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Polarized basis sets for high-level-correlated calculations of molecular electric properties

VIII. Elements of the group IIb: Zn, Cd, Hg

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Summary. The first-order polarized basis sets are generated for Zn, Cd, and Hg and their performance is tested in high-level-correlated calculations of electric dipole polarizabilities of these atoms. The present results calculated at the level of the non-relativistic CCSD(T) approximation with 12 explicitly correlated electrons are: 40.4 a.u. for Zn, 56.3 a.u. for Cd, and 58.0 a.u. for Hg. Upon including the relativistic and electron correlation–relativistic corrections within the quasirelativistic scheme based on the mass–velocity and Darwin terms these values are reduced to 37.9 a.u., 47.6 and 31.8 a.u., respectively. The derived polarized basis sets have been also used for the evaluation of the dipole polarizability of singly and doubly positive ions of the group IIb elements and are recommended for calculations of interaction energies and interaction-induced electric properties in both neutral and charged systems.

Key words: Polarized basis sets – Electric dipole polarizabilities of Zn, Cd, Hg, and their positive ions – Electron correlation effects on atomic properties – Relativistic effects on atomic properties

1 Introduction

In the truncated basis set approximation for atomic and molecular wave functions the usual way of increasing the accuracy of calculations goes through the basis set extension. This approach shortly faces the problem of physical limitations of the available resources. An intermediate solution to this dilemma is to use property-oriented basis sets. Most of the standard basis sets are energy-oriented, for they usually follow from the optimization of their parameters with respect to atomic or molecular energies. A recent example of such standardized high-quality sets is given by the so-called approximate natural orbitals [1]. Hovever, their performance in calculations of other than energy properties is usually less satisfactory [2, 3].

It is known [4] that accurate calculations of response properties for the external electric field perturbation require that the basis sets used for this purpose are to be specifically tailored. They must be both diffuse enough to permit a proper description of the perturbation effect on the outer part of the electron density distribution and tight enough to properly account for the electron correlation effects. A systematic procedure for the generation of relatively small basis sets for the calculation of atomic and electric properties has been proposed some years ago [5, 6] and successfully applied to most atoms of the main groups of the periodic table [5–11]. These so-called polarized basis sets have been demonstrated to perform well in calculations of dipole and quadrupole moments and electric dipole polarizabilities. Moreover, for systems involving heavy atoms the polarized basis sets have been shown to correctly predict the relativistic contribution to different electric properties.

The interest in atomic and molecular electric properties and basis sets which permit their sufficiently accurate calculation is mostly driven by different models of intermolecular interactions. Electric properties of the interacting subsystems enter different models of interactions in the form of parameters. Moreover, as argued by van Duijneveldt-van der Rijdt and van Duijneveldt [12], once the given basis set is capable of correctly predicting the major electric properties of the interacting subsystems it should also be appropriate for the calculation of the weak interaction energies. The same applies to calculations of the interaction-induced electric properties of weakly bound systems. In this context one should mention the growing interest in different properties of weakly bound complexes of the group IIb metal atoms [13, 14]. This makes the development of polarized basis sets for these atoms timely and desirable.

The procedure used for the generation of polarized basis for Zn, Cd, and Hg follows essentially that used for other atoms [5, 7]. However, the presence of the next-to-valence $(n-1)d^{10}$ shell makes certain details of the present basis set generation different from the earlier ones. A brief survey of the procedure employed for the derivation of polarized basis sets for Zn, Cd, and Hg is given in Sect. 2. The methodology of testing the performance of the basis sets derived in this paper and certain computational aspects of the present study are surveyed in Sect. 3. In Sect. 4 the first-order polarized basis sets are tested against their performance in calculations of atomic dipole polarizabilities at different levels of approximation with respect to the treatment of the electron correlation contribution. The relativistic corrections are evaluated as well. The results of our study are compared with earlier data by other authors and summarized in Sect. 5.

2 Generation of polarized basis sets

The method of the generation of polarized basis sets for Zn, Cd, and Hg used in this study heavily relies on the experience gained in our earlier studies of polarized basis sets [5–10]. However, certain features of the electronic structure of these elements lead to some modifications of the standardized procedure used for atoms of the main groups of the periodic table. In addition to correctly representing the polarization of the outer ns^2 shell the generated basis sets must be appropriate for describing both the field-induced polarization of the $(n-1)d^{10}$ shell and the so-called core-polarization effects [15].

The initial GTO basis set of Zn is the energy-optimized (14.9.3) set of Huzinaga [16] while those of Cd (17.12.8) and Hg (19.14.10.5) are taken from the basis set optimization study of Gropen [17]. In all cases the flexibility of the s-subsets in the valence region was enhanced by adding one diffuse s-type GTO and another one in the region of the most distant node of the valence ns orbital. The orbital exponents for diffuse s-type GTOs are obtained from the geometric continuation of the s-orbital exponent series. In the case of Zn and Cd the orbital exponents for the additional *s*-type GTOs in the outermost node region follow from the upward continuation of the approximate geometric series. For Hg the corresponding *s*-type orbital exponent has been taken simply as the arithmetic average of the two nearest exponents of the initial basis set. This extension of the initial *s*-subsets was accompanied by contractions in the core region. For Zn ten highest-exponent GTOs are contracted into three CGTOs with contraction coefficients read from 1*s*, 2*s*, and 3s SCF eigenvectors. In a similar way 1*s*, 2*s*, 3*s*, and 4s SCF eigenvectors of Cd were employed to contract 12 highest-exponent GTOs and 1*s* through 5*s* SCF eigenvectors of Hg were used for contracting 13 highest-exponent GTOs of its *s*-subset.

The *p*-orbital exponents of initial basis sets are rather high and used for the purpose of representing the core *p*-type orbitals. No *p*-type functions are initially available for the polarization of the valence shell *ns* orbitals. For this reason the *p*-subsets of all atoms were extended by three diffuse GTOs with orbital exponents matching those of the three most diffuse *s*-type functions. This procedure is a consequence of the basis set polarization ideas [5, 6] and supplies *p*-type functions appropriate for describing the polarization of the *ns* valence shell of the given atom. Additionally, the diffuse *p*-functions may also be used for representing the valence *np* orbitals. The extension of the *p*-subset was accompanied by its contraction in the core region. Two (2*p*, 3*p*), three (2*p*–4*p*), and four (2*p*–5*p*) CGTOs were constructed for Zn, Cd, and Hg, respectively, with contraction coefficients read from the corresponding SCF eigenvectors. The number of contracted highest-exponent primitive GTOs is seven for Zn, nine for Cd, and ten for Hg. For all these atoms the final *p*-subsets are essentially uncontracted in the valence (*np*) and subvalence ($(n-1)p$) shells.

In our earlier studies of polarized basis sets for elements of the main groups IVa through VIIa the attention was focused on the generation of the *d*-type polarization functions [5, 6, 8–10]. For these elements the major contribution to electric dipole polarizabilities comes from the electric-field-induced polarization of the valence *p*-shell. In the present case, however, this polarization mechanism is much less important. Thus, the initial *d*-subsets were only extended by one diffuse *d*-type GTO with the orbital exponent obtained from the geometric progression rule. This was followed by contracting the highest-exponent GTOs. For Zn a single CGTO was produced by contracting the corresponding four GTOs with contraction coefficients read from the 3*d* SCF eigenvector. Two CGTOs (3*d* and 4*d*) were obtained for Cd by contracting six highest-exponent GTOs and for Hg three CGTOs (3*d*, 4*d*, and 5*d*) follow from contracting seven highest-exponent GTOs.

The *f*-subset of Hg has been contracted to two CGTOs with orbital exponents read from the 4*f* SCF eigenvector. However, for all atoms of the IIb group the polarization of the next-to-valence *d*-shell is expected to bring significant contribution to polarizabilities. Hence, the basis sets generated so far need to be extended by the *f*-type polarization functions determined by what is referred to as the first-order polarization of the $(n-1)d$ shell. This procedure follows to a great extent the method used earlier for generating *d*-type polarization functions for elements of the IVa through VIIa groups of the periodic table [5, 6, 8–10]. The *f*-type polarization functions are assumed to be of the form of two CGTOs, each built of two primitive GTOs with orbital exponents matching those of the most diffuse region of the corresponding $(n-1)d$ orbital. The contraction coefficients are determined by considering the first-order electric field polarization of the $(n-1)d$ orbital, i.e., in complete analogy to the determination of the *d*-type polarization functions for the main group elements. This means that the initial LCAO coefficients of the $(n-1)d$

SCF eigenvector are scaled by the inverse square root of the corresponding orbital exponent [5, 6]. The same method has been used in our earlier studies of polarized basis sets for the elements of the fourth and fifth rows of the periodic table [9, 10].

The present method of the generation of polarized basis sets for elements of the IIb group leads finally to the following GTO/CGTO basis sets: [16.12.6.4/9.7.3.2] for Zn (PolZn), [19.15.9.4/11.9.5.2] for Cd (PolCd), and [21.17.11.9/13.11.7.4] for Hg (PolHg). The details of their composition are given in the Appendix.

One should recall that the main reason for the development of the polarized basis sets is to use them in accurate calculations of basic electric properties of molecules and to study intermolecular interaction energies. From this point of view the performance of the generated basis sets at the level of atomic calculations provides a direct check on their possible usefulness.

Above all the first-order polarized basis sets must be flexible enough to account for the electric-field-induced polarization of the electron density distribution at the SCF level. Moreover, they should properly account for the valence correlation contribution to polarizabilities as well as for the core-polarization effects [15]. With the increasing nuclear charge the relativistic contribution to electric dipole polarizabilities becomes important [18, 19] and this should also be reliably predicted in calculations with polarized basis sets developed in this study. All these aspects of the performance of polarized sets for Zn, Cd, and Hg will be considered by computing their electric dipole polarizabilities at different levels of approximation.

3 Methods and approximations

The reliability of the computed polarizability data depends primarily on the composition and flexibility of the basis set. Thus, to qualify the polarized basis sets of this paper several parallel calculations of atomic dipole polarizabilities have been carried out with the corresponding completely uncontracted GTO bases. These comparative studies have been performed at both the SCF and different correlated levels of approximation. The electron correlation corrections to the SCF values of atomic polarizabilities have been calculated by a variety of high-level correlated techniques ranging from different *n*th order many-body perturbation theory (MBPTn) approaches to the coupled cluster (CC) methods [20–23]. The highest level of approximation with respect to the electron correlation contribution is represented by the results of the CCSD(T) method [22, 23]. The results obtained by other methods (MBPTn,CCSD) are helpful in qualifying the reliability of the CCSD(T) values of atomic polarizabilities.

In addition to single reference MBPT/CC studies we have carried out some complementary calculations by using the CAS SCF [24] method followed by the second-order multireference perturbation CASPT2 approach [25, 26]. These calculations are helpful in analyzing the possible effect of the near-degeneracy between ns^2 and np^2 valence configurations of the group IIb atoms.

The electron correlation contribution to the dipole polarizability as recovered by the given method depends also on the number of correlated electrons. It is obvious that both the SCF and electron correlation contributions from very deep cores are negligible. However, considering explicitly the electron correlation contribution of the $(n-1)d^{10}$ shell and the accompanying core-polarization effects is necessary. The contribution of the $(n-1)s^2$ and $(n-1)p^6$ shells may be of some importance as well. For this reason the present calculations have been carried out with 12 and 20 explicitly correlated electrons.

For the present series of atoms the relativistic contribution to the electric dipole polarizability becomes important and this has been estimated by using the method developed in our earlier papers [18, 27]. The method is based on a quasirelativistic scalar (Cowan–Griffin [31]) approximation to the relativistic hamiltonian. This approximation, which accounts for the lowest-order contribution due to mass–velocity and Darwin (MVD) terms, has been found to give quite reliable values of the relativistic correction to electric properties whose values are determined primarily by the electron distribution in the valence shell [19, 32]. The present calculations of the relativistic correction to the dipole polarizability of the group IIb atoms combine both the pure relativistic effects as estimated at the level of the SCF approximation and the mixed relativistic-correlation contributions [19, 27, 32].

The methodology of calculations closely follows that employed in our earlier studies of atomic and molecular electric properties [5, 6, 10, 18]. The polarizability results are obtained by using the finite electric field perturbation followed by the numerical differentiation of the field-dependent energies. A similar finite field perturbation method [27] has been used to obtain mixed relativistic-correlation corrections to the dipole polarizability. All calculations reported in this paper have been carried out with the MOLCAS-2 system of quantum chemistry programs [28] which includes codes for MBPT/CC [28, 29] and CC methods [30].

4 Calculations of atomic dipole polarizabilities

The results of MBPT/CC calculations of the electric dipole polarizability of Zn, Cd, and Hg are presented in Tables 1, 2, and 3, respectively. They include the non-relativistic SCF values, electron correlation corrections calculated at the level of MBPT2, MBPT3, SDQ4, CCSD, MBPT4, and CCSD(T) approximations [20, 22, 23], and relativistic and relativistic-correlation corrections obtained from the quasirelativistic (MVD) approach [18, 27].

In order to investigate the effect of contractions the SCF and non-relativistic MBPT/CC calculations have been carried out with both the derived polarized basis sets (PolZn, PolCd, PolHg) and with their completely uncontracted GTO counterparts. On comparing the corresponding results for 12 correlated electrons one finds that the contraction effect is essentially negligible at the SCF HF level of approximation, i.e., in the worst case (Hg) it amounts to less than 0.3 a.u. In non-relativistic MBPT/CC calculations the contraction effects become slightly larger. However, at the level of the CCSD(T) approximation the contraction effect is only of the order of 1–2% of the final non-relativistic CCSD(T) result. This appears to be a reasonable compromise between the basis set size and the accuracy of the calculated polarizabilities. One should also take into account that the CCSD(T) method by no means exhausts the electron correlation contribution to dipole polarizabilities. Going beyond this approximation might also affect our results to some extent. However, a rather small difference between the T_3 contributions evaluated at the MBPT4 and CCSD(T) levels of approximation indicates that the higher-level CC methods [20] would not substantially change the present values.

The basis set contraction effect on the SCF values of the relativistic (MVD) contribution is again negligibly small. The mixed relativistic-correlation

Table 1. MBPT/CC calculations of the electric dipole polarizability of Zn(^{1}S). All values in a.u.

Method	Basis set: Correlated shells:	(16.12.6.4) $3d^{10}4s^2$	PolZn[a] $3d^{10}4s^2$	PolZn[a] $3s^23p^63d^{10}4s^2$
SCF		53.54	53.39	53.39
Electron correlation corrections				
MBPT2		– 14.93	– 15.38	– 16.53
MBPT3		– 12.35	– 13.25	– 13.10
SDQ4		– 13.13	– 13.84	– 15.42
CCSD		– 11.35	– 11.79	– 12.07
MBPT4		– 15.00	– 15.69	– 17.65
CCSD(T)		– 12.64	– 10.58	– 10.87
Quasirelativistic corrections				
SCF		– 3.18	– 3.29	– 3.29
MBPT2			0.68	0.68
MBPT3			0.81	0.82
SDQ4			0.70	0.71
CCSD			0.71	0.71
MBPT4			0.70	0.73
CCSD(T)			0.66	0.66
Total				
CCSD(T)[b]		40.90	40.39	40.13
CCSD(T)[c]			37.86	37.61

[a] First-order polarized [16.12.6.4/9.7.3.2] GTO/CGTO basis set of Zn derived in this paper.

[b] Non-relativistic results calculated at the level of the CCSD(T) approximation.

[c] Quasirelativistic results including the MVD relativistic correction and mixed relativistic–correlation contributions evaluated at the level of the CCSD(T) approximation.

contributions are small by themselves. Thus, the contraction effect on the mixed terms is not expected to be important. This has also been found in our earlier studies of the relativistic-correlation contribution to dipole polarizabilities of heavy atoms [10, 19, 32].

The SCF HF dipole polarizabilities of the group IIb elements are strongly affected by the electron correlation contribution. This contribution is negative and in the CCSD(T) approximation it reduces the SCF HF results by about 25%. The magnitude of the electron correlation contribution depends on the level of approximation and the number of explicitly correlated shells.

It can be seen that for Cd and Hg the lowest-order MBPT2 method overestimates to some extent the magnitude of the (negative) electron correlation contribution, while for Zn the MBPT2 correction is rather close to those obtained from other methods. This can be interpreted in terms of the increasing importance of the ns^0sp^2 configuration which worsens the assumption of the single configuration reference used in our calculations. In order to verify this interpretation we have carried out the second-order perturbation calculations (CASPT2) [25, 26] with a multiconfiguration reference function generated by the CAS SCF method [24]. This reference function is the full CI wave function for two valence electrons in the active space comprising the *nsnp* shell [24]. All core orbitals including the $(n-1)d^{10}$ shell are considered to belong to the inactive orbital subspace. In

Table 2. MBPT/CC calculations of the electric dipole polarizability of Cd(^{1}S). All values in a.u.

Method	Basis set: Correlated shells:	(19.15.9.4) $4d^{10}5s^2$	PolCd[a] $4d^{10}5s^2$	PolCd[a] $4s^24p^64d^{10}5s^2$
SCF		75.12	74.98	74.98
Electron correlation corrections				
MBPT2		− 25.21	− 26.00	− 28.07
MBPT3		− 19.21	− 20.18	− 20.87
SDQ4		− 16.93	− 17.58	− 19.08
CCSD		− 16.34	− 16.79	− 17.59
MBPT4		− 18.79	− 19.47	− 21.56
CCSD(T)		− 18.21	− 18.68	− 19.62
Quasirelativistic corrections				
SCF		− 12.15	− 12.20	− 12.20
MBPT2			4.30	4.43
MBPT3			3.90	4.06
SDQ4			3.36	3.51
CCSD			3.17	3.24
MBPT4			3.61	3.84
CCSD(T)			3.53	3.64
Total				
CCSD(T)[b]		56.91	56.30	55.36
CCSD(T)[c]			47.63	46.80

[a] First-order polarized [19.15.9.4/11.9.5.2] GTO/CGTO basis set of Cd derived in this paper.

[b] Non-relativistic results calculated at the level of the CCSD(T) approximation

[c] Quasirelativistic results including the MVD relativistic correction and mixed relativistic–correlation contributions evaluated at the level of the CCSD(T) approximation

subsequent CASPT2 calculations excitations were allowed from the active space and the $(n-1)d^{10}$ shell. These CAS SCF/CASPT2 results are compared with the MBPT2 and CCSD(T) data in Table 4.

Limiting the treatment of the electron correlation contribution to the level of the valence CAS SCF approximation is obviously insufficient. However, for the present CAS SCF reference function the second-order treatment of the electron correlation contribution from the $(n-1)d^{10}$ shell makes the CAS SCF/CASPT2 results comparable with those of the single reference CCSD(T) method. The CAS SCF reference removes the major part of the near-degeneracy effect and the remaining electron correlation contributions to the dipole polarizability of the group IIb atoms can be treated reasonably well by the CASPT2 method. With respect to the $(n-1)d^{10}$ shell this method closely resembles the single configuration MBPT2 approach and our results show that the core correlation contributions to the dipole polarizability can be satisfactorily accounted for in the low-order perturbation scheme.

The dependence of the pure electron correlation contribution to dipole polarizabilities on the number of correlated shells has been studied by comparing the results evaluated with either 12 ($(n-1)d^{10}ns^2$) or 20 ($(n-1)s^2(n-1)p^6$-$(n-1)d^{10}ns^2$) explicitly correlated electrons. The corresponding results are presented in the last two columns of Tables 1–3. Including the $(n-1)s^2(n-1)p^6$ shell increases the (negative) value of the electron correlation contribution to dipole

Table 3. MBPT/CC calculations of the electric dipole polarizability of Hg(^{1}S). All values in a.u.

Method	Basis set: Correlated shells:	(21.17.11.9) $5d^{10}6s^2$	PolHg[a] $5d^{10}6s^2$	PolHg[a] $5s^25p^65d^{10}6s^2$
SCF		79.57	79.27	79.27
Electron correlation corrections				
MBPT2		– 30.07	– 30.88	– 33.25
MBPT3		– 22.78	– 23.88	– 24.60
SDQ4		– 19.42	– 20.19	– 21.72
CCSD		– 18.75	– 19.28	– 20.16
MBPT4		– 21.26	– 22.09	– 24.31
CCSD(T)		– 20.69	– 21.29	– 22.36
Quasirelativistic corrections				
SCF		– 38.32	– 38.58	– 38.58
MBPT2			16.52	17.25
MBPT3			13.89	14.58
SDQ4			11.59	12.25
CCSD			11.00	11.39
MBPT4			12.70	13.65
CCSD(T)			12.43	12.91
Total				
CCSD(T)[b]		58.88	57.98	56.91
CCSD(T)[c]			31.82	31.24

[a] First-order polarized [21.17.11.9/13.11.7.4] GTO/CGTO basis set of Hg derived in this paper
[b] Non-relativistic results calculated at the level of the CCSD(T) approximation
[c] Quasirelativistic results including the MVD relativistic correction and mixed relativistic–correlation contributions evaluated at the level of the CCSD(T) approximation

polarizabilities. However, at the level of the CCSD(T) approximation this effect is rather small and possibly can be neglected in most studies. Our results can be related to the use of pseudopotential methods [14] and indicate that without a major deterioration of their electric properties the group IIb atoms can be considered as effectively 12-electron systems. The same conclusion applies therefore to calculations of interaction energies involving these atoms.

In the non-relativistic approximation both the SCF and correlated data form a similar pattern with the dipole polarizability values increasing with the nuclear charge. However, it is known [19, 32] that with the increase of the nuclear charge there is a significant increase of the relativistic contribution to atomic dipole polarizabilities. The present results provide a direct illustration of this effect. At the level of the SCF HF approximation the (MVD) relativistic contribution is only about – 6% for Zn while it increases to about – 40% for Hg. Thus, for Hg the MVD correction becomes more important than the electron correlation contribution, both being large and negative.

In the case of simultaneously large electron correlation and relativistic corrections to electric properties one can expect that the magnitude of the electron correlation contribution can be substantially affected by relativistic effects [19, 27, 32]. According to our data these mixed relativistic–correlation contributions are positive and diminish the effect of the pure correlation and MVD SCF HF corrections. For Zn the mixed relativistic–correlation contribution is essentially

Table 4. Dipole polarizability calculations with polarized basis sets. A comparison of the CAS SCF/CASPT2 results with single reference MBPT2 and CCSD(T) data. All values in a.u.

Atom	CAS SCF[a]	CASPT2[b]	MBPT2[c]	CCSD(T)[d]
Non-relativistic results				
Zn	46.63	39.85	38.01	40.39
Cd	65.37	55.24	48.98	56.30
Hg	68.87	56.53	48.39	57.98
Quasirelativistic results[e]				
Zn	44.09	36.99	35.40	37.86
Cd	56.35	46.28	41.08	47.63
Hg	41.25	29.70	26.33	31.82

[a] In CAS SCF calculations all shells through $(n-1)d^{10}$ belong to the inactive orbital subspace. The active orbital subspace is built from the *nsnp* shell orbitals and describes the two valence electrons

[b] The sum of the CAS SCF result and the corresponding CASPT2 corrections. In CASPT2 calculations double excitations are also allowed from the $(n-1)d^{10}$ shell

[c] Single reference MBPT2 calulations with 12 explicitly correlated electrons. For details see Tables 1–3

[d] Single reference CCSD(T) calulations with 12 explicitly correlated electrons. For details see Tables 1–3

[e] Both the pure (SCF HF) relativistic and mixed relativistic–correlation contributions are included

negligible. However, already for Cd it reduces the MVD SCF HF correction by about 4 a.u. Neglecting these mixed terms for Hg would lead to much too low values of its dipole polarizability. One should also note that most of the mixed relativistic–correlation correction comes from the $(n-1)d^{10}ns^2$ shells. The contribution of the $(n-1)s^2(n-1)p^6$ shells evaluated at the level of the CCSD(T) approximation ranges from less than 0.01 a.u. for Zn to about 0.5 a.u. for Hg. Hence, one can conclude that the calculation of the mixed relativistic–correlation contribution to the dipole polarizability can be satisfactorily carried out with only 12 electrons explicitly correlated.

From the data presented in Table 4 the valence shell near-degeneracy effects can be seen to be of certain importance for mixed relativistic–correlation contribution to the dipole polarizability of Hg. This contribution as predicted by the single reference MBPT2 method is by about 4 a.u. higher than the CCSD(T) result (Table 3). For Cd (Table 2) this difference amounts to only about 0.8 a.u. and is completely negligible for Zn (Table 1). It follows from the CAS SCF/CASPT2 data of Table 4 that most of the difference between CCSD(T) and MBPT2 results for Hg is recovered by using the multiconfiguration approach in the valence space followed by the second-order perturbation treatment of the remaining electron correlation contribution.

Among the methods employed in this paper the CCSD(T) approach represents the highest level of approximation with respect to the treatment of the electron correlation effects. According to the final quasirelativistic CCSD(T) results of our study the predicted sequence of polarizabilities is $\alpha_{\mathrm{Hg}} < \alpha_{\mathrm{Zn}} < \alpha_{\mathrm{Cd}}$ while the non-relativistic treatment leads to the monotonic increase of polarizabilities with the

Table 5. Dipole polarizabilities of singly and doubly positive ions of the group IIb elements. All values in a.u.

Method	Zn^+	Cd^+	Hg^+	Zn^{2+}	Cd^{2+}	Hg^{2+}
Non-relativistic results						
SCF HF	24.83	37.12	40.05	2.132	4.450	6.086
MBPT4				2.658	4.776	6.721
Quasirelativistic results[a]						
SCF HF	23.09	30.65	17.52	2.206	4.668	6.421
MBPT4				2.732	4.994	7.056

[a] The relativistic (MVD) correction has been evaluated only at the level of the SCF HF approximation

increasing nuclear charge. A similar relativistic effect has been found also in the case of elements of the main groups Ia and IIa [19, 32]. Since the dipole polarizability is approximately related to the size of atoms one can say that cadmium is the largest atom among the elements of the group IIb.

In addition to a rather comprehensive study of dipole polarizabilities of the neutral atoms of the group IIb we have also carried out some limited study of their positively charged ions. For singly ionized atoms only the SCF HF data including the MVD corrections have been calculated. The doubly positive species have been considered at the level of the MBPT4 approximation with respect to pure correlation effects while the relativistic corrections have been estimated from the SCF HF MVD data. The corresponding results are collected in Table 5.

The dipole polarizabilities of singly positive ions essentially follow the pattern already discussed for neutral atoms, the corresponding values being about half of those for the neutral systems. The pure relativistic effect calculated in the MVD approximation causes their considerable reduction. As a consequence Cd^+ turns out to be the most polarizable ion in the series. The negative sign of the MVD correction is a consequence of the relativistic contraction of the valence *ns* orbital [33] and dominates the total relativistic contribution to dipole polarizabilities of singly positive ions of the group IIb elements. The relativistic effect on the $(n-1)d^{10}$ shell should lead to its expansion and some (relatively small) positive relativistic contribution to polarizability. In addition to relativistic corrections one can also expect a considerable contribution due to electron correlation and mixed relativistic–correlation effects [11]. Hence, the present MVD-corrected SCF HF results give only some preliminary information about the magnitude of dipole polarizabilities of the singly ionized systems.

The polarizability data for doubly charged species bring about certain interesting features. The MVD correction is positive for all ions and explicitly shows the relativistic effect on $(n-1)d^{10}$ shells [33]. This is accompanied by positive electron correlation corrections. Since both these corrections are small the mixed relativistic-correlation contributions will be essentially negligible and has not been considered in this study. The dipole polarizabilities of the doubly positive ions increase monotonically with their nuclear charge. The relativistic MVD correction is comparable to the MBPT4 correlation contribution already for Cd^{2+} and becomes dominant for Hg^{2+}. In view of rather small values of these corrections, the present MVD-corrected MBPT4 data for dipole polarizabilities of Zn^{2+}, Cd^{2+}, and Hg^{2+}

Table 6. Comparison of the non-relativistic and quasirelativistic HF dipole polarizabilities calculated with polarized basis sets of this paper with numerical Hartree–Fock and Dirac–Hartree–Fock data. All values in a.u.

Method	Zn	Cd	Hg
Non-relativistic results			
SCF HF[a]	53.39	74.98	79.27
Numerical HF[b]	53.4	75	80
Quasirelativistic/relativistic results			
SCF HF[c]	50.10	62.78	40.69
Numerical DHF[d]	50.4	62	43

[a] SCF HF results of this paper calculated with polarized basis sets

[b] Numerical non-relativistic SCF HF results from Ref. [35]

[c] SCF HF results of this paper including the MVD correction for relativistic effects

[d] Numerical Dirac–Hartree–Fock results from Ref. [35]

are quite reliable. Let us also add that most of the results for positive ions calculated with polarized basis sets have been checked against the corresponding data obtained with the corresponding fully uncontracted sets. Only very small differences have been found indicating that the polarized basis sets of this paper are equally useful in calculations for both neutral and ionized species.

5 Comparison with other polarizability data. Conclusions

The purpose of extensive calculations of the electric dipole polarizabilities of Zn, Cd, Hg, and their ions was mainly to test the performance of the polarized basis sets generated in this study. Our attention was so far primarily focused on rather formal aspects of the basis set contraction effect and its influence on different contributions to the dipole polarizability. The reliability of different corrections was verified only by comparing our results in different approximations. However, both the relativistic and electron correlation contributions are calculated only approximately and one would like to have some external measure of the quality of our basis sets and polarizability results.

The experimental values of dipole polarizabilities for systems studied in this paper are either unknown or insufficiently reliable. The available experimental dipole polarizability of Hg is about 34 a.u. [34] (see also Ref. [14]) and agrees well with our quasirelativistic CCSD(T) result of 31.8 a.u. (see Table 3). In this context the numerical HF and Dirac–Hartree–Fock (DHF) polarizability values calculated by Desclaux et al. [35] are of great help, for they permit a direct verification of the quality of our polarized basis sets and of the validity of the MVD approximation. A comparison of these results with our data is presented in Table 6.

Our non-relativistic calculations with polarized basis sets developed in this study give essentially the same results as those obtained by Desclaux et al. [35] by numerically integrating the HF equations. On comparing our MVD SCF HF with DHF results one finds that the MVD approximation works well for Zn and Cd. Even in the case of a rather heavy atom like Hg the difference between the MVD

SCF HF and DHF data is only of the order of 2–3 a.u. Interestingly enough this is about the same as the difference between our quasirelativistic CCSD(T) polarizability of Hg (31.8 a.u.) and the experimental result (34 a.u.). The comparison presented in Table 6 shows that the polarized basis sets of Zn, Cd, and Hg are indeed of sufficiently high quality to give reliable results for atomic polarizabilities at the level of the HF approximation. Also the MVD approximation appears to be quite reliable.

The majority of theoretical data for dipole polarizabilities of the group IIb elements follows from calculations with effective core potentials (ECP) [14, 36, 37]. Konowalow et al. [36] have studied the electron correlation and relativistic effects on dipole polarizabilities of the group IIb atoms by using the valence multiconfiguration (MC)SCF method and 2-electron ECPs. The effect of the d^{10} shell has been considered only for Hg in the framework of the 12-electron ECPs. The MC SCF results obtained with empirical relativistic 2-electron ECPs (Zn: 35.1 a.u.; Cd: 42.5 a.u.; Hg: 36.2 a.u. [36]) show correct trends with respect to the Z-dependence of the dipole polarizability and agree qualitatively with the present quasirelativistic CCSD(T) data. On using the 12-electron ECPs for Hg Konowalow et al. [36] calculated its polarizability as equal to 31.8 a.u.

Several theoretical studies have been reported for the dipole polarizability of Hg. The 2-electron ECP calculations by Maeder and Kutzelnigg [37] gave the polarizability value of 32.8 a.u. Recently Schwerdtfeger et al. [14] have carried out a comprehensive ECP study of the dipole polarizability of Hg with 20-electron ECPs. The electron correlation effects were treated at the level of MBPTn ($n = 2$–4), QCISD, and QCISD(T) methods. The non-relativistic QCISD(T) result of these authors (57.76 a.u.) compares well with the present non-relativistic CCSD(T) value of 56.91 a.u. (20 electrons correlated, see Table 3). Their QCISD(T) result (33.44 a.u.) with relativistic 20-electron ECPs is, however, about 2 a.u. higher than the corresponding CCSD(T) value (31.24 a.u.) of this paper. It is worthwhile to mention that such a difference occurs already at the level of the non-relativistic SCF HF approximation. The non-relativistic SCF HF result of Schwerdtfeger and Pyykkö (81.29 a.u.) is by about 2 a.u. higher than the present value (79.27 a.u.) obtained in all electron calculations with the PolHg basis set. The higher non-relativistic SCF HF polarizability value calculated by Schwerdtfeger and Pyykkö can be interpreted as resulting from the use of too soft ECPs. On the other hand, one could argue that the lower value obtained from our calculations is due to some basis set truncation effects. However, several attempts to increase the flexibility of the uncontracted counterpart of the PolHg basis set have failed to produce the SCF HF dipole polarizability higher than 80 a.u.

It appears to be of interest to compare our polarizability data with the so-called recommended values of Miller and Bederson [38]. For Zn the recommended value is 38.5 a.u. and compares well with the present quasirelativistic CCSD(T) results (37.86 a.u., 37.61 a.u., see Table 1). However, the recommended dipole polarizabilty of Cd (40.5 a.u.) is much lower than the present values (47.63 a.u., 46.80 a.u., see Table 2) and needs to be corrected. For Hg the recommended dipole polarizability corresponds to its experimental value and, as discussed earlier in this section, agrees reasonably well with our quasirelativistic CCSD(T) data.

The main result of this paper is the first-order polarized basis sets for the group IIb atoms whose details are given in the Appendix. These basis sets were shown to perform satisfactorily at both the SCF HF and different correlated levels of approximation. The contraction effects have been found to be relatively small. The quasirelativistic (MVD) estimates of relativistic corrections to dipole

Table 7. First-order polarized [16.12.6.4/9.7.3.2] GTO/CGTO basis set (PolZn) for zinc

GTO	CGTO	Exponent	Contraction coefficients		
s subset					
1	1–3	322679.10	0.0003161	– 0.0000979	0.0000368
2		48663.558	0.0024285	– 0.0007485	0.0002837
3		11166.082	0.0123911	– 0.0038821	0.0014576
4		3208.8831	0.0485712	– 0.0153564	0.0058655
5		1069.5126	0.1479921	– 0.0506439	0.0191051
6		396.66584	0.3250939	– 0.1255657	0.0496913
7		159.92496	0.4061928	– 0.2291848	0.0902554
8		68.610341	0.1937377	– 0.1103823	0.0555846
9		23.690661	0.0143465	0.5407636	– 0.3406232
10		10.038526	– 0.0020383	0.5835458	– 0.4692264
11	4	2.7728690	1.0		
12	5	1.0871093	1.0		
13	6	0.426200	1.0		
14	7	0.14532845	1.0		
15	8	0.0507459	1.0		
16	9	0.017719	1.0		
p-subset					
1	1–2	2208.5972	0.0026157	0.0009837	
2		528.03016	0.0208369	0.0078341	
3		172.54422	0.0948808	0.0371585	
4		66.149786	0.2683111	0.1087578	
5		27.715181	0.4353094	0.1951371	
6		12.190621	0.3133438	0.0840062	
7		4.9602890	0.0550264	– 0.3584633	
8	3	2.0663549	1.0		
9	4	0.79142986	1.0		
10	5	0.145328	1.0		
11	6	0.050746	1.0		
12	7	0.017719	1.0		
d-subset					
1	1	58.305471	0.0274318		
2		16.474188	0.1506560		
3		5.5608782	0.3671806		
4		1.8975641	0.4656488		
5	2	0.55727732	1.0		
6	3	0.163661	1.0		
f-subset					
1	1	5.560878	0.155707		
2		1.897564	0.338034		
3	2	0.557277	0.420498		
4		0.163661	0.105305		

polarizabilities compare well with other data. They show that the MVD approximation gives most of the relativistic correction to polarizabilities of the closed-shell systems. It is also worth attention that the mixed relativistic–correlation contributions to dipole polarizabilities of the group IIb elements are by no means negligible.

Table 8. First-order polarized [19.15.9.4/11.9.5.2] GTO/CGTO basis set (PolCd) for cadmium

GTO	CGTO	Exponent[a]	Contraction coefficients[a]			
s-subset						
1	1–4	0.26966473(+ 7)	0.730733(− 4)	− 0.235290(− 4)	0.102647(− 4)	− 0.433151(− 5)
2		0.39716818(+ 6)	0.586111(− 3)	− 0.189518(− 3)	0.824358(− 4)	− 0.348412(− 4)
3		0.87165314(+ 5)	0.327460(− 2)	− 0.105601(− 2)	0.461437(− 3)	− 0.194612(− 3)
4		0.23333882(+ 5)	0.148410(− 1)	− 0.485720(− 2)	0.211360(− 2)	− 0.894077(− 3)
5		0.71327509(+ 4)	0.559388(− 1)	− 0.186383(− 1)	0.819325(− 2)	− 0.345658(− 2)
6		0.24263210(+ 4)	0.167182(+ 0)	− 0.603976(− 1)	0.265892(− 1)	− 0.112883(− 1)
7		0.90602687(+ 3)	0.351326(+ 0)	− 0.148517(+ 0)	0.678580(− 1)	− 0.287749(− 1)
8		0.36744488(+ 3)	0.396089(+ 0)	− 0.247376(+ 0)	0.116938(+ 0)	− 0.506895(− 1)
9		0.15964308(+ 3)	0.151261(+ 0)	− 0.745082(− 1)	0.442607(− 1)	− 0.185387(− 1)
10		0.64314338(+ 2)	0.770122(− 2)	0.545882(+ 0)	− 0.414862(+ 0)	0.191594(+ 0)
11		0.29090498(+ 2)	− 0.329872(− 3)	0.560877(+ 0)	− 0.566116(+ 0)	0.299140(+ 0)
12		0.10383109(+ 2)	0.442936(− 4)	0.777871(− 1)	0.579765(+ 0)	− 0.444927(+ 0)
13	5	0.51857168(+ 1)	1.0			
14	6	0.17235995(+ 1)	1.0			
15	7	0.7436723 (+ 0)	1.0			
16	8	0.320868 (+ 0)	1.0			
17	9	0.1172635 (+ 0)	1.0			
18	10	0.424395 (− 1)	1.0			
19	11	0.15360 (− 1)	1.0			
p-subset						
1	1–3	0.18879856(+ 5)	0.352057(− 3)	0.162560(− 3)	0.642288(− 4)	
2		0.45781388(+ 4)	0.296780(− 2)	0.132052(− 2)	0.537917(− 3)	
3		0.14846041(+ 4)	0.167402(− 1)	0.787531(− 2)	0.311194(− 2)	
4		0.56323368(+ 3)	0.626626(− 1)	0.279776(− 1)	0.117363(− 1)	
5		0.34065261(+ 3)	0.381806(− 1)	0.226943(− 1)	0.804164(− 2)	
6		0.19501957(+ 3)	0.235741(+ 0)	0.112163(+ 0)	0.474681(− 1)	
7		0.84455826(+ 2)	0.434542(+ 0)	0.246877(+ 0)	0.100139(+ 0)	
8		0.37130829(+ 2)	0.336302(+ 0)	0.917251(− 1)	0.352881(− 1)	
9		0.14452454(+ 2)	0.579846(− 1)	− 0.517705(+ 0)	− 0.319717(+ 0)	

Table 8. (Continued)

GTO	CGTO	Exponent[a]	Contraction coefficients[a]	
10	4	0.62890997(+ 1)	1.0	
11	5	0.20519356(+ 1)	1.0	
12	6	0.7438697 (+ 0)	1.0	
13	7	0.1172635 (+ 0)	1.0	
14	8	0.424395 (− 1)	1.0	
15	9	0.15360 (− 1)	1.0	
d-subset				
1	1-2	0.57877186(+ 3)	− 0.395919(− 2)	− 0.135725(− 2)
2		0.16731679(+ 3)	− 0.356614(− 1)	− 0.122403(− 1)
3		0.59938384(+ 2)	− 0.164631(+ 0)	− 0.578854(− 1)
4		0.23520380(+ 2)	− 0.406206(+ 0)	− 0.141739(+ 0)
5		0.94516036(+ 1)	− 0.475100(+ 0)	− 0.138268(+ 0)
6		0.36396557(+ 1)	− 0.153300(+ 0)	0.224174(+ 0)
7	3	0.13373112(+ 1)	1.0	
8	4	0.4185349 (+ 0)	1.0	
9	5	0.130988 (+ 0)	1.0	
f-subset				
1	1	0.3639656 (+ 1)	0.116442(+ 0)	
2		0.1337311 (+ 1)	0.505667(+ 0)	
3	2	0.418535 (+ 0)	0.597537(+ 0)	
4		0.130988 (+ 0)	0.112968(+ 0)	

[a] The numbers in parentheses give the power of ten accompanying the given entry

Table 9. First-order polarized [21.17.11.9/13.11.7.4] GTO/CGTO basis set (PolHg) for mercury

GTO	CGTO	Exponent[a]	Contraction coefficients[a]				
s-subset							
1	1–5	0.94998897(+ 7)	0.544068(− 4)	0.180660(− 4)	− 0.858550(− 5)	0.427650(− 5)	0.182804(− 5)
2		0.14085815(+ 7)	0.431678(− 3)	0.144664(− 3)	− 0.685723(− 4)	0.341933(− 4)	0.146011(− 4)
3		0.31224217(+ 6)	0.237557(− 2)	0.787865(− 3)	− 0.374959(− 3)	0.186705(− 3)	0.798449(− 4)
4		0.84765340(+ 5)	0.105822(− 1)	0.358849(− 2)	− 0.170148(− 2)	0.849047(− 3)	0.362441(− 3)
5		0.26389035(+ 5)	0.393660(− 1)	0.133519(− 1)	− 0.638777(− 2)	0.318234(− 2)	0.136188(− 2)
6		0.91661112(+ 4)	0.119646(+ 0)	0.438925(− 1)	− 0.210165(− 1)	0.105226(− 1)	0.449214(− 2)
7		0.34817789(+ 4)	0.277612(+ 0)	0.111908(+ 0)	− 0.552418(− 1)	0.276876(− 1)	0.118800(− 1)
8		0.14165063(+ 4)	0.410425(+ 0)	0.232370(+ 0)	− 0.118550(+ 0)	0.604438(− 1)	0.258655(− 1)
9		0.60008268(+ 3)	0.262989(+ 0)	0.180582(+ 0)	− 0.104842(+ 0)	0.541404(− 1)	0.235870(− 1)
10		0.20737130(+ 3)	0.282275(− 1)	− 0.462404(+ 0)	0.387786(+ 0)	− 0.218143(+ 0)	− 0.969058(− 1)
11		0.96896340(+ 2)	− 0.644496(− 2)	− 0.631415(+ 0)	0.700840(+ 0)	− 0.452289(+ 0)	− 0.203380(+ 0)
12		0.34782672(+ 2)	0.345368(− 2)	− 0.128594(+ 0)	− 0.594128(+ 0)	0.648895(+ 0)	0.321810(+ 0)
13		0.18868997(+ 2)	− 0.270562(− 2)	0.480440(− 1)	− 0.720429(+ 0)	0.898645(+ 0)	0.512274(+ 0)
14	6	0.80205980(+ 1)	1.0				
15	7	0.42275907(+ 1)	1.0				
16	8	0.13057630(+ 1)	1.0				
17	9	0.6047389 (+ 0)	1.0				
18	10	0.352824 (+ 0)	1.0				
19	11	0.1009094 (+ 0)	1.0				
20	12	0.368773 (− 1)	1.0				
21	13	0.13477 (− 1)	1.0				
p-subset							
1	1–4	0.73262682(+ 5)	0.213606(− 3)	0.107874(− 3)	0.530885(− 4)	− 0.214023(− 4)	
2		0.17078800(+ 5)	0.197154(− 2)	0.994940(− 3)	0.494571(− 3)	− 0.196499(− 3)	
3		0.53541727(+ 4)	0.119448(− 1)	0.611289(− 2)	0.301967(− 2)	− 0.121709(− 2)	
4		0.19588228(+ 4)	0.533276(− 1)	0.278647(− 1)	0.139599(− 1)	− 0.556007(− 2)	
5		0.79590756(+ 3)	0.171561(+ 0)	0.947124(− 1)	0.476169(− 1)	− 0.192827(− 1)	
6		0.34912051(+ 3)	0.361076(+ 0)	0.214952(+ 0)	0.111629(+ 0)	− 0.446124(− 1)	
7		0.16187452(+ 3)	0.400525(+ 0)	0.240912(+ 0)	0.121840(+ 0)	− 0.506016(− 1)	
8		0.77508827(+ 2)	0.161760(+ 0)	− 0.155144(+ 0)	− 0.125461(+ 0)	0.597057(− 1)	

Table 9. (Continued)

GTO	CGTO	Exponent[a]	Contraction coefficients[a]			
9		0.37749779(+ 2)	0.109387(− 1)	− 0.620042(+ 0)	− 0.532576(+ 0)	0.229804(+ 0)
10		0.18864161(+ 2)	0.943887(− 3)	− 0.340415(+ 0)	− 0.887320(− 1)	0.351531(− 1)
11	5	0.85572345(+ 1)	1.0			
12	6	0.40781769(+ 1)	1.0			
13	7	0.14423865(+ 1)	1.0			
14	8	0.5445733 (+ 0)	1.0			
15	9	0.100909 (+ 0)	1.0			
16	10	0.36877 (− 1)	1.0			
17	11	0.13477 (− 1)	1.0			
d-subset						
1	1–3	0.47966911(+ 4)	0.533220(− 3)	0.285793(− 3)	− 0.882410(− 4	
2		0.13591414(+ 4)	0.630278(− 2)	0.319309(− 2)	− 0.103598(− 2)	
3		0.47328686(+ 3)	0.452773(− 1)	0.242592(− 1)	− 0.764302(− 2)	
4		0.18246073(+ 3)	0.198704(+ 0)	0.105815(+ 0)	− 0.343397(− 1)	
5		0.75149950(+ 2)	0.455402(+ 0)	0.252729(+ 0)	− 0.797240(− 1)	
6		0.32185264(+ 2)	0.421461(+ 0)	0.923948(− 1)	− 0.242524(− 1)	
7		0.12670732(+ 2)	0.858264(− 1)	− 0.544313(+ 0)	0.238742(+ 0)	
8	4	0.51390016(+ 1)	1.0			
9	5	0.14813481(+ 1)	1.0			
10	6	0.4452387(+ 0)	1.0			
11	7	0.133822(+ 0)	1.0			
f-subset						
1	1	0.16505605(+ 3)	0.212856(− 1)			
2		0.54797342(+ 2)	0.131610(+ 0)			
3		0.21145428(+ 2)	0.366964(+ 0)			
4	2	0.82595480(+ 1)	0.501235(+ 0)			
5		0.29666792(+ 1)	0.288736(+ 0)			
6	3	0.51390016(+ 1)	− 0.050237(+ 0)			
7		0.14813481(+ 1)	0.492730(+ 0)			
8	4	0.4452387 (+ 0)	0.791640(+ 0)			
9		0.133822 (+ 0)	0.187679(+ 0)			

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[a] The numbers in parentheses give the power of ten accompanying the given entry

A limited study of positively charged ions of the group IIb elements indicates that the PolMe (Me = Zn, Cd, Hg) basis sets (see Tables 7–9) correctly represent the influence of the ionic charge on the dipole polarizability. Thus, the basis sets generated in this study can be used in investigations of interactions involving both neutral species and positively charged ions of the group IIb elements.

Appendix

The first-order polarized basis sets for Zn, Cd, and Hg generated in the present study are listed in Tables 7, 8, and 9, respectively. The procedure used in their generation is described in Sect. 2 of this paper and follows the ideas presented in our earlier papers [5–10]. The present PolMe (Me = Zn, Cd, Hg) basis sets will be available as a part of the basis set library of the MOLCAS system of quantum chemistry programs [28]. They are primarily recommended for use in calculations of interaction energies and interaction-induced electric properties in weakly interacting systems.

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