Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION

Electron correlation and vibrational effects in predictions of paramagnetic NMR shifts

Aleksander Jaworski,* Niklas Hedin

Department of Materials and Environmental Chemistry,
Stockholm University, SE-106 91 Stockholm, Sweden

*Corresponding author: *aleksander.jaworski@mmk.su.se*

Contents

Table S1 Convergence of ^{14}N hyperfine (A_{con}) and quadrupole (χ) coupling constants (MHz) for cyanomethyl radical at the DLPNO-CCSD(HFC1)/aug-cc-pVTZ-J level of theory with respect to the completeness of auxiliary basis sets; molecular geometry optimized at the CCSD(T)/aug-cc-pCVTZ level of theory

AuxJ basis set	AuxC basis set	A_{con}	χ
AutoAux	aug-cc-pCVDZ/C	9.32	−4.28
AutoAux	aug-cc-pCVTZ/C	9.20	−4.28
AutoAux	aug-cc-pCVQZ/C	9.17	−4.28
AutoAux	aug-cc-pCV5Z/C	9.17	−4.28
AutoAux	AutoAux	9.17	−4.28
def2/J	AutoAux	9.17	−4.29
SARC/J	AutoAux	9.17	−4.28

Table S2 ^{1}H and ^{13}C NMR shieldings for the eclipsed conformer of Cp_2Fe (ferrocene); molecular geometry optimized at the PBE0-D4/cc-pVTZ level of theory

		CH_4				Cp_2Fe					
		^{1}H		^{13}C		^{1}H			^{13}C		
Method	Basis set	σ_{orb}	$\sigma_{orb,\,zpv}$[a]	σ_{orb}	$\sigma_{orb,\,zpv}$[a]	σ_{orb}	$\sigma_{orb,\,zpv}$[a]	δ	σ_{orb}	$\sigma_{orb,\,zpv}$[a]	δ
PBE	pcSseg-1	31.37	−0.61	189.34	−3.47	27.49	−0.51	5.94	104.12	−3.53	76.63
PBE0	pcSseg-1	31.33	−0.61	190.92	−3.47	27.82	−0.51	5.57	114.38	−3.53	67.95
PBE0	pcSseg-2	31.25	−0.61	191.82	−3.47	27.73	−0.51	5.59	111.65	−3.53	71.58
PBE0	pcSseg-3	31.30	−0.61	191.48	−3.47	27.67	−0.51	5.69	111.14	−3.53	71.75
PBE0	pcSseg-4	31.30	−0.61	191.44	−3.47	27.67	−0.51	5.69	111.12	−3.53	71.73
DSD-PBEP86	pcSseg-2	31.28	−0.61	197.02	−3.47	24.40	−0.51	8.95	60.63	−3.53	127.80
HF	pcSseg-2	31.46	−0.61	194.45	−3.47	33.33	−0.51	0.20	216.24	−3.53	−30.38
MP2	pcSseg-2	31.24	−0.61	200.61	−3.47	−9.20	−0.51	42.51	−566.51	−3.53	758.53
SCS-MP2	pcSseg-2	31.32	−0.61	198.73	−3.47	−5.77	−0.51	39.15	−500.32	−3.53	690.46
Experiment								~4.2			~68

[a]vibrational corrections to orbital shielding calculated at the VPT2 PBE0-D4/cc-pVTZ//PBE0/pcSseg-2 level

Table S3 Cyanomethyl radical

N	-1.983162	0.208926	0.000000
C	-0.811141	0.246261	0.000000
C	0.579652	0.290493	0.000000
H	1.085689	1.243113	0.000000
H	1.145183	-0.628055	0.000000

Table S4 $[V(H_2O)_6]^{2+}$

V	-0.653134	0.377780	0.049941
O	-1.687545	2.256213	0.010824
O	-0.486197	0.511879	2.183767
O	-2.531829	-0.637011	0.267518
O	0.381064	-1.500691	0.089163
O	1.225288	1.392973	-0.167703
O	-0.820526	0.244162	-2.083927
H	-1.292634	3.129395	-0.077086
H	-0.063481	-0.126958	2.766314
H	-3.093176	-0.966484	-0.441315
H	1.332166	-1.629290	0.017993
H	1.657598	1.620935	-0.996750
H	-0.498550	-0.471460	-2.641028
H	-1.243378	0.883815	-2.665480
H	-2.638708	2.384409	0.081920
H	1.786811	1.722164	0.541122
H	-0.014191	-2.373716	0.177066
H	-0.808558	1.228146	2.739818
H	-2.963937	-0.865355	1.096567

Table S5: $[Cr(H_2O)_6]^{3+}$

Cr	-0.653312	0.377942	0.049934
O	-1.613789	2.126362	0.015216
O	-0.492470	0.504635	2.034655
O	-2.400458	-0.567205	0.251994
O	0.307162	-1.370480	0.084636
O	1.093836	1.323082	-0.152121
O	-0.814143	0.251258	-1.934789
H	-1.206681	3.003392	-0.074308
H	-0.067504	-0.145910	2.616990
H	-2.960810	-0.895344	-0.469971
H	1.267690	-1.494814	0.014753
H	1.527412	1.549878	-0.990869
H	-0.482634	-0.472720	-2.490597
H	-1.239117	0.901801	-2.517119
H	-2.574316	2.250699	0.085104
H	1.654182	1.651226	0.569846
H	-0.099943	-2.247511	0.174164
H	-0.823987	1.228611	2.590462
H	-2.834035	-0.793996	1.090743

Table S6: $[Mn(H_2O)_8]^{2+}$

Mn	-0.653313	0.377935	0.049911
O	-1.712055	2.297903	0.011787
O	-0.478747	0.517617	2.230640
O	-2.576888	-0.657777	0.270998
O	0.405554	-1.541972	0.088239
O	1.270227	1.413728	-0.171243
O	-0.827998	0.238152	-2.130791
H	-1.321377	3.173383	-0.077477
H	-0.059116	-0.120993	2.816431
H	-3.138902	-0.987867	-0.437652
H	1.357007	-1.672296	0.018649
H	1.707918	1.643451	-0.997507
H	-0.503858	-0.475222	-2.690339
H	-1.247613	0.876772	-2.716584
H	-2.663502	2.428287	0.081341
H	1.832256	1.743800	0.537404
H	0.014935	-2.417482	0.177474
H	-0.802874	1.231002	2.790179
H	-3.014570	-0.887515	1.097263

Table S7: $[Yb(H_2O)_8]^{3+}$

Yb	-0.571261	0.221571	0.032463
O	0.650891	1.731933	1.351865
O	-1.120287	2.383058	-0.727768
O	-2.903436	0.430646	0.219776
O	-1.289718	-2.032082	-0.050452
O	1.241543	-1.110295	0.758934
O	1.254456	0.763827	-1.370936
O	-1.118454	-0.240104	2.275320
O	-1.283052	-0.167693	-2.188912
H	0.508103	1.924188	2.289300
H	-1.563885	2.617653	-1.555198
H	-3.549437	-0.275591	0.361478
H	-1.497259	-2.604700	0.701103
H	2.060174	-0.825763	1.188746
H	1.331997	1.532220	-1.953576
H	-0.965078	3.217843	-0.263836
H	1.398100	2.282907	1.079369
H	-0.554795	-0.659654	2.940588
H	-2.184710	-0.324378	-2.502540
H	-1.948346	-0.028234	2.725468
H	2.074611	0.262828	-1.481999
H	1.326688	-2.064869	0.626578
H	-1.443500	-2.565868	-0.842588
H	-3.414162	1.250709	0.166306
H	-0.711527	-0.251734	-2.964993

Table S8: Eclipsed Cp_2V

V	0.000000	0.000000	0.000000
C	-0.742794	-0.942403	1.931032
C	-1.124140	0.419878	1.930815
C	0.670633	-1.000721	1.927834
C	1.162913	0.325525	1.925699
C	0.053658	1.203557	1.927509
H	2.202379	0.616467	1.922736
H	0.098252	2.282058	1.926543
H	-2.136087	0.795510	1.933059
H	-1.412787	-1.788712	1.933167
H	1.268524	-1.899431	1.926857
C	-0.744023	-0.941375	-1.931059
C	-1.123451	0.421442	-1.930874
C	0.669321	-1.001683	-1.927791
C	1.163466	0.323870	-1.925647

C	0.055449	1.203462	-1.927521
H	2.203341	0.613348	-1.922635
H	0.101562	2.281899	-1.926564
H	-1.415206	-1.786740	-1.933218
H	-2.134867	0.798497	-1.933175
H	1.265946	-1.901234	-1.926778

Table S9: Stagerred Cp_2V

V	0.000000	0.000000	0.000000
C	-0.400221	-1.134789	1.929645
C	-1.203540	0.029619	1.929208
C	0.955383	-0.730619	1.930229
C	0.989955	0.683495	1.930105
C	-0.344306	1.153420	1.929483
H	1.878511	1.296414	1.929193
H	-0.652587	2.187901	1.928106
H	-2.282654	0.056049	1.927739
H	-0.758772	-2.152934	1.928593
H	1.812852	-1.386317	1.929478
C	-1.013598	-0.648093	-1.929999
C	-0.929454	0.763940	-1.929876
C	0.303375	-1.164522	-1.929725
C	1.201485	-0.071542	-1.929395
C	0.439478	1.120313	-1.929452
H	2.279007	-0.135768	-1.928194
H	0.833460	2.125278	-1.928292
H	-1.923101	-1.229484	-1.929074
H	-1.763439	1.449256	-1.928763
H	0.575227	-2.209168	-1.928662

Table S10: CoSOD model E

Co	0.000000	0.000000	0.000000
C	-1.304370	-3.831830	-0.760260
C	-0.955630	-2.368510	-0.905200
O	-0.011660	-1.932930	-0.153390
O	-1.579070	-1.630820	-1.686810
N	1.125440	0.367760	1.668030
N	-1.899570	0.333790	0.683950
N	0.815640	1.030240	-1.554570
H	5.053450	1.183760	1.372220
C	4.885730	0.137480	1.075900
H	5.532970	-0.083940	0.216000
C	3.423740	-0.112250	0.730910
C	2.486750	0.202300	1.849000
C	2.763150	0.374020	3.183460
C	0.604030	0.632220	2.859320
N	1.563520	0.639980	3.791580
H	5.216070	-0.505640	1.906970
H	3.132590	0.490890	-0.144630
H	3.276750	-1.166100	0.432890
H	3.694340	0.324530	3.740260
H	-0.444430	0.827800	3.071350
H	1.422760	0.815820	4.780660
H	-3.020050	2.280140	-2.969800
C	-3.128270	1.507480	-2.192100
C	-4.512530	0.991990	-2.242810
O	-5.494250	1.715520	-2.135960
C	-2.824610	2.147410	-0.826930
C	-2.927730	1.167680	0.291930
C	-4.044850	0.839580	1.021920
C	-2.387780	-0.476490	1.615490
N	-3.677260	-0.192800	1.842330
H	-2.392490	0.717360	-2.400120
H	-1.821330	2.597350	-0.839340
H	-3.541150	2.963100	-0.653080
H	-5.051620	1.247630	1.004290
H	-1.842270	-1.269270	2.124930
H	-4.274310	-0.666820	2.511700
N	-4.560590	-0.338450	-2.403790
C	-5.821270	-0.974520	-2.470100
H	-5.833300	-1.754260	-3.246900
H	-3.703450	-0.879320	-2.315120
H	-6.109230	-1.446030	-1.513590
H	-6.577930	-0.218680	-2.711920
H	-2.925180	-1.741380	-6.336320
C	-2.487270	-1.849510	-5.337100
C	-0.987700	-1.713690	-5.436840
O	-0.367820	-2.017960	-6.444060
H	-2.712700	-2.860340	-4.962910
H	-2.933490	-1.120000	-4.647140
N	-0.342320	-1.262760	-4.319640
C	1.076730	-1.486510	-4.248100
C	1.332540	-3.008850	-4.120610
O	0.530010	-3.719080	-3.529980
C	1.677370	-0.891340	-2.957140
C	1.454610	0.561150	-2.691330

C	1.907140	1.647860	-3.399310
C	0.893880	2.353950	-1.581060
N	1.540040	2.754260	-2.682440
H	-0.846890	-1.321170	-3.429200
H	1.564750	-1.082710	-5.146550
H	1.287300	-1.459720	-2.098470
H	2.763070	-1.079130	-2.982440
H	2.462020	1.717260	-4.330710
H	0.514250	3.035980	-0.822860
H	1.730690	3.718880	-2.933090
N	2.511670	-3.495210	-4.565260
C	2.771730	-4.919510	-4.529100
C	2.958570	-5.537290	-3.139290
O	2.867200	-6.743370	-3.004110
H	3.683210	-5.125170	-5.107250
H	3.098410	-2.909130	-5.147490
H	1.946880	-5.482470	-4.990050
N	3.234310	-4.692600	-2.112850
C	3.336730	-5.132510	-0.739100
C	2.076760	-4.962920	0.093880
O	2.132080	-5.044160	1.312840
H	3.311920	-3.704960	-2.322440
H	3.577510	-6.206970	-0.747080
H	4.155310	-4.613750	-0.220750
N	0.942080	-4.772380	-0.597080
C	-0.327270	-4.651510	0.067900
H	-0.762570	-5.649570	0.253330
H	0.970520	-4.682270	-1.610390
H	-0.153860	-4.186030	1.048250
H	-1.419840	-4.243340	-1.775020
H	-2.306620	-3.872750	-0.302520

Table S11: CoSOD model F

Co	0.000000	0.000000	0.000000
C	3.774690	0.418420	-1.592570
C	2.337650	0.053930	-1.326440
O	1.690160	0.807250	-0.524860
O	1.814800	-0.947720	-1.853390
N	-0.531380	1.168860	1.587880
N	0.649900	-1.721180	0.899820
N	-1.477750	-0.073430	-1.398870
H	-3.323090	3.851800	0.997570
C	-2.414260	4.269790	0.540730
H	-2.689970	4.745170	-0.411180
C	-1.360680	3.190130	0.319130
C	-0.959110	2.483250	1.571360
C	-0.924380	2.957930	2.859990
C	-0.247980	0.865980	2.848700
N	-0.471820	1.923430	3.636910
H	-2.036860	5.064470	1.203360
H	-1.732480	2.437290	-0.394050
H	-0.458750	3.628190	-0.145090
H	-1.172140	3.928790	3.279340
H	0.103850	-0.095440	3.215380
H	-0.333230	1.949150	4.641480
H	-1.282830	-4.107030	-2.081370
C	-0.450260	-3.656210	-1.523270
C	0.761190	-4.549690	-1.675630
O	0.676750	-5.759520	-1.508110
C	-0.829280	-3.562810	-0.034280
C	0.282850	-3.050350	0.817340
C	1.184180	-3.786960	1.547650
C	1.744390	-1.664980	1.649340
N	2.087610	-2.893880	2.057120
H	-0.256870	-2.652180	-1.930880
H	-1.722490	-2.933470	0.088780
H	-1.099090	-4.567300	0.321860
H	1.255250	-4.856970	1.722210
H	2.305310	-0.765220	1.898300
H	2.884650	-3.117530	2.643690
N	1.917840	-3.908310	-1.949820
C	3.170740	-4.610210	-2.043270
H	3.718680	-4.317440	-2.951790
H	1.926190	-2.886630	-1.951530
H	3.815720	-4.411480	-1.170510
H	2.959750	-5.686180	-2.080160
H	1.832340	-3.267650	-6.142120
C	1.958740	-2.549210	-5.323270
C	1.141620	-1.320990	-5.604870
O	0.860420	-0.944220	-6.732100
H	3.020830	-2.259660	-5.282130
H	1.696050	-3.019170	-4.365720
N	0.746530	-0.632820	-4.500790
C	0.202740	0.673790	-4.657270
C	1.340120	1.712870	-4.944520
O	2.474180	1.507200	-4.538000
C	-0.416830	1.172970	-3.332650

C	-1.494010	0.338680	-2.722050
C	-2.694940	-0.043040	-3.267650
C	-2.640640	-0.666040	-1.161380
N	-3.389700	-0.670210	-2.269480
H	1.185090	-0.844870	-3.600090
H	-0.530620	0.676850	-5.477390
H	0.388990	1.294100	-2.592920
H	-0.820370	2.183250	-3.509440
H	-3.105190	0.092430	-4.264370
H	-2.966990	-1.081910	-0.210360
H	-4.320890	-1.065590	-2.346610
N	0.988660	2.895080	-5.514560
C	1.958740	3.946790	-5.815270
C	2.604340	4.609880	-4.615330
O	3.653790	5.214770	-4.734420
H	1.450270	4.723590	-6.402750
H	0.068670	2.971240	-5.932470
H	2.784880	3.554110	-6.427200
N	1.928300	4.497030	-3.450310
C	2.442740	5.018790	-2.222270
C	3.089180	3.991260	-1.289030
O	3.247560	4.263180	-0.107870
H	1.051240	3.991840	-3.455210
H	3.219230	5.758990	-2.470060
H	1.663990	5.534640	-1.642920
N	3.490730	2.836440	-1.855580
C	4.164740	1.800790	-1.103270
H	5.259810	1.917850	-1.186380
H	3.318210	2.673970	-2.845570
H	3.897660	1.938300	-0.047130
H	3.952780	0.301350	-2.672830
H	4.397640	-0.345020	-1.096930

Table S12: CH_4

C	-0.009688	0.019687	-0.015115
H	1.046244	0.257503	-0.134597
H	-0.501753	0.819463	0.536298
H	-0.111373	-0.915406	0.533597
H	-0.471889	-0.082788	-0.995776

Table S13: Eclipsed Cp_2Fe

Fe	0.006391	0.001200	0.000001
C	-0.742424	-0.945682	1.649043
C	-1.124967	0.421762	1.649275
C	0.676246	-1.004533	1.648103
C	1.170640	0.326575	1.647537
C	0.057400	1.208126	1.648416
H	2.209082	0.617023	1.623052
H	0.102118	2.285518	1.624812
H	-2.135854	0.797148	1.626593
H	-1.411949	-1.790981	1.626006
H	1.273357	-1.902428	1.624069
C	-0.743307	-0.944936	-1.649070
C	-1.124454	0.422899	-1.649337
C	0.675302	-1.005237	-1.648059
C	1.171056	0.325365	-1.647479
C	0.058717	1.208053	-1.648425
H	2.209792	0.614754	-1.622948
H	0.104536	2.285400	-1.624836
H	-1.413696	-1.789550	-1.626060
H	-2.134958	0.799316	-1.626715
H	1.271492	-1.903743	-1.623988