

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

II. Second-row atoms: Si through Cl

Andrzej J. Sadlej

Theoretical Chemistry, Chemical Centre, University of Lund, Box 124, S-221 00 Lund, Sweden

Received July 3, 1990/Accepted October 29, 1990

Summary. The basis set polarization approach is employed for the generation of medium-size polarized GTO/CGTO basis sets for calculations of molecular dipole moments and polarizabilities. The excellent performance of the [13.10.4/7.5.2] GTO/CGTO polarized basis sets derived for Si through Cl is illustrated by the atomic polarizability results and SCF and MBPT data for dipole moments and polarizabilities of the second-row atom hydrides. The possible applications of the electric-property oriented polarized basis sets are discussed. The basis set data for Si through Cl are those for H and C through F append the paper.

Key words: Polarized basis sets – Molecular electric properties – Dipole moments and polarizabilities of the second-row hydrides – Basis set polarization approach

1. Introduction

Over the past years a considerable amount of effort has been invested into generation of highly efficient basis sets for molecular calculations [1–3]. The finite and acceptably small size of algebraic problems required by the majority of computational methods for the solution of the Schrödinger equation anticipates a certain balance between the basis set dimension, its flexibility, and the level of accuracy to be achieved [4].

The high-quality almost-all-purpose basis sets recently advocated by Almlöf and Taylor [2] and Widmark et al. [3] are obviously indispensable for benchmarking purposes [5]. However, the excellent performance of those (atomic natural orbital, ANO) basis sets [2, 3] in calculations of energies and diverse properties of atoms and molecules [5] is achieved at the expense of their relatively large size and a considerable amount of time spent on the integral evaluation. Both these factors become particularly important in accurate calculations of atomic and molecular properties. Then, the truncation of ANO basis sets usually results in a significant deterioration of the calculated properties.

Another direction of the basis set development and standardization is based on a more pragmatic philosophy and has been pursued by the present author and his collaborators [6–8]. It is accepted that the overall high quality of large

all-purpose basis sets can be to some extent sacrificed in favour of accurately predicting only certain selected properties of atoms and molecules. This approach leads to purpose-oriented basis sets which are tailored specifically for the given type of properties and whose size is anticipated to be small enough to permit calculations for relatively large systems.

For several properties the generation of property-oriented basis sets is greatly facilitated by recognizing that the basis functions themselves are or can be made dependent on the perturbation related to the property of interest [9–11]. The basis set generation method [6, 8] which follows from this observation is referred to as the basis set polarization technique. When combined with certain additional rules [8] this approach gives rather compact basis sets suitable for calculations of atomic and molecular properties. In particular, a series of medium-size Gaussian (GTO/CGTO) basis sets has been devised recently for H ([6.4/3.2]) and C through F ([10.6.4/5.3.2]) for the purpose of reliable high-level correlated calculations of molecular dipole moments, dipole polarizabilities [8, 12], and intermolecular interactions [13].

In the present paper the basis set polarization method is employed for the generation of compact electric-property-oriented medium-size basis sets for Si through Cl. The method, which has been extensively described and discussed elsewhere [8], is surveyed briefly in Sect. 2. The derived medium-size ([13.10.4/7.5.2]) polarized basis sets are examined in Sect. 3 with respect to their performance in calculations of atomic polarizabilities. Their efficiency is further illustrated by SCF and many-body perturbation theory (MBPT) results for dipole moments and polarizabilities of HCl, H₂S, PH₃, and SiH₄ which are presented in Sect. 4. A summary of main results of the present study and a survey of different plausible applications of the medium-size polarized basis sets are given in Sect. 5. The details of the basis set data are tabulated in the Appendix.

2. Survey of the basis set polarization method

A detailed description and discussion of the basis set polarization method for the generation of GTO/CGTO sets for calculations of molecular electric properties can be found in Ref. [8]. The method, which was initially used for the construction of large GTO/CGTO basis sets in highly accurate calculations of molecular electric properties [6, 7], is based on the following considerations.

First, the given (initial) GTO/CGTO basis set is assumed to have a known analytic dependence on the external perturbation pertinent for the property of interest [8–11, 14, 15]. This could be, for instance, the natural geometry dependence of nucleus-centred basis sets. In the case of the external electric field perturbation such a dependence can be derived from the harmonic oscillator model [8–11]. The initial GTO/CGTO basis set is assumed to be large enough to give a reasonable qualitative description of molecules in terms of their energies and/or geometries. However, the initial set can be quite deficient for predictions of molecular electric properties. The double-zeta quality GTO/CGTO basis sets [16, 17] appear to be good candidates for the initial choice. Even upon their extension (polarization) they will be small enough to permit calculations of molecular electric properties for interestingly large systems.

Once the initial basis set is chosen and its perturbation dependence is known the next step involves its extension which is guessed from the Hellmann–Feynman

theorem [14, 15, 18]. Suppose that calculations of properties are carried out by a method which virtually satisfies the Hellmann–Feynman theorem as long as the basis set itself does not depend on the external perturbation. If it does, the first-order property formulae will additionally involve terms with the first-order derivatives of basis functions with respect to the perturbations strength [14, 15, 18]. Those terms would approximately vanish or at least their contribution would be diminished if the initial basis set were augmented by the first-derivatives of all basis functions. Thus, the initial set and the first-order derivative set combine into a general (first-order) polarized basis set. Obviously, this procedure can be continued to higher orders. However, it has been found that completely satisfactory results for electric dipole moments and polarizabilities can be obtained with first-order polarized basis sets [8].

The above-described procedure would lead to a significant extension of the initial basis set if not complemented by some additional rules which have been deduced from a number of numerical experiments [8]. Those “empirical” rules for the derivation of polarized basis sets for calculations of dipole moments and polarizabilities can be summarized as follows:

(i) The given primitive GTO basis set should be contracted to the minimal acceptable size. A double-zeta contraction appears to be a reasonable choice [8, 16, 17] and is employed in this paper.

(ii) The GTO/CGTO basis set chosen in (i) should be in most cases extended by at least one diffuse function in each shell. The diffuse GTOs are left uncontracted and their exponents are conveniently determined from the corresponding even-tempered sequences. In the present case the *s* and *p* shells of the double-zeta GTO/CGTO basis set are extended by one diffuse GTO each.

(iii) The polarization functions whose contraction coefficients follow from the derivatives of SCF HF orbitals calculated in the extended basis set of (ii), are to be generated only for the outermost occupied shell of the given atom [8].

(iv) Several primitive GTOs with high orbital components can be removed from polarization functions obtained in (iii). According to the experience gained in earlier studies it is advisable to retain at least two primitive GTOs. For calculations at the correlated level retaining four primitive polarization GTOs is recommended [8] and followed in the present case.

(v) The polarization function obtained according to (iii) and (iv), which is a single contract of four primitive GTOs, should be decontracted into two CGTOs ($4 \rightarrow 2 + 2$). No decontraction appears to be needed for polarization functions built from only two primitive GTOs.

A detailed documentation leading to those empirical rules has been given in Ref. [8]. Some of them can be given a firm validation, some others are merely based on different numerical experiments. An a posteriori proof of their validity is given by the results of SCF and MBPT calculations of molecular dipole moments and polarizabilities [8–13] for molecules containing hydrogen and C through F. Those results are very close to either experimental or the best theoretical data. In the present paper the same rules are used to generate medium-size polarized basis sets for Si through Cl for the purpose of reliable calculations of basic electric properties for molecules containing the second-row atoms.

The basis set polarization method is devised for the generation of rather small sets for the given type of molecular properties. Its present exposition is virtually limited to the case of low-order molecular electric properties. However, the method has a rather general character and can be employed for the basis set generation for other molecular properties [11], though the corresponding additional rules may undergo some modifications. Some of those ideas [11] have been recently investigated by Lazzeretti and Zanasi [19]. Finally, one should stress that the basis set polarization technique which relies on small initial basis sets is by no means meant to produce exceptionally accurate results. Simply, one cannot go beyond some limits imposed by the choice of the initial basis set. However, the current experience with calculations of dipole moments and dipole polarizabilities [8, 13] indicates that the medium-size polarized basis sets given the corresponding results within a few per cent of the best available data. It is also worth while to mention that the same polarized basis sets [8] give unexpectedly good molecular quadrupole moments [20].

3. Polarized basis sets for Si through Cl and their examination in calculations of atomic polarizabilities

The polarized basis set for Si through Cl have been derived following the rules presented in Sect. 2. The orbital exponents and contraction coefficients for those basis sets are given in the Appendix. The initial sets are the [12.9/6.4] GTO/CGTO basis sets of McLean and Chandler [17] derived from the (12.9) primitive GTO basis sets of Huzinaga [21]. Such a choice is compatible with that made in the case of the first-row atoms [8]. According to the rule (ii) the initial sets have been augmented by diffuse *s* and *p* GTOs leading to [13.10/7.5] GTO/CGTO sets.

It has been found previously that the determination of contraction coefficients in polarization functions should be rather based on the SCF HF orbitals of the negative ion which corresponds to the given atom [8]. Several arguments in favour of such a procedure have been given and different pilot calculations have confirmed its validity for the second-row atoms considered in this paper.

The polarization of the $3p$ SCF HF atomic orbitals determined in the [13.10/7.5] GTO/CGTO basis set carried out according to the general scheme [6, 8] would result in a contracted *d*-type polarization function expanded in terms of 10 primitive GTOs. Most of the contraction coefficients entering this polarization function are, however, negligibly small and thus the rule (iv) of Sect. 2 can be naturally applied. Since the present basis sets are being devised for calculations at the correlated level, four lowest-exponent *d*-type GTOs have been retained in polarization functions. Finally, the rule (v) of Sect. 2 has been applied leading to what is referred to as the medium-size polarized basis sets. Those [13.10.4/7.5.2] GTO/CGTO basis sets are still small enough to permit molecular calculations of dipole moments and polarizabilities for systems with several second-row atoms.

A useful preliminary information about the performance of the polarized basis set in molecular calculations can be obtained already at the atomic level. For this purpose, the derived basis sets have been first used to calculate the electric dipole polarizability of Si through Cl at the level of the restricted open-shell SCF HF method. The results are shown in Table 1 and compared

Table 1. SCF calculations of atomic dipole polarizabilities for Si through Cl with [13.10.4/7.5.2] polarized basis sets. All values in au

Atom	Term		This work ^a	Ref. [22]
Si	³ P	$M_L = 0$	32.40	
		$M_L = \pm 1$	41.06	
		Average ^b	38.17	38.83 ^c
P	⁴ S		25.08	25.41
S	³ P	$M_L = 0$	21.44	
		$M_L = \pm 1$	17.87	
		Average	19.06	19.17
Cl	² P	$M_L = 0$	13.01	
		$M_L = \pm 1$	14.72	
		Average	14.15	14.20

^a Dipole polarizabilities have been calculated as the numerical derivatives of induced dipole moments. All calculations have been carried out using molecular programs with $D_{2h}(C_{2v})$ symmetry [23]

^b Rotational average: $\alpha_{Av} = \frac{1}{3}[\alpha(M_L = 0) + 2\alpha(M_L = \pm 1)]$

^c The SCF values of the dipole polarizability components do not seem to have been reported in Ref. [22]. The polarizability anisotropy data shown in Table 1 of that paper correspond rather to the correlated-level calculations

with large basis set calculations of Reinsch and Meyer [22]. The agreement between the two sets of calculated average values of the dipole polarizability (α) is highly satisfactory. Some deterioration which can be observed for P and Si has its origin in the way of choosing the d -type CGTOs for the present polarized basis sets.

The d -type CGTOs are assumed to represent the polarization of the outermost valence shell of the given atom. On passing from Cl to Si the contribution of the L shell to the total atomic polarizability increases. However, the d components of polarized basis sets derived according to the rules of Sect. 2 are not able to properly account for the core and core-valence contributions to the total polarizability. This would presumably require adding to the present basis sets another d -type CGTOs involving GTOs with higher orbital exponents. On the other hand, it is important to have the polarized basis sets of relatively small size rather than to care for inaccuracies of less than two per cent.

The compilation of the atomic polarizability data obtained in this paper confirms the expected excellent performance of medium-size polarized basis sets at the level of the SCF HF approximation. The simultaneous presence of d -type GTOs with relatively high values of orbital exponents (see Appendix) should help to recover a considerable portion of the electron correlation contribution to atomic polarizabilities. However, it is more convenient to carry out the corresponding studies at the correlated level in the case of closed-shell systems. Hence, the investigation of the present medium-size polarized basis sets at the correlated level will be performed for dipole moments and polarizabilities of the second-row hydrides.

It should be stressed that the present atomic SCF results are obtained without any basis set optimization. The orbital exponents and contraction coefficients in polarization functions follow directly from the assumed form of the electric field dependence of GTOs [8, 9]. Moreover, the final shape of polarized basis sets for Si through Cl is determined by using precisely the same rules as those which have been employed for the derivation of polarized basis sets for C through F.

The results presented in Table 1 clearly show that the polarized basis sets of this paper should perform well in molecular SCF calculations of dipole moments and polarizabilities. Since not too much is known about electric properties of molecules involving the second-row atoms, even the SCF level of approximation is fairly attractive. However, the experience with similar basis sets derived for H and C through F indicates that one should also expect the present basis sets to be equally efficient at the correlated level of approximation [8].

4. Molecular calculations with polarized basis sets: dipole moments and polarizabilities of the second-row atom hydrides

In order to examine the performance of polarized basis sets for Si through Cl in molecular applications the dipole moments and polarizabilities of the second-row atom hydrides have been computed. The SCF results are corrected for the electron correlation contribution by using the MBPT method through the complete fourth-order in the correlation perturbation [24–27]. All results for molecular electric properties have been obtained by using the finite-field perturbation approach at the level of the MBPT approximation [26]. The corresponding computational details are virtually the same as in Ref. [8]. The data tabulated in this section comprise the SCF values and the results calculated at the level of the second- (MPBT(2)), third- (MBPT(3)), and fourth-order (MBPT(4)) approximations for the electron correlation contribution. Also the approximate fourth-order results obtained in the SDQ-MBPT(4) approach [24–27] are presented. The electron correlation effects are accounted for only for the valence-shell electrons; the other orbitals, which are principally the heavy atom core orbitals, are left uncorrelated. This approximation is consistent with the present way of choosing the polarization functions.

For the sake of completeness the calculated total energy values are compiled in Table 2. They simply reflect the quality of the initial basis sets used for the generation of polarized sets. There are several more accurate calculations of SCF and correlation energies for the second-row atom hydrides [28, 29, 35]. A survey of different energy data can be found in the recent paper by Feller et al. [28]. The accuracy of the SCF energy, and in particular, the amount of the valence correlation energy recovered in calculations with polarized basis sets are rather low. Those basis sets are not tailored for energy-oriented calculations and this is the sacrifice one has to make in order to stay within reasonably small (medium-size) basis set dimensions.

Of primary importance for the present study are the dipole moment and polarizability results collected in Tables 3 and 4, respectively. The dipole moment values calculated in this paper are compared with the recent SCF, SD-CI, and MRSD-CI data of Feller et al. [28]. The basis sets employed by these authors (see footnote b to Table 3) are 2–3 times larger than the polarized sets of the

Table 2. Total energies of the second-row atom hydrides computed with polarized basis sets in different approximations^{a,b}. All values in au

Method	Total energy (E)			
	HCl ^c (+460.)	H ₂ S ^d (+398.)	PH ₃ ^e (+342.)	SiH ₄ ^f (+291.)
SCF	-0.09424	-0.69834	-0.47224	-0.24238
MBPT(2)	-0.25309	-0.85044	-0.61103	-0.35980
MBPT(3)	-0.26901	-0.87087	-0.64595	-0.38563
MBPT(4)	-0.27265	-0.87667	-0.64343	-0.39288
SDQ-MBPT(4)	-0.26931	-0.87275	-0.63999	-0.39102

^a The [10.4/3.2] polarized basis set is used for H [8]

^b Only valence-shell correlation contributions are included. The K and L shells of heavy atoms are left uncorrelated

^c Bond distance $R(\text{HCl}) = 1.2746 \text{ \AA} = 2.4086 \text{ au}$ [30]

^d Geometry: $R(\text{SH}) = 1.3280 \text{ \AA} = 2.5096 \text{ au}$, $\angle \text{HSH} = 92.2^\circ$ [31]. The molecular geometry given in Ref. [32] leads to insignificant changes in the calculated electric properties of H₂S

^e Geometry: $R(\text{PH}) = 1.42002 \text{ \AA} = 2.68345 \text{ au}$, $\angle \text{HPH} = 93.3452^\circ$ [33]

^f Geometry: $R(\text{SiH}) = 1.48111 \text{ \AA} = 2.79889 \text{ au}$, T_d symmetry [34]

Table 3. Dipole moments of the second-row atom hydrides.^a All values in au

Method	Dipole moment (μ)		
	HCl	H ₂ S	PH ₃
This work			
SCF	0.4743	0.4367	0.2815
MBPT(2)	0.4510	0.4085	0.2439
MBPT(3)	0.4461	0.39971	0.2293
MBPT(4)	0.4351	0.3897	0.2240
SDQ-MBPT(4)	0.4414	0.3955	0.2264
Reference data			
SCF [28] ^b	0.4767	0.4297	0.2638
SD-CI [28] ^{b,c}	0.4585	0.4139	0.2390
MRSD-CI [28] ^{b,c}	0.4570	0.4081	0.2353
Expt. [36]	0.441	0.401	0.227

^a See footnotes a–c to Table 2

^b Large basis set calculations. The following basis sets have been used [28]: HCl: H[10.3.2/6.3.1], Cl[23.15.4.2/14.11.5.2]; H₂S: H[10.3.2/6.3.1], S[21.14.4.2/12.10.4.2]; PH₃: H[10.3/6.3], P[21.14.4/12.10.4]

^c All electrons correlated. We have calculated the L-shell contribution to the dipole moment values with polarized basis sets at the level of the MBPT(4) approximation. The corresponding estimates of the core contribution are equal to -0.003 au , -0.005 au , and -0.006 au for HCl, H₂S, and PH₃, respectively

Table 4. Dipole polarizabilities of the second-row atom hydrides.^a All values in au

Method	Dipole polarizability (α)									
	HCl ^b		H ₂ S ^c		PH ₃ ^d		SiH ₄			
	α_{xx}	α_{zz}	α	α_{xx}	α_{yy}	α_{zz}	α	α_{xx}	α_{zz}	α
This work										
SCF	16.04	17.91	16.66	23.69	23.85	23.39	23.64	29.58	30.59	29.92
MBPT(2)	16.77	18.44	17.33	24.21	25.14	24.20	24.52	30.06	31.79	30.64
MBPT(3)	16.66	18.34	17.22	24.04	24.92	24.02	24.33	29.87	31.48	30.41
MBPT(4)	16.83	18.50	17.39	24.16	25.13	24.16	24.48	29.90	31.56	30.45
SDQ-MBPT(4)	16.66	18.36	17.23	24.00	24.86	23.97	24.28	29.78	31.32	30.29
Reference results										
SCF		17.93 ^e		22.9	22.7	22.1	22.5 ^f			
MBPT(4)		18.15 ^e								
	16.763	18.405	17.310 ^g							
Expt.	16.8	19.0	17.5 ^h							
	19.6	21.1	20.1 ⁱ				25.5 ^h			

^a See footnotes a–f to Table 2

^b The molecule lies on the z axis of the coordinate system

^c The molecule lies in the xz plane with the C_2 symmetry axis coinciding with the z axis of the coordinate system

^d The C_3 symmetry axis coincides with the z axis of the coordinate system

^e SCF/MBPT data obtained with a large polarized basis set (H[11.5.2/7.4.2], Cl[15.12.7.2/15.12.5.2]) used in relativistic calculations on HCl [40]

^f SCF calculations of Ahlström et al. [42]. An inspection of their data for other molecules indicates that the result for HCl is too low

^g Polarized basis set calculations [43]

^h Ref. [41]

ⁱ Ref. [44]

present paper and in terms of total molecular energies the results of Feller et al. surpass the accuracy of all earlier calculations. An inspection of the GTO orbital exponents used in Ref. [28] shows, however, that they were chosen mostly in the energy-oriented way. This is presumably one of the reasons that Feller et al. recover less correlation contribution to the dipole moment in their all-electron SD-CI and MRSD-CI calculations than could be expected. Since the vibrational contribution to dipole moments of HCl and H₂S is positive, the accurate vibrationless data should fall below the experimental values as our MBPT(4) results do. Another reason for rather unexpected relations between the calculated dipole moments of Feller et al. and the experimental ones could be the use of the Hellmann–Feynman theorem at the level of the SD-CI and MRSD-CI approximations [37].

The dipole moment data calculated in this paper with polarized basis sets are, within the estimated [38] magnitude of rovibrational corrections, very close to the experimental values. This proves the reliability of polarized basis sets in SCF and correlated-level calculations of the second-row atom hydrides. Another support towards this conclusion comes from the numerical SCF dipole moment of HCl (0.4638 au [39]). Thus, the usefulness of the present polarized basis sets for Si through Cl in high-level correlated calculations of molecular dipole moments appears to be beyond any doubt. The results, similarly to those obtained for the first-row atom hydrides [8], are within a few percent equal to either experimental [36] or accurate theoretical data [39]. This is achieved with the basis set size which permits the corresponding calculations for fairly large systems.

It is rather difficult to make firm conclusions with respect to the performance of polarized basis sets in calculations of the dipole polarizability of the second-row atom hydrides. The reference experimental data are uncertain and accurate theoretical results are quite rare. However, the MBPT dipole moment values obtained in this paper indicate that the first-order wave function response to the electric field perturbation is correctly accounted for by the polarized sets. Hence, the SCF HF results for the dipole polarizability should be almost as accurate as the dipole moment data. Moreover, the first-order electric-field-perturbed wave function gives the dominant contribution to the electron correlation corrections computed in the MBPT approximation [26, 27]. Those two observations make a sound basis for believing that the polarizability values listed in Table 4 are of remarkably high accuracy. This is supported by the large polarized basis set data for HCl [40] and the results obtained in previous calculations for the first-row atom hydrides [8]. Thus, the polarizability data calculated with the present polarized basis sets are expected to be within a few percent close to the exact vibrationless data. The use of those basis sets in reliable calculations of molecular dipole moments and polarizabilities is strongly recommended.

Finally, let us mention a rather remarkable feature of the MBPT data for dipole polarizabilities of the second-row atom hydrides. Almost all correlation contribution to the dipole polarizability is recovered in the second-order approach and the differences between the MBPT(n) results for various values on n are insignificant. This pattern of the MBPT correlation perturbation series for dipole polarizabilities makes the present results trustworthy within the limits of basis set truncation to the s -, p -, and d -type functions. The results obtained recently for HCl in large basis set calculations of relativistic effects [40] indicate that the correlation contribution due to f -type GTOs is rather small.

5. Summary and conclusions. Possible applications of medium-size polarized basis sets

In the present study the [13.10.4/7.5.2] GTO/CGTO (medium-size) polarized basis sets for calculations of dipole moments and polarizabilities have been derived for the second-row atoms Si through Cl. Their derivation is based on a set of simple rules determined in earlier investigations [8] for the first-row atoms. No orbital exponent optimization is involved and the *d*-type polarization functions follow directly from the known initial GTO/CGTO basis set and its analytic dependence on the external perturbation strength [8, 9].

The performance of polarized basis sets generated in this study has been examined in calculations of atomic dipole polarizabilities, leading to very encouraging results. Molecular dipole moments and polarizabilities of the second-row atom hydrides have been calculated at the SCF and MBPT levels of approximation. Whenever reliably more accurate theoretical data or trustworthy experimental results for those properties are available, the performance of medium-size polarized basis sets turns out to be exceptionally good.

The polarized basis sets represent the purpose-oriented CGTO sets for reliable calculations of molecular dipole moments and polarizabilities. Their high efficiency is achieved at the expense of less accurate energies. The predictions concerning other molecular properties are rather uncertain. However, the uniform character of the electron density distribution which is a consequence of the basis set polarization scheme [6–8], can lead to reasonably accurate values for higher multipole moments. This has been confirmed in recent SCF and MBPT calculations of molecular quadrupole moments [20]. On the other hand, the calculation of quadrupole polarizabilities would require a further extension of the present polarized basis sets by some *f*-type functions. Their orbital exponents and contraction coefficients can be determined from the electric-field gradient dependence of GTOs [10]. An analogous basis set polarization scheme has been proposed by Woliński et al. [10] for calculations of intramolecular electric fields and forces. This approach has revived [19] the interest in calculations of infrared intensities via the electric field derivatives of the Hellmann–Feynman forces.

To summarize, let us stress that the generation of polarized basis sets is primarily based on the following three steps: (i) the choice of the initial GTO/CGTO basis set and its eventual extension by some diffuse GTOs, (ii) the identification of the basis set dependence on the relevant external perturbations, and (iii) the generation of polarization functions appropriate for the properties of interest. Hence, once the initial GTO/CGTO basis set is selected, its polarized counterpart can be obtained without any major effort.

So far the polarized medium-size GTO/CGTO basis sets have been generated for H, C through F [8], and in the present paper, for Si through Cl. The attempts to use the same set of rules for the generation of polarized basis sets for alkali and alkaline-earth metals have shown that the core polarization effects must be taken into account, thus leading to some modifications of the rules presented in Sect. 2 [45]. The need for a different treatment of the alkali and alkaline-earth atoms is rather obvious from the above-mentioned deterioration of the atomic polarizability data in the sequence Cl, S, P, and Si.

An immediate application of polarized basis sets is obviously the computation of reliable values of molecular dipole moments and polarizabilities, and perhaps also the evaluation of molecular quadrupole moments [20]. Once those basic electric properties are known to be accurately predicted in calculations with

polarized basis sets, one can attempt the evaluation of intermolecular interaction energies [13, 43, 46]. Initially, this was one of the major objectives of the basis set polarization studies and the recent results [13] and yet unpublished investigations of different van der Waals systems [47] are very encouraging. Some problems which occur in calculations of interaction energies in weakly bound systems with polarized basis sets have been discussed elsewhere [8, 13]. The results available so far show that the polarized basis sets can give reliable predictions of energies and geometries for weak molecular complexes.

The polarized basis sets, whose details are given in the Appendix to this paper, will become a part of the basis set library in the forthcoming edition of the MOLCAS system [23].

Appendix

The medium-size polarized basis sets for H and the first-row atoms C through F have been published in the previous paper. This paper has appeared in a memorial issue [8] of a national journal which is rather infrequently seen in the libraries abroad. Thus, in order to facilitate the access to those basis sets they are listed once more in Table 5 of this appendix.

The polarized basis sets for the second-row atoms Si through Cl which follow from the present investigations are shown in Table 6. They can be still truncated to the [13.10.2/7.5.1] size by removing the two highest-exponent d functions. However, the current experience shows that such basis sets can eventually be useful only at the level of the SCF approximation. The truncation of the d subspace considerably affects the electron correlation contribution to molecular dipole moments and polarizabilities.

O	1	1	10662.285	0.000799	1	1	34.856463	0.015648	1	1	2.3062	0.20270
	2	2	1599.7097	0.006153	2	2	7.843131	0.098197	2	2	0.7232	0.57910
	3	3	364.72526	0.031157	3	3	2.306249	0.307768	2	1	0.2149	0.78545
	4	4	103.65179	0.115596	4	4	0.723164	0.492470	2	2	0.0639	0.53387
	5	5	33.905805	0.301552	2	1	0.214882	1.				
	2	1	12.287469	0.444870	3	1	0.063850	1.				
	2	2	4.756805	0.243172								
	3	1	1.004271	1.								
	4	1	0.300686	1.								
	5	1	0.090030	1.								
F	1	1	13521.523	0.000801	1	1	44.147303	0.016509	1	1	2.9532	0.18354
	2	2	2028.6916	0.006164	2	2	9.993426	0.103481	2	2	0.9186	0.51058
	3	3	462.37392	0.031244	3	3	2.953246	0.315418	2	1	0.2668	0.69925
	4	4	131.37366	0.116081	4	4	0.918597	0.489353		2	0.0775	0.42926
	5	5	42.974531	0.303589	2	1	0.266824	1.				
	2	1	15.571440	0.445904	3	1	0.077500	1.				
	2	2	6.032232	0.239115								
	3	1	1.307215	1.								
	4	1	0.388869	1.								
	5	1	0.115680	1.								

^a Except for the most diffuse GTO all orbital exponents and contraction coefficients are taken from Ref. [48]. The standard segmented contraction scheme is employed. The orbital exponent of the most diffuse GTO is determined from the appropriate geometric progression

^b Except for the most diffuse GTO all orbital exponents and contraction coefficients for C through F are taken from Ref. [48] the standard segmented contraction scheme is employed. The orbital exponent of the most diffuse *p*-type GTO for C through F is determined from the appropriate geometric progression. The *p*-type CGTOs of H are determined according to the method described in Ref. [8]

^c All *d*-type polarization functions are obtained according to the method described in Ref. [8]

Table 6. Polarized basis sets for Si through Cl

		<i>s</i> subset ^a			<i>p</i> subset ^a			<i>d</i> subset ^b					
		CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient
Si	1	1	1	69379.23	0.000757	1	1	335.480	0.003616	1	1	0.5050	0.2261
		2	2	10354.94	0.005932		2	78.900	0.027866		2	0.1863	1.0759
		3	3	2333.88	0.031088		3	24.988	0.118678				
		4	4	657.14	0.124966		4	9.2197	0.298750	2	1	0.0654	0.1636
		5	5	214.30	0.386896		5	3.6211	0.441192		2	0.0230	0.1077
		6	6	77.6290	0.554890		6	1.4513	0.312701				
	2	1	1	77.629	0.177882	2	1	0.5050	1.				
		2	2	30.631	0.627756								
		3	3	12.801	0.247631		3	1	0.1863	1.			
	3	1	1	3.9269	1.		4	1	0.0654	1.			
	4	1	1	1.4523	1.		5	1	0.0230	1.			
	5	1	1	0.2562	1.								
	6	1	1	0.0943	1.								
	7	1	1	0.0347	1.								
P	1	1	1	77492.43	0.000787	1	1	384.840	0.003765	1	1	0.5979	0.3093
		2	2	11605.79	0.006109		2	90.552	0.029010		2	0.2292	0.9715
		3	3	2645.96	0.031368		3	28.806	0.122953				
		4	4	754.98	0.124291		4	10.688	0.306470	2	1	0.0838	0.1278
		5	5	248.75	0.380682		5	4.2521	0.441349		2	0.0306	0.0774
		6	6	91.157	0.559989		6	1.7405	0.295817				

Table 6 (continued)

<i>s</i> subset ^a			<i>p</i> subset ^a			<i>d</i> subset ^b					
CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient
Cl	1	105818.8	0.000743	1	1	589.78	0.002982	1	1	0.9528	0.2853
	2	15872.0	0.005754		2	139.85	0.023375		2	0.3580	0.8169
	3	3619.70	0.029674		3	47.795	0.103998				
	4	1030.80	0.117991		4	16.612	0.284430	2	1	0.1250	0.1013
	5	339.910	0.365319		5	6.5995	0.450686		2	0.0436	0.0430
	6	124.538	0.581146		6	2.7141	0.323064				
2	1	124.538	0.137543	2	1	0.9528	1.				
	2	49.514	0.622920								
	3	20.806	0.290106		3	1	0.3580	1.			
3	1	6.4648	1.		4	1	0.1250	1.			
4	1	2.5254	1.		5	1	0.0436	1.			
5	1	0.5378	1.								
6	1	0.1935	1.								
7	1	0.0696	1.								

^a Except for the most diffuse GTO all orbital exponents and contraction coefficients are taken from Ref. [17]. The standard segmented contraction scheme is employed. The orbital exponent of the most diffuse GTO is determined from the appropriate geometric progression

^b All *d*-type functions are obtained according to the method described in this paper

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