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

VII. Elements of the group Ib: Cu, Ag, Au

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Summary. The first-order polarized basis sets PolMe are generated for elements (Me = Cu, Ag, Au) of group Ib of the periodic table by using the basis set polarization method developed in earlier papers. The performance of these basis sets is extensively tested in calculations of atomic dipole polarizabilities with particular attention given to the evaluation of the electron correlation and relativistic contributions. The extension by the g-type polarization functions (PolMe-g sets) is devised for use in accurate calculations of atomic and molecular electric properties. The (negative) electron correlation contribution to dipole polarizabilities of all elements of group Ib, as calculated at the level of the spin adapted coupled cluster method with single and double excitations and non-iterative corrections for the contribution of the T_3 clusters (SA CCSD(T)), remains at the same level relative to the ROHF data. The pure relativistic correction to the ROHF results, evaluated within the quasirelativistic approximation involving the mass–velocity and Darwin corrections, is negative and rapidly increases with increase of the nuclear charge. Its large negative value is, for heavier systems, partly compensated by a positive contribution from the mixed relativistic–correlation terms. Our relativistically corrected SA CCSD(T) calculations predict the following values of the dipole polarizability in the coinage metal series: 46, 51, and 29 a.u., for Cu, Ag, and Au. The present results for Cu and Ag agree well with recent pseudopotential calculations by Schwerdtfeger and Bowmaker. However, for Au our result is by about 6 a.u. lower than that obtained by using 19-electron relativistic potentials. Several possible reasons for this discrepancy are discussed. The PolMe and PolMe-g basis sets are also used to calculate electric dipole polarizabilities of the singly positive ions of group Ib elements. The results obtained in the quasirelativistic CCSD(T) approximation are 6.6, 9.2, and 11.8 a.u. for Cu^+, Ag^+, and Au^+, respectively. These values follow the pattern expected for the series of ions whose polarizability is dominated by the next-to-valence d shell.

1 Introduction

The calculation of atomic and molecular electric properties belongs to the most important areas of computational quantum chemistry. These properties, i.e., electric moments and polarizabilities [1], are obviously of interest by themselves. Their calculations also provide a way of testing different computational methods. Moreover, the study of atomic and molecular electric properties is closely related to the investigation of intermolecular interactions [1–3].

Most calculations of atomic and molecular electric properties are carried out within the truncated basis set approximation. To achieve a high accuracy of the calculated electric properties, particular attention has to be given to the basis set composition and flexibility [3–5]. The commonly used energy-optimized basis sets usually do not meet the corresponding criteria [4, 5] and need to be considerably extended. Some years ago a systematic method for the extension of the energy-optimized GTO/CGTO basis sets for the purpose of accurate calculations of atomic and molecular electric properties has been devised [5, 6] and applied to the generation of what is called the first-order polarized basis sets for most elements of the main groups of the periodic table [6–10]. These basis sets are of relatively modest size and have been shown to perform well in both SCF HF and high-level-correlated calculations of basic atomic and molecular electric properties. Very recently the analogous approach has been successfully used to generate the polarized GTO/CGTO basis sets for the elements of group IIb [11].

The generation of the first-order polarized basis sets for elements of group Ib essentially follows the procedure developed in our earlier paper [11] and does not bring too much novelty. However, the fact that group Ib atoms have the open-shell electronic structure makes the evaluation of their electric properties considerably different from the methodological point of view. The methods for high-level-correlated calculations for open-shell systems are not that well developed as those used for the closed-shell atoms and molecules. Thus, most attention will be focused on the use of different methodologies.

The investigation of the performance of the polarized basis sets designed in this study will be limited to calculations of electric dipole polarizabilities of group Ib atoms and their singly positive ions. Several other atomic and molecular applications of these basis sets will be reported in a separate paper [12]. The computational methods used in this paper for the calculation of electric properties of open-shell atoms and their singly positive (closed-shell) ions are briefly surveyed in Sect. 2. Some details of the procedure used to generate the polarized basis sets of this paper are given in Sect. 3 and followed by the analysis of the basis set contraction and extension effects upon dipole polarizabilities of the neutral atoms. This preliminary investigation of the basis set quality has been carried out at the level of the restricted open-shell Hartree–Fock (ROHF) method with the electron correlation contribution calculated by using the second-order perturbation approach (CASPT2 [13, 14]).

Once the quality of the generated polarized basis sets (PolMe, Me = Cu, Ag, Au) is established, they will be used in accurate high-level-correlated calculations of the electric dipole polarizability of Cu, Ag, and Au. The results of these studies are reported in Sect. 4. The methods employed in these calculations comprise the large active space CASSCF approach [15] followed by the second-order CASPT2 treatment [13, 14] and the coupled cluster (CC) techniques [16] for open-shell systems [17–19]. The non-relativistic calculations of atomic polarizabilities are accompanied by the evaluation of the relativistic [20]

and correlation–relativistic [21] corrections. In Sect. 5 we survey our results for dipole polarizabilities of singly positive ions of group Ib metals. The paper is summarized in Sect. 6. The details of the PolMe basis sets and their counterparts extended by the g-type polarization functions (PolMe-g) are given in the Appendix.

2 Methods and approximations

Any electric property can be defined in terms of derivatives of the total energy of the given system embedded in the appropriate perturbing field. Thus, the survey of methods used in the present study can be limited to those employed for the calculation of the total atomic energies.

In atomic calculations the lowest-order method is the ROHF approximation which is equivalent to the CASSCF approach [15] with one electron in the active orbital space consisting of a single valence ns orbital and all core orbitals considered as belonging to the inactive orbital subspace. We have also carried out some large active space CASSCF calculations with the attempt to correlate explicitly the next-to-valence $(n-1)d^{10}$ shell. However, for moderately large CASSCF CI wave functions with up to about half a million of Slater determinants, this method does not bring significant improvement over the ROHF approximation. In this respect the methods based directly on the ideas of the perturbation improvement of the reference function [16] appear to be far more promising.

Given the reference function calculated by the CASSCF (ROHF) method one can improve upon it by using the second-order perturbation treatment. Such a method has been recently developed for completely general CASSCF reference functions and is known as the CASPT2 approach [13, 14]. The way of treating the doubly occupied orbitals (frozen or inactive orbitals [13, 15]) may be different in CASSCF and CASPT2 calculations. Hence, it is convenient to introduce the following symbol which combines all necessary information:

$$[(F_{CASSCF}/I_{CASSCF}/A_{CASSCF}/D_{CASSCF})|(F_{CASPT2}/I_{CASPT2}/A_{CASPT2}/D_{CASPT2})].$$

For the method X, X = CASSCF, CASPT2, the symbols F_X, I_X, A_X, and D_X denote the frozen, inactive, active, and deleted orbital subspaces [15], respectively. A bar in the middle separates the information about the reference function from that about the way of performing the CASPT2 calculations. The number of electrons in the active space is determined by the total number of electrons in the system and the number of frozen and inactive orbitals. Moreover, in calculations with large basis sets a certain number of secondary (virtual) orbitals can be deleted without significantly affecting the computed data.

The CASSCF/CASPT2 method has been used in this study for both the ROHF and the large active space CASSCF reference functions. In the first case its purpose was to account for the electron correlation contribution of the next-to-valence shell. For the large active space CASSCF reference functions the purpose of the CASPT2 approach was to improve upon the dynamic correlation contribution which is already partly accounted for at the CASSCF level of approximation.

On the methodological side of performing large space CASCCF calculations for systems with a complicated pattern of the electron correlation, one should remark that the ROHF/CASPT2 calculation gives as a by-product a set of approximate natural orbitals. They provide very useful information concerning the choice of the active orbital subspace in subsequent large active space

CASSCF calculations [22]. The method has its roots in the procedure developed by Adamowicz et al. [23] and Jensen et al. [24] and was used to determine the composition of the active orbital space for correlating 11 electrons of the $(n - 1)d^{10}ns^1$ configuration. A similar procedure has been found to be very useful in our earlier studies of atomic electric properties [22].

The disadvantage of the CASSCF method is that it shortly reaches the limit of managable CI functions while the amount of the recovered dynamic correlation effects may be still relatively low. Then, the second-order CASPT2 method may not be capable of accounting for a sufficiently large part of the remaining electron correlation contribution. In this respect the coupled cluster methods are definitely more powerful [16]. They are of well-established reputation in calculations of the electron correlation contribution to energies and other properties of the closed-shell systems [16, 25–27].

Recently, the CC approach has been extended to deal with open-shell systems for which the reference function can be written as a single determinant. This is precisely the case of the ROHF wave function for atoms studied in this paper. The details of the ROHF CC approach with spin adapted amplitudes (SA) and including the T_1 and T_2 clusters (SA CCSD) are described in our recent papers [17, 18]. The latest developments in this area have led to the non-iterative scheme (SA CCSD(T)) which accounts for the effect of the T_3 clusters [19]. The particular version of the SA CCSD(T) method which is employed in this study uses the energy denominators defined in terms of the diagonal elements of the Fock operator of the ROHF method [19]. One should add that similar approaches, although without the spin symmetry adaptation, have been developed by Bartlett and his co-workers [28].

The SA CCSD and SA CCSD(T) methods for the single determinant ROHF reference state represent direct counterparts of the CCSD and CCSD(T) schemes used in the case of the closed-shell systems [16, 25–27]. The current numerical experience with these methods shows that their performance for open-shell systems should be quite as good as in the case of the single determinant closed-shell reference [17–19]. The reliability of CC calculations of dipole polarizabilities even in difficult cases with a significant portion of quasidegeneracy was demonstrated in a recent paper [29]. The present atoms, however, represent by no means difficult cases that can be recognized by quite low T_1 and T_2 amplitudes obtained in actual calculations. Also, convergence was excellent. Since both methods are of infinite order in terms of the T_1 and T_2 clusters they are definitely more efficient than the CASPT2 approach based on the single determinant ROHF reference. However, if certain correlation effects are already included in the multiconfiguration CASSCF wave function the CASSCF/CASPT2 and SA CC approaches may become competitive. It has been found in our recent study of dipole polarizabilities of group IIb atoms [11] that with the CASSCF reference function generated for two electrons in the $nsnp$ active space and the CASPT2 treatment including the $(n - 1)d^{10}$ shell the corresponding results are very close to those of the CCSD(T) approach with the single determinant HF reference function. Similar comparisons between different methods will also be discussed in this paper.

For the series of atoms considered in this paper the relativistic effects on their electric properties become important [30]. Their contribution to atomic dipole polarizabilities has been evaluated by using the quasirelativistic scheme [20] based on the mass–velocity and Darwin (MVD) [31] terms in the Pauli hamiltonian. This approach has been found to work exceptionally well for electric properties of the closed-shell systems [20, 32]. More recent applications to the calculation of

relativistic corrections to dipole polarizabilities of alkali metals [33] bring about a similar conclusion supporting the use of this method for atoms of the Ib group.

For atoms as heavy as Au the relativistic contribution to the dipole polarizability becomes very large [34] and will be at least comparable with the electron correlation effect. Thus, the relativistic effect on the electron correlation contribution has to be taken into account as well. These mixed relativistic–correlation contributions have been evaluated in this paper by using the numerical method developed in our earlier studies [21, 32, 33].

Essentially the same strategy has been followed in calculations of electric dipole polarizabilities for singly positive ions of the group Ib metals. The electronic ground state of all these systems is well described by the closed shell KL ... $(n - 1)$ $s^2(n - 1)p^6(n - 1)d^{10}$ configuration. Thus, the standard single reference CCSD and CCSD(T) methods [16, 25–27] have been used to obtain the electron correlation and mixed relativistic–correlation contributions to their dipole polarizabilities.

The calculation of atomic dipole polarizabilities has been carried out mostly by using the finite field perturbation techniques with the electric properties evaluated as the numerical derivatives of the field-dependent energies. A similar approach is also used to obtain the mixed relativistic–correlation corrections [21, 32, 33]. The accuracy of the numerical differentiation was checked within ROHF and CASSCF calculations by comparing the numerical derivatives of energy with those of the induced dipole moments. More details in this respect can be found in our earlier papers [21, 32, 33]. For the sake of different comparisons the ROHF/CASPT2, CASSCF/CASPT2, and ROHF/CC results for neutral atoms will be presented with one decimal accuracy. However, because of some convergence problems which occur in ROHF (CASSCF) calculations the numerical errors make the last decimal of our final results rather uncertain. For positively charged species the calculated data are accurate at least within the reported number of decimals.

The CASSCF/CASPT2 calculations have been carried out with the MOLCAS system of quantum chemistry programs [35]. The SA CCSD and SA CCSD(T) codes have been developed by the Bratislava group [17–19] and linked to the MOLCAS system. For the closed-shell ions investigated in this paper the CCSD and CCSD(T) calculations [16, 27] have been performed with the (molecular) TITAN code [36] integrated to the MOLCAS system.

3 First-order polarized basis sets for Cu, Ag, and Au. Preliminary testing in atomic calculations

The method employed for the generation of the first–order polarized basis sets for Cu, Ag, and Au follows step by step the procedure used for the elements of group IIb [11]. The initial energy–optimized GTO basis sets of Huzinaga (Cu [37]) and Gropen (Ag, Au [38]) have been first extended in the valence region by some diffuse GTOs, then contracted and augmented with f-type polarization CGTOs derived according to the ideas of the basis set polarization method [5, 6, 11]. One should also mention that the s-subsets of the initial GTO basis sets have been additionally augmented by a single GTO in the region of the outermost node of the valence s orbital. This increase of the basis set flexibility is particularly recommended in quasirelativistic calculations in the MVD approximation because of the relativistic contraction of the ns orbital and the accompanying shift of its nodes [30].

For Cu the initial (14.9.5) GTO basis set leads to the polarized GTO/CGTO set (PolCu) of the form [16.12.6.4/9.7.3.2]. In the same way, the initial (17.12.8) GTO basis set of Ag [38] is converted into the [19.15.9.4/11.9.5.2] polarized GTO/CGTO set (PolAg) and the (19.14.10.5) GTO set of Au [38] becomes the polarized GTO/CGTO set (PolAu) of the form [21.17.11.9/13.11.7.4]. The orbital exponents and contraction coefficients for the PolMe basis sets of this paper are given in the Appendix. They will also be available as a part of the basis set library of the MOLCAS system of programs [35].

The basis set quality is the most important factor in accurate calculations of atomic and molecular electric properties. For this reason we have carried out an extensive testing of the quality of the derived PolMe basis sets. The electric dipole polarizability has been taken as a representative atomic electric property. Indeed, according to our earlier studies [5–11], once the basis set is capable of accurately predicting atomic dipole polarizabilities its use in molecular calculations guarantees correct results for molecular dipole moments and polarizabilities. Also the molecular quadrupole moments, calculated with basis sets qualified by the atomic polarizability criterion, turn out to be quite accurate [39].

Most of the preliminary testing has been carried out at the level of the ROHF/CASPT2 approximation. Although the CASPT2 scheme with a single determinant reference function may not qualify as a high-level-correlated approach and may not account sufficiently for the electron correlation contribution to atomic polarizabilities, it should reflect the dependence of different contributions on the basis set structure and composition. The ROHF/CASPT2 calculations should at least indicate the major deficiencies of the given basis set and suggest a way of its improvement.

It has been found that the calculated atomic dipole polarizabilities are essentially insensitive to the increase of the basis set diffuseness. This follows partly from the method used to generate the first-order polarized basis sets [5, 6, 11]. Of the other important factors affecting the quality of PolMe basis sets one should consider the basis set contraction effects and the possible need for higher angular momentum polarization functions.

On passing from fully uncontracted GTO to PolMe basis sets we have employed strong contractions in the spirit of the generalized contraction scheme [40]. This way of contracting the primitive GTO sets resembles the ideas underlying the generation of the so-called averaged natural orbital (ANO) basis sets [41–43]. However, as shown by the data given in the Appendix, the contractions of the primitive set are limited to the core region while the basis set functions describing the valence and next-to-valence shells are left essentially uncontracted. The deep core region is obviously insignificant for non-relativistic electric dipole polarizabilities. The possible contribution of the next-to-valence s and p shells should be well accounted for within the present structure of the PolMe basis sets. On the other hand, the strong contractions in the core region may be of some importance for the accuracy of the evaluated relativistic and correlation–relativistic corrections to the dipole polarizability of the group Ib elements.

The basis set contraction effects have been checked by comparing the atomic dipole polarizabilities calculated with PolMe basis sets and with their fully uncontracted (GTO) counterparts. The corresponding ROHF/CASPT2 results for Cu, Ag, and Au can be found in Tables 1, 2, and 3, respectively. These data comprise the calculated ROHF polarizabilities, the MVD corrections evaluated in this approximation (MVD/ROHF), the pure electron correlation contributions (CASPT2), and the mixed relativistic–correlation corrections (MVD/CASPT2). In order to

Table 1. ROHF/CASPT2 study of the basis set and core-correlation contributions to the dipole polarizability of $Cu(^2S)$. All values in a.u.

Method/contribution[b]	Basis set[a]							
	PolCu		GTO		PolCu-g		GTO-g	
$n =$ [c]	11	19	11	19	11	19	11	19
ROHF		76.1		76.4		76.1		76.4
MVD/ROHF		−6.7		−6.5		−6.7		−6.5
Pure electron correlation contribution CASPT2	−39.7	−43.6	−39.5	−43.1	−40.8	−44.7	−40.5	−44.1
Mixed relativistic–correlation contribution MVD/CASPT2	2.7	2.9	2.8	3.0	2.8	3.0	3.0	3.3
Total ROHF/CASPT2 nr[d]	36.4	32.5	37.0	33.4	35.2	31.4	35.9	32.3
qr[e]	32.3	28.7	33.3	29.9	31.3	27.7	32.4	29.1
qr,est[f]							32.3	28.9

[a] PolMe, Me = Cu, denotes the first-order polarized basis set, GTO corresponds to its fully uncontracted counterparts. Similarly, PolMe-g, Me = Cu, denotes the PolMe basis set complemented with the g-type polarization functions and GTO-g is its fully uncontracted counterpart
[b] See text for the explanation of symbols
[c] The number of explicitly correlated electrons in CASPT2 calculations
[d] Non-relativistic result for the given number of correlated electrons
[e] Quasirelativistic (MVD) result for the given number of correlated electrons
[f] Estimated from the data for PolMe, GTO, and PolMe-g basis sets. See text

Table 2. ROHF/CASPT2 study of the basis set and core-correlation contributions to the dipole polarizability of Ag(^{2}S). All values in a.u.

Method/contribution[b]	Basis set[a]							
	PolAg		GTO		PolAg-g		GTO-g	
$n =$ [c]	11	19	11	19	11	19	11	19
ROHF	103.8		104.0		103.8		104.0	
MVD/ROHF	−24.8		−24.7		−24.8		−24.7	
Pure electron correlation contribution								
CAST2	−59.7	−66.2	−59.1	−65.4	−61.4	−68.1	−60.9	−67.3
Mixed relativistic–correlation contribution								
MVD/CASPT2	14.3	15.5	14.3	15.4	15.3	16.4	15.2	16.4
Total ROHF/CASPT2								
nr[d]	44.1	37.6	44.9	38.6	42.1	35.7	43.2	36.8
qr[e]	33.6	28.3	34.5	29.3	32.6	27.3	33.6	28.4
qr,est[f]							33.5	28.3

[a] PolMe, Me = Ag, denotes the first-order polarized basis set, GTO corresponds to its fully uncontracted counterparts. Similarly, PolMe-g, Me = Ag, denotes the PolMe basis set complemented with the g-type polarization functions and GTO-g is its fully uncontracted counterpart

[b,c,d,e,f] See the corresponding footnotes to Table 1

Table 3. ROHF/CASPT2 study of the basis set and core-correlation contributions to the dipole polarizability of Au(^{2}S). All values in a.u.

Method/contribution[b]	Basis set[a]							
	PolAu		GTO		PolAu-g		GTO-g	
$n =$[c]	11	19	11	19	11	19	11	19
ROHF		101.2		101.9		101.2		101.9
MVD/ROHF		−71.9		−70.9		−71.8		−72.1
Pure electron correlation contribution CASPT2	−60.2	−66.6	−59.7	−65.9	−61.7	−68.1	−60.9	−67.3
Mixed relativistic–correlation contribution MVD/CASPT2	50.2	54.3	49.7	53.8	53.0	57.2	53.4	57.8
Total ROHF/CASPT2 nr[d]	41.0	34.6	42.2	36.0	39.5	33.2	40.9	34.5
qr[e]	19.3	17.1	21.0	18.8	20.7	18.6	22.2	20.5
qr,est[f]							22.4	20.3

[a] PolMe, Me = Au, denotes the first-order polarized basis set, GTO corresponds to its fully uncontracted counterparts. Similarly, PolMe-g, Me = Au, denotes the PolMe basis set complemented with the g-type polarization functions and GTO-g is its fully uncontracted counterpart
[b,c,d,e,f] See the corresponding footnotes to Table 1

investigate the electron correlation and relativistic contributions arising from the next-to-valence s and p shells we have carried out two series of ROHF/CASPT2 calculations for each of the basis sets. According to the notation introduced in Sect. 2 these calculations correspond to the following selection of the orbital sub-spaces:

$$[(- /K \ldots (n - 1)d^{10}/ns^1/ -)|(K \ldots (n - 1)p^6/(n - 1)d^{10}/ns^1/ -)]$$

with 11 electrons correlated at the level of the CASPT2 approximation and

$$[(- /K \ldots (n - 1)d^{10}/ns^1/ -)|(K \ldots /(n - 1)s^2(n - 1)p^6(n - 1)d^{10}/ns^1/ -)]$$

for 19 correlated electrons. All orbitals have been fully optimized at the level of the ROHF reference function.

It follows from the PolMe and GTO data of Tables 1–3 that the contraction effect is rather small for the ROHF dipole polarizabilities. In the worst case (Au) a full de-contraction of the PolMe basis set increases the calculated dipole polariza-bility by $+ 0.7$ a.u. The basis set contraction effect is also of a similar magnitude for MVD/ROHF and CASPT2 corrections. Upon de-contracting the PolMe basis set they both become less negative. The de-contraction effect on the mixed relativ-istic–correlation correction (MVD/CASPT2) is small and essentially negligible for Cu and Ag while for Au it contributes about $- 0.5$ a.u. The effect of de-contracting the PolMe basis sets on the final non–relativistic ROHF/CASPT2 results with 11 correlated electrons is $+ 0.6$, $+ 0.8$, and $+ 1.2$ a.u. for Cu, Ag, and Au, respec-tively. In the quasirelativistic approximation with the same number of correlated electrons these numbers become $+ 1.0$, $+ 0.9$, and $+ 1.7$ a.u., respectively. For 19 correlated electrons the basis set de-contraction contributions are of similar magnitude.

It will be shown in the next section that the second-order approach tends to overshoot the magnitude of the pure correlation and mixed relativistic–correlation effects on the dipole polarizability. Thus, the corrections for the basis set de-contraction as given by the ROHF/CASPT2 data should be considered as their upper limits. Moreover, the calculation of atomic dipole polarizabilities is a rather severe test on the basis set flexibility and one can expect that the role of the contraction effect should be quite negligible in most of the molecular applications. Hence, the contracted PolMe sets derived in this study appear to offer a reasonable compromise between the accuracy of the computed data and the computational effort involved in high-level-correlated calculations with large basis sets.

Although the problem of the contribution due to electron correlation in deeper than $(n - 1)d^{10}$ shells is not directly related to the present investigation of the PolMe basis set quality some of the relevant data are given in Tables 1–3. The core-polarization [44] and core correlation effects are represented by the difference between the ROHF/CASPT2 results with 11 and 19 electrons correlated at the level of the CASPT2 method. According to both the PolMe and GTO data of Tables 1–3 the contribution of the $(n - 1)s^2(n - 1)p^6$ shell is by no means negli-gible and amounts to about $- 3$ a.u. for Cu, $- 5$ a.u. for Ag, and $- 2$ a.u. for Au. With the reservation for the possible inadequacy of the ROHF/CASPT2 approach these data suggest that this contribution needs to be evaluated in any accurate study of atomic and molecular electric properties. In the context of the effective core potential methods (ECP) [45] the present data suggest that 19-electron rather than 11-electron ECPs should be used for atoms of group Ib. However, it will be shown in the next section that the contribution of the $(n - 1)s^2(n - 1)p^6$ core is

reduced when including the higher-order electron correlation effects. Moreover, certain favourable cancellations between the increase of the negative pure correlation corrections and the increase of the positive mixed relativistic–correlation contributions can make the $(n-1)s^2(n-1)p^6$ core effect on the total dipole polarizability almost negligible.

A useful by-product of the ROHF/CASPT2 calculation is the approximate natural orbitals of the CASPT2 method and their occupation numbers [13, 14, 22]. As discussed in Sect. 2 they provide a method for the choice of the active orbital subspaces for large active space CASSCF/CASPT2 calculations. They also indicate the relative importance of different correlating orbitals. On analysing the CASPT2 orbitals from 11-electron ROHF/CASPT2 calculations we have found that the most important correlating shell for Ag and Au is of the f-type. This means that in these atoms the angular correlation effect on the $(n-1)d^{10}$ shell dominates over the radial correlation. The latter has been found to be the most important one in the case of the Cu atom. However, one should mention that for all three atoms there is a group of correlating shells of the p-, d-, and f-type of very similar occupation numbers (about 0.01) and in principle all of them together with the occupied $(n-1)$ d^{10} and ns^1 shells should be used to build the active space in CASSCF calculations with 11 electrons. The resulting size of the CASSCF CI wave function is, unfortunately, quite beyond any manageable size.

The importance of the f-type correlating shell suggests indirectly that their electric-field-induced polarization may affect the calculated polarizabilities. To account for this polarization the PolMe basis sets need to be extended by the appropriate set of the g-type polarization functions. Since the correlating f-type orbitals involve dominantly the f-type polarization functions, the corresponding g-type polarization functions can be produced by applying the basis set polarization scheme [5, 6] to these two f-type CGTOs derived for PolMe sets. This method applied to the PolMe sets derived so far has led to their extension by four primitive g-type GTOs contracted to two CGTOs. Their orbital exponents and contraction coefficients are given in the Appendix. The g-extended PolMe sets will be referred to by the symbol PolMe-g. Their fully uncontracted counterparts will be denoted by GTO-g.

Both PolMe-g and GTO-g basis sets have been used in ROHF/CASPT2 calculations and the corresponding polarizability calculations are shown in the last two columns of Tables 1–3. In comparison with the PolMe and GTO data including the g-type polarization functions reduces the total polarizabilities of Cu and Ag by about 1–2 a.u. The same is observed for non-relativistic dipole polarizability of Au. However, in the quasirelativistic approximation the presence of the g-type polarization functions leads to the increase of its value by about 1.5 a.u.

The g-extension of the PolMe basis sets increases their size by 28 additional spherical CGTOs and may lead to basis sets of prohibitively large size to be used in high-level-correlated molecular calculations. Most likely their effect will be to some extent quenched in higher than ROHF/CASPT2 approximations. Moreover, for Cu and Ag the g-function effect (negative) will be compensated by the basis set de-contraction effect (positive). Only in the case of Au both these effects may result in a relatively large modification of the dipole polarizability calculated with the PolAu basis set (about $+3$ a.u., see Table 3).

In the context of different polarizability data collected in Tables 1–3 one should mention the approximate additivity of the basis set de-contraction and g-extension effects. The corresponding corrections as obtained from differences between the PolMe and GTO (the basis set de-contraction correction) and the PolMe and

PolMe-g (the g-extension correction) data lead to the estimates for the results expected from GTO-g basis sets. These estimates agree very well with the directly calculated polarizabilities. This observation will be used in Sect. 4 to obtain a set of increments which, when added to the results calculated with PolMe basis sets, approximately account for their de-contraction and extension by the g-type polarization functions.

The ROHF/CASPT2 data reported in this section indicate that in most of the molecular calculations the least extensive PolMe basis sets should provide acceptable, i.e., within a few percent, accuracy of the calculated electric properties (molecular dipole and quadrupole moments and dipole polarizabilities). Only when aiming at an accuracy better than a few per cent one should use the g-extended basis sets. The 11-electron approximation for the electron correlation contribution should then be preferably replaced by the 19-electron treatment including explicitly the $(n-1)s^2(n-1)p^6$ shell.

4. High-level-correlated calculations of atomic dipole polarizabilities

It has been documented in Sect. 3 that neither the PolMe basis set de-contraction nor their extension by the g-type polarization functions lead to dramatic changes in the calculated atomic polarizability data. There are some indications that including the core-polarization/correlation effects may be of some importance in highly accurate studies of molecular electric properties. So far, however, we have not addressed directly the question of the absolute accuracy of our results presented in Sect. 3. The magnitude of different calculated corrections to ROHF dipole polarizabilities indicates that the ROH/CASPT2 level of approximation combined with the MVD treatment of the relativistic contribution may not be sufficiently accurate.

Not too much freedom is left with respect to the evaluation of the relativistic contribution to dipole polarizabilities. In this context one should recall that these contributions are calculated in the first-order approximation in the MVD perturbation operator [20, 21, 32, 33]. Going beyond that order in the perturbation treatment of relativistic contributions to atomic and molecular electric properties, while retaining the simple form of the relativistic MVD perturbation, would be incompatible with the spirit of the MVD approximation [46]. On the other hand, this simple first-order approximation has been found to work rather well for several atoms as heavy as the ones considered in this paper [32, 33]. Hence, no attempt will be made to improve upon the MVD approximation for the relativistic contribution and our attention will be mostly focused on the treatment of the electron correlation contribution.

It can be seen from the data presented in Tables 1–3 that the electron correlation correction to the non-relativistic ROHF data is of the order of about 50–60% of the ROHF values. This suggests that the second-order treatment (CASPT2) may be overshooting the magnitude of the (negative) electron correlation contribution. The mixed relativistic–correlation contribution (positive) can be affected in a similar way. In the case of closed-shell systems such unusually large second-order correlation corrections would indicate that the electron correlation perturbation series has a very poor convergence pattern [47]. A similar reasoning should also apply to the ROHF/CASPT2 data.

One of the possible ways to check the reliability of the ROHF/CASPT2 data is to improve upon the reference function by using the CASSCF method. However,

as was already pointed out in Sect. 2, such a way of improvement shortly faces insurmountable dimensionality problems while the CASSCF wave function takes into account only a little of the important correlation effects. In the present case the spherical symmetry causes that all orbitals of the given strongly occupied or correlating shell have to be simultaneously included in the active space. The CASSCF reference function must, therefore, account for correlating of at least 11 electrons of the $(n-1)d^{10}ns^1$ configuration. This requires that a suitable active orbital space will be relatively small and limited to $(n-1)d$, ns, and the most important correlating orbitals (shells).

It has already been mentioned that the analysis of the approximate natural orbitals obtained from 11-electron CASPT2 calculations with the ROHF reference function shows that for each atom studied in this paper there are three correlating shells of almost the same importance. The differences between the occupation numbers for these correlating orbitals are small. For Cu the $4d$ correlating shell slightly dominates over the $4p$ and $4f$ shells, while for Ag and Au the f-type correlating shells become marginally dominant. With the available computational resources we could simultaneously include only one of these correlating shells in the active space. Hence, the "large active space" CASSCF calculations for Cu correspond to 11 electrons in the active space comprising the $3d$, $4s$, and $4d$ shells. For Ag and Au the corresponding CASSCF wave functions were calculated for 11 electrons in $(4d5s4f)$ and $(5d6s5f)$ active spaces, respectively. The CASSCF calculations have been followed by the second-order CASPT2 treatment with the electron correlation contribution considered either within the 11- or 19-electron model. The 19-electron calculations account for the second-order electron correlation contribution due to core electrons of the $(n-1)p^2(n-1)p^6$ shells. The results obtained with PolMe basis sets are presented in Table 4.

In comparison with the ROHF/CASPT2 data of Tables 1–3 one finds that the CASSCF/CASPT2 results for Cu differ markedly from those for Ag and Au. The electron correlation effects accounted for in the CASSCF approximation reduce the non-relativistic ROHF dipole polarizability of Cu by about 8 a.u. while for Ag and Au a small increase of their non-relativistic ROHF polarizabilities is observed. Moreover, replacing the ROHF reference function in CASPT2 calculations by its CASSCF counterpart leads to the reduction of the (negative) pure electron correlation contribution. For Cu this contribution is reduced by almost 50%, indicating the importance of the d-type correlating shell. The corresponding changes for Ag and Au, whose active spaces involve the f-type correlating shells, are much smaller. According to these data it would be desirable to use much larger active space comprising simultaneously the d- and f-type correlating shells.

The reduction of the (negative) pure electron correlation contribution is accompanied by some decrease of the (positive) mixed relativistic–correlation correction to the CASSCF dipole polarizability. However, the sum of CASPT2 and MVD/CASPT2 corrections calculated with the CASSCF reference function is definitely less negative than that obtained in the ROHF/CASPT2 approximation (see Tables 1–3). This leads finally to the total CASSCF/CASPT2 dipole polarizabilities higher than those calculated with the ROHF reference.

Evidently the CASSCF/CASPT2 level of approximation with the present choice of the active orbital space does not saturate the electron correlation effect on the dipole polarizability. Extending the size of the active space would lead to a prohibitively large number of configurations in the CASSCF CI wave function. One is thus left with the possibility to limit the reference function to the lowest order of approximation (ROHF) and to include the electron correlation effects by

Table 4. Large active space CASSCF/CASPT2 calculations of the electric dipole polarizability of Cu(^{2}S), Ag(^{2}S), and Au(^{2}S) with PolMe basis sets. All values in a.u.

Method/contribution[a]		Atom					
		Cu		Ag		Au	
	$n =$ [b]	11	19	11	19	11	19
CASSCF			67.9		106.8		103.4
MVD/CASSCF			−7.6		−23.4		−72.4
Pure electron correlation contribution CASPT2		−21.3	−24.0	−51.9	−58.0	−54.2	−60.5
Mixed relativistic–correlation contribution MVD/CASPT2		−1.2	−1.1	12.3	14.1	44.6	48.8
Total CASSCF/CASPT2	nr[c]	46.6	43.9	54.9	48.8	49.3	42.9
	qr[d]	37.7	35.1	43.9	39.5	21.5	19.5

[a] The symbol MVD/CASSCF denotes the MVD correction evaluated with the CASSCF wave function. Similarly, MVD/CASPT2(n) is the mixed relativistic–correlation correction evaluted in the CASPT2 approximation with n correlated electrons
[b] The number of explicitly correlated electrons in CASPT2 calculations
[c] The sum of all non-relativistic (CASSCF and CASPT2) contributions
[d] The sum of all non-relativistic (CASSCF and CASPT2) and relativistic (MVD/CASSCF and MVD/CASPT2) contributions

using methods which are, in this respect, more efficient than the CASPT2 scheme. This is again supported by the ROHF/CASPT2 data which show that the weight of the (ROHF) reference in the first-order corrected wave function is relatively large (more than 90%). Moreover, the experience in the area of the closed-shell systems shows that computational methods based on a single configuration reference function and either high- or infinite-order perturbation treatment of the electron correlation are indeed very successful in predicting electron correlation contributions to atomic and molecular properties [16].

According to the conclusions which follow from our CASSCF/CASPT2 results we have carried out the polarizability calculations by using the SA CCSD method with the ROHF reference function [17–19]. The effect of the T_3 clusters has been accounted for in a non-iterative way (SA CCSD(T) [18, 19]). The results calculated with PolMe basis sets are summarized in Table 5. To facilitate their discussion and comparison with our ROHF/CASPT2 and CASSCF/CASPT2 data the pure correlation and mixed relativistic correlation contributions to dipole polarizabilities of Cu, Ag, and Au, computed in all these approximations, are separately compiled in Table 6. The ROHF/CASPT2 data calculated with PolMe basis sets are complemented by corrections for the basis set de-contraction and its extension by the g-type polarization functions. The CASSCF/CASPT2 electron correlation and relativistic–correlation corrections presented in Table 6 are given with respect to the ROHF and MVD/ROHF values, respectively, and thus account for the electron correlation contribution at both CASSCF and CASPT2 levels of approximation.

Table 5. ROHF/SA CC calculations of the electric dipole polarizability of $Cu(^2S)$, $Ag(^2S)$, and $Au(^2S)$ with PolMe basis sets. All values in a.u.

Method/contribution[a]		Atom					
		Cu		Ag		Au	
	$n =$ [b]	11	19	11	19	11	19
ROHF			76.1		103.8		101.2
MVD/ROHF			− 6.7		− 24.8		− 71.9
Pure electron correlation contributions CCSD		− 23.0	− 24.3	− 32.5	− 35.2	− 31.9	− 34.4
T_3-CCSD(T)		− 2.7	− 2.3	− 3.7	− 3.7	− 3.1	− 3.1
Mixed relativistic– correlation contributions MVD/							
CCSD		2.1	2.1	9.0	9.7	28.8	31.1
MVD/T_3-CCSD(T)		0.4	0.4	1.0	1.0	3.2	3.3
Total ROHF/CC	nr[c]	50.3	49.5	67.6	64.9	66.3	63.7
	qr[d]	46.1	45.4	52.8	50.8	26.3	26.3

[a] The symbol CCSD denotes contributions calculated at the level of the SA CCSD approximation as described in Sect. 2. The symbol T_3-CCSD(T) refers to non-iterative corrections for the T_3 clusters as defined in the SA CCSD(T) approximation [18, 19]. See Sect. 2 for details
[b] The number of explicitly correlated electrons in CC calculations
[c] The sum of all (ROHF, CCSD, and T_3-CCSD(T)) non-relativistic contributions
[d] The sum of all non-relativistic (ROHF, CCSD, and T_3-CCSD(T)) and relativistic (MVD/ROHF, MVD/CCSD, and MVD/T_3-CCSD(T)) contributions

As expected on the basis of the ROHF/CASPT2 and CASSCF/CASPT2 data the infinite order treatment of contributions due to single (T_1) and double (T_2) excitations within the SA CCSD method leads to a dramatic reduction of the pure electron correlation contribution to dipole polarizabilities which amounts to more than 40% of the ROHF/CASPT2 values for the pure correlation correction. The contribution of triple excitations (T_3) is negative and relatively small and this can be regarded as an indication of the saturation of the pure electron correlation contribution to dipole polarizabilities at the level of the CCSD(T) approximation. It is interesting to note that relative to the ROHF polarizabilities the total CCSD(T) (pure) correlation correction is of very similar magnitude for all atoms of the Ib group. For 11 correlated electrons this correction amounts to 33.9, 34.8, and 34.6% of the ROHF polarizabilities of Cu, Ag, and Au, respectively.

For the mixed relativistic–correlation contributions the observed pattern of changes of their positive values essentially parallels that discussed for the pure correlation contribution. However, because of the interplay between the relativistic and electron correlation effects the corresponding contributions rapidly increase with the nuclear charge. This makes the sum of the pure electron correlation and mixed relativistic–correlation contributions large and negative for Cu (dominant electron correlation effect) and very small for Au (near-equivalence between the two effects). As a result the relativistic Ag atom turns out to be the most polarizable

Table 6. The pure electron correlation and mixed relativistic–correlation contributions to the dipole polarizability of $Cu(^2S)$, $Ag(^2S)$, and $Au(^2S)$ as calculated in ROHF/CASPT2, CASSCF/CASPT2, and SA CCSD(T) approximations with PolMe basis sets. All values in a.u.

Method/contribution[a]	Atom					
	Cu		Ag		Au	
$n =$ [b]	11	19	11	19	11	19
Pure electron correlation contribution[c]						
ROHF/CASPT2[d]	− 39.7	− 43.6	− 59.7	− 66.2	60.2	− 66.6
	(− 0.8)	(− 0.5)	(− 1.2)	(− 1.1)	(− 0.7)	(− 0.7)
CASSCF/CASPT2[e]	− 29.5	− 32.2	− 48.9	− 55.0	− 51.9	− 58.3
ROHF/CC[f]	− 25.8	− 26.5	− 36.2	− 38.9	− 35.0	− 37.5
Mixed relativistic–correlation contribution[c]						
ROHF/CASPT2[d]	2.7	2.9	14.3	15.5	50.2	54.3
	(+ 0.3)	(+ 0.4)	(+ 0.9)	(+ 0.9)	(+ 3.2)	(+ 3.5)
CASSCF/CASPT2[g]	− 2.2	− 3.1	13.8	15.5	44.1	48.7
ROHF/CC[f]	2.5	2.5	10.0	10.9	32.0	34.4

[a] For the definition of symbols see text and Tables 1–5
[b] The number of explicitly correlated electrons in CASPT2 and CC calculations
[c] Total contributions calculated in the given approximation
[d] The numbers in parentheses correspond to corrections for the de-contraction and g-extension of the PolMe basis sets as obtained from the data of Tables 1–3. For correcting the CC results they will be reduced proportionally to the ratio of the corresponding ROHF/CC and ROHF/CASPT2 contributions
[e] Defined with respect to the ROHF level of approximation
[f] Include both CCSD and T_3-CCSD(T) contributions
[g] Defined with respect to the MVD/ROHF level of approximation

in the series, while for Au its relatively small polarizability arises primarily from the large negative value of the MVD/ROHF contribution to the non-relativistic ROHF result. The present SA CCSD(T) calculations with either 11 or 19 correlated electrons establish therefore the following sequence of dipole polarizabilities:

$$\alpha_{Ag} > \alpha_{Cu} > \alpha_{Au}.$$

This sequence is not affected by the contribution of the $(n - 1)s^2(n - 1)p^6$ core and follows the pattern observed in our calculations for the group IIb atoms [11].

　　All the results presented in Table 5 have been obtained with PolMe basis sets. According to the data of Tables 1–3 the contraction effect accompanying the generation of these sets leads to some reduction of the non-relativistic ROHF polarizability. There are also small changes in the MVD/ROHF corrections. The effect of the extension by the g-type polarization functions is essentially negligible. All these effects influence the ROHF/CC data at the level of the ROHF approximation and can be accounted for by a set of corrections applied to the quasirelativistic ROHF results calculated with PolMe basis sets. From Tables 1–3 one obtains + 0.5 a.u. for Cu, + 0.3 a.u. for Ag, and + 0.5 a.u. for Au. These values follow directly from the ROHF and MVD/ROHF data presented in Tables 1–3 for

PolMe and GTO-g basis sets and should be added to the present ROHF and ROHF/CC results of Table 5.

One can also try to indirectly establish a set of corrections which account for the basis set de-contraction and g-extension effects at the level of the CC approximation. For this purpose let us first consider the pure electron correlation contributions as calculated within the ROHF/CASPT2 approximation. From the 11-electron non-relativistic ROHF/CASPT2 data compiled in Table 6 one learns that the de-contraction and g-extension effects contribute -0.8, -1.2, and -0.7 a.u. for Cu, Ag, and Au, respectively. For the 19-electron model the corresponding numbers are -0.5, -1.1, and -0.7 a.u. Simultaneously, de-contracting and g-extending the PolMe basis sets affects the quasirelativistic correlation contributions to the dipole polarizability of Cu, Ag, and Au by $+0.3(+0.4)$, $+0.9(+0.9)$, and $+3.2(+3.5)$ a.u., respectively, in the 11-(19-)electron CASPT2 treatment.

It follows from the data of Table 6 that on passing from the ROHF/CASPT2 to ROHF/CC approximation the absolute values of the pure correlation and mixed relativistic–correlation corrections become much smaller. One can expect that the de-contraction and g-extension effects will be reduced proportionally to the magnitude of the corresponding ROHF/CASPT2 and ROHF/CC data. Within this assumption the corrections to be applied to the pure ROHF/CC correlation contributions will be $-0.5(-0.3)$, $-0.7(-0.6)$, and $-0.4(-0.4)$ a.u. for Cu, Ag, and Au, respectively. For the mixed relativistic–correlation contribution the corresponding numbers are $+0.3(+0.3)$, $+0.7(+0.6)$, and $+2.0(+2.2)$ a.u. The values in parentheses refer to 19-electron CC calculations. Upon adding these corrections to those evaluated at the level of the MVD/ROHF approximation (*vide supra*) one obtains a set of increments which should reasonably well account for the de-contraction and g-extension of the PolMe sets in the ROHF/CC approximation.

The increments to be added to the final ROHF/CC data of Table 5 are thus $+0.3(+0.5)$ for Cu, $+0.3(+0.3)$ for Ag, and $+2.1(+2.3)$ a.u. for Au. Owing to the mutual cancellation of the separate increments for the pure correlation and mixed relativistic–correlation contribution to dipole polarizabilities of Cu and Ag the estimated quasirelativistic data for these atoms hardly differ from the directly calculated polarizabilities. However, for Au the present correction scheme shows that both de-contracting and extending the PolMe basis set by the g-type polarization functions will markedly increase the calculated dipole polarizability.

The approximate correction scheme used in this paper avoids very demanding CC calculations with extended uncontracted basis sets. Its reliability is to some extent verified by a similar correction scheme used for the ROHF/CASPT2 data (see Tables 1–3) which was verified by the corresponding direct calculations. Our final ROHF/CC results in both non-relativistic and quasirelativistic (MVD) approximations, including the estimated polarizability values, are presented in Table 7. Within the numerical accuracy of our calculations (see Sect. 2) the last decimal of these polarizability data is uncertain within about ± 0.2 a.u. Within these limits there is principally no difference between the 11- and 19-electron calculations for Cu and Au. Indeed, for Cu the $(n-1)s^2(n-1)p^6$ core brings only a small contribution to both pure correlation and mixed relativistic-correlation corrections (see Table 6). However, for Au the pattern is a little more complicated. According to the data of Table 6 both corrections are markedly changed by the $(n-1)s^2(n-1)p^6$ core polarization. The mutual cancellation of these changes makes the Au dipole polarizability looking insensitive to the core

Table 7. A summary of the calculated polarizability data for Cu, Ag, and Au and their comparison with pseudopotential calculations of Schwerdtfeger and Bowmaker. All values in a.u.

Method		Atom		
		Cu	Ag	Au
This work				
ROHF	nr[a]	76.1	103.8	101.2
	qr[b]	69.4	79.0	29.3
	qr,est[c]	69.9	79.3	29.8
ROHF/CC[d]	nr[a]	49.5 (50.3)	64.9 (67.6)	63.7 (66.3)
	qr[b]	45.4 (46.1)	50.8 (52.8)	26.3 (26.3)
	qr,est[c]	45.9 (46.4)	51.1 (53.1)	28.6 (28.4)
Schwerdtfeger and Bowmaker [48]				
SCF HF	nr-pp[e]	73.6	105.4	103.7
	r-pp[f]	67.5	82.5	46.7
QCISD(T)	nr-pp[e]	49.7	65.0	64.1
	r-pp[f]	45.0	52.2	35.1

[a] Non-relativistic results
[b] Quasirelativistic results obtained in the MVD approximation
[c] Estimated values with approximate corrections for the basis set de-contraction and its extension by the g-type polarization functions. See text and footnote c to Table 6
[d] Results obtained in ROHF/SA CCSD calculations with the perturbative (T_3-CCSD(T)) correction for the contribution from T_3 [17–19]. The numbers in parentheses correspond to the 11-electron treatment of the electron correlation contribution
[e] Calculations with non-relativistic pseudopotentials
[f] Calculations with relativistic pseudopotentials

correlation effects. No such cancellation occurs for Ag and the $(n-1)s^2(n-1)p^6$ core polarization lowers its dipole polarizability by about 2 a.u.

Table 7 summarizes our best results calculated at different levels of approximation. This summary comprises the ROHF and MVD/ROHF results, the non-relativistic ROHF/CC data, and their quasirelativistic counterparts obtained in the MVD approximation. No experimental data for dipole polarizabilities of the coinage metal atoms seem to be available. The comparison of our data with theoretical calculations by other authors is limited to the very recent study by Schwerdtfeger and Bowmaker [48]. The accuracy of most of the earlier data, which are surveyed by Schwerdtfeger and Bowmaker [48], does not seem to be high enough for drawing any conclusions concerning our results. The (recommended) polarizability values listed in review articles by Teachout and Pack [49] and Miller and Bederson [50] are based on calculations performed by using the Kirkwood–Pople–Schofield method [51] and can be considered only as the order-of-magnitude estimates [50, 52].

Schwerdtfeger and Bowmaker [48] have carried out their calculations by using different high-level-correlated methods within the framework of the 19-electron pseudopotential approximation. The relativistic contributions have been studied by parallel calculations with non-relativistic and relativistic pseudopotentials. The results, given the same or a very similar level of approximation, are expected to be

similar to those of our non-relativistic and MVD-corrected studies. Out of a variety of different approximations analysed by Schwerdfeger and Bowmaker we shall consider only their ROHF and QCISD(T) results. The former ones should be directly comparable to our ROHF and MVD/ROHF values, while the latter should not be much different from those obtained in this paper by using the SA CCSD(T) method.

At the level of the non-relativistic HF approximation the pseudopotential results agree reasonably well with the present all electron data, although some unexpected features occur. In spite of using a more diffuse valence basis set than the one employed in the present study, Schwerdfeger and Bowmaker obtain an HF value of the dipole polarizability of Cu lower than ours. On the other hand, their HF values for Ag and Au are slightly higher than those calculated in the present study. As indicated in Sect. 3 the PolMe sets have been checked against their extension by diffuse functions and no significant changes in the calculated dipole polarizabilities have been found. However, in view of our recent calculations of the dipole polarizability of Hg [11] it appears that for relatively large cores, like those in Ag and Au, the pseudopotential methods tend to overestimate the extension of orbital tails [11, 54].

A comparison of relativistic contributions at the level of the HF approximation shows that the MVD perturbation [20] and relativistic pseudopotential [53] methods lead to similar results for Cu and Ag. For Au the HF relativistic corrections estimated from these two methods are, however, considerably different. In principle one could agree with the comment made by Schwerdtfeger and Bowmaker [48] on the basis of our earlier MVD/ROHF data [34] that this is a consequence of the deterioration of the MVD approximation. On the other hand, the MVD method has been found to be accurate within less than 2 a.u. for Hg [11, 55]. There is hardly any reason to expect that the MVD approximation works better for a heavier atom of similar electronic structure than for Au. Similar arguments can be forwarded on the basis of other atomic calculations [32, 33] and their comparison with numerical Dirac–Hartree–Fock data [55]. However, this would only provide indirect arguments in favour of the MVD approximation. The reason for the discrepancy between the MVD/ROHF and pseudopotential data, which further affects the results at the correlated levels of approximation, needs to be analysed in terms of explicit Dirac–Hartree–Fock calculations [56].

With the allowance made for differences between the relativistic pseudopotential and MVD approaches and differences between the methods used in calculations at the correlated level of approximation, our final results for Cu and Ag agree well with those obtained by Schwerdtfeger and Bowmaker. The difference in the result calculated for Au is by no means related to the basis set deficiencies. Hence, the SA CC calculations of electric dipole polarizabilities of the group Ib metals confirm the correctness of PolMe basis sets. The effect of their de-contraction and extension by the g-type polarization functions, as estimated on the basis of the ROHF/CASPT2 data, is negligible for Cu and Ag and relatively small for Au.

5 Dipole polarizabilities of the singly positive ions of the group Ib metals

In most of their compounds the group Ib metals carry a formal positive charge. Thus, in terms of molecular applications of PolMe and PolMe-g sets, they should also be suitable for reliable predictions of the polarization of positively charged species. In order to investigate the performance of the first-order polarized basis

Table 8. Dipole polarizabilities of Cu^+, Ag^+, and Au^+. The present CCSD(T) results calculated with PolMe and PolMe-g basis sets and their comparison with the 18-electron pseudopotential calculations of Schwerdtfeger and Bowmaker. All values in a.u.

Method	$n =$ [a]	Cu+ 10	Cu+ 18	Ag+ 10	Ag+ 18	Au+ 10	Au+ 18
This work, PolMe basis sets							
SCF HF	nr[b]	4.86		7.78		9.57	
	qr[c]	5.05		8.23		10.78	
CC[d]	nr[b]	6.30	6.31	8.40	8.68	10.12	10.41
	qr[c]	6.58	6.57	8.93	9.20	11.51	11.79
This work, PolMe-g basis sets							
SCF HF	nr[b]	4.86		7.78		9.57	
	qr[c]	5.05		8.23		10.79	
CC[d]	nr[b]	6.34	6.31	8.47	8.68	10.24	10.45
	qr[c]	6.62	6.57	9.00	9.21	11.64	11.82
Schwerdtfeger and Bowmaker [48]							
SCF HF	nr-pp[e]	4.59		6.88		9.04	
	r-pp[f]	4.79		7.29		10.59	
QCISD(T)	nr-pp[e]	—	5.74	—	7.56	—	9.65
	r-pp[f]	—	6.00	—	7.96	—	11.60

[a] The number of correlated electrons in CCSD(T) and QCISD(T) calculations
[b] Non-relativistic results
[c] Quasirelativistic results obtained in the MVD approximation
[d] Results obtained in the single-reference closed-shell CCSD calculations with the perturbative $(T_3$-CCSD(T)) correction for the contribution from T_3 [26, 27]
[e] Calculations with non-relativistic pseudopotentials
[f] Calculations with relativistic pseudopotentials

set, we have carried out the dipole polarizability calculations for Cu^+, Ag^+, and Au^+. This study of the singly positive ions with the closed-shell structure has been carried out at the level of the single reference CCSD(T) approximation. Both the PolMe and g-extended PolMe-g sets were used while the electron correlation effects have been studied in the 10- (only the $(n-1)d^{10}$ shell correlated) and 18-electron $((n-1)s^2(n-1)p^6(n-1)d^{10}$ electrons correlated) models. Our results are summarized in Table 8.

The polarizabilities of positive ions are obviously much smaller than those of the neutral species. They are primarily determined by the polarization of the d shell. The reduced SCF HF values are accompanied by rather small positive corrections due to the electron correlation effects in this shell. The electron correlation contribution from the $(n-1)s^2(n-1)p^6$ shell slightly decreases the polarizability of Cu and increases those of Ag and Au by about 0.2–0.3 a.u. The relativistic expansion of the outer d shell [30] is manifested by the positive value of the MVD contribution. The same applies to the mixed relativistic–correlation corrections. This causes that the ionic polarizabilities in this series increase monotonically

with the nuclear charge. There is only a small change of the calculated CC polarizabilities upon the g-extension of the PolMe sets.

Our SCF HF and CC results are compared in Table 8 with the pseudopotential data of Schwerdtfeger and Bowmaker [48]. Although the differences between the two sets of calculations are small they appear to have a rather random character. The reason for such a behaviour becomes clear after inspecting the basis sets used by Schwerdtfeger and Bowmaker. Their basis sets contain hardly any functions suitable for extensive treatment of both the polarization and correlation effects in the outer d shell. For this reason already their SCF HF data are lower than the ones obtained in our study. In the same way the use of inappropriate basis sets affects the non-relativistic electron correlation contributions. On the other hand, the SCF HF relativistic corrections calculated by Schwerdtfeger and Bowmaker are reasonably close to those obtained in this study within the MVD approximation.

In the context of some discrepancies between the present and pseudopotential data for the dipole polarizability of Au one should point out that the MVD correction for Au^+ (+ 1.2 a.u.) is slightly smaller than the one which follows from the pseudopotential approach (+ 1.5 a.u.). The opposite ordering of these corrections has been found for Au with ours being by about 15 a.u. more negative than the value resulting from calculations of Schwerdtfeger and Bowmaker (see Table 7).

In most molecules the coinage metals are formally positively charged and the polarizability data for their positive ions bring some information about the extent of the intramolecular polarization effects. A rather small dependence of the calculated ionic polarizabilities on the $(n-1)s^2(n-1)p^6$ core correlation contribution and the g-extension of the PolMe sets indicates that both of them can be neglected in calculations for polar species of the form Me^+X^- [57].

6 Summary and conclusions

The investigations presented in this paper had two main purposes. The first one was to generate the first-order polarized basis sets for the group Ib metals which would be fully compatible with polarized sets designed for other atoms. This goal has been achieved by following the rules developed in our earlier studies in this area. The performance of the PolMe basis sets has been first investigated at the level of the ROHF/CASPT2 approximation. It has been found that for accurate calculations of atomic dipole polarizabilities a further extension of the PolMe basis sets by the g-type polarization functions may be desirable. On the basis of the ROHF/CASPT2 calculations with fully de-contracted and g-extended PolMe sets we could conclude that the contraction and g-extension effects are approximately additive.

It also follows from our preliminary ROHF/CASPT2 calculations that for all atoms of group Ib of the periodic table there is a very large pure correlation contribution to their dipole polarizabilities which considerably lowers the corresponding ROHF values. This is accompanied by the negative pure relativistic MVD/ROHF contribution whose importance rapidly increases with the nuclear charge. While still being small for Cu in comparison with the pure correlation contribution, it becomes the dominant correction to the dipole polarizability of Au. The ROHF/CASPT2 calculations also reveal the importance of the mixed relativistic–correlation contribution to dipole polarizabilities of the coinage metals. This contribution is relatively negligible for Cu and for Au it becomes comparable, although of opposite sign, with the pure electron correlation contribution.

   The large values of the electron correlation contribution to dipole polarizabilities as found in ROHF/CASPT2 calculations indicate that this simple second-order method may overestimate their importance. This has been illustrated by CASSCF/CASPT2 data obtained with extended active orbital spaces and for 11 electrons correlated at the level of the CASSCF reference function. However, one finds that for the leading $(n-1)d^{10}ns^1$ configuration there are at least three $(p, d,$ and $f)$ correlating shells of similar importance. Since the corresponding CASSCF reference functions for 19 explicitly correlated electrons become prohibitively sizable, the CASSCF/CASPT2 approach to the determination of the accurate polarizability data for the coinage metals becomes futile. In this context the use of the higher- or infinite-order perturbation-type techniques with the ROHF reference function becomes of great advantage. In the present study we have employed the recently developed ROHF/SA CCSD(T) method which accounts for infinite-order treatment of the T_1 and T_2 cluster operators and corrects the results perturbatively for the effect of the T_3 clusters.

   On applying the SA CCSD(T) method one finds that both the pure electron correlation and mixed relativistic–correlation contributions to the dipole polarizability become considerably smaller than the values calculated in the ROHF/CASPT2 approximation. The contribution due to T_3 clusters is rather small and one can conclude that the SA CCSD(T) corrections are well converged in terms of the cluster expansion.

   The pure relativistic and mixed relativistic–correlation corrections to dipole polarizabilities are calculated in this study by using the quasirelativistic approach based on the MVD approximation. For the sake of internal consistency such an approach is, by definition, of the first-order in the relativistic perturbation. This may obviously raise some questions concerning the reliability of the MVD approximations for atoms as heavy as Au. However, this simple method appears to work well in all cases when the MVD data could be directly compared with the Dirac–Hartree–Fock results and there is no reason to expect its sudden failure in the present case.

   Our SA CCSD(T) calculations with estimated corrections for the basis set de-contraction and g-extension effects lead to the following results for electric dipole polarizabilities of the group Ib atoms. The Ag atom turns out to be the most polarizable in this series with the polarizability value of about 51 a.u. and is closely followed by Cu whose polarizability is about 46 a.u. The least polarizable is the gold atom (about 29 a.u.). Its low polarizability is mainly due to very large relativistic contribution, i.e., due to relativistic shrinkage of the ns valence shell. The calculated sequence of atomic polarizabilities matches that for the group IIb atoms.

   The ROHF and SA CCSD(T) results of this paper have been compared with recent 19-electron pseudopotential SCF HF and QCISD(T) calculations of Schwerdtfeger and Bowmaker. While our results for Cu and Ag agree very well with the values obtained by these authors, the Au dipole polarizability obtained in the pseudopotential calculations turns out to be by about 6 a.u. higher than the present result. Although Schwerdtfeger and Bowmaker seem to blame the MVD approximation, the reasons for this discrepancy seem to be uncertain.

   The atomic calculations have been complemented by a study of dipole polarizabilities of the positive ions of the coinage metals. The results for ions form a regular pattern with all MVD, electron correlation and mixed relativistic–correlation corrections to the SCF HF polarizabilities being positive. This follows the pattern observed for dipole polarizabilities of the doubly positive ions of group IIb and agrees with qualitative ideas concerning the so-called relativistic expansion

Table 9. First-order polarized [16.12.6.4/9.7.3.2] GTO/CGTO basis set for copper (PolCu)

GTO	CGTO	Exponent	Contraction coeffficients		
s subset					
1	1–3	310 252.93	0.0003052	− 0.0000941	0.0000353
2		46 637.712	0.0023575	− 0.0007238	0.0002733
3		10 652.747	0.0121189	− 0.0037810	0.0014147
4		3045.9213	0.0478425	− 0.0150578	0.0057286
5		1011.5187	0.1464166	− 0.0498353	0.0187338
6		374.52120	0.3228334	− 0.1237886	0.0487539
7		150.89684	0.4067805	− 0.2271207	0.0890756
8		64.633174	0.1976664	− 0.1140293	0.0565255
9		22.117173	0.0150049	0.5351433	− 0.3329111
10		9.3453475	− 0.0021961	0.5885575	− 0.4741771
11	4	2.5692979	1.0		
12	5	1.0124632	1.0		
13	6	0.39897300	1.0		
14	7	0.13828203	1.0		
15	8	0.04887468	1.0		
16	9	0.01727400	1.0		
p subset					
1	1–2	2033.6501	0.0026638	0.0009958	
2		484.71107	0.0212953	0.0079569	
3		158.02207	0.0966912	0.0376479	
4		60.562742	0.2707524	0.1090117	
5		25.387743	0.4349332	0.1938554	
6		11.172029	0.3107569	0.0819186	
7		4.5361622	0.0539096	− 0.3594412	
8	3	1.8931355	1.0		
9	4	0.72779079	1.0		
10	5	0.13828203	1.0		
11	6	0.04887468	1.0		
12	7	0.01727400	1.0		
d subset					
1	1	53.555631	0.0270941		
2		15.101581	0.1485655		
3		5.0892342	0.3642737		
4		1.7406786	0.4663714		
5	2	0.51338127	1.0		
6	3	0.15141200	1.0		
f subset					
1	1	5.0892342	0.1614740		
2		1.7406786	0.3534860		
3	2	0.51338127	0.4820910		
4		0.15141200	0.2301080		

of the outer d shell. It should also be mentioned that the corresponding results of Schwerdtfeger and Bowmaker show explictly some deficiencies of basis sets used in their calculations on positively charged species.

The first-order polarized PolMe basis sets generated in this study appear to be appropriate for calculations of molecular electric properties by using high-level-

Table 10. First-order polarized [19.15.9.4/11.9.5.2] GTO/CGTO basis set for copper (PolAg)

GTO	CGTO	Exponent	Contraction coeffficients			
s subset						
1	1–4	2 466 447.8	0.0000773	− 0.0000248	0.0000108	− 0.0000045
2		365 128.37	0.0006164	− 0.0001992	0.0000861	− 0.0000359
3		80 073.473	0.0034645	− 0.0011139	0.0004849	− 0.0002014
4		21 268.394	0.0159111	− 0.0052113	0.0022532	− 0.0009406
5		6434.1100	0.0605951	− 0.0201592	0.0088345	− 0.0036705
6		2166.3029	0.1812448	− 0.0660625	0.0288997	− 0.0121167
7		800.83475	0.3722569	− 0.1598627	0.0731574	− 0.0305269
8		321.88857	0.3871661	− 0.2562944	0.1205071	− 0.0518408
9		139.16735	0.1222898	− 0.0158776	0.0154099	− 0.0049937
10		54.807387	0.0048193	0.6307829	− 0.5084717	0.2319137
11		24.693249	− 0.0005585	0.4699661	− 0.4520614	0.2460600
12		8.7455636	0.0002655	0.0496180	0.7698641	− 0.6237119
13	5	4.3406869	1.0			
14	6	1.4361951	1.0			
15	7	0.6203987	1.0			
16	8	0.2679960	1.0			
17	9	0.1001000	1.0			
18	10	0.0364142	1.0			
19	11	0.0132470	1.0			
p subset						
1	1–3	15 926.060	0.0004412	− 0.0002038	0.0000786	
2		3877.1796	0.0035632	− 0.0015608	0.0006279	
3		1348.7612	0.0165421	− 0.0078519	0.0030135	
4		546.91358	0.0610534	− 0.0268763	0.0111039	
5		282.57251	0.0704096	− 0.0406741	0.0144626	
6		176.15632	0.2144127	− 0.0968123	0.0415179	
7		78.878744	0.4403446	− 0.2538017	0.0998586	
8		34.122269	0.3305021	− 0.0664769	0.0246276	
9		12.737152	0.0483618	0.5754612	− 0.3541106	
10	4	5.4645251	1.0			
11	5	1.7446082	1.0			
12	6	0.6323319	1.0			
13	7	0.1001000	1.0			
14	8	0.0364142	1.0			
15	9	0.0132470	1.0			
d subset						
1	1–2	513.26732	0.0044901	0.0014529		
2		151.89997	0.0379343	0.0122621		
3		54.850920	0.1721028	0.0570882		
4		21.319618	0.4209702	0.1378088		
5		8.4550623	0.4671162	0.1254130		
6		3.2668348	0.1376360	− 0.2288042		
7	3	1.1758928	1.0			
8	4	0.3616256	1.0			
9	5	0.1112120	1.0			
f subset						
1	1	3.2668348	0.1265903			
2		1.1758928	0.5223211			
3	2	0.3616256	0.6617001			
4		0.1112120	0.1934398			

Table 11. First-order polarized [21.17.11.9/13.11.7.4] GTO/CGTO basis set for gold (PolAu)

GTO	CGTO	Exponent	Contraction coefficients				
s subset							
1	1–5	9 424 086.3	0.0000537	− 0.0000178	− 0.0000085	− 0.0000042	0.0000018
2		1 375 442.2	0.0004322	− 0.0001447	− 0.0000685	− 0.0000340	0.0000143
3		306 690.80	0.0023297	− 0.0007721	− 0.0003671	− 0.0001821	0.0000766
4		84 491.492	0.0102003	− 0.0034565	− 0.0016357	− 0.0008134	0.0003417
5		26 543.620	0.0376640	− 0.0127533	− 0.0060953	− 0.0030244	0.0012733
6		9304.6797	0.1134110	− 0.0414511	− 0.0197943	− 0.0098757	0.0041498
7		3564.1327	0.2657618	− 0.1060533	− 0.0522321	− 0.0260599	0.0109966
8		1445.9715	0.4121903	− 0.2279979	− 0.1156615	− 0.0587150	0.0247376
9		603.64506	0.2793042	− 0.1946214	− 0.1121897	− 0.0576172	0.0246215
10		204.91458	0.0308444	0.4530458	0.3770000	0.2104062	− 0.0917269
11		94.866768	− 0.0071454	0.6397221	0.7099466	0.4569177	− 0.2024194
12		35.234607	0.0038141	0.1240073	− 0.4991837	− 0.5463992	0.2659279
13		19.540386	− 0.0026593	− 0.0361427	− 0.7958021	− 0.9454262	0.5149869
14	6	7.2801752	1.0				
15	7	3.8905484	1.0				
16	8	1.2522517	1.0				
17	9	0.5531111	1.0				
18	10	0.3143090	1.0				
19	11	0.0755071	1.0				
20	12	0.0285347	1.0				
21	13	0.0107835	1.0				
p subset							
1	1–4	72 158.456	0.0002096	0.0001058	0.0000518	0.0000205	
2		16 873.054	0.0019156	0.0009640	0.0004773	0.0001856	
3		5336.5550	0.0113928	0.0058233	0.0028626	0.0011308	
4		1970.9859	0.0503094	0.0261829	0.0130615	0.0050900	
5		806.33572	0.1621994	0.0891964	0.0445905	0.0176942	
6		355.52526	0.3475775	0.2051116	0.1059343	0.0414006	
7		165.79167	0.4030827	0.2469651	0.1250347	0.0509081	
8		80.216366	0.1804524	− 0.1089125	− 0.0921319	− 0.0441752	

Table 11. (Continued)

GTO	CGTO	Exponent	Contraction coefficients			
9		38.790536	0.0168200	-0.6068369	-0.5147861	-0.2167580
10		19.337199	0.0002351	-0.3810263	-0.1546511	-0.0671985
11	5	8.6522832	1.0			
12	6	4.0697338	1.0			
13	7	1.3807124	1.0			
14	8	0.5097264	1.0			
15	9	0.0755071	1.0			
16	10	0.0285347	1.0			
17	11	0.0107835	1.0			
d subset						
1	1–3	4726.8080	0.0005232	0.0002784	-0.0000810	
2		1329.0893	0.0062279	0.0031336	-0.0009613	
3		464.65094	0.0441568	0.0234954	-0.0069768	
4		180.03014	0.1963176	0.1023247	-0.0313694	
5		74.171925	0.4517318	0.2490388	-0.0740675	
6		31.616362	0.4290563	0.1006551	-0.0261785	
7		12.357104	0.0887405	-0.5397306	0.2226998	
8	4	4.9448522	1.0			
9	5	1.3681377	1.0			
10	6	0.3899109	1.0			
11	7	0.1111246	1.0			
f subset						
1	1	164.57891	0.0196780			
2		54.510867	0.1244727			
3		20.887159	0.3587654			
4	2	8.0698463	0.5055694			
5		2.8511552	0.3045673			
6	3	4.9448522	-0.0494710			
7		1.3681377	0.4997800			
8	4	0.3899109	0.8697170			
9		0.1111246	0.2601720			

Table 12. Complementary g-type first-order polarization functions for Cu, Ag, and Au

GTO	CGTO	Cu		Ag		Au	
		Exponent	Contraction coefficients	Exponent	Contraction coefficients	Exponent	Contraction coefficients
g subset							
1	1	5.0892342	0.1614740	3.2668348	0.1265903	4.9448522	− 0.0494710
2		1.7406786	0.3534860	1.1758928	0.5223211	1.3681377	0.4997800
3	2	0.51338127	0.4820910	0.3616256	0.6617001	0.3899109	0.8697170
4		0.15141200	0.2301080	0.1112120	0.1934398	0.1111246	0.2601720

correlated methods combined with approximate (MVD) treatment of the relativistic contribution. The present data suggest that in most cases the correlated-level calculations can be carried out with only 11 electrons of the coinage metal atom being explicitly taken into consideration. However, when using the low-order methods one can expect the $(n-1)s^2(n-1)p^6$ to bring artificially large contribution to the calculated properties. Also the effect of the g-extension of the PolMe basis sets is rather small and should not be of major importance in calculations of molecular electric properties. A study of electric properties of different molecules involving the group Ib atoms will be published separately [12].

7 Appendix

The first-order polarized basis sets for Cu, Ag, and Au, generated in the present study, are listed in Tables 9, 10, and 11, 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, 6, 11]. In accurate calculations of atomic and molecular properties they may need to be still extended by the addition of the g-type polarization functions which are given in Table 12. The present PolMe (Me = Cu, Ag, Au) and g-extended PolMe-g basis sets will be available as a part of the basis set library of the MOLCAS system of the quantum chemistry programs [35]. They are primarily recommended for use in calculations of electric properties for systems involving group Ib atoms [12]. Another area where the basis sets developed in this study can be useful is the calculation of interaction energies and interaction-induced electric properties in weakly interacting systems combined with the study of relativistic effects upon them [58].

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