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Correlated and gauge origin independent calculations of magnetic properties

II. Shielding constants of simple singly bonded molecules

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Summary. We have applied a gauge origin invariant method for calculations of nuclear magnetic shielding constants to the singly bonded molecules BF, F_2, BH_3, CH_4, NH_3, H_2O, and HF as well as to the ^1H shielding constants of HCN and C_2H_2. The calculations were performed at the RPA and second order polarization propagator (SOPPA) level of theory. For most molecules the correlation contribution in SOPPA is less diamagnetic than in the comparable MP2 calculations. For F_2, SOPPA gives a large paramagnetic correlation correction whereas the MP2 method gives a very small correlation contribution. For all molecules agreement with experimental results is generally improved at the SOPPA level compared to RPA. We have also demonstrated that second order gauge origin invariant, common and local origin (SOLO) methods do not necessarily give the same shielding even in the limit of a converged basis set.

Key words: Magnetic shieldings – *Ab initio* – Polarization propagator methods – SOPPA – Gauge origin invariant

1 Introduction

In the first paper of this series [1] we applied a method for consistently correlated calculations [2] of magnetizabilities and gauge origin independent nuclear magnetic shielding constants to the triply bonded molecules CO, N_2, HCN, CN^- and HCCH. We systematically investigated the basis set dependence of this new method and found that inclusion of *p*- and *d*-functions with large exponents is important for the convergence of the sum-over-states diamagnetic contribution to the nuclear magnetic shielding, whereas it is necessary to include diffuse *d*-functions for the corresponding sum-over-states diamagnetic contribution to the magnetizability. Universal atomic basis sets containing these functions were developed and applied to all of the molecules studied. The effect of electron correlation was

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** *Permanent address*: J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic investigated within the second order polarization propagator approximation (SOPPA) [3]. We found that SOPPA gives a much smaller overall diamagnetic correlation contribution to the nuclear magnetic shielding constants of the heavy atoms in the triply bonded molecules than comparable MP2 and MC-based calculations. We found an overall paramagnetic correlation correction to the magnetizability.

In a second paper [4] we applied this method in combination with the coupled cluster polarization propagator approximations (CCDPPA/CCSDPPA) [5] to the potential temperature independent van Vleck paramagnetism of closed shell diatomic hydrides with six valence electrons. We have found that BH, CH^+ and SiH^+ are paramagnetic, MgH^-, AlH and GeH^+ are diamagnetic and BeH^- is a borderline case tilting towards paramagnetism. In the present paper we apply the gauge origin invariant method for calculations of nuclear magnetic shielding constants and the basis sets developed in the first paper [1] to seven simply singly bonded molecules: BF, F_2, BH_3, CH_4, NH_3, H_2O, and HF as well as to HCN and C_2H_2.

From second-order perturbation theory one obtains two contributions to the nuclear magnetic shielding tensor [6]: the so-called diamagnetic ($\boldsymbol{\sigma}^{\mathrm{d}}$) and paramagnetic ($\boldsymbol{\sigma}^{\mathrm{p}}$) terms

$$\begin{aligned}\boldsymbol{\sigma}_K(\boldsymbol{R}) &= \boldsymbol{\sigma}_K^{\mathrm{d}}(\boldsymbol{R})+\boldsymbol{\sigma}_K^{\mathrm{p}}(\boldsymbol{R})\\ &= \frac{e^2\mu_0}{8\pi m_{\mathrm{e}}}\left\langle 0\left|(\boldsymbol{r}-\boldsymbol{R})\cdot\frac{(\boldsymbol{r}-\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\,\mathbf{1}-(\boldsymbol{r}-\boldsymbol{R})\frac{(\boldsymbol{r}-\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\right|0\right\rangle\\ &\quad+\frac{e^2\mu_0}{4\pi m_{\mathrm{e}}^2}\sum_{n\neq 0}\frac{\left\langle 0\left|\dfrac{\boldsymbol{l}(\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\right|n\right\rangle\langle n|\boldsymbol{l}(\boldsymbol{R})|0\rangle}{E_0-E_n},\end{aligned} \tag{1}$$

where all operators are given in the second quantization notation. Here $\boldsymbol{l}(\boldsymbol{R}_K)=(\boldsymbol{r}-\boldsymbol{R}_K)\times\boldsymbol{p}$ is the angular momentum operator defined with respect to the position of the nucleus K while $\boldsymbol{l}(\boldsymbol{R})=(\boldsymbol{r}-\boldsymbol{R})\times\boldsymbol{p}$ is defined with respect to the gauge origin $\boldsymbol{R}$. The two contributions to the magnetic shielding tensor are linear in $\boldsymbol{R}$. Only their sum, however, is an observable and must therefore be independent of the choice of $\boldsymbol{R}$ when exact eigenstates of the Hamiltonian are used in Eq. (1). This also holds for all methods which fulfill the off-diagonal hypervirial relation, such as the coupled perturbed Hartree–Fock/random phase approximation (CHF/RPA) or its multireference generalization (MC-RPA) in the limit of a complete basis set. In all other cases, there will remain a net gauge origin dependence of the total nuclear magnetic shielding constant

$$\boldsymbol{\sigma}_K(\boldsymbol{R}')=\boldsymbol{\sigma}_K(\boldsymbol{R})+\boldsymbol{C}_1^{\sigma}\cdot(\boldsymbol{R}'-\boldsymbol{R}). \tag{2}$$

The linear $\boldsymbol{C}_1^{\sigma}$ gauge origin dependence vector can be calculated directly [7, 8] and it is thus possible to obtain the nuclear magnetic shielding constant for any gauge origin from a calculation at a single gauge origin.

Geertsen [2] recently proposed a method for the calculation of the trace of the nuclear magnetic shielding tensor which eliminates the gauge origin problem. The gauge origin independence is obtained by reformulating the diamagnetic contribution in Eq. (1) as a sum-over-states so that it has a form similar to the paramagnetic contribution

$$\sigma_K^{\mathrm{d}}(\boldsymbol{R})=\tfrac{1}{3}\sum_{i=x,y,z}\frac{e^2\mu_0}{4\pi m_{\mathrm{e}}^2}\sum_{n\neq 0}\frac{\left\langle 0\left|\left(\frac{(\boldsymbol{r}-\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\times \boldsymbol{l}(\boldsymbol{R})+\boldsymbol{O}^{\sigma}+\boldsymbol{O}_H^{\sigma}\right)_i\right| n\right\rangle \langle n|(\boldsymbol{p})_i|0\rangle}{E_0-E_n}. \tag{3}$$

The gauge origin independence of the trace of the nuclear magnetic shielding constant is ensured by the operator

$$\boldsymbol{O}^{\sigma}=\left\{\frac{(\boldsymbol{r}-\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\times\boldsymbol{R}\right\}\times\boldsymbol{p}. \tag{4}$$

The operator $(\boldsymbol{r}-\boldsymbol{R}_K)/|\boldsymbol{r}-\boldsymbol{R}_K|^3\times\boldsymbol{l}(\boldsymbol{R})+\boldsymbol{O}^{\sigma}$ is not Hermitian and a computationally more convenient Hermitian expressions can be obtained by also including the operator [2]

$$\boldsymbol{O}_H^{\sigma}=-\frac{\mathrm{i}h}{2\pi}\left\{\frac{\boldsymbol{r}}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}+\frac{3}{2}\frac{\boldsymbol{r}-\boldsymbol{R}_K}{|\boldsymbol{r}-\boldsymbol{R}_K|^5}\times\{(\boldsymbol{r}-\boldsymbol{R}_K)\times\boldsymbol{r}\}+\frac{4\pi}{3}\,\delta\,(\boldsymbol{r}-\boldsymbol{R}_K)\boldsymbol{r}\right\}. \tag{5}$$

However, the operators $\boldsymbol{O}^{\sigma}$ and $\boldsymbol{O}_H^{\sigma}$ introduce a linear dependence on the position of the origin of the coordinate system in Geertsen's reformulated diamagnetic term. This linear dependence on the origin of the coordinate system was first pointed out by Lazzeretti et al. [9]. Adding the additional operator

$$\boldsymbol{O}_2^{\sigma}=-\left\{\frac{(\boldsymbol{r}-\boldsymbol{R}_K)}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\times\boldsymbol{r}\right\}\times\boldsymbol{p} \tag{6}$$

removes the linear dependence on the coordinate system in $\boldsymbol{O}^{\sigma}$. We may add this operator because the trace of $[\boldsymbol{r}, \boldsymbol{O}_2^{\sigma}]=0$ in a complete basis set which means that it does not change the trace of $\boldsymbol{\sigma}^{\mathrm{d}}$ [1, 2]. A final Hermitian, gauge origin and coordinate system invariant expression for the nuclear magnetic shielding constant can then be obtained using the operator

$$\frac{\boldsymbol{r}-\boldsymbol{R}_K}{|\boldsymbol{r}-\boldsymbol{R}_K|^3}\times\boldsymbol{l}(\boldsymbol{R})+\boldsymbol{O}^{\sigma}+\boldsymbol{O}_2^{\sigma}-\frac{\mathrm{i}h}{2\pi}\frac{\boldsymbol{r}-\boldsymbol{R}_K}{|\boldsymbol{r}-\boldsymbol{R}_K|^3} \tag{7}$$

for the diamagnetic contribution in Eq. (3). This operator is, as shown in an earlier publication [1], identical to the operator suggested by Smith et al. [10]. The calculations reported here were performed using the operator in Eq. (7).

The reformulation of $\boldsymbol{\sigma}^{\mathrm{d}}$ relies on certain operator relations [1] which are strictly fulfilled for exact states and for all methods which fulfill hypervirial relations in the limit of a complete basis set. Calculations of the diamagnetic term as a ground state average value (Eq. (1)) with and SCF wavefunction and as sum-over-states (Eq. (3)) at the RPA level will therefore converge to the same limit only in a complete basis set.

In addition to the gauge and coordinate origin independence, the present approach has the advantage that one may use the *same* correlated sum-over-states method to calculate both the paramagnetic and the diamagnetic contributions to the magnetic properties [11] and thus obtain a similar advantage as in MP2- and MC-based calculations of shieldings.

Sum-over-states expressions like Eqs. (1) and (3) are zero-energy limits of a polarization propagator [3] or linear response function [12]

$$\langle\langle \boldsymbol{P}; \boldsymbol{Q} \rangle\rangle_E = \sum_{n \neq 0} \left\{ \frac{\langle 0|\boldsymbol{P}|n\rangle\langle n|\boldsymbol{Q}|0\rangle}{E + E_0 - E_n} - \frac{\langle 0|\boldsymbol{Q}|n\rangle\langle n|\boldsymbol{P}|0\rangle}{E + E_n - E_0} \right\}. \tag{9}$$

We thus calculate the nuclear magnetic shielding constant from the following polarization propagators:

$$\sigma_K^{\mathrm{p}}(\boldsymbol{R}) = \tfrac{1}{3} \sum_{i=x,y,z} \frac{e^2\mu_0}{8\pi m_e^2} \left\langle\!\!\left\langle \left(\frac{\boldsymbol{l}(\boldsymbol{R}_K)}{|\boldsymbol{r} - \boldsymbol{R}_K|^3} \right)_i ; (\boldsymbol{l}(\boldsymbol{R}))_i \right\rangle\!\!\right\rangle_{E=0}, \tag{10}$$

$$\sigma_K^{\mathrm{d}}(\boldsymbol{R}) = \tfrac{1}{3} \sum_{i=x,y,z} \frac{e^2\mu_0}{8\pi m_{\mathrm{e}}^2} \left\langle\!\!\left\langle \left(\frac{\boldsymbol{r} - \boldsymbol{R}_K}{|\boldsymbol{r} - \boldsymbol{R}_K|^3} \times \boldsymbol{l}(\boldsymbol{R}) + \boldsymbol{O}^\sigma + \boldsymbol{O}_2^\sigma - \frac{\mathrm{i}h}{2\pi} \frac{\boldsymbol{r} - \boldsymbol{R}_K}{|\boldsymbol{r} - \boldsymbol{R}_K|^3} \right)_i ; (\boldsymbol{p})_i \right\rangle\!\!\right\rangle_{E=0}. \tag{11}$$

These polarization propagators may be evaluated using a superoperator formulation of the linear response function [3]. Electron correlation is included in our calculations by means of perturbation theory. As zeroth-order reference state we use an SCF wavefunction and as perturbation the fluctuation potential. The polarization propagator is evaluated through 2nd order in the fluctuation potential. In first order we obtain the random phase approximation (RPA), which is equivalent to the coupled Hartree–Fock method (CHF). In second order we obtain the second order polarization propagator approximation (SOPPA) [3]. Higher order terms are also contained in SOPPA in addition to all contributions up to and including second order and several additional series of diagrams are summed to infinite order in SOPPA compared with RPA. These collective excitation effects [13] have no corresponding counterpart in MP2 analytical derivative calculations as they are primarily caused by the requirement that the poles of the polarization propagators, i.e. the excitation energies, are correct to second order [3]. A similar condition is not invoked in the MP2 calculation of second order properties.

2 Computational details

All calculations have been performed with the Odense version of the RPAC 9.0 program package [14, 1]. The atomic integrals and molecular orbital energies were obtained from the Gaussian 92 program system [15], which was interfaced with the RPAC program. We use 5 spherical *d*- and 7 spherical *f*-functions. The calculations were performed at experimental equilibrium geometries taken from Refs. [16–18] (Ref. [18] for CH_4) with the exception of BH_3 where we used the MP2 optimized geometry in our basis set. For further details see the footnotes of Table 1. The W_4 term [3] is not included in the SOPPA calculations of the shielding constants.

In the first paper [1] we systematically tested basis sets for correlated calculations of the magnetizability and nuclear magnetic shielding constants using the gauge origin independent method. Our final basis sets gave good agreement between the ground state average value, Eq. (1), and sum over states results, Eq. (3), of the diamagnetic term for the molecules studied and also seemed to be converged at the SOPPA level. We thus used them in the present study without further optimization. The reader is refered to Ref. [1] for a detailed description of the basis

Table 1. Total energies and Thomas–Reiche–Kuhn sum rules[a]

	Basis set[b]	#[c]	E_{SCF}	ΔE_{MP2}	$S^{M}_{RPA}(0)$
BF[d]	$sp_{tt}d_{td}f_2$	150	-124.167220	-0.446529	13.9981
F_2[e]	$sp_{tt}d_{td}f_2$	150	-198.770975	-0.675943	17.9973
BH_3[f]	$sp_{tt}d_{td}f_2/sp_td$	141	-26.402240	-0.162729	7.9942
CH_4[g]	$sp_{tt}d_{td}f_2/sp_td$	163	-40.216499	-0.254858	9.9962
NH_3[h]	$sp_{tt}d_{td}f_2/sp_td$	141	-56.223936	-0.298855	9.9967
H_2O[i]	$sp_{tt}d_{td}f_2/sp_td$	119	-76.066200	-0.332326	9.9960
HF[k]	$sp_{tt}d_{td}f_2/sp_td$	97	-100.069451	-0.350180	9.9970
HCN[l]	$sp_{tt}d_{td}f_2/sp_td$	172	-92.914292	-0.462389	13.9981
C_2H_2[m]	$sp_{tt}d_{td}f_2/sp_t$	184	-76.854576	-0.418465	13.9966

[a] E_{SCF} is the Hartree–Fock SCF total energy, ΔE_{MP2} is the MP2 correlation energy and $S^{M}_{RPA}(0)$ is the RPA value of the Thomas–Reiche–Kuhn sum rule in the mixed representation. E_{SCF} and ΔE_{MP2} are in atomic units: 1 au of $E = E_h \approx 4.35975 \times 10^{-18}$ J.

[b] For the definitions of the basis sets see Table 1 and Table 2 in Ref. [1]. The symbol in front and after the solidus refers to the basis sets centered on the heavy atoms and on the hydrogen atoms, respectively.

[c] The number of contracted Gaussian-type functions.

[d] $R_{BF} = 1.2625$ Å [16]

[e] $R_{FF} = 1.41193$ Å [16]

[f] $R_{BH} = 1.18281215$ Å, $\angle$HBH = 120°

[g] $R_{CH} = 1.086$ Å [18]

[h] $R_{NH} = 1.0124$ Å, $\angle$HNH = 106.67° [17]

[i] $R_{OH} = 0.9572$ Å, $\angle$HOH = 104.52° [17]

[k] $R_{FH} = 0.9168$ Å [16]

[l] $R_{CH} = 1.064$ Å, $R_{CN} = 1.156$ Å [17]

[m] $R_{CC} = 1.203$ Å, $R_{CH} = 1.060$ Å [17]

sets for hydrogen, carbon, nitrogen and oxygen. The basis sets for boron and fluorine were derived in the same way. We started with the 11*s*7*p* basis sets from van Duijneveldt [19] and contracted the *s*-functions with the four largest exponents into one function. The *s*-functions with the three smallest exponents were replaced by an even tempered set of four functions ($\zeta_s = 0.696162$, 0.280732, 0.113207, 0.045652 for boron and $\zeta_s = 2.713189$, 1.076494, 0.427114, 0.169463 for fluorine). We then added two tight *p*-functions with exponents $\zeta_p = 656$, 152 for boron and $\zeta_p = 2473$, 581 for fluorine. Finally, the 3*d* and 2*f* basis sets from Dunning [20] augmented with two *d*-functions ($\zeta_d = 3.065$, 0.052 for boron and $\zeta_d = 14.574$, 0.199 for fluorine) were added.

In Table I we give the SCF total energies, the MP2 correlation energy and the Thomas–Reiche–Kuhn (TRK) sum rule, $S(0)$, for all molecules. Calculated at the RPA level with a complete basis set, the TRK sum rule is equal to the number of electrons and can therefore be used as a criterion for the completeness of a basis set. A second and in this case more direct criterion is provided by the agreement between calculations using the ground state average value expression for the diamagnetic contribution (Eq. (1)) with an SCF wavefunction, on the one hand, and evaluating the sum-over-states expression (Eq. (11)) at the RPA level on the other. The latter criterion applied to the diamagnetic contribution to the nuclear magnetic shielding constant at the RPA level demonstrates the completeness of the basis set as the two diamagnetic contributions differ by only ~0.3% for the ^{1}H shielding constants (Table 3) and (~0.2%) for the non-hydrogen shielding constants (Table 2). We can, therefore, conclude that the basis sets also give a good and

Table 2. Gauge origin invariant and common origin nuclear magnetic shielding constant[a]

	RPA					SOPPA				Exp.[g]
	σ^d	σ^d_{SCF}	σ^p	σ	σ_{com}	σ^d	σ^p	σ	σ_{com}	σ
^{11}B: BH_3	226.21	226.64	−196.11	30.10	30.53	226.58	−214.12	12.47	12.52	
BF	268.03	268.50	−193.17	74.86	75.33	269.08	−203.19	65.90	65.31	
^{13}C: CH_4[b]	296.01	296.51	−101.95	194.05	194.56	296.91	−100.92	195.99	195.59	195.1 [27] (3.6 [27])
^{15}N: NH_3[c]	353.55	354.11	−93.54	260.61	260.56	354.01	−87.96	266.04	266.14	264.54 [30] (8.81 [41])
^{17}O: H_2O[d]	415.35	416.07	−90.61	324.73	325.46	415.08	−84.45	330.62	331.62	344.0 [28] (13.6 [42])
^{19}F: HF[e]	481.33	482.26	−69.73	411.60	412.53	480.21	−68.71	411.50	413.55	410 ± 6 [29] (11.2 [29])
BF	506.84	507.81	−385.07	121.77	122.74	505.58	−403.16	102.42	104.65	
F_2[f]	528.69	529.73	−700.00	−171.30	−170.26	528.11	−780.17	−252.06	−250.44	−232.8 [36] (40 [33])

[a] σ^d is the sum-over-states diamagnetic contribution calculated from Eq. (11), σ^d_{SCF} is the diamagnetic term calculated as a SCF ground state average value from Eq. (1), σ^p is the paramagnetic contribution calculated from Eq. (10), σ is the gauge origin invariant nuclear magnetic shielding constant (the sum of σ^d and σ^p), whereas σ_{com} is the common origin gauge dependent nuclear magnetic shielding constant (the sum of σ^d_{SCF} and σ^p), all given in ppm. The gauge origin was placed at the nucleus.

[b] *Cf.* the IGLO (193.82 ppm) and MC-IGLO (198.39 ppm) result of van Wüllen [21]; the GIAO-SCF (195.7 ppm) and GIAO-MBPT(2) (201.5 ppm) result of Gauss [24].

[c] *Cf.* the gauge origin dependent SCF (261.61 ppm) and MP2 (275.04 ppm) result of Cybulski and Bishop [22]; the IGLO (257.79 ppm) and MC-IGLO (264.75 ppm) result of van Wüllen [21]

[d] *Cf.* the gauge origin dependent SCF (327.96 ppm) and MP2 (344.87 ppm) result of Cybulski and Bishop [22]; the IGLO (321.39 ppm) and MC-IGLO (323.04 ppm) result of van Wüllen [21]; the GIAO-SCF (323.18 ppm) and GIAO-MBPT(2) (339.79 ppm) result of Gauss [24]

[e] *Cf.* the gauge origin dependent RPA (413.04 ppm) and SOPPA (414.38 ppm) result of Oddershede and Geertsen [7]; the gauge origin dependent SCF (414.14 ppm) and MP2 (424.36 ppm) result of Cybulski and Bishop [22]; the IGLO (411.19 ppm) and MC-IGLO (402.67 ppm) result of van Wüllen [21]

[f] *Cf.* the gauge origin dependent SCF (−170.05 ppm) and MP2 (−169.57 ppm) result of Cybulski and Bishop [22]; the IGLO (−165.32 ppm) and MC-IGLO (−204.32 ppm) result of van Wüllen [21]

[g] The experimental shieldings are σ_0 (300 K) values. In parenthesis we have given the magnitude of the rovibrational correction (in ppm) $\sigma_e - \sigma_0$ estimated in the references listed in the parenthesis. For a discussion of rovibrational corrections to σ see Jameson's review [43]. Note that the σ_e value is the one that can be directly compared with the calculated shielding.

Table 3. Gauge origin invariant and common origin ^1H nuclear magnetic shielding constant[a]

	RPA					SOPPA				Exp.[h]
^1H	σ^d	σ^d_{SCF}	σ^p	σ	σ_{com}	σ^d	σ^p	σ	σ_{com}	σ
BH_3	69.13	69.35	−44.74	24.39	24.61	69.22	−45.51	23.71	23.84	
CH_4[b]	87.61	87.83	−56.22	31.39	31.62	87.72	−56.53	31.20	31.31	30.61 [37]
NH_3[c]	95.23	95.49	−63.88	31.36	31.61	95.24	−64.03	31.21	31.46	
H_2O[d]	102.23	102.55	−71.89	30.34	30.66	102.26	−71.64	30.61	30.91	30.05 [37] (0.58 [42])
HF[e]	108.15	108.52	−80.15	28.00	28.37	108.22	−79.13	29.08	29.38	28.5±0.2 [37]
HCN[f]	99.45	99.66	−70.43	29.02	29.23	99.61	−70.48	29.13	29.18	28.32 [39]
C_2H_2[g]	98.78	99.14	−68.59	30.19	30.55	98.55	−68.52	30.04	30.62	29.26 [38]

[a] see footnote [a] of Table 2.

[b] *Cf.* the IGLO (31.22 ppm) and MC-IGLO (31.13 ppm) result of van Wüllen [21]

[c] *Cf.* the gauge origin dependent SCF (31.57 ppm) and MP2 (31.56 ppm) result of Cybulski and Bishop [22]; the IGLO (30.95 ppm) and MC-IGLO (31.00 ppm) result of van Wüllen [21]

[d] *Cf.* the gauge origin dependent SCF (30.70 ppm) and MP2 (30.97 ppm) result of Cybulski and Bishop [22]; the IGLO (29.89 ppm) and MC-IGLO (30.47 ppm) result of van Wüllen [21]

[e] *Cf.* the gauge origin dependent RPA (27.68 ppm) and SOPPA (28.05 ppm) result of Oddershede and Geertsen [7]; the gauge origin dependent SCF (28.45 ppm) and MP2 (29.32 ppm) result of Cybulski and Bishop [22]; the IGLO (27.77 ppm) and MC-IGLO (29.26 ppm) result of van Wüllen [21]

[f] *Cf.* the gauge origin dependent SCF (29.21 ppm) and MP2 (29.24 ppm) result of Cybulski and Bishop [22]

[g] *Cf.* the IGLO result of Schindler and Kutzelnigg [25] (30.04 ppm)

[h] see footnote [g] of Table 2

balanced description of the magnetic properties of these cases, without being specially optimized for the individual molecules.

3 Results

There is little difference between our RPA results for the nuclear magnetic shielding constants (Tables 2 and 3) and other comparable uncorrelated calculations [7, 21–25] (see footnotes of Tables 4 and 5). The previous common origin RPA and SOPPA calculation of the ^1H shielding constant in HCN [26] was performed in a smaller basis set and is thus not of the same quality as the present results.

In our previous study of triply bonded systems [1] we found that SOPPA gives much smaller diamagnetic correlation corrections than MP2 [22, 24] or MC-IGLO [21]. A similar but weaker trend can be observed also for the non-hydrogen

Table 4. Comparison between LORG/SOLO and the corresponding common origin method for the nuclear magnetic shielding constant[a]

	SCF/RPA	SCF/SOPPA	LORG	SOLO	Full LORG	Full SOLO
^{11}BF: BH_3	30.53	12.52	30.53	12.52	30.45	12.70
BF_3	75.32	65.31	75.01	64.61	75.03	65.17
^{13}C: CH_4	194.56	195.59	194.56	195.59	194.50	190.76
^{15}N: NH_3	260.56	266.14	260.56	266.14	260.51	260.39
^{17}O: H_2O	325.46	331.62	325.46	331.62	325.52	327.50
^{19}F: HF	412.53	413.55	412.53	413.55	412.68	411.66
BF	122.74	104.65	122.72	113.08	122.80	116.56
F_2	−170.26	−250.44	−170.35	−250.89	−170.24	−242.77

[a] SCF/RPA is the common origin gauge dependent nuclear magnetic shielding constant denoted σ_{com} in Table 3. SCF/SOPPA is the analogous approximation where the paramagnetic contribution is calculated at the SOPPA level. For the definition of LORG, SOLO, full LORG and full SOLO see Ref. [40]. For an explanation of differences between the SOLO/full SOLO/SOPPA results see the text. All nuclear magnetic shielding constants are given in ppm. The core and σ orbitals were localized separately.

Table 5. Comparison between LORG/SOLO and the corresponding common origin method for ^1H nuclear magnetic shielding[a]

	SCF/RPA	SCF/SOPPA	LORG	SOLO	Full LORG	Full SOLO
BH_3	24.61	23.84	24.58	24.02	24.56	24.00
CH_4	31.62	31.31	31.56	31.57	31.52	31.49
NH_3	31.61	31.46	31.53	31.60	31.48	31.40
H_2O	30.66	30.91	30.57	30.86	30.50	30.52
HF	28.37	29.38	28.19	29.07	28.08	28.54
HCN	29.23	29.18	29.12	29.64	29.08	29.48
C_2H_2	30.55	30.62	30.30	30.64	30.24	30.45

[a] See footnote of Table 4.

shielding constants in the singly bonded molecules studied here (Table 2). MP2 [22, 24] always gives a positive correlation correction, whereas SOPPA predicts a smaller positive contribution for CH_4, NH_3 and H_2O as well as a small negative correction for HF and a large negative correction for F_2. Correlation at the SOPPA levels also reduces the ^{11}B and ^{19}F shielding constants in BH_3 and BF. The MC-IGLO calculations [21] seem to support the smaller correction of SOPPA for H_2O and the paramagnetic corrections for HF and F_2 but not for NH_3.

SOPPA improves the agreement with the experimental absolute shielding constants for CH_4 [27], H_2O [28], HF [29] and NH_3 [30]. The shielding, however, is not a directly measurable quantity. Instead, a direct comparison would involve the calculation of the related [7] spin rotation constant and also its ro-vibrational dependence. This was done previously for NH_3 [31] for which another comparison between theory and experiment has been performed by calculating the temperature dependence of the nitrogen shielding [32]. Since vibrational corrections are known to be important [33] for the nuclear magnetic shielding in F_2, we have used this molecule to illustrate the magnitude of the vibrational corrections. We calculated the shielding constant for seven different geometries (R_{FF}, $R_{FF} \pm 0.1a_0$, $R_{FF} \pm 0.2a_0$, $R_{FF} \pm 0.3a_0$) and calculated the zero-point-vibrational average by numerical integration over the ground ro-vibrational wavefunction [34], which was obtained from an experimental RKR potential [35]. These averaged results (RPA: -200.4 ppm, SOPPA: -290.9 ppm) can than be compared with the experimental value for the vibrational ground state (-232.8 ppm [36]). Contrary to what we normally find SOPPA apparently gives a too negative correlation correction in this case. We find, however, that the computed vibrational correction at the SOPPA level, -39 ppm, is in very good agreement with the value obtained from the temperature dependence of σ, -40 ppm [33].

The effect of correlation on the ^1H shieldings constants (Table 3) is small, an observation also confirmed by the previously mentioned MP2 and MC-IGLO calculations. SOPPA gives a paramagnetic correlation contribution to the hydrogen shielding constant in CH_4, C_2H_2 and NH_3 and a diamagnetic contribution for H_2O, HF, and HCN. The agreement with the experimental absolute shielding constants [37–39] is fair.

In Tables 4 and 5 we compare gauge origin dependent, common origin RPA and SOPPA results with LORG/SOLO [40] and full LORG/full SOLO calculations using the same basis set. The diamagnetic term is calculated as an SCF ground state average value in all three approaches (the two local origins and the common origin) and thus only the paramagnetic term is correlated in a SOLO or in a gauge origin dependent, common origin SOPPA calculation. In the limit of a complete basis set, LORG, full LORG and gauge origin dependent, common origin RPA calculations will converge to the same result, because the operator relations used in the derivation of LORG and full LORG are fulfilled in the limit of a complete basis set at the RPA level and the SCF wavefunction is the RPA reference state. This is, however, not the case for SOLO, full SOLO and gauge origin dependent, common origin SOPPA. The main reason [40] is that some terms in the paramagnetic contribution of the common origin method are transformed into diamagnetic like terms in the local origin methods and are thus calculated at the SCF level and not at the correlated level applied to the calculation of σ^p in SOLO/full SOLO. As expected Table 4 shows the good agreement between all methods at the RPA level and also between common origin SOPPA and SOLO with the exception of BF. Full SOLO, however, deviates clearly from the other two methods and predicts in some cases even a different sign of the correlation correction. For the ^1H shielding constants in Table 5, however, all three methods give basically the same result, due to the smallness of the correlation contribution.

4 Conclusions

Using a gauge origin invariant method, we have calculated the nuclear magnetic shielding constants of BF, F_2, HF, H_2O, NH_3, CH_4 and BH_3 as well as the ^1H shielding constants in HCN and C_2H_2. Correlation was included in our calculations by means of the second order polarization propagator approximation (SOPPA). We used basis sets which have been optimized previously for correlated, gauge origin invariant calculations of magnetic properties.

For the nuclear magnetic shielding constants, the correlation contribution is less diamagnetic at the SOPPA level than at the MP2 level and, with the exception of NH_3, in better agreement with MC-IGLO calculations. However, the differences between SOPPA and the other methods as well as the experimental results are much smaller than what we found in our previous study on triply bonded systems. The only exception is the shielding constant of F_2, where SOPPA gives a large paramagnetic correlation correction (-80.76 ppm) compared with a weakly diamagnetic contribution ($+0.48$ ppm) from MP2.

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