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Standardized basis sets for high-level-correlated relativistic calculations of atomic and molecular electric properties in the spin-averaged Douglas-Kroll approximation

II. Groups Ia and IIa

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Abstract. The technique previously developed for the generation of the so-called first-order polarized basis sets for accurate non-relativistic calculations of molecular electric properties is used to obtain similar basis sets suitable for calculations in the Douglas-Kroll no-pair approximation. The corresponding (relativistic) basis sets are constructed for atoms of groups Ia and IIa of the Periodic Table and tested in calculations of atomic and ionic polarizabilities. Also the first ionization potential of the group Ia and the first and second ionization potential of the group IIa metals have been evaluated to provide additional qualification of the generated basis sets. The present results are compared with earlier non-relativistic and quasirelativistic data and the role of the relativistic effect is discussed.

Key words: Polarized basis sets – Relativistic effects – Douglas-Kroll approximation – Ionization potentials of group Ia and IIa metals

1 Introduction

Until recently the development of standardized Gaussian basis sets for the purpose of high-level-correlated calculations of atomic and molecular electric properties has been essentially limited to the non-relativistic level of approximation [1–8]. These so-called (first-order) polarized basis sets [1, 2] originate from the idea of the internal electric-field dependence of the basis set functions [9, 10] and have been successfully used in different atomic and molecular calculations. In contrast to other Gaussian basis sets developed in the past [11–13], the polarized sets are not meant simultaneously to give highly accurate results for a variety of different atomic and molecular properties. With acceptably small size they are principally oriented towards achieving high-quality results for basic atomic and molecular electric properties like dipole and quadrupole moments and dipole polarizabilities. The (first-order) polarized basis sets developed for non-relativistic calculations will be hereafter referred to as the non-relativistic polarized sets (PolX), where X stands for the chemical symbol of the atom.

Starting from the third row of the Periodic Table some attention should be given to the relativistic contribution to the calculated atomic and molecular electric properties [4–8]. In earlier studies we evaluated this contribution by using a simple method [14, 15] developed on the basis of what is called the mass-velocity-Darwin (MVD) approximation [16–19]. With increasing value of the nuclear charge (Z) the role of the higher-order relativistic effects becomes important and the MVD approximation, which is accurate through the second order in the fine structure constant α, becomes less and less appropriate. In addition to higher-order relativistic terms in the Hamiltonian, one must also take into account the relativistic change in the wave function. This problem can be approached by using the latest developments in perturbation theory for relativistic effects [20–23]. However, in the case of perturbative calculations of relativistic corrections to properties one faces all the problems of the multiple perturbation theory; an atomic or molecular property calculated at the correlated level of approximation arises then as the result of the triple perturbation scheme with the three perturbations referring to (1) the property itself, (2) relativistic effects, and (3) the electron correlation correction [15]. It is, therefore far more convenient to use methods of non-perturbative character, in particular those which can be formulated in the framework of the variation principle. In this respect the method developed by Douglas and Kroll [24] and thoroughly analysed by Sucher et al. [25, 26] appears to be a very convenient choice, as shown by numerous studies of Hess and his co-workers [27–30].

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The major computational advantage of the Douglas-Kroll (DK) approach in its one-component (spin-free) form advocated by Hess et al. [27, 28] is that the relativistic terms alter only the one-electron part of the Hamiltonian. Moreover, the operators which appear in the DK method are non-singular [31]. This makes the DK method suitable for the use in variational calculations and immediately poses the problem of the basis set choice. It has already been shown by Hess et al. [30, 32] that the standard sets of contracted Gaussian (CGTO) functions are usually inappropriate in relativistic calculations based on the DK Hamiltonian. The same conclusion follows from our earlier paper in this series [33].

It is well known that calculations of atomic and molecular electric properties are particularly demanding in terms of the basis set composition and diffuseness [34]. On the other hand, most of the electric properties of interest are determined by the electron distribution in outer electronic shells. Hence, a careful optimization of orbital exponents (see e.g. [32]) is not as necessary as in energy-oriented calculations. For valence-determined properties in closed-shell systems the relativistic effects, though sometimes appreciably large, are of secondary character. By this reasoning we have based the strategy of the determination of "relativistic" CGTO basis sets [33] on the assumption that the uncontracted Gaussian (GTO) basis set are the same as in the non-relativistic case. Thus, only the contraction coefficients need to be determined. This assumption has been used for the generation of "relativistic" polarized basis sets (NpPol) for atoms of groups Ib and IIb of the Periodic Table [33]. In the present paper the same method is used to generate NpPol basis sets for atoms of groups, Ia and IIa.

Some details of the basis set generation are briefly described in Sect. 2 along with certain computational details of the present study. In Sect. 3 the results obtained with these NpPol sets for atomic and ionic polarizabilities will be presented. They are accompanied by the calculated ionization potential data. Both these features of atoms are directly related to their behaviour upon formation of molecules and determine the usefulness of the NpPol sets in molecular calculations. Particular attention will be given to the increased importance of the relativistic effect on the calculated properties with the increase of Z. On the basis of the present results we shall also discuss the range of validity of the MVD approximation used in our earlier estimations of the relativistic effect on atomic and molecular electric properties [35, 36]. The paper is summarized and concluded in Sect. 4.

2 Generation of the first-order polarized basis sets for DK calculations: methods and computational details

The general strategy of the NpPol basis set generation is essentially the same as that used in the determination of their non-relativistic counterparts [3, 35, 36]. Certain steps, however, could have been omitted by using the experience gained in non-relativistic calculations. Among them is the choice of orbital exponents in the extension of initial basis sets. In most cases these are assumed to be the same as those of polarized (Pol) basis sets for non-relativistic calculations. Only in the case of the Ba atom one more diffuse s-type function with the orbital exponent of 0.00371 has been added to the set described in Ref. [35]. Simultaneously the number of generally contracted s-type CGTOs has been reduced by one. This removes some linear dependencies between basis set functions found in our earlier calculations and saves the general structure of the polarized basis set for Ba.

One may raise some objections concerning the use of the same set of primitive GTOs for both Pol and NpPol sets. In the case of relatively light atoms (Li, Be, Na, Mg) the relativistic effect on valence-determined properties is negligible. Thus, although these basis sets may be deficient in high exponents, the neglected effects are relatively unimportant. For heavier atoms the very initial sets [37, 38] are quite rich in high-exponent Gaussians and for the present purpose there is no need for their further extension in this region of the orbital exponent values.

The assumed target structure of the polarized CGTO basis sets is of the form [5.3.2], [7.5.2], [9.7.2], [11.9.4], [13.11.6], for the first-, second-, third-, fourth-, and fifth-row atoms, respectively. For Fr the final polarized basis set is [15.13.8.2]. In the notation employed in this paper for CGTO sets, $[N_s.N_p.N_d.N_f]$, the subsequent entries denote the number of CGTOs with the indicated angular momentum quantum number. All these basis sets have been obtained by starting from some initial primitive set. It most cases the initial GTO set had to be extended by some diffuse p-type GTOs for the representation of the valence p-type orbital. These extended GTO sets were afterwards transformed into GTO/CGTO sets by partial contraction of the high-exponent GTOs, i.e. those which represent mostly the core orbitals, while leaving the low-exponent part essentially uncontracted.

The representation of the core orbitals, i.e. of the orbitals of all fully occupied shells, is assumed to be in the form of generalized contractions of the primitive set [11, 12, 39], though restricted only to a certain range of GTOs with the highest orbital exponents. The contraction coefficients have been determined in Douglas-Kroll/self-consistent field/Hartree-Fock (DK-SCF-HF) calculations with extended initial GTO sets. This way of determining the contraction coefficients takes into account the important relativistic effects which predominantly affect the core orbitals [40]. Let n_l be the number of primitive functions of the type l, $l = s,p,d,\ldots$, in the *final polarized* set. Then, for the primitive GTO set of the form $(n_s.n_p.n_d\ldots)$ the contraction coefficients for core orbitals follow from calculations with the primitive GTO set of the form $(n_s{-}1.n_p{-}1.n_d{-}4\ldots)$. The resulting contracted set is of the form $[n_s{-}1.n_p{-}1.n_d{-}4\ldots/N_s{-}1.N_p{-}1.N_d{-}2\ldots]$ and has been afterwards completed by one diffuse s-type and one diffuse p-type GTO. This gives the "unpolarized" GTO/CGTO set of the form $[n_s.n_p.n_d{-}4\ldots/N_s.N_p.N_d{-}2\ldots]$. The background of this strategy is described and documented in earlier papers on the generation of Pol sets for non-relativistic calculations of electric properties [1, 3] and is supported by numerous pilot calculations of different electric properties of atoms.

Table 1. Details of the generation of standardized first-order polarized (NpPol) basis sets for relativistic calculations of atomic and molecular electric properties

Atom	Uncontracted GTO sets			Contracted sets		
	Initial	[Ref.]	Extended[a]	Initial[b]	Extended[c]	Final (NpPol)[d]
Li	(9)	[72]	(9.5)	[9.5/4.2]	[10.6/5.3]	[10.6.4/5.3.2]
Na	(12.9)	[73]	(12.9)	[12.9/6.4]	[13.10/7.5]	[13.10.4/7.5.2]
K	(14.9)	[37]	(14.12)	[14.12/8.6]	[15.13/9.7]	[15.13.4/9.7.2]
Rb	(17.11.6)	[37]	(17.14.6)	[17.14.6/10.8.2]	[18.15.6/11.9.2]	[18.15.10/11.9.4]
Cs	(21.15.8)	[36]	(22.17.8)	[22.17.8/12.10.4]	[23.18.8/13.11.4]	[23.18.12/13.11.6]
Fr	(24.17.13.8)	[36]	(25.20.13.8)	[25.20.13.8/14.12.6.2]	[26.21.13.8/15.13.6.2]	[26.21.17.8/15.13.8.2]
Be	(9)	[72]	(9.5)	[9.5/4.2]	[10.6/5.3]	[10.6.4/5.3.2]
Mg	(12.9)	[73]	(12.9)	[12.9/6.4]	[13.10/7.5]	[13.10.4/7.5.2]
Ca	(14.9)	[37]	(14.12)	[14.12/8.6]	[15.13/9.7]	[15.13.4/9.7.2]
Sr	(17.11.6)	[37]	(17.14.6)	[17.14.6/10.8.2]	[18.15.6/11.9.2]	[18.15.10/11.9.4]
Ba	(20.17.8)	[35]	(20.17.8)	[20.17.8/12.10.4]	[21.18.8/13.11.4]	[21.18.12/13.11.6]

[a] This extension, whenever carried out, amounts to adding some diffuse *s*- and *p*-type functions in order to (1) increase the flexibility of the initial set determined in energy-oriented calculations, (2) provide uncontracted Gaussians (GTOs) appropriate for the representation of the valence *p*-type orbital. For details see Refs. [3, 35, 36]. Only in the case of Na and Mg have the initial basis sets of McLean and Chandler [73] already been derived by extending the sets of Huzinaga [37]

[b] Contraction of the extended GTO set of the previous column with contraction coefficients determined from Douglas-Kroll, Self Consistent field Hartree-Fock (DK-SCF-HF) eigenvectors which follow from calculations with the extended GTO sets

[c] Extension of the initial contracted Gaussian (CGTO) set by one diffuse *s*-function and one diffuse *p*-function

[d] The final NpPol sets with the *d*-type polarization functions determined from DK-SCF-HF eigenvector calculated with extended CGTO sets of the previous column

The physics of the electric field polarization of the electronic distribution [9] tells us that the major effects will be associated with the valence shell. In the case of the group Ia and IIa atoms the polarization of the next-to-valence is also quite important [41]. The deeper shells hardly contribute the response of these atoms to weak electric fields. For this reason only the *d*-type polarization functions have been added to the "unpolarized" GTO/CGTO sets leading to final NpPol sets of the form $[n_s.n_p.n_d\ldots/N_s.N_p.N_d\ldots]$. For each atom the polarization set includes two *d*-type CGTOs, each composed of two GTOs and derived according to the method described in our earlier papers [3, 35, 36] in the context of the Pol basis set generation of non-relativistic calculations.

The different steps in the NpPol basis set generation are summarized in Table 1. Some further details concerning the range of contractions and the choice of orbital exponents and contraction coefficients for polarization functions can be found in our earlier papers [3, 35, 36]. All basis set details are available upon request from the authors[1] and on the http page[2]. They will be also a part of the basis set library of future releases of the MOLCAS system of quantum chemistry programs [42].

The basis set generation step relies on SCF-HF calculations in the framework of the one-component DK approximation [28–30, 32]. The illustration of the performance of these basis sets, as presented in Sect. 3, is based on calculations performed by using one of the most reliable post-HF methods, the coupled cluster scheme (CC) with iterative evaluation of the one- (T_1) and two-particle (T_2) cluster amplitudes (CCSD) [43] and perturbative estimation of the effect of the three-particle (T_3) cluster amplitudes according to what is known as the CCSD(T) scheme [44]. The CCSD and CCSD(T) methods with restricted Hartree-Fock (RHF)-SCF wave functions are nowadays a fairly routine tool for accurate evaluation of the electron correlation contribution to energies and other properties of many-electron closed shell systems [43, 45–48]. They have been used in our earlier quasirelativistic calculations for the group IIa atoms [35].

Until recently most of our quasirelativistic studies for open shell systems have been carried out only at the level of the restricted open-shell Hartree-Fock (ROHF) SCF approximation. For the group Ia atoms [36] some calculations have been performed within the CASPT2 scheme [49, 50]. However, with the next-to-valence orbitals and appropriate correlating orbitals included in the active orbital space of the reference function, such calculations represent a formidable task. Owing to the recent developments [51–53] in the area of the CC approximation for open shell systems the same level of sophistication as that used for closed shells could also have been reached in the present study for the group Ia elements. The results reported in Sect. 3 for the group Ia elements and for singly ionized group IIa atoms have been obtained at the level of the CCSD(T) approximation with ROHF reference function and complete spin projection [53].

The physical properties of atoms and ions considered in this paper are primarily determined by the electronic structure of the atomic valence shell. However, calculation of these properties [35, 36] reveals that the valence-shell approximation offers at best only a qualitative description. It is well recognized, for example, that the so-called core-polarization effects [41, 54, 55] must be

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[2] Network address: http://www.qch.fns.uniba.sk/NpPol_bases.txt

taken into account to achieve a fair accuracy of the calculated data. This means that the study of the electron correlation contribution must be extended to electrons of inner atomic shells. The results of our earlier calculations [35, 36, 56] as well as the pseudopotential methods [57, 58] show that most valence properties of the group Ia and IIa atoms and their compounds can be quite accurately computed if the electron correlation effects due to next-to-valence shell are included. This approximation is used in calculations reported in this paper, i.e. the correlated level CC calculations include either $(n-1)s^2ns^x$ (Li, Be and their ions) or $(n-1)s^2(n-1)p^6ns^x$ (other atoms and ions), $x = 0, 1$, or 2, electrons. In this context it is also worthwhile to point out that the NpPol basis sets derived in this paper are essentially uncontracted in the next-to-valence region and should provide a reasonable description of the electron correlation effects there.

The basis set development is primarily carried out for their use in relativistic calculations of molecular electric properties. A suitable test of their flexibility can therefore be achieved by the calculation of electric dipole polarizabilities of neutral atoms and ions resulting from the removal of valence electrons. The corresponding calculations have been carried out using the numerical finite-field perturbation technique [59]. The numerical values of the electric field strength used in the present study are in the range of 0.0001–0.01 atomic units (a.u.), depending on the magnitude of the calculated dipole polarizability. For systems with relatively low polarizabilities a parabolic fit of the field-dependent energies is usually sufficient for achieving high enough accuracy of the polarizability data. For highly polarizable atoms a quartic fit has been used to reduce the contamination by higher-order polarizabilities.

The calculations reported in this paper have been carried out using the MOLCAS system of quantum chemistry programs [42] with several other codes linked to it. The additional integrals needed for DK calculations and the routines for building the matrix of the DK-Fock Hamiltonian have been written by Hess [60]. The closed-shell CCSD(T) results follow from the TITAN code [61] linked to the MOLCAS system. The ROHF-CCSD(T) calculations have been carried out using the corresponding set of programs written by P. Neogrády [62] and installed by him within the MOLCAS system of programs.

3 A study of the performance of the NpPol basis sets: results and discussion

Among different properties of isolated atoms and ions, which may characterize their ability to undergo chemical reactions and elucidate the electronic structure of the resulting compounds, the polarizability, ionization potential (IP), and electron affinity (EA) are particularly important. The long-range interactions of neutral and ionized species are well characterized by dipole polarizabilities. At shorter ranges the possibility of the intermolecular charge transfer during the formation of the chemical bond can be interpreted in terms of IPs and EAs. The EA values of the group Ia and IIa atoms are in most cases so small that any reliable theoretical prediction would require more sophisticated treatment than that used in this paper. Hence, the present study of the performance of the NpPol basis set will be limited to calculations of electric dipole polarizabilities and IPs.

Both polarizabilities and IPs are quite sensitive to details of the description of the electronic structure of the given system and for this reason provide a good probe for different approximations. In the present study they will be used to determine the level of flexibility of the generated NpPol sets. This will be carried out by comparing the corresponding results obtained with the final NpPol sets and with their fully uncontracted GTO counterparts (GTO-NpPol) at both SCF-HF and correlated levels of approximation.

The polarization of the valence shell of heavy atoms and ions is also quite sensitive of relativistic effects. These will be investigated at two different levels of approximation for basis sets. Once the contractions leading to either Pol or NpPol bases are performed, a direct comparison of the results obtained in non-relativistic and relativistic calculations and the estimation of the magnitude of the relativistic effect will depend on the way in which the basis set functions are contracted. Although such estimates of relativistic effects are frequently acceptable [63, 64] the right approach is to compare the non-relativistic and relativistic data calculated with the allowance made for complete flexibility of the given basis set, e.e. calculated with fully uncontracted sets of the same composition. For this reason a series of comparative non-relativistic calculations will be carried out with non-relativistic Pol sets and with their fully uncontracted counterparts (GTO-Pol).

The present results are obtained in the framework of the DK approximation for relativistic effects. This approximation is definitely more sophisticated than the simplest MVD approach [14, 15] used in our earlier investigations [35, 36]. The results of this study can be therefore used to validate our previous conclusions concerning the use of the MVD approximation in calculations of the valence-determined atomic and molecular properties [14, 15, 35, 36]. A comparison of the present DK and earlier MVD data will shed some light on the reliability of the MVD approximation in calculations of the valence properties of atoms and ions.

3.1 Dipole polarizabilities of atoms and atomic ions

The dipole polarizability results presented in this section are selected primarily for the purpose of illustrating the performance of the NpPol sets in comparison with their fully uncontracted GTO sets. However, the numerical material gathered in our calculations also offers the possibility of discussing different aspects of the methods used to calculate relativistic corrections of atomic and molecular properties and the magnitude of these effects. On the other hand, only marginal attention will be given to the comparison of the present data with experimental results and calculations by other authors. This subject has already been well covered in our earlier papers on quasirelativistic calculations of atomic dipole polarizabilities [3, 35, 36]. The present results will only be used to strengthen some arguments in favour of the MVD approximation for calculations of the relativistic contribution to valence-determined properties.

For the sake of completeness the NpPol basis sets are studied here for all atoms of groups Ia and IIa of the Periodic Table. However, the static (spin-independent) relativistic effects are essentially of no importance for polarizabilities of atoms of the first- and second-row, and quite negligible for the third-row atoms. Additionally, one should bear in mind that in most applications one would be interested primarily in the relativistic contribution to the energy changes induced by some other perturbation. Hence, only if the absolute relativistic correction to energies is large may one expect important relativistic contributions to the energy differences.

The calculated polarizability data for neutral atoms are collected in Tables 2 and 3. The corresponding results for ions resulting from the removal of the valence electrons are presented in Tables 4 and 5. These tables offer a comparison between the results obtained with fully uncontracted GTO sets and their GTO/CGTO counterparts (either Pol or NpPol sets) in both non-relativistic and relativistic DK calculations. The comparison is limited to the level of the SCF-HF and CCSD(T) approximations.

At the level of the SCF-HF approximation the contraction of the basis set leading to either Pol or NpPol sets has essentially a negligible effect on the calculated values of atomic polarizabilities of neutral atoms. It is obvious, however, that using exactly the same contracted sets in SCF calculations for positive ions must lead to some deterioration of their polarizabilities in comparison with the results obtained with fully uncontracted sets. As seen from Tables 4 and 5 this deterioration is quite large for Li^+ and Be^{2+} and rapidly diminishes with the increase of the number of atomic shells and the total number of available functions. Fortunately enough, the dipole polarizabilities of light singly positive ions of the group Ia metals and those of light doubly positive ions of the group IIa elements are very small. Their contribution to molecular polarizabilities of highly ionic molecules is therefore very small and insignificant; the total molecular polarizabilities are primarily due to the contribution of their negatively charged constituents [65].

The basis set contraction effects become more visible at the level of the CCSD(T) approximation since the magnitude of the electron correlation effects depends

Table 2. Dipole polarizabilities of the group Ia atoms. A study of the basis set contraction effects in non-relativistic (NR) and relativistic (DK) calculations at the restricted open-shell Hartree-Fock (ROHF) and ROHF-CCSD(T) levels of approximation. All values in a.u.

Atom	Method:	NR	DK	NR	DK
	Basis set:	GTO[a]	GTO[a]	Pol[b]	NpPol[c]
ROHF-SCF results					
Li		169.5	169.4	171.9	168.3
Na		190.5	189.5	191.0	189.0
K		416.7	409.2	416.1	409.1
Rb		524.2	484.8	523.7	484.3
Cs		806.8	670.6	806.1	670.1
Fr		964.0	541.9	964.0	544.0
ROHF-CCSD(T) results					
Li		163.8	163.8	171.8	168.4
Na		166.0	165.0	166.1	164.4
K		307.1	301.5	298.9	294.4
Rb		358.1	332.1	352.1	326.3
Cs		507.7	428.4	496.3	418.0
Fr		584.2	350.4	573.8	347.4

[a] Fully uncontracted GTO basis sets. These are the same for both Pol and NpPol sets. See text for details and references

[b] Non-relativistic polarized GTO/CGTO basis sets

[c] Relativistic polarized GTO/CGTO basis sets derived in this study

Table 3. Dipole polarizabilities of the group IIa atoms. A study of the basis set contraction effects in non-relativistic (NR) and relativistic (DK) calculations at the restricted Hartree-Fock (RHF) and RHF-CCSD(T) levels of approximation. All values in a.u.

Atom	Method:	NR	DK	NR	DK
	Basis set:	GTO[a]	GTO[a]	Pol[b]	NpPol[c]
RHF-SCF results					
Be		44.90	44.87	44.53	44.28
Mg		81.70	81.26	81.74	81.23
Ca		185.2	182.6	185.2	182.6
Sr		245.6	232.2	245.5	232.2
Ba		366.4	323.0	366.4	323.0
RHF-CCSD(T) results					
Be		37.28	37.26	37.34	37.13
Mg		71.37	71.02	72.21	71.78
Ca		155.9	153.8	150.5	148.3
Sr		206.9	195.6	199.6	188.8
Ba		312.2	273.4	302.0	265.5

[a,b,c] See the corresponding footnotes to Table 2

Table 4. Dipole polarizabilities of the singly positive ions of the group Ia atoms. A study of the basis set contraction effects in non-relativistic (NR) and relativistic (DK) calculations at the RHF and RHF-CCSD(T) levels of approximation. All values in a.u.

Atom	Method:	NR	DK	NR	DK
	Basis set:	GTO[a]	GTO[a]	Pol[b]	NpPol[c]
RHF-SCF results					
Li^+		0.188	0.188	0.057	0.058
Na^+		0.908	0.909	0.789	0.790
K^+		5.14	5.14	5.04	4.95
Rb^+		8.95	8.87	8.36	8.29
Cs^+		16.03	15.63	15.30	14.93
Fr^+		20.89	19.43	20.46	19.01
RHF-CCSD(T) results					
Li^+		0.191	0.191	0.060	0.061
Na^+		0.969	0.969	0.828	0.829
K^+		5.21	5.21	5.17	5.05
Rb^+		8.97	8.91	8.38	8.32
Cs^+		16.03	15.68	15.29	14.98
Fr^+		20.91	19.62	20.48	19.19

[a,b,c] See the corresponding footnotes to Table 2

Table 5. Dipole polarizabilities of the singly and doubly positive ions of the group IIa atoms. A study of the basis set contraction effect in non-relativistic (NR) and relativistic (DK) calculations at the RHF-ROHF and RHF-ROHF-CCSD(T) levels of approximation. All values in a.u.

Atom	Method:	NR	DK	NR	DK
	Basis set:	GTO[a]	GTO[a]	Pol[b]	NpPol[c]
Singly positive ions: ROHF-SCF results					
Be^+		24.71	24.68	24.30	24.10
Mg^+		38.91	38.61	38.88	38.56
Ca^+		98.27	96.15	98.17	96.08
Sr^+		131.6	121.0	131.5	121.0
Ba^+		211.6	173.9	211.4	173.7
Singly positive ions: ROHF-CCSD(T) results					
Be^+		24.20	24.18	24.31	24.12
Mg^+		35.65	35.39	35.61	35.32
Ca^+		79.35	77.74	77.32	75.71
Sr^+		101.4	94.11	98.69	91.58
Ba^+		152.6	129.6	149.1	126.2
Doubly positive ions: RHF-SCF results					
Be^{2+}		0.051	0.051	0.012	0.012
Mg^{2+}		0.456	0.456	0.415	0.415
Ca^{2+}		3.08	3.07	3.06	3.01
Sr^{2+}		5.84	5.76	5.61	5.53
Ba^{2+}		10.78	10.42	10.38	10.02
Doubly positive ions: RHF-CCSD(T) results					
Be^{2+}		0.052	0.052	0.012	0.012
Mg^{2+}		0.474	0.474	0.427	0.427
Ca^{2+}		3.09	3.08	3.11	3.05
Sr^{2+}		5.80	5.73	5.59	5.52
Ba^{2+}		10.68	10.36	10.30	9.97

[a,b,c] See the corresponding footnotes to Table 2

considerably on the number and shape of the available (virtual) orbitals. However, the basis set contraction effect is still relatively small as compared to the magnitude of the final atomic polarizabilities and is very similar for both non-relativistic and relativistic DK results. It should be stressed that the NpPol sets generated in this study are designed for relativistic calculations of molecular electric properties rather than for the most accurate determination of the corresponding atomic data. Hence, some deterioration of atomic properties on passing from GTO to Pol and NpPol sets is by no means disturbing.

The data of Tables 2–5 provide important information about the magnitude of the relativistic effect on atomic and ionic polarizabilities. This can be estimated as a difference between relativistic and non-relativistic results at the given level of the treatment of the electron correlation. One should stress, however, that a judicious evaluation of the magnitude of the relativistic contribution to dipole polarizabilities can only be made in calculations with fully uncontracted sets, optimized independently at the non-relativistic and relativistic (DK) levels of approximation. It is quite remarkable that the relativistic theory predicts caesium rather than francium to be the most polarizable alkali metal atom (see Table 2). The dipole polarizability of francium as calculated within the CCSD(T) DK scheme turns out to be considerably lower than the corresponding value for caesium.

The unconstrained basis set optimization carried out with the DK Hamiltonian [32, 66] leads to very high exponent values, in particular for the *s*-type GTOs. These may obviously be important in calculations of total energies but should not considerably affect the valence properties. Thus, as long as the generated basis sets are designed for calculations of the valence-determined properties, using the same parent GTO basis set for both Pol and NpPol sets, a reasonable approximation can be made. The effect of replacing the non-relativistic core Hamiltonian by its DK counterpart is then approximately accounted for by the change in contraction coefficients. Because of this approximation a direct comparison of the non-relativistic data for Pol sets with the DK results for NpPol sets can lead to rather misleading conclusions concerning the value of very small relativistic contributions (e.g. for Li, Be). In such cases the absolute error due to incomplete basis set optimization may be larger than the total of the relativistic effect on the calculated polarizability. For heavier atoms such a comparison becomes, however, quite meaningful since the absolute value of the relativistic correction becomes much larger than the above-mentioned inaccuracies.

For heavier atoms of the present series the relativistic and correlation-relativistic effect on dipole polarizabilities has been calculated earlier by using the MVD approximation [14, 15, 35, 36] which accounts only for relativistic contributions of the first order in the square of the fine structure constant. A comparison of earlier MVD data with the present DK results is presented in Table 6. These data are accompained by a survey of different experimental values for atomic dipole polarizabilities. This comparison with experimental results is solely for the purpose of documenting the reliability of the NpPol bases developed in this paper.

The best validated is the mutual comparison of the SCF results calculated in MVD and DK approximations. As shown by the SCF data of Table 6 the results of both approximations do not differ significantly. Even in the case of atoms as heavy as Cs, Ba, and Fr, the performance of the simple first-order perturbation (MVD) treatment of the relativistic contribution to their dipole polarizabilities is excellent. One needs to take into account that at the level of the SCF-HF approximation the MVD approach [14] amounts to the evaluation of the electric-field derivatives of the expectation value of the MVD operator. This expectation value is determined by using non-relativistic SCF eigenvectors obtained in calculations with Pol basis sets. The SCF-HF-DK results combine the effect of the basis set change, i.e. the use of the relativistic NpPol basis set, and that resulting from the direct presence (through infinite order in the fine structure constant) of relativistic terms in the DK Hamiltonian. Thus, the present SCF-HF results lend additional support to our earlier claims concerning the validity of the MVD approximation in calculations of the relativistic contribution to valence-determined atomic and molecular properties [14, 15, 35, 36].

Table 6. Dipole polarizabilities of selected heavier atoms of groups Ia and IIa as calculated in the quasirelativistic mass-velocity-Darwin (MVD) and relativistic DK approximation at the SCF and correlated levels of approximation and their comparison with experimental data. All values in a.u.

Atom	SCF		Correlated		Experimental
	NR + MVD[a]	DK[b]	NR + MVD[c]	DK[d]	
Group Ia atoms					
K	408.3	409.1	295.5	294.4	292.9 ± 6.1 [74], 305.0 ± 21.6 [75]
Rb	487.4	484.3	333.6 (330.2)	326.3	319.2 ± 6.1 [74], 328.7 ± 22.9 [75]
Cs	674.0	670.1	422.6 (413.6)	418.0	402.2 ± 8.1 [74], 427.2 ± 31.0 [75]
Fr	548.7	544.0	350.3 (325.7)	347.4	
Group IIa atoms					
Ca	182.5	182.6	145.3 (152)	148.2	167 ± 17 [76], 154 [77], 155.9 [78]
Sr	232.4	232.2	186.4 (190)	188.8	186 ± 15 [79], 192 [77]
Ba	323.3	323.0	261.4 (273)	265.4	268 ± 22 [79], 242 [77]

[a] Non-relativistic calculations with polarized (Pol) basis sets and relativistic effects estimated from the MVD correction to SCF energies [14, 36, 35]

[b] SCF-DK calculations with NpPol basis sets of this paper

[c] Correlated level calculations in the MVD approximation using different methods and Pol basis sets The results for the group Ia metals have been obtained within the CASSCF + CASPT2 approximations [36]. Those for the group IIa atoms follow from the use of the CCSDT-1a (Ca, Sr) and CCSD + T(CCSD) (Ba) methods. The numbers in parentheses correspond either to calculations with Pol basis sets augmented by the *f*-type polarization functions (group Ia [36]) or to estimates obtained from extended basis sets (group IIa [35]).

[d] CCSD(T)-DK calculations with NpPol basis sets of this paper

The reference correlated MVD results of Table 6, i.e those including the direct MVD contribution and its effect on the electron correlation to dipole polarizabilities, have been obtained by a variety of different methods for the calculation of the electron correlation effect [35, 36]. Thus, the differences between the correlated MVD and CCSD(T)-DK values may also to some extent arise from the incomplete compatibility of the methods used for the study of the electron correlation and correlation-relativistic contributions. With the allowance made for this source of differences one can conclude that the previous correlated MVD data are in excellent agreement with the present CCSD(T)-DK results; the differences are at most of the order of magnitude of the uncertainty which follows from the basis set contractions.

The reference correlated results of Table 6 include also some data obtained with extended basis sets and including the electron correlation contributions from deeper-than-valence and next-to-valence electronic shells [35, 36]. Both of them have certain effect upon the accuracy of the calculated atomic polarizabilities which increases with the value of the nuclear charge. In the case of Fr correlating the $5d^{10}$ shell, accompanied by the basis set extension by the appropriate *f*-type polarization functions, lowers its polarizability by 25 a.u. [36]. However, with the NpPol sets designed for routine relativistic calculations of molecular electric properties their further extension by, e.g. *f*-type polarization functions and combined with correlating the *d*-shells is not recommended. It would lead to prohibitively large molecular basis sets with only a small gain in accuracy of the determined molecular properties. Calculations of electric dipole moments and polarizabilities of the alkali metal fluorides [67] show that such extensions have a rather negligible effect.

The present DK results are compared in Table 6 with several experimental data. Because of the closeness of the DK and MVD results this comparison brings about essentially the same conclusions as presented in our earlier papers [35, 36]. Our CCSD(T)-DK values are in the range of those obtained in experimental studies, although the accuracy of the experimental data is usually rather low. The present results, in spite of some limitations imposed on the size and flexibility of the NpPol sets, also appear to be superior to most of the other theoretical data which have been comprehensively reviewed in Refs. [35, 36]. In particular, the SCF-HF-DK value of the dipole polarizability of Cs confirms our earlier conclusions concerning the accuracy of the approximate Dirac-Hartree-Fock (DHF) result of Desclaux et al. [68]. For the reasons discussed in Ref. [36] the DHF value of the dipole polarizability of Cs appears to be about 40–50 a.u. too low.

The dipole polarizability results for the group Ia and IIa atoms discussed in this section show that the (relativistic) NpPol basis sets derived in this study are sufficiently flexible to account for the mutual polarization effect occurring upon the formation of either covalent or ionic bonds. The comparison of the present data with earlier calculations with more extended basis sets and more extensive treatment of the electron correlation effects [35, 36] shows that a further extension of the NpPol sets is rather impractical for the purpose of routine calculations of molecular electric properties. It is quite obvious that the error of a few percent in predicting dipole polarizabilities of free atoms may only insignificantly change the polarization pattern in their compounds.

3.2 Ionization potentials

Most compounds formed by the alkali and alkaline earth metals are highly ionic and therefore the basis sets used in relativistic molecular calculations must properly account for the possibility of the intermolecular charge transfer. This feature is well represented by the atomic IPs. The calculated valence IPs of atoms studied in this paper are presented in Tables 7 and 8.

Table 7 summarizes the computed values of the first IP of the group Ia atoms as obtained in non-relativistic SCF, SCF-DK, non-relativistic CCSD(T), and CCSD(T)-DK calculations with Pol and NpPol basis sets, respectively. The calculated values are also compared with experimental data [69]. A similar survey of the first and second IP data for the group IIa atoms is given in Table 8. For all atoms and all levels of ionization considered in this study the basis set contraction effects in both non-relativistic and relativistic DK calculations are essentially negligible. Thus, the magnitude of the relativistic effect can be quite reliably estimated from the difference between DK and non-relativistic results calculated with the respective contracted sets.

Table 7. The first ionization potential of the group Ia atoms. A study of the basis set contraction effects in non-relativistic (NR) and relativistic (DK) calculations at the RHF and RHF-CCSD(T) levels of approximation and comparison with experimental data. All values in eV

Atom	Method:	NR	DK	NR	DK	Experimental[a]
	Basis set:	GTO[b]	GTO[b]	Pol[c]	NpPol[d]	
RHF/ROHF-SCF results						
Li		5.34	5.34	5.32	5.34	
Na		4.95	4.95	4.94	4.95	
K		4.00	4.02	4.01	4.02	
Rb		3.74	3.80	3.74	3.80	
Cs		3.36	3.47	3.36	3.47	
Fr		3.20	3.56	3.20	3.56	
RHF/ROHF-CCSD(T) results						
Li		5.39	5.39	5.32	5.34	5.392
Na		5.11	5.12	5.10	5.11	5.139
K		4.27	4.28	4.27	4.29	4.341
Rb		4.04	4.11	4.03	4.10	4.177
Cs		3.66	3.80	3.66	3.80	3.894
Fr		3.51	3.92	3.51	3.92	

[a] Taken from Ref. [69]

[b] Fully uncontracted GTO basis sets. These are the same for both Pol and NpPol sets. See text for details and references

[c] Non-relativistic polarized GTO/CGTO basis sets

[d] Relativistic polarized GTO/CGTO basis sets derived in this study

Table 8. The first and second ionization potentials of the group IIa atoms. A study of the basis set contraction effects in non-relativistic (NR) and relativistic (DK) calculations at the RHF and RHF CCSD(T) levels of approximation and comparison with experimental data. All values in eV

Atom	Method:	NR	DK	NR	DK	Experimental[a]
	Basis set:	GTO[b]	GTO[b]	Pol[c]	NpPol[d]	
The first ionization potential:						
RHF/ROHF-SCF results						
Be		8.05	8.05	8.03	8.05	
Mg		6.61	6.62	6.61	6.62	
Ca		5.12	5.14	5.12	5.14	
Sr		4.68	4.75	4.68	4.75	
Ba		4.14	4.29	4.14	4.29	
RHF/ROHF-CCSD(T) results						
Be		9.28	9.28	9.19	9.21	9.322
Mg		7.60	7.61	7.57	7.58	7.646
Ca		6.00	6.02	5.97	5.99	6.113
Sr		5.52	5.59	5.47	5.54	5.695
Ba		4.93	5.06	4.88	5.01	5.212
The second ionization potential:						
RHF/ROHF-SCF results						
Be		18.12	18.12	18.10	18.12	
Mg		14.72	14.74	14.72	14.74	
Ca		11.31	11.35	11.31	11.35	
Sr		10.29	10.44	10.29	10.44	
Ba		9.07	9.36	9.07	9.36	
RHF/ROHF-CCSD(T) results						
Be		18.19	18.19	18.10	18.12	18.211
Mg		14.97	14.99	14.94	14.97	15.035
Ca		11.72	11.77	11.72	11.77	11.871
Sr		10.74	10.90	10.74	10.90	11.030
Ba		9.52	9.83	9.51	9.82	10.004

[a,b,c,d] See the corresponding footnotes to Table 7

A comparison of the present CCSD(T)-DK data with the experimental values shows that the total effect of inaccuracies introduced by the basis set truncation, incomplete treatment of the electron correlation effect (e.g. neglecting the electron correlation contribution due to deeper-than-valence and next-to-valence shells), and the approximate treatment of the relativistic contribution, in the worst cases amounts to about 0.2 eV. The calculated IPs are systematically lower than the observed ones. However, in view of molecular applications of the generated NpPol sets these discrepancies are rather irrelevant.

In comparison with very large relativistic contributions to atomic dipole polarizabilities the effect of relativity on IPs of the group Ia and IIa atoms is rather small. The magnitude of the relativistic effect on the IP of the group Ia and IIa atoms is also much smaller than that for atoms of group Ib [70, 71]. The pattern of these effects which follows from our data agrees with general ideas [40] concerning the trends in relativistic contributions to the ionization energy for the *ns* valence shells. The non-relativistic theory predicts that among the group Ia metals Fr should have the lowest IP of about 3.51 eV. The nuclear charge dependence of the relativistic contribution to the ionization energy causes the IP values to reach their minimum for Cs. This pattern of relativistic contributions to IPs parallels that observed for dipole polarizabilities. The relativistic theory predicts Cs to be the most polarizable atom among alkali metals and to have the lowest IP (see Tables 2 and 7).

The largest value of the relativistic correction to IPs is calculated for Fr (ca. 0.4 eV) while for Cs and Ba this correction amounts to only about 0.15 eV. Thus, the electronegativity of the heavy elements of groups Ia and IIa is not significantly affected by their "relativistic character". From the point of view of the basis set quality the results of this section show that the NpPol basis sets should properly reflect the electronegativity differences among alkali metal and alkaline earth atoms and, thus, should lead to a reliable description of the charge distribution and polarity of molecules.

4 Summary and conclusions

In this study we have generated the first-order polarized basis sets for atoms of groups Ia and IIa of the Periodic Table. These so-called NpPol basis sets are specifically devised for relativistic calculations within the DK approximation. Their performance has been tested in calculations of atomic dipole polarizabilities and IPs.

It has been shown that the contraction of the parent GTO sets leading to the NpPol basis sets has a relatively small effect on the properties studied in this paper. Most attention has been given to the performance of the NpPol bases in calculations of atomic dipole polarizabilities. The present results calculated at the level of the CCSD(T)-DK approximation agree with the available experimental data. This agreement shows that in spite of neglecting certain electron correlation contributions and truncating the basis sets one can expect quite high accuracy in calculations of molecular electric properties.

A comparison of the present DK polarizability values with our earlier MVD results confirms that the MVD approximation can be quite safely used to obtain reliable values of the relativistic contribution to atomic and molecular properties whose values are dominated by the valence-shell polarization.

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