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Implementation of the IPPP–CLOPPA–INDO/S method for the study of indirect nuclear spin coupling constants and its application to molecules containing tin nuclei

Edith L. Botek [a], Gustavo A. Aucar [a,*], Marshall G. Cory [b], Michael C. Zerner [b]

[a] *Departamento de Física, FCENyA, Universidad Nacional del Nordeste, Campus Universitario,*
Avenida Libertad 5500 (3400) Corrientes, Argentina
[b] *Quantum Theory Project, University of Florida, Gainesville, FL, USA*

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Abstract

The inner projection of the polarization propagator, using contributions from localized orbitals, IPPP–CLOPPA, and using the intermediate neglect of the differential overlap model parameterized for spectroscopy, INDO/S, was implemented and used to calculate indirect nuclear spin coupling constants. The resulting model was tested on a group of small- and medium-size model compounds by comparing its performance with that of other semi-empirical methods and experiments where available. It is shown that in general the INDO/S approximation with the use of $S^2_{\mathrm{N}}(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$ atomic parameters taken from the INDO and AM1 approaches is the most suitable scheme to describe coupling constants. The introduction of atomic parameters for $S^2_{\mathrm{N}}(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$ in the case of heavy nuclei like Sn, is a critical step. The correction of the bonding beta parameter for this nucleus was also necessary within the INDO/S approximation to improve the accuracy and to better account for indirect relativistic effects. The application of this parameterization was accomplished in a series of tetrastannacyclohexanes and different pathways for coupling transmission were analyzed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Indirect nuclear spin coupling constants; IPPP–CLOPPA–INDO/S; Atomic parameters; Relativistic effects

1. Introduction

In spite of the great diversity of methods available at present [1–8] for the theoretical study of coupling constants, limitations still exist. These limitations are related to three sources: (a) schemes applied for the calculation of the ground-state wavefunction, (b) approximations made for the perturbative computation and (c) the treatment of molecules containing heavy atoms that require the introduction of relativistic effects.

The use of both wavefunctions and perturbative schemes of high quality such as those employed in ab initio methods is aimed at obtaining the best possible agreement with experimental data. However, the reliability of the results depends on the atomic basis size employed [9]. Accuracy implies a great number of atomic functions per atom and the resulting calculations are not feasible for even medium-size organometallic complexes, let alone the larger complexes of our interest.

On the other hand, a correct qualitative description of the electronic structure of large molecules can be obtained using semi-empirical methods, which considerably reduce computational requirements [10]. Parameters obtained in an empirical fashion take into account effects not included explicitly within the Hamiltonian used (such as the influence of large basis sets, dynamic correlation and relativistic effects in heavy atoms [11]). This fact makes these models especially interesting for application in the study of complexes containing a great number of atoms, and particularly heavy atoms.

At this point the implementation of IPPP [12–14] (inner projection of the polarization propagator)–CLOPPA (contributions from localized orbitals within the polarization propagator approach) [15]–INDO/S

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* Corresponding author.

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(intermediate neglect of the differential overlap model parameterized for spectroscopy) [16,17] method becomes a promising alternative, even more than its precursors IPPP–CLOPPA–INDO [18] and IPPP–CLOPPA–MNDO [6]/AM1 [7]/PM3 [8]. This is because: (a) the great deal of atoms parameterized under the INDO/S scheme opens the way to the possible study of complexes containing various types of atoms such as transition metals [19,20] or lanthanides [21], (b) the perturbative approach together with such wavefunctions to describe the values of the coupling constants performs adequately, and (c) this model is parameterized on optical properties and thus should produce an accurate propagator.

The aim of this article is to present the IPPP–CLOPPA–INDO/S method and examine its performance on various small- and medium-size molecules, analyzing the introduction of certain combinations of the atomic parameters $S^2_{\mathrm{N}}(0)$, the square of the contact term, and $\langle r_{\mathrm{N}}^{-3}\rangle$. A particular case is discussed in detail: tin parameterization and the criteria applied for the parameters, a scheme that appears to be appropriate for other heavy atoms. The model is then applied to calculate Sn–Sn coupling constants in tetrastannacyclohexanes and the IPPP–CLOPPA method is used to analyze the different pathways for transmitting these couplings.

2. Method of calculation

In the first step of the IPPP–CLOPPA–INDO/S method the electronic wavefunction is calculated using the INDO/S model. The second step is to perform a unitary transformation on the canonical molecular orbitals (MOs) to obtain localized molecular orbitals (LMOs), which resemble the intuitive chemical concepts of bonds, thorough bonding and antibonding orbitals and lone pairs. The localization procedure used in this work is that of Engelmann and Contreras [12]. A third step consists of calculating the polarization propagator using the RPA [22] theory to calculate a given property such as the coupling constants within a fragment of interest by means of the inner projections technique [23] onto the subspace defined by the LMOs of the fragment. This subspace can be as large as we choose, and might contain the whole system.

Considering an isotropic phase, the local contribution (contribution from a fragment) to the coupling constant between nuclei N and N′ has the form [18]

$$J_{\mathrm{L,NN'}} = J^{\mathrm{FC}}_{\mathrm{L,NN'}} + J^{\mathrm{PSO}}_{\mathrm{L,NN'}} + J^{\mathrm{SD}}_{\mathrm{L,NN'}} \tag{1}$$

where the superscripts FC, PSO and SD designate the Fermi contact, paramagnetic spin–orbit and spin–dipolar interactions, respectively. Each component of Eq. (1) can be expressed as

$$J^{X}_{\mathrm{L,NN'}} = (\Omega_X/3) \sum_{ia \le jb}^{\mathrm{local}} \sum_{\alpha} V^{X,\alpha\alpha}_{iajb,\mathrm{NN'}}\,{}^{n}W_{iajb} \tag{2}$$

where each term in the sum defines a ‘coupling pathway’ and involves two virtual excitations $i \to a$ and $j \to b$ with i,j (a, b) occupied (vacant) LMOs that belong to the fragment. The constant Ω_X contains between others the gyromagnetic constants of nuclei N and N′ [6]. Each term of Eq. (2) can be factored in the following way:

$$J^{X}_{ia,jb;\mathrm{NN'}} = U^{X}_{ia,\mathrm{N}}\,{}^{n}W_{ia,jb}\,U^{X}_{jb,\mathrm{N'}} \tag{3}$$

where$U^{X\alpha\beta}_{ia,\mathrm{N}}$ is the perturbation matrix element or ‘perturbator’, see below, which is a measure of the strength of the $i \to a$ virtual excitation due to the perturbation X, ${}^{n}W_{ia,jb}$ is a matrix element of the propagator projected on the LMOs of the fragment and n indicates its singlet $(n = 1)$ or triplet $(n = 3)$ character [18]. This propagator gives the response of the molecular fragment connecting two virtual excitations $i \to a$ and $j \to b$. For a CLOPPA calculation the propagator matrix is evaluated in such a way that the whole molecule is described in terms of LMOs.

The perturbators within the CLOPPA method are implemented at the semi-empirical level using a one-center approximation, and they have the form:

$$\begin{aligned} U^{FC}_{ia,\mathrm{N}} &= \langle i|\delta(\vec{R}_{\mathrm{N}})|a\rangle = C^{\mathrm{s}}_{i\mathrm{N}}C^{\mathrm{s}}_{a\mathrm{N}}S^2_{\mathrm{N}}(0) \\ U^{PSO,\alpha}_{ia,\mathrm{N}} &= i\langle r_{\mathrm{N}}^{-3}\rangle(C^{\alpha}_{i\mathrm{N}}C^{\gamma}_{a\mathrm{N}} - C^{\gamma}_{i\mathrm{N}}C^{\beta}_{a\mathrm{N}})\varepsilon_{\alpha\beta\gamma} \\ U^{SD,\alpha\beta}_{ia,\mathrm{N}} &= \frac{1}{5}\langle r_{\mathrm{N}}^{-3}\rangle f(C^{x}_{p}, C^{y}_{p}, C^{z}_{p}) \end{aligned} \tag{4}$$

where α,β and γ refer to Cartesian coordinates, coefficients $C^{s}_{i(a)\mathrm{N}}$ are those of ‘s’ type belonging to atom N, $C^{\alpha}_{i(a)\mathrm{N}}$ is the atomic coefficient np$_{\alpha}$, $\varepsilon_{\alpha\beta\gamma}$ is the anti-symmetric tensor and ‘f’ is a function of ‘np’ type atomic coefficients for ‘i’ and ‘a’ LMOs. The electronic density at the site of nucleus N, $S^2_{\mathrm{N}}(0)$, together with $\langle r_{\mathrm{N}}^{-3}\rangle$, where ‘$r$’ is the distance between an electron of a ‘p’ type orbital and the nucleus, are atomic parameters and are fit empirically.

Relativistic effects must be taken into account when calculating spin couplings between nuclei when at least one of them is ‘heavy’. Following the ideas of Lee et al. [24], electrons in the valence region can be treated non-relativistically. Indirect relativistic effects can be considered through the semi-empirical parameters of the wavefunction as in the MNDO [25] and AM1 [26] approaches. Besides, direct relativistic effects, which are important in the region close to the nuclei, are considered in such methods, when used to evaluate coupling constants [6,7], through MCDF [11] ab initio calculated $S^2_{\mathrm{N}}(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$ atomic parameters. In the case of the INDO approximation, where only Se and Te atoms are considered heavy, this type of effect is taken into account in the parameterization of Galasso et al. [27], where the mentioned parameters are empirically adjusted to reproduce experimental values of coupling constants [28]. Such atomic parameters had not been systematically examined before in the INDO/S method for the study of coupling constants, and this point will be examined in the following section.

3. Results and discussion

3.1. General comments

ZINDO, the computer program used, was not specifically parameterized for the calculation of coupling constants. For this reason it is important to analyze which $S^2_N(0)$ and $\langle r_N^{-3}\rangle$ parameters should be used for calculating the perturbators. Table 1 contains a list of the values for such parameters used for the different semi-empirical approaches in the calculation of coupling constants involving several different nuclei. INDO/S values for $S^2_N(0)$ correspond to the values of atomic density for 's' type orbitals in this approximation. The largest discrepancies occur for O, F and Sn.

In Table 2 a comparative study of coupling constants contributions (FC, SD and PSO terms) is given. The values reported in this Table were calculated using the $S^2_N(0)$ and $\langle r_N^{-3}\rangle$ parameters corresponding to the different semi-empirical approximations as shown in Table 1.

All the geometries of compounds that appear in Table 2 were optimized using the AM1 method. The IPPP–CLOPPA method was implemented for the unsaturated compounds in such a way that the electronic π systems were excluded from the polarization propagator calculation in order to avoid instabilities of non-singlet type that occur in these systems. The detailed reasons for this are described in the literature [29].

From Table 2 the following general arguments can be made. ^1J(CH) INDO/S coupling constants are in good agreement with experimental values, even improving the results obtained with INDO approximation. A similar statement is also valid for ^2J(CH) and ^2J(HH) cases. It should be pointed out that ^1J(CF) values calculated with the INDO/S wavefunction and $S^2_N(0)$ and $\langle r_N^{-3}\rangle$ parameters from the AM1* and INDO methods are also in good agreement with experimental results (data not shown). The $S^2_F(0)$ parameter calculated with the INDO/S wavefunction is nearly one-half of the value used in AM1* and causes the INDO method to underestimate coupling constants compared with experiment. It is also noted that good values of ^1J(SiH) compared with experiment are obtained with the $S^2_{Si}(0)$ parameter from the INDO method and the INDO/S wavefunction (data not shown). Coupling constants involving I and Br calculated using the INDO/S and AM1 wavefunctions yield instabilities. Coupling constants involving N and P atoms appear to be satisfactorily described by the AM1 wavefunction. Coupling constants between F and H are underestimated in all cases, which is likely a consequence of the one-center approximation used in our semi-empirical methods, as the non-contact contributions to coupling constant is null for the cases where at least one hydrogen atom is involved. This approximation seems to be a limitation in this case because it is known from the literature that these contributions are important in FH couplings. As an example, in an ab initio SOPPA (second-order polarization propagator approach) calculation for the FH molecule, the FC term is 338.3 Hz, the SD term is negligible, but the PSO term is 195.7 Hz [30].

As expected, the AM1* method is the best in reproducing couplings involving Sn atoms [31]. Besides, its $S^2_{Sn}(0)$ parameter, which takes into account direct relativistic effects, is related to core orbital contraction; indirect relativistic effects are considered through the semi-empirical parameters of the wavefunction. Bearing in mind these considerations, a further analysis to improve the coupling constant values involving tin atoms is presented using INDO/S wavefunction. The following discussion is also feasible for the analysis of coupling constants in compounds containing Se, Cl, Br, I and other heavy atoms.

Table 1
$S^2_N(0)$ and $\langle r_N^{-3}\rangle$ atomic parameters used with different semi-empirical approaches

	$S^2_N(0)$			$\langle r^{-3}\rangle$	
N	AM1* [11]	INDO [10]	INDO/S	AM1* [11]	INDO [10]
H	0.55	0.37	0.55	1.00	1.00
C	2.77	4.03	3.02	1.69	2.88
N	6.93	6.93	5.26	2.20	7.24
O	4.95	12.07	8.39	4.95	4.95
F	21.31	21.31	12.58	7.54	5.95
Si	3.81	3.81	4.09	2.04	2.04
P	3.26	5.63	5.16	2.38	3.32
Cl	11.01	10.64	10.18	6.77	6.71
Sn	18.00		1.76	6.99	

Table 2
Comparison of calculated J values for several small molecules using both different semi-empirical approximations and parameterizations for $S_{\mathrm{N}}^2(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$[a]

			INDO/S [b]	INDO/S(A) [c]	AM1* [d]	INDO/S(I) [e]	INDO [f]	Exp.
C_2H_6		FC	19.78	16.63	24.49	35.32	49.42	
	^1J(CC)	SD	1.71	0.59	1.01	1.71	1.49	
		PSO	−0.98	−0.39	−1.00	−0.98	−2.70	
		Total	20.51	16.84	24.51	36.05	48.20	34.60 [5]
	^1J(CH)		126.72	116.17	178.80	114.63	117.99	124.90 [5]
	^2J(CH)		−2.23	−2.05	−12.27	−2.02	−7.18	−4.50 [5]
	^2J(HH)		−5.76	−5.75	−50.82	−2.64	−6.19	−13.00 [5]
C_2H_4		FC	29.51	18.50	95.88	39.28	86.42	
	^1J(CC)	SD	0.94	59.86	20.48	0.94	7.61	
		PSO	−1.07	−10.00	−11.07	−1.07	−17.70	
		Total	29.38	68.35	105.29	39.15	76.33	67.60 [5]
	^1J(CH)		165.97	132.03	247.83	130.28	153.24	156.40 [35]
	^2J(CH)		1.12	1.66	−58.46	1.64	−11.54	−2.40 [5]
	^2J(HH)		18.38	19.20	−57.21	8.80	2.29	2.50 [5]
CH_3F		FC	−108.67	−168.84	−151.17	−246.02	−250.12	
	^1J(FC)	SD	14.81	11.03	13.10	14.81	19.94	
		PSO	7.06	5.26	−23.07	7.06	−14.16	
		Total	−86.80	−152.56	−161.14	−224.15	−244.34	−157.50 [35]
	^1J(CH)		148.20	135.86	189.62	134.06	139.98	149.10 [35]
	^2J(FH)		5.24	8.87	8.71	6.01	4.40	46.36 [35]
SiH_4	^1J(SiH)		−285.00	−264.99	−513.90	−179.45	−163.30	−202.50 [36]
Si_2H_6		FC	220.27	190.52	495.76	190.52	63.92	
	^1J(SiSi)	SD	2.89	2.89	4.80	2.89	0.65	
		PSO	−0.42	−0.42	−1.00	−0.42	−0.76	
		Total	222.75	193.00	499.56	193.00	63.80	88.30 [36]
	^1J(SiH)		−248.78	−231.33	−605.08	−156.66	−148.44	−197.71 [36]
$SiHF_3$	^1J(SiH)		−626.80	−582.79	−452.08	−394.67	−259.64	−381.70 [36]
HCN	^1J(CH)		267.00	298.11	280.95	294.16	235.40	274.00 [5]
	^2J(NH)		7.04	24.55	14.56	16.62	11.42	±8.60 [5]
		FC	16.50	−7.01	14.90	−10.21	6.26	
	^1J(NC)	SD	−0.89	−15.54	−6.59	− −0.89	−18.98	
		PSO	0.00	−12.30	−4.15	0.00	−14.23	
		Total	15.61	−34.85	4.16	−11.10	−26.94	−18.60 [5]
CH_3NH_2	^1J(NH)		−29.82	−39.29	−67.70	−26.61	−36.61	
		FC	1.78	2.15	−1.83	3.13	−5.09	
	^1J(NC)	SD	−1.44	−0.26	−0.35	−1.44	−1.49	
		PSO	1.06	0.19	0.89	1.06	3.62	
		Total	1.40	2.08	−1.30	2.75	−2.96	−4.50 [35]
NH_3	^1J(NH)		−31.52	−41.53	−64.73	−28.13	−38.94	−61.23 [11]
	^2J(HH)		−8.99	−8.99	−18.14	−4.12	−7.01	−10.40 [11]
PH_3	^1J(PH)		22.80	14.43	94.08	16.84	17.03	184.76 [11]
	^2J(HH)		−14.78	−14.78	−78.07	−6.78	−13.87	−13.80 [11]
H_2O	^1J(OH)		−46.58	−27.44	−48.17	−45.34	−8.73	−78.97 [11]
C_2OH_2		FC	9.45	5.10	30.08	18.14		
	^1J(OC)	SD	25.49	14.98	0.00	25.49		
		PSO	10.87	6.39	0.00	10.87		
		Total	45.80	26.47	30.08	54.50		22.00 [37]
	^1J(CH)		243.88	223.57	217.30	220.61		171.50 [37]
	^2J(HH)		−21.87	−21.86	−32.21	−10.03		−15.80 [37]
FH	^1J(FH)		196.06	332.11	141.40	224.91	18.62	530.00 [35]
SnH_4	^1J(SnH)		−86.24	−881.80	−2500.00			−1930 [32]
HCl	^1J(ClH)		−47.30		−19.53		−9.68	+41.47 [11]
HBr	^1J(BrH)		−622.85		−351.90			±57.68 [11]
HI	^1J(IH)		−891.18		−1564.92			

[a] All couplings in Hz.

[b] Values calculated with INDO/S wavefunction. $S_{\mathrm{N}}^2(0)$ parameter calculated with atomic functions of such approximation and $\langle r_{\mathrm{N}}^{-3}\rangle$ taken from INDO method.

[c] Values calculated with INDO/S wavefunction. $S_{\mathrm{N}}^2(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$ parameters taken from MNDO/AM1* methods.

[d] Values calculated with RPA–AM1* method.

[e] Values calculated with INDO/S wavefunction. $S_{\mathrm{N}}^2(0)$ and $\langle r_{\mathrm{N}}^{-3}\rangle$ parameters are taken from INDO method.

[f] Values calculated with RPA–INDO method.

3.2. Analysis of tin bond parameter

For molecules containing atoms with a large atomic number such as tin ($Z = 50$), relativistic effects are important [32]. The INDO/S parameters for tin are crude and have not yet been published; some results of couplings involving heavy atoms are displayed in Table 2, and they are in poor agreement with experiment. It might be noted that the $S^2_{\mathrm{Sn}}(0)$ parameter taken from MCDF [11] calculations (used for AM1*) improves only slightly the calculated $^1J(\mathrm{SnH})$ coupling with the INDO/S wavefunction. At this point, it might be expected that some modifications of the semi-empirical parameters that determine the wavefunction are necessary. Toward this goal, the INDO/S beta bonding (resonance integral) parameter for Sn was compared with their corresponding values used in AM1*. In the AM1* $\beta(\mathrm{s}) = -3.23$ eV and $\beta(\mathrm{p}) = -4.29$ eV, while within INDO/S the default value is $\beta(\mathrm{s}) = \beta(\mathrm{p}) = -23.00$ eV. This leads to a large difference in the one-electron terms of the Fock matrix, and suggests a re-examination of the INDO/S values. It was found that $\beta(\mathrm{s}) = \beta(\mathrm{p}) = -8.00$ eV yields coupling constants involving Sn atoms in good agreement with experimental results, and has little effect on the calculated electronic spectroscopy of Sn-containing model compounds. Table 3 displays some of the results obtained and compares them with AM1* and experimental values. With the value for β, an INDO/S geometry optimization of SnH_4 gives an interatomic distance of Sn–H = 1.758 Å, which compares very well with the experimental value for such a distance, i.e. 1.701 Å [32]. The experimental value is obtained theoretically in the optimization of SnH_4 molecule when the bonding parameter used for Sn is -11.00 eV. Some coupling constants were calculated with $\beta = -8.00$ eV and $\beta = -11.00$ eV parameters for Sn and a comparison between them is shown in Table 4.

Table 3
Comparison between coupling constants calculated with RPA–AM1* and RPA–INDO/S methods with $S^2_{\mathrm{Sn}}(0)$ taken from AM1* and $\beta = -8.00$ eV [a]

		AM1*	INDO/S	Exp.
SnH_4 [b]	$^1J(\mathrm{Sn–H})$	−2500.00	−2164.00	−1930.00 [32]
	$^2J(\mathrm{H–H})$	65.00	33.10	15.30 [32]
$SnMe_4$	$^1J(\mathrm{Sn–C})$	−300.31	−378.03	−337.80 [38]
	$^2J(\mathrm{Sn–H})$	137.30	36.22	54.00 [36]
$SnMeH_3$	$^1J(\mathrm{Sn–H})$	−2388.73	−1860.70	−1852.00 [39]

[a] Geometries optimized with AM1*. All couplings in Hz.

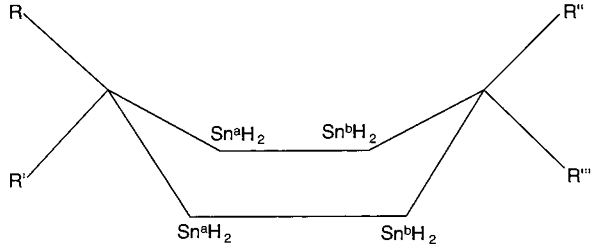
[b] Experimental interatomic distance Sn–H of 1.701 Å was used and angles were optimized with AM1*.

Table 4
Comparison between couplings involving Sn atoms with $\beta = -8$ and -11 eV [a]

J exp.		J ($\beta = -8.00$)	J ($\beta = -11.00$)
SnH_4			
−1930.00 [32]	$^1J(\mathrm{Sn–H})$	−2164.00	−1756.00
15.30 [32]	$^2J(\mathrm{H–H})$	33.10	15.38
$SnMe_4$			
−337.80 [38]	$^1J(\mathrm{Sn–C})$	−378.03	−306.00
+54.00 [36]	$^2J(\mathrm{Sn–H})$	36.22	30.15
$SnMeH_3$			
	$^1J(\mathrm{Sn–C})$	−473.69	−349.35
−1852.00 [39]	$^1J(\mathrm{Sn–H})$	−1862.00	−1562.00
	$^2J(\mathrm{Sn–H})$	36.70	28.00
$O(SnMe_3)_2$			
±440.00 [36]	$^2J(\mathrm{Sn–Sn})$	−259.99	−146.14
$S(SnMe_3)_2$			
±218.00 [36]	$^2J(\mathrm{Sn–Sn})$	−237.04	−90.88
Sn_2Me_6			
4460.00 [36]	$^1J(\mathrm{Sn–Sn})$	4500.09	2860.64
−244.00 [36]	$^1J(\mathrm{Sn–C})$	−311.00	−272.15
48.00 [36]	$^2J(\mathrm{Sn–H})$	40.00	30.00

[a] All couplings in Hz.

In general, both columns of Table 4, with $\beta = -8.00$ eV and $\beta = -11.00$ eV, are in good agreement with the experimental values. In this re-parameterization of Sn the following reasoning is considered. The use of experimental interatomic distance in the SnH_4 molecule allows one to consider relativistic effects originating in the scalar Hamiltonian terms like mass velocity and Darwin, that directly relate to the relativistic contraction of bond distances in a systematic and empirical fashion. Furthermore, Kirpekar et al. [32] have found a value of about -1700 Hz for $^1J(\mathrm{SnH})$ in SnH_4 with ab initio calculations at the correlated level of approximation and they showed that spin–orbit contributions to that coupling are about 1%. The inclusion of a further correction due to indirect relativistic effects is obviously needed. On the other hand, values obtained using the INDO/S approach of $^1J(\mathrm{SnH}) = -1756$ and -2164 Hz with $\beta = -11.00$ and -8.00 eV, respectively, are both close to its experimental value of -1930 Hz. A more acute re-parameterization of the INDO/S model for Sn would yield a closer value for the coupling constant with a bond parameter between -8.00 and -11.00 eV. It could be feasible, at this point, to fit this parameter to reproduce experimental data of coupling constants instead of interatomic distances because the former appear to be more sensitive to such a change than the latter. This can be verified with the variation of Sn–H distances and coupling constants in SnH_4 when the bond parameter varies from -8.00 to -11.00 eV.



Scheme 1.

Table 5
Compounds examined in this study, see Scheme 1

Compound	R	R′	R″	R‴
1	H	H	H	H
2	H	H	H	Me
2′	H	H	Me	H
3	H	H	Me	Me
4a	H	Me	H	Me
4a′	Me	H	Me	H
4b	H	Me	H	Me
5	H	Me	Me	Me
6	Me	Me	Me	Me
7	H_2C=		H_2C=	

It should be pointed out that this analysis has been carried out considering only ^1J(SnH) in SnH_4 because of the lack of experimental data available, as far as we know, on the geometries of compounds containing tin.

3.3. Sample application

For the reasons above, we adopt $\beta = -11.00$ eV and carry out INDO/S calculations of one, two and three bond coupling constants between tin atoms in 1,2,4,5-tetrastannacyclohexanes, which were measured by Mitchell et al. [33]. In order to study the question related to the additivity of different pathways of coupling transmission in Sn–Sn couplings, it appears to be very important to analyze ^{2+4}J(SnSn) and their signs for geminal couplings in these cycles, as well as $^{3+}$ 3J(SnSn) for vicinal values.

Model compounds and their enumeration for the different substituents involved in the coupling constants analyzed are shown in Scheme 1 and Table 5, respectively. In all cases the model compounds used contain hydrogens replacing methyl groups bonded to tin atoms. Such a replacement diminishes computing time and does not considerably affect the Sn–C–Sn angle to which geminal Sn–Sn coupling constants are particularly sensitive [34].

Coupling constants calculated with both INDO/S ($\beta = -11.00$ eV) and AM1* approaches compared with experimental values in several tetrastannacyclohexanes are presented in Table 6. INDO/S type calculations with boat-like (INDO/S(B)) and chair-like (INDO/S(C)) conformations were performed because it is only known (from Ref. [33]) that compounds **1** and **4a** exist in boat conformation. Calculations with both conformations could be useful to predict the conformations of the other compounds.

From Table 6 it is observed that ^1J(SnSn) coupling constants are described well using the INDO/S model. For this kind of coupling the values calculated with AM1* seriously underestimate experimental data.

Geminal J(Sn–Sn) coupling constants are of great interest (see Ref. [33]) because of the drawbacks involved in their sign assignation and the existence of different pathways of transmission that contribute to such couplings in cyclic compounds. Table 6 displays, in parentheses, the signs given by Mitchell et al.

The RPA-AM1* results of geminal Sn–Sn coupling constants overestimate experimental values and have a monotonic variation when substituents are introduced; they have negative sign in all cases. Otherwise, the values of J obtained within the RPA-INDO/S method vary considerably when substituents are introduced, and, in general, they are closer to the variation range of the experimental data. Moreover, a sign change is observed in passing from compounds series **1**–**6** in this series.

The ^2J(Sn–Sn) coupling presents three main mechanisms of transmission in these cycles: through space contribution (TS) [18], through two bonds (TB2) and through four bonds (TB4) contributions. In the case denoted by ^2J(Sn^b–Sn^b) in Table 6 the pathway involving two bonds is Sn^b–C–Sn^b and that of four bonds involves Sn^b–Sn^a–C–Sn^a–Sn^b. The IPPP–CLOPPA method allows one to study such coupling pathways, so subspaces were defined as follows (see Scheme 2): TS = $(1+2+3+4)$, TB2 = $(1+2+3+4+5+6)$-TS and TB4 = $(1+2+3+4+7+8+9+10)$–TS. Only bonding orbitals are detailed.

In Table 7 an analysis of transmission pathways for ^2J(Sn^b–Sn^b) is given for compounds **1**, **2** and **3** in the boat conformation.

It is clear that there are large contributions from the pathways through space and through four bonds to ^2J(Sn^b–Sn^b) and there is good agreement between the sum of the three contributions and the total value calculated. The values obtained from the sum of the different pathways appear additive. In the cases where the RPA–INDO/S results of ^2J(Sn–Sn) are in good agreement with experimental trends, one might conclude that it is possible to analyze coupling transmission with the IPPP–CLOPPA method. The deviation of these geminal couplings from the experimental trends would originate, in particular, from contribution of two bonds pathway to ^2J(Sn^b–Sn^b). It is noted in Table 7 that such contributions vary more than contributions TS and TB4 (even in sign) with the introduction of the substituent groups.

Vicinal Sn–Sn calculated coupling constants show good semiquantitative agreement with the experimental trend predicting positives values for the series of compounds **1**–**6** when the INDO/S wavefunction is used.

It is important to remark that the geometrical structures of these rings are not well known. That makes it difficult to analyze the coupling constants studied since the results are sensitive to structure. This is particularly important in the case of geminal couplings because it is well known [34] that they are very sensitive to geometric and substituent changes. Such dependence is also observed for vicinal couplings.

Table 6
Comparison between coupling constants calculated with the INDO/S approximation for the boat, INDO/S(B), and chair, INDO/S(C), conformations and AM1* approximation [a]

Compound	INDO/S(B)	INDO/S(C)	AM1*	Exp.
^1J(Sn–Sn)				
1	3961.60	4000.00	2558.40	4245.00
2	3613.00	3548.70	2460.00	3828.00
2′	3931.00		2463.50	
3	3564.60	3598.00	2315.10	3600.00
4a	3226.00		2333.30	3560.00
4a′	3831.50		2296.20	
4b		3975.20		3568.00
5	3525.25	3582.70	2172.18	3275.00
6	3276.11	3272.00	2091.54	3010.00
7 [b]	3231.50	3513.50	2675.00	3707.00
^2J(Sn^a–Sn^a)				
1	−215.70	−218.00	−635.00	157.00(−)
2	−134.20	−114.40	−600.60	112.00(−)
2′	−207.90		−634.60	
3	−139.40	−115.90	−601.50	81.00(−)
4a	−96.70		−556.40	11.00(±)
4a′	−111.00		−600.70	
4b		−103.70		17.00(±)
5	0.83	20.00	−551.51	51.00(−)
6	138.26	80.00	−467.46	268.00(−)
7 [b]	355.50	321.00	−445.50	859.00(+)
^2J(Sn^b–Sn^b)				
1	−215.70	−218.00	−635.00	157.00(+)
2	−194.30	−253.40	−621.30	43.00(+)
2′	−116.70		−608.80	
3	−38.30	−117.30	−541.70	136.00(−)
4a	−96.70		−556.40	11.00(±)
4a′	−111.00		−600.70	
4b		−103.70		17.00(±)
5	−30.69	−102.30	−540.69	215.00(−)
6	138.26	80.00	−467.46	268.00(−)
7 [b]	355.50	321.00	−445.50	859.00(+)
^3J(Sn–Sn)				
1	86.80	86.70	10.40	102.00
2	36.90	25.00	−37.90	53.00
2′	77.70		−7.80	
3	34.00	35.40	−53.30	
4a	4.70		−71.57	14.00
4a′	62.20		−28.80	
4b		73.70		21.00
5	24.49	23.10	66.70	18.00
6	5.89	4.50	88.91	40.00
7 [b]	−20.20	−13.10	26.50	202.00

[a] All geometries were optimized with AM1* method. All couplings in Hz. Experimental values are taken from Ref. [33].

[b] In Ref. [33] substituents are $Ph_2C=$ instead of $H_2C=$.

4. Conclusions

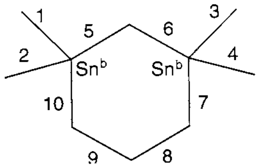
The implementation of the IPPP–CLOPPA–INDO/S method for the study of indirect spin–spin coupling constants yields satisfactory results when tested in a group of small- and medium-size molecules adopting different values for the atomic parameters $S_N^2(0)$ and $\langle r_N^{-3} \rangle$. In general, a careful choice of these parameters must be made for the different nuclei involved to further refine the model.

In the case of coupling constants involving Sn, these considerations are not enough to take into account all the relativistic effects through such parameters. It was found necessary to refine some of the atomic parameters of the INDO/S model in order to calculate results closer to experiment.

In particular, it was straightforward to modify the INDO/S β parameter for Sn, in such a way that little effect on calculated geometry or spectroscopy resulted. A detailed analysis leads to the conclusion that the optimal value for this parameter lies between -8.00 and -11.00 eV.

When the values of $\beta = -11.00$ eV and $S_N^2(0)$ from MCDF are taken for the Sn nucleus for a homologous group of tetrastannacyclohexanes, very acceptable results are obtained. These calculations allow us to conclude that this method is very promising for use in the analysis of J in these organometallic complexes. These initial successes suggest that minor changes in the resonance integrals of the INDO/S Hamiltonian might prove very profitable.

It might be of value to refine the parameters of the theory, not only the resonance integral β, but also perhaps the spin–orbit value and the value of $\langle r_N^{-3} \rangle$ for Sn based on experimental information on well-characterized systems. For the moment we do not do that, recognizing that our results are already good for values of β between -8 and -11 eV for systems that are reasonably well characterized, and a shortage of experimental data on which to fine tune such parameters.



Scheme 2.

Table 7
Different contributions to $^2J(\mathrm{Sn^b}–\mathrm{Sn^b})$ coupling for compounds **1**–**3**

	TS	TB2	TB4	TS+TB2+TB4	Total
1	−50.60	−121.60	−61.90	−234.10	−215.70
2	−32.20	−48.50	−78.30	−159.00	−194.30
3	−36.30	66.60	−70.70	−40.40	−38.30

Another approach would be to systematically fit the parameters of the theory to data involving molecules containing atoms of the forth row, assuming all such parameters are smooth functions of atomic number. This we will do, but it is outside the scope of the present paper.

From this analysis we believe it should be possible to perform theoretical studies of medium-size and quite large molecules containing heavy atoms, and it should be possible to study a great diversity of compounds. This observation is due to the wide range of nuclei parameterized for the INDO/S wavefunction calculation including transition metals and the lanthanides [40]. The inclusion of relativistic effects in the INDO/S model should make these studies particularly attractive.

Before concluding, it is necessary to once again point out that the calculation of coupling constants is quite sensitive to geometry. In these initial studies we have used geometries obtained from the AM1 model Hamiltonian. Nevertheless, we know that spectroscopy is not well reproduced using geometries from this model, and is vastly improved using either experimental geometry, or those obtained from density functional theory using such exchange and correlation potentials such as those found in BLYP and B3LYP. We will need to examine these structures to determine if our resulting deviations from experiment in the calculation of coupling constants are from the coupling constant theory we use, from the INDO/S model, or simply from poor starting geometry.

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