Supporting Material: Improving the calculation of Electron Paramagnetic Resonance hyperfine coupling tensors for d-block metals†

Erik Donovan Hedegård,[a,b] **Jacob Kongsted,**[a] **and Stephan P. A. Sauer***[b]

[a] *University of Southern Denmark, Institute for Physics, Chemistry and Pharmacy, Campusvej 55, Odense, Denmark. Fax: +45 66158780; Tel: +45 65503520; E-mail: edh@ifk.sdu.dk*
[b] *University of Copenhagen, Department of Chemistry, Universitetsparken 5, Copenhagen, Denmark. E-mail: sauer@kiku.dk; http://sites.google.com/site/spasauer*

Table 1 Contraction schemes for the used basis sets

Row.	aug-cc-pVTZ-Juc	aug-cc-pVTZ-J	aug-cc-pCVTZ	aug-cc-pVTZ	CP(PPP)	IGLOIII
H	Uncontracted	(13s3p1d)/	-	(6s3p2d)/	-	(6s2p)/
	aug-cc-pVTZ-J	[6s3p1d]	-	[4s3p2d]	-	[4s2p]
B-F	Uncontracted	(21s8p3d1f)/	(13s8p4d2f)/	(11s6p3d2f)/	-	(11s7p2d)/
	aug-cc-pVTZ-J	[9s5p3d1f]	[7s6p4d2f]	[5s4p3d2f]	-	[7s6p2d]
Al-Cl	Uncontracted	(25s12p6d1f)/	(18s12p5d3f)/	(16s10p3d2f)/	-	-
	aug-cc-pVTZ-J	[10s7p6d1f]	[8s7p5d3f]	[6s5p3d2f]	-	-
Sc-Zn	Uncontracted	(25s17p10d3f2g)/	(21s17p9d4f3g)/	(21s17p9d3f2g)/	(17s11p5d1f)/	-
	aug-cc-pVTZ-J	[17s10p7d3f2g]	[10s9p7d4f3g]	[8s7p5d3f2g]	[17s7p3d1f]	-

Table 2 Number of primitives and contracted functions in each of the used basis set combinations

Molecule	Basis	aug-cc-pVTZ-Juc	aug-cc-pVTZ-J	aug-cc-pCVTZ	aug-cc-pVTZ	CP(PPP)	CP(PPP)/J
MnO	Primitive	230	287	614	567	124	149
	Contracted	230	167	186	139	95	106
ZnF	Primitive	230	287	xxx	567	xxx	xxx
	Contracted	230	167	xxx	139	xxx	xxx
TiF_3	Primitive	356	421	699	??	208	283
	Contracted	356	259	231	??	165	198
$[Cr(CO)_4]^+$	Primitive	664	756	1167	1029	418	752
	Contracted	664	489	599	461	148	520
$Mn(CO)_5$	Primitive	788	890	1325	1161	502	752
	Contracted	788	581	717	553	410	520
$[Fe(CO)_5]^+$	Primitive	788	890	1325	1161	502	752
	Contracted	788	581	717	553	410	520
$Ni(H)(CO)_3$	Primitive	567	649	1032	922	346	511
	Contracted	567	417	504	392	124	356
$Cu(CO)_3$	Primitive	540	622	1009	897	334	484
	Contracted	540	397	481	369	270	336
$[V(H_2O)_6]^{2+}$	Primitive	624	706	1093	981	418	568
	Contracted	600	457	541	429	330	396
$[Mn(H_2O)_6]^{2+}$	Primitive	624	706	1093	981	418	568
	Contracted	600	457	541	429	330	396
$[Cr(NO)(H_2O)_5]^{2+}$	Primitive	672	759	1158	1033	446	621
	Contracted	652	493	590	465	355	432
$[Cr(NS)(H_2O)_5]^{2+}$	Primitive	689	828	xxx	1089	340	690
	Contracted	669	515	xxx	469	234	454
$Cu(acac)_2$	Primitive	944	1016	1379	1293	778	878
	Contracted	716	605	663	577	500	544
$[Cu(en)_2]^{2+}$	Primitive	700	772	1135	1049	534	634
	Contracted	588	477	535	449	372	416
$[Cu(NH_3)_4]^{2+}$	Primitive	500	572	935	849	334	434
	Contracted	476	365	423	337	260	304
$V(O)(acac)_2$	Primitive	1006	1083	1458	1359	820	945
	Contracted	778	651	722	623	535	590
$Cr(N)(acac)_2$	Primitive	1006	1083	1458	1359	820	945
	Contracted	778	651	722	623	535	590
$[Mn(N)(CN)_4]^-$	Primitive	726	823	1246	1095	460	685
	Contracted	726	535	658	507	375	474
$Fe(NO)(Me_2dtc)_2$	Primitive	792	1098	1481	1321	570	960
	Contracted	704	597	657	497	418	536
$V(S_2C_2H_2)_3$	Primitive	942	1336	1717	1533	688	1198
	Contracted	810	697	745	561	492	636
$[Ni(mnt)_2]^-$	Primitive	1000	1280	1639	1505	802	1142
	Contracted	760	669	703	569	512	608
$Cu(Me_2dtc)_2$	Primitive	912	1192	1551	1417	714	1054
	Contracted	728	637	671	537	480	576

Table 3 Mean absolute deviation (MAD), maximum deviation and fit parameters for each of the used functionals and basis sets for A^{SD} (in MHz)

	aug-cc-pVTZ			aug-cc-pCVTZ			aug-cc-pVTZ-J			CP(PPP)		
	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}	A_{11}^{SD}	A_{22}^{SD}	A_{33}^{SD}
BP86												
MAD	14.49	13.67	25.74	13.03	12.83	23.52	12.96	12.68	23.32	12.42	12.16	22.02
Max	70.15	74.89	145.16	67.68	63.03	130.82	68.21	63.52	131.84	61.04	56.47	117.61
slope	1.0944	1.1486	1.2689	1.0709	1.0967	1.1275	1.0782	1.1021	1.1567	1.0540	1.0722	1.1042
R^2	0.9479	0.9671	0.9414	0.9507	0.9652	0.9651	0.9661	0.9664	0.9596	0.9536	0.9672	0.9688
BLYP												
MAD	14.27	13.98	26.37	12.68	12.81	23.46	12.70	12.54	23.26	12.26	11.99	21.82
Max	77.07	72.43	149.62	69.88	65.32	135.31	70.32	65.73	136.17	62.85	58.39	121.35
slope	1.12505	1.14616	1.5294	1.0874	1.1119	1.1391	1.0952	1.1154	1.1567	1.0669	1.0828	1.1123
R^2	0.95429	0.96599	0.8569	0.9553	0.9670	0.9674	0.9575	0.9682	0.9596	0.9574	0.9688	0.9695
B3LYP												
MAD	22.45	23.16	43.77	20.76	21.32	40.63	20.66	21.11	40.28	19.97	20.23	38.28
Max	123.05	126.76	249.93	117.01	113.37	230.49	117.29	113.56	230.96	108.22	104.61	212.95
slope	1.23266	1.29797	1.1650	1.1971	1.2463	1.2781	1.2025	1.2506	1.2260	1.1690	1.2126	1.2455
R^2	0.91974	0.9346	0.9647	0.9205	0.9386	0.9378	0.9223	0.9398	0.9449	0.9237	0.9415	0.9412
PBE												
MAD	13.94	14.44	26.12	13.23	13.02	23.91	13.16	12.88	23.71	12.97	12.11	22.37
Max	70.11	74.96	145.18	67.87	63.10	131.08	68.37	63.57	132.05	61.11	56.47	117.69
slope	1.10355	1.14118	1.1763	1.0731	1.0988	1.1297	1.0796	1.1038	1.4741	1.0537	1.0733	1.2455(!)
R^2	0.95194	0.96114	0.9660	0.9502	0.9645	0.9655	0.9522	0.9656	0.8678	0.9528	0.9665	0.9680
PBE0												
MAD	26.21	25.81	50.19	24.63	23.71	46.61	24.46	23.55	46.24	23.04	23.29	44.14
Max	137.81	134.19	272.11	127.24	123.70	251.05	127.52	123.89	251.52	118.66	115.14	233.91
slope	1.25707	1.31766	1.3241	1.2166	1.2673	1.3080	1.2205	1.2717	1.1329	1.1838	1.2392	1.1052
R^2	0.89483	0.92242	0.9355	0.8976	0.9252	0.9232	0.8995	0.9267	0.9670	0.9033	0.9266	0.9273
TPSS												
MAD	16.25	16.04	29.84	14.96	14.77	27.35	15.48	15.23	28.22	14.30	13.92	25.47
Max	84.38	79.45	163.94	76.35	71.47	147.93	76.40	71.48	147.99	68.86	64.13	133.10
slope	1.12685	1.16014	1.1667	1.0857	1.1198	1.1516	1.094	1.1222	1.2825	1.0671	1.0943	1.2759
R^2	0.93835	0.95603	0.9641	0.9394	0.9571	0.9579	0.9413	0.9602	0.9389	0.9439	0.9605	0.9620
TPSSh												
MAD	20.42	20.63	38.91	18.89	19.05	35.86	18.73	18.80	35.39	18.08	18.02	33.61
Max	108.95	104.60	213.66	99.53	95.22	194.86	99.53	95.14	194.79	91.22	87.01	178.35
slope	1.18475	1.23247	1.3558	1.1401	1.1884	1.2221	1.1494	1.1888	1.1346	1.1188	1.1593	1.1278
R^2	0.91956	0.94101	0.9203	0.9216	0.9426	0.9430	0.9227	0.9464	0.9663	0.9267	0.9468	0.9479
B2PLYP												
MAD	40.29	39.47	77.16	35.37	34.54	67.26	36.79	35.90	70.01	35.93	34.85	67.26
Max	187.26	184.60	371.97	172.73	170.21	343.05	172.57	169.97	342.65	164.63	162.06	326.80
slope	1.36843	1.47709	1.19474	1.3429	1.4439	1.4971	1.3252	1.4220	1.3116	1.2834	1.3794	1.1944
R^2	0.80600	0.85554	0.95671	0.8365	0.8888	0.8900	0.8187	0.8673	0.9244	0.8147	0.8694	0.8708