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# Theoretical analysis of NMR shieldings of group-11 metal halides on MX ( $M = \text{Cu, Ag, Au}$ ; $X = \text{H, F, Cl, Br, I}$ ) molecular systems, and the appearance of quasi instabilities on AuF

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Accurate calculations of nuclear magnetic shieldings of group-11 metal halides,  $\sigma(M; MX)$  ( $M = \text{Cu, Ag, Au}$ ;  $X = \text{H, F, Cl, Br, I}$ ) were performed with relativistic and nonrelativistic theoretical schemes in order to learn more about the importance of the involved electronic mechanisms that underlies such shieldings. We applied state of the art schemes: polarization propagators at random phase level of approach (PP-RPA); Spin-free Hamiltonian (SF); linear response elimination of small component (LRESC) and density functional theory (DFT) with two different functionals: B3LYP and PBE0. Results from DFT calculations are not close to those from the relativistic polarization propagator calculations at RPA level of approach (RelPP-RPA), in line with previous results. The spin-orbit (SO) contribution to shielding constant is important only for  $MF$  molecules ( $M = \text{Cu, Ag, Au}$ ). Different electronic mechanisms are considered within the LRESC method, bunched in two groups: core- and ligand-dependent. For the analysed shieldings the core-dependent electronic mechanisms are the most important ones; being the ligand-dependent only important for  $MF$  molecules. An out of range value for  $\sigma(\text{Au})$  is found in AuF. It was previously reported in the literature, either originated in the large fluorine electronegativity together with large spin-orbit coupling contributions; or, due to Fermi-contact contributions. We argue here that such unexpected large value is an artifact originated in the appearance of quasi instabilities, and show how to handle this apparent problem.

## 1 Introduction

NMR spectroscopic parameters are useful tools for describing electronic structure of atoms and molecules. The nuclear magnetic shieldings,  $\sigma$ , are of considerable interest in molecular science and theoretical chemistry. When heavy atoms are involved, relativistic effects must be included in the calculation of  $\sigma$ .<sup>1–6</sup>

Some properties of noble metal halides have been studied with a variety of theoretical methods. Highly correlated Hamiltonians, like Møller-Plesset or  $\text{MP}_n$   $n = 2, 3, 4$ ; and coupled cluster including single and double contributions or CCSD, and CCSD(T), have been used to calculate dissociation energies, harmonic vibrational frequencies of the electronic ground states, electronic structure and transition energies.<sup>7–9</sup> For these properties relativistic effects were included only via scalar potentials or by using first order perturbative corrections to the estimation of some electronic mechanisms.<sup>10</sup>

For group-11 metal atoms it is well known that properties of Au atoms in Au-containing molecules may be very differ-

ent from those of Ag- or Cu-containing compounds. This is the case for NMR spectroscopic parameters. For gold atom relativistic effects are larger than for the other elements of the group, and such effects are dominant compared with electron correlation even for systems with a large number of electrons.<sup>11,12</sup>

Few years ago David and Restrepo reported relativistic effects on the nuclear magnetic shieldings of  $MF$  ( $M = \text{Cu, Ag, Au}$ ) compounds. They applied the Dirac-Hartree-Fock (DHF) method at random phase level of approach (RPA)<sup>13</sup> and did not find very large relativistic effects on the shielding constant,  $\sigma(M; M = \text{Cu, Ag})$ . For  $\sigma(\text{Au})$  in AuF molecule an unexpected very large value was found. They proposed that the high electronegativity of the fluorine atom in addition to the spin-orbit (SO) coupling would increase the paramagnetic component of  $\sigma$  reporting such a very large value. As known, within the relativistic domain, the nuclear magnetic shielding constant can be splitted up into contributions from both virtual negative- and positive-energy electronic states, that are related with the diamagnetic and paramagnetic components, respectively.<sup>14</sup> The large value of  $\sigma(\text{Au})$  in AuF arises from the positive-energy electronic contributions (paramagnetic term).  $\sigma(\text{Au}; \text{AuF})$  is more than twice larger than  $\sigma(\text{Au})$  on AuCl, AuBr, and AuI. The smaller value of  $\sigma(\text{Au})$  on these last compounds would be related with the smaller electronegativity of the ligand, and such effect on AuF would be very strong.

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In a more recent work, Yoshizawa and Sakaki studied in some detail the nuclear magnetic shieldings of the whole group-11 metal halides, applying two-component relativistic density functional theory (DFT) with the second-order Douglas-Kroll-Hess (DKH2) one-electron Hamiltonian.<sup>15</sup> They also found the same unexpected large value of  $\sigma(\text{Au})$  in AuF and stated that it arises from the Fermi contact (FC) term, which gives a much larger contribution in AuF than in the other group-11 metal halides. From their analysis they conclude that it must come from transitions related with some specific molecular orbitals that have small orbital energy separation.

An enhancement of the SO effect due to large electronegativity has been found in NMR shielding constants in some molecular systems,<sup>16</sup> although it is not always the case.<sup>3</sup> Shall it be the case in metal halides? Given previous explanations proposed in the literature, a high interest appears to shed some light on whether SO effects may be enhanced by electronegativity of fluorine atom in AuF. It is not clear the fact that in this case SO effects should be related with electronegativity and this does not seem to be the case. The proposed enhancement mechanism which involve together SO and electronegativity for nuclear magnetic shielding constants, has not yet been elucidated; so, another theoretical justification of what is happening may be necessary.

The contribution of SO effects to magnetic shieldings are fully included in a 4c Hamiltonian and is not taken into account in a Spin-Free, SF, Hamiltonian.<sup>17</sup> In this way, SO contributions can be estimated as a difference among perturbative calculations with the 4c Hamiltonian and SF Hamiltonian.<sup>13,18</sup>

The SF Hamiltonian, first proposed by Dyall, is very useful for obtaining contributions that come from the SO mechanism within the relativistic framework.<sup>17</sup> The SO is only one of several electronic mechanisms responsible for relativistic effects on  $\sigma$ . When one wants to include its contributions, the LRESC model is one of the most reliable methods of choice.<sup>19,20</sup> It permits to analyse contributions from the core and also from the environment. In this way spin-orbit effects are roughly obtained from 4c methods, as a crude estimation based on the difference among the full and the spin-free calculations,<sup>18</sup> or from the LRESC model which is more accurate.

Theoretical studies of NMR spectroscopic parameters in compounds which are of interest for organic and inorganic chemistry is many times plagued with problems of instabilities or quasi instabilities, QIs. These are artifacts that several times do appear on calculations performed at RPA level of approach when the restricted Hartree-Fock (RHF) electronic ground state of the molecular system is not (or is quite close to) the lowest energy state, but a triplet state is (more close to) the lowest.<sup>21</sup> In general this fact disturbs the output of calculations of FC or SD contributions to NMR J-couplings and makes them overvalued. It is then necessary to overcome the problem with some other scheme.<sup>22</sup> In the case of magnetic shieldings calculated within the relativistic regime, both FC

and SD mechanisms shall be involved with the SO correction as also other triplet-type corrections.

QI problems are more usual when calculations are applied on unsaturated molecules, though they could also appear in calculations on saturated molecular systems.<sup>23</sup> The usual way to overcome this problem by *ab initio* methods is to use post-RPA schemes (*i.e.* including more electron correlation). There is also another way to tackle it, which was proposed for medium- and large-size systems and consist of using a more crude approximation.<sup>24</sup> The reason for doing it, is subtle and shall be explained schematically in the next section. Within the polarization propagator formalism two options were developed for going through QI problems: the pure zeroth order approach (PZOA) and the second order polarization propagator approach (SOPPA), though SOPPA is not implemented yet for relativistic calculations.<sup>14</sup>

In this work we give an accurate analysis of the electronic origin of relativistic effects on the NMR shieldings of the following family of compounds:  $MX$  ( $M = \text{Cu, Ag, Au}$ ;  $X = \text{H, F, Cl, Br, I}$ ) by applying state of the art theoretical models. Special care is taken on the analysis of how large are core- and ligand-dependent contributions to such relativistic effects. We shall also show that the unexpectedly large value of  $\sigma(\text{Au}; \text{AuF})$  is an artifact that can be related to the appearance of quasi instabilities.

The structure of the article is as follows. First we give in section 2 a schematic overview of theoretical methods we have worked with. Then we present all the computational details regarding this paper. In Section 4 we discuss the main Results, and finally we give our concluding remarks in Section 5.

## 2 Theory

### 2.1 Polarization propagators. Relativistic formalism

The nuclear magnetic shielding constant,  $\sigma$ , can be calculated within both, the relativistic and nonrelativistic regime, using the polarization propagator formalism. For this response property the perturbative Hamiltonians involved are the external magnetic field and the magnetic moment due to the nuclear spin.<sup>14</sup> Within the nonrelativistic regime the contributions to  $\sigma$  are computed considering the excitations from occupied electronic states to virtual electronic states. On the other hand, within the relativistic regime there are two different type of excitations to be considered: the one that arises from occupied and bounded electronic states and goes to virtual and positive-energy electronic states, and the other that goes to virtual and negative-energy electronic states.

Within the relativistic polarization propagator approach, RelPPA, the explicit short hand expression of the nuclear magnetic shielding of a nucleus  $M$  reads<sup>14</sup>

$$\sigma_M = e^2 \left\langle \left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle \right\rangle \quad (1)$$

**Table 1** LRESC corrections to NMR shielding constants.

$\sigma = \sigma_p + \sigma_d$	Zeroth-order Singlet	First-order		Third-order	
		Singlet	Triplet	Singlet	Triplet
$\sigma_p$	--	$\sigma_p^{S(1)} = \sigma_p^{OZK} + \sigma_p^{PSOK}$	$\sigma_p^{T(1)} = \sigma_p^{SZK} + \sigma_p^{BSO}$	$\sigma_p^{S(3)} = \sigma_p^{PSO}$	$\sigma_p^{T(3)} = \sigma_p^{SO}$
$\sigma_d$	$\sigma_d^{S(0)} = \sigma_d^{DIAK}$	$\sigma_d^{S(1)} = \sigma_d^{MV} + \sigma_d^{DW}$	--	--	--

This equation can be reexpressed in such a way that all virtual electronic excitations to be considered are written explicitly. The excitations involving occupied electronic states and virtual positive-energy electronic states will give the paramagnetic component; and those involving negative-energy electronic states will give the diamagnetic component. They are known as *ee* and *ep* contributions, respectively.<sup>14</sup>

In the RelPPA formalism one can include electron correlation at different levels. The pure zeroth-order approach (PZOA) is equivalent to the sum-over-states scheme. The random phase approximation (RPA) which is consistent till first-order in electron correlation. They are actually implemented in computational codes as the DIRAC.<sup>25</sup>

## 2.2 LRESC method for relativistic corrections to shielding constants

The starting point to appropriately include most of relativistic corrections to  $\sigma$  within the LRESC model is to consider a molecular system under the action of both, the uniform external magnetic field ( $\vec{B}$ ) and the magnetic moments of all nuclei ( $\vec{\mu}_M$ ) in a relativistic many-body framework.<sup>19</sup> In this way, the important interactions are taken into account when the relativistic Hamiltonian of the total system is transformed from 4- to 2-components. In doing so, one gets the unperturbed molecular Hamiltonian and a perturbation containing both magnetic interactions. The LRESC model takes into account the elimination of the small component scheme on all matrix elements involved in a response function, as well as the contributions that can be derived from the manifold space where *N* electron–positron pairs can be created over the ground state. These states are coupled with the *N*-electron ground state via both, the magnetic interaction and the Breit operator in the unperturbed molecular Hamiltonian. A detailed description of this scheme was published elsewhere (see Refs.<sup>19,20</sup>).

The whole list of relativistic corrections to both, paramagnetic and diamagnetic terms ( $\sigma_p$  and  $\sigma_d$ ) that come from one-body operators, are presented in Table 1. Detailed descriptions about this separation and also the origin of the whole LRESC corrections are discussed in Ref.<sup>5</sup>. Such corrections can be

clustered as both, first- and third-order in response theory, and also as a dependence of their spin character, being this singlet or triplet. From now on we will consider the LRESC corrections in accordance with all terms that are given in Table 1.

There are several leading relativistic corrections that are now well known within the LRESC model. We shall give a step further and divide them as core- and ligand-dependent.<sup>26</sup> Those corrections that have almost the same value when the number or type of halogen-substituents varies, bunched as core-dependent:  $\sigma_p^{T(1)}$ ,  $\sigma_d^{S(1)}$  and  $\sigma_d^{S(0)}$ . On the other hand we named ligand-dependent to those corrections which have a strong dependence with the substituents:  $\sigma_p^{S(1)}$ ,  $\sigma_p^{T(3)}$  and  $\sigma_p^{S(3)}$ . The typical SO term is ligand-dependent as it should be.

## 2.3 Quasi instabilities

As mentioned above when one perform calculations at RPA level of approach on unsaturated systems, overvalued J-couplings may appear. It could also happen in saturated systems. The reason is subtle, though it is well known as a mathematical problem and fortunately some vaccines were developed. It does appear when the eigenvalue of the principal propagator is less than 0.11, or equivalently the value of the following expression  $v_{ia,jb} = (\langle aj|bi \rangle + \langle ab|ji \rangle) / (\epsilon_a - \epsilon_i)$  is larger than 0.75. In the last case what happens is a rate of convergency in calculations that becomes much lower. Indices *i* and *j* are related with occupied molecular orbitals, MOs, and *a* and *b* are related with unoccupied MOs.  $\epsilon_i$  and  $\epsilon_a$  correspond to MO energies.

In ref.<sup>24</sup> it was shown that, when one of the two-electron integrals (coulombic or exchange) is neglected the QI disappears. So, one of the vaccines is not exclusively related with electron correlation in itself though it is more related with the way to diminish  $v_{ia,jb}$  and so, to overcome the mathematical problem. One should also mention that QI usually appears when the system contain  $\pi$ -like bonds.

### 3 Computational details

Our calculations were performed with four-component, 4c, and two-components, 2c, methods. We used both, DIRAC<sup>25</sup> and DALTON<sup>27,28</sup> suite of programs.

**Table 2** Bond lengths in  $MX$  model compounds  $M = \text{Cu, Ag, Au}$  and  $X = \text{H, F, Cl, Br, I}$ .

	H	F	Cl	Br	I
Cu	1.4626 <sup>a</sup>	1.7449 <sup>a</sup>	2.0512 <sup>a</sup>	2.1734 <sup>a</sup>	2.3383 <sup>a</sup>
Ag	1.6170 <sup>a</sup>	1.9832 <sup>a</sup>	2.2808 <sup>a</sup>	2.3931 <sup>a</sup>	2.5446 <sup>a</sup>
Au	1.5237 <sup>a</sup>	1.9184 <sup>b</sup>	2.1990 <sup>b</sup>	2.3184 <sup>c</sup>	2.4711 <sup>d</sup>

<sup>a</sup> Taken from Ref. <sup>29</sup>; <sup>b</sup> Taken from Ref. <sup>30</sup>;

<sup>c</sup> Taken from Ref. <sup>31</sup>; <sup>d</sup> Taken from Ref. <sup>32</sup>

The geometries used in this work are presented in Table 2 and were taken from Refs. <sup>29–32</sup>

#### 3.1 4c shielding calculations, geometries and basis set convergence

The 4c shielding calculations were carried out with the DIRAC program package.<sup>25</sup> They were performed at RPA level of approach of the polarization propagator formalism and hereafter expressed as 4c-RPA. 4c-DFT calculations were carried out using two different hybrid functionals, B3LYP and PBE0, including different amounts of HF exchange, *i.e.* 20 % and 25 % respectively.

We found a combination of optimized basis sets to be the best choice to reproduce converged results for 4c shielding calculations. For hydrogen and halogen atoms we used an optimized version of Sadlej's basis set, as already published in other of our works<sup>3,26,33</sup> Shortly, we started with uncontracted Sadlej's basis set<sup>34</sup>, and including then tight and diffuse gaussian functions to get converged results. The scheme applied for including such orbitals was the addition of tight basis functions to *s, p, d, f* blocks with related exponents as  $\alpha_{i+1}/\alpha_i = 3$ , starting from the largest exponent of each block as stated in Refs.<sup>3,26,33</sup> No diffuse basis functions were necessary (*d* and *f* blocks) compared to significantly changing of shielding constants. The small components were generated from the large components basis set applying the UKB prescription, as standard procedure in Dirac code.<sup>35</sup>

For metal atoms we used: optimized Ahlrichs basis set<sup>36</sup> (19s14p11d8f3g) for Cu atom; optimized Huckel basis set (20s16p12d7f5g) for Ag; and optimized Faegri basis set<sup>37</sup> (22s18p14d9f4g) for Au atom. To ensure convergence for the shielding constant of each nucleus, we optimized each basis set as shown in Tables 3 and 4. For Cu atom we used Ahlrichs basis set with tight and diffuse functions added. For Ag atom we used Huckel basis set at the starting point to obtain the convergency.

In Table 3 and Table 4 we show the dependence of both

paramagnetic and diamagnetic components of  $\sigma(\text{Cu})$  and  $\sigma(\text{Ag})$  with the size of the basis set. We carried out calculations applying both prescriptions, the restricted kinetic balance (RKB) and unrestricted kinetic balance (UKB). Calculations of  $\sigma(\text{Cu})$  converge to similar values with both prescriptions when the size of the basis set increases. Calculations with both such prescriptions give almost the same value for the paramagnetic component but they are very different for the diamagnetic one. This makes mandatory to increase the size of the basis set in such a way to get converged values of  $\sigma(\text{Cu})$ .

#### 3.2 LRESC shielding calculations

LRESC shielding calculations were carried out with the Dalton suite of programs.<sup>27,28</sup> We used similar basis set to that published in a previous paper for hydrogen, halogen and metal atoms.<sup>26</sup> In fact, the basis set used in this work is smaller than the previous one, but ensuring the same quality of the LRESC results. Namely, we have taken out tight functions of *s* and *p* character: 2 *s-type* tight functions for H and F, and 2 *s-type* and *p-type* tight functions for Cl, Br, and I.

## 4 Results and discussion

#### 4.1 Nuclear magnetic shieldings of group-11 metal atoms

In Table 5 we present results for  $\sigma(M)$ , on group-11 metal halides,  $MX$  ( $M = \text{Cu, Ag, Au}$ ;  $X = \text{H, F, Cl, Br, I}$ ) within the relativistic regime applying the 4c-RPA formalism, and DFT methods with two different functionals, B3LYP and PBE0. LRESC results are also shown in this Table.

One of our aims in this section is to highlight which differences exist among 4c-RPA, 4c-DFT and LRESC descriptions, with those obtained in previous works using DKH2 with HF and DFT;<sup>13,15</sup> aiming to point out new insights originated in such methodological differences.

Calculations with 4c-RPA method are different to 4c-DFT ones, which is in agreement with previous results.<sup>4,6,38</sup> They are also close to those obtained using 4c methods<sup>13</sup> and with DKH2-HF method<sup>15</sup>, though there is a difference in results on about 20 % applying DKH2-B3LYP method.<sup>15</sup>

The differences among our 4c-RPA results and those 4c-RPA reported by David and Restrepo are within 10 % of difference. Also this agreement still happens for  $\sigma(\text{Au})$  in AuF, where the total shielding constant has an extremely large magnitude. Gold atom containing molecules needs a more detailed analysis which will be given further in this Section.

For CuF and AgF molecules, our results are over those of David and Restrepo, but still close to what Yoshizawa and Sakaki reported via DKH2-HF method. When compared with results using DKH2-B3LYP method the difference reaches 16 % for CuCl molecule.  $\sigma(\text{Au})$  has a very large value in AuF molecule, being more than two times compared with other gold containing systems, as previously shown.<sup>13,15</sup> For

**Table 3** 4c-RPA basis set convergence for  $\sigma(\text{Cu})$  in CuH with both RKB and UKB prescriptions.

basis set Ahlrichs	RKB			UKB		
	$\sigma_d$	$\sigma_p$	$\sigma_t$	$\sigma_d$	$\sigma_p$	$\sigma_t$
17s10p6d	1879.83	-93.16	1786.67	2292.41	-92.57	2199.84
19s11p6d	1879.18	-90.65	1788.53	2291.86	-89.93	2201.93
19s14p7d	2005.53	-130.04	1875.49	2289.18	-121.59	2167.59
19s14p9d1f	2078.00	-124.67	1953.33	2283.61	-122.20	2161.41
19s14p9d4f	2180.80	-122.84	2057.96	2283.53	-123.12	2160.41
19s14p9d6f1g	2262.66	-115.20	2147.46	2283.13	-115.40	2167.73
19s14p9d7f2g	2269.41	-111.01	2158.40	2283.01	-111.28	2171.73
19s14p11d8f3g	2280.56	-109.82	2170.74	2282.89	-110.10	2172.80

**Table 4** 4c-RPA basis set convergence for  $\sigma(\text{Ag})$  in AgH with both RKB and UKB prescriptions.

basis set Huckel	RKB			UKB		
	$\sigma_d$	$\sigma_p$	$\sigma_t$	$\sigma_d$	$\sigma_p$	$\sigma_t$
15s12p6d	3278.96	-88.08	3190.88	4282.95	-82.91	4200.04
18s14p6d	3241.00	338.30	3579.30	4270.12	344.32	4614.44
18s15p7d	3408.02	260.47	3668.48	4265.14	270.93	4536.08
18s15p10d5f	4069.79	292.56	4362.36	4240.25	298.40	4538.65
19s15p11d6f	4083.12	384.53	4467.65	4224.41	390.52	4614.93
20s16p12d6f2g	4113.99	582.21	4696.19	4222.25	579.69	4801.94
20s16p12d6f4g	4204.43	582.22	4786.66	4222.16	579.85	4802.02
20s16p12d7f5g	4222.39	582.95	4805.34	4222.72	580.83	4803.55

all other AuX ( $X = \text{H, Cl, Br, I}$ ) molecular systems, the differences between our 4c-RPA and 4c-DFT values are among 9 % to 12 %. There is a difference close to 3 % with respect to results published by David and Restrepo, and such a difference grows up to 5 % (DKH2-HF) and 18 % (DKH2-B3LYP) when compared with results of Yoshizawa and Sakaki.

On the other hand, the LRESC values are in very good agreement with 4c-RPA calculations for Cu and Ag containing systems. In these cases the differences are less than 3 %. For AuX ( $X = \text{H, Cl, Br, I}$ ) molecular systems, such a difference grows up close to 20 % because LRESC method does not reproduce in suitable form the nuclear magnetic shieldings of atoms belonging to the sixth row of the Periodic Table.<sup>3,38</sup> For AuF molecule the difference among 4c-RPA and LRESC values is completely out of range.

Differences between 4c-RPA and the methods mentioned above have different origins. The 4c-DFT values do not reproduce the 4c-RPA in a reliable way because the functionals were parameterized within the nonrelativistic regime, showing that they are not suitable for calculations of nuclear magnetic shieldings in heavy-atom containing molecular systems. 4c-DFT shieldings are smaller than 4c-RPA ones for not so heavy molecular systems, but when the weight of the molecule grows up 4c-DFT and 4c-RPA values become closer. For heavy molecular systems like AgBr, AgI and AuI, 4c-DFT results are larger than the 4c-RPA ones, which is in agreement with

previous results at Ref.<sup>6,15</sup>

With respect to the shielding values of this work and those reported by David and Restrepo, the difference might be assessed due to the basis sets they used.<sup>13</sup> The  $f$  and  $g$  orbital functions give differences in shielding calculations that can be of 10 % when the basis set is not fully optimized. The poor quality of a basis set for Cu atom could produce small differences between relativistic and nonrelativistic values, like the 16 ppm reported by David and Restrepo.<sup>13</sup>

We have shown in previous works that when RKB prescription is used, a very large basis set is necessary in order to obtain reliable results for nuclear magnetic shieldings within the relativistic domain.<sup>35</sup> Such basis sets must be constructed adding specially  $d$  and  $f$  tight functions aiming to correctly describe virtual electronic states. The lack of this procedure produces differences in more than 10 % at the end. A basis set problem could be responsible for the difference between the present work and those results reported previously<sup>13</sup>. For CuF, AgF and AuF molecules, the differences of our values with respect to those reported by David and Restrepo are 10 %, 8 % and 4 % respectively.

## 4.2 Relativistic effects on the nuclear magnetic shieldings

Relativistic effects on  $\sigma(M)$  ( $\Delta^X \sigma(M)$ ) may be computed as the percentual difference between a scheme  $X$  and 4-

**Table 5** NMR magnetic shieldings,  $\sigma(M)$ , in  $MX$  model compounds  $M = \text{Cu, Ag, Au}$  and  $X = \text{H, F, Cl, Br, I}$ . [1] 4c calculations taken from Ref. 13; [2] DKH2 at HF/DFT level, taken from Ref. 15.

M	method	H	F	Cl	Br	I
Cu	4c-RPA	2172.80	1985.34	2027.46	2086.65	2147.71
	4c-PBE0	1834.81	1168.10	1671.51	1854.47	2081.48
	4c-B3LYP	1756.23	985.95	1595.38	1814.82	2102.92
	LRESC	2218.29	2009.72	2063.48	2121.10	2184.58
	4c-RPA <sup>[1]</sup>	–	1787.0	–	–	–
	DKH2-HF <sup>[2]</sup>	–	2043	2005	2060	2112
	DKH2-B3LYP <sup>[2]</sup>	–	1754	1708	1899	2166
Ag	4c-RPA	4803.55	5017.69	4827.98	4841.57	4844.06
	4c-PBE0	4817.79	4882.02	4763.02	4940.04	5144.01
	4c-B3LYP	4798.22	4858.11	4769.71	5017.02	5292.18
	LRESC	4933.67	5124.98	4920.68	4912.46	4900.66
	4c-RPA <sup>[1]</sup>	–	4633.7	–	–	–
	DKH2-HF <sup>[2]</sup>	–	5047	4825	4830	4830
	DKH2-B3LYP <sup>[2]</sup>	–	4987	4794	5082	5425
Au	4c-RPA	13926.54	32910.32	15394.77	14851.83	14969.76
	4c-PBE0	14057.70	18098.34	13501.70	14455.09	15840.75
	4c-B3LYP	14175.22	18222.70	13443.57	14701.90	16374.60
	LRESC	11839.83	12607.76	11933.11	11899.62	11800.59
	4c-RPA <sup>[1]</sup>	–	31610.8	14937.3	14458.9	14454.0
	DKH2-HF <sup>[2]</sup>	–	32635	16130	15501	15523
	DKH2-B3LYP <sup>[2]</sup>	–	25527	14437	15712	17669

component results,

$$\Delta^X \sigma(M) = \frac{\sigma^{4c}(M) - \sigma^X(M)}{\sigma^X(M)} \quad (2)$$

Table 6 shows calculations of nuclear magnetic shieldings at relativistic (4c-RPA) and non relativistic (NR, HF) levels for the metal atom. It also include the corresponding relativistic effects evaluated with Eq. 2 among 4c-RPA and NR-HF schemes ( $\Delta^{NR} \sigma$ ). For nonrelativistic calculations, the speed of light was multiplied by an scaling factor of 10 in such a way to consider its value equal to  $10c$  ( $c = 137.0359998$  au). We do it in order to obtain values in the NR limit with the same scheme of calculation.

Relativistic effects on  $\sigma(\text{Cu})$  has almost the same value for the whole family of  $\text{CuX}$  (around 8 %) diatomics, with the only exception of  $\sigma(\text{Cu})$  in the  $\text{CuF}$  molecule. This means that relativistic effects are not very much dependent on the heavy-halogen substituent, which is also observed for  $\sigma(\text{Ag})$  where relativistic effects are among 15 % and 20 % on the whole  $\text{AgX}$  set. However, for gold-atom containing molecules, relativistic effects grow up as expected, between 63 % and 87 %, excluding  $\sigma(\text{Au})$  in  $\text{AuF}$ . Therefore the heavy atom effect on vicinal heavy atom (so called HAVHA effect<sup>3,35</sup>) is important for this kind of compounds. But  $\sigma(\text{Au})$  in  $\text{AuF}$  molecule needs a special treatment as  $\sigma^{4c}(\text{Au})$  is around four times  $\sigma^{NR}(\text{Au})$ .

In Table 7 we show results of shielding calculations with both, 4c-RPA and Spin-free Hamiltonian.<sup>17</sup> In the same Table we also show both components of  $\sigma(M)$ , meaning diamagnetic and paramagnetic terms together with its total value for the whole set of molecular systems. For Cu-containing molecules the diamagnetic term,  $\sigma_d$  has almost the same value for all systems with differences of less than 2 ppm. In the case of the paramagnetic terms variations that depend on the halogen substituents are observed. The largest variation is obtained for the  $\text{CuF}$  molecule. In Ag-containing molecules the behavior of  $\sigma(\text{Ag})$  is similar.  $\sigma_d$  has almost the same value for 4c-RPA and SF Hamiltonians (close to 4 ppm). The paramagnetic contribution reaches its maximum variation for  $\text{AgF}$  molecule.

The relativistic effects given by  $\Delta^{SF} \sigma(M)$  for the total shielding in the whole serie of molecules is close to 2 %, with the exception of shieldings for  $\text{CuF}$ . This means that the spin dependent contributions are not important for these shielding constants.

For Au-containing molecules the absolute value of relativistic effects of spin-dependent contributions might be roughly assessed as  $\sigma^{4c} - \sigma^{SF}$ . In the case of  $\text{AuF}$ , these contributions are the largest within the  $\text{AuX}$  group. The spin-dependent corrections of  $\sigma_d$  are close to 100 ppm in the whole serie. As observed when full relativistic effects are included, a huge contribution to  $\sigma_p(\text{Au})$  in  $\text{AuF}$  is obtained. One may be tempted to consider that SO effects are unusually large in this case

**Table 6** Relativistic (4c-RPA) versus nonrelativistic (Hartree-Fock) calculations of  $\sigma(M)$ , and their corresponding relativistic effects.

$MX$	4c-RPA			NR-HF			$\Delta^{NR}\sigma(M)$ (eq.2)	
	$\sigma_d$	$\sigma_p$	$\sigma^t$	$\sigma_d$	$\sigma_p$	$\sigma^t$		
Cu	H	2282.89	-110.10	2172.80	2409.17	-381.54	2027.63	7.2%
	F	2330.85	-345.51	1985.34	2450.88	-693.15	1757.73	12.9%
	Cl	2359.69	-332.23	2027.46	2479.83	-606.80	1873.03	8.2%
	Br	2432.26	-345.61	2086.65	2553.11	-623.40	1929.71	8.1%
	I	2492.53	-344.82	2147.71	2614.64	-642.49	1972.15	8.9%
Ag	H	4222.72	580.83	4803.55	4660.78	-507.06	4153.72	15.6%
	F	4258.09	759.61	5019.70	4697.39	-477.31	4220.08	18.9%
	Cl	4285.28	542.70	4827.98	4724.42	-641.21	4083.21	18.2%
	Br	4351.82	489.75	4841.57	4791.65	-718.99	4072.67	18.9%
	I	4409.57	435.69	4845.26	4849.76	-811.84	4037.92	20.0%
Au	H	7926.44	6000.10	13926.54	9533.90	-1024.47	8509.43	63.7%
	F	7965.02	24945.30	32910.32	9571.83	-1032.67	8539.16	285.4%
	Cl	7992.41	7402.36	15394.77	9599.95	-1364.10	8235.85	86.9%
	Br	8060.78	6791.05	14879.83	9668.98	-1415.25	8253.74	80.3%
	I	8119.04	6850.72	14957.76	9728.41	-1506.23	8222.18	81.9%

given that these results are in good agreement with previous results.<sup>13,15</sup>

**Table 7** Relativistic 4c-RPA and Spin-free calculations of  $\sigma(M)$ .

$MX$	4c-RPA			Spin free			
	$\sigma_d$	$\sigma_p$	$\sigma^t$	$\sigma_d$	$\sigma_p$	$\sigma^t$	
Cu	H	2282.89	-110.10	2172.80	2280.96	-154.32	2126.64
	F	2330.85	-345.51	1985.34	2328.92	-549.65	1779.27
	Cl	2359.69	-332.23	2027.46	2357.81	-368.38	1989.43
	Br	2432.26	-345.61	2086.65	2430.48	-366.14	2064.34
	I	2492.53	-344.82	2147.71	2490.91	-362.45	2128.46
Ag	H	4222.72	580.83	4803.55	4226.82	679.51	4906.33
	F	4258.09	759.61	5019.70	4262.30	646.80	4909.10
	Cl	4285.28	542.70	4827.98	4289.33	509.14	4798.47
	Br	4351.82	489.75	4841.57	4356.00	452.30	4808.30
	I	4409.57	435.69	4845.26	4413.99	391.14	4805.14
Au	H	7926.44	6000.10	13926.54	8035.24	5952.72	13987.96
	F	7965.02	24945.30	32910.32	8065.30	4733.84	12799.14
	Cl	7992.41	7402.36	15394.77	8092.14	5427.45	13519.59
	Br	8060.78	6791.05	14879.83	8160.74	5643.05	13803.79
	I	8119.04	6850.72	14957.76	8213.73	5866.38	14080.11

We should also mention that both  $\sigma_d$  and  $\sigma_p$  do not change significantly in  $AuX$  ( $X = H, F, Cl, Br, I$ ) family of compounds, except for  $\sigma_p(Au; AuF)$ . We will take special attention to this particular case in section 4.4 analysing the relativistic contributions to  $\sigma(Au)$  in  $AuF$  with the LRESC method.

### 4.3 LRESC analysis of electronic contributions to $\sigma$

In the last section we showed the spin-dependent contributions to the nuclear magnetic shielding of metal atoms. In this section we want to explore which other electronic mechanism might be responsible for the total relativistic effects. We shall consider that the LRESC model is one of the most reliable methods, developed to analyse the different electronic mechanisms underlying the relativistic effects that should be

included in the calculation of  $\sigma$ . This is valid even for heavy-atom containing molecular systems with atoms belonging down to the sixth row of the Periodic Table.<sup>3,19,26</sup>

In Table 8 we present the whole LRESC relativistic corrections together with the nonrelativistic contributions for all metallic atoms. We grouped the corrections in two types: “core-” and “ligand-” dependent, as we did in Ref.<sup>26</sup>. Corrections that are almost the same when the number, or type, of halogen-substituent varies are named “core-dependent”; and corrections showing a strong dependence with the substituents are named “ligand-dependent”. In the last two columns of Table 8 total LRESC and 4c-RPA shielding constant values are presented.

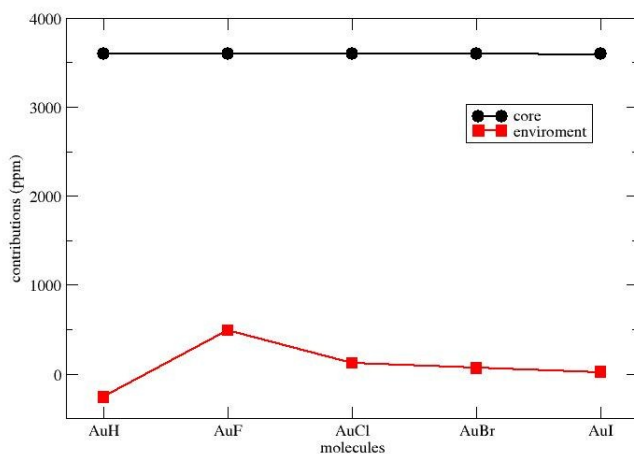
The main relativistic corrections to the total magnetic shielding for the whole set of studied  $MX$  molecules are core-dependent. They give the largest contribution to the total value of  $\sigma^{LRESC}$  and grow up when the metallic atom becomes heavier. As expected the ligand-dependent corrections vary with the substituent. In Fig. 1 the behavior of these contributions for gold-containing molecules are shown. It is also observed that  $\sigma(M; MX)$  have a small dependence with the type of the halogen substituent ( $X = H, Cl, Br, I$ ), but when the metallic atom is bounded to fluorine, important ligand-dependent contributions do appear, as shown in Fig. 2. It is observed that the total amount of  $\sigma^{LRESC}(M, MF)$  corrections is larger in MF systems than the same LRESC corrections at the rest of the  $MX$  group. In all cases the SO is the main one. Such SO effects are more positive in the whole set of molecular systems when the halogen is  $X = F$ . Furthermore, when the weight of the molecule increases few other important electronic mechanisms do become important.

In Table 8 we can see that  $\sigma_p^{T(3)} = 512$  ppm, which is the



**Table 8** Leading relativistic corrections obtained with the LRESC model, to  $\sigma(M)$  in  $MX$  model compounds ( $M = \text{Cu, Ag, Au}$ ;  $X = \text{H, F, Cl, Br, I}$ )

$MX$	$\sigma^{nr}$	core			ligand			core <sup>a</sup>	ligand <sup>b</sup>	LRESC	4c
		$\sigma_p^{T(1)}$	$\sigma_d^{S(1)}$	$\sigma_d^{S(0)}$	$\sigma_p^{S(1)}$	$\sigma_p^{T(3)}$	$\sigma_p^{S(3)}$				
CuH	2025.22	334.83	61.07	-212.56	23.88	32.52	-46.67	183.34	9.73	2218.29	2172.80
CuF	1757.05	334.52	61.01	-212.56	23.85	165.57	-119.72	182.97	69.71	2009.72	1985.34
CuCl	1870.41	334.90	61.05	-212.66	24.81	36.54	-51.57	183.29	9.78	2063.48	2027.46
CuBr	1926.78	335.11	61.07	-213.19	25.85	19.89	-34.42	183.00	11.32	2121.10	2086.65
CuI	1962.91	335.33	61.11	-214.17	27.72	26.99	-15.30	182.26	39.42	2184.58	2147.71
AgH	4157.66	1458.70	283.45	-940.72	119.45	-75.85	-69.02	801.43	-25.42	4933.67	4803.55
AgF	4229.29	1458.67	283.35	-940.69	110.02	52.02	-67.67	801.32	94.37	5124.98	5019.70
AgCl	4087.53	1458.69	283.40	-940.79	120.15	-2.44	-83.41	801.30	31.85	4920.68	4827.98
AgBr	4076.90	1458.88	283.43	-941.27	120.15	-13.72	-71.90	801.03	34.53	4912.46	4841.57
AgI	4037.13	1459.10	283.47	-942.19	124.32	-6.25	-54.92	800.38	63.15	4900.66	4845.26
AuH	8504.87	6754.09	1446.27	-4605.67	689.58	-562.38	-386.93	3594.69	-259.74	11839.83	13926.54
AuF	8525.31	6753.71	1446.27	-4605.58	645.17	512.43	-669.23	3594.08	488.38	12607.76	32910.32
AuCl	8219.15	6753.58	1446.12	-4605.69	697.01	-28.08	-548.99	3594.01	119.94	11933.11	15394.77
AuBr	8240.89	6753.87	1446.19	-4606.19	703.53	-162.71	-475.97	3593.88	64.85	11899.62	14879.83
AuI	8186.00	6754.22	1446.27	-4605.13	719.12	-296.28	-401.64	3593.38	21.21	11800.59	14957.76

<sup>a</sup> Core-dependent contributions given by  $\sigma_p^{T(1)} + \sigma_d^{S(1)} + \sigma_d^{S(0)}$ <sup>b</sup> Ligand-dependent contributions given by  $\sigma_p^{S(1)} + \sigma_p^{T(3)} + \sigma_p^{S(3)}$ **Fig. 1** Core- and ligand-dependent contribution to  $\sigma(\text{Au})$  in  $\text{AuX}$  ( $X = \text{H, F, Cl, Br, I}$ ) model compounds.

total SO contribution obtained with the LRESC model (SD + FC contributions). Even though the SO effect within the LRESC model is one of the most sensible contributions in the whole series of molecules, it is very small as compared with the contribution of 20000 ppm obtained for  $\sigma(\text{Au})$  (see Table 7).

This fact seems to indicate the existence of a different origin for this likely unphysical result.

#### 4.4 Quasi instabilities on the calculations of $\sigma(\text{Au}; \text{AuF})$

As mentioned above very large values of  $\sigma(\text{Au})$  in the AuF molecular system were previously reported.<sup>13,15</sup> This fact was related by the authors to the large electronegativity of fluorine atom together with a very large value of the SO contribution. On the other hand it is expected that all group-11 metal halides should have similar electronic properties. So, there are no reason for getting a huge value of  $\sigma(\text{Au})$  only in AuF system. This could be related with a QI problem and this is why do not appears in CuF and AgF molecules. As suggested in Ref.<sup>22</sup> QIs could be avoided including more electronic correlation in the calculations or, working with a more crude approximation, like PZOA. So, for molecular systems that contain heavy atoms, like AuF, when shielding calculations are performed at different levels of the theory of polarization propagators (RPA and PZOA levels) we would be able to know whether QI are involved in them.

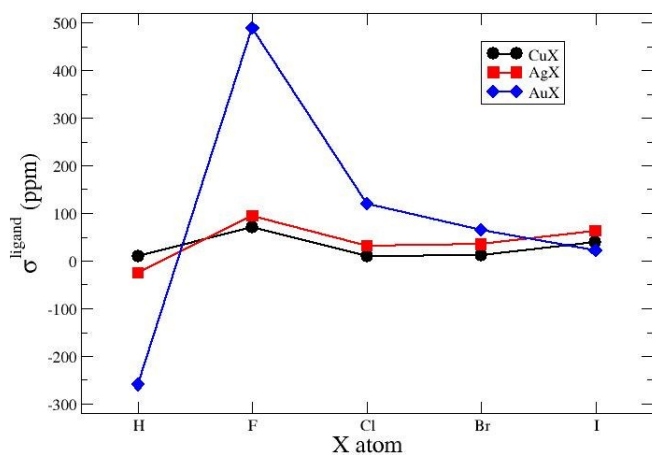
We did calculate  $\sigma(\text{Au})$  in the whole set of gold-containing molecules, at PZOA level of approach. In Table 9 we show results of calculations with 4c-PPA scheme at both levels, RPA and PZOA. The diamagnetic component of  $\sigma(\text{Au})$  does not change much in the whole set of molecules, meaning that  $\sigma_d$  is not highly dependent on electron correlation. On the other hand, the paramagnetic component changes its value, showing

**Table 9** Diamagnetic and paramagnetic contributions to  $\sigma(\text{Au}; \text{AuX})$ 

molecule	4c-RPA			4c-PZOA		
	$\sigma_d$	$\sigma_p$	$\sigma^t$	$\sigma_d$	$\sigma_p$	$\sigma^t$
AuH	7926.44	6000.10	13926.54	7921.00	6525.67	14446.67
AuF	7965.02	24945.30	32910.32	7958.45	6961.97	14920.42
AuCl	7992.41	7402.36	15394.77	7986.76	6351.26	14338.02
AuBr	8060.78	6791.05	14879.83	8055.24	6352.22	14407.46
AuI	8119.04	6850.72	14957.76	8113.63	6410.03	14523.66

a dependency on electron correlation. Such effect is not larger than 1100 ppm, excluding the AuF molecule, as can be seen in Table 9. There is only one value that appears completely different:  $\sigma_p(\text{Au}; \text{AuF})$  for calculations with the 4c-RPA method. On the other hand the value of  $\sigma_p(\text{Au}; \text{AuF})$  at PZOA level does not show such a behavior. This is what happens when calculations have problems of QL.

Considering that the value of the calculation of  $\sigma(\text{Au}; \text{AuF})$  with the LRESC method should be close to 20 % lower than the 4c-RPA (Table 8) and the fact that no large contributions are observed when electron correlation is not considered, we can state that the best theoretical value of  $\sigma_p(\text{Au}; \text{AuF})$  shall be between 7200 ppm and 8200 ppm. Then, the best number for  $\sigma^{4c}(\text{Au}; \text{AuF})$  should be between 15000 ppm and 16000 ppm. On the other hand, gold has a single isotope which has a nuclear spin of 3/2 and therefore a quadrupole moment. As a result of fast quadrupole relaxation, the resonances are extremely broad and weak and there are not experimental values in this kind of compounds.

**Fig. 2** Ligand-dependent contributions to  $\sigma(M)$  in  $MX$  model compounds ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ).

## 5 Conclusions

We have studied the nuclear magnetic shieldings of the group-11 metal atoms in  $MX$  ( $M = \text{Cu}, \text{Ag}, \text{Au}; X = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) molecular systems with different state of the arte theoretical approaches. We have focused our study on relativistic effects and the electronic origin of their contributions.

Small differences between our values and those reported previously<sup>13,15</sup> were found, probably coming from differences in the convergence of the basis sets used.

We applied 4c methodology and also the LRESC model to the analysis of the electronic origin of NMR shieldings of heavy atoms. As observed in our previous results on other heavy-atom containing systems, results of 4c-DFT calculations are not quite close to the 4c-RPA ones. These last one are more reliable as compared with experiments. Also, as it is well-known, relativistic effects increases when the weight of the molecule grows up. Still such effects are slightly dependent on the heavy halogen substituent atom.

In 4c calculations, the spin-dependent contribution is only important for  $MF$  molecules ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ). For the other halogen substituents such contributions are not so large. Another interesting finding is related with core- vs ligand-dependent mechanisms that are more important in this set of molecules. The analysis of relativistic effects given by LRESC method shows that the most important contributions come from core-dependent electronic mechanism. The ligand-dependent ones are only important for  $MF$  molecules ( $M = \text{Cu}, \text{Ag}, \text{Au}$ ).

As published in recent articles and also observed in our calculations, an unexpected and very large contribution to  $\sigma_p(\text{Au}; \text{AuF})$  arises in spin-dependent terms, when calculations are performed with 4c methods. This large contribution does not appear when calculations are performed within the LRESC model and also when electron correlation is not considered (PZOA level of approach). Given the reliability of the LRESC method, the unexpectedly large value of  $\sigma_p(\text{Au}; \text{AuF})$  that appears only for this compound in the whole serie, and the fact that such a large contribution is not observed when electron correlation on the calculation of the magnetic property is not considered, we can state that a quasi instability problem does appear in this case. When a remedy previously used in similar cases was applied the best theoretical value of  $\sigma_p(\text{Au}; \text{AuF})$  is

reduced to close to 7100 ppm. This may be the first time that a QI problem is reported in calculations of magnetic properties of gold-containing molecules. It is a QI of non-singlet type that arise due to the introduction of operators that are of triplet-type, as the SO and FC, in the relativistic corrections of NMR magnetic shieldings.

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