NMR espectroscopic parameters of HX and Si(Sn)X_4 (X = H, F, Cl, Br and I) and SnBr$_{4-n}$I$_n$ model compounds

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A B S T R A C T

The NMR spectroscopic parameters are largely influenced by relativistic effects. They are highly dependent on the electronic behavior inside the spatial regions occupied by nuclei.

Full relativistic calculations of indirect nuclear spin–spin couplings at random phase level of approach (RPA) in the title compounds with reoptimized Dyall cVTZ basis sets are given. A comparison with the results of calculations with other basis sets that are mostly used within the non-relativistic (NR) domain is presented. We analyzed the dependence of that couplings with the speed of light over the whole range of values, from the full relativistic to the NR regimes. Within this last regime, calculations at the second-order level of approach (SOPPA) indicated that electron correlation effects may not be as important for nuclear magnetic shieldings, but they must be included with care for J-coupling calculations. From these calculations, we determined that relativity enlarges the electron correlation effects of the J-couplings of HBr and HI.

Because the results of nuclear magnetic shielding calculations within polarization propagators at the RPA level were reliable, we were able to show a new and easy procedure to obtain absolute nuclear magnetic shieldings on reference compounds for both Si and Sn nuclei: σ[Si(CH$_3$)$_4$] = 421.28 ± 29.33 ppm and σ[Sn(CH$_3$)$_4$] = 3814.96 ± 79.12 ppm. They were obtained from experimental chemical shifts and accurate nuclear magnetic shielding calculations on different molecular systems.

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1. Introduction

During approximately the last ten years, increasing interest has been paid to both the development and application of formalisms that include relativistic effects on the calculations of molecular properties. Nuclear magnetic resonance (NMR) spectroscopic para meters are the most sensitive to such effects and have been included from the outset [1–3] or as a perturbation [4–6].

It is well known that within the NR regime, the results of NMR J-coupling calculations are highly dependent on the quality of the basis set and the amount of electron correlation. At the relativistic level, both dependences seem to be different from what we know of the NR domain.

Currently, satisfactory basis sets are available to obtain converged results of the calculation of NMR spectroscopic parameters, although they may not converge to the same values provided the fact that they are finite in size. For this reason, it is important to determine the reliability of calculations of such parameters versus different schemes of basis sets, and whether such basis set depen-

dence is similar in the relativistic and non-relativistic regimes. In this article, we will show that one should be very careful in evaluating results obtained with optimized basis sets.

The calculation of magnetic properties within a relativistic domain requires the consideration of either kinetic balance [7–10] or magnetic balance [11–15] between large and small components of the basis sets. There are different types of balance, and they give equivalent results when properly included [16]. However, they are only important for nuclear magnetic shieldings but not J-coupling calculations. This may be the case because J-couplings are independent of the external magnetic field. We will show some calculations that highlight this fact.

One can determine absolute nuclear magnetic shieldings using theoretical calculations, although, currently, this cannot be experimentally performed. The formal definition of σ does produce such a constraint; it gives a measure of how much the molecular electronic environment of a nucleus modifies (shielding or deshielding) the magnitude of the external magnetic field at the nuclear position.

The usual way for an experimentalist to determine absolute magnetic shieldings begins with the measured values of spin-rotation constants, from which they obtain paramagnetic contributions to

the shielding, σ^p. By combining this (experimentally based) value with the calculated (theoretically based) value of the diamagnetic contribution, σ^d, one gets the total (experimental and theoretical mixed result) value: $\sigma = \sigma^p + \sigma^d$. This general procedure does not work properly when heavy atoms are involved [17]. Another important parameter the experimentalist can measure with high accuracy is the chemical shift, which is defined as the difference in shieldings of the same type of nuclei in two different environments, with one of them being well known. The problem here again is the lack of an absolute shielding obtained from experiments. Thus, it would be of interest to accurately obtain such an absolute shielding. We show in this article an easy procedure to obtain reliable values of absolute magnetic shieldings for reference molecular systems using a mix of theoretical and experimental results.

This article is organized as follows: in Section 2 we give a brief introduction to the relativistic polarization propagator formalism at different levels of approach in the electronic correlation, and the procedure from which one can obtain the value of reference of nuclear magnetic shieldings from experimental chemical shifts and reliable theoretical calculations. The main results together with an analysis of trends of σ and J-calculations are given in Section 4. The main conclusions are highlighted in Section 5.

2. Theory

Both NMR spectroscopic parameters can be expressed in a similar manner within the relativistic polarization propagator approach, RPPA [1,18]. Depending on the value of the speed of light ($c \to nc$), one obtains full relativistic ($n = 1$) or NR ($n = 10$) results. There is a smooth and continuous connection of results between these two extreme values. In the first article on the relativistic theory of polarization propagators, it was analitically shown that one can determine NR expressions by making c go to infinity. Numerical calculations confirmed this finding several times and for different molecular systems. The relativistic theory of polarization propagators is given in more detail elsewhere [1].

Within the relativistic version of the polarization propagator approach, the explicit expressions of both NMR spectroscopic parameters are

$$\mathbf{J}_{MN} = \frac{e^2 h^2}{h} \gamma_M \gamma_N \left\langle\!\!\left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_M}{r_M^3} ; \frac{\boldsymbol{\alpha} \times \mathbf{r}_N}{r_N^3} \right\rangle\!\!\right\rangle \tag{1}$$

and

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

From these equations one concludes that within the RPPA approach, there is only one electronic mechanism involved in each of the two NMR spectroscopic parameters.

We can write both parameters in terms of the so-called *perturbators* (in the equation below expressed as **b**) and the *principal propagator* (the matrix **P** ($E = 0$)) [1]

$$J_{MN} = \tilde{\mathbf{b}}_M^J \mathbf{P}^J(E=0)\mathbf{b}_N^J + c.c.$$
$$\sigma_M = \tilde{\mathbf{b}}_M^\sigma \mathbf{P}^\sigma(E=0)\mathbf{b}^B + c.c. \tag{3}$$

Early in the development of relativistic polarization propagators, it was shown that the non-relativistic limit is obtained by making $c \to \infty$ on both the perturbators and principal propagators [18]

$$\mathbf{b}_M^R \to \mathbf{b}_M^{NR} \tag{4}$$

and

$$\mathbf{P}^R(E=0) \to \mathbf{P}^{NR}(E=0) \tag{5}$$

The explicit form of the principal propagator matrix at the RPA (random phase approximation) level of approach (which is the first order in a perturbative expansion of propagators) is

$$\mathbf{P}^R(E=0) = \begin{pmatrix} \mathbf{A} & \mathbf{B}^* \\ \mathbf{B} & \mathbf{A}^* \end{pmatrix}^{-1} \tag{6}$$

with the matrix elements of matrices **A** and **B**

$$\mathbf{A}_{ia,jb} = -\left\langle 0 \left| \left[a_i^\dagger a_a, \left[a_b^\dagger a_j, H_0 \right] \right] \right| 0 \right\rangle = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + \langle aj\|ib\rangle \tag{7}$$

and

$$\mathbf{B}_{ia,jb} = -\left\langle 0 \left| \left[a_i^\dagger a_a, \left[a_j^\dagger a_b, H_0 \right] \right] \right| 0 \right\rangle = \langle ji\|ab\rangle \tag{8}$$

The RPA level of approach is obtained when considering the reference state as the Dirac–Hartree–Fock or $|0\rangle = |DHF\rangle$ and the manifold of excitation operators truncated up to single-excitation operators. Subindices $a,b, \ldots$ refer to unoccupied DHF orbitals and $i, j, \ldots$ stands for occupied DHF orbitals.

The SOPPA (second order polarization propagator approximation) level of approach, which is consistent up to the second order in electron correlation, is obtained when $|0\rangle = |DHF\rangle + |0^{(1)}\rangle$ and the manifold of excitation operators is truncated up to double excitations [1].

One of the interesting features of RPPA is the fact that paramagnetic-like terms are obtained when excitations are taken only to positive-energy electronic states. In a similar manner, diamagnetic-like contributions are obtained from excitations only to negative-energy electronic states.

To obtain well-defined energy spectra, which also means to avoid the so-called "variational collapse", one should include a relationship between large and small components of the basis set in four component calculations. This relationship must ensures that the kinetic energy will be properly described in the non-relativistic limit ($n = 10$ in our case).

There are at least two ways to do this: the kinetically balanced small component basis set [7–10,19,20] and the magnetically balanced small component basis set [11–15]. The former does not include the external magnetic field, while the latter does.

Recently, Sun et al. published an article with a discussion of four types of kinetically balanced basis sets [16] along with the numerical performance of each of them, although only for a completely ionized Rn atom.

Within the RPPA formalism it is not necessary to use magnetically balanced basis sets because in the matrix elements of Eq. (6), the matrix representation of the principal propagator, *i.e.* **P**, is defined in terms of the unperturbed Hamiltonian (see Eqs. (7) and (8)). The other type of matrix elements, the property matrix elements (*i.e.* $\mathbf{b}_{ia}$, being a a virtual positive- or virtual negative-energy MO) are also defined in terms of the unperturbed molecular system [21].

It can thus clearly be seen that within the RPPA formalism, one should consider the kinetic balance prescription or any variant of it, but not the magnetic balance, to obtain proper non-relativistic limits of both matrix elements that intervene in the calculation of response properties.

If one expands both the large and small components of Dirac's 4-spinors in a 2-spinor basis $\left\{\chi_\mu^L, \chi_\mu^S\right\}$, one has

$$\Psi^L = \sum_{\mu=1}^{n_L} a_\mu^L \chi_\mu^L, \quad \Psi^S = \sum_{\mu=1}^{n_S} a_\mu^S \chi_\mu^S \tag{9}$$

where n_L and n_S need not to be equal each other. The relationship between χ_μ^L and χ_μ^S given by the kinetic balance prescription can be written in the NR limit as

$$\chi_\mu^S = \frac{1}{2mc}(\sigma \cdot \mathbf{p})\chi_\mu^L \tag{10}$$

or

$$\lim_{c\to\infty} c\chi_\mu^S = \frac{1}{2m}(\sigma \cdot \mathbf{p})\chi_\mu^L \tag{11}$$

If Gaussian basis sets are considered for large component functions with angular quantum number ℓ, one obtains two small component functions with $\ell + 1$ and $\ell - 1$ angular quantum numbers

$$\chi_\mu^L \propto \eta^L(r) = \{G_\ell\} \Rightarrow \chi_\mu^S \propto \eta^S(r) = \{c_{\ell-1}G_{\ell-1} + c_{\ell+1}G_{\ell+1}\} \tag{12}$$

where $c_{\ell-1}$ and $c_{\ell+1}$ are constants and $\eta(r)$ is the radial part of a spherical Gaussian 2-spinor [22]. In this case, the kinetic balance prescription is known as *restricted kinetic balance* (RKB). There is also another possibility where both types of small basis functions are separate functions *i.e.*

$$\chi_\mu^L \propto \eta_\mu^L(r) = \{G_\ell\} \Rightarrow \chi_\mu^S \propto \eta_\mu^S(r) = \{c_{\ell-1}G_{\ell-1}\} \cup \{c_{\ell+1}G_{\ell+1}\} \tag{13}$$

in which case the kinetic balance prescription is known as *unrestricted kinetic balance* (UKB). For the RKB prescription, there is a 1:1 relationship between large and small component basis set. For the UKB prescription, each generated Gaussian function is independently used as a basis function and produces approximately 1:2 relationship between the size of the large and small component basis sets depending on the number of s-type Gaussian functions. This fact increases the size of the small component basis set and improves the description of the negative-energy spectra.

The chemical shift of a nucleus in two different molecular environments is calculated using the following approximated expression

$$\delta^{exp/theo} = \sigma^{ref} - \sigma \tag{14}$$

The chemical shift δ^{exp} is directly obtained from experiments and the value of absolute magnetic shieldings, while σ^{ref} and σ are obtained through indirect measurements. The paramagnetic component of σ is usually obtained from the spin-rotation constants and magnetic shieldings of free atoms [23,24]. However, diamagnetic contributions to the shielding are obtained from theoretical calculations.

From Eq. (14), the reference value of the magnetic shielding of an atom in a given molecular system can be calculated as

$$\sigma^{ref} = \delta^{exp} + \sigma \tag{15}$$

Results from this last expression arise as a combination of experimental and theoretical values. We will apply it for the calculation of $\sigma(X)$ in $X\mathrm{Me}_4$ (X = Si, Sn) model compounds.

3. Computational details

All calculations of NMR nuclear magnetic shieldings and indirect J-couplings were performed with the DIRAC program package [25]. Non-relativistic calculations were performed with the DALTON program package [26].

The speed of light was taken as c = 137.0359998 a.u., and to obtain the NR limit, the speed of light was modified, with nc (n = 1,...10). The NR limit is usually obtained for n = 10.

The geometries for the XY_4 (X = Si, Sn; Y = F, Cl, Br, I) model compounds were optimized using the module OPTMIZE of the DIRAC code, and for the $\mathrm{SnBr}_{4-n}\mathrm{I}_n$, n = 1, ... 3 model compounds, the tetrahedron geometries were used with bond lengths taken from the SnBr_4 and SnI_4 model compounds. For the other systems, experimental geometries were used and taken from Ref. [27]. For the tetrahedron compounds, the gauge origin was placed at the position of the central heavy atom. For linear molecules, $\mathrm{H}X$ (X = F, Br, I), it was placed at the position of the heavy nucleus.

The Gaussian nuclear model was considered in all calculations, though our magnetic perturbative Hamiltonians did not include any corrections due to the finite nuclear model.

The UKB prescriptions were applied to generate small component basis sets from large component basis sets in the four-component calculations. Different basis sets were used for calculation of the J-couplings, the Dyall [28], Sadlej [29], and aug-cc-pVTZ-Jun3 [4] basis sets. However, only (optimized) Sadlej basis sets, Sadlej-pVTZ-OS [21], were chosen for four-component shielding calculations in the systems $\mathrm{Si(Sn)Y}_4$ and $\mathrm{SnBr}_n\mathrm{I}_{4-n}$.

The Dyall-cVTZ basis set was used in J-coupling calculations and several more tight and diffuse Gaussian functions were included to obtain converged results. The scheme to include more Gaussian functions was typical: (i) tight basis functions were added to the s, p, d, and f blocks with exponents related as α_{i+1}/α_i = 3 from the largest exponent of each block; (ii) diffuse basis functions were added to p, d, and f blocks following the same relationship between the exponents: α_i/α_{i-1} = 3. For shielding calculations, some other optimized basis set were taken from Refs. [21,30].

The aug-cc-pVTZ-Jun3 basis set [4] was built from complete uncontraction and the addition of both tight and diffuse functions of the aug-cc-pVTZ-J basis set of Ref. [31]. Tight and diffuse functions were included following the relationship between exponents given by α_{i+1}/α_i = 2, although in a few cases, this relationship was taken as equal to 3. The criterium for selecting factors 2 or 3 was consideration of the final value of the new exponent.

4. Results and discussions

In the next subsection, we will first show the results of four-component calculations of NMR espectroscopic parameters for heavy-atom-containing systems. Some of them did contain more than four heavy atoms. To our knowledge, this information is given for the first time.

To obtain reliable shielding calculations of such systems, we developed a large enough and converged basis set, based on the Sadlej basis set for fourth and fifth-row elements [21,30]. The results of calculations with such a basis set were in good agreement with those obtained with the original Dyall basis set [28]. Therefore, reliable results were obtained by working with this basis set for systems that contain more than three or four heavy atoms. A new proposal of reference values for nuclear magnetic shieldings is also given. Our calculated chemical shifts fits quite well with experimental measurements.

4.1. Improving basis set for relativistic J-couplings and shieldings

We chose the recently published Dyall basis set as the starting basis set, and then searched for convergence on J-coupling calculations [28]. We added tight s and p type functions and then diffuse p, d and f functions, as shown in Fig. 1. A clear pattern was evident, and it seemed to indicate direct and indirect relativistic effects on atoms: s and p type orbitals did contract on the nucleus, but d and f orbitals were expanded. However, this must be considered with caution. One should consider the scheme shown in Fig. 1 in order to obtain converged J-coupling calculations. We applied the following nomenclature nlm, where n and m means the number of tight and diffuse functions, respectively, added to the l-type orbital. 2p3 means two tight and three diffuse functions added to the basic p-type functions belonging to the Dyall-··· basis set.

We coined Dyall-···-J or Sadlej-···-J for the optimized basis sets. Results from the Dyall-cVTZ-J basis set were quite close to those of the non-optimized Dyall basis set for the whole range of values of the speed of light, nc. This means that both branchs of the energy pattern (positive-energy and negative-energy) were quite well
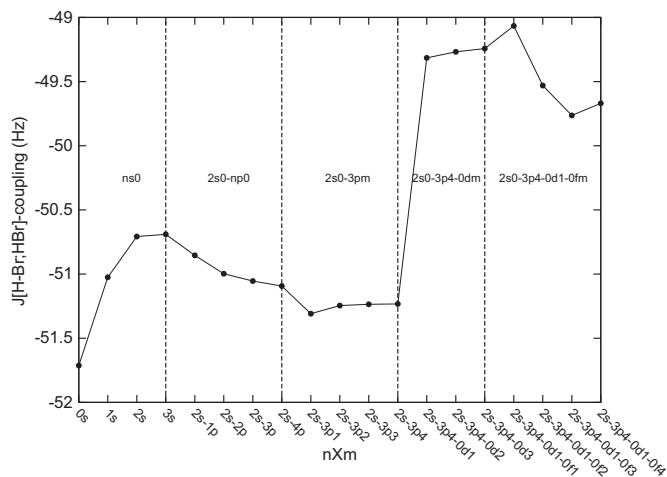
Fig. 1. Optimization of Dyall-cVTZ basis set (Dyall-cVTZ-J) for J(HBr).

Fig. 3. Basis set and velocity of light ($c \rightarrow nc$) dependence of J(HI) for the HI molecule.

reproduced. In Figs. 2 and 3, we observed that the difference between results of calculations with Dyall-cVTZ and Dyall-cVTZ-J in the whole spectra (considering $n = 1,2,\ldots 10$) was always the same. This was not the case for other basis sets, meaning that the small components obtained from them through the application of kinetic balance are not able to reproduce the contributions from the negative-energy spectra with high accuracy. In other words, one cannot obtain reliable results within the relativistic domain from such basis sets, even though they are known to be good enough for calculations within the NR domain.

4.2. Basis set and speed of light dependence of J-couplings and shieldings

The results of relativistic and NR calculations of both NMR spectroscopic parameters for HX (X = F, Br, I) systems are shown in Table 1. Several optimized basis set were considered. We also show the results at the RPA and SOPPA levels of approach within the NR regime.

For the HF molecule, relativistic effects are quite small, as observed from the difference between the values of both parameters calculated within both the relativistic and NR domains. The total relativistic effect is close to 1% for σ(F) and only 0.25% for J(HF).
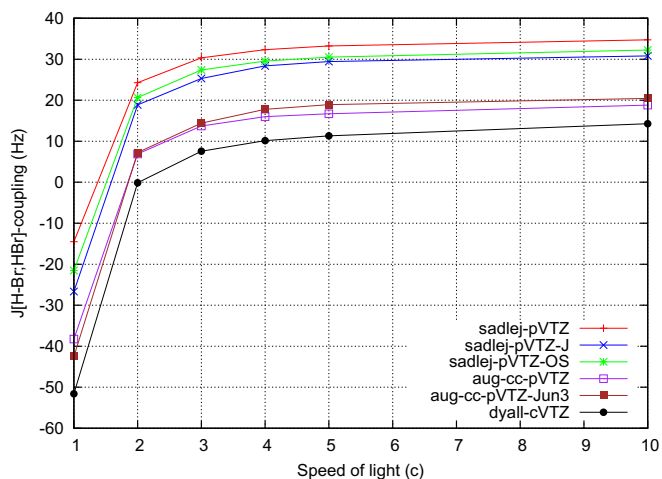
In the NR regime, J-coupling calculations are much more dependent on the quality of basis sets as compared to the nuclear magnetic shieldings. In the relativistic regime the behavior of such parameters is the same, as observed in Figs. 2–4.

Indeed, the results of J-coupling calculations were enlarged, as observed in Figs. 2 and 3, and also when comparing both Figures with each other. In the case of J(HI), Fig. 3 shows that there was a difference of more than 50 Hz between the results of calculations with Sadlej-pVTZ and Dyall-cVTZ within the relativistic regime compared to a difference of around 20 Hz in its NR counterpart. A similar behavior was observed for J(HBr).

The behaviour of magnetic shieldings as a function of the speed of light, nc (see Figs. 4 and 5 where calculations were performed with the gauge origin placed on the site of the heavy atom), is such that no large differences were found for either of Dyall's basis sets. A different behavior was observed when other basis sets were applied. In these cases, the results of shielding calculations with $n = 10$ were closer than that with $n = 1$. This means that usual NR basis set are not as good for full relativistic calculations as those developed within this last regime.

It is also interesting to observe that these less accurate results for the usual NR basis set were more pronounced when the gauge origin was placed at the site of the hydrogen nucleus for σ(H) (see Fig. 6).

In order to evaluate the results obtained with the Dirac package, and also the nice figures one obtains by varying the speed of light in theoretical calculations, with other schemes of calculations, we performed calculations of NMR J-couplings and shieldings by applying the Dalton package. They are shown in Table 1, where a nice fitting is observed.

At the moment, correlation effects at the SOPPA level of approach are only obtainable within the NR domain. In the case of HF, they decreased J(HF) by around 100 Hz, but for HBr, the effect was opposite: $J^{RPA/SOPPA}$(HBr) = 12.58 Hz/55.84 Hz. Previous and preliminary calculations of J(HBr) [1] were based on the Sadlej-pVTZ-J basis set. They suggested that when including correlation effects at the SOPPA level, and assuming that correlation is not modified very much by relativity, theoretical results would be close to experimental measurements. It appears now that working with a larger and converged basis set, like Dyall-cVTZ-J, one obtain relativistic RPA values that are more negative than those obtained with the Sadlej basis set, and the SOPPA-RPA values in the NR domain were also much smaller. One should thus infer that correlation effects are enlarged by relativistic effects or other effects

Fig. 2. Basis set and velocity of light ($c \rightarrow nc$) dependence of J(HBr) for the HBr molecule.

Table 1
$\sigma(X)$ and J(HX) at the RPA (relativistic and NR) and SOPPA (NR) levels of approach for X (X = F, Br, I).

Basis	Relativistic		lim NR		Non relativistic			
	RPA		RPA		RPA		SOPPA	
	σ	J	σ	J	σ	J	σ	J
HF system								
Sadlej-pVTZ	418.91	606.34	414.85	607.11	414.92	608.04	420.49	503.57
Sadlej-pVTZ-OS	418.91	606.34	414.85	607.11	414.92	608.04	416.93	503.57
Sadlej-pVTZ-J	419.14	666.89	414.82	667.50	414.89	668.75	416.29	547.66
Aug-cc-pVTZ	418.36[a]	605.84	414.24	606.59	415.36	607.57	417.26	498.02
HBr system								
Sadlej-pVTZ	2925.44	−14.51	2634.38	34.73	2635.82	34.60	2622.95	89.69
Sadlej-pVTZ-OS	2937.67	−21.54	2635.65	32.25	2634.18	32.01	2616.63	68.67
Sadlej-pVTZ-J	2942.24	−26.66	2634.34	30.82	2635.60	30.58	2622.73	92.49
Aug-cc-pVTZ	2945.71	−38.25	2638.45	18.81	2635.28	18.56	2628.62	85.91
Aug-cc-pVTZ-Jun3	2952.16	−42.49	2637.14	20.46	2633.96	20.07	2620.20	65.77
Dyall-cVTZ	2944.72	−51.60	2632.94	14.26	2634.18	12.58	2618.92	55.84
Dyall-cVTZ-J	2945.66[b]	−49.67	2637.65	15.21	2633.68	14.90	2619.29	57.45
HI system								
Sadlej-pVTZ	5772.98	−214.93	4535.51	−17.40	4537.96	−18.34	4500.45	9.36
Sadlej-pVTZ$_J$	5841.41	−256.40	4542.67	−25.90	4537.51	−27.50	4490.01	6.08
Dyall-cVTZ	5860.34[c]	−276.01	4541.53	−31.68	4540.11	−31.43	4498.50	13.54

[a] σ(F) = 415.3 ppm [3], 416.2 ppm [13].
[b] σ(Br) = 2879.4 ppm [3], 2899.4 ppm [13].
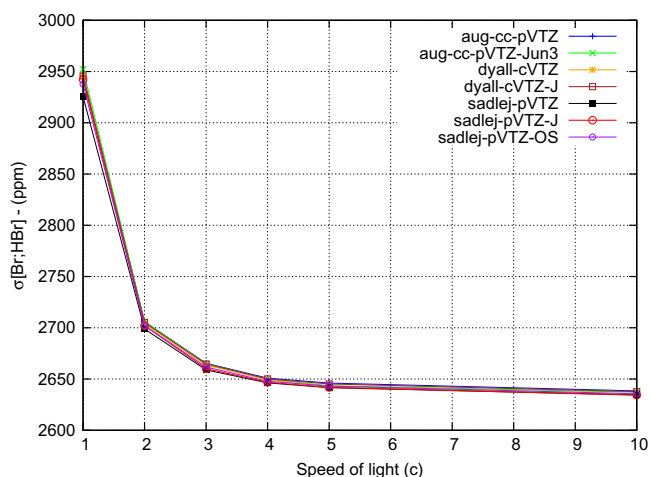[c] σ(I) = 5654.3 ppm [3], 5716.3 ppm [13].

Fig. 4. Basis set and velocity of light ($c \to$ nc) dependence of σ(Br) for the HBr molecule.

Fig. 5. Basis set and velocity of light ($c \to$ nc) dependence of σ(H) for the HBr molecule. The gauge origin was on Br.

must be considered in order to obtain theoretical results closer to experimental results.

Nuclear magnetic shieldings do not change very much by including correlation effects. $\sigma^{SOPPA-RPA}$(F/Br/I) = −20.27 ppm ($\simeq$0.5%)/−6.66 ppm ($\simeq$0.25%)/−41.61 ppm ($\simeq$0.9%). Relativistic effects on $\sigma(X)$ were 1% for X = F, 10% for X = Br and 22% for X = I. Our value for σ(Br) = 2945.66 ppm with Dyall-cVTZ-J and 2937.67 ppm with Sadlej-pVTZ-OS (2879.4 ppm from Ref. [3] and 2899.4 ppm from Ref. [13]).

Calculation of σ(H; HBr) with the Dyall-cVTZ-J basis set and with the gauge origin on Br provided a value of 35.9 ppm (its value with Dyall-cVTZ and the gauge origin on H was 39.31 ppm), which is close to previous findings: 34.91 ppm from Ref. [3] and 36.4 ppm from Ref. [13].

4.3. Absolute magnetic shieldings on reference compounds

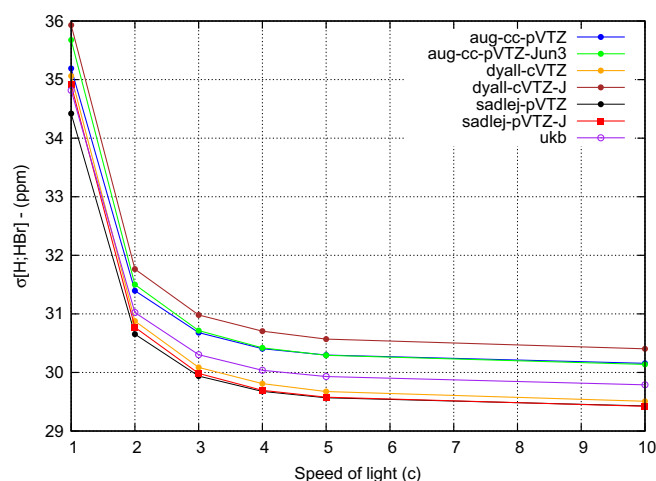As explained in Section 2, chemical shifts arise from the nuclear magnetic shielding calculation of the same nucleus in two different molecular systems, one being the reference. In Table 2, the total paramagnetic and diamagnetic components of σ(Si) in SiX_4 (X = H, F, Cl, Br, I) are shown. One can take any system as the reference. Here, we used SiH$_4$.

In the case of SiX_4, σ^d smoothly became more positive as X became heavier. Conversely σ^p, showed the opposite behavior, with SiI$_4$ as an exception. Thus, σ did not vary much until X = I, where it changed quite a bit compared with σ (Si; SiH$_4$). The chemical shift obtained as $\sigma^{ref} - \sigma$ does not adequately fit with experimental data.

A similar behavior was observed for σ^d (Sn) in the series of compounds shown in Table 2, but σ^p did not show a smooth negative tendency as X, Y became heavier. The system SnCl$_4$, σ^d (Sn) became more and more positive, and its sign changed for SnI$_4$ (209.48 ppm). Therefore, the calculated δ(Sn) does not adequately reproduce δ^{exp}(Sn).

Given that $\delta^{theo} = \sigma^{ref} - \sigma$, we calculated σ^{ref} (Si; Sn) as in Eq. (15). In Table 3, different values of such references are shown.
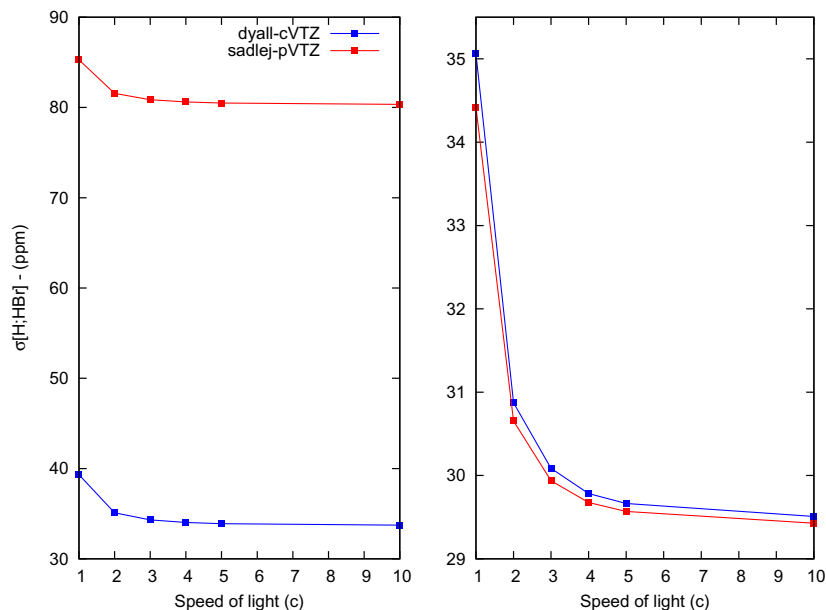
Fig. 6. Dependence of $\sigma(H)$ with different basis sets and the value of the velocity of light. To the left, the gauge origin was on H. To the right, the gauge origin was on Br.

Table 2
Calculated magnetic shieldings and chemical shifts of Si and Sn in SiX_4, SnX_4 and $SnBr_{4-n}I_n$ molecular systems.

Molecule	σ^d	σ^p	σ	$\sigma^t(ZORA)$	$\delta(Si)$	$\delta(Si)$		$\delta(Si)^{exp}$
SiH_4	884.86	−396.01	489.09		0.00			0.00
SiF_4	1074.91	−553.95	520.96		−31.87			−99.1
$SiCl_4$	1170.41	−742.33	428.09		61.00			−10.1
$SiBr_4$	1451.25	−959.63	491.62		−2.53			−83.7
SiI_4	1664.14	−908.78	755.36		−266.27			−336.3
Molecule	σ^d	σ^p	σ^t	$\sigma^t(ZORA)$	$\delta(Sn)$	$\delta(Sn)$		$\delta(Sn)^{exp}$
SnH_4	4582.76	−456.62	4126.14	3433.7[a] 3381[b]	0.00	0.00	0	0
SnF_4	4741.50	−376.98	4364.52	–	−238.38	–	–	–
$SnCl_4$	4833.24	−844.71	3988.53	3149.0[a] 2960[b]	137.61	275.8[a]	422[b]	350
$SnBr_4$	5084.82	−604.10	4480.72	3446.7[a] 3723[b]	−354.58	−21.9[a]	−341[b]	−138
$SnBr_3I$	5135.39	−350.30	4785.10	3688.0[a]	−658.96	−263.2[a]	–	−416
$SnBr_2I_2$	5185.96	−131.80	5054.16	3933.2[a]	−928.02	−508.4[a]	–	−687
$SnBrI_3$	5236.52	59.67	5296.20	4185.8[a]	−1170.06	−761.0[a]	–	−947
SnI_4	5287.04	225.83	5512.86	4442.4[a] 4942[b]	−1386.72	−1017.5[a]	−1561[b]	−1201

[a] Results taken from Ref. [32].
[b] Results taken from Ref. [33].

Table 3
Nuclear magnetic shieldings of Si and Sn nuclei in their reference systems.

Molecule	$\sigma[Si; Si(CH_3)_4]^a$
SiH_4	479.19
SiF_4	411.96
$SiCl_4$	408.09
$SiBr_4$	398.02
SiI_4	409.16
Molecule	$\sigma[Sn; Sn(CH_3)_4]^a$
SnH_4	3626.14
SnF_4	
$SnCl_4$	3838.53
$SnBr_4$	3842.72
$SnBr_3I$	3869.10
$SnBr_2I_2$	3867.16
$SnBrI_3$	3849.20
SnI_4	3811.86

[a] Results of calculations with Eq. (15).

Table 4
Chemical shifts of Si and Sn in SiX_4, SnX_4 and $SnBr_{4-n}I_n$ molecular systems taken from the average calculated values of reference (Eq. (16)).

Molecule	σ	$\delta(Si)$	$\delta(Si)^{exp}$
SiH_4	489.09	−67.81	−9.9
SiF_4	520.96	−99.68	−109.0
$SiCl_4$	428.09	−6.81	−20.0
$SiBr_4$	491.62	−70.34	−93.6
SiI_4	755.36	−334.08	−346.2
Molecule	σ^t	$\delta(Sn)$	$\delta(Sn)^{exp}$
SnH_4	4126.14	−311.18	−500
SnF_4	4364.52	−549.56	–
$SnCl_4$	3988.53	−173.57	−150
$SnBr_4$	4480.72	−665.76	−638
$SnBr_3I$	4785.10	−970.14	−916
$SnBr_2I_2$	5054.16	−1239.20	−1187
$SnBrI_3$	5356.90	−1541.94	−1447
SnI_4	5528.08	−1713.12	−1701
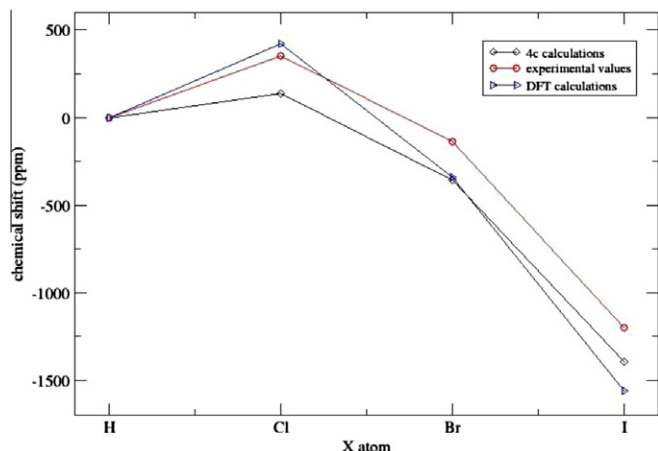
Fig. 7. Experimental and theoretical chemical shift of Sn in SnX_4 (X = H, Cl, Br, I).

The average values are

$$\sigma[Si(CH_3)_4] = 421.28 \pm 29.33 \text{ ppm}$$
$$\sigma[Sn(CH_3)_4] = 3814.96 \pm 79.12 \text{ ppm}(2.1\%) \qquad (16)$$

The chemical shift of Sn in SnH_4 was not directly obtained from experiments [33]. If its value is disregarded

$$\sigma[Sn(CH_3)_4] = 3846.43 \pm 19.25 (\simeq 0.5\%) \text{ ppm} \qquad (17)$$

When calculating chemical shifts from such references and those magnetic shielding, we calculated new results, which showed a close fit between theory and experiments. These results are shown in Table 4. The best correspondences were obtained for SiI_4 and SnI_4. Our calculated values of σ^{ref} allowed us to reproduce semiquantitatively experimental measurements of δ.

When chemical shift were calculated applying Eq. (14), our results were close to experiments and follows them more closely (see Fig. 7)-as compared to previous results obtained with the ZORA-SO scheme [33].

5. Concluding remarks

Absolute NMR magnetic shieldings may be obtained from theory or experiments, although in this last case, there is no specific measurement whose output provides this data. The measurement of spin-rotation constants, which are related to the paramagnetic component of σ via a NR relationship developed long ago, and calculation of the diamagnetic component, give what is known as *experimental* magnetic shieldings. Instead, what can actually be measured is the chemical shift.

In this article we showed a procedure to obtain absolute magnetic shieldings of reference compounds through the addition of measured experimental chemical shifts and accurate calculation of magnetic shieldings. We obtained σ(Si; Si (CH$_3$)$_4$) = 421.28 $\pm$ 29.33 ppm and σ(Sn; Sn (CH$_3$)$_4$) = 3814.96 $\pm$ 79.12 ppm.

These results for Sn are much larger than previously calculated values or those taken from experiments, which considering the above metioned NR relationship, do not work in the relativistic domain.

Analysis of the influence of basis sets and electron correlation on both NMR spectroscopic parameters was performed for small systems like HX (X = F, Br, I). We improved Dyall's basis set to obtain converged J-coupling results. Medium-sized optimized basis sets that work fairly well within the NR domain are no longer good choices.

From our results, it becomes apparent that relativistic effects enlarge the electron correlation on J-couplings. We showed this by comparing the influence on J-couplings within the NR domain.

We also showed the results of accurate calculations of nuclear magnetic shieldings of molecular systems that contained more than three heavy atoms. Our results were not very close to previous ZORA-SO calculations. We believe that our method provides better results because: (i) the tendency of the chemical shift we obtain is closer to that of experimental values, and (ii) the shielding of Si and Sn for reference compounds has a very small dispersion.

Acknowledgments

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