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Finite nucleus effects, relativistic effects and picture change error in the IOTC/DKH2 contact spin densities of Cu, Ag, Au atoms

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Abstract: Sensitivity of contact spin density as well as electron density to the size of nucleus is investigated using the Gaussian model of nucleus and the point charge nucleus model. Scalar Infinite Order Two Component and scalar second order Douglas-Kroll-Hess quasirelativistic contact spin densities (spin densities at the nucleus) of Cu, Ag and Au atoms are considered. The non-relativistic contact spin densities and the valence *s*-orbital contact densities of Kramers restricted orbitals (Cu, Ag, Au atoms) are presented as well. The picture change error in the quasirelativistic calculations of spin densities is corrected by analytic means. Uncontracted triple-zeta UTZ+N*s* basis sets are employed, where N is the number of additional tight *s* Gaussians. In addition, the impact of tight *p* and *d* Gaussians is briefly discussed.

Keywords: contact spin density, nucleus model, PCE correction, picture change error

Introduction

The last two decades were in the sign of a rapid development of relativistic methods in computational chemistry [Pyykkö 1988, Schwerdtfeger (Ed.) 2002, Dyall and Faegri 2007, Reiher and Wolf 2009]. In this paper, 2nd order Douglas-Kroll-Hess (DKH2) [Foldy and Wouthuysen 1950, Douglas and Kroll 1974, Hess 1985, Nakajima and Hirao 2000, Wolf et al. 2002, Reiher and Wolf 2004a, Reiher and Wolf 2004b] and Infinite-Order Two-Component (IOTC) [Barysz et al. 1997, Barysz and Sadlej 2001, Barysz and Sadlej 2002, Iliaš and Saue 2007, Kedziera and Barysz 2007] quasirelativistic approaches, based on the diagonalization of $\hat{H}_D$, are employed.

Relativistic effects play a non negligible role in systems containing heavy atoms [Pyykkö 1988, Schwerdtfeger (Ed.) 2002, Dyall and Faegri 2007, Reiher and Wolf 2009, Iliaš et al. 2010]. Foremostly, electron density at the nucleus and properties directly related to core electrons are mostly sensitive to the relativistic effects. In the case of contact electron density (electron density at the nucleus), relativistic effects, picture change error (PCE), sensitivity to the size of the nucleus and the basis set quality at the nucleus have been already studied for a number of atoms [Mastalerz et al. 2010, Bučinský et al. 2011, Peng and Reiher 2011, Malček et al. 2013] and/or simple molecules [Mastalerz et al. 2008, Knecht et al. 2011]. The finite size nucleus model (FN) has to be included [Mastalerz et al. 2008, Mastalerz et al. 2010, Bučinský et al. 2011, Knecht et al. 2011, Malček et al. 2013] because relativistic contact electron density has a weak singularity at the point charge (PCH) nucleus [Kutzelnigg 2004, Mastalerz et al. 2010, Bučinský et al. 2011], *i.e.* the relativistic wave function is square integrable but infinite at PCH nucleus. This weak singularity is in the case of finite basis set approach (LCAO using Gaussian functions centered by atoms) coupled with the so-called basis set artifact [Mastalerz et al. 2008], *i.e.* the LCAO based electron density cannot have a weak singularity contrary to an analytic or numeric [Dyall et al. 1989] solution of the Dirac version of Schrödinger equation.

In addition, calculations at quasirelativistic DKH and/or IOTC level of theory have to take into account the "picture change" of the wave function (PCE), *i.e.* the unitary transformation of $\hat{H}_D$ affects also the wave function [Barysz and Sadlej 2001, Wolf and Reiher 2006a, Wolf and Reiher 2006b]. The formal mapping between the expectation value of a general property operator $\hat{X}$ (it can be also $\hat{H}_D$ itself) in the Dirac picture (Ψ) and the DKH/IOTC picture ($\tilde{\Psi}$) [Barysz and Sadlej 2001, Bučinský et al. 2010, Bučinský et al. 2011] reads:

$$\langle \Psi | \hat{X} | \Psi \rangle = \langle \Psi | U^{+} U \hat{X} U^{+} U | \Psi \rangle = \langle \tilde{\Psi} | U \hat{X} U^{+} | \tilde{\Psi} \rangle \qquad (1)$$

The relation ("change of picture") between the transformed DKH/IOTC spinor $\tilde{\Psi}$ and the Dirac 4-component spinor Ψ is following:

$$\tilde{\Psi} = U\Psi \qquad (2)$$

To avoid PCE in the DKH/IOTC calculations of properties the transformation of the property operator can be performed as shown in the Equation 1. This PCE correction is actually performed by means of correcting the matrix representation

of the property operator [Wolf and Reiher 2006a, Wolf and Reiher 2006b]. An alternative option is to move the DKH/IOTC spinor back to the Dirac picture [Barysz et al. 2009].

In this regard, the proper behavior of the spin densities reflecting the size of nucleus, the basis set quality at the nucleus and the behavior of the basis set artifact has not been analyzed yet in full detail. The spin densities (as well as electron densities) have been already reported for a coordination copper compound and the copper atom at the DKH2 level of theory [Bučinský et al. 2012], including PCE correction, but using only the PCH model of nucleus and only two tight *s* Gaussian functions. Besides this, the contact electron and spin densities of coinage metal atoms have been studied quite extensively in [Malček et al. 2013] which accounted for the relativistic effects as well as a comparison of both the FN and PCH nucleus model. Nevertheless, the impact of the tight *s* Gaussian functions on the values of contact electron and spin densities has been considered less systematically. Herein the contact densities of Cu, Ag and Au are revisited, with the focus on their sensitivity to the inclusion of tight *s* Gaussian functions with the finite basis set. Besides this, the extent of relativistic effects, PCE as well as effects of the size of the nucleus are presented.

Computational details

The DKH2 calculations were performed in the standard manner as was introduced by Hess and coworkers [Hess 1985, Wolf et al. 2002, Reiher and Wolf 2004a, Reiher and Wolf 2004b]. The calculations at the IOTC level of theory were based on the approach of Barysz and Sadlej [Barysz et al. 1997, Barysz and Sadlej 2001, Barysz and Sadlej 2002, Kedziera and Barysz 2007] and the IOTC *Y* matrix was obtained by iterative means [Barysz and Sadlej 2002]. All calculations were performed at the scalar (1-component) level of theory.

The Cu, Ag, Au atoms (with spin multiplicity 2) were calculated in the electron configuration [RG](N-1) $d^{10}Ns^1$, where RG means the electron configuration of the closest previous rare gas. Actually, in the case of copper the $[Ar]3d^94s^2$ electron configuration is energetically more preferred than $[Ar]3d^{10}4s^1$ [Visscher and Dyall 1997]. Nevertheless, in this paper only the $[Ar]3d^{10}4s^1$ electron configuration of copper is considered.

The 1-component UHF DKH/IOTC and nonrelativistic calculations were obtained with the TONTO package [Jayatilaka and Grimwood 2000]. The DCH (Dirac-Coulomb Hamiltonian) calculations were performed in Dirac10 [Saue et al. 2010] and Grasp90 [Dyall et al. 1989] packages. The parameters of the Gaussian nucleus model were taken from Visscher and Dyall [Visscher and Dyall 1997]. The uncontracted triple-zeta (UTZ) basis sets of Peterson *et al.* [Balabanov and Peterson 2005, Peterson and Puzzarini 2005] were employed at the finite basis set level of theory. For more accurate description of contact densities it is found necessary to expand the original basis sets with additional tight *s*-type Gaussian functions [Mastalerz et al. 2008, Bučinský et al. 2011, Knecht et al. 2011]. Besides the effects of extra *s* Gaussians, also the effect of extra *p* and *d* tight Gaussians will be briefly considered. Exponents of these tight *s*, *p* and *d* Gaussian functions were obtained by assuming a geometric (even tempered) series for the two largest exponents of the original UTZ basis sets [Balabanov and Peterson 2005, Peterson and Puzzarini 2005].

In the case of contact spin density, the following operator has been corrected for PCE:

$$\hat{\rho}_s(\mathbf{r}) = \sum_{i=1}^{N} \delta^{(3)}(\mathbf{r}_i - \mathbf{r})\boldsymbol{\sigma}_z \tag{3}$$

where $\boldsymbol{r}$ is general position, $\boldsymbol{r}_i$ is the position of *i*-th electron, $\delta^{(3)}$ is Dirac delta function and $\boldsymbol{\sigma}_z$ is the Pauli *z* matrix. More details on the analytic PCE correction of electron density can be found in the literature [Mastalerz et al. 2008, Mastalerz et al. 2010, Seino et al. 2010, Bučinský et al. 2010, Knecht et al. 2011]. Actually, the difference between the analytic PCE correction of the spin and electron density is only in the usage of the spin density matrix $\mathbf{D}_s = \mathbf{D}_\alpha - \mathbf{D}_\beta$ instead of the electron density matrix $\mathbf{D}_e = \mathbf{D}_\alpha + \mathbf{D}_\beta$ in the evaluation of the density. The PCE correction of the matrix representation of the electron/spin density operator (essentially the σ function) remains the same [Bučinský et al. 2011, Bučinský et al. 2012].

The following notation for the spin/electron density will be used throughout the manuscript:

- NR means non-relativistic values
- $DKH2_0$ employs only U_0 — the free particle Foldy-Wouthuysen (fpFW) transformation within the PCE correction
- $DKH2_1$ employs U_0U_1 — the fpFW and the first order Douglas-Kroll transformations (D K 1) within the PCE correction
- DKH2 employs $U_0U_1U_2$ — the fpFW, DK1 and the second order Douglas-Kroll transformations (DK2) within the PCE correction
- $DKH2_{PCE}$ represents PCE contaminated DKH2 values
- IOTC uses U_0U_1 — the fpFW and the IOTC transformations within the PCE correction
- $IOTC_{PCE}$ represents PCE contaminated IOTC values

Results & Discussions

Cu atom

The impact of the size of the nucleus (both FN and PCH) and of the basis set quality (UTZ+N*s*) on the UHF contact spin densities at the IOTC and NR level of theory are presented in Figures 1a and 1b. The contact spin/electron densities at NR, DKH2 and IOTC levels of theory (including UTZ and UTZ+10*s* basis sets only and the FN and PCH nucleus models) are compared in the Table 1 and Table 2. Furthermore, the impact of the inclusion of tight *s*, *p*, *d* Gaussians on the contact spin density of copper is shown in Table 3 and the individual orbital contributions are presented in the Table 4.

Impact of the size of nucleus and basis set quality

The IOTC contact spin density is nearly a linear function of the number of tight *s* Gaussians which are added to the original UTZ basis set in the case of the PCH model of nucleus, see Figure 1a. This confirms that not only the relativistic electron density [Mastalerz et al. 2008, Knecht et al. 2011, Bučinský et al. 2011] but also the spin density [Kutzelnigg 2004] has a singular behavior at and/or near to the PCH nucleus. Note that regardless of the nucleus model, the relativistic values of contact spin/electron densities are quite similar in the case of UTZ basis set, while in the case of UTZ+10*s* basis set the impact of the nucleus model is obvious (singular behavior of density at nucleus), see Table 1 and Table 2.

In the case of the FN model, the first two added tight *s* Gaussians have a significant influence on the contact spin density of Cu, while the following *s* Gaussian functions cause only small oscillations of the contact spin density value (see Figure 1b). This has been found also for the contact electron densities of radon [Bučinský et al. 2011] and iron atoms [Mastalerz et al. 2010]. Such saturation of the value of the contact density is closely related to a situation when the exponent values of the tight *s* Gaussians reach the exponent of the Gaussian nucleus [Knecht, Saue, van Wüllen, personal communications].

The influence of the FN model as well as the inclusion of tight *s* Gaussians on the NR contact spin/electron densities is negligible (impact is less than 1 %), see Figures 1(a), 1(b) and Tables 1, 2. The influence of additional tight *p* Gaussians on the contact spin density of copper was found negligible and tight *d* Gaussians have no influence on the contact spin density at all, see Table 3. Nonetheless, the additional tight *p* Gaussians have been found important in the case of relativistic calculations of hyperfine coupling constants [Malkin et al. 2004, Malkin et al. 2006]. In addition, the impact of tight *p* Gaussians is found more pronounced in the contact electron densities [Mastalerz et al. 2010] when using contracted basis sets. Last but not least, the considered electron configuration of copper is of pure *s* character, what can also cause a smaller contribution of higher angular momentum tight Gaussians to the contact densities.

Relativistic effects and PCE

Obviously, PCE cannot be neglected in the IOTC/DKH2 calculations of contact spin/electron density of Cu, see Tables 1 and 2. The PCE contaminated ($IOTC_{PCE}$ and $DKH2_{PCE}$) contact electron/spin densities are overestimated in comparison with IOTC and DKH2 values by a factor of roughly two in the case of the FN nucleus model (for both

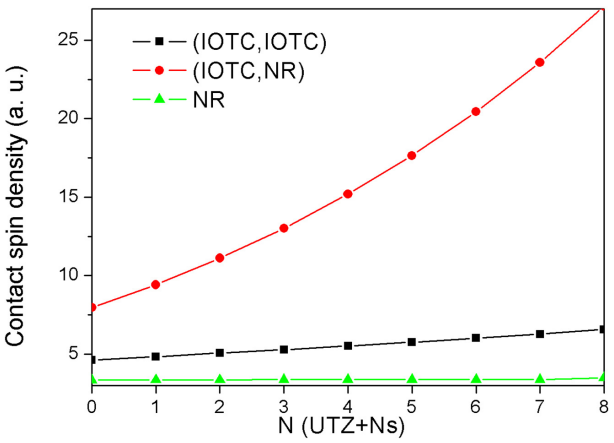

Fig. 1a. The dependence of IOTC contact spin density at the PCH nucleus of Cu on the number of additional tight *s* Gaussians within the UTZ+Ns basis set.

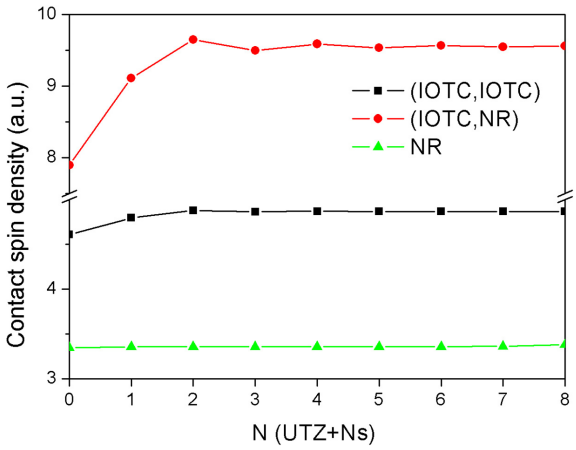

Fig. 1b. The dependence of IOTC contact spin density at the FN nucleus of Cu on the number of additional tight *s* Gaussians within the UTZ+Ns basis set.

Tab. 1. Scalar NR, IOTC and DKH2 contact spin densities of Cu, Ag, Au (in a.u.) at UHF level of theory. The impact of relativistic effects including PCE, nucleus model and the number of tight *s* Gaussian functions.

Cu							
	NR	$IOTC_{PCE}$	IOTC	$DKH2_{PCE}$	$DKH2_0$	$DKH2_1$	DKH2
UTZ[a]	3.3460[d]	7.9111[d]	4.6114[d]	7.8931	6.2112	4.3096	4.6585
UTZ+10s[a]	3.3581[c]	9.5113	4.8691	9.5113	7.2205	4.2785	4.9934
UTZ[b]	3.3482[d]	7.9568[d]	4.6193[d]	7.9381	6.2400	4.3117	4.6674
UTZ+10s[b]	3.3717[c]	36.0282	7.3366	33.4004	21.1026	–1.4652	11.0473
Ag							
	NR	$IOTC_{PCE}$	IOTC	$DKH2_{PCE}$	$DKH2_0$	$DKH2_1$	DKH2
UTZ[a]	5.4138[d]	34.2910[d]	13.7498[d]	33.8305	22.9164	10.4577	14.7594
UTZ+6s[a]	5.4135	33.8880	13.6972	33.4427	22.6903	10.4965	14.6738
Au							
	NR	$IOTC_{PCE}$	IOTC	$DKH2_{PCE}$	$DKH2_0$	$DKH2_1$	DKH2
UTZ[a]	9.8166[d]	362.6563[d]	119.8741[d]	350.3748	207.0734	79.8522	136.1980
UTZ+4s[a]	9.8182	362.7617	119.8860	350.4256	207.0787	79.8508	136.2009

[a]Finite nucleus (FN) model

[b]Point charge (PCH) nucleus model

[c]Results obtained for the UTZ+6*s* basis set

[d]Ref. [Malček et al. 2013]

Tab. 2. Scalar NR, IOTC and DKH2 contact electron densities of Cu atom (in a.u.) at UHF level of theory. The impact of relativistic effects including PCE, nucleus model and the number of tight *s* Gaussian functions

Cu							
	NR	$IOTC_{PCE}$	IOTC	$DKH2_{PCE}$	$DKH2_0$	$DKH2_1$	DKH2
UTZ[a]	16497.76[d]	35862.20[d]	20996.62[d]	35780.84	28309.57	19612.28	21214.46
UTZ+10s[a]	16558.70[c]	43132.44	22167.47	43132.44	32904.14	19464.50	22738.61
UTZ[b]	16508.27[d]	36069.64[d]	21032.37[d]	35985.06	28440.54	19621.50	21254.46
UTZ+10s[b]	16624.10[c]	162171.32	32579.81	150256.64	95278.65	–7777.43	49621.44

[a]Finite nucleus (FN) model

[b]Point charge (PCH) nucleus model

[c]Results obtained for the UTZ+6*s* basis set

[d]Ref. [Malček et al. 2013]

UTZ and UTZ+10s basis sets) and in the case of the PCH model when using the UTZ basis set. PCE in the PCH UTZ+10*s* IOTC/DKH2 calculations of contact spin densities is even more dramatic (more than a factor of three).

PCE corrected IOTC and DKH2 contact spin densities at the FN model are in a good agreement with each other (the difference is around 3 %, relative to the IOTC value). In the case of PCH nucleus model in the connection with the UTZ+10*s* basis set, this difference is considerably larger (around 50 %), see Table 1. The $DKH2_1$ contact densities are in a better agreement with the DKH2 level of theory than the $DKH2_0$ one in the case of the FN model. Similar results are found also for the PCH nucleus model if the tight *s* Gaussians are not included (a large basis set artifact). In the case of the highly augmented (UTZ+10*s*) basis set, the PCH $DKH2_1$ contact spin/electron density of Cu is negative (see Tables 1, 2). This is completely in agreement with the study [Bučinský et al. 2011], where this phenomenon was discussed in more detail. Particularly, some of the terms created in the DK1 transformation within the PCE correction of the total electron density at the PCH nucleus are large in value and negative, and need to be counter-balanced by the terms from the DK2 transformation [Wolf and Reiher 2006a, Wolf and Reiher 2006b, Bučinský et al. 2010, Bučinský et al. 2011] if more tight *s* Gaussians are included in the basis set. This shows on the failure of the

Tab. 3. The impact of tight *s*, *p* and *d* Gaussian functions on the value of contact spin density of Cu atom at the IOTC/FN level of theory for both FN and PCH nucleus model

Cu		
Basis set	FN	PCH
UTZ	4.6114[a]	4.6193[a]
UTZ+1s	4.7960	4.8365
UTZ+2s	4.8783[a]	5.0646[a]
UTZ+2s1p	4.8783	5.0646
UTZ+2s2p	4.8782	5.0646
UTZ+3s	4.8651	5.2839
UTZ+4s	4.8707[a]	5.5246[a]
UTZ+4s2p	4.8706	5.5245
UTZ+4s2p1d	4.8705	5.5244
UTZ+4s2p2d	4.8705	5.5244
UTZ+5s	4.8683	5.7594
UTZ+6s	4.8693	6.0220

[a]Ref. [Malček et al. 2013]

DK1 PCE correction for the DKH2 wave function and the need to account for the DK2 transformation. The found trends of the contact spin density, in regards of relativistic effects, PCE, nucleus size and basis set quality at the nucleus are similar to the ones found for the electron density [Mastalerz et al. 2010, Knecht et al. 2011, Bučinský et al. 2011, Bučinský et al. 2012].

An interesting point is also the contribution of individual orbitals to the contact UHF spin density. Of course, the unpaired electron in the 4s shell has the dominant contribution, see Table 4. For comparison, the contact spin density of the DCH 4s spinorbitals is also shown in Table 4. Nonetheless, remaining *s* orbitals have non-negligible contributions to the UHF contact spin density as well (spin polarization), all together about 11.3 %. The contributions from scalar *p* orbitals are negligible (see Table 4), although they have a non-zero contact electron density [Mastalerz et al. 2010, Bučinský et al. 2011], see Table 4. It is worth to point out that the PCE corrected scalar *p* orbitals

Tab. 4. The orbital contributions to the value of contact spin densities of Cu, Ag, Au atoms at the IOTC/FN level of theory, using UTZ+10s basis sets ($\rho_{\alpha,i}$ is α-electron density and $\rho_{s,i}$ is spin density).

	Cu		**Ag**		**Au**	
i	$\rho_{\alpha,i}$	$\rho_{s,i}$	$\rho_{\alpha,i}$	$\rho_{s,i}$	$\rho_{\alpha,i}$	$\rho_{s,i}$
1s	9959.7898	0.1260	63936.2298	0.2281	900425.8618	1.4734
2s	978.6343	0.2515	7343.6122	0.2872	134915.9235	1.2831
2p	1.6054	0.0002	28.2004	0.0004	814.3607	0.0021
	1.6054	0.0002	28.2004	0.0004	814.3607	0.0021
	1.6054	0.0002	28.2004	0.0004	814.3607	0.0021
3s	137.9501	0.1723	1390.8536	0.3086	30922.5224	1.3778
3p	0.2187	–0.0006	5.7680	–0.0002	214.4885	0.0003
	0.2187	–0.0006	5.7680	–0.0002	214.4885	0.0003
	0.2187	–0.0006	5.7680	–0.0002	214.4885	0.0003
4s	4.3204	4.3204	242.9496	0.7559	7714.2856	1.8349
4p			0.8957	–0.0024	52.7849	–0.0067
			0.8957	–0.0024	52.7849	–0.0067
			0.8957	–0.0024	52.7849	–0.0067
5s			12.1239	12.1239	1439.0052	7.1303
5p					8.3296	–0.0332
					8.3296	–0.0332
					8.3296	–0.0332
6s					106.8887	106.8887
LL		4.8701		13.7036		119.9882
SS		–0.0011		–0.0064		–0.1125
Total		4.8691		13.6972		119.8757
ns(DCH)[a]	4.3154		12.1209		108.3584	
ns(DCH)[b]	4.2869		12.1801		108.3649	

[a]Valence *s* orbital density from Grasp90 package [Dyall et al. 1989]

[b]Valence *s* orbital density from Dirac10 package [Saue et al. 2010]

have an underestimated *s* character in comparison with 2- or 4-component $p_{1/2}$ orbitals [Bučinský et al. 2011]. The small contribution of the *p* orbitals can be further seen in the small (SS) component vs. large (LL) component contribution to the contact spin density, which can be obtained either by summing up separately the contributions of *s* and *p* orbitals separately.

Ag and Au atoms

The contact spin densities of Ag and Au atoms are shown in Tables 5 and 6, respectively, with emphasis on the relativistic effects (IOTC vs. NR), the quality of the basis set and the model of nucleus. The orbital contributions to the contact spin densities are shown in Table 4.

Size of the nucleus and the basis set quality at the nucleus

The UTZ+N*s* basis set was in the case of silver and gold atoms expanded by max. 6*s* and/or 4*s* Gaussian functions, respectively. Like in the case of Cu, expanding the basis set with *p* or *d* functions has also a negligible effect on the contact spin/electron density. Contrary to Cu, FN IOTC/DKH2 contact spin densities of Ag and Au are not affected by the additional tight *s* Gaussians and are oscillatory for all UTZ+N*s* basis sets (see Tables 1, 5 and 6). This is caused by the fact, that the largest exponents in the original UTZ basis sets of Ag and Au ($2.5914 \times 10^{+08}$ and $5.1452 \times 10^{+10}$, respectively) are already larger than the exponents of the Gaussian nucleus ($2.0389 \times 10^{+08}$ and $1.4223 \times 10^{+08}$) [Malček et al. 2013].

Differences between the IOTC contact spin densities obtained for the FN and PCH nucleus models are mostly pronounced for the Au atom (see Table 6). The PCH IOTC contact spin density is approx. 2.3-times bigger than the FN IOTC one in the case of Ag (UTZ+6*s*). In the case of Au (UTZ+4*s*) this factor (PCH vs. FN) is nearly 18. This is completely in agreement with the fact that with the growing atomic number the inclusion of the FN model becomes more important in regard of the singular behavior of the relativistic densities at the PCH nucleus model. This obviously holds also for the spin and not only for the electron density, hand in hand with the *s* electron configuration of the studied atoms. NR spin/electron densities of Ag and Au atoms are by less than 1 % affected by the effect of the size of nucleus.

Tab. 5. Scalar NR and IOTC contact spin densities of Ag atom (in a.u.) at UHF level of theory. The impact of relativistic effects including PCE, nucleus model and the number of tight *s* Gaussian functions.

Rel. approach	IOTC		$IOTC_{PCE}$		NR	
Nucleus model	FN	PCH	FN	PCH	FN	PCH
UTZ	13.7498[a]	15.5432[a]	34.2910[a]	45.7752[a]	5.4138[a]	5.4456[a]
UTZ+1s	13.6692	17.3913	33.5686	58.8208	5.4135	5.4470
UTZ+2s	13.7037[a]	19.5250[a]	34.0210[a]	75.4426[a]	5.4137	5.4498
UTZ+3s	13.6883	21.8333	33.7380	95.8020	5.4136	5.4502
UTZ+4s	13.6952[a]	24.5031[a]	33.9104[a]	121.3030[a]	5.4134	5.4513
UTZ+5s	13.6921	27.5890	33.8070	153.7370	5.4140	5.4516
UTZ+6s	13.6936	30.7447	33.8683	191.6559	5.4135	5.4521

[a]Ref. [Malček et al. 2013]

Tab. 6. Scalar NR and IOTC contact spin densities of Au atom (in a.u.) at UHF level of theory. The impact of relativistic effects including PCE, nucleus model and the number of tight *s* Gaussian functions.

Rel. approach	IOTC		$IOTC_{PCE}$		NR	
Nucleus model	FN	PCH	FN	PCH	FN	PCH
UTZ	119.8741[a]	500.4707[a]	362.6565[a]	2728.8416[a]	9.8166[a]	9.9694[a]
UTZ+1s	119.8881	715.4043	362.8430	4410.1196	9.8181	9.9693
UTZ+2s	119.8823[a]	1032.3769[a]	362.7231[a]	7151.5267[a]	9.8176	9.9695
UTZ+3s	119.8844	1478.0086	362.7952	11500.1425	9.8175	9.9695
UTZ+4s	119.8860[a]	2134.7824[a]	362.7617[a]	18521.6598[a]	9.8182	9.9700

[a]Ref. [Malček et al. 2013]

Relativistic effects and PCE

Differences between NR and IOTC contact spin densities are, as expected, far larger in the case of Au than in the cases of Ag or Cu. The NR contact spin density of Ag accounts for about 40 %, while for Au it is only around 8 %, of the value obtained at the IOTC level of theory. The PCE contaminated $IOTC_{PCE}$ contact spin density at FN is about three times larger than the PCE corrected one for both the Ag and Au atoms, see Tables 5 and 6, respectively. In the case of PCH nucleus model, PCE is much more pronounced because of the "singular behavior" of the contact spin density (similar holds also for the electron density, not shown).

In the case of DKH2 calculations of contact spin density the trends of PCE and the order of the PCE correction agree well with those found for the copper atom, see Table 1. This means that in the case of the FN model, the DKH2 contact spin density is in good agreement with the more rigorous IOTC value. The $DKH2_1$ contact spin density is underestimated and $DKH2_0$ overestimated in comparison with the IOTC level of theory. The PCE contaminated $DKH2_{PCE}$ and $IOTC_{PCE}$ contact spin densities are close each other and $DKH2_{PCE}$ is slightly smaller than $IOTC_{PCE}$ contact spin density. Herein, only the results for the FN model have been considered.

The orbital contributions to the IOTC FN contact spin densities of Ag and Au are shown in Table 4. As it holds for the Cu atom, the dominant contribution to the contact spin density comes from the unpaired valence *s* electron. The remaining *s* orbitals contribute again by about 11.5 % and 10.8 % (Ag and Au, respectively) to the final value of the spin density. The contribution of PCE corrected *p* orbitals (small component) to the contact spin density is even in the case of Au less than 0.1 %. The 5*s* and 6*s* IOTC contact orbital densities of Ag and Au, respectively, agree well with the DCH values, see Table 4. Small differences are caused mostly by the missing two electron terms of DCH within the IOTC transformation [Seino and Hada 2008, Seino et al. 2010].

Conclusions

The key factors in the calculations of contact spin densities of the coinage metal (Cu, Ag, Au) atoms are the inclusion of relativistic effects hand in hand with the inclusion of finite model of nucleus. In addition, in the case of quasirelativistic calculations like DKH2 and/or IOTC the treatment of PCE shall not be forgotten. In accordance with the previous paper [Bučinský et al. 2011], the PCH $DKH2_1$ contact electron/spin densities are "ill behaved" (negative) if tight enough *s* Gaussians (N) are included in the UTZ+Ns basis set.

Furthermore, the expansion of the basis set by tight *s* Gaussians in the FN DKH2/IOTC calculations is of importance in the case of the Cu atom. At least two tight *s* Gaussians are required to achieve reasonable convergence of contact spin density of Cu. Because the original UTZ basis sets for Ag and Au [Balabanov and Petersen 2005, Petersen and Puzzarini 2005] contain larger *s* Gaussian exponents than the exponents in the Gaussian nucleus (FN) model [Visscher and Dyall 1997], the additional tight *s* Gaussians have not a dramatic effect on their contact spin/electron density values. In the case of PCH nucleus model the analytic/numeric contact spin density at the relativistic level of theory is singular at the nucleus, *i.e.* contact spin density is nearly a linear function of the number of extra tight *s* Gaussian functions added to the basis set. Additional *p* or *d* Gaussians have a negligible influence on the contact spin densities of the studied atoms.

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