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All-electron and relativistic pseudopotential studies for the group 1 element polarizabilities from K to element 119

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Two-component and scalar relativistic energy-consistent pseudopotentials for the group 1 elements from K to element 119 are presented using nine electrons for the valence space definition. The accuracy of such an approximation is discussed for dipole polarizabilities and ionization potentials obtained at the coupled-cluster level as compared to experimental and all-electron Douglas–Kroll results. © 2005 American Institute of Physics. [DOI: 10.1063/1.1856451]

I. INTRODUCTION

The way of developing a valence-only formalism for atoms and molecules is by the use of pseudopotentials, which is the preferred choice in the calculation of heavy element containing systems.^{1,2} One of the biggest advantages of the pseudopotential method is attributed to the computational savings in integral calculations by replacing the core electrons by an effective potential.^{3,4} Perhaps more importantly the pseudopotentials can be generated to account for the main relativistic effects, which can be easily incorporated into the pseudopotential scheme.^{5–7}

As for the group 1 elements, such advances have resulted in the generation of small-core (nine-valence electron) energy-consistent scalar relativistic pseudopotentials by Leininger *et al.*,⁸ where the relativistic effects were accounted for by a one-component (scalar) relativistic Hamiltonian.⁹ These pseudopotentials have been used in molecular and solid state calculations involving homonuclear/heteronuclear dimers, hydrides, and halides^{8,10} of the group 1 elements.

In the present study, we have generated small-core nine-valence electron energy-consistent pseudopotentials of the group 1 elements from K to element 119 (E119), using the Dirac–Coulomb multiconfiguration Hartree–Fock (DC-MCHF) method.¹¹ These include *j*-averaged pseudopotentials (ARPP) and two-component spin-orbit coupled pseudopotentials (SOPP). Core-polarization potentials^{12–14} were also generated for Cs to E119. The accuracy and reliability of these pseudopotentials together with our optimized valence basis sets were tested for the static electric dipole polarizabilities and ground state ionization potentials of the group 1 elements from K to E119. Polarizabilities are quite sensitive to the model applied, and a comparison to all-electron (AE) and/or experimental values give a clear indication of the reliability of the pseudopotential approximation.

It must be stressed that the basis set requirements for the dipole polarizability in all-electron calculations are severe. The accuracy of the calculated dipole polarizabilities¹⁵ criti-

cally depend on the quality of the basis sets used and this resulted in the generation of sets such as the first-order polarized basis sets of Sadlej and Urban¹⁶ or the atomic natural orbital (ANO) type basis sets of Roos *et al.*¹⁷ Following our basis set study of the positively charged group 1 elements,^{18,19} we have decided to investigate basis set effects on the static dipole polarizabilities of the group 1 elements at the coupled-cluster (CC) all-electron level within the Douglas–Kroll (DK) relativistic formalism.

II. METHODS

A. All-electron method and atomic basis sets

In the present study, the scalar relativistic effects in AE calculations were accounted for by modifying the one-electron integrals via a no-pair DK operator,^{20,21}

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

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

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

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

W_i is the integral operator with kernel,

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

and E_i is defined as

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

$\{a, b\}$ 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.

Electron correlation was treated by applying second-order Møller–Plesset perturbation theory (MP2) and CC with

single and double excitations (CCSD) plus perturbative triples [CCSD(T)].²² The active space in the CC calculations were (unless stated otherwise): no frozen core for K, frozen KL core for Rb, KLM frozen core for Cs, and KLMN frozen core for Fr and E119. All virtual orbitals with orbital energies higher than 1000 a.u. were deleted in the correlation procedure. All AE calculations were performed with the MOLCAS program package.²³

The importance of basis sets in calculating polarizabilities is well documented.^{16,24} We therefore decided to carefully study basis set effects on atomic polarizabilities of the neutral group 1 elements at the relativistic DK level. This was carried out by modifying our previously developed DK all-electron basis sets²⁵ in such a way that the basis set exponents were tight enough to result in converged polarizabilities. The necessary range of exponents for each angular momentum subset was determined by monitoring the convergence behavior of the group 1 dipole polarizabilities with respect to the basis set expansion at the DK Hartree–Fock (HF) and DK-MP2 level. Particular attention was given to the influence of polarization functions on the dipole polarizabilities by extending the original basis sets with *g*-type functions and beyond. The present basis set modification is as follows. For K, the original DK basis set was extended by one *s*-type function (0.07) and three *d*-type functions (4.1168, 1.556, 0.081 26), leading to a (17*s*14*p*7*d*) Gaussian-type orbital (GTO) set. This GTO set was further augmented by five *f*-type functions (4.1168, 1.556, 0.612 19, 0.223 05, 0.081 26), giving a final (17*s*14*p*7*d*5*f*) GTO set. For Rb, the original DK basis set was modified by replacing six *s*-type functions (3.130 680, 1.423 036, 0.646 835, 0.31, 0.15, 0.08), by five (3.946 150, 1.844 039, 0.692 172, 0.276 767, 0.0791), and by deleting one function (0.006 404) in order primarily to eliminate linear dependencies. This (22*s*15*p*11*d*4*f*) GTO set was further augmented by four additional *f*-type functions (0.211 26, 0.071, 0.025 49, 0.008 86) and five *g*-type functions (17.659 46, 6.359 740, 2.431 531, 0.721 516 6, 0.211 26), leading to a (22*s*15*p*11*d*8*f*5*g*) GTO set. The original DK basis set of Cs was extended with one *d*-type function (0.0498) and six *f*-type functions (30.342, 0.3469, 0.133 84, 0.049 804, 0.019 921 7, 0.007 685 9). In order to test the influence of *g* functions, this (27*s*19*p*13*d*10*f*) GTO set was augmented with five *g*-type functions (5.6225, 2.373 08, 0.916 18, 0.3469, 0.133 84), leading to a final (27*s*19*p*13*d*10*f*5*g*) GTO set. For Fr, an additional *d*-type function (0.052 867) and four additional diffuse *f*-type functions (0.361 091, 0.134 774, 0.052 867 2, 0.022 028) were added to the original DK basis set. The influence of *g*-type functions was tested more extensively than previously carried out,²⁵ by an addition of seven *g*-type functions. The resulting GTO set was (31*s*22*p*19*d*14*f*7*g*). For E119, a new (31*s*29*p*23*d*17*f*11*g*) GTO set was obtained by an energy minimization using a modified four-component relativistic GRASP code.²⁶ This GTO set was contracted to a [17*s*16*p*14*d*17*f*11*g*] set.

All GTO sets were generally contracted. The contraction coefficients were obtained from relativistic Douglas–Kroll

TABLE I. All-electron basis sets and contraction schemes.

Basis set contraction schemes	
K	(17 <i>s</i> 14 <i>p</i> 7 <i>d</i> 5 <i>f</i>)/[12 <i>s</i> 12 <i>p</i> 7 <i>d</i> 5 <i>f</i>]
Rb	(22 <i>s</i> 15 <i>p</i> 11 <i>d</i> 8 <i>f</i> 5 <i>g</i>)/[14 <i>s</i> 11 <i>p</i> 9 <i>d</i> 8 <i>f</i> 5 <i>g</i>]
Cs	(27 <i>s</i> 19 <i>p</i> 13 <i>d</i> 10 <i>f</i> 5 <i>g</i>)/[13 <i>s</i> 11 <i>p</i> 9 <i>d</i> 10 <i>f</i> 5 <i>g</i>]
Fr	(31 <i>s</i> 22 <i>p</i> 19 <i>d</i> 14 <i>f</i> 7 <i>g</i>)/[15 <i>s</i> 13 <i>p</i> 11 <i>d</i> 11 <i>f</i> 7 <i>g</i>]
E119	(31 <i>s</i> 29 <i>p</i> 23 <i>d</i> 17 <i>f</i> 11 <i>g</i>)/[17 <i>s</i> 16 <i>p</i> 14 <i>d</i> 17 <i>f</i> 11 <i>g</i>]

calculations. Our optimized final basis sets along with the contraction schemes are summarized in Table I.

B. Pseudopotentials and corresponding valence basis sets

In the present study, the following valence model Hamiltonian (in atomic units) was used,

$$H_v = -\frac{1}{2} \sum_i \Delta_i + \sum_i V_{pp}(i) + \sum_{i < j} \frac{1}{r_{ij}} + V_{CPP}, \quad (5)$$

where *i, j* are valence electron indices and $V_{pp}(i)$ is a semilocal pseudopotential. For a *j*-dependent two-component SOPP, we use the following ansatz for the pseudopotential (*pp*) $V_{pp}(i)$ of the form

$$V_{\text{SOPP}}(i) = -\frac{Q_c}{r_i} + \sum_{klj} B_{klj} \exp(-\beta_{klj} r_i^2) P_{lj}(i), \quad (6)$$

where Q_c denotes the core charge of a specific atom (in our case $Q_c=9$ for all atoms), and P_{lj} is the projection operator acting on the Hilbert subspace of angular symmetry *l* and *j* = *l* ± 1/2. *k* is a simple expansion parameter which determines the number of Gaussian functions used, with a maximum *k* value for each (*lj*) to be 2. For a *j*-averaged pseudopotential, ARPP, the above ansatz largely remains the same with the *j* dependence dropped out,

$$\begin{aligned} V_{PP} &= V_{\text{ARPP}} + \Delta V_{\text{SOPP}} \\ &= -\frac{Q_c}{r_i} + \sum_{kl} A_{kl} \exp(-\alpha_{kl} r_i^2) P_l(i) + \Delta V_{\text{SOPP}}. \end{aligned} \quad (7)$$

In both cases, these essentially form a linear combination of Gaussian functions with adjustable parameters. The spin-orbit correction ΔV_{SOPP} then is,

$$\begin{aligned} \Delta V_{\text{SOPP}}(i) &= \sum_{kl} [C_{kl(l+1/2)} \exp(-\gamma_{kl(l+1/2)} r_i^2) \\ &\quad + C_{kl(l-1/2)} \exp(-\gamma_{kl(l-1/2)} r_i^2)] P_l(i) \vec{l}_i \vec{s}_i P_l(i). \end{aligned} \quad (8)$$

In order to construct a series of reference data to which the pseudopotential parameters are adjusted, the all-electron reference valence energies, defined as $E_{\text{val},nm}^{\text{AE}} = E_{\text{total},nm} - E_{\text{core}}$ of a number of different electronic states for each element were obtained numerically in all-electron multiconfiguration Dirac–Coulomb–Hartree–Fock (DC–HF) calculations, using a modified version of the finite-difference atomic GRASP code.²⁶ Here, relativistic effects are included at a four-component level using the Dirac–Coulomb Hamil-

tonian, with Breit interaction terms in the low frequency limit correct to first order.²⁷ Average level type of calculations were performed with GRASP, which includes all configuration state functions resulting from a given nonrelativistic configuration. For the case of SOPPs, individual j -dependent energies were used, whereas the ARPPs are obtained from j averaging the SOPPs (hence increasing the number of Gaussian functions for each l to a maximum of 4). Note that ARPPs may also be constructed from j -averaged energies.⁴ The pseudopotential parameters were then fitted in a least-square sense such that the following function is minimized with respect to B_{klj} and β_{klj} as shown in Eqs. (6),

$$S = \sum_m \sum_n w_{nm} [E_{nm}^{PP} - E_{val,nm}^{AE}]^2. \quad (9)$$

Here, m and n are orbital configurations and relativistic states of a given orbital configuration, and E_{nm}^{PP} and $E_{val,nm}^{AE}$ are valence energies from the pseudopotential and all-electron calculations, respectively. w_{nm} are respective individual and configurational weights. We used equal weights for all states of a specific nonrelativistic configuration. By an augmented-Hessian-like procedure based on the derivatives of E_{nm}^{PP} with respect to B_{ljk} and β_{ljk} , a new set of parameters resulting in a smaller value of S was obtained. This typically involves some hundred iteration steps, achieving a near minimum value of S . Such methods have been used recently in the generation of energy-consistent pseudopotentials for the group 11–18 atoms^{28–31} using a small core definition, i.e., for the main group elements the valence space is defined as $(n-1)spd(n)sp$. In the present study, the valence shell of the group 1 elements consists of nine electrons.

In order to address the issue on the transferability of pseudopotentials to the subsequent molecular level, we have included in our reference energy data spectrum, the singly and doubly charged cations and the anion for s , p , and d projectors. These configurations are important, for example, in the calculation of ionic compounds such as CsF. The f and g projectors were adjusted to the valence energies arising from various configurations of the $6+$ ions with a single f or g electron outside the s^2 closed shell to obtain a better convergence. The maximum value of parameter l in Eq. (6) has been chosen to be 3 for K and Rb, and 4 for Cs, Fr, and E119. The pseudopotential parameters for the ARPPs and SOPP as defined as in Eqs. (7) and (8) are listed in Table II. Note that the k numbering is with respect to the ARPP notation. As a demonstration, the reference states used for the generation of the cesium pseudopotential are given in Table III. We mention that fitting the f and g projectors for element 119 was not straightforward and we had serious convergence problems in the numerical self-consistent-field (SCF) procedure. There are other local minima, some with quite small exponents in the f projector, leading to very similar polarizabilities.

Up to this point, core-valence correlation and core-polarization effects are neglected in V_{pp} . This, however, may not be such a good approximation, especially for the heavier alkali atoms where the core becomes increasingly more polarizable. Therefore, the last term in Eq. (5), V_{CPP} , is introduced in order to account for the dynamic polarization of the

atomic core by the valence electrons. The following local form of the effective core-polarization potential (CPP) for an atom is used as demonstrated by Müller *et al.*¹²

$$V_{CPP} = -\frac{1}{2} \alpha_D \tilde{f}^2, \quad \text{where } \tilde{f} = -\sum_i \frac{\vec{r}_i}{r_i^3} [1 - \exp(-\delta r_i^2)]^2. \quad (10)$$

α_D is the static dipole polarizability of the specific core and \tilde{f} is the electric field generated by the valence electrons. A cutoff parameter for the electric field is used to avoid divergence of the integrals caused by the valence electrons at the origin. Further details on the pseudopotential fitting procedures and the numerical values of the parameters can be found in the works by Fuentealba, Stoll, and Schwerdtfeger.^{13,14,32} Following our small-core definition of M^{9+} , the CPPs were included only for Cs, Fr, and E119. The dipole polarizabilities of the M^{9+} core were obtained in AE CCSD(T) calculations using the present all-electron basis sets and a finite-field technique using a dipole point charge model.²⁵ The M^{8+} ionization potentials determined in AE CCSD(T) calculations were used as input data for adjusting the cutoff parameter. The CPP parameters used in the present study are listed in Table IV.

So far any errors due to the finite basis set expansion have been avoided by our numerical calculations in the generation of the pseudopotentials. These pseudopotentials need to be accompanied with accurate valence basis sets for the subsequent molecular calculations. The exponents for these valence basis sets were directly taken from the relativistic all-electron basis sets developed in this study, omitting the high-exponent functions which do not contribute greatly to the total electronic energy. These valence basis sets are presented in Table V where the contraction coefficients were obtained from pseudopotential HF calculations. All pseudopotential calculations were performed with the MOLPRO program package.³³

In order to demonstrate the accuracy of our present pseudopotential approximation, the HF valence energies of selected states of the group 1 elements calculated by numerical all-electron and pseudopotential methods are listed in Table VI. Also in Table VII orbital energies ε and expectation values $\langle r \rangle$ from all-electron DC-HF and pseudopotential calculations for the ground state alkali elements are listed for comparison. The pseudopotential error, ΔE^{PP} , is well below 0.01 eV for K and Rb. From Cs onwards, ΔE^{PP} of some of the states starts to exceed 0.01 eV. The problematic configurations for elements up to Cs seem to be the doubly charged configuration of $(n-1)s^2p^5$. For the heavier elements, the pseudopotential error of the negatively charged $(n)s^2$ configuration exceeds that of the doubly charged $(n-1)s^2p^5$ configuration. Also evident from Table VI is the relatively large pseudopotential errors associated with element 119. In particular, the pseudopotential valence energy of the ground state configuration of $7s^27p^68s^1$ for E119 deviates from the all-electron case by as much as 0.026 eV. Three other states listed in Table VI for E119 have pseudopotential errors in excess of 0.01 eV. It is therefore evident that for the heaviest elements a smaller core definition is required to achieve

TABLE II. The ARPP and SOPP parameters of the group 1 elements (see text for details). The SOPP parameters already contain the commonly used prefactor of $2/(2l+1)$.

	<i>i</i>	<i>j</i>	<i>k</i>	A_{kl}	α_{kl}/γ_{klj}	C_{klj}
K	<i>s</i>	1/2	1	91.144 930 956 159 7	6.882 798 724 586 71	
		1/2	1	9.674 728 404 352 93	4.726 860 935 382 62	−19.349 456 808 705 9
	<i>p</i>	3/2	2	20.569 141 944 695 5	4.845 267 085 850 88	20.569 141 944 695 5
		3/2	1	−2.542 646 075 672 58	8.707 542 695 709 42	2.542 646 075 672 58
	<i>d</i>	5/2	2	−3.464 046 662 570 23	8.310 839 526 122 56	−2.309 364 441 713 48
		3/2	3	−2.542 646 075 672 50	8.707 542 695 709 29	2.542 646 075 672 50
		5/2	4	−3.464 046 662 572 40	8.310 839 526 123 74	−2.309 364 441 714 94
	<i>f</i>	5/2	1	−16.555 281 536 913 6	13.939 669 152 724 9	11.036 854 357 942 4
		7/2	2	−36.621 153 099 844 3	16.629 551 418 346 5	−18.310 576 549 922 2
Rb	<i>s</i>	1/2	1	89.503 949 586 582 0	5.031 683 377 034 07	
		1/2	2	0.437 903 605 407 40	2.015 185 434 389 94	
	<i>p</i>	1/2	1	19.520 470 196 343 8	4.383 544 458 875 11	−39.040 940 392 687 7
		3/2	2	39.038 955 357 373 2	4.332 659 280 071 95	39.038 955 357 373 2
		1/2	3	0.170 609 341 094 21	1.374 288 087 822 54	−0.341 218 682 188 42
		3/2	4	0.418 499 875 580 78	1.225 772 391 016 97	0.418 499 875 580 78
	<i>d</i>	3/2	1	10.482 661 239 202 7	3.415 601 371 470 31	−10.482 661 239 202 7
		5/2	2	15.724 060 278 127 6	3.412 863 366 363 59	10.482 706 852 085 0
		3/2	3	0.266 082 838 442 97	1.030 504 898 889 13	−0.266 082 838 442 97
		5/2	4	0.408 802 184 428 97	1.019 872 163 088 08	0.272 534 789 619 31
	<i>f</i>	5/2	1	−4.478 284 427 952 90	3.574 403 408 814 03	2.985 522 951 968 60
		7/2	2	−5.956 907 509 284 51	3.565 710 590 642 82	−2.978 453 754 642 26
Cs	<i>s</i>	1/2	1	84.547 722 330 315 8	4.081 119 213 165 74	
		1/2	2	16.654 034 969 716 5	2.421 522 383 391 16	
	<i>p</i>	1/2	1	52.349 630 743 380 7	5.533 972 644 202 38	−104.699 261 486 761
		3/2	2	104.699 413 178 443	5.506 794 383 746 37	104.699 413 178 443
		1/2	3	8.806 557 724 631 47	2.280 961 579 685 69	−17.613 115 449 262 9
		3/2	4	17.616 611 106 475 0	2.103 490 504 835 49	17.616 611 106 475 0
	<i>d</i>	3/2	1	5.268 985 512 742 28	1.813 149 410 142 54	−5.268 985 512 742 28
		5/2	2	7.903 641 922 169 04	1.807 721 683 677 06	5.269 094 614 779 36
		3/2	3	1.336 431 280 634 16	0.872 904 030 508 32	−1.336 431 280 634 16
		5/2	4	2.005 651 327 711 43	0.858 720 278 751 06	1.337 100 885 140 95
	<i>f</i>	5/2	1	−16.497 654 298 015 9	5.217 083 860 292 41	10.998 436 198 677 3
		7/2	2	−23.308 131 339 402 3	5.148 196 479 007 71	−11.654 065 669 701 2
		5/2	3	−2.236 827 345 761 40	1.580 599 468 911 57	1.491 218 230 507 60
		7/2	4	−2.226 941 952 298 75	1.347 895 923 476 92	−1.113 470 976 149 37
	<i>g</i>	7/2	1	−2.504 198 722 343 14	1.807 739 822 053 58	1.252 099 361 171 57
		9/2	2	−3.138 244 523 917 73	1.805 061 309 262 78	−1.255 297 809 567 09
Fr	<i>s</i>	1/2	1	84.518 087 072 558 0	4.188 321 670 974 92	
		1/2	2	16.079 176 322 525 6	2.032 715 709 488 50	
	<i>p</i>	1/2	1	52.351 810 585 153 3	5.275 461 936 325 70	−104.703 621 170 307
		3/2	2	104.705 104 394 027	5.084 425 052 983 42	104.705 104 394 027
		1/2	3	8.877 332 658 960 87	2.146 984 148 452 80	−17.754 665 317 921 7
		3/2	4	18.091 692 783 975 4	1.733 211 697 977 42	18.091 692 783 975 4
	<i>d</i>	3/2	1	5.294 775 002 479 84	2.079 148 856 002 51	−5.294 775 002 479 84
		5/2	2	7.950 402 797 503 08	1.886 428 196 280 81	5.300 268 531 668 72
		3/2	3	1.632 423 051 957 65	0.644 610 997 336 63	−1.632 423 051 957 65
		5/2	4	2.624 185 902 892 39	0.643 592 303 343 99	1.749 457 268 594 92
	<i>f</i>	5/2	1	−6.923 464 425 306 64	4.414 495 881 185 79	4.615 642 950 204 43
		7/2	2	−9.021 819 015 770 29	4.502 002 449 911 52	−4.510 909 507 885 14
		5/2	3	−1.258 463 385 923 10	0.901 233 517 219 90	0.838 975 590 615 40
		7/2	4	−1.639 240 216 703 86	0.875 093 960 592 36	−0.819 620 108 351 93
	<i>g</i>	7/2	1	−4.127 370 571 216 89	1.592 432 236 911 71	2.063 685 285 608 45
		9/2	2	−5.004 549 561 285 37	1.562 577 006 403 62	−2.001 819 824 514 15
119	<i>s</i>	1/2	1	100.411 612 769 238	3.449 522 772 030 20	
		1/2	1	62.967 933 900 146 7	4.217 827 015 049 44	−125.935 867 800 293
	<i>p</i>	3/2	2	107.741 467 003 175	3.050 533 592 237 54	107.741 467 003 175
		1/2	3	9.123 591 062 773 33	3.754 857 504 228 00	−18.247 182 125 546 7

TABLE II. (Continued.)

	<i>i</i>	<i>j</i>	<i>k</i>	A_{kl}	α_{kl}/γ_{klj}	C_{klj}
<i>d</i>		3/2	4	17.969 319 742 806 1	1.536 864 249 726 50	17.969 319 742 806 1
		3/2	1	4.156 600 882 880 96	0.734 246 100 170 44	-4.156 600 882 880 96
		5/2	2	3.036 245 186 642 24	0.499 923 751 330 90	2.024 163 457 761 50
		3/2	3	2.125 815 242 300 26	3.380 157 389 806 59	-2.125 815 242 300 26
<i>f</i>		5/2	4	3.501 216 835 176 94	3.883 729 576 323 82	2.334 144 556 784 63
		5/2	1	8.863 964 834 134 41	4.012 269 097 996 40	-5.909 309 889 422 94
		7/2	2	11.712 688 162 462 7	3.810 433 555 228 35	5.856 344 081 231 37
		5/2	3	-0.448 403 465 436 78	0.316 010 790 185 67	0.298 935 643 624 52
<i>g</i>		7/2	4	-0.451 838 040 829 37	0.235 066 781 320 92	-0.225 919 020 164 69
		7/2	1	-96.730 930 955 556 0	10.894 670 762 442 4	48.365 465 477 778 0
		9/2	2	-124.011 352 008 100	10.880 297 288 911 1	-49.604 540 803 240 0
		7/2	3	-8.161 952 900 508 00	1.582 646 957 542 00	4.080 976 450 254 00
		9/2	4	-9.455 367 758 646 78	1.509 582 684 317 12	-3.782 147 103 458 71

higher accuracies. However, the agreement between the AE and PP methods for the ground state $p_{1/2}$ - $p_{3/2}$ fine structure splitting is satisfactory in all cases as shown in Table VII.

III. DIPOLE POLARIZABILITIES

A. All-electron results

The calculated values of the group 1 static dipole polarizabilities together with the corresponding atomic basis sets are presented in Table VIII. We mention the anomaly in the trend of the dipole polarizabilities with increasing nuclear charge, where the dipole polarizability is the largest for Cs and decreases thereon to Fr and to E119, attributed to the relativistic contraction of the valence *s* shell (see Ref. 25 for details). In order to clearly demonstrate the effects of our basis set modifications, the dipole polarizabilities are compared with the values resulting from the original basis sets used in our previous work,²⁵ as shown in the first row for each element in Table IX. In Table VIII, the influence of polarization functions is shown in separate rows labeled *l*, where *l* is the maximum angular momentum used for that basis set. In the last row for each element, our final basis sets are further augmented by an additional hard and diffuse function. These basis sets are denoted l^* . The resulting dipole polarizabilities demonstrate that these values are converged with respect to the basis set expansion and hence are of near basis set limit quality. The remaining error comes mostly from the neglect of spin-orbit coupling and from the coupled-cluster approximation used. The values are shown to two decimal places to make small changes more transparent.

At the HF level the previously used basis sets already bear the converged dipole polarizabilities with respect to the basis set expansion up to angular momentum $l=2$ for K and 3 for Rb to Fr. As expected the highest angular momentum functions have little effect on the HF dipole polarizabilities. However, for E119, the new basis set yields a dipole polarizability smaller than the original set even at the HF level, clearly demonstrating the deficiencies of the previous basis set used.

At the correlated level, the present basis sets lead to a significant improvement over the previous dipole polarizabilities.²⁵ This is expected as the convergence of the dipole polarizability with respect to the basis set expansion is slower at the correlated level, and a larger number of high angular momentum functions are needed. Indeed, the effects of additional *f*- and *g*-type functions to dipole polarizabilities are evident. The importance of *g*-type functions grows from Rb to E119. For E119, these *g*-type functions reduce the dipole polarizability by more than 10% at the DK-MP2 level. The influence of higher angular momentum functions is such that the dipole polarizability of E119 is reduced by 1.69 a.u. at the DK-MP2 level upon inclusion of nine *h*-type functions. This is further reduced by 0.40 a.u. when seven *i*-type functions were added. The convergence pattern in the dipole polarizability is therefore clearly established in terms of polarization functions. As mentioned earlier due to a very high computational demand with such extensive basis sets, the influence of *h*- and *i*-type functions was investigated at the MP2 level only.

Overall, electron correlation effects reduce the dipole

TABLE III. Configurations of chosen reference states for the adjustment of the Cs pseudopotential.

Cs	$5s^25p^66s^1$	$5s^25p^66p^1$	$5s^25p^67s^1$	$5s^25p^67p^1$	$5s^25p^56s^2$
	$5s^25p^56s^16p^1$	$5s^25p^56p^2$	$5s^25p^65d^1$	$5s^25p^66d^1$	$5s^25p^55d^16s^1$
	$5s^25p^55d^2$	$5s^25p^55d^16p^1$			
Cs ⁺	$5s^25p^6$	$5s^25p^56s^1$	$5s^25p^56p^1$	$5s^25p^55d^1$	
Cs ²⁺	$5s^25p^5$	$5s^25p^46s^1$	$5s^25p^46p^1$	$5s^25p^45d^1$	
Cs ⁻	$5s^25p^66s^2$				
Cs ⁶⁺	$5s^24f^1$	$5s^25f^1$	$5s^26f^1$	$5s^27f^1$	
Cs ⁶⁺	$5s^25g^1$	$5s^26g^1$	$5s^27g^1$		

TABLE IV. Parameters for the CPP. See text for explanations. All values are in atomic units.

	α_D	δ
Cs	0.6935	1.4702
Fr	1.2500	1.1636
E119	2.2474	0.5726

polarizabilities substantially due to the contraction of the valence shell. That is, in the correlated case the valence electrons are more tightly bound to the nucleus and this leads to a smaller change in the total electronic energy as a response to the applied external electric field, $\Delta E^{\text{corr}}(F) < \Delta E^{\text{HF}}(F)$, where ΔE is the total electronic energy difference at zero field and at a nonzero field strength F . The largest electron correlation effect is expected for the heaviest element, E119. This is however not the case as shown in Table IX, with the dipole polarizability of Fr showing the largest electron correlation contribution. Here, relativistic effects significantly reduce dipole polarizabilities for the group 1 elements and alter the electron correlation contributions. Clearly, these two effects are not additive.

In order to demonstrate that our present dipole polarizabilities are of basis set limit quality, we performed additional calculations applying the larger basis sets l^* as shown in Table VIII at the DK-MP2 level. The change in the dipole polarizabilities from the l to l^* basis sets is well below 1 a.u. for all elements.

Our final basis sets, namely, set f for K and set g for Rb to E119 were used in subsequent CCSD(T) calculations, which are summarized in Table IX together with values from previous basis set calculations and other theoretical and experimental values where available. Overall, the DK-CCSD(T) polarizabilities are in excellent agreement with the best experimental values^{34,35} available. Errors caused by the finite basis set expansion are well below the experimental uncertainty. Noteworthy is the calculation by Derevianko *et al.*³⁶ and Safronova *et al.*³⁷ They performed accurate calculations of group 1 atom polarizabilities, adopting high precision experimental values for the dipole matrix elements of principal transitions with error bars estimated from the experimental accuracy of these matrix elements. Their values for the heavier elements have much smaller error bars than given experimental values and are in excellent agreement with our DK-CCSD(T) values. The present dipole polarizabilities for Cs and Fr seem to be slightly smaller in comparison with the values of Derevianko *et al.*³⁶ One source of the discrepancy is from the neglect of spin-orbit coupling effects in our calculations, where an increase in the dipole polarizabilities is expected due to a splitting of the next-to-valence p orbital into $p_{1/2}$ and $p_{3/2}$. Coincidentally, our calculated dipole polarizabilities agree better with the purely theoretical values of Derevianko *et al.* than their other values adopting experimental dipole matrix elements.

In the polarization caused by an external electric field, it is the outer region of electronic density that is of the most importance. However, it is crucial to take into consideration the inner shell polarization, which significantly alters the va-

lence region. For example, it has been suggested that for Cs, the inclusion of $(n-2)d^{10}$ shell in the electron correlation procedure is important and the omission of such leads to overestimated dipole polarizabilities by as much as 9 a.u. at the CASPT2 level of theory.²⁴ As for coupled-cluster calculations, electron correlation of the next-to-valence $(n-1)$ shell has been commonly included in the past to achieve higher accuracies.³⁸ In order to extend this investigation to Fr and E119, we have calculated the dipole polarizability of these elements with various sizes of active space in the correlation step. The results are shown in Table X. At the DK-MP2 level, the dipole polarizability shows a strong dependency on the choice of active space. Upon inclusion of the $(n-3)$ shell in electron correlation (compare frozen core KLMN and KLM for Fr), the dipole polarizability decreases by 4%. As many as 59 electrons need to be correlated in order to obtain a satisfying convergence. Therefore it is clear that for Fr, the $(n-3)$ shell as well as the $(n-2)$ shell is of significant importance in electron correlation at the DK-MP2 level. Surprisingly, this effect is somewhat less profound at the DK-CCSD/CCSD(T) level of theory. Correlation of the $(n-3)$ shell (i.e., KLM frozen core for Fr) has a negligible effect on the dipole polarizability. However, correlation of the $(n-2)$ shell decreases the dipole polarizability by 5%. In other words, as many as 27 electrons need to be correlated at the DK-CCSD/CCSD(T) step in order to obtain a highly accurate dipole polarizability for Fr. For E119 the requirement for inner shell correlation seems to be even more severe. At the DK-MP2 level, correlation of $(n-4)$ shell is critical in order to obtain converged values within 0.2 a.u. Omission of such a shell leads to an overestimated dipole polarizability by 1.65 a.u. at the DK-MP2 level, which is less than 1.5% of the total dipole polarizability. Consequently, at least 91 electrons are to be correlated in the MP2 procedure. At the DK-CCSD/CCSD(T) level, the frozen KLMN5s²5p⁶5d¹⁰ core offers the smallest correlation space without affecting the dipole polarizability too severely. Note that the 5f orbitals were automatically included in the correlation procedure as they lie higher in energy than the 6s orbital. A smaller correlation space, for example, frozen KLMNOP core results in an overestimated dipole polarizability by more than 4% at the DK-CCSD(T) level. Therefore, the minimum number of electrons that need to be correlated for E119 is at least 41. Interestingly, there emerges a common feature from this investigation. That is, at the DK-MP2 level, the maximum depth of frozen core allowed for obtaining reliable dipole polarizabilities is, according to Sadlej and co-workers,²⁴ the KLM frozen core for Cs, and this remains unchanged for Fr and E119. On the contrary, the DK-CCSD/CCSD(T) results show that the number of electrons to be correlated does not increase but remains constant from Cs to E119. As a result, no more than 27 valence electrons (if we accept that the 5f electrons can be left out for E119) need to be correlated regardless of the nuclear charge to obtain reasonable accurate dipole polarizabilities. For example, for Cs our DK-CCSD(T) calculation shows dipole polarizabilities of 396.02 and 409.32 a.u. for frozen cores KLM (i.e., 27 electrons correlated) and KLMN (i.e., 9 electrons correlated), respec-

TABLE V. Valence basis sets for the adjusted pseudopotentials.

	Exponents					Coefficients	
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>s</i>	<i>p</i>
K	180.900 80	65.912 33	1.556 00	0.612 19		0.001 19	0.001 32
	71.217 69	24.598 63	0.612 19	0.223 05		−0.000 50	0.002 48
	29.384 28	9.882 28	0.223 05	0.081 26		0.002 69	0.014 06
	8.699 24	4.116 75	0.081 26			0.069 04	−0.067 81
	3.473 30	1.556 00	0.029 61				
	0.814 56	0.612 19					
	0.318 92	0.223 05					
	0.070 00	0.081 26					
	0.035 48	0.029 61					
	0.016 39	0.010 79					
	0.007 57	0.003 93					
Rb	240.216 80	46.597 79	0.859 43	2.431 53	0.721 52	0.001 544	0.003 055
	106.111 20	20.619 47	0.608 15	0.721 52		−0.003 275	−0.008 262
	40.822 35	8.545 80	0.211 26	0.211 26		0.012 417	0.035 584
	18.695 21	3.727 81	0.071 00			−0.037 286	−0.128 646
	7.850 89	1.626 09	0.025 49			0.154 375	
	3.946 15	0.608 15				−0.204 712	
	1.844 04	0.211 26					
	0.692 17	0.073 39					
	0.276 77	0.025 49					
	0.079 10	0.008 86					
	0.038 89						
	0.019 63						
	0.009 91						
Cs	132.350 22	38.616 74	0.916 18	0.916 18	0.916 18	−0.000 589	0.000 326
	67.030 35	18.515 06	0.346 92	0.346 92	0.346 92	0.002 513	−0.001 341
	33.464 64	9.139 09	0.133 84	0.133 84		−0.006 236	0.001 814
	14.568 73	4.129 33	0.049 80			0.017 078	0.043 747
	7.458 85	1.929 19	0.019 92			−0.031 642	
	3.001 49	0.811 87					
	1.461 08	0.346 92					
	0.402 21	0.133 84					
	0.175 58	0.051 64					
	0.045 84	0.019 92					
	0.020 01	0.007 69					
	0.008 74						
Fr	205.233 45	71.292 30	2.609 75	1.218 51	0.346 92	0.000 315	0.000 585
	103.066 81	36.898 36	1.218 51	0.511 82	0.133 84	−0.001 437	−0.002 577
	46.537 48	18.715 67	0.511 82	0.361 09	0.049 80	0.005 138	0.007 488
	24.831 04	9.523 76	0.361 09	0.134 77		−0.011 684	−0.021 315
	11.069 22	4.831 62	0.134 77	0.052 87		0.032 420	0.067 796
	5.942 40	2.292 43	0.052 87			−0.065 536	
	2.281 95	1.084 59	0.022 03				
	1.191 59	0.361 09	0.010 22				
	0.337 91	0.134 77					
	0.151 65	0.047 47					
	0.047 47	0.022 03					
	0.022 03	0.010 22					
	0.010 22	0.004 74					
	0.004 74						
E119	537.560 00	229.880 00	68.405 00	3.926 00	2.173 30	−0.000 309	0.000 217
	262.870 00	114.890 00	35.201 00	1.790 20	0.984 64	0.001 754	−0.001 015
	132.780 00	57.947 00	18.468 00	0.869 22	0.402 68	−0.005 661	0.003 012
	68.405 00	29.643 00	9.386 20	0.366 08	0.171 60	0.014 471	−0.007 506
	35.201 00	15.300 00	4.692 30	0.159 57	0.078 39	−0.033 358	0.017 634
	18.468 00	7.849 30	2.173 30	0.066 95		0.072 083	−0.043 376

TABLE V. (Continued.)

Exponents					Coefficients	
<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>s</i>	<i>p</i>
9.386 20	3.926 00	0.984 64			−0.168 738	
4.692 30	1.790 20	0.402 68				
2.173 30	0.869 22	0.171 60				
0.984 64	0.366 08	0.078 39				
0.402 68	0.159 57	0.039 20				
0.171 60	0.066 95	0.019 60				
0.078 39	0.033 48	0.009 32				
0.039 20	0.016 44					
0.019 60	0.008 22					
0.009 32	0.003 92					
0.004 66						

tively. Hence, single reference MP2 is not useful for obtaining correlation contributions from inner shells.

The present DK-CCSD(T) values of the group 1 first ionization potentials are presented in Table XI, together with the results from the previous basis set²⁵ and experimental values.³⁹ The theoretical values were taken from the Fock-space coupled-cluster work by Kaldor and co-workers.⁴⁰ The data in Table XI shows a monotonic decrease in the ionization potential from K to Cs. Due to relativistic effects, this

TABLE VI. Valence HF energies obtained in numerical all-electron DCHF calculation (E^{AE}) and numerical pseudopotential calculations (E^{PP}) in atomic units. ΔE^{PP} is the pseudopotential error in eV. All values are spin-orbit averaged.

	Valence State	E^{AE}	E^{PP}	ΔE^{PP}
K	$3s^2 3p^6 4s^1$	−28.038 939 389 8	−28.039 018 035 9	−0.002 14
K	$3s^2 3p^6 4p^1$	−27.986 772 596 5	−27.986 600 767 3	0.004 68
K ⁺	$3s^2 3p^6$	−27.164 704 684 8	−27.164 866 118 3	−0.004 39
K ⁺⁺	$3s^2 3p^5$	−26.766 009 853 1	−26.765 776 430 3	0.006 35
K [−]	$3s^2 3p^6 4s^2$	−28.036 066 959 8	−28.036 160 192 6	−0.002 54
Rb	$4s^2 4p^6 5s^1$	−23.799 309 049 9	−23.799 367 108 3	−0.001 58
Rb	$4s^2 4p^6 5p^1$	−23.749 930 149 9	−23.749 840 974 8	0.002 43
Rb ⁺	$4s^2 4p^6$	−23.659 668 149 9	−23.659 566 949 4	0.002 75
Rb ⁺⁺	$4s^2 4p^5$	−22.683 367 483 2	−22.683 266 196 5	0.002 76
Rb [−]	$4s^2 4p^6 5s^2$	−23.796 760 149 9	−23.796 826 809 1	−0.001 81
Cs	$5s^2 5p^6 6s^1$	−19.859 285 384 7	−19.859 916 728 0	−0.017 18
Cs	$5s^2 5p^6 6p^1$	−19.815 905 818 0	−19.815 861 755 0	0.001 20
Cs ⁺	$5s^2 5p^6$	−19.731 515 084 7	−19.731 542 879 1	−0.000 76
Cs ⁺⁺	$5s^2 5p^5$	−18.894 317 118 0	−18.893 598 746 9	0.019 55
Cs [−]	$5s^2 5p^6 6s^2$	−19.857 081 184 7	−19.857 719 417 1	−0.017 37
Fr	$6s^2 6p^6 7s^1$	−18.922 263 524 3	−18.922 161 089 5	0.002 79
Fr	$6s^2 6p^6 7p^1$	−18.872 704 191 0	−18.873 186 712 6	−0.013 13
Fr ⁺	$6s^2 6p^6$	−18.790 454 524 3	−18.790 776 407 5	−0.008 76
Fr ⁺⁺	$6s^2 6p^5$	−18.000 585 191 0	−18.000 441 963 0	0.003 90
Fr [−]	$6s^2 6p^6 7s^2$	−18.920 554 524 3	−18.920 352 321 0	0.005 50
E119	$7s^2 7p^6 8s^1$	−18.689 913 368 7	−18.688 954 505 3	0.026 09
E119	$7s^2 7p^6 8p^1$	−18.615 532 368 7	−18.615 720 789 6	−0.005 13
E119 ⁺	$7s^2 7p^6$	−18.534 339 368 7	−18.533 920 586 6	0.011 40
E119 ⁺⁺	$7s^2 7p^5$	−17.756 583 035 4	−17.755 437 257 6	0.031 18
E119 [−]	$7s^2 7p^6 8s^2$	−18.693 232 368 7	−18.691 810 316 4	0.038 70

downward trend is reversed for the two heaviest elements Fr and E119. This trend is also in accordance with the trend in the dipole polarizabilities as noted by Fricke,⁴¹ where ionization potentials increase with decreasing dipole polarizabilities.

To conclude this section, we point out that the present basis set modifications as outlined in Sec. II significantly improve the agreement with experimental results. The discrepancy between the calculated and the experimental values is reduced by as much as a factor of 5 compared to our previous study.²⁵ The calculated ionization potentials are, however, still underestimated compared with the experimental values, but this discrepancy is relatively small and only about 0.01 eV for elements up to Cs and 0.04 eV for Fr. In comparison with the theoretical values of Kaldor and co-workers⁴⁰ estimated at the DC-CCSD level, the present scalar relativistic ionization potentials are underestimated due to the neglect of spin-orbit coupling and other important relativistic and quantum electrodynamic effects.

TABLE VII. Comparison of spin-orbit coupled orbital energies ε (a.u.) and r -expectation values from all-electron DC-HF and pseudopotential calculations for the ground state of the alkali atoms.

		AE		PP	
		− ε	$\langle r \rangle$	− ε	$\langle r \rangle$
K	$3p_{1/2}$	0.960 538 33	1.430 323 0	0.958 413 13	1.435 125 0
	$3p_{3/2}$	0.949 559 82	1.438 469 6	0.947 827 59	1.445 617 4
	$4s$	0.148 029 08	5.224 021 5	0.148 357 85	5.214 915 7
Rb	$4p_{1/2}$	0.832 308 47	1.703 492 6	0.829 414 89	1.723 311 5
	$4p_{3/2}$	0.796 273 32	1.739 146 7	0.794 480 98	1.755 335 4
	$5s$	0.140 044 15	5.544 989 7	0.140 183 13	5.541 392 9
Cs	$5p_{1/2}$	0.726 703 20	2.028 915 9	0.722 778 17	2.065 564 9
	$5p_{3/2}$	0.659 368 06	2.119 221 5	0.657 454 17	2.154 194 2
	$6s$	0.128 239 25	6.084 533 5	0.128 835 22	6.058 055 9
Fr	$6p_{1/2}$	0.759 989 69	2.062 276 1	0.754 896 42	2.086 269 1
	$6p_{3/2}$	0.566 758 18	2.342 228 4	0.565 788 16	2.370 778 9
	$7s$	0.132 711 87	5.922 037 3	0.132 367 83	5.927 242 4
E119	$7p_{1/2}$	0.954 906 60	1.945 457 0	0.942 094 11	1.938 270 8
	$7p_{3/2}$	0.434 709 17	2.704 839 9	0.433 972 30	2.741 280 8
	$8s$	0.159 015 21	5.198 906 7	0.158 151 31	5.195 293 8

TABLE VIII. The calculated scalar relativistic all-electron static dipole polarizabilities of the group 1 elements. All values are in atomic units.

	Basis set	DK-HF	DK-MP2
K ^a	(16s14p4d)/[12s12p4d]	409.05	277.47
	<i>d</i> (17s14p7d)/[12s12p7d]	410.29	271.80
	<i>f</i> (17s14p7d5f)/[12s12p7d5f]	410.30	261.31
	<i>f</i> [*] (19s16p9d7f)/[14s14p9d7f]	410.41	261.18
Rb ^a	(24s15p11d4f)/[17s12p9d4f]	483.77	267.32
	<i>f</i> (22s15p11d8f)/[14s11p9d8f]	484.29	258.25
	<i>g</i> (22s15p11d8f5g)/[14s11p9d8f5g]	484.29	254.35
	<i>g</i> [*] (24s17p13d10f7g)/[16s13p11d10f7g]	484.46	254.48
Cs ^a	(27s19p12d4f)/[13s11p8d4f]	670.88	279.64
	<i>f</i> (27s19p13d10f)/[13s11p8d10f]	671.52	254.97
	<i>g</i> (27s19p13d10f5g)/[13s11p9d10f5g]	671.52	245.78
	<i>g</i> [*] (29s21p15d12f7g)/[15s13p11d12f7g]	672.07	246.52
Fr ^a	(31s22p18d10f)/[15s13p10d7f]	542.99	193.51
	<i>f</i> (31s22p19d14f)/[15s13p11d11f]	543.41	177.73
	<i>g</i> (31s22p19d14f7g)/[15s13p11d11f7g]	543.42	165.38
	<i>g</i> [*] (33s24p21d16f9g)/[17s15p13d13f9g]	543.45	164.78
E119 ^a	(27s22p17d11f)/[17s13p10d7f]	252.76	130.45
	<i>f</i> (13s29p23d17f)/[17s16p14d17f]	244.36	114.15
	<i>g</i> (31s29p23d17f11g)/[17s16p14d17f11g]	244.38	101.94
	<i>g</i> [*] (33s31p25d19f13g)/[19s18p16d19f13g]	243.84	101.90
	<i>h</i> (31s29p23d17f11g9h)/[17s16p14d17f11g9h]	244.38	100.25
	<i>i</i> (31s29p23d17f11g9h7i)/[17s16p14d17f11g9h7i]	244.38	99.86

^aReference 25.

TABLE IX. All-electron dipole polarizabilities of the alkali elements from K to E119 calculated with our current basis sets. For comparison, the dipole polarizabilities from previous basis set calculations and other theoretical and experimental values are listed. All values are in atomic units.

		DK-HF	DK-MP2	DK-CCSD	DK-CCSD(T)
K	Previous basis set ^a	409.05	277.47	307.22	301.28
	Present basis set	410.29	261.35	303.24	291.12
	Theor./expt. ^b				290.2±8
	Expt. ^{c,d}				293±6
Rb	Previous basis set ^a	483.77	267.32	341.14	324.24
	Present basis set	484.28	253.60	335.81	316.17
	Theor./expt. ^b				318.6±6
	Expt. ^{c,d}				319±6
Cs	Previous basis set ^a	670.88	279.64	444.09	411.87 ^e
	Present basis set	671.52	245.78	435.27	396.02
	Theor./expt. ^b				399.9±1.9
	Expt. ^{c,d}				401±0.6
Fr	Previous basis set ^a	542.99	193.51	355.44	329.17
	Present basis set	543.42	165.38	347.59	315.23
	Theor./expt. ^b				317.8±2.4
E119	Previous basis set ^a	252.76	130.45	191.34	184.83
	Present basis set	244.38	101.94	176.53	165.98

^aReference 25.^bReference 36.^cReference 34.^dReference 35.^eReference 45.

TABLE X. The dipole polarizability of Fr and element 119 resulting from various active orbital space definitions. All values are in atomic units.

Atom	Frozen core	DKMP2	DKCCSD	DKCCSD(T)
Fr	KLMNO	234.04	356.12	331.67
	KLMN	172.50	347.58	315.23
	KLM	165.30	348.34	315.18
	None	164.81
E119	KLMNOP	137.73	179.88	173.00
	KLMN5s5p5d	103.54	176.51	165.96
	KLMN	103.39	176.53	165.98
	KLM	101.93	176.08	165.48
	KL	101.74
	K	101.73
	None	101.73

B. Pseudopotential results

Our frozen-core definition reduces the alkali metals to nine-valence electrons systems which of course will limit the accuracy for the calculated dipole polarizabilities. As a test case we chose Rb where frozen-core all-electron calculations were carried out with nine-valence electrons included in the valence space, Table XII. Here the core remains unchanged as an external electric field is applied. The basis set used for these calculations is slightly smaller. The respective HF and CCSD/CCSD(T) calculations reveal that frozen-core effects lead only to a slight decrease in the dipole polarizabilities due to the omission of the core polarization. However, more interesting is the comparison of 9 vs 27 electrons in the electron correlation procedure. As discussed above for Cs to E119, the active correlation space required for reliable dipole polarizabilities exceeds far beyond nine-valence electrons and omission of the ($n-2$) shell in correlation results in overestimated dipole polarizabilities.

Let us now turn to the dipole polarizabilities calculated by using the small-core nine-valence electron pseudopotentials with the accompanying valence basis sets, which can be found in Table XIII together with the corresponding all-electron values. The ARPP dipole polarizabilities at the CCSD(T) level agree with the all-electron results within 1% for the elements up to Cs. Although it is not apparent from the results obtained for K, the overestimation of the dipole polarizabilities by the ARPP is in line with the correlation of only nine-valence electrons. The use of a CPP to account for

TABLE XI. Calculated all-electron DK-CCSD(T) values of the ground state ionization potentials. The present values are compared to the previous values from Ref. 25 and other theoretical and experimental values. All values are in eV.

	K	Rb	Cs	Fr	E119
Previous basis set ^a	4.284	4.137	3.821	3.975	4.540
Present basis set	4.336	4.167	3.881	4.038	4.713
Theor. ^b	4.343	4.181	3.898	4.072	...
Expt. ^c	4.341	4.177	3.894	4.073	...

^aReference 25.

^bRelativistic Fock-space coupled-cluster singles and doubles approximation starting from a Dirac-Coulomb-Breit Hamiltonian, from Ref. 40.

^cReference 39.

TABLE XII. The dipole polarizabilities of Rb. All values are in atomic units.

	9 VE frozen-core ^a	9 VE in correlation ^b	27 VE in correlation ^c
DK-HF	484.11	484.30	484.30
DK-CCSD	337.62	337.73	336.56
DK-CCSD(T)	319.89	319.99	316.97

^aFrozen-core calculation with nine-valence electrons.

^bNo frozen-core with nine-valence-electrons (VE) correlated.

^cNo frozen-core with 27 valence-electrons correlated.

core-polarization and core-valence correlation for Cs overcompensates these effects and results in a slight underestimation in the dipole polarizability. Nonetheless the pseudopotential errors remain just over 1%. For Fr, the ARPP results do not agree so well with the AE values. This is not surprising as demonstrated by the all-electron DK-CCSD(T) calculations where electron correlation from deeper core levels have to be considered. Therefore, for the nine-valence electron case, the ARPP dipole polarizability should be compared with the AE results of KLMNO frozen core in Table X. The use of a CPP reduces the ARPP dipole polarizability of Fr similar to the correlation of ($n-2$) shell in the AE calculation. Consequently, the ARPP+CPP dipole polarizability agrees well with the all-electron result within 0.5%. For E119, the dipole polarizability is underestimated by the ARPP, with a discrepancy of less than 1% to the all-electron result at the CCSD(T) level. Hence, the agreement becomes poorer with the use of a CPP as the dipole polarizability is further reduced. There is obviously some error compensation involved and for this heavy element, one has to choose a smaller core definition in order to produce more accurate results. The present pseudopotential results for the dipole polarizabilities for K to Cs are also compared with other

TABLE XIII. The dipole polarizabilities of the group 1 elements calculated by the use of the small-core nine-valence electron scalar relativistic pseudopotentials, ARPP. The values are compared with the all-electron results at the scalar relativistic DK level taken from Table IX. All values are in atomic units.

		ARPP	ARPP+CPP	AE
K	HF	406.37	...	410.17
	CCSD	301.89	...	303.24
	CCSD(T)	290.68	...	291.12
Rb	HF	482.27	...	484.28
	CCSD	337.09	...	335.81
	CCSD(T)	319.09	...	316.17
Cs	HF	654.27	613.80	671.52
	CCSD	429.04	415.65	435.27
	CCSD(T)	395.10	390.79	396.02
Fr	HF	548.70	488.50	543.42
	CCSD	357.04	334.72	347.59
	CCSD(T)	327.94	316.70	315.23
E119	HF	229.77	209.34	244.38
	CCSD	172.35	164.37	176.53
	CCSD(T)	163.69	159.01	165.98

TABLE XIV. The dipole polarizabilities of the group 1 elements from K to Cs derived from relativistic pseudopotential calculations and compared with other pseudopotential and experimental values. All values are in atomic units.

	K	Rb	Cs
This work ^a	290.7	319.1	395.1
Christiansen ^{b,c}	...	336	414
Dolg ^{d,e}	292	316	404
Fuentealba ^{f,g}	293	321	402
Expt. ^{h,i}	293±6	319±6	401±0.6

^aRelativistic energy-consistent nine-valence pseudopotential results using finite basis sets at the CCSD(T) level.

^bRelativistic shape-consistent nine-valence electron pseudopotentials results calculated with finite basis sets at the CISD level.

^cReference 46.

^dRelativistic four-component energy-adjusted one-valence electron pseudopotential results including a core-valence correlation calculated at the Dirac–Hartree–Fock–Roothaan level with finite basis sets.

^eReference 42.

^fRelativistic one-valence electron semiempirical pseudopotential results including core-valence correlation calculated with finite basis sets.

^gReference 47.

^hReference 34.

ⁱReference 35.

pseudopotential results and experimental values in Table XIV. In comparison with the experimental values, Dolg's results⁴² seem to yield the best agreement despite the use of a large-core definition.

We may compare to the already published shape-consistent relativistic nine-valence electron pseudopotentials for Rb and Cs by Christiansen and co-workers.^{43,44} Here the CISD polarizabilities were obtained with much smaller basis sets and are much larger than our values. We therefore decided to perform CCSD(T) calculations using these shape-consistent pseudopotentials together with our large basis sets. For Rb and Cs we obtain 318.5 and 404.2 a.u., respectively, in good agreement with experiment.

The calculated group 1 ground state ionization potentials using our pseudopotentials together with the corresponding valence basis sets are presented and compared with all-electron and experimental values in Table XV. At the CCSD(T) level, the discrepancy between the ARPP and the all-electron ionization potentials is relatively small for K to Cs, but larger for Fr and E119, amounting up to 0.03 eV. The agreement between ARPP+CPP and the all-electron result

for Cs at the CCSD(T) level is slightly poorer than that without the use of a CPP. However, the agreement with the experimental value improves with the use of the CPP. For Fr, inclusion of core-valence correlation clearly improves the agreement with the AE result and the experimental value within 0.02 eV. For E119, the use of a CPP worsens the agreement with the all-electron result as the positive core-valence contribution increases the already overestimated ARPP result. This also follows the trend observed in the dipole polarizability, where the underestimated ARPP result becomes even smaller by core-valence correlation. This error comes most likely from the pseudopotential adjustment and not from the CPP. Nonetheless, the present pseudopotentials seem to give more accurate ionization potentials than other large-core pseudopotentials also shown in Table XV. A comparison using the shape-consistent relativistic nine-valence electron pseudopotentials for Rb and Cs by Christiansen and co-workers^{43,44} together with our large basis sets give ionization potentials of 4.162 and 3.868 eV for Rb and Cs, respectively, at the CCSD(T) level of theory in good agreement with experiment.

IV. CONCLUSION

The accuracy of calculated dipole polarizabilities severely depends on the quality of basis sets and electron correlation method used. In particular, correlation contribution from the $(n-2)$ shell needs to be included in all-electron calculations to obtain accurate dipole polarizabilities. Although the use of a core-polarization potential does improve the accuracy, it is clear that for the heavier elements further improvements need to include the lower $(n-2)$ shell in the valence space. However, the nine-valence electron spin-orbit coupled pseudopotentials presented here offer an economic way for molecular calculations and will be very useful in future investigations on alkaline cluster systems. Applications of our pseudopotentials to the molecular framework are currently under way.

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TABLE XV. Ionization potentials of the group 1 elements from ARPP and ARPP+CPP calculations. The values are compared with the present AE values and other PP results. The experimental values are taken from Ref. 39. All values are in eV.

	ARPP		ARPP+CPP CCSD(T)	DK-AE		Other PP	Expt.
	HF	CCSD(T)		HF	CCSD(T)		
K	4.029	4.333	...	4.020	4.336	4.278 ^a	4.341
Rb	3.805	4.161	...	3.801	4.167	4.135 ^a	4.177
Cs	3.488	3.884	3.901	3.473	3.881	3.880 ^b	3.894
Fr	3.559	4.013	4.056	3.565	4.038	...	4.073
E119	4.183	4.716	4.761	4.134	4.713

^aNine-valence pseudopotentials. Correlation was treated at the CCSD(T) level. See Ref. 10.

^bCalculated with nine-valence pseudopotentials and a CPP. Correlation was treated at the CISD level. See Ref. 48.

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