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Four-component and scalar relativistic Douglas-Kroll calculations for static dipole polarizabilities of the alkaline-earth-metal elements and their ions from Ca^n to Ra^n $(n=0,+1,+2)$

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Static dipole polarizabilities for the neutral and ionized M, M^+, and M^{2+} group 2 elements from $M=\mathrm{Ca}$ to Ra are predicted from relativistic coupled-cluster calculations using finite field techniques together with carefully optimized Gaussian-type basis sets. Useful relations between the dipole polarizability and the ionization potential are established.

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I. INTRODUCTION

The importance of atomic polarizabilities has long been recognized in the field of electromagnetic field-matter interactions, optical properties, and collision phenomena, to name a few [1]. Its use extends to broad areas of chemistry and physics including atomic scattering processes [2], refractive indices [3], ion mobility in gases, dielectric constants, and van der Waals constants [4], as well as accounting for electron correlation effects through core-polarization in model/pseudopotential methods [5,6] and transition moment calculations [7]. Useful relationships between polarizabilities and various physical quantities such as ionization potentials are also being studied [8]. The experimental determination of dipole polarizabilities has resulted in various techniques such as dielectric constant measurements [9], Rayleigh scattering [10], beam deflection [11,12], atom interferometry [13], and position sensitive time-of-flight measurements [14]. The application and the accuracy of these methods are, however, subject to specific cases. Further difficulties arise when dealing with charged ions, as dipole polarizabilities are not subject to direct experimental determination. In this case one must resort to the purely theoretical, empirical, or semiempirical determination of crystal polarizabilities containing the ion of interest. Here, complications arise from the nonadditive nature of individual free ionic polarizabilities in its crystalline environment, and the results can only be shown according to the polarizabilities of the ionic counterparts in the crystalline structure [15]. Hence from an experimental point of view it is currently not possible to determine accurate polarizabilities for ions except for simple one valence-electron systems where the sum-over-states equation for the dipole polarizability can be used.

The theoretical determination of polarizabilities has incorporated a large range of methods [16] derived from either wave-function based or density-functional theory [17], often in connection with the pseudopotential approximation for the heavier atoms, and using either finite field [18,19] or response theory [20,21]. For few-electron atoms, more sophisticated relativistic all-order methods for electron correlation including quantum electrodynamic effects lead to high precision results [22–24]. Theoretical studies of dipole polarizabilities have somewhat overtaken experimental advances as noted by Miller *et al.* [25], at least for the alkali-metal atoms and their isoelectronic sequences. This is mainly due to the simplicity of dealing with a single valence electron, where the sum-over-states equation can effectively be used. As noted by Dalgarno and Kingston [26], it takes advantage of the fact that in a single-active-electron environment, the oscillator strengths for the first $ns \rightarrow np$ transition are large and close to unity, implying that the oscillator strengths for the $ns \rightarrow n'p$ $(n' > n)$ transitions become rapidly smaller with increasing n' [27]. However, for many-electron valence systems it has remained a challenging field to obtain reasonably accurate dipole polarizabilities from first-principle relativistic quantum theory due to large electron correlation and relativistic effects associated with this property. Furthermore, spin-orbit coupling has not been incorporated rigorously except for few-electron systems as mentioned before.

As for the alkaline-earth metals, many of the theoretical studies have been limited to the evaluation of open-shell M^+ ions [28–30] with a single valence electron for the reasons mentioned above. There is a set of purely *ab initio* values of dipole polarizabilities available for the alkaline-earth metals up to Ba and their singly and doubly charged ions by Sadlej and co-workers [31,32]. This study incorporated electron correlation at the coupled-cluster (CC) level of theory and scalar relativistic effects approximated by the use of the scalar relativistic Douglas-Kroll (DK) operator. These are the most accurate polarizabilities available so far for the heavier group-2 elements. However, they tend to depend on the basis-set expansion and the contraction scheme and at the time did not include spin-orbit (SO) coupling effects. Another study by Mahan [33] adopted the density-functional formalism to modify the Sternheimer equation for atomic polarizabilities [34] in order to account for the self-consistent field. It was confirmed in this study that electron correlation reduces the dipole polarizabilities typically by 40% for closed-shell atoms and ions. More recently, Roos and coworkers [35] have evaluated atomic natural orbital-type basis sets for the alkaline-earth metals up to Ra. However, the application of their basis sets to dipole polarizabilities at the relativistic DK level using complete-active-space second-order perturbation (CASPT2) theory yields larger discrepancies from the other known theoretical values.

On the semiempirical side are the calculations of dipole polarizabilities by summation of experimental oscillator

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strengths. Early attempts by Altick [36] and Cohen [37] have established lower and upper bounds for the dipole polarizabilities (α_D) of Sr and Ba with accuracies of about 16% in Altick's case and 6% in Cohen's case for both atoms. Their lower bounds coincided with one another whereas Altick's upper bound was much higher than that of Cohen's. It was noted that the semiempirical results are typically underestimated in the case of Ba [38] but are overestimated for Ca [39]. On the experimental side, electric deflection studies have been a long-standing method of choice as has been for the alkali metals. A study by Miller *et al.* [40] and Schwartz *et al.* [41] revealed that Cohen's semiempirical values were seriously underestimated and were able to reduce Altick's margin of error of 16% to about 8% for Sr and Ba, yielding $\alpha_{\mathrm{D}}(\mathrm{Sr}) = 186.26 \pm 14.85$ and $\alpha_{\mathrm{D}}(\mathrm{Ba}) = 267.92 \pm 21.60$ a.u. They have later measured, using the same method, the dipole polarizability of Ca with a somewhat larger error at $\alpha_{\mathrm{D}}(\mathrm{Ca}) = 168.71 \pm 16.87$ [40]. We point out that for the lighter elements Be [42] and Mg [43] reliable values of dipole polarizabilities are available.

In order to clarify the current situation for the alkaline-earth elements we decided to reinvestigate the static dipole polarizabilities of these elements from Ca to Ra and their singly and doubly charged ions, using a scalar relativistic Douglas-Kroll Hamiltonian H_{DK}, within coupled-cluster theory and a finite field approach. Spin-orbit coupling was accounted for by employing a relativistic four-component formalism using the Dirac-Coulomb Hamiltonian H_{DC} within second-order many-body Rayleigh-Schrödinger perturbation theory (MBPT2) to account for electron correlation. It must be stressed that in *ab initio* calculations the accuracy of dipole polarizabilities depends critically on the quality of basis sets used as pointed out by Sadlej and co-workers [44]. We have therefore carefully devised and tested the basis-set expansion by employing a tight basis-set convergence threshold of about 1 a.u. in the dipole polarizabilities of the neutral elements.

II. THEORY

Scalar relativistic effects were accounted for by modifying the one-electron integrals in the Hartree-Fock scheme [45] via a no-pair Douglas-Kroll (DK) operator [46,47] (in atomic units)

$$H_{DK} = \sum_i \left[E_i - mc^2 + V_{\mathrm{eff}}^{\mathrm{SF}}(i)\right] + \sum_{i<j} r_{ij}^{-1}, \tag{1}$$

where the one-particle effective spin-free potential $V_{\mathrm{eff}}^{\mathrm{SF}}$ is

$$V_{\mathrm{eff}}^{\mathrm{SF}}(i) = -A_i[V_{\mathrm{ext}}(i) + \vec{R}_i V_{\mathrm{ext}}(i)\vec{R}_i]A_i - \frac{1}{2}\bigl\{\{E_i, W_i\}, W_i\bigr\},$$

$$A_i = \left(\frac{mc^2 + E_i}{2E_i}\right)^{1/2}, \quad \vec{R} = \frac{c\vec{p}_i}{mc^2 + E_i}. \tag{2}$$

W_i is the integral operator with kernel,

$$W(\vec{p}_i, \vec{p}_i') = A_i(\vec{R}_i - \vec{R}_i')A_i' \frac{V_{\mathrm{ext}}(\vec{p}_i, \vec{p}_i')}{E_i + \vec{E}_i'}, \tag{3}$$

and E_i is defined as

$$E_i = (p_i^2 c^2 + m^2 c^4)^{1/2}. \tag{4}$$

$\{a, b\}$ is the anticommutator of a and b, SF denotes the spin-free DK approximation, and $V_{\mathrm{ext}}(\vec{p}_i, \vec{p}_i')$ is the Fourier transform of the external potential [46].

In order to account for spin-orbit coupling, four-component relativistic Dirac-Coulomb (DC) Hartree-Fock (HF), and MBPT2 calculations [48] were performed for the closed-shell atoms M and M^{2+} and for the heavier open-shell atoms Ba^+ and Ra^+ [49] using the standard Dirac-Coulomb operator,

$$H_{DC} = \sum_i \{c\vec{\alpha}_i\vec{p}_i + c^2\beta_i + V_{\mathrm{ext}}(i)\} + \sum_{i<j} r_{ij}^{-1}, \tag{5}$$

where $\vec{\alpha}$ and β are the well-known Dirac matrices. A Gaussian nuclear model with nuclear exponents as given by Visscher and Dyall [50] was used. The values obtained from Eq. (5) are then compared with scalar relativistic Douglas-Kroll calculations.

The appropriate active orbital space for the electron correlation procedure was tested at the MBPT2 level of theory and chosen such that the change in the dipole polarizability is much smaller than 1.0 a.u. In detail: for Ca a full active orbital space, for Sr the (KL) shell, and for Ba and Ra the (KLM) shell were kept frozen with orbitals deleted in the virtual space greater than 1000 a.u.

Finite electric homogeneous fields of $F = 0.0$, 0.001, 0.002, and 0.004 a.u. were used to obtain dipole polarizabilities by numeric differentiation. For this procedure one has to use very tight convergence criteria for the total electronic energy E and the density matrix D in the SCF process, i.e., $\Delta E < 10^{-11} - 10^{-10}$ a.u. depending on the element chosen, and $D_{ij} < 10^{-8}$ a.u.

III. BASIS-SET EFFECTS

The construction of basis sets is an important issue in the determination of accurate polarizabilities. The starting primitive GTO (Gaussian type orbital) basis-set exponents for all elements were taken from Refs. [51–53]. These exponents were then re-optimized by an energy minimization procedure within a numerical four-component procedure using the operator as defined in Eq. (5) to obtain relativistic GTO sets of dual-family type [54]. These energy optimized basis sets were tested against ground-state electronic energies at the numerical DC-HF limit as tabulated in Table I. Such large basis sets are, however, computationally too demanding for finite field perturbation calculations at the coupled-cluster level because of the broken atomic symmetry. Some hard exponents necessary in the energy minimization may be deleted without affecting the final value of the polarizability. Additional diffuse functions become more critical in order to correctly describe the polarization in the valence region. Furthermore, the exponents in the GTO basis set need to be tight

TABLE I. A comparison between calculated numerical and finite basis-set total electronic energies at the Dirac-Coulomb-Hartree-Fock level of theory (in a.u.).

	Basis set	Total electronic energies	
		DC-HF numerical	DC-HF finite basis
Ca	(20*s*15*p*8*d*)	−679.7101602882	−679.7052677615
Sr	(21*s*16*p*11*d*9*f*)	−3178.080046946	−3178.073284531
Ba	(26*s*22*p*17*d*13*f*)	−8135.645897280	−8135.636298367
Ra	(31*s*24*p*20*d*14*f*)	−25028.18780985	−25028.17080236

enough to accurately account for the core polarization. Therefore the energy optimized basis sets are carefully tailored to suit the calculation of dipole polarizabilities. The idea here is to devise small enough basis sets suitable for high-level calculations, which are, within a desired threshold, converged with respect to the dipole polarizability. This is accomplished in a systematic manner by determining the upper and lower limits of the exponents for each angular momentum subset in separate polarizability calculations at a lower level of theory. The same procedure is applied to additional polarization functions required for correctly describing valence polarization. This gives us an understanding of the convergence behavior of dipole polarizabilities with respect to the finite basis-set expansion, which, in turn, enables us to estimate the errors caused by basis-set deficiencies if desired. We have therefore performed a series of test calculations at the DK-MBPT2 level for each element, monitoring the convergence behavior of the polarizability. Typically over 20 basis sets were tested until a desired convergence threshold was reached. In short, the resulting basis sets were as follows: For Ca, Sr, Ba, and Ra, we have used a (20*s*15*p*8*d*), (21*s*16*p*11*d*9*f*), (26*s*22*p*17*d*13*f*), and (31*s*24*p*20*d*14*f*) GTO set, respectively. These GTO sets were generally contracted (GC) to a [15*s*12*p*10*d*9*f*], [17*s*16*p*13*d*13*f*], and [19*s*16*p*15*d*11*f*] GC-GTO set for the nonrelativistic (NR) calculation of Sr, Ba, and Ra, respectively. For the relativistic calculations of Ba and Ra, a somewhat heavier contraction scheme of respective [16*s*15*p*12*d*13*f*] and [18*s*15*p*14*d*10*f*] was used in order to improve on linear dependencies and to keep computational costs low for the subsequent coupled-cluster calculations. No basis set contraction was used for the lightest element in this series, Ca. The influence of polarization functions was tested by expanding the above GTO/GC-GTO sets by adding five *f*-, three *g*-, ten *g*-, and eleven *g*-type functions for Ca, Sr, Ba, and Ra, respectively.

For the calculations involving the charged ions M^+ and M^{2+}, the initial basis exponents were taken from the corresponding neutral elements. However, the range of the exponents, especially for the polarization functions, were modified slightly along with the contraction scheme to account for the more compact wave function. For the NR and DK calculations of Ca and Sr the basis sets used were the same as the neutral case; a (25*s*21*p*16*d*8*f*5*g*)/[16*s*15*p*12*d*8*f*5*g*] set for both the NR and DK calculations of Ba and a (31*s*24*p*20*d*12*f*8*g*)/[18*s*16*p*15*d*9*f*8*g*] set for the NR calculations and a (31*s*24*p*20*d*12*f*8*g*)/[18*s*15*p*14*d*9*f*8*g*] set for the DK calculations of Ra. Again, a slightly heavier contraction for the relativistic Ra calculations was to improve on linear dependencies. In all cases, the contraction coefficients were obtained in separate nonrelativistic and relativistic Douglas-Kroll self-consistent calculations.

Spin-orbit effects are expected to be rather small for the group-2 elements containing valence *ns* electrons. Hence, for the dipole polarizabilities including spin-orbit effects, we have used uncontracted basis sets for a better comparison with Douglas-Kroll results at the HF and MBPT2 level of theory. We only included basis functions up to $l=3$ (i.e., *f*-type functions) as the computational demand was very high for the four-component calculations. The large component exponents were taken from the above basis sets whereas the small component exponents were generated from the large components by a linear transformation and a projection [55] equivalent to the kinetic balance condition [56].

The static dipole polarizabilities of the neutral, singly charged, and doubly charged group-2 elements calculated with various basis sets are presented in Tables II–IV. For each element, we first list the dipole polarizabilities resulting from the uncontracted basis sets, labeled *uncntr* (except for Ca where uncontracted basis sets were used throughout). Then the dipole polarizabilities following a specific basis set contraction are given. The contracted basis sets are labeled by l, where l denotes the highest angular momentum quantum number given within that basis set. These GC-GTO's were further augmented by one high and one diffuse exponent in each angular momentum subset, giving basis sets l^*. The dipole polarizabilities resulting from these l^* sets are listed to demonstrate that set l gives the converged dipole polarizability within about 0.5 a.u. It is reminded that the convergence of the dipole polarizability with respect to the basis-set expansion was studied at the MBPT2 level of theory only. The high level correlation calculations at the CCSD(T) level were performed with smaller basis sets which expand up to *g*-type functions for the heavier elements. Although a further expansion of the basis sets to *h*-type functions and beyond is unlikely to affect greatly the overall quality of the present dipole polarizabilities, the influence of the *h*- and *i*-type functions was tested for Ra and is discussed later in this section.

Let us first consider the dipole polarizabilities of the neutral elements listed in Table II. For these elements the dipole polarizability remains virtually unchanged upon the basis-set contraction. For Ca, set d contains enough functions up to $l=2$ as revealed by a negligible difference in dipole polarizabilities between set d and d^*. The influence of *f*-type functions is negligible at the HF level, and is still small, less than 0.5 a.u. at the MBPT2 level of theory. For elements from Sr to Ra, a comparison between set f and f^* confirms that the dipole polarizability is converged within basis functions up to $l=3$ as a further augmentation of set f to f^* shows no significant change at all levels of theory within about 0.1 a.u. The influence of *g*-type functions (compare set f and g) appears to be small for both Sr and Ba, contributing less than 1% to the dipole polarizability. For Ra, however, the *g*-type functions reduce the dipole polarizability by a larger margin of 1.6% at the DK-MBPT2 level. Further augmentation of set g to g^* shows no change in the dipole polarizability and

TABLE II. The calculated nonrelativistic and scalar relativistic static dipole polarizabilities of the neutral group-2 elements from Ca to Ra (in a.u.; 1 a.u. = 0.148 18 Å^3).

		Nonrelativistic			Scalar relativistic		
	l	Basis set	HF	MBPT2	Basis set	HF	MBPT2
Ca	*d*	(20*s*15*p*8*d*)	185.45	142.57	(20*s*15*p*8*d*)	182.86	140.69
	d^*	(22*s*17*p*10*d*)	185.46	142.64	(22*s*17*p*10*d*)	182.87	140.70
	f	(20*s*15*p*8*d*5*f*)	185.45	143.06	(20*s*15*p*8*d*5*f*)	182.86	141.17
	f^*	(22*s*17*p*10*d*7*f*)	185.46	143.11	(22*s*17*p*10*d*7*f*)	182.87	141.16
Sr	*uncntr*	(21*s*16*p*11*d*9*f*)	246.06	176.63	(21*s*16*p*11*d*9*f*)	232.88	170.51
	f	(21*s*16*p*11*d*9*f*)/ [15*s*12*p*10*d*9*f*]	246.06	179.67	(21*s*16*p*11*d*9*f*)/ [15*s*12*p*10*d*9*f*]	232.88	170.53
	f^*	(23*s*18*p*13*d*11*f*)/ [17*s*14*p*12*d*11*f*]	246.08	179.65	(23*s*18*p*13*d*11*f*)/ [17*s*14*p*12*d*11*f*]	232.92	170.57
	g	(21*s*16*p*11*d*9*f*3*g*)/ [15*s*12*p*10*d*9*f*3*g*]	246.06	178.30	(21*s*16*p*11*d*9*f*3*g*)/ [15*s*12*p*10*d*9*f*3*g*]	232.88	169.20
	g^*	(23*s*18*p*13*d*11*f*5*g*)/ [17*s*14*p*12*d*11*f*5*g*]	246.06	178.66	(23*s*18*p*13*d*11*f*5*g*)/ [17*s*14*p*12*d*11*f*5*g*]	232.88	169.46
Ba	*uncntr*	(26*s*22*p*17*d*13*f*)	368.02	244.14	(26*s*22*p*17*d*13*f*)	324.67	217.11
	f	(26*s*22*p*17*d*13*f*)/ [17*s*16*p*13*d*13*f*]	368.02	244.13	(26*s*22*p*17*d*13*f*)/ [16*s*15*p*12*d*13*f*]	324.66	217.11
	f^*	(28*s*24*p*19*d*15*f*)/ [19*s*18*p*15*d*15*f*]	368.05	244.13	(28*s*24*p*19*d*15*f*)/ [18*s*17*p*14*d*15*f*]	324.68	217.12
	g	(26*s*22*p*17*d*13*f*10*g*)/ [17*s*16*p*13*d*13*f*10*g*]	368.02	243.75	(26*s*22*p*17*d*13*f*10*g*)/ [16*s*15*p*12*d*13*f*10*g*]	324.66	216.51
	g^*	(28*s*24*p*19*d*15*f*12*g*)/ [19*s*18*p*15*d*15*f*12*g*]	368.02	243.76	(28*s*24*p*19*d*15*f*12*g*)/ [18*s*17*p*14*d*15*f*12*g*]	324.66	216.52
Ra	*uncntr*	(31*s*24*p*20*d*14*f*)	440.85	279.75	(31*s*24*p*20*d*14*f*)	300.56	199.42
	f	(31*s*24*p*20*d*14*f*)/ [19*s*16*p*15*d*11*f*]	440.85	279.72	(31*s*24*p*20*d*14*f*)/ [18*s*15*p*14*d*10*f*]	300.56	199.44
	f^*	(33*s*26*p*22*d*16*f*)/ [21*s*18*p*17*d*13*f*]	440.87	279.75	(33*s*26*p*22*d*16*f*)/ [20*s*17*p*16*d*12*f*]	300.57	199.44
	g	(31*s*24*p*20*d*14*f*11*g*)/ [19*s*16*p*15*d*11*f*11*g*]	440.86	277.37	(31*s*24*p*20*d*14*f*11*g*)/ [18*s*15*p*14*d*10*f*11*g*]	300.57	196.31
	g^*	(33*s*26*p*22*d*16*f*13*g*)/ [21*s*18*p*17*d*13*f*13*g*]	440.86	277.42	(33*s*26*p*22*d*16*f*13*g*)/ [20*s*17*p*16*d*12*f*13*g*]	300.57	196.31

this gives us confidence that set *g* contains a sufficient number of basis exponents for the dipole polarizability calculations for Ra. The influence of *h*-type functions was also tested for Ra by adding eight *h*-type functions to set *g*. The resulting dipole polarizability at the DK-MBPT2 level was 195.06 a.u., which is 1.3 a.u. lower than the dipole polarizability of set *g*. When this basis set was further augmented with five *i*-type functions, the dipole polarizability was further reduced by 0.3 a.u. at the same level of theory. This means that the dipole polarizability of Ra is converged with respect to the basis-set expansion to a level of about 1 a.u. with the inclusion of the *h*-type functions. Due to high computational demands, the influence of *h*-type functions was considered only at the MBPT2 level. The final basis sets chosen for the CCSD(T) calculations were set *f* for Ca, and set *g* for Sr, Ba, and Ra as shown in Table II. Additional basis set effects are taken into account only for the final recommended polarizabilities.

For all singly charged ions, the dipole polarizabilities remain virtually unaffected by the basis set contraction (Table III) and basis sets labeled *l* cover the necessary range of exponents for all angular momentum type up to *l* as an augmentation to l^* shows no significant change in the dipole polarizability. The influence of polarization functions seems to be larger for the charged ions. For example, at the nonrelativistic MBPT2 level, the dipole polarizability of Ca$^+$ is reduced by 1.7 a.u. upon addition of *f*-type functions, which amounts to 2.4%. This is more than an order of magnitude larger than the basis set convergence up to *d*-type functions and therefore these *f*-type functions are important. A reduction of the Ca$^+$ dipole polarizability by *f*-type functions is also observed at the relativistic level as shown in Table III.

TABLE III. The calculated static dipole polarizabilities of the singly charged group-2 elements from Ca$^+$ to Ra$^+$ (in a.u.).

		Nonrelativistic			Scalar relativistic		
	l	Basis set	HF	MBPT2	Basis set	HF	MBPT2
Ca$^+$	d	$(20s15p8d)$	98.64	73.84	$(20s15p8d)$	96.46	72.28
	d^*	$(22s17p10d)$	98.65	73.90	$(22s17p10d)$	96.47	72.34
	f	$(20s15p8d5f)$	98.64	72.16	$(20s15p8d5f)$	96.46	70.62
	f^*	$(22s17p10d7f)$	98.65	72.19	$(22s17p10d7f)$	96.47	70.66
Sr$^+$	*uncntr*	$(21s16p11d9f)$	132.15	87.06	$(21s16p11d9f)$	121.33	80.67
	f	$(21s16p11d9f)/[15s12p10d9f]$	132.15	87.07	$(21s16p11d9f)/[15s12p10d9f]$	121.33	80.68
	f^*	$(23s18p13d11f)/[17s14p12d11f]$	132.16	87.07	$(23s18p13d11f)/[17s14p12d11f]$	121.34	80.68
	g	$(21s16p11d9f3g)/[15s12p10d9f3g]$	132.15	86.21	$(21s16p11d9f3g)/[15s12p10d9f3g]$	121.33	79.89
	g^*	$(23s18p13d11f5g)/[17s14p12d11f5g]$	132.16	86.26	$(23s18p13d11f5g)/[17s14p12d11f5g]$	121.34	79.91
Ba$^+$	*uncntr*	$(25s21p16d8f)$	213.47	112.81	$(25s21p16d8f)$	174.64	96.69
	f	$(25s21p16d8f)/[16s15p12d8f]$	213.47	112.82	$(25s21p16d8f)/[16s15p12d8f]$	174.64	96.70
	f^*	$(27s23p18d10f)/[18s17p14d10f]$	213.47	112.81	$(27s23p18d10f)/[18s17p14d10f]$	174.65	96.68
	g	$(25s21p16d8f5g)/[16s15p12d8f5g]$	213.47	110.60	$(25s21p16d8f5g)/[16s15p12d8f5g]$	174.64	94.94
	g^*	$(27s23p18d10f7g)/[18s17p14d10f7g]$	213.47	110.56	$(27s23p18d10f7g)/[18s17p14d10f7g]$	174.65	94.94
Ra$^+$	*uncntr*	$(31s24p20d14f)$	440.85	279.75	$(31s24p20d12f)$	145.46	82.61
	f	$(31s24p20d12f)/[19s16p15d9f]$	256.80	125.25	$(31s24p20d12f)/[18s15p14d9f]$	145.46	82.61
	f^*	$(33s26p22d14f)/[21s18p17d11f]$	256.80	125.25	$(33s26p22d14f)/[20s17p16d11f]$	145.47	82.60
	g	$(31s24p20d12f8g)/[19s16p15d9f8g]$	257.00	123.23	$(31s24p20d12f8g)/[18s15p14d9f8g]$	145.47	79.80
	g^*	$(33s26p22d14f10g)/[21s18p17d11f10g]$	257.00	123.22	$(33s26p22d9f10g)/[20s17p16d11f10g]$	145.47	79.81

For Sr$^+$, there is a slight decrease in the nonrelativistic dipole polarizability at the MBPT2 level upon addition of g-type functions. This decrease is small, less than 1 a.u., but is significantly larger when compared with the basis-set convergence up to f-type functions. The g-type functions were therefore included in the final basis set. Similarly, at the relativistic level, three g-type functions were needed to obtain a convergence margin smaller than the reduction in dipole polarizability caused by the inclusion of the g-type functions. The influence of g-type functions becomes larger for Ba$^+$ and Ra$^+$ as expected with increasing number of electrons. More precisely, the g-type functions reduce the dipole polarizability of Ba$^+$ by 2.2 and 1.8 a.u. at the nonrelativistic and relativistic MBPT2 level, respectively. For Ra$^+$, the influence of g-type functions amounts to 2.8 a.u. at the relativistic MBPT2 level. The influence of h-type functions was tested for Ra$^+$ by adding seven h-type functions to set g. The resulting dipole polarizability was 79.12 a.u. at the DK-MBPT2 level. This is only 0.68 a.u. smaller than the dipole polarizability from set g. The h-type functions were therefore considered only for basis-set corrections at the MBPT2 level of theory.

The static dipole polarizabilities of the doubly charged group-2 elements resulting from various basis sets are presented in Table IV. The values here are shown to three decimal places to make small changes more transparent. For Ca^{2+}, the dipole polarizability is slightly increased upon addition of f-type functions at the correlated level. For Sr^{2+}, the dipole polarizability is unaffected by the inclusion of g-type functions within 0.007 a.u. For Ba^{2+} and Ra^{2+}, the influence of g-type functions is small as the dipole polarizability is decreased by about 0.025 and 0.07 a.u. for respective Ba^{2+} and Ra^{2+} at the correlated level. The influence of h-type functions was tested for Ra^{2+} at the DK-MBPT2 level, by

TABLE IV. The calculated static dipole polarizabilities of the doubly charged group-2 elements from Ca^{2+} to Ra^{2+} (in a.u.).

		Nonrelativistic			Scalar relativistic		
	l	Basis set	HF	MBPT2	Basis set	HF	MBPT2
Ca^{2+}	d	$(20s15p8d)$	3.255	3.221	$(20s15p8d)$	3.248	3.216
	d^*	$(22s17p10d)$	3.260	3.215	$(22s17p10d)$	3.253	3.208
	f	$(20s15p8d5f)$	3.255	3.262	$(20s15p8d5f)$	3.248	3.260
	f^*	$(22s17p10d7f)$	3.260	3.263	$(22s17p10d7f)$	3.253	3.254
Sr^{2+}	*uncntr*	$(21s16p11d9f)$	5.866	5.845	$(21s16p11d9f)$	5.790	5.768
	f	$(21s16p11d9f)/[15s12p10d9f]$	5.866	5.847	$(21s16p11d9f)/[15s12p10d9f]$	5.790	5.768
	f^*	$(23s18p13d11f)/[17s14p12d11f]$	5.868	5.845	$(23s18p13d11f)/[17s14p12d11f]$	5.791	5.770
	g	$(21s16p11d9f3g)/[15s12p10d9f3g]$	5.866	5.841	$(21s16p11d9f3g)/[15s12p10d9f3g]$	5.790	5.761
Ba^{2+}	*uncntr*	$(25s21p16d8f)$	10.913	10.788	$(25s21p16d8f)$	10.559	10.475
	f	$(25s21p16d8f)/[16s15p12d8f]$	10.913	10.788	$(25s21p16d8f)/[16s15p12d8f]$	10.559	10.475
	f^*	$(27s23p18d10f)/[18s17p14d10f]$	10.914	10.787	$(27s23p18d10f)/[18s17p14d10f]$	10.559	10.477
	g	$(25s21p16d8f5g)/[16s15p12d8f5g]$	10.913	10.764	$(25s21p16d8f5g)/[16s15p12d8f5g]$	10.559	10.449
	g^*	$(27s23p18d10f7g)/[18s17p14d10f7g]$	10.913	10.762	$(27s23p18d10f7g)/[18s17p14d10f7g]$	10.559	10.447
Ra^{2+}	*uncntr*	$(31s24p20d12f)$	14.628	14.480	$(31s24p20d12f)$	13.360	13.381
	f	$(31s24p20d12f)/[19s16p15d9f]$	14.628	14.480	$(31s24p20d12f)/[18s15p14d9f]$	13.360	13.379
	f^*	$(33s26p22d14f)/[21s18p17d11f]$	14.628	14.487	$(33s26p22d14f)/[20s17p16d11f]$	13.360	13.379
	g	$(31s24p20d12f8g)/[19s16p15d9f8g]$	14.628	14.410	$(31s24p20d12f8g)/[18s15p14d9f8g]$	13.360	13.314
	g^*	$(33s26p22d14f10g)/[21s18p17d11f10g]$	14.628	14.403	$(33s26p22d14f10g)/[20s17p16d11f10g]$	13.360	13.308

adding six h-type functions to set g. The resulting dipole polarizability of 13.29 a.u. is virtually identical to that of set g. Therefore h-type functions were ignored in the subsequent CCSD/CCSD(T) calculations for Ra^{2+}.

IV. STATIC DIPOLE POLARIZABILITIES

A. Neutral elements

The calculated dipole polarizabilities of the neutral group-2 elements from Ca to Ra are presented in Table V. As expected, at the nonrelativistic level, the dipole polarizabilities show a monotonic increase from Ca to Ra; see Fig. 1. The importance of electron correlation effects is evident as the dipole polarizabilities are significantly reduced at the correlated level. Correlation effects at the nonrelativistic level are more profound for the heavier elements as depicted in Fig. 2. At the nonrelativistic MBPT2 level, the dipole polarizabilities are reduced by as much as 38% (for Ra) from the HF results. Due to a slow convergence of the many-body expansion [31], however, electron correlation effects are overestimated at the MBPT2 level (by sometimes more than a factor of 2) in comparison with the more accurate coupled-cluster results. Also evident is the importance of perturbative triples, without which the correlation is underestimated. These contributions account for as much as 18% (for Ra) of the total electron correlation effects at the relativistic CCSD(T) level. This suggests that in order to further improve the results here, quadruple contributions will have to be included in all future studies.

The results in Table V and Fig. 3 demonstrate the importance of scalar relativistic effects [31]. The relativistic valence s shell contraction leads to smaller dipole polarizabilities for all elements in comparison with the nonrelativistic case. This effect is present even for a relatively light element of Ca with a decrease in the dipole polarizability by 1.4%. Although the scalar relativistic contribution to the dipole polarizability of Ca is quite negligible, it remains larger than

TABLE V. The calculated dipole polarizabilities of the neutral group-2 elements at the nonrelativistic, relativistic Douglas-Kroll and Dirac-Coulomb level of theory (in a.u.). For a direct comparison of the DC with DK results see basis set labeled *uncntr* in Table II.

		Ca	Sr	Ba	Ra
NR	Basis set	$(20s15p8d5f)$	$(21s16p11d9f3g)$/ $[15s12p10d9f3g]$	$(26s22p17d13f10g)$/ $[17s16p13d13f10g]$	$(31s24p20d14f11g)$/ $[19s16p15d11f11g]$
	HF	185.45	246.06	368.02	440.86
	MBPT2	143.06	178.30	243.75	277.37
	CCSD	161.81	215.43	323.41	387.43
	CCSD(T)	160.01	210.64	316.21	378.46
DK	Basis set	$(20s15p8d5f)$	$(21s16p11d9f3g)$/ $[15s12p10d9f3g]$	$(26s22p17d13f10g)$/ $[16s15p12d13f10g]$	$(31s24p20d14f11g)$/ $[18s15p14d10f11g]$
	HF	182.86	232.88	324.66	300.57
	MBPT2	141.17	169.20	216.51	196.31
	CCSD	162.24	203.53	282.11	257.67
	CCSD(T)	158.00	198.85	273.85	248.56
DC	Basis set	$(20s15p8d5f)$	$(21s16p11d9f)$	$(26s22p17d13f)$	$(31s24p20d14f)$
	HF	182.79	232.66	323.82	299.59
	MBPT2	141.05	170.38	216.72	198.64

the errors caused by the use of a finite basis set in this study. Scalar relativistic effects increase with the increasing nuclear charge and become non-negligible from the fourth-row atom Sr which exhibits a 5.4% decrease in the dipole polarizability. For Ba, relativistic effects grow by a factor of 2 from Sr and become of similar size to electron correlation. Of particular interest is the scalar relativistic contribution to the dipole polarizability of the sixth-row atom, Ra. For this element, relativistic effects begin to dominate over electron correlation. Here, the relativistic contribution is, in fact, more than twice as large as the correlation contribution. Such large relativistic effects cause the dipole polarizability of Ra to be smaller than that of Ba and a monotonic increase in the dipole polarizabilities is no longer observed at the relativistic level as shown in Fig. 1. The well-known Z^2 dependence of relativistic effects is depicted in Fig. 3 at the CCSD(T) level. Even larger relativistic effects are therefore expected for the heaviest group-2 element with nuclear charge 120.

In our relativistic DK scheme, spin-orbit coupling effects are ignored. In order to test the influence of such effects, relativistic four-component DC-HF and DC-MBPT2 calculations were performed. Due to the extensiveness of the DC-HF and DC-MBPT2 calculations, the smaller, uncontracted basis sets for heavy elements, which contain only up to $l=3$-type functions (i.e., set f for Ca and set *uncntr* for Sr to Ra in Table II) were used. This avoids errors resulting from the contraction scheme and makes a direct comparison between DK and DC results more reliable. As shown in Table V, SO coupling effects are almost negligible for all neutral elements.

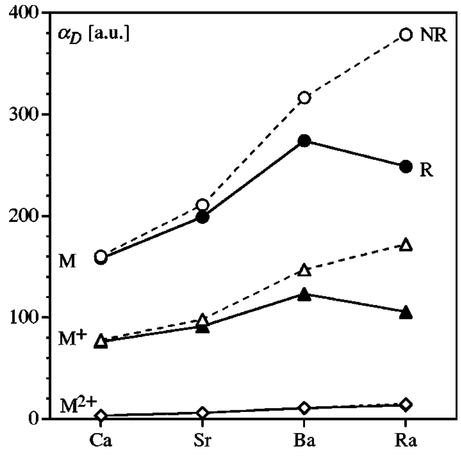

FIG. 1. Nonrelativistic (dashed lines) and scalar relativistic (solid lines) static dipole polarizabilities of the neutral and charged group-2 elements at the CCSD(T) level of theory. For the M^{2+} ions spin-orbit corrections from MBPT2 calculations are included.

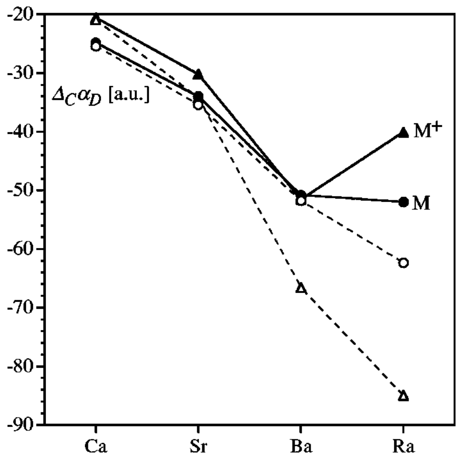

FIG. 2. Electron correlation contributions to the dipole polarizability at the relativistic (solid lines) and nonrelativistic (dashed lines) level of theory for the neutral, M, and positively charged, M^+, atoms.

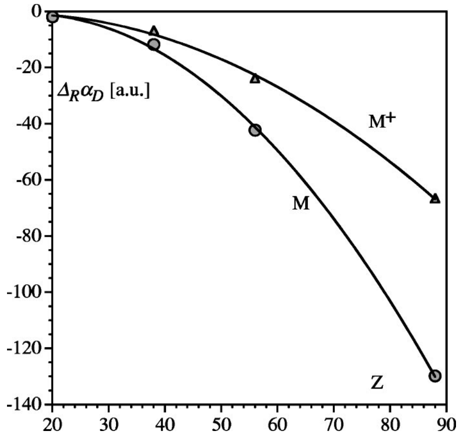

FIG. 3. Scalar relativistic contributions to the dipole polarizability at the coupled cluster level of theory for the neutral, M, and positively charged, M^+, atoms as a function of the nuclear charge Z.

The present DK-CCSD(T) values of the dipole polarizabilities of the neutral group-2 elements are compared with experimental and other theoretical values in Table VI. The values given by Hyman [38] derived from the summation of oscillator strength are systematically underestimated. The present values lie within the experimental uncertainties of Miller and Bederson [40,41] obtained by the electric deflection method. The most direct comparison of our calculated dipole polarizabilities could be made with the DK-CCSD(T) values of Sadlej and co-workers [31]. They have noted that their results may only be insignificantly improved by basis-set extension. On the contrary, the present study demonstrates that the dipole polarizabilities are quite sensitive to the choice of basis sets and the errors caused by the use of finite basis sets could only be minimized by a systematic investigation of the convergence behavior of the dipole polarizabilities with respect to the basis-set expansion. A recent study by Roos *et al.* [35] which adopted a multiconfigurational complete-active-space second-order perturbation theory approach (CASPT2) with their newly generated atomic natural orbital (ANO)-type basis sets systematically overestimates the dipole polarizabilities. For Ra, there is no experimental dipole polarizability available. There is, however, an unpublished theoretical value [57] of $\alpha_D(\mathrm{Ra}) = 258.5$ a.u., which has been calculated by using relativistic linear response theory. This gives confidence in our present results for Ra.

B. Singly charged ions

The static dipole polarizabilities of the singly charged group-2 elements are presented in Table VII. Again we see a monotonic increase in the dipole polarizabilities from Ca^+ to Ra^+ at the nonrelativistic level; see Fig. 1. In comparison to the neutral elements, the dipole polarizabilities of the singly charged ions are significantly smaller by up to 50% as the remaining valence s electron feels less screening from the nuclear charge. Electron correlation effects reduce the dipole polarizabilities by as much as 38% at the relativistic CCSD(T) level. This is much larger compared to the neutral atoms where the correlation contribution only amounts to a maximum of 18%. Again, MBPT2 overestimates electron correlation effects and the importance of the perturbative triples in the coupled-cluster procedure is easily seen from Table VII. Interestingly, the relative correlation contribution to the dipole polarizabilities of the singly charged group-2 elements is similar to that of the neutral group-1 elements [58], both having the same valence electron configuration of ns^1.

Figure 1 again highlights the importance of relativistic effects for these ions. Even for a light ion like Ca^+, the dipole polarizability is reduced by 1.8 a.u. at the CCSD(T) level of theory. This is similar in magnitude, for example, to the basis-set effects of f-type functions (1.7 a.u. at the DK-MBPT2 level), and is therefore considered non-negligible in an accurate determination of the Ca^+ dipole polarizability. As one expects, relativistic effects grow with increasing nuclear charge and become more visible for Sr^+ and Ba^+; see Fig. 3. Up to Ba^+, the largest contribution to the dipole polarizability comes from electron correlation effects, which dominate over relativistic effects. For Ra^+, however, relativistic effects become the most important contribution to the dipole polarizability, dominating over correlation effects, and the upward trend in the nonrelativistic polarizabilities going down the group in the periodic table is no longer continued at the relativistic level. That is, the dipole polarizability of Ra^+ is smaller than that of Ba^+ as depicted in Fig. 1.

It is well known that relativity significantly alters electron correlation effects and the two effects are nonadditive. This is demonstrated by comparing the correlation contribution to the dipole polarizabilities estimated at the relativistic level with that estimated at the nonrelativistic level in Fig. 2. In particular, Ra^+ experiences smaller correlation effects than Ba^+ at the relativistic level whereas correlation effects increase from Ba^+ to Ra^+ at the nonrelativistic level. As the

TABLE VI. The calculated static dipole polarizabilities of the neutral group-2 elements at the DK-CCSD(T) level in comparison with other values (in a.u.). For the methods used, see text.

	Method	Ref.	Ca	Sr	Ba	Ra
This work	DK-CCSD(T)		158.0	198.9	273.9	248.6
Theor.	DK-CCSD(T)	[31]	152.0	194.0	277.1	
	DK-CASPT2	[35]	163	210	312	283
Expt.	SOS[a]	[38]	153.9	191.4	241.5	
		[40,41]	167±17	186±15	268±22	

[a] Indirectly determined using the sum-over-states approach.

TABLE VII. The calculated static dipole polarizabilities of the singly charged group-2 elements (in a.u.).

		Ca$^+$	Sr$^+$	Ba$^+$	Ra$^+$
NR	Basis set	$(20s15p8d5f)$	$(21s16p11d9f3g)/$ $[15s12p10d9f3g]$	$(25s21p16d8f5g)/$ $[16s15p12d8f5g]$	$(31s24p20d12f8g)/$ $[19s16p15d9f8g]$
	HF	98.64	132.15	213.47	257.00
	MBPT2	72.16	86.21	110.60	123.23
	CCSD	79.65	101.58	148.24	186.00
	CCSD(T)	77.71	97.91	146.88	172.00
DK	Basis set	$(20s15p8d5f)$	$(21s16p11d9f3g)/$ $[15s12p10d9f3g]$	$(25s21p16d8f5g)/$ $[16s15p12d8f5g]$	$(31s24p20d12f8g)/$ $[18s15p14d9f8g]$
	HF	96.46	121.33	174.64	145.47
	MBPT2	70.62	79.89	94.94	79.80
	CCSD	77.75	94.31	129.92	110.48
	CCSD(T)	75.88	91.10	123.07	105.37

valence *s* orbital of Ra$^+$ undergoes relativistic contraction, the extent to which electron correlation causes the valence shell to contract is reduced and smaller correlation effects are observed for Ra$^+$ than for Ba$^+$. Interestingly, a similar trend in electron correlation effects is observed for the neutral group-1 elements where correlation effects at the relativistic level increase from K to Cs, but smaller correlation effects are observed for Fr and even smaller effects for the group-1 element 119 with increasing relativistic effects [59].

In order to test for spin-orbit (SO) coupling, four-component open-shell relativistic calculations were performed for Ba$^+$ and Ra$^+$. This was carried out with the uncontracted basis sets, *uncntr* in Table III. For Ba$^+$, the DC-HF calculation results in a dipole polarizability of 174.28 a.u. This is 0.36 a.u. smaller than the scalar relativistic result of 174.64 a.u. with the same basis set. For Ra$^+$, DC-HF calculation yields 144.73 a.u., 0.74 a.u. smaller than the DK counterpart.

The present dipole polarizabilities of the singly charged group-2 elements are compared with other values in Table VIII. As can be seen, the present values agree reasonably well with the DK-CCSD(T) values of Sadlej and co-workers [32], except for Ba$^+$ where their dipole polarizability seems to be overestimated due to basis-set deficiencies. Tang *et al.* [60] have used a rather different approach to calculate dipole polarizabilities. They evaluated multipolar matrix elements using simple one-particle wave functions within an effective potential approximation. It is interesting that such an approximation gives accurate values as these are in excellent agreement with our results. This gives confidence for our predicted dipole polarizability of Ra$^+$.

TABLE VIII. The dipole polarizabilities of the singly charged group-2 elements. The values are compared to other theoretical values (in a.u.).

	Method	Ca$^+$	Sr$^+$	Ba$^+$	Ra$^+$
This work	DK-CCSD(T)	75.88	91.10	123.07	105.37
Theor. [32]	DK-CCSD(T)	75.71	91.58	126.2	
Theor. [60]	SOS-OPA[a]	75.50	91.47	124.7	

[a] Sum-over-states approach within a one-particle approximation using an effective potential.

C. Doubly charged ions

The static dipole polarizabilities of the doubly charged group-2 elements from Ca^{2+} to Ra^{2+} are presented in Table IX. The nonrelativistic results show that the dipole polarizability increases monotonically from Ca^{2+} to Ra^{2+}; see Fig. 1. Electron correlation contributions to the dipole polarizability at the nonrelativistic level are negative, reducing the dipole polarizabilities from the HF values for all ions, except for Ca^{2+}; see Fig. 4. For Ca^{2+}, there is an increase in the dipole polarizability due to electron correlation at the CCSD(T) level of theory. It is interesting to note that Sadlej's results [32] also show a positive correlation contribution to the dipole polarizability of Be^{2+} and Mg^{2+} as well as Ca^{2+}. This sign change in the correlation contribution to the dipole polarizabilities was also noted in the singly charged group-1 elements [61] which have the same $(n-1)s^2p^6$ valence electron configuration as the present case. Electron correlation effects are small, for example amounting to only 1% for the dipole polarizability of Ra^{2+} at the nonrelativistic CCSD(T) level. The small effect of electron correlation is attributed to the much larger gap between the highest occupied and the lowest unoccupied molecular orbitals for the doubly charged group-2 ions than for the neutral or singly positive elements.

Figure 4 depicts scalar relativistic and spin-orbit coupling effects at the correlated level as well as electron correlation effects at the nonrelativistic and relativistic CCSD(T) level for comparison. It is easy to see that for Ca^{2+} scalar relativistic effects are very small. For Sr^{2+}, these effects grow and reduce the dipole polarizability due to the overall relativistic contraction of the $(n-1)p$ shell. Although the scalar relativistic contribution to the dipole polarizability of Sr^{2+} is small, it dominates over electron correlation by more than an order of magnitude. For Ba^{2+} and Ra^{2+}, scalar relativistic effects become increasingly more important and account for up to 9% of the dipole polarizability at the HF level. This is still

TABLE IX. The calculated static polarizabilities of the doubly charged group-2 elements at the nonrelativistic, relativistic Douglas-Kroll and Dirac-Coulomb level of theory (in a.u.). For a direct comparison of the DC with DK results, see basis set labeled *uncntr.* in Table IV.

		Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
NR	Basis set	$(20s15p8d5f)$	$(21s16p11d9f)/$ $[15s12p10d9f]$	$(25s21p16d8f5g)/$ $[16s15p12d8f5g]$	$(31s24p20d12f8g)/$ $[19s16p15d9f8g]$
	HF	3.255	5.866	10.913	14.628
	MBPT2	3.262	5.847	10.764	14.410
	CCSD	3.260	5.859	10.781	14.471
	CCSD(T)	3.263	5.864	10.796	14.496
DK	Basis set	$(20s15p8d5f)$	$(21s16p11d9f)/$ $[15s12p10d9f]$	$(25s21p16d8f5g)/$ $[16s15p12d8f5g]$	$(31s24p20d12f8g)/$ $[18s15p14d9f8g]$
	HF	3.248	5.790	10.559	13.360
	MBPT2	3.260	5.768	10.449	13.314
	CCSD	3.259	5.787	10.474	13.328
	CCSD(T)	3.262	5.792	10.491	13.361
DC	Basis set	$(20s15p8d5f)$	$(21s16p11d9f)$	$(25s21p16d8f)$	$(31s24p20d12f)$
	HF	3.248	5.795	10.603	13.809
	MBPT2	3.256	5.780	10.516	13.779

small in comparison with the scalar relativistic contributions for the neutral or singly charged group-2 elements, as one expects from a relatively small relativistic contraction of the $(n-1)p$ shell compared to *ns* shell. Such small relativistic effects do not cause any anomaly in the dipole polarizability trend. As a result, the dipole polarizability increases monotonically from Ca^{2+} to Ra^{2+} at the relativistic level. Spin-orbit coupling contributions are negligible for Ca^{2+} (the tiny decrease in the polarizability due to spin-orbit effects in our calculations probably reflects numerical instabilities in the finite field method) and also for Sr^{2+}, but are more visible for Ba^{2+}, where an increase in the dipole polarizability is observed from the spin-free DK scheme. Here, SO effects are still small and it is electron correlation that dominates over SO coupling effects. The SO coupling is, however, almost twice as large as the basis-set effects caused by *g*-type functions. For Ra^{2+}, SO coupling effects grow by an order of magnitude from Ba^{2+} and finally start to dominate over electron correlation. The largest contribution to the dipole polarizability, however, still comes from scalar relativistic effects. Overall, the SO contribution increases the dipole polarizability from the spin-free DK counterpart, and is due to the expansion of the $p_{3/2}$ shell which experiences an increased screening from the nucleus by the relativistically contracted *s* and $p_{1/2}$ orbitals.

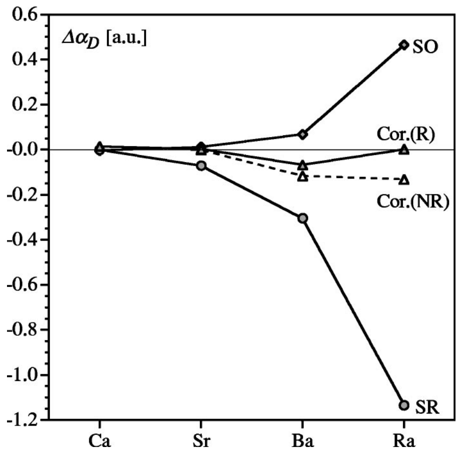

FIG. 4. Electron correlation and relativistic contributions to the dipole polarizabilities of the doubly charged group-2 elements (in a.u.).

In contrast to the nonrelativistic results, electron correlation contributions at the relativistic level increase only up to Ba^{2+} and then decrease for Ra^{2+}, see Fig. 4. Furthermore, these contributions to the dipole polarizability are negative up to Ba^{2+}. For Ra^{2+}, however, there is a sudden change in the trend of electron correlation effects, which results in a slightly positive contribution at the DK-CCSD(T) level. A similar behavior in electron correlation at the relativistic level has been reported for the $(n-1)$ valence system of the singly charged group-1 elements [59]. It is interesting to note such an anomaly in the electron correlation contribution caused by relativity as the situation only arises with a complete removal of the valence *ns* shell such as in the dipole polarizability of the respective singly and doubly charged group-1 and -2 ions. This clearly demonstrates the nonadditivity of electron correlation and relativistic effects.

The static dipole polarizabilities of the doubly charged group-2 elements corrected for spin-orbit corrections are compared with other theoretical values in Table X. Our dipole polarizabilities show excellent agreement with the numerical values of Mahan [64]. The estimated (experimental) values in Table X depend on the crystalline environment.

V. IONIZATION POTENTIALS

The accuracy of our calculated polarizabilities can be estimated from the accuracy of the calculated ionization poten-

TABLE X. Dipole polarizabilities of the doubly charged group-2 elements. The values are compared with other theoretical and estimated experimental values. All values are in a.u.

	Method	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
This work	DK+SO-CCSD(T)[a]	3.258	5.804	10.532	13.735
Theor. [64]	Numerical	3.307	5.871	10.528	
Theor. [32]	DK-CCSD(T)	3.05	5.52	9.97	
Est. [15,65]		3.523	5.669	11.675	

[a] Spin-orbit correction from MBPT2 results.

tials. We note that the relationship between dipole polarizabilities and ionization potentials was suggested by Dalgarno and Kingston [26], using the oscillator strength formula for systems exhibiting strong $ns \rightarrow sp$ transition of single valence electron systems. We pointed out before that for a one valence-electron case one obtains approximately the following relationship [58]:

$$\alpha_D = c_1 I^{-2} + c_2, \tag{6}$$

where c_1 and c_2 are adjustable constants and I is the ionization potential. In a similar way we obtain relativistic effects in dipole polarizabilities by the following relation:

$$\frac{\alpha_D^{NR}}{\alpha_D^{R}} = c_3\left(\frac{I_R}{I_{NR}}\right)^2 + c_4. \tag{7}$$

The basis sets for the ionization potential calculations were chosen to be the same as the final CCSD(T) dipole polarizabilities calculations. The ground-state first ionization potentials of the neutral group-2 elements are presented in Table XI together with experimental values [62,67].

At the nonrelativistic level, the ionization potentials show a monotonic decrease with increasing nuclear charge. This downward trend in ionization potentials is in accordance with the upward trend in the dipole polarizabilities from Ca to Ra at the nonrelativistic level as shown in Eq. (6). For the Ca ionization potential, relativistic effects are small as expected, but the deviation of the nonrelativistic value from experiment is halved by the consideration of such effects. Relativistic effects for Ra give rise to an anomalous trend in ionization potentials as noted before [66]. The present DK-CCSD(T) values tend to be slightly underestimated in comparison with experimental values. The agreement between the two sets of data is excellent, however, with a discrepancy of no more than 0.02 eV. The theoretical values in Table XI obtained by Fock-space Dirac-Coulomb-Breit calculations of Kaldor *et al.* [66] slightly overestimate the ionization potentials compared with experimental values. Another theoretical value of 5.278 eV for the ionization potential of Ra [63] also gives support for our value.

TABLE XI. The calculated ground-state first ionization potentials of the neutral group-2 elements (in eV).

	Method	Ca	Sr	Ba	Ra
This work	NR-HF	5.121	4.677	4.135	3.908
	NR-CCSD	6.002	5.522	4.947	4.701
	NR-CCSD(T)	6.074	5.607	5.054	4.815
	DK-HF	5.140	4.748	4.277	4.336
	DK-CCSD	6.022	5.593	5.092	5.139
	DC-CCSD(T)	6.093	5.678	5.194	5.238
Theor. [66]	DCB-FS-CCSD			5.327	5.369
Expt. [62,67]		6.113	5.695	5.212	

TABLE XII. The calculated ionization potentials of the singly charged group-2 elements compared with other values (in eV).

	Method	Ca^{+}	Sr^{+}	Ba^{+}	Ra^{+}
This work	NR-HF	11.31	10.29	9.06	8.55
	NR-CCSD	11.77	10.80	9.60	9.09
	NR-CCSD(T)	11.81	10.85	9.66	9.16
	DK-HF	11.35	10.44	9.36	9.42
	DK-CCSD	11.82	10.97	9.93	10.04
	DK-CCSD(T)	11.85	11.01	9.99	10.10
Theor. [66]	DCB-FS-CCSD			10.03	10.17
Expt. [68–70]		11.87	11.03	10.00	10.15

The linear relationship in Eq. (6) is almost perfectly satisfied with a correlation coefficient of 0.9997,

$$\frac{\alpha_D^{NR}}{\alpha_D^{R}} = 2.036\left(\frac{I_R}{I_{NR}}\right)^2 - 1.041. \tag{8}$$

The fact that the $\alpha_D^{NR}/\alpha_D^{R}$ is quadratically dependent on I_R/I_{NR} means that the ratio $\alpha_D^{NR}/\alpha_D^{R}$ grows faster than the ratio I_R/I_{NR}, which rationalizes the fact that relativistic effects in dipole polarizabilities are so important.

The calculated second ionization potentials of the singly charged group-2 elements are presented in Table XII together with other theoretical values. These will not be discussed in detail here, as the trends are basically the same compared to the neutral elements. Note, however, that for Ra^{+} relativistic effects become larger in magnitude than electron correlation effects. According to Eq. (6), the change in dipole polarizabilities between the neutral and singly charged group-2 elements is related to the ionization potentials, which we approximate by the following equation (in a.u.):

$$\Delta\alpha_D = c_5(I_0^{-2} - I_1^{-2}) + c_6, \tag{9}$$

where $\Delta\alpha_D = \alpha_D(\text{neutral elements}) - \alpha_D(\text{singly charged ions})$ and I_0 and I_1 are the first and second ionization potentials, respectively. The linear relationship between the two valence properties is almost perfectly satisfied with $c_5 = 6417.4$ and $c_6 = -64.611$ and a correlation coefficient of 0.9997.

VI. CONCLUSION

Given the large experimental uncertainties, it is of interest to obtain more accurate theoretical values for dipole polarizabilities, which could serve as future reference values. In this study we presented the dipole polarizabilities of the neutral, singly, and doubly charged group-2 elements from Ca to Ra

TABLE XIII. Recommended dipole polarizabilities of the group-2 elements (in a.u.).

M	$\alpha_D(M)$	$\alpha_D(M^+)$	$\alpha_D(M^{2+})$
Ca	157.9	75.9	3.25
Sr	199.0	91.1	5.80
Ba	273.5	122.7	10.5
Ra	246.2	104.0	13.7

together with the ground-state first and second ionization potentials calculated using specifically optimized and tailored GTO basis sets. Much effort has gone into obtaining dipole polarizabilities which are converged with respect to the basis-set expansion. We present our recommended dipole polarizabilities in Table XIII, which are adjusted to reflect all contributions to the dipole polarizability including electron correlation and relativistic effects as well as basis-set effects. To improve our results even further, calculations have to go beyond the relativistic CCSD(T) method.

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