Supporting Information

An efficient DFT method of predicting the one-, two- and three-bond indirect spin-spin coupling constants involving fluorine nucleus in fluoroalkanes†

Adam Gryff-Keller* and Przemysław Szczeciński

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland

Table S1. The experimental and theoretically predicted values of NMR parameters[a] for fluoromethane. The molecular geometry optimization and NMR parameter calculations were performed using the same DFT method.

Method	B3LYP				PBE0				BHandH				Exp.
	s	*m*	*m'*	*l*	*s*	*m*	*m'*	*l*	*s*	*m*	*m'*	*l*	
σ(F)	460.2	462.5		463.0	467.6	469.5		470.1	487.4	488.9		490.2	471.0[b]
σ(C)	108.6	108.1		103.6	115.9	115.2		110.5	120.7	120.2		116.7	110.3[c]
σ(H)	27.5	27.2		27.2	27.4	27.2		27.2	27.4	27.1		27.1	26.7[d]
J(C,F)	-214.1	-213.7	-230.7	-226.2	-216.1	-214.2	-230.6	-226.8	-186.5	-183.2	-197.8	-193.9	-163.0[e]
J(C,H)	139.1	140.2	155.8	155.3	132.2	132.4	145.3	144.9	129.3	130.2	144.6	144.8	147.3[e]
J(F,H)	47.6	47.4	53.3	53.4	46.7	46.7	51.9	51.8	47.1	46.8	53.5	53.9	46.5[e]

[a] σ in ppm, J in Hz
[b] Ref. 55.
[c] Ref. 46.
[d] Calculated as: $\sigma(CH_3F)_{gas}=\sigma(X)_{gas}-\delta(X)_{solvent}+\delta(CH_3F)_{solvent}$, i.e. assuming the same solvent effect for CH_3F and X (X=CH_2F_2 or CHF_3), and using the experimental data of refs 56, 57 and 58.
[e] Ref. 13.
m' = aug-cc-pVTZ-J

* E-mail: agryff@ch.pw.edu.pl

Table S2. The experimental and theoretically predicted values of NMR parameters[a] for difluoromethane. The molecular geometry optimization and NMR parameter calculations were performed using the same DFT method.

Method	B3LYP				PBE1PBE				BHandH				Exp.[b]
	s	*m*	*m'*	*l*	*s*	*m*	*m'*	*l*	*s*	*m*	*m'*	*l*	
σ(F)	321.7	324.6		321.9	330.8	333.4		330.8	348.5	350.6		349.0	338.9
σ(C)	67.3	66.6		60.6	75.9	75.1		68.7	83.0	82.1		77.3	77.7
σ(H)	26.1	25.7		25.7	26.0	25.7		25.7	26.2	25.8		25.8	25.3
J(F,C)	-296.9	-292.3	-314.0	-311.3	-289.2	-283.9	-303.9	-302.1	-243.7	-237.6	-254.2	-251.6	-234.6
J(C,H)	170.9	171.6	190.9	190.1	162.3	161.9	178.1	177.5	156.1	156.7	174.1	174.1	180.4
J(F,H)	50.0	49.4	57.2	57.1	48.6	48.3	55.0	54.7	48.4	47.8	55.9	56.1	50.2
J(F,F)	284.5	274.4	297.4	311.9	294.9	285.0	305.6	317.5	334.8	322.0	356.7	370.7	346.2[c]

[a] σ in ppm, *J* in Hz

[b] Ref. 57.

[c] Calculated value; ref. 13.

m' = aug-cc-pVTZ-J

Table S3. The experimental and theoretically predicted values of NMR parameters[a] for trifluoromethane. The molecular geometry optimization and NMR parameter calculations were performed using the same DFT method.

Method	B3LYP			PBE1PBE			BHandH			Exp.[b]
	s	*m*	*l*	*s*	*m*	*l*	*s*	*m*	*l*	
σ(F)	253.4	257.6	252.8	263.2	267.1	262.5	280.7	283.7	280.4	274.1
σ(C)	56.3	55.9	48.8	65.6	64.8	57.4	74.8	73.7	68.1	68.7
σ(H)	25.3	24.9	24.9	25.3	24.9	24.9	25.6	25.1	25.1	24.5
J(F,C)	-350.2	-340.7	-363.2	-334.9	-325.2	-346.5	-272.5	-262.4	-277.4	-272.3
J(C,H)	225.2	223.8	250.1	213.3	210.8	232.8	201.8	200.6	224.1	235.6
J(F,H)	77.1	76.4	88.3	75.3	74.7	84.8	75.0	74.6	86.4	79.9
J(F,F)	45.4	37.1	59.5	62.1	53.3	72.2	122.7	109.9	145.7	152.4[c]

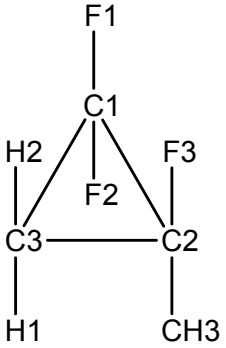
[a] σ in ppm, *J* in Hz
[b] Ref. 56
[c] Calculated value; ref. 13.

Table S4. The experimental and theoretically predicted values of NMR parameters[a] for tetrafluoromethane. The molecular geometry optimization and NMR parameter calculations were performed using the same DFT method.

Method	B3LYP			PBE1PBE			BHandH			Exp.
	s	*m*	*l*	*s*	*m*	*l*	*s*	*m*	*l*	
σ(F)	234.6	240.7	235.3	244.7	250.4	245.0	263.5	268.3	264.3	250[b]
σ(C)	49.6	49.6	41.8	59.3	59.0	51.0	69.9	69.1	63.0	64[b]
J(F,C)	-353.8	-342.7	-363.5	-332.2	-321.3	-341.0	-250.6	-239.9	-250.7	259.4[c]
J(F,F)	-53.3	-59.1	-44.7	-35.0	-41.2	-29.5	35.7	26.4	54.4	

[a] σ in ppm, *J* in Hz
[b] Ref. 31.
[c] Ref. 46.

Table S5. Comparison of calculated and experimental values of spin-spin coupling constants for 1,1,2-trifluoro-2-methylcyclopropane.



Constant					Constant				
	B3LYP/s	PBE0/l	BHandH/s	Exp.[a]		B3LYP/s	PBE0/l	BHandH/s	Exp.[a]
^{2}J(F-1,F-2)	94.6	127.9	159.4	168.7	^{3}J(F-2,$\underline{C}H_3$)	4.0	3.7	5.0	3.8
^{3}J(F-2,F-3)	10.9	13.6	10.7	14.0	^{3}J(F-1,$\underline{C}H_3$)	-1.5	-1.4	-1.6	-0.9
^{3}J(F-1,F-3)	-1.6	-1.8	0.8		^{2}J(F-3,$\underline{C}H_3$)	16.6	21.3	19.9	22.2
^{1}J(F-2,C-1)	-368.5	-364.1	-278.1	-295.2	^{3}J(F-2,H-1)	1.5	3.2	2.7	5.1
^{1}J(F-1,C-1)	-366.6	-360.4	-275.8	-293.5	^{3}J(F-1,H-1)	15.9	18.6	19.1	17.7
^{2}J(F-3,C-1)	4.3	7.8	6.6	10.2	^{3}J(F-3,H-1)	22.5	25.9	25.6	24.2
^{2}J(F-2,C-3)	5.1	8.6	8.3	10.8[b]	^{3}J(F-2,H-2)	13.5	15.5	15.1	15.0
^{2}J(F-1,C-3)	4.1	7.5	7.7	9.9[b]	^{3}J(F-1,H-2)	3.2	5.4	5.0	7.5
^{2}J(F-3,C-3)	7.9	11.4	10.60	13.2[b]	^{3}J(F-3,H-2)	8.7	11.0	10.4	14.0
^{2}J(F2,C-2)	6.1	10.0	9.7	13.2	^{4}J(F-2,C$\underline{H}_3$)	2.0	1.8	1.8	
^{2}J(F-1,C-2)	5.4	7.9	6.7	9.3	^{4}J(F-1,C$\underline{H}_3$)	2.2	3.0	2.1	2.6
^{1}J(F-3,C-2)	-286.8	-292.4	-228.0	-234.0	^{3}J(F-3,C$\underline{H}_3$)	17.5	19.9	18.7	-

[a]Refs. 50 and 53.

[b] Assignment different than in ref. 50.

Table S6. Comparison of calculated and experimental[a] values of selected spin-spin coupling constants for fluoronorbornanes in $CDCl_3$ solution.

Molecule	Method	$^1J(F,C)$	$^2J(F,C)$	$^3J(F,C^{syn})$	$^3J(F,C^{anti})$	$^2J(F,H)$
7-Fluoronorbornan	Exp	-192.3	15.9	2.1	9.0	60.2
	B3LYP/*s*	-227.5	11.7	2.2	5.4	59.6
	BHandH/*s*	-188.8	15.3	3.3	7.2	56.9
syn-7-Fluoronorbornen	Exp.	-199.6	16.2	0.0	6.1	60.4
	B3LYP/*s*	-238.5	12.0	0.8	2.5	62.1
	BHandH/*s*	-198.0	15.8	0.9	4.2	59.3
anti-7-Fluoronorbornen	Exp.	-210.4	17.2	0.0	9.0	60.2
	B3LYP/*s*	-247.0	13.1	-1.1	5.6	60.7
	BHandH/*s*	-205.1	16.6	0.2	7.8	58.4
7-Fluorobornadien	Exp.	-228.3	16.8	-1.2	4.4	unavailable
	B3LYP/*s*	-268.5	12.5	-1.5	0.8	66.7
	BHandH/*s*	-224.7	16.1	-1.5	2.5	64.6

[a] Ref. 59.

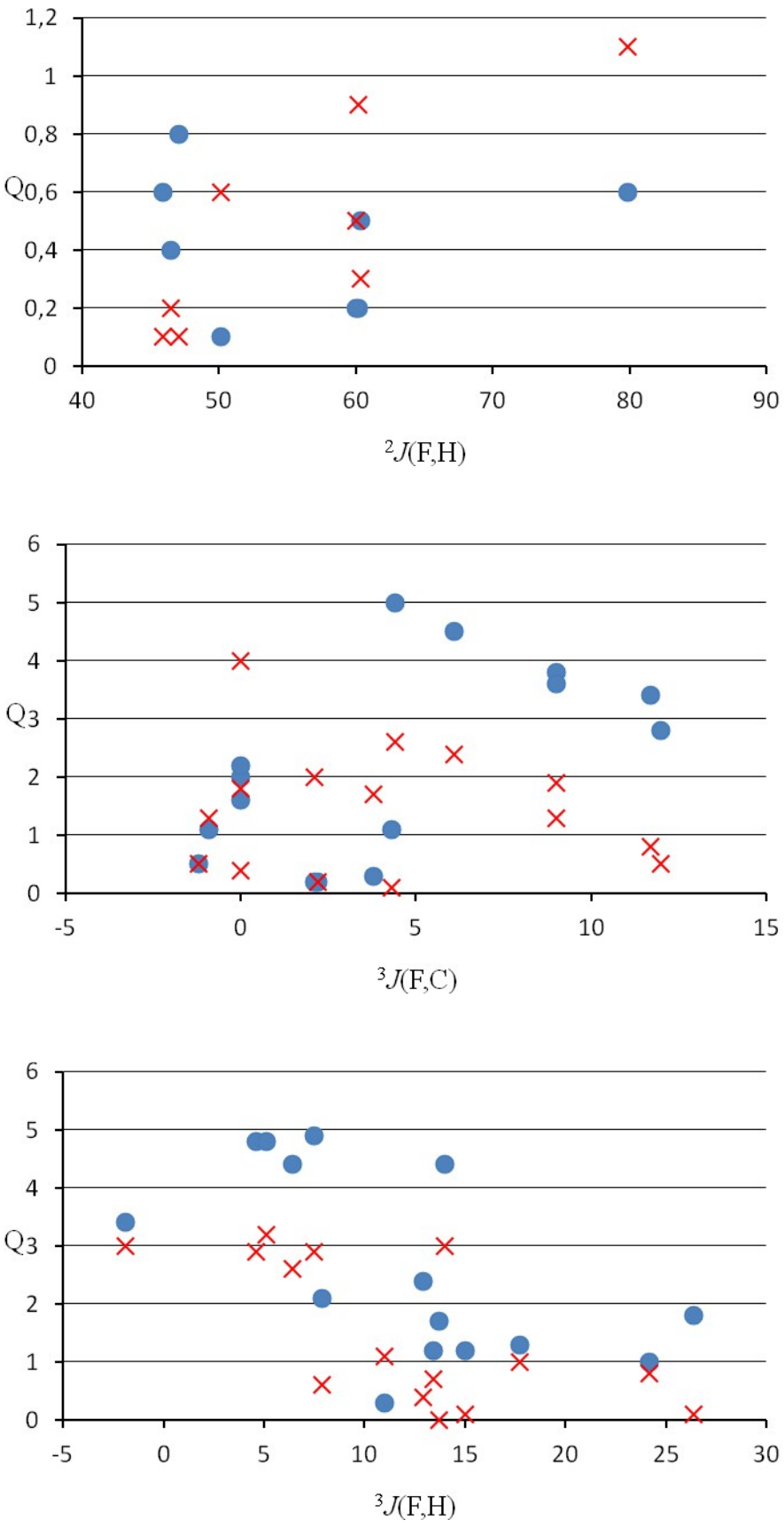


Figure S1. Accuracy, as defined by Q parameter, of calculated values of different coupling constants; × - BHandH/*s*, ● – B3LYP/*s*.