Determination of the dipole polarizability of the alkali-metal negative ions

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We present electric dipole polarizabilities (α_d) of the alkali-metal negative ions, from H$^-$ to Fr$^-$, by employing four-component relativistic many-body methods. Differences in the results are shown by considering Dirac-Coulomb (DC) Hamiltonian, DC Hamiltonian with the Breit interaction, and DC Hamiltonian with the lower-order quantum electrodynamics interactions. At first, these interactions are included self-consistently in the Dirac-Hartree-Fock (DHF) method, and then electron correlation effects are incorporated over the DHF wave functions in the second-order many-body perturbation theory, random phase approximation, and coupled-cluster (CC) theory. Roles of electron correlation effects and relativistic corrections are analyzed using the above many-body methods with size of the ions. We finally quote precise values of α_d of the above negative ions by estimating uncertainties to the CC results, and compare them with other calculations wherever available.

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I. INTRODUCTION

There are several experimental techniques available to produce negative alkali-metal ions in the laboratory. The techniques to produce these ions have been engineered time to time over the several decades [1,2]. Electron affinities (EAs) of these systems have been measured very precisely [3–7]. Photoabsorption spectra of these ions have also been extensively investigated both theoretically and experimentally, in order to understand their structures [8–11]. Starting from the 1970s, a series of studies on the photodetachment of negative lithium (Li$^-$), sodium (Na$^-$), and potassium (K$^-$) ions have been conducted by several groups [5,12–15]. Theoretical results from these lighter ions were in excellent agreement with the corresponding experimental values. By solving a set of coupled equations, Norcross had predicted the existence of bound excited states in negative alkali-metal ions [16]. This was later conformed by Greene [17], by applying a combined approach of jj coupling in the R-matrix method and generalized quantum-defect theory while attempting to describe photodetachment spectra of negative rubidium (Rb$^-$), cesium (Cs$^-$), and francium (Fr$^-$) ions. Later, another study [18] disproved the existence of such states in these ions by reanalyzing the calculations using the Dirac R-matrix method. Instead, the authors of the work suggested that the lowest excited state of the above alkali-metal negative ions is a multiplet of ${}^3P^o_J$-shape resonance. This work clearly demonstrated the importance of relativistic effects for accurate calculations of atomic properties in these ions. Similarly, several studies on negative hydrogen (H$^-$) ion have been carried out [19,20], and its applications [21,22] and production sources are well known to the physicists [23,24].

Apart from EAs and photodetachment cross sections, there is scarcity in the atomic data of the negative alkali-metal ions. Alkali-metal atoms have a closed shell and a valence orbital in their electronic configurations. Owing to this, it is relatively simpler to calculate atomic wave functions of these atoms. However, it is challenging to determine atomic wave functions of the alkaline earth-metal atoms due to strong electron correlations among the valence electrons in such systems. The negative alkali-metal ions are isoelectronic to the alkaline earth-metal atoms.

Electric dipole polarizability (α_d) is a very useful property of any atomic system. This quantity has been measured very precisely [25] in the alkali-metal atoms as well as in the singly charged positive alkaline earth-metal ions, and with reasonable accuracy in the alkaline earth-metal atoms. However, there has not been a single measurement of α_d carried out thus far in any of the negative alkali-metal ions due to difficulties in setting up their experiments. There are no full relativistic calculations of α_d available in these ions, and only a few nonrelativistic calculations have been reported in the lighter H$^-$ [26–28], Li$^-$ [13,29,30], Na$^-$ [13], and K$^-$[13] ions. Except the high-precision calculations in H$^-$, the reported values of other ions are not very reliable.

Calculations of α_d in the alkali-metal atoms are in very good agreement with the experiments [31,32]. The reason for this is that one can easily use their experimental energies and electric dipole (E1) matrix elements inferring from the lifetime measurements of their atomic states in the evaluation of α_d values using the sum-over-states approach. It is possible to adopt the sum-over-states approach in these atoms because they possess a large number of bound states in contrast to the negative alkali-metal ions. *Ab initio* procedures demonstrate that the electron correlation and the relativistic effects are pronounced, and they need to be accounted for, in order to determine α_d values of alkaline earth-metal atoms [33–35], which are isoelectronic systems to the negative alkali-metal ions. A few calculations of the α_d values of some heavier negative ions of the coinage metal atoms have been reported by Sadlej and coworkers [36,37], by employing a variety of methods including the coupled-cluster (CC) theory. In another study by Schwerdtfeger and Bowmaker [38], these

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quantities were also evaluated by using total angular momentum j-averaged relativistic pseudopotentials in the configuration interaction (CI) method. These works highlight about the unusually large electron correlation and relativistic effects in the determination of α_d values in the negative ions compared to their counterisoelectronic neutral atoms. But the relativistic effects were estimated only approximately in these calculations. Recently, we had evaluated α_d values of Cl^- and Au^- by applying a number of relativistic many-body methods at different levels of approximation to demonstrate the roles of electron correlations for their accurate determination. Here, we intend to determine α_d values of all the negative alkali-metal ions very accurately.

II. THEORY

It is not possible to adopt a finite-field (FF) approach to determine α_d of atomic states by preserving spherical symmetry property and treating parity as a good quantum number. Thus, the spherical symmetry of the systems is exploited in Refs. [36–38] in order to adopt the FF procedure for the determination of α_d of negative ions. Also, the FF approach introduces large uncertainty to the calculation of α_d, which stems from both numerical differentiation as well as neglecting higher-order perturbation corrections in the evaluation of the second-order perturbed energy due to external electric field, in a brute-force manner. To overcome these problems in the determination of α_d while retaining spherical symmetry behavior of atomic orbitals, we follow a perturbative approach in which the total Hamiltonian of the system is defined in the presence of a weak external electric field $\vec{\mathcal{E}}$ as $H = H_{\text{at}} + \vec{D} \cdot \vec{\mathcal{E}}$ with the atomic Hamiltonian H_{at} and electric dipole operator D in a similar framework as Dalgarno and Lewis [39]. In such case, the wave function and energy of an atomic state can be expressed as

$$|\Psi_0\rangle = \big|\Psi_0^{(0)}\big\rangle + |\vec{\mathcal{E}}|\big|\Psi_0^{(1)}\big\rangle + \cdots, \tag{1}$$

and

$$E_0 = E_0^{(0)} + |\vec{\mathcal{E}}|E_0^{(1)} + \tfrac{1}{2}|\vec{\mathcal{E}}|^2 E_0^{(2)} \cdots, \tag{2}$$

respectively, where superscripts (0), (1), etc., denote order of $\vec{\mathcal{E}}$ in the expansion. Since D is an odd-parity operator, $E_0^{(1)} = 0$ and the second-order energy is traditionally given by $E_0^{(2)} \equiv \alpha_d$. It follows that α_d can be evaluated in the perturbative approach as [34]

$$\alpha_d = 2\frac{\big\langle\Psi_0^{(0)}\big|D\big|\Psi_0^{(1)}\big\rangle}{\big\langle\Psi_0^{(0)}\big|\Psi_0^{(0)}\big\rangle}. \tag{3}$$

Thus, it is imperative to determine both the unperturbed wave function $|\Psi_0^{(0)}\rangle$ of H_{at} and the first-order perturbed wave function $|\Psi_0^{(1)}\rangle$ due to D very reliably for an accurate evaluation of α_d. Instead of using the sum-over-states approach to determine $|\Psi_0^{(1)}\rangle$, we would like to solve it as the solution to the first-order inhomogeneous perturbed equation given by

$$\big(H_{\text{at}} - E_0^{(0)}\big)\big|\Psi_0^{(1)}\big\rangle = -D\big|\Psi_0^{(0)}\big\rangle. \tag{4}$$

Though the solution of this equation appears to be similar to the procedure adopted by Dalgarno and Lewis [39], it can be kept in mind that we only obtain the first-order wave function $|\Psi_0^{(1)}\rangle$ for Eq. (3) instead of determining $E_0^{(2)}$ directly.

III. METHODS FOR CALCULATIONS

The many-electron atomic wave function can be obtained by

$$|\Psi_0\rangle = \Omega_0|\Phi_0\rangle, \tag{5}$$

where $|\Phi_0\rangle$ is a mean-field wave function, which is obtained here by the Dirac-Hartree-Fock (DHF) method, and Ω_0 is known as the wave operator that is responsible for accounting for electron correlation effects due to the interactions that are neglected in the determination of $|\Phi_0\rangle$. Likewise, for the wave function, we can expand Ω_0 in the presence of weak electric field $\vec{\mathcal{E}}$ as

$$\Omega_0 = \Omega_0^{(0)} + |\vec{\mathcal{E}}|\Omega_0^{(1)} + \cdots. \tag{6}$$

Using this, we can write the unperturbed and the first-order perturbed wave function as

$$\big|\Psi_0^{(0)}\big\rangle = \Omega_0^{(0)}|\Phi_0\rangle \quad \text{and} \quad \big|\Psi_0^{(1)}\big\rangle = \Omega_0^{(1)}|\Phi_0\rangle. \tag{7}$$

In the n^{th}-order perturbation theory, we express [35]

$$\Omega^{(0)} = \sum_{k=0}^{n} \Omega^{(k,0)} \quad \text{and} \quad \Omega^{(1)} = \sum_{k=0}^{n-1} \Omega^{(k,1)}, \tag{8}$$

with $\Omega^{(0,0)} = 1$, $\Omega^{(1,0)} = 0$, and $\Omega^{(0,1)} = \sum_{p,a} \frac{\langle\Phi_a^p|D|\Phi_0\rangle}{\epsilon_a^{(0)} - \epsilon_p^{(0)}}$ for all the occupied orbitals denoted by the index a and unoccupied orbitals denoted by the index p. In the second-order relativistic perturbation theory [RMBPT(2) method] that accounts for the lowest-order electron correlation effects [35] in the many-body theory, it corresponds to $n = 1$ in the above summations.

We present results from two all-order many-body methods: relativistic random-phase approximation (RRPA) and relativistic CC (RCC) theory. The RCC theory incorporates electron correlation effects more rigorously, while RRPA has traditionally been employed to capture these effects due to the core polarization only, which can be done to all orders in a computationally much less expensive way. The correlation effects arising through RRPA also represent the orbital relaxation effects that arise naturally in the mixed-parity orbitals of the DHF method in the FF procedure. In our RRPA implementation [40,41], they are contained in $\Omega_0^{(0)} = 1$ and $\Omega^{(1)} = \sum_{k=0}^{\infty} \sum_{p,a} \Omega_{a\to p}^{(k,1)}$. Here, $a \to p$ 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 $|\Phi_0\rangle$. The RCC theory implicitly includes correlation effects arising through RRPA along with other correlation effects such as pair-correlation effects to all orders and is known as the gold standard method of many-body theory for its capabilities of producing accurate results in multielectron systems. In this theory, the wave operators are given by [40,42]

$$\Omega^{(0)} = e^{T^{(0)}} \quad \text{and} \quad \Omega^{(1)} = e^{T^{(0)}} T^{(1)}, \tag{9}$$

respectively. We consider only singles and doubles excitations in the RCC calculations (RCCSD method) by expressing

$$T^{(0)} = T_1^{(0)} + T_2^{(0)} \quad \text{and} \quad T^{(1)} = T_1^{(1)} + T_2^{(1)}, \tag{10}$$

where subscripts (1) and (2) denote the level of excitation. In this method, α_d determined as

$$\alpha_d = 2\frac{\langle\Phi_0|\Omega^{(0)\dagger}D\Omega^{(1)}|\Phi_0\rangle}{\langle\Phi_0|\Omega^{(0)\dagger}\Omega^{(0)}|\Phi_0\rangle} = 2\langle\Phi_0|(\overbrace{D^{(0)}}\,T^{(1)})_c|\Phi_0\rangle, \quad (11)$$

where $\overbrace{D^{(0)}} = e^{T^{\dagger(0)}}De^{T^{(0)}}$ is a nontruncating series. We have adopted an iterative procedure to take into account contributions from this nonterminating series self-consistently, as described in our earlier works on α_d calculations in the closed-shell atoms [42,43].

For the evaluation of $|\Psi_0\rangle$, we consider first the Dirac-Coulomb (DC) Hamiltonian, given by

$$H^{\rm DC} = \sum_i [c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i + (\beta_i - 1)c^2 + V_n(r_i)] + \sum_{i,j>i}\frac{1}{r_{ij}}, \quad (12)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β are the usual Dirac matrices, $\mathbf{p}_i$ is the single-particle momentum operator, $V_n(r_i)$ denotes the nuclear potential, and $\frac{1}{r_{ij}}$ represents the Coulomb potential between two electrons located at the $i^{\rm th}$ and $j^{\rm th}$ positions. We estimate the Breit interaction by using the Dirac-Coulomb-Breit (DCB) Hamiltonian ($H^{\rm DCB} = H^{\rm DC} + V^B$) by defining the potential,

$$V^B = -\sum_{j>i}\frac{[\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i\cdot\hat{\mathbf{r}}_{\mathbf{ij}})(\boldsymbol{\alpha}_j\cdot\hat{\mathbf{r}}_{\mathbf{ij}})]}{2r_{ij}}, \quad (13)$$

where $\hat{\mathbf{r}}_{\mathbf{ij}}$ is the unit vector along $\mathbf{r}_{\mathbf{ij}}$. Similarly, contributions from the quantum electrodynamics (QED) effects are estimated using the Dirac-Coulomb–QED (DCQ) Hamiltonian ($H^{\rm DCQ} = H^{\rm DC} + V^Q$) by considering $V^Q = V_{\rm VP} + V_{\rm SE}$ with the vacuum polarization interaction potential $V_{\rm VP}$ and the self-energy interaction potential $V_{\rm SE}$. We use the model potentials for $V_{\rm VP}$ and $V_{\rm SE}$ as defined in Refs. [44,45].

We use Gaussian-type orbitals (GTOs), as defined in Ref. [46], to obtain the single-particle orbitals. We have considered orbitals up to h-angular momentum symmetry (orbital angular momentum $l = 5$) to carry out all the calculations. We have used 40 GTOs for each symmetry to obtain the DHF wave function. However, we have frozen high-lying orbitals beyond energy 3000 atomic units (a.u.) to account for electron correlation effects through the employed many-body methods. We have verified contributions from these neglected orbitals using RRPA and they are found to be extremely small. These contributions are included in the uncertainty estimation later.

TABLE I. Calculated α_d values (in ea_0^3) of the negative alkali-metal ions from the DHF, RMBPT(2), RRPA, and RCCSD methods. Results from the DC, DCB, and DCQ Hamiltonians are listed separately to highlight the roles of Breit and QED interactions in the determination of α_d of the above ions.

Method	DC	DCB	DCQ
	H^- ion		
DHF	44.41	44.61	44.41
RMBPT(2)	66.35	66.35	66.35
RRPA	91.13	91.13	91.13
RCCSD	206.14	206.16	206.15
	Li^- ion		
DHF	500.90	500.94	500.91
RMBPT(2)	764.68	764.74	764.70
RRPA	1176.68	1176.76	1176.70
RCCSD	794.06	794.08	794.07
	Na^- ion		
DHF	605.91	606.00	606.03
RMBPT(2)	923.52	923.66	923.72
RRPA	1447.69	1447.92	1448.01
RCCSD	952.54	952.63	952.67
	K^- ion		
DHF	1053.39	1053.58	1053.89
RMBPT(2)	1586.91	1587.18	1587.68
RRPA	2565.41	2565.88	2566.66
RCCSD	1353.69	1353.84	1354.19
	Rb^- ion		
DHF	1214.16	1214.43	1215.40
RMBPT(2)	1816.88	1817.22	1818.75
RRPA	2968.55	2969.21	2971.66
RCCSD	1506.57	1506.75	1507.88
	Cs^- ion		
DHF	1534.15	1534.48	1537.06
RMBPT(2)	2271.42	2271.78	2275.81
RRPA	3770.88	3771.71	3778.25
RCCSD	1800.42	1800.54	1803.59
	Fr^- ion		
DHF	1357.23	1357.78	1357.33
RMBPT(2)	1990.66	1991.21	1990.77
RRPA	3308.49	3309.76	3308.69
RCCSD	1619.04	1619.16	1619.03

IV. RESULTS AND DISCUSSION

In Table I, we present α_d values of all the negative alkali-metal ions in a.u., ea_0^3, from the DHF, RMBPT(2), RRPA, and RCCSD methods using the DC, DCB, and DCQ Hamiltonians. It can be seen from this table that the DHF method gives lower values in all the ions, and the electron correlation contributions enhance their magnitudes. Except in the H^- ion, the RRPA yields the largest value for each ion. The results from the RMBPT(2) method are also larger than the values obtained using the RCCSD method, except in the lighter H^- and Li^- ions. It can be recalled that the results from the RMBPT(2) method are actually the lowest-order core-polarization terms and results from RRPA are the contributions from the all-order core-polarization effects including the DHF value. Thus, the huge differences between the results from the RMBPT(2) and RRPA methods imply that the core-polarization effects arising through the higher-order perturbation theory are quite strong in the negative alkali-metal ions. Since RRPA values are the mean-field contributions (i.e., DHF values) in the FF procedure, it would require immense efforts to attain convergence in the values by evaluating the property in the FF framework than in the perturbation approach through a many-body method as adopted here. Nonetheless, the RCCSD method implicitly

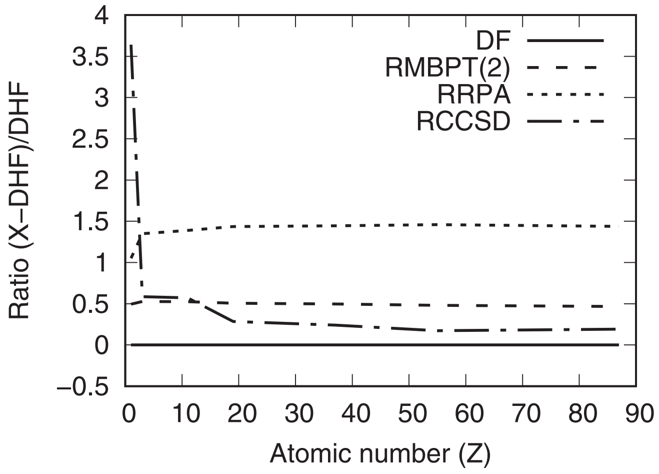

FIG. 1. (X-DHF)/DHF values, where X represents contributions from the DHF, RMBPT(2), RRPA, and RCCSD methods, against the atomic number (Z) of the negative alkali-metal ions. Values from the DHF method act as reference (zero line on x axis) for comparison of correlation contributions incorporated at different levels of many-body methods.

incorporates the RRPA contributions in addition to correlation effects due to non-RRPA effects such as those from the pair correlations. Large differences between the RRPA and RCCSD results indicate that the non-RRPA contributions are also substantially large, but with the opposite sign than that of the RRPA contributions. As a result, the final results in the RCCSD method come out to be smaller than the RMBPT(2) values in the heavier ions.

The electron correlation effects in the simplest two-electron H$^-$ ion, which is analogous to the He atom, shows a unique trend than the rest of the ions. In this system, the inclusion of electron correlation effects increases the α_d values gradually through the RMBPT(2), RRPA, and RCCSD methods. Recently, we have evaluated this property for the negative chlorine (Cl$^-$) and gold (Au$^-$) ions by employing the above many-body methods [41]. We find similar trends in the electron correlation effects in H$^-$ and Cl$^-$, but the correlation contributions at different levels of approximations in the many-body theory are found to be quite large in H$^-$ compared to Cl$^-$. The DHF value of α_d was larger than the RCCSD value in Au$^-$, in contrast to the trend seen in the negative alkali-metal ions. In Fig. 1, we plot the fractional differences of the results from the DC Hamiltonian from different methods against the atomic number (Z) of the negative alkali-metal ions. This shows that scaling of correlation contributions through RMBPT(2) and RRPA varies linearly with the size of the considered systems, but no particular trend is followed by the contributions from the RCCSD method.

We notice from Table I that both the higher-order relativistic effects due to the Breit and QED interactions do not contribute significantly to α_d of the considered ions. However, the trends in the results from different approximations in many-body theories demonstrate that the estimated corrections from the Breit and QED interactions vary in different methods. It is, therefore, not prudent to estimate corrections due to these relativistic effects by applying lower-order many-body methods as done in literature quite often.

TABLE II. Contributions from the DC Hamiltonian through different RCC terms in the determination of α_d (in ea_0^3) of the negative alkali-metal ions. The differences between the sum of the contributions from the mentioned terms and the final values from the RCCSD method given using the DC Hamiltonian in Table I correspond to the contributions from the remaining RCC terms that are not shown explicitly here.

Ion	$DT_1^{(1)}$	$T_1^{(0)\dagger}DT_1^{(1)}$	$T_2^{(0)\dagger}DT_1^{(1)}$	$T_1^{(0)\dagger}DT_2^{(1)}$	$T_2^{(0)\dagger}DT_2^{(1)}$
H$^-$	149.59	30.47	−3.88	−1.99	32.25
Li$^-$	968.86	−146.32	−108.09	25.45	127.48
Na$^-$	1160.42	−193.82	−118.33	34.24	133.65
K$^-$	1741.75	−358.37	−204.67	69.89	197.74
Rb$^-$	1948.21	−414.85	−224.50	82.39	209.90
Cs$^-$	2351.13	−516.10	−278.24	105.36	250.74
Fr$^-$	2076.99	−448.47	−214.02	87.29	190.49

To gain a deeper insight into the behavior of electron correlation effects in the determination of α_d of the negative alkali-metal ions, we present contributions from different RCC terms in Table II by using the DC Hamiltonian. Contributions from the higher-order nonlinear RCC terms are not given explicitly, but their importance can be found from the differences in the results after summing contributions from the shown terms and the final RCCSD values from the DC Hamiltonian given in Table I. Contrasting behaviors of correlation effects between H$^-$ and other ions can be visibly noticeable. The first term, $DT_1^{(1)}$, includes the DHF value, and the leading-order RRPA and non-RRPA correlation contributions [34]. This is the reason for the seemingly dominant contribution of the term over all others. Though the overall trend of correlation effects between H$^-$ and Cl$^-$ was earlier found to be similar, comparison of individual contributions from various RCC terms of the above table and that given in Ref. [41] for Cl$^-$ does not suggest the same. In the Cl$^-$ ion, the $DT_1^{(1)}$ term accounts for almost all of the α_d value in the RCCSD method, whereas in H$^-$, almost all the RCC terms are found to be significant. Also, it can be found from Ref. [41] that only the first three terms contribute mostly to the determination of α_d in the heavier Au$^-$ ion, where contributions from the $T_2^{(0)\dagger}DT_1^{(1)}$ RCC term are found to be quite large in the alkali-metal negative ions. We plot contributions from the above RCC terms in Fig. 2 to demonstrate their roles quantitatively in different ions. For this purpose, we have plotted the $DT_1^{(1)}$ value after subtracting the DHF result. As seen, the magnitudes of the correlation effects are slowly increasing with the size of the system through each RCC term, with the only exception being the trend from Cs$^-$ to Fr$^-$.

In Table III, we quote the final values along with uncertainties by considering the RCCSD results from the DC, DCB, and DCQ Hamiltonians of our calculations. The uncertainties are estimated by extrapolating contributions from the finite-size basis functions that were used and the neglected higher-level excitations (especially from the triple excitations). Our final values are compared with the available literature results in the same table. It is worth noting again that due to complication in measuring α_d of the negative ions,

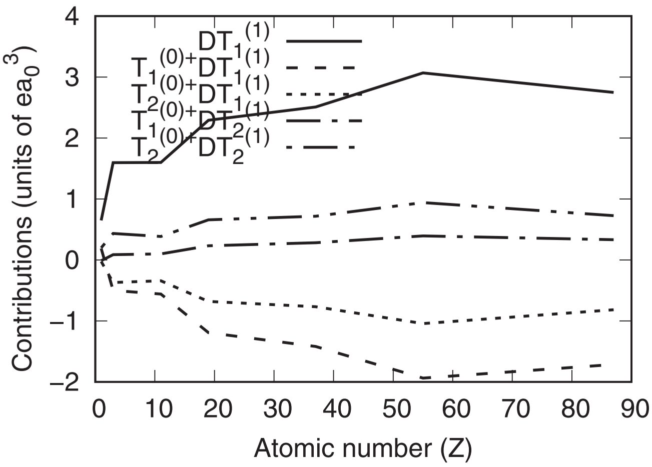

FIG. 2. Plot demonstrating correlation contributions arising through the leading order RCC terms against Z of the negative alkali-metal ions. The DHF value is subtracted from the first term to show only its correlation contribution.

there are no experimental values available until date and calculations are reported only for a few lighter negative ions by employing lower-order nonrelativistic many-body methods. We find that among the negative alkali-metal ions, precise results are available only for H^-, by applying few-body methods. Though the RCC theory is not apt to investigate electron correlation effects in H^-, the applied RCCSD method in this work is the complete *ansatz* of the RCC theory for this ion. Thus, its result can serve as the benchmark to our calculations for other ions. A very good agreement of our result with the reported precise value [28] implies reliability in the calculation using the RCCSD method. In this context, we would like to emphasize here that the DHF, RMBPT(2), and RRPA results are far off from the RCCSD result in this ion. The entire uncertainty to its α_d value arises due to construction of basis functions owing to its point-size nucleus in contrast to other ions. An old theoretical study presents α_d values of Li^-, Na^-, and K^- by analyzing photodetachment cross sections in both the length and velocity gauge approximations [13]. Values from both the gauge expressions differ widely, raising questions about their accuracies. Two more calculations for α_d of Li^- using CI methods are found in literature [29,30]. However, results from both the CI calculations are far apart and much outside of the quoted error bars. Thus, these results cannot be used assuredly for any application of this ion. Our α_d value of Li^- matches well with the velocity gauge result of Ref. [13] and calculation by Ågren *et al.* [30], but this agreement could be coincidental as large disagreements between our calculations, performed in length gauge, with the results from gauges of Ref. [13] are seen in the Na^- and K^- ions. To our knowledge, there are no theoretical studies on α_d of Rb^-, Cs^-, and Fr^- available in the literature to make comparative analysis with our calculations.

TABLE III. The recommended α_d values (in ea_0^3) of negative alkali-metal ions from this work. Previous calculations using nonrelativistic methods are also given for comparison. The estimated uncertainties are quoted in parentheses.

Ion	This work	Others
H^-	206.2(5)	206.165 [26], 206.37683 [27] 206.1487618(37) [28]
Li^-	794(2)	832[a] [13], 798[b] [13], 650(50) [29] 798(5) [30]
Na^-	953(5)	989[a] [13], 1058[b] [13]
K^-	1354(7)	1805[a] [13], 1757[b] [13]
Rb^-	1508(8)	
Cs^-	1804(10)	
Fr^-	1620(10)	

[a] From the length gauge calculation.
[b] From the velocity gauge calculation.

We would also like to make an analogy among the roles of electron correlation effects played in the determination of α_d values of the positively charged ions and neutral atoms belonging to the isoelectronic sequence of the considered negative ions. Comparing the calculations in the positively charged ions and alkaline earth-metal atoms from our earlier work [35], and that with the results for the undertaken negative ions reported in this work, we find that the Breit and QED contributions are negligibly small in all these three types of systems belonging to the same isoelectronic sequence. The correlation trends are found to be almost similar among these systems, but the final results are found to be at least an order bigger in the negative ions than their positively charged counterparts and neutral atoms [25,34,35]. This implies that the negative ions are highly polarized and very sensitive to an applied electric field.

V. CONCLUSION

We have evaluated electric dipole polarizabilities of all the negative alkali-metal ions very accurately. Propagations of electron correlation effects are investigated from lower order to all order in perturbation in the determination of these quantities by employing a relativistic second-order perturbation theory, random phase approximation, and coupled-cluster method on the Dirac-Hartree-Fock calculation. Trends of correlation effects from these methods and through different terms of the coupled-cluster approach are demonstrated quantitatively. It shows that the roles of electron correlation effects follow almost similar trends in all ions except in H^-, on which they bestow a completely different trend. Random-phase approximation predicts the values by huge magnitudes, while the coupled-cluster method gave moderate values. This clearly suggests that there are huge cancelations among the electron correlation effects arising through the pair-correlation and core-polarization effects. It also demonstrates that magnitudes of the correlation effects increase with the size of the system with an exception in the trend from Cs^- to Fr^-. We have also compared electron correlation trends in the determination of the above-mentioned quantities among the negative alkali-metal ions, and their isoelectronic positively charged ions and neutral atoms. This comparison shows that electric dipole polarizabilities in the above ions are about an order larger than the values of their respective positively charged ions and neutral atoms indicating that negative alkali-metal ions are highly polarized. Higher-order relativistic corrections due to the Breit and quantum electrodynamics interactions are found to be negligibly small, but their magnitudes are observed to be modified with the electron correlation effects. There are only a few existing calculations of the investigated property available for the lighter ions. Since it is extremely difficult to measure the electric dipole polarizabilities of the negative alkali-metal ions, our estimated precise values of these quantities will be very useful to the applications of these ions. Our results can be further improved after including contributions from the triple excitations.

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