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

VI. Fifth-row atoms: Pb through At

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Summary. The first-order polarized basis sets for the use in high-level-correlated investigations of molecular electric properties have been generated for Pb, Bi, Po, and At. The performance of the standard [10.17.14.5/13.11.8.2] and extended [20.17.14.9/13.11.8.4] basis sets has been examined in nonrelativistic and quasirelativistic calculations for atoms and simple closed-shell hydrides. The relativistic contributions to electric dipole properties of those systems have been evaluated by using the recently developed quasirelativistic scheme. The predicted dipole polarizability of At is in good agreement with the results of other relativistic calculations. The calculated quasirelativistic dipole moments of BiH_3 (-0.499 a.u.), PoH_2 (-0.207 a.u.), and AtH ($+0.036$ a.u.) involve a significant relativistic contribution which amounts to -0.230 a.u., -0.177 a.u., and -0.097 a.u., respectively. The basis set details append this paper. They are also available as a part of the basis set library of the MOLCAS system.

Key words: Polarized basis sets – Atomic dipole polarizabilities of Pb, Bi, Po, and At – Molecular electric properties – Dipole moments and polarizabilities of the fifth-row hydrides – Relativistic contributions to atomic and molecular properties – PbH_4 – BiH_3 – PoH_2 – AtH

1. Introduction

In a series of recent papers [1–5] the basis set polarization method [1, 6] has been used to generate relatively compact GTO/CGTO basis sets for the purpose of accurate calculations of basic electric properties of molecules. These so-called medium-size (first-order) polarized basis sets have been found to give high quality results for molecular dipole and quadrupole moments and dipole polarizabilities [1–5, 7–9] at both the SCF HF and different correlated levels of approximation.

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The fifth-row atoms, for which the polarized basis sets are to be developed in this paper, appear to be rather exotic for routine quantum chemical calculations. However, even for Po and At their chemistry is well developed [10, 11] and the possibility of performing accurate calculations on their compounds seems to be both attractive and useful. Moreover, the study of relativistic contributions [12, 13] to different properties of molecules involving the fifth-row atoms is of particular interest and importance.

The method of the basis set generation, which is used in the present study, has been comprehensively described in earlier papers of this series [1–5]. A brief account of some details pertinent to its application to the fifth-order atoms is given in Sect. 2 while the generated basis sets are listed in the Appendix. The main attention is focused on the documentation of the performance of those basis sets in calculations of atomic dipole polarizabilities (Sect. 3) and molecular dipole moments and polarizabilities (Sect. 4). In the latter case the relevant molecular electric properties are calculated for the series of hydrides AH_n. Since there are hardly any experimental data available for comparison with the present results, most of our conclusions will be based on a mutual cross-examination of theoretical data. Considerable attention will be given to the estimates of the relativistic contribution to atomic and molecular electric properties. A summary of our investigations and the main conclusions are presented in Sect. 5.

2. The basis set generation and computational details

The method used for the generation of the so-called (first-order) polarized basis sets for the fifth-row atoms follows essentially the procedure employed in Part V of this series [5]. The general aspects of this method have been extensively discussed in our earlier papers [1, 2, 6]. For the reason of their compactness the polarized basis set derived in this study will be referred to as medium size sets.

The initial GTO sets for Pb through At are the energy-optimized (19.16.10.5) sets of Gropen [14]. Following the method used for the fourth-row atoms, the initial primitive sets have been contracted to the [19.16.10.5/12.10.6.2] GTO/CGTO form by using the Raffenetti contraction scheme [15] with the contraction coefficients read from the SCF HF eigenvectors for occupied atomic orbitals computed in the primitive set. The contraction in the *s* subset comprises 12 highest-exponent GTO's and is used to generate five *s*-type CGTO's. In the *p* subset the Raffenetti scheme is applied to 10 highest-exponent GTO's out of which four *p*-type CGTO's are obtained. In the *d* subset 6 highest-exponent GTO's are contracted to two *d*-type CGTO's. For the *f* subset we have employed a split-shell contraction scheme leading from 5 GTO's to two $(5 \rightarrow 3 + 2)$ *f*-type CGTO's.

The GTO/CGTO set obtained in such a way is principally uncontracted in the valence and next-to-valence shells of the fifth-row atoms. To increase its diffuseness in the valence region, one diffuse *s* GTO and one diffuse *p* GTO have been added. Their exponents follow from approximate geometric progressions in the respective subsets. The resulting [20.17.10.5/13.11.6.2] GTO/CGTO basis sets have been used to obtain the SCF HF AO's for the ground state of negative ions Pb^- through At^- [1, 2]. The valence-shell polarization functions, i.e., the respective *d*-type CGTO's have been generated from the 6*p* SCF HF AO of each negative ions. According to the procedure devised in earlier papers of this series [1, 2, 5], the *d*-type polarization set is assumed to consist of 4 primitives contracted to two ($4 \rightarrow 2+2$) *d*-type GTO's with the contraction coefficients determined by the basis set polarization method [1, 2, 6]. This method results finally in [20.17.14.5/13.11.8.2] first-order polarized basis sets which append this paper.

Our previous studies of the third- [4] and fourth-row [5] atoms indicate that the calculated atomic and molecular properties may be considerably affected by the polarization of the next-to-valence shell. To account for the polarization of $5d^{10}$ shell the polarized basis sets generated so far need to be extended by *f*-type polarization functions. On applying the basis set polarization method to 5*d* SCF HF AO's one obtains the appropriate polarization functions which are assumed to be two *f*-type CGTO's built ($4 \rightarrow 2+2$) from 4 primitive GTO's which cover the most important range of orbital exponents contributing to the 5*d* SCF HF AO of the given atom. This results in extended [20.17.14.9/13.11.8.4] polarized basis sets. The details of the *f*-type polarization functions of those extended polarized basis sets are given in Table 1.

All atomic and molecular calculations have been carried out by using the MOLCAS system of quantum chemistry programs [16, 17]. The *s*-components of *d*-type CGTO's and the *p*-components of *f*-type CGTO's have been removed at the integral generation level [18], leading to a considerable reduction of the basis set size. For contracted basis sets generated in this study some near-linear dependences in the *s* and *p* subsets occur. They have been systematically removed with the threshold of 10^{-6} used for the eigenvalues of the overlap matrix. This threshold leads to the removal of one *s*-type and one *p*-type functions.

The calculation of electric properties of the 5th-row atoms and their hydrides has been carried out by using the finite field perturbation method as described in earlier papers. The study of atomic dipole polarizabilities has been performed at the SCF HF level of approximation. The dipole moments and dipole polarizabilities of the fifth-row atom hydrides have been investigated at both the SCF HF and different correlated levels of approximation. To obtain the electron correlation contributions to molecular electric properties we have employed different finite-order many-body perturbation theory (MBPT) methods [19]. The corresponding calculations have been carried out in the second- (MBPT2), third- (MBPT3), and complete fourth-order (MBPT4) approximations. Also the results

Table 1. The *f*-type polarization functions for the fifth-row atoms derived by applying the basis set polarization method to 5*d* SCF HF AO's[a]

GTO	CGTO	Pb		Bi		Po		At	
		α_i[b]	c_i[c]	α_i	c_i	α_i	c_i	α_i	c_i
1	1	14.25898	0.06508	14.42043	0.06918	14.78087	0.07113	14.98556	0.07458
2		5.95199	0.06600	6.08952	0.06315	6.32164	0.06394	6.47152	0.06057
3	2	1.84584	0.42785	1.94419	0.43085	2.08955	0.41951	2.18774	0.42249
4		0.60512	0.73909	0.65797	0.68009	0.72670	0.63967	0.77864	0.59350

[a] Upon adding those polarization functions to the (valence) polarization sets (see Appendix) one obtains the extended [20.17.14.9/13.11.8.4] polarized basis sets

[b] Orbital exponents

[c] Contraction coefficients

of incomplete fourth-order approach, with single-, double-, and quadruple-substitutions only (SDQ-MBPT4) [19], will be presented.

The MBPT calculations of molecular electric properties have been carried out in two different approximations with respect to the number of correlated electrons. The first series of calculations has been performed with the standard, [20.17.14.5/13.11.8.2] polarized sets as given in the Appendix and amounts to correlating only the ten valence electrons in each hydride. The second series of MBPT calculations has used the extended [20.17.14.9/13.11.8.4] basis sets of this paper combined with the explicit correlation of the $5d^{10}$ shell of heavy atoms. It should be added that the [6.4/3.2] basis set of H employed in our studies of hydrides is the polarized GTO/CGTO set derived in Part I of this series [1, 2].

For atoms as heavy as those studied in this paper one has to consider the relativistic contributions. Recently, we have demonstrated [20] that a simple quasirelativistic method, based on the so-called Cowan–Griffin approximation [12, 20, 21] to the relativistic hamiltonian is capable of giving very reliable estimates of relativistic corrections to atomic and molecular electric properties. This method, which is comprehensively described in Ref. [20], will be used in the present study to obtain relativistic corrections to molecular dipole moments and polarizabilities. Also some estimates of those contributions to atomic dipole polarizabilities will be calculated and discussed.

Among other computational details one should also mention that all present molecular calculations have been performed at molecular equilibrium geometries which are estimated from different theoretical and empirical data. This brings about some additional uncertainty of the calculated values of molecular electric properties and indicates that the discussion of their reliability should be rather focused on the cross-examination of different theoretical results.

3. Atomic calculations

The main purpose of atomic SCF HF calculations presented in this section is to investigate the effect of contractions and the importance of the polarization of atomic $5d^{10}$ shells. Once the polarized basis sets are found to be saturated enough for reliable calculations of atomic dipole polarizabilities, their performance in calculations of molecular dipole properties should be equally satisfactory. This feature of polarized basis sets has been well exemplified in our earlier studies and stresses the importance of preliminary atomic calculations.

The dipole polarizabilities of Pb (^3P), Bi (^4S), Po (^3P), and At (^2P) have been calculated with four basis sets which differ from each other either by the presence of contractions or by the extent of polarization. The results for the 'valence' polarized basis sets [20.17.14.5/13.11.8.2] (see Appendix) will be compared with those obtained by using their completely uncontracted (20.17.14.5) counterparts. An analogous comparison is carried out for the extended [20.17.14.9/13.11.8.4] polarized sets (see Appendix and Table 1) and their fully uncontracted (20.17.14.9) counterparts. Our non-relativistic open-shell SCF HF results are presented in Table 2. They are accompanied by the estimates of the relativistic contribution to dipole polarizabilities evaluated from the second derivatives of the electric-field-dependent corrections to atomic SCF HF energies [5, 20].

The nonrelativistic data of Table 2 show that the contraction scheme used to generate the polarized basis sets of this paper essentially does not affect the calculated polarizability values. Also including the f-type polarization functions

Table 2. Atomic dipole polarizabilities from SCF HF calculations in different polarized GTO and GTO/CGTO basis sets. The estimated relativistic corrections are given in parentheses. All values in a.u.

Atom	State	Basis set[a]			
		(20.17.14.5)	[20.17.14.5/ 13.11.8.2][b]	(20.17.14.9)	[20.17.14.9/ 13.11.8.4][c]
Pb ^3P	$M_L = 0$	58.56	57.81	58.81	58.14
		(−11.84)[d]	(−11.34)	(−12.40)	(−12.18)
	$M_L = \pm 1$	72.02	71.52	72.05	71.51
		(−5.36)	(−4.90)	(−5.18)	(−5.37)
Bi ^4S	$M_L = 0$	53.33	52.86	53.34	52.85
		(−6.24)	(−5.88)	(−8.46)	(−6.08)
Po ^3P	$M_L = 0$	51.53	51.38	51.54	51.50
		(−1.16)	(−1.24)	(−0.60)	(−0.94)
	$M_L = \pm 1$	44.63	44.45	44.58	44.41
		(−4.34)	(−4.62)	(−4.62)	(−4.58)
At ^2P	$M_L = 0$	37.41	37.33	37.38	37.30
		(−4.10)	(−4.09)	(−3.34)	(−3.89)
	$M_L = \pm 1$	41.19	41.11	41.21	41.18
		(−1.50)	(−1.92)	(−2.00)	(−1.72)

[a] For the basis set description see Sect. 2

[b] The standard (valence) polarized GTO/CGTO basis set of this paper. See Appendix

[c] The extended polarized GTO/CGTO basis set of this paper. See Appendix and Table 1

[d] Approximate relativistic correction calculated according to the method described in Ref. [20]

is virtually inconsequential at the level of the SCF HF approximation, although they might be needed to properly account for the core-polarization effects in correlated-level molecular calculations. However, as long as the calculations of dipole properties are carried out in the SCF HF approximation, the use of the less demanding [20.17.14.9/13.11.8.4] polarized basis sets can be recommended.

One may raise some objections against the quasirelativistic method used to calculate the relativistic contribution to atomic dipole polarizabilities [20]. This method does not take into account the spin-orbit interaction effects which might be of considerable importance for open-shell configurations of the fifth-row atoms [12, 13, 22]. Additionally, the Cowan–Griffin approximation for the hamiltonian tends to deteriorate for heavy nuclei. With all those reservations one can consider the relativistic corrections listed in Table 2 only as estimates of the relativistic effect on atomic dipole polarizability of the fifth-row atoms. Surprisingly enough our quasirelativistic results for the dipole polarizability of astatine (33.41 a.u. for $M_L = 0$ and 39.46 a.u. for $M_L = \pm 1$ with extended polarized GTO/CGTO basis set) agree well with the j-averaged relativistic results of Stevens and Krauss (33.7 a.u. for $M_L = 0$ and 38.5 a.u. for $M_L = \pm 1$ [23]). There are no comparable relativistic results for other atoms of the present series and more general conclusions based on the data for astatine would be rather premature.

The pattern of the present nonrelativistic and quasirelativistic results for atomic dipole polarizabilities is essentially similar to that observed for the corresponding fourth-row atoms [5]. The polarizabilities of the Pb, Bi, Po, and At are somewhat larger than those of Sn, Sb, Te, and I, respectively. The role of relativistic effects becomes more important for heavier atoms and those effects must be accounted for in molecular calculations.

With exception of astatine no reliable polarizability data for the fifth-row atoms seem to be available. The average polarizabilities (Pb: 42.38 a.u., Bi: 37.52 a.u., Po: 33.81 a.u., and At: 29.52 a.u.) have been calculated by Thorhallsson et al. [24] in the framework of the Kirkwood–Pople–Schofield approximation [25] and their reliability is very uncertain. For comparison, the present nonrelativistic average SCF HF values are 67.05 a.u., 52.85 a.u., 46.77 a.u., and 39.89 a.u. for Pb, Bi, Po, and At, respectively. This shows that the method used by Thorhallsson et al. [24] gives only the order-of-magnitude estimates of atomic dipole polarizabilities.

4. Molecular calculations. Dipole moments and polarizabilities of hydrides

The results of the dipole moment calculations for polar hydrides AH_n of the fifth-row atoms are presented in Table 3. The dipole moment values obtained with extended polarized basis sets are only slightly different from those obtained with standard (valence) sets. The main portion of those differences is accounted for within the SCF HF approximation. On the other hand, the SCF HF relativistic corrections are virtually independent of the choice among the two polarized basis sets.

The electron correlation contribution to dipole moments is rather small and corrections to their nonrelativistic SCF HF values are dominated by the relativistic contribution. For BiH_3 both the nonrelativistic and quasirelativistic dipole moments are negative (see footnote a to Table 3) the latter being about twice as large as the nonrelativistic dipole moment. The negative sign of the dipole moment of BiH_3 perfectly fits to the behaviour of the Group Va hydrides; the dipole moments change from the positive value for NH_3 [1], smaller positive values for PH_3 [2] and AsH_3 [4] to small negative value for SbH_3 [5] and relatively large negative dipole for BiH_3. This regularity has been also observed by Dai and Balasubramanian [26] on the basis of their relativistic multireference CI (RCI) [30] calculations with relativistic effective core potentials. Similar regularities follow for the series of the Group VIa [1, 2, 4, 5, 27] and Group VIIa [1, 2, 4, 5] hydrides.

No experimental dipole moments seem to be available for molecules studied in this paper. Thus, the only confirmation of the accurate performance of polarized basis sets generated in this study can be obtained form the RCI results of Balasubramanian et al. [26, 27]. Their results for BiH_3 and PoH_2 are rather close to ours, although the differences appear to be somewhat too large if one assumes that the present basis sets perform equally well as for the lighter atoms [1–5]. In all previous studies of polar hydrides with polarized basis sets our results were usually within ± 0.02 a.u. close to the experimental data. In the non-relativistic approximation one would expect that also for the present series of molecules the accuracy of calculations with polarized basis sets should be similar to that achieved for lighter systems. However, the approximate treatment of relativistic effects employed in this study makes such conclusions uncertain. Thus, one would rather consider the RCI data [26, 27] as a benchmark for our calculations.

Table 3. Nonrelativistic and quasirelativistic dipole moments of the fifth-row hydrides. The relativistic corrections estimated at the level of the SCF HF approximation are given in parentheses. All values in a.u.[a]

Molecule[b]	Method[c]	This work		Reference results
		Standard polarized basis set[d]	Extended polarized basis set[e]	
BiH_3	SCF	−0.2152 (−0.2275)	−0.2344 (−0.2302)	
	MBPT2	−0.2231	−0.2769	
	MBPT3	−0.2475	−0.2806	
	SDQ-MBPT4	−0.2439	−0.2699	
	MBPT4	−0.2417	−0.2687	
	Total[f]	−0.4692	−0.4989	−0.448[g]
PoH_2	SCF	+0.0454 (−0.1781)	+0.0336 (−0.1773)	
	MBPT2	+0.0088	−0.0148	
	MBPT3	−0.0145	−0.0285	
	SDQ-MBPT4	−0.0140	−0.0240	
	MBPT4	−0.0174	−0.0297	
	Total[f]	−0.1955	−0.2070	−0.105[h]
AtH	SCF	+0.1987 (−0.0982)	+0.1924 (−0.0974)	
	MBPT2	−0.1594	+0.1540	
	MBPT3	+0.1472	+0.1419	
	SDQ-MBPT4	+0.1454	+0.1412	
	MBPT4	+0.1396	+0.1330	
	Total[f]	+0.0414	+0.0356	

[a] The positive sign of the dipole moment corresponds to the polarity $+\mathrm{AH}_n-$. 1 a.u. of dipole moment = 2.5414 Debye

[b] The following geometries have been assumed in present calculations.

BiH_3: R(Bi-H) = 1.865 Å ≅ 3.52434, a.u., $\angle$HBiH = 90.3°, C_{3v} symmetry. Theoretical optimized geometry from RCI calculations of Dai and Balasubramanian [26]. The C_3 axis is the z axis of the coordinate system.

PoH_2: R(Po-H) = 1.835 Å ≅ 3.46765, a.u., $\angle$HPoH = 90.0°, C_{2v} symmetry. Theoretical optimized geometry from RCI calculations of Sumathi and Balasubramanian [27]. The molecule lies in the xz plane with the symmetry axis coinciding with the z axis of the coordinate system.

AtH: R(At-H) = 1.71 Å ≅ 3.23143, a.u. Theoretical bond distance as estimated by Lippincott and Dayhoff [28]. The $C_{\infty v}$ symmetry axis coincides with the z axis of the coordinate system

[c] For the explanation of symbols see text

[d] The standard (valence) polarized [20.17.14.5/13.11.8.2] basis set (see Appendix). The correlation contribution to the dipole moment has been calculated in the valence approximation (8 electrons correlated)

[e] The extended polarized [20.17.14.9/13.11.8.4] basis set (see Appendix and Table 1). The correlation contribution has been computed in the valence $+5d^{10}$ approximation (18 electrons correlated)

[f] Estimated total quasirelativistic dipole moment obtained as a sum of the non-relativistic MBPT4 result and the SCF HF relativistic correction [20]

[g] Theoretical dipole moment obtained from relativistic multireference CI (RCI) calculations by Dai and Balasubramanian [26]. The sign of the dipole moment reported by those authors has been changed to comply with the present convention. See text

[h] Theoretical dipole moment obtained from RCI calculations by Sumathi and Balasubramanian [27]

Similar discrepancies between the RCI data and MBPT4 results calculated with polarized basis sets have been, however, observed earlier [4, 5] for lighter hydrides. The existence of accurate experimental dipole moments for those molecules resolved them in favor of our calculations and proved the excellent performance of polarized basis sets in high-level-correlated studies of molecular dipole properties. In the case of the fourth-row hydrides [5] such comparisons have given strong support to the quasirelativistic method for the calculation of relativistic corrections [20].

It has been indicated [4, 5] that one of the sources of discrepancies between our MBPT4 results and the RCI data could be the unlinked [19] contributions to RCI dipole moments [31]. However, in the present case the corresponding corrections [19, 31], estimated from the fourth-order renormalization term in the Rayleigh–Schrödinger perturbation expansion, have been found to be negligible. A part of the observed discrepancies can be eventually explained by the use of the Hellmann–Feynman theorem [32] in RCI calculations of dipole moments. Also the basis sets used by Balasubramanian et al. [26, 27] may not be as flexible as those employed in the present study.

The large value of the estimated relativistic correction to dipole moments of BiH_3 and PoH_2 suggests that the relativistic effects may affect the electron correlation terms. This would lead to a mixed correlation-relativistic correction [33] whose sign is likely to be positive for both BiH_3 and PoH_2. However, it is not excluded that a part of the observed differences follows simply from the inadequacy of the quasirelativistic method applied to very heavy elements. Even so, the results obtained in this study of molecular dipole moments are quite acceptable. Future studies of other molecules involving heavy atoms may resolve the present ambiguities.

The results of the dipole polarizability calculations or AH_n are presented in Table 4. Since there are no other data for comparison, the present results will be only briefly analysed. Most of the dipole polarizability can be seen to follow from nonrelativistic SCF HF calculations. The electron correlation and relativistic corrections to SCF HF results are of little importance for separate components. However, one should note that the relativistic contribution is anisotropic, and thus, may significantly affect the nonrelativistic results for the polarizability anisotropy.

The dipole polarizability of AH_n is primarily predicted by the polarizability of the heavy atom. The A–H bonding results in near-spherical symmetry of polarizability tensors for the fifth-row atom hydrides as compared to relatively large anisotropy of atomic dipole polarizabilities (see Table 2). This effect has been already observed in lighter homologous hydrides and becomes even more pronounced for the present series of molecules.

The dipole moment and polarizability results can be complemented by the SCF HF data for molecular quadrupole moments [34]. For the standard (valence) polarized sets and the quadrupole moment origin at the heavy atom our nonrelativistic SCF HF values are as follows. BiH_3: $\Theta = \Theta_{zz} = -2.225$ a.u., PoH_2: $\Theta_{xx} = -3.920$ a.u., $\Theta_{yy} = 2.918$ a.u., $\Theta_{zz} = 1.002$ a.u., and AtH: $\Theta = \Theta_{zz} = 3.901$ a.u. For the extended polarized basis sets the corresponding results are -2.184 a.u. for BiH_3, -3.851 a.u., -2.860 a.u., and 0.990 a.u. for PoH_2, and 3.822 a.u. for AtH. The influence of the basis set extension is relatively small and confirms our earlier conclusions [4, 5, 8] concerning the reliability of nonrelativistic SF HF quadrupole moments computed with polarized basis sets.

Table 4. SCF HF and MBPT calculations of the dipole polarizability tensor ($\alpha_{\mu\nu}$) for the fifth-row hydrides. The SCF HF relativistic corrections are given in parentheses. All values in a.u.[a]

Molecule[b]	Method[c]	Basis set					
		Standard polarized[d]			Extended polarized[e]		
PbH_4[f]		$\alpha_{xx}=\alpha_{yy}=\alpha_{zz}$			$\alpha_{xx}=\alpha_{yy}=\alpha_{zz}$		
	SCF	43.67			44.16		
		(+2.33)			(+2.23)		
	MBPT2	45.55			46.38		
	MBPT3	45.30			45.85		
	SDQ-MBPT4	45.32			46.04		
	MBPT4	45.50			46.29		
	Total[g]	47.83			48.52		
BiH_3		$\alpha_{xx}=\alpha_{yy}$	α_{zz}		$\alpha_{xx}=\alpha_{yy}$	α_{zz}	
	SCF	55.84	55.10		55.65	55.21	
		(−2.22)	(−0.38)		(−2.25)	(−0.55)	
	MBPT2	56.05	56.45		55.27	56.60	
	MBPT3	55.89	56.27		55.34	56.08	
	SDQ-MBPT4	55.81	56.12		55.30	55.94	
	MBPT4	55.94	56.40		55.44	56.31	
	Total[g]	53.72	56.02		53.19	55.76	
PoH_2		α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}
	SCF	51.84	53.70	52.41	51.90	53.57	52.33
		(−2.15)	(−1.86)	(−1.02)	(−2.06)	(−1.84)	(−1.02)
	MBPT2	53.21	53.82	52.92	52.23	53.01	52.65
	MBPT3	53.28	53.61	53.08	52.62	53.15	52.51
	SDQ-MBPT4	53.26	53.55	52.92	52.36	53.00	52.34
	MBPT4	53.65	53.73	52.82	52.87	53.20	52.64
	Total[g]	51.50	51.87	51.80	50.81	51.36	51.62
AtH		$\alpha_{xx}=\alpha_{yy}$	α_{zz}		$\alpha_{xx}=\alpha_{yy}$	α_{zz}	
	SCF	41.86	44.55		41.91	44.48	
		(−2.08)	(−1.61)		(−2.05)	(−1.65)	
	MBPT2	42.44	45.22		41.63	44.39	
	MBPT3	42.57	44.95		42.16	44.60	
	SDQ-MBPT4	42.64	44.98		41.98	44.50	
	MBPT4	42.87	45.19		42.28	44.75	
	Total[g]	40.79	43.58		40.23	43.10	

[a] 1 a.u. of dipole polarizability = 0.14818 Å^3

[b–e] See corresponding footnotes to Table 3

[f] The bond distance of 1.742 Å ≅ 3.2919 a.u. follows from recent Dirac–Hartree–Fock calculations by Dyall et al. [29] and is close to other theoretical values [12]

[g] Estimated quasirelativistic values of the dipole polarizability obtained as a sum of non-relativistic MBPT4 results and SCF HF relativistic corrections

Our recent studies of the Group Ib hydrides have shown that their quadrupole moments can be considerably modified by the influence of relativistic effects [35]. For the present series of hydrides the relativistic corrections to quadrupole moments are (*i*) negligible for AtH (−0.016 a.u.), (*ii*) moderate for PoH_2 (−0.342 a.u. and +0.279 a.u. for Θ_{yy} and Θ_{zz}, respectively), and (*iii*) large for

BiH_3 (+0.678 a.u.). All those results have been obtained with the extended polarized basis sets and the calculated changes reflect the increasing metallic character of the heavy atom.

This completes the illustration of the performance of polarized basis sets derived in this study for the fifth-row atoms. With limited amount of sufficiently accurate data for comparisons, the conclusions presented in Sect. 5, cannot be that firm as those obtained for lighter atoms. Most of the results discussed in this section appear, however, to be internally consistent and acceptable.

5. Summary and conclusions

The first-order polarized basis sets have been generated for Pb, Bi, Po, and At by applying the basis set polarization method [6] and some complementary rules [1, 2, 5] to energy-optimized GTO basis sets of Gropen [14]. The so-called standard [20.17.14.5/13.11.8.2] polarized basis sets have been devised for the purpose of valence-shell calculations. To account for the core-polarization effect the extended [20.17.14.9/13.11.8.4] polarized basis sets have been obtained by using the same approach [5].

The validity of the assumed contraction schemes has been examined in calculations of atomic dipole polarizabilities. It has been shown that the Raffenetti-type contractions used for deep-core orbitals lead to negligible changes in atomic polarizabilities as compared with the values computed in fully uncontracted basis sets. The calculated atomic dipole polarizabilities for the Pb through At are the most accurate nonrelativistic SCF HF results calculated for those atoms.

The pilot atomic calculations have also included a study of relativistic effects on the dipole polarizability within a quasirelativistic approach used in our earlier papers [20]. Although this approach does not account for the spin-orbit contribution, very encouraging results have been obtained for At. The present data have been found to be in good agreement with explicitly relativistic calculations on At by Stevens and Krauss [23]. Thus one can expect that the quasirelativistic approximation may lead to realistic estimates of relativistic contributions to electric properties of closed shell molecules for which the spin-orbit coupling terms should be of lesser importance. The relativistic contributions to atomic dipole polarizabilities have been shown to insignificantly depend on the basis set contraction and composition. They have been found to be essentially the same for both the standard and extended polarized sets.

It is interesting to note that the relativistic contribution to atomic dipole polarizabilities has (for rotationally averaged values) the largest value for Pb and diminishes along the series of atoms. One concludes that for molecules involving the studied fifth-row atoms the largest effect on their electric properties is to be expected for lead compounds.

The testing of the performance of polarized basis sets in molecular calculations has been carried out for the standard series of AH_n closed-shell hydrides. The dipole moments and dipole polarizabilities of those molecules have been calculated at the SCF HF and different correlated levels of approximation. The relativistic contribution to those properties has been estimated within the quasirelativistic SCF HF method [20]. The results obtained for dipole moments of BiH_3 and PoH_2 have been compared with the RCI data of Balasubramanian et al. [26, 27]. Our results differ from the RCI data by about 0.05 a.u. for BiH_3

and by about 0.1 a.u. for PoH_2. The possible sources of those discrepancies have been investigated.

It is clear that both the RCI and the present approach involve a variety of approximations, each of them being approximate in a different way. Hence, if one considers the RCI data as a benchmark for our results, the performance of the derived polarized basis sets can be classified as good enough to predict the magnitude of relativistically-corrected electric properties for molecules involving the fifth-row atoms. With the growing interest in properties of heavy elements and their compounds the basis sets generated in this study are a useful supplement to those already available for lighter atoms.

To summarize the results of our molecular calculations let us mention the following general features of the computed dipole moments and polarizabilities. In general, the electron correlation contribution to those properties has been found to be relatively small and in particular much less important than the estimated relativistic contributions. The core-polarization contribution to dipole moments might be of some importance for BiH_3 while being negligible for PoH_2 and AtH. One can expect that in the case of polar compounds of lead the role of core-polarization effects will be significant. On the other hand, corrections to nonrelativistic SCF HF dipole moments of such compounds will be dominated by relativistic terms.

For molecular dipole polarizabilities their total values are reasonably well predicted in the nonrelativistic SCF HF approximation; both the electron correlation and relativistic corrections constituting at most a few percent of our final quasirelativistic MBPT4 results. The polarizability data of AH_n molecules studied in this paper are not expected to be significantly modified by improvements in either basis sets or methods used for their calculation. The present data provide the recommended dipole polarizability values for molecules studied in this paper.

As shown by the cross-examination of different basis sets and methods, the polarized sets generated in this study are likely to perform well in high-level-correlated nonrelativistic calculations of electric properties. No firm conclusion can be drawn with respect to their performance in relativistic calculations. The quasirelativistic results of this paper show, however, that a significant portion of relativistic contributions to dipole moments of heavy molecules can be recovered.

The basis sets derived in this study open the possibility of accurate nonrelativistic and quasirelativistic investigations on electric properties of the heavy element compounds. Though still quite exotic, such systems are widely investigated experimentally [10, 11]. Of particular interest appears to be the study of the electronic structure and properties of simple molecules involving lead, e.g., lead chalcogenides, whose importance is well recognized in chemistry and physics.

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Appendix

The details of polarized basis sets generated in this paper for Pb, Bi, Po, and At are given in Tables A.1–A.4. Those so-called standard polarized basis sets are recommended for SCF HF calculations and for valence-only correlated studies. The extended basis sets can be obtained by adding the *f*-type polarization functions listed in Table 1. Those extended sets are recommended for calculations of molecular dipole moments and polarizabilities including the correlation contributions due to the next-to-valence shells of heavy atoms.

The basis sets for Pb through At constitute a part of the basis set library of the MOLCAS system [16].

Table A.1. First-order polarized [2.17.14.5/13.11.8.2] GTO/CGTO basis set for lead

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1−5	10208720.	.000053	.000018	.000008	−.000004	.000002
2		1526905.4	.000414	.000139	.000066	−.000033	.000015
3		340584.61	.002254	.000750	.000358	−.000180	.000079
4		93707.809	.009797	.003316	.001574	−.000791	.000348
5		29681.270	.035825	.012184	.005854	−.002936	.001294
6		10426.952	.108954	.039603	.018956	−.009560	.004212
7		3976.0750	.259539	.103773	.051372	−.025912	.011437
8		1618.7788	.403197	.218069	.110497	−.056689	.025065
9		687.51568	.292833	.209559	.121050	−.062846	.027992
10		236.73026	.041742	−.379078	−.314517	.176533	−.080193
11		109.40898	−.010503	−.699172	−.749570	.481225	−.224590
12		36.201095	.006596	−.162716	.531008	−.618645	.327030
13	6	20.657198	1.				
14	7	7.7462394	1.				
15	8	4.2299116	1.				
16	9	1.6749791	1.				
17	10	.77134800	1.				
18	11	.18549969	1.				
19	12	.07096126	1.				
20	13	.02714560	1.				
p subset							
1	1−4	18767.709	.001818	.000921	.000462	.000191	
2		80209.616	.000199	.000101	.000050	.000021	
3		5937.3450	.010840	.005562	.002770	.001158	
4		2195.7001	.047836	.025030	.012646	.005255	
5		901.63193	.154719	.085243	.043161	.018127	
6		398.72506	.338120	.200405	.104776	.043775	
7		185.55823	.410593	.253055	.130352	.055603	
8		88.685407	.192404	−.089194	−.081909	−.040816	
9		43.240355	.016074	−.600736	−.515040	−.235871	
10		21.610825	.001637	−.395368	−.185725	−.078931	
11	5	9.8681563	1.				
12	6	4.7934843	1.				
13	7	1.8299713	1.				
14	8	.76161271	1.				
15	9	.17869533	1.				
16	10	.05933931	1.				
17	11	.01970479	1.				
d subset							
1	1−2	5267.6211	.000490	.000266			
2		1479.6313	.005982	.003071			
3		512.28876	.043403	.023559			
4		197.65006	.192372	.103802			
5		81.969436	.442704	.249731			
6		35.648486	.428531	.111588			
7	3	14.258977	1.				
8	4	5.9519853	1.				
9	5	1.8458420	1.				
10	6	.60512269	1.				
11	7	.76161	−.15306				
12		.17870	1.06715				
13	8	.05934	2.23554				
14		.01970	1.35723				
f subset							
1	1	163.05935	.025734				
2		54.230856	.151327				
3		21.148600	.389126				
4	2	8.4336050	.487679				
5		3.1331156	.250481				

Table A.2. First-order polarized [2.17.14.5/13.11.8.2] GTO/CGTO basis set for bismuth

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	10176927.	.000055	.000018	.000009	−.000004	.000002
2		1515322.0	.000430	.000144	.000069	−.000035	.000015
3		339566.67	.002323	.000733	.000370	−.000186	.000083
4		93880.328	.010032	.003401	.001616	−.000815	.000364
5		29878.560	.036436	.012394	.005967	−.003006	.001344
6		10530.252	.110501	.040280	.019294	−.009755	.004359
7		4017.6218	.262487	.105139	.052198	−.026462	.011857
8		1637.7872	.403057	.219905	.111518	−.057322	.025697
9		698.12863	.288545	.205129	.119363	−.062490	.028298
10		240.11366	.040672	−.386757	−.324889	.184445	−.085261
11		111.50704	−.010370	−.694483	−.740633	.475357	−.224881
12		35.736259	.006816	−.167794	.611487	−.708026	.380099
13	6	20.458210	1.				
14	7	8.4921587	1.				
15	8	4.7032570	1.				
16	9	1.7072317	1.				
17	10	.82739050	1.				
18	11	.22583838	1.				
19	12	.08054797	1.				
20	13	.02872840	1.				
p subset							
1	1–4	18757.914	.001906	.000967	.000487	.000206	
2		80110.813	.000208	.000105	.000053	.000022	
3		5934.2456	.011254	.005784	.002893	.001233	
4		2208.5978	.049019	.025720	.013050	.005527	
5		909.37420	.157864	.087211	.044366	.018996	
6		402.47944	.342047	.203618	.106966	.045557	
7		187.37659	.409384	.251485	.129953	.056532	
8		89.390242	.186616	−.102653	−.092124	−.046524	
9		43.731648	.013966	−.606419	−.523768	−.244856	
10		21.867500	.001957	−.383247	−.166996	−.070585	
11	5	10.048275	1.				
12	6	4.9120633	1.				
13	7	1.9165877	1.				
14	8	.81766057	1.				
15	9	.20717706	1.				
16	10	.07151496	1.				
17	11	.02468608	1.				
d subset							
1	1–2	5222.3946	.000531	−.000290			
2		1461.8129	.006503	−.003364			
3		506.30576	.046572	−.025453			
4		195.99131	.201558	−.109595			
5		81.647826	.448912	−.254545			
6		35.745524	.415597	−.096211			
7	3	14.420430	1.				
8	4	6.0895161	1.				
9	5	1.9441886	1.				
10	6	.65797307	1.				
11	7	.81766	.15948				
12		.20718	−1.12750				
13	8	.07151	−1.88749				
14		.02469	−1.08192				
f subset							
1	1	162.96888	.027833				
2		54.323144	.160089				
3		21.276302	.398533				
4	2	8.5579530	.480991				
5		3.2265185	.233999				

Table A.3. First-order polarized [2.17.14.5/13.11.8.2] GTO/CGTO basis set for polonium

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	10147462.	.000057	.000019	.000009	.000005	−.000002
2		1508418.1	.000445	.000149	.000071	.000036	−.000016
3		339064.81	.002388	.000796	.000381	.000192	−.000087
4		94389.636	.010204	.003459	.001648	.000834	−.000378
5		30204.647	.036905	.012578	.006054	.003060	−.001387
6		10661.010	.111821	.040773	.019596	.009946	−.004507
7		4075.3468	.263670	.106048	.052610	.026752	−.012151
8		1667.3611	.402068	.219615	.111980	.057810	−.026289
9		712.69345	.286478	.205151	.118645	.062243	−.028561
10		246.61525	.040474	−.388928	−.322555	−.183370	.085891
11		114.51769	−.010641	−.687619	−.749983	−.485152	.233175
12		39.773182	.006979	−.159574	.469175	.538067	−.291375
13	6	22.757103	1.				
14	7	8.9256617	1.				
15	8	4.9559058	1.				
16	9	1.8437346	1.				
17	10	.90851021	1.				
18	11	.23961861	1.				
19	12	.09481913	1.				
20	13	.03752074	1.				
p subset							
1	1–4	18704.791	.001982	.001008	.000509	−.000219	
2		79719.133	.000220	.000112	.000056	−.000024	
3		5963.7221	.011593	.005968	.002999	−.001300	
4		2225.6930	.050109	.026361	.013428	−.005791	
5		920.88730	.159515	.088335	.045152	−.019668	
6		408.94093	.343568	.205236	.108265	−.046967	
7		190.63085	.408437	.250487	.130028	−.057487	
8		90.886142	.183704	−.109220	−.097925	.049989	
9		44.638647	.012835	−.607591	−.527115	.251790	
10		22.370667	.002226	−.377977	−.162772	.068332	
11	5	10.382566	1.				
12	6	5.1125154	1.				
13	7	2.0571713	1.				
14	8	.90034222	1.				
15	9	.24718975	1.				
16	10	.08349407	1.				
17	11	.02820206	1.				
d subset							
1	1–2	5107.5638	.000595	−.000325			
2		1423.6732	.007260	−.003793			
3		495.24132	.050621	−.027821			
4		193.41200	.210891	−.115709			
5		81.366679	.452003	−.256933			
6		35.996808	.402067	−.084245			
7	3	14.780874	1.				
8	4	6.3216393	1.				
9	5	2.0895515	1.				
10	6	.72669572	1.				
11	7	.90034	−.18121				
12		.24719	1.07647				
13	8	.08349	1.80647				
14		.02820	.84389				
f subset							
1	1	163.22891	.029854				
2		54.719457	.166927				
3		21.619694	.403180				
4	2	8.7952535	.474850				
5		3.3628341	.223378				

Table A.4. First-order polarized [2.17.14.5/13.11.8.2] GTO/CGTO basis set for astatine

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	10091062.	.000059	.000020	–.000009	–.000005	–.000002
2		1502667.9	.000460	.000154	–.000074	–.000037	–.000017
3		339957.12	.002439	.000813	–.000390	–.000198	–.000091
4		94893.604	.010456	.003549	–.001692	–.000859	–.000394
5		30337.438	.037678	.012850	–.006197	–.003142	–.001444
6		10744.494	.113530	.041497	–.019960	–.010167	–.004668
7		4109.6703	.266874	.107642	–.053547	–.027320	–.012577
8		1684.0699	.401979	.221361	–.112987	–.058567	–.026988
9		721.86706	.281844	.201166	–.117175	–.061673	–.028698
10		250.38251	.038780	–.398468	.333755	.190597	.090571
11		116.32881	–.010026	–.682762	.743936	.484629	.236252
12		39.944751	.006495	–.155626	–.518142	–.602598	–.331878
13	6	22.833203	1.				
14	7	8.8768669	1.				
15	8	4.9668397	1.				
16	9	1.9445859	1.				
17	10	.96935840	1.				
18	11	.26999310	1.				
19	12	.10755789	1.				
20	13	.04284813	1.				
p subset							
1	1–4	18709.470	.002063	.001051	.000533	–.000233	
2		79695.936	.000229	.000117	.000059	–.000026	
3		5979.7809	.011991	.006181	.003120	–.001376	
4		2237.2501	.051481	.027165	.013892	–.006089	
5		927.73469	.162690	.090304	.046382	–.020554	
6		412.64004	.347083	.208334	.110373	–.048663	
7		192.51291	.406897	.248158	.129261	–.058203	
8		91.600505	.178294	–.121116	–.107669	.055945	
9		45.312523	.010798	–.608440	–.530290	.257261	
10		22.788781	.002702	–.369422	–.154502	.066460	
11	5	10.729663	1.				
12	6	5.3312557	1.				
13	7	2.1471083	1.				
14	8	.95791244	1.				
15	9	.27541427	1.				
16	10	.09321300	1.				
17	11	.03154762	1.				
d subset							
1	1–2	4999.7298	.000660	–.000362			
2		1397.8562	.007933	–.004175			
3		489.10601	.054024	–.029889			
4		192.25790	.219105	–.121108			
5		81.338354	.456102	–.260291			
6		36.195417	.390522	–.070197			
7	3	14.985560	1.				
8	4	6.4715217	1.				
9	5	2.1877427	1.				
10	6	.77863648	1.				
11	7	.95791	–.17760				
12	8	.27541	1.09285				
13	9	.09321	1.67313				
14	10	.03155	.65759				
f subset							
1	1	164.62329	.031571				
2		55.288695	.173947				
3		21.906243	.410650				
4	2	8.9715446	.468875				
5		3.4730438	.210258				