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On the convergence of FPT-DFT calculations of the Fermi contact contribution to NMR coupling constants

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Abstract. Calculations of the Fermi contact term of NMR couplings, $J^{FC}(MN)$, using a single FC perturbation within the Finite Perturbation Theory-DFT frameworks are only reliable if they do not depend either on **a)** the size of the perturbation, and **b)** whether the perturbation is placed at the site of the M or N nucleus. In this short communication these two points are addressed by studying the $^{1}J^{FC}(MN)$ and $^{2}J^{FC}(MN)$ linear response behavior in a set of small molecules. It is shown how such a linearity depends on the size of the finite perturbation, the basis set employed, and the chosen nucleus site. The dependence of SCF convergence requirements on the size of the perturbation is also discussed. Calculations are carried out employing the B3LYP and B3PW91 hybrid functionals and results are compared with both state-of-the-art calculations and experimental values.

Key words: NMR couplings – Fermi contact – FPT – DFT – Ab initio

The relevance of NMR coupling constants as probes to determine several structural aspects of biologically important compounds has increased notably during the last few years [1]. There are two main reasons that define such a trend, namely, the use of sophisticated experimental techniques which allow the measurement of NMR coupling constants in compounds fully enriched with ^{13}C and ^{15}N isotopes [2], and the possibility of using very efficient computational algorithms in very high performance computing systems to complement these experimental measurements [3].

Current approaches to calculate spin-spin coupling constants were recently reviewed [4] and the importance of including electron correlation effects to obtain accurate calculated values was stressed. At present highly sophisticated methods that include all four contributions to couplings are known to yield reliable theoretical values; however, within the current computational resources calculations in biologically important compounds they are prohibitively demanding. For this reason, for coupling constants whose trends are known to be largely determined by the FC term behavior, one of the most extended approaches to calculate them is the Pople et al.'s [5] FPT method [6]. The FPT procedure must be implemented within methods that yield correlated energies for spin-unrestricted molecular states based either on post-Hartree-Fock methods or on the DFT formalism.

The suitability of the DFT-based methods to reproduce a large variety of molecular properties [7] encouraged using them for calculating NMR parameters [6, 8–11] yielding quite promising results. However, the results obtained in early work dealing with the calculation of couplings within the DFT-FPT approach suggested that some difficulties can be met if some subtle points are not addressed properly.

In the current literature two different implementations of the FPT approach to calculate the FC contribution, $J^{FC}(MN)$, are commonly used, namely,

- **i)** to add a finite FC perturbation, as given in Eq. 1, to the one-electron Hamiltonian before performing an unrestricted SCF calculation. The FC perturbation must be placed at the site of one of the two coupled nuclei, e.g., N (single perturbation); the resulting spin-density at the site of nucleus M is proportional to $J^{FC}(MN)$ [12].
- **ii)** To add two of such finite FC perturbations placed at the site of each coupled nucleus, M and N (double perturbation).

This last implementation has the obvious drawback that, for obtaining all couplings in a given molecule, it requires a markedly larger number of calculations than using just only one perturbation.

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$$h_{FC} = \lambda \sum_{k} \delta(\mathbf{r}_{kN})\mathbf{S}_k \cdot \mathrm{I}_N \tag{1}$$

When implementing the single perturbation approach, **i)**, the calculated $J^{FC}(MN)$ value should not depend either on

a) the size of the perturbation, λ, and
b) whether the perturbation is placed at the site of the M or N nucleus.

Since these two points, although obvious as they could be, are not discussed in detail in the current literature, they are addressed in this short communication, together with additional convergence requirements on the SCF calculation owing to the presence of the electron spin-dependent finite perturbation. If the double perturbation approach is implemented, these two conditions should also hold, although problems associated with point **b)** can be overlooked.

In order to determine which conditions must be fulfilled in the single perturbation DFT-FPT approach to satisfy points **a)** and **b)**, in this work $J^{FC}(MN)$ values were evaluated in a selected set of small molecules. To this end, two links of the Gaussian 98 [13] suite of programs were slightly modified to implement the single perturbation FPT approach. It should be noted that, with this modification, $J^{FC}(MN)$ can be calculated either at the DFT or Hartree-Fock/post-Hartree-Fock levels implemented in the Gaussian 98 package. Calculations were carried out using both the DFT/B3LYP [14, 15] and DFT/B3PW91 [14, 16] functionals, using the NASA-Ames-ANO basis set [17] with full decontracted s and p functions, yielding (8s6p4d)/[8s6p1d] and (13s8p6d)/[13s8p3d] basis set quality for H and for F, C N, and O, respectively. The set of chosen molecules was selected taking care that very sophisticated and reliable calculations as well as experimental values of their couplings are known from the literature. Comparisons of calculated values of $J^{FC}(MN)$ contributions to one-bond couplings for different perturbation sizes and for different perturbation sites are displayed in Table 1. They are also compared with values obtained from state-of-the-art calculations and with the "FC-experimental value". General good agreement was found between DFT-FPT values and the corresponding state-of-the-art calculations for the whole set of molecules studied, with the exception of $^1J(CF)$ in methyl fluoride which is algebraically underestimated. The FC contributions to two-bond couplings in the same compounds are displayed in Table 2, where a very good agreement between DFT-FPT results and state-of-the art calculations is observed.

From calculations shown in Table 1 and Table 2 it is inferred that points **a)** and **b)** mentioned above can be satisfied using a sufficiently small finite perturbation. However, a small perturbation induces a small spin density at the sites of other nuclei, which requires a tight SCF convergence criterion to be accurately calculated. If this requirement is not imposed, the SCF procedure can stop before the spin density is adequately represented. It is important to note that this convergence problem may be overlooked if the double perturbation approach is employed.

With the basis set employed [17], points **a)** and **b)** mentioned above are satisfied for one-bond and two-bond couplings using a perturbation of 10^{-4} au; however, the appropriate size of the perturbation to be used strongly depends on the chosen basis set. For instance, in methane using the fully decontracted GAMESS-pVTZ basis set [24] including tight s functions [19], when the perturbation is placed at the C nucleus site the calculated FC term of $^1J(CH)$ depends on λ as follows. For $\lambda = 5 \times 10^{-5}$, $^1J(CH) = 126.14$ Hz; while for $\lambda = 10^{-5}$ and $\lambda = 10^{-6}$, $^1J(CH) = 121.87$ Hz and $^1J(CH) = 121.69$ Hz, respectively, are obtained. On the other hand, when the perturbation is placed at the proton site, with $\lambda = 10^{-4}$, $^1J(CH) = 121.81$ Hz; and with $\lambda = 10^{-6}$, $^1J(CH) = 121.63$ Hz, are obtained. The values shown above suggest that for calculating the FC terms of $^1J(XH)$ couplings it is preferable to place the

Table 1. $^1J^{FC}(MN)$ contribution to one-bond couplings in the chosen set of small molecules calculated with the FPT approach and the B3LYP and B3PW91 functionals (the basis set is described in the text) for different perturbation sizes, λ, and different perturbed nucleus[a]

Functional	M/N[b]	λ (au)	CH_4 $^1J(CH)$	CH_3F $^1J(CH)$	CH_3F $^1J(CF)$	C_2H_4 $^1J(CH)$	H_2O $^1J(OH)$	NH_3 $^1J(NH)$	CO $^1J(CO)$
B3LYP	Y	10^{-3}	126.79	149.29	−286.65	159.25	−62.10	41.92	11.04
B3LYP	X	10^{-3}	125.59	147.86	−283.90	157.75	−61.14	41.39	10.88
B3LYP	Y	10^{-4}	125.59	147.86	−281.21	157.76	−61.14	41.39	10.74
B3LYP	**X**	$\mathbf{10^{-4}}$	**125.57**	**147.83**	**−281.17**	**157.74**	**−61.13**	**41.38**	**10.74**
B3PW91	**X**	$\mathbf{10^{-4}}$	**115.54**	**137.00**	**−282.31**	**146.78**	**−55.37**	**38.03**	**13.75**
Reference calculation			118.85[c]	136.44[d]	−226.16[d]	151.37[d]	−65.45[e]	40.19[e]	7.00[e]
FC (Experimental)[f]			119.09	148.39	−214.10	155.48	−64.05	41.98	7.90
Experimental[g]			120.87[h]	149.1	−157.5	156.4	−73.5	43.6	16.4

[a] Coupling constants are in Hz. Values in bold correspond to the most reliable calculation. Geometrical structures of CH_4, C_2H_4 and CH_3F were optimized at the B3LYP/cc-pVTZ level; those of H_2O, NH_3 and CO were taken from Ref. [18]

[b] Perturbation site: X stands for the lighter atom between M and N

[c] Taken from Ref. [19]

[d] Taken from Ref. [20]

[e] Taken from Ref. [21]

[f] FC(Experimental) = J(exp.) − (non-Fermi), where exp. stands for the measured value taken from [22]

[g] Taken from Ref. [22]

[h] The estimated rovibrational contributions were subtracted. Taken from Ref. [23]

Table 2. $^{2}J^{FC}$(MN) contribution to two-bond couplings in the chosen set of small molecules calculated with the FPT approach and the B3LYP and B3PW91 functionals (the basis set is described in the text) for different perturbation sizes, λ, and different perturbed nucleus[a]

Functional	M/N[b]	λ (au)	CH_4 $^{2}J(HH)$	CH_3F $^{2}J(FH)$	C_2H_4 $^{2}J(CH)$	H_2O $^{2}J(HH)$	NH_3 $^{2}J(HH)$
B3LYP	Y	10^{-3}	–	44.16	0.51	–	–
B3LYP	X	10^{-3}	−13.15	43.33	0.50	−9.84	−11.20
B3LYP	Y	10^{-4}	–	43.34	0.50	–	–
B3LYP	**X**	$\mathbf{10^{-4}}$	**−13.59**	**43.32**	**0.50**	**−9.83**	**−11.19**
B3PW91	**X**	$\mathbf{10^{-4}}$	**−13.56**	**40.19**	**−0.17**	**−9.44**	**−11.03**
Reference calculation			−13.87[c]	41.7[d]	−0.90[d]	−11.12[e]	−11.72[e]
FC (Experimental)[f]			−12.63	39.06	−0.68	−7.51	−9.61
Experimental[g]			−11.99[h]	46.36	−2.4	−7.2	−10.0

[a] Coupling constants are in Hz. Values in bold correspond to the most reliable calculation. Geometrical structures of CH_4, C_2H_4 and CH_3F were optimized at the B3LYP/cc-pVTZ level; those of H_2O and NH_3 were taken from Ref. [18]

[b] Perturbation site: X stands for the lighter atom between M and N

[c] Taken from Ref. [19]

[d] Taken from Ref. [20]

[e] Taken from Ref. [21]

[f] FC (Experimental) = J(exp.) − J(non-Fermi), where exp. stands for the measured value taken from [22]

[g] Taken from Ref. [22]

[h] The estimated rovibrational contributions were subtracted. Taken from Ref. [23]

finite perturbation at the proton rather than at the X nucleus site, since in so doing, the condition of perturbation size independence is satisfied with larger values of λ. Consequently, in this way a larger spin density is induced at the site of other nuclei that can be accurately reproduced without requiring strict convergence criteria.

As a final remark it is stressed that, when the points commented above are properly taken into account, the Gaussian 98 package of programs [13] can easily be modified to obtain a very efficient code for calculating the Fermi contact contribution to nuclear spin-spin couplings involving light nuclei where relativistic effects can be neglected.

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