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Accurate State Energetics in Spin-Crossover Systems using Pure Density Functional Theory

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Electronic Supplementary Information

A text file containing *xyz* files with the optimized structures and an xlsx file with the calculated and experimental bond distances.

Table S1. High- and low-spin energy differences (in kcal/mol) using s1-s20 molecular models (positive values indicate a low-spin ground state) using the twenty-five KTBM0-KTBM24 exchange functionals + SCAN correlation using PBE+MB optimized geometry. The last row has the sum of energy differences. The functionals with the best results are highlighted in bold.

KTBM	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	GAP
s1	13.1	12.9	12.2	9.6	13.0	14.1	13.2	11.0	8.9	8.8	12.3	11.5	9.9	7.7	**6.6**	11.2	10.4	8.6	6.9	**6.2**	9.2	8.2	7.4	6.4	**5.8**	-6.6
s2	13.3	13.1	12.1	8.1	9.4	13.8	13.2	10.8	7.4	6.1	12.8	12.0	10.0	7.1	**5.3**	12.3	11.5	9.1	6.6	**5.3**	10.2	8.9	7.7	6.2	**4.8**	-11.2
s3	13.6	13.4	12.4	8.5	9.7	14.1	13.6	11.4	8.0	6.8	13.5	12.8	10.9	8.1	**6.4**	13.4	12.6	10.4	7.8	**6.5**	11.6	10.3	9.1	7.5	**5.7**	-11.0
s4	11.4	11.2	10.2	6.2	7.2	11.8	11.4	9.1	5.7	4.5	11.4	10.6	8.8	6.0	**4.3**	11.3	10.6	8.4	5.8	**4.5**	9.6	8.3	7.1	5.5	**3.5**	-13.4
s5	25.1	24.8	23.6	18.4	21.3	26.9	25.5	21.5	17.1	15.0	24.2	22.8	19.7	15.1	**12.2**	22.7	21.0	17.5	13.8	**11.9**	18.5	16.6	15.0	12.9	**9.7**	-11.9
s6	27.0	26.7	25.4	19.7	22.6	28.6	27.2	23.0	18.3	16.3	25.9	24.5	21.1	16.5	**13.6**	24.3	22.6	18.9	15.2	**13.3**	20.0	18.1	16.4	14.3	**11.4**	-11.0
s7	27.4	27.1	25.7	19.7	22.2	28.8	27.4	23.2	18.3	16.1	26.2	24.7	21.3	16.5	**13.6**	24.6	22.9	19.0	15.2	**13.3**	20.2	18.2	16.5	14.4	**11.6**	-11.4
s8	21.5	21.1	19.4	12.0	11.9	22.1	21.4	17.5	11.2	8.1	21.6	20.4	17.1	12.0	**8.9**	21.9	20.6	16.5	12.0	**9.4**	18.7	16.4	14.4	11.5	**7.2**	-21.2
s9	29.1	28.7	26.9	19.3	20.5	29.9	28.9	24.5	18.3	15.5	28.6	27.2	23.7	18.4	**15.3**	28.3	26.8	22.6	18.0	**15.6**	24.7	22.3	20.2	17.3	**13.8**	-15.7
s10	24.1	23.7	22.0	14.7	15.5	24.9	24.0	19.9	13.8	11.1	23.9	22.6	19.3	14.3	**11.3**	23.9	22.6	18.5	14.1	**11.7**	20.6	18.4	16.4	13.5	**9.5**	-19.2
s11	17.5	17.2	15.9	10.4	13.6	18.9	17.5	13.6	9.0	7.2	16.2	14.9	11.8	7.4	**4.7**	14.7	13.2	9.8	6.1	**4.4**	11.0	9.1	7.4	5.3	**3.6**	-20.3
s12	20.2	19.9	18.4	12.3	16.3	21.6	20.2	16.1	11.1	9.8	19.1	17.7	14.6	9.9	**7.4**	17.8	16.3	12.7	8.8	**7.1**	14.3	12.1	10.3	8.0	**6.2**	-21.8
s13	22.3	22.0	20.7	15.6	19.7	24.0	22.4	18.3	14.1	12.7	20.7	19.2	16.2	11.8	**9.3**	18.8	17.2	13.8	10.3	**8.8**	14.9	12.9	11.4	9.5	**8.2**	-14.3
s14	23.7	23.4	21.8	15.4	18.5	25.0	23.6	19.2	14.0	12.3	22.4	20.9	17.6	12.8	**10.3**	21.0	19.4	15.7	11.7	**10.0**	17.2	15.1	13.2	11.0	**9.3**	-17.5
s15	14.1	13.9	12.9	8.4	12.0	15.3	14.0	10.7	6.9	5.8	12.5	11.4	8.9	5.0	**2.7**	10.8	9.6	6.7	3.5	**2.2**	7.7	6.0	4.5	2.9	**2.8**	-18.6
s16	12.7	12.6	12.0	9.5	12.6	14.2	12.7	9.6	7.8	6.9	10.4	9.3	7.1	4.3	**2.9**	7.6	6.2	4.0	2.4	**2.1**	3.9	2.9	2.2	1.8	**2.3**	-6.1
s17	11.7	11.5	11.0	8.3	9.9	12.6	11.6	9.0	7.0	5.9	10.0	9.1	7.1	4.7	**3.4**	8.1	6.9	4.9	3.3	**2.9**	5.0	4.1	3.4	2.9	**2.8**	-5.6
s18	12.1	12.0	11.4	8.7	11.6	13.6	12.1	8.9	7.0	5.9	9.8	8.7	6.4	3.5	**2.0**	7.1	5.6	3.3	1.6	**1.1**	3.3	2.2	1.4	0.9	**1.3**	-7.4
s19	16.7	16.6	16.1	14.0	18.2	18.4	16.9	14.0	12.5	12.2	14.7	13.6	11.7	9.2	**8.1**	12.2	10.8	8.9	7.4	**7.2**	8.9	7.9	7.2	6.7	**7.1**	-3.4
s20	19.5	14.9	14.3	11.5	14.0	16.3	15.1	12.4	10.3	9.3	13.6	12.7	10.7	8.1	**6.7**	11.9	10.7	8.7	6.9	**6.2**	9.0	7.9	7.1	6.3	**5.7**	-4.7
sum	376.1	366.6	344.4	250.1	299.4	394.8	371.8	303.8	226.8	196.3	349.7	326.4	273.9	198.3	154.8	323.9	297.5	238.0	177.3	149.6	258.5	225.9	198.3	164.5	132.3	-

Table S2. Normalized training weights for the KBTM meta-GGA family of exchange functionals (from SI of ref.1)

functional	w lattice parameter	w cohesive energy	w bandgap
KTBM0	0.0	1.0	0.0
KTBM1	0.32	0.95	0.0
KTBM2	0.71	0.71	0.0
KTBM3	0.95	0.32	0.0
KTBM4	1.0	0.0	0.0
KTBM5	0.0	0.97	0.02
KTBM6	0.3	0.9	0.03
KTBM7	0.67	0.67	0.03
KTBM8	0.9	0.3	0.03
KTBM9	0.97	0.0	0.02
KTBM10	0.0	0.83	0.06
KTBM11	0.24	0.73	0.06
KTBM12	0.51	0.51	0.07
KTBM13	0.73	0.24	0.06
KTBM14	0.83	0.0	0.06
KTBM15	0.0	0.55	0.08
KTBM16	0.15	0.44	0.09
KTBM17	0.3	0.3	0.09
KTBM18	0.44	0.15	0.09
KTBM19	0.55	0.0	0.08
KTBM20	0.0	0.24	0.1
KTBM21	0.06	0.18	0.1
KTBM22	0.12	0.12	0.1
KTBM23	0.18	0.06	0.1
KTBM24	0.24	0.0	0.1
KTBM_GAP	0.019	0.0062	0.1

Table S3. Experimental transition temperatures $T_{1/2}$ (in K). Estimation of the difference of the electronic energy to reproduce the experimental $T_{1/2}$. Such value can be calculated as the difference of thermal corrections to free energy (thermal corrections to translational, rotational and electronic energy + zero-point correction + translational, rotational and electronic entropy). Two DFT methods[2 3] has been adopted by changing functional, basis set [4, 5 6] and dispersion contribution[7] to check the relatively small changes with the methodology. For the discussion in the main text, the B3LYP values will be employed because such approach was benchmarked as the best to reproduce the vibrational frequencies that are the main contribution to such energy difference through the zero-point correction and entropic terms.[8]

Molecular System	**ref.**	**Exp. $T_{1/2}$**	**B3LYP+GD3 6-311G**	**TPSSh def2-TZVP**
s1 $[Cr^{II}(L_{s1})_2I_2]$	9	171	1.7	2.5
s2 $[Mn^{III}(L_{s2})]$	10, 11	45	1.2	1.2
s3 $[Mn^{III}(L_{s3})]^{+1}$	12	175	2.7	2.8
s4 $[Mn^{III}(L_{s4})]^{+1}$	13	131	2.3	2.4
s5 $[Mn^{II}(L_{s5})_2]$	14	303	7.9	7.4
s6 $[Mn^{II}(L_{s6})_2]$	15	215	6.4	5.8
s7 $[Mn^{II}(L_{s7})_2]$	15	325	8.3	7.0
s8 $[Fe^{III}(L_{s8})]^{+1}$	16	200	2.9	3.6
s9 $[Fe^{III}(L_{s9a})(L_{s9b})_2]^{+1}$	17	200	4.0	5.1
s10 $[Fe^{III}(L_{s10})_2]^{+1}$	18	164	3.1	3.9
s11 $[Fe^{II}(L_{s11})_2(NCS)_2]$	19	176.5	4.3	4.7
s12 $[Fe(L_{s12})_4(NCS)_2]$	20	109	5.4	5.1
s13 $[Fe^{II}(L_{s13})_2]^{+2}$	21	256	5.3	5.9
s14 $[Fe^{II}(L_{s14a})(L_{s14b})]$	22	160	4.0	4.7
s15 $[Fe^{II}(L_{s15})_2(NCS)_2]$	23	118	1.7	3.4
s16 $[Co^{II}(L_{s16})_2]^{+2}$	24	200	2.0	2.3
s17 $[Co^{II}(L_{s17})(py)_2]$	25	121	1.2	1.3
s18 $[Co^{II}(L_{s18})_2]^{+2}$	26	172.4	1.6	1.9
s19 $[Co^{II}(L_{s19})_2]$	27	150	1.5	2.1
s20 $[Co^{II}(L_{s20})_2]^{+2}$	28	250	1.7	1.9

Table S4. High- and low-spin states energy differences (in kcal/mol, positive values indicate a low-spin ground state) calculated with exchange-correlation functionals especially devoted to reproduce bandgaps including the KTBM_GAP functional with large weight for the bandgap error proposed by Kovács et al. [1]

Molecular System	**ref.**	**KTBM_GAP // PBE+MB**	**TASK //PBE+MB**	**mBEEF // PBE+MB**	**HLE17 // PBE+MB**
s1 $[Cr^{II}(L_{s1})_2I_2]$	9	-6.6	-28.7	5.2	-6.3
s2 $[Mn^{III}(L_{s2})]$	10, 11	-11.2	-27.3	4.4	-3.0
s3 $[Mn^{III}(L_{s3})]^{+1}$	12	-11.0	-27.3	3.3	-4.6
s4 $[Mn^{III}(L_{s4})]^{+1}$	13	-13.4	-30.0	1.0	-6.8
s5 $[Mn^{II}(L_{s5})_2]$	14	-11.9	-30.7	13.1	-1.0
s6 $[Mn^{II}(L_{s6})_2]$	15	-11.0	-34.5	13.6	-1.9
s7 $[Mn^{II}(L_{s7})_2]$	15	-11.4	-37.3	12.4	-1.9
s8 $[Fe^{III}(L_{s8})]^{+1}$	16	-21.2	-43.5	9.2	2.3
s9 $[Fe^{III}(L_{s9a})(L_{s9b})_2]^{+1}$	17	-15.7	-43.7	14.9	5.6
s10 $[Fe^{III}(L_{s10})_2]^{+1}$	18	-19.2	-29.7	11.4	1.8
s11 $[Fe^{II}(L_{s11})_2(NCS)_2]$	19	-20.3	-35.3	12.8	0.0
s12 $[Fe(L_{s12})_4(NCS)_2]$	20	-21.8	-46.9	12.7	-4.8
s13 $[Fe^{II}(L_{s13})_2]^{+2}$	21	-14.3	-27.3	20.4	2.3
s14 $[Fe^{II}(L_{s14a})(L_{s14b})]$	22	-17.5	-40.6	17.7	1.7
s15 $[Fe^{II}(L_{s15})_2(NCS)_2]$	23	-18.6	-33.6	11.5	1.4
s16 $[Co^{II}(L_{s16})_2]^{+2}$	24	-6.1	-6.9	13.5	0.8
s17 $[Co^{II}(L_{s17})(py)_2]$	25	-5.6	-8.9	12.0	0.4
s18 $[Co^{II}(L_{s18})_2]^{+2}$	26	-7.4	-8.1	13.3	0.2
s19 $[Co^{II}(L_{s19})_2]$	27	-3.4	-7.3	24.1	2.0
s20 $[Co^{II}(L_{s20})_2]^{+2}$	28	-4.7	-8.7	12.3	3.9

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