

Hybrid density functional and EXX-OEP calculations of NMR shieldings using Slater-type orbitals and ZORA

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1 Calculation of the two-electron integrals with the STOs

Fitting of the density to the auxiliary basis set:

$$\rho(\mathbf{r}) \approx \bar{\rho}(\mathbf{r}) = \sum_i c_i f_i(\mathbf{r}) \quad , \quad (1)$$

$$\Delta = \iint (\rho - \bar{\rho})^2 d\tau_1 \quad , \quad (2)$$

$$\Delta = \iint (\rho - \bar{\rho}) \frac{1}{r_{12}} (\rho - \bar{\rho}) d\tau_1 d\tau_2 = (\rho - \bar{\rho} | \rho - \bar{\rho}) \quad , \quad (3)$$

$$J\phi(1) = \phi(1) \sum_i c_i \int \frac{f_i(2)}{r_{12}} d\tau_2 \quad . \quad (4)$$

$$K_{\mu\sigma} = \sum_{\nu\lambda} P_{\nu\lambda}(\mu\nu|\sigma\lambda) , \quad (5)$$

Fitting of each atomic orbital pair to the auxiliary basis set:

$$\Omega_{\mu\nu} = \left(\mu\nu - \sum_i c_i^{\mu\nu} f_i \middle| \mu\nu - \sum_i c_i^{\mu\nu} f_i \right)^{\mathbf{a}} , \quad (6)$$

$$c_i^{\mu\nu} = \sum_j (V^{-1})_{ij} (f_j | \mu\nu) , \quad (7)$$

$$(\mu\nu|\sigma\lambda) = \sum_i (\mu\nu|f_i) c_i^{\sigma\lambda} . \quad (8)$$

The double fitting formula:

$$(\mu\nu|\sigma\lambda) = \sum_{ij} c_i^{\mu\nu} (f_i|f_j) c_j^{\sigma\lambda} , \quad (9)$$

$$K_{\mu\sigma} \approx \sum_{\nu\lambda} \sum_{ij} P_{\nu\lambda} c_i^{\mu\nu} (f_i|f_j) c_j^{\sigma\lambda} . \quad (10)$$

^aM. A. Watson, N. C. Handy, and A. J. Cohen, J. Chem. Phys. **119**, 6475 (2003)

Table 1: Isotropic shielding constants (ppm); DZP basis set; GIAOs; B3LYP

Molecule	Atom	Our	Others ^a	Experiment ^a
HF	F	412.10	411.7	419.7 ± 6
N ₂	N	-48.32	-48.8	-59.6 ± 1.5
CO	C	6.95	-6.9	2.8 ± 0.9
	O	-26.76	-26.8	-36.7 ± 17.2
H ₂ O	O	328.26	328.5	357.6 ± 17.2
NH ₃	N	268.25	268.3	273.3 ± 0.1
CH ₄	C	200.67	202.3	198.4 ± 0.9
LiH	Li	94.07	94.0	
F ₂	F	-193.28	-192.9	-192.8
CO ₂	C	65.61	66.1	58.8
	O	232.77	233.5	243.4
HCN	C	84.14	84.6	82.1
H ₂ CO	C	-2.78	-2.6	-4.4 ± 3
	O	-365.08	-362.6	-375 ± 100
C ₂ H ₄	C	70.02	71.7	
	H	25.84	26.0	

^a M. A. Watson, N. C. Handy, A. J. Cohen, and T. Helgaker, J. Chem. Phys. **120**, 7252 (2004)

Table 2: Isotropic shieldings and chemical shifts (ppm); TZP basis set; GIAOs

Molecule	B3LYP		PBE0		BP86	BLYP	HF	Expt ^a
	Our	Others ^a	Our	Others ^a				
TiCl ₄	-911	-985	-848	-934	-907	-934	-332	
TiCl ₃ CH ₃	-1373	-1462	-1320	-1421	-1357	-1375	-829	
δ	462	477	472	488	450	441	497	613
MnO ₄ ⁻	-4624	-4822	-4847	-5068	-3485	-3555	-37543	
Mn(CO) ₆ ⁺	-2432	-2636	-2522	-2748	-1568	-1660	-6605	
δ	-2192	-2186	-2325	-2320	-1917	-1895	-30938	-1445
Cr(CO) ₆	-971	-1018	-957	-1021	-575	-642	-2713	
CrO ₄ ²⁻	-2898	-3038	-2948	-3106	-2371	-2418	-6511	
δ	1927	2020	1991	2086	1796	1776	3798	1795
VOCl ₃	-2095	-2214	-2092	-2223	-1795	-1834	-3403	
VOF ₃	-1254	-1340	-1250	-1343	-1111	-1134	-2342	
δ	-841	-873	-842	-881	-684	-700	-1061	-757
VOCl ₃	-2095	-2214	-2092	-2223	-1795	-1834	-3403	
VF ₅	-1163	-1234	-1133	-1207	-1108	-1131	-736	
δ	-932	-980	-959	-1016	-687	-703	-2667	-895

^a A. M. Teale, A. J. Cohen, and D. J. Tozer, J. Chem. Phys. **126**, 074101 (2007)

8s6p4d Wachters GTO basis on the metal and 6-31G(*d*, *p*) on the ligands

Table 3: ^{31}P NMR chemical shifts (ppm); TZ2P basis set; GIAOs; ZORA scalar

Molecule	PBE0	B3LYP	revPBE	BLYP	HF+PBEc	HF	Expt ^a
P_4	-537.7	-539.7	-522.1	-527.1	-584.7	-593.1	-552.
PN	356.9	334.5	304.7	299.0	461.6	425.8	275.
PH_3	-266.1	-266.1	-266.1	-266.1	-266.1	-266.1	-266.
PF_3	82.44	73.56	84.22	80.10	39.56	24.62	106.
PCl_3	224.5	235.8	233.0	251.8	145.5	142.4	217.
PBr_3	273.8	296.7	286.5	317.2	176.3	180.0	226.
PI_3	269.7	306.9	341.2	341.2	123.1	132.3	176.
$\text{Si}(\text{PH}_2)_4$	-244.9	-238.8	-237.0	-228.7	-277.3	-271.7	-205.
$\text{P}(\text{CH}_3)_3$	-88.10	-79.68	-79.53	-68.0	-131.3	-123.3	-63.
$\text{OP}(\text{CH}_3)_3$	-7.86	-8.79	-9.52	-5.24	-38.50	-42.83	36.
$\text{P}(\text{OCH}_3)_3$	118.7	112.7	112.0	118.6	77.15	64.33	140.
$\text{OP}(\text{OCH}_3)_3$	-9.22	-16.77	-11.05	-13.61	-41.39	-51.69	0.
PF_6^{1-}	-139.9	-148.4	-125.2	-131.2	-203.0	-215.3	-145.
PH_4^{1+}	-155.7	-159.1	-152.4	-154.7	-172.7	-178.5	-105.
$\text{P}(\text{CH}_3)_4^{1+}$	-4.98	-2.85	-0.67	6.50	-69.17	-68.07	25.
RMSD	42.2	48.6	43.5	54.5	76.9	74.1	

^a S. Patchkovskii and T. Ziegler, J. Phys. Chem. A **106**, 1088 (2002)

Table 4: ^{195}Pt NMR shifts (ppm) relative to $\text{cis-PtCl}_2(\text{SMe}_2)_2$; TZP; ZORA SO

Molecule	BP86	B3LYP	BLYP	Expt ^b
$\text{cis-PtBr}_2(\text{SMe}_2)_2$	-352.37	-388.43	-360.53	-328
$\text{trans-PtI}_2(\text{SMe}_2)_2$	-1112.86	-1068.06	-1147.18	-1601
$\text{cis-PtCl}_2(\text{NH}_3)_2$	1283.67	1535.80	1420.04	1447
$\text{trans-PtCl}_2(\text{NH}_3)_2$	1202.55	1526.35	1288.62	1450
$\text{cis-PtBr}_2(\text{NH}_3)_2$	802.49	1031.40	925.86	1092
$\text{cis-PtI}_2(\text{NH}_3)_2$	-137.24	20.52	-44.88	283
$\text{cis-PtCl}_2(\text{PMe}_3)_2$	-362.23	-598.17	-383.29	-857
$\text{trans-PtCl}_2(\text{PMe}_3)_2$	-202.89	-297.14	-187.51	-399
$\text{cis-PtBr}_2(\text{PMe}_3)_2$	-582.34	-869.12	-618.92	-1085
$\text{trans-PtBr}_2(\text{PMe}_3)_2$	-749.74	-837.28	-743.89	-922
$\text{cis-PtI}_2(\text{PMe}_3)_2$	-911.75	-1256.27	-975.03	-1037
$\text{trans-PtI}_2(\text{PMe}_3)_2$	-1700.15	-1816.40	-1729.96	-1988
$\text{cis-PtCl}_2(\text{AsMe}_3)_2$	-392.22	-554.92	-404.70	-740
$\text{trans-PtCl}_2(\text{AsMe}_3)_2$	-120.31	-131.54	-93.47	-229
$\text{cis-PtBr}_2(\text{AsMe}_3)_2$	-686.61	-878.56	-709.01	-1074
$\text{trans-PtBr}_2(\text{AsMe}_3)_2$	-684.68	-705.10	-666.0	-827
$\text{trans-PtI}_2(\text{AsMe}_3)_2$	-1721.28	-1795.25	-1736.59	-1967

^b T. M. Gilbert and T. Ziegler, J. Phys. Chem. A **103**, 7535 (1999)

2 Response properties from the IVO and Hartree-Fock methods

We assume a set of occupied and virtual orbitals satisfying

$$F^0|i^0\rangle = \varepsilon_i^0|i^0\rangle, \quad (11)$$

$$F^0|a^0\rangle = \varepsilon_a^0|a^0\rangle. \quad (12)$$

For a perturbation Θ we have

$$A_{ai,bj} = (\varepsilon_i^0 - \varepsilon_a^0)\delta_{ij}\delta_{ab} - \left(\frac{\partial F_{ai}}{\partial X_{bj}} \right)_{\Theta=0}, \quad (13)$$

$$B_{ai,bj} = - \left(\frac{\partial F_{ai}}{\partial Y_{bj}} \right)_{\Theta=0}, \quad (14)$$

$$(A + B)(X + Y) = 2V \text{ (real)}, \quad (15)$$

$$(A - B)(Y - X) = -2V \text{ (imaginary)}. \quad (16)$$

In the IVO method we add a term F' to the one-electron operator F^0

$$F' = (1 - \sum_k^{\text{occ}} |k\rangle\langle k|) \Omega (1 - \sum_i^{\text{occ}} |i\rangle\langle i|) , \quad (17)$$

that does not effect the occupied orbitals

$$\tilde{F}^0 |i^0\rangle = F^0 |i^0\rangle + F' |i^0\rangle = \varepsilon_i^0 |i^0\rangle , \quad (18)$$

and rotates the virtual orbitals by the unitary transformation R

$$\tilde{F}^0 |\tilde{a}^0\rangle = F^0 |\tilde{a}^0\rangle + F' |\tilde{a}^0\rangle = \varepsilon_{\tilde{a}}^0 |\tilde{a}^0\rangle , \quad (19)$$

$$|a^0\rangle = R |\tilde{a}^0\rangle . \quad (20)$$

For a perturbation Θ we have

$$\tilde{A}_{\tilde{a}i, \tilde{b}j} = (\varepsilon_i^0 - \varepsilon_{\tilde{a}}^0) \delta_{ij} \delta_{\tilde{a}\tilde{b}} - \left(\frac{\partial \tilde{F}_{\tilde{a}i}}{\partial X_{\tilde{b}j}} \right)_{\Theta=0} = R A_{ai, bj} R^\dagger , \quad (21)$$

$$\tilde{B}_{\tilde{a}i, \tilde{b}j} = - \left(\frac{\partial \tilde{F}_{\tilde{a}i}}{\partial Y_{\tilde{b}j}} \right)_{\Theta=0} = R B_{ai, bj} R^\dagger . \quad (22)$$

- Real perturbation

$$R^\dagger(\tilde{X} + \tilde{Y}) = X + Y \quad , \quad (23)$$

$$\langle \Theta' \rangle = \sum_a^{\text{virt}} \sum_i^{\text{occ}} (X + Y)_{ai} \langle i^0 | \Theta' | a^0 \rangle = \sum_{\tilde{a}}^{\text{virt}} \sum_i^{\text{occ}} (\tilde{X} + \tilde{Y})_{\tilde{a}i} \langle i^0 | \Theta' | \tilde{a}^0 \rangle \quad . \quad (24)$$

- Imaginary perturbation

$$R^\dagger(\tilde{Y} - \tilde{X}) = Y - X \quad , \quad (25)$$

$$\langle \Xi' \rangle = \sum_a^{\text{virt}} \sum_i^{\text{occ}} (X - Y)_{ai} \langle i^0 | \Xi' | a^0 \rangle = \sum_{\tilde{a}}^{\text{virt}} \sum_i^{\text{occ}} (\tilde{X} - \tilde{Y})_{\tilde{a}i} \langle i^0 | \Xi' | \tilde{a}^0 \rangle \quad . \quad (26)$$

3 Response properties from the EXX-OEP and Hartree-Fock methods

We assume that there is such a potential v_{OEP} which satisfies:

$$\langle a^0 | v_{\text{OEP}} - \hat{K} | i^0 \rangle = \langle a^0 | \hat{F}_{\text{OEP}} - \hat{F}_{\text{HF}} | i^0 \rangle = 0 . \quad (27)$$

Here, \hat{K} is the Hartree-Fock exchange operator, $|i^0\rangle$ and $|a^0\rangle$ are the occupied and virtual Hartree-Fock orbitals. For the first order perturbation theory:

$$\langle a^0 | \hat{F}_{\text{OEP}}^{(1)} - \hat{F}_{\text{HF}}^{(1)} | i^0 \rangle + \langle a^{(1)} | \hat{F}_{\text{OEP}} - \hat{F}_{\text{HF}} | i^0 \rangle + \langle a^0 | \hat{F}_{\text{OEP}} - \hat{F}_{\text{HF}} | i^{(1)} \rangle = 0 . \quad (28)$$

The unitary transformation R that transforms the EXX-OEP Kohn-Sham orbitals into the Hartree-Fock orbitals:

$$|a^0 i^0\rangle = R | \tilde{a}^0 \tilde{i}^0 \rangle . \quad (29)$$

- Real perturbation

$$\begin{aligned}
 R^\dagger (\tilde{A}_{\tilde{a}\tilde{i},\tilde{b}\tilde{j}}^{\text{OEP}} + \tilde{B}_{\tilde{a}\tilde{i},\tilde{b}\tilde{j}}^{\text{OEP}}) R &= \delta_{ij} \delta_{ab} (\varepsilon_i^0 - \varepsilon_a^0) - K_{ai,jb}^{\text{HF}} - K_{ai,bj}^{\text{HF}} \\
 &= A_{ai,bj}^{\text{HF}} + B_{ai,bj}^{\text{HF}} ,
 \end{aligned} \tag{30}$$

$$R^\dagger (\tilde{X}^{\text{OEP}} + \tilde{Y}^{\text{OEP}}) = X^{\text{HF}} + Y^{\text{HF}} . \tag{31}$$

- Imaginary perturbation

$$\begin{aligned}
 R^\dagger (\tilde{A}_{\tilde{a}\tilde{i},\tilde{b}\tilde{j}}^{\text{OEP}} - \tilde{B}_{\tilde{a}\tilde{i},\tilde{b}\tilde{j}}^{\text{OEP}}) R &= \delta_{ij} \delta_{ab} (\varepsilon_i^0 - \varepsilon_a^0) + K_{ai,jb}^{\text{HF}} - K_{ai,bj}^{\text{HF}} \\
 &= A_{ai,bj}^{\text{HF}} - B_{ai,bj}^{\text{HF}} ,
 \end{aligned} \tag{32}$$

$$R^\dagger (\tilde{Y}^{\text{OEP}} - \tilde{X}^{\text{OEP}}) = Y^{\text{HF}} - X^{\text{HF}} . \tag{33}$$

4 Finite basis set EXX-OEP method

The local exchange potential is expressed in terms of the fit functions, $f_m(\mathbf{r})$

$$v_{\text{OEP}}(\mathbf{r}) = \sum_m^M b_m f_m(\mathbf{r}) \quad (34)$$

The b_m coefficients are obtained from a solution of a system of linear equations

$$\sum_m^M X_{nm} b_m = t_n \quad , \quad n = 1, 2, \dots, M \quad . \quad (35)$$

Equation (35) corresponds to the discretized functional derivative $\delta E_{\text{EXX}}/\delta\rho^{\text{a}}$. We have used Slater-type orbitals for $f_m(\mathbf{r})$ and for orbital basis sets. Two variants of the EXX-OEP algorithms have been implemented in the Amsterdam Density Functional (ADF) package.

^aS. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999);
A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

- Exact OEP ^a

$$X_{nm} = \sum_i^{\text{occ}} \sum_a^{\text{virt}} \frac{\langle \phi_i | f_n | \phi_a \rangle \langle \phi_a | f_m | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} \quad (36)$$

$$t_n = \sum_i^{\text{occ}} \sum_a^{\text{virt}} \frac{\langle \phi_i | f_n | \phi_a \rangle \langle \phi_a | \hat{K} | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} \quad (37)$$

- Common energy denominator approximation (CEDA) ^b

$$X_{nm} = \sum_i^{\text{occ}} \langle \phi_i | f_n f_m | \phi_i \rangle - \sum_{ij}^{\text{occ}} \langle \phi_i | f_n | \phi_j \rangle \langle \phi_j | f_m | \phi_i \rangle \quad (38)$$

$$t_n = \sum_i^{\text{occ}} \langle \phi_i | f_n \hat{K} | \phi_i \rangle - \sum_{ij}^{\text{occ}} \langle \phi_i | f_n | \phi_j \rangle \langle \phi_j | \hat{K} | \phi_i \rangle \quad (39)$$

^aS. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999); A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

^bV. N. Staroverov, G. E. Scuseria, and E. R. Davidson, J. Chem. Phys. **125**, 081104 (2006); A. F. Izmaylov et al., J. Chem. Phys. **126**, 084107 (2007).

5 Results of calculations

Table 5: Isotropic shielding constants, σ (ppm); HOMO-LUMO gaps, Δ_{HL} (in eV); differences of the total energies with respect to the Hartree-Fock, Δ_E (in atomic units); DZ basis set; GIAOs

Mol.	N	exact OEP			CEDA			Hartree-Fock	
		σ	Δ_{HL}	Δ_E	σ	Δ_{HL}	Δ_E	σ	Δ_{HL}
H ₂	H	27.24	13.6	0.000	27.59	13.3	0.001	27.24	21.8
LiH ²⁺	Li	95.20	58.6	0.000	95.19	53.9	0.001	95.19	63.0
	H	0.02			0.02			0.02	
BeH ₂ ⁴⁺	Be	130.59	114.	0.000	130.58	120.	0.000	130.58	134.
	H	0.00			0.00			0.00	

$$E_{total}^{HF}(\text{H}_2) = -1.842$$

$$E_{total}^{HF}(\text{LiH}^{2+}) = -7.899$$

$$E_{total}^{HF}(\text{BeH}_2^{4+}) = -15.188$$

Table 6: σ (ppm); Δ_{HL} (eV); Δ_E (atomic units); DZP basis set; GIAOs

Mol.	N	exact OEP			CEDA			Hartree-Fock		Exp.
		σ	Δ_{HL}	Δ_E	σ	Δ_{HL}	Δ_E	σ	Δ_{HL}	
N ₂	N	22.00	10.1	0.015	-23.02	8.97	0.013	-82.47	20.9	-59.6
F ₂	F	-39.22	6.54	0.021	-151.7	4.18	0.018	-171.4	20.2	-192.8
HF	F	417.4	14.2	0.008	422.7	13.3	0.007	407.8	21.6	419.7
CO	C	45.04	8.66	0.011	15.81	7.57	0.008	-12.03	18.9	2.8
	O	52.42			20.68			-50.36		-36.7
CO ₂	C	88.56	10.3	0.023	82.73	9.66	0.018	59.12	20.3	58.8
	O	263.2			245.0			227.2		243.4
NH ₃	N	287.8	9.51	0.005	293.1	9.83	0.009	267.6	15.6	273.3
CH ₄	C	213.1	13.8	0.0001	225.1	13.6	0.006	207.9	18.8	198.4
H ₂ O	O	354.8	10.9	0.009	350.1	10.6	0.008	322.3	17.7	357.6
HCN	C	122.4	8.82	0.015	105.7	8.52	0.014	81.91	18.0	82.1
	N	44.31			24.59			-14.46		-20.4
H ₂ CO	O	-96.72	5.35	0.010	-174.2	4.40	0.017	-374.8	15.2	-375.0
	C	51.12			27.18			4.26		-4.4
C ₂ H ₂	C	177.6	7.58	0.0001	166.5	7.29	0.011	135.5	16.1	117.2
C ₂ H ₄	C	125.6	6.29	0.006	112.8	5.98	0.017	78.63	14.4	64.5
RMS (ppm)		92.0			59.6			15.4		

Table 7: Statistical evaluation of the Hartree-Fock results for isotropic NMR chemical shifts, in comparison with exact OEP and CEDA values; TZ2P basis set; GIAOs

	C	H	N	O	F
Number of data points	49	19	18	18	12
Hartree-Fock					
σ_{ref} (ppm)	194.8	31.25	-111.3	13.23	388.7
average abs. error (ppm)	9.48	0.36	51.6	438.3	19.9
RMS error (ppm)	12.9	0.43	71.0	707.4	29.0
RMS/range (percent)	4.85	3.39	8.88	19.2	4.34
exact OEP					
σ_{ref} (ppm)	225.0	31.19	-16.38	469.7	433.3
average abs. error (ppm)	20.1	0.52	21.3	86.4	42.0
RMS error (ppm)	22.1	0.73	25.8	138.8	40.6
RMS/range (percent)	10.3	5.82	4.15	13.8	9.14
CEDA					
σ_{ref} (ppm)	220.4	30.81	-40.26	362.9	392.0
average abs. error (ppm)	19.8	0.49	13.7	45.8	20.2
RMS error (ppm)	20.5	0.62	16.4	59.4	25.2
RMS/range (percent)	9.69	4.43	2.29	4.05	3.85

Table 8: Statistical evaluation of the CEDA results for isotropic NMR chemical shifts, in comparison with BP86 and B3LYP values; TZ2P basis set; GIAOs

	C	H	N	O	F
Number of data points	49	19	18	18	12
CEDA					
σ_{ref} (ppm)	220.4	30.81	-40.26	362.9	392.0
average abs. error (ppm)	19.8	0.49	13.7	45.8	20.2
RMS error (ppm)	20.5	0.62	16.4	59.4	25.2
RMS/range (percent)	9.69	4.43	2.29	4.05	3.85
BP86					
σ_{ref} (ppm)	187.0	31.14	-89.37	223.4	318.3
average abs. error (ppm)	5.44	0.34	31.5	85.2	15.9
RMS error (ppm)	7.96	0.45	69.5	108.3	22.2
RMS/range (percent)	3.41	3.58	6.95	5.78	2.99
B3LYP					
σ_{ref} (ppm)	184.0	31.23	-99.35	183.3	329.7
average abs. error (ppm)	6.41	0.26	27.1	118.3	14.8
RMS error (ppm)	8.76	0.33	48.9	153.9	19.3
RMS/range (percent)	3.60	2.61	5.36	7.12	2.63

Table 9: Comparison of the CEDA to the SIC-VWN and SIC-BP86; TZ2P; GIAOs

	C	H	N	O	F
Number of data points	49	19	18	18	12
CEDA					
σ_{ref} (ppm)	220.4	30.81	-40.26	362.9	392.0
average abs. error (ppm)	19.8	0.49	13.7	45.8	20.2
RMS error (ppm)	20.5	0.62	16.4	59.4	25.2
RMS/range (percent)	9.69	4.43	2.29	4.05	3.85
SIC-VWN ^a					
σ_{ref} (ppm)	189.4	30.36	-63.2	323.2	350.4
average abs. error (ppm)	5.0	0.27	13.6	46.1	11.3
RMS error (ppm)	7.1	0.44	21.3	70.1	14.5
RMS/range (percent)	3.0	3.6	3.0	4.2	2.1
SIC-BP86 ^b					
σ_{ref} (ppm)	199.3	30.86	-39.1	373.4	369.6
average abs. error (ppm)	5.3	0.17	12.8	53.3	9.6
RMS error (ppm)	6.6	0.24	17.0	79.4	12.3
RMS/range (percent)	2.8	1.9	2.5	4.8	1.7

^a S. Patchkovskii, J. Autschbach, and T. Ziegler, J. Chem. Phys. **115**, 26 (2001)^b S. Patchkovskii and T. Ziegler, J. Phys. Chem. A **106**, 1088 (2002)

6 Summary

- 1) The static second order response properties from the Hartree-Fock (HF) and EXX-OEP methods coincide in the limit of the perfect fit of the nonlocal HF exchange potential into the local one.
- 2) The improved virtual orbitals method does not change the static second order response properties when compared to the HF values.
- 3) Separate rotations of the occupied and the virtual orbitals do not change any static response property, while they change (reduce) the HOMO-LUMO gaps.
- 4) For two electron systems the EXX-OEP and the HF methods afford similar NMR shielding constants although the HOMO-LUMO gaps are different.
- 5) For the many electron systems the EXX-OEP and the HF methods affords different chemical shifts as we are unable to perform an exact fit of the HF potential. This deviation has the consequence that the HF method afford better chemical shifts for H, C and F atoms whereas the EXX-OEP shifts are better compared to experiment for O and N atoms.