

Electron-correlation and relativistic contributions to atomic dipole polarizabilities: Alkali-metal atoms

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Electric-dipole polarizabilities of K, Rb, Cs, and Fr are calculated in the framework of the quasirelativistic method based on mass-velocity and Darwin terms in the Pauli Hamiltonian. The electron-correlation contribution due to atomic cores is taken into account at two levels of approximation. The next-to-valence-shell contributions follow from the appropriate complete active-space multiconfiguration self-consistent-field calculations while the remaining core correlation effects are evaluated by using a second-order-perturbation method. Both pure relativistic and mixed correlation-relativistic contributions are evaluated. The present nonrelativistic results for K (44.6 \AA^3), Rb (60.8 \AA^3), Cs (72.8 \AA^3), and Fr (81.8 \AA^3) are reduced by 0.8 \AA^3 , 11.3 \AA^3 , 11.5 \AA^3 , and 33.5 \AA^3 , respectively, due to relativistic and correlation-relativistic corrections. The quasirelativistic results for K, Rb, and Cs are in good agreement with experimental data. The predicted dipole polarizability of Fr is 48.3 \AA^3 . Additionally, polarized basis sets for Cs and Fr for calculations of molecular electric properties have been generated in this study.

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I. INTRODUCTION

The dipole polarizability is undoubtedly one of the most important and interesting electric properties of atoms [1]. It accounts for the main part of their response to external perturbations which can be modeled in terms of electric fields [2]. For this reason atomic dipole polarizabilities are natural ingredients of interaction potentials for atomic scattering studies [3].

Most of the dipole polarizability reflects the electric-field response of atomic valence shells and the core and core-valence contributions are usually of secondary importance. This is certainly true for atoms of main groups *Va* through *VIII* [4]. However, already for the main group *IVa* the core contributions to the dipole polarizability of the second- and higher-row atoms become of some importance [4]. It is well established [4,5] that a pure valence-electron approximation is unsuitable for dipole polarizabilities of the group-*Ia* and group *IIa* atoms. With the increasing nuclear charge *Z* a substantial contribution to the dipole polarizability arises also from relativistic effects [6,7].

The purpose of the present study ranges from the plain numerical calculation of accurate polarizability data for alkali-metal atoms to the investigation of the validity of methods for the determination of the electron-correlation [8,9] and relativistic [10,11] contributions. Some attention is also given to the development of polarized basis sets [12,13] of Gaussian-type orbitals (GTO's) for calculations of atomic and molecular electric properties and supplements our earlier investigations [13] in this area.

The dipole polarizability of Li and Na has been widely

studied by several other authors and a survey of the corresponding theoretical and experimental data can be found in Refs. [1,4,5,14]. It also follows from relativistic Dirac-Hartree-Fock (DHF) calculations of Desclaux, Laaksonen, and Pyykkö [6] that the relativistic contribution to the dipole polarizability of Li and Na is virtually negligible. Thus these two atoms are excluded from present investigations.

The recent study of polarizabilities of the alkaline-earth metals [7] shows that a noticeable relativistic contribution is observed already for the third-row atoms. For this reason the present study comprises potassium and all heavier metals of group *Ia*. Including Fr is mainly a matter of curiosity, as the corresponding data are rather unlikely to be used.

The methods employed in our calculations are surveyed in Sec. II. The polarized basis sets of contracted Gaussian-type orbitals (CGTO's) for K and Rb have been generated in our earlier investigation [13]. Those for Cs and Fr are derived in this paper and the pertinent details are given in Sec. III. In Sec. IV the polarizability data of this paper are presented and their reliability is analyzed. The paper is summarized in Sec. V.

II. METHODS AND COMPUTATIONAL METHODOLOGY

In general, the methods used in this paper are based on the perturbation treatment of electron-correlation and relativistic contributions with respect to the given approximate reference state calculated by some approximate method *M*. The latter may by itself account for

some part of the electron correlation while the rest of it is to be obtained in a perturbation treatment. This approach has been recently used in calculations of valence-state electric-dipole polarizabilities and quadrupole moments of the first- and second-row atoms [15].

The relativistic contribution to atomic polarizabilities has been obtained in the framework of the quasirelativistic method [10,11] based solely on the mass-velocity and Darwin (MVD) terms of the Pauli approximation to the relativistic Hamiltonian [16].

In what follows some details of methods used in this study will be discussed in terms of their applicability and reliability. Since the dipole polarizability α of an atomic S state is given by [1,2]

$$\alpha = - \left[\frac{\partial^2 E(\mathbf{F})}{\partial F_\mu \partial F_\mu} \right]_{\mathbf{F}=0}, \quad (1)$$

where $E(\mathbf{F})$ is the total electronic energy as a function of the electric-field strength \mathbf{F} , most of the discussion will be carried out with reference to the methods of computing $E(\mathbf{F})$.

A. Evaluation of the electron-correlation contribution to dipole-polarizabilities

In the nonrelativistic approximation the total polarizability α_{nr} is expressed as a sum of the result obtained by some method M , $\alpha_{\text{nr},M}$, and perturbation corrections, $\alpha_{\text{nr},M\text{-PT}}$, with respect to the reference state obtained by that method:

$$\alpha_{\text{nr}} = \alpha_{\text{nr},M} + \alpha_{\text{nr},M\text{-PT}}. \quad (2)$$

If the reference method M corresponds to some formal Hamiltonian $H_{\text{nr}}^{(0)}$, the perturbation corrections $\alpha_{\text{nr},M\text{-PT}}$ can be given a series expansion ordered with respect to the (correlation) perturbation operator W_{nr} ,

$$W_{\text{nr}} = H_{\text{nr}} - H_{\text{nr}}^{(0)}, \quad (3)$$

where H_{nr} is the total nonrelativistic electronic Hamiltonian of the system. Hence, one can write

$$\alpha_{\text{nr},M\text{-PT}} = \sum_i \alpha_{\text{nr},M\text{-PT}i} \quad (4)$$

(with i denoting the order of the perturbation correction). Furthermore, if M satisfies the Brillouin condition [17], the series in (4) begins with the second-order term [18].

By choosing the method M one can shift the amount of the electron-correlation contribution carried by the two terms of Eq. (2). In particular, if M is the restricted Hartree-Fock (RHF) method, then the total of the electron-correlation contribution will have to be recovered by the perturbation term (4). Since in most cases the series (4) is replaced by N th-order truncated expansion, the RHF reference requires a rather high-order perturbation treatment.

If the method M accounts for the electron-correlation effects to a certain level, one can anticipate that the perturbation series in (4) can be truncated at relatively low order without considerable loss of accuracy. This is the main idea behind the recently developed second-order

perturbation-theory (PT2) approach based on complete-active-space (CAS) self-consistent-field (SCF) wave functions [8,9]. The success of the method, which is hereafter referred to as CASPT2, strongly depends on the quality of the CASSCF reference space.

The following terminology will be used in the analysis of the dependence between the structure of the CASSCF reference state and the efficiency of the second-order treatment of the pertinent residual correlation (3). The total available space of one-particle states is subdivided into four classes—the frozen, inactive, active, and secondary orbital subspaces [19]. The frozen orbitals are always doubly occupied and are not optimized at the level of the CASSCF approximation. No excitations from the frozen subspace are allowed in CASPT2. The inactive orbitals are doubly occupied and optimized in CASSCF and excitations from this subspace are allowed in CASPT2 [8,9]. It is worth noting that some inactive CASSCF orbitals may be frozen in the CASPT2 approximation.

The active orbital subspace is used to build the full configuration-interaction (CI) wave function for a given number of electrons. The secondary space is used to fully optimize the CASSCF wave function and to generate single and double excitations from the reference state at the level of the CASPT2 approach [8,9].

The partition of the orbital space and the number of electrons in the active subspace completely define the CASSCF wave function of the chosen spin-space symmetry. For the 2S ground state of alkali atoms the minimum active space is that with a single valence orbital ns . Since in the present paper all inner-shell orbitals are considered to be inactive in the CASSCF method, such a wave function will be equivalent to that of the open-shell RHF approximation. The inner-shell orbitals may then remain all inactive in CASPT2 or partly frozen. Both approximations will be studied in this paper with the freezing restricted to all but $(n-2)d^{10}$, $(n-1)s^2$, and $(n-1)p^6$ shells ($3s^23p^6$ in the case of K).

The subsequent plausible candidate for the reference state is the CASSCF wave function for the $\{(n-1)p, ns\}$ subspace of occupied orbitals. By using the method described in Ref. [15] the major correlating orbitals have been found to be $(n-1)d$ and np , leading to the active orbital subspace $\{(n-1)p, ns, (n-1)d, np\}$ for seven electrons. The inactive CASSCF orbitals are either left inactive or partly frozen at the CASPT2 level of approximation. In the latter case only the $(n-2)d^{10}$ and $(n-1)s^2$, shells are left inactive.

The largest active space considered in this paper consists of $\{(n-1)s, (n-1)p, ns, (n-1)d, np, (n+1)s\}$ orbitals for nine electrons. The CASPT2 calculations for this active space are quite time demanding and the corresponding studies have consequently been somewhat restricted. In all these CASPT2 calculations only the $(n-2)d^{10}$ shell was left inactive with all other inner shells frozen. The most complete study of the interplay between correlation contributions from the CASSCF and perturbation approaches has been performed for Cs. The analysis of the corresponding nonrelativistic and quasirelativistic corrections has been used to set up guide lines for calculations on other atoms.

B. Quasirelativistic treatment of pure relativistic and correlation-relativistic contributions to the dipole polarizability

The quasirelativistic treatment of relativistic contributions to electric properties, as developed in our recent papers [10,11] and demonstrated in a variety of applications [7,10,11,20,21], takes advantage of the spatial distinction between relativistic and electric-field perturbations. As long as the spin-orbit coupling can be neglected, the MVD operator [10,11] gives the major part of the relativistic effect. Moreover, it heavily weights the inner regions of the atomic-electron-density distribution while the electric-field perturbation affects primarily the outer (valence) region. This distinction has been demonstrated to lead to excellent quasirelativistic estimates of the relativistic contribution to polarizabilities of alkaline-earth-metal atoms [7] within the SCF approximation.

Obviously, the quasirelativistic treatment must fail for the nuclear charge Z approaching the value of about 137 a.u. However, present experience shows that even for Au ($Z=79$) the quasirelativistic method performs quite well [21]. Some deterioration of the dipole-moment results which has been recently found for PbO could presumably be attributed to either the spin-orbit-coupling effects or to nonadditivity of relativistic and electron-correlation contributions to electric properties. In the present case, the quasirelativistic results for Fr may tell more about the range of applicability of the method based on the MVD perturbation.

In the quasirelativistic approach the nonrelativistic Hamiltonian H is replaced by

$$H_{\text{qr}} = H_{\text{nr}} + \sigma H_{\text{MVD}} . \quad (5)$$

Thus the CASSCF approach will lead to the following counterpart of Eq. (3):

$$H_{\text{qr}} = H^{(0)}(\sigma) + W(\sigma) , \quad (6)$$

where σ is the ordering parameter for the MVD perturbation H_{MVD} . As a consequence, the total quasirelativistic dipole polarizability α depends on σ and can be expressed as

$$\alpha(\sigma) = \alpha_{\text{M}}(\sigma) + \alpha_{\text{M-PT}}(\sigma) , \quad (7)$$

with both terms on the right-hand side assumed to be analytic in σ ,

$$\alpha_{\text{M}}(\sigma) = \sum_{k=0}^{\infty} \sigma^k \alpha_{\text{M}}^{(k)} , \quad (8a)$$

$$\alpha_{\text{M-PT}}(\sigma) = \sum_{k=0}^{\infty} \sigma^k \alpha_{\text{M-PT}}^{(k)} . \quad (8b)$$

Since the MVD operator is of the first order in c^{-2} , the expansions (8a) and (8b) should be truncated at that order as well [10,11]. Thus, setting $\sigma=1$, one obtains the first-order quasirelativistic approximation to α ,

$$\alpha \cong \alpha_{\text{M}}^{(0)} + \alpha_{\text{M}}^{(1)} + \alpha_{\text{M-PT}}^{(0)} + \alpha_{\text{M-PT}}^{(1)} , \quad (9)$$

where the correlation perturbation expansion (4) applies to both $\alpha_{\text{M-PT}}^{(0)}$ and $\alpha_{\text{M-PT}}^{(1)}$.

For M representing the RHF method all the electron-correlation contribution follows from $\alpha_{\text{M-PT}}(\sigma)$, while for methods going beyond this approximation the electron-correlation effects will be redistributed between $\alpha_{\text{M}}(\sigma)$ and $\alpha_{\text{M-PT}}(\sigma)$.

There may be several objections with respect to the present treatment of the interplay between electron-correlation and relativistic effects. Certainly, whenever the spin-orbit coupling becomes of importance, the quasirelativistic approximation based solely on MVD terms is expected to fail. On the other hand, the splitting of $l-\frac{1}{2}$ and $l+\frac{1}{2}$ levels is not expected to be important for inner (closed) shells [22] and the contribution from these to the total dipole polarizability is small anyway. In the present case the valence part is represented by a single ns orbital and it is the relativistic contraction of this orbital that yields the dominant contribution to the lowering of nonrelativistic dipole polarizabilities [7,16].

C. Computational aspects

All calculations reported in this paper have been carried out by using the finite-field numerical perturbation method as described in our earlier papers [10,11]. This technique is used for both electric field and MVD perturbations. The field-strength values used in this paper are a little higher than those employed in earlier studies for closed-shell systems [7,11]. The CASSCF and CASPT2 energies have been calculated for electric fields 0.0, 0.001, and 0.002 a.u. with the quasirelativistic perturbation strength of 0.0 and ± 0.01 a.u. (for K and Rb) and ± 0.005 a.u. (for Cs and Fr) and then fitted for each value of σ to a quartic polynomial in F . The derivatives of the CASSCF energy have been checked against the derivatives of the CASSCF dipole moment with respect to σ . Another verification of the CASSCF data is provided by second derivatives of the first-order MVD correction with respect to the electric-field strength [7,10,11]. The agreement between those three sources of the first-order relativistic correction to dipole polarizability is taken as a measure of the accuracy of our numerical data. It has been found that the corresponding differences are at most of the order of 0.2%. A similar accuracy is expected for numerical derivatives of CASPT2 energies.

All polarizability calculations have been performed by using the MOLCAS-2 system of quantum-chemistry programs [23]. This system, devised primarily for molecular calculations, requires treating atoms in symmetry groups not higher than D_{2h} . The optimization of orbital exponents in initial *spd* and *spdf* GTO basis sets for Cs and Fr, respectively, has been carried out by the methods outlined in Ref. [24].

III. BASIS SETS

All calculations reported in this paper have been carried out using contracted sets of Gaussian functions. It is known [12,14] that in evaluation of atomic and molecular electric properties particular care needs to be taken of sufficient flexibility of the basis set. A standardization of the basis-set generation for such calculations has been

proposed recently [12], leading to what is called the (first-order) polarized basis sets. Such basis sets are already available for K and Rb. Those for Cs and Fr have been generated in this paper starting from energy-optimized sets of approximately double- ζ quality.

A. Potassium and rubidium

The polarized (*spd*) basis set for potassium [13] has been derived earlier and is used without any modification in this study. The suitability of this [15.13.4/3.7.2] GTO/CGTO set has already been demonstrated in RHF SCF calculations on K and in correlated-level calculations for KH [13,25]. This basis set and the Rb bases below are available in the MOLCAS-2 [23] basis-set library.

The original [18.15.10/11.3.4] polarized basis set for Rb is taken from Ref. [13]. Because one of the purposes of this study is to investigate the role of core-polarization effects involving the $3d^{10}$ shell, the initial set has been augmented by appropriate *f*-type polarization functions generated by applying the basis-set polarization method

[12] to $3d$ RHF SCF orbitals of Rb. The two *f*-type polarization functions are

$$f_1 = 0.08\,775(14.1054) + 0.19\,320(5.5366),$$

$$f_2 = 0.19\,873(2.2397) + 0.06\,384(0.8594)$$

The numbers in parentheses are the orbital exponents of primitive *f*-type GTO's while those in front of them are the contraction coefficients. The augmented (*spdf*) polarized set of Rb is therefore [18.15.10.4/11.9.4.2].

B. Cesium and francium

The generation of polarized (*spd*) and (*spdf*) sets follows the rules described previously [7,12,13] and consists of the following three steps: (i) generalized contraction of initial energy-optimized sets, (ii) addition of diffuse *s* and *p* functions, and (iii) determination of polarization functions for outer *p* shells and the $(n-2)d^{10}$ shell.

The initial (21.15.8) GTO set [$E_{\text{RHF}}(^2S) = -7553.900\,53$ a.u.] has been contracted to a [11.9.2]

TABLE I. First-order polarized [23.18.12.4/13.11.6.2] GTO/CGTO basis set for cesium. The (*spd*) polarized basis set can be obtained by removing the *f*-type GTO's.

GTO	CGTO	Exponent	Contraction coefficients			
<i>s</i> subset						
1	1-4	18 018 184.2	0.000 009 5	0.000 003 1	0.000 001 4	0.000 000 6
2		2 698 241.36	0.000 074 2	0.000 024 2	0.000 010 8	0.000 005 0
3		614 059.535	0.000 389 9	0.000 127 0	0.000 056 9	0.000 026 3
4		173 927.900	0.001 643 6	0.000 536 5	0.000 241 2	0.000 111 0
5		56 739.082 3	0.005 950 8	0.001 948 1	0.000 873 8	0.000 403 7
6		20 481.201 5	0.019 054 7	0.006 317 0	0.002 848 3	0.001 310 7
7		7 986.413 01	0.054 243 5	0.018 433 1	0.008 306 0	0.003 845 9
8		3 310.8212 2	0.133 629 0	0.048 382 7	0.022 116 1	0.010 193 0
9		1 442.310 16	0.265 623 0	0.109 149 0	0.050 509 0	0.023 570 7
10		654.023 073	0.364 094 0	0.195 398 0	0.095 111 8	0.044 262 1
11		304.041 333	0.256 777 0	0.194 059 0	0.099 939 7	0.048 406 1
12		132.350 219	0.049 596 0	-0.155 127 0	-0.095 531 2	-0.490 884 2
13		67.030 350 4	-0.005 282 9	-0.589 003 0	-0.526 235 0	-0.274 671 0
14		33.464 640 0	0.002 669 5	-0.397 561 0	-0.431 629 0	-0.268 047 0
15	5	14.568 725 9	1.0			
16	6	7.458 851 12	1.0			
17	7	3.001 490 96	1.0			
18	8	1.461 0830 1	1.0			
19	9	0.402 209 42	1.0			
20	10	0.175 580 56	1.0			
21	11	0.045 835	1.0			
22	12	0.0200 091 8	1.0			
23	13	0.008 735	1.0			
<i>p</i> subset						
1	1-3	29 904.687 5	0.000 262 9	0.000 123 7	0.000 055 4	
2		7 084.517 30	0.002 309 4	0.001 086 9	0.000 489 7	
3		2 299.176 74	0.012 851 5	0.006 125 7	0.002 750 8	
4		877.155 521	0.052 470 8	0.025 504 0	0.011 569 5	
5		370.647 956	0.158 414 0	0.080 813 8	0.036 775 4	
6		167.623 191	0.329 064 0	0.179 004 0	0.083 393 9	
7		79.458 439 4	0.395 249 0	0.225 337 0	0.104 223 0	
8		38.616 742 5	0.201 967 0	-0.035 943 6	-0.035 285 5	

TABLE I (Continued).

GTO	CGTO	Exponent	Contraction coefficients		
9		18.515 060 2	0.026 320 4	-0.516 314 0	-0.359 461 0
10		9.139 090 91	0.000 352 9	-0.477 959 0	-0.323 333 0
11	4	4.129 325 41	1.0		
12	5	1.929 193 85	1.0		
13	6	0.811 869 55	1.0		
14	7	0.346 916 39	1.0		
15	8	0.133 841 82	1.0		
16	9	0.051 636 7	1.0		
17	10	0.019 921 7	1.0		
18	11	0.007 685 9	1.0		
<i>d</i> subset					
1	1-2	638.157 487	0.006 302 4	-0.002 741 8	
2		191.608 245	0.049 366 0	-0.021 816 9	
3		72.488 068 8	0.194 327 0	-0.087 402 2	
4		30.342 141 0	0.412 736 0	-0.185 749 0	
5		13.238 863 5	0.428 200 0	-0.140 377 0	
6		5.622 501 76	0.133 923 0	0.288 626 0	
7	3	2.373 086 59	1.0		
8	4	0.916 181 10	1.0		
9	5	0.346 916 39	0.116 830		
10		0.133 841 82	0.098 540		
11	6	0.019 921 7	0.519 964		
12		0.007 685 9	0.314 661		
<i>f</i> subset					
1	1	13.238 86	-0.038 581		
2		5.622 502	0.121 722		
3	2	2.373 087	0.388 874		
4		0.916 181	0.293 876		

CGTO set and extended by two diffuse *s*-type and three diffuse *p*-type GTO's, thus leading to a [23.18.8/13.11.2] CGTO set [$E_{\text{RHF}}(^2S) = -7553.90084$ a.u.]. Two *d*-type polarization CGTO's have been generated from *5p* and *6p* atomic orbitals of Cs(2S) and Cs(2P), respectively. This leads [7,12,13] to a (*spd*) polarized basis set of the form [23.18.12/13.11.4], which is compatible with the Sr polarized set of Ref. [7]. To account for the $4d^{10}$ core-polarization effects two *f*-type polarization CGTO's [7] have been generated, and they give the (*spdf*) polarized set of the form [23.18.12.4/13.11.4.2]. Both (*spd*) and (*spdf*) polarized basis sets for Cs are presented in Table I.

The corresponding basis sets for Fr have been obtained in an analogous way as for Cs. Both the *d*-extended and *df*-extended sets are derived from the energy-optimized (24.17.13.8) GTO set [$E_{\text{RHF}}(^2S) = -22475.84862$ a.u.] which has been contracted to a [13.9.6.2] GTO set and augmented with diffuse *s*- and *p*-type functions to give a [26.21.13.8/15.13.6.2] GTO/CGTO set [$E_{\text{RHF}}(^2S) = -22475.84900$ a.u.]. Out of this set the *d*- and *df*-polarized sets of the form [26.21.17.8/15.13.8.2] and [26.21.17.12/15.13.8.4], respectively, have been generated. The orbital exponents and contraction coefficients are given in Table II.

By the method of their derivation [12,13] the *d*-polarized sets account for the field-induced polarization of outer *s* and *p* shells. The flexibility of the description of these shells is ensured by leaving most *s*- and *p*-type GTO's with low exponents uncontracted. The *df*-polarized sets additionally account for the field-induced polarization of $(n-2)d^{10}$ shells. The use of generalized contractions, as shown in our earlier papers [7,21] and confirmed by the results presented in Sec. IV, has only a small effect on the relativistic contribution to dipole polarizabilities of alkali metals.

IV. RESULTS. EVALUATION OF THE RELIABILITY OF THE CALCULATED POLARIZABILITY DATA

The presentation of numerical data follows the partition defined by Eq. (9). The results shown in Tables III and IV are subdivided into nonrelativistic contributions as calculated by CASSCF and CASPT2 methods, i.e.,

$$\alpha_{\text{M}}^{(0)} + \alpha_{\text{M-PT}}^{(0)} = \alpha_{\text{CASSCF}}^{(0)} + \alpha_{\text{CASPT2}}^{(0)}, \quad (10)$$

and what is called the relativistic contributions, which are approximated by the first-order quasirelativistic re-

TABLE II. First-order polarized [26.21.17.12/15.13.8.4] GTO/CGTO basis set for francium. The numbers in brackets give the power of 10 accompanying the given entry. A basis set which does not account for the polarization of the 5*d* shell can be obtained by removing the last four *f*-type GTO's.

GTO	CGTO	Exponent	Contraction coefficients				
<i>s</i> subset							
1	1-5	0.519 902 283[+8]	0.800 923 [-5]	-0.267 971[-5]	0.128 324[-5]	0.655 215[-6]	0.308 372[-6]
2		0.778 522 721[+7]	0.622 755[-4]	-0.208 354[-4]	0.998 772[-5]	0.509 584[-5]	0.239 894[-5]
3		0.177 170 151[+7]	0.327 448[-3]	-0.109 617[-3]	0.524 727[-4]	0.268 020[-4]	0.126 127[-4]
4		0.501 817 629[+6]	0.138 109[-2]	-0.462 822[-3]	0.222 023[-3]	0.113 246[-3]	0.533 196[-4]
5		0.163 704 385[+6]	0.500 554[-2]	-0.168 421[-2]	0.806 435[-3]	0.412 147[-3]	0.193 936[-3]
6		0.590 925 831[+5]	0.160 848[-1]	-0.546 308[-2]	0.262 772[-2]	0.134 044[-2]	0.631 298[-3]
7		0.230 421 470[+5]	0.461 545[-1]	-0.160 604[-1]	0.772 551[-2]	0.395 535[-2]	0.186 151[-2]
8		0.955 227 062[+4]	0.115 902[+0]	-0.425 580[-1]	0.207 401[-1]	0.106 058[-1]	0.499 985[-2]
9		0.416 173 242[+4]	0.239 591[+0]	-0.989 143[-1]	0.488 398[-1]	0.251 978[-1]	0.118 762[-1]
10		0.188 806 699[+4]	0.356 004[+0]	-0.185 707[+0]	0.961 467[-1]	0.498 113[-1]	0.235 820[-1]
11		0.881 602 891[+3]	0.291 223[+0]	-0.219 427[+0]	0.120 776[+0]	0.644 816[-1]	0.305 810[-1]
12		0.405 734 450[+3]	0.762 196[-1]	0.471 897[-1]	-0.301 202[-1]	-0.181 244[-1]	-0.854 306[-2]
13		0.205 233 445[+3]	-0.289 925[-2]	0.546 948[+0]	-0.501 909[+0]	-0.296 954[+0]	-0.145 989[+0]
14		0.103 066 810[+3]	0.255 355[-2]	0.500 140[+0]	-0.604 981[+0]	-0.416 280[+0]	-0.210 608[+0]
15		0.465 374 781[+2]	-0.153 103[-2]	0.833 508[-1]	0.523 577[+0]	0.555 612[+0]	0.310 691[+0]
16		0.248 310 377[+2]	0.962 018[-3]	-0.114 439[-1]	0.806 229[+0]	0.107 869[+1]	0.664 625[+0]
17	6	0.110 692 200[+2]	1.0				
18	7	0.594 239 642[+1]	1.0				
19	8	0.228 194 840[+1]	1.0				
20	9	0.119 158 993[+1]	1.0				
21	10	0.337 905 297	1.0				
22	11	0.151 649 993	1.0				
23	12	0.474 708 000[-1]	1.0				
24	13	0.220 277 975[-1]	1.0				
25	14	0.102 215 185[-1]	1.0				
26	15	0.474 310 000[-2]	1.0				
<i>p</i> subset							
1	1-4	0.106 044 417[+6]	-0.150 838[-3]	0.769 776[-4]	0.391 778[-4]	0.176 973[-4]	
2		0.251 136 654[+5]	-0.133 534[-2]	0.681 418[-3]	0.346 780[-3]	0.157 593[-3]	
3		0.815 438 543[+4]	-0.757 975[-2]	0.390 983[-2]	0.199 506[-2]	0.901 829[-3]	
4		0.311 741 758[+4]	-0.322 674[-1]	0.169 007[-1]	0.865 572[-2]	0.393 964[-2]	
5		0.132 234 593[+4]	-0.105 461[+0]	0.575 698[-1]	0.297 856[-1]	0.135 050[-1]	
6		0.602 971 370[+3]	-0.252 404[+0]	0.146 357[+0]	0.769 073[-1]	0.352 647[-1]	
7		0.289 498 046[+3]	-0.388 505[+0]	0.244 803[+0]	0.131 653[+0]	0.600 383[-1]	
8		0.143 957 601[+3]	-0.303 915[+0]	0.129 195[+0]	0.582 805[-1]	0.265 621[-1]	
9		0.712 922 966[+2]	-0.803 595[-1]	-0.356 091[+0]	-0.293 266[+0]	-0.151 550[+0]	
10		0.368 983 593[+2]	-0.343 651[-4]	-0.580 572[+0]	-0.507 290[+0]	-0.254 384[+0]	
11		0.187 156 664[+2]	-0.161 064[-2]	-0.210 517[+0]	0.137 035[+0]	0.112 377[+0]	
12		0.952 376 353[+1]	0.103 010[-2]	-0.931 576[-2]	0.739 691[+0]	0.614 533[+0]	
13	5	0.483 162 337[+1]	1.0				
14	6	0.229 242 994[+1]	1.0				
15	7	0.108 459 331[+1]	1.0				
16	8	0.361 090 962[+0]	1.0				
17	9	0.134 773 553[+0]	1.0				
18	10	0.474 708 000[-1]	1.0				
19	11	0.220 277 975[-1]	1.0				
20	12	0.102 215 185[-1]	1.0				
21	13	0.474 310 000[-2]	1.0				
<i>d</i> subset							
1	1-2	0.611 735 956[+4]	-0.459 047[-3]	-0.246 637[-3]			
2		0.185 205 638[+4]	-0.443 897[-2]	-0.240 943[-2]			
3		0.724 226 431[+3]	-0.251 769[-1]	-0.137 725[-1]			

TABLE II (Continued).

GTO	CGTO	Exponent	Contraction coefficients	
4		0.321 814 803[+3]	-0.950 631[-1]	-0.532 519[-1]
5		0.154 434 352[+3]	-0.242 232[+0]	-0.138 225[+0]
6		0.775 020 935[+2]	-0.387 560[+0]	-0.215 654[+0]
7		0.400 923 735[+2]	-0.328 430[+0]	-0.944 443[-1]
8		0.207 097 071[+2]	-0.113 483[+0]	0.296 407[+0]
9		0.105 859 654[+2]	-0.994 924[-2]	0.526 547[+0]
10	3	0.539 040 583[+1]	1.0	
11	4	0.260 975 371[+1]	1.0	
12	5	0.121 851 031[+1]	1.0	
13	6	0.511 821 378[+0]	1.0	
14	7	0.361 091 000[+0]	0.114 7970[+0]	
15		0.134 774 000[+0]	0.135 1830[+0]	
16	8	0.220 280 000[-1]	0.383 0940[+0]	
17		0.102 220 000[-1]	0.450 2800[+0]	
<i>f</i> subset				
1	1	0.635 258 368[+3]	0.156 248[-2]	
2		0.222 350 513[+3]	0.140 800[-1]	
3		0.957 847 815[+3]	0.655 637[-1]	
4		0.450 793 487[+2]	0.187 845[+0]	
5	2	0.222 060 626[+2]	0.337 320[+0]	
6		0.109 955 403[+2]	0.384 596[+0]	
7		0.534 161 135[+1]	0.244 145[+0]	
8		0.239 269 542[+1]	0.603 122[-1]	
9	3	0.539 040 583[+1]	-0.631 500[-2]	
10		0.260 975 371[+1]	0.302 345[+0]	
11	4	0.121 851 031[+1]	0.459 934[+0]	
12		0.511 821 378[+0]	0.200 798[+0]	

TABLE III. Calculations of the dipole polarizability of Cs(2S). A study of different approximations. All polarizability data in a.u. (1. a.u. of dipole polarizability $\cong 0.14818 \text{ \AA}^3$).

Basis set	Orbital subspaces		Contributions						
	Active in	Frozen in	Nonrelativistic			Relativistic			
	CASSCF ^a	CASPT2 ^b	CASSCF	CASPT2	Total	CASSCF	CASPT2	Total	Total
[23.18.12] ^c	{6s} ^d	None	806.7	-420.2	386.5	-135.4	+80.1	-55.3	331.2
	{5p6s5d6p}	None	621.8	-110.7	511.1	-107.0	+27.0	-80.0	431.0
	{5p6s5d6p}	{KLM4s ² 4p ⁶ }	621.8	-114.7	507.1	-107.0	+28.6	-78.4	428.7
	{5s5p6s5d6p7s}	None	609.7			-104.0			
[23.18.12/13.11.6] ^e	{6s} ^d	None	806.0	-443.8	362.1	-132.0	+85.9	-46.1	316.0
	{5p6s5d6p}	None	600.0	-99.2	500.2	-99.7	+23.5	-76.2	424.6
	{5p6s5d6p}	{KLM4s ² 4p ⁶ }	600.0	-103.9	496.2	-99.7	+26.2	-73.6	422.6
	{5s5p6s5d6p7s}	{KLM4s ² 4p ⁶ }	594.7	-83.9	510.8	-97.7			
[23.18.12.4/13.11.6.2] ^f	{5p6s5d6p}	{KLM4s ² 4p ⁶ }	600.5	-109.0	491.6	-99.7	+21.7	-78.0	413.6

^aAll remaining core orbitals are inactive in CASSCF calculations. The sequence of orbitals in the active space follows from the nonincreasing sequence of occupation numbers.

^bThe active orbital subspace is the same as in CASSCF calculations. The inactive orbital space in CASPT2 follows from the difference between inactive CASSCF and frozen CASPT2 orbital subspaces.

^cUncontracted polarized GTO basis set determined in this paper.

^dOpen-shell RHF calculation.

^espd polarized GTO/CGTO basis set of this paper.

^fspdf polarized GTO/CGTO basis set of this paper.

TABLE IV. Calculations of the dipole polarizability of $K(^2S)$, $Rb(^2S)$, and $Fr(^2S)$. All data in a.u.

Atom/basis set	Orbital subspaces		Contributions						
	Active in	Frozen in	Nonrelativistic			Relativistic			
	CASSCF	CASPT2	CASSCF	CASPT2	Total	CASSCF	CASPT2	Total	Total
K(2S)									
[15.13.4/3.7.2]	{4s}	{KL}	416.1	-141.7	274.4	-7.8	+3.3	-4.5	269.9
	{3p4s3d4p}	{KL}	335.3	-34.2	301.1	-6.8	+1.2	-5.6	295.5
Rb(2S)									
[18.15.10/11.3.4]	{5s}	{KL3s ² 3p ⁶ }	523.7	-230.6	233.1	-36.3	+16.8	-19.4	273.6
	{4p5s4d5p}	{KL3s ² 3p ⁶ }	410.3	-52.3	358.1	-30.4	+5.9	-24.5	333.6
[18.15.10.4/11.9.4.2]	{4p5s4d5p}	{KL3s ² 3p ⁶ }	410.5	-55.1	355.1	-30.4	+5.5	-24.8	330.2
Fr(2S)									
[26.21.17.8]	{7s}	None	964.3	-599.0	365.3	-415.6	+292.3	-127.3	238.0
	{6p7s6d7p}	{KLMN5s ² 5p ⁶ }	710.2	-135.7	574.5	-310.2	+83.5	-226.7	347.8
[26.21.17.8/15.13.8.2]	{6p7s6d7p}	{KLMN5s ² 5p ⁶ }	703.5	-135.7	567.8	-306.7	+89.2	-217.5	350.3
[26.21.17.12/15.13.8.4]	{6p7s6d7p}	{KLMN5s ² 5p ⁶ }	704.4	-152.8	551.6	-307.4	+81.6	-225.8	325.7

sults. Thus, in the present tabular data,

$$\alpha_M^{(1)} + \alpha_{M-PT}^{(1)} = \alpha_{CASSCF}^{(1)} + \alpha_{CASPT2}^{(1)} \quad (11)$$

While the first term on the right-hand side of Eq. (1) gives the pure first-order MVD contribution and the corresponding mixed correlation-relativistic corrections for the given active orbital space, the second term accounts for mixed correlation-relativistic effect arising from the core orbitals. Only in the case of the $\{ns\}$ active space, i.e., with the CASSCF being equivalent to the open-shell RHF method, the CASPT2 contributions can be clearly interpreted as the core and core-valence (core-polarization) [5] terms.

Among the alkali-metal atoms studied in this paper, Cs(2S) occupies a rather special position. Both the core-polarization and relativistic contributions to its dipole polarizability are either known [6] or expected [5] to be large. Hence, most of the approximations used in our calculations have been carefully investigated for Cs. It is anticipated that once a given approximation is found to be reasonably safe for Cs, its use for K and Rb should be even more valid. No extensive scan of the reliability of different approximations has been carried out for Fr, as the quasirelativistic approach may not be entirely appropriate for this case.

We have studied the following three factors which may affect the calculated dipole polarizability of Cs: (i) the basis-set contraction effect, (ii) the effect of the electron correlation as partitioned between the CASSCF and CASPT2 contributions, and (iii) the core-polarization contribution from the $4d^{10}$ shell. Also, the influence of freezing deep core orbitals in CASPT2 calculations has been investigated. All data pertinent to these effects are collected in Table III. Some missing entries result from excessive demands on computational resources for the corresponding calculations.

The pure valence nonrelativistic CASSCF approximation overestimates the dipole polarizability of Cs(2S) by almost a factor of 2. The core-correlation correction as

estimated from the CASPT2 results for the $\{6s\}$ active space is much too negative. Their sum (386.5 a.u.) for the uncontracted [23.18.12] GTO set and 362.1 a.u. for the polarized [23.18.12/13.11.6] set) is fortuitously close to the final quasirelativistic results for largest basis sets and largest active spaces (see last column of Table III). Increasing the size of the active space stabilizes the nonrelativistic CASSCF + CASPT2 result for [23.18.12] GTO set at approximately 500 a.u. Simultaneously, the total first-order relativistic correction becomes stabilized at the value of about -80 a.u. The effect of freezing the inner shells $\{KLM4s^24p^6\}$ in CASPT2 calculations lowers the total nonrelativistic value by about 4 a.u. The relativistic contribution becomes less negative by about 2 a.u. One can conclude that freezing the deep core orbitals has a rather negligible effect on the final quasirelativistic result.

The effect of the contraction of the [23.18.12] basis set depends on the choice of the active space and can be estimated at the value of about -11 a.u. for the total nonrelativistic results with the $\{5p6s5d6p\}$ active space. On comparing these results with those for the $\{6s\}$ active space (lowering by about 24 a.u. upon contraction) one finds that the contraction effect on the nonrelativistic CASSCF + CASPT2 result diminishes with the increase of the active orbital subspace. Thus one can safely consider the value of +11 a.u. as an upper limit for the change in the nonrelativistic result upon fully decontracting the spd polarized basis set. Simultaneously, one finds that the same correction to the relativistic contribution should not be more negative than about -4 a.u.

On extending the spd polarized basis set with f -type polarization functions one finds that the nonrelativistic result is lowered by about 5 a.u. while the total relativistic correction becomes about 4 a.u. more negative. The change in the total dipole polarizability arising from the polarization of the $4d^{10}$ shell amounts to about -9 a.u. and will be at least partly canceled by the basis-set contraction effect. On the other hand, increasing the size of the active space would presumably reduce the total polarizability.

Summarizing different estimates which follow from the data of Table III we conclude that the total relativistically corrected dipole polarizability of $\text{Cs}(^2S)$ should be in the range of 410–420 a.u. It also follows that calculations with the *spd* polarized basis set and the $\{5p6s5d6p\}$ active space give a reasonable estimate of the result which would follow from uncontracted basis-set calculations with much larger active spaces. One should also remark that the failure of the CASSCF + CASPT2 calculations with the minimal $\{6s\}$ active space gives some warning with regard to the reliability of low-order results with unrestricted Hartree-Fock reference.

Much less extensive analysis of the influence of different approximations on the calculated dipole polarizability has been carried out for K, Rb, and Fr. The (*spd*) polarized basis sets for K and Rb have been examined in our earlier paper [13]. The polarized basis sets generated in this study for Fr are examined in present calculations of its dipole polarizability. Moreover, in order to investigate the magnitude of the core-polarization effect due to $3d^{10}$ shell, the polarizability of $\text{Rb}(^2S)$ has been calculated with the polarized basis set augmented by *f*-type functions (see Sec. III). Results of the dipole polarizability calculations for K, Rb, and Fr are collected in Table IV.

The general pattern of the dependence of the dipole polarizability data for K, Rb, and Fr on the basis-set features and the size of the active orbital subspace follows that discussed for Cs. One can expect that upon a further extension of the active space the nonrelativistic CASSCF + CASPT2 values should to some extent increase; the corresponding changes should be very small for K, but may contribute significantly to the dipole polarizability of Fr. Increasing the size of the active space leads to an increase in the negative first-order CASSCF + CASPT2 relativistic contribution. This compensates to some extent for the corresponding increase of the nonrelativistic result. Including the $(n-2)d^{10}$ core-polarization effect in calculations on Rb and Fr has a similar contribution as in the case of Cs. This effect reduces the total polarizability of Rb and Fr.

There are experimental values of the dipole polarizability available for K, Rb, and Cs [1]. A comparison of our results with experimental data will be presented in Sec. V. Most theoretical calculations for heavier alkali-metal atoms have been carried out with different effective pseudopotentials. Surveys of these results may be found in Refs. [1,4,5,26]. Since the pseudopotential methods usually involve several uncertainties, the corresponding data should not be used as the major reference to qualify the present results.

All electron calculations at the RHF and correlated levels of approximation have been performed by Reinsch and Meyer [4] for $\text{K}(^2S)$. The RHF result for the dipole polarizability of $\text{K}(^2S)$ computed by Reinsch and Meyer (418.0 a.u. with *spd* GTO/CGTO basis set) agrees well with the present value of 416.1 a.u. However, the contribution of intershell correlation effects calculated by these authors amounts to -130.4 a.u., and gives the nonrelativistic dipole polarizability of $\text{K}(^2S)$ equal to 287.6 a.u., i.e., about 13 a.u. lower than the nonrelativistic value of

the present paper. This discrepancy may to some extent follow from the method used in early papers of Meyer and co-workers [4,5] to evaluate the dipole polarizability from an approximate dipole-moment formula [27,28].

For evaluating the reliability of the calculated relativistic contribution to dipole polarizabilities of alkali-metal atoms, the numerical DHF results of Desclaux, Laaksonen, and Pyykkö [6] are of only limited usefulness. The nonrelativistic result for $\text{Cs}(^2S)$ reported by these authors (757 a.u.) is about 50 a.u. lower than the present RHF value (806.7 a.u., see Table III). The DHF result of Desclaux, Laaksonen, and Pyykkö is 622 a.u. Thus their (total) pure relativistic contribution to α of $\text{Cs}(^2S)$ is about -135 a.u. and perfectly agrees with the first-order quasirelativistic value of this study (-135.4 a.u., see Table III).

Nonrelativistic RHF values for K and Rb have not been given by Desclaux, Laaksonen, and Pyykkö [6] while their DHF data are 394 and 463 a.u., respectively. The present quasirelativistic RHF values from Table IV are 408.3 a.u. for $\text{K}(^2S)$ and 486.7 a.u. for Rb. By analogy with the above-mentioned discrepancies for Cs one may conclude that the DHF values of Ref. [6] are most likely affected in a similar manner.

The nonrelativistic RHF and the DHF results of Desclaux, Laaksonen, and Pyykkö [6] turn out to be systematically too low. In the calculations carried out by these authors only one orbital of the given symmetry could be perturbed. Their calculations therefore correspond to what is known as the uncoupled Hartree-Fock (UCHF) approximation [29] to the fully coupled Hartree-Fock (CHF) solution of the perturbation problem. The UCHF dipole polarizabilities [29] are usually lower than the corresponding CHF results. Indeed, on performing open-shell RHF-UCHF calculations with polarization restrictions to only the $6s$ valence orbital, we obtain a dipole polarizability of 751.6 a.u. for Cs, in good agreement with the value of 757 a.u. reported by Desclaux, Laaksonen, and Pyykkö [6].

The importance of the electron-correlation contribution to dipole polarizabilities of alkali-metal atoms arising from the next-to-valence shell has been stressed by Christiansen and Pitzer [30]. Their results with explicit correlation of the valence and next-to-valence shells and the rest of the core approximated by relativistic pseudopotentials have been found to differ from the experimental data in the worst case (Rb) by +5%. Because the method used by Christiansen and Pitzer (within the approximations inherent in their approach) combines both the electron-correlation and relativistic effects, their data should be compatible with those of this paper. Indeed the dipole-polarizability results of Christiansen and Pitzer [30] (K: 287.5 a.u., Rb: 336.1 a.u., Cs: 413.7 a.u.) compare well with the present values calculated for the $\{(n-1)p\ ns\ (n-1)dnp\}$ active space (see the last column of Tables III and IV).

Among different approximation methods of including the core-polarization and relativistic effects one should also mention the results obtained by Fuentealba [31] with a semiempirical effective core potential. This method treats the alkali-metal atoms as a one-electron problem

and all electron-correlation (including core-polarization) and relativistic effects are embedded in empirical parameters of the pseudopotential. Indeed, the method nearly reproduces the experimental polarizability data for Li through Cs. However, it provides little information about the mutual interplay of the electron-correlation and relativistic contributions to the dipole polarizability of alkali-metal atoms. Similar, essentially one-electron methods have recently been used by Zhou and Norcross [32], who obtained excellent results for the dipole polarizability of Cs.

V. SUMMARY AND CONCLUSIONS

The dipole-polarizability results calculated in this paper are summarized in Table V. They are compared with experimental data of Molof *et al.* [33] and Hall and Zorn [34] obtained by using two different measurement techniques. The quasirelativistic data of this paper correspond to the sum of CASSCF and CASPT2 nonrelativistic and first-order MVD contributions calculated with the $\{(n-1)p\ ns(n-1)d\ np\}$ active space. The core-correlation effects and the corresponding mixed correlation-relativistic contributions include $(n-2)d^{10}$ and $(n-1)s^2$ shells.

The present all-electron first-order quasirelativistic results for K, Rb, and Cs agree well with the experimental values. The data of Table V show that including the relativistic corrections to the dipole polarizability is important already for Rb and indispensable for heavier atoms of group Ia.

Experimental data for the dipole polarizability of Fr are rather unlikely to become available and it is difficult to assess the quality of our quasirelativistic result for this atom. The quasirelativistic approach works well for K, Rb, and Cs, and although some deterioration of its validity for higher values of Z is expected, the present α value for Fr should not be far from the exact result. Our quasirelativistic calculations predict a relativistic contribution to α of Fr as large as -41% of the nonrelativistic result. For the validation of this value even DHF calcu-

lations of Fr dipole polarizability [6] would be of great help.

In their 1988 review article Miller and Bederson [1] quote (yet unpublished) results of Doolen and Liberman, who on the basis of relativistic pseudopotential calculations predicted a decrease of 18% in the polarizability of Fr as compared to that of Cs. According to our quasirelativistic correlated data of Table V the relativistic and electron-correlation contributions make the dipole polarizability of Fr about 21% lower than the calculated value for Cs.

The present all-electron calculations avoid any reference to effective core potentials and the detailed analysis of different results presented in Tables III and IV adds to the validation of pseudopotential methods. The semiempirical pseudopotentials [31] may obviously be very successful even in the valence-electron approximation. However, there is no systematic way of their improvement. The *ab initio* pseudopotential methods [30] may efficiently account for core-polarization and relativistic effects of deeper core electrons. The observation of Christiansen and Pitzer [30] that in calculations on alkali-metal atoms one needs to consider explicitly the next-to-valence shell is confirmed and documented by the present data. However, the occupation-number analysis of the CASPT2 one-particle density matrix shows that while explicit correlation is necessary to $(n-1)p^6$ pairs the effect for the $(n-1)s^2$ pair is quite negligible.

It is also interesting to compare the relative contributions due to electron-correlation and relativistic effects. According to the data of Tables III and IV the electron-correlation contribution to the RHF polarizabilities systematically increases with Z , as does the (negative) pure (RHF) relativistic correction. However, the latter is accompanied by the increase of the (positive) correlation-relativistic correction. Consequently, the pure electron-correlation term makes a dominant contribution to the lowering of the RHF dipole polarizability even for Fr.

On the computational side the results of this paper provide another [8,9,15,35] illustration of the efficiency of the CASPT2 approach. Once the dominant electron-correlation effects are accounted for at the level of the CASSCF method, the remaining correlation is adequately described by the second-order single-state multireference CASPT2 treatment. This provides an all-electron *ab initio* alternative to effective core potentials.

Finally, let us mention that as part of this study we have generated first-order polarized basis sets for Cs and Fr which complete the polarized basis-set library [7,13,23] for the group-Ia elements. These basis sets are devised primarily for high-level correlated calculations of molecular electric properties. Because of the highly ionic character of compounds with alkali-metal atoms, the contraction effects discussed in Sec. IV will be rather insignificant. For the same reason the relativistic contribution to molecular electric properties will be significantly reduced, making the pseudorelativistic MVD method quite reliable.

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TABLE V. Comparison of the calculated dipole polarizability data with experimental values. All polarizabilities in \AA^3 .

Atom	This work		Experimental	
	A^a	B^b	Molof <i>et al.</i> (Ref. [33])	Hall and Zorn (Ref. [34])
K ^c	44.6	43.8	43.4±0.9	45.2±3.2
Rb ^d	60.8	48.9	47.3±0.9	48.7±3.4
Cs ^e	72.8	61.3	59.6±1.2	63.3±4.6
Fr ^f	81.8	48.3		

^aNonrelativistic values.

^bFirst-order MVD quasirelativistic results.

^cBasis set: [15.13.4/9.7.2]; active space $\{3p4s3d4p\}$; frozen in CASPT2: $\{KL\}$.

^dBasis set: [18.15.10.4/11.9.4.2]; active space $\{4p5s4d5p\}$; frozen in CASPT2: $\{KL3s^23p^6\}$.

^eBasis set: [23.18.12.4/13.11.6.2]; active space $\{5p6s5d6p\}$; frozen in CASPT2: $\{KLM4s^24p^6\}$.

^fBasis set: [26.21.17.12/15.13.8.4]; active space $\{6p7s6d7p\}$; frozen in CASPT2: $\{KLMN5s^25p^6\}$.

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- [1] T. M. Miller and B. Bederson, *Adv. At. Mol. Phys.* **13**, 1 (1977); **25**, 37 (1988), and references therein.
- [2] A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1969).
- [3] J. Cooper and R. N. Zare, *Atomic Collision Processes* (Gordon and Breach, New York, 1969); *Atomic Physics with Positions*, edited by W. Hubectson and E. A. G. Armour (Plenum, New York, 1987).
- [4] E.-A. Reinsch and W. Meyer, *Phys. Rev. A* **14**, 915 (1976).
- [5] W. Müller, J. Flesch, and W. Meyer, *J. Chem. Phys.* **80**, 3297 (1984).
- [6] J. P. Desclaux, L. Laaksonen, and P. Pyykkö, *J. Phys. B* **14**, 419 (1981).
- [7] A. J. Sadlej, M. Urban, and O. Gropen, *Phys. Rev. A* **44**, 5547 (1991).
- [8] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990).
- [9] K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
- [10] V. Kellö and A. J. Sadlej, *J. Chem. Phys.* **93**, 8112 (1990).
- [11] A. J. Sadlej and M. Urban, *Chem. Phys. Lett.* **176**, 293 (1991).
- [12] A. J. Sadlej, *Coll. Czech. Chem. Commun.* **53**, 1995 (1988); A. J. Sadlej, *Theor. Chim. Acta* **79**, 123 (1991).
- [13] A. J. Sadlej and M. Urban, *J. Mol. Struct. (Theochem.)* **234**, 147 (1991).
- [14] H.-J. Werner and W. Meyer, *Phys. Rev. A* **13**, 13 (1976).
- [15] K. Andersson and A. J. Sadlej, *Phys. Rev. A* **46**, 2356 (1992).
- [16] P. Pyykkö, *Chem. Rev.* **88**, 563 (1988); I. Grant, in *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1988), Vol. 2, p. 1.
- [17] B. Levy and G. Berthier, *Int. J. Quantum Chem.* **2**, 307 (1968).
- [18] A. J. Sadlej, *J. Chem. Phys.* **75**, 320 (1981); A. J. Sadlej, *Int. J. Quantum Chem.* **23**, 147 (1983).
- [19] B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- [20] V. Kellö and A. J. Sadlej, *J. Chem. Phys.* **95**, 8248 (1991); *Mol. Phys.* **75**, 209 (1992); A. J. Sadlej, *J. Chem. Phys.* **36**, 2048 (1992).
- [21] A. J. Sadlej, *J. Chem. Phys.* **95**, 2614 (1991).
- [22] W. J. Stevens and M. Krauss, *J. Phys. B* **16**, 2321 (1983).
- [23] K. Andersson, M. P. Fülscher, R. Lindh, P.-Å. Malmqvist, J. Olsen, B. O. Roos, A. J. Sadlej, and P.-O. Widmark, MOLCAS System of Quantum Chemistry Programs, Release O2 (Theoretical Chemistry, University of Lund, Sweden, 1992) (unpublished).
- [24] K. Faegri, Jr. and J. Almlöf, *J. Comp. Chem.* **7**, 396, (1986).
- [25] M. Urban and A. J. Sadlej, *J. Chem. Phys.* **95**, 5490 (1991).
- [26] F. Maeder and W. Kutzelnigg, *Chem. Phys.* **42**, 95 (1979).
- [27] R. Jaquet, W. Kutzelnigg, and V. Staemmler, *Theor. Chim. Acta* **54**, 205 (1980).
- [28] The discrepancies which may result from using approximate expressions for the induced moment and the Hellmann-Feynman theorem are discussed in G. H. F. Diercksen and A. J. Sadlej, *Chem. Phys.* **77**, 429 (1989). See also P.-O. Nerbrant, B. O. Roos, and A. J. Sadlej, *Int. J. Quantum Chem.* **15**, 135 (1979); G. H. F. Diercksen and A. J. Sadlej, *Chem. Phys.* **59**, 29 (1981).
- [29] P. W. Langhoff and R. P. Hurst, *Phys. Rev.* **139A**, 1415 (1965).
- [30] P. A. Christiansen and K. S. Pitzer, *Chem. Phys. Lett.* **85**, 434 (1982).
- [31] P. Fuentealba, *J. Phys. B* **15**, L555 (1982).
- [32] H. L. Zhou and D. W. Norcross, *Phys. Rev. A* **40**, 5048 (1989), and references therein.
- [33] R. W. Molof, H. L. Schwartz, T. M. Miller, and B. Bederson, *Phys. Rev. A* **10**, 1131 (1974).
- [34] W. D. Hall and J. C. Zorn, *Phys. Rev. A* **10**, 1141 (1974).
- [35] B. O. Roos, K. Andersson, and M. P. Fülscher, *Chem. Phys. Lett.* **192**, 5 (1992); P. Bozowski, K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **97**, (1992); K. Andersson and B. O. Roos, *Int. J. Quantum Chem.* (to be published).