

# RPA AM1 calculations of NMR spin–spin coupling constants: geminal $^{119}\text{Sn}$ – $^{119}\text{Sn}$ couplings

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Received 9 October 1995; revised 8 April 1996

## Abstract

In this paper a method for calculation of NMR spin–spin coupling constants is implemented at the random phase approximation (RPA) using the semiempirical AM1 approach with localized molecular orbitals. It is found that for tin-containing molecules the AM1 ground state wave function is near a Hartree–Fock instability of the non-singlet type. A method to circumvent this condition is presented and the resulting approach is applied to study a few structural and substituent effects on geminal  $^2J(^{119}\text{Sn}^{119}\text{Sn})$  couplings known from the literature. Results thus obtained show several trends which are in fair agreement with those known experimentally.

**Keywords:** Tin; NMR; Spin–spin couplings; Molecular orbital calculations; Geometrical dependence; RPA AM1 calculations

## 1. Introduction

The large increase in the sensitivity of NMR spectrometers that has taken place during the last two decades has made it possible to measure systematically almost all naturally occurring magnetic isotopes [1]. Among them, a relevant place is occupied by the spin-1/2 most abundant isotopes of tin, i.e.  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$ . Spin–spin coupling constants involving such isotopes were found in many cases to strongly depend on the molecular structure [2,3].

It is well known that the theoretical analysis of spin–spin coupling constants may increase notably the scope of NMR spectroscopy to study molecular structural problems if it is used to complement experimental observations. However, shortcomings of present theoretical approaches to study in a precise way these coupling constants and their trends along the Periodic Table are well known [4,5], especially when heavy atoms are involved. Although new formulations based on first principles to achieve this goal are promising [6,7], they

seem to be far beyond the actual computing facilities to be used systematically to complement experimental work. For this reason, it seems to be quite interesting to resort to only approximate approaches based on semiempirical methods to obtain insight into electronic mechanisms defining spin–spin coupling constants. Along this line, a few years ago the method of ‘contributions from localized orbitals within the polarization propagator approach’ (CLOPPA) [8] was extended for use with MNDO [9] ground state wave functions and several trends of couplings involving a few heavy atoms were described [10–12].

In this paper the possibility of using AM1 wave functions [13] to implement a similar approach for couplings involving  $^{119}\text{Sn}$  nuclei is discussed. AM1 tin parameters were reported a few years ago [14]. In the present work such parameters are found to yield greatly exaggerated values for these types of coupling. Such large values are thought to originate in ‘quasi-instabilities’ of the non-singlet type [15] of the AM1 ground state wave functions for tin containing compounds. This point is discussed in the Section 2, where a way to overcome this condition for this particular case is presented. In order to test the resulting approach, it is applied to study, from a theoretical point of view, several structural and substituent effects on  $^2J(\text{SnSn})$  coupling constants. These couplings are chosen owing

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to the wealth of data known in the literature which show that they strongly depend, both in magnitude and sign, on different geometrical and substituent effects [2,3,16–20]. In fact, absolute values of such couplings are known to range from 0 to 35 000 Hz [2,3]. Calculations are carried out in a few model compounds which are chosen intending to mimic experimental examples known in the literature. In order to shorten the expressions, the tin isotopes involved in couplings considered in this work are not explicitly shown, although in all cases they refer to  $^{119}\text{Sn}$ .

## 2. Method of calculation

The polarization propagator approach to calculate second order contributions to spin–spin coupling constants using semiempirical ground state wave functions was described in detail in previous papers [21,22]. When this approach is used together with localized molecular orbitals, important insight into physico-chemical factors affecting coupling constants can be obtained [11]. The resulting approach was dubbed ‘the CLOPPA method’ and it was first [8] implemented at the INDO level [23]. With such an approach, spin–spin coupling constants in molecules containing first and second row atoms, as well as Se and/or Te atoms, can be calculated and different transmission mechanisms studied. A similar approach [10] was afterwards implemented at the MNDO level [9] which allowed the study of compounds containing a few heavier atoms [10–12]. In this paper a similar approach is implemented at the AM1 level. As this implementation closely parallels those at the INDO [8] and MNDO [10–12] levels, only a brief description is given here, stressing differences and similarities with previous versions.

Within the CLOPPA method, the spin–spin coupling constant between nuclei  $N$  and  $N'$ ,  $J(NN')$  can be written as a sum of contributions originating in two virtual excitations  $i \rightarrow a$ ,  $j \rightarrow b$ , as in Eq. (1).

$$J(NN') = \sum_{ia,jb} J_{ia,jb}(NN') \quad (1)$$

where  $i, j$  ( $a, b$ ) are occupied (vacant) LMOs representing bonds or lone pairs (antibonding orbitals), provided a valence minimum basis set is employed and only elements belonging to Group IV or beyond are considered. The sum in Eq. (1) runs over all occupied and vacant LMOs belonging to the molecule under study.

An expression like Eq. (1) holds for each of the Fermi contact (FC), the paramagnetic spin orbital (PSO), and spin dipolar (SD) interactions. In all three cases each  $J_{ia,jb}(NN')$  term can be factored into ‘perturbators’  $U$  and the polarization propagator  $P$  [8,22] terms,

Eq. (2). The respective ‘perturbators’ are given in Eqs. (3a), (3b) and (3c).

$$J_{ia,jb}^X(NN') = U_{ia,N}^X {}^n P_{ia,jb} U_{jb,N'}^X \quad (2)$$

$$U_{ia,N}^{\text{FC}} = \langle i | \delta(\vec{r}_N) | a \rangle \quad (3a)$$

$$U_{ia,N}^{\text{PSO},\alpha} = \left\langle i \left| \frac{L_N^\alpha}{i\hbar r_N^3} \right| a \right\rangle \quad (3b)$$

$$U_{ia,N}^{\text{SD},\alpha\beta} = \left\langle i \left| \frac{3n_{N\alpha}n_{N\beta} - \delta_{\alpha\beta}}{r_N^3} \right| a \right\rangle \quad (3c)$$

where  $n_{N\alpha} = r_{N\alpha}/r_N$ , and  $\alpha$  and  $\beta$  are Cartesian components. The remaining symbols have their usual meaning.

The matrix elements of the singlet and triplet polarization propagators  ${}^n P_{ia,jb}$  can be written as

$${}^n P_{ia,jb} = ({}^n A \pm {}^n B)^{-1} \quad (4)$$

where the triplet polarization propagator,  $n = 3$ , with the lower sign corresponds to the FC and SD terms, and the singlet polarization propagator,  $n = 1$ , with the upper sign corresponds to the PSO term. At the random phase approximation (RPA) matrices  ${}^n A$  and  ${}^n B$  are calculated from the Hartree–Fock solution, or from one of its approximations, as shown in Eqs. (5a), (5b), (5c) and (5d) [24].

$${}^1 A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} + 2 \langle aj | ib \rangle - \langle aj | bi \rangle \quad (5a)$$

$${}^1 B_{ia,jb} = \langle ab | ji \rangle - 2 \langle ab | ij \rangle \quad (5b)$$

$${}^3 A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} - \langle aj | bi \rangle \quad (5c)$$

$${}^3 B_{ia,jb} = \langle ab | ji \rangle \quad (5d)$$

In the present approach the ground state wave function is calculated at the AM1 [13] level. However, MNDO, instead of AM1, Sn parameters are used. The reason for this change in Sn parameters is explained below. As in previous CLOPPA implementations [8,10–12], the polarization propagator is evaluated at the RPA level. Two-electron integrals entering in Eqs. (5a), (5b), (5c) and (5d) are calculated in a consistent form with the AM1 approximation. The ‘perturbators’, Eqs. (3a), (3b) and (3c), are evaluated using the monocentric approximation [25]. Besides, both the electronic density at the site of the nucleus  $N$ ,  $S_N^2(0)$  and  $\langle r_N^{-3} \rangle$ , i.e. the mean value of  $r_N^{-3}$  where  $r_N$  is the distance from an electron in a p-type orbital to the corresponding nucleus  $N$ , are considered as atomic parameters and their values taken from relativistic multiconfigurational Dirac Fock (MCDF) ab initio calculations [26]. For tin atoms these parameters are, in a.u., 18.0000 and 6.9888 respectively.

It is well known that relativistic effects are important when dealing with coupling constants involving heavy

Table 1

Comparison between calculated coupling constants using AM1 and MNDO tin parameters within the RPA AM1 approach in compounds of type  $\text{Me}_3\text{Sn-X}$ ; experimental values taken from the literature are also shown <sup>a</sup>

X	<sup>1</sup> $J(\text{Sn-C})_{\text{Mc}}$ (Hz)			<sup>2</sup> $J(\text{Sn-H})_{\text{Mc}}$ (Hz)			<sup>1</sup> $J(\text{Sn-X})$ (Hz)		
	Exp.	AM1	AM1*	Exp.	AM1	AM1*	Exp.	AM1	AM1*
H	-352 <sup>b</sup>	-930	-360	+56 <sup>b</sup>	+390	+160	-1744 <sup>b</sup>	-4858	-2310
SnMe <sub>3</sub>	-244 <sup>c</sup>	-890	-295	+48 <sup>c</sup>	+391	+150	+4460 <sup>c</sup>	+2103	+2640
Me <sup>3</sup>	-337 <sup>d</sup>	-900	-340	+54 <sup>d</sup>	+368	+150	-337 <sup>d</sup>	-900	-340

<sup>a</sup> All calculations were carried out using the respective optimized geometries. AM1\* stands for the AM1 approach where AM1 tin parameters were replaced by the MNDO parameters. <sup>b</sup> Taken from Ref. [30]. <sup>c</sup> Taken from Ref. [31]. <sup>d</sup> Taken from Ref. [32].

nuclei [27]. With the approach presented here, relativistic effects are taken into account following the ideas of Balasubramanian and Pitzer [28]. Electrons in the valence region are treated non-relativistically. Indirect relativistic effects are taken into account through the empirical parameters of the AM1 method. Direct relativistic effects, which are important in the region where the interactions between magnetic nuclei and electrons that define coupling constants take place, are taken into account through the MCDF calculated  $S_N^2(0)$  and  $\langle r_N^{-3} \rangle$  atomic parameters.

To implement this approach, the MOPAC program [29], where the AM1 Sn parameters [14] were introduced, was appropriately modified. However, when carrying out calculations of spin-spin coupling constants in a variety of tin-containing molecules, notably overestimated values were found. A few examples are given in Table 1 for compounds of type  $\text{Me}_3\text{SnX}$ . The origin of such conspicuously overestimated values was traced to a 'quasi-unstable' condition of the non-singlet type [15] of the AM1 ground state wave function in tin-containing molecules. This condition was verified by determining the smallest eigenvalues of the corresponding  ${}^3P_{\alpha,\beta}$  matrix [4,5]. In order to find out which is the origin of the 'quasi-instability' problem, a detailed comparison between MNDO and AM1 Sn parameters was carried out. The following points are worth noting.

One of the main differences between the MNDO and AM1 approaches is that in the latter a number of different spherical Gaussians are assigned to several atoms which are intended to correct the excessive repulsions at van der Waals' distances observed in the former. Parameters defining these spherical Gaussians were also optimized with all other parameters in the AM1 approach. For this reason, the number of AM1 parameters for most atoms is larger than that of MNDO ones. However, this is not the case for tin atoms, where the number and type of AM1 parameters is exactly the same as in the MNDO method. This indicates that a successful parameterization for tin atoms was achieved without modifying the core-core repulsion term. Most of the tin AM1 parameters agree within a few percent with those of MNDO. However, in both methods a notable difference for the bonding parameters for p-type

orbitals,  $\beta_p$ , is observed. In fact, the AM1  $\beta_p(\text{Sn})$  parameter is about one-half the MNDO  $\beta_p(\text{Sn})$  one. Small values for the bonding parameter corresponding to p-type orbitals were reported previously to yield either instabilities or 'quasi-instabilities' of the non-singlet type [15,33].

Taking into account these considerations, in this work the AM1 Sn parameters were replaced in the AM1 method by the MNDO ones. In this way the 'quasi-instability' condition for the AM1 wave functions of tin-containing molecules is overcome while keeping the advantages of the AM1 approach. With this 'mixed' approach, many calculations of coupling constants involving a tin nucleus were carried out and a conspicuous improvement was observed in their values compared with results obtained using the same approach but with the AM1 tin parameters. A few results are displayed in Table 1. For  $J(\text{SnX})$  couplings (X different from H), they correspond to the sum of the FC, PSO and SD terms. However, it is important to stress that all these couplings are found to be, by far, dominated by the FC interaction. Non-contact contributions amount only to a few percent. For couplings involving at least one H nucleus, non-contact contributions are identically zero due to the approximations involved in this approach. The overvalued geminal  $J(\text{SnH})$  couplings displayed in Table 1 suggest that they may be affected by quasi-instabilities that do not affect the corresponding  ${}^1J(\text{SnC})$  couplings.

### 3. Results and discussion

In order to test the ability of the 'mixed' approach delineated above, RPA AM1\*, a few structural and substituent dependencies of geminal  ${}^2J(\text{SnSn})$  couplings are studied in this section. As quoted above, values for these types of coupling are spread over a very large range, and they strongly depend both on substituent and on structural effects. One of the important advantages of a theoretical analysis like that presented in this paper is the possibility of studying both effects separately. As non-contact contributions to all  ${}^2J(\text{SnSn})$  couplings studied in this work are found to be, by far, much

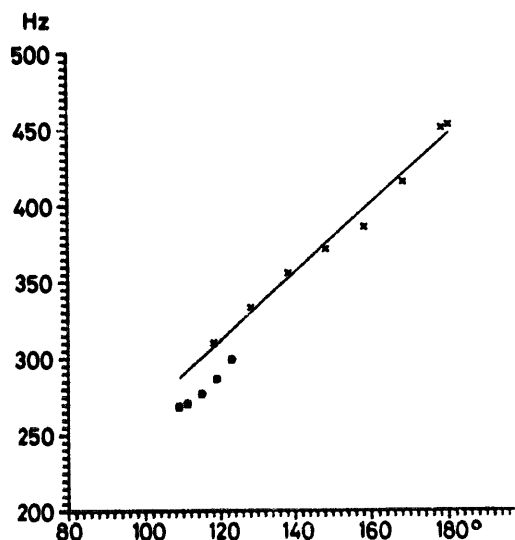


Fig. 1. Sn-X-Sn angle dependence of the absolute value of  $^2J(\text{SnSn})$  couplings in  $\text{Me}_3\text{Sn-O-SnMe}_3$  (x) and in  $\text{Me}_3\text{Sn-S-SnMe}_3$  (\*). It should be recalled that the actual signs of these couplings were not determined experimentally. The present calculations yield negative couplings.

smaller, in absolute value, than the corresponding FC term, only total couplings, i.e. the sum of the PSO, SD and FC terms are shown.

A detailed study of the dependence of  $^2J(\text{SnSn})$  couplings on Sn-X-Sn moieties (X = O, S, Se, Te) was reported by Mitchell and coworkers [20]. For X = O, a linear relationship was established, Eq. (6), using some absolute values of  $^2J(\text{SnSn})$  couplings measured in solution and others in solid state for compounds of type  $\text{RSn-O-SnR}'$  with the corresponding Sn-O-Sn angles  $\theta$  measured in solid state. This angle strongly depends on the nature of substituents R and R', which include linear fragments as well as organic groups. It is important to recall that only the absolute values of these couplings were determined experimentally. Calculations presented in this paper yield them as negative.

$$\theta = 0.086^2J(\text{SnSn}) + 98.6 \quad (6)$$

$$r^2 = 0.990, n = 8$$

where  $\theta$  is measured in degrees and  $^2J(\text{SnSn})$  in hertz.

In Fig. 1 the 'mixed' AM1 dependence of  $^2J(\text{SnSn})$  on the Sn-O-Sn angle in the model compound  $\text{Me}_3\text{Sn-O-SnMe}_3$ , which is intended to mimic the actual molecules, is displayed. Values for different angles were obtained as follows. Firstly, the geometry of this model compound was fully optimized with the AM1 method, i.e. using MNDO tin parameters. Then, the different points were obtained by increasing the Sn-O-Sn angle while keeping fixed all other geometrical parameters. In all cases it was found that the total  $^2J(\text{SnSn})$  coupling is, by far, dominated by the FC

interaction. A linear regression of calculated  $^2J(\text{Sn-O-Sn})$  vs. the Sn-O-Sn angle  $\theta$  yields

$$\theta = -0.437^2J(\text{SnSn}) - 15.763 \quad (7)$$

$$r^2 = 0.984, n = 8$$

where  $\theta$  is measured in degrees and  $^2J(\text{SnSn})$  in hertz.

When comparing Eq. (6) and Eq. (7) the following facts should be stressed. Both equations correspond to linear correlations, and the absolute value of the corresponding coupling increases with increasing Sn-O-Sn angle. However, these equations differ notably: the calculated couplings are undervalued compared with the experimental values. For instance, at the optimized AM1 geometry of  $\text{Me}_3\text{Sn-O-SnMe}_3$ , where the Sn-O-Sn angle is  $119^\circ$ , the calculated coupling only amounts to  $-310\text{ Hz}$ , while for this compound the experimental value is  $418\text{ Hz}$  [20]. For larger angles, the departure between calculated and experimental values is more significant. However, it should be recalled that experimental couplings may show significant electronic and geometric effects which are not present in the model compound. For instance, actual geometrical effects could introduce important changes in the hybridization of the tin atoms which in turn may also have important effects on couplings involving any of these two atoms. Also, it is important to recall that the regression of Eq. (6) was obtained [20] using some absolute values of  $^2J(\text{SnSn})$  couplings measured in solution and others in solid state, and that the Sn-O-Sn angles were always measured in solid state.

Fig. 1 also displays the RPA AM1  $^2J(\text{SnSn})$  couplings vs. the Sn-S-Sn angle in  $\text{Me}_3\text{Sn-S-SnMe}_3$ . Calculations were carried out using the same procedure as that employed in the oxygen-containing compound. The AM1 optimized geometry renders an Sn-S-Sn angle of  $109^\circ$ . For this geometry the calculated coupling is  $-268\text{ Hz}$ . When the Sn-S-Sn angle is increased to  $123^\circ$ , a coupling of  $-298\text{ Hz}$  is calculated. When comparing these couplings with the experimental values it should be noted that measurements have only been carried out in compounds where the Sn-S-Sn angle ranges from  $85.8$  to  $116.5^\circ$  [20]. The respective couplings range, in absolute value, from 207 to 217 Hz, i.e. in this case the calculated absolute values are somewhat overvalued.

When comparing the calculated values at the optimized geometries for the  $\text{Me}_3\text{Sn-O-SnMe}_3$  and  $\text{Me}_3\text{Sn-S-SnMe}_3$  compounds it is observed that the trend given by the replacement in the coupling pathway of the oxygen atom by the sulfur atom is correctly reproduced, although only on a qualitative basis.

Another well-known problem is the large range of variations observed in  $^2J(\text{SnSn})$  couplings in non-cyclic hydrazines of type  $(\text{Me}_3\text{Sn})_2\text{N-NXY}$ . These couplings are assumed to be highly sensitive to the interaction of

Table 2

RPA AM1\* calculated geminal Sn–Sn coupling constants in  $(\text{H}_3\text{Sn})_2\text{N–N–X}_2$  ( $\text{X} = \text{SiH}_3, \text{PbH}_3, \text{SnH}_3, \text{H}, \text{CH}_3, \text{F}$ ). Experimental values of related compounds are given in parentheses; the calculated charge in the  $\text{NX}_2$  moiety is also shown

X	$^2J(\text{SnSn})$ (Hz)	N– $\text{X}_2$ charge
$\text{SiH}_3$	–1064.4	0.1076
$\text{PbH}_3$	–964.8	–0.0313
$\text{SnH}_3$	–671.7 (972) <sup>b</sup>	–0.0002
H	–631.2 (486) <sup>c</sup>	0.1466
$\text{CH}_3$	–535.4	0.1499
F	–409.4	0.2877

<sup>a</sup> Charge in a.u. The tin parameters are those of the MNDO method.

<sup>b</sup> In  $(\text{SnMe}_3)_2\text{N–N}(\text{SnMe}_3)_2$ , taken from Ref. [17]. <sup>c</sup> In  $(\text{SnMe}_3)_2\text{N–NMe}_2$ , taken from Ref. [17].

the lone pairs of both N atoms [17]. In this paper the RPA AM1\* approach is applied to study in a separate way the following two effects on  $^2J(\text{SnSn})$  couplings in these types of hydrazine: (a) the substituent effect for a fixed geometrical structure; (b) the orientational effect of both N lone pairs. In order to study the electronic substituent effects, hydrazines of type  $(\text{H}_3\text{Sn})_2\text{N–NX}_2$  are taken as model compounds with  $\text{X} = \text{SiH}_3, \text{PbH}_3, \text{SnH}_3, \text{H}, \text{CH}_3$  and F. Their geometries were built up as follows. Keeping fixed the lone-pair–N–N–lone-pair dihedral angle at  $0^\circ$ , the remaining geometrical parameters for  $\text{X} = \text{SnH}_3$  were optimized. For other substituents the same geometry for the  $(\text{H}_3\text{Sn})_2\text{N}$  moiety was taken and the X structure was built up from typical values. In this way only electronic substituent effects are present in couplings thus calculated. They are shown in Table 2, where a large sensitivity of these couplings to electronic substituent effects is observed. The net charge in the  $\text{NX}_2$  moieties is also reported in the same table. It is observed that, with the exception of  $\text{X} = \text{SiH}_3$ , they follow the same trend. This different behavior of a silicon-containing compound suggests that in this case the AM1 parameterization also yields an instability problem to the ground state wave function. This suggestion is further supported when comparing the AM1 and MNDO  $\beta_p(\text{Si})$  bonding parameters, the former being about one-third of the latter. It is interesting to recall that for some Si-containing compounds the INDO ground state wave function also presents a 'quasi-instability' condition [34].

To study the N lone-pairs orientational effect on  $^2J(\text{SnSn})$  couplings,  $(\text{H}_3\text{Sn})_2\text{N–NH}_2$  is taken as a model compound. The geometry for the  $0^\circ$  conformation was built-up as described above. Geometries for other conformations were obtained from the  $0^\circ$  one by applying rigid rotations around the N–N bond. Couplings thus obtained are plotted in Fig. 2, where sign changes for dihedral angles ca.  $60^\circ$  and  $135^\circ$  are observed. The maximum algebraic value is found at ca.  $105^\circ$ , which corresponds to a minimum interaction be-

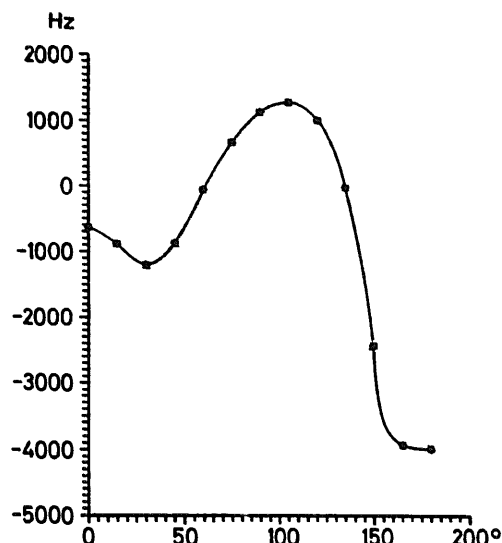


Fig. 2.  $^2J(\text{SnSn})$  couplings vs. the dihedral angle between the lone pairs of the N atoms in  $(\text{H}_3\text{Sn})_2\text{N–NH}_2$ .

tween the N lone-pairs. Two minima are observed for  $0^\circ$  and  $180^\circ$ . For these two dihedral angles, maxima for the s character of the N lone pair in the Sn–N–Sn moiety are also observed. Therefore, this coupling is found to be algebraically larger, the larger is the p character of the N lone pair.

$^2J(\text{SnSn})$  couplings in compounds of type  $(\text{Me}_3\text{Sn})_{4-n}\text{ER}_n$  depend strongly both on the nature of the Group IV E element and on n, the number of alkyl groups attached to E [18]. In this work this trend is studied in compounds of type  $(\text{H}_3\text{Sn})_{4-n}\text{EMe}_n$ , with  $n = 0-2$ , and  $\text{E} = \text{C}, \text{Sn}$ . In each case, coupling constants are calculated using the optimized AM1\* geometries. Results thus obtained are displayed in Table 3. It is observed that the increase in the number of  $\text{SnH}_3$  groups attached to the central E atom yields more negative  $^2J(\text{SnSn})$  couplings closely paralleling the experimental trend reported by Wrackmeyer [18]. Also, the change in sign when the central  $\text{E} = \text{C}$  atom is replaced by  $\text{E} = \text{Sn}$  is adequately reproduced.

In order to get insight into the mechanisms that define geminal  $^2J(\text{SnSn})$  couplings, CLOPPA analyses were attempted in all problems discussed above. At this point it is important to recall that the number of terms

Table 3

Dependence of RPA AM1\* calculated  $^2J(\text{SnSn})$  (Hz) couplings on n in  $\text{Me}_n\text{–E}(\text{SnH}_3)_{4-n}$  ( $n = 0-2$ ;  $\text{E} = \text{C}, \text{Sn}$ ). Experimental values of related compounds are given in parentheses<sup>a</sup>

E	$\text{Me}_2\text{–E}(\text{SnH}_3)_2$	$\text{Me–E}(\text{SnH}_3)_3$	$\text{E}(\text{SnH}_3)_4$
C	–486 (–19) <sup>b</sup>	–649 (–230) <sup>c</sup>	–753 (–325) <sup>d</sup>
Sn	+213 (+763) <sup>e</sup>	+122 (+259) <sup>f</sup>	+13 (+20) <sup>g</sup>

<sup>a</sup> The experimental values are taken from Ref. [18]. <sup>b</sup> In  $\text{Me}_2\text{C}(\text{SnMe}_3)_2$ . <sup>c</sup> In  $\text{EtC}(\text{SnMe}_3)_3$ . <sup>d</sup> In  $\text{C}(\text{SnMe}_3)_4$ . <sup>e</sup> In  $\text{Me}_2\text{Sn}(\text{SnMe}_3)_2$ . <sup>f</sup> In  $\text{EtSn}(\text{SnMe}_3)_3$ . <sup>g</sup> In  $\text{Sn}(\text{SnMe}_3)_4$ .

entering into the sum of Eq. (1) amounts to  $nm \cdot (nm + 1)/2$ , where  $n$  and  $m$  stand for the number of occupied and vacant molecular orbitals respectively, obtained with the MO approach used to calculate the ground state wave function. As for any medium-sized molecule, this total number of terms is very large; Eq. (1) only yields a clear picture of factors defining a given trend in cases when such a sum is, by far, dominated by only a few terms. Unfortunately, this is not the case for those types of coupling where the FC part of Eq. (1) is built up from several tens of positive and negative terms, all of them of a magnitude close to or larger than the total value. However, such a feature seems to reflect an actual physical fact and, apparently, the notably large range for these types of coupling originates in the different degree of cancellations of positive and negative terms that take place owing to different physico-chemical properties of each compound.

#### 4. Concluding remarks

The perturbative calculation of the three second-order contributions to NMR spin–spin coupling constants within the polarization propagator approach at the RPA level, together with the use of localized molecular orbitals, constitute the background of the CLOPPA approach [8]. This method, at least in principle, can be implemented using any unideterminantal ground state wave function, whether it is an *ab initio* or a semiempirical one. If this implementation is intended to be useful for the experimentalist to complement NMR measurements, then for the time being the use of a semiempirical approach seems to be mandatory, especially if heavy-atom-containing molecules are to be studied. Among the different possibilities, the implementation of the CLOPPA approach within the AM1 method is quite appealing owing to the widespread use of this semiempirical approach to study other molecular properties. However, ground state AM1 wave functions of tin-containing molecules are found to be close to Hartree–Fock instabilities of the non-singlet type. To overcome this condition, in this work the AM1 Sn parameters were replaced by the MNDO Sn ones in the AM1 method.

This 'mixed' RPA AM1 approach was applied in the present work to study a few known trends of  $^2J(\text{SnSn})$  coupling constants. Such trends are reproduced, at least on a semiquantitative base. This is a remarkable fact, since difficulties in describing geminal coupling constants theoretically are well known [4]. The CLOPPA analysis, Eq. (1), of the FC term of these types of coupling shows that they are built up from many terms of opposite signs and magnitudes close to the total FC contribution. On the one hand, this shows that  $^2J(\text{SnSn})$  couplings are very difficult to describe accurately, and, on the other hand, it provides a rationalization for the

large range observed experimentally for such couplings [3].

Results presented in this paper are encouraging and suggest that the RPA AM1 method can be an adequate approach to complement NMR measurements. However, to be useful for spectroscopists, the implementation of this method should be easy enough in such a way that researchers with a very general background in molecular orbital theory can apply it to specific problems. To this end, a subprogram to be coupled to MOPAC [29] will soon be deposited in an international distribution center.

#### Acknowledgements

Economic support from UBACYT and CONICET, as well as fellowships from SECYT-UNNE (E.B.) and CONICET (S.G.), are gratefully acknowledged.

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