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REGULAR ARTICLE

Reduced-size polarized basis sets for calculations of molecular electric properties. IV. First-row transition metals

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Abstract Recent studies of the perturbation-dependent basis sets have indicated the possibility of a significant reduction of the size of the usual CGTO sets without considerable loss of accuracy in calculations of molecular electric properties. The resulting (ZPolX) basis sets have been developed for several atoms of the first and second row of the Periodic Table. The same method of the ZPolX basis set generation is extended for the first-row transition metals and the corresponding contracted ZPolX basis sets of the size [6s5p3d1f] are determined for both nonrelativistic and scalar relativistic calculations. The performance of the ZPolX basis sets is verified in calculations on the first-row transition metal oxides at the level of the ROHF, ROHF/CASPT2, and ROHF/CCSD(T) approximations. Also the study of the dipole polarizability of $TiCl_4$ confirms the excellent features of these very compact basis sets. The ZPolX basis sets for nonrelativistic and relativistic calculations of molecular electric properties are available on the web page http://www.chem.uni.torun.pl/zchk/basis-sets.html.

Keywords ZPolX basis sets · Dipole moment and polarizability calculations · First-row transition metals · First-row transition metal oxides

1 Introduction

The experimental determination of molecular properties faces a variety of difficulties and limitations and molecular electric properties are particularly difficult to measure. Their numerical values are usually derived from some model of the measured feature and rarely come directly from the experimental data [1]. The gas phase measurements, which lead to presumably most accurate data for molecular electric properties, are limited to small molecules. The data from measurements in liquids and solids are uncertain because of intermolecular interactions which may significantly modify the isolated molecule data. All this clearly indicates the importance of the computational determination of molecular electric properties.

Though for large polyatomic molecules the calculated electric property data may not be required to be of very high accuracy, to obtain their reliable values could be a difficult task. The main problem affecting the computing times is the size of basis sets which need to be used. First, the basis sets used in calculations of molecular electric properties must comprise sufficiently diffuse functions which properly describe the electron density distribution far away from the nuclei. Second, to describe the electric field effects one must include atomic polarization functions, i.e., atomic functions of the higher angular momentum value. These conditions result in very large all-purpose basis sets [2–9], which can be used to calculate any molecular property with high accuracy. Simultaneously the size of these basis sets significantly reduces the range of their applicability.

Another direction of the basis set development is to standardize them for certain type of molecular properties and to limit their size by weakening the stringent accuracy requirements which are characteristic for all-purpose sets. This direction appears to have been pioneered by Pople et al. by the

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development of relatively small Gaussian basis sets, mostly for the purpose of the theoretical determination of molecular geometries [10,11]. In the case of molecular electric properties a similar idea underlies the development of the so-called polarized basis set (PolX, where X stands for the element symbol) [12–14].

The PolX sets have been developed by considering the electric-field-dependence of exact solutions for the harmonic oscillator in a static homogeneous electric field [15]. Recently, this approach has been extended to time-dependent problems [16]. This extension has revealed some new useful features of the electric-field-dependence of Gaussian orbitals and suggested that certain reduction of the size of PolX basis sets is possible without seriously affecting the accuracy of the calculated dipole moments and dipole polarizabilities [17,18]. These new electric-property-oriented basis sets (referred to as ZPolX sets) are, by one-third smaller, than the PolX bases. Yet they give almost the same accuracy of the calculated molecular properties [17,18]. This line of the basis set development is continued in the present paper by the generation and testing of the ZPolX for the first-row of transition elements (X = Sc through Zn). With the wide range of applications of the electronic structure computational methods for transition metal compounds [19–23], the development of these basis sets appears to be worth pursuing.

The paper is organized in the following way. In Sect. 2, a brief survey of the main principles underlying the generation of ZPolX basis sets is given and the general method is detailed for the first-row transition metals. In the case of these elements the relativistic effects may already be of some importance and for this reason the ZPolX basis sets are obtained for both nonrelativistic and relativistic calculations. The relativistic effects are accounted for in the framework of the scalar approximation to the infinite-order two-component (IOTC) method [24]. The main computational aspects of calculations reported in this paper are summarized in Sect. 3. The results of different atomic and molecular calculations with ZPolX and ZPolX_iotc basis sets are presented and discussed in Sect. 4. The ZPolX (ZPolX_iotc) sets generated in this study are first tested in the calculations of dipole polarizabilities for transition metal atoms and then used in calculations of dipole moments and polarizabilities of their oxides. Additional test of the performance of ZPolX basis sets is obtained in the calculations of the electric dipole polarizability of the titanium chloride molecule, whose different electric properties have been recently studied by Hohm and Maroulis [25]. The results calculated with the ZPol_iotc basis set are also compared with the polarizability values computed with large, systematically extended basis sets. The paper is summarized in Sect. 5. All basis set data can be accessed at web addresses [26] or received directly from the authors.

2 The generation of ZPolX basis sets

2.1 Generation of the reduced-size polarized (ZPolX) basis sets

The idea of the reduced-size polarized basis sets presented in [17] is based on a simple physical model of a harmonic oscillator embedded in the external electric field [15]. This model has been used earlier to generate the PolX basis set. However, its use required either very large extended initial basis sets [27] or a rather extensive preprocessing of the initial basis set [12,13]. The question how to overcome this preprocessing of the initial basis set follows from the recent study of the time-dependent electric field perturbations [16]. These investigations have also indicated that some further reduction of the size of PolX sets, without significant deterioration of the calculated electric properties, is possible. This line of development is followed in the present paper.

The polarized basis sets are obtained from some source set of Gaussian functions, which is sufficiently flexible to describe the electronic structure of the isolated atom. Since both PolX and ZPolX are required to be "small", a primitive set of Gaussians (GTO) used, e.g., to obtain double–ζ (DZ) quality contracted (CGTO) atomic basis sets, is considered to be a reasonable choice for the source set. However, the external electric field perturbation affects mostly the outer part of the electron-density distribution, and thus, extending the source set by some diffuse functions for valence shells is appropriate. This leads to what is called the extended source set of primitive Gaussian functions, $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$. In the absence of the external electric field, i.e., for $\mathbf{F}=\mathbf{0}$, each of these functions of the electron coordinate vector $\mathbf{r}$ is defined by its origin $\mathbf{R}_\mu(\mathbf{0})$, orbital exponent α_μ, and the angular momentum quantum number l. These functions are used to obtain the eigenvectors $u(\mathbf{r};\mathbf{0})$ in the absence of the external electric field,

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

Once these eigenvectors are determined, the next step is to consider the shape of their dependence on the external electric field [12,13,17,18,27]. Owing to the proposed model [15,16] of the field-dependence of the initial source basis set,

$$G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\rightarrow G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu), \tag{2}$$

the eigenvectors $u(\mathbf{r};\mathbf{0})$ become field-dependent,

$$u(\mathbf{r};\mathbf{0})\rightarrow u(\mathbf{r};\mathbf{F})=\sum_\mu c_\mu(\mathbf{F})G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu), \tag{3}$$

through both the expansion coefficients and basis set functions.

The usual methods of the electronic structure theory assume that the basis set functions are field-independent and this is compensated by the use of several polarization functions in the $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ set. The opposite end is to assume that essentially all of the field-dependence is in $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu)\}$ and the change in the expansion coefficients follows solely from the orthonormality conditions [28]. Then, for each one-electron function $u(\mathbf{r};\mathbf{F})$, which is determined by the expansion into the augmented source set $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ and used to build many-electron determinantal functions of the given molecule, one can determine the explicit form of the first-order perturbed term, $u^{(1)}(\mathbf{r};\mathbf{0})$

$$u^{(1)}(\mathbf{r};\mathbf{0}) \sim \sum_{n=1} b_n(f_{n-}^{(1)} + f_{n+}^{(1)}), \tag{4}$$

with

$$f_{n\pm} = \sum_{\mu} c_\mu(\mathbf{0})\alpha_\mu^{-n+1\mp 1/2} G_{\mu,l\pm 1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu). \tag{5}$$

The functions contributing to (4) must be linearly independent. Thus, the summation in (4) and (5) is actually limited by the number of uncontracted functions in the $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ set.

The field-independent first-order perturbed orbitals (4) can be considered as the additional (polarization) functions, which should be used to supplement the augmented source set $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$. Because of the use of the explicit electric-field-dependence of the $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu)\}$ set, these compact (polarization) functions correctly represent the first-order system response to the external electric field perturbation. Thus, if the augmented source set $\{G_{\mu,l}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu)\}$ were extended by $u^{(1)}(\mathbf{r};\mathbf{0})$ functions, one would obtain what is called the polarized basis set. This basis set is obviously independent of the external electric field and can be used in routine calculations of molecular electric properties.

There are several ways of reducing the size of the initial source set augmented with polarization functions of (4). First, the augmented source set can be contracted in the usual way, though one should take care that the lowest-exponent basis set functions are left uncontracted. Second, the number of polarization functions can be reduced by the consideration of the mechanism of the polarization of atomic shells. The main polarization effect comes from the valence one-electron functions. Thus, the contracted polarization functions (4) can be limited to the valence part of the occupied atomic orbitals. One should also recognize that the f_{n-} contribution to (4) will mostly reproduce basis functions which are already present in the initial source set. Hence, the f_{n+} contribution should be sufficient for the representation of the polarization effect due to the external electric field. As already mentioned, the range of values of n is limited by the number of initial basis functions used in (1). Moreover, the importance of different functions f_{n+} varies with n. The most important [16] contribution has been found to be due to $n = 2$. This observation is underlying the structure of ZPolX basis sets which appear to be the most compact polarized basis sets for realistic calculations of molecular electric properties.

2.2 ZPolX basis sets for the first-row transition metal atoms

The method described in Sect. 2.1 can be applied at any level of the generation of atomic eigenvectors. The polarization functions can be generated for atomic valence SCF HF orbitals. One can also build them for atomic orbitals which follow from multiconfiguration SCF calculations and obtain polarization functions for weakly occupied correlating orbitals. In the present study, the method is based on restricted open shell Hartree–Fock (ROHF) eigenvectors calculated for the investigated transition metal atoms.

The choice of the source basis set is to a large extent irrelevant, for the method described in Sect. 2.1 applies equally well to any initial set of functions. Hence, the source basis set could be any of the usual optimized basis sets, which is considered to be good enough for calculations of molecular energies and geometries. The ZPolX basis sets generated in this paper are derived from the $(14s9p5d)$ sets of energy-optimized uncontracted Gaussian functions of Huzinaga [29,30].

The determination of orbital exponents from the requirement of the ROHF SCF energy minimum heavily weighs the high-exponent Gaussian functions. Thus, the source sets require some preprocessing oriented towards the increase of their flexibility in the outer region of the electron density distribution. For this reason the source subset of each transition metal atom was extended by one diffuse s-type and one diffuse d-type Gaussian functions with orbital exponents determined by the geometric progression rule. One may note that no extension is done for the p subset. This subset is used mostly for the description of inner p shells and increasing its diffuseness does not appear to be necessary.

The s and d extension of the initial set results in what is called the augmented source sets of the form $(15s9p6d)$, which are then contracted to the VTZ form $[15s9p6d/6s4p3d]$. In each subset the two Gaussian functions with lowest orbital exponents are left uncontracted. This way of contracting the augmented source set saves the flexibility of the outer region [12–14].

For the first-row transition metal atoms most of the polarization response comes from the valence $3d$ and $4s$ shells. Hence, the corresponding eigenvectors are used to determine the polarization functions f_{n+} defined by (5). As already mentioned, the major polarization effects come from functions with $n = 2$, i.e.,

$$f_{2+} = \sum_{\mu=1}^{m} c_\mu(\mathbf{0})\alpha_\mu^{-3/2} G_{\mu,l+1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu), \tag{6}$$

where in principle the summation should include all orbitals of the given value of l which are present in the augmented source set. However, the numerical experiments [17,18] show that no major deterioration of the atomic polarizability data occurs if this summation is restricted to three most diffuse primitive Gaussian functions of the given value of l. Hence, once the $3d$ and $4s$ eigenvectors in the fully uncontracted augmented source set are available from field-independent ROHF SCF calculations, the polarization functions are determined by simple scaling of the corresponding expansion coefficients. The orbital exponents remain the same as those in the polarized shell, i.e., the three lowest s-type exponents for the p-type and the three lowest d-type exponents for the f-type polarization functions. This produces highly compact contracted polarization functions $[3p/1p]$ and $[3f/1f]$ for the $4s$ and $3d$ shells, respectively, and finally results in what is called the ZPolX basis sets of the form $[15s12p6d3\mathrm{f}/6\mathrm{s}5p3d1f]$.

2.3 ZPolX basis sets for relativistic calculations

The first-row transition metal atoms and their compounds are already heavy enough to exhibit certain difference between nonrelativistic and relativistic calculations of their properties. Hence, it is worthwhile to develop parallel ZPolX basis sets for the corresponding relativistic calculations with the purpose to evaluate the relativistic contribution to molecular dipole moments and dipole polarizabilities. However, some problems arise because of the diversity of relativistic computational methods, which are currently in use [24,31–33]. In principle, one would have to develop different basis sets for different exact or approximate relativistic approaches.

Certain limitation of the large number of possible "relativistic" basis sets can be achieved by recalling the goal of the present developments; the ZPolX basis sets are generated for reliable approximate calculations of molecular electric properties. Hence, developing their counterpart for four-component relativistic calculations based on the Dirac-Coulomb or Dirac-Breit approximations [31] would not be appropriate. It is rather the very popular two-component relativistic methods [24,32] which should be used in this context.

Most of the two-component methods of relativistic theory [24,32,33] are based on the some approximate transformations of the one-electron Dirac hamiltonian [32,34]. Hence, each approximate two-component approach would in principle require the use of a different basis set. This problem is, however, solved by referring the relativistic ZPolX sets to the exact infinite-order two-component (IOTC) approach [35–37]. The IOTC scheme is the ultimate goal of all approximate two-component relativistic theories and for a single electron moving in the external Coulomb potential is fully equivalent to the Dirac theory "for electrons only" [38]. The relativistic ZPolX basis sets of this paper, ZPol_iotc, are defined for the use in calculations based on fully decoupled relativistic two-component IOTC hamiltonian. One should note, however, that for lighter atoms the difference between fully decoupled IOTC and approximate schemes [24,32–34,37] is small.

In principle, the generation of ZPolX_iotc basis sets should use the set of Gaussian orbital exponents, which are optimized with the IOTC hamiltonian. However, with primitive Gaussian functions of relatively high orbital exponents, which are already present in the initial Huzinaga basis set [29] and the focus on valence shell properties, the relativistic reoptimization of orbital exponents appears to be unnecessary. Thus, the only difference between ZPolX and ZPolX_iotc basis sets will be in contraction coefficients. All other details of the generation of ZPolX_iotc basis sets are exactly the same as in the case of ZPolX for nonrelativistic calculations.

The ZPol_iotc basis sets are generated by using the contraction coefficients obtained from SCF IOTC calculations in the so-called spin-free approximation [36]. Since the first-row transition metal atoms do not exhibit very large scalar relativistic effects, the same basis sets can be used in the context of different approximate two-component methods based on the Douglas–Kroll approximation [32,34,39–41]. It is worthwhile to note that at variance with four-component methods based on the Dirac hamiltonian, the IOTC and related approaches do not require explicit determination of what is called the small component basis set [42]. Thus, the dimensionality of spin-free relativistic problems remains the same as that of the nonrelativistic schemes. In the IOTC method the small component basis set is generated internally through the full kinetic balance [42] and does not influence the dimension of the two-component hamiltonian matrix [36,37].

3 Computational details

All of the dipole moment and dipole polarizability results presented in this paper follow from finite-field calculations with the external electric field strength equal to ±0.001 au. Moreover, both atomic and molecular electric properties have been carried out by using molecular codes [43,44] based on Abelian symmetry groups. This means that in the presence of the finite electric field perturbation the highest available symmetry groups are either C_{2v} or C_2. The use of the C_2 symmetry group permits the averaging over different configurations which lead to the same atomic or molecular term.

The test calculations of atomic dipole polarizabilities have been all performed at the level of the ROHF approximation. In the case of the dipole moments of the first-row transition metal oxides this study has been extended by including the electron correlation contribution within the ROHF CCSD(T) scheme of Neogrády et al. [45,46], which is coded into Molcas suite of quantum chemistry programs [43,44]. This method, however, requires that the reference function is represented by a single (high-spin) determinant and could not have been used for some of the investigated transition metal oxides. One can use, however, approximate approach in which the single determinant reference function is built as a symmetry broken solution in C_{2v} symmetry. Both these cases can be simultaneously studied by using the second-order perturbation method (CASPT2) [47,48] based on the (multideterminant) complete active space (CAS) SCF reference function with the active orbital space generated from valence orbitals of the appropriate symmetry. In all correlated-level calculations for transition metal oxides the 1σ, 2σ, 3σ, 4σ, and 1π doubly occupied orbitals are left uncorrelated.

The spin-free IOTC calculations have been performed with the same assumptions as those used in the nonrelativistic case and carried out by using the Molcas codes with the modified one-electron electron hamiltonian[1]. The picture change contributions [49,50] have not been taken into account. It has been demonstrated earlier [51] that these contributions to relativistic dipole moments and polarizabilities are negligible.

In calculations on transition metal oxides (MeO) we have used the values of interatomic distances R_{MeO} reported by Bauschlicher and Maitre [52], i.e., $R_{\mathrm{ScO}} = 3.174$ au, $R_{\mathrm{TiO}} = 3.077$ au, $R_{\mathrm{VO}} = 3.027$ au, $R_{\mathrm{CrO}} = 3.087$ au, $R_{\mathrm{MnO}} = 3.146$ au, $R_{\mathrm{FeO}} = 3.041$ au, $R_{\mathrm{CoO}} = 3.063$ au, $R_{\mathrm{NiO}} = 3.073$ au, $R_{\mathrm{CuO}} = 3.347$ au, and $R_{\mathrm{ZnO}} = 3.248$ au [53]. This choice of bond distances permits direct comparison between our results and those of Bauschlicher and Maitre [52].

The other illustrative molecular calculation of electric properties has been carried out for the $TiCl_4$ molecule studied recently by Hohm and Maroulis [25]. The molecule is assumed to be of tetrahedral symmetry with the experimental value of the Ti–Cl bond distance ($R_{\mathrm{TiCl}} = 2.17$ Å), i.e., the same as used by the other authors. This closed-shell molecule is also used to check the ZPolX_iotc results with respect to those obtained with systematically extended relativistic ANO (R-ANO) basis sets of Widmark and Roos [54].

4 Results and discussion

4.1 Atomic calculations

The main purpose of the calculation of atomic polarizabilities for the first-row transition metal atoms is to investigate the overall performance of the ZPolX basis set and to determine their possible deficiencies. Obviously, the small and very compact ZPolX basis sets are not highly suitable for accurate calculations of atomic dipole polarizabilities and deviations from the accurate reference data of Stiehler and Hinze [55] of the order of a few per cent seem fully acceptable. The comparison of the present nonrelativistic results for different M_L components of the atomic dipole polarizability tensor and its isotropic rotational average with the numerical nonrelativistic data of Stiehler and Hinze are presented in Table 1. Additionally, we have also included more recent ROHF results by Kłos [56]. The latter have been calculated by using large Gaussian basis sets and the finite-field perturbation method. Some other nonrelativistic and relativistic data for Cu and Zn will also be used for comparison [57–59].

On inspecting the nonrelativistic data of Table 1 one finds that the ZPolX results are systematically a little lower than the corresponding reference values. Only in the case of Cr($3d^5 4s^1$: ^{7}S) and Cu($3d^{10} 4s^1$: ^{2}S), the difference between the present and reference results of Stiehler and Hinze [55] exceeds that observed for the other atoms and amounts to about 6 and 5%, respectively. The origin of these somewhat larger differences has been investigated by considering other configurations and atomic terms.

Since most of the dipole polarizability of the ground atomic terms comes from the contribution of the 4*s* atomic orbital, its diffuseness is of particular importance for the determination of the *p*-type polarization functions. To increase its diffuseness one may consider the electronic configuration in which the 4*s* orbital becomes doubly occupied. In the case of Cr, this gives the atomic term ^5D. If the *p*-type and *f*-type polarization functions are determined from eigenvectors of Cr($3d^4 4s^2$: ^{5}D) the calculated polarizability value of the Cr($3d^5 4s^1$: ^{7}S) term increases by almost 2 au and approaches the result of Stiehler and Hinze (see Table 1). The same is observed for Cu if the polarization functions are determined from ROHF eigenvectors of Cu($3d^9 4s^2$: ^{2}D). However, taking into account the small size of the ZPolX sets these improvements are marginal. The final ZPolX basis sets are therefore based on polarization functions derived from ROHF eigenvectors for the ground state term of each atom. These are the basis sets which will be used in molecular applications.

The results of the investigation of the role of relativistic contributions to the ground state atomic dipole polarizability are presented in Table 2. This contribution, $\Delta\alpha_{rel}(M_L)$, is defined as the difference between the relativistic (rel) and

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[1] The IOTC method was implemented in the local version of the Molcas.5.4 system of programs by D. Kędziera (Department of Quantum Chemistry, Institute of Chemistry, Nicolaus Copernicus University, Toruń, Poland, 2003) and by D. Kędziera and V. Kellö in Molcas.6.5. The corresponding patches for Molcas.5 and Molcas.6 releases of Molcas can be obtained directly either from D. Kędziera (E–mail: teodar@chem.uni.torun.pl) or from V. Kellö (E–mail: kelloe@fns.uniba.sk)

Table 1 Nonrelativistic dipole polarizabilities of the first-row transition metals. (all values in au)

	$\alpha_{nrel}(M_L)$				
	$M_L = 0$	$M_L = 1$	$M_L = 2$	$M_L = 3$	Av
Sc					
	143.46[a]	146.68	154.75	–	149.26
[55]	145.03	148.13	155.86	–	150.60
[56]	145.38	148.03	155.97	–	150.68
Ti					
	125.77	126.11[a]	128.36	129.97[a]	127.81
[55]	127.45	128.12	129.48	131.44	129.36
[56]	127.75	128.15	129.36	131.38	129.36
V					
	112.74	112.36[a]	112.04	110.01[a]	111.65
[55]	114.95	114.30	113.19	111.36	113.23
[56]	114.44	114.09	113.04	111.30	113.04
Cr [b]					
	106.26	–	–	–	106.26
[55]	112.88	–	–	–	112.88
Mn					
	89.20	–	–	–	89.20
[55]	90.14	–	–	–	90.14
Fe					
	76.64	77.56[a]	80.48	–	78.54
[55]	77.62	78.60	81.62	–	79.61
Co					
	69.52	69.75[a]	70.50	71.18[a]	70.34
[55]	70.59	70.96	71.49	72.35	71.46
Ni					
	63.99	63.87[a]	63.66	62.85[a]	63.54
[55]	65.39	65.16	64.68	63.94	64.71
[56]	65.22	65.07	64.61	63.85	64.61
Cu [c]					
	73.46	–	–	–	73.46
[55]	77.19	–	–	–	77.19
[56]	76.18	–	–	–	76.18
Zn					
	53.22	–	–	–	53.22
[55]	54.07	–	–	–	54.07

[a] Determined from the data for two explicitly calculated components. See text

[b] The reported value corresponds to polarization functions derived from ROHF eigenvectors for the ^7S term of the $3d^54s^1$ configuration. With polarization functions determined from ROHF eigenvectors of Cr($3d^44s^2$: ^5D) the ground state polarizability is 107.96 au. See text

[c] The reported value corresponds to polarization functions derived from ROHF eigenvectors for the ^2S term of the $3d^{10}4s^1$ configuration. With polarization functions determined from ROHF eigenvectors of Cu($3d^94s^2$: ^2D) the ground state polarizability is 75.68 au. See text

nonrelativistic ($nrel$) results,

$$\Delta\alpha_{rel}(M_L) = \alpha_{rel}(M_L) - \alpha_{nrel}(M_L). \qquad (7)$$

Our spin-free IOTC results are compared with the data of Kłos [56] obtained in the framework of the so-called Douglas-Kroll-Hess method of the second-order in the external Coulomb field (DKH2) [24,39,41]. Since the studied transition metal atoms correspond to relatively small values of the nuclear charge, the difference between DKH2 and IOTC dipole polarizabilities is very small [60]. Thus, the difference between the present results and those of Kłos is primarily due to different basis sets used in calculations. In spite of at least twice as large basis sets employed by Kłos [56] his relativistic corrections are essentially the same as those obtained with ZPolX_iotc basis sets of this paper.

In the context of our atomic calculations we would like to add some comments on the use of the exact formula for M_L component of the dipole polarizability of certain atomic term which is characterized by the angular quantum number L, total spin quantum number S and the total angular momentum quantum number J. In the representation which diagonalizes the $\hat{J}^2$ and $\hat{J}_z$ operators the M_J component, $\alpha(M_J)$, of the parallel atomic dipole polarizability α can be expressed in terms of three parameters [61–63],

$$\alpha(M_J) = (J^2 - M_J^2)A + M_J^2 B + (J^2 - 2J + 1 - M_J^2)C. \qquad (8)$$

In the representation which simultaneously diagonalizes $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ operators (8) becomes a two-parameter formula,

$$\alpha(M_L) = (L^2 - M_L^2)A + (L^2 - 2L + 1 - M_L^2)C \qquad (9)$$

and is independent of the M_S quantum number. This is the case considered in this paper as well as in calculations presented by Kłos [56]. In both cases no spin-orbit coupling is taken into account. However, on using (9) to determine A and C from two M_L components of the dipole polarizability obtained from finite-field calculations with molecular programs one faces some unavoidable symmetry problem.

The formula derived by Bederson [61–63] follows from the perturbation expansion of the atomic energy in the presence of the external electric field and assumes that both the reference function and all intermediate states belong to well-defined representations of the full O(3) symmetry group. This assumption is automatically violated if the external electric field is included in the framework of the finite-field perturbation theory. Then, the highest symmetry group which can be used becomes $C_{\infty v}$. In general, the electronic configurations which generate the symmetry adapted functions of this group will not exploit all of the available degenerate orbitals. In consequence, some symmetry breaking must occur which causes that the core orbitals will be different for different

Table 2 Relativistic dipole polarizabilities of the first-row transition metals (all values in au)

	$\alpha_{rel}(M_L)$					$\Delta\alpha_{rel}(M_L)$				
	$M_L = 0$	$M_L = 1$	$M_L = 2$	$M_L = 3$	Av	$M_L = 0$	$M_L = 1$	$M_L = 2$	$M_L = 3$	Av
Sc										
	140.66[a]	143.88	151.82	–	146.41	−2.80	−2.80	−2.93	–	−2.85
[56]	142.59	145.19	153.00	–	147.79	−2.79	−2.84	−2.97	–	−2.89
Ti										
	122.82	123.13[a]	125.37	126.95[a]	124.82	−2.95	−2.98	−2.99	−3.02	−2.99
[56]	124.80	125.20	126.39	128.38	126.39	−2.95	−2.95	−2.97	−3.00	−2.97
V										
	109.68	109.30[a]	109.00	107.00[a]	108.61	−3.06	−3.06	−3.04	−3.01	−3.04
[56]	111.42	111.07	110.05	108.33	110.05	−3.02	−3.02	−2.99	−2.97	−2.99
Cr[b]										
	100.70	–	–	–	100.70	−5.56	–	–	–	−5.56
Mn										
	86.08	–	–	–	86.08	−3.12	–	–	–	−3.12
Fe										
	73.60	74.48[a]	77.28	–	75.42	−3.04	−3.08	−3.20	–	−3.12
Co										
	66.38	66.60[a]	67.34	67.98[a]	67.17	−3.14	−3.15	−3.16	−3.20	−3.17
Ni										
	60.84	60.71[a]	60.52	59.75[a]	60.40	−3.15	−3.16	−3.14	−3.10	−3.14
[56]	62.09	61.94	61.51	60.78	61.51	−3.13	−3.13	−3.10	−3.07	−3.10
Cu[c]										
	67.40	–	–	–	67.40	−6.06	–	–	–	−6.06
[56]	70.03	–	–	–	70.03	−6.15	–	–	–	−6.15
Zn										
	50.04	–	–	–	50.04	−3.18	–	–	–	−3.18

[a] Determined from the data for two explicitly calculated components. See text

[b] The reported value corresponds to polarization functions derived from ROHF eigenvectors for the ^7S term of the $3d^5 4s^1$ configuration. With polarization functions determined from ROHF eigenvectors of Cr($3d^4 4s^2$: ^5D) the ground state polarizability is 102.08 au. See text

[c] The reported value corresponds to polarization functions derived from ROHF eigenvectors for the ^2S term of the $3d^{10} 4s^1$ configuration. With polarization functions determined from ROHF eigenvectors of Cu($3d^9 4s^2$: ^2D) the ground state polarizability is 69.48 au. See text

configurations in the valence shell and will differ from fully symmetric solutions in the $O(3)$ group.

To give some example, let us consider ($3d^2 4s^2$) configuration of Ti, which leads to the lowest energy ^{3}F term in $O(3)$ with all M_L components fully equivalent. In the $C_{\infty v}$ group $M_L = 3$ component will correspond to the ($3d^1_{+2} 3d^1_{+1} 4s^2$) configuration and will transform according to the Φ representation. The $M_L = 2$ component will be generated by the ($3d^1_{+2} 3d^1_0 4s^2$) configuration and will belong to the Δ representation in $C_{\infty v}$. In both these cases, the occupation of valence orbitals is different and influences the core orbitals in a different way. This asymmetry remains in the limit of the vanishing external electric field since there is no continuous transition from the $C_{\infty v}$ symmetry group to the full rotation group $O(3)$. In consequence Bederson's formula (9) will be only *approximately* satisfied for polarizability components evaluated in finite-field calculations.

It appears that Stiehler and Hinze [55] were aware of this problem and never tried to find A and C parameters from their numerical finite-field results. All components of atomic dipole polarizabilities reported in their paper follow from direct finite-field calculations in $C_{\infty v}$ symmetry and for $L \geq 2$ different $\alpha(M_L)$ pairs result in different sets of A and C. Another approximate method to circumvent the core symmetry breaking effect in finite-field calculations was employed by Kłos [56], who determined A and C from the calculated Σ ($M_L = 0$) component and the rotational average of the atomic dipole polarizability, and then used them to determine the other components of $\alpha(M_L)$ (see Summary of [56]). According to the direct data of Stiehler and Hinze [55], this method may lead to errors of the order of 1–2 au.

One more problem which occurs in the case of 'molecular' finite-field calculations of atomic dipole polarizabilities relates to the use of lower than $C_{\infty v}$ symmetry groups. For the software used in this paper [43,44], the highest symmetry group which can be used in such calculations is C_{2v}. This causes two problems. First, the equivalent configurations, *e.g.*, those of Π_x and Π_y symmetry need to be averaged. Such an averaging can be accomplished only by using the C_2 subgroup. The C_{2v} symmetry used by Kłos does not permit the averaging over the two branches of Π, Δ, and higher two-dimensional representations of the full $C_{\infty v}$ group. The second problem is the mixing of orbitals of different $C_{\infty v}$ symmetry, which fall into the same representation of the C_{2v} group. The latter problem occurs in calculations with the software [43,44] used in this paper. We have found that in some cases the separation of d_{z^2} and $d_{x^2-y^2}$ components was impossible in spite of using different 'cleanup' options available in Molcas programs. In all these cases the missing components of $\alpha(M_L)$ have been evaluated from (9) with A and C available from the direct results for other components. Details of this procedure can be found in footnotes to Tables 1 and 2. According to the data of Stiehler and Hinze [55] and the values of A and C derived from different pairs of M_L components of their atomic polarizabilities, this approximate handling of symmetry problems leads to relatively small inaccuracies.

On summarizing our calculated results of Tables 1 and 2 one needs to recall the aim of this paper, i.e., the generation of highly compact basis sets for calculations of molecular dipolar electric properties. The ZPolX are certainly not the best choice for *accurate* atomic calculations. However, in most cases the calculated atomic dipole polarizabilities agree within a few percent with the accurate numerical data of Stiehler and Hinze. This level of accuracy should be sufficient for achieving at least similar accuracy in calculations of dipole moments and dipole polarizabilities of the transition metal compounds.

4.2 Dipole moments of transition metal oxides

This section illustrates the performance of ZPolX basis sets in calculations of dipole moments of the first-row transition metal oxides. The reference data are those obtained in large basis set (unrestricted) CCSD(T) (UCCSD(T)) calculations of Bauschlicher and Maitre [52].

For all oxides whose ground electronic state can be represented by a single (high spin case) Slater determinant the corresponding ROHF calculations have been followed by the CCSD(T) determination of the electron correlation contribution by using the ROHF CCSD(T) approach of Neogrády et al. [45,46] (see Sect. 3). The inspection of the ground state electronic configurations of the first-row transition metal oxides shows that this high-level correlated method can be used for ScO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1$: ${}^2\Sigma^+$), VO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1 1\delta^2$: ${}^4\Sigma^-$), MnO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1 4\pi^2 1\delta^2$: ${}^6\Sigma^+$), NiO ($\ldots 3\pi^4 8\sigma^2 9\sigma^2 4\pi^2 1\delta^4$: ${}^3\Sigma^-$), and the closed shell ZnO ($\ldots 3\pi^4 8\sigma^2 9\sigma^2 4\pi^4 1\delta^4$: ${}^1\Sigma^+$) molecule. For the other molecules, TiO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1 1\delta^1$: ${}^3\Delta$), CrO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1 4\pi^1 1\delta^2$: ${}^5\Pi$), FeO ($\ldots 3\pi^4 8\sigma^2 9\sigma^1 4\pi^2 1\delta^3$: ${}^5\Delta$), CoO ($\ldots 3\pi^4 8\sigma^2 9\sigma^2 4\pi^2 1\delta^3$: ${}^4\Delta$), and CuO ($\ldots 3\pi^4 8\sigma^2 9\sigma^2 4\pi^3 1\delta^4$: ${}^2\Pi$), the ROHF reference function is build of two Slater determinants and cannot be directly used in the context of the ROHF CCSD(T) method which assumes that the reference function is a single determinant.

One of the possibilities to employ the very efficient CCSD(T) method is to use a single determinant reference function of broken symmetry, which corresponds to certain particular choice of orbital occupations (active orbital space) in C_{2v} symmetry. The effect of the symmetry breaking can be estimated by comparing the symmetry-broken ROHF results (C_{2v}) with those obtained in state-averaged ROHF data calculated in the C_2 symmetry. Its effect on the electron correlation contribution can be similarly estimated at the level of the second-order perturbation theory (CASPT2 [47,48]) by comparing the single determinant ROHF/CASPT2 data of broken symmetry with the state-averaged CASPT2 results for the two-determinant ROHF reference function averaged over two states. This averaging can be done only by reducing the symmetry group to C_2 and may require some particular choice of the active orbital space. The choice of the active orbital space for ROHF/CASPT2 calculations is explained in Table 3, where the ground-state configurations (molecular terms) are those established by Bauschlicher and Maitre [52] and Gutsev et al. [64] in their extensive analysis of the electronic structure of molecules considered in this paper.

The nonrelativistic results for dipole moments of the first-row transition metal oxides are presented in Table 4 and compared with the results of Bauschlicher and Maitre [52] and Gutsev et al. [64]. Several other nonrelativistic dipole moment results are available [65–67]. However, only the UCCSD(T) data of Bauschlicher and Maitre are useful for the purpose of the present study of the performance of ZPolX basis sets for transition metal compounds. The UCCSD(T) method used by Bauschlicher and Maitre is not much different from the ROHF CCSD(T) approach employed in our calculations. Although one may expect some spin contamination of the UCCSD(T) results, the major difference between the present data and those of Bauschlicher and Maitre is in basis sets. Those of Bauschlicher and Maitre are much larger than the present highly compact ZPolX sets. Hence, the data of Table 4 help to assess the ZPolX basis set performance at the same or comparable level of the electronic structure theory. The other comparative results [65–67], though presumably of good accuracy, correspond to diverse computational methods and basis sets and are not suitable for the purpose of the sole basis set performance study.

On comparing the present ROHF CCSD(T) results with UCCSD(T) data one finds that the dipole moments evaluated with ZPolX basis sets are very close to those calculated by Bauschlicher and Maitre [52]. This is another indication that the present ZPolX basis sets should be useful for calculation of electric dipole moments of transition metal compounds at the correlated level of approximation.

The ROHF/CASPT2 (CASSCF/CASPT2) results of Table 4 are in most cases significantly different from the

Table 3 The first-row transition metal oxides. The ground state electronic configuration and the choice of orbital subspaces for ROHF/CASSCF reference functions

Molecule	Term	Configuration[a]	Orbital subspaces [b]	
			C_{2v}	C_2
ScO	$^2\Sigma^+$	[CaO]$9\sigma^1$	(0,0,0,0/8,3,3,0/1,0,0,0; 1)	
TiO	$^3\Delta$	[CaO]$9\sigma^1 1\delta^1$	(0,0,0,0/8,3,3,0/1,0,0,1; 2)[c]	(0,0/8,6/3,0; 2)
VO	$^4\Sigma^-$	[CaO]$9\sigma^1 1\delta^2$	(0,0,0,0/8,3,3,0/2,0,0,1; 3)	
CrO	$^5\Pi$	[CaO]$9\sigma^1 4\pi^1 1\delta^2$	(0,0,0,0/8,3,3,0/2,1,0,1; 4)[d]	(0,0/8,6/3,2; 4)
MnO	$^6\Sigma^+$	[CaO]$9\sigma^1 4\pi^2 1\delta^2$	(0,0,0,0/8,3,3,0/2,1,1,1; 5)	
FeO	$^5\Delta$	[CaO]$9\sigma^1 4\pi^2 1\delta^3$	(0,0,0,0/9,3,3,0/1,1,1,1; 4)[c,d]	(0,0/8,6/3,2; 6)
CoO	$^4\Delta$	[CaO]$9\sigma^2 4\pi^2 1\delta^3$	(0,0,0,0/10,3,3,0/0,1,1,1; 3)[c,e]	(0,0/9,6/2,2; 5)
NiO	$^3\Sigma^-$	[CaO]$9\sigma^2 4\pi^2 1\delta^4$	(0,0,0,0/10,3,3,1/0,1,1,0; 2)[f]	
CuO	$^2\Pi$	[CaO]$9\sigma^2 4\pi^3 1\delta^4$	(0,0,0,0/10,3,4,1/0,1,0,0; 1)[c,g]	(0,0/11,6/0,2; 3)
ZnO	$^1\Sigma^+$	[CaO]$9\sigma^2 4\pi^4 1\delta^4$	(0,0,0,0/10,4,4,1/0,0,0,0; 0)	

[a] [CaO] denotes the electronic configuration of CaO, i.e., $1\sigma^2 2\sigma^2 \ldots 7\sigma^2\ 8\sigma^2 1\pi^4 2\pi^4 3\pi^4$

[b] The symbol $(f_1, f_2, \ldots / i_1, i_2, \ldots / a_1, a_2, \ldots ; N)$ defines the selection of the frozen (f_k), inactive (i_k), and active (a_k) orbital subspaces for different representations of the given symmetry group. In C_{2v} symmetry the order of representations is: z, x, y, xy. The active space is used to describe N electrons

[c] Symmetry-broken solution. Two equivalent configurations in C_{2v} symmetry

[d] The doubly occupied $1\delta_{x^2-y^2}$ has been shifted to the inactive subspace

[e] Both, 9σ and $1\delta_{x^2-y^2}$ shifted to the inactive subspace

[f] 9σ, $1\delta_{x^2-y^2}$ and $1\delta_{xy}$ shifted to the inactive subspace

[g] Only π_x orbital is left in the active subspace

corresponding CCSD(T) data; the CrO molecule is the most striking example. Obviously, the CASPT2 results calculated with the minimal active space can be improved by increasing its size and the number of electrons which are explicitly correlated in the CASSCF approximation for the reference function. For some of the oxides (ScO, TiO, MnO, CoO, CuO, ZnO) studied in this paper, the active space comprising 8σ, 9σ, 10σ, 1π, 2π, and 1δ valence orbitals leads to the dipole moment values comparable to those obtained in CCSD(T) calculations. For some others (VO, CrO, FeO, NiO) adding 11σ and/or 3π orbitals is necessary. Particularly difficult is the case of CrO. Several exploratory CASSCF/CASPT2 calculations performed with ZPolX basis sets show essentially the same pattern as the earlier dipole moment studies with large basis sets by Steimle et al. [68], Bauschlicher et al. [67], and Bauschlicher and Maitre [52]. This gives further support for the recommendation of ZPolX basis sets for reliable calculations on transition metal compounds.

The scalar relativistic IOTC values of the dipole moment obtained in ROHF (two–state CASSCF), ROHF/CASPT2 (CASSCF/CASPT2), and ROHF/CCSD(T) approximations are presented in Table 5. The relativistic effect on atomic dipole polarizabilities is relatively small (see Table 2) and one would therefore expect small relativistic contributions to dipole moments of the transition metal oxides. However, the magnitude of the relativistic contribution strongly depends on the level of approximation and in most cases is significantly reduced on passing from the ROHF to ROHF/CASPT2 and CCSD(T) approximations. This reflects the electron correlation effect on the electronic structure of the transition metal oxides and shows the importance of the interplay between relativistic and electron correlation effects [69].

Comparisons between experimental and theoretical results for the transition metal oxides have been extensively discussed by other authors [20,22,52,64,65,67,68,70]. The experimental data are incomplete and their accuracy is in some cases disputable [52]. However, it is pleasing to note that the present scalar relativistic CCSD(T) result for the dipole moment of CrO (1.502 au, Table 5) is in good agreement with the experimental value of 3.88 ± 0.13 D ≈ 1.53 ± 0.05 au [68]. The best nonrelativistic UCCSD(T) result of Bauschlicher and Maitre (1.530 au) [52] is also in good agreement with the experimental value. This agreement would further improve upon the addition of the relativistic correction (−0.035 au, Table 5) calculated in this paper. Accurate experimental value [71] of the dipole moment of VO (3.355±0.014 D ≈ 1.320 ± 0.006 au) is also available and almost perfectly agrees with the present IOTC CCSD(T) result (1.316 au, Table 5) as well as with the nonrelativistic UCCSD(T) result of Bauschlicher and Maitre (1.317 au, [52]).

The recent experimental J-resolved results for FeO (4.50± 0.03 D ≈ 1.77 ± 0.01 au and 4.29 ± 0.05 ≈ 1.69 ± 0.02 au for $X^5\Delta_4$ and $X^5\Delta_3$ states, respectively [72]), combined with the older value of the dipole moment (4.7 ± 0.2 D ≈ 1.85 ± 0.08 au [73]) for the $X^5\Delta_2$ lead to the J-averaged [74] result of about 1.76 au. Taking into account the uncertainty

Table 4 Nonrelativistic dipole moments of the first-row transition metal oxides in different approximations (all data in au)

Molecule	Term	ZPolX results[a]			[52][d]
		ROHF/CASSCF[b]	CASPT2[c]	CCSD(T)[c]	
ScO	$^2\Sigma^+$	1.793	1.417	1.570	1.54
TiO	$^3\Delta$	1.698	1.205		
		(1.698)	(1.207)	(1.358)	1.38
VO	$^4\Sigma^-$	1.872	1.260	1.317	1.42
CrO	$^5\Pi$	3.238	0.882		
		(3.211)	(0.781)	(1.537)	1.53
MnO	$^6\Sigma^+$	3.590	1.918	2.042	1.96
FeO	$^5\Delta$	3.526	1.840		
		(3.528)	(1.859)	(2.019)	
CoO	$^4\Delta$	3.124	2.020		
		(3.124)	(2.018)	(1.854)	
NiO	$^3\Sigma^-$	3.255	2.114	1.876	
CuO	$^2\Pi$	2.414	2.065		
		(2.414)	(2.064)	(2.065)	2.01
ZnO	$^1\Sigma^+$	2.774	2.690	2.165	2.11[e]

[a] The numbers in parentheses correspond to symmetry broken calculations with high-spin single determinant reference function of C_{2v} symmetry. See Table 3 and text

[b] Either high-spin single determinant function or average over two determinants generated in C_2 symmetry

[c] The reference function as described in Footnote b. See text

[d] Large basis set UCCSD(T) results of Bauschlicher and Maitre [52]. The data of these authors have been converted from Debye to atomic units (1 au = 2.54175 D)

[e] This CCSD(T) result is reported in [64]

of the experimental dipole moment for the $X^5\Delta_2$ state, this J-averaged value is reasonably close to the present IOTC CCSD(T) result of 1.934 au (see Table 5).

For other oxides, one finds the experimental values of the ground state dipole moment of ScO (4.55 ± 0.08 D $\approx 1.79\pm0.03$ au [20,22,75]) and TiO (2.96 ± 0.05 D $\approx 1.16\pm0.02$ au [20,22,76]). Both of them are by about 0.2 au higher than the IOTC CCSD(T) results of this study and the nonrelativistic values reported by Bauschlicher and Maitre [52]. In the case of Cu, the experimental dipole moment of the $X^2\Pi_{3/2}$ state is 4.45 ± 0.30 D $\approx 1.75\pm0.12$ au [22,77] and is lower by about 0.25 au than the present scalar IOTC CCSD(T) result. The latter, however, reasonably agrees with the nonrelativistic value computed by Bauschlicher and Maitre [52]. All these discrepancies between theoretical data and experimental values cannot be resolved on the basis of present calculations with small basis sets and we rather focus on the comparison with the results of Bauschlicher and Maitre [52].

The agreement between our results, the UCCSD(T) data computed with large basis sets, and the accurate experimental values strongly suggests that the very small ZPolX basis sets can be used for realistic predictions of the polarity of the first-row transition metal compounds. One should note that the determination of electric properties of the transition metal oxides is a very difficult task [20,22,52]. The calculated results strongly depend on approximations used in calculations of molecular wave functions and/or energies. Most of the oxides studied in this paper have a very complicated electronic structure whose representation by a single electronic configuration may strongly influence the performance

Table 5 Scalar relativistic IOTC dipole moments (μ_{rel}) of the first-row transition metal oxides in different approximations. Also the relativistic contribution ($\Delta\mu_{\text{rel}}$) calculated with the data of Table 4 is reported. All results in au

Molecule	Term	ROHF/CASSCF[a,b]		CASPT2[a,c]		CCSD(T)[a,c]	
		μ_{rel}	$\Delta\mu_{\text{rel}}$	μ_{rel}	$\Delta\mu_{\text{rel}}$	μ_{rel}	$\Delta\mu_{\text{rel}}$
ScO	$^2\Sigma^+$	1.931	0.138	1.422	0.005	1.595	0.025
TiO	$^3\Delta$	1.843	0.145	1.201	−0.004		
		(1.842)	(0.144)	(1.202)	(−0.005)	(1.377)	(0.019)
VO	$^4\Sigma^-$	2.033	0.161	1.167	−0.093	1.316	−0.001
CrO	$^5\Pi$	3.217	−0.021	0.834	−0.048		
		(3.189)	(−0.022)	(0.681)	(−0.100)	(1.502)	(−0.035)
MnO	$^6\Sigma^+$	3.540	−0.049	1.855	−0.063	1.955	−0.087
FeO	$^5\Delta$	3.501	−0.025	1.769	−0.071		
		(3.504)	(−0.024)	(1.786)	(−0.072)	(1.934)	(−0.085)
CoO	$^4\Delta$	3.022	−0.102	2.121	0.101		
		(3.022)	(−0.102)	(2.131)	(0.113)	(1.824)	(−0.030)
NiO	$^3\Sigma^-$	3.136	−0.119	2.255	0.141	1.884	0.008
CuO	$^2\Pi$	2.469	0.055	2.047	−0.018		
		(2.485)	(0.071)	(2.032)	(−0.032)	(2.019)	(−0.046)
ZnO	$^1\Sigma^+$	2.598	−0.176	2.703	0.013	2.047	−0.118

[a] The numbers in parentheses correspond to symmetry-broken calculations with high-spin single determinant reference function of C_{2v} symmetry. See Table 3 and text

[b] Either high-spin single determinant function or average over two determinants of C_2 symmetry

[c] The reference function as described in Footnote b. See text

of the correlated-level methods. The assessment of the reliability of the single configuration CCSD(T) method, though partly provided by the data of Table 4, is obviously far from complete.

For the present study, the dipole moment values calculated by Bauschlicher and Maitre [52] are considered to be the reference theoretical data. They are used to show that within essentially the same computational method the ZPolX and large basis sets of Bauschlicher and Maitre give very similar results. It is presently fashionable to investigate the performance of different methods and accuracy limits by using systematic sequences of extended basis sets [6] combined with different extrapolation techniques [78–80]. The transition metal oxides, however, do not seem to be particularly suitable for these investigations. The basis set extension, though systematic, may lead to significant differences in the electronic structure of these systems and the pattern of convergence may be considerably affected by the assumptions of the single configuration methods. In this respect, one may also have purely formal reservations; the union of large and diffuse atomic basis sets will unavoidably result in linear dependencies in the molecular basis set, whose (numerical) removal may considerably affect the convergence pattern for the calculated property.

4.3 Dipole polarizabilities of transition metal oxides

The calculated ROHF (CASSCF) and ROHF/CCSD(T) results for the parallel component of the dipole polarizability of the first-row transition metal oxides are presented in Table 6. Both the nonrelativistic and scalar relativistic values are reported. They correspond to the same choice of active orbital spaces as that used in dipole moment calculations presented in Tables 4 and 5. The selection of the orbital subspaces is explained in Table 3.

In the case of the ROHF/CCSD(T) results for molecules, whose ground state wave function is represented by the space-averaged ROHF wave function built of two determinants, only the polarizability values obtained from broken symmetry (C_{2v}) single determinant reference functions are given. The magnitude of the symmetry breaking effect can be guessed from the comparison of the symmetry-broken C_{2v} and averaged C_2 ROHF data (Table 6) and is quite small. Hence, the symmetry-broken ROHF/CCSD(T) results can be anticipated to be close to the corresponding data which would follow from calculations with full molecular symmetry.

There seem to be no other polarizability data available for the comparison of our results. Hence, the discussion of the ZPolX data is limited to a few remarks concerning the electron correlation and relativistic effects on the dipole polarizability. On comparing the ROHF/CASSCF results with the CCSD(T) values, one finds that the magnitude and sign of the electron correlation contribution to the parallel polarizability of the first-row transition metal oxides strongly depends on their electronic structure. For some of the oxides (ScO, TiO, CrO, MnO, FeO, and CuO) this contribution is positive, whereas its value is negative for VO, CoO, NiO, and ZnO. There is no obvious relation between the electron correlation contribution to dipole moments (Tables 4 and 5) and its effect on the dipole polarizability. The increase of the dipole polarizability due to the electron correlation contribution can be interpreted in terms of the correlation-induced enhancement of the participation of the 4*s* orbital of the metal atom; this orbital gives the dominant part of the atomic dipole polarizability of the transition metal atoms.

Table 6 Nonrelativistic and scalar relativistic results for the parallel component of the dipole polarizabilities (in au) of the first-row transition metal oxides

Molecule	Nonrelativistic results		Scalar relativistic results	
	ROHF/CASSCF	CCSD(T)	ROHF/CASSCF	CCSD(T)
ScO ($^2\Sigma^+$)	87.59	92.42	85.56	89.90
TiO ($^3\Delta$)	82.58		80.09	
	(82.52)	(83.50)	(80.10)	(80.31)
VO ($^4\Sigma^-$)	96.09	79.43	91.00	75.65
CrO ($^5\Pi$)	70.27		69.55	
	(71.32)	(79.17)	(71.01)	(71.77)
MnO($^6\Sigma^+$)	57.70	71.73	59.93	66.10
FeO ($^5\Delta$)	45.17		48.43	
	(45.10)	(57.93)	(48.39)	(55.79)
CoO ($^4\Delta$)	64.31		67.62	
	(64.31)	(51.76)	(67.62)	(54.21)
NiO ($^3\Sigma^-$)	56.14	32.38	62.05	37.00
CuO($^2\Pi$)	20.19		20.07	
	(20.28)	(36.44)	(20.40)	(38.71)
ZnO ($^1\Sigma^+$)	75.06	63.96	72.42	58.79

The relativistic contribution to the parallel dipole polarizability of the first-row transition metal oxides is usually of the order of a few units. However, both its magnitude and sign depend significantly on the level of approximation. For instance, in the case of FeO the relativistic effect of the ROHF value of its polarizability is positive, whereas at the level of the CCSD(T) approximation one obtains the negative value of the relativistic contribution.

4.4 Electric properties of $TiCl_4$

The last example of the use of ZPolX basis sets developed in this paper refers to recent calculations of different electric properties of the transition metal chlorides reported by Hohm and Maroulis [25]. These authors have calculated several electric properties of $TiCl_4$ at the level of the SCF HF and MP2 approximations with three different basis sets of increasing size and diffuseness. In present comparisons we

Table 7 Electric dipole polarizability of $TiCl_4$. (all values in au)

Method	This work		[25][a]	R-ANO results [b]		
	Nonrelativistic[c]	IOTC [d]	Nonrelativistic	A[e]	B[f]	C[g]
SCF HF	83.70	83.45	84.73	84.58	84.41	84.41
MP2–32e	101.86	101.19	100.83	99.34	98.87	98.49
MP2–40e	102.38	101.70	–	100.50	100.18	99.88
CCSD(T)–32e	101.73	101.28	–	99.63	98.46	97.77

[a] Calculations with T2 basis set of [25]

[b] ITOC calculations with systematically extended R-ANO basis sets [54] (AJ Sadlej and BO Roos, 2007, Unpublished results)

[c] Results calculated with ZPolX basis sets for Cl and Ti

[d] Results calculated with ZPolX_iotc basis sets for Cl and Ti

[e] [10s9p8d6f] R-ANO basis set for Ti and [8s7p5d] R-ANO basis set for Cl [54]

[f] [10s9p8d6f4g] R-ANO basis set for Ti and [8s7p5d4f] R-ANO basis set for Cl [54]

[g] [10s9p8d6f4g2h] R-ANO basis set for Ti and [8s7p5d4f2g] R-ANO basis set for Cl [54]

shall refer only to the dipole polarizability data obtained with the T2 basis set of Hohm and Maroulis [25]. This basis set comprises a total of 209 spherical Gaussians, whereas the corresponding molecular ZPolX basis sets lead to only 131 spherical Gaussians.

The results obtained in our SCF HF, MP2, and CCSD(T) calculations with ZPolX basis sets and the data of Hohm and Maroulis [25] are shown in Table 7. The MP2 data of these authors correspond to correlating all valence electrons of Cl and four electrons of Ti, (MP2-32e). To investigate the possible effects due to the $3s^2 3p^6$ shell of Ti, we have also carried out the corresponding MP2 calculations with 40 correlated electrons (MP2-40e). The present CCSD(T) values correspond to the correlation effect due to 32 valence electrons.

The nonrelativistic SCF HF results obtained with ZPolX basis set are by about 1 au lower than those reported by Hohm and Maroulis [25]. On the other hand, our nonrelativistic MP2-32e results are by about 1 au higher than the corresponding reference value. Taking into account the significant difference in the basis set size, the ZPolX results can be considered as being of almost the same quality as those reported by Hohm and Maroulis. One should note however, that the $3s^2 3p^6$ correlation contribution, which has been neglected by these authors, will lead to the increase of the dipole polarizability by about 0.5 au. Simultaneously, the relativistic effects will reduce the MP2-40e result by about the same amount. Also the higher–order correlation effects, as indicated by the present CCSD(T) data (Table 7), do not appear particularly important. Let us also mention that the relativistic IOTC CCSD(T) result calculated in the present paper (101.3 au) is in excellent agreement with the experimental value (101.4 au) [25] of the dipole polarizability of $TiCl_4$.

The $TiCl_4$ molecule is a closed shell system for which the single determinant reference in MP2 and CCSD(T) calculations should not raise any objections. Hence, at variance with the study of dipole moments and polarizabilities of the transition metal oxides, one can also consider the reliability of the present data by their comparison with the results calculated with systematically extended sequences of large basis sets. Basis sets suitable for relativistic second-order Douglas–Kroll (DK2) [24,34] calculations have been recently generated by Widmark and Roos [54] and they are used in the present investigations. One should mention, that for the relatively light atoms in $TiCl_4$ and the electric property which is primarily determined by the valence contribution, the difference between IOTC and DK2 schemes is fully negligible.

The results reported in the last three columns of Table 7 show a nice convergence pattern. The IOTC SCF value of the dipole polarizability converges to about 84.41 au. This result is by about 1 au higher than that computed with the ZPolX_iotc basis set. A the level of the CCSD(T) approximation the polarizability value calculated with the largest R–ANO basis set (column C of Table 7) is by about 3% lower than the ZPolX_iotc result. This difference appears to be fully acceptable for the basis set, which involves only 131 basis functions as compared to the R–ANO set of 577 spherical Gaussians.

Finally, one should note that the IOTC CCSD(T) result (98.35 au) for the largest R-ANO basis set does not compare with the experimental dipole polarizability of $TiCl_4$ (101.4 au [25]) that well as the ZPolX_iotc value (101.28 au). Obviously, the 32-electron CCSD(T) approximation does not exhaust all electron correlation contributions. Another reason could be that our calculations neglect the vibrational contribution to the dipole polarizability. This would increase the calculated polarizability value.

5 Summary and conclusions

In the present study, we have designed very compact basis sets for the first-row transition metal atoms. These basis sets, combined with those determined earlier for the first-and second-row atoms [17,18], can be used in nonrelativistic and scalar relativistic high-level correlated molecular calculations. Their performance was first tested in calculations of atomic polarizabilities. Then, they were used in calculations of the dipole moments and polarizabilities of the first-row transition metal oxides. Finally, the ZPolX basis sets were employed to calculate the dipole polarizability of $TiCl_4$.

Obviously, the ZPolX basis sets are not designed for accurate calculations of atomic polarizabilities. The difference between the present ZPolX and large basis set results, which is in most cases of the order of about 2–3%, is quite acceptable and does not seem to affect the accuracy of the calculated molecular dipole moments and polarizabilities. Hence, the ZPolX basis sets developed in this study can be safely recommended for calculations of dipole moments and polarizabilities of the first-row transition metal compounds [23,81].

Let us also mention that the present ZPolX are supposedly the smallest sets which can be used in reliable calculations of molecular dipole moments and polarizabilities. Obviously, they can be extended by additional polarization functions by using the method developed in our earlier papers [16–18]. Given some initial basis set of sufficiently diffuse form, this method can be used to obtain one or more polarization functions which are suitable for the description of the electric field polarization of the electron density distribution.

The present study is based on the use of traditional methods of the wave function theory. However, the common experience shows that basis sets developed in the framework of these methods perform very well also in the case of the density functional calculations. The use of ZPolX basis sets in the context of the density functional theory methods would further extend the range of their applicability in calculations of molecular electric properties. On the other hand, the polarizability data obtained within the density functional scheme do not seem to be highly reliable [20].

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