Barriers to Predictive High-throughput Screening for Spin-crossover

Daniel Mejía-Rodríguez,[1, 2, a)] Angel Albavera-Mata,[1, 3, b)] Eric Fonseca,[1, 3] Dian-Teng Chen,[1, 2] H-P. Cheng,[1, 2]
Richard G. Hennig,[1, 3, c)] and S.B. Trickey[1, 2, d)]
[1)] *Center for Molecular Magnetic Quantum Materials, Quantum Theory Project, University of Florida, Gainesville, FL 32611*
[2)] *Department of Physics, University of Florida, Gainesville, FL 32611*
[3)] *Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611*

(Dated: 15 October 2021; use with Revision B.8; not for circulation outside M^2QM)

I. [MN(TAA)] EXPERIMENTAL INFORMATION

A. Reported structure

The crystal structure of [Mn(taa)] has been reported by two groups, namely Sim and Sinn[1] (denoted "JACS" hereafter) and more recently by Guionneau et al.[2] (denoted "PRB" hereafter). The JACS structure was room temperature, hence high-temperature, high-spin (HT-HS). The PRB HT-HS crystal structure data is deposited in the Cambridge Crystallographic Data Centre with identification number 266994. Both crystal structures have $I\bar{4}3d$ symmetry. The JACS crystal lattice parameter, 20.309 Å, is slightly larger than the PRB value, 20.282 Å.

Table I shows the Cartesian coordinates of symmetry-unique atoms for both the JACS and PRB crystal structures. As a graphical aid, Figure 1(a) shows the 3-D structure corresponding to PRB with atoms labeled as in Table I. To facilitate further the comparison between the JACS and PRB structures, Table II shows the bond lengths for the heavy atoms. [Aside: Sim and Sinn misreported the C(3)–C(4) bond length: its value in their Table II does not correspond to the fractional coordinates given in their Table I. All the JACS bond lengths shown here were recalculated from their Table I. The C(3)–C(4) value shown here is correct.]

TABLE I: Cartesian coordinates [Å] for the symmetry unique atoms of the [Mn(taa)] crystal in the HT-HS phase. The coordinates place the Mn atom at the origin and align the C_3 axis along z.

Atom	JACS[1]			PRB[2]		
	x	y	z	x	y	z
Mn	0.000	0.000	0.000	0.000	0.000	0.000
N(1)	0.515	-1.672	-1.073	0.514	-1.668	-1.072
N(7)	1.707	-0.694	1.105	1.701	-0.690	1.069
N(10)	0.000	0.000	3.261	0.000	0.000	3.233
C(2)	1.677	-2.315	-0.599	1.642	-2.321	-0.604
C(3)	1.915	-3.406	-1.361	1.901	-3.438	-1.367
C(4)	0.969	-3.465	-2.320	0.910	-3.479	-2.341
C(5)	0.126	-2.368	-2.108	0.084	-2.392	-2.120
C(6)	2.254	-1.698	0.545	2.245	-1.739	0.545
C(8)	2.251	-0.101	2.312	2.261	-0.092	2.280
C(9)	1.374	-0.389	3.468	1.369	-0.408	3.468
H(3)	2.797	-4.169	-1.428	2.598	-4.043	-1.253
H(4)	0.762	-4.010	-2.988	0.820	-4.116	-3.012
H(5)	-0.545	-2.129	-2.519	-0.667	-2.189	-2.627
H(6)	2.865	-1.927	0.811	3.017	-2.105	0.912
H(81)	3.238	-0.377	2.242	3.151	-0.443	2.436
H(82)	2.075	0.856	2.242	2.331	0.868	2.169
H(91)	1.742	0.158	4.200	1.709	0.049	4.254
H(92)	1.456	-1.327	3.590	1.392	-1.362	3.641

[a)] Electronic mail: daniel.mejia@pnnl.gov
[b)] Electronic mail: aalbaveramata@ufl.edu
[c)] Electronic mail: rhennig@ufl.edu
[d)] Electronic mail: trickey@qtp.ufl.edu

TABLE II: [Mn(taa)] bond distances [Å] for bonds among non-Hydrogen atoms. Values are for the HT-HS phase.

	JACS	PRB
Mn–N(1)	2.053	2.048
Mn–N(7)	2.148	2.124
Mn–N(10)	3.261	3.233
N(1)–C(2)	1.410	1.386
N(1)–C(5)	1.307	1.345
N(7)–C(6)	1.273	1.293
N(7)–C(8)	1.451	1.462
N(10)–C(9)	1.442	1.448
C(2)–C(3)	1.352	1.377
C(2)–C(6)	1.422	1.422
C(3)–C(4)	1.349	1.390
C(4)–C(5)	1.399	1.383
C(8)–C(9)	1.480	1.519

Note that one [Mn(taa)] molecule can be seen as having three equivalent *arms* that stem from the N(10) atom. Each arm is a bidentate ligand, with N(1) expected to have anionic character (the deprotonated pyrrole position) and N(7) neutral character (the imine position). The presence of the three bidentate moieties introduces the possibility of Λ/Δ optical isomerism (colloquially known as propeller twist isomerism). Due to the achiral $I\bar{4}3d$ spacegroup, both JACS and PRB crystals show a 50:50 ordered mixture of the stereoisomers.

Nota bene: The bond lengths quoted in the main text as well as below are either low-temperature low-spin (LT-LS) or low-temperature high-spin (LT-HS), corresponding to Crystallographic Information Files with identification numbers 266992 and 266995, respectively. Beware of the mistaken annotations in 266995 and ascertain the actual system state by comparison with Table I of Ref. 2.

B. Spin-crossover energy estimates

To our knowledge, three experimental values for ΔE_{HL} have appeared in the literature. Recently Otsuki et al.[3] reported $\Delta E_{\mathrm{HL}} \approx 10$ meV by fitting to dielectric and magnetostriction measurements. This differs from an earlier value from what appears to be the same laboratory[4] (see page 627) but determined by different methods, namely 30 meV.

Yu et al.[5] recently redetermined ΔE_{HL} to lie between 50 and 100 meV in order to be consistent with the measured SCO $T_c \approx 50$ K[1] after taking into account Jahn-Teller, spin manifold, and vibrational energy contributions.

For the purposes of this study, we conclude that $\Delta E_{\mathrm{HL}} = 50 \pm 20$ meV is a reasonable present-day target range for calculations.

II. DETAILS OF CODES UTILIZED

The deMon2k code[6] is an all-electron molecular DFT code that uses variational Coulomb fitting and an auxiliary basis set to avoid 4-center integrals.[7] Our calculations used a locally modified developers' version and were done in the unrestricted Kohn-Sham (UKS) framework. The XC potential was integrated using the orbital basis (keyword `VXCTYPE BASIS`) scheme, not the auxiliary basis. Determination of the numerical integration grid is discussed below; see Section III A. Ionic position relaxations were performed in Cartesian coordinates with default convergence thresholds that include 0.3 mHartree/Bohr (15.4 meV/Å) root-mean-square force, 0.45 mHartree/Bohr (23.1 meV/Å) maximum force, as well as either a change in energy between steps below 10^{-6} Hartree or a root-mean-square displacement below 0.00120 Bohr. The automatically generated GEN-A2* auxiliary basis set[8] was used to compute the Coulomb integrals and potential. That auxiliary function set should ensure the reproduction of enthalpies of formation within 0.1 kcal/mol (4.3 meV) of results from a conventional KS implementation (i.e., without robust Coloumb fitting of an auxiliary density) for small to medium-sized molecules (less than 20 atoms).

The NWChem calculations used the UKS scheme and an SCF convergence threshold of 10^{-7} Hartree. Variational Coulomb fitting again was used, with the `Weigend Coulomb Fitting` auxiliary basis.[9] Distinct from deMon2k, the variational Coulomb fitting scheme in NWChem is constrained explicitly to preserve the total charge. The ionic relaxation employed redundant internal coordinates and the default convergence thresholds for the residual forces

TABLE III: Definition of the PBE PAWs used. The column headed *Valence* lists the reference atomic configurations for the valence electrons of the potentials. Columns headed s, p, and d list the number of partial waves N_l and their respective cutoff radii r_c^l. The column headed E_{cut} shows the default energy cutoff of the plane-wave basis set.

		$N_l \times r_c^l$			
Element	Valence	s	p	d	E_{cut}
H	$1s^1$	2×1.1	1×1.1		250
C	$2s^2\, 3p^2$	2×1.2	2×1.5		400
N	$2s^2\, 3p^3$	2×1.2	2×1.5		400
Mn	$4s^1\, 3d^6$	2×2.3	2×2.3	2×2.3	270
Mn_pv	$3p^6\, 4s^1\, 3d^6$	2×2.3	2×2.0	2×2.3	270

and displacements were used. The thresholds for the ionic relaxation match those of deMon2k. However, NWChem also enforces a maximum displacement criterion, regardless of the change in energy between two consecutive steps. When starting from a structure with C_3 point group symmetry, one must deactivate use of symmetry adaptation (`noautosym`) explicitly. Otherwise, the code will constrain the molecule to maintain the same point group along the ionic relaxation, thereby leading to metastable structures that lack the Jahn-Teller symmetry-breaking distortions.

The Gaussian09[10] calculations used the UKS scheme with an `UltraFine` grid to integrate the XC potential. The ionic relaxations also employed redundant internal coordinates with default convergence thresholds and no symmetry constraints (`NoSymmetry` keyword). Those thresholds match those of deMon2k and NWChem. However, Gaussian09 stops the relaxation when one of two criteria is met: i) all four values (maximum force, RMS force, maximum displacement, and RMS displacement) are smaller than their respective thresholds, or ii) the maximum force and RMS force are two orders of magnitude smaller than their respective thresholds regardless of the values of the displacement.

We started the relaxations from structures relaxed with VASP using the PBE DFA and unless otherwise noted, results with gaussian-type orbitals correspond to the `def2-QZVP` basis with a converged grid for the given functional. For NWChem, in particular, this means `medium`, `fine`, and `custom` for PBE, r^{2}SCAN (r^{2}SCAN-L), and SCAN (SCAN-L), respectively.

Isolated molecule calculations with periodic boundary conditions were performed using VASP 5.4.4.[11] Each molecule was placed inside a 20×20×20 Å^3 cubic cell, with the threefold molecular rotation axis aligned along the (111) direction. The plane wave kinetic energy cutoff was set at 600 eV, aspherical corrections were activated (keyword `LASPH=.TRUE.`), the precision tolerance was "accurate" (`PREC=Accurate`), and the smearing value was 0.02 eV. Since very small energy differences are at issue, projection operators were evaluated in reciprocal space (`LREAL=.FALSE.`), and the convergence criterion tightened to an energy difference below 10^{-6} eV between successive electronic minimization steps. Dipole-dipole corrections for the energy and the potential also were included (`LDIPOL=.TRUE.`, `IDIPOL=4`. To remove symmetry constraints, symmetrization of the charge density with the `ISYM=0` keyword was deactivated explicitly. Alternatively, one may distort the cubic box to remain orthorhombic but with three different lengths ($20 \times 20.5 \times 21.0$ Å^3) and use a tiny smearing value (0.001 eV, for example). Ionic relaxations were stopped when the maximum force was less than 0.02 eV/Å(`EDIFFG=-0.02`). Note that VASP does not include the displacement as a convergence criterion for the ionic relaxations.

As is conventional in VASP calculations, PBE PAW data sets were used throughout. (PAW data sets for r^{2}SCAN, SCAN, their deorbitalized versions, and other meta-GGAs are unavailable in VASP.) The PAWs correspond to VASP version 54. For H, C, and N, we used the PAW potentials that describe the outer-shell electrons as valence electrons. For Mn, we used both the PAW potential that includes the outer shell electrons as valence and the one that also includes the semicore $3p$-shell to the valence. No significant difference was found between the predicted ΔE_{HL} values obtained with those two Mn PAW potentials. Table III shows the reference atomic electronic configuration for the valence used to generate the PAWs, the default energy cutoffs, and cutoff radii.

In most cases, irrespective of the code, ionic relaxations (optimizations) were started from the isolated molecular structures corresponding to the LT-LS and LT-HS crystal structures,[2] see Section I A. For the ramped U calculations, the structural relaxations at the new U started from the equilibrium configuration found at the preceding U value. Moreover, the ramping started with $U = 0$ and the symmetric molecular structure.

TABLE IV: Definition of the numerical integration grids used in NWChem, deMon2k, and Gaussian09. The first entry inside the parentheses gives the number of radial shells while the second one gives the number of angular points per radial shell. The letter *p* (for pruning) means that grid points are discarded if their corresponding weights are small.

NWChem

	Medium	Fine	XFine	Custom
H	(45,434)p	(60,590)p	(100,1202)p	(200,590)p
C	(49,434)p	(70,590)p	(100,1454)p	(200,590)p
N	(49,434)p	(70,590)p	(100,1454)p	(200,590)p
Mn	(112,590)p	(140,974)p	(160,1454)p	(200,590)p

deMon2k

	Coarse	Medium	Fine	Reference
H	(50,194)p	(75,302)p	(99,590)p	(200,1202)
C	(50,194)p	(75,302)p	(99,590)p	(200,1202)
N	(50,194)p	(75,302)p	(99,590)p	(200,1202)
Mn	(50,194)p	(75,302)p	(99,590)p	(200,1202)

Gaussian09

	Coarse	Fine	UltraFine	SuperFine
H	(35,110)p	(75,302)p	(99,590)p	(175,974)p
C	(35,110)p	(75,302)p	(99,590)p	(175,974)p
N	(35,110)p	(75,302)p	(99,590)p	(175,974)p
Mn	(35,110)p	(75,302)p	(99,590)p	(250,974)p

TABLE V: ΔE_{HL} for [Mn(taa)] (meV) using three pre-defined XC grids in NWChem. Caution: these are small-basis set results solely to demonstrate grid effects.

Grid	PBE	SCAN	r^{2}SCAN
`medium`	404	-236	120
`fine`	409	684	118
`xfine`	406	371	109

III. COMPUTATIONAL BEHAVIOR AND SENSITIVITIES

A. Grids

Typically, convergence of total energies to μHartree accuracy is obtained with more than 200 radial shells per atom, while convergence of the gradients to μHartree/Bohr accuracy requires around 300 radial shells per atom.[12] Definitions of the numerical integration grids used in this work with NWChem, deMon2k, and Gaussian09 are given in Table IV. Note that all three codes use Lebedev angular quadratures[13–16] for the tabulated grids.

One of the motivations for constructing r^{2}SCAN was to reduce those grid sensitivities.[17] Table V shows the SCO energy splitting obtained with PBE, SCAN, and r^{2}SCAN for three pre-defined grids in NWChem. We caution that because the small double-zeta basis set cc-pVDZ was used, that table serves *only* the purpose of showing grid sensitivity. Immediately it makes evident that SCAN needs a grid quality comparable to, or better than, the `xfine` one defined in Table IV. In contrast, the default numerical integration grid in NWChem is the `medium` one. The custom grid listed in Table IV yields a converged SCAN SCO energy splitting (343 meV) with the same cc-pVDZ basis set but with a computational cost similar to the `fine` pre-defined setting. A further contrast is that r^{2}SCAN yields good results even with the `medium` quality grid.

In VASP, the radial grid used inside the PAW spheres is logarithmic and depends on the specific `POTCAR` being used. All of the potentials used in this work have radial grids with at least 355 points. A consequence of this large number of radial points is that the numerical integration of the SCAN potential inside the PAW spheres is well converged. The azimuthal coordinate is discretized on an equally spaced grid, and the inclination coordinate is integrated with

TABLE VI: ΔE_{HL} values (meV) using two families of systematic basis sets.

Basis set	PBE	SCAN	r^2SCAN
`cc-pVDZ`	404	343	118
`cc-pVTZ`	448	398	157
`cc-pVQZ`	450	429	131
`def2-SVP`	445	400	146
`def2-TZVP`	444	390	130
`def2-QZVP`	440	389	134

TABLE VII: Predicted SCO energies, ΔE_{HL} (meV) using different plane-wave kinetic energy cutoffs in VASP.

Cutoff (eV)	PBE	SCAN	r^2SCAN
400	457	402	156
500	458	404	156
600	458	408	158
700	460	409	159

Gauss-Legendre quadrature. We found this angular discretization to be well-suited to describe the SCAN functional. The accuracy of the XC grid for the valence region is determined by the kinetic energy cutoff of the plane wave basis and the precision setting or by manual definition of the "fine grid" (`NGXF, NGYF, NGZF`). The "accurate" precision setting that we used yields a "fine grid" with eight times more points than the standard Fourier grid defined by the kinetic energy cutoff. VASP uses a second support grid for the evaluation of the augmentation charges. Selecting `ADDGRID=.TRUE.` ensures that this support grid has eight times more points than the "fine grid." We found that when `PREC=Accurate` is used, SCAN results are stable with a kinetic energy cutoff of at least 600 eV (see Sec. VI below). Using `ADDGRID=.TRUE.` was beneficial for SCAN and SCAN-L ionic relaxations, but no significant change in the SCO energy splitting was found. Use of the keyword `ADDGRID=.TRUE.` was not necessary to obtain stable ionic relaxations with either r^2SCAN or r^2SCAN-L.

B. Basis sets

It is possible to find contradictory statements about the importance of the basis set for predicting the ΔE_{HL} for several complexes. Those contradictions may be rooted both in the definition of the energy difference that one deems converged and the specific family of basis sets being compared. Previously, Cirera, Via Nadal, and Ruiz showed that the simple addition of polarization functions to the def2-tzv basis set changed the [Mn(taa)] ΔE_{HL} from the TPSSh DFA by as much as 122 meV: see the Supporting Information in Ref. [18]. However, Amabilino and Deeth concluded that extending the basis set beyond the double-zeta def2-SVP "does not appear to be required".[19]

Given this context, we did a systematic study of basis set dependence with two widely used families of Gaussian-type basis sets with polarization functions: the Dunning-type correlation-consistent polarized `cc-pVXZ` family, and the Karlsruhe `def2` family. Gaussian09 and NWChem were used. Table VI shows the ΔE_{HL} values obtained with PBE, SCAN, and r^2SCAN using converged numerical integration grids. The effect of increasing the basis set size within a given family is similar among the three functionals. Quality improvement of the Dunning-type sets led to a relative stabilization of the LS configuration by as much as 80 meV. In contrast, results obtained with the Karlsruhe family did not vary more than 15 meV. A notable difference between these two basis set families is that a tight d function is not present in the Mn bases of the Dunning-type family. We recommend against the use of the `cc-pVXZ` family in favor of the `def2` one.

Convergence studies with respect to the kinetic energy cutoff were carried out in VASP for PBE, SCAN, and r^2SCAN DFAs. The resulting ΔE_{HL} values are summarized in Table VII. We determined that use of the 600 eV cutoff was sufficient to have a satisfactory description of the forces acting on the ions, especially for the SCAN DFA. For purposes of systematic comparison, we used the same value for r^2SCAN.

IV. SCF CONVERGENCE

At each ionic configuration relaxation step, NWChem calculations converged without issues. On the other hand, deMon2k calculations were slow to converge despite the use of different convergence acceleration and stabilization techniques (Hartree damping `MIXING`, Pulay mixing `DIIS`, and level-shifting `SHIFT`). We traced this ill behavior to the quasi-linear-dependencies found in the auxiliary function set, but neither the default numerical solver `MATINV NUMERICAL` nor the use of the `MATINV ANALYTIC` approach helped. The solution was to mix approaches. The inverse of the fitting matrix was computed explicitly at *each* ionic configuration relaxation step but used as a preconditioner for the numerical solver [Aside: the default approach is to compute the inverse only at the first ionic relaxation step, use that as an approximate inverse, and update it with the BFGS algorithm for the subsequent steps. Another possible solution might be to use the MINRES solver `MATINV MINRES` available since deMon2k version 6.0.]

Despite the use of the UKS approach, the resulting KS state spin-contamination is low irrespective of the DFA. In all cases, the LS $\langle S^2 \rangle$ deviates about 2 % from the expected value, while the HS $\langle S^2 \rangle$ deviates by less than 1 %.

An important deMon2k technical point is that forces from SCAN and SCAN-L must include the numerical integration weight derivatives. That is not the default behavior of the code. Failure to include those derivatives results in an oscillatory ionic relaxation with both functionals. In contrast, r^{2}SCAN and r^{2}SCAN-L calculations did not need the computation of those derivatives.

Gaussian09 calculations ran smoothly with default parameters across all the DFAs tested. Relative to the other codes tested, Gaussian09 calculations ran with little requirement of user directives and achieved similar results concerning the SCO energies. All Gaussian09 calculations required more electronic and ionic steps for the HS species than for the LS species. By contrast, calculations with the TPSS DFA did not converge successfully on the first attempt. Achieving convergence of the revTPSS functional required the calculation to be started from the relaxed geometry using TPSS.

VASP convergence proceeded without issues for PBE and SCAN. SCAN-L and r^{2}SCAN-L calculations required a couple of hundred iterations in the first three electronic minimizations, but that is an oddity of Laplacian-dependent functionals in combination with large vacuum regions and is not particular to the [Mn(taa)] system. However, r^{2}SCAN-L needed fewer iterations than SCAN-L to converge subsequent ionic steps. The iteration count can be reduced dramatically by taking the density obtained with a different DFA as starting point.

Originally, ionic relaxations in VASP with SCAN and SCAN-L stopped with a “zero-curvature error message”. We traced the origin of this issue to a small bug present in almost all spin-polarized meta-GGA correlation functionals implemented in VASP. In particular, the SCAN implementation in VASP assumes that

$$\begin{aligned}\frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial \nabla n_\sigma} &= \frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial |\nabla n_\sigma|}\frac{\partial |\nabla n_\sigma|}{\partial \nabla n_\sigma} \\ &= \frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial |\nabla n|^2}\frac{\partial |\nabla n|^2}{\partial |\nabla n_\sigma|}\frac{\nabla n_\sigma}{|\nabla n_\sigma|}\end{aligned} \tag{1}$$

where e_c is the correlation energy density, σ labels the spin channel, and the absence of subscripts in n, ∇n, and τ indicates that they refer to the sum of both spin channels. This expression fails to recognize that $|\nabla n|^2$ also changes when the angle between ∇n_σ and $\nabla n_{\sigma'}$ changes. The VASP implementation tries to compensate for that by using

$$\frac{\partial |\nabla n|^2}{\partial |\nabla n_\sigma|} = 2|\nabla n_\sigma| + 2\frac{\nabla n_\sigma \cdot \nabla n_{\sigma'}}{|\nabla n_\sigma|}. \tag{2}$$

However, the correct result is obtainable straightforwardly by using

$$\begin{aligned}\frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial \nabla n_\sigma} &= \frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial |\nabla n|^2}\frac{\partial |\nabla n|^2}{\partial \nabla n_\sigma} \\ &= 2\frac{\partial e_c(n,|\nabla n|^2,\tau)}{\partial |\nabla n|^2}\nabla n\end{aligned} \tag{3}$$

instead of Equations (1) and (2). Correction of this bug removed the “zero curvature error” problem. [Aside: VASP includes this fix since version 6.1.]

V. SYMMETRIC STRUCTURE CALCULATED RESULTS

For the symmetry-preserving calculations, Tables VIII and IX list the bond distances among heavy atoms (Å) for low- and high-spin respectively.

TABLE VIII: Distances [Å] between pairs of heavy atoms in the low-spin configuration preserving the C_3 point group. Reference values were taken from the LT-LS crystal reported in Ref. [2]. The bottom line lists the value of the similarity index; see text for details.

	Ref.	VASP			deMon2k			NWChem		
		PBE	SCAN	SCAN-L	PBE	SCAN	SCAN-L	PBE	SCAN	SCAN-L
Mn–N(1)	1.975	1.970	1.950	1.961	1.971	1.954	1.961	1.974	1.954	1.956
Mn–N(7)	2.027	2.018	2.009	2.005	2.018	2.007	2.009	2.023	2.010	2.004
Mn–N(10)	3.284	3.465	3.405	3.354	3.465	3.399	3.359	3.452	3.378	3.375
N(1)–C(2)	1.388	1.392	1.384	1.393	1.391	1.383	1.390	1.391	1.383	1.392
N(1)–C(5)	1.351	1.351	1.343	1.350	1.349	1.341	1.347	1.350	1.342	1.349
N(7)–C(6)	1.299	1.318	1.309	1.317	1.318	1.308	1.314	1.318	1.309	1.317
N(7)–C(8)	1.469	1.450	1.446	1.455	1.450	1.443	1.451	1.450	1.444	1.453
N(10)–C(9)	1.443	1.441	1.436	1.444	1.441	1.434	1.440	1.440	1.435	1.441
C(2)–C(3)	1.403	1.411	1.402	1.406	1.411	1.402	1.406	1.411	1.403	1.408
C(2)–C(6)	1.426	1.408	1.401	1.403	1.408	1.401	1.404	1.408	1.401	1.405
C(3)–C(4)	1.405	1.402	1.395	1.399	1.401	1.394	1.397	1.401	1.396	1.399
C(4)–C(5)	1.407	1.412	1.404	1.409	1.412	1.403	1.408	1.412	1.404	1.409
C(8)–C(9)	1.528	1.545	1.532	1.539	1.545	1.532	1.537	1.545	1.531	1.538
Similarity		0.991	0.991	0.993	0.991	0.991	0.993			

TABLE IX: Distances [Å] between pairs of heavy atoms in the high-spin configuration preserving the C_3 point group. Reference values were taken from the LT-HS crystal data reported in Ref. [2]. The bottom line lists the value of the similarity index; see text for details.

	Ref.	VASP			deMon2k			NWChem		
		PBE	SCAN	SCAN-L	PBE	SCAN	SCAN-L	PBE	SCAN	SCAN-L
Mn–N(1)	2.054	2.058	2.048	2.044	2.066	2.047	2.043	2.069	2.051	2.040
Mn–N(7)	2.121	2.149	2.121	2.117	2.145	2.125	2.119	2.155	2.135	2.126
Mn–N(10)	3.241	3.495	3.363	3.314	3.479	3.373	3.364	3.380	3.331	3.295
N(1)–C(2)	1.385	1.388	1.382	1.389	1.388	1.380	1.387	1.387	1.379	1.387
N(1)–C(5)	1.343	1.351	1.342	1.350	1.350	1.340	1.348	1.350	1.340	1.348
N(7)–C(6)	1.295	1.310	1.301	1.309	1.310	1.300	1.307	1.310	1.300	1.308
N(7)–C(8)	1.464	1.448	1.442	1.453	1.447	1.440	1.449	1.448	1.442	1.451
N(10)–C(9)	1.452	1.442	1.439	1.448	1.443	1.437	1.443	1.445	1.438	1.446
C(2)–C(3)	1.400	1.410	1.402	1.406	1.410	1.401	1.405	1.411	1.401	1.405
C(2)–C(6)	1.427	1.414	1.406	1.408	1.414	1.406	1.409	1.413	1.405	1.408
C(3)–C(4)	1.408	1.403	1.396	1.400	1.402	1.394	1.399	1.402	1.395	1.399
C(4)–C(5)	1.405	1.410	1.403	1.407	1.411	1.401	1.406	1.411	1.402	1.406
C(8)–C(9)	1.530	1.544	1.531	1.538	1.545	1.530	1.536	1.541	1.529	1.533
Similarity		0.985	0.992	0.994	0.985	0.992	0.992			

To provide quantitative comparison with the experimentally reported distances, similarity indices between the relaxed geometries and the corresponding reference one were obtained using the algorithm in deMon2k. To compute the similarity index, deMon2k first minimizes the sum of absolute deviations of calculated positions from the reference atomic positions by translations, rotations, and permutations. This step minimizes misalignment error. The resulting sum then is mapped to the interval $(0, 1]$, with 1 corresponding to identical structures (see Ref. 20 for more details). The results for the symmetry-preserving structures are shown in the last lines of Tables VIII and IX.

VI. BOND LENGTHS AND DEVIATIONS FOR VARIOUS DFAS

Tables X, XI, XII, XIII, and XIV compare individual bond lengths for PBE, SCAN, SCAN-L, r^{2}SCAN, and r^{2}SCAN-L respectively from NWChem and VASP for the unsymmetric structure. One point to note is that PBE in either code yields structures with larger Mn–N(10) distances than from any of the meta-GGAs. That atomic pair is not bonded directly, which leads to the assumption that the enlarged bond behavior is linked directly to a comparatively poor description of non-covalent interactions by PBE. The meta-GGAs provide improvement, but a significant difference with experiment remains, a fact which supports the determination that van der Waals corrections should be included regardless of the DFA chosen.

TABLE X: Individual PBE bond lengths.

		Low-spin			High-spin		
	Bond	Arm 1	Arm 2	Arm 3	Arm 1	Arm 2	Arm 3
NWChem	Mn–N(1)	1.987	1.968	1.968	2.218	1.993	1.998
	Mn–N(7)	2.028	2.028	2.016	2.052	2.077	2.363
	Mn–N(10)		3.458			3.436	
	N(1)–C(2)	1.390	1.389	1.395	1.386	1.390	1.388
	N(1)–C(5)	1.346	1.353	1.348	1.344	1.350	1.357
	N(7)–C(6)	1.318	1.314	1.320	1.319	1.314	1.298
	N(7)–C(8)	1.449	1.449	1.451	1.452	1.451	1.440
	N(10)–C(9)	1.440	1.440	1.440	1.443	1.441	1.446
	C(2)–C(3)	1.414	1.407	1.412	1.418	1.409	1.405
	C(2)–C(6)	1.405	1.413	1.405	1.406	1.409	1.425
	C(3)–C(4)	1.398	1.406	1.400	1.396	1.402	1.407
	C(4)–C(5)	1.416	1.408	1.414	1.418	1.410	1.404
	C(8)–C(9)	1.546	1.544	1.545	1.542	1.543	1.545
VASP	Mn–N(1)	1.965	1.983	1.966	1.992	1.986	2.210
	Mn–N(7)	2.009	2.027	2.024	2.368	2.073	2.055
	Mn–N(10)		3.474		3.463		
	N(1)–C(2)	1.397	1.391	1.390	1.389	1.391	1.387
	N(1)–C(5)	1.349	1.347	1.354	1.358	1.351	1.345
	N(7)–C(6)	1.321	1.318	1.315	1.298	1.315	1.319
	N(7)–C(8)	1.452	1.450	1.450	1.442	1.452	1.454
	N(10)–C(9)	1.441	1.441	1.441	1.446	1.442	1.443
	C(2)–C(3)	1.412	1.415	1.408	1.406	1.409	1.418
	C(2)–C(6)	1.406	1.406	1.414	1.426	1.409	1.406
	C(3)–C(4)	1.401	1.399	1.407	1.408	1.403	1.397
	C(4)–C(5)	1.414	1.416	1.408	1.404	1.410	1.419
	C(8)–C(9)	1.546	1.547	1.546	1.546	1.544	1.542

The following three tables (XV, XVI, XVII) show deviations of calculated bond lengths for the PBE, SCAN, and SCAN-L DFAs as calculated from VASP, deMon2k, NWChem, and Gaussian9. The reference values are from the Crystallographic Information Files 266992 (LT-LS) and 266995 (LT-HS) associated with Ref. 2.

Finally, Table XVIII shows that in the LS case, the similarity indices for all three DFAs are quite close, but PBE is distinctly poorer in the high-spin case. At the risk of perhaps over-reading the outcome, r^{2}SCAN structures have the highest similarity indices, followed closely by the two de-deorbitalized DFAs.

TABLE XI: Individual SCAN bond lengths.

			Low-spin			High-spin	
	Bond	Arm 1	Arm 2	Arm 3	Arm 1	Arm 2	Arm 3
NWChem	Mn–N(1)	1.968	1.949	1.968	2.131	1.953	2.062
	Mn–N(7)	2.024	2.019	2.012	2.014	2.151	2.256
	Mn–N(10)			3.381	3.309		
	N(1)–C(2)	1.380	1.383	1.386	1.382	1.384	1.378
	N(1)–C(5)	1.339	1.344	1.338	1.336	1.345	1.344
	N(7)–C(6)	1.306	1.305	1.310	1.310	1.298	1.292
	N(7)–C(8)	1.444	1.444	1.444	1.447	1.441	1.436
	N(10)–C(9)	1.434	1.435	1.435	1.439	1.439	1.442
	C(2)–C(3)	1.404	1.398	1.406	1.408	1.399	1.401
	C(2)–C(6)	1.403	1.407	1.398	1.398	1.407	1.414
	C(3)–C(4)	1.394	1.399	1.391	1.391	1.399	1.399
	C(4)–C(5)	1.406	1.401	1.408	1.410	1.400	1.401
	C(8)–C(9)	1.532	1.531	1.531	1.527	1.531	1.530
VASP	Mn–N(1)	1.946	1.966	1.948	1.991	1.966	2.181
	Mn–N(7)	1.998	2.018	2.017	2.333	2.067	2.021
	Mn–N(10)	3.429	3.429	3.429	3.413		
	N(1)–C(2)	1.388	1.382	1.383	1.381	1.384	1.381
	N(1)–C(5)	1.34	1.339	1.345	1.349	1.343	1.337
	N(7)–C(6)	1.312	1.307	1.305	1.290	1.304	1.310
	N(7)–C(8)	1.446	1.445	1.445	1.438	1.446	1.449
	N(10)–C(9)	1.435	1.435	1.435	1.440	1.436	1.438
	C(2)–C(3)	1.404	1.404	1.399	1.396	1.399	1.408
	C(2)–C(6)	1.398	1.400	1.406	1.417	1.402	1.398
	C(3)–C(4)	1.393	1.393	1.399	1.401	1.396	1.390
	C(4)–C(5)	1.406	1.407	1.400	1.396	1.401	1.410
	C(8)–C(9)	1.532	1.533	1.532	1.532	1.53	1.530

TABLE XII: Individual SCAN-L bond lengths.

			Low-spin			High-spin	
	Bond	Arm 1	Arm 2	Arm 3	Arm 1	Arm 2	Arm 3
NWChem	Mn–N(1)	1.950	1.968	1.952	1.972	2.979	2.191
	Mn–N(7)	2.016	2.012	2.002	2.051	2.317	2.033
	Mn–N(10)		3.359			3.309	
	N(1)–C(2)	1.388	1.389	1.395	1.390	1.388	1.387
	N(1)–C(5)	1.351	1.344	1.346	1.348	1.355	1.342
	N(7)–C(6)	1.312	1.316	1.317	1.313	1.297	1.317
	N(7)–C(8)	1.451	1.452	1.453	1.454	1.444	1.455
	N(10)–C(9)	1.441	1.441	1.441	1.444	1.448	1.446
	C(2)–C(3)	1.403	1.410	1.407	1.405	1.400	1.413
	C(2)–C(6)	1.409	1.402	1.402	1.404	1.420	1.401
	C(3)–C(4)	1.403	1.395	1.396	1.399	1.404	1.393
	C(4)–C(5)	1.404	1.412	1.410	1.406	1.400	1.414
	C(8)–C(9)	1.536	1.537	1.536	1.535	1.536	1.533
VASP	Mn–N(1)	1.972	1.971	1.951	2.149	2.036	1.966
	Mn–N(7)	2.017	1.998	2.014	2.083	2.031	2.247
	Mn–N(10)		3.404			3.364	
	N(1)–C(2)	1.390	1.394	1.397	1.387	1.393	1.392
	N(1)–C(5)	1.353	1.345	1.350	1.344	1.351	1.359
	N(7)–C(6)	1.313	1.319	1.317	1.316	1.316	1.299
	N(7)–C(8)	1.453	1.455	1.456	1.457	1.457	1.446
	N(10)–C(9)	1.443	1.443	1.442	1.447	1.445	1.449
	C(2)–C(3)	1.403	1.410	1.404	1.413	1.406	1.400
	C(2)–C(6)	1.407	1.400	1.402	1.406	1.400	1.417
	C(3)–C(4)	1.401	1.394	1.399	1.396	1.397	1.405
	C(4)–C(5)	1.407	1.415	1.408	1.412	1.410	1.401
	C(8)–C(9)	1.541	1.542	1.539	1.540	1.538	1.540

TABLE XIII: Individual r^{2}SCAN bond lengths.

			Low-spin			High-spin	
	Bond	Arm 1	Arm 2	Arm 3	Arm 1	Arm 2	Arm 3
NWChem	Mn–N(1)	1.956	1.974	1.957	1.985	1.991	2.202
	Mn–N(7)	2.023	2.023	2.009	2.067	2.318	2.046
	Mn–N(10)		3.379			3.346	
	N(1)–C(2)	1.382	1.382	1.387	1.383	1.381	1.380
	N(1)–C(5)	1.345	1.339	1.340	1.342	1.349	1.337
	N(7)–C(6)	1.305	1.308	1.311	1.306	1.291	1.310
	N(7)–C(8)	1.445	1.445	1.446	1.447	1.437	1.448
	N(10)–C(9)	1.436	1.436	1.436	1.438	1.442	1.440
	C(2)–C(3)	1.400	1.406	1.405	1.402	1.399	1.410
	C(2)–C(6)	1.408	1.402	1.401	1.404	1.419	1.401
	C(3)–C(4)	1.400	1.393	1.394	1.396	1.401	1.390
	C(4)–C(5)	1.402	1.409	1.408	1.404	1.398	1.412
	C(8)–C(9)	1.536	1.537	1.536	1.535	1.536	1.533
VASP	Mn–N(1)	1.954	1.955	1.972	1.978	1.989	2.189
	Mn–N(7)	2.004	2.021	2.02	2.066	2.331	2.037
	Mn–N(10)		3.404			3.394	
	N(1)–C(2)	1.390	1.384	1.385	1.386	1.383	1.383
	N(1)–C(5)	1.343	1.347	1.341	1.344	1.351	1.339
	N(7)–C(6)	1.314	1.308	1.311	1.308	1.293	1.313
	N(7)–C(8)	1.448	1.447	1.447	1.449	1.439	1.451
	N(10)–C(9)	1.438	1.438	1.438	1.440	1.444	1.441
	C(2)–C(3)	1.406	1.402	1.408	1.403	1.400	1.412
	C(2)–C(6)	1.401	1.409	1.402	1.406	1.421	1.402
	C(3)–C(4)	1.395	1.401	1.394	1.398	1.403	1.392
	C(4)–C(5)	1.409	1.403	1.410	1.404	1.399	1.413
	C(8)–C(9)	1.537	1.537	1.538	1.537	1.538	1.536

TABLE XIV: Individual r^{2}SCAN-L bond lengths.

			Low-spin			High-spin	
	Bond	Arm 1	Arm 2	Arm 3	Arm 1	Arm 2	Arm 3
NWChem	Mn–N(1)	1.951	1.97	1.953	1.982	2.196	1.977
	Mn–N(7)	2.018	2.015	2.004	2.321	2.038	2.058
	Mn–N(10)		3.369			3.322	
	N(1)–C(2)	1.387	1.388	1.393	1.386	1.385	1.389
	N(1)–C(5)	1.350	1.343	1.345	1.354	1.341	1.347
	N(7)–C(6)	1.311	1.315	1.317	1.296	1.316	1.311
	N(7)–C(8)	1.449	1.449	1.451	1.442	1.453	1.451
	N(10)–C(9)	1.439	1.439	1.440	1.446	1.444	1.442
	C(2)–C(3)	1.403	1.410	1.407	1.401	1.413	1.405
	C(2)–C(6)	1.409	1.402	1.402	1.42	1.401	1.404
	C(3)–C(4)	1.402	1.395	1.396	1.404	1.392	1.399
	C(4)–C(5)	1.404	1.412	1.41	1.400	1.414	1.406
	C(8)–C(9)	1.538	1.539	1.538	1.538	1.534	1.536
VASP	Mn–N(1)	1.956	1.954	1.972	1.974	1.985	2.186
	Mn–N(7)	2.002	2.017	2.019	2.062	2.328	2.032
	Mn–N(10)		3.400			3.389	
	N(1)–C(2)	1.396	1.39	1.389	1.391	1.388	1.388
	N(1)–C(5)	1.345	1.352	1.345	1.349	1.357	1.343
	N(7)–C(6)	1.319	1.312	1.315	1.312	1.297	1.317
	N(7)–C(8)	1.453	1.452	1.451	1.453	1.444	1.456
	N(10)–C(9)	1.441	1.441	1.440	1.443	1.447	1.444
	C(2)–C(3)	1.409	1.403	1.410	1.404	1.401	1.413
	C(2)–C(6)	1.402	1.410	1.404	1.406	1.422	1.403
	C(3)–C(4)	1.397	1.404	1.397	1.401	1.406	1.394
	C(4)–C(5)	1.412	1.405	1.412	1.406	1.401	1.415
	C(8)–C(9)	1.540	1.540	1.541	1.539	1.54	1.537

TABLE XV: Average bond length deviation (Å) with respect to experiment obtained with PBE.

	Low-spin					High-spin				
	Ref.	VASP	deMon2k	NWChem	Gaussian	Ref.	VASP	deMon2k	NWChem	Gaussian
Mn–N(1)	1.975	−0.004	+0.001	−0.001	−0.002	2.054	+0.009	+0.014	+0.016	+0.017
Mn–N(7)	2.027	−0.007	−0.004	−0.003	−0.003	2.121	+0.044	+0.040	+0.043	+0.042
Mn–N(10)	3.284	+0.190	+0.199	+0.174	+0.176	3.241	+0.222	+0.226	+0.195	+0.197
N(1)–C(2)	1.388	+0.005	+0.004	+0.003		1.385	+0.004	+0.004	+0.003	
N(1)–C(5)	1.351	−0.001	−0.002	−0.002		1.343	+0.008	+0.007	+0.007	
N(7)–C(6)	1.299	+0.019	+0.018	+0.018		1.295	+0.016	+0.015	+0.015	
N(7)–C(8)	1.469	−0.018	−0.020	−0.019		1.464	−0.015	−0.017	−0.016	
N(10)–C(9)	1.443	−0.002	−0.003	−0.003		1.452	−0.008	−0.009	−0.009	

TABLE XVI: Average bond length deviation (Å) with respect to experiment obtained with SCAN.

	Low-spin				High-spin			
	Ref.	VASP	deMon2k	NWChem	Ref.	VASP	deMon2k	NWChem
Mn–N(1)	1.975	−0.022	−0.014	−0.013	2.054	−0.008	−0.002	−0.005
Mn–N(7)	2.027	−0.016	−0.012	−0.009	2.121	+0.019	+0.018	+0.019
Mn–N(10)	3.284	+0.145	+0.118	+0.097	3.241	+0.172	+0.134	+0.068
N(1)–C(2)	1.388	−0.004	−0.006	−0.005	1.385	−0.003	−0.004	−0.004
N(1)–C(5)	1.351	−0.010	−0.012	−0.011	1.343	0.000	−0.001	−0.001
N(7)–C(6)	1.299	+0.009	+0.006	+0.008	1.295	+0.006	+0.005	+0.005
N(7)–C(8)	1.469	−0.024	−0.027	−0.025	1.464	−0.020	−0.022	−0.023
N(10)–C(9)	1.443	−0.008	−0.009	−0.008	1.452	−0.014	−0.015	−0.012

TABLE XVII: Average bond length deviation (Å) with respect to experiment obtained with SCAN-L.

	Low-spin				High-spin			
	Ref.	VASP	deMon2k	NWChem	Ref.	VASP	deMon2k	NWChem
Mn–N(1)	1.975	−0.010	−0.015	−0.018	2.054	−0.004	−0.006	−0.007
Mn–N(7)	2.027	−0.017	−0.018	−0.017	2.121	−0.001	+0.011	+0.013
Mn–N(10)	3.284	+0.101	+0.089	+0.075	3.241	+0.123	+0.102	+0.068
N(1)–C(2)	1.388	+0.006	+0.003	+0.003	1.385	+0.006	+0.002	+0.003
N(1)–C(5)	1.351	−0.002	−0.005	−0.004	1.343	+0.008	+0.005	+0.006
N(7)–C(6)	1.299	+0.017	+0.015	+0.016	1.295	+0.015	+0.013	+0.014
N(7)–C(8)	1.469	−0.014	−0.019	−0.017	1.464	−0.011	−0.014	−0.013
N(10)–C(9)	1.443	0.000	−0.003	−0.002	1.452	−0.005	−0.008	−0.006

TABLE XVIII: Similarity indices

DFA	LS	HS
PBE	0.930	0.842
SCAN	0.919	0.844
SCAN-L	0.927	0.812
r^2SCAN	0.930	0.848
r^2SCAN-L	0.926	0.818
SCAN-D3(BJ)	0.920	0.845
TPSSh[a]	0.936	0.900
TPSSh-D3(BJ)[b]	0.921	0.850
JACS[c]	NA	0.924
PRB[d]	1.000	1.000

[a] Reference [18]

[b] Reference [19]

[c] Reference [1]

[d] Reference [2]

[1] P. G. Sim and E. Sinn, J. Am. Chem. Soc. **103**, 241 (1981).

[2] P. Guionneau, M. Marchivie, Y. Garcia, J. A. K. Howard, and D. Chasseau, Phys. Rev. B **72**, 214408 (2005).

[3] Y. Otsuki, S. Kimura, S. Awaji, and M. Nakano, AIP Advances **9**, 85219 (2019).

[4] M. Nakano, G. Matsubayashi, and T. Matsuo, Adv. Quantum Chem. **44**, 617 (2003).

[5] J.-X. Yu, D.-T. Chen, J. Gu, J. Chen, J. Jiang, L. Zhang, , X. Zhang, Y. Yu, V. S. Zapf, and H.-P. Cheng, Phys. Rev. Lett. **124**, 227201 (2020).

[6] A. M. Köster, G. Geudtner, A. Alvarez-Ibarra, P. Calaminici, M. E. Casida, J. Carmona-Espíndola, V. D. Dominguez, R. Flores-Moreno, G. U. Gamboa, A. Goursot, A. Ipatov, T. Heine, A. de la Lande, F. Janetzko, J. M. del Campo, D. Mejía-Rodríguez, J. U. Reveles, J. Vasquez-Perez, A. Vela, B. Zuniga-Gutierrez, and D. R. Salahub, The deMon developers, Cinvestav, Mexico City (2018).

[7] B. Dunlap, J. Conolly, and J. Sabin, J. Chem. Phys. **71**, 3396 (1979).

[8] P. Calaminici, F. Janetzko, A. M. Köster, R. Mejía-Olvera, and B. Zuniga-Gutierrez, J. Chem. Phys. **126**, 044108 (2007).

[9] F. Weigend, Phys. Chem. Chem. Phys. **8**, 1057 (2006).

[10] M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, Sonnenberg, J. L. Hada, and F. D. J., Gaussian, Inc., Wallingford, CT, 2009 (1988).

[11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[12] J. G. Brandenburg, J. E. Bates, J. Sun, and J. P. Perdew, Phys. Rev. B **94**, 115144 (2016).

[13] V. Lebedev, Zh. Vychisl. Mat. Mat. Fix. **15**, 48 (1975).

[14] V. Lebedev, Zh. Vychisl. Mat. Mat. Fix. **16**, 293 (1976).

[15] V. Lebedev, Sibirsk. Mat. Zh. **18**, 132 (1977).

[16] V. Lebedev and D. Laikov, Dokl. Math. **366**, 741 (1999).

[17] J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, and J. Sun, J. Phys. Chem. Lett. **11**, 8208 (2020).

[18] J. Cirera, M. Via Nadal, and E. Ruiz, Inorg. Chem. **57**, 14097 (2018).

[19] S. Amabilino and R. J. Deeth, Inorg. Chem. **56**, 2602 (2017).

[20] J. Vásquez-Pérez, G. U. Gamboa Martínez, A. M. Köster, and P. Calaminici, J. Chem. Phys. **131**, 124126 (2009).