Supporting Information

for

Mean Value Ensemble Hubbard-U Correction for Spin-Crossover Molecules

Angel Albavera-Mata ,[†,‡] Richard G. Hennig ,[*,†,‡] and S.B. Trickey [*,†,¶]

†*Center for Molecular Magnetic Quantum Materials, Quantum Theory Project, University of Florida, Gainesville, Florida 32611*

‡*Department of Materials Science and Engineering, University of Florida, 1885 Stadium Road, Gainesville, Florida 32611*

¶*Department of Physics and Department of Chemistry, University of Florida, P.O. Box 118435, Gainesville, Florida 32611*

E-mail: rhennig@ufl.edu; trickey@ufl.edu

Table S1: Element and valence electrons, Z_{val}, of the projector augmented wave potentials.

Element	Z_{val}	Potential
H	1	PAW_PBE H 15Jun2001
B	3	PAW_PBE B 06Sep2000
C	4	PAW_PBE C 08Apr2002
N	5	PAW_PBE N 08Apr2002
O	6	PAW_PBE O 08Apr2002
F	7	PAW_PBE F 08Apr2002
P	5	PAW_PBE P 06Sep2000
S	6	PAW_PBE S 06Sep2000
Cl	7	PAW_PBE Cl 06Sep2000
Cr	14	PAW_PBE Cr_sv 23Jul2007
Mn	15	PAW_PBE Mn_sv 23Jul2007
Fe	16	PAW_PBE Fe_sv 23Jul2007
Co	17	PAW_PBE Co_sv 23Jul2007
Ni	16	PAW_PBE Ni_pv 06Sep2000
Br	7	PAW_PBE Br 06Sep2000
I	7	PAW_PBE I 08Apr2002

Table S2: Calculated $U_{eff} = U - J$, in units of eV, from linear response on the low- (LS), high- (HS) and mean value ensemble spin (MS) states for PBE.

Complex	Ion	LS	HS	MS
$[Cr(ddpd)_2][BF_4]_2$	Cr^{II}	5.83	5.73	1.45
$[Cr(Cp^{iPr_4})_2]$	Cr^{II}	5.18	4.92	1.30
$[Cr(I_2)(depe)_2]$	Cr^{II}	5.46	5.16	1.35
$[Cr(Ind^{Me-2})_2]$	Cr^{II}	5.19	5.11	1.30
$[Mn(L_1tren)]$	Mn^{III}	5.03	4.82	1.28
$[Mn(3,5\text{-diBr-sal}_2323)][BF_4]$	Mn^{III}	5.01	4.88	1.26
$[Mn(L_2)][PF_6]$	Mn^{III}	5.02	4.88	1.27
$[Mn(imSQ^{OMe})_2Cl]$	Mn^{III}	5.45	5.31	1.35
$[Mn(Cp^{1\text{-}Me})_2]$	Mn^{II}	4.41	3.96	1.12
$[Mn(Cp^{1\text{-}tBu})_2]$	Mn^{II}	4.41	3.58	1.13
$[Mn(Cp^{1,3\text{-}tBu})_2]$	Mn^{II}	4.54	3.90	1.14
$[Mn(L\text{-}N_3O_2)_2(CN)_2{\cdot}H_2O]$	Mn^{II}	5.33	6.43	1.42
$[Fe(acac)_2(trien)][PF_6]$	Fe^{III}	7.56	7.56	1.93
$[Fe(qsal\text{-}Br)_2][NO_3]$	Fe^{III}	7.75	7.67	2.01
$[Fe(3\text{-}OMe\text{-}salen)_2][PF_6]$	Fe^{III}	7.73	7.75	1.95
$[Fe(qsal\text{-}5\text{-}OMe)_2][BF_4]$	Fe^{III}	7.71	7.89	1.98
$[Fe(phen)_2(NCS)_2]$	Fe^{II}	7.88	8.21	2.03
$[Fe(stpy)_2(NCS)_2]$	Fe^{II}	7.98	8.47	2.06
$[Fe(bpp)_3][BF_4]_2$	Fe^{II}	7.52	7.64	1.92
$[Fe(H_2B(pz)_2)_2(bipy)]$	Fe^{II}	7.82	8.28	2.02
$[Fe(tzpy)_2(NCS)_2]$	Fe^{II}	7.87	8.32	2.04
$[Fe(tBu_2qsal)_2]$	Fe^{II}	8.08	8.01	2.04
$[Fe(L_3)_3][ClO_4]_2$	Fe^{II}	7.77	7.69	1.96
$[Co(NAd)(Tp^{tBu,Me})]$	Co^{III}	6.82	6.42	1.63
$[Co(^{Ar}L)(NtBu)]$	Co^{III}	6.54	6.18	1.57
$[Co(terpy)_2]$	Co^{II}	6.60	6.54	1.66
$[Co(H_2(fsa)_2en)(Py)_2]$	Co^{II}	6.49	6.27	1.59
$[Co(terpyrindone)_2][ClO_4]_2$	Co^{II}	6.61	6.28	1.62
$[Co(papl)_2]$	Co^{II}	6.60	6.82	1.66
$[Co(MeO\text{-}terpy)_2][BF_4]_2$	Co^{II}	6.60	6.25	1.60
$[Co(PM\text{-}BiA)_2][NCS]_2$	Co^{II}	6.56	7.01	1.74
$[Ni(\alpha\text{-}phpyNO)_2Br_2]$	Ni^{II}	7.15	6.44	1.64
$[Ni(phpyNO)_2Cl_2]$	Ni^{II}	6.84	6.41	1.67
$[Ni(\beta\text{-}phpyNO)_2Br_2]$	Ni^{II}	6.96	6.31	1.67

ddpd = N,N′-dimethyl-N,N′-dipyridine-2-yl-pyridine-2,6-diamine, Cp^{iPr_4} = tetraisopropylcyclopentadienide, depe = 1,2-bis(diethylphosphino)ethane, Ind^{Me-2} = bis(2-methylindenyl), L_1tren = tris(2-((pyrrol-2yl)methyleneamino)ethyl)amine, 3,5-diBr-sal$_2$323 = 2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)bis(4,6-dibromophenolato), L_2 = (2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)diphenol), $imSQ^{OMe}$ = 4,6-di-*tert*-butyl-N-(2-methoxyphenyl)-o-aminophenol, $Cp^{1\text{-}Me}$ = methylcyclopentadiene, $Cp^{1\text{-}tBu}$ = *tert*-butylcyclopentadienyl, $Cp^{1,3\text{-}tBu}$ = *tert*-butylcyclopenta-1,3-diene, L-N_3O_2 = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene, acac = acetylacetonate, trien = triethylenetetramine, qsal-Br = (N-8-quino-lyl)-5-Br-salicylaldiminate, 3-OMe-salen = (2-((((2-(ethylamino)ethyl)imino)methyl)-6-methoxyphenolato-N,N′,O), qsal-5-OMe = N-(8-quino-lyl)salicylaldiminate, phen = phenanthroline, stpy = 4-styrylpyridine, bpp = (2,6-di(pyrazol-1-yl)pyridine), $H_2B(pz)_2$ = dihydrogen bis(pyrazol-1-yl)borate, bipy = bipyridine, tzpy = (3-(2-pyridyl)(1,2,3)triazolo(1,5-a)pyridine), tBu_2qsal = 2,4-di(*tert*-butyl)-6-((quinoline-8-ylimino)methyl)phenol, L_3 = 1-acetic ethyl-2-(pyridine-2-yl)-imidazole, Ad = 1-adamantyl, $Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl,5-methyl-pyrazol-1-yl)borate, ^{Ar}L = 5-mesityl-1,9-(2,4,6-triphenylphenyl)dipyrrin, terpy = terpyridine, H_2(fsa)$_2$en = 3-formylsalicylic acid-ethylendiamine, papl = 1-(2-pyridylazo)-2-phenanthrol, MeO-terpy = 4′-methoxy-2,2′:6′,2″-terpyridine, PM-BiA = *cis*-bis(thiocyanato)bis(N-(2-pyridylmethylene)aminobiphenyl), α-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase α, phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide, β-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase β.

Table S3: Differences in HOMO-LUMO gap, $\Delta\varepsilon_{\mathrm{gap}}$, in units of eV, between results calculated with PBE+U_{eff} and results with PBE, $[\Delta\varepsilon_{\mathrm{gap}}(\mathrm{PBE}{+}U_{eff})] - [\Delta\varepsilon_{\mathrm{gap}}(\mathrm{PBE})]$, for the low-spin (LS) and high-spin (HS) states.

Complex	Ion	LS	HS
$[Cr(ddpd)_2][BF_4]_2$	Cr^{II}	0.09	0.34
$[Cr(Cp^{iPr_4})_2]$	Cr^{II}	0.35	0.35
$[Cr(I_2)(depe)_2]$	Cr^{II}	0.32	0.53
$[Cr(Ind^{Me-2})_2]$	Cr^{II}	0.13	0.51
$[Mn(L_1tren)]$	Mn^{III}	0.51	0.54
$[Mn(3,5\text{-diBr-sal}_2323)][BF_4]$	Mn^{III}	0.52	0.21
$[Mn(L_2)][PF_6]$	Mn^{III}	0.45	0.17
$[Mn(imSQ^{OMe})_2Cl]$	Mn^{III}	-0.11	0.10
$[Mn(Cp^{1\text{-}Me})_2]$	Mn^{II}	0.61	0.50
$[Mn(Cp^{1\text{-}t\mathrm{Bu}})_2]$	Mn^{II}	0.60	0.50
$[Mn(Cp^{1,3\text{-}t\mathrm{Bu}})_2]$	Mn^{II}	0.61	0.51
$[Mn(L\text{-}N_3O_2)_2(CN)_2{\cdot}H_2O]$	Mn^{II}	0.22	0.18
$[Fe(acac)_2(trien)][PF_6]$	Fe^{III}	0.88	0.70
$[Fe(qsal\text{-Br})_2][NO_3]$	Fe^{III}	0.41	0.22
$[Fe(3\text{-OMe-salen})_2][PF_6]$	Fe^{III}	0.65	0.30
$[Fe(qsal\text{-}5\text{-OMe})_2][BF_4]$	Fe^{III}	0.41	0.22
$[Fe(phen)_2(NCS)_2]$	Fe^{II}	-0.02	0.01
$[Fe(stpy)_2(NCS)_2]$	Fe^{II}	0.08	0.23
$[Fe(bpp)_3][BF_4]_2$	Fe^{II}	0.22	-0.11
$[Fe(H_2B(pz)_2)_2(bipy)]$	Fe^{II}	0.28	0.37
$[Fe(tzpy)_2(NCS)_2]$	Fe^{II}	0.08	0.14
$[Fe(t\mathrm{Bu}_2qsal)_2]$	Fe^{II}	0.12	0.12
$[Fe(L_3)_3][ClO_4]_2$	Fe^{II}	0.30	0.71
$[Co(NAd)(Tp^{t\mathrm{Bu,Me}})]$	Co^{III}	0.03	0.31
$[Co(^{\mathrm{Ar}}L)(Nt\mathrm{Bu})]$	Co^{III}	0.58	0.61
$[Co(terpy)_2]$	Co^{II}	-0.03	-0.01
$[Co(H_2(fsa)_2en)(Py)_2]$	Co^{II}	0.37	0.76
$[Co(terpyrindone)_2][ClO_4]_2$	Co^{II}	-0.32	0.19
$[Co(papl)_2]$	Co^{II}	-0.01	0.23
$[Co(MeO\text{-terpy})_2][BF_4]_2$	Co^{II}	0.08	0.47
$[Co(PM\text{-BiA})_2][NCS]_2$	Co^{II}	-0.01	0.04
$[Ni(\alpha\text{-phpyNO})_2Br_2]$	Ni^{II}	-0.14	0.10
$[Ni(phpyNO)_2Cl_2]$	Ni^{II}	0.00	0.15
$[Ni(\beta\text{-phpyNO})_2Br_2]$	Ni^{II}	-0.27	0.10

ddpd = N,N′-dimethyl-N,N′-dipyridine-2-yl-pyridine-2,6-diamine, Cp^{iPr_4} = tetraisopropylcyclopentadienide, depe = 1,2-bis(diethylphosphino)ethane, Ind^{Me-2} = bis(2-methylindenyl), L_1tren = tris(2-((pyrrol-2yl)methyleneamino)ethyl)amine, 3,5-diBr-sal_2323 = 2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)bis(4,6-dibromophenolato), L_2 = (2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)diphenol), $imSQ^{OMe}$ = 4,6-di-*tert*-butyl-N-(2-methoxyphenyl)-o-aminophenol, $Cp^{1\text{-Me}}$ = methylcyclopentadiene, $Cp^{1\text{-}t\mathrm{Bu}}$ = *tert*-butylcyclopentadienyl, $Cp^{1,3\text{-}t\mathrm{Bu}}$ = *tert*-butylcyclopenta-1,3-diene, L-N_3O_2 = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene, acac = acetylacetonate, trien = triethylenetetramine, qsal-Br = (N-8-quino-lyl)-5-Br-salicylaldiminate, 3-OMe-salen = (2-(((2-(ethylamino)ethyl)imino)methyl)-6-methoxyphenolato-N,N′,O), qsal-5-OMe = N-(8-quino-lyl)salicylaldiminate, phen = phenanthroline, stpy = 4-styrylpyridine, bpp = (2,6-di(pyrazol-1-yl)pyridine), $H_2B(pz)_2$ = dihydrogen bis(pyrazol-1-yl)borate, bipy = bipyridine, tzpy = (3-(2-pyridyl)(1,2,3)triazolo(1,5-a)pyridine), $t\mathrm{Bu}_2$qsal = 2,4-di(*tert*-butyl)-6-((quinoline-8-ylimino)methyl)phenol, L_3 = 1-acetic ethyl-2-(pyridine-2-yl)-imidazole, Ad = 1-adamantyl, $Tp^{t\mathrm{Bu,Me}}$ = hydrotris(3-*tert*-butyl,5-methyl-pyrazol-1-yl)borate, $^{\mathrm{Ar}}L$ = 5-mesityl-1,9-(2,4,6-triphenylphenyl)dipyrrin, terpy = terpyridine, $H_2(fsa)_2en$ = 3-formylsalicylic acid-ethylendiamine, papl = 1-(2-pyridylazo)-2-phenanthrol, MeO-terpy = 4′-methoxy-2,2′:6′,2″-terpyridine, PM-BiA = *cis*-bis(thiocyanato)bis(N-(2-pyridylmethylene)aminobiphenyl), α-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase α, phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide, β-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase β.

Table S4: Spin-crossover energies, ΔE_{HL}, in units of eV, calculated with the PBE and PBE+U_{eff} density functional approximations.

			PBE+U_{eff}		
Complex	Ion	PBE	LS	HS	MS
$[Cr(ddpd)_2][BF_4]_2$	Cr^{II}	0.46	-0.59	-0.58	0.25
$[Cr(Cp^{iPr_4})_2]$	Cr^{II}	0.68	-0.68	-0.61	0.34
$[Cr(I_2)(depe)_2]$	Cr^{II}	0.44	-0.70	-0.65	0.12
$[Cr(Ind^{Me-2})_2]$	Cr^{II}	0.16	-0.89	-0.87	-0.11
$[Mn(L_1tren)]$	Mn^{III}	0.50	-0.51	-0.47	0.20
$[Mn(3,5\text{-diBr-sal}_2323)][BF_4]$	Mn^{III}	0.50	-0.53	-0.51	0.20
$[Mn(L_2)][PF_6]$	Mn^{III}	0.53	-0.49	-0.47	0.25
$[Mn(imSQ^{OMe})_2Cl]$	Mn^{III}	0.55	0.26	0.26	0.43
$[Mn(Cp^{1\text{-}Me})_2]$	Mn^{II}	1.15	-0.91	-0.70	0.64
$[Mn(Cp^{1\text{-}t\mathrm{Bu}})_2]$	Mn^{II}	1.09	-0.96	-0.58	0.58
$[Mn(Cp^{1,3\text{-}t\mathrm{Bu}})_2]$	Mn^{II}	1.09	-1.03	-0.74	0.56
$[Mn(L\text{-}N_3O_2)_2(CN)_2\cdot H_2O]$	Mn^{II}	1.06	-1.41	-1.78	0.41
$[Fe(acac)_2(trien)][PF_6]$	Fe^{III}	0.48	-1.17	-1.17	0.06
$[Fe(qsal\text{-}Br)_2][NO_3]$	Fe^{III}	1.03	-1.20	-1.14	0.39
$[Fe(3\text{-}OMe\text{-}salen)_2][PF_6]$	Fe^{III}	0.99	-1.14	-1.14	0.37
$[Fe(qsal\text{-}5\text{-}OMe)_2][BF_4]$	Fe^{III}	0.95	-1.20	-1.24	0.32
$[Fe(phen)_2(NCS)_2]$	Fe^{II}	0.89	-1.38	-1.41	0.14
$[Fe(stpy)_2(NCS)_2]$	Fe^{II}	0.83	-1.38	-1.43	0.05
$[Fe(bpp)_3][BF_4]_2$	Fe^{II}	1.15	-1.27	-1.31	0.38
$[Fe(H_2B(pz)_2)_2(bipy)]$	Fe^{II}	0.70	-1.26	-1.31	0.24
$[Fe(tzpy)_2(NCS)_2]$	Fe^{II}	0.95	-1.40	-1.45	0.21
$[Fe(t\mathrm{Bu}_2qsal)_2]$	Fe^{II}	0.90	-1.40	-1.39	0.14
$[Fe(L_3)_3][ClO_4]_2$	Fe^{II}	1.36	-1.17	-1.15	0.56
$[Co(NAd)(Tp^{t\mathrm{Bu,Me}})]$	Co^{III}	0.27	-0.91	-0.57	-0.02
$[Co(^{Ar}L)(Nt\mathrm{Bu})]$	Co^{III}	0.50	-0.48	-0.44	0.21
$[Co(terpy)_2]$	Co^{II}	-0.03	-0.02	-0.02	-0.03
$[Co(H_2(fsa)_2en)(Py)_2]$	Co^{II}	0.53	-0.63	-0.60	0.22
$[Co(terpyrindone)_2][ClO_4]_2$	Co^{II}	0.70	-0.65	-0.61	0.31
$[Co(papl)_2]$	Co^{II}	1.00	-1.10	-1.18	0.86
$[Co(MeO\text{-}terpy)_2][BF_4]_2$	Co^{II}	0.76	-0.61	-0.57	0.36
$[Co(PM\text{-}BiA)_2][NCS]_2$	Co^{II}	0.38	-1.57	-1.71	-0.10
$[Ni(\alpha\text{-}phpyNO)_2Br_2]$	Ni^{II}	0.25	-0.60	-0.58	0.05
$[Ni(phpyNO)_2Cl_2]$	Ni^{II}	0.27	-0.59	-0.60	-0.04
$[Ni(\beta\text{-}phpyNO)_2Br_2]$	Ni^{II}	0.15	0.04	0.04	0.06

ddpd = N,N′-dimethyl-N,N′-dipyridine-2-yl-pyridine-2,6-diamine, Cp^{iPr_4} = tetraisopropylcyclopentadienide, depe = 1,2-bis(diethylphosphino)ethane, Ind^{Me-2} = bis(2-methylindenyl), L_1tren = tris(2-((pyrrol-2yl)methyleneamino)ethyl)amine, 3,5-diBr-sal$_2$323 = 2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)bis(4,6-dibromophenolato), L_2 = (2,2′-(2,6,9,13-tetraazatetradeca-1,13-diene-1,14-diyl)diphenol), $imSQ^{OMe}$ = 4,6-di-*tert*-butyl-N-(2-methoxyphenyl)-o-aminophenol, $Cp^{1\text{-}Me}$ = methylcyclopentadiene, $Cp^{1\text{-}t\mathrm{Bu}}$ = *tert*-butylcyclopentadienyl, $Cp^{1,3\text{-}t\mathrm{Bu}}$ = *tert*-butylcyclopenta-1,3-diene, L-N_3O_2 = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene, acac = acetylacetonate, trien = triethylenetetramine, qsal-Br = (N-8-quino-lyl)-5-Br-salicylaldiminate, 3-OMe-salen = (2-(((2-(ethylamino)ethyl)imino)methyl)-6-methoxyphenolato-N,N′,O), qsal-5-OMe = N-(8-quino-lyl)salicylaldiminate, phen = phenanthroline, stpy = 4-styrylpyridine, bpp = (2,6-di(pyrazol-1-yl)pyridine), $H_2B(pz)_2$ = dihydrogen bis(pyrazol-1-yl)borate, bipy = bipyridine, tzpy = (3-(2-pyridyl)(1,2,3)triazolo(1,5-a)pyridine), $t\mathrm{Bu}_2$qsal = 2,4-di(*tert*-butyl)-6-((quinoline-8-ylimino)methyl)phenol, L_3 = 1-acetic ethyl-2-(pyridine-2-yl)-imidazole, Ad = 1-adamantyl, $Tp^{t\mathrm{Bu,Me}}$ = hydrotris(3-*tert*-butyl,5-methyl-pyrazol-1-yl)borate, ^{Ar}L = 5-mesityl-1,9-(2,4,6-triphenylphenyl)dipyrrin, terpy = terpyridine, H_2(fsa)$_2$en = 3-formylsalicylic acid-ethylendiamine, papl = 1-(2-pyridylazo)-2-phenanthrol, MeO-terpy = 4′-methoxy-2,2′:6′,2″-terpyridine, PM-BiA = *cis*-bis(thiocyanato)bis(N-(2-pyridylmethylene)aminobiphenyl), α-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase α, phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide, β-phpyNO = *tert*-butyl 5-phenyl-2-pyridyl nitroxide phase β.