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Ab-initio SOS-CI Calculations of Magnetic Properties of the First- and Second-Row Hydrides

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Non-empirical SOS-CI calculations based on Nakatsuji's theory are reported for the nuclear spin–spin coupling constants, (considering all the four spin-interactions), magnetic shielding constants and magnetic susceptibilities of all the first- and second-row hydrides. The calculated values, except for ^{2}J(HH), correlate satisfactorily with the available experimental data and with the corresponding CHF results, and prove that the SOS-CI model according to Nakatsuji may be a convenient alternative to the time-consuming CHF procedures in order to get accurate estimates of second-order magnetic properties.

Key words: SOS-CI Nakatsuji's formalism – Magnetic properties.

1. Introduction

Nakatsuji [1] has shown that the second-order energy of the CHF theory can also be written exactly in a simple sum-over-states configuration-interaction (SOS-CI) perturbation formula, (Eq. (50) of his paper), if one considers all the singly-excited configurations and at the same time introduces doubly-excited configurations in a restricted way. This correspondence allows the bypassing of the differences that arise in the second-order properties as calculated by the CHF procedures, e.g. via the Finite Perturbation Theory (FPT), and the conventional SOS perturbation treatments, as claimed earlier by Ditchfield et al. [2]. Furthermore, the computational simplicity of Nakatsuji's SOS-CI approach, requiring a non-iterative procedure, seems attractive since it could provide a promising alternative to the time-consuming CHF computations, especially for the calculations of second-order magnetic properties of large molecules, for which there is a current widespread interest.

Recently, Fukui et al. [3] have used Nakatsuji's approach to calculate at *ab-initio* level the magnetic shielding constants of CH_4, NH_3, H_2O, and HF and the nuclear spin–spin coupling constants of some simple hydrocarbons with the semiempirical INDO method and considering the only Fermi-contact perturbation operator. In both cases, these authors have reproduced well the corresponding FPT results. In the present paper we report an extended application of Nakatsuji's approach to the non-empirical calculation of the magnetic shielding constants (σ), magnetic susceptibilities (χ), and nuclear spin–spin coupling constants (J), taking into account all the four mechanisms of spin information transmission, namely the Fermi-contact (FC), "diamagnetic" (OD) and "paramagnetic" (OP) orbital–dipole, and spin-dipole (SD) interactions, for the entire series of the first- and second-row hydrides. This sample of molecules has been selected to give the opportunity to check the SOS-CI results by comparison with corresponding CHF *ab-initio* results and so to test the actual convenience and accuracy of Nakatsuji's formalism in evaluating magnetic properties.

2. Computational Details

The various magnetic properties have been evaluated using the SOS-CI perturbation technique according to Nakatsuji [1]. In particular, as an example of application for a spin-free perturbation, the paramagnetic orbital–dipole (OP) contribution to the nuclear spin–spin coupling constant between nuclei A and B is given by:

$$J(\mathrm{OP}) = -(4\gamma_A\gamma_B\beta^2 h/3\pi^2)\sum_n E_n^{-1} \sum_{i,j}^{\mathrm{occ}} \sum_{k,l}^{\mathrm{unocc}} c_{ik,n}c_{jl,n}\langle i|r_A^{-3}L_A|k\rangle\langle i|r_B^{-3}L_B|j\rangle$$

where $c_{ik,n}$ is the coefficient of the singlet excitation $i \rightarrow k$ in the nth eigenstate of the H matrix defined as follows:

$$H_{ik,jl} = \langle {}^1\psi_i^k|\boldsymbol{H}_0|\psi_j^l\rangle - \langle {}^1\psi_0|\boldsymbol{H}_0|{}^1\psi_{ij}^{kl}\rangle - \delta_{ij}\delta_{kl}\langle {}^1\psi_0|\boldsymbol{H}_0|{}^1\psi_0\rangle$$

where $\boldsymbol{H}_0$ is the unperturbed Hamiltonian, ${}^1\psi_0$ the GS wavefunction, ${}^1\psi_i^k$ the singlet state formed by promoting one electron from the ith occupied MO to the kth virtual one, and ${}^1\psi_{ij}^{kl}$ is the doubly-excited singlet configuration $\| \cdots ikjl(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)/2 \cdots \|$ in standard notation. On the other hand, for the case of a spin-dependent perturbation, e.g. the Fermi-contact contribution to the nuclear spin–spin coupling constant between nuclei A and B, the following expression can be derived from the Nakatsuji formula:

$$J(FC) = -(64\gamma_A\gamma_B\beta^2 h/9)\sum_n E_n^{-1} \sum_{i,j}^{\mathrm{occ}} \sum_{k,l}^{\mathrm{unocc}} c_{ik,n}c_{jl,n}\langle i|\delta(r_A)|k\rangle\langle l|\delta(r_B)|j\rangle$$

where $c_{ik,n}$ is the coefficient of the triplet excitation $i \rightarrow k$ in the nth eigenstate of the H matrix defined as follows:

$$H_{ik,jl} = \langle {}^3\psi_i^k|\boldsymbol{H}_0|{}^3\psi_j^l\rangle + \langle {}^1\psi_0|\boldsymbol{H}_0|\psi_{ij}^{kl}\rangle - \delta_{ij}\delta_{kl}\langle {}^1\psi_0|\boldsymbol{H}_0|{}^1\psi_0\rangle$$

where ψ_{ij}^{kl} is the doubly-excited state defined by $\| \cdots ikjl(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)/2 \cdots \|$ in standard notation. For the computations we have utilized three different basis sets: the contracted Gaussian 6-31G basis set for atoms H to F and Si [4], the 4-31G basis set for atoms P, S, and Cl [5], and the minimal STO-5G basis set [6] for atoms Na, Mg, and Al, for which no basis set of the split-valence N-31 type is as yet available. All integrals required for the evaluation of the various matrix elements were calculated using standard methods [7–9].[1] The calculations were performed with the origin of the coordinates at the centre of mass of the molecules and using gaugeless Gaussian functions. Experimental geometries were used, if known, otherwise theoretical structures were assumed [10, 11, and Refs. therein].

3. Results and Discussion

The SOS-CI treatment of Nakatsuji has yielded calculated values of the one-bond X—H nuclear spin–spin coupling constants of LiH to HF and of SiH_4 to HCl (Table 1) in fair agreement with the available experimental values, suggesting that the N-31G split-valence basis sets are flexible enough for the purpose of describing satisfactorily all the four types of spin interactions. The results obtained for the second-row hydrides NaH, MgH_2, and AlH_3 with the minimal basis set STO-5G are probably of lower quality, as expected however from the inherent inferiority of this basis set. The absolute magnitudes of the indirectly bonded H—H coupling constants (Table 2) are systematically overestimated relative to their experimental counterparts: this situation has, however, been encountered

Table 1. SOS-CI values of $^1J(XH)$ in the first- and second-row hydrides (Hz)[a]

Molecule	FC	SD	OP	OD	Total	Exper.
LiH	209.43	0.09	−0.06	0.03	209.49	
BeH_2	−65.39	−0.08	0.08	0.02	−65.38	
BH_3	163.62	0.37	−1.76	0.09	162.31	(137)[b] [25]
CH_4	166.40	−0.08	1.38	0.38	168.07	125.0 [26]
NH_3	−72.28	0.08	−2.51	−0.19	−74.91	−61.1 [27]
H_2O	−73.93	1.70	−10.90	−0.34	−83.47	−79 [28]
HF	259.20	−24.17	191.66	3.42	430.11	530 [29]
NaH	2417.23	0.08	−0.54	−0.10	2406.78	
MgH_2	−421.94	0.01	0.10	0.02	−421.81	
AlH_3	864.91	0.03	−1.70	−0.01	863.22	
SiH_4	−242.01	0.02	0.65	−0.10	−241.43	−202.5 [30]
PH_3	156.10	−2.68	3.96	0.28	157.67	182 [31]
H_2S	24.56	−0.80	4.03	0.07	27.86	
HCl	14.38	−0.84	14.00	0.11	27.65	41 [32]

[a] The X nuclei are: ^7Li, ^9Be, ^{11}B, ^{13}C, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{33}S, ^{35}Cl.
[b] The quoted value refers to B_2H_6.

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[1] In addition to the errors in some formulas of Refs. [7] and [8] pointed out by Lee and Schulman [13], we found two other errors. In Eq. 3.2 of Ref. [7], for the case $l_1 + l_2 = 4$, G_1 should be amended to $-f_1p - f_2/2\gamma - 3pf_3/2\gamma - 3/2\gamma^2$. The formula for $V_4(2, 2)$ at page 8 of Ref. [8], should be amended to: $V_4(2, 2) = \cdots + 180p^2 + 48p^4\gamma$.

Table 2. SOS-CI values of $^2J(HH)$ in the first- and second-row hydrides (Hz)

Molecule	FC	SD	OP	OD	Total	Exper.
BeH_2	41.35	−0.04	0.47	−2.08	39.69	
BH_3	−9.80	0.29	0.37	−2.43	−11.57	
CH_4	−35.44	0.69	1.17	−3.27	−36.85	−12.4 [33]
NH_3	−28.92	1.39	1.98	−5.12	−30.33	−10.4 [27]
H_2O	−24.18	0.94	3.31	−6.38	−27.30	−7.2 [34]
MgH_2	250.51	−0.01	0.14	−2.69	250.64	
AlH_3	104.17	0.07	0.08	−2.22	102.10	
SiH_4	−17.70	0.10	0.21	−2.16	−19.55	−2.8 [35]
PH_3	−46.82	0.26	0.28	−1.08	−47.37	−13.2 [36]
H_2S	−48.77	0.28	0.68	−0.71	−48.51	

frequently in the vast majority of perturbational calculations and has been rationalized in terms of the insufficient account of the electron correlation contribution to the FC term [12]. The trend of the geminal H—H coupling constant over the range of molecules studied seems however qualitatively reproduced.

Comparison of the present values of the OP and SD contributions to the coupling constants of CH_4, H_2O, and HF with those calculated by Lee and Schulman [13] with the CHF-PT using the same 6-31 basis set shows that the SOS-CI treatment reproduces the CHF values quite well.

Furthermore, the present results for CH_4 to HF and for SiH_4 to HCl compare reasonably well also with the SCF-Perturbation Method results achieved by Guest et al. [14, 15] employing very large basis sets. Signs, absolute values, trends and relative importance of the various contributions to the coupling constants both along and between these two series of molecules are also in noticeable agreement with the CHF [14, 15] and SCF-PT [16, 17] results.

In order to assess the sensitivity of the SOS-CI results to the basis set, we have repeated some of the calculations by adding to the 6-31G basis set a group of single Gaussian 2p functions (exponent 1.1 [18]) on the hydrogen and/or a group of single Gaussian 3d functions (exponent 0.8 [18]) on the heavy atom. We found that the non-contact terms are much less sensitive to the basis set than the FC term and that the FC term appears far more dependent upon the basis set for the $^1J(HF)$ than for any other coupling constant, in agreement with previous theoretical conclusions [13–15].

A further comment worth noting refers to the hitherto neglected "diamagnetic" orbital-dipole (OD) contribution to the coupling constant. The present non-empirical results over the range of molecules examined seem to indicate that the OD term provides actually a quite negligible contribution both to the various X—H coupling constants and to the geminal H—H coupling constants, but with the noticeable exception of the hydrides CH_4, NH_3, and H_2O, for which significant contributions are forecast by the theory. (These comparatively large values are,

Table 3. Basis set dependence of the "diamagnetic" orbital term (Hz)

Molecule	J	STO-5G	4-31	6-31	6-31 (*H*, *p*)	6-31 (*X*, *d*)	6-31 (*H*, *p*; *X*, *d*)
HF	^{1}J(HF)	6.04	3.42	3.42	1.87	3.26	2.14
H_2O	^{1}J(OH)	−0.55	−0.35	−0.34	−0.19	−0.22	−0.16
	^{2}J(HH)	−6.39	−6.35	−6.38	−7.05	−6.89	−7.17
NH_3	^{1}J(NH)	−0.25	−0.19	−0.19	−0.12	−0.13	−0.10
	^{2}J(HH)	−4.81	−4.76	−5.12	−5.43	−5.06	−5.26

on the other hand, in agreement with those obtained by Matsuoka and Aoyama [9] with different basis sets.) The present findings afford, therefore, further quantitative corroboration to the assumption usually invoked of very scarce importance of the OD contribution to the various coupling constants, apart from the cases where the other three terms almost cancel each other. The sample data collected in Table 3 provide a preliminary, certainly not exhaustive, idea about the basis set dependence of the OD contribution. A greater sensitivity seems to be associated to the ^{1}J(XH), and particularly in the case of ^{1}J(HF), than to the geminal H—H coupling constants.

It is well known that the total computed values of both the magnetic shielding constants and magnetic susceptibilities are very sensitive to the basis set quality and to the gauge origin [19]. Use of extended basis sets of gaugeless Gaussian functions, including polarization functions all over the atoms, or use of gauge-invariant AO's are necessary to get accurate estimates of the paramagnetic contributions of these magnetic properties with a high degree of gauge independence. At any rate, the search of highly accurate reproduction of these observables was beyond the main scope of this work, i.e. to investigate the capability of the SOS-CI treatment according to Nakatsuji's proposal to give acceptable results by mimicking those provided by the CHF procedures. For the present series of hydrides the centre of mass is assumed as gauge origin; in this respect, it is, however, worthwhile mentioning that for the series BeH_2 to HF the best gauge origin was predicted theoretically [20] to lie exactly at, or close to the heavy atom, i.e. quite near to the centre of mass. On the other hand, the diamagnetic terms of both σ and χ are almost insensible to the quality of the basis set, so also the present reduced basis sets of STO-N31G or STO-NG type are sufficient to get accurate results.

It is then gratifying to note that the SOS-CI method (Table 4) was able to duplicate the values for the magnetic shielding constants of the nuclei C, N, O, and F in the relative hydrides, as obtained by Ditchfield et al. [21] with the FPT and the 4-31 basis set. The present results are also very similar to the double-zeta values obtained for both the proton and the heavy nucleus in some first-row hydrides by a CHF procedure [22]. For the second-row hydrides, our values of σ(H), 27.9 ppm (SiH_4), 30.5 (PH_3), 30.7 (H_2S), and 30.0 (HCl), are close to the CHF results obtained with very large basis sets: 28.1 ppm (SiH_4), 30.2

Table 4. SOS-CI values of the magnetic shielding constants (ppm) in the first- and second-row hydrides

	X nucleus			H nucleus		
	σ^d	σ^p	σ	σ^d	σ^p	σ
LiH	107.27	−10.72	96.55	27.17	−0.74	26.43
BeH_2	164.73	−63.10	101.63	25.29	−0.89	24.40
BH_3	226.83	−165.64	61.19	27.77	−7.26	20.51
CH_4	296.61	−75.00	221.61	30.24	−1.50	28.74
NH_3	353.75	−109.64	244.11	28.89	−0.22	28.67
H_2O	415.69	−146.52	269.17	27.02	1.88	28.90
HF	482.29	−132.94	349.35	24.14	4.74	28.88
NaH	627.15	−64.40	562.75	33.70	0.14	33.84
MgH_2	715.18	−246.25	468.93	27.99	−0.09	27.90
AlH_3	804.74	−443.00	361.74	28.96	−1.36	27.60
SiH_4	899.54	−361.53	538.01	29.82	−1.96	27.86
PH_3	980.28	−358.60	621.68	31.85	−1.35	30.50
H_2S	1064.15	−395.07	669.08	29.80	0.95	30.75
HCl	1149.64	−289.32	860.32	25.87	4.12	29.99

(PH_3), 30.7 (H_2S), and 30.1 (HCl) [23]; less satisfactory is instead the similar comparison for the heavy nucleus: this discrepancy is however not surprising, due to the important role played by the *d* polarization functions in the heavy atom in determining the value of such a magnetic property.

Also the SOS-CI values of the magnetic susceptibilities for the first-row hydrides (Table 5) compare reasonably well with the CHF estimates obtained with a double-zeta basis set and the same gauge origin [24].

In spite of the inherent limitations, due to the restricted basis sets adopted and the use of gaugeless functions, on the whole the present non-empirical calculations mimic quite satisfactorily the corresponding CHF results. From the body of these findings, it can therefore be argued that the SOS-CI procedure according to the proposal by Nakatsuji [1] may be actually a practical alternative, computationally more economic over the very time-consuming CHF procedures, to achieve reasonably accurate values for second-order magnetic properties even in larger molecules.

Table 5. SOS-CI values of the diamagnetic susceptibilities (10^{-6} cm^3/mol) in the first- and second-row hydrides

Molecule	χ^d	χ^p	χ	Molecule	χ^d	χ^p	χ
LiH	−16.80	4.91	−11.89	NaH	−24.37	0.81	−23.56
BeH_2	−23.80	10.97	−12.83	MgH_2	−36.51	3.84	−32.67
BH_3	−27.04	14.97	−12.07	AlH_3	−45.16	7.17	−37.99
CH_4	−28.20	4.09	−24.11	SiH_4	−55.08	10.63	−44.45
NH_3	−20.79	1.82	−18.97	PH_3	−44.06	5.06	−39.00
H_2O	−15.06	0.95	−14.11	H_2S	−34.36	2.86	−31.50
HF	−10.48	0.44	−10.04	HCl	−26.52	1.16	−25.36

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