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Reduced–size polarized basis sets for calculations of molecular electric properties. III. Second–row atoms

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Abstract Reduced–size polarized (ZmPolX) basis sets are developed for the second–row atoms X = Si, P, S, and Cl. The generation of these basis sets follows from a simple physical model of the polarization effect of the external electric field which leads to highly compact polarization functions to be added to the chosen initial basis set. The performance of the ZmPolX sets has been investigated in calculations of molecular dipole moments and polarizabilities. Only a small deterioration of the quality of the calculated molecular electric properties has been found. Simultaneously the size of the present reduced–size ZmPolX basis sets is about one-third smaller than that of the usual polarized (PolX) sets. This reduction considerably widens the range of applications of the ZmPolX sets in calculations of molecular dipole moments, dipole polarizabilities, and related properties.

Keywords ZmPolX basis sets · Dipole moment and polarizability calculations · Second–row atoms

1 Introduction

Most of computational quantum chemistry is nowadays practiced in the framework of the algebraic approximation for single–particle wave functions, i.e. by using expansions into Gaussian basis sets. The accuracy of the calculated data crucially depends on the basis set composition and flexibility [1]. Both these factors affect the basis set size, which in turn determines the computational effort and limits the maximum size of molecules for which the given calculations can be carried out.

There are two ways of considering the basis set problem. One of them is oriented towards large basis sets which can be expected to lead to highly accurate data. This route is well exemplified by systematic sequences of *correlation-consistent* basis sets of Dunning and his coworkers [2]. Their tremendous success lies in the possibility of studying the complete basis set limits for energies and other properties of many-electron systems in terms of what is called the cardinal number X [2–4]. Unfortunately, the size of correlation-consistent basis sets grows rapidly with X and limits the range of highly accurate calculations to small systems (< ten atoms). In particular, the calculation of atomic and molecular electric properties needs a further extension of the correlation consistent sets which results in what is called the *augmented correlation-consistent* basis sets [5]. Already for moderate values of X the size of these basis sets becomes prohibitively large.

The other way of handling the basis set problem is more pragmatic and oriented towards moderately accurate calculations of selected properties for larger, but more interesting, molecules. This route leads to medium–sized property–oriented basis sets which usually sacrifice the very high accuracy of the computed data and offer significant gains in the computational effort involved. This idea underlies the development of the so–called *polarized* basis sets (PolX, where X stands for the element symbol) [6–9] for calculations of low–multipole electric properties of molecules. These basis sets follow from relatively small initial sets, which are extended by diffuse valence functions and augmented by polarization functions. The success of the PolX basis sets is primarily due to the choice of these polarization functions; the method of their generation follows from the well-defined physical model of the electric field polarization effect [10].

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In spite of their relatively small size, the PolX basis sets have been found to yield molecular dipole moments and polarizabilities of the accuracy comparable to that obtained with much larger augmented correlation consistent sets. Until recently any considerable reduction of the size of PolX basis sets, which would not be accompanied by a significant loss of accuracy of the property data, appeared to be rather unlikely. New ideas came from the study of the explicit time–dependence of basis set functions for calculations of frequency–dependent response functions [11]. It has been found that the dominant contribution to the static dipole polarizability actually follows from a single polarization function adapted to sufficiently diffuse valence orbitals. This observation has been used in our recent paper [12] to generate the reduced–size polarized basis sets (ZmPolX) for H, C, N, O, and F. They are one-third smaller than that of the original PolX sets. The deterioration of the calculated molecular dipole moments, dipole polarizabilities [12], and Raman intensities [13] compared to the results obtained with PolX sets have been found to be essentially insignificant.

The method used to generate the ZPolX sets for hydrogen and the first–row atoms is employed in the present study to obtain reduced–size (ZmPolX) basis sets for selected second–row atoms: Si, P, S, and Cl. A brief description of it is given in Sect. 2 and followed by some details of the generation of the ZmPolX basis sets. Extensive performance tests in calculations of molecular dipole moments and dipole polarizabilities are presented in Sect. 3. These tests lead to our final conclusions concerning the usefulness of ZmPolX basis sets in calculations of molecular dipole moments, polarizabilities, and related properties of molecules.

2 ZPolX basis sets

2.1 The generation of polarization functions

The general principles of the generation of the reduced–size polarized basis sets have been comprehensively described in Part I of this series [12] and only a brief summary will be given here. The method is based on certain observations concerning basis sets with explicit dependence on the external electric field ($\mathbf{F}$) [10]. This dependence can be modeled analytically [10,14] by the known solutions for the harmonic oscillator in the external homogeneous electric field and then used to determine the electric–field–dependence of exponential (Slater–type) functions [14].

Once the dependence of (Gaussian) basis set functions on the external electric field is established, every ordinary (field–independent, $\mathbf{F}=\mathbf{0}$) Gaussian basis set $\{G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ is transformed into a set of field–dependent functions $\{G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu)\}$ with the same orbital exponents α_μ and the origins $\mathbf{R}_\mu$ shifted in the field:

$$\mathbf{R}_\mu(\mathbf{0}) \to \mathbf{R}_\mu(\mathbf{F}) = \mathbf{R}_\mu(\mathbf{0}) - \lambda(\alpha_\mu)\mathbf{F}, \tag{1}$$

where $\lambda(\alpha_\mu)$ is in general a power series in α_μ. In the case of the harmonic oscillator $\lambda(\alpha_\mu) = 0.25\alpha_\mu^{-2}$. The field–dependent Gaussian basis set can be directly used in field–dependent calculations of atomic and molecular energies and the electric properties of interest can be derived as the appropriate energy derivatives [15].

With the field–dependent basis set $\{G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu)\}$ the usual field–independent single–particle functions, $u(\mathbf{r};\mathbf{0})$, of the given method (SCF, MC SCF, DFT),

$$u(\mathbf{r};\mathbf{0}) = \sum_\mu c_\mu(\mathbf{0}) G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu), \tag{2}$$

acquire a field–dependence of the form:

$$u(\mathbf{r};\mathbf{F}) = \sum_\mu c_\mu(\mathbf{F}) G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu). \tag{3}$$

It is important to note that in such a way the initial single–particle functions (2) and the field–dependence of the basis set fully determine the form of the field–dependent orbitals of the given method. This feature can be used to obtain derivatives of $u(\mathbf{r};\mathbf{F})$ with respect to the components of $\mathbf{F}$, i.e., the polarization functions which need to be added to the original field–independent set $\{G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ in order to properly describe the external perturbation effect. In the first–order with respect to $\mathbf{F}$ one obtains:

$$\begin{aligned} u^{(1)}(\mathbf{r};\mathbf{0}) &= \sum_\mu c_\mu^{(1)}(\mathbf{0}) G_\mu(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu) \\ &\quad + \sum_\mu c_\mu(\mathbf{0}) G_\mu^{(1)}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu), \end{aligned} \tag{4}$$

where $G_\mu^{(1)}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)$ is the first derivative of the field–dependent GTO, evaluated at $\mathbf{F}=\mathbf{0}$. One should note that the first term in the right-hand-side of this equation is a linear combination of field–independent basis functions which are already present in the initial basis set. Hence, the first–order polarization function appropriate for the unperturbed orbital $u(\mathbf{r};\mathbf{0})$ can be simplified to:

$$u^{(1)}(\mathbf{r};\mathbf{0}) \approx \sum_\mu c_\mu(\mathbf{0}) G_\mu^{(1)}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu). \tag{5}$$

Owing to the form of GTOs and their dependence (1) on the external field the derivative functions in (5) can be explicitly calculated. Let $G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu)$ be a field–dependent normalized GTO with the angular momentum quantum number l. Then,

$$\begin{aligned} G_{\mu,l}^{(1)}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu) &= \alpha_\mu\lambda(\alpha_\mu)[a_{l-1}G_{\mu,l-1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu) \\ &\quad + a_{l+1}G_{\mu,l+1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)], \end{aligned} \tag{6}$$

where $G_{\mu,l\mp1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)$ denote normalized GTOs with the angular momentum quantum number shifted by ∓1. Thus, the numerical coefficients $a_{l\mp1}$ are proportional to the ratios of the GTO normalization constants $N_{\mu,l}/N_{\mu,l\mp1}$, i.e., to $\alpha_\mu^{\pm1/2}$.

To fully determine the first–order polarization function (5) one needs to know the analytic form of $\lambda(\alpha_\mu)$. It has recently been found [11] that $\lambda(\alpha_\mu)$ can be written as:

$$\lambda(\alpha_\mu) = \sum_{n=1}^{\infty} \frac{b_n}{\alpha_\mu^n} \tag{7}$$

with coefficients b_n being independent of α_μ. Hence, the first–order polarization function (5) for the unperturbed orbital $u(\mathbf{r};\mathbf{0})$ becomes:

$$u^{(1)}(\mathbf{r};\mathbf{0}) \approx \sum_{n=1}^{\infty} b_n (f_{n-}^{(1)} + f_{n+}^{(1)}), \tag{8}$$

where

$$f_{n\pm} = \sum_{\mu} c_\mu(\mathbf{0}) \alpha_\mu^{-n+1\mp 1/2} G_{\mu,l\pm 1}(\mathbf{r}; \mathbf{R}_\mu(\mathbf{0}), \alpha_\mu). \tag{9}$$

It is noteworthy that owing to the known analytic form of the field–dependence of GTOs, each separate function $f_{n\mp}^{(1)}$ is fully determined in its contracted compact form. These functions can be considered as the polarization basis set functions to be added to the initial basis set of unperturbed orbitals. The infinite summation in (9) is actually limited to the finite number of terms because of the use of finite basis sets. To further reduce the number of polarization functions $f_{n\mp}$ one can refer to some general features of atomic basis sets and the electronic structure of atoms.

First, let us note that because of the shell structure of atomic orbitals, the f_{n-} components of the polarization set are already present in the initial set of functions. Hence, the polarization set can be reduced to some finite number of f_{n+} functions. Second, one should recall that the response of atoms and molecules to external electric fields is primarily determined by the response of their valence shells. Hence, the present method for the generation of polarization functions can be applied to valence orbitals only [6–8, 12]. Additional rules are used to generate polarized basis sets of certain assumed structure and will be exemplified by the generation of ZmPolX sets for the second–row atoms.

In general, the generation of polarized basis sets consists of a series of steps. With the chosen initial fully uncontracted GTO basis set one obtains a set of atomic orbitals. Usually these are the occupied SCF HF orbitals, although one could equally well use the (occupied) MC SCF or DFT orbitals. The GTO–expanded atomic orbitals are then used to obtain certain number of polarization functions f_{n+} by applying Eq. (9) with $n = 1, 2, \ldots$. The final polarized basis set comprises partly or fully contracted initial basis set functions and polarization functions. One should mention that the method described in this section can be applied to any initial basis set. Its flexibility determines to a large extent the quality of the final polarized basis set. Moreover, the method can be used to obtain polarization functions for (strongly) occupied orbitals as well as for weakly occupied correlating orbitals. Hence, the present method can be also employed for the generation of suitable augmented sets from the ordinary correlation consistent sets of Dunning [2]. Let us also mention that the scheme described in this section can be extended to higher orders with respect to the external electric field perturbation, leading to polarization functions suitable in calculations of molecular hyperpolarizabilities [16].

2.2 ZmPolX basis sets for the second–row atoms

The ZmPolX sets introduced in Part I of this series [12] represent a particular case of polarized basis sets which are likely to be the smallest basis sets suitable for calculations of molecular dipole moments and polarizabilities without significant deterioration in the accuracy of these properties. Although their generation can start with any sufficiently flexible initial GTO basis set, the present ZmPolX sets are derived from (12s9p) sets of Huzinaga [17, 18].

In the first step, the flexibility of the initial GTO sets is enhanced by augmenting them with one diffuse s–type GTO and one diffuse p–type GTO; the orbital exponents are determined from the approximate geometric progression which follows from the two lowest exponents in the original s and p subsets of the $(12s9p)$ set. The resulting $(13s10p)$ set is used in SCF HF calculations on neutral atoms. In the case of the ZmPolX sets it is assumed that the most important polarization functions f_{n+} are those obtained for the highest–energy $3p$ valence orbital. The polarization functions (p-type functions) for the $3s$ valence orbital are to a large extent present in the original set, i.e. these are the GTOs that build the valence $3p$ atomic orbital.

The study of time–dependent basis sets for oscillatory electromagnetic field perturbations [11] has revealed that of all the polarization functions (9), the dominant contribution to the atomic dipole polarizability comes from the contracted function f_{n+} with $n = 2$,

$$f_{2+} = \sum_{\mu=1}^{m} c_\mu(\mathbf{0}) \alpha_\mu^{-3/2} G_{\mu,l+1}(\mathbf{r}; \mathbf{R}_\mu(\mathbf{0}), \alpha_\mu), \tag{10}$$

where in the present case $l = 1$ and m is the dimension of the p–type GTO set in the extended $(13s10p)$ GTO basis set for the second–row atoms. The coefficients $c_\mu(\mathbf{0})$ are those of the $3p$ SCF atomic orbital.

In the next step of the basis set derivation, the s and p subsets are contracted to $[5s4p]$. The first three s–type CGTOs are formed of 11 primitive GTOs with the highest values of the orbital exponents. The two most diffuse s–type functions are left uncontracted. Similarly, the two p–type CGTOs are built of 8 highest–exponents GTOs and two most diffuse p–type GTOs are left uncontracted. This way of contracting the primitive $(13s10p)$ subset follows from the experience gained in the generation of PolX basis sets [6–8] and makes the resulting $[13s10p/5s4p]$ GTO/CGTO subset sufficiently diffuse and flexible to describe the outer regions of the electronic density distribution.

Upon adding a single d–type CGTO determined according to Eq. (10) one obtains a polarized basis set of the form $[13s10p10d/5s4p1d]$. At this point one notes that the scaling of the coefficients in (10) by $\alpha_\mu^{-3/2}$ will strongly diminish the role of GTOs with high orbital exponents and enhance the contribution of diffuse d–type GTOs. Hence, the primitive $(10d)$ GTO subset is likely to be truncated to only a few low–exponent functions. The numerical experiments show that only three d–type GTOs with the lowest valuesof orbital

Table 1 SCF HF dipole polarizabilities of Si through Cl. A study of the basis set truncation and contraction effects. All values in a.u.

Basis set[a]	Si(^{3}P)	P(^{4}S)	S(^{3}P)	Cl(^{2}P)
$M_L = 0$ component				
$(13s10p10d)$	32.89	25.47	21.58	13.10
$[13s10p10d/5s4p10d]$	32.86	25.45	21.58	13.10
$[13s10p10d/5s4p1d]$[b]	32.57	25.25	21.07	12.91
$[13s10p9d/5s4p1d]$	32.57	25.25	21.07	12.91
$[13s10p8d/5s4p1d]$	32.57	25.25	21.07	12.91
$[13s10p7d/5s4p1d]$	32.57	25.25	21.07	12.91
$[13s10p6d/5s4p1d]$	32.57	25.25	21.07	12.91
$[13s10p5d/5s4p1d]$	32.61	25.25	21.08	12.91
$[13s10p4d/5s4p1d]$	32.62	25.26	21.09	12.92
$[13s10p3d/5s4p1d]$	32.56	25.25	20.91	12.88
$[13s10p2d/5s4p1d]$	31.63	24.81	19.55	12.42
$[13s10p1d/5s4p1d]$	23.22	19.10	12.21	7.95
$[13s10p4d/7s5p2d]$[c]	32.40	25.08	21.44	13.01
$M_L = \pm 1$ component				
$(13s10p10d)$	41.81		18.03	14.84
$[13s10p10d/5s4p10d]$	41.78		18.03	14.83
$[13s10p10d/5s4p1d]$[b]	41.52		17.77	14.52
$[13s10p9d/5s4p1d]$	41.52		17.77	14.52
$[13s10p8d/5s4p1d]$	41.52		17.77	14.52
$[13s10p7d/5s4p1d]$	41.52		17.77	14.52
$[13s10p6d/5s4p1d]$	41.52		17.77	14.52
$[13s10p5d/5s4p1d]$	41.56		17.78	14.52
$[13s10p4d/5s4p1d]$	41.57		17.78	14.53
$[13s10p3d/5s4p1d]$	41.55		17.75	14.40
$[13s10p2d/5s4p1d]$	41.03		17.28	13.42
$[13s10p1d/5s4p1d]$	32.69		11.99	7.65
$[13s10p4d/7s5p2d]$[c]	41.06		17.87	14.72

[a] In $[13s10pm_dd/5s4p1d]$ m_d is the number of primitive d functions contributing to the polarization function and corresponds to the removal of $10 - m_d$ highest–exponent GTOs from the d subset

[b] The contraction coefficient at the highest–exponent d–type GTO is about 10^8–times smaller than the largest contraction coeffcient

[c] Results obtained with PolX basis sets [7]. The PolX used in present calculations are taken from the PolX Basis Set Library [9,20] and differ from those of Ref. [7] by the way of handling contractions. This, however, leads to only marginal (of the order of 0.01 a.u.) differences in the calculated polarizabilities. See also Ref. [8,9]

exponents make a significant contribution to the contracted d–type functions. The corresponding numerical data are given in Table 1.

All numerical data of Table 1 correspond to derivatives of the field–dependent energy calculated for the external electric field strength equal to 0.001 a.u. Through all decimals displayed in Table 1 these results agree with the derivatives of the induced dipole moment. The data of Table 1 have been obtained from restricted open shell HF calculations by using the RASSCF code of MOLCAS [19].

The SCF HF atomic polarizability values presented in Table 1 show that the contraction of the sp subset has a negligible effect on the calculated data. This can be seen from the comparison of the calculated atomic polarizabilities with fully uncontracted $(13s10p10d)$ and partly contracted $[13s10p10d/5s4p10d]$ sets. With the latter basis set considered as a reference, we have studied the effect of contracting the d subset to a single polarization function according to Eq. (10) and then removing one–by–one the highest–exponent primitive d functions. The data of Table 1 show that the contraction of the d subset to a single d–type polarization function diminishes the polarizability values by about 1–2%. However, the removal of up to seven highest–exponent d–type GTOs from the polarization function has practically no influence on the calculated polarizabilities. Hence, the $[13s10p3d/5s4p1d]$ becomes a suitable candidate for a reduced–size polarized ZmPolX (Z3PolX) basis set. Also the removal of eight highest–exponent d–type functions which leads to the $[13s10p2d/5s4p1d]$ (Z2PolX) set gives quite acceptable values of atomic polarizabilities. However, the gain in computing times with Z2PolX sets as compared to Z3PolX bases is insignificant [13] and, if not mentioned otherwise, the latter will now be referred to as the standard ZPolX basis sets.

The ZmPolX basis set data for m ranging from 10 to 1 are also compared with the results obtained using the PolX sets [7]. One finds that, at least in atomic calculations, the performance of the Z3PolX (= ZPolX) sets is practically as good as that of the earlier PolX sets. It is worth noting that the size of the PolX sets for the second–row atoms amounts to 32 (spherical) functions whereas that of the ZPolX sets equals to only 22 functions. Hence, passing from PolX to ZPolX sets means the reduction of the basis set size by approximately one third does not result in any major deterioration of the accuracy of the atomic polarizability data. One may therefore expect this will also hold in molecular calculations.

Table 2 Dipole moments of the second–row hydrides. Results of SCF HF and MP2 calculations with different basis sets. All values in a.u.

Basis set	Molecule[a]		
	PH_3	H_2S	HCl
SCF HF results			
Z2PolX[b]	0.375	0.533	0.546
Z3PolX[c]	0.305	0.441	0.467
Z3PolX(uncontr.)[d]	0.300	0.458	0.492
$(13s10p10d)$[e]	0.262	0.422	0.466
PolX[f]	0.281	0.436	0.474
aug–cc–pVDZ[g]	0.282	0.448	0.488
aug–cc–pVTZ[g]	0.267	0.429	0.472
MP2 results[h]			
Z2PolX[b]	0.335	0.484	0.496
Z3PolX[c]	0.281	0.417	0.437
Z3PolX(uncontr.)[d]	0.274	0.427	0.461
$(13s10p10d)$[e]	0.222	0.385	0.436
PolX[f]	0.249	0.408	0.451
aug–cc–pVDZ[g]	0.251	0.420	0.461
aug–cc–pVTZ[g]	0.241	0.396	0.439
MP2 results[i]			
PolX[f]	0.243	0.404	0.449
aug–cc–pCVDZ[g]	0.244	0.416	0.460
aug–cc–pCVTZ[g]	0.229	0.388	0.435

[a] All molecular geometries taken from Ref. [7]

[b] Z2PolX ([$13s10p2d/5s4p1d$]) basis sets for the second–row atoms and the Z2PolH ([$6s2p/3s1p$]) basis set for H

[c] ZPolX (Z3PolX) basis sets for all atoms

[d] Fully uncontracted ZPolX (Z3PolX) basis sets for all atoms, i.e., $(13s10p3d)$ and $(6s3p)$ sets for the second–row atoms and H, respectively

[e] Fully uncontracted polarized basis sets with full size polarization functions. The compatible basis set for H is $(6s6p)$ [12]

[f] PolX basis sets ([$6s4p/3s2p$] for H and [$13s10p4d/7s5p2d$] for the second–row atoms [7]. The PolX used in present calculations are taken from the PolX Basis Set Library [9,20] and differ from those of Ref. [7] by the way of handling contractions. This, however, leads to only marginal differences in the calculated dipole moments and polarizabilities. See also Ref. [8]

[g] Dunning's augmented correlation consistent valence and core–valence basis sets [5] as available form EMSL Basis Set Library [21]

[h] Only eight valence electrons are correlated in MP2 calculations

[i] 16 valence and subvalence electrons are correlated in MP2 calculations

3 Dipole moment and polarizability calculations with ZPolX basis sets. Performance tests

To firmly establish the quality and usefulness of the ZPolX (Z3PolX and Z2PolX) sets described in Sect. 2, we have carried out several test calculations of molecular dipole moments and polarizabilities. The corresponding ZPolX basis sets used for H and the first–row atoms in the studied molecules are those developed in part I [12]. The present comparisons will be carried out for molecular electric properties calculated at the level of the SCF HF and MP2 approximations, i.e., the approximations that are most likely to be used for large molecules. The MP2 data will also indicate the possible use of the ZPolX basis sets in DFT calculations of molecular electric properties [13].

The molecular data reported in this paper correspond to finite–field perturbation calculations and have been systematically obtained with the field strength values of 0.001 a.u. At the level of the SCF HF approximation the energy derivatives have been checked against the expectation values of the dipole moment and its derivatives. All calculations have been performed with the MOLCAS software [19].

3.1 Hydrides of the second–row elements

The dipole moment results for the second–row hydrides, PH_3, H_2S, and HCl, calculated with Z2PolX and Z3PolX basis sets are presented in Table 2. They are compared with the results obtained with fully uncontracted Z3PolX sets, i.e., $(13s10p3d)$ and $(6s3p)$ for the second–row atoms and hydrogen [12], respectively. Also the results for fully uncontracted sets containing ten d–type polarization functions for the second–row atoms and six p–type polarization functions for H [12] are presented. The reference data include the results obtained with PolX basis sets [7,8,20] and Dunning's augmented correlation consistent valence (aug–cc-pVXZ) and core–valence (aug–cc–pCVXZ) bases with $X = 2$ (D) and $X = 3$ (T).

Two series of MP2 calculations have been carried out in order to investigate the importance of the core–valence electron correlation contribution. The first series of MP2 calculations corresp onds to correlating only the eight valence electrons of the studied molecules. The second series extends the electron correlation to the subvalence $2s^2 2p^6$ shell of the second–row atom, i.e., corresponds to correlating 16 electrons.

Table 3 Dipole polarizabilities of the second–row hydrides. Results of SCF HF and MP2 calculations with different basis sets. All values in a.u.

Basis set	Molecule [a]							
	SiH$_4$	PH$_3$		H$_2$S			HCl	
	α	α_{xx}	α_{zz}	α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{zz}
SCF HF results								
Z2PolX[b]	30.15	29.09	29.40	22.04	23.18	22.41	14.84	17.28
Z3PolX[c]	30.03	29.26	29.61	23.42	23.18	22.50	15.78	17.36
Z3PolX(uncontr.)[d]	30.13	29.64	30.48	23.51	23.71	23.37	15.85	17.90
(13s10p10d)[e]	29.70	29.45	30.57	24.14	23.71	23.44	16.21	17.93
PolX[f]	29.96	29.58	30.58	23.86	23.69	23.39	16.05	17.91
aug–cc–pVDZ[g]	29.98	29.15	29.80	22.63	22.70	22.25	14.71	17.06
aug–cc–pVTZ[g]	29.79	29.48	30.41	23.71	23.52	23.20	15.81	17.74
MP2 results[h]								
Z2PolX[b]	31.46	30.42	32.32	25.25	24.42	24.13	16.66	18.29
Z3PolX[c]	31.57	30.52	32.12	26.11	24.34	24.09	17.30	18.38
Z3PolX(uncontr.)[d]	31.28	30.31	31.95	25.09	24.36	24.34	16.72	18.55
(13s10p10d)[e]	30.63	29.90	31.66	25.37	24.19	24.20	16.87	18.43
PolX[f]	30.98	30.06	31.78	25.14	24.21	24.20	16.77	18.45
aug–cc–pVDZ[g]	30.97	29.61	30.95	23.58	23.02	22.88	15.16	17.46
aug–cc–pVTZ[g]	30.77	29.97	31.49	24.77	24.00	23.92	16.48	18.23
MP2 results[i]								
PolX[f]	31.03	30.09	31.84	25.21	24.24	24.24	16.81	18.47
aug–cc–pCVDZ[g]	31.04	29.58	30.96	23.58	23.01	22.88	15.16	17.45
aug–cc–pCVTZ[g]	30.84	29.90	31.47	24.76	23.96	23.91	16.48	18.22

[a] See the corresponding footnote to Table 2. The orientation of the coordinate axes is as follows. PH$_3$: the z axis coincides with the C$_3$ symmetry axis, H$_2$S: the z axis coincides with the C$_2$ symmetry axis; the molecule lies in the yz plane; HCl: the molecule lies along the z axis

[b–i] See the corresponding footnotes to Table 2

In spite of a rather small deterioration of the atomic polarizability data observed on passing from Z3PolX to Z2PolX basis sets, the calculated dipole moments of the second–row hydrides show that the Z2PolX sets are not sufficiently flexible to account for the intramolecular polarization of the electron density distribution. Thus, on the basis of the data of Table 2 one could not recommend the Z2PolX sets for calculations of dipole moments in molecules containing the second–row atoms. The Z3PolX sets give, however, acceptable values of dipole moments. At the level of the SCF HF approximation their performance is at most by about 0.02 a.u. worse than that of the much larger PolX sets and this may increase to about 0.03 a.u. in the MP2 approximation.

The core–valence correlation contribution is unlikely to be correctly predicted in MP2 calculations with ZPolX basis sets since the single d–type polarization function is appropriate only for describing the external electric field effect on the valence $3p$ orbital. Including one more polarization function selected according to the shape of the $2p$ SCF HF orbital would increase the total basis set size. Under the assumption that the ZPolX sets should be as small as possible, some sacrifice arising from the neglect of the core–valence contribution to the calculated electric properties appears to be acceptable. The magnitude of this contribution can be estimated from the MP2 data presented in Table 2.

In addition to MP2 calculations in the valence approximation with PolX augmented correllation consistent valence basis sets of Dunning, we have also carried out similar MP2 calculations with 16 correlated electrons (eight valence electrons and eight L–shell electrons of the second–row atom). The PolX basis sets involve two d–type polarization functions with high enough orbital exponents to at least partly account for the polarization of the L shell. For the same reason the valence aug–cc–pVXZ sets of Dunning were replaced by their core–valence counterparts (aug–cc-pCVXZ). The differences between the valence–only and core–valence MP2 data show that the core–valence contribution to the dipole moments of hydrides amounts to about -0.01 a.u. for PH$_3$ and becomes negligible for HCl.

The results of a similar study of dipole polarizabilities of the second–row hydrides are presented in Table 3. The dipole polarizabilities of these molecules calculated with Z3PolX (ZPolX) basis sets are, in most cases, close to the data obtained with PolX and Dunning's sets. Moreover, in the dipole polarizability calculations the performance of the Z2PolX sets is also acceptable. However, as has been already mentioned, the Z2PolX and Z3PolX basis sets differ only by the number of primitive GTOs in the d–type polarization CGTO and this difference affects only the timing of calculations and may not be worth exploiting. Let us also note that the core–valence contribution to dipole polarizabilities of the second–row hydrides is, in terms of the overall accuracy of the present data, of negligible importance.

3.2 Diatomic and polyatomic molecules with second–row elements

Additional documentation of the performance of the ZmPolX ($m = 2, 3$) sets developed in this study is given by the

Table 4 Dipole moments of selected diatomic and polyatomic molecules with second–row elements. Results of SCF HF and MP2 calculations with different basis sets. All values in a.u.

Molecule[b]	Basis set[a]				
	Z2PolX	Z3PolX (ZPolX)	PolX	aug–cc–pVDZ	aug–cc–pVTZ
SCF HF results[c]					
CS	0.513	0.595	0.626	0.614	0.628
				(0.618)	(0.640)
SiS	0.941	0.853	0.879	0.890	0.899
				(0.890)	(0.896)
PCl_3	0.387	0.254	0.252	0.262	0.248
				(0.261)	–[d]
SO_2	0.853	0.768	0.782	0.798	0.797
				(0.797)	(0.790)
H_2CS	0.929	0.884	0.855	0.871	0.850
				(0.867)	(0.842)
Cl_2CO	0.521	0.568	0.597	0.595	0.606
				(0.598)	(0.612)
MP2 results[e]					
CS	0.937	0.937	0.879	0.876	0.887
			(0.883)	(0.876)	(0.890)
SiS	0.530	0.546	0.603	0.610	0.629
			(0.607)	(0.621)	(0.650)
PCl_3	0.312	0.203	0.233	0.235	0.206
			(0.236)	(0.243)	–[d]
SO_2	0.673	0.593	0.602	0.622	0.614
			(0.605)	(0.622)	(0.608)
H_2CS	0.662	0.659	0.655	0.660	0.645
			(0.650)	(0.660)	(0.642)
Cl_2CO	0.398	0.411	0.432	0.436	0.453
			(0.434)	(0.436)	(0.455)

[a] The ZmPolX basis sets for the first–row atoms are those of Ref. [12]. See also footnote f to Table 2

[b] The following molecular geometries are assumed in calculations: CS: $R_{CS} = 2.900540$ a.u., [22]; SiS; $R_{SiS} = 3.645848$ a.u. [22]; PCl_3: $R_{PCl} = 3.860710$ a.u., ∠(ClPCl) = 100.105° [22]; SO_2: $R_{SO} = 2.706277$ a.u., ∠(OSO) = 119.5° [22]; H_2CS: $R_{CS} = 3.043971$ a.u., $R_{CH} = 2.064525$ a.u., ∠(HCH) = 116.87^o [23]; Cl_2CO: $R_{CO} = 2.221562$ a.u., $R_{CCl} = 3.284533$ a.u., ∠(ClCCl) = 111.79° [24]. The dipole moment axis is assumed to be the z axis of the coordinate system. The SO_2, H_2CS, and Cl_2CO molecules are placed in the yz plane

[c] The values in parentheses are the SCF HF dipole moments calculated with the corresponding aug–cc–pCVXZ basis sets of Dunning

[d] Not calculated

[e] For each molecule the first row of entries gives the valence MP2 results. The numbers in parentheses include the core correlation contribution due to the L–shells of the second–row atoms. In calculations with Dunning's basis sets these results correspond to the use of the aug–cc–pCVXZ sets

dipole moment and polarizability data for selected diatomic and polyatomic molecules involving second–row elements. In these calculations the ZmPolX basis sets for H and the first–row atoms are those presented in Part I [12]. The main series of the present results corresponds to SCF HF and valence MP2 approximations. Similarly as in the case of the second–row hydrides the estimates of the core–valence contributions have been obtained from MP2 calculations which include the L–shell electron correlation contributions. Also all numerical data presented in this section follow from finite field calculations with the field strength values of 0.001 a.u. and have been obtained by using the MOLCAS set of quantum chemistry programs [19].

The dipole moment data are displayed in Table 4. The ZmPolX results calculated at the level of the SCF HF and valence MP2 approximations are compared there with the corresponding data obtained with the usual PolX and with Dunning's aug–cc–pVDZ and aug–cc-pVTZ basis sets. The core–valence contributions to molecular dipole moments can be estimated by comparing the valence MP2 data for aug–cc–pVXZ sets and the MP2 results calculated with aug–cc–pCVXZ basis sets and double excitations extended to the L–shell orbital of the second–row atoms. One finds that the core–valence contribution to molecular dipole moments is usually quite small. Only in the case of SiS does it become of the order of 0.02 a.u.

In a similar way to the earlier results for the second–row hydrides, the dipole moment data show that the Z2PolX basis sets lead to rather poor results. However, the Z3PolX sets give quite acceptable accuracy taking into account their small size. The calculated results are usually within about 0.02–0.04 a.u. of the PolX and aug–cc-pVDZ data.

The dipole polarizability results are collected in Tables 5, 6, and 7, their values resemble the pattern already discussed for the hydrides. Both the Z2PolX and Z3PolX basis sets perform rather well for molecular polarizabilities and can be used to obtain dipole polarizabilty and related data for larger molecules. The accuracy of these results is usually between that obtained with the DZ- and TZ-augmented correlation-consistent valence basis sets of Dunning and close

Table 5 Dipole polarizabilities of selected diatomic molecules with second–row elements. Results of SCF HF and MP2 calculations with different basis sets. All values in a.u.

Molecule[b]		Basis set[a]				
		Z2PolX	Z3PolX (ZPolX)	PolX	aug–cc–pVDZ	aug–cc–pVTZ
SCF HF results [c]						
Cl_2	α_{xx}	21.77	23.42	23.79	22.24 (22.28)	23.57 (23.67)
	α_{zz}	42.52	41.89	42.10	40.57 (40.55)	41.77 (41.80)
CS	α_{xx}	22.64	23.84	23.56	22.97 (22.99)	23.78 (23.84)
	α_{zz}	35.47	34.43	36.96	36.57 (36.59)	36.95 (37.00)
SiS	α_{xx}	39.89	41.32	40.97	40.06 (40.09)	41.37 (41.46)
	α_{zz}	61.97	59.94	63.39	62.82 (62.87)	63.06 (63.14)
MP2 results [d]						
Cl_2	α_{xx}	24.38	25.54	24.97 (25.03)	22.97 (22.96)	24.66 (24.68)
	α_{zz}	41.76	42.17	41.54 (41.60)	39.65 (39.63)	41.24 (41.31)
CS	α_{xx}	23.67	24.47	23.31 (24.48)	22.89 (22.87)	23.60 (23.60)
	α_{zz}	37.59	36.93	37.88 (36.95)	37.62 (37.63)	37.64 (37.64)
SiS	α_{xx}	41.89	42.82	40.93 (42.86)	40.12 (39.99)	41.61 (41.33)
	α_{zz}	69.59	67.43	68.46 (67.47)	68.00 (68.07)	67.80 (67.83)

[a–c] See the corresponding footnotes to Table 4. For Cl_2 the bond distance value assumed in calculations is $R_{\mathrm{ClCl}} = 3.756586$ a.u. [22]. The molecule is lying on the z axis of the coordinate system

[d] See footnote e to Table 4

to the accuracy of the PolX data. Taking into account the small size of the ZPolX basis sets, dipole moments and polarizabilities agree well with those obtained with larger sets. It is worth stressing that the ZPolX sets are not designed for highly accurate calculations of molecular electric properties. Their purpose is to permit systematic and moderately accurate calculations of these properties for larger molecules of chemical interest.

4 Conclusions

The performance of the ZPolX basis sets derived in this study for the second–row atoms has been investigated in calculations of molecular dipole moments and polarizabilities. These basis sets have been found to offer acceptable accuracy of the calculated molecular electric properties and to considerably widen the area of possible applications in computational quantum chemistry. The ZPolX sets are likely to be the smallest polarized basis sets which can be used in large–scale SCF HF, post–HF, and DFT calculations of molecular dipole moments, dipole polarizabilities, and related properties without major deterioration of the quality of the computed data.

The need for the reduced–size polarized basis sets came from calculations of the Raman spectra of large organic molecules [25,26]. The usual PolX sets have been found to give good results for both frequencies and intensities in the Raman spectra [27]. However, their size was still too big to handle larger systems that are of interest to experimentalists. The resulting demand for the reduction of the size of PolX set without any major deterioration of their useful features came along with the investigation of the explicit time–dependence of basis sets for calculations of atomic and molecular response functions [11]. The observation that, for static polarizabilities, the set of polarization functions (9) is dominated by one component (10) initiated our search for reduced size of PolX sets and led to the idea of ZPolX basis sets [12].

Obviously, as shown by the present data and those for the molecules comprising the first–row elements, in comparison with the PolX values there was some deterioration in the accuracy of the dipole moment and polarizability results. However, the new reduced–size polarized basis sets generated for H and the first–row atoms have been found to perform very well in theoretical simulations of the Raman spectra. Similar investigations, with ZPolX basis sets reported in this paper, are being carried out for molecules containing second-row elements [28] and early results are very promising.

The generation of the ZPolX sets described in this paper was aimed at finding the smallest basis sets capable of systematically reproducing dipole moments and polarizability data. The method used here is by no means restricted to small basis sets and can be used to obtain polarized basis sets of

Table 6 Dipole polarizabilities of selected polyatomic molecules with second–row elements. Results of SCF HF calculations with different basis sets. All values in a.u.

Molecule[b]		Basis set [a]				
		Z2PolX	Z3PolX (ZPolX)	PolX	aug–cc–pVDZ	aug–cc–pVTZ
SCF HF results [c]						
CCl_4	α	63.38	64.77	66.06	64.29	65.81
					(64.35)	(66.02)
$SiCl_4$	α	68.87	70.88	71.59	69.76	70.93
					(69.89)	– [d]
CS_2	α_{xx}	33.56	35.66	36.31	34.83	36.48
					(34.87)	(36.61)
	α_{zz}	89.82	89.02	92.79	92.32	93.01
					(92.47)	(93.39)
PCl_3	α_{xx}	69.52	70.59	71.43	69.80	70.99
					(69.82)	–[d]
	α_{zz}	49.93	52.34	53.25	51.55	53.08
					(51.58)	–[d]
SO_2	α_{xx}	17.94	18.48	18.34	17.66	18.39
					(17.65)	(18.40)
	α_{yy}	33.94	32.57	31.98	31.71	31.59
					(31.63)	(31.35)
	α_{zz}	19.71	20.21	20.75	20.22	20.67
					(20.23)	(20.68)
H_2CS	α_{xx}	25.65	26.58	26.80	25.49	26.75
					(25.50)	(26.79)
	α_{yy}	28.68	29.73	30.40	28.87	30.26
					(28.90)	(30.33)
	α_{zz}	45.78	45.32	46.80	46.41	46.84
					(46.43)	(46.89)
Cl_2CO	α_{xx}	28.63	30.27	30.57	29.38	30.43
					(29.41)	(30.52)
	α_{yy}	50.24	50.56	51.50	50.42	51.38
					(50.45)	(51.49)
	α_{zz}	42.22	42.84	43.94	42.77	43.74
					(42.81)	(43.85)

[a–d] See the corresponding footnotes to Tables 4 and 5. The additional geometry data are: CCl_4: $R_{\mathrm{CCl}} = 3.339146$ a.u. [22]; $SiCl_4$: $R_{\mathrm{SiCl}} = 3.815357$ a.u. [22]. Both these molecules are assumed to have tetrahedral symmetry

very high quality. Once some initial basis set without polarization functions is selected, the corresponding polarized sets can be obtained by applying Eq. (9). There are, however, some conditions which need to be satisfied.

The most important condition is that the reference (unpolarized) basis set must be sufficiently diffuse to correctly describe the remote regions of the electron density distribution. In the present case the initial $[13s10p/5s4p]$ set is of the triple–zeta quality in the valence region. This is perhaps the least extended initial basis set which can be used for the generation of polarization functions. Its further extension by diffuse s– and p–type functions would make it suitable for the generation of higher–order polarization functions [16].

With the selected initial basis set one then generates polarization functions according to the method described in Sect. 3.1. This step does not need to be restricted to the generation of just one polarization function [11] for the outermost valence orbital. The method used here to obtain ZmPolX sets can be applied to any atomic orbital and can produce several polarization functions. This would lead to high-quality polarized basis sets of quite large size but that was not the aim of the present study.

The method [12] used here to generate the ZmPolX basis sets can be in principle used for any element. In the case of the Group Ia and IIa elements one may need to add polarization functions to describe the contribution due to the subvalence shell. A similar condition also applies to the generation of the ZPolX sets for transition metals. Studies in this direction are in progress.

Finally, let us stress that the present approach to the generation of basis sets appropriate for calculations of molecular electric properties is rooted in a well defined model of the polarization of the electronic density distribution by the external electric field [10, 11, 14]. The ad hoc choice of polarization functions or their optimizations is replaced by their generation according to this model. The model physics involved in the present approach is the most important factor which determines the efficiency of the ZmPolX sets.

The ZmPolX basis sets presented in this study as well as those generated earlier for H and the first–row atoms can be either downloaded from the Bratislava Basis Set Library [20] or obtained directly from the authors. A survey of different polarized basis sets will be published elsewhere [9].

Table 7 Dipole polarizabilities of selected polyatomic molecules with second–row elements. Results of MP2 calculations with different basis sets. All values in a.u.

Molecule [b]		Basis set[a]				
		Z2PolX	Z3PolX (ZPolX)	PolX	aug–cc–pVDZ	aug–cc–pVTZ
MP2 results[c]						
CCl_4	α	68.39	69.76	69.29	67.09	69.02
				(69.42)	(67.10)	(69.11)
$SiCl_4$	α	76.56	77.76	76.41	74.15	75.78
				(76.61)	(74.28)	–[d]
CS_2	α_{xx}	35.98	37.23	36.45	34.82	36.59
				(37.27)	(34.79)	(36.59)
	α_{zz}	100.37	99.62	98.46	98.14	97.85
				(99.71)	(98.06)	(97.72)
PCl_3	α_{xx}	75.23	76.24	75.45	73.37	75.10
				(75.59)	(73.36)	–[d]
	α_{zz}	55.16	56.79	56.12	54.06	55.87
				(56.24)	(54.05)	–[d]
SO_2	α_{xx}	19.76	20.01	19.58	18.74	19.51
				(20.02)	(18.71)	(19.44)
	α_{yy}	36.03	34.82	35.01	34.55	34.43
				(34.81)	(34.53)	(34.27)
	α_{zz}	23.26	23.46	23.65	22.93	23.30
				(23.47)	(22.92)	(23.27)
H_2CS	α_{xx}	26.39	26.82	26.29	24.88	26.23
				(26.84)	(24.86)	(26.22)
	α_{yy}	30.87	31.64	31.44	29.70	31.04
				(31.67)	(29.70)	(31.05)
	α_{zz}	42.92	43.55	44.17	43.71	43.91
				(43.56)	(43.70)	(43.92)
Cl_2CO	α_{xx}	31.75	32.73	32.05	30.51	31.80
				(32.75)	(30.50)	(31.81)
	α_{yy}	56.22	56.75	56.18	54.77	56.00
				(56.79)	(54.77)	(56.07)
	α_{zz}	46.34	46.78	47.00	45.43	46.60
				(46.81)	(45.43)	(46.62)

[a,b] See the corresponding footnotes to Tables 4, 5, and 6

[c] See footnote e to Table 4

[c] Not calculated

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