies. However, it is extremely difficult to determine these matrix elements accurately with confidence because it requires careful handling of a large number of configuration-state functions (CSFs). Furthermore, these contributions are usually estimated by dividing the electronic configurations into a core and few valence electrons [33,34]. This enables us to estimate different contributions separately by using varieties of many-body methods. Obviously, this cannot explain the true behaviors of all the correlation effects in equal footings. In contrast, the present method considers the V^N potential and treats all the associated correlations among the electrons in the uniform manner.

The other famous approach for determining α is by using the finite $\vec{\mathcal{E}}$ perturbation method in which the second-order differentiation of the total energy E_0 of the ground state needs to be estimated in the presence of the electric field (finite field method); i.e.,

$$\alpha = -\left(\frac{\partial^2 E_0(|\vec{\mathcal{E}}|)}{\partial|\vec{\mathcal{E}}|\partial|\vec{\mathcal{E}}|}\right)_{|\vec{\mathcal{E}}|=0}, \tag{4}$$

which requires numerical calculations for a smaller arbitrary value of $\vec{\mathcal{E}}$. This is a typical procedure of calculating α by using the molecular methods based on the Cartesian coordinate systems where the atomic states do not possess definite parity. In contrast, it is a convoluted procedure of determining α of the atomic systems in the relativistic formalism if we wish to describe the method exclusively in the spherical coordinates.

Our methodology to determine α lies in the technique of calculating $|\Psi_0^{(1)}\rangle$ and to supplant the ideology of obtaining it as the solution of the inhomogeneous equation

$$(H - E_0^{(0)})|\Psi_0^{(1)}\rangle = -D|\Psi_0^{(0)}\rangle \tag{5}$$

through the matrix mechanism in the four-component relativistic theory described by the spherical polar coordinate system. By approximating the total wave function of the ground state as $|\Psi_0\rangle \simeq |\Psi_0^{(0)}\rangle + \lambda|\Psi_0^{(1)}\rangle$, we have

$$\alpha = \frac{\langle\Psi_0|D|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}, \tag{6}$$

where λ denotes the order of perturbation in D which has to be set as one to determine α.

III. METHODS OF CALCULATIONS

We consider the Dirac–Fock (DF) wave function $|\Phi_0\rangle$ as the starting point for the MBPT(3), RPA, and CC methods employed. In the CC calculations, we consider only the single and double excitations with the linear-terms approximation (LCCSD method) and accounting for all the nonlinear terms (CCSD method). Details on the DF, MBPT(3), LCCSD, and CCSD methods for the calculation of α are discussed elaborately in our previous work [30]. Here, we explain the RPA approach adopted to evaluate α and to ameliorate the CCSD results by estimating contributions from the important triples excitations perturbatively (CCSD$_p$T method).

In the RPA method, we perturb the ith single-particle wave function $|\phi_i^0\rangle$ of $|\Phi_0\rangle$ and its energy ϵ_i^0 due to the external operator D as

$$|\phi_i^0\rangle \rightarrow |\phi_i^0\rangle + \lambda|\phi_i^1\rangle, \tag{7}$$

$$\epsilon_i^0 \rightarrow \epsilon_i^0 + \lambda\epsilon_i^1, \tag{8}$$

where $|\phi_i^1\rangle$ and ϵ_i^1 are the first-order corrections to $|\phi_i^0\rangle$ and ϵ_i^0, respectively. Owing to the fact that D is an odd-parity operator, $\epsilon_i^1 = 0$. It can be shown that the equation to solve $|\phi_i^1\rangle$ is given by

$$(h_0 + U_{\rm DF} - \epsilon_i^0)|\phi_i^1\rangle = (-D - U_{\rm DF}^1)|\phi_i^0\rangle, \tag{9}$$

where $U_{\rm DF}^1$ is defined by

$$U_{\rm DF}^1|\phi_i^0\rangle = \sum_b^{N_c}\Big(\langle\phi_b^0|\frac{1}{r_{12}}|\phi_b^1\rangle|\phi_i^0\rangle - \langle\phi_b^0|\frac{1}{r_{12}}|\phi_i^0\rangle|\phi_b^1\rangle + \langle\phi_b^1|\frac{1}{r_{12}}|\phi_b^0\rangle|\phi_i^0\rangle - \langle\phi_b^1|\frac{1}{r_{12}}|\phi_i^0\rangle|\phi_b^0\rangle\Big), \tag{10}$$

with N_c representing the number of occupied orbitals present in the system.

We can write the single-particle perturbed wave function in terms of the unperturbed single-particle wave functions as

$$|\phi_i^1\rangle = \sum_{j\neq i} C_i^j|\phi_j^0\rangle, \tag{11}$$

where the C_i^js are the expansion coefficients. In the RPA approach, we write

$$\sum_{j\neq i} C_i^j(h_0 + U_{\rm DF} - \epsilon_j^0)|\phi_j^0\rangle = (-D - U_{\rm DF}^1)|\phi_i^0\rangle, \tag{12}$$

and solve this equation self-consistently to obtain the C_i^j coefficients with infinity orders of contributions from the Coulomb interaction conforming their initial solutions as the above perturbed DF method.

In the Bloch-wave-operator representation [35], we can express $|\Psi_0^{(1)}\rangle = \Omega_{\rm RPA}^{(1)}|\Phi_0\rangle$ with the definition of $\Omega_{\rm RPA}^{(1)}$ as

$$\Omega_{\rm RPA}^{(1)} = \sum_{k}^{\infty}\sum_{p,a}\Omega_{a\to p}^{(k,1)} = \sum_{p,a}\Omega_{a\to p}^{(0,1)} + \sum_{k=1}^{\infty}\sum_{pq,ab}\left\{\frac{\left[\langle pb|\frac{1}{r_{12}}|aq\rangle - \langle pb|\frac{1}{r_{12}}|qa\rangle\right]\Omega_{b\to q}^{(k-1,1)}}{\epsilon_p^0 - \epsilon_a^0} + \frac{\Omega_{b\to q}^{(k-1,1)^\dagger}\left[\langle pq|\frac{1}{r_{12}}|ab\rangle - \langle pq|\frac{1}{r_{12}}|ba\rangle\right]}{\epsilon_p^0 - \epsilon_a^0}\right\}, \quad (13)$$

where the a and p indices represent for the occupied and unoccupied orbitals, respectively, $a \to p$ means replacement of an occupied orbital a from $|\Phi_0\rangle$ by a virtual orbital p which alternatively refers to a singly excited state with respect to $|\Phi_0\rangle$ and $\Omega_{a\to p}^{(0,1)} = \langle\phi_p^0|D|\phi_a^0\rangle/(\epsilon_p^0 - \epsilon_a^0)$. In the above formulation, all order contributions are estimated by evaluating the second term self-consistently. It is obvious from this that the RPA method picks-up a certain class of singly excited configurations congregating the core-polarization correlation effects to all orders.

By using the above RPA wave operator, we evaluate α by

$$\alpha = 2\langle\Phi_0|\Omega^{(0,0)^\dagger}D\Omega_{\rm RPA}^{(1)}|\Phi_0\rangle = 2\langle\Phi_0|D\Omega_{\rm RPA}^{(1)}|\Phi_0\rangle. \quad (14)$$

The impediment of this method is that it encapsulates contributions to $|\Psi_0^{(1)}\rangle$ from the correlation effects due to the Coulomb interaction to all orders, but only from the core-polarization effects through the singly excited configurations. However, it approximates the bra state $|\Psi_0^{(0)}\rangle$ of Eq. (2) to the mean-field wave function $|\Phi_0\rangle$.

The first-order perturbed wave function as in the CC method is given by

$$\left|\Psi_0^{(1)}\right\rangle = e^{T^{(0)}}T^{(1)}|\Phi_0\rangle, \quad (15)$$

where $T^{(0)}$ and $T^{(1)}$ are the excitation operators from the reference state $|\Phi_0\rangle$ that take care of contributions from the Coulomb interactions and Coulomb interactions along with from the perturbed D operator, respectively. We have given relevant diagrams and explained computational procedures to calculate amplitudes of the $T^{(0)}$ operators in Ref. [30] for the CCSD method. The $T^{(1)}$ amplitudes are solved by using the equations

$$\left\langle\Phi_0^\tau\right|\overline{H_{\rm N}^{\rm DC}}T^{(1)}|\Phi_0\rangle = -\left\langle\Phi_0^\tau\right|\overline{D}|\Phi_0\rangle, \quad (16)$$

where $H_{\rm N}^{\rm DC}$ is the normal-ordered DC Hamiltonian, $\overline{O} = (Oe^{T^{(0)}})_{\rm con}$ where "con" means only the connected terms and $|\Phi_0^\tau\rangle$ corresponds to the excited configurations with τ referring to excitations from $|\Phi_0\rangle$. For the LCCSD and CCSD methods ($\tau = 1,2$), the CC operators are denoted by

$$T^{(0)} = T_1^{(0)} + T_2^{(0)} \text{ and } T^{(1)} = T_1^{(1)} + T_2^{(1)}. \quad (17)$$

TABLE I. Universal GTO parameters for all the angular-momentum symmetries in the calculations of DF wave functions for B$^+$, C^{+2}, Al$^+$, and Si^{+2}.

	B$^+$	C^{+2}	Al$^+$	Si^{+2}
η_0	0.00525	0.00425	0.00525	0.00425
ζ	2.73	2.67	2.72	2.67

In order to estimate the dominant contributions from the triple-excited configurations, we define an excitation operator perturbatively in the CC framework as follows:

$$T_3^{(0),\rm pert} = \frac{1}{3!}\sum_{abc}^{pqr}\frac{\left(\overline{H_{\rm N}^{\rm DC}T_2^{(0)}}\right)_{abc}^{pqr}}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \quad (18)$$

and contract it with the D operator to calculate the amplitudes of the $T_2^{(1)}$ perturbed CC operator in a self-consistent procedure considering it in Eq. (16) as part of $\overline{D}$. We refer to this approach as the CCSD$_p$T method in this work.

IV. RESULTS AND DISCUSSION

We use the Gaussian-type orbitals (GTOs) to calculate the single-particle DF wave functions by using

$$\left|\phi_{n,\kappa}^0(r)\right\rangle = \frac{1}{r}\sum_\nu\begin{pmatrix} C_{n,\kappa}^L N_L f_\nu(r)\chi_{\kappa,m} \\ C_{n,-\kappa}^S N_S\left(\frac{d}{dr} + \frac{\kappa}{r}\right)f_\nu(r)\chi_{-\kappa,m}\end{pmatrix}, \quad (19)$$

where n and κ are the principle and angular quantum numbers, respectively, $C_{n,\kappa}^L$ and $C_{n,\kappa}^S$ are the expansion coefficients, N_L and N_S are the normalization constants of the respective large and small components of the wave function, and $\chi_{n,\kappa}$ are the spherical harmonics. Suitable η_ν are chosen to construct the GTOs, $f_\nu(r) = r^l e^{-\eta_\nu r^2}$, to obtain well-behaved radial functions of the orbitals by imposing the even-tempering condition $\eta_\nu = \eta_0\zeta^{\nu-1}$ for the exponents with two guessed parameters η_0 and ζ. We have taken 35 GTOs for each angular-momentum symmetry with the η_0 and ζ parameters given in Tables I and II for different atomic systems.

Furthermore, the radial grid points for the numerical calculations are defined nonuniformly as

$$r_i = r_0[e^{h(i-1)} - 1], \quad (20)$$

where r_0 is the starting point inside the nucleus at which the wave function becomes finite and h is the step size. We consider the Fermi charge-density distribution $\rho(r)$ to calculate the nuclear potential for the electrons as

$$\rho_{\rm nuc}(r) = \frac{\rho_0}{1 + e^{(r-c)/a}}, \quad (21)$$

TABLE II. GTO parameters for the respective angular-momentum symmetries in the calculations of DF wave functions for Zn, Ga$^+$, Ge^{+2}, Cd, In$^+$, and Sn^{+2}.

	s	p	d	f	g
η_0	0.007	0.008	0.0018	0.009	0.007
ζ	2.53	2.55	2.66	2.70	2.77

TABLE III. Comparison of the dipole polarizabilities of the considered systems between the calculations carried out by using the different many-body methods listed in the first column and experimental results. Contributions from the Breit interactions are estimated by using the RPA method and are given as δ_B. Uncertainties in our CCSD$_p$T results are given in parentheses.

Method	B^+	C^{+2}	Al^+	Si^{+2}	Zn
Our work					
DF	8.142	3.282	19.514	9.683	37.317
MBPT(3)	9.720	3.804	21.752	10.482	34.421
RPA	11.374	4.503	26.289	12.476	50.846
LCCSD	11.875	4.886	26.118	12.847	38.739
CCSD	10.413	4.213	24.299	11.893	38.701
CCSD$_p$T	**10.395 (22)**	**4.244 (11)**	**24.26 (5)**	**11.880 (28)**	**38.666 (96)**
δ_B	0.002	0.001	0.007	0.003	0.056
Others					
CHF	9.448 [36]	3.347 [36]			
MP4			24.206 (2.42) [37]		
DK,CASPT2					38.4 [38]
CI	9.975 [39]		24.12 [40], 24.405 [39]	11.567 [33], 11.75 [40]	
CICP	9.64 (3) [41]		24.14 (12) [42]	11.668 [43]	38.12 [44]
CI+MBPT	9.613 [39]		24.030 [39]	11.502 [33]	
CI + all orders	9.624 [39]		24.048 [39]	11.670 (13) [33]	
CCSD					39.27 [45]
CCSD(T)					39.2 (8) [46], 38.01 [45], 37.6 [47]
Expt.			24.20 (75) [48][a]	11.669 (9) [43], 11.666 (4) [49][b]	38.8 (3) [46]

Method	Ga^+	Ge^{+2}	Cd	In^+	Sn^{+2}
Our work					
DF	17.148	10.085	49.647	25.734	16.445
MBPT(3)	15.796	8.884	35.728	18.374	12.095
RPA	21.780	12.011	63.743	29.570	17.941
LCCSD	19.138	11.520	45.086	25.360	15.978
CCSD	18.455	10.890	45.898	24.246	15.537
CCSD$_p$T	**18.441(39)**	**10.883(16)**	**45.86(15)**	**24.11(51)**	**15.526(41)**
δ_B	0.019	0.006	0.104	0.036	0.019
Others					
DK,CASPT2			46.9 [38]		
CI				26.27 [39]	
CICP	17.95 (34) [34]		44.63 [44]		
CI+MBPT				23.83 [39]	
CI+all order				24.01 [39]	
CCSD			48.09 [45]	24.065 (1.70) [50]	
CCSD(T)			46.25 [45], 46.8 [47]		
CCSDTQ				24.14 (8) [51]	
Expt.			49.65 (1.49) [52]		

[a] Estimated from the measured oscillator strengths.

[b] Obtained by reanalyzing data of Ref. [49].

with the normalization constant ρ_0, the half-density radius c and parameter a is related with the skin thickness of the nucleus. In our calculations, we have taken $a \approx 0.5234$ fm and $c = \{[5(0.836A^{1/3} + 0.570)^2 - 7\pi^2 a^2]/3\}^{1/2}$ fm for the atomic mass of the system A. By using these values, we determine ρ_0 as

$$\rho_0 = Z\left[\frac{4}{3}\pi c^3\left(1 + \frac{a^2\pi^2}{c^2} + \frac{6a^3}{c^3}S_3\right)\right]^{-1}, \qquad (22)$$

where Z is the atomic number and $S_3 = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^3} e^{-nc/a}$. We use 1200 grid points, $r_0 = 2 \times 10^{-6}$ au and maximum radial functions up to 500 au with $h = 0.016$ au in the numerical calculations. This defines 258 grid points within the c value to describe the wave functions smoothly both inside and outside the atomic nucleus.

Our final results using all the considered methods along with the available experimental values for Al^+, Si^{+2}, Zn, and Cd and from the other calculations are given in Table III. We recommend our CCSD$_p$T method results are the more accurate results compared to other methods employed by us on the basis of the degree of its capability to include correlation effects than the other approximated methods. To ascertain lucidity in the accuracies of the results from our calculations, we also provide uncertainties associated with our results by estimating neglected contributions from the finite basis size, triples excitations, and Breit interactions. These uncertainties are given in the parentheses alongside the CCSD$_p$T results in the above table. The value that is referred to as the experimental result for Al^+ is not directly obtained from the measurement [48]; rather it is estimated by summing over the experimental values of the oscillator strengths and has a relatively large uncertainty compared to some of the reported calculations. There are two high-precision results reported as the experimental values for the Si^{+2} ion [43,49]; however, the value reported in Ref. [49] is obtained from the analysis of the energy intervals measurement using the resonant Stark ionization spectroscopy (RESIS) technique while the other value [43] is reported by reanalyzing the data of Ref. [49], which is about 0.03% larger than the former value. The only available experimental result of the ground state α of Zn is measured using an interferometric technique by Goebel *et al.* [46]. Similarly there is also one measurement of α available for Cd by using a technique of dispersive Fourier-transform spectroscopy, but the reported uncertainty in this experimental value is comparatively large [52]. Nevertheless, when we compare our CCSD$_p$T results with all these experimental values, they match very well within their reported error bars except for Cd. There are no experimental results available for the other considered ions to compare them against our calculations.

There are also a number of calculations of α available from many groups that used varieties of many-body approaches among which some of them are based on either the lower-order methods or considering the nonrelativistic mechanics. All these results are listed in Table III along with the information about their employed methods. We only discuss a few of these calculations to demonstrate the differences and similarities of the present method with others. An old calculation of α in B^+ was reported by Epstein *et al.* [36] based on the coupled perturbed Hartree–Fock (CHF) method while Cheng *et al.* had employed a configuration interaction method considering a semi-empirical core-polarization potential (CICP) method to evaluate it more precisely [41]. Later, Safronova *et al.* used a combined CI and LCCSD methods (CI + all-order method) to determine α of B^+ ion [39]. However, the CCSD$_p$T result seems to be larger than all other calculations. Our analysis suggests that the differences in these results are mainly due to inclusion of the pair-correlation effects to all orders in our CC method. For the C^{+2} ion, we find only one theoretical result reported by Epstein *et al.*, who use the same CHF method. Our result for C^{+2} is also slightly larger then the value reported by the above calculation. To date, Al^+ is the most precise ion clock in the world [5] for which a couple of high-precision calculations have been reported on the determination of α of this ion by attempting to push down the uncertainty in the blackbody radiation (BBR) shift of the respective ion-clock transition [39,50,51]. Among them, calculations carried out by Mihaly *et al.* is based on the relativistic CC method considering up to quadrupole excitations and the finite-field approach [51]. However, calculations carried out in this work are based on the Cartesian coordinate system and minimizing the energies in the numerical differentiation approach in contrast to the present CCSD$_p$T method, where the matrix elements of D are evaluated in the spherical coordinate system. Calculations reported by Yu *et al.* use the same approach of Ref. [51] but consider a different set of single-particle orbitals [50]. Safronova *et al.* have employed the CI + all-order approach to calculate α for Al^+. There are also other theoretical results that have been reported based on varieties of many-body methods such as CCSD, CICP, CI, etc. both in nonrelativistic and relativistic mechanics [37,40,42]. We find excellent agreement among all the theoretical results. Some of these methods have also been employed to calculate α for Si^{+2} [33,40,42], which are in perfect agreement with the experimental results. However, our CCSD$_p$T value is a little larger than the experimental result. In fact, our estimated contributions from the Breit interaction using the RPA method, given in Table III as δ_B, are about 0.02% to 0.03%, in accordance with the findings by Safronova *et al.* [33]. We found only one more calculation of α in Ga^+ by using the CICP method [34] to compare with our result. Although values from both calculations are very close, they do not agree within their reported uncertainties. Calculations for Cd are reported by many groups, including the latest one by Roos *et al.* who used the the Douglas–Kroll–Hess (DKH) Hamiltonian in their method [38]. Calculations by Ye *et al.* [44] are based on the relativistic formalism in the CICP method. All theoretical results are consistent and show good agreement with each other, suggesting that the experimental result could have been overestimated. Therefore, it is important to have another measurement of the polarizability of Cd to resolve this ambiguity. Again there has also been an effort made for the precise determination of α in In^+ to estimate the BBR shift accurately for its proposed atomic clock transition [39]. Our result agrees nicely with this calculation, but our estimated uncertainty for this result is comparatively big owing to the fact that contributions from the triples are estimated to be large and the calculations exhibit a slight convergence problem with the finite size basis used. As discussed earlier, calculations carried out in Ref. [39] are based on the CI + all-order method. We could not find any other calculations of α of the ground states of the Ge^{+2} and Sn^{+2} ions to make comparative analyses with our results.

To assimilate the underlying roles of the electron-correlation behavior in the evaluation of α of the ground states of the considered systems, we systematically present the calculated values of the dipole polarizabilities in Table III from the DF, MBPT(3), RPA, LCCSD, and CCSD methods. So, the differences between the CCSD results and the values quoted from the CCSD$_p$T method are the contributions from the partial triple excitations. Obviously, these differences are small in magnitude, implying that the contributions from the unaccounted-for higher-order excitations are very small. The lowest-order DF results are smaller in magnitude in the lighter systems but their trends revert in the Cd iso-electronic systems with respect to their corresponding CCSD results. Also, the MBPT(3) results do not follow a steady trend. In the B^+, C^{+2}, Al^+, and Si^{+2} ions, the correlation effects enhance the α values in the MBPT(3) method from their DF results while the MBPT(3) results are smaller than the DF values in the other systems. It is also found that the electron-correlation trends in B^+ and C^{+2} are different than its corresponding iso-electronic neutral Be atom reported by us earlier [30]. For example, the MBPT(3) result for Be is smaller than its DF result, while this trend is the other way around for the B^+ and C^{+2} ions. Similar observations are also noticed in the Mg atom and among their iso-electronic Al^+ and Si^{+2} ions. As has been stated earlier, RPA is a nonperturbative method embracing the core-polarization effects to all orders, but we find that the results are overestimated in this method compared to the CCSD results; more precisely from the experimental values given in Table III. We understand these differences as the contributions from the pair-correlation effects that are absent in the RPA method, but they are accounted for intrinsically to all orders as the integral part of the CCSD method. The role of the pair-correlation effects in the determination of α is verified by examining contributions from the individual MBPT(3) diagrams. From these results, we find that the non-RPA contributions are larger than the differences between the RPA and CCSD results which are reported in Table III. This demonstrates as big cancellations among the lower-order and higher-order pair-correlation contributions in the CCSD method bestowing a modest size of contributions to α, but they appear to be very significant in the heavier systems to attribute accuracies in the results. To demonstrate the roles of the nonlinear terms to procure high-precision α values in the considered ions, we have also given the results from the LCCSD method in the above table. Although LCCSD is an all-order perturbative method, it omits higher-order core-polarization and pair-correlation effects that crop up through the nonlinear terms involving $T^{(0)}T^{(0)}$ or higher powers of $T^{(0)}$. Consequently, this method also overestimates the results like the RPA method. The LCCSD results in B^+ and C^{+2} are larger than the RPA values, but the LCCSD values are smaller than the RPA results in the other cases. This clearly demonstrates intermittent trends of the correlation effects in the determination of α of the systems belonging to a particular group of elements in the periodic table to another through a given many-body method as well as when they are studied by using the methods with different levels of approximations. To manifest contributions from the correlation effects through various many-body methods quantitatively, we portray the results obtained for α in the considered systems by using these methods in a histogram, as shown in Fig. 1. This clearly bespeaks about the lopsided trend in the estimation of α of the considered systems. Again, we also plot the α values of the singly and doubly charged ions separately in Figs. 2 and 3 in order to make a comparative analysis in the propagation of correlation effects through the employed methods in these elements that belong to two different groups of the periodic table. This figure shows that the contributions from the correlation effects in the singly charged and doubly charged ions do not exactly follow similar trends.

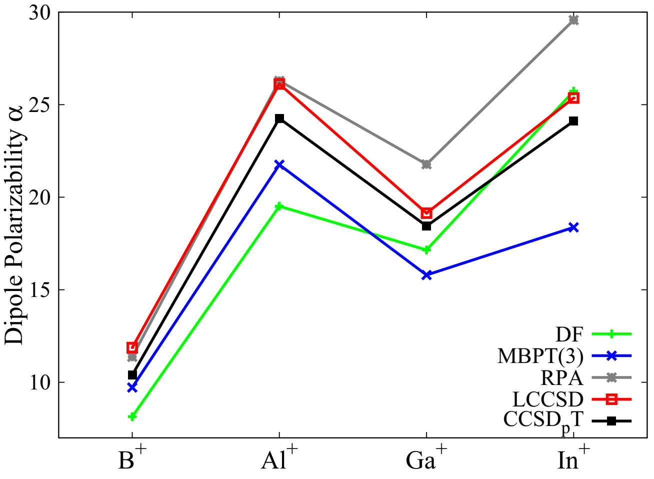

FIG. 2. (Color online) Trends in the calculations of dipole polarizabilities α from the employed many-body methods for the considered singly charged ions.

Finally, we would like to discuss the trends in the correlation effects coming through various CCSD$_p$T terms. We give contributions explicitly from the individual CC terms of linear form and the rest as "Others" in Table IV. Clearly, this table shows that the first term $DT^{(1)}$ gives the dominant contribution because it subsumes all the leading-order core-polarization and pair-correlation effects along with the DF result. The next dominant contributing term is $T_2^{(0)\dagger} DT_1^{(1)}$ which incorporates some contributions from the correlation effects emanated at the MBPT(2) level and possesses opposite signs from the $DT^{(1)}$ contributions, causing cancellations between them. It

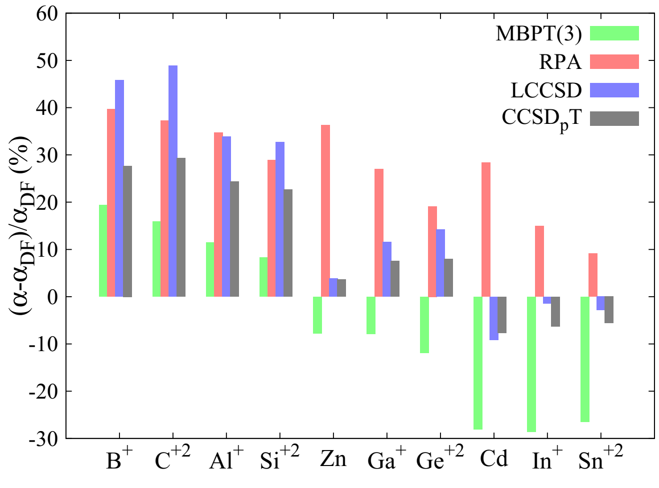

FIG. 1. (Color online) Histogram showing $(\alpha - \alpha_D)/\alpha_D$ (in percent) with different many-body methods against the considered atomic systems.

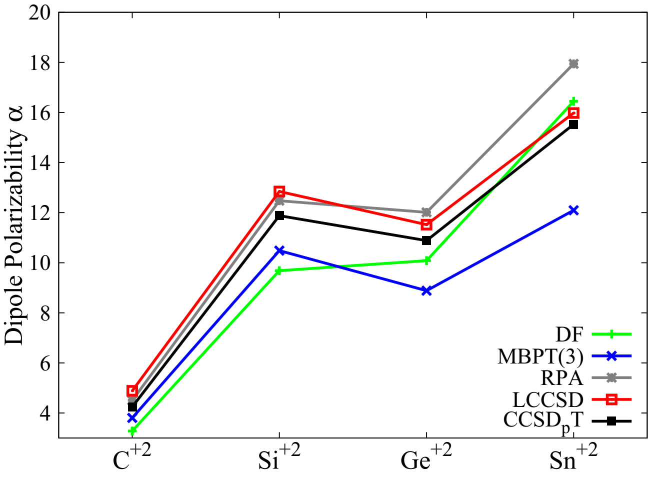

FIG. 3. (Color online) Trends in the calculations of dipole polarizabilities α from the employed many-body methods for the considered doubly charged ions.

TABLE IV. Contributions to α of the ground state of considered atomic systems from various CCSD$_p$T terms.

System	$DT_1^{(1)}$ +c.c.	$T_1^{(0)\dagger} DT_1^{(1)}$ +c.c.	$T_2^{(0)\dagger} DT_1^{(1)}$ +c.c.	$T_2^{(0)\dagger} DT_2^{(1)}$ +c.c.	Others
B$^+$	10.848	−0.194	−1.679	0.774	0.646
C^{+2}	4.392	−0.047	−0.668	0.274	0.29
Al$^+$	25.855	−0.519	−3.166	1.523	0.567
Si^{+2}	12.589	−0.160	−1.475	0.666	0.260
Zn	43.812	−2.458	−5.286	2.047	0.551
Ga$^+$	20.223	−0.545	−2.409	0.837	0.335
Ge^{+2}	11.846	−0.198	−1.363	0.476	0.122
Cd	52.963	−3.346	−6.985	2.262	0.962
In$^+$	27.134	−0.882	−3.647	1.064	0.441
Sn^{+2}	17.249	−0.366	−2.286	0.603	0.326

is also worth mentioning that contributions coming from the $T_2^{(0)\dagger} DT_2^{(1)}$ term corresponds to the higher-order perturbation and also accounts contributions from the doubly excited intermediate states. As seen from the table, these contributions are non-negligible suggesting that they should also be estimated accurately for accomplishing high-precision results and the sum-over-states approach may not be able to augment these contributions suitably in the considered systems. Contributions from the other nonlinear CC terms at the final property evaluation level seem to be slender, although the differences between the LCCSD and CCSD results emphasize their importance for accurate calculations of the atomic wave functions in the considered systems.

V. CONCLUSION

We employed a variety of many-body methods to incorporate the correlation effects at different levels of approximations to unravel the role of the correlation effects and follow up their trends to achieve very accurate calculations of the dipole polarizabilities of three groups of elements in the periodic table. We find the trends in which the correlation effects behave with respect to the mean-field level of the calculations are different in one set of iso-electronic systems to another when they are studied by using a given many-body method. Also, our calculations reveal that inclusion of both the core-polarization and pair-correlation effects to all orders are equally important for securing high-precision dipole polarizabilities in the considered systems and the core-polarization effects play the pivotal role among them. Contributions from the doubly excited states are found to be non-negligible, implying that a sum-over-states approach may not be pertinent to carry out these studies. Our results obtained using the singles, doubles, and important triples approximation in the coupled-cluster method agree very well with the available experimental values in some of the systems except for cadmium and doubly ionized silicon. In fact none of the reported theoretical results for cadmium agree with the measurement; however, there seems to be reasonable agreement among all theoretical results. This argues for further experimental investigation of the cadmium result. In a few systems, there are no experimental results available yet and the precise reported values in the present work can serve as exemples for their prospective measurements.

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[1] S. A. Diddams *et al.*, Science **293**, 825 (2001).
[2] P. Gill *et al.*, Meas. Sci. Technol. **14**, 1174 (2003).
[3] P. Gill, Metrologia **42**, S125 (2005).
[4] T. Rosenband *et al.*, Phys. Rev. Lett. **98**, 220801 (2007).
[5] T. Rosenband *et al.*, Science **319**, 1808 (2008).
[6] K. D. Bonin and V. V. Kresin, *Electric Dipole Polarizabilities of Atoms, Molecules and Clusters* (World Scientific, Singapore, 1997).
[7] C. J. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases* (Cambridge University Press, Cambridge, 2008).
[8] A. A. Madej and J. E. Bernard, in *Frequency Measurement and Control*, in Topics in Applied Physics, edited by Andre N. Luiten (Springer, Berlin, 2001), Vol. 79, p. 153195.
[9] W. D. Hall and J. C. Zorn, Phys. Rev. A **10**, 1141 (1974).
[10] R. W. Molof, H. L. Schwartz, T. M. Miller, and B. Bederson, Phys. Rev. A **10**, 1131 (1974).
[11] T. M. Miller and B. Bederson, Phys. Rev. A **14**, 1572 (1976).
[12] H. L. Schwartz, T. M. Miller, and B. Bederson, Phys. Rev. A **10**, 1924 (1974).
[13] A. D. Cronin, J. Schmiedmayer, and D. E. Pritchard, Rev. Mod. Phys. **81**, 1051 (2009).
[14] C. R. Ekstrom, J. Schmiedmayer, M. S. Chapman, T. D. Hammond, and D. E. Pritchard, Phys. Rev. A **51**, 3883 (1995).
[15] J. M. Amini and H. Gould, Phys. Rev. Lett. **91**, 153001 (2003).
[16] A. Dalgarno, Adv. Phys. **11**, 281 (1962).
[17] A. Dalgarno and H. A. J. McIntyre, Proc. Phys. Soc., London **85**, 47 (1965).
[18] H. J. Monkhorst, Int. J. Quantum Chem. **12(S11)**, 421 (1977).
[19] E. Dalgaard and H. J. Monkhorst, Phys. Rev. A **28**, 1217 (1983).
[20] B. Kundu and D. Mukherjee, Chem. Phys. Lett. **179**, 468 (1991).
[21] H. Koch, R. Kobayashi, A. Sánchez de Merás, and P. Jørgensen, J. Chem. Phys. **100**, 4393 (1994).
[22] R. Kobayashi, H. Koch, and P. Jørgensen, J. Chem. Phys. **101**, 4956 (1994).
[23] B. Datta, P. Sen, and D. Mukherjee, J. Phys. Chem. **99**, 6441 (1995).
[24] K. Kowalski, J. R. Hammond, and W. A. de Jong, J. Chem. Phys. **127**, 164105 (2007).
[25] J. R. Hammond, Ph.D. thesis, The University of Chicago, 2009 (unpublished).
[26] I. S. Lim and P. Schwerdtfeger, Phys. Rev. A **70**, 062501 (2004).

[27] I. S. Lim, H. Stoll, and P. Schwerdtfeger, J. Chem. Phys. **124**, 034107 (2006).
[28] B. K. Sahoo, Chem. Phys. Lett. **448**, 144 (2007).
[29] B. K. Sahoo and B. P. Das, Phys. Rev. A **77**, 062516 (2008).
[30] Y. Singh, B. K. Sahoo, and B. P. Das, Phys. Rev. A **88**, 062504 (2013).
[31] S. Chattopadhyay, B. K. Mani, and D. Angom, Phys. Rev. A **87**, 062504 (2013).
[32] S. Chattopadhyay, B. K. Mani, and D. Angom, Phys. Rev. A **89**, 022506 (2014).
[33] M. S. Safronova, S. G. Porsev, M. G. Kozlov, and C. W. Clark, Phys. Rev. A **85**, 052506 (2012).
[34] Y. Cheng and J. Mitroy, J. Phys. B: At., Mol. Opt. Phys. **46**, 185004 (2013).
[35] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).
[36] S. T. Epstein and R. E. Johnson, J. Chem. Phys. **47**, 2275 (1967).
[37] E. F. Archibong and A. J. Thakkar, Phys. Rev. A **44**, 5478 (1991).
[38] B. O. Roos, R. Lindh, P-Å. Malmqvist, V. Veryazov, and P.-O. Widmark, J. Phys. Chem. A **109**, 6575 (2005).
[39] M. S. Safronova, M. G. Kozlov, and C. W. Clark, Phys. Rev. Lett. **107**, 143006 (2011).
[40] L. Hamonou and A. Hibbert, J. Phys. B: At., Mol. Opt. Phys. **41**, 245004 (2008).
[41] Y. Cheng and J. Mitroy, Phys. Rev. A **86**, 052505 (2012).
[42] J. Mitroy, J. Y. Zhang, M. W. J. Bromley, and K. G. Rollin, Eur. Phys. J. D **53**, 15 (2009).
[43] J. Mitroy, Phys. Rev. A **78**, 052515 (2008).
[44] A. Ye and G. Wang, Phys. Rev. A **78**, 014502 (2008).
[45] M. Seth, P. Schwerdtfeger, and M. Dolg, J. Chem. Phys. **106**, 3623 (1997).
[46] D. Goebel, U. Hohm, and G. Maroulis, Phys. Rev. A **54**, 1973 (1996).
[47] V. Kellö and A. J. Sadlej, Theor. Chim. Acta **91**, 353 (1995).
[48] N. Reshetnikov, L. J. Curtis, M. S. Brown, and R. E. Irving, Phys. Scr. **77**, 015301 (2008).
[49] R. A. Komara, M. A. Gearba, C. W. Fehrenbach, and S. R. Lundeen, J. Phys. B: At., Mol. Opt. Phys. **38**, S87 (2005).
[50] Y. M. Yu, B. B. Suo, and H. Fan, Phys. Rev. A **88**, 052518 (2013).
[51] M. Kállay, H. S. Nataraj, B. K. Sahoo, B. P. Das, and L. Visscher, Phys. Rev. A **83**, 030503(R) (2011).
[52] D. Goebel and U. Hohm, Phys. Rev. A **52**, 3691 (1995).