Relativistic and electron correlation effects on the NMR shieldings of molecules containing Sn and Pb atoms

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Abstract

The reference values for NMR magnetic shieldings, σ^{ref}, are of highest importance when theoretical analysis of chemical shifts are envisaged. The fact that the non relativistically valid relationship among spin-rotation constants and magnetic shieldings is not any longer valid for heavy atoms makes that the search for σ^{ref} for such atoms needs new strategies to follow.

We present here results of σ^{ref} that were obtained applying an own simple procedure which mix accurate experimental chemical shifts (δ) and theoretical magnetic shieldings (σ). We calculated $\sigma(\text{Sn})$ and $\sigma(\text{Pb})$ in a family of heavy-halogen containing molecules. We found out that $\sigma^{ref}(\text{Sn}; \text{Sn}(\text{CH}_3)_4)$ in gas phase should be close to 3864.11 $\pm$ 20.05 ppm (0.5 %). For Pb atom, $\sigma^{ref}(\text{Pb}; \text{Pb}(\text{CH}_3)_4)$ should be close to 14475.1 ppm $\pm$ 500.7. Such theoretical values correspond to calculations with the relativistic

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polarization propagator method, RelPPA, at RPA level of approach. They are closer to experimental values as compared to those obtained applying few different functionals like PBE0, B3LYP, BLYP, BP86, KT2 and KT3 of the density functional theory.

We studied tin and lead shieldings of the $XY_{4-n}Z_n$ (X = Sn, Pb; Y, Z = H, F, Cl, Br, I) and $PbH_{4-n}I_n$ (n = 0, 1, 2, 3, 4) family of compounds with four-component functionals as implemented in the DIRAC code. For these systems results of calculations with RelPPA-RPA are more reliable than the DFT ones. We argue on why those DFT functionals must be modified in order to obtain more accurate results of NMR magnetic shieldings within the relativistic regime: first, there is a dependence among both, electron correlation and relativistic effects that should be introduced in some way in the functionals; and second, the DIRAC code uses standard non-relativistic functionals and the functionals B3LYP and PBE0 were parameterized only with data taken from light elements. It can explain why they are not able to properly introduce relativistic effects on nuclear magnetic shieldings.

We finally show that in the analysis of magnetic shieldings for the family of compounds mentioned above, one must consider the newest and so called heavy-atom effect on vicinal heavy atoms, HAVHA. Such effects are among the most important relativistic effects in these kind of compounds.

Introduction

The nuclear magnetic resonance (NMR) spectroscopic parameters, the indirect J-coupling and the nuclear magnetic shielding, σ, provide valuable information about the molecular electronic structure, and also information of great usefulness in structure elucidation. For tin and lead containing compounds the determination of structural geometries needs reliable results for both the chemical shifts, δ and the absolute value of magnetic shieldings in their reference compounds, $\sigma[(\text{Sn/Pb}); (\text{Sn/Pb})(\text{CH}_3)_4]$.

Even though an experimental method was recently published from which magnetic shield-

ings are directly obtainable,[1,2] it is the chemical shift the most usually measured parameter. The nuclear magnetic shieldings are usually obtained by theoretical calculations and the chemical shifts as a difference between magnetic shieldings of a given nucleus in an specific molecule with that of the same nucleus in another molecule taken as a reference, the same used by experimentalists.[3]

For light elements, measured magnetic shieldings are indirectly obtainable through a relationship first published by Flygare[4] between measured spin-rotation constants and the paramagnetic component of the shielding. The diamagnetic component is then obtained by as accurate as possible calculation of the free atom. This experimental/theoretical relationship to get semiempirical magnetic shieldings does not work when heavy atoms are involved.[5,6]

In the past years a fairly broad range of reference values for $\sigma(\mathrm{Sn})$ were published. Some of them were proposed based on theoretical calculations[7–13] and others based on a mixture between spin-rotation measurements and theoretical calculations of free atoms.[14]

A new absolute shielding constant of tin in its reference compound, $\mathrm{Sn(CH_3)_4}$ was recently published by Malkin $et\ al.$[13] They furthermore proposed a new shielding scale for $\mathrm{SnH_4}$, $\mathrm{Sn(CH_3)_4}$ and $\mathrm{SnCl_4}$ model compounds which have a difference of around 1000 ppm with respect to the old shielding scale obtained by applying the nonrelativistic relationship with spin-rotation constants. How can this new (theoretical) scale be corroborated? One should be aware that at the moment there is no actual "pure" experimental value for checking it. The last published experimental value[15] was in fact estimated by applying the above mentioned semiempirical procedure. The smallest theoretical values are close to 2500 ppm[8,9,11] and the highest values are close to 3500 ppm.[10,12,13] Which one is closer to the most accurate reference value? One of the aims of this article is related with a possible answer to this enquiry.

As happens with the shielding of tin atom, it is also of interest to search for the absolute scale of lead shieldings. The problem with this last element is that there are not enough experimental chemical shifts available for the simplest lead centered tetrahalides, in order

to apply our procedure. Fortunately reasonable correlations among NMR chemical shifts of different elements belonging to the fourth main group of the periodic table were found.[16,17] In this manner the NMR analysis of tin and lead containing molecules can usually be made together. Bern Wrackmeyer published a serie of review articles with a large amount of chemical shifts data for Sn and Pb containing compounds.[18–21] Based on experimental measurements a linear relationship between the chemical shift of Sn(IV) and Pb(IV) for comparable tin and lead compounds were proposed.[16,22] We should emphasis here that tin chemical shifts cover a range of approximately 6500 ppm, from +4000 to −2500 ppm, using tetramethyltin $(Sn(CH_3)_4)$ as a reference and ^{207}Pb chemical shift cover a range of approximately 17000 ppm, from +11000 to −6000 ppm with tetramethyllead, $Pb(CH_3)_4$, as a reference.

There is an ever increasing interest in the development of theoretical schemes which should give a better treatment of relativistic and electron correlation effects on magnetic molecular properties. They may be divided into two sets, *i.e.* four-component and two-component, though there is also a distinction among those methods. They may also be based on the electronic wave function or on electron density obtained through the DFT formalism.[23–25] A third option is the polarization propagator that must be considered though it is not formally based on similar grounds.[26]

Concerning the calculation of magnetic properties of heavy atom containing molecules, Nakatsuji and coauthors were among the first to study the electronic origin of $\sigma(Sn)$ on SnX_4 model compounds.[7] They worked out an *ab initio* unrestricted Hartree-Fock, UHF method that included SO effects by finite perturbation theory. They showed that the SO effect would increase $\sigma(Sn)$ two orders of magnitud from SnH_4 to SnI_4. Calculated values without the spin-orbit correction do not satisfactorily reproduce the experimental values of the chemical shifts when the halogen atom is heavy. For compounds in which Sn is directly bonded to heavy atoms (Br and I) relativistic effects play a decisive role.

From that simple methodology one can go ahead to one of the most accurate four-component methods, recently published by Malkin and coauthors.[27] This last method was

also improved by including non-collinear spin magnetization and employing London atomic orbitals to ensure gauge origin independence.[28] An almost complete survey of wave function-based (4c and 2c) methods for the calculation of molecular property calculations was recently published.[29]

On the other hand, the relativistic polarization propagator formalism (RelPPA)[30–32] is one of the most reliable method for the calculation of nuclear magnetic shieldings within the four-component relativistic level.[12,33,34] This formalism was implemented at random phase approximation, RPA, or consistent first order of approach in the DIRAC code.[35] Applying this approach, benchmark shielding calculations of usual elements were published during the last ten years.[33,34,36–39]

Density functional theory, DFT, is usually the method of choice for calculation of NMR properties in medium-size heavy-atom containing molecules because it includes electron correlation at an affordable computational cost. Some two-component DFT and wave function based methods are available[25,40–43] though not all of them were tested for Sn or Pb containing molecules. They were developed in order to assess the study of medium-size systems or to analyze NR-like electronic mechanisms that may explain tendences or absolute values of magnetic shieldings.[23,44] It is, therefore, of interest to assess whether different DFT functionals are a valuable tool in quantitative predictions of Sn and Pb NMR properties.

There are several functionals available for DFT calculations of magnetic properties, some of them uses the zeroth order regular approximation (ZORA) method.[45–47] But ZORA calculations are not suitable for absolute shielding of heavy atoms, though they can be used safely for chemical shifts in most application scenarios.[48]

In order to learn on the performance of DFT methods to get quantitative predictions of ^{119}Sn NMR properties, Bagno *et al.* carried out calculations using DFT as implemented in the Amsterdam density functional (ADF) code,[49] in which frozen-core, as well as all-electron, Slater basis sets are available for all atoms of interest. Relativistic effects were included by means of the ZORA method up to spin-orbit coupling.[11] Bagno and coauthors found that

calculated ^{119}Sn chemical shifts generally correlate well with experimental values, except when several heavy halogen atoms, especially iodine, are bounded to tin.

Some recent studies about the performance of DFT calculations on NMR spectroscopic parameters of heavy-atom containing molecules showed that DFT gives lower shielding constants as compared with HF results.[39,50–53] On the other hand Arcisauskaite *et al.* have shown that for linear mercury containing molecules the difference between HF and DFT results increase with a more accurate treatment of relativistic corrections.[54]

In a recent review Jameson and de Dios highlighted that, despite the great success of global hybrid functionals, *e.g.*, B3LYP and PBE0, in predicting various molecular properties, they turned out not to be sufficiently flexible. They remarked the fact that it is usually not possible to find a unique constant for the amount of exact-exchange admixture that provides consistently high accuracy for different properties as well as for different classes of systems.[25] Some bibliography with examples for the performance of local hybrids in the description of NMR properties were provided. Admixtures of 40-45 % exact exchange (in contrast to the default 25 % in PBE0) were required to obtain theoretical chemical shifts in better agreement with experiments.[55]

The new KT1-3 functionals were published by Tozer group.[56–59] They developed functionals that were designed to provide high-quality shieldings. They showed that KT3 gives good quality ^{77}Se shielding tensors without including exchange functionals. One important point to mention here is the fact that the whole set of KT functionals were applied to the study of NMR shieldings of not so heavy atoms.

As a continuation of previous studies developed in our research group, concerning the analysis of the influence of electron correlation on NMR spectroscopic parameters together with its relationship with relativistic effects, we performed DFT calculations using DFT functionals as implemented in the DIRAC code. We have considered some functionals, like the exchange-correlation functional that are introduced in the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA),[60] and the popular semi-empirical hybrid

Becke3-Lee-Yang-Parr (B3LYP) functional.[61,62]

We will also show and analyze the new effect that becomes apparent when the molecular system under study do contain more than two vicinal heavy atoms, the so called heavy-atom effect on a vicinal heavy atom or HAVHA. We consider as vicinal two atoms that are connected by one bond.[33,34] There are other two relativistic effects on shieldings which are related with electronic effects due to the presence of heavy atoms: i) a heavy atom (relativistic) effect on a vicinal light atom, coined HALA,[63,64] and ii) a heavy-atom effect on the heavy-atom itself, coined HAHA.[65] The first effect is mostly due to spin-orbit interactions, and the second one do contain few new mechanisms that involve the electronic behaviour of core electrons. The electronic mechanisms involved in the HAVHA effect are treated in more detail in a submitted manuscript.[66] In this article we show the importance of such effect on magnetic shieldings in tin and lead tetrahalides family of compounds.

The structure of the article is as follows. We first give an schematic overview of the methods applied. Then we shall start presenting results calculations of tin and lead NMR shieldings. From such results together with experimental chemical shifts we obtained absolute magnetic shieldings of tin and lead applying the method proposed in Ref.[12] The likely relationship among electron correlation with relativistic effects and the HAVHA effect are analyzed in subsections. The last section is devoted to highlight the main findings.

Theoretical methods and computational details

We applied two different formalisms for calculating the NMR magnetic shieldings within a theoretical four-component relativistic level, being them the RelPPA approach and six different DFT functionals as implemented in DIRAC code, *e.g.* PBE0, B3LYP, BLYP, BP86, KT2 and KT3.

In the following section we give a very short introduction of both general formalisms.

Relativistic polarization propagator

Any static second-order molecular property can be studied with the relativistic (or nonrelativistic when only light atoms are involved) formalism of polarization propagators.[26,30,32] One of its advantages is the fact that NR values can be obtained directly from relativistic calculations making c, the velocity of light, scale to infinity.

The four-component relativistic expression of the NMR nuclear magnetic shielding of the nucleus M, σ_M is obtained as

$$\sigma_M = e^2 \left\langle\!\!\left\langle \frac{\alpha \times \mathbf{r_M}}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle\!\!\right\rangle \tag{1}$$

From this equation one realize that only one electronic mechanism is involved in the calculations. There is no formal distinction between dia and paramagnetic terms.[31]

All terms of Eq.(1) can be calculated at different levels of approach depending on the fluctuation potential, *i.e.* pure zeroth-order (PZOA), consistent first-order or random phase approximation (RPA), second-order level of approach (SOPPA), etc. The fluctuation potential represents the difference between the Coulomb and the self-consistent field (SCF) potential. This means that at RPA level of approach electron correlation is introduced to first order in the fluctuation potential, though the actual expressions are the same as that obtained by the coupled-Hartree-Fock scheme.[32] At the moment only the relativistic RPA level of approach, RelPPA-RPA was implemented in the DIRAC code.

Density functional theory and different functionals

When applying the Kohn-Sham density functional theory, DFT, one assumes that the exact universal exchange-correlation functional could not be known, and needs to be modeled based on different grounds. The usual prescription to do that was to design them to best reproduce experimental values of some properties. So a good performance of a particular functional for one property may not translate into a good performance for another.

In the generalized gradient approximation (GGA) the exchange-correlation functional is built including the density gradient, in addition to the electron density. Two commonly used GGA exchange-correlation functionals are the Becke-Lee-Yang-Parr (BLYP) functional[62,67] and the Perdew-Burke-Ernzerhof (PBE) functional.[60]

There are several exchange-correlation functionals. Nonempirical, like the KT1 of Keal and Tozer,[56] and semiempirical, like the KT2[56] and the B3LYP.[61,62] Tozer and coauthors also developed a new semiempirical generalized gradient, named KT3.[58]

The nonempirical PBE0 functional[68] is based on the PBE with 25 % of exact exchange.

DIRAC code uses standard nonrelativistic functionals. Various studies on electron kinematics, potential energy, bond lengths, vibrational frequencies and binding energies of diatomic molecules indicate that relativistic corrections to the exchange-correlation functionals have a negligible effect on spectroscopic constants, at least for non-heavy-atom-containing compounds.[69–71]

Early studies show that calculations performed with four-component DFT schemes reduce the shielding constants of heavy atoms in molecules. The conclusion that DFT gives lower shielding constants compared to HF has been reported previously.[39,50–54] In addition, hybrid functionals containing exact HF exchange lead to smaller reductions compared to GGA/BP86 and therefore give results which are in better agreement with HF, especially PBE0 which has a larger percentage of HF exchange than B3LYP.

Computational details

The geometries of the $XY_{4-n}Z_n$ (X = Sn, Pb; Y, Z = H, F, Cl, Br, I) and $PbH_{4-n}I_n$ (n = 0, 1, 2, 3, 4) model compounds were obtained from experimental measurements[72] or from calculations. In Table I of Supplementary material we especify which molecules were optimized.

The optimization of geometries were carried out at relativistic level with optimized Sadlej's[73] basis set, except for Pb atom where Faegri's basis set[74] were used, and Dirac-

Hartree-Fock Hamiltonian using the module OPTMIZE in the Dirac code.[35] The small component basis sets were obtained from the large component applying the restricted kinetic balance scheme (RKB).

For molecular systems containig a combination of Cl, Br and I atoms, the bond angles were assumed to be tetrahedral and X-Cl, X-Br and X-I distances are assumed to be the same as the corresponding distances in XCl$_4$, XBr$_4$ and XI$_4$ (X = Sn, Pb) respectively. The gauge origin was placed at the position of the center of the molecules for all tetrahedric compounds.

Calculations of nuclear magnetic shieldings were performed with the RelPPA formalism at RPA level of approach, which means consistent at first order in electron correlation. Calculations at DFT level of theory were performed using the DFT module in the DIRAC program. The functionals used were KT2, KT3, BP86, BLYP, B3LYP and PBE0. The last two ones are hybrid functionals including different amounts of HF exchange. The finite-size nucleus model of Gaussian type and uncontracted basis sets were used.

For property calculations, the small components basis sets were generated applying the unrestricted kinetic balance (UKB) prescription because it increases the size of the small component basis sets and so improves the description of the negative-energy space and the diamagnetic component.[33] The basis sets used were the same that were used in previous works.[12,34,75] Again, Sadlej's basis sets were chosen for all cases[73] except for Pb atom where Faegri's basis set[74] were used. Several more tight and diffuse Gaussian functions were included to get converged results. The scheme for including more Gaussian functions was the usual one: i) tight basis functions were added to s, p, d, f and g (only for Pb atom) blocks with exponents related as $\alpha_{i+1}/\alpha_i = 3$ from the largest exponent of each block; ii) diffuse basis functions were not necessary to include in shielding calculations in the d and f blocks because they don't change the shielding values significantly.

For nonrelativistic calculations (NR) the speed of light was taken as 10 times c ($c = 137.0359998$ a.u.) in order to obtain the NR limits that converge to the exact NR values

within the same scheme of calculation.

The whole basis sets with all previous considerations and all geometrical parameters used in calculations are given as Supporting Information.

Results and discussion

In order to learn about the performance of few different functionals for the calculation of σ, in 1 and 2 we show results obtained using the relativistic variant of the polarization propagator formalism, RelPPA at the RPA level of approach, and the DFT formalism with six different functionals which contain different amounts of electron exchange-correlation. In an earlier study we analyzed the performance of different functionals within the NR domain using Breit-Pauli-Perturbation-Theoy (BPPT) and comparing them with four component calculations.[39] We found that when the amount of HF exchange increases, the results become closer to the four-component ones, for $M(CH_3)_4$ (M = Zn, Cd, Hg) molecular systems.

We studied some model compounds that correspond to tetrahedric geometry: XY_4 (X = Sn, Pb; Y = H, F, Cl, Br, I) in relativistic and nonrelativistic domain. We obtained the absolute shieldings for Sn and Pb atoms by applying the previous scheme published in Ref.[12] The still open enquiry concerning the relationship between electron correlation and relativistic effects is addressed from an analysis of results from DFT, SOPPA and RelPPA-RPA methods. We treated molecular systems with more than two heavy elements. This gave us the opportunity to learn more on some features of the HAVHA effect.

Magnetic shieldings of SnX_4 and PbX_4 (X = H, F, Cl, Br and I)

In 1 we show that the nuclear magnetic shielding grows up when the substituent atom becomes heavier, as was shown earlier by other authors and by ourselves.[7,11,12] The NR values have an inverse halogen dependence, which is opposite to the experimental one. Still the whole set of DFT values and that obtained by the RelPPA formalism are not close each

other, though for SnI_4 they are.

The results obtained by Malkin and coauthors[13] using a similar approach are close to our DFT/BP86 ones. The small difference may be due to the fact that we use different codes, basis sets and geometries. On the other hand, the differences between RelPPA-RPA and DFT results increase with a more accurate treatment of relativistic corrections. The largest differences are thus observed in the four-component calculations.

The analysis of both terms, paramagnetic and diamagnetic, shows that the diamagnetic one has almost exactly the same value in both kind of methods (for all six functionals) for each molecular system. This means that such a component does not have a high dependence with electron correlation. This is in line with what is well known for light and medium size systems.[9,11,33] The diamagnetic component grows up when the molecular system become heavier, being the rate of increase, from SnH_4 to SnI_4, quite similar in both regimes, relativistic and NR and close to 15 %. This behaviour is little different from what was observed in Ref.[7] where its variation was found to be less than 1.5 %. The paramagnetic contribution is highly dependent on both, the number and type of substituent halogen atoms.

1 shows that BP86 values are close to BLYP ones, and KT2 and KT3 values are close to B3LYP and PBE0 ones. Henceforth we will consider only values calculated with PBE0, B3LYP and BLYP functionals and with this we will analyze the performance of DFT when the functionals include different amounts of HF exchange.

As observed in 1, results of calculations with three DFT functionals follow a similar behavior, and they are not close to the corresponding to the RelPPA-RPA ones. A remarkable result was obtained for SnI_4 where all numbers are close each other and they become positive; so they turned out to be of a diamagnetic-type. From Fig. 2 one can see that such a behavior is the same as the total value of $\sigma(Sn; SnX_4)$. What paramagnetic-like electronic mechanism is then responsible for such behavior? It would likely be related to the spin-orbit mechanism, the SO-FC mechanism.[34]

As observed in some other molecular systems, relativistic effects are different in their

Table 1: Nuclear magnetic shieldings of Sn. All values are given in ppm

Molecular system	Rel			NR		
	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
SnH$_4$ [a]						
RPA	4582.76	-456.62	4126.14	5098.65	-1818.49	3280.15
PBE0	4583.89	-691.20	3892.69	5098.78	-2001.07	3097.71
B3LYP	4583.95	-749.76	3834.19	5098.93	-2041.79	3057.14
BLYP	4584.00	-814.98	3769.02	5099.03	-2097.88	3001.15
BP86	4584.16	-802.45	3781.71	5099.09	-2092.92	3006.17
KT2	4590.51	-696.80	3893.71	5107.30	-1992.81	3114.48
KT3	4590.94	-718.78	3872.16	5107.25	-2010.50	3096.75
SnF$_4$						
RPA	4741.50	-376.98	4364.52	5265.63	-1810.21	3455.42
PBE0	4742.29	-829.44	3912.85	5266.70	-2158.34	3108.37
B3LYP	4742.38	-871.07	3871.31	5266.77	-2194.35	3072.41
BLYP	4742.58	-1004.24	3738.34	5267.20	-2291.30	2975.90
BP86	4742.76	-1018.04	3724.72	5267.44	-2302.59	2964.85
KT2	4749.24	-923.50	3825.74	5266.20	-2199.57	3066.62
KT3	4749.48	-864.46	3885.02	5275.42	-2158.09	3117.33
SnCl$_4$ [b]						
RPA	4833.24	-844.71	3988.53	5353.51	-2381.14	2972.37
PBE0	4833.99	-1285.81	3548.18	5355.11	-2738.06	2617.05
B3LYP	4834.11	-1344.80	3489.31	5354.46	-2797.57	2556.89
BLYP	4834.26	-1449.84	3384.42	5354.81	-2884.06	2470.75
BP86	4834.41	-1446.26	3388.15	5350.04	-2847.11	2502.93
KT2	4840.88	-1334.96	3505.91	5358.23	-2731.56	2626.67
KT3	4841.11	-1287.54	3553.57	5358.14	-2673.74	2684.41
SnBr$_4$ [c]						
RPA	5084.82	-604.10	4480.72	5602.91	-2760.61	2842.30
PBE0	5085.48	-859.77	4225.71	5603.60	-3119.85	2483.74
B3LYP	5085.61	-843.80	4241.81	5603.65	-3206.94	2396.71
BLYP	5085.76	-841.60	4244.15	5603.89	-3292.84	2311.05
BP86	5085.89	-865.20	4220.69	5350.04	-2847.11	2502.93
KT2	5092.36	-830.92	4261.44	5612.28	-3138.39	2473.88
KT3	5092.62	-812.54	4280.08	5612.21	-3090.84	2521.37
SnI$_4$						
RPA	5287.04	225.83	5512.86	5810.00	-3121.43	2688.57
PBE0	5287.58	198.73	5486.32	5810.02	-3421.48	2388.54
B3LYP	5287.66	251.80	5539.46	5810.16	-3583.94	2226.22
BLYP	5287.77	276.84	5564.61	5810.38	-3661.84	2148.54
BP86	5287.89	257.79	5545.68	5810.49	-3557.76	2252.73
KT2	5294.35	277.43	5571.77	5818.69	-3417.22	2401.48
KT3	5294.62	246.37	5540.99	5818.64	-3382.63	2436.01

[a]: Other theoretical results of σ^t: 3039 ppm taken from Ref.,[8] 3381 ppm taken from Ref.,[11] 4018 taken from Ref.[10] (with an estimated error of 100 ppm[76]), 3815 ppm calculated with BP86 in Ref.[13]
[b]: Other theoretical results of σ^t: 2960 ppm taken from Ref.,[11] 3457 ppm calculated with BP86 in Ref.[13]
[c]: Other theoretical result of σ^t: 3723 ppm taken from Ref.[11]
[d]: Other theoretical result of σ^t: 4942 taken from Ref.[11]

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absolute values and behavior, for both terms of the theoretical shielding.[32] The diamagnetic contribution becomes more negative and the paramagnetic one becomes more positive, when relativistic effects are included. This means that relativistic effects make the diamagnetic contributions "more paramagnetic" and the other way around for the paramagnetic contributions. The amount of such effects depends on the number and weight of the substituents. For SnX_4 model compounds, the total relativistic effect $(\sigma^R - \sigma^{NR})/\sigma^{NR})$ is of 26 % when X = H, F. For X = Cl it is 34 %; for X = Br, it is 58 % and for X = I it is 105 %.

Relativistic effects have almost the same values for the diamagnetic component in the whole SnX_4 serie, but the paramagnetic component strongly depends on the heavy atom substituent.

Table 1 also shows the dependence of paramagnetic component with the electronic correlation, though for heavy molecular systems such a dependency diminishes quite a bit. This may indicate that one could calculate nuclear magnetic shieldings for heavy systems in a computationally cheaper way, using DFT methodology (B3LYP or PBE0 functionals) to obtain reliable results. We shall discuss in Section how important is the relationship between relativistic effects and electron correlation, for an accurate reproduction of experimental results.

Previous calculations of relativistic effects on $\sigma(Sn)$ of SnX_4 molecular systems have a different rate of increase. Our results are closer, in percentage, to that of Ref.,[11] being them of 20.5, 25.5, 36.6 and 51.2 % in our RelPPA-RPA calculations and for X = H, Cl, Br and I (14.7, 22.1, 42.1 and 61.0 % in Ref.[11]). Such a percentage is quite different in Ref.:[7] 0.3, 1.4, 13.8 and 36.2 % respectively. In these percentages the relativistic value was taken as the reference.

The whole analysis given above is even more enforced by the results shown in 2. There we see a higher dependence of the paramagnetic contributions to relativistic effects. Furthermore the diamagnetic component increases its value only 8.4 % from PbH_4 to PbI_4, and they seem to be quite independent of the electron correlation, even for the heaviest molecular systems.

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Table 2: Nuclear magnetic shielding of Pb in PbX_4 (X = H, F, Cl, Br and I). All values in ppm

Molecular system	Rel			NR		
	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
PbH_4 [a]						
RPA	8286.99	4644.85	12931.84	10040.66	-3157.53	6883.13
PBE0	8288.56	3831.17	12119.74	10040.65	-3437.31	6603.33
B3LYP	8288.70	3712.16	12000.86	10040.57	-3492.62	6547.95
BLYP	8288.87	3407.68	11696.55	10040.55	-3583.46	6457.09
PbF_4						
RPA	8438.04	6107.84	14545.88	10192.06	-2771.55	7420.51
PBE0	8440.00	3902.14	12342.14	10192.30	-3387.66	6804.64
B3LYP	8440.19	3757.84	12198.03	10192.24	-3447.10	6745.14
BLYP	8440.55	3048.83	11489.38	10192.36	-3625.07	6567.28
$PbCl_4$						
RPA	8533.93	5168.68	13702.60	10288.71	-3743.46	6545.25
PBE0	8535.59	2964.53	11500.12	10288.09	-4437.68	5850.41
B3LYP	8535.80	2818.09	11353.89	10288.88	-4489.55	5799.33
BLYP	8536.04	2236.28	10772.33	10288.98	-4641.50	5647.48
$PbBr_4$						
RPA	8784.20	7021.47	15805.67	10540.26	-4321.57	6218.69
PBE0	8786.04	5623.87	14409.91	10540.62	-4954.95	5585.67
B3LYP	8785.86	5693.68	14479.55	10540.59	-5068.61	5471.98
BLYP	8786.11	5506.01	14292.12	10540.70	-5223.55	5317.15
PbI_4						
RPA	8984.45	9654.45	18638.90	10744.53	-4740.08	6004.45
PBE0	8986.00	9018.65	18004.65	10744.91	-5343.21	5401.70
B3LYP	8985.87	9021.20	18007.07	10744.89	-5488.57	5256.32
BLYP	8986.08	8583.18	17569.26	10745.00	-5625.77	5119.23

[a] Few results taken from Ref.:[10] σ^{Rel} = 10091.51 ppm and σ^{NR} = 6965.05 ppm. It is known that the perturbational approach underestimates relativistic effects for elements of row 6th.

The paramagnetic component increases its value very much when the substituents of the molecular models become heavier. For PbH_4, $\sigma^p(Pb) = 4644.85$ ppm, being $\sigma^p(Pb) = 9654.45$ ppm for PbI_4. This corresponds to an increase of 107 % from the lightest to the heaviest molecular system. On the other hand, we can see also in Table 2 that the dependence of the shieldings with the electron correlation decreases when the molecular system becomes heavier. For PbH_4 the difference between RelPPA-RPA and BLYP (0 % HF exchange) is 27 %, but for PbI_4 such a difference is only 11 %. In addition to this result we also observe that, the largest difference on the total nuclear magnetic shielding of the heaviest molecule is of only 5.7 % between RelPPA-RPA and DFT (BLYP) values.

On the other hand, the compared the running time for the first step of our calculations (wave function) and observe that they are close among DFT and RelPPA methods. Some times this is not the case though for shielding calculations, the DFT running times are smaller than the corresponding for RelPPA-RPA. Such a difference depends on the functional used in the calculations. For our heaviest systems, like SnI_4 and PbI_4, when B3LYP is the chosen functional, its running time for shielding calculations are 40% and 60% smaller than those for RelPPA-RPA, respectively. If we chose the BLYP functional the running time is 90% smaller than that of RelPPA-RPA. This means that one can get a large saving of computational time when using such functionals though they give qualitative or good tendences for the shieldings.

The main results of the analysis given above become more apparent in Figs. 1-4. They show that, the calculations of σ with different methods converge to closer values for tin atom, and to less closer values for lead atom when the four substituents belong to the 4th or the 5th row of the Periodic Table. For the paramagnetic component such a pattern is quite similar because, as was mentioned above, the diamagnetic component has a tenous and also small dependence with the electron correlation, even for the heaviest molecular system.

In Fig. 5 we show the NR limit of paramagnetic components. We observe that a similar mechanism does appear and so the physics behind it seems to be the same in all cases, as was also observed for atoms belonging to the same row of the Periodic Table (Xe, I, Te,

Sb and Sn).[32] This means that relativistic effects on σ^p are such that the paramagnetic contribution become more positive when the system becomes heavier. Figure 5 shows the relativistic value of $\sigma^p(\text{Pb}; \text{PbI}_4) > \sigma^p(\text{Pb}; \text{PbH}_4)$, and $\sigma^p(\text{Sn}; \text{SnI}_4) > \sigma^p(\text{Sn}; \text{SnH}_4)$. On the other hand the NR behavior is such that its tendence is opposite. So, being the value of σ^p of the heaviest molecule the most paramagnetic within the NR regime, it becomes the most diamagnetic within the relativistic regime.

There is still a difference among the values of σ^p obtained by DFT functionals and those obtained by RelPPA-RPA. The former are unable to properly reproduce the experimental chemical shifts, and the differences arise from the paramagnetic terms as can be seen in Tables 1 and 2.

In the DFT module of the DIRAC code, standard non-relativistic functionals are used. This option was based on previous studies [17, 18, 19] which indicated that relativistic corrections to the exchange-correlation functionals have a negligible effect on spectroscopic constants that do not depend on the core.

In the case of NMR magnetic shieldings there are different core-dependent electronic mechanisms which are responsible of important relativistic effects. They should be properly incorporated in the functionals, and as mentioned they are not still included in the implementation.

Absolute values for references of Sn and Pb magnetic shieldings

In an earlier paper we presented an scheme from which the reference value of the absolute value of $\sigma(\text{Sn})$ in the tetramethyltin compound, $\text{Sn}(\text{CH}_3)_4$ can be obtained.[12] It consider a combination of theoretical calculations of magnetic shieldings with experimental chemical shifts for the tin atom in different molecular systems. In the present article, we show an improvement of such study including twice more molecules, and so a more precise average value is then obtained.

The chemical shift of a nucleus is related with the difference of magnetic shieldings in

two different molecular environments; one of them is taken as a reference

$$\delta^{theo} = \frac{\sigma^{ref} - \sigma}{1 - \sigma^{ref}} \qquad (2)$$

Chemical shifts are then theoretically obtained by the calculation of σ of a given atom in two different electronic environments. The main difficulty is to obtain reliable reference values. For the most accurate reference values it is necessary a method that properly include relativistic and electron correlation effects. At the moment such a method does not exist. So we proposed one mixed scheme from theoretical and experimental results.

From the last equation, and considering experimental instead of theoretical chemical shifts, the reference shieldings are calculated as

$$\sigma^{ref} = \frac{\delta^{theo} + \sigma}{1 + \delta^{theo}}$$

In the case of $\sigma(\text{Sn})$ we considered the following expression

$$\sigma^{ref}[Sn; Sn(CH_3)_4] = \frac{\delta^{exp} + \sigma(Sn)}{1 + \delta^{exp}} \qquad (3)$$

Applying the last equation we are then able to calculate $\sigma^{ref}(\text{Sn})$ in many molecular systems at four-component relativistic level. There exist in the literature a great amount of experimental data for tin atom-containing molecules, but in such molecular systems theoretical calculations at four-component relativistic level are very expensive and sometimes it is impossible to compute them.

Absolute value for $\sigma^{ref}(\text{Sn})$

In 3 we show results of calculations of $\sigma^{ref}(\text{Sn})$ with different DFT functionals and RelPPA-RPA method, for fifteen different molecular systems. From these results the values of reference are obtained applying Eq. (3). Then the RelPPA-RPA average value, $\sigma[\text{Sn}(\text{CH}_3)_4]$

= 3864.11 ± 20.05 ppm (0.52 %) is obtained. We found a very small dispersion, meaning a reliable average value. Our new value is close to that obtained previously.[12] By applying the same procedure to calculations with the three functionals we obtained the following values for $\sigma^{ref}[\mathrm{Sn(CH_3)_4}]$: 1) PBE0, 3608.98 ± 109.10 ppm (3.02 %); 2) B3LYP, 3627.69 ± 142.40 ppm (3.93 %) and 3) BLYP, 3609.06 ± 178.72 ppm (4.95 %). These results show that the RelPPA-RPA $\sigma^{ref}(\mathrm{Sn})$ has the smallest dispersion.

Table 3: Experimental chemical shift, magnetic shieldings and reference values of Sn atom in a serie of heavy atom containing molecules

		RPA		PBE0		B3LYP		BLYP	
Molecule	δ^{exp}	σ	$\sigma[\mathrm{SnMe_4}]$	σ	$\sigma[\mathrm{SnMe_4}]$	σ	$\sigma[\mathrm{SnMe_4}]$	σ	$\sigma[\mathrm{SnMe_4}]$
$\mathrm{SnCl_4}$	-150	3988.53	3839.11	3548.18	3398.69	3489.31	3339.81	3384.42	3234.91
$\mathrm{SnCl_3Br}$	-263	4116.30	3854.31	3715.32	3453.22	3678.10	3416.00	3601.17	3339.05
$\mathrm{SnCl_2Br_2}$	-385	4238.81	3855.29	3885.38	3501.73	3868.01	3484.35	3818.28	3434.60
$\mathrm{SnClBr_3}$	-508	4361.01	3854.97	4056.08	3549.88	4056.54	3550.34	4033.23	3527.02
$\mathrm{SnCl_3I}$	-557	4438.04	3883.20	4072.09	3517.05	4071.76	3516.72	4015.42	3460.35
$\mathrm{SnBr_4}$	-638	4480.72	3845.72	4225.71	3590.00	4241.81	3606.11	4244.15	3608.45
$\mathrm{SnCl_2BrI}$	-672	4554.98	3885.59	4240.05	3570.45	4254.93	3585.34	4222.63	3553.02
$\mathrm{SnClBr_2I}$	-796	4673.13	3880.22	4406.92	3613.80	4434.77	3641.67	4425.71	3632.60
$\mathrm{SnBr_3I}$	-916	4785.10	3872.65	4571.50	3658.85	4610.13	3697.52	4623.65	3711.05
$\mathrm{SnCl_2I_2}$	-955	4844.11	3892.83	4580.10	3628.57	4616.87	3665.37	4597.10	3645.58
$\mathrm{SnClBrI_2}$	-1068	4952.19	3888.34	4740.30	3676.23	4785.42	3721.39	4786.09	3722.07
$\mathrm{SnBr_2I_2}$	-1187	5054.16	3871.76	4896.53	3713.94	4947.89	3765.69	4968.43	3785.92
$\mathrm{SnClI_3}$	-1347	5206.40	3864.59	5054.67	3712.67	5108.35	3766.42	5115.02	3773.10
$\mathrm{SnBrI_3}$	-1447	5296.20	3854.78	5199.46	3757.90	5255.13	3813.65	5279.37	3837.92
$\mathrm{SnI_4}$	-1701	5512.86	3818.36	5486.32	3791.77	5539.46	3845.00	5564.61	3870.19

[a]: The reference values are obtained applying Eq. 3 for each scheme, DFT and RelPPA-RPA.

We are able now to go one step further and calculate again chemical shifts within the RelPPA-RPA level but using the reference value $\sigma^{ref}(\mathrm{Sn})$ computed above. In 4 we show results of calculations of $\sigma^{ref}(\mathrm{Sn})$ in the same molecular systems at RelPPA-RPA level and also with the different DFT functionals mentioned above.

A good fitting between theoretical and experimental values for the tin chemical shift, $\delta(\mathrm{Sn})$ is obtained at RelPPA-RPA level. The largest difference is only 46 ppm for $\mathrm{SnI_4}$. For $\mathrm{SnClI_3}$ such a difference is close to 0. The average deviation over all molecular systems is only 17 ppm. In 6 we show the excellent agreement with experimental values that arises

when we use the calculated $\sigma^{ref}(\text{Sn})$ with RelPPA-RPA as the reference value.

As observed in 4 the DFT chemical shifts are not in good agreement with experimental values for light systems, although its performance is improved when the weight of the molecules grows up, as expected from the analysis given in the last Section. For the lightest molecule, SnCl$_4$, the DFT chemical shift is positive and the experimental one is negative. Indeed, there is a large difference between all values obtained with the DFT functionals. The performance of BLYP is quite poor and that shows an important electron correlation effect. For heavier systems the performance of DFT calculations is improved and the results obtained with different functionals are closer each other, and to experiments. In the case of heavier molecular systems the calculated chemical shifts are in good agreement with experiments, and the differences between them are very small.

Table 4: Magnetic shieldings and chemical shifts of tin atom with respect to the reference value

molecule	RPA	δ	PBE0	δ	B3LYP	δ	BLYP	δ	δ^{exp}
$SnCl_4$	3988.53	-124.90	3548.18	317.16	3489.31	376.25	3384.42	481.55	-150
$SnCl_3Br$	4116.30	-253.17	3715.32	149.36	3678.10	186.73	3601.17	263.96	-263
$SnCl_2Br_2$	4238.81	-376.15	3885.38	-21.35	3868.01	-3.92	3818.28	46.01	-385
$SnClBr_3$	4361.01	-498.83	4056.08	-192.71	4056.54	-193.18	4033.23	-169.78	-508
$SnCl_3I$	4438.04	-576.16	4072.09	-208.79	4071.76	-208.46	4015.42	-151.90	-557
$SnBr_4$	4480.72	-619.00	4225.71	-363.00	4241.81	-379.17	4244.15	-381.51	-638
$SnCl_2BrI$	4554.98	-693.55	4240.05	-377.54	4254.93	-392.34	4222.63	-359.91	-672
$SnClBr_2I$	4673.13	-812.16	4406.92	-544.92	4434.77	-572.87	4425.71	-563.78	-796
$SnBr_3I$	4785.10	-924.56	4571.50	-710.13	4610.13	-748.91	4623.65	-762.49	-916
$SnCl_2I_2$	4844.11	-983.80	4580.10	-718.77	4616.87	-755.68	4597.10	-735.83	-955
$SnClBrI_2$	4952.19	-1092.30	4740.30	-879.59	4785.42	-924.88	4786.09	-925.56	-1068
$SnBr_2I_2$	5054.16	-1194.67	4896.53	-1036.42	4947.89	-1087.98	4968.43	-1108.60	-1187
$SnClI_3$	5206.40	-1347.50	5054.67	-1195.18	5108.35	-1249.07	5115.02	-1255.76	-1347
$SnBrI_3$	5296.20	-1437.65	5199.46	-1340.53	5255.13	-1396.42	5279.37	-1420.75	-1447
SnI_4	5512.86	-1655.15	5486.32	-1628.50	5539.46	-1681.85	5564.61	-1707.10	-1701

[a]: Experimental data taken from Ref. [77]
[b]: Experimental data taken from Ref. [78,79]

These results are related with previous findings of Bagno *et al.*[11] For the family of molecules Me$_{4n}$SnX_n, upon increasing the number of halogen atoms the spin-orbit contribution becomes more important, being the highest that for the heaviest halogens. These authors also mentioned that the results of nonrelativistic calculations of tin chemical shifts

are in very good agreement with those obtained at the relativistic ZORA-SC level.

From the analysis given above (see also 6), we can say that the results obtained with RPPA formalism at RPA level of approach can be taken as benchmark relativistic calculations for the absolute nuclear magnetic shielding, as well as chemical shift, even for very heavy molecular systems.

In 7 we show the behavior of different theoretical chemical shift as compared with experimental chemical shift. In this case theoretical chemical shifts were obtained from Eq. 2 though considering the reference value obtained with each theoretical method. We observe that a different slope appears for the results of three DFT functionals as compared with experimental and RelPPA-RPA method.

Absolute value for σ^{ref}(Pb)

To our knowledge there are no experimental values for σ(Pb) of the model compounds analyzed here. Based on previous experimental values, Mitchell has suggested the following relationship between the chemical shift of four-coordinated Sn and Pb atoms:[16]

δ^{207}Pb[IV] = 2.424 $\cdot$ δ^{119}Sn[IV] + 74.8 (ppm)

Applying this relationship and using our results of δ^{119}Sn[IV] taken from 4, we are now able to obtain δ(Pb) theoretically in some $PbY_{4-n}Z_n$ (Y, Z = F, Cl, Br, I; $n = 0, ..., 4$) model compounds. Then the reference value for the shielding of Pb in the reference compound can be obtained from the expression

$$\sigma^{ref}[Pb; Pb(CH_3)_4] = \frac{\delta^{exp} + \sigma(Pb)}{1 + \delta^{exp}} \tag{4}$$

They are shown in 5.

From such twelve values one get an average, σ^{ref}(Pb) = 14475.1 ppm $\pm$ 500.7 ppm (3.5%).

We can now compare our results, calculated applying Eq. 2, with few previous one. Our

Table 5: Chemical shifts and reference values of Pb atom. All values in ppm

Molecule	δ	σ^{ref}	Molecule	δ	σ^{ref}
$PbCl_4$	-288.8	13417.7	$PbCl_3I$	-1275.4	14672.7
$PbCl_3Br$	-562.7	14309.3	$PbCl_2I_2$	-2240.1	15034.9
$PbCl_2Br_2$	-858.4	14023.3	$PbBr_2I_2$	-2802.5	14939.0
$PbClBr_3$	-1156.6	15366.2	$PbClI_3$	-3178.2	14951.9
$PbBr_4$	-1471.7	14355.1	$PbBrI_3$	-3432.7	14857.1
$PbBr_3I$	-2145.6	14819.0	PbI_4	-4048.4	14649.8

values for the chemical shifts of Pb in PbX_4 model compounds when X = Cl, Br and I are

772 ppm, -1331 ppm and -4164 ppm respectively, which are quite differente of that published

in Ref.[80] -721 ppm, -4825 ppm and -7241 ppm respectively. The difference is of $\simeq$ 3000 ppm

for the heavier systems.

Electron correlation and relativistic effects

There is an interesting long-standing challenge concerning the likely relationship between

electron correlation and relativistic effects. Are both effects independent each other? In this

section we will give few insights that may help to answer such a question.

As shown in 1, considering the difference among DFT and RelPPA-RPA values as a

gross measure of the electron correlation, EC, contribution one observes that such a measure

has different behavior depending on what regime one is considering, *i.e.* relativistic or NR.

Within the NR regime the EC is quite stable (among 10-20 %) for all functionals though

within the relativistic regime this pattern is modified: $\cong$ 40 % for X = H, and Cl; $\cong$ 60 %

for X = F; $\cong$ 30 % for X = Br and 13 % for X = I.

On the other hand relativistic effects, RE, within RelPPA at RPA level are $\cong$ 75 % for

σ^p when X = H, F and Br. For X = Cl the percentage of such effect goes down to $\cong$ 65

% but for X = I the RE becomes higher than 100 % (107 %). In the whole set of SnX_4

(X = H, F, Cl and Br) molecules the RE obtained from DFT functionals are smaller than

that from the RPA ones. Results of calculations for the system with X = I give a different

behavior, meaning that RE in both methodologies would be quite similar.

So, the SnI_4 is the unique compound of the serie analyzed here for which EC effects ($\simeq$ 10 %) at both levels, R and NR, and the amount of RE calculated by RelPPA-RPA and all functionals give quite similar numbers ($\simeq$ 107 %) for the paramagnetic component. This last compound is the only one for which experimental and theoretical results are close each other.

In 8 we show the behavior of the difference among NR values of typical DFT functionals (including SOPPA in this case) and the Non-RelPPA-RPA values. In 9 we do it for four-component DFT and RelPPA-RPA. Within the NR regime all differences follow the same pattern being the Non-RelSOPPA values closer to the Non-RelPPA-RPA ones. Within the relativistic regime the behavior is similar for the lightest substituents though it changes drastically when the halogen substituents becomes heavier. Specially for $X = I$ the difference among DFT and RelPPA-RPA are very small.

This fact may explain why for such iodine containing molecules we obtained the best fitting between theoretical and experimental results. σ^p is the term which is most important to be properly calculated for getting accurate theoretical results. Its behavior defines whether experimental and theoretical methods will fit each other more closely. One should be aware that the relativistic functionals does not include the whole branch of relativistic effects on their expressions.

The HAVHA effect

From results presented in 2 and 6 we can analyze the percentage of relativistic effects, $\%RE$ on $\sigma(\mathrm{Pb})$ in the usual way[34]

$$\%RE\sigma = \frac{\sigma^R - \sigma^{NR}}{\sigma^{NR}} \tag{5}$$

Then we obtain the following values for $\sigma(\mathrm{Pb};\ \mathrm{Pb}X_4)$: 87.88 %, 96.02 %, 121.84 %, 154.16 % and 210.42 % when $X = $ H, F, Cl, Br and I, respectively.

Table 6: Nuclear magnetic shielding of Pb for PbH$_{4-n}$I$_n$ with n = 0-4

Molecular system	Rel			NR		
	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
PbH$_4$						
RPA	8286.99	4644.85	12931.84	10040.66	-3157.53	6883.13
PBE0	8288.56	3831.17	12119.74	10040.65	-3437.31	6603.33
B3LYP	8288.70	3712.16	12000.86	10040.57	-3492.62	6547.95
BLYP	8288.87	3407.68	11696.55	10040.55	-3583.46	6457.09
PbH$_3$I						
RPA	8643.41	4798.83	13262.24	10218.80	-3607.44	6611.36
PBE0	8464.50	3711.69	12176.19	10218.49	-4040.29	6178.20
B3LYP	8464.69	3655.19	12119.89	10218.43	-4115.71	6102.72
BLYP	8464.90	3338.78	11803.68	10218.45	-4245.90	5972.55
PbH$_2$I$_2$						
RPA	8633.31	5499.68	14132.99	10390.31	-4021.61	6368.70
PBE0	8634.75	4198.56	12833.31	10390.51	-4585.05	5805.46
B3LYP	8634.96	4231.83	12866.80	10390.47	-4688.03	5702.44
BLYP	8635.18	3924.71	12559.90	10390.52	-4857.79	5532.73
PbHI$_3$						
RPA	8803.25	7363.13	16166.38	10561.66	-4409.86	6151.80
PBE0	8804.57	6106.14	14910.71	10561.96	-5054.58	5507.38
B3LYP	8804.75	6181.91	14986.66	10561.93	-5186.16	5375.77
BLYP	8804.96	5834.30	14639.26	10562.01	-5366.96	5195.06
PbI$_4$						
RPA	8984.45	9654.45	18638.90	10744.53	-4740.08	6004.45
PBE0	8986.00	9018.65	18004.65	10744.91	-5343.21	5401.70
B3LYP	8985.87	9021.20	18007.07	10744.89	-5488.57	5256.32
BLYP	8986.08	8583.18	17569.26	10745.00	-5625.77	5119.23

In the same manner, the HAVHA effect is related with the weight of the halogen substituents. For the set of molecules analized here such effect is calculated as the difference $^{\%RE}\sigma(\text{Pb; Pb}X_4)$ - $^{\%RE}\sigma(\text{Pb; PbH}_4)$ or $^{\%RE}\sigma(\text{Pb; PbH}_{4-n}\text{I}_n)$ - $^{\%RE}\sigma(\text{Pb; PbH}_4)$

In the first set of molecules, $^{HAVHA}\sigma(\text{Pb; Pb}X_4) = 8.14\%, 33.96\%, 66.28\%$ and 122.54% for $X = $ F, Cl, Br and I, respectively. Such a variation is mainly due to the paramagnetic component. The values of the diamagnetic ones vary in a very small percentage (close to 8.4%) from the lightest (PbH_4) to the heaviest (PbI_4) system. On the other hand, the paramagnetic component increase its value more than twice for the same set of compounds.

The same analysis can be performed for the set of $\text{PbH}_{4-n}\text{I}_n$ (n = 0-4) molecules. When n = 1, $^{\%RE}\sigma(\text{Pb}) = 104.01\%$, and $^{HAVHA}\sigma(\text{Pb}) = 16.13\%$. From these results it is apparent that the effect produced by four iodine atoms on the lead shielding is not four times the effect produced by only one iodine atom. This is confirmed from the analysis of the other members of the $\text{PbH}_{4-n}\text{I}_n$ serie.

For n = 2, $^{\%RE}\sigma(\text{Pb}) = 121.91$ % and $^{HAVHA}\sigma(\text{Pb}) = 34.03$ %. Finally for n = 3, $^{\%RE}\sigma(\text{Pb}) = 162.79$ % and $^{HAVHA}\sigma(\text{Pb}) = 74.91$ %. The values given above show that the addition of iodine atoms on $\text{PbH}_{4-n}\text{I}_n$ model compounds does not produce additive effects on the nuclear magnetic shielding of the central Pb atom.

In 10 we show the amount of relativistic effects (in percentage) for the $\text{SnH}_{4-n}X_n$ ($X = $ H, F, Cl, Br and I) series. It is seen that such effects depend on the type of halogen substituent and its number. The largest effects are obtained for $X = $ I. The dependence with the number of halogen substituents is not the same for the different halogen. The relativistic effects depend in very different way with the number and type of halogen substituents.

The behavior of the HAVHA effect as a function of the number of iodine atoms on the nuclear magnetic shielding, $\sigma(\text{Pb})$ for the $\text{PbH}_{4-n}\text{I}_n$ family of compounds is shown in 11. There is no a linear relationship between the number of iodine atoms and the magnitud of the HAVHA effect. In other words, those effects are non additive. The actual relationship is set by a quadratic function as observed in 11.

Concluding remarks

Given the still large differences among the lately proposed (published) absolute values for the NMR shielding of tin and lead containing molecules, one needs to search for more accurate theoretical methods. One also needs to obtain their reference values, meaning the NMR shielding of tin and lead in tetramethyltin and tetramethyllead molecules. The search for such theoretical NMR shieldings needs also to include the likely dependence of such spectroscopic parameter with both effects, relativistic and electron correlation. One also needs to search for its mutual dependence.

We have undertaken during the last few years a systematic study, based on the RelPPA formalism at RPA level of approach, to establish a reliable range of values for the shielding of heavy atoms in molecules that contain more than two heavy atoms. This search drove us to propose a new effect, the heavy atom effect on vicinal heavy atom, HAVHA, being vicinal two atoms that are connected by one bond. We have studied molecules belonging to the families $XH_{4-n}Y_n$, $XY_{4-n}Z_n$ (X = C, Ge, Si, Sn and Pb; Y = H, F, Cl, Br and I; Z = F, Cl, Br and I). So we considered the halogen as the only type of substituents.

The aims of this article were focused to answer the following enquiries:

i) What is the performance of different four-component DFT functionals, as implemented in the DIRAC code, in reproducing NMR magnetic shieldings of tin and lead containing molecules of the type Sn/PbX_4 (X = H, F, Cl, Br and I) and PbI$_{4-n}$H$_n$ (n = 0,...4)?

ii) Which is the most accurate value (or short range of values) of σ^{ref}[Sn/Pb; Sn/PbCH$_3$)$_4$] to consider as the reference for the shieldings of tin and lead atoms?

iii) What about the chemical shift of such shieldings in different halogen substitued tin and lead molecular systems?

iv) What kind of relationship is expected to relate relativistic and electron correlation effects? Are they mutually dependent?

v) How large are the HAVHA effects on the set of molecules studied here?

We performed state of the art calculations with different four-component DFT functionals

and RelPPA at RPA level of approach as are implemented in the DIRAC code. Large enough basis set were used to get as converged results as possible. A previously proposed scheme (it applies experimental chemical shifts and theoretical magnetic shieldings) was used to obtain the value of reference for $\sigma(\text{Sn/Pb})$ in the usual tetramethyltin/lead compounds.

We want to highlight the following findings:

1. The RelPPA-RPA scheme gives reliable results as compared with experiments. The pattern of chemical shifts is better followed when done with such approach instead of DFT. We argue that the DFT functionals should include the different electronic mechanisms that take account of relativistic effects. In other words, the actual different functionals as implemented in computational codes does not properly include relativistic effects. This fact should be corrected, specially when studying magnetic properties in heavy-atom containing molecules.

2. The best reference value obtained with the RelPPA-RPA approach for the shielding of Sn and Pb are:

$\sigma[\text{Sn}; \text{Sn}(\text{CH}_3)_4] = 3864.11 \pm 20.05$ ppm (0.5 %)

$\sigma[\text{Pb}; \text{Pb}(\text{CH}_3)_4] = 14475.1$ ppm ± 500.7 ppm (3.5%)

3. There is a new and consistent pattern for the paramagnetic behavior of $\sigma(\text{Sn/Pb})$ of XY_4 ($X = $ Sn, Pb; $Y = $ H, I) molecules. The NR most paramagnetic contribution becomes the relativistic most diamagnetic one. It comes from the heaviest system analyzed. So relativistic effects are the largest for the heaviest systems though it invert the type of contribution to the shielding: being paramagnetic within the NR domain it becomes more diamagnetic (or diamagnetic) within the relativistic regime.

4. There seems to be a non-linear dependence among relativistic and electron correlation effects. They need to be studied more deeply. There are different type of dependences when substituents are lighter than iodine in halogen substitued XY_4 ($X = $ Sn, Pb; $Y = $ H, I) systems.

5. The HAVHA effect is mostly due to paramagnetic-like contributions. It has a quadratic

dependence with the number of iodine atoms in $Sn(Pb)H_nI_{4-n}$ model compounds.

Acknowledgement

References

(1) Jackowski, K.; M.Jaszunski,; Wilczek, M. *J. Phys. Chem. A* **2010**, *114*, 2471.

(2) Jaszunski, M.; Antusek, A.; Garbacz, P.; Jackowski, K.; Makulski, W.; Wilczek, M. *Prog NMR Spectr.* **2012**, *67*, 49.

(3) Contreras, R. H.; Ferraro, M. B.; de Azúa, M. C. R.; Aucar, G. A. In *High Resolution NMR Spectroscopy: Understanding Molecules and their Electronic Structures*; Contreras, R., Ed.; Elsevier: Amsterdam, 2013; Chapter 2.

(4) Flygare, W. H. *J. Chem. Phys.* **1964**, *41*, 793.

(5) Bryce, D. L.; Wasylishen, R. E. *J. Molec. Struct.* **2002**, *602*, 463.

(6) Aucar, I. A.; Gomez, S. S.; de Azúa, M. C. R.; Giribet, C. G. *J. Chem. Phys.* **2012**, *136*, 204119.

(7) Kaneko, H.; Hada, M.; Nakajima, T.; Nakatsuji, H. *Chem. Phys. Lett.* **1996**, *261*, 1.

(8) Vivas-Reyes, R.; Proft, F. D.; Biesemans, M.; Willem, R.; Geerlings, P. *J. Phys. Chem. A* **2002**, *106*, 2753.

(9) Avalle, P.; Harris, R. K.; Karadakov, P.; Wilson, P. *J. Phys. Chem. Chem. Phys.* **2002**, *4*, 5925.

(10) Jaszunski, M.; Ruud, K. *Molec. Phys.* **2006**, *104*, 2139.

(11) Bagno, A.; Casella, G.; Saielli, G. *J. Chem. Theory Comput.* **2006**, *2*, 37.

(12) Maldonado, A. F.; Gimenez, C. A.; Aucar, G. A. *Chem. Phys.* **2012**, *395*, 75.

(13) Malkin, E.; Komorovsky, S.; Repisky, M.; Demissie, T.; Ruud, K. *J. Phys. Chem. Let.* **2013**, *4*, 459.

(14) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653.

(15) Makulski, W. *J. of Molec. Structure* **2012**, *45*, 1017.

(16) Mitchell, T. N. *J. of Organomet. Chem.* **1983**, *255*, 279.

(17) Watkinson, P. J.; Mackay, K. M. *J. of Organom. Chem.* **1984**, *275*, 39.

(18) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

(19) Wrackmeyer, B.; Horschler, K. *Annu. Rep. NMR Spectrosc.* **1989**, *22*, 249.

(20) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1999**, *38*, 203.

(21) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **2002**, *47*, 2.

(22) Kennedy, J. D.; Mcfarlane, W.; Pyne, G. S. *J. Chem. Soc. Dalton Trans.* **1977**, 2332.

(23) Vaara, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5399.

(24) Autschbach, J.; Zheng, S. *Annu. Rep. NMR Spectrosc.* **2009**, *67*, 1.

(25) de Dios, A. C.; Jameson, C. J. *Annu. Rep. NMR Spectrosc.* **2012**, *77*, 1.

(26) Aucar, G. A. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4420.

(27) Komorovský,; Repiský, M.; Malkina, O. L.; Malkin, V. G. *J. Chem. Phys.* **2010**, *132*, 154101.

(28) Olejniczak, M.; Bast, R.; Saue, T.; Pecul, M. *J. Chem. Phys.* **2012**, *136*, 014108.

(29) Helgaker, T.; Coriani, S.; Jørgensen, P.; Kristensen, K.; Olsen, J.; Ruud, K. *Chem. Rev.* **2012**, *112*, 543.

(30) Aucar, G. A.; Oddershede, J. *Int. J. Quantum Chem.* **1993**, *47*, 425.

(31) Aucar, G. A.; Saue, T.; Visscher, L.; Jensen, H. J. A. *J. Chem. Phys.* **1999**, *110*, 6208.

(32) Aucar, G. A.; Romero, R. H.; Maldonado, A. F. *Int. Rev. on Phys. Chem.* **2010**, *29*, 1.

(33) Maldonado, A. F.; Aucar, G. A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5615.

(34) Melo, J. I.; Maldonado, A.; Aucar, G. A. *Theor. Chem. Acc.* **2011**, *129*, 483.

(35) Saue, T. et al. DIRAC is a *relativistic ab initio electronic structure program*, Release DIRAC10 (University of Southern Denmark, Odense, 2010), `http://dirac.chem.sdu.dk`.

(36) Gomez, S. S.; Romero, R. H.; Aucar, G. A. *J. Chem. Phys.* **2002**, *117*, 7942.

(37) Gomez, S. S.; Maldonado, A. F.; Aucar, G. A. *J. Chem. Phys.* **2005**, *123*, 214108.

(38) Gomez, S. S.; Aucar, G. A. *J. Chem. Phys.* **2011**, *134*, 204314.

(39) Roukala, J.; Maldonado, A. F.; Vaara, J.; Aucar, G. A.; Lantto, P. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21016.

(40) Autschbach, J.; Ziegler, T. *Encyclopedia of NMR* **2002**, *9*, 306.

(41) Xiao, Y.; Sun, Q.; Liu, W. *Theo. Chem. Acc.* **2012**, *131*, 1080.

(42) Maeda, H.; Ootani, Y.; Fukui, H. *J. Chem. Phys.* **2008**, *128*, 129903.

(43) Seino, J.; Hada, M. *J. Chem. Phys.* **2010**, *132*, 174105.

(44) Melo, J. I.; de Azúa, M. C. R.; Giribet, C. G.; Aucar, G. A.; Romero, R. H. *J. Chem. Phys.* **2003**, *118*, 471.

(45) Chang, C.; Pelissier, M.; Durand, M. *Phys. Scr.* **1986**, *34*, 394.

(46) van Lenthe, E.; Baerends, E.; Snijders, J. *J. Chem. Phys.* **1993**, *99*, 4597.

(47) van Lenthe, E.; Baerends, E.; Snijders, J. *J. Chem. Phys.* **1994**, *101*, 9783.

(48) Autschbach, J. *Molec. Phys.* **2013**, *111*, 2544.

(49) Baerends, E. J.; et al., Amsterdam Density Functional (ADF), Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. `http://www.scm.com`.

(50) Bühl, M.; Kaupp, M.; Malkina, O. L.; Malkin, V. G. *J. Comput. Chem.* **1999**, *20*, 91.

(51) Sanders, L. K.; Oldfield, E. *J. Phys. Chem. A* **2001**, *105*, 8098.

(52) Auer, A. A.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2003**, *118*, 10407.

(53) Tossell, J. A. *Phys. Chem. Miner.* **2004**, *31*, 41.

(54) Arcisauskaite, V.; Melo, J. I.; Hemmingsen, L.; Sauer, S. P. A. *J. Chem. Phys.* **2011**, *135*, 044306.

(55) Vicha, J.; Patzschke, M.; Marek, R. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7740.

(56) Teal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2003**, *119*, 3015.

(57) Teal, T. W.; Tozer, D. J.; Helgaker, T. *Chem. Phys. Lett.* **2004**, *391*, 374.

(58) Teal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2004**, *121*, 5654.

(59) J.Peach, M.; Kattirzi, J. A.; Teal, T. W.; Tozer, D. J. *J. Phys Chem. A* **2010**, *114*, 7179.

(60) Perdew, J.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(61) Becke, A. *J. Chem. Phys.* **1993**, *98*, 5648.

(62) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785.

(63) Pyykkö, P.; Görling, A.; Rösch, N. *Molec. Phys.* **1987**, *61*, 195.

(64) Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem. Eur. J.* **1998**, *4*, 118.

(65) Edlund, U.; Lejon, T.; Pyykkö, P.; Venkatachalam, T. K.; Buncel, E. *J. Am. Chem. Soc.* **1987**, *109*, 5982.

(66) Maldonado, A. F.; Aucar, G. A.; Melo, J. I. *J. Mol. Model* **2014**, In press.

(67) Becke, A. J. *J. Chem. Phys.* **1988**, *38*, 3098.

(68) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(69) Varga, S.; Fricke, B.; Nakamatsu, H.; Mukoyama, T.; Anton, J.; Geschke, D.; Heitmann, A.; Engel, E.; Bastug, T. *J. Chem. Phys.* **2000**, *112*, 3499.

(70) Varga, S.; Engel, E.; Sepp, W.-D.; Fricke, B. *Phys. Rev. A* **1999**, *59*, 4288.

(71) Mayer, M.; Häberlen, O. D.; Rösch, N. *Phys. Rev. A* **1996**, *54*, 4775.

(72) Sutton, L. E. *Tables of Interatomic Distances and Configurations in Molecules and Ions*; The Chemical Society, London, 1995.

(73) Sadlej, A. J. *Theor. Chim. Acta* **1991**, *79*, 123.

(74) Fægri, K. private communication; see also `http://folk.uio.no/knutf/bases/one`.

(75) Maldonado, A. F.; Gimenez, C. A.; Aucar, G. A. *J. Chem. Phys.* **2012**, *136*, 224110.

(76) Jaszunski, M.; Jackowski, K. *Lecture Notes in Phys.* **2008**, *745*, 233.

(77) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 326.

(78) Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the periodic table*; Harris, R., Mann, B. E., Eds.; Academic Press, New York, 1978; p 309.

(79) Kennedy, J. D.; MacFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum. New York, 1987; p 305.

(80) Rodriguez-Fortea, A.; Alemany, P.; Ziegler, T. *J. Phys. Chem. A* **1999**, *103*, 8288.

Figure 1: Behavior of $\sigma^p(\text{Sn})$ in SnX_4 model compounds, calculated with RelPPA-RPA and DFT methods.
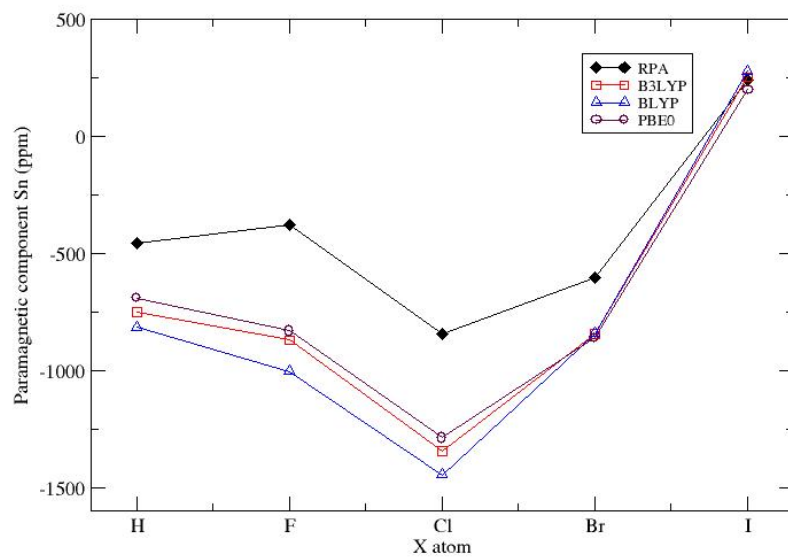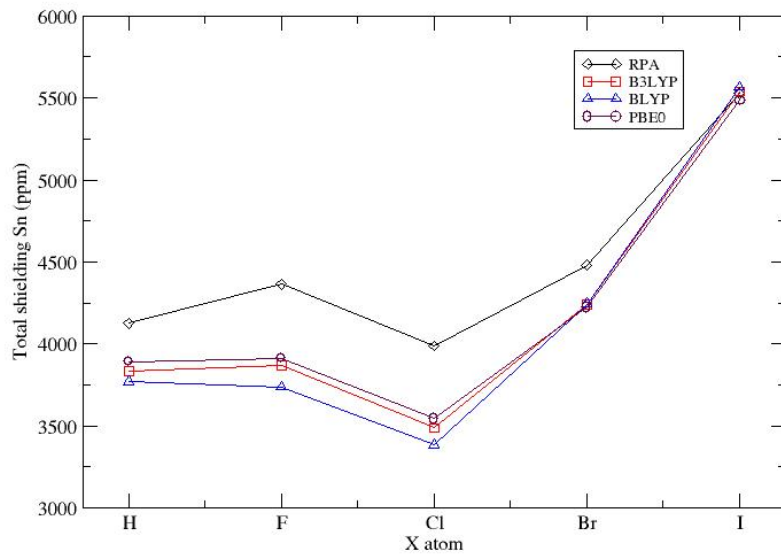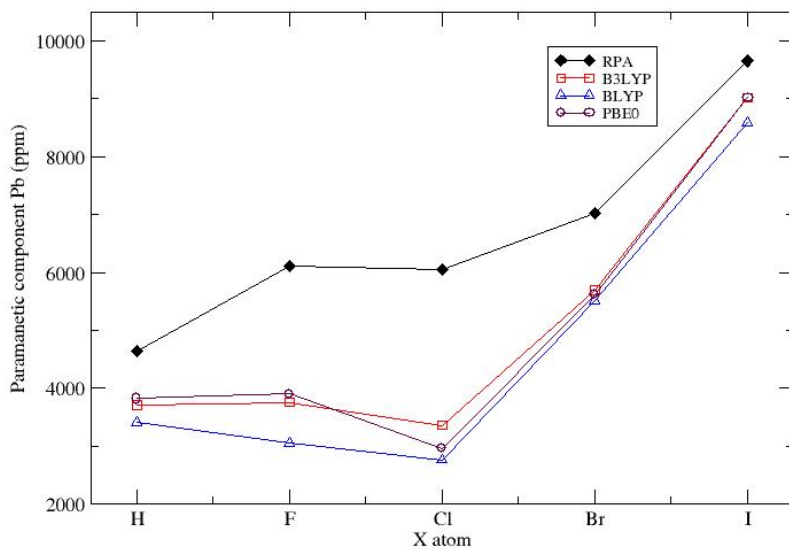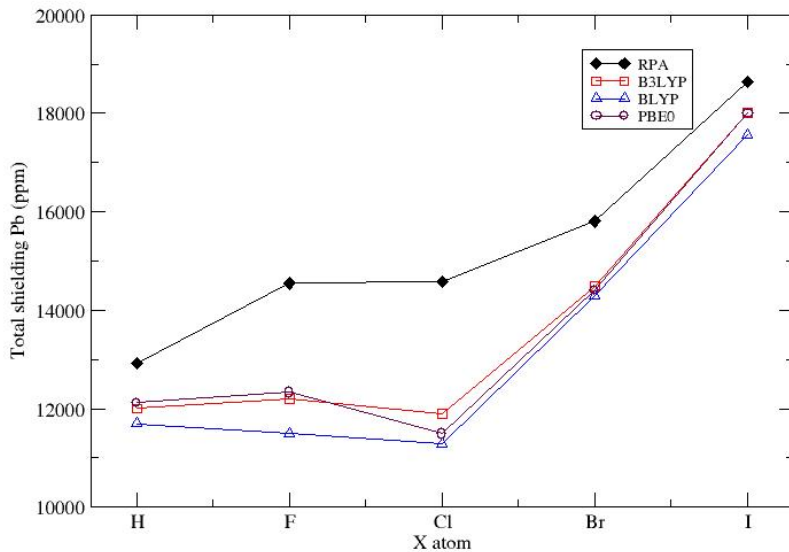
Figure 2: Behavior of $\sigma^t(Sn)$ in SnX_4 model compounds, calculated with RelPPA-RPA and DFT methods.

Figure 3: Behavior of $\sigma^p(Pb)$ in PbX_4 model compounds, calculated with RelPPA-RPA and DFT methods.

Figure 4: Behavior of $\sigma^t(\text{Pb})$ in $\text{Pb}X_4$ model compounds, calculated with RelPPA-RPA and DFT methods.

Figure 5: NR limit of $\sigma^p(\text{Sn/Pb})$ in the $(\text{Sn/Pb})X_4$ (X = H, I) model compounds, calculated with RelPPA-RPA method.
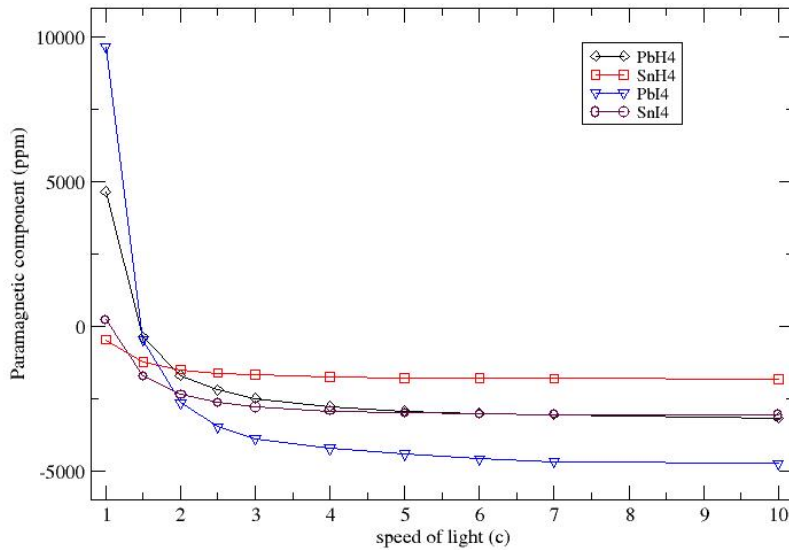
Figure 6: Chemical shift of Sn in the fifteen molecular systems of 3.
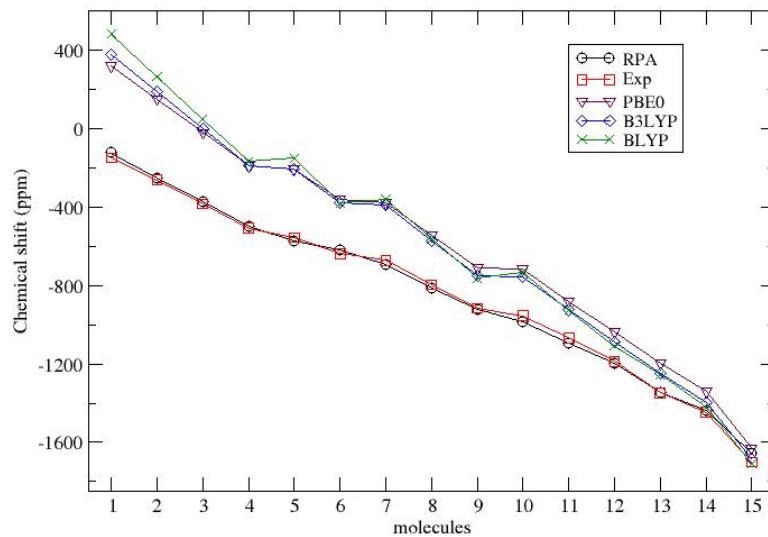
Figure 7: Theoretical vs. experimental values of $\delta(\text{Sn})$. The red line indicates the perfect agreement.
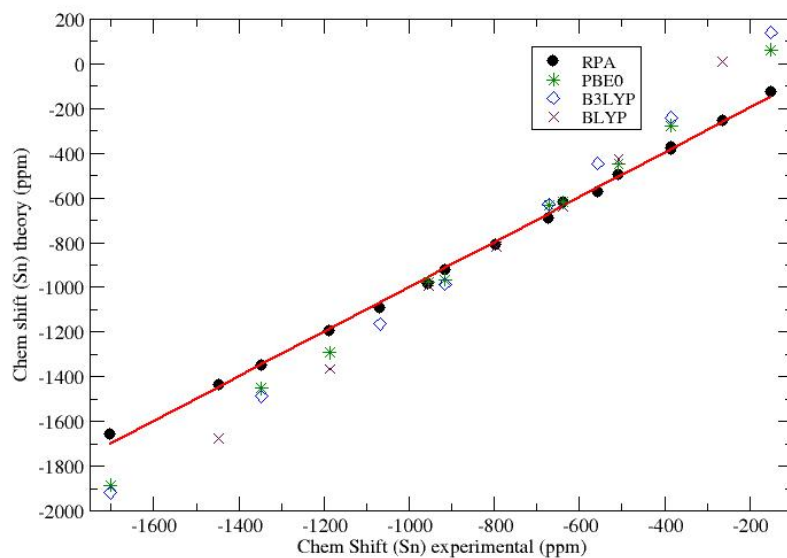
Figure 8: Differences between non relativistic DFT and SOPPA values, with NRPPA-RPA values for $\sigma(\text{Sn})$ in $\text{Sn}X_4$ (X = H, F, Cl, Br and I).
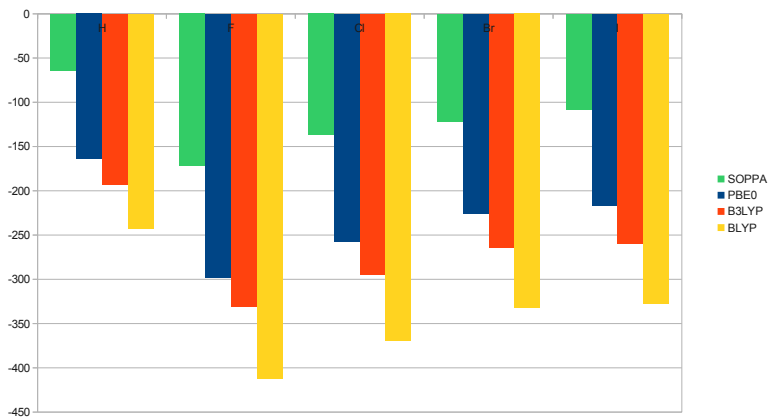
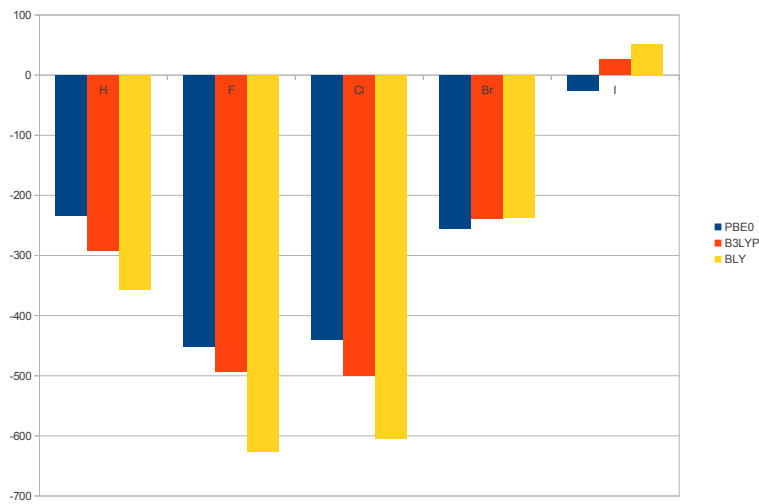Figure 9: Differences between relativistic DFT and RelPPA-RPA values for $\sigma(\text{Sn})$ in $\text{Sn}X_4$ (X = H, F, Cl, Br and I)

Figure 10: Percentage of relativistic effects on $\sigma(\text{Sn})$ as a function of X and n in $\text{SnH}_{4-n}X_n$ for $X = $ H, F, Cl, Br and I.
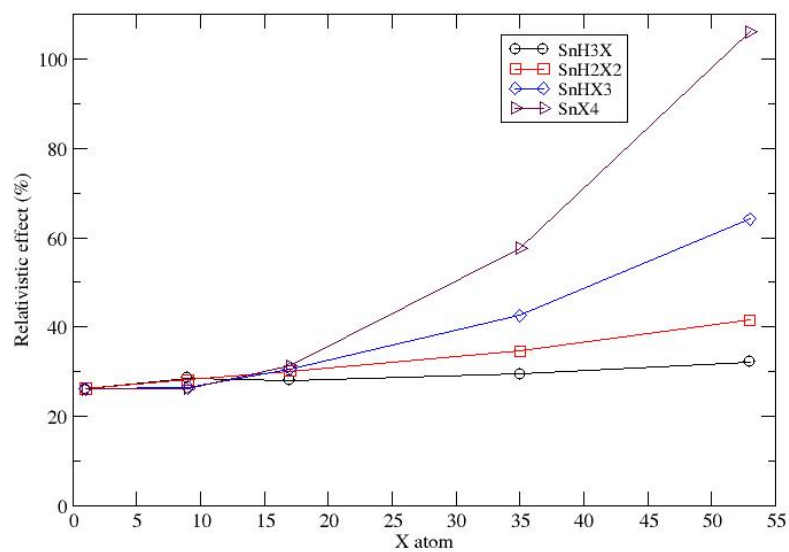
Figure 11: Dependence of $^{HAVHA}\sigma(\text{Pb})$ with the number of iodine atoms in $\text{PbH}_{4-n}\,\text{I}_n(n = 0,...4)$.