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Electron correlation and relativistic effects in the coinage metal compounds.

I. The coinage metal hydrides

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Summary. The first-order polarized basis sets of the coinage metal atoms have been used to perform high-level-correlated calculations of the dipole moment in the series of the MeH (Me = Cu, Ag, Au) molecules. The relativistic effects were accounted for by using the quasirelativistic approach based on the mass–velocity and Darwin terms in both the SCF HF and correlated level approximations. The non-relativistic coupled cluster calculations with complete treatment of one- and two-body clusters and perturbative correction for the three-body terms (CCSD(T) predict the following sequence of the dipole moment data: 1.13 a.u. for CuH, 1.35 a.u. for AgH, and 1.21 a.u. for AuH. Upon including the relativistic correction the calculated dipole moments turn out to be 1.05 a.u. for CuH, 1.14 for AgH, and 0.64 a.u. for AuH. The influence of the electron correlation and relativistic effects on the electronic distribution in the MeH molecules is discussed. A comparison of calculations with different number of explicitly correlated electrons gives an approximate scheme for the estimation of the core polarization/correlation contribution.

Key words: Dipole moments of CuH, AgH, AuH – Electron correlation effects – Relativistic effects – Polarized basis sets

1. Introduction

In our recent study [1], we have derived the first-order polarized [2, 3] GTO/CGTO basis sets for the group Ib (coinage) metals. These basis sets (PolMe, Me = Cu, Ag, Au) are primarily designed for high-level-correlated calculations of major atomic and molecular electric properties [4]. So far, the performance of the PolMe basis sets has been studied only in calculations of electric dipole polarizabilities of the coinage metal atoms and their singly positive ions [1]. The atomic results have been found to exhibit a regular and consistent pattern of different contributions to atomic polarizabilities. The present study will supply additional information concerning the performance of the PolMe basis sets in calculations of molecular electric properties. Moreover, owing to the uniform character of the PolMe basis sets for all atoms of the coinage metal group, the present calculations are also aimed at providing a homogeneous illustration and interpretation of the role of the electron correlation and relativistic effects and their mutual interplay in the series of the coinage metal hydrides.

In recent years the dipole moments of the coinage metal hydrides, MeH, have been extensively investigated at different levels of approximation [5–15]. Some of the computed dipole moments are presumably of good accuracy [8, 10, 11, 14, 15]. In the absence of the experimental dipole moment data, they are the only reference for the present results and can be used for verifying both the PolMe basis set quality and certain approximations involved in our calculations.

In the non-relativistic approximation there are two major factors affecting the accuracy of the computed electric properties. One of them is the basis set size and flexibility. The second important factor affecting the accuracy of the computed dipole moments is the way and extent of treating the electron correlation contributions.

In the present case the basis set size and flexibility problem is to a large extent taken care of by the method [2, 3] used to generate the PolMe basis sets [1]. However, our atomic calculations [1] have indicated certain importance of a further extension of the standard PolMe basis sets by the g-type polarization functions (PolMe-g basis sets of Ref. [1]). The effect of this extension will be investigated for molecules studied in this paper.

Concerning the study of the electron correlation contribution to the dipole moment of the MeH molecules, we have selected three methods of increasing reliability. The lowest-level technique is the second-order perturbation (MBPT2) [16] treatment of the electron correlation contribution. The other two methods are the coupled cluster (CC) techniques [16–19], i.e., the CCSD and CCSD(T) approaches, whose high efficiency in treating the electron correlation effects has been proven in numerous calculations [16–20].

The study of the performance of different methods is combined with parallel investigations of the importance of the core correlation effects. The MBPT2, CCSD, and CCSD(T) calculations will be performed with correlation effects accounted for 20 (correlating the $(n-1)s^2(n-1)p^6(n-1)d^{10}$ shell of Me and the σ bonding orbital of MeH), 12 (correlating the $(n-1)d^{10}$ shell of Me and the σ bonding orbital of MeH), and two (only the bonding σ orbital of MeH being correlated) electrons. These investigations of the extent to which the electron correlation effects are taken into account will also shed some light on the expected reliability of different pesudopotentials [5, 21–23].

In the case of molecules involving heavy atoms there is one more factor which affects their electronic structure. With the increasing nuclear charge Z of the heavy atom the relativistic effect on the electronic structure becomes of considerable importance [24]. For large values of Z the relativistic contribution to atomic and molecular electric properties may even dominate over the pure electron correlation effect [1, 15, 25–28]. Then, also the relativistic effect on the electron correlation contribution, i.e., the mixed correlation–relativistic correction must be taken into account [14].

Some years ago we have developed a simple method to account for the relativistic contribution to atomic and molecular properties [12]. This method, which is based on the quasirelativistic (mass–velocity + Darwin terms, MVD) approximation [24, 30] to the relativistic hamiltonian, profits from the fact that the relativistic and external electric field perturbations operate in relatively disjoint regions of the electron density distribution [12]. This simple MVD approximation has been found to give correct estimates of the relativistic contribution to different atomic and molecular electric properties [12, 15, 26–28, 31–33]. Its extension [14] to the calculation of the mixed correlation-relativistic contribution gives the major part of the corresponding effect on atomic and molecular electric properties [14, 15, 25–27, 34]. Relying on our earlier experience, the MVD approximation will be used in this study for the evaluation of the relativistic and mixed correlation–relativistic corrections to the dipole moment of the coinage metal hydrides.

A brief survey of the computational methods employed in the present study is given in Section 2 and accompanied by some details concerning the evaluation of the relativistic, electron correlation, and mixed correlation-relativistic contributions to dipole moments. The results for the dipole moments of the coinage metal hydrides, evaluated at the experimental values of the Me–H bond distance, are presented in Sect. 3 and their dependence on different approximations involved in calculations of the electronic structure of the coinage metal compounds is discussed. A comparison of our results with the best available reference data and general discussion of the relative importance of the electron correlation and relativistic effects and of their mutual interplay are given in Sect. 4. A summary of our investigations and conclusions follow in Sect. 5.

2. Computational methods and methodology

All molecules investigated in this study are of the closed shell type and at least in the vicinity of the equilibrium bond distance the single configuration Hartree–Fock (SCF HF) approximation accounts well for their non-relativistic electronic structure. The electron correlation effects, which are then mostly of the dynamic character, can be investigated in the framework of the single configuration reference many-body perturbation theory or coupled cluster methods [16–19]. As already mentioned in Sect. 1 the present calculations are performed at the level of the MBPT2, CCSD, and CCSD(T) approximations. The highest level approximation is represented by the CCSD(T) method, i.e., the CC method with the complete treatment of the T_1 and T_2 clusters [16] and the perturbative correction for T_3 evaluated with the CCSD amplitudes [18, 19]. For systems whose electronic structure is well represented already at the level of the SCF HF approximation the CCSD(T) method is known to account properly for the major part of the dynamic correlation contribution to their energies and properties. Let us also recall that all correlated-level calculations have been carried out with either 2, 12, or 20 explicitly correlated electrons.

The heavy metal first-order polarized basis sets PolMe are taken from Ref. [1] and have the following GTO/CGTO structure: [16.12.6.4/9.7.3.2] for Cu, [19.15.9.4/11.9.5.2] for Ag, and [21.17.11.9/13.11.7.4] for Au. Their g-extended counterparts [1] have additionally 4 g-type GTOs contracted to two CGTOs. All the corresponding details can be found in Ref. [1]. For all hydride molecules, we have used the polarized [6.4/3.2] hydrogen basis set (PolH) of Refs. [2, 3] (see also Ref. [22] in Ref. [35]).

No particular attention is given to the calculation of non-relativistic and MVD-corrected total energies. Although the electron correlation treatment is carried out to relatively high level of approximation, the quasirelativistic method used for the evaluation of the SCF HF relativistic and mixed correlation–relativistic contributions to energies is not considered to be highly suitable for accurate calculations of the potential energy curves. Some exploratory calculations of the minimum energy bond distance have been performed for AgH (PolAg and PolH basis sets, 12 correlated electrons) leading to the non-relativistic CCSD(T) bond distance of 3.261 a.u. The quasirelativistic (MVD) result at the same level of approximation is 3.127 a.u. (includes both the MVD/SCF HF and mixed correlation–relativistic contributions; the latter being evaluated at the level of the CCSD(T) method). Although the MVD approximation correctly reflects the direction of the relativistic effect on the equilibrium bond distance, the calculated value of $R_{\min}$ differs by about -0.07 a.u. from the experimental result. A similar conclusion follows from MVD/SCF HF calculations of Martin [36]. With the attention focused on the study of different contributions to dipole moments of the MeH molecules all calculations have been carried out at the experimental values of the bond distance: 1.463 Å ≈ 2.7647 a.u. for CuH, 1.618 Å ≈ 3.058 a.u. for AgH, and 1.524 Å ≈ 2.880 a.u. for AuH [37].

All dipole moment calculations for the hydride molecules have been carried out by using the finite-field numerical perturbation scheme. The dipole moments have been evaluated as the finite difference approximations to the energy derivatives with energies calculated for the electric field strength along the bond equal to ± 0.001. With the convergence threshold for the SCF HF density matrices and the CC amplitudes set equal to 10^{-9}, the numerical method used in this study gives about 5 stable decimals for non-relativistic dipole moments and at least 2 stable decimals for relativistic corrections. Since some of the contributions to the total molecular dipole moment are relatively small, most of our results will be presented with three decimal accuracy.

The evaluation of the relativistic contribution to the dipole moment has been performed within the finite-field perturbation scheme applied to both the external electric field and MVD perturbations. The numerical strength of the MVD perturbation used for all molecules studied in this paper was equal to ± 0.005. The first-order relativistic corrections to SCF HF, MBPT2, CCSD, and CCSD(T) dipole moments have been obtained as the second-order derivatives of the corresponding energies $E(F, W)$ with respect to the electric field (F) and MVD (W) perturbations. At the level of the SCF HF approximation the accuracy of the numerically evaluated derivatives has been checked against the corresponding values obtained from the first-order derivatives of the electric-field-dependent SCF HF MVD correction [12, 14]; the latter being evaluated directly from the Hellmann–Feynman theorem [12].

All numerical calculations have been carried out by using the MOLCAS system of quantum chemistry programs [38] combined with CCSD and CCSD(T) codes of the TITAN package [39]. The PolMe and PolMe-g basis sets used in our calculations [1] will be available in subsequent editions of the basis set library of the MOLCAS system.

3. Calculations of the dipole moment of the coinage metal hydrides

In order to assess the importance of the g-extension of the PolMe basis sets we have carried out two series of calculations of the dipole moment of the MeH molcules. The first one uses the standard PolMe [1] and PolH [2, 3, 38] basis sets. In the second series the PolMe sets have been replaced by their g-extended counterparts. As regards the extent of the electron correlation all these calculations correspond to correlating explicitly 20 electrons which in the reference function occupy the highest energy orbitals, i.e., the σ bonding orbital of the Me–H bond and the orbitals of the next-to-valence shell of the metal atom. The results which are

Table 1. Dipole moments of the coinage metal hydrides. Calculations with PolMe amd PolMe-g basis sets for the heavy atom and the PolH basis set for hydrogen. The MBPT2, CCSD, and CCSD(T) data correspond to the explicit correlation of 20 electrons.[a] All values in a.u.

Method/contribution		CuH		AgH		AuH	
	Me basis set:	PolCu	PolCu-g	PolAg	PolAg-g	PolAu	PolAu-g
SCF HF		1.596	1.593	1.814	1.810	1.669	1.656
MVD/SCF HF		− 0.066	− 0.066	− 0.174	− 0.175	− 0.520	− 0.525
Electron correlation contributions							
MBPT2		− 0.454	− 0.463	− 0.425	− 0.436	− 0.442	− 0.449
CCSD		− 0.393	− 0.393	− 0.388	− 0.385	− 0.389	− 0.378
T_3-CCSD(T)		− 0.068	− 0.073	− 0.071	− 0.080	− 0.058	− 0.069
CCSD(T)		− 0.461	− 0.466	− 0.459	− 0.465	− 0.447	− 0.447
Correlation-relativistic contributions							
MVD/MBPT2		− 0.028	− 0.028	− 0.051	− 0.050	− 0.113	− 0.103
MVD/CCSD		− 0.018	− 0.017	− 0.033	− 0.030	− 0.059	− 0.047
MVD/T_3-CCSD(T)		0.001	0.000	− 0.005	− 0.005	− 0.001	− 0.002
MVD/CCSD(T)		− 0.017	− 0.016	− 0.037	− 0.035	− 0.060	− 0.049
Total							
SCF + CCSD(T)	nr[b]	1.134	1.127	1.355	1.345	1.222	1.209
	qr[c]	1.052	1.044	1.144	1.135	0.642	0.635

[a] The positive sign of the dipole moment is associated with the Me^+H^- polarization. All results obtained at the experimental values of the bond distance [37]. See text for details and the explanation of symbols

[b] Non-relativistic results

[c] Quasirelativistic results including MVD/SCF HF and mixed correlation-relativistic MVD/CCSD(T) corrections

presented in Table 1 will be considered as a reference for all other approximations investigated in this study. The display of our results comprises the SCF HF dipole moments, the total pure correlation corrections as calculated in the MBPT2 and CCSD approximations, the T_3 correction as obtained from the CCSD(T) scheme, and the total electron correlation contribution computed at the level of the CCSD(T) method. A similar set of data accounts for relativistic (MVD/SCF HF) and correlation–relativistic corrections to the dipole moment. The final total values correspond to molecular dipole moments computed in either non-relativistic (SCF HF + CCSD(T)) or quasirelativistic (SCF HF + MVD/SCF HF + CCSD(T) + MVD/CCSD(T)) approximations.

The results presented in Table 1 confirm the acceptable quality of the PolMe basis sets for the group Ib atoms. Their extension by two g-type polarization CGTOs is of little importance for both the SCF HF results and different corrections. The effect of these functions at the level of the MVD CCSD(T) approximation amounts to at most 0.01 a.u. In view of the uncertainties involved by the use of the quasirelativistic MVD method such a difference between the PolMe and PolMe-g results is essentially irrelevant.

The discussion of different contributions to the MeH dipole moment and of their dependence on the nuclear charge of the heavy atom will be postponed to

Table 2. Pure electron correlation contributions to the dipole moment of the coinage metal hydrides and their dependence on the number of explicitly correlated electrons (N_{corr}). All values in a.u.[a]

Molecule	N_{corr}	Method/contribution			
		MBPT2	CCSD	T_3^b	CCSD(T)
CuH	20	−0.454	−0.393	−0.068	−0.461
	12	−0.413	−0.373	−0.077	−0.450
	2	−0.082	−0.144	–	−0.144
AgH	20	−0.425	−0.388	−0.071	−0.459
	12	−0.376	−0.356	−0.062	−0.418
	2	−0.074	−0.131	–	−0.131
AuH	20	−0.442	−0.389	−0.058	−0.447
	12	−0.393	−0.356	−0.051	−0.407
	2	−0.062	−0.110	–	−0.110

[a] See Footnote a to Table 1.

[b] The T_3 contribution calculated in the CCSD(T) approximation

Sect. 4. At present we shall focus our attention on certain approximations concerning the treatment of the electron correlation effects. Let us note that the pure electron correlation contribution to the MeH dipole moments is, for either of the methods used for its evaluation, almost independent of the heavy atom. This is a consequence of the electron correlation effect on the dipole polarizability of these atoms which also parallels the changes in their electronegativity [29]. It has been found [1] that the percentage of change of the SCF HF dipole polarizability due to electron correlation effects in the valence and next-to-valence shells is nearly the same for all coinage metal atoms. Thus, the electron correlation effect should bring nearly the same change in the polarization of the negatively charged hydrogen in MeH compounds. The validity of this interpretation is confirmed by the data of Table 1.

It is also a rather striking feature of the pure electron correlation contributions (20 correlated electrons) that the presumably best CCSD(T) results are almost the same as those obtained in the lowest-order MBPT2 approximation. This coincidence, though rather fortuitous, occurs rather frequently in calculations of the electron correlation contribution to atomic and molecular electric properties whenever the SCF HF reference function provides a good and stable initial approximation. This behaviour suggests that at least certain part of the electron correlation contribution can be evaluated by a low-order theory while the higher-order treatment can be limited at a relatively small number of electrons. This procedure has been used in our earlier studies to estimate the electron correlation contribution due to low-energy core electrons [12, 14, 15, 33]. The reliability and limits of this approximate treatment of the electron correlation contribution to molecular electric properties will be investigated.

In Table 2 we have collected the non-relativistic MBPT2, CCSD, T_3-CCSD(T), and total CCSD(T) corrections to dipole moments of the coinage metal hydrides calculated with different number of explicitly correlated electrons. These results correspond to calculations with PolMe basis sets. Corrections calculated with PolMe-g sets are insignificantly different from these data. The analogous set of data

Table 3. Mixed correlation–relativistic contributions to the dipole moment of the coinage metal hydrides and their dependence on the number of explicitly correlated electrons (N_{corr}). All values in a.u.[a]

Molecule	N_{corr}	Method/contribution[b]			
		MBPT2	CCSD	T_3^c	CCSD(T)
CuH	20	– 0.028	– 0.018	0.001	– 0.017
	12	– 0.026	– 0.017	– 0.003	– 0.020
	2	– 0.002	– 0.004	–	– 0.004
AgH	20	– 0.052	– 0.033	– 0.005	– 0.037
	12	– 0.047	– 0.032	– 0.004	– 0.036
	2	– 0.003	– 0.006	–	– 0.006
AuH	20	– 0.113	– 0.059	– 0.001	– 0.060
	12	– 0.102	– 0.059	– 0.001	– 0.060
	2	0.006	0.007	–	0.007

[a] See Footnote a to Table 1

[b] Quasirelativistic (MVD) corrections. See text

[c] The T_3 contribution calculated in the CCSD(T) approximation

for mixed correlation-relativistic correction computed in the MVD approximation is presented in Table 3. By using these data one can discuss certain approximate methods for the evaluation of the electron correlation and correlation-relativistic contributions to electric properties of the coinage metal compounds.

Although the perturbative evaluation of the T_3 contribution in the CCSD(T) scheme is much less time consuming than any of the iterative CCSDT methods [16, 40, 41], the computational effort involved sharply increases with the number of explicitly correlated electrons and the size of the basis set. On the other hand, the second-order MBPT2 calculations are fast, inexpensive, and can be easily carried out for very large basis sets [42]. Thus, one can contemplate a combination of the MBPT2 and any of the high-level correlated methods in which the latter is used for only a small number of electrons while the rest of the correlation contribution is accounted for at the level of the MBPT2 approximation. Such a combination of methods is quite suitable in the case of the valence-shell-determined atomic and molecular properties, i.e., the multipole moments and multipole polarizabilities [4]; both the SCF HF and electron correlation contributions to the total value of the given electric property rapidly decrease as one moves down from the valence and/or next-to-valence shells.

Suppose that the total number of explicitly correlated electrons is N and N_1 of them are correlated by using come high-level-correlated approach M. The remaining $N_2 = N - N_1$ electrons will be correlated by some method m, which is anticipated to be less demanding than the method M. Then, an estimate $P_{\mathrm{est}}(N_1, N_2)$, of the electron correlation contribution $P(M, N)$, which could have been calculated by the method M used for all N electrons, is given by

$$\begin{aligned} P_{\mathrm{est}}(N_1, N_2) &= P(M, N_1) + [P(m, N) - P(m, N_1)] \\ &= P(M, N_1) - \Delta P(m, N - N_2), \end{aligned} \tag{1}$$

Table 4. Estimates of the dipole moment of the coinage metal hydrides based on CCSDT(T) calculations for N_1 electrons of the highest energy orbital levels and MBPT2 corrections for $N_2 = 20 - N_1$ electrons of deeper shells. All values in a.u.[a]

Method[b]	N_1	N_2	CuH	AgH	AuH
Non-relativistic results					
Estimated	2	18	1.079	1.334	1.179
Estimated	12	8	1.105	1.348	1.213
Calculated[c]	20	0	1.134	1.355	1.222
Quasirelativistic results					
Estimated	2	18	0.983	1.104	0.547
Estimated	12	8	1.017	1.133	0.622
Calculated[d]	20	0	1.052	1.144	0.642

[a] The data of this table are based on the PolMe results presented in Tables 1–3.

[b] For details of the method used to estimate the dipole moment values, see Sect. 3.

[c] Non-relativistic CCSD(T) reference results obtained with 20 correlated electrons; see Table 1.

[d] Quasirelativistic (MVD) reference CCSD(T) results obtained with 20 correlated electrons; see Table 1.

where $P(x, y)$ is the electron correlation contribution calculated by the method x while correlating y electrons and

$$\Delta P(m, N - N_2) = P(m, N) - P(m, N_1) \tag{2}$$

is the differential effect calculated by the method m.

In the present case, Eq. (1) will be used for M = CCSD(T) and m = MBPT2 with $N = 20$ and N_1 equal to either 2 or 12. For $N_1 = 2$ only the electrons of the bonding σ orbital of the Me–H bond are correlated at the level of the CCSD(T) (≡ CCSD) method while the correlation contribution due to the next-to-valence shell of Me (18 electrons) is assumed to be accounted for at the level of the MBPT2 approximation. In the case of $N_1 = 12$ the CCSD(T) method is applied to electrons of the Me–H bond and the $(n-1)d^{10}$ shell of the heavy atom. These estimates are compared in Table 4 with directly calculated CCSD(T) dipole moments ($N_1 = 20$, see Table 1). The results presented in Table 4 are obtained with PolMe basis sets for heavy atoms. The same features are exhibited by the results calculated with PolMe-g sets.

The estimates presented in Table 4 are quite encouraging. Even for the CCSD(T) (≡ CCSD) treatment covering only the two electrons of the σ bonding orbital, the estimates of the remaining electron correlation contribution, as calculated by the MBPT2 method, are reasonably good. Some deterioration of these data occurs in the quasirelativitic approximation and it looks that the MBPT2 treatment of the mixed correlation–relativistic contribution due to the next-to valence shell of Me overshoots the (negative) value of the corresponding correction. This is efficiently remedied if 12 electrons are correlated at the level of the CCSD(T) approximation.

The choice of N_1 and N_2 in the estimation procedure (1) depends on the desired accuracy. For larger molecules involving the coinage metal atoms, one will have to sacrifice the accuracy demands and then the CCCSD(T) treatment of the valence part accompanied by the MBPT2 evaluation of the core polarization/correlation effects offers a reasonable compromise. One should also mention that the present data give certain support to the strategy of the complete active space (CAS)SCF calculations [43] followed by the second-order (CASPT2) [44, 45] treatment of the remaining electron correlation effects. The present study shows that the method based on Eq. (1) should work well for properties determined primarily by the electron distribution in the valence shell. The application of the present method to the total energy of the given state at the given geometry will be obviously less successful.

4. Discussion and comparison with reference results

One of the major objectives of the investigation of the coinage metal atoms and their compounds and the most attractive aspect of these studies is the exploration of the role of relativistic effects [24]. Most of qualitative discussions of the non-relativistic electronic structure are carried out by using single-particle (orbital) models. Such models can obviously be extended to account for the dominant part of the relativistic effect [24]. However, for both the electron correlation and relativistic effects on the electronic structure the computational approach is the only way to determine their magnitude and mutual importance. The case study of the dipole moment in the series of the coinage metal hydrides offers a possibility of exploration of certain regularities. The dipole moment values and their changes upon including the electron correlation and relativistic effects reflect the changes in the electron density distribution and our results can be interpreted in terms of its modification.

The main features of the electron density distribution in MeH molecules are qualitatively predicted at the level of the non-relativistic SCF HF approximation. It can bee seen from the most elaborate non-relativistic data of Table 1 that the pure electron correlation effect does not produce any marked qualitative changes. All SCF HF dipole moments are lowered by approximately the same amount. This shows that the non-relativistic electronic structure of all MeH molecules is very similar. The amount of the charge transfer from Me to H is decreased in the correlated-level picture. However, the sequence of dipole moments:

$$\mu(\mathrm{CuH}) < \mu(\mathrm{AuH}) < \mu(\mathrm{AgH})$$

remains the same as predicted in the non-relativistic SCF HF approximation. One should recall that the dipole moment values have been calculated at the experimental values of the bond distance. Hence, the sequence of the non-relativistic dipole moment data is, to some extent, a consequence of differences in the MeH bond length. The experimental bond length in AuH is shorter than in AgH predominantly due to relativistic effects [24, 46]. Additional reason for the absence of the monotonic dependence of the MeH dipole moments on the Z value of Me can be sought in differences between non-relativistic values of the ionization potential of Ag and Au [47]. The non-relativistic ionization potentials of the two atoms calculated with PolMe basis sets in the CCSD(T) approximation turn out to be almost the same (ca. 0.25 a.u. [47]) suggesting that, at the given Me–H separation, there should be a similar amount of charge transfer from Me to H. With the AuH bond length shorter than that in AgH, one concludes then that their non-relativistic dipole moments should satisfy the relation found in our calculations.

A similar qualitative interpretation can be given for the CuH non-relativistic dipole moment which turns out to have the smallest value in the series. Among the coinage metal atoms Cu is found to have the highest value of the non-relativistic ionization potential (ca. 0.28 a.u. [47]). However, this value is not significantly higher than the above-mentioned non-relativistic results for Ag and Au. However, the Cu–H bond equilibrium bond distance, as used in our calculations, is much shorter than the experimental bond distances in AgH and AuH (see Sect. 2). These two factors appear to make the non-relativistic CuH dipole moment smaller than the non-relativistic dipole moments of AuH and AgH.

The influence of the electron correlation on the charge distribution in the hydride molecules can be also analysed from the point of view of the negatively charged hydrogen atom. The electron correlation effect leads to the shrinkage of the diffuse electron density distribution in the vicinity of this atom. This makes the hydrogen end of MeH less polarizable by the positive charge carried by the Me atom and in consequence the dipole induced at H is reduced.

This interpretation of the non-relativistic dipole moment data shows that the non-relativistic electronic structure of all coinage metal hydrides is essentially similar. There is also a great deal of similarity in the non-relativistic polarization pattern of the coinage metal atoms [1]. The important differences in the electronic structure of these atoms and their compounds are a consequence of relativistic effects whose contribution rapidly increases with the Z value of the heavy atom [24].

Our quasirelativistic calculations predict the following sequence of the MeH dipole moments:

$$\mu(\mathrm{AuH}) \ll \mu(\mathrm{CuH}) \sim \mu(\mathrm{AgH}).$$

The relativistic effect on the dipole moment of Cu in both SCF HF and CCSD(T) approximations is quite small (see Table 1). Slightly larger is the corresponding effect in AgH and makes its quasirelativistic dipole moment not too much different from that of CuH. If the allowance were made for the Cu–H bond being shorter and Ag–H, the quasirelativistic dipole moments of the two molecules, at the same separation between hydrogen and the heavy atom, would turn out to be practically the same, showing that the relativity makes silver resembling in its behaviour copper [24]. This is reflected by experimental, i.e. trully relativistic, values of the ionization potentials [48] and electron affinities of the two atoms [49].

A dramatic, both quantitative and qualitative, change due to relativistic effect is found for the AgH molecule. Most of the total relativistic (MVD) correction to its non-relativistic dipole moment is recovered at the level of the MVD/SCF HF approximation. The mixed correlation–relativistic contribution brings some further lowering of the AgH dipole moment. However, the value of this lowering is rather small. In this context one should mention that for the dipole polarizability of Au [1, 29], this contribution is of utmost importance while for the Au^+ ion it becomes almost negligible [1, 29]. Thus, in the AuH molecule, where the Au atom carries some positive effective charge, the importance of the mixed correlation-relativistic correction to the non-relativistic data should be diminished as well. The difference between the relativistic and non-relativistic dipole moments of AuH reflects also the corresponding differences in the ionization potential [47, 48, 50] and electron affinity [47, 51, 52] of Au.

The discussion of the relativistic effect on the dipole moment of the coinage metal hydrides is based on the results obtained in the MVD approximation and anticipates its validity for atoms as heavy as Au. Certain justification of this

Table 5. Dipole moments of the coinage metal hydrides. A comparison of the present quasirelativistic CCSD(T) results with other theoretical data. All values in a.u.

Molecule	This work[a]	Reference results
CuH	1.04	1.05[b], 1.24(1.2)[c]
AgH	1.14	1.141[d], 1.160[e], 1.126[f], 1.328[g], 1.204[h]
AuH	0.64	0.78(0.63)[i], 0.62[j]

[a] The quasirelativistic CCSD(T) results computed with PolMe-g basis sets at the experimental values of the bond distance in MeH; see Table 1

[b] Relativistic ACPF result of Ref. [11] at the bond distance of 2.90 a.u. This value vill be reduced by about 0.04 a.u. for the bond distance used in the present study

[c] Relativistic MR SDCI result of Ref. [11] at the bond distance of 2.90 a.u. The difference between this MR SCDI value and the ACPF result gives an estimate of the unlinked contribution (− 0.19 a.u.) present in the MR SDCI dipole moment. The value given in parentheses is the result at the experimental bond distance read from Fig. 2 of Ref. [11]

[d] CPF result calculated with 12-electron relativistic effective core potentials [8]

[e] MCPF result calculated with 12-electron RECPs for Ag [8]

[f] Estimated quasirelativistic result based on the fourth-order MBPT calculations with MVD corrections [14]

[g] MR SDCI result of Ref. [8] calculated with 12-electron RECPs. According to the CPF data of the same paper the unlinked terms contribute about − 0.17 a.u.

[h] Relativistic CASSCF/SO CI result calculated at the distance of 3.092 a.u.

[i] Relativistic MR SDCI calculations at the distance of 2.9 a.u. [10]. The value in parentheses is the MR SDCI result corrected approximately for unlinked contributions; see text and Ref. [15]

[j] Estimated quasirelativistic result based on the fourth-order MBPT approach with MVD corrections [15]

assumption is given by our earlier calculations. For example, the SCF HF polarizability of Hg, corrected for relativistic effects via the MVD approximation (79.3 a.u. [53]), agrees very well with the numerical Dirac–Hartree–Fock (DHF) results (80 a.u. [54]). Another support to the validity of the MVD approximation for atoms as heavy as Au follows from the comparison of the MVD/SCF HF and DHF data for the PbO molecule [55]. There seems to be no reason to expect that the MVD approximation fails just for Au [1, 29]. Let us also add that the validity of the quasirelativistic MVD approximation for the evaluation of the relativistic correction to atomic and molecular electric properties of systems with lighter atoms is already well documented [1, 26–28, 31–34, 53]. In spite of several successful applications of the MVD correction in different studies of atomic and molecular electric properties, one must be aware that the method represents a rather crude approximation to the true relativistic theory and must finally fail for large values of Z.

No experimental dipole moment data for the coinage metal hydrides are available. Thus, the theoretical prediction of their correct values is quite challenging. Some insight into the absolute accuracy of our results can be gained by comparing them with the results of other authors. Table 5 compares the results of our most advanced calculations (PolMe-g basis sets, CCSD(T) calculations with MVD corrections at both the SCF HF and correlated levels of approximation) with the reference data of sufficiently high quality. Unfortunately, most of the reference results compiled in this table are not directly comparable with the values obtained in this study because of differences in the assumed or computed bond distances. Nevertheless, they are helpful in drawing some conclusions concerning the accuracy of our results.

Highly accurate calculations of the dipole moment of CuH have been carried out by Marian [11], who employed the averaged coupled pair functional (ACPF) [56] and multireference singles and doubles (MR SD) CI methods in the framework of the so-called no-pair spinless relativistic hamiltonian [57]. The published data refer to the bond distance of 2.9 a.u. which is considerably longer (by ca. 0.14 a.u.) than the value used in our calculations. From Fig. 2 in Ref. [11] one finds that the MR SDCI result at the experimental value of the bond distance should be about 1.2 a.u. and this gives the estimated value of 1.01 a.u. for the relativistic ACPF method. According to Marian [11] the ACPF value of the dipole moment of the ground electronic state of CuH is more reliable than the MR SDCI result. The agreement between our quasirelativistic calculations for CuH and the relativistic ACPF result of Marian [11] is good in spite of differences in both basis sets and methods. From the MR SDCI and ACPF data one can also estimate that the unlinked terms present in the MR SDCI values contribute about -0.19 a.u.

There are quite a few rather accurate results available for the dipole moment of AgH. Langhoff et al. [8] have performed CPF, (modified) (M)CPF, and MR SDCI calculations at the experimental bond distance using 12-electron relativistic effective core potentials (RECPs) to account for relativistic effects. Their CPF and MCPF results are in complete agreement with present predictions. The MR SDCI result is much higher than the other values because of the contribution due to unlinked terms. From the difference between the MR SDCI and CPF(MCPF) data of Langhoff et al. [8], one obtains an estimate of this contribution as $-0.19(-0.17)$ a.u. The present result agrees also very well with the earlier quasirelativistic estimate [14] based on the fourth-order MBPT treatment of the electron correlation contribution to the dipole moment. Balasubramanian [13] obtained the AgH dipole moment of 1.204 a.u. at the bond distance of 3.092 a.u. by using a relativistic MR SDCI method combined with RECPs. His result suffers from the unlinked contribution in a similar way as the other limited CI values.

The no-pair spin-free relativistic hamiltonian has been used by Jensen and Hess [57] in MR SDCI calculations of the dipole moment of AuH. Their result at the bond distance of 2.9 a.u. is higher than the present value. However, upon adding the unlinked contribution of -0.15 a.u. as estimated in Ref. [15] the two results are brought into excellent agreement. Also the earlier quasirelativistic MBPT estimate [15] agrees well with present calculations.

There are several other theoretical data available for dipole moments of the coinage metal hydrides. However, most of them are either obtained at much lower levels of theory [5, 7] or follow from advanced calculations with very poor basis sets [9]. A fairly comprehensive survey of different calculations for AgH and AuH can be found in Refs. [14, 15]. One should also mention the pseudopotential calculations by Schwerdtfeger et al. [23]. However, their non-relativistic SCF result (2.030 a.u.) is already much larger than the well established value obtained in all-electron calculations [15]. Häberlen and Rösch [58] have recently used the Douglas–Kroll transformation [59] in the framework of the density functional theory. At the level of the least approximate method (vn3 [58]) their value for the dipole moment of AuH is 0.455 a.u. Though the method used by Häberlen and Rösch may give better estimates of relativistic corrections than the MVD approximation, the treatment of the electron correlation in the density functional methods brings about several uncertainties.

To summarize the discussion of the data presented in Table 5, let us point out that most of other calculations can be brought into agreement with our results provided certain estimated corrections are applied. This agreement occurs in spite of differences in treating both the electron correlation and relativistic effects.

5. Summary and conclusions

The PolMe and PolMe-g basis sets derived in our earlier study have been used in calculations of dipole moments of the coinage metal hydrides. The electron correlation effects in the valence and next-to-valence shells have been accounted for at the level of the CCSD(T) approximation while the relativistic corrections have been evaluated in the framework of the quasirelativistic MVD approach. A comparison of the present data with other high-level-correlated relativistic and quasirelativistic calculations indicates the usefulness of the MVD approximation even for systems as heavy as AgH.

A great deal of attention was given to the extent to which the core correlation effects should be explicitly calculated. The two-electron valence treatment has been found to be insufficient for correct predictions of the electron density distribution in the coinage metal hydrides. By correlating the σ Me–H bonds and the $(n-1)d^{10}$ electrons of the metal atom one is able to account for the dominant part of the core polarization/correlation contribution to the dipole moment. However, accurate calculations need to be performed at the level of explicitly correlating the valence and full next-to-valence shells. This favours the use of 19-electron pseudopotentials [29] for the coinage metal atoms.

It has been shown, however, that reasonable results for the MeH dipole moments can be obtained by estimating the deep core contributions at the level of the MBPT2 approximation while the high-level-correlated treatment is limited to either 12 or 2 electrons. This method, though obviously approximate, is a candidate for calculations on larger molecules containing heavy metals.

Different regularities in the calculated electron correlation and relativistic contributions to the dipole moments of the MeH molecules have been discussed. Owing to the uniform character of the first-order polarized basis sets this discussion brings a consistent picture of the relative importance of these contributions in different molecules. It has been found that the pure electron correlation effects change the SCF HF dipole moments by nearly the same amount independently of the Me atom. The SCF HF relativistic contribution rapidly increases with the Z value of Me. For AuH this correction becomes larger than the electron correlation effect. The mixed correlation–relativistic contributions have been found to be small for all hydride molecules.

The present quasirelativistic CCSD(T) calculations predict the AuH dipole moment to have the smallest value in the series of the MeH molecules. This is mainly due to large relativistic contribution to its value. For the other two molecules their dipole moments are predicted to be close to each other and definitely larger that the dipole moment of AuH. This is in correspondence to the electron correlation and relativistic effects on the electron density distribution and other properties of the coinage metal atoms.

The investigations reported in this paper give a test on the performance of the PolMe basis sets in high-level-correlated calculations for molecules involving heavy atoms. They show that the g-extension of these basis sets is of only little importance and may be neglected in calculations of molecular electric properties. The quasirelativistic MVD approximation is found to be acceptably accurate. Thus, the PolMe sets are expected to give accurate and valuable results in high-level-correlated quasirelativistic calculations on other compounds of the coinage metal atoms.

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