SUPPLEMENTARY MATERIAL

Through-space spin–spin coupling constants involving fluorine: benchmarking DFT functionals

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Table 1. Oxime-Ph: individual coupling constants and their relative deviations from the experimental values, Δ, calculated with various methods and the pcJ-2 basis set

Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0	SOPPA	SOPPA (CCSD)	Exp
Through-bond coupling												
^{1}J(N C7)	5.18	0.38	1.53	-0.30	-12.73	-5.28	-7.08	-8.97	-5.54	-6.58	-7.62	(-)2.3
^{3}J(F H3)	10.43	11.95	11.76	10.66	10.15	11.53	11.05	10.30	9.32	8.00	7.52	10.4
^{3}J(H4 H3)	11.07	9.16	9.07	8.32	9.87	9.83	9.97	10.20	9.47	8.99	8.69	8.2
^{3}J(H5 H4)	9.29	7.87	7.80	7.20	8.72	8.61	8.80	9.05	8.26	7.95	7.70	7.4
^{3}J(H6 H5)	10.29	8.62	8.55	7.92	9.57	9.45	9.67	9.94	9.08	8.81	8.52	7.6
^{4}J(F H4)	5.56	5.02	4.86	4.29	5.56	5.19	4.93	5.29	5.38	4.82	4.87	5.3
^{4}J(F H6)	8.19	7.38	7.12	6.37	7.65	7.34	6.86	7.14	7.42	6.52	6.43	7.2
^{4}J(H5 H3)	1.49	1.20	1.20	0.78	0.54	1.05	0.79	0.56	0.86	0.77	0.64	1.2
^{4}J(H6 H4)	2.48	1.91	1.90	1.36	0.95	1.64	1.27	0.97	1.41	1.22	1.03	1.8
^{4}J(N F)	0.20	0.46	0.49	0.29	-3.17	-0.74	-1.79	-2.87	-1.40	-0.28	-0.93	(-)3.2
Δ values												
^{1}J(N C7)	-3.252	-1.165	-1.665	-0.870	4.535	1.296	2.078	2.900	1.409	1.861	2.313	
^{3}J(F H3)	0.003	0.149	0.131	0.025	-0.024	0.109	0.063	-0.010	-0.104	-0.231	-0.277	
^{3}J(H4 H3)	0.350	0.117	0.106	0.015	0.204	0.199	0.216	0.244	0.155	0.096	0.060	
^{3}J(H5 H4)	0.255	0.064	0.054	-0.027	0.178	0.164	0.189	0.223	0.116	0.074	0.041	
^{3}J(H6 H5)	0.354	0.134	0.125	0.042	0.259	0.243	0.272	0.308	0.195	0.159	0.121	
^{4}J(F H4)	0.049	-0.053	-0.083	-0.191	0.049	-0.021	-0.070	-0.002	0.015	-0.091	-0.081	
^{4}J(F H6)	0.138	0.025	-0.011	-0.115	0.063	0.019	-0.047	-0.008	0.031	-0.094	-0.107	
^{4}J(H5 H3)	0.242	0.000	0.000	-0.350	-0.550	-0.125	-0.342	-0.533	-0.283	-0.358	-0.467	
^{4}J(H6 H4)	0.378	0.061	0.056	-0.244	-0.472	-0.089	-0.294	-0.461	-0.217	-0.322	-0.428	
^{4}J(F N)	-1.063	-1.144	-1.153	-1.091	-0.009	-0.769	-0.441	-0.103	-0.563	-0.913	-0.709	
MARD												
	1.106	0.523	0.645	0.467	1.457	0.493	0.699	0.955	0.502	0.681	0.798	
MARE												
	3.252	1.165	1.665	1.091	4.535	1.296	2.078	2.900	1.409	1.861	2.313	

[a] Experimental data taken from ref. [1]

Table 2. Flubenzimine: individual coupling constants and their relative deviations from the experimental values, Δ, calculated with various methods and the pcJ-2 basis set

Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0	Exp
Through-bond coupling										
^{1}J(Cf1 F1)	-389.14	-371.59	-377.01	-396.07	-283.86	-341.84	-325.03	-316.41	-331.87	(-)255.8
^{1}J(Cf2 F2)	-393.69	-375.84	-381.25	-400.44	-288.42	-346.23	-329.41	-320.85	-336.23	(-)262.9
^{2}J(F1 N4)	-15.80	-20.77	-19.85	-19.39	-23.68	-22.48	-22.78	-22.91	-21.74	-23.2
^{2}J(F2 N5)	-15.29	-20.12	-19.26	-18.66	-22.10	-21.38	-21.70	-21.72	-20.60	-20.0
^{3}J(C4 F1)	4.69	6.74	6.45	5.61	7.47	7.19	7.38	7.47	7.23	8.2
^{3}J(C5 F2)	2.39	5.02	4.58	3.85	6.26	5.51	5.40	5.52	5.65	8.6
Through-space coupling										
^{5}J(F1 N5)	-5.89	-6.49	-6.58	-7.42	-7.14	-7.12	-7.21	-7.16	-6.24	-7.8
Δ values										
^{1}J(Cf1 F1)	0.521	0.453	0.474	0.548	0.110	0.336	0.271	0.237	0.297	
^{1}J(Cf2 F2)	0.497	0.430	0.450	0.523	0.097	0.317	0.253	0.220	0.279	
^{2}J(F1 N4)	-0.319	-0.105	-0.144	-0.164	0.021	-0.031	-0.018	-0.012	-0.063	
^{2}J(F2 N5)	-0.235	0.006	-0.037	-0.067	0.105	0.069	0.085	0.086	0.030	
^{3}J(C4 F1)	-0.428	-0.178	-0.214	-0.315	-0.089	-0.123	-0.100	-0.089	-0.118	
^{3}J(C5 F2)	-0.722	-0.416	-0.467	-0.552	-0.272	-0.359	-0.372	-0.358	-0.343	
^{5}J(F1 N5)	-0.245	-0.167	-0.157	-0.049	-0.085	-0.088	-0.075	-0.082	-0.200	
MARD										
	0.454	0.301	0.325	0.380	0.132	0.230	0.207	0.191	0.221	
MARE										
	0.722	0.453	0.474	0.552	0.272	0.359	0.372	0.358	0.343	

[a] Experimental data taken from ref. [2]

Table 3. Phosphine-Ph: individual coupling constants and their relative deviations from the experimental values, Δ, calculated with various methods and the pcJ-2 basis set

Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0	Exp
Through-bond coupling										
^{1}J(C1 P)	-96.63	-105.59	-105.12	-72.11	-64.02	-88.46	-83.49	-78.06	-82.35	-57.0
^{1}J(C7 F(C))	-400.03	-388.86	-393.42	-409.73	-300.23	-358.25	-340.71	-331.70	-346.98	-274.7
^{2}J(C1 F(P))	-0.45	5.07	4.04	4.32	16.15	10.31	12.02	13.82	12.61	9.9
^{2}J(C6 P)	9.06	9.45	9.47	10.17	8.36	9.25	8.68	8.44	8.76	10.1
^{3}J(C3 P)	1.81	2.40	2.41	3.78	4.03	3.27	3.63	3.82	3.59	2.4
^{3}J(C3 F(C))	1.87	3.57	3.40	3.85	6.42	5.07	5.48	5.90	4.90	5.3
^{3}J(C6 F(P))	6.16	7.77	7.63	8.84	9.38	8.74	9.04	9.30	8.33	11.1
^{3}J(C7 P)	-3.50	-2.78	-2.68	-2.60	-2.53	-2.53	-2.39	-2.26	-2.40	(-)2.5
^{4}J(C7 F(P))	-0.89	-0.65	-0.64	-0.82	-1.14	-0.77	-0.87	-0.96	-0.83	(-)0.7
^{5}J(C4 F(P))	-0.23	0.26	0.09	0.77	1.43	0.76	0.83	1.07	0.89	1.8
Through-space coupling										
^{4}J(F(C) P)	66.04	71.50	73.72	87.72	78.88	78.51	77.67	77.23	68.79	68.3
^{5}J(F(P) F(C))	6.61	7.83	7.58	7.19	8.71	7.93	7.90	7.91	7.77	8.3
Δ values										
^{1}J(C1 P)	0.695	0.852	0.844	0.265	0.123	0.552	0.465	0.369	0.445	
^{1}J(C7 F(C))	0.456	0.416	0.432	0.492	0.093	0.304	0.240	0.207	0.263	
^{2}J(C1 F(P))	-1.045	-0.488	-0.592	-0.564	0.631	0.041	0.214	0.396	0.274	
^{2}J(C6 P)	-0.103	-0.064	-0.062	0.007	-0.172	-0.084	-0.141	-0.164	-0.133	
^{3}J(C3 P)	-0.246	0.000	0.004	0.575	0.679	0.363	0.513	0.592	0.496	
^{3}J(C3 F(C))	-0.648	-0.326	-0.359	-0.273	0.211	-0.043	0.034	0.113	-0.076	
^{3}J(C6 F(P))	-0.445	-0.300	-0.313	-0.204	-0.155	-0.213	-0.186	-0.162	-0.250	
^{3}J(C7 P)	0.400	0.112	0.072	0.040	0.012	0.012	-0.044	-0.096	-0.040	
^{4}J(C7 F(P))	0.271	-0.071	-0.086	0.171	0.629	0.100	0.243	0.371	0.186	
^{5}J(C4 F(P))	-1.128	-0.856	-0.950	-0.572	-0.206	-0.578	-0.539	-0.406	-0.506	
^{4}J(F(C) P)	-0.033	0.047	0.079	0.284	0.155	0.149	0.137	0.131	0.007	
^{5}J(F(P) F(C))	-0.203	-0.057	-0.086	-0.133	0.050	-0.045	-0.049	-0.047	-0.064	
MARD										
	0.579	0.418	0.448	0.357	0.347	0.282	0.290	0.300	0.284	
MARE										
	1.128	0.856	0.950	0.575	0.679	0.578	0.539	0.592	0.506	

[a] Experimental data taken from ref. [3]

Table 4. Selen-Naph: individual coupling constants and their relative deviations from the experimental values, Δ, calculated with various methods and the pcJ-2 basis set

Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0	Exp
Through-space coupling										
^{4}J(F Se)	276.73	301.17	304.70	322.62	320.00	319.97	331.74	329.11	293.17	276.7
^{5}J(F C11)	15.26	17.62	17.20	19.64	20.72	20.40	20.93	21.32	18.80	14.9
Δ values										
^{4}J(F Se)	0.000	0.088	0.101	0.166	0.156	0.156	0.199	0.189	0.060	
^{5}J(F C11)	0.024	0.183	0.154	0.318	0.391	0.369	0.405	0.431	0.262	
MARD										
	0.017	0.143	0.131	0.254	0.298	0.283	0.319	0.333	0.190	
MARE										
	0.024	0.183	0.154	0.318	0.391	0.369	0.405	0.431	0.262	

[a] Experimental data taken from ref. [4]

Table 5. Contributions to the through-space spin-spin coupling constants

	Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0
oxime-Ph (syn)										
	F and N	-19.25	-20.62	-21.02	-23.54	-25.88	-23.81	-24.87	-25.73	-21.57
	FC	-14.83	-16.74	-17.10	-19.82	-20.25	-19.51	-19.94	-20.12	-16.78
	PSO	-1.45	-1.51	-1.53	-1.38	-1.36	-1.41	-1.34	-1.28	-1.43
	SD	-2.83	-2.22	-2.25	-2.20	-4.14	-2.74	-3.45	-4.20	-3.20
oxime-Ind										
	F and N	6.31	6.95	7.17	8.62	10.04	8.82	9.47	10.02	7.77
	FC	4.17	5.18	5.38	6.89	7.16	6.73	6.96	7.11	5.40
	PSO	0.46	0.46	0.46	0.41	0.46	0.45	0.45	0.43	0.46
	SD	1.59	1.22	1.24	1.23	2.32	1.55	1.96	2.38	1.81
oxime-Bnz										
	F and N	42.37	44.72	44.82	46.76	42.87	45.22	44.76	43.41	40.58
	FC	42.58	44.68	44.78	46.86	44.29	45.70	45.77	44.88	41.26
	PSO	0.06	0.17	0.17	0.13	-0.29	-0.06	-0.19	-0.22	-0.08
	SD	-0.44	-0.30	-0.30	-0.39	-1.29	-0.57	-0.98	-1.42	-0.76
perfluoro										
	F′ and F	85.12	100.62	102.16	96.64	95.07	102.70	101.56	100.07	93.23
	FC	29.67	42.91	44.25	44.44	56.89	55.88	58.37	59.99	47.92
	PSO	31.14	35.47	35.62	32.08	24.03	28.61	26.27	24.51	27.84
	SD	23.36	21.28	21.34	19.16	13.21	17.27	15.97	14.63	16.52
di-F-Naph										
	F and F	45.95	63.25	65.21	65.44	60.23	69.02	66.46	63.88	57.19
	FC	32.37	48.10	49.87	53.42	61.30	62.01	64.65	65.90	50.99
	PSO	9.28	11.23	11.37	10.15	2.73	5.91	4.04	3.40	6.75
	SD	3.33	2.93	2.97	0.90	-4.78	0.14	-3.20	-6.43	-1.51
di-F-Naph-NO_2										
	F and F	74.00	94.85	96.62	96.25	89.88	99.73	96.45	93.71	85.46
	FC	51.39	70.06	71.56	75.56	87.92	86.86	91.03	92.74	73.78
	PSO	15.54	18.45	18.59	16.74	4.77	10.15	6.72	5.66	10.65
	SD	5.98	5.25	5.37	2.87	-3.90	1.64	-2.39	-5.79	-0.06
acenaphtene										
	F and F	20.23	31.18	32.87	34.18	25.47	34.19	30.67	27.53	25.36
	FC	11.71	21.13	22.81	26.29	27.66	29.78	30.61	30.99	22.10
	PSO	7.76	9.13	9.22	8.26	3.86	5.79	4.71	4.27	6.33
	SD	-0.07	0.06	-0.02	-1.21	-6.90	-2.24	-5.49	-8.61	-3.90
acenaphthylene										
	F and F	45.72	53.77	55.12	52.96	40.30	50.78	44.70	41.20	42.99
	FC	8.40	16.35	17.93	20.14	22.73	24.29	24.92	25.41	17.56
	PSO	27.29	28.84	28.72	25.76	17.17	21.45	18.42	16.97	21.43
	SD	9.21	7.73	7.63	6.22	-0.36	4.24	0.58	-2.01	3.22
selen-Naph										
	F and Se	276.73	301.17	304.70	322.62	320.00	319.97	331.74	329.11	293.17
	FC	271.78	294.97	298.43	317.13	317.91	315.30	328.22	326.91	289.89
	PSO	9.70	10.27	10.34	9.74	8.99	9.62	9.69	9.43	9.01
	SD	-4.97	-4.29	-4.29	-4.47	-7.12	-5.17	-6.39	-7.45	-5.95
	C and F	15.26	17.62	17.20	19.64	20.72	20.40	20.93	21.32	18.80
	FC	13.76	16.19	15.75	18.36	19.76	19.19	19.86	20.29	17.66
	PSO	0.60	0.63	0.63	0.60	0.38	0.50	0.40	0.38	0.48
	SD	1.40	1.30	1.32	1.18	1.07	1.20	1.16	1.14	1.16

table 5 continued

	Coupling	KT2	PBE	BP86	B97-D	BHandH	B3LYP	CAM-B3LYP	CAM-B3LYPx	PBE0
		Coupling constants averaged over a few nuclei								
flubenzimine										
J = (a+2b)/3										
	F1 and N5	-0.48	-0.55	-0.55	-0.48	-0.11	-0.34	-0.35	-0.31	-0.22
	FC	-0.41	-0.53	-0.53	-0.46	-0.08	-0.33	-0.33	-0.27	-0.22
	PSO	-0.02	-0.01	-0.01	-0.01	0.01	0.00	0.01	0.01	0.01
	SD	-0.09	-0.06	-0.06	-0.06	-0.09	-0.07	-0.08	-0.09	-0.07
	F1b and N5	-8.60	-9.47	-9.59	-10.89	-10.65	-10.51	-10.65	-10.59	-9.24
	FC	-9.46	-10.25	-10.37	-11.65	-11.59	-11.37	-11.51	-11.46	-10.13
	PSO	0.72	0.70	0.70	0.68	0.88	0.79	0.81	0.81	0.80
	SD	0.36	0.31	0.31	0.31	0.29	0.30	0.28	0.29	0.32
azobenzene										
J = (a+b)/2										
	F′ and F1	-0.33	2.28	3.82	4.56	2.84	5.05	4.93	5.43	2.28
	FC	1.48	4.08	5.64	5.77	4.08	6.53	6.34	6.73	3.68
	PSO	-2.88	-2.95	-2.89	-2.65	-2.38	-2.64	-2.58	-2.44	-2.48
	SD	0.07	0.14	0.06	0.43	0.13	0.15	0.16	0.14	0.08
	F′ and F2	5.04	5.27	5.19	4.36	5.54	5.18	5.17	5.17	5.13
	FC	0.74	1.18	1.07	0.57	2.17	1.60	1.65	1.83	1.78
	PSO	3.11	2.98	3.02	2.66	2.57	2.66	2.61	2.49	2.54
	SD	1.48	1.41	1.39	1.42	1.10	1.22	1.20	1.15	1.11
phosphine-Ph										
J = (a+b+c)/3										
	F1p and F1c	0.79	1.00	0.96	0.78	0.35	0.65	0.63	0.55	0.58
	FC	1.02	1.27	1.22	1.01	0.44	0.83	0.77	0.67	0.73
	PSO	0.67	0.67	0.68	0.70	0.81	0.75	0.78	0.80	0.76
	SD	0.04	0.00	0.00	0.02	0.04	0.02	0.02	0.03	0.03
	F1p and F2c	4.96	5.55	5.35	5.38	6.63	5.87	5.80	5.76	5.60
	FC	6.65	7.16	6.92	6.94	8.04	7.24	7.06	7.05	7.04
	PSO	-0.16	-0.31	-0.30	-0.22	0.23	0.11	0.33	0.33	0.02
	SD	-1.57	-1.34	-1.31	-1.39	-1.67	-1.52	-1.63	-1.66	-1.49
	F1p and F3c	14.09	16.94	16.44	15.42	19.16	17.26	17.26	17.42	17.12
	FC	6.02	8.81	8.39	8.40	13.85	11.09	12.00	12.68	10.92
	PSO	10.25	10.23	10.13	9.12	7.42	8.25	7.38	6.87	8.27
	SD	-1.26	-1.20	-1.17	-1.19	-1.20	-1.17	-1.21	-1.22	-1.16
J = (a+2b)/3										
	F1c and P	7.15	7.84	7.80	7.53	3.24	5.79	5.62	5.01	4.62
	FC	7.21	8.02	7.97	7.67	3.31	5.90	5.70	5.08	4.73
	PSO	0.18	0.14	0.14	0.16	0.19	0.18	0.21	0.20	0.18
	SD	0.05	-0.03	-0.03	0.00	0.02	-0.01	0.00	0.01	0.00
	F2c and P	95.49	103.33	106.68	127.82	116.70	114.87	113.69	113.34	100.88
	FC	96.94	104.70	108.03	129.40	118.08	116.21	115.03	114.72	102.25
	PSO	-0.90	-0.87	-0.88	-0.87	-0.61	-0.74	-0.65	-0.63	-0.72
	SD	-1.09	-1.02	-1.01	-1.24	-1.30	-1.13	-1.22	-1.28	-1.19

References

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