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

V. Fourth-row atoms: Sn through I

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Abstract. The basis set polarization method is used to generate the first-order polarized basis sets for Sn, Sb, Te, and I. The standard (spd) and extended (spdf) versions of those basis sets are derived for the purpose of calculations of dipole moments and dipole polarizabilities for molecules involving the fourth-row atoms. The verification of the performance of the generated polarized basis sets is achieved mainly by a cross-examination of different atomic and molecular results calculated in this paper. The role of the core-polarization and relativistic effects is investigated. It is shown that the relativistic contribution to dipole moments of the fourth-row hydrides is commensurate with the contribution due to electron correlation and must be explicitly considered in accurate calculations. The detailed basis set data for Sn through I are presented in the Appendix.

Key words: Polarized basis sets – Molecular electric properties – Relativistic effects on electric properties – Dipole polarizabilities of Sn, Sb, Te, and I – Dipole moments and polarizabilities of the fourth-row atom hydrides (SnH_4, SbH_3, H_2Te, HI) – Core-polarization effects

1. Introduction

Over the past few years a series of relatively small yet highly efficient contracted Gaussian (CG) basis sets has been developed in this laboratory [1–4] for the purpose of accurate, high-level-correlated calculations of molecular electric properties. All of those GTO/CGTO (Gaussian Type Orbital) basis sets (H, C, N, O, F [1, 2]; Si, P, S, Cl [2], Li, Na, K, Rb, Be, Mg, Ca, Sr [3], Ge, As, Se, Br [4]) have been generated from standard, 2-zeta-type energy-optimized sets of atomic functions, by using the basis set polarization method [1, 5]. Their generation is facilitated by a set of rules [1, 2] which can be applied to any given initial GTO basis set. The corresponding details can be found in [1–4].

The performance of the so-called medium-size polarized basis sets for the first-, second-, and third-row atoms has been well documented in molecular calculations of dipole moments and dipole polarizabilities performed at the SCF HF (self-consistent field Hartree–Fock) and different correlated levels of approximation [1, 2, 4]. Also, the calculated quadrupole moments turn out to be exceptionally good [6]. In the case of the alkali and alkaline-earth atoms [3], a similar documentation has been achieved in terms of excellent results for the major electric dipole properties of diatomic hydrides [3] and other molecules [7]. Another area of applications is represented by the recent studies of molecular interactions [8, 9].

In the present paper, the basis set polarization method [5] is used for the generation of polarized basis sets for Sn, Sb, Te, and I. The growing interest in the electronic structure and properties of molecules containing heavy atoms [10, 11] appears to make this extension of our previous studies worthwhile and timely. Most details of the basis set generation method employed in this paper are virtually the same as those discussed earlier [3]. Some of them, which are relevant for the present study, will be surveyed in Sect. 2. The documentation of the performance of the derived basis sets in atomic calculations is given in Sect. 3. In contrast to the evaluation of atomic data carried out in our earlier papers [1–3], there are hardly any accurate values available for dipole polarizabilities of the atoms considered in this paper. This limits our conclusions concerning the performance of those basis sets. The same also applies to the majority of the molecular results for dipole moments and polarizabilities of simple hydrides (SnH_4, SbH_3, TeH_2, and HI) that are presented in Sect. 4. Only in the case of HI can the computed dipole moment be compared with a reliable experimental value. Thus, certain conclusions will be based on those derived earlier [1–4, 6, 7, 9] and on the uniform character of the method used to generate the polarized basis sets.

The rather high nuclear charge of the fourth-row atoms makes relativistic effects [12, 13] non-negligible. Those effects have been already discussed for the third-row atoms and their compounds [4]. In the present paper the relativistic contribution to electric dipole properties is investigated at both atomic (Sect. 3) and molecular (Sect. 4) levels by using a recently developed quasirelativistic approach [14, 15].

The conclusions of this study are presented in Sect. 5. The basis sets generated for the fourth-row atoms are tabulated in the Appendix. They are a part of the standard basis set library of the second release [16] of the MOLCAS system of quantum chemistry programs [17] developed in this laboratory.

2. The generation of polarized basis sets

The general strategy used to generate the so-called polarized basis sets closely follows that employed in our earlier studies [1–4]. The initial basis sets for the fourth-row atoms are the energy-optimized and fully uncontracted (18.14.8) GTO sets of Huzinaga [18]. The reduction of their size is accomplished by their contraction to the 2-zeta size [18.14.8/10.8.4]. Following the experience gained during the generation of polarized sets for the third-row atoms, we have employed the Raffenetti [19], rather than the standard segmented, contraction scheme: 13 highest-exponent GTO's of the *s* subset have been contracted to 5 CGTO's, 10 highest-exponent *p*-type GTO's have been contracted to 4 CGTO's, and all *d*-type GTO's of the primitive set have been converted into two groups of two CGTO's. The contraction coefficients follow from the occupied SCF HF atomic orbitals determined in the primitive GTO set of the given atom. The details can be read from the Tables that append this paper. The use of the Raffenetti-type contraction minimizes the energy loss which accompanies the

Table 1. The *f*-type polarization functions for the fourth-row atoms derived using the basis set polarization method applied to 4*d* atomic orbitals

GTO	CGTO	Sn		Sb		Te		I	
		α_i[a]	c_i[b]	α_i[a]	c_i[b]	α_i[a]	c_i[b]	α_i[a]	c_i[b]
1	1	6.28011	0.010380	6.83812	0.007635	7.39940	0.005371	7.81544	0.003896
2		2.77694	0.242860	3.06085	0.231355	3.34930	0.220977	3.74282	0.197839
3	2	1.15345	0.473750	1.29517	0.451003	1.44359	0.429852	1.65959	0.408254
4		0.42870	0.350400	0.49325	0.312806	0.56017	0.283734	0.65266	0.275083

[a] Orbital exponent of the *i*-th *f*-type GTO

[b] Contraction coefficient for the *i*-th *f*-type GTO

contraction procedure. Those contractions can be efficiently handled by the MOLCAS integral package [16].

The [18.14.8/10.8.4] GTO/CGTO sets have been then extended by one diffuse *s*-type GOT and one diffuse *p*-type GTO [1, 2], the orbital exponents (see Appendix) being determined from the corresponding approximate even-tempered sequences. The basis set polarization method [1, 5] has been applied to those contracted sets through the first-order terms with respect to the electric field strength [20]. By analogy with our previous studies it was anticipated that the polarization set comprising 4 *d*-type functions could be contracted to two *d*-type CGTO's. The contraction coefficients follow directly from the basis set polarization method and SCF HF calculations on the negative ion corresponding to the given atom [1, 2, 5]. The resulting (first-order) polarized basis sets of the size [19.15.12/11.9.6] are given in the Appendix. They will be hereafter referred to as the medium-size polarized sets. Taking into account the size of atoms considered in this paper and the dimension of the original GTO sets, the term 'medium-size', used in a relative sense, appears to still be appropriate. However, when compared with what is termed the medium size sets for the first- and second-row atoms, the present basis sets turn out to be rather large.

Polarizing only the *s* and *p* shells of atoms may not be sufficient in the present case. In order to investigate the effect of the field-induced polarization of *d* shells an extended (*spdf*) basis set has been generated. The basis set polarization method has been applied to the 4*d* shell [1, 4, 5] and gave a set of 4 *f*-type GTO's, contracted afterwards to two CGTO's. The corresponding orbital exponents and contraction coefficients, which have been derived according to the same method as that used to obtain the standard (valence) polarized basis sets, are presented in Table 1. They complement the basis set data given in the Appendix. In addition to the [19.15.12.4/11.9.6.2] GTO/CGTO polarized basis set, we have also investigated its fully uncontracted (19.15.12.4) counterpart. All four polarized basis sets, i.e., the uncontracted GTO and contracted GTO/CGTO sets, are examined in Sect. 3 with respect to their performance in the calculation of atomic dipole polarizabilities.

3. Atomic dipole polarizabilities

The appropriateness of basis sets derived in this study for calculations of molecular dipole properties can be to a large extent concluded from their performance at the atomic level. For most atoms investigated in our previous paper we could profit from the existence of reliable reference values for atomic dipole polarizabilities. No such data seem to be available for the fourth-row atoms. The tabulated and recommended [21, 22] dipole polarizabilities of those atoms follow from highly approximate calculations of Thorhallsson et al. [23] and do not seem to be worth referring to. Their inaccuracy is virtually undetermined [22]. Hence, the validation of the present polarized basis sets has to go through the internal examination of the stability of calculated dipole polarizabilities with respect to different basis set extensions and modifications.

We have carried out [16, 17] the SCF HF dipole polarizability calculations for the ground electronic states of Sn, Sb, Te, and I in both the fully uncontracted (19.15.12) polarized GTO basis set and in the [19.15.12/11.6.9] GTO/CGTO set derived in Sect. 2. The results of those calculations, which follow the method used in our previous studies [1–4], are compiled in Table 2. The first two columns of the dipole polarizability data of Table 2 indeed show that there is virtually no deterioration of our results upon contracting the primitive set. Thus, one can conclude that the contraction scheme used for the generation of those (*spd*) polarized sets is appropriate for the present purposes.

The use of (*spd*) polarized sets eliminates, however, most of the possible effect due to the response of *d* shells of the fourth-row atoms. In order to investigate this effect we have repeated all calculations with the uncontracted (19.15.12.4) and contracted [19.15.12.4/11.9.6.2] (*spdf*) sets described in Sect. 2. The corresponding results are presented in the last two columns of Table 2. It can be concluded from those data that the (field-induced) polarization of *d* shells

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

Atom	State		Basis set[a]			
			(19.15.12)	[19.15.12/11.9.6][b]	(19.15.12.4)	[19.15.12.4/11.9.6.2]
Sn	^3P	$M_L = 0$	50.76	50.28	51.08	50.58
			(−3.36)[c]	(−3.36)	(−3.25)	(−3.47)
		$M_L = \pm 1$	63.23	62.72	63.25	62.72
			(−1.24)	(−1.29)	(−1.21)	(−1.26)
Sb	^4S	$M_L = 0$	45.47	44.99	45.49	44.99
			(−1.56)	(−1.60)	(−1.58)	(−1.58)
Te	^3P	$M_L = 0$	43.10	42.97	42.97	43.02
			(−0.04)	(−0.08)	(−0.03)	(−0.08)
		$M_L = \pm 1$	36.96	36.77	36.91	36.75
			(−1.23)	(−1.28)	(−1.23)	(−1.27)
I	^2P	$M_L = 0$	30.26	30.18	30.25	30.18
			(−1.00)	(−1.05)	(−1.01)	(−1.03)
		$M_L \pm 1$	33.55	33.50	33.53	33.54
			(−0.30)	(−0.33)	(−0.34)	(−0.31)

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

[b] The standard first-order polarized (*spd*) basis set

[c] Approximate relativistic correction calculated according to [14]. This correction does not include the spin-orbit interaction term. See text

makes hardly any contribution to total dipole polarizabilities at the SCF HF level of approximation. However, the present SCF HF atomic data do not tell anything about the core-polarization effects [24] which are likely to affect the polarizability values at the correlated levels of approximation [3]. This will be investigated in the context of our molecular calculations of dipole moments and dipole polarizabilities.

The relatively large nuclear charge of atoms considered in this paper can lead to a significant relativistic contribution to their electric properties [12]. In order to gain some idea about the size of those effects in future molecular calculations we have computed approximate relativistic corrections to the dipole polarizability of all four atoms. The results, which correspond to the first-order quasirelativistic approach [14], based on the so-called Cowan–Griffin Hamiltonian [25], are shown in Table 2. They are not meant to be fully representative of the total relativistic contribution to atomic dipole polarizabilities, since the spin-orbit and several other terms are not included in the Cowan–Griffin approximation. On the other hand, in calculations of electric properties of closed-shell molecules, the major part of the relevant relativistic correction comes from the two terms (the mass-velocity and Darwin corrections) considered in the present atomic study. It is therefore quite pleasing to note that this relativistic contribution evaluated at the level of the SCF HF approximation is almost independent of both the contraction of GTO basis sets and their extension by the *f*-type polarization functions.

According to the results presented in Table 2, one can expect a satisfactory performance of (*spd*) GTO/CGTO polarized basis sets in SCF HF molecular calculations of electric dipole properties. Using larger and computationally more demanding (*spdf*) GTO/CGTO sets would only marginally change the corresponding SCF HF data. However, the extended basis sets might be indispensable for accurate calculations of molecular dipole moments and polarizabilities at the correlated level of approximation. Let us also mention that the present atomic SCF HF data for dipole polarizabilities should be considered as the current most accurate reference values. Their negligibly small dependence on the basis set variation and the general uniformness of polarized basis sets [1-4] indicate that the atomic data presented in Table 2 should be very close to the corresponding HF limits.

4. Molecular dipole moments and polarizabilities: SnH_4, SbH_3, H_2Te, and HI

In our earlier papers [1–4] the calculation of dipole moments and polarizabilities of simple hydrides AH_n served as a measure of the performance of the derived basis sets. In the case of the fourth-row atoms even the reference dipole moment data for the AH_n hydrides are very scarce. Thus, the present calculations are considered to a large extent as an attempt to predict the basic electric properties of those molecules.

The dipole moment results obtained in this paper are collected in Table 3. A similar compilation of the dipole polarizability data is given in Table 4. All calculations have been carried out at the experimental equilibrium geometries as indicated in the Tables. The calculated data comprise the SCF HF and different correlated results. The details of those calculations are virtually the same as those given in earlier papers of this series [1–4].

The electron correlation contribution to molecular dipole properties has been estimated by using the many-body perturbation theory (MBPT) methods

Table 3. SCF HF and MBPT calculations of dipole moments for the fourth-row hydrides. The relativistic corrections estimated at the level of the SCF HF approximation are shown in parentheses. All values in a.u.[a]

Molecule[b]	Method[c]	Basis set	
		(*spd*)[d]	(*spdf*)[e]
SbH_3[f]	SCF	0.0039 (−0.0796)	−0.0139 (−0.0813)
	MBPT2	−0.0326	−0.0790
	MBPT3	−0.0472	−0.0787
	SDQ-MBPT4	−0.0482	−0.0739
	MBPT4	−0.0482	−0.0730
H_2Te[g]	SCF	0.1755 (−0.0622)	0.1650 (−0.0624)
	MBPT2	0.1273	0.1095
	MBPT3	0.1145	0.1004
	SDQ-MBPT4	0.1129	0.1026
	MBPT4	0.1084	0.0977
HI[h]	SCF	0.2625 (−0.0394)	0.2571 (−0.0393)
	MBPT2	0.2215	0.2188
	MBPT3	0.2137	0.2075
	SDQ-MBPT4	0.2109	0.2062
	MBPT4	0.2049	0.1993

[a] 1 a.u. of dipole moment = 2.5414 debye

[b] The following experimental equilibrium geometries have been used. SbH_3: $R(\mathrm{Sb-H}) = 1.7039$ Å $\simeq 3.2199$ a.u., $\sphericalangle \mathrm{HSbH} = 91.6°$ [29], C_{3v} symmetry. The symmetry axis coincides with the z axis of the coordinate system. H_2Te: $R(\mathrm{Te-H}) = 1.658$ Å $\simeq 3.1332$ a.u., $\sphericalangle \mathrm{HTeH} = 90.25°$ [30], C_{2v} symmetry. The molecule lies in the xz plane of the coordinate system with the z axis coinciding with the C_2 symmetry axis. HI: $R(\mathrm{H-I}) = 1.609$ Å $\simeq 3.040$ a.u. [31], $C_{\infty v}$ symmetry. The main symmetry axis is the z axis of the coordinate system. The positive sign of the dipole moment means that dipole's positive end is oriented towards the hydrogen atom(s)

[c] For the explanation of symbols see text. The values in parentheses are the first-order relativistic corrections to the SCF HF dipole moments [14]. The other data are the total dipole moments as computed according to the given approximation. To obtain the final estimates the relativistic correction has to be added

[d] The standard [19.15.12/11.9.6] polarized GTO/CGTO basis sets developed in this paper are used for the heavy atom. The hydrogen basis set is the [6.4/3.2] polarized GTO/CGTO set taken from [1, 2]. Only the valence shell correlation effects are included at the level of the MBPT treatment

[e] The extended [19.15.12.4/11.9.6.2] polarized basis set developed in this study is used for the heavy atom. The hydrogen basis set is the [6.4/3.2] polarized GTO/CGTO set taken from [1, 2]. The correlated level calculations correspond to correlating the valence and $4d^{10}$ shells

[f] Neither experimental nor theoretical dipole moment data appear to be available

[g] The dipole moment of H_2Te has been recently calculated by Sumathi and Balasubramanian [32] in the relativistic MR CI approach based on the use of relativistic core pseudopotentials. Their value of 0.105 a.u. is about 0.06 a.u. higher than the present relativistically corrected MBPT4 result for the (*spdf*) polarized basis set. See text

[h] The experimental value of the HI dipole moment is 0.1760 a.u. [33]. A survey of different theoretical data can be found in [14]. See text

[26, 27]. Our calculations have been performed [16, 17, 27] at the level of the second, third-, and complete fourth-order approximation in the MBPT expansion. Those are referred to by MBPT2, MBPT3, and MBPT4 symbols, respectively. This sequence of the correlated MBPT results provides useful information

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

Molecule[b]	Method[c]	Basis set					
		$(spd)^d$			$(spdf)^e$		
SnH_4[f]		$\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$			$\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$		
	SCF	41.27			41.66		
		(+0.86)			(+0.88)		
	MBPT2	42.46			43.70		
	MBPT3	42.60			43.30		
	MDQ-MBPT4	42.63			43.44		
	MBPT4	42.76			43.66		
SbH_3		$\alpha_{xx} = \alpha_{yy}$	α_{zz}		$\alpha_{xx} = \alpha_{yy}$	α_{zz}	
	SCF	46.51	46.59		46.35	46.65	
		(−0.64)	(−0.06)		(−0.71)	(−0.11)	
	MBPT2	47.00	47.96		46.31	47.97	
	MBPT3	46.86	47.78		46.32	47.52	
	SDQ-MBPT4	46.78	47.63		46.28	47.38	
	MBPT4	46.89	47.86		46.41	47.68	
H_2Te		α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}
	SCF	43.29	43.93	42.72	43.19	43.96	42.67
		(−0.50)	(−0.38)	(−0.22)	(−0.50)	(−0.36)	(−0.22)
	MBPT2	43.76	45.40	43.61	43.09	44.59	43.25
	MBPT3	43.59	45.39	43.46	43.16	44.78	43.10
	SDQ-MBPT4	43.51	45.31	43.37	43.03	44.53	42.96
	MBPT4	43.67	45.61	43.57	43.20	44.88	43.19
HI[g]		$\alpha_{xx} = \alpha_{yy}$	α_{zz}		$\alpha_{xx} = \alpha_{yy}$	α_{zz}	
	SCF	34.48	37.03		34.50	36.99	
		(−0.39)	(−0.34)		(−0.39)	(−0.34)	
	MBPT2	35.24	37.64		34.68	37.18	
	MBPT3	35.29	37.53		34.97	37.25	
	SDQ-MBPT4	35.30	37.52		34.80	37.15	
	MBPT4	35.49	37.70		35.02	37.34	

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

[b–e] See the corresponding footnotes to Table 3

[f] Experimental equilibrium geometry: R(Sn–H) = 1.7108 Å ≃ 3.2329 a.u. [30], T_d symmetry

[g] The non-relativistic SCF and MBPT4 results of [14] for the parallel component (α_{zz}) of the dipole polarizability tensor are 37.13 a.u. and 38.15 a.u., respectively. The SCF HF first-order relativistic correction of [14] is −0.31 a.u. See text

concerning the convergence of the electron correlation perturbation series for the investigated properties. Another estimate of the expected accuracy of the highest-order, i.e., MBPT4, results is given by their comparison with those obtained in an approximate fourth-order approach, which is based on singly-, doubly-, and quadruply-substituted intermediate states (SDQ-MBPT4). The difference between the MBPT4 and SDQ-MBPT4 data is equal to the fourth-order contribution due to triply-substituted intermediate states [26] and gives an approximate measure of their importance in higher-order approximations [26]. As shown by the data of Tables 3 and 4 this difference is indeed small and provides an estimate of error bounds for MBPT4 corrections to dipole moments and polarizabilities.

The MBPT correlation contributions to molecular electric properties have been studied at two levels of approximation with respect to the number of explicitly correlated electrons. The standard (*spd*) polarized GTO/CGTO set derived in Sect. 2 has been used for MBPT studies in the valence approximation (8 correlated electrons). With the (*spdf*) polarized GTO/CGTO set the $4d^{10}$ shell has been included at the correlated level of approximation (18 correlated electrons). The latter case corresponds to the explicit treatment of the core and core-valence correlation contribution to molecular electric properties.

As shown by the dipole moment data the basis set extension gives a negative contribution at the SCF HF level which varies from about -0.005 a.u. for HI to about -0.018 a.u. for SbH_3, indicating the increasing polarization of the $4d^{10}$ shell. The net core-polarization (correlation) effect, as estimated at the level of the MBPT4 method, is negligibly small for HI and H_2Te. However, for SbH_3 the core-polarization contribution becomes comparable to that which follows from the basis set extension at the SCF HF level of approximation. Both these effects must be accounted for in accurate calculations of the dipole moment of SbH_3.

The pattern of the basis set dependence and the importance of core-polarization effects for the dipole polarizability of the fourth-row hydrides are very similar to those observed in the dipole moment calculations. The contribution of the $4d^{10}$ shell at both the SCF and HF levels of approximation is relatively small. The relativistic corrections to dipole moments and polarizabilities of the fourth-row atom hydrides appear to be of particular interest. The SCF HF data obtained by using the first-order quasirelativistic approach developed in our recent studies [14, 15] are given in Tables 3 and 4. We have also calculated the mixed relativistic-correlation corrections [15] to our non-relativistic data. However, the corresponding numbers are more than an order of magnitude smaller than the SCF HF corrections, and thus, completely negligible.

The decrease of the relativistic contribution to the dipole moment of the fourth-row atom hydrides (see Table 3) on passing from SbH_3 to HI is somewhat puzzling. This is just opposite to what one would expect on the basis of simple considerations involving the nuclear charge of the heavy atom [12, 13]. However, if one takes into account the lone pair contributions to the dipole moment, the sequence of relativistic corrections to dipole moments becomes quite reasonable; in SbH_3 most of the dipole moment comes from the lone pair hybrid on Sb and this will be mostly affected by the relativistic shrinkage of the 5*s* orbital. In other words, the relativistic data of Table 3 can be interpreted in terms of the relativisitic effect on the hybridization of the lone pair orbital of the heavy atom.

The relativistic effect on the dipole polarizability of the fourth-row atom hydrides is rather small (see Table 4). In most cases the relativistic contribution is negative and reflects the relativistic shrinkage of atomic orbitals. The corresponding corrections are usually much smaller than those calculated for free atoms (see Table 2). However, in the case of SnH_4 the relativistic contribution to its dipole polarizability is positive. This change of sign of the relativistic contribution in the series HI, H_2Te, SbH_3, and SnH_4 appears again to originate from the lone pair effect. It is worthwhile noting that the *zz*-component of the dipole polarizability steadily becomes less negative on passing from HI to SbH_3. Hence, the effect observed for SnH_4 is a rather secondary effect of the shrunken density on Sn on the outer shell of the electron density distribution, i.e., on the region of the four hydrogen atoms. Let us also add that a similar trend has been noted for relativistic corrections to the dipole polarizability of the third-row atoms, though the corresponding numbers are much smaller than in the present case.

A reliable experimental value (0.1760 a.u. [33]) is available for the dipole moment of HI. On correcting our MBPT4 result (0.1993 a.u., Table 3), calculated with the (*spdf*) polarized basis set, for the relativistic contribution (-0.0393 a.u., Table 3) one obtains 0.1600 a.u. The same method applied at the level of the SDQ-MBPT4 approximation gives 0.1669 a.u.; both results are in good agreement with the experimental value. This is virtually the only 'external' proof of the reliability of polarized basis sets developed in the present paper. The dipole moment computed with the (*spd*) polarized basis set will be about 0.005 a.u. higher than that obtained with the (*spdf*) set. There are also several theoretical results computed by other authors which range between 0.157 a.u. and 0.194 a.u. The corresponding data are surveyed and analysed in [14]. For the purpose of the present discussion, let us only mention that the relativistic MR CI method accompanied by the use of relativistic core pseudopotentials [13] gives the HI dipole moment as either 0.181 a.u. [34] or 0.194 a.u. [35]; both results being slightly larger than the experimental value. All those data clearly indicate the appropriateness of both (*spd*) and (*spdf*) polarized basis sets of this paper for reliable calculations of molecular dipole moments.

The dipole moment of H_2Te has been recently calculated by Sumathi and Balasubramanian [32] who employed the relativistic MR CI approach and relativistic core pseudopotentials. Their result (0.105 a.u.) is about 0.06 a.u. higher than the present MBPT4 value corrected for the relativistic contribution (0.0462 a.u. for the (*spd*) basis set and 0.0353 a.u. for the (*spdf*) basis set, see Table 3). A similar discrepancy has been previously noted for H_2Se [4]; Balsubramanian's relativistic result [36] was about 0.1 a.u. higher than the MBPT4 value computed with the corresponding polarized basis set. However, in the case of H_2Se the available experimental value could have been used to show the correctness of the MBPT calculation with polarized basis sets. In conclusion, it also appears that the dipole moment result for H_2Te as calculated in the present paper is more reliable than that computed by Sumathi and Balasubramanian.

The parallel component of the dipole polarizability of HI has recently been calculated by using MBPT methods and relativistic corrections in a paper by Kellö and Sadlej [14]. Those authors employed a much larger basis set on both H and I and their non-relativistic results are slightly higher than the values obtained in this study (see footnote g to Table 4). However, both the SCF HF value of the parallel dipole polarizability of HI and the first-order relativistic correction to it are virtually the same in both calculations. This gives another indication of the reliability of the present approach.

As a by-product of our SCF HF calculations of properties of the fourth-row atom hydrides we have also obtained the quadrupole moments of those molecules. The non-relativistic SCF HF results are: $\Theta_{xx} = 1.084$ a.u., $\Theta_{zz} = -2.168$ a.u. for SbH_3, $\Theta_{xx} = 0.976$ a.u., $\Theta_{yy} = -3.720$ a.u., $\Theta_{zz} = 2.744$ a.u. for H_2Te, and $\Theta_{xx} = -1.854$ a.u., $\Theta_{zz} = 3.707$ a.u. for HI. Those values correspond to calculations with (*spd*) polarized basis sets and the origin of the coordinate system chosen at the nuclear centre of mass. The corresponding data for the (*spdf*) sets read: $\Theta_{xx} = 1.064$ a.u., $\Theta_{zz} = -2.131$ a.u. for SbH_3, $\Theta_{xx} = 0.961$ a.u., $\Theta_{yy} = -3.657$ a.u., $\Theta_{zz} = 2.697$ a.u. for H_2Te, and $\Theta_{xx} = -1.822$ a.u., $\Theta_{zz} = 3.643$ a.u. for HI. It is worthwhile noting a rather negligible basis set dependence of the calculated quadrupole moment data. This supports our previous conclusions concerning the reliability of the quadrupole moment data computed with polarized basis sets [2, 4, 6]. No attempt has been made to calculate the correlation and relativistic corrections to molecular quadrupole moments. However, it has been found in our recent study of AuH that the relativistic contribution to the quadrupole moment is much larger than that for the dipole moment of this molecule. Similar effects might be expected for molecules involving the fourth-row atoms.

5. Current applications. Conclusions

The polarized basis sets derived in this study for the fourth-row atoms are currently being used in investigations of intermolecular interactions. The major electric properties of OCTe, SCTe, and CTe_2 (dipole and quadrupole moments and dipole polarizabilities) have been calculated [37] in relation to interactions of those systems with other polar and non-polar species. One of the interesting findings is that although the CTe_2 molecule resembles formally its iso-valent counterpart CO_2, the charge distribution and several electric properties turn out to be quite different.

Another current application of the derived polarized basis sets is the study of interactions in the CO···HI system. For the linear configuration of the dimer the energy minima are predicted for both IH···CO and CO···HI. The first of those two structures has a minimum of about -1.8 mH at the H···C distance of 5.11 a.u. The second structure gives a shallow minimum of about -0.9 mH at the O···H distance of approximately 5.2 a.u. (MBPT4 results [38]).

Those two examples illustrate the major goal underlying the generation of medium-size polarized basis sets. In addition to calculations of molecular electric properties, the main area of their applications is to be the calculation of intermolecular interaction energies and other interaction properties. Obviously, the present polarized basis sets give a rather large basis set superposition contribution to interaction energies [9]. However, the secondary basis set superposition effect [39], i.e., the basis set superposition contribution to interaction properties, is virtually zero. Thus, the polarized basis sets give a very reliable tool for accurate calculations of dipole moment and polarizability surfaces for interacting species. This indicates their applicability to theoretical studies of infrared and Raman spectra of such systems. The present paper extends the range of possible applications to molecules involving fourth-row atoms.

The verification of the quality of polarized basis sets generated in this study has been carried out mostly in terms of the cross-examination of different data. Thus, our conclusions concerning the performance of the first-order polarized basis sets for the fourth-row atoms are not as firm as in the case of previously derived sets for lighter atoms. However, the available reference data show the present basis sets should give the main molecular electric properties not worse than those obtained for molecules built from the first-, second-, and third-row atoms [1–4].

The major novelty brought by the fourth-row atoms is the importance of the relativistic contribution to different properties. This has been calculated in the present paper by using the first-order quasirelativistic approach [14, 15]. It has been documented that the relativistic contribution is quite stable with respect to both the contraction and extension of basis sets.

It appears that for the majority of qualitative purposes the less computer-time demanding (*spd*) polarized basis sets can be employed. For the purpose of accurate calculations the use of the extended (*spdf*) polarized basis sets of this paper is recommended. This is obviously necessary whenever the property calculations are meant to account for the core-polarization effects at the correlated level of approximation.

Further development in the area of medium-size polarized basis sets may lead to their consideration for the fifth-row atoms. However, molecules involving fifth-row atoms are either rare or unstable. On the other hand, it might be worthwhile continuing the approach of this work in the study of relativistic contributions to different properties. This contribution is expected to dominate the electron correlation effects in the electric properties of molecules involving the fifth-row atoms.

The (*spd*) first-order polarized basis sets for Sn through I are given in the Appendix to this paper. They are included in the basis set library of the second release of the MOLCAS system of quantum chemistry programs [16]. Their extension to the appropriate (*spdf*) sets can be accomplished with the aid of the data presented in Table 1.

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Appendix

The details of the (*spd*) polarized basis sets generated in this paper for Sn, Sb, Te, and I are presented in Tables A, B, C, and D, respectively. These basis sets take into account one of the unique advantages of the MOLCAS integral code which permits the efficient handling of the Raffenetti-type contractions. The (*spd*) sets, whenever necessary, can be extended to the corresponding (*spdf*) polarized sets by using the data of Table 1.

Table A. First-order polarized [19.15.12/11.9.6] GTO/CGTO basis set for tin

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	899821.66	0.0003171	−0.0001027	0.0000451	−0.0000196	−0.0000057
2		134984.99	0.0024542	−0.0007940	0.0003498	−0.0001519	−0.0000444
3		30894.687	0.0125308	−0.0041012	0.0018034	−0.0007832	−0.0002289
4		8884.5899	0.0490344	−0.0163241	0.0072300	−0.0031431	−0.0009183
5		2970.8316	0.1483326	−0.0530849	0.0235920	−0.0102703	−0.0030036
6		1114.3989	0.3205279	−0.1318363	0.0604148	−0.0264382	−0.0077309
7		457.49766	0.3999731	−0.2335835	0.1108669	−0.0489543	−0.0143645
8		201.14673	0.1988844	−0.1324689	0.0724148	−0.0327790	−0.0096064
9		76.951888	0.0179062	0.4745137	−0.3474649	0.1669511	0.0495391
10		34.627033	−0.0028864	0.6214301	−0.6342873	0.3338854	0.1014565
11		12.709521	0.0016815	0.1121186	0.3778088	−0.2676719	−0.0872059
12		6.7445922	−0.0014366	−0.0297494	0.8205402	−0.8936390	−0.3068572
13		2.8589584	0.0009646	0.0144162	0.1569332	0.1252524	0.0684718
14	6	1.4649553	1.0				
15	7	0.5482545	1.0				
16	8	0.4970868	1.0				
17	9	0.1612089	1.0				
18	10	0.0680632	1.0				
19	11	0.028737	1.0				
p subset							
1	1–4	6555.3605	0.0025781	0.0011867	0.0004945	−0.0001149	
2		1572.5554	0.0205342	0.0095279	0.0039733	−0.0009222	
3		518.87112	0.0947403	0.0456649	0.0191961	−0.0044678	
4		201.79386	0.2672822	0.1359994	0.0577300	−0.0134276	
5		87.860501	0.4214396	0.2349656	0.1019275	−0.0238707	
6		40.765381	0.3077676	0.1051300	0.0373197	−0.0082584	
7		18.522327	0.0666156	−0.3751055	−0.2223105	0.0538259	
8		8.9900952	−0.0015574	−0.5650153	−0.3848178	0.0974260	
9		4.3941855	0.0018794	−0.1915481	0.0581870	−0.0292863	
10		2.1610510	−0.0010383	−0.0106883	0.5876685	−0.1732536	
11	5	1.0168061	1.0				
12	6	0.4415798	1.0				
13	7	0.1650588	1.0				
14	8	0.0589605	1.0				
15	9	0.021061	1.0				
d subset							
1	1–2	313.59189	0.0168137	0.0062995			
2		93.029929	0.1119063	0.0429247			
3		34.699209	0.3339019	0.1287688			
4		14.308712	0.4721659	0.1719142			
5	3–4	6.2801124	0.2617913	0.0260230			
6		2.7769449	0.0367596	0.4047028			
7		1.1534475	0.0012999	0.5088044			
8		0.4286993	−0.0001541	0.2294249			
9	5	0.44158	0.12519				
10		0.16506	1.15562				
11	6	0.0589605	0.19425				
12		0.021061	0.12250				

Table B. First-order polarized [19.15.12/11.9.6] GTO/CGTO basis set for antimony

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	937975.11	−0.0003163	0.0001026	−0.0000453	0.0000199	0.0000062
2		141220.76	−0.0024307	0.0007873	−0.0003483	0.0001533	0.0000476
3		32433.012	−0.0123809	0.0040585	−0.0017927	0.0007891	0.0002450
4		9334.5594	−0.0484525	0.0161443	−0.0071806	0.0031619	0.0009813
5		3122.3022	−0.1468909	0.0526207	−0.0234931	0.0103682	0.0032221
6		1169.7278	−0.3192445	0.1311856	−0.0603530	0.0267424	0.0083057
7		479.56797	−0.4007104	0.2338806	−0.1115674	0.0499946	0.0155953
8		210.71500	−0.2012277	0.1340401	−0.0733613	0.0334858	0.0104084
9		80.254076	−0.0183861	−0.4734877	0.3487065	−0.1694917	−0.0534133
10		36.187742	0.0030423	−0.6225744	0.6395280	−0.3436074	−0.1113060
11		13.164129	−0.0017135	−0.1128803	−0.4086383	0.3052706	0.1069484
12		6.8895312	0.0014370	0.0312486	−0.8180623	0.9094680	0.3333489
13		2.7977351	−0.0010430	−0.0167245	−0.1329101	−0.2615642	−0.1329571
14	6	1.4606731	1.0				
15	7	0.6514449	1.0				
16	8	0.4579382	1.0				
17	9	0.1806266	1.0				
18	10	0.0783207	1.0				
19	11	0.033960	1.0				
p subset							
1	1–4	6754.9329	0.0026221	−0.0012131	−0.0005139	0.0001328	
2		1629.8164	0.0206143	−0.0096238	−0.0040820	0.0010540	
3		541.11515	0.0942772	−0.0456751	−0.0195214	0.0050516	
4		211.37093	0.2651591	−0.1358077	−0.0586617	0.0151841	
5		92.398824	0.4190345	−0.2345223	−0.1034238	0.0269217	
6		43.035643	0.3095054	−0.1108588	−0.0409752	0.0101937	
7		19.780810	0.0688357	0.3640495	0.2209034	−0.0598906	
8		9.6201993	−0.0007617	0.5713013	0.3954266	−0.1112942	
9		4.7016732	0.0015567	0.1981136	−0.0484394	0.0294663	
10		2.3339768	−0.0008689	0.0112215	−0.5949310	0.2010653	
11	5	1.0999764	1.0				
12	6	0.4623662	1.0				
13	7	0.1851735	1.0				
14	8	0.0687746	1.0				
15	9	0.025543	1.0				
d subset							
1	1–2	331.88981	−0.0165619	−0.0064375			
2		98.366642	−0.1111384	−0.0442383			
3		36.798758	−0.3308190	−0.1325055			
4		15.340436	−0.4664939	−0.1768039			
5	3–4	6.8381205	−0.2657970	0.0199642			
6		3.0608489	−0.0408344	0.4047620			
7		1.2951671	−0.0011371	0.5132661			
8		0.4932548	0.0000689	0.2196904			
9	5	0.462366	0.19784				
10		0.185174	1.18499				
11	6	0.068775	0.16053				
12		0.025543	0.09176				

Table C. First-order polarized [19.15.12/11.9.6] GTO/CGTO basis set for tellurium

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	978822.88	−0.0003143	0.0001021	−0.0000453	−0.0000202	0.0000066
2		147828.00	−0.0024070	0.0007806	−0.0003469	−0.0001546	0.0000505
3		34015.467	−0.0122364	0.0040170	−0.0017813	−0.0007940	0.0002594
4		9798.9016	−0.0478978	0.0159735	−0.0071372	−0.0031826	0.0010391
5		3276.8736	−0.1455861	0.0522006	−0.0233901	−0.0104538	0.0034180
6		1226.4017	−0.3178680	0.1305206	−0.0603423	−0.0270770	0.0088466
7		502.27506	−0.4013723	0.2340650	−0.1119595	−0.0508166	0.0166815
8		220.57164	−0.2035352	0.1357521	−0.0749639	−0.0346582	0.0113307
9		83.669102	−0.0189369	−0.4721342	0.3513796	0.1731847	−0.0574438
10		37.810205	0.0032727	−0.6236111	0.6394285	0.3489708	−0.1192071
11		13.574922	−0.0019592	−0.1172671	−0.4122502	−0.3179603	0.1183222
12		7.2966932	0.0017045	0.0368232	−0.8055617	−0.9051359	0.3500455
13		2.8917326	−0.0014090	−0.0222932	−0.1583094	0.2407511	−0.1312831
14	6	1.6043893	1.0				
15	7	0.7881579	1.0				
16	8	0.5553914	1.0				
17	9	0.2212502	1.0				
18	10	0.0913273	1.0				
19	11	0.0376979	1.0				
p subset							
1	1–4	7003.1556	0.0026412	0.0012279	−0.0005282	−0.0001480	
2		1694.6925	0.0205837	0.0096659	−0.0041652	−0.0011673	
3		564.80973	0.0938945	0.0457054	−0.0198392	−0.0055669	
4		220.99327	0.2636880	0.1359368	−0.0596812	−0.0167761	
5		96.942841	0.4171862	0.2342577	−0.1049086	−0.0295902	
6		45.224205	0.3112651	0.1160592	−0.0443706	−0.0121399	
7		21.038604	0.0694667	−0.3566303	0.2211556	0.0656478	
8		10.214355	0.0007714	−0.5796918	0.4076291	0.1240375	
9		4.9427469	0.0007236	−0.2012531	−0.0513357	−0.0323610	
10		2.4813817	−0.0004106	−0.0089392	−0.5998766	−0.2275135	
11	5	1.1921537	1.0				
12	6	0.5195231	1.0				
13	7	0.2167987	1.0				
14	8	0.0802522	1.0				
15	9	0.0297069	1.0				
d subset							
1	1–2	347.73554	0.0165234	0.0066361			
2		103.87251	0.1093631	0.0449861			
3		39.238498	0.3249199	0.1346119			
4		16.482706	0.4645236	0.1825784			
5	3–4	7.3994044	0.2708094	0.0146096			
6		3.3493018	0.0436736	0.4044130			
7		1.4435871	0.0012780	0.5164642			
8		0.5601709	−0.0000716	0.2123596			
9	5	0.519523	0.216264				
10		0.216799	1.125548				
11	6	0.080252	0.147472				
12		0.029707	0.071054				

Table D. First-order polarized [19.15.12/11.9.6] GTO/CGTO basis set for iodine

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	1024924.8	−0.0003112	0.0001012	−0.0000451	−0.0000203	0.0000069
2		154843.13	−0.0023822	0.0007736	−0.0003451	−0.0001556	0.0000529
3		35646.336	−0.0121028	0.0039784	−0.0017715	−0.0007992	0.0002719
4		10272.630	−0.0473906	0.0158201	−0.0070961	−0.0032017	0.0010883
5		3434.4769	−0.1443574	0.0517979	−0.0233084	−0.0105449	0.0035900
6		1284.4313	−0.3164481	0.1298812	−0.0602625	−0.0273582	0.0093065
7		525.64189	−0.4018988	0.2340313	−0.1124651	−0.0516988	0.0176738
8		230.74127	−0.2058581	0.1378589	−0.0761724	−0.0355751	0.0121096
9		87.255217	−0.0195178	−0.4704590	0.3515680	0.1753485	−0.0605902
10		39.494464	0.0035105	−0.6244144	0.6449758	0.3578347	−0.1275278
11		14.254520	−0.0021503	−0.1186834	−0.4140994	−0.3285772	0.1280144
12		7.6466089	0.0019077	0.0377119	−0.8084290	−0.9202006	0.3725377
13		3.0500598	−0.0017174	−0.0247635	−0.1559773	0.2478261	−0.1394091
14	6	1.7326181	1.0				
15	7	0.8768236	0.0				
16	8	0.6349930	0.0				
17	9	0.2564976	0.0				
18	10	0.1061169	1.0				
19	11	0.0439022	0.0				
p subset							
1	1–4	7299.0410	0.0026316	0.0012293	0.0005366	0.0001599	
2		1767.8671	0.0204925	0.0096738	0.0042285	0.0012612	
3		590.09433	0.0932057	0.0455881	0.0200867	0.0059946	
4		231.49387	0.2616339	0.1356119	0.0603974	0.0180769	
5		101.73176	0.4158847	0.2345662	0.1067446	0.0320064	
6		47.569119	0.3128182	0.1201292	0.0467467	0.0137283	
7		22.275404	0.0714857	−0.3495375	−0.2201150	−0.0700630	
8		10.840897	0.0010960	−0.5837640	−0.4207903	−0.1360543	
9		5.2379498	0.0006345	−0.2062012	0.0628580	0.0381252	
10		2.5466334	−0.0003811	−0.8572306	0.6434501	0.2700960	
11	5	1.2106848	1.0				
12	6	0.5744092	0.0				
13	7	0.2465331	0.0				
14	8	0.0913532	1.0				
15	9	0.0338511	0.0				
d subset							
1	1–2	370.37639	0.0160789	0.0066648			
2		109.71047	0.1091329	0.0461780			
3		41.199216	0.3277467	0.1405037			
4		17.284607	0.4658406	0.1865116			
5	3–4	7.8154415	0.2640157	0.0108920			
6		3.7428153	0.0438970	0.3827473			
7		1.6595878	0.0030830	0.5259328			
8		0.6526591	−0.0004230	0.2222319			
9	5	0.574409	0.248065				
10		0.246533	1.072953				
11	6	0.091353	0.136634				
12							
		0.033851	0.054360				

References

1. Sadlej AJ (1988) Coll Czech Chem Commun 53:1995, and references therein. Part I of this series
2. Sadlej AJ (1991) Theor Chim Acta 79:123 and references therein. Part II of this series
3. Sadlej AJ, Urban M (1991) J Mol Struct (Theochem) (in press) and references therein. Part III of this series
4. Sadlej AJ (1991) Theor Chim Acta 81:45 and references therein. Part IV of this series
5. Roos BO, Sadlej AJ (1985) Chem Phys 94:43
6. Woliński K, Sadlej AJ, Karlström G (1991) Mol Phys 72:425
7. Fowler PW, Sadlej AJ (1991) Mol Phys 73:43
8. Chałasiński G, Cybulski SM, Szcześniak MM, Scheiner S (1989) J Chem Phys 91:7048
9. Sadlej J, Roos BO (1989) Theor Chim Acta 76:173
10. Joyce BA (1985) Rep Prog Phys 48:1637; Berkowitz J (1988) J Chem Phys 89:7065
11. Balasubramanian K (1989) Chem Rev 89:1801
12. Pyykkö P (1978) Adv Quantum Chem 11:353; Pyykkö P (1986) Relativistic theory of atoms and molecules. Springer, Berlin Heidelberg New York
13. Balasubramanian K, Pitzer KS (1987) Adv Chem Phys 67:287
14. Kellö V, Sadlej AJ (1990) J Chem Phys 93:8122
15. Sadlej AJ, Urban M (1991) Chem Phys Lett 176:293
16. Andersson K, Fülscher M, Lindh R, Malmqvist P-Å, Olsen J, Roos BO, Sadlej AJ, Widmark P-O (1991) MOLCAS system of quantum chemistry programs. Release 2. Theoretical Chemistry, University of Lund, Lund, Sweden and IBM Sweden
17. Almlöf J, Karlström G, Malmqvist P-Å, Roos B, Sadlej AJ, Widmark P-O (1990) MOLCAS system of quantum chemistry programs. Release 1; Roos BO, Karlström G, Malmqvist P-Å, Sadlej AJ, Widmark P-O (1990) In: Clementi E (ed) Modern techniques in computational chemistry: MOTECC$^{\mathrm{tm}}$-90. ESCOM, Leiden, p. 533
18. Huzinaga S (1971) Technical Report. Department of Chemistry, University of Alberta, Edmonton, Canada. The original basis sets of Huzinaga are partly contracted in *s* and *p* subsets. For the present purposes the corresponding fully uncontracted basis sets are employed
19. Raffenetti RC (1973) J Chem Phys 58:4452
20. Sadlej AJ (1977) Chem Phys Lett 47:50
21. Teachout RR, Pack RT (1971) Atomic Data 3:195
22. Miller TM, Bederson B (1977) Adv At Mol Phys 13:1
23. Thorhallsson J, Fisk, C, Fraga S (1968) J Chem Phys 49:1987
24. Muller W, Flesch J, Meyer W (1984) J Chem Phys 80:3297, and references therein
25. Cowan RD, Griffin DC (1976) J Opt Soc Am 66:1010; Martin RL (1983) J Phys Chem 87:750
26. Urban M, Černušák I, Kellö V, Noga J (1987) In: Wilson S (ed) Methods in computational chemistry, vol. 1. Plenum Press, New York, p. 117, and references therein
27. The original version of the MBPT package used in this paper within the MOLCAS system of programs [16, 17] is due to M. Urban, V. Kellö, I. Černušák, and J. Noga. Department of Physical Chemistry, Faculty of Science, Comenius University, Bratislava, Czechoslovakia; see also [26, 28]
28. Urban M, Hubač I, Kellö V, Noga J (1980) J Chem Phys 72:3378; Noga J (1983) Comput Phys Commun 29:117
29. Helminger P, Beeson EL, Gordy W (1971) Phys Rev A 3:122
30. Landoldt-Börnstein (1974) Zahlenwerte und Funktionen. Vol. II/7, Springer, Berlin Heidelberg New York
31. Huber KP, Herzberg G (1978) Molecular spectra and structure. Vol. 4, Van Nostrand-Reinhold, New York
32. Sumathi K, Balasubramanian K (1990) J Chem Phys 92:6604
33. Ogilvie JF, Rodwell WP, Tipping RH (1980) J Chem Phys 73:5221
34. Chapman D, Balasubramanian K, Lin SH (1988) Phys Rev A 38:6098
35. Chapman D, Balasubramanian K, Lin SH (1987) J Chem Phys 87:5325
36. Balasubramanian K, Liao MZ (1988) J Phys Chem 92:4595
37. Sadlej J (1991) J Mol Struct (Theochem) (in press)
38. Sadlej AJ (unpublished results)
39. Karlström G, Sadlej AJ (1982) Theor Chim Acta 61:1