

Relativistic coupled-cluster static dipole polarizabilities of the alkali metals from Li to element 119

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Static dipole polarizabilities α_D of the first main group elements from Li down to superheavy element 119 were calculated using a relativistic Douglas-Kroll Hamiltonian within an open-shell coupled-cluster theory. Spin-orbit effects were investigated using a fully relativistic four-component Dirac-Hartree-Fock scheme. Our final recommended values for the dipole polarizabilities from Li to Cs should be more accurate than currently available experimental data. Relativistic effects in α_D are roughly $\sim Z^2$ and we establish a clear relationship for relativistic and electron correlation effects between the dipole polarizability and the ionization potential of the neutral atom. Spin-orbit effects become non-negligible for Fr and element 119. For the latter, relativistic effects clearly dominate over electron correlation resulting in a very small α_D value comparable to that of sodium. [S1050-2947(99)03610-0]

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I. INTRODUCTION

Multipole polarizabilities are important for a number of optical properties and for the description of long-range forces in weakly interacting systems. However, an accurate calculation of static or dynamic multipole polarizabilities for heavy atoms or molecules, including heavy atoms, still remains a great challenge to theoreticians because electron correlation and relativistic effects become increasingly important for heavy elements [1,2]. On the experimental side, Miller and Bederson noted that experimentalists are still lagging behind theorists in dealing with atomic polarizabilities [3].

Concerning the static dipole polarizabilities of the neutral alkali-metal atoms there are two sets of experimental data by Molof *et al.* [4] and Zorn and co-workers [5,6], which have error bars of a few percent. There are also a number of theoretical studies [7,8] for H [9,10], Li [8,10–17], Na [8,10,13,15,16], K [1,10,13], Rb [1,13,18], Cs [1,18], and Fr [1]. Noteworthy are the calculations by Kellö *et al.* [1] for K, Rb, Cs, and Fr at the complete active space second-order perturbation theory (CASPT2) level using the mass-velocity and Darwin (MVD) terms of the Pauli Hamiltonian [19] to account for scalar relativistic effects. Dalgarno and Kingston noted that for one-valence electron systems like the alkali-metal atoms the sum-over-state formula for the dipole polarizability α_D can be approximated (in a.u.) by, [20],

$$\alpha_D = \int \frac{f_{0k}}{(E_0 - E_k)^2} \approx f_{2_s \rightarrow 2_p} (E_{2_s} - E_{2_p})^{-2}. \quad (1)$$

The integral runs over all discrete and continuum states, f_{0k} is the oscillator strength between the ground state $|0\rangle$ and the excited state $|k\rangle$, and E_k are the corresponding eigenvalues. More precisely we have

$$\begin{aligned} \alpha_D &= c_1 (E_0 - E_1)^{-2} + c_2 \\ &= c_1 I_0^{-2} \left(1 - \frac{I_1}{I_0} \right)^{-2} + c_2 = c_1 I_0^{-2} + c_2', \end{aligned} \quad (2)$$

where I_0 is the (first) ionization potential of the atom in its electronic ground state, and I_1 is the (first) ionization potential of the atom in its first electronic excited state with non-zero oscillator strength. The constants c_1 and c_2 are positive ($c_1 = f_{01}$) and c_2 is assumed to be small compared to the first term in expression (2) [21]. Dalgarno and Kingston noted that Eq. (1) works well for the alkali-metal atoms [20], and it was shown recently that this approximation works reasonably well for the group-11 metals Cu, Ag, and Au [22]. Equation (2) is interesting since it suggests a relationship between the polarizability and the first ionization potential. It was Fricke who first pointed out that static dipole polarizabilities correlate strongly with the first ionization potential [23] i.e., the polarizability decreases with increasing ionization potential as Eq. (2) suggests. $\alpha_D \sim I^{-2}$ also implies that the dipole polarizability is related to Pearson's hardness [24] η , $\alpha_D \sim \eta^{-2}$, although a recent study rather suggests $\alpha_D \sim \eta^{-3}$ [25]. Anyway, the experimental ionization potentials from H to Cs show a monotonic decrease [26], in accordance with the monotonic increase of the dipole polarizabilities [4–6].

The recent CASPT2 calculations by Kellö *et al.* suggest that for the element francium there appears to be an anomaly in the trend of the group-1 dipole polarizabilities due to relativistic effects [1], as indicated earlier by Miller and Bederson [3]. If we accept an almost linear relationship between the dipole polarizability and the ionization potential as im-

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TABLE I. A comparison between calculated numerical and finite basis-set total electronic energies at the nonrelativistic level of theory. (All values are in a.u.)

	Basis-set contraction schemes		Total electronic energies	
	NR	DK	NR numerical	NR finite basis
Li	11s7p4d/8s7p4d	11s7p4d/8s7p4d	-7.432 727	-7.432 418
Na	14s11p4d/11s10p4d	14s11p4d/11s10p4d	-161.858 912	-161.854 055
K	16s14p4d/12s12p4d	16s14p4d/12s12p4d	-599.164 787	-599.156 347
Rb	23s15p11d4f/17s12p9d4f	24s15p11d4f/17s12p9d4f	-2938.357 454	-2938.293 005
Cs	26s18p12d4f/16s11p8d4f	27s19p12d4f/13s11p8d4f	-7553.933 658	-7553.903 317
Fr	26s21p17d10f/15s13p10d7f	31s22p18d10f/15s13p10d7f	-22 475.858 712	-22 475.849 538
119	27s22p17d11f/17s13p10d7f	27s22p17d11f/17s13p10d7f	-47 258.448 972	-47 258.444 464

plied by Eq. (2), we can try to approximate relativistic effects as follows (the coefficient c_2 is assumed to be small):

$$\frac{\alpha_D^{\text{NR}}}{\alpha_D^{\text{R}}} = a \frac{I_R^2}{I_{\text{NR}}^2} + b, \quad (3)$$

where a and b are constants to be determined. This relation for single valence-electron systems has the following important consequences: (i) if relativistic (or electron correlation) effects increase the atomic ionization potential, the dipole polarizability will decrease; (ii) it is well known that relativistic effects in ionization potentials behave like $\Delta_R I \sim Z^2$. Because of the quadratic dependency in Eq.(3), relativistic effects in dipole polarizabilities should be larger percentage-wise compared to ionization potentials. This was verified recently for the group-11 metals [22].

In order to investigate relativistic effects in dipole polarizabilities in detail, we decided to perform accurate coupled-cluster calculations for the first ionization potentials and the static dipole polarizabilities of all group-1 metals from Li down to the superheavy element $Z=119$ using large basis sets within a relativistic Douglas-Kroll (DK) formalism [27]. While it has been shown recently that the first-order Pauli Hamiltonian is not adequate for the heaviest elements, the scalar relativistic Douglas-Kroll operator performs extremely well even for superheavy elements like element 111 [28].

II. METHOD

The scalar relativistic (spin-free) part of the no-pair Douglas-Kroll (DK) operator [29],

$$H_+^1 = \sum_i [E_i - mc^2 + V_{\text{eff}}^{\text{SF}}(i)] + \sum_{i<j} \frac{1}{r_{ij}} \quad (4)$$

was implemented in the MOLCAS3 program package [30], modifying only the one-electron integrals. Here $V_{\text{eff}}^{\text{SF}}$ is the one-particle effective spin-free (external) potential with

$$V_{\text{eff}}^{\text{SF}}(i) = -A_i(V_{\text{ext}}(i) + \vec{R}_i V_{\text{ext}}(i) \vec{R}_i) A_i - \frac{1}{2} \{ \{ E_i, W_{ij} \}, W_i \},$$

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

W_i is the intergral operator with kernel

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

and E_i is defined in the usual way,

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

$\{a, b\}$ denotes the anticommutator of a and b , SF denotes the spin-free DK approximation, and $V_{\text{ext}}(\vec{p}_i, \vec{p}'_i)$ is the Fourier-transform of the external potential [31].

A general contraction scheme for all basis sets was used and is summarized in Table I. The contraction coefficients were obtained from either a nonrelativistic or a relativistic DK self-consistent-field (SCF) calculation. The original GTO (Gaussian-type orbital) basis-set exponents for lithium, sodium, and potassium were taken from Ref. [13] and extended by one s function (0.003) and one p function (0.002) to allow for more flexibility in the diffuse region. The relativistic DK basis sets for these atoms were identical to the nonrelativistic ones. For the nonrelativistic calculations of rubidium the original basis set of Sadlej and Urban [13] was extended by two diffuse s functions (0.003 365, 0.0013). This GTO set was further augmented by four f -type polarization functions (14.1054, 5.5366, 2.2397, 0.8594) [1]. For the relativistic calculations of rubidium the first two hardest s functions of the original Sadlej-Urban basis set were removed and replaced by three s -type functions (1 843 444.8, 307 240.8, 61 448.16) for a better description of the core region. The original cesium GTO set was taken from Ref. [1] and extended by three s -type diffuse functions (0.003 813, 0.001 665, 0.000 727). To account for the relativistic effects, this GTO set was modified by replacing the two hardest s functions with six new s -type functions (25 325 100 000.0, 3 088 422 749.0, 428 947 604.0, 68 086 921.27, 14 379 440.23, 2 579 050.047) and the hardest p function with two new p -type functions (141 690.346, 28 338.0692). The initial francium GTO basis set from Ref. [1] was modified slightly by removing two of the f -type functions with exponents 5.341 611 35 and 0.239 269 542. For relativistic francium calculations this GTO set was extended by replacing the three hardest s functions with eight new s -type functions (358 861 000 000.0, 44 857 600 000.0, 6 144 876 662.0, 903 658 332.6, 150 609 722.1, 28 416 928.7, 6 458 392.886, 1 655 998.176), the two hardest p functions with three new functions (492 909.3, 98 581.86, 25 277.4), and finally the hardest d function with two new functions (26 669.611 87,

TABLE II. Atomic ionization potentials (I) and static dipole polarizabilities (α_D) at various levels of theory. Ionization potentials I in units of eV; dipole polarizabilities α_D in a.u.. The numerical HF and DHF (Dirac-HF) results for the ionization potentials are given in italics below the finite basis set HF and DKHF results. The H dipole polarizabilities are derived analytically [9,10]. Experimental ionization potentials from Ref. [26]. UCHF denotes the HF (DHF in the relativistic case) calculation using a completely uncontracted basis set.

		I_{NR}	I_R	α_D^{NR}	α_D^R			I_{NR}	I_R	α_D^{NR}	α_D^R
H	HF	13.6057	13.6050	4.50000	4.49975	CCSD	4.0413	4.1089	370.37	341.14	
	Expt.		13.5984			CCSD(T)	4.0681	4.1366	352.12	324.24	
Li	HF	5.3416	5.3420	169.50	169.45	Expt.		4.1772		319±6, ^a 329±23 ^b	
		<i>5.3419</i>	<i>5.3424</i>			Cs HF	3.3557	3.4733	806.81	670.88	
	UCHF(DHF)			169.42	169.35		<i>3.3560</i>	<i>3.4774</i>			
	MP2	5.3791	5.3795	164.49	164.44	UCHF(DHF)			806.76	668.14	
	CCSD	5.3843	5.3847	163.89	163.84	MP2	3.7076	3.8541	409.28	327.02	
	CCSD(T)	5.3850	5.3854	163.80	163.74	CCSD	3.6563	3.7952	548.00	444.09	
	Full-CI			163.73		CCSD(T)	3.6808	3.8207	516.08	432.71	
	Expt.		5.3917		164±4, ^a 148±13 ^b	Expt.		3.8939		402±8, ^a 427±31 ^b	
						Fr HF	3.2003	3.5645	963.64	542.99	
Na	HF	4.9486	4.9548	190.49	189.37		<i>3.1989</i>	<i>3.5880</i>			
		<i>4.9511</i>	<i>4.9574</i>			HF+ g^c		3.5645		542.98	
	UCHF(DHF)			190.55	189.41	UCHF(DHF)			963.63	530.02	
	MP2	5.0943	5.1013	165.83	164.82	MP2	3.5735	4.0292	327.18	193.51	
	CCSD	5.1016	5.1085	166.96	165.97	CCSD	3.5121	3.9428	610.56	355.44	
	CCSD(T)	5.1093	5.1162	165.89	164.89	CCSD+ g^c		3.9373		358.72	
	CCSD(TQ)			166.12		CCSD(T)	3.5420	3.9772	554.74	329.17	
	Expt.		5.1391		159±3.5, ^a 165±12 ^b	CCSD(T)+ g^c		3.9748		330.70	
K	HF	4.0046	4.0192	416.60	409.05	Expt.		4.0728			
		<i>4.0057</i>	<i>4.0205</i>			119 HF	2.9822	4.1060	1219.23	252.76	
	UCHF(DHF)			416.60	408.89		<i>2.9858</i>	<i>4.2423</i>			
	MP2	4.2620	4.2792	282.84	277.47	HF+ g^c		4.1060		252.76	
	CCSD	4.2556	4.2725	312.93	307.22	UCHF(DHF)			1219.23	237.22	
	CCSD(T)	4.2672	4.2841	306.77	301.28	MP2	3.3499	4.6635	412.09	130.45	
	Expt.		4.3407		293±6, ^a 305±22 ^b	CCSD	3.2894	4.5077	756.66	191.34	
						CCSD+ g^c		4.5083		191.40	
Rb	HF	3.7445	3.8015	522.39	483.77	CCSD(T)	3.3119	4.5384	693.94	184.83	
		<i>3.7422</i>	<i>3.8002</i>			CCSD(T)+ g^c		4.5398		184.54	
	UCHF(DHF)			522.36	483.07						
	MP2	4.0740	4.1442	290.73	267.32						

^aMolof *et al.* [4].

^bZorn *et al.* [5,6].

^cAn additional set of three g functions contracted to one was added to the basis set.

7408.225 52). We obtained the exponents for the element 119 by minimizing the total electronic energy at the nonrelativistic level [32]. The exponents obtained were used for both nonrelativistic and relativistic calculations. Note that for this element we had to use a somehow smaller basis set compared to the other elements because of the large number of electrons involved. A comparison between numerical Hartree-Fock (HF) total energies obtained by using the multiconfiguration Hartree-Fock (MCHF) program [33] and our finite basis set results show that the basis sets used are of almost HF limit quality; see Table I. In order to check the influence of g functions to correlate the occupied f orbitals, we added a contracted (3 g)→(1 g) function for Fr and element 119 using the three lowest f exponents in each case (denoted as + g).

In this DK scheme spin-orbit effects are neglected. These are of second-order and are expected to be small for the ground state valence properties (such as dipole polarizabil-

ities) of alkali metals. In order to test the influence of spin-orbit coupling we performed fully relativistic open-shell Dirac-Hartree-Fock calculations (DHF) [34] for all elements using the standard Dirac operator,

$$D = \sum_i \{c \tilde{\alpha}_i \vec{p}_i + c^2 \beta_i + V_{\text{ext}}(i)\} + \sum_{i < j} \frac{1}{r_{ij}}, \quad (5)$$

where α and β are the well-known Dirac matrices [35]. Equation (4) can be obtained by a unitary transformation from Eq. (5) [29]. For the Dirac-Hartree-Fock (DHF) calculations the same basis sets as described above were used but in uncontracted form (UCDHF). However, for element 119 the total electronic energy was 41 a.u. above the DHF limit obtained from numerical DHF calculations using GRASP [36]. We therefore added two more hard p functions yielding a basis set with energy only 3.4 a.u. above the DHF limit. These two p functions were important for a more accurate

description of the $2p_{1/2}$ orbital and increased the DHF polarizability by $\Delta\alpha = +1.45$ a.u. In contrast, they are negligible in the DK calculations, $\Delta\alpha = +0.27$ a.u. All DHF calculations were performed with the Dirac program [34], applying a Gaussian nuclear model with nuclear exponents as given by Visscher and Dylla [37]. The resulting Gaussian basis set has been used in a spherical and uncontracted form for the large component functions, and the small component basis sets were generated from the large component set using a linear transformation and a projection [38] that is equivalent to the restricted kinetic balance (RKB) condition [35,39]. In order to obtain the effect of the basis-set contraction we also carried out uncontracted HF calculations for all elements.

The static dipole polarizabilities of each atom were calculated by applying a point charge model where two charges are placed with opposite sign at a large distance (100 a.u.) from the atom in order to achieve near homogeneity of the electric-dipole field. The electric-field strengths of 0.000, ± 0.001 , ± 0.002 , and ± 0.004 a.u. were used for each atom, yielding seven points to be fitted to a fourth-order polynomial $E(F)$ of total electronic energy E as a function of electric-field strength F . Second derivatives of these polynomials were taken at Hartree-Fock, many-body perturbation theory (second-order Møller-Plesset, MP2) and the coupled-cluster CCSD and CCSD(T) level [40] to obtain the static dipole polarizabilities. The error introduced by the small inhomogeneity created by our point charge model is less than 0.1 a.u., as tested at the nonrelativistic level using homogeneous electric-field perturbations. Nevertheless, we tabulate the dipole polarizabilities to two significant figures in order to make the small relativistic effects for the lighter elements more transparent. Single and double excitation were properly spin adapted in CCSD. The diagonal Fock matrix elements were taken as denominators in the perturbative estimates of triples [40]. For Li we checked the accuracy for treating the triples perturbatively by a full configuration interaction treatment (full-CI) for the nonrelativistic case. For Na we investigated the quadruple contributions in the CCSD procedure by performing nonrelativistic CCSD(TQ) calculations [41]. Calculations on the positively charged atoms were performed in order to obtain the first ionization potential of each atom. The active orbital space in the coupled-cluster calculations was chosen as follows: Li, Na, and K fully active; frozen KL core for Rb and Cs; frozen KLM core for Fr; and frozen KLMN core for element 119. This means that we have correlated altogether 59 electrons in Fr and element 119. The reason for increasing the number of correlated electrons for the heavier elements is that core polarization increases with increasing nuclear charge.

III. RESULTS

The calculated ionization potentials I and static dipole polarizabilities α_D for the elements H to 119 are shown in Table II. The relativistic coupled-cluster polarizabilities are shown in Fig. 1 together with the experimental values. Up to the element cesium all our Douglas-Kroll CCSD(T) polarizabilities lie within the experimentally estimated values. This gives us confidence for the predicted dipole polarizabilities of the elements Fr and element 119. For Cs, spin-orbit effects start to become significant and for Fr and element 119

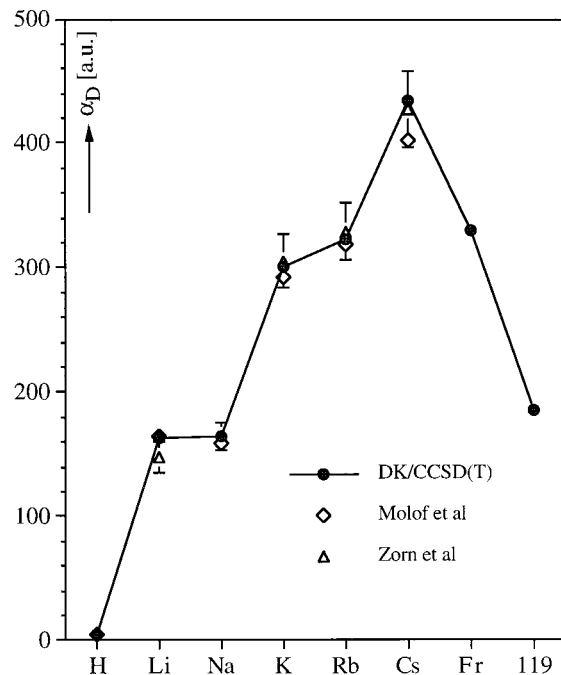


FIG. 1. A comparison between theoretical DK/CCSD(T) and experimental dipole polarizabilities measured by Molof *et al.* [4] and Zorn *et al.* [5,6]. The experimental error bars are given as well.

spin-orbit contributions cannot be neglected anymore. The influence of adding g functions in order to correlate the occupied f space is very small, as the data in Table II show. We also investigated the accuracy of the CCSD(T) procedure by performing full-CI calculations for Li and CCSD(TQ) calculations for Na, which leads only to minor changes compared to the CCSD(T) treatment. Furthermore, the basis-set contraction leads only to minor changes as a comparison between HF and UCHF at the nonrelativistic level shows. Considering our high-quality basis sets and the high-quality treatment of relativistic and electron correlation effects, we are confident that our results are more accurate than previously published experimental or theoretical data. Nevertheless, if we take the most accurate calculated values published by other authors so far, we see good agreement [in a.u.; our DK CCSD(T) values are given in parentheses for comparison]: Li NR/CCSD(T) 164.25 [14], NR Hylleras basis 164.11 (163.74) [42], Na NR/PNO-CEPA 165.02 (164.89) [15], K MVD/CASPT2 295.5 (301.27) [1], Rb MVD/CASPT2 330.2 (323.57) [1], Cs MVD/CASPT2 413.6 (433.97) [1]; Fr MVD/CASPT2 325.7 (329.17) [1]. Our recommended dipole polarizabilities for all group-1 elements are summarized in Table III. We mention that for sodium the dipole polarizability has recently been determined by atomic interference that gave 162.7(4) a.u. [43]. Our recommended

TABLE III. Recommended dipole polarizabilities (α_D) calculated from relativistic CCSD(T) including spin-orbit contributions at the DHF level (in a.u.).

	H	Li	Na	K	Rb	Cs	Fr	119
α_D	4.49975 ^a	164 ^b	165	301	324	430	318	169

^aReferences [9,10].

^bReference [42].

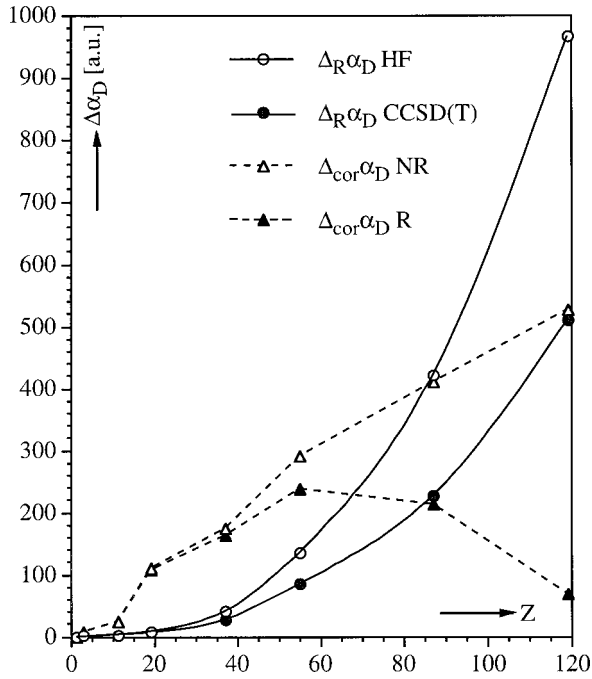


FIG. 2. Scalar relativistic Δ_R and correlation Δ_{cor} contributions to the dipole polarizability as a function of the nuclear charge Z .

value of 165 a.u. shows that our polarizabilities could be in error by a maximum of 2–3 a.u.

Figure 2 depicts relativistic (at the HF and correlated levels) and electron correlation effects (at the nonrelativistic and relativistic levels) on dipole polarizabilities. We note several important trends:

(i) At the nonrelativistic level the correlation contribution to the dipole polarizability is monotonically increasing, as one would expect. A reasonable fit is obtained using (α_D in a.u.)

$$\alpha_D \approx 4.5Z + 150 \quad (6)$$

for the CCSD(T) values of Li up to element 119.

(ii) Relativistic effects $\Delta_R \alpha_D$ increase approximately $\sim Z^2$ at both the HF and CCSD(T) levels. A polynomial fit for the CCSD(T) results gives (α_D in a.u.),

$$\Delta_R \alpha_D = \alpha_D^{\text{NR}} - \alpha_D^{\text{R}} = -2.275 \times 10^{-2} + 2.30 \times 10^{-2} Z^2 + 8.83 \times 10^{-7} Z^4, \quad (7)$$

with a root-mean-square error of 9.6 a.u. and a very small fourth-order contribution. This large increase leads finally to an anomaly as pointed out by Kellö *et al.* [1]; i.e., from Cs to Fr the polarizability suddenly decreases and this downward trend remains for element 119, as shown in Fig. 1. In fact, superheavy element 119 has a similar dipole polarizability, as Na and relativistic effects for this element account for more than 967 a.u. (143 \AA^3).

(iii) Relativistic effects lead to a contraction of the valence s orbital, which is $\sim Z^2$. This results in a relativistic decrease of the correlation contribution and therefore again to an anomaly in $\Delta_{\text{cor}} \alpha_D$ at the relativistic level, as shown in Fig. 2. Because relativistic effects significantly change

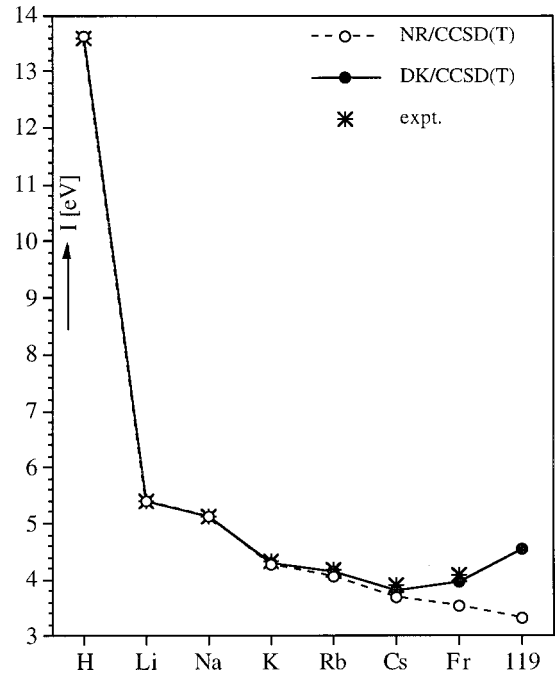


FIG. 3. A comparison between theoretical NR and DK CCSD(T) and experimental ionization potentials [26].

electron-correlation contributions, especially for dipole polarizabilities, both effects no longer additive.

(iv) In comparison to relativistic effects, correlation effects for α_D dominate up to Cs and become similar in size for Fr. Element 119 clearly shows large relativistic and smaller electron-correlation effects.

(v) A comparison between second-order Rayleigh-Schrödinger perturbation theory for electron correlation

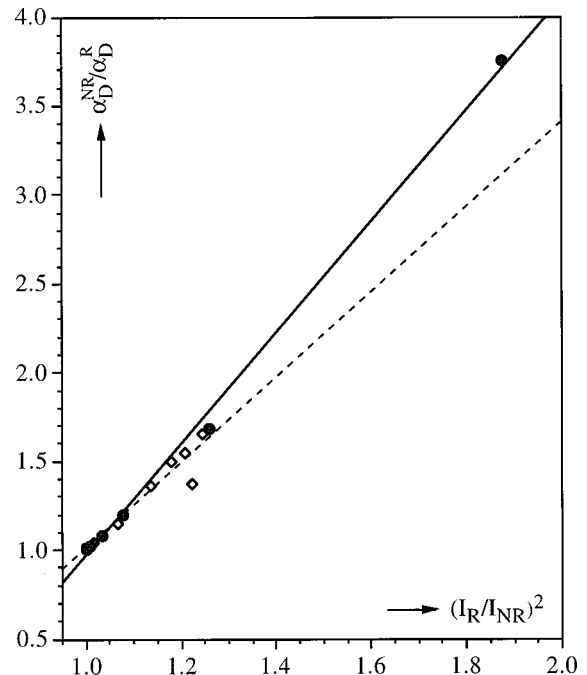


FIG. 4. Relation between relativistic changes in α_D and I according to Eq. (3). Also shown on this graph (dashed line; values shown as diamonds) is the effect of electron correlation; i.e., $\alpha_D^{\text{DK}}/\alpha_D^{\text{DKCCSD(T)}}$ versus $I_{\text{DKCCSD(T)}}^2/I_{\text{DK}}^2$.

(MP2) and coupled cluster [CCSD(T)] shows that the MP2 method is not very reliable; in other words, the perturbation expansion converges slowly, especially for the heavier elements. Except for Li, the MP2 method overestimates the electron-correlation contribution [as compared with CCSD(T)] to polarizabilities. The same is true for the ionization potentials of Rb, Cs, Fr, and 119.

The nonrelativistic and relativistic ionization potentials are shown in Fig. 3. Again, our DK/CCSD(T) values are in good agreement with experimental results (see also Ref. [44] for accurate fully relativistic coupled-cluster calculations). Analyzing the errors due to basis-set incompleteness and the relativistic electron-correlation procedure applied for the elements Li to Fr, we predict an ionization potential of ~ 4.65 eV for element 119. In accordance with the trend in the dipole polarizabilities, the ionization potentials change from the expected downward trend with increasing nuclear charge to an increase for the two heaviest atoms Fr and element 119. The relativistic change in the ionization potentials is $\sim Z^2$, as expected (I in eV),

$$\Delta_R I = I^{\text{NR}} - I^R \approx -2.7 \times 10^{-5} Z^2 - 4.2 \times 10^{-9} Z^4. \quad (8)$$

Figure 4 shows a plot defined by Eq. (3). As can be seen, this simple relationship is almost perfectly fulfilled and we have

$$\frac{\alpha_D^{\text{NR}}}{\alpha_D^R} \approx 3.130 \frac{I_R^2}{I_{\text{NR}}^2} - 2.156, \quad (9)$$

with a root-mean-square error of only 0.12. Thus the large relativistic effect in α_D can be derived from the (quadratic) relativistic change in the ionization potential as a direct result of the relativistic s -orbital contraction. Figure 4 also shows a nice linear behavior for the electron correlation effects,

$$\frac{\alpha_D^{\text{DK}}}{\alpha_D^{\text{DKCCSD(T)}}} \approx 2.39 \frac{I_{\text{DKCCSD(T)}}^2}{I_{\text{DK}}^2} - 1.39. \quad (10)$$

We conclude that for one-valence electron systems like the group-1 metals the trend in dipole polarizabilities, including changes due to relativistic and electron correlation effects, can be understood from similar trends in their first ionization potentials.

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