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Medium-size polarized basis sets for high-level-correlated calculations of molecular electric properties

IV. Third-row atoms: Ge through Br

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Summary. The basis set polarization method is used to derive the first-order polarized basis sets for Ge through Br for calculations of atomic and molecular electric properties. The performance of the [15.12.9/9.7.4] GTO/CGTO basis sets generated in this study is verified in calculations of atomic dipole polarizabilities and dipole moments and polarizabilities of the third-row atom hydrides. Whenever accurate reference data are available for comparison, the excellent performance of the derived first-order polarized basis sets is demonstrated. The role of the core polarization and relativistic contributions to atomic and molecular is also investigated. The detailed basis set data for Ge through Br are given in Appendix.

Key words: Polarized basis sets – Molecular electric properties – Atomic polarizabilities of Ge, As, Se, and Br – Dipole moments and polarizabilities of the third-row atom hydrides – Basis set polarization approach – Core polarization effects for the third-row elements – Relativistic effects for the third-row elements

1. Introduction

The recent developments in the generation and standardization of Gaussian basis sets for molecular calculations show two major trends. One of them is the generation of (large) high-quality Gaussian-type/contracted Gaussian-type (GTO/CGTO) basis sets of very wide applicability for accurate studies of atoms and molecules at both the self-consistent field Hartree–Fock (SCF HF) and correlated levels of approximation [1–3]. Another direction in the basis set standardization has a more pragmatic character and favours relatively small purpose-oriented GTO/CGTO basis sets [4, 5]; in most cases the main purpose being the calculation of molecular geometries and related parameters [5].

It is commonly appreciated that the electric properties of atoms and molecules, i.e., their multipole moments and polarizabilities [6], play an important role in different areas of chemistry and molecular physics. Their accurate prediction has long been one of the major goals of quantum chemical calculations. However, even in the case of molecular dipole moments the performance of small standardized basis sets is usually very poor [5]. Following the pioneering studies of Werner and Meyer [7] one usually expects that accurate predictions of atomic and molecular electric properties will require the use of large, highly diffuse and flexible basis sets [7–9], whose size easily poses insurmountable computational problems and significantly limits the range of possible applications. An intermediate solution for the basis set standardization in calculations of basic electric properties of atoms and molecules has been recently pursued by the present author [10, 11].

The basis set standardization for calculations of atomic and molecular electric properties follows from the ideas of what is known as the basis set polarization method [12]. Once some reasonably good (usually rather small and energy-oriented) GTO/CGTO basis set is known, e.g., a double-zeta GTO/CGTO set, the corresponding polarized basis set of a predetermined size is almost automatically generated from the known orbital exponents and atomic SCF HF eigenvectors [10, 11]. This method does not involve any additional optimization of the basis set parameters; the analytic form of the polarization functions follows immediately from the recognition of the possible electric-field-dependence of Gaussian functions in the initial basis set [13, 14]. Moreover, it has been found [10, 11] that, for the purpose of accurate calculations of dipole moments and dipole polarizabilities, only the first-order electric-field-dependence of the initial basis set needs to be taken into account; the resulting GTO/CGTO basis sets being termed the first-order polarized sets. Several simple rules for their generation have been devised and used to derive relatively small (medium-size) polarized GTO/CGTO basis sets for H ([6.4/3.2]), C through F ([10.6.4/5.3.2]) [10, 11], Si through Cl ([13.10.4/7.5.2]) [11], and alkali (Li, Na, K, Rb) and alkaline-earth (Be, Mg, Ca, Sr) metals [15]. The performance of these medium-size polarized basis sets has been carefully checked in calculations of atomic and molecular electric properties in SCF HF and different correlated approximations. The first-order polarized basis sets for the first-row atoms have also been found to perform exceptionally well in calculations of molecular quadrupole moments [16]. The previous experience indicates that the generation of medium-size polarized basis sets for calculations of atomic and molecular electric properties is worth pursuing.

In the present paper the basis set polarization method is used to derive the first-order polarized GTO/CGTO basis sets for the third-row atoms: Ge through Br. The main principles of the method are the same as those devised in our earlier studies [10, 11, 15]. Some technical differences, which are described in the next section, reflect certain features of the initial GTO sets [17]. The derived polarized basis sets of the form [15.12.9/9.7.4] are examined in calculations of atomic dipole polarizabilities and molecular dipole moments and polarizabilities. The corresponding data for Ge, As, Se, Br, and GeH_4, AsH_3, SeH_2, and HBr are presented in Sect. 3. The conclusions of this study are given in Sect. 4. The basis set data are given in detail in Tables A–D of the Appendix.

2. The generation of the first-order polarized basis sets for the third-row atoms

The principles of the method employed in this study for the generation of the first-order polarized basis sets from the given GTO/CGTO atomic sets are comprehensively described in the earlier papers [10, 11] of this series. They follow from the ideas of the basis set polarization method [12, 18] supplemented by certain 'empirical' rules [10, 11, 15].

The overall quality of the resulting polarized basis set is to some extent predefined by the choice of the initial GTO/CGTO basis set. The polarized basis sets for the first-row atoms [10] were generated from the double-zeta contractions of (9*s*5*p*) GTO sets of van Duijneveldt [19]. The generation of similar basis sets for the second-row atoms [11] was greatly facilitated by the availability of the optimized double-zeta contractions [20] of (12*s*9*p*) GTO sets of Huzinaga [12]. Since no contractions of a similar quality seem to be available for the third-row atoms the approach employed in this paper differs slightly from the previous ones.

The initial primitive GTO basis sets for Ge through Br of the size (14*s*11*p*5*d*) have been taken from Huzinaga's compilation [17]. Their quality is similar to that of the (9*s*5*p*) and (12*s*9*p*) GTO sets employed for the first- and second-row atoms, respectively. To avoid the optimization of the contractions to the anticipated double-zeta size, i.e. [14.11.5/8.6.2], we employed the Raffenetti contraction scheme [22] to the first ten highest exponent *s*-type GTO's. This leads to 4 CGTO's: the contraction coefficients being taken directly from the SCF HF eigenvectors for 1*s*, 2*s*, 3*s*, and 4*s* AO's. In a similar way the first eight highest-exponent *p*-type GTO's have been contracted to 3 *p*-type CGTO's. In the *d* subset a segmented contraction of 5 *d*-type GTO's to the corresponding two $(3+2)$ CGTO's has been employed following the ideas of the double-zeta contraction scheme. The resulting [14.11.5/8.6.2] GTO/CGTO sets are virtually uncontracted in the valence part as required by the rules of the basis set polarization method [10, 11]. They constitute the initial GTO/CGTO atomic basis sets used for the generation of the corresponding first-order polarized sets.

According to the rules developed in our previous studies [10, 11], the initial sets are first augmented by one diffuse *s* GTO and one diffuse *p* GTO with their orbital exponents determined from approximate geometric progressions in the corresponding subsets. The resulting [15.12.5/9.7.2] sets are then used to determine the SCF HF eigenvectors for negative ions of all atoms under consideration. The basis set polarization method is then applied to the valence 4*p* SCF AO with the assumption that the *d*-type first-order polarization functions are represented by two CGTO's based on 4 primitive *d*-type GTO's whose orbital exponents match the maxima of the 4*p* AO in the given negative ion. The origins of this procedure are explained and documented in earlier papers of this series [10, 11] and belong to the set of pragmatic rules for the generation of the first-order polarized basis sets.

The procedure employed in this study finally gives the [15.12.9/9.7.4] GTO/CGTO first-order polarized basis sets for Ge through Br which are listed in the Appendix. Previous experience has suggested that no additional polarization functions are needed for the initial *s*-type AO's; the initial *p*-subset is good enough for that purpose. To account for the polarization of the 3*d* shell one would need to consider the *f*-type first-order polarization functions. However, the numerical experiments described in the next section show that their effect on the calculated dipole moments and polarizabilities is virtually negligible.

The polarized basis sets derived in this study will be referred to as the medium-size (first-order) polarized sets. Their performance with respect to the calculation of other than electric properties of atoms and molecules should reflect that of the initial GTO/CGTO sets derived from Huzinaga's Tables [17]. The size of the present [15.12.9/9.7.4] basis set amounts to 54 (50 after deleting the *s*-components of the *d*-type CGTO's) CGTO's per third-row atom. Such basis sets are easily manageable in calculations for fairly sizeable molecules. According to our previous results for the first- and second-row atoms and the similarity of the valence-shell structure of atoms considered in this paper one can expect the performance of basis sets derived in the present study to be at least satisfactory. This gives a chance for low-cost and reasonably accurate predictions of basic electric properties for molecules involving the third-row atoms. Some illustration of this point will be presented in the next section.

3. Calculations of atomic and molecular electric properties

3.1. Computational details

The computational methods employed in this study are principally the same as those used and described in the earlier papers of this series [10, 11, 15]. All calculations have been carried out by using the MOLCAS system of quantum chemistry programs [23–26].

The examination of the performance of the first-order polarized basis sets has been carried out in two steps. First, we have performed a series of open-shell restricted Hartree–Fock (RHF) calculations of atomic dipole polarizabilities with the dipole polarizabilities being derived as the numerical first-order derivatives of the external-field-induced dipole moments and verified against the second-order derivatives of the field-dependent RHF energies. Those data are used to obtain a preliminary qualification of the derived basis sets and have been followed by molecular calculations for the third-row atom hydrides.

The molecular calculations for GeH_4, AsH_3, H_2Se, and HBr have been carried out at both the SCF HF and different correlated levels of approximation. The electron correlation contribution to dipole moments and polarizabilities has been calculated by using the many-body perturbation theory (MBPT) method [25, 27]. In order to analyse the convergence of the electron correlation perturbation series for dipole moments and polarizabilities of the third-row hydrides, the results of different MBPT approximations have been investigated. Those data are used to draw conclusions about the performance of the first-order polarized sets at different correlated levels of approximation.

The SCF HF and MBPT results for molecular dipole moments are obtained by using the finite-field perturbation approach. An external electric field strength of 0.002 a.u. was found appropriate to achieve the numerical accuracy which corresponds to the stability of the last decimal of all data tabulated in this section. At the level of SCF HF approximation the numerical stability of the dipole moment and polarizability results obtained from the energy derivatives has been cross-examined against the results of the Hellmann–Feynman theorem.

In both atomic and molecular calculations the s components of the d-type CGTO's and the p components of the f-type CGTO's have been removed from the basis set. The first-order [6.4/3.2] GTO/CGTO basis sets of hydrogen employed in the hydride calculations is the same as described in Part I of this series [10]. Its high performance in atomic and molecular calculations of electric properties is already well established [10, 11, 15].

3.2. Atomic dipole polarizabilities for Ge *through* Br

The most important verification of the performance of the first-order polarized basis sets follows from calculations of atomic electric properties [10, 11]. A basis set which performs reasonably well in calculations of atomic dipole polarizabilities should certainly give fairly accurate data for low-multipole low-order molecular electric properties.

When verifying the first-order polarized basis sets for the first- and second-row atoms [10, 11] the calculated dipole polarizability data could have been compared with a variety of accurate results of other authors. There seem to be no such data available for the third-row atoms. The values computed long ago by Thorhallsson et al. [28] follow from the Kirkwood–Pople–Schofield method [29]. By analysing the corresponding results for the second-row atoms one can conclude that the Kirkwood–Pople–Schofield scheme tends to overestimate the accurate RHF data by about 20% [11, 28–30]. The source of the recommended values of polarizabilities for Ge through Br in the review article of Miller and Bederson [32] appears to be undefined (see footnote e of Table 1).

Since no reliable reference values of atomic dipole polarizabilities are available for the third-row atoms, we have chosen to carry out an internal cross-examination of our data calculated with the [15.12.9/9.7.4] GTO/CGTO basis sets (as given in the Appendix) with the results computed with the corresponding completely uncontracted GTO sets. The results of those calculations are presented in Table 1. The differences between the dipole polarizabilities calculated with the two basis sets are virtually negligible, and thus, give a clear confirmation of the

Table 1. SCF RHF calculations of atomic dipole polarizabilities for Ge through Br using different Gaussian basis sets. All values in a.u. (1 a.u. of dipole polarizability $\simeq 0.14818$ Å^3)

Atom		This work				[31][e]
		A[a]	B[b]	C[c]	D[d]	
Ge	^3P, $M_L = 0$	34.00	34.26	34.09	34.34	
	$M_L = \pm 1$	45.05	45.27	45.07	45.30	
	Average[f]	41.37	41.60	41.41	41.65	42.90
As	^4S	30.23	30.40	30.27	30.43	30.46
Se	^3P, $M_L = 0$	28.42	28.52	28.44	28.48	
	$M_L = \pm 1$	23.56	23.65	23.57	23.61	
	Average	25.18	25.27	25.19	25.23	26.65
Br	^2P, $M_L = 0$	18.56	18.62	18.56	18.60	
	$M_L = \pm 1$	21.08	21.16	21.11	21.15	
	Average	20.24	20.31	20.26	20.30	21.55

[a] First-order polarized [15.12.9/9.7.4] GTO/CGTO basis set of this paper

[b] Completely decontracted first-order polarized (*spd*) basis set: (15.12.9)

[c] First-order GTO/CGTO polarized basis set augmented with the *f*-type polarization CGTO's: [15.12.9.4/9.7.4.2]. See text for details

[d] Completely decontracted (*spdf*) polarized basis set: (15.12.9.4)

[e] The origin set of those recommended values tabulated in [31] is uncertain. Though they are claimed to follow from calculations by Meyer et al. [7, 30], no such data seem to have seen computed by these authors. It appears that the recommended values of Miller and Bederson correspond to the scaled results of the Kirkwood–Pople–Schofield approximation [28, 29]. If so, they should approximate the corresponding accurate SCF RHF data relatively well

[f] Rotational average: $\frac{1}{3}[\alpha(M_L = 0) + 2\alpha(M_L = \pm 1)]$, where α denotes the dipole polarizability

appropriateness of the first-order polarized basis sets of this paper. In principle this could have been expected on the basis of our previous tests for the first- and second-row atoms. The method used to derive the first-order polarized basis sets for Ge through Br is principally the same as that employed for the other atoms and the quality of the basis sets is expected to be similar.

The comparison of the polarizability data obtained with the [15.12.9/9.7.4] basis sets (column A of Table 1) with those calculated by using the completely uncontracted (15.12.9) GTO sets also shows that the polarization of 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* atomic shells is either negligible or well accounted for within the present contracted basis set approximation. The completely uncontracted basis sets include a wide enough range of orbital exponents in the *p*- and *d*-subsets to provide the polarization functions for those shells. What remains to be investigated is the possible contribution to the atomic dipole polarizabilities from the polarization of the 3*d* shell.

In order to study the 3*d* shell contribution to atomic dipole polarizability of Ge through Br the [15.12.9/9.7.4] polarized sets have been augmented with two *f*-type polarization CGTO's generated from four *f*-type GTO's using the basis set polarization method [10–12] applied, this time, to 3*d* AO's. The GTO exponents and contraction coefficients for those *f*-type polarization functions are listed in Table 2. Adding the *f*-type polarization CGTO's to the initial (*spd*) first-order polarized basis sets results in extended (*spdf*) GTO/CGTO sets of the form [15.12.9.4/9.7.4.2]. The dipole polarizability results calculated with those extended basis sets are given in column C of Table 1.

Finally, to avoid the possible uncertainties resulting from the contraction of the primitive GTO sets, we carried out the dipole polarizability calculations in completely uncontracted (*spdf*) (15.12.9.4) GTO basis sets. The results of those calculations are listed in column D of Table 1. A mutual comparison of different computed polarizability values shows that the performance of the [15.12.9/9.7.4] first-order polarized basis sets is almost as good as that of fully uncontracted (*spdf*) sets. Hence, there seems to be no need to augment the contracted sets with additional *f*-type polarization GTO's.

There is one more factor whose relevance for calculations of electric properties of the third row atoms and their compounds needs to be investigated, namely the contribution of relativistic effects. In comparison with the first- and second-row atoms, the nuclear charge of the third-row atoms is large enough that the relativistic contribution to basic electric properties may not be negligible [32]. The relativistic effect on the dipole polarizability of the third-row atoms has been

Table 2. The *f*-type polarization functions for the third-row atoms derived according to the basis set polarization method applied to 3*d* AO's

GTO	CGTO	Ge		As		Se		Br	
		α_i[a]	c_i[b]	α_i	c_i	α_i	c_i	α_i	c_i
1	1	19.3564	0.03766	20.8895	0.03751	22.5360	0.03700	27.8391	0.02844
2		6.60001	0.16123	7.21765	0.14953	7.88759	0.14444	9.85107	0.12123
3	2	2.28841	0.31091	2.56930	0.29045	2.86378	0.27334	3.61019	0.25277
4		0.74115	0.29311	0.86394	0.25202	0.99035	0.21968	1.25154	0.22158

[a] GTO orbital exponents. [b] Contraction coefficients.

investigated in this paper using the recently developed quasirelativistic approach [33]. The estimated relativistic contribution to the dipole polarizabilities of Ge through Br has been found to be of the order of at most 2% of the computed RHF polarizabilities: the spin-orbit interaction effects being neglected [33]. This gives an order of magnitude estimate of the relativistic contribution to molecular dipole moments for systems involving the third-row atoms. It is clear that among the different corrections to the non-relativistic RHF molecular dipole moments (and/or dipole polarizabilities) the electron correlation contribution is definitely dominant.

3.3. Molecular dipole moments and polarizabilities: GeH_4, AsH_3, H_2Se, HBr

The simple hydrides of the third-row atoms supply a very useful set of test molecules for the investigation of the performance of the first-order polarized basis sets devised in this paper. Reliable experimental data and several accurate theoretical values of dipole moments for polar hydrides are available and can be used to verify the assumptions of this work. The reference dipole polarizability data are rather scarce and seem to be known only for the HBr molecule. This will to some extent limit the generality of our conclusions. On the other hand, the previous results for the first- and second-row atom hydrides [10, 11] give indirect support to the high accuracy claimed for the present polarizability data and make our conclusions more general than they would be solely on the basis of the available reference values.

All molecular calculations have been carried out for the experimental equilibrium geometries taken from [34]. The dipole moments and polarizabilities have been calculated in the SCF HF and MBPT approximations according to the computational scheme outlined in Sect. 3.1. The MBPT study of the electron correlation contribution to molecular electric properties has been completely carried through to fourth-order with respect to the electron correlation perturbation [25, 27, 35]. The use of the numerical finite-field approach gives directly what is known as the pure electron correlation corrections to the corresponding SCF HF property values [36, 37]; all self-consistency effects are automatically accounted for at the level of the SCF HF approximation [36].

The calculated dipole moment data for AsH_3, H_2Se, and HBr are presented in Table 3 and comprise the results of the SCF HF approximation and the second- (MBPT(2)), third- (MBPT(3)), and complete fourth-order (MBPT(4)) perturbation methods [25, 27, 35]. We have also included the approximate SDQ-MBPT(4) data [25, 35] whose comparison with the MBPT(4) results gives useful information concerning the importance of triply excited intermediate states and helps to assess the reliability of the MBPT(4) electron correlation corrections [35]. Both the experimental and theoretical dipole moments of other authors are compared with the values obtained in this study. The present high-level correlated results are in excellent agreement with the experimental data. A relatively small difference between the MBPT(4) and SDQ-MBPT(4) values can be considered as an indication of rather good convergence of the electron correlation perturbation series for the dipole moment of the third-row atom hydrides. Further support for this conclusion is obtained from the MBPT(3) data of Table 3.

The dipole moment results calculated in the present paper compare well with the majority of other accurate theoretical data. The only puzzling difference is

Table 3. Dipole moments of the third-row atom hydrides. All values in a.u. (1 a.u. of dipole moment ≃ 2.5414 D)

Molecule[b]	This work[a]		Reference results	
	Method[c]		Method	
AsH_3	SCF	0.1588	Exptl.	0.085 ± 0.001 [38][d]
	MBPT(2)	0.1200		
	MBPT(3)	0.1057		
	MBPT(4)	0.1014		
	SDQ-MBPT(4)	0.1034		
H_2Se	SCF	0.3216	Exptl.	0.247 ± 0.001 [39][e]
	MBPT(2)	0.2783	SCF HF	0.359 [40]
	MBPT(3)	0.2673	CEPA	0.279 [41][f]
	MBPT(4)	0.2593		0.276 [41][g]
	SDQ-MBPT(4)	0.2642	MR-CI	0.335 [42][h]
HBr	SCF	0.3820	Exptl.	0.3218 [43]
	MBPT(2)	0.3462	CEPA	0.323 [44]
	MBPT(3)	0.3394	ACPF	0.3255 [45]
	MBPT(4)	0.3303	MR-CI	0.323 [46]
	SDQ-MBPT(4)	0.3356	MBPT(4)	0.323 [33]

[a] Calculations with the [15.12.9/9.7.4] first-order polarized basis sets for the third-row atoms and the [6.4/3.2] polarized basic sets [10, 11] for H. At the MBPT level of approximation only the valence correlation effects are taken into account

[b] All molecular geometry data correspond to the experimental equilibrium values and are taken from [34]:

AsH_3 R(As-H) = 2.855 a.u., $\sphericalangle$ HAsH = 92.08°; the z axis of the coordinate system coincides with the C_3 symmetry axis.

H_2Se R(Se-H) = 2.759 a.u., $\sphericalangle$ HSeH = 90.27°; the molecule lies in the xz plane with the z axis of the coordinate system coinciding with the C_2 symmetry axis.

HBr R(Br-H) = 2.673 a.u.; the molecule lies on the z axis of the coordinate system

[c] See text for the explanation of abbreviations

[d] This value corresponds to the $v = 0$ vibrational level. The vibration correction to the equilibrium geometry dipole moment appears to be negligibly small [38]

[e] This value follows from the Stark effect measurement for D_2Se.

[f] Equilibrium geometry value calculated at the theoretical molecular geometry obtained by using the CEPA approximation. The CEPA equilibrium geometry of H_2Se is almost the same as the experimental one [41]

[g] Theoretical dipole moment for the lowest vibrational level of H_2Se

[h] MR-CI result calculated with the relativistic effective core potential for Se. See text for further comments

[i] Vibrationless value for the equilibrium geometry of HBr

[j] MR-CI result calculated with the relativistic effective core potential for Br

[k] MBPT result calculated with the [17.14.8.2/17.14.6.2] GTO/CGTO basis set for Br and the [11.7.2/7.4.2] GTO/CGTO basis set for H

observed between the multi-reference CI (MR-CI) and the present MBPT(4) value of the dipole moment for H_2Se. By using virtually the same method Balasubramanian et al. [46] have obtained excellent result for HBr while the value calculated for H_2Se [42] is by almost 0.1 a.u. higher than the experimental dipole moment. This discrepancy may partly originate from the method used to evaluate the MR-CI dipole moment which assumes that the MR-CI wave function satisfies the Hellmann–Feynman theorem. This assumption may produce errors as large as that in Balasubramanian and Liao's calculations [42] for H_2Se [47, 48]. Also the unlinked cluster contributions [49] which have not been removed from the MR-CI value for H_2Se may to be some extent responsible for the high MR-CI dipole moment of H_2Se. Some additional comments on this subject can be found in [33].

The values of the MBPT(4) dipole moments of this work for AsH_3, H_2Se, and HBr are only 0.016 a.u., 0.012 a.u., and 0.008 a.u. higher than the corresponding experimental results. Since the data reported in Table 3 correspond to the valence MBPT approximation, this sequence of differences can be looked upon as arising from the core polarization effects [50] whose importance is expected to diminish on passing from As to Br. In order to investigate those effects the MBPT(4) calculations of the dipole moment were also carried out including with the $3d^{10}$ shell at the correlated level of approximation. To allow for the polarization of the d-type core orbitals the corresponding MBPT calculations have been performed with the extended [15.12.9.4/9.7.4.2] first-order polarized basis sets described in Sect. 3.2. The SCF and MBPT(4) results for the two polarized basis sets of this paper are collected in Table 4 and compared with the experimental data.

It follows from the data of Table 4 that the f-type polarization functions reduce the SCF values of molecular dipole moment. This negative SCF contribution of the $3d^{10}$ shell polarization is partly counterbalanced by the diminished total MBPT(4) electron correlation correction. The final MBPT(4) results for the (*spdf*) basis set are uniformly about 0.01 a.u. higher than the experimental dipole moments. This difference may to some extent arise from the relativistic contribution [33, 51]. The corresponding estimated corrections calculated at the SCF level of approximation are negative and vary between −0.01 a.u. and −0.02 a.u. [33, 41].

According to the results presented in Tables 3 and 4 both the (*spd*) and (*spdf*) first-order polarized basis sets determined in this paper perform excellently in calculations of dipole moments for the test series of the third-row atom

Table 4. Dipole moments of the third-row atom hydrides: the effect of the f-type polarization functions and the $3d^{10}$ shell correlation contributions. All values in a.u.

Molecule[a]	This work			Exptl.
	Method	A[b]	B[c]	
AsH_3	SCF	0.1588	0.1509	
	MBPT(4)	0.1014	0.0986	0.085 ± 0.001 [38]
H_2Se	SCF	0.3216	0.3171	
	MBPT(4)	0.2593	0.2606	0.247 ± 0.001 [39]
HBr	SCF	0.3820	0.3798	
	MBPT(4)	0.3303	0.3311	0.3218 [43]

[a] See footnote b to Table 3

[b] Calculated with the [15.12.9/9.7.4] first-order polarized basis sets for the third-row atoms. See also footnote a to Table 3

[c] Calculated with the [15.12.9.4/9.7.4.2] first-order polarized basis sets for the third-row atoms. The MBPT results include the electron correlation contribution due to $3d^{10}$ and valence shells

hydrides. The much smaller (*spd*) sets are only marginally worse than the (*spdf*) basis sets and are preferable in molecular calculations. Their high performance has been more recently confirmed in calculations of molecular electric properties of OCSe and SCSe and interactions with polar species [52]. It should also be noted that those features of the first-order polarized basis sets for the third-row closely follow the excellent performance of analogous basis sets for the first- and second-row atoms [10, 11].

Another electric property which should be correctly predicted in molecular calculations with first-order polarized basis sets is the dipole polarizability (α). The results obtained in this study for the dipole polarizability tensors of GeH_4, AsH_3, H_2Se, and HBr are presented in Table 5. The dipole polarizability is one of the most fundamental response properties of molecules [6] and its importance for the prediction of the molecular interaction effects is well recognized [53]. It is also anticipated that a successful calculation of intermolecular interaction energies can only be achieved if the selected subsystem basis sets predict the principal electric properties of the interacting species well enough [54]. The expected major application of the first-order polarized basis sets appears to be the study of weak molecular interactions [10, 52, 55, 59], and thus,

Table 5. Electric dipole polarizability (α) of the third-row atom hydrides. All values in a.u.

Molecule[b]	This work[a]					Reference results
	Method[c]	α_{xx}	α_{yy}	α_{zz}	α^d	
GeH_4[e]	SCF	32.99[f]			32.99	
	MBPT(2)	33.99			33.99	
	MBPT(3)	34.04			34.04	
	MBPT(4)	34.13			34.13	
	SDQ-MBPT(4)	34.02			34.02	
AsH_3	SCF	34.29[g]		35.36	34.65	
	MBPT(2)	34.82		36.66	35.43	
	MBPT(3)	34.67		36.45	35.26	
	MBPT(4)	34.71		36.53	35.32	
	SDQ-MBPT(4)	34.58		36.30	35.15	
H_2Se	SCF	30.16	30.63	29.93	30.24	Exptl. $\alpha = 32.2$ [57]
	MBPT(2)	30.70	32.12	30.78	31.20	Semiempirical: $\alpha_{xx} = 34.8$, $\alpha_{yy} = 25.6$,
	MBPT(3)	30.56	32.04	30.66	31.09	$\alpha_{zz} = 33.3$ [56]
	MBPT(4)	30.67	32.27	30.79	31.24	
	SDQ-MBPT(4)	30.51	31.98	30.60	31.03	
HBr	SCF	22.38[g]		24.53	23.10	Exptl. $\alpha_{xx} = 22.9$, $\alpha_{zz} = 25.5$ [45, 58]
	MBPT(2)	23.22		25.12	23.85	SCF: $\alpha_{xx} = 22.18$, $\alpha_{zz} = 24.34$ [45]
	MBPT(3)	23.20		25.05	23.81	$\alpha_{zz} = 24.74$ [33]
	MBPT(4)	23.37		25.21	23.98	ACPF: $\alpha_{zz} = 24.55$ [45]
	SDQ-MBPT(4)	23.20		25.06	23.82	MBPT(4): $\alpha_{zz} = 25.37$ [33][h]

[a, b, c] See the corresponding footnotes to Table 3

[d] Rotational average of the dipole polarizability tensor

[e] Experimental bond length R(Ge-H) = 2.882 a.u.

[f] $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$

[g] $\alpha_{xx} = \alpha_{yy}$

[h] See footnote k to Table 3

the accurate prediction of molecular dipole polarizabilities represents one of the basic requirements with respect to their performance.

The reference data for our calculations of molecular dipole polarizabilities of the third-row atom hydrides are principally limited to those for the HBr molecule [33, 45, 58]. The experimental average dipole polarizability of H_2Se from [57] is rather uncertain and the theoretical data seem to be limited to semiempirical results of Rhee et al. [56]. Guessing from the dipole moment of H_2Se calculated by Rhee et al. (0.61 a.u. [56] as compared to the experimental value of 0.247 a.u. [39]) the credibility of their polarizability data is rather low. No credible polarizability values seem to be available for GeH_4 and AsH_3.

With the comparison of the dipole polarizability values limited virtually to the HBr molecule the present conclusions concerning the performance of the first-order polarized basis sets for the third-row atoms are not as well documented as in the case of the first- and second-row elements. However, for HBr and SCF and MBPT(4) results of this paper agree well with the corresponding data calculated with much larger basis sets [33]. Also their agreement with the SCF and ACPF values obtained recently by Bacskay [45] is very satisfactory. The values of the polarizability tensor of HBr calculated in this work agree almost perfectly with the available experimental data [45, 58]. Owing to the uniform quality of the first-order polarized basis sets for different atoms [10, 11] a similar accuracy should be expected for other third-row atom hydrides.

It is worthwhile mentioning certain general features of the calculated dipole polarizability values. Above all, the correlation perturbation series for the dipole polarizability tensor has a very nice convergence pattern. It appears that for all molecules listed in Table 5 the higher than the second-order correlation corrections are virtually negligible. Moreover, the electron correlation contribution to the dipole polarizability tensors of the third-row atom hydrides represents a much smaller fraction of the total polarizability than in the case of the first- and second-row hydrides. For all the molecules studied in this paper, the polarizability tensors are almost isotropic, indicating that most of the polarization effects arises from the heavy atom. This is accompanied by a rather low polarity of the pertinent molecules (see Table 3). Hence, in interactions with other species the third-row atom hydrides can be reasonably well represented by nonpolar polarizable charge distributions. However, in contrast to the near-isotropic polarizability tensors of AsH_3, H_2Se, and HBr, the second moments of the charge distribution in those molecules are highly anisotropic. The calculated SCF quadrupole moments of AsH_3 and HBr (for the origin at the nuclear centre of mass evaluated from the natural abundance atomic masses) are equal to -1.70 a.u. and 3.28 a.u., respectively. The components of the quadrupole moment tensor of H_2Se are found to be $\theta_{xx} = 2.32$ a.u., $\theta_{yy} = -3.34$ a.u., and $\theta_{zz} = 1.02$ a.u. (see footnote b of Table 3 for the definition of the coordinate system assumed for H_2Se).

All calculations reported in Table 5 have been carried out with the (*spd*) polarized basis sets. The electron correlation contribution has been evaluated in the valence approximation. The changes in the computed dipole polarizability which arise from the use of the extended (*spdf*) sets and the $3d^{10}$ shell correlation effects have been found to usually be smaller than 1% of the total polarizability value. Those two effects slightly lower the dipole polarizability of HBr, H_2Se, and AsH_3 while increasing the α value for GeH_4 a little. Since including the two *f*-type polarization functions in the basis set and correlating the $3d^{10}$ shell considerably increases the computational effort involved, the resulting improvement does not seem to be particularly important. Both the dipole moment and polarizability values calculated with the [15.12.9/9.7.4] (*spd*) basis sets are completely satisfactory.

Finally, let us mention that the relativistic effects on the dipole polarizability of the third-row atom hydrides, as estimated by using the quasirelativistic SCF approximation, are virtually negligible [33]. They decrease the corresponding non-relativistic results by less than 0.1 a.u. and do not seem to deserve any particular attention. They are much smaller than the estimates obtained for the isolated third-row atoms (see Sect. 3.2). The formation of chemical bonds appears to diminish the importance of the relativistic effect on the dipole polarizability.

4. Summary

In this paper a series of compact and relatively small basis sets, tailored for accurate calculations of atomic and molecular electric properties, has been derived for the third-row atoms: Ge through Br. Those so-called first-order polarized (medium-size) basis sets have been generated by using the basis set polarization approach accompanied by certain additional rules which have been developed in our earlier studies.

The performance of the first-order polarized basis sets of Ge through Br has been carefully examined in atomic calculations and the present restricted Hartree–Fock data for atomic dipole polarizabilities appear to be close to the corresponding HF limits. A similar conclusion was previously reached for the first-order polarized sets of the first- and second-row atoms.

The generated first-order polarized basis sets were then applied to the calculation of basic electric properties of the third-row atom hydrides. A comparison with available experimental and accurate theoretical data for molecular dipole amounts and polarizabilities shows that the MBPT(4) results calculated with the [15.12.9/9.7.4] polarized basis sets for Ge through Br are suitable for high-level-correlated calculations of molecular dipole moments and dipole polarizabilities. There are also some indications that the uniform character of those basis sets may lead to fairly accurate values of molecular quadrupole moments [16].

The possible contribution of the core-polarization effects has been investigated for dipole moments and polarizabilities of the third-row atom hydrides by using extended [15.12.9.4/9.7.4.2] polarized basis sets and correlating the $3d^{10}$ atomic shells. For the third-row atom hydrides those effects have been found to be relatively small and their contribution is considered to be negligible in comparison with several other uncertainties of the finite-order MBPT approach. A similar conclusion applies to the role of the relativistic contribution to electric properties of the third-row atom hydrides.

The demonstrated excellent performance of the first-order polarized basis sets in calculations of atomic and molecular electric properties indicates their possible usefulness in calculations of intermolecular interactions for weakly interacting systems. Indeed, the first-order polarized basis sets for the first-row atoms have been shown to give very satisfactory interaction energy data [55, 59]. The calculation of intermolecular interaction energies and interaction induced properties is to be the major area of the future use of the polarized basis sets derived in this study. The detailed basis set data for Ge through Br are listed in the

Appendix. The generation of extended (*spdf*) polarized basis sets can be achieved with the aid of the data of Table 2.

Predicting the molecular interaction energies also requires [53, 54] that the higher multipole moments of each subsystem are represented accurately enough by the given basis set. Obviously, no condition which would satisfy this requirement for molecular quadrupole and higher multipole moments is directly built into the present basis set generation scheme. The appropriate extension of this scheme for calculations of quadrupole moments and polarizabilities follows immediately from the known [14] basis set dependence on the electric field gradient perturbation and will add *f*-type functions to the present (*spd*) sets and *f*- and *g*-type functions to the present (*spdf*) sets. However, there are some indications that the basis sets derived from the first-order electric field polarization scheme may give, at least at the level of the SCF HF approximation, fairly reasonable results for molecular quadrupole moments [16]. This appears to result from the following two factors. (i) The first-order electric field polarization scheme provides a uniformly diffuse extension of the original basis set. As indicated by the dipole moment data this leads to an improved molecular electron density distribution at the level of the SCF HF approximation. The resulting second moments of the electron density distribution should be improved as well. (ii) The second important factor follows from the definition of the quadrupole moment [53]. The differences of cartesian second moments calculated with a uniformly diffuse basis set should not be highly sensitive to the presence of higher angular momentum basis functions. Such an interpretation, though fairly plausible in the case of SCF HF results [16], may not be satisfactory at the correlated level of approximation. On the other hand, in the case of relatively bulky molecules the electron correlation correction to the diagonal components of the quadrupole moment tensor is quite small [16]. This seems to also be a by-product of the quadrupole moment definition.

The derivation of similar first-order polarized basis sets for the fourth-row atoms (Sn through I) is currently under investigation. In comparison with the third-row atoms, the relativistic contribution to electric properties of systems involving the fourth-row atoms is definitely non-negligible and must be taken into account in accurate predictions of dipole moments and polarizabilities. Thus, for fourth-row (Sn through I) and heavier elements polarized basis sets must properly describe (i) the charge polarization effects, (ii) electron correlation contribution to the charge polarization, and (iii) the relativistic contribution. To simultaneously satisfy these three conditions may lead to the first-order polarized basis sets which are considerably larger than those which have been devised for the first-, second-, and third-row atoms.

Appendix

The first-order polarized [15.12.9/9.7.4] basis sets for Ge through Br are presented in Tables A to D. The details of their derivation can be found in Sect. 2 and in the earlier papers of this series [10, 11, 15]. An extension to the [15.12.9.4/9.7.4.2] (*spdf*) form can be achieved by adding the *f*-type polarization functions presented in Table 2. However, the present investigations show that sufficiently accurate data can be obtained with the (*spd*)-type polarized sets which are recommended for accurate high-level-correlated calculations of electric properties and molecular interactions.

Table A. The first-order polarized [15.12.9/9.7.4] GTO/CGTO basis set for Ge

GTO	CGTO	Exponent	Contraction coefficients			
s subset						
1	1 ÷ 4	348299.8	0.0003383	0.0001055	0.0000405	0.0000104
2		52638.12	0.0025792	0.0008002	0.0003099	0.0000792
3		12018.36	0.0134593	0.0042524	0.0016283	0.0004163
4		3406.951	0.0526727	0.0167878	0.0065612	0.0016758
5		1157.699	0.1512606	0.0525514	0.0201835	0.0051718
6		442.1850	0.3225121	0.1257423	0.0511386	0.0130977
7		180.0446	0.4068147	0.2342057	0.0937554	0.0242756
8		76.50783	0.1889964	0.1027861	0.0554130	0.0143390
9		26.77091	0.0114588	−0.5563724	−0.3692429	−0.1002602
10		11.43546	−0.0010655	−0.5695571	−0.4528432	−0.1323443
11	5	3.023474	1.0			
12	6	1.159275	1.0			
13	7	0.241695	1.0			
14	8	0.082681	1.0			
15	9	0.028284	1.0			
p subset						
1	1 ÷ 3	2581.751	0.0025342	−0.0009805	−0.0001945	
2		620.9984	0.0199240	−0.0077373	−0.0015199	
3		203.7177	0.0921153	−0.0370860	−0.0073988	
4		77.57168	0.2670416	−0.1121499	−0.0221507	
5		32.38502	0.4374929	−0.2010281	−0.0411436	
6		14.24833	0.3129736	−0.0908530	−0.0147554	
7		6.010788	0.0558649	0.3507104	0.0795689	
8		2.561509	0.0000316	0.5582308	0.1540492	
9	4	1.061296	1.0			
10	5	0.282632	1.0			
11	6	0.084551	1.0			
12	7	0.025294	1.0			
d subset						
1	1	68.53021	0.0301959			
2		19.35644	0.1657003			
3		6.600014	0.3971127			
4	2	2.288409	0.4703261			
5		0.741149	0.2523345			
6	3	1.06130	−0.02450			
7		0.28263	0.76234			
8	4	0.08455	0.19214			
9		0.02529	0.14193			

Table B. The first-order polarized [15.12.9/9.7.4] GTO/CGTO basis set for As

GTO	CGTO	Contraction coefficients				
s subset						
1	1 ÷ 4	373201.1	0.0003371	0.0001055	0.0000410	−0.0000113
2		54939.83	0.0027018	0.0008416	0.0003289	−0.0000904
3		12270.63	0.0141257	0.0044758	0.0017368	−0.0004774
4		3538.010	0.0532252	0.0170473	0.0067152	−0.0018466
5		1218.193	0.1523040	0.0530786	0.0207147	−0.0057037
6		464.8529	0.3263965	0.1284161	0.0524490	−0.0144806
7		189.4323	0.4028654	0.2336762	0.0958017	−0.0266239
8		81.75079	0.1853815	0.1013469	0.0527402	−0.0148682
9		28.83275	0.0132875	−0.5472122	−0.3591681	0.1057078
10		12.45438	−0.0019340	−0.5715411	−0.4826202	0.1512379
11	5	3.677003	1.0			
12	6	1.552864	1.0			
13	7	0.291144	1.0			
14	8	0.107232	1.0			
15	9	0.039495	1.0			
p subset						
1	1 ÷ 3	2782.858	0.0024863	−0.0009764	−0.0002187	
2		669.0384	0.0197457	−0.0077851	−0.0017204	
3		218.7985	0.0915011	−0.0373990	−0.0084307	
4		83.48981	0.2656987	−0.1133623	−0.0251727	
5		34.92050	0.4355429	−0.2033940	−0.0472648	
6		15.48738	0.3132782	−0.0937084	−0.0164231	
7		6.570163	0.0595995	0.3459266	0.0875009	
8		2.841880	−0.0007508	0.5571049	0.1818443	
9	4	1.210419	1.0			
10	5	0.328250	1.0			
11	6	0.103361	1.0			
12	7	0.032547	1.0			
d subset						
1	1	73.62860	0.0315097			
2		20.88949	0.1714495			
3		7.217652	0.4017342			
4	2	2.569304	0.4655653			
5		0.863941	0.2342530			
6	3	1.21042	−0.01396			
7		0.32825	0.82417			
8	4	0.10336	0.16009			
9		0.03255	0.10592			

Table C. The first-order polarized [15.12.9/9.7.4] GTO/CGTO basis set for Se

GTO	CGTO	Exponent	Contraction coefficients			
s subset						
1	1 ÷ 4	373064.5	0.0003645	0.0001144	0.0000449	0.0000131
2		55085.14	0.0028724	0.0008977	0.0003544	0.0001034
3		12592.85	0.0144645	0.0045980	0.0018041	0.0005269
4		3699.059	0.0536980	0.0172673	0.0068668	0.0020057
5		1277.820	0.1545309	0.0540553	0.0213582	0.0062493
6		486.7047	0.3297180	0.1307919	0.0538925	0.0158045
7		198.6806	0.4006442	0.2344816	0.0976695	0.0288697
8		86.13051	0.1812354	0.0981841	0.0511442	0.0152959
9		30.72411	0.0129547	−0.5485378	−0.3627238	−0.1136170
10		13.32537	−0.0019021	−0.5684272	−0.4937134	−0.1656001
11	5	4.103203	1.0			
12	6	1.760131	1.0			
13	7	0.352896	1.0			
14	8	0.131568	1.0			
15	9	0.049052	1.0			
p subset						
1	1 ÷ 3	2975.594	0.0024786	−0.0009868	0.0002401	
2		713.7165	0.0197102	−0.0078882	0.0018939	
3		233.8993	0.0911422	−0.0377738	0.0092517	
4		89.31284	0.2658265	−0.1152657	0.0278305	
5		37.33775	0.4365449	−0.2066787	0.0522325	
6		16.58343	0.3116260	−0.0948790	0.0179079	
7		7.125157	0.0596090	0.3464229	−0.0961145	
8		3.103954	−0.0002812	0.5611639	−0.2037544	
9	4	1.339101	1.0			
10	5	0.387547	1.0			
11	6	0.119992	1.0			
12	7	0.037152	1.0			
d subset						
1	1	78.71959	0.0327398			
2		22.53607	0.1756588			
3		7.887587	0.4056571			
4	2	2.863780	0.4625696			
5		0.990345	0.2186191			
6	3	1.33910	−0.00820			
7		0.38755	0.81387			
8	4	0.11999	0.14805			
9		0.03715	0.07972			

Table D. The first-order polarized [15.12.9/9.7.4] GTO/CGTO basis set for Br

GTO	CGTO	Exponent	Contraction coefficients			
s subset						
1	1 ÷ 4	379677.7	0.0003842	−0.0001208	0.0000480	−0.0000147
2		56125.18	0.0030003	−0.0009411	0.0003749	−0.0001147
3		12967.35	0.0148907	−0.0047442	0.0018827	−0.0005766
4		3836.082	0.0547746	−0.0177026	0.0070977	−0.0021735
5		1331.996	0.1567715	−0.0549918	0.0220139	−0.0067547
6		508.0421	0.3328099	−0.1333894	0.0553369	−0.0170164
7		207.7812	0.3985678	−0.2345111	0.0995058	−0.0308665
8		90.42185	0.1765368	−0.0972103	0.0498142	−0.0156180
9		33.00437	0.0124906	0.5425917	−0.3574409	0.1175750
10		14.35639	−0.0017219	0.5718584	−0.5171876	0.1828625
11	5	4.728525	1.0			
12	6	2.032967	1.0			
13	7	0.412706	1.0			
14	8	0.156142	1.0			
15	9	0.059074	1.0			
p subset						
1	1 ÷ 3	3167.910	0.0024643	−0.0009940	0.0002588	
2		762.5044	0.0195907	−0.0079501	0.0020438	
3		249.3963	0.0911694	−0.0382891	0.0100386	
4		95.23177	0.2656020	−0.1169117	0.0302452	
5		39.92301	0.4355430	−0.2090161	0.0565897	
6		17.78166	0.3117761	−0.0968376	0.0195855	
7		7.677264	0.0602091	0.3512283	−0.1056535	
8		3.342064	−0.0019929	0.5698537	−0.2254965	
9	4	1.442422	1.0			
10	5	0.442320	1.0			
11	6	0.137772	1.0			
12	7	0.042913	1.0			
d subset						
1	1	96.15001	0.0265128			
2		27.83908	0.1500642			
3		9.851067	0.3804896			
4	2	3.610187	0.4802772			
5		1.251544	0.2478854			
6	3	1.4424	0.00395			
7		0.4423	0.80388			
8	4	0.1378	0.13480			
9		0.0429	0.06231			

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