

AM1* parameters for manganese and iron

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Abstract We report the parameterization of AM1* for the elements manganese and iron. The basis sets for both metals contain one set each of *s*-, *p*- and *d*-orbitals. AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Mo, I and Au. The performance and typical errors of AM1* are discussed for Mn and Fe, and are compared with available NDDO Hamiltonians.

Keywords AM1* · Iron parameters
Manganese parameters · Semiempirical MO theory

Introduction

We have introduced AM1* [1–7] as an extension of AM1 [8] that uses *d*-orbitals for the elements P, S, Cl, [1] Al, Si, Ti and Zr, [2] Cu and Zn, [3] Br and I, [4] V and Cr, [5] Co and Ni, [6] and Au [7]. The AM1* parameters that are available for molybdenum are a slight modification of Voityuk and Röscher's AM1(d) parameter set [9] to include the AM1* core-core parameters for interactions between Mo and new AM1* elements. The rationalization behind AM1* is to retain the

advantages of AM1 (good energies for hydrogen bonds, higher rotation barriers for π -systems than MNDO [10, 11] or PM3 [12–14]) for first-row elements, improved performance over AM1 for compounds that contain second-row and heavier elements, and to provide a published parameterization for an AM1-like method for the transition metals. As a continuation of this work, we now report AM1* parameters for manganese and iron. Both manganese and iron are important in the chemistry of organometallic and biological catalysts, and play a very important role in biochemical systems especially in the active sites of enzymes [15, 16].

Theory

AM1* for the two new elements uses the same basic theory as outlined previously [1, 2]. As for other element–H interactions, the core–core repulsion potential for the Mn–H and Fe–H interactions use a distance-dependent term δ_{ij} , rather than the constant term used for core–core potentials for most other interactions in AM1* [1]. This distance-dependent δ_{ij} was also used for the Mo–H and interaction in AM1(d) [9] and for Ti–H, V–H, Cr–H, Co–H, Ni–H, Cu–H, Zn–H, Br–H, Zr–H, Mo–H, I–H and Au–H in AM1* [2–7]. The core–core terms for Mn–H and Fe–H are thus:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + r_{ij} \delta_{ij} \exp(-\alpha_{ij} r_{ij})] \quad (1)$$

where all terms have the same meaning as given in reference [1].

The standard MNDO/d formula is used for all other core–core interactions:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + \delta_{ij} \exp(-\alpha_{ij} r_{ij})] \quad (2)$$

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The parameterization techniques were those reported in references [1] and [2] and will not be described further here.

Parameterization data

The target values used for parameterization and their sources are defined in Tables S1–S3 of the electronic supplementary material (ESM). We used heats of formation, Koopmans' theorem ionization potentials, dipole moments and geometrical variables as we did for the Ti, Zr, Cu, Zn, Br, I, V, Cr, Co, Ni and Au parameterizations [2–7]. Because the experimental data for heats of formation of compounds of these two metals are relatively sparse, we also extended our parameterization data using a small series of model compounds whose heats of formation we derived from DFT calculations. [17] As before [1–7], we checked that experimental values for heats of formation were reasonable using DFT calculations.

DFT calculations used the Gaussian 03 suite of programs [18] with the LANL2DZ basis set and standard effective core potentials [19–22] augmented by a set of polarization functions [23] (designated LANL2DZ+pol) and the B3LYP hybrid functional [24–26].

Experimental parameterization data for manganese and iron were taken largely from the NIST Webbook [27], but also from the OpenMopac collection [28]; other experimental and theoretical sources are given in Tables S1–S3.

The energetic parameterization data and their sources are given in Table S1 of the ESM. In addition to the energetic data, geometries, dipole moments and ionization potentials taken from the above sources, crystal structures from the Cambridge Structural Database (CSD) [29] were also used in the parameterization to ensure that not only the energetic and electronic properties for the “prototype” compounds, but also the structures of large manganese and iron compounds are well produced.

Results

Table 1 shows the optimized AM1* parameters. Geometries were optimized with the new AM1* parameterization using VAMP 10.0 [30], while PM5 calculations used LinMOPAC2.0 [31]. Since PM5 was not parameterized for manganese, it was used only for iron compounds. The calculations with PM6 used MOPAC2009 [32]. We give related errors for each property, i.e., heats of formation, ionization potentials, dipole moments, geometries as the mean unsigned error (MUE) and mean signed error (MSE). MUE is used to measure the scatter of the calculated results relative to the experimental values, whereas MSE indicates the direction of any systematic deviation of the predictions from experiment.

Manganese

Heats of formation

The calculated heats of formation for our training set of manganese compounds are shown in Table 2. We have compared our results with Stewart's published PM6 method [33].

AM1* reproduces the heats of formation for the training set of manganese compounds used in parameterization better than PM6. However, we note that this comparison is not strictly valid as it is based on the current parameterization data. As can be seen from Table 2, the AM1* parameterization data set contains 86 compounds, of which 44 are taken from the original PM6 parameterization data set. These data convincingly demonstrate the influence of the extent of the training data. AM1* performs significantly better for its extended training set, whereas PM6 performs better for the subset for which it was trained. This situation is unavoidable and is a direct consequence of the relative paucity of data for parameterizing semiempirical MO techniques for transition metals.

Both AM1* and PM6 tend to give positive systematic errors for manganese-containing compounds. For AM1* with a MSE of 2.3 kcal mol⁻¹, this tendency is less pronounced than for PM6 (MSE of 9.8 kcal mol⁻¹).

The MUE for the AM1* parameterization dataset is 32.3 kcal mol⁻¹, compared with 51.0 kcal mol⁻¹ for PM6. PM6 produces especially large errors for the compounds that were not included in its original training set.

The largest errors for AM1* are found mainly for Mn³⁺, Mn²⁺ and Mn⁺ (−167.3, 161.1 and 95.8 kcal mol⁻¹, respectively). Since the ionization potentials (and hence the heats of formation of the cations) of manganese are important determinants of the reactivity of manganese centres, these errors are important. However, we could not detect serious systematic trends caused by these errors. Molecules that give the largest positive errors for AM1* are MnF₃⁻ (113.7 kcal mol⁻¹), MnCl₂O (89.5 kcal mol⁻¹), MnF₂⁻ (79.5 kcal mol⁻¹), MnCl₂ (76.5 kcal mol⁻¹), MnF₂ (75.8 kcal mol⁻¹), MnC₇H₅SO₄ (Mn(Cp)(CO)₂(SO₂), CPCSMN,) (68.2 kcal mol⁻¹), MnO₂⁻ (59.1 kcal mol⁻¹), MnH (58.1 kcal mol⁻¹) and MnH⁻ (55.5 kcal mol⁻¹). The largest negative errors are found for MnC₇N₂H₁₂S₄⁻ (Mn(C₃N₂H₄)(C₂H₄S₂)₂⁻, COWHOL) (−141.9 kcal mol⁻¹), trans-Mn(H₂O)₄Cl₂ (−121.5 kcal mol⁻¹), MnZr (−93.2 kcal mol⁻¹), MnC₉H₁₂O (Mn(CO)(C₄H₆)₂, BUTMNC) (−65.5 kcal mol⁻¹), trans-Mn(H₂O)₄Br₂ (−61.2 kcal mol⁻¹) and MnF₅⁻ (−60.3 kcal mol⁻¹). AM1* uses the unchanged AM1 parameterization for the elements H, C, N, O and F, which limits the possible accuracy of the parameterization. The large errors with the compounds containing these elements are not surprising, as we have

Table 1 AM1* parameters for the elements Mn and Fe

Parameter	Mn	Fe
U _{ss} [eV]	-33.2275445	-99.00
U _{pp} [eV]	-27.2535784	-38.200
U _{dd} [eV]	-69.8244104	-83.10
ζ _s [bohr ⁻¹]	1.9646322	2.8351398
ζ _p [bohr ⁻¹]	18.8965365	37.1808614
ζ _d [bohr ⁻¹]	1.2348158	2.2895425
β _s [eV]	-8.1782339	-20.4335137
β _p [eV]	-21.7780791	-66.1689990
β _d [eV]	-6.2336234	-26.5282533
g _{ss} [eV]	5.0059282	8.4047951
g _{pp} [eV]	13.6386827	10.4447975
g _{sp} [eV]	12.3772691	7.6833614
g _{p2} [eV]	96.0815576	13.9440172
h _{sp} [eV]	4.5810741	1.6747978
z _{sn} [bohr ⁻¹]	26.0703955	75.1015032
z _{pn} [bohr ⁻¹]	1.9830213	0.7086051
z _{dn} [bohr ⁻¹]	1.9132012	1.4519328
ρ(core) [bohr ⁻¹]	1.2307875	1.0769040
ΔH _f ^o (atom) [kcal mol ⁻¹]	67.701	99.3
F _{sd} ⁰ [eV]	3.3270203	14.1017174
G _{sd} ² [eV]	1.8796412	13.4789419
α(ij)		
H	4.1317380	3.6162132
C	2.8147514	4.0432263
N	1.8883089	3.8755726
O	3.0560315	4.9080254
F	2.5828364	5.3397259
Al	3.5620838	2.0238999
Si	4.2623991	2.6259521
P	2.4072008	2.9339288
S	2.7156160	2.7835642
Cl	2.5923979	2.4937637
Ti	2.3993667	1.4496317
V	3.8190630	1.9484452
Cr	2.7010078	2.0835714
Mn	3.1647134	2.4029678
Fe	2.4029678	3.3225842
Co	2.2792673	2.6623880
Ni	4.5772694	4.4251916
Cu	2.2179615	4.1806484
Zn	4.5907029	4.4519730
Br	3.6890036	2.8134065
Zr	2.6907788	1.7761525
Mo	3.0996586	1.9309316
I	4.1561815	3.5275630
Au	3.0829513	2.8842586
δ(ij)		
H	-12.2571050	-10.2036220
C	3.8500280	41.7471647

Table 1 (continued)

Parameter	Mn	Fe
N	0.6216587	18.5709816
O	6.1303519	98.7945881
F	1.8592303	98.4859864
Al	32.1147597	4.4417867
Si	79.1063414	7.6467930
P	2.9611118	21.4786698
S	3.7385117	8.4757133
Cl	2.4354976	3.7093945
Ti	1.5477850	1.1499629
V	127.1273363	5.0747072
Cr	7.1369564	3.3205625
Mn	5.9226904	4.7319791
Fe	4.7319791	20.2552175
Co	2.1958330	8.1077071
Ni	265.4707317	178.9982694
Cu	1.8893296	96.7779734
Zn	87.3866849	52.0532649
Br	25.1186833	4.3023002
Zr	3.2445347	2.7554220
Mo	14.0341168	3.2515086
I	53.7439446	43.5771427
Au	10.1393842	7.0870550

pointed out in previous parameterizations [3–6]. As found for other metals, the large errors in pure AM1* element-containing compounds are likely to be a consequence of our sequential parameterization strategy, in contrast to the simultaneous parameterization used for PM6 [33].

Ionization potentials and dipole moments

A comparison of the calculated and experimental Koopmans’ theorem ionization potentials and dipole moments for AM1* and PM6 are given Table 3.

AM1* with an MUE of 1.66 eV performs better than PM6 (MUE of 2.07 eV) for Koopmans’ theorem ionization potentials. Both AM1* and PM6 tend to underestimate ionization potentials for manganese-containing compounds. However, this tendency is more serious for PM6 with an MSE of -2.02 eV, compared to the AM1* MSE of -0.77 eV.

Large AM1* errors are found for MnF₂ (-3.06 eV), MnF₃ (-4.00 eV) and MnF₄ (-3.88 eV). This may be an indirect result of using the original AM1 parameters for fluorine. However, PM6 also produces very large errors for MnF₂ (-2.84 eV), MnF₃ (-4.45 eV) and MnF₄ (-6.59 eV). Since both methods produce these large errors in the same direction, this may be result from possible erroneous reference values given in NIST [27].

Table 2 Calculated AM1* and PM6 heats of formation and errors compared with our target values for the manganese-containing compounds used to parameterize AM1* (all values kcal mol⁻¹). Errors are classified by coloring the boxes in which they appear. *Green*

Errors lower than 10 kcal mol⁻¹, *yellow* 10–20 kcal mol⁻¹, *pink* greater than 20 kcal mol⁻¹. The codenames within parentheses indicate the Cambridge Structural Database (CSD)-names of the compounds

Compound	Target ΔH_f	AM1*		PM6	
		ΔH_f	Error	ΔH_f	Error
Mn	67.7	67.7	0.0	67.7	0.0
Mn ⁻	90.2	151.8	61.6	97.9	7.7
Mn ⁺	239.1	334.9	95.8	224.8	-14.3
Mn ²⁺	599.8	760.9	161.1	566.7	-33.1
Mn ³⁺	1376.0	1208.7	-167.3	1053.2	-322.8
Mn ₂	184.3	203.7	19.4	128.2	-56.1
MnH	57.3	115.4	58.1	114.2	56.9
MnH ⁻	41.2	96.7	55.5	124.2	83.0
MnH ₂	114.1	117.0	2.9	114.6	0.5
Mn(C ₅ H ₅) ₂	66.2	100.8	34.6	95.4	29.2
MnN	123.1	121.1	-2.0	99.2	-23.9
Mn(NH ₃) ₆ ²⁺	269.5	275.4	5.9	229.9	-39.6
MnO ₂ ⁻	-62.1	-3.0	59.1	-35.3	26.8
MnO ₃ ⁻	-127.1	-97.5	29.6	-127.7	-0.6
MnO ₄ ⁻	-158.4	-149.7	8.7	-168.8	-10.4
Mn(H ₂ O) ₆ ²⁺	65.7	9.6	-56.1	50.6	-15.1
Mn(CO) ₃ ⁻	-54.8	-58.6	-3.8	-113.0	-58.1
Mn(CO) ₄ ⁻	-122.3	-131.1	-8.7	-157.7	-35.3
Mn(CO) ₅	-178.0	-152.9	25.1	-174.4	3.6
Mn(CO) ₅ H	-176.8	-180.2	-3.4	-170.4	6.4
Mn(CO) ₆ ⁺	-49.7	-67.8	-18.1	-78.8	-29.1
Mn(CO) ₅ CH ₃	-179.5	-196.5	-17.0	-179.5	0.0
Mn(CO) ₅ C ₆ H ₅	-140.8	-169.9	-29.1	-151.3	-10.5
Mn(CO) ₅ (C ₆ H ₅ CH ₂)	-151.9	-173.7	-21.8	-154.6	-2.7
Mn(CO) ₅ COCH ₃	-215.3	-228.5	-13.2	-230.3	-15.0
Mn(CO) ₅ (C ₆ H ₅ CO)	-173.2	-195.1	-21.9	-192.3	-19.1
MnC ₁₅ H ₂₁ O ₆ (Mn(acac) ₃)	-285.2	-280.0	5.2	-267.2	18.0
MnC ₆ H ₈ O ₁₀ ⁻ (KAMMND)	-543.1	-576.9	-33.8	-537.4	5.7
MnC ₉ H ₁₂ O (BUTMNC)	11.9	-53.6	-65.5	22.8	10.9
MnC ₈ H ₅ O ₃ (cyclopentadienyl manganese tricarbonyl)	-115.2	-65.3	49.9	-81.5	33.7
MnC ₉ H ₇ O ₃ (HEXMNC)	-95.5	-89.4	6.1	-83.9	11.6
Mn ₂ (CO) ₉	-314.5	-310.0	4.5	-323.3	-8.8
Mn ₂ (CO) ₁₀	-385.9	-378.7	7.2	-336.8	49.1
Mn(NO)	8.5	47.9	39.4	98.1	89.6
Mn(CO)(NO) ₃	-60.6	-52.9	7.7	-23.0	37.6
MnC ₁₀ N ₂ H ₁₂ O ₈ ⁻ (EDTMNK01)	-388.3	-407.0	-18.7	-413.1	-24.8
MnF ₂	-126.2	-50.4	75.8	-76.8	49.4
MnF ₂ ⁻	-226.0	-146.5	79.5	-106.1	119.9
MnF ₃	-188.0	-173.3	14.7	-139.0	49.0
MnF ₃ ⁻	-272.2	-158.5	113.7	-164.8	107.4
MnF ₄	-231.0	-280.9	-49.9	-170.0	61.0
MnF ₄ ⁻	-343.6	-308.5	35.1	-250.3	93.3
MnF ₅ ⁻	-373.0	-433.3	-60.3	-300.3	72.7
Mn ₂ F ₅ ⁻	-448.3	-440.7	7.6	-257.2	191.1
Mn ₂ F ₇ ⁻	-600.0	-630.6	-30.6	-392.6	207.4
MnOF ₂	-125.8	-120.5	5.3	-114.7	11.1
Mn(H ₂ O) ₄ F ₂ trans	-333.2	-366.8	-33.6	-315.4	17.8
MnC ₇ HO ₅ F ₂ (CDFVMN)	-252.2	-273.1	-20.9	-314.4	-62.2
Mn(CO) ₅ CF ₃	-330.5	-355.7	-25.2	-363.7	-33.2

Table 3 Calculated AM1* and PM6 Koopmans' theorem ionization potentials and dipole moments for manganese-containing compounds. The errors are color-coded as follows: *green* up to 0.5 eV or 0.5 Debye; *yellow* between 0.5 and 1.0; *pink* larger than 1.0

Compound	Target	AM1*		PM6	
			Error		Error
Koopmans' Theorem Ionization Potentials for Manganese Compounds (eV)					
MnH	7.80	9.39	1.59	5.82	-1.98
MnO	8.70	10.58	1.88	7.66	-1.04
Mn(CO) ₅	8.10	9.18	1.08	7.44	-0.66
Mn(CO) ₅ H	8.85	8.71	-0.14	8.44	-0.41
MnF ₂	11.40	8.34	-3.06	8.56	-2.84
MnF ₃	12.60	8.60	-4.00	8.15	-4.45
MnF ₄	13.50	9.62	-3.88	6.91	-6.59
MnCl ₂	11.03	9.67	-1.36	8.11	-2.92
Mn(CO) ₅ Br	8.83	8.52	-0.31	8.74	-0.09
MnBr ₂	10.30	9.70	-0.60	8.78	-1.52
Mn(CO) ₅ I	8.40	8.71	0.31	8.65	0.25
		AM1*		PM6	
N=11					
MSE		-0.77		-2.02	
MUE		1.66		2.07	
Dipole Moments for Manganese Compounds (Debye)					
MnH	0.50	0.75	0.25	0.99	0.49
MnN	3.07	4.38	1.31	3.98	0.91
MnNO	5.89	4.46	-1.43	4.45	-1.44
MnO	4.72	4.57	-0.15	3.74	-0.98
MnOH	0.40	1.64	1.24	3.13	2.73
MnF	2.27	0.67	-1.60	4.23	1.96
MnOF ₂	0.53	4.56	4.03	0.61	0.08
MnAl	1.67	1.60	-0.07	0.19	-1.48
MnSi	3.27	2.85	-0.42	4.03	0.76
MnSiH	3.15	2.75	-0.40	4.03	0.88
MnSiH ₂	3.22	2.54	-0.68	3.96	0.74
MnP	2.54	2.88	0.34	2.70	0.16
MnPH	4.34	3.12	-1.22	2.97	-1.37
MnS	4.22	3.91	-0.31	1.56	-2.66
MnCl	2.36	0.81	-1.55	3.59	1.23
MnBr	4.29	3.10	-1.19	7.72	3.43
MnOBr ₂	0.51	2.12	1.61	0.56	0.05
MnI	4.25	1.68	-2.57	2.13	-2.12
MnOI ₂	0.94	4.30	3.36	0.30	-0.64
		AM1*		PM6	
N=19					
MSE		0.03		0.14	
MUE		1.25		1.27	

AM1* with an MSE of 0.03 Debye shows no significant tendency to systematic errors for dipole moments of manganese compounds, whereas PM6 gives a positive systematic error of 0.14 Debye (MSE). AM1* and PM6 perform comparably, with MUEs of 1.25 and

1.27 Debye, respectively. The largest AM1* errors are found for MnOF₂ (4.03 Debye), MnOI₂ (3.36 Debye) and MnI (-2.57 Debye). The large error for MnOF₂ may be an indirect result of using original AM1 parameters for oxygen and fluorine. However, the large errors for iodine-

Table 4 Calculated AM1* and PM6 bond lengths and angles for manganese-containing compounds. The codenames within parentheses indicate the CSD-names of the compounds. The errors are color-coded as follows: *green* up to 0.05 Å or 0.5°; *yellow* between 0.05–0.1 Å or 0.5–1.0°; *pink* larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*		PM6	
				Error		Error
Mn ₂	Mn-Mn	2.29	2.40	0.11	2.89	0.60
MnH	Mn-H	1.74	1.91	0.18	1.68	-0.05
MnH ⁻	Mn-H	1.77	1.83	0.06	1.66	-0.11
Mn(C ₅ H ₅) ₂	Mn-C	2.42	2.79	0.37	2.37	-0.05
MnO ₂ ⁻	Mn-O	1.62	1.86	0.24	1.63	0.02
MnO ₃ ⁻	Mn-O	1.59	1.85	0.26	1.62	0.03
MnO ₄ ⁻	Mn-O	1.64	1.86	0.22	1.63	-0.01
Mn(H ₂ O) ₆ ²⁺	Mn-O	2.14	2.21	0.07	2.15	0.01
	Mn-O	2.19	2.23	0.04	2.17	-0.02
	Mn-O	2.20	2.27	0.07	2.17	-0.03
Mn(CH ₃)O ₃	Mn=O	1.59	1.84	0.25	1.60	0.01
	Mn-C	1.99	1.91	-0.08	1.93	-0.06
Mn(CO) ₃ ⁻	Mn-C	1.82	1.97	0.16	1.82	0.01
Mn(CO) ₅	Mn-C	1.82	1.89	0.07	1.85	0.03
	Mn-C	1.86	1.90	0.04	1.89	0.03
Mn(CO) ₅ H	Mn-C	1.86	1.93	0.07	1.84	-0.02
	Mn-C	1.85	1.92	0.07	1.86	0.01
	H-Mn-C	85.5	90.7	5.2	83.5	-2.0
Mn(CO) ₅ CH ₃	Mn-C	1.83	1.90	0.07	1.85	0.02
	Mn-C	1.85	1.94	0.09	1.85	0.00
	Mn-C	2.19	1.99	-0.21	2.08	-0.12
Mn(CO) ₆ ⁺	Mn-C	1.91	1.95	0.04	1.89	-0.02
	Mn(CO) ₅ C ₆ H ₅	Mn-C	1.83	1.90	0.07	1.85
	Mn-C	1.85	1.94	0.09	1.86	0.01
	Mn-C	2.15	1.99	-0.16	1.99	-0.16
Mn(CO) ₅ (C ₆ H ₅ CH ₂)	Mn-C	1.82	1.90	0.08	1.85	0.03
	Mn-C	1.85	1.94	0.09	1.85	0.00
	Mn-C	2.26	2.02	-0.24	2.09	-0.17
Mn(CO) ₅ COCH ₃	Mn-C	1.84	1.91	0.07	1.85	0.01
	Mn-C	1.85	1.93	0.08	1.88	0.03
	Mn-C	2.17	2.02	-0.15	1.97	-0.20
Mn(CO) ₅ (C ₆ H ₅ CO)	Mn-C	1.84	1.90	0.07	1.86	0.02
	Mn-C	1.85	1.93	0.08	1.87	0.02
	Mn-C	2.18	2.03	-0.15	1.97	-0.20
MnC ₆ H ₈ O ₁₀ ⁻ (KAMMND)	Mn-O	1.90	2.07	0.17	1.93	0.03
	Mn-O	2.30	2.28	-0.02	2.44	0.14
	O-Mn-O	91.7	74.1	-17.6	88.3	-3.4
MnC ₉ H ₁₂ O (BUTMNC)	Mn-C	1.81	1.92	0.11	1.81	0.00
	Mn-C	2.15	1.98	-0.17	2.11	-0.04
Mn(CO) ₃ Cp (CPMNCO)	Mn-C(ring)	2.14	2.21	0.07	2.16	0.02
	Mn-C(O)	1.79	1.93	0.14	1.81	0.02
	C-Mn-C	91.4	101.0	9.6	92.6	1.2
MnC ₉ H ₇ O ₃ (HEXMNC)	Mn-C	2.15	2.12	-0.03	2.17	0.02
	Mn-C	1.78	1.92	0.14	1.82	0.04
Mn ₂ C ₈ H ₁₂ O ₈ (Mn ₂ (Ac) ₄)	Mn-Mn	3.31	2.43	-0.88	3.28	-0.03
Mn ₂ (CO) ₁₀	Mn-Mn	2.89	2.36	-0.53	2.70	-0.19
Mn ₂ (CO) ₁₀ C ₂ (JIPVOT)	Mn-C	1.86	1.93	0.07	1.84	-0.02
	Mn-C	1.83	1.90	0.07	1.83	0.00
	C-Mn-C	85.9	87.6	1.7	85.4	-0.5

Table 4 (continued)

Compound	Variable	Target	AM1*		PM6	
				Error		Error
MnN	Mn#N	1.59	1.52	-0.07	1.57	-0.02
MnNO	Mn-N	1.73	1.76	0.03	1.74	0.01
Mn(NH ₃) ₆ ²⁺	Mn-N	2.16	2.21	0.05	2.15	-0.01
Mn(CO)(NO) ₃	Mn-N	1.70	1.67	-0.03	1.64	-0.06
	Mn-C	1.87	1.94	0.06	1.93	0.06
	C-Mn-N	106.0	92.9	-13.1	107.7	1.8
MnC ₁₀ N ₂ H ₁₂ O ₈ ⁻ (EDTMNK01)	Mn-O	2.02	2.15	0.13	1.95	-0.07
	Mn-O	1.89	2.16	0.27	1.98	0.09
	Mn-N	2.24	2.11	-0.13	2.10	-0.14
	O-Mn-O	88.3	89.7	1.4	84.2	-4.1
	N-Mn-O	77.5	82.2	4.7	83.7	6.2
MnC ₁₂ N ₂ H ₁₂ O ₆ (XOYHAU)	Mn-O	2.15	2.19	0.04	2.33	0.18
	Mn-N	2.26	1.81	-0.45	1.84	-0.42
	O-Mn-O	85.4	66.7	-18.7	62.5	-22.9
MnC ₁₂ N ₂ H ₁₆ O ₄ (Mn phenanthroline tetrahydrate)	Mn-O	2.16	2.33	0.17	3.45	1.29
MnF	Mn-F	1.82	2.14	0.32	1.87	0.05
MnF ₂	Mn-F	1.79	1.84	0.05	1.78	-0.01
MnF ₂ ⁻	Mn-F	1.86	1.88	0.03	1.83	-0.03
MnOF ₂	Mn-O	1.55	1.89	0.34	1.57	0.02
	Mn-F	1.72	1.79	0.06	1.73	0.01
	O-Mn-F	121.3	102.0	-19.3	124.1	2.8
Mn(H ₂ O) ₄ F ₂ trans	Mn-F	1.98	1.87	-0.11	1.78	-0.20
	Mn-O	2.13	2.35	0.22	2.34	0.21
MnC ₇ HO ₅ F ₂ (CDFVMN)	Mn-C	1.72	1.90	0.18	1.85	0.13
	Mn-C	1.77	1.94	0.17	1.86	0.09
	Mn-C	1.94	2.03	0.09	1.97	0.03
	C-Mn-C	93.8	87.6	-6.2	93.3	-0.5
MnF ₃	Mn-F	1.79	1.79	0.00	1.76	-0.03
	F-Mn-F	120.0	141.7	21.7	136.1	16.1
MnC ₇ O ₇ F ₃ (FACMNA)	Mn-C	1.81	1.89	0.08	1.82	0.01
	Mn-O	2.03	2.29	0.26	2.05	0.02
Mn ₂ (CO) ₈ (CF ₂) ₂ (DOFPET)	Mn-Mn	2.66	2.42	-0.24	2.73	0.07
	Mn-C(F ₂)	2.02	2.10	0.08	1.98	-0.04
	Mn-C(O)	1.88	1.96	0.08	1.87	-0.01
	C-Mn-Mn	49.4	54.8	5.4	46.4	-3.0
MnAl	Mn-Al	2.34	2.34	0.00	2.05	-0.28
Mn(AlH ₂) ₂	Mn-Al	2.41	2.42	0.00	2.15	-0.26
MnSi	Mn-Si	2.34	2.25	-0.10	2.45	0.11
MnSiH	Mn-Si	2.34	2.34	0.00	2.51	0.17
MnSiH ₂	Mn-Si	2.38	2.44	0.06	2.60	0.22
MnSi ₂ C ₉ H ₁₅ O ₅ (KIRYUF)	Mn-Si	2.34	2.39	0.05	2.34	0.00
	Mn-O	2.95	2.99	0.04	2.99	0.04
	Si-Mn-Si	71.2	81.5	10.3	68.8	-2.4
MnP	Mn-P	1.97	2.06	0.09	2.15	0.18
MnPH	Mn-P	2.22	2.21	-0.02	2.23	0.01
MnS	Mn-S	1.99	2.14	0.15	2.01	0.02
MnS ₂	Mn-S	2.20	2.00	-0.20	2.02	-0.18
MnC ₉ H ₁₁ SO ₂ (VALXAI)	Mn-S	2.27	2.25	-0.02	2.18	-0.09
	Mn-C(O)	1.77	2.01	0.24	1.79	0.02
	Mn-C(C ₄)	2.12	2.10	-0.02	2.19	0.07
MnC ₇ H ₅ SO ₄ (CPCSMN)	Mn-S	2.04	2.38	0.34	2.10	0.06
	Mn-C	1.79	1.99	0.20	1.82	0.03
	Mn-C'	2.10	2.10	0.00	2.18	0.08

Table 4 (continued)

Compound	Variable	Target	AM1*		PM6	
				Error		Error
	S-Mn-C	91.0	80.8	-10.1	92.6	1.6
MnC ₇ N ₂ H ₁₂ S ₄ ⁻ (COWHOL)	Mn-S	2.32	2.33	0.01	2.28	-0.04
	S-Mn-S	157.5	144.9	-12.6	156.2	-1.3
MnC ₇ H ₁₀ S ₂ ClO ₃ (GEQLUJ)	Mn-S	2.39	2.35	-0.04	2.26	-0.13
	Mn-C	1.80	1.92	0.12	1.79	-0.01
	Mn-Cl	2.38	2.17	-0.21	2.31	-0.07
	S-Mn-Cl	92.2	87.7	-4.5	88.6	-3.6
MnC ₄ N ₂ H ₈ S ₂ O ₆ (WIFSEJ)	Mn-S	2.61	2.26	-0.35	2.21	-0.40
	Mn-O	2.20	2.23	0.03	2.13	-0.07
	O-Mn-S	87.3	111.8	24.5	80.6	-6.7
MnCl	Mn-Cl	2.12	2.31	0.19	2.13	0.01
Mn(CO) ₅ Cl (ZOSWEJ)	Mn-Cl	2.37	2.13	-0.24	2.23	-0.14
	Mn-C	1.81	1.91	0.10	1.83	0.02
	Mn-C	1.89	1.94	0.05	1.86	-0.03
Mn(H ₂ O) ₄ Cl ₂ trans	Mn-Cl	2.36	2.21	-0.15	1.98	-0.38
	Mn-O	2.10	2.33	0.23	2.21	0.11
	Mn-O	2.50	2.41	-0.09	3.70	1.20
	Mn-O	2.52	2.59	0.07	3.79	1.27
Mn ₂ Cl ₄	Mn-Mn	2.29	2.38	0.09	2.49	0.20
	Mn-Cl	2.13	2.10	-0.03	1.96	-0.18
MnCl ₂ O	Mn-O	1.55	1.89	0.34	1.57	0.02
	Mn-Cl	2.10	2.08	-0.02	1.87	-0.23
	O-Mn-Cl	121.5	86.3	-35.1	119.1	-2.3
MnC ₁₂ N ₄ H ₁₂ Cl ₂ O (MUPYUR)	Mn-Cl	2.47	2.12	-0.35	2.15	-0.32
	Mn-N(py)	2.26	1.81	-0.45	1.92	-0.34
	Mn-N'	2.34	1.94	-0.40	1.94	-0.40
	N-Mn-N'	95.2	96.2	1.0	94.7	-0.5
MnTi	Mn-Ti	2.25	2.25	0.00	3.62	1.37
MnV ₂	Mn-V	2.28	2.21	-0.07	4.90	2.62
MnCr	Mn-Cr	2.35	2.35	0.00	5.90	3.55
MnCo	Mn-Co	2.44	2.27	-0.18	3.39	0.95
MnNi	Mn-Ni	2.50	2.41	-0.08	6.02	3.52
MnCu	Mn-Cu	2.50	2.50	0.00	7.67	5.17
MnZn	Mn-Zn	2.62	2.62	0.00	2.29	-0.33
MnBr	Mn-Br	2.25	2.41	0.16	2.56	0.31
MnBr ₂	Mn-Br	2.34	2.33	-0.01	2.23	-0.11
MnOBr ₂	Mn-Br	2.24	2.29	0.05	2.31	0.07
	Mn-O	1.55	1.88	0.33	1.56	0.01
	O-Mn-Br	120.7	104.2	-16.5	125.5	4.8
Mn(H ₂ O) ₄ Br ₂ trans	Mn-Br	2.50	2.40	-0.10	2.45	-0.05
	Mn-O	2.10	2.23	0.13	2.08	-0.02
Mn(CO) ₅ Br	Mn-Br	2.56	2.39	-0.17	2.49	-0.07
	Mn-C	1.82	1.90	0.09	1.82	0.01
	Mn-C'	1.88	1.94	0.07	1.86	-0.01
MnBr ₄ ²⁻ (PYDMNB)	Mn-Br	2.50	2.43	-0.07	2.44	-0.06
MnAlC ₆ Br ₃ O ₅ (CMNCXA10)	Mn-Al	3.53	3.63	0.10	3.45	-0.08
	Mn-C	1.95	1.97	0.02	1.92	-0.03
	Mn-C'	1.87	1.93	0.06	1.87	0.00
	Br-Al-Mn	140.2	117.0	-23.2	126.9	-13.3
MnZr	Mn-Zr	2.43	2.43	0.00	3.02	0.59
MnMo	Mn-Mo	2.27	2.27	0.00	4.71	2.44
MnI	Mn-I	2.46	2.49	0.04	2.29	-0.17

Table 4 (continued)

Compound	Variable	Target	AM1*		PM6	
				Error		Error
MnO ₂	Mn-I	2.45	2.33	-0.12	2.44	-0.01
	Mn-O	1.55	1.89	0.34	1.55	0.00
	O-Mn-I	120.1	112.7	-7.4	116.1	-4.0
Mn(H ₂ O) ₄ I ₂ trans	Mn-I	2.73	2.44	-0.29	2.52	-0.21
	Mn-O	2.08	2.27	0.19	2.24	0.16
Mn(CO) ₅ I (VUCFAA)	Mn-I	2.69	2.39	-0.30	2.62	-0.07
	Mn-C	1.84	1.91	0.07	1.82	-0.02
MnC ₁₃ N ₂ H ₈ O ₃ I (YOMHEN)	Mn-I	2.72	2.36	-0.36	2.70	-0.02
	Mn-N	2.05	1.98	-0.07	1.92	-0.13
	Mn-C	1.77	1.93	0.16	1.84	0.07
	I-Mn-N	87.7	87.1	-0.6	83.3	-4.4
Mn ₂ (CO) ₈ I ₂ (SIZYUV)	Mn-Mn	3.98	3.98	0.00	3.96	-0.02
	Mn-I	2.70	2.51	-0.19	2.66	-0.04
	Mn-C	1.88	1.93	0.05	1.85	-0.03
	I-Mn-Mn	42.6	37.8	-4.8	43.6	1.0
MnI(SH)	Mn-I	2.41	2.36	-0.05	2.41	0.00
	Mn-S	2.10	2.27	0.17	2.05	-0.05
	I-Mn-S	115.6	146.2	30.6	101.6	-14.0
MnI(F)(PH ₂)(SH)	Mn-I	2.50	2.39	-0.12	2.46	-0.04
	Mn-F	1.75	1.79	0.04	1.73	-0.02
	Mn-P	2.27	2.25	-0.02	2.28	0.01
	Mn-S	2.16	2.22	0.06	2.16	0.00
			AM1*		PM6	
N=151						
MSE bond length			0.02		0.14	
MUE bond length			0.13		0.24	
N=25						
MSE bond angle			-3.0		-2.1	
MUE bond angle			12.2		5.0	

containing compounds are not surprising and result from the known weakness [4, 5] of the AM1* parameterization in reproducing dipole moments for iodine-containing compounds.

Geometries

Table 4 shows a comparison of AM1* and PM6 results in reproducing the geometries of the manganese-containing compounds.

Both AM1* and PM6 overestimate bond lengths to manganese systematically by 0.02 and 0.14 Å, respectively. AM1*, with an MUE of 0.13 Å performs better than PM6 (MUE of 0.24 Å) for bond lengths. Here we note that PM6 reproduces bond lengths as very long for the manganese-transition metal diatomic compounds. The parameterization dataset of PM6 clearly does not cover these model compounds, which seriously affects statistics. For the bond

angles, PM6 with an MUE of 5.0° performs quite well, compared with AM1* (MUE=12.2°). AM1* and PM6 reproduce bond angles for manganese-containing compounds that are on average 3.0° and 2.1° too small.

Iron

Heats of formation

The results obtained for heats of formation of iron-containing compounds are shown in Table 5. We have compared our results with Stewart's published PM6 method [33] and also the unpublished PM5 method implemented in LinMopac [31].

AM1* reproduces the heats of formation of the training set of iron compounds used in parameterization better than both PM6 and PM5. Once again, one must consider that this comparison is not strictly valid as it is based on the

Table 5 Calculated AM1*, PM6 and PM5 heats of formation and errors compared with our target values for the iron-containing compounds used to parameterize AM1* (all values kcal mol⁻¹). Errors are classified by coloring the boxes in which they appear. *Green*

indicates errors lower than 10 kcal mol⁻¹, *yellow* 10–20 kcal mol⁻¹, *pink* greater than 20 kcal mol⁻¹. The codenames within parentheses indicate the CSD-names of the compounds

Compound	Target ΔH_f°	AM1*		PM6		PM5	
		ΔH_f°	Error	ΔH_f°	Error	ΔH_f°	Error
Fe	99.3	99.3	0.0	99.3	0.0	99.3	0.0
Fe ⁺	281.6	251.5	-30.1	262.3	-19.3	282.2	0.6
Fe ⁻	92.0	160.3	68.3	201.3	109.3	140.7	48.7
Fe ²⁺	654.6	697.5	42.9	637.4	-17.2	647.3	-7.3
Fe ³⁺	1361.0	1361.6	0.6	1358.0	-3.0	1349.7	-11.3
Fe ₂	180.0	164.3	-15.7	210.5	30.5	207.5	27.5
FeH	113.9	90.4	-23.5	145.9	32.0	123.7	9.8
FeH ⁻	91.1	100.4	9.3	193.0	101.9	102.2	11.1
FeCH ₃	71.0	51.7	-19.3	109.6	38.6	79.9	8.9
FeC ₅ H ₅	88.0	82.5	-5.5	110.7	22.7	142.6	54.6
Fe(C ₅ H ₅) ₂	57.9	67.2	9.3	49.3	-8.6	102.3	44.3
Fe(C ₅ H ₅) ₂ ⁺	210.2	250.4	40.2	252.0	41.8	294.3	84.1
FeO	60.0	32.8	-27.2	69.2	9.2	61.0	1.0
FeO ⁺	265.0	289.8	24.8	246.0	-19.0	259.3	-5.7
FeO ⁻	31.0	81.7	50.7	94.1	63.1	44.0	13.0
FeO ₂ ⁻	-30.0	-26.9	3.1	48.0	78.0	-18.8	11.2
FeOH	32.0	13.5	-18.5	28.5	-3.5	37.6	5.6
Fe(OH) ₂	-79.0	-83.3	-4.3	-56.5	22.5	-50.4	28.6
Fe(H ₂ O) ₄ (OH) ₂	-294.0	-327.1	-33.1	-334.5	-40.5	-294.5	-0.5
Fe(H ₂ O) ₅ (OH)	-162.2	-222.7	-60.5	-194.9	-32.7	-183.3	-21.1
Fe(H ₂ O) ₆ ²⁺	64.8	-4.3	-69.1	90.8	26.0	39.4	-25.4
Fe(H ₂ O) ₆ ³⁺	492.6	466.0	-26.7	455.0	-37.6	415.8	-76.8
Fe(CO) ₄ H ₂	-131.0	-129.8	1.2	-82.7	48.3	-130.9	0.1
Fe(CO)	63.9	26.1	-37.8	59.1	-4.8	60.4	-3.5
Fe(CO) ⁻	34.8	2.0	-32.8	94.1	59.3	42.4	7.6
Fe(CO) ₂	0.2	6.7	6.5	-3.4	-3.6	1.9	1.7
Fe(CO) ₂ ⁻	-27.3	-76.6	-49.3	15.9	43.2	-43.8	-16.5
Fe(CO) ₃	-55.8	-57.3	-1.5	-32.0	23.8	-41.0	14.8
Fe(CO) ₃ ⁻	-99.2	-124.1	-24.9	-50.2	49.0	-103.6	-4.4
Fe(CO) ₄	-105.1	-148.7	-43.6	-127.5	-22.4	-108.0	-2.9
Fe(CO) ₄ ⁻	-160.9	-205.1	-44.2	-139.2	21.7	-173.0	-12.1
Fe(CO) ₄ ²⁻	-115.1	-125.9	-10.8	-114.6	0.5	-127.3	-12.2
Fe(CO) ₅	-174.0	-181.1	-7.2	-188.4	-14.4	-138.1	35.8
FeC ₆ O ₁₂ ³⁻ (Fe(III)(Ox) ₃)	-506.7	-554.5	-47.8	-510.4	-3.7	-618.7	-112.0
FeC ₆ H ₃ O ₁₂ (H ₃ Fe(III)(Ox) ₃)	-516.8	-481.2	35.6	-501.4	15.4	-505.4	11.4
Fe(CO) ₄ C ₂ H ₄	-129.2	-142.1	-12.9	-133.4	-4.2	-128.5	0.7
FeC ₈ H ₂ O ₆ (FCPEN0)	-173.8	-211.7	-37.9	-170.4	3.4	-210.0	-36.2
FeC ₁₀ H ₁₄ O ₄ (bis(acetylacetonate)iron)	-198.0	-97.2	100.8	-178.2	19.8	-150.6	47.4
FeC ₁₅ H ₂₁ O ₆ ⁻ (Fe(II)(Acac) ₃ anion)	-340.2	-331.6	8.6	-317.9	22.3	-340.3	-0.1
Fe ₂ (CO) ₉	-319.2	-322.7	-3.5	-378.8	-59.6	-324.1	-4.9
Fe(NH ₃) ₆ ²⁺	266.4	258.1	-8.3	284.2	17.8	247.0	-19.4
Fe(CN) ₆ ³⁻	374.3	156.5	-217.8	337.0	-37.3	126.8	-247.5
Fe(CN) ₆ ⁴⁻	484.5	361.2	-123.3	494.5	10.0	318.1	-166.4
FeC ₆ N ₆ H ₂₄ ²⁺ (Fe(II)en) ₃	283.9	290.6	6.7	286.9	3.0	283.8	-0.1
FeC ₃₆ N ₆ H ₂₄ ²⁺ (Ferrous tris(ortho phenanthroline))	451.2	535.5	84.3	428.1	-23.1	489.1	37.9
FeC ₈ NH ₅ O ₂ (ACODUR)	-12.1	-12.0	0.1	-9.2	2.9	-5.1	7.0
FeC ₉ NH ₈ O ₂ ⁺ (CPACFE)	113.2	147.1	33.9	96.1	-17.1	145.4	32.2
Fe(CO) ₂ (NO) ₂	-75.0	-72.8	2.2	-62.3	12.7	-2.9	72.1
FeC ₁₆ N ₅ H ₁₁ O ₄	-53.9	8.2	62.1	-54.8	-0.9	-31.2	22.7
FeC ₇ NH ₅ O ₅ (CNOFEA)	-89.2	-57.0	32.2	-94.6	-5.4	-65.6	23.6
FeC ₁₀ N ₂ H ₁₂ O ₈ ⁻ (Iron(III)EDTA)	-405.6	-377.8	27.9	-404.1	1.5	-425.7	-20.1
FeN	174.3	139.8	-34.5	113.5	-60.8	159.5	-14.8
FeN ⁺	348.8	340.5	-8.3	294.5	-54.3	326.5	-22.3
FeN ⁻	123.7	147.8	24.1	162.4	38.7	135.0	11.3
FeF	11.4	44.6	33.2	22.1	10.7	9.9	-1.5

Table 5 (continued)

Compound	Target ΔH_f°	AM1*		PM6		PM5	
		ΔH_f°	Error	ΔH_f°	Error	ΔH_f°	Error
Fe(H ₂ O) ₅ F ⁺	-184.7	-252.6	-67.9	-214.0	-29.3	-212.6	-27.9
FeF ₂	-93.1	-97.1	-4.0	-80.7	12.4	-95.8	-2.7
FeF ₃	-196.2	-159.3	36.9	-162.1	34.1	-185.6	10.6
FeF ₆ ³⁻	-175.3	-175.3	0.0	-177.2	-1.9	-323.5	-148.2
FeAl	157.8	161.1	3.3	181.0	23.2	181.6	23.8
Fe(AlH ₂) ₂	216.8	214.8	-2.0	299.6	82.8	169.9	-46.9
FeSiH	133.7	121.6	-12.1	190.5	56.8	162.1	28.4
FeSiH ₂	125.6	122.9	-2.7	184.7	59.1	146.7	21.1
Fe(SiH ₃) ₂	126.7	133.4	6.7	234.7	108.0	136.0	9.3
FeP	156.9	157.0	0.1	29.8	-127.1	174.0	17.1
FePH	104.6	104.4	-0.2	56.8	-47.8	126.3	21.7
FeS	88.6	55.0	-33.6	137.0	48.4	101.1	12.5
FeC ₉ H ₁₀ SO ₂ (CEYTFE)	-59.3	-42.6	16.7	-39.5	19.8	-36.1	23.2
FeC ₁₂ H ₁₄ S ₄ O ₂ (CIBGAV10)	-73.1	-73.1	0.0	-88.8	-15.7	-64.0	9.1
FeCl	60.0	51.4	-8.6	52.5	-7.5	50.7	-9.3
FeCl ₂	-33.7	33.7	67.4	12.6	46.3	-24.0	9.7
FeCl ₃	-60.5	-5.7	54.8	-37.9	22.6	-59.8	0.7
FeCl ₄ ²⁻ (GOXLUA)	-105.2	-106.9	-1.7	-100.8	4.4	-187.2	-82.0
FeCl ₆ ³⁻	-56.5	-109.4	-52.9	-54.3	2.2	-177.8	-121.3
Fe(H ₂ O) ₅ Cl ⁺	-148.4	-208.0	-59.6	-146.3	2.1	-175.4	-27.0
FeC ₆ N ₂ H ₁₈ Cl ₃ (FINJIV)	-91.7	-74.4	17.3	-104.0	-12.3	-126.7	-35.0
FeTi	179.7	179.8	0.1	140.2	-39.5	153.7	-26.0
FeV	146.0	146.0	0.0	250.8	104.8	171.9	25.9
FeCr	215.2	215.2	0.0	216.4	1.2	-20.1	-235.3
FeCo	158.4	158.4	0.0	133.9	-24.5	-11.3	-169.7
FeNi	93.6	93.6	0.0	199.4	105.8	178.5	84.9
FeCu	140.7	140.7	0.0	180.0	39.3	83.8	-56.9
FeZn	119.7	129.6	9.9	113.1	-6.6	180.9	61.2
FeBr	44.7	51.9	7.2	83.7	39.0	58.6	13.9
FeBr ₂	-9.9	-16.5	-6.6	55.9	65.8	62.3	72.2
Fe ₂ Br ₄	-60.5	-60.5	0.0	-23.5	37.0	-35.2	25.3
FeC ₆ H ₅ BrO ₃ (ALCFEA)	-110.8	-122.7	-11.9	-119.6	-8.8	-132.4	-21.6
Fe(H ₂ O) ₅ Br ⁺	-137.9	-211.7	-73.8	-141.7	-3.8	-165.0	-27.1
Fe(H ₂ O) ₄ Br ₂	-248.8	-239.4	9.5	-293.3	-44.5	-281.1	-32.3
FeZr	206.1	180.3	-25.8	311.3	105.2	314.0	107.9
FeMo	251.3	251.2	-0.1	242.5	-8.8	317.4	66.1
Fe(CO) ₃ (C ₃ H ₅)I	-82.1	-86.7	-4.6	-81.0	1.1	-67.1	15.0
FeC ₆ H ₅ IO ₃ (ALCOFE10)	-97.1	-79.1	18.0	-100.2	-3.1	-108.1	-11.0
Fe(CO) ₄ I ₂	-151.9	-127.6	24.3	-140.5	11.4	-166.4	-14.5
Fe ₂ I ₄	2.0	74.1	72.1	16.5	14.5	18.8	16.8
FeI ₂	21.0	77.7	56.7	125.4	104.4	47.3	26.3
FeI	52.9	91.2	38.3	107.2	54.3	78.3	25.4
FeMn	126.6	126.7	0.1	161.6	35.0	-	-
		AM1*		PM6		PM5	
N=98							
Most positive error		100.8		109.3		107.9	
Most negative error		-217.8		-127.1		-247.5	
MSE		-3.1		13.7		-5.5	
MUE		26.5		31.6		34.5	
RMSD		41.4		43.6		57.4	
Results for the PM6 parameterization set (N=55)							
MSE		-6.3		1.6		-13.5	
MUE		32.4		17.8		33.8	
RMSD		48.9		23.5		57.6	

Table 6 Calculated AM1*, PM6 and PM5 Koopmans' theorem ionization potentials and dipole moments for iron-containing compounds. The errors are color-coded as follows: *green* up to 0.5 eV or 0.5 Debye; *yellow* between 0.5 and 1.0; *pink* larger than 1.0

Compound	Target	AM1*		PM6		PM5	
			Error		Error		Error
Koopmans' Theorem Ionization Potentials for Manganese Compounds (eV)							
Fe(CO) ₄ H ₂	9.65	9.36	-0.29	9.70	0.05	9.72	0.07
Fe(CO) ₂	6.68	8.01	1.33	8.07	1.39	8.51	1.83
Fe(CO) ₄	8.48	9.90	1.42	9.02	0.54	9.78	1.30
Fe(CO) ₅	8.60	9.76	1.16	9.23	0.63	9.21	0.61
FeBr ₂	9.70	10.05	0.35	9.23	-0.47	11.02	1.32
Fe ₂ Br ₄	12.60	11.04	-1.56	7.11	-5.49	10.53	-2.07
Fe(CO) ₄ H ₂	9.65	9.46	-0.19	9.70	0.05	9.72	0.07
FeCl ₂	10.10	11.21	1.11	8.38	-1.72	11.09	0.99
		AM1*		PM6		PM5	
N=8							
MSE		0.42		-0.63		0.52	
MUE		0.93		1.29		1.03	
Dipole Moments for Manganese Compounds (Debye)							
FeO	7.50	6.62	-0.88	4.44	-3.06	4.95	-2.55
FeCH ₃	0.90	0.67	-0.23	0.48	-0.42	1.58	0.68
Fe(CO) ₄ C ₂ H ₄	1.50	2.02	0.52	3.25	1.75	1.16	-0.34
FeO ₂ (3B1)	2.00	0.91	-1.09	3.33	1.33	0.74	-1.26
FeO ₂ (5B2)	3.40	5.06	1.66	2.10	-1.30	4.94	1.54
Fe(CO) ₃ C ₄ H ₆	2.10	0.36	-1.74	4.41	2.31	1.73	-0.37
FeC ₆ NH ₃ O ₄ (Fe(CO) ₄ acetonitrile)	5.00	7.67	2.67	5.13	0.13	6.61	1.61
FeF	4.19	3.82	-0.37	5.00	0.81	4.53	0.34
FeO ₂ F ₂	1.60	3.04	1.44	2.00	0.40	2.34	0.74
FeC ₁₀ PH ₁₅ O ₄ (Fe(CO) ₄ (PEt ₃))	5.20	5.93	0.73	1.56	-3.64	5.10	-0.10
FeCl	4.51	5.98	1.47	1.06	-3.45	4.59	0.08
FeCl ₂ O ₂	0.22	0.42	0.20	2.70	2.48	1.65	1.43
FeBr	4.18	4.41	0.23	1.12	-3.06	6.17	1.99
Fel	4.20	3.97	-0.23	5.05	0.85	5.24	1.04
		AM1*		PM6		PM5	
N=14							
MSE		0.31		-0.35		0.34	
MUE		0.96		1.79		1.01	

current parameterization data, which sometimes differ from those used in PM6 and PM5. As can be seen from Table 5, the AM1* parameterization data set contains 98 compounds, of which 55 are taken from the original PM6 parameterization data set. Since PM5 is unpublished, we do not know whether these data cover the original PM5 parameterization dataset. These data demonstrate the influence of the extent of the training data. AM1* with MUE of 26.5 kcal mol⁻¹ performs significantly better for its extended training set than PM6 and PM5 (MUEs of 31.6 and 34.5 kcal mol⁻¹, respectively), whereas PM6 performs better (MUE=17.8 kcal mol⁻¹) than AM1* and PM5 (MUEs of 32.4 and 33.8 kcal mol⁻¹, respectively) for the subset for which it was trained. As before, we note that this situation is unavoidable.

AM1* and PM5 underestimate heats of formation for iron compounds by only 3.1 and 5.5 kcal mol⁻¹, respectively. On the other hand, PM6 systematically predicts the heats of formation of iron compounds to be too positive, with MSE of 13.7 kcal mol⁻¹. The largest positive errors for AM1* are found for the compounds FeC₁₀H₁₄O₄ [bis(acetylacetonate)iron; 100.8 kcal mol⁻¹], FeC₃₆N₆H₂₄²⁺ [ferrous tris(*ortho* phenanthroline); 84.3 kcal mol⁻¹], Fe₂I₄ (72.1 kcal mol⁻¹), Fe⁻ (68.3 kcal mol⁻¹) and FeCl₂ (67.4 kcal mol⁻¹). The largest negative errors for AM1* are found for Fe(CN)₆³⁻ (-217.8 kcal mol⁻¹), Fe(CN)₆⁴⁻ (-123.3 kcal mol⁻¹), Fe(H₂O)₅Br⁺ (-73.8 kcal mol⁻¹), Fe(H₂O)₆²⁺ (-69.1 kcal mol⁻¹) and Fe(H₂O)₅F⁺ (-67.9 kcal mol⁻¹). The large negative errors with oxygen-containing compounds are not surprising, as pointed out in our previous

Table 7 Calculated AM1*, PM6 and PM5 bond lengths and angles for iron-containing compounds. The codenames within parentheses indicate the CSD-names of the compounds. The errors are color-

coded as follows: *green* up to 0.05 Å or 0.5°; *yellow* between 0.05–0.1 Å or 0.5–1.0°; *pink* larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*		PM6		PM5	
				Error		Error		Error
Fe ₂	Fe-Fe	2.19	2.02	-0.17	2.35	0.17	1.83	-0.36
FeH	Fe-H	1.63	1.63	0.00	1.08	-0.55	1.70	0.07
FeH ⁻	Fe-H	1.69	1.69	0.00	1.98	0.29	1.70	0.01
FeH ⁺	Fe-H	1.60	1.53	-0.07	1.16	-0.44	1.58	-0.02
FeCH ₃	Fe-C	1.97	1.90	-0.07	2.12	0.15	1.94	-0.03
FeC ₅ H ₅	Fe-C	2.17	2.05	-0.13	2.06	-0.11	2.03	-0.14
Fe(C ₅ H ₅) ₂	Fe-C	2.06	2.12	0.06	2.06	0.00	2.22	0.16
Fe(III)Cp ₂ ⁺	Fe-C	2.06	1.99	-0.07	2.05	-0.01	2.08	0.02
FeO	Fe-O	1.62	1.76	0.14	1.66	0.04	1.63	0.00
FeO ⁻	Fe-O	1.69	1.74	0.05	1.79	0.10	1.73	0.04
FeO ⁺	Fe-O	1.56	1.75	0.19	1.65	0.09	1.65	0.09
FeO ₂ ⁻	Fe-O	1.71	1.77	0.06	1.71	0.00	1.72	0.01
FeOH	Fe-O	1.83	1.83	0.00	1.61	-0.22	1.77	-0.06
Fe(OH) ₂	Fe-O	1.78	1.85	0.08	1.81	0.03	1.79	0.02
Fe(H ₂ O) ₄ (OH) ₂	Fe-O	2.02	1.93	-0.09	1.66	-0.36	1.94	-0.08
	Fe-O	2.08	2.13	0.05	3.17	1.09	2.32	0.24
Fe(H ₂ O) ₅ (OH)	Fe-O	1.95	1.85	-0.10	1.83	-0.12	1.92	-0.03
	Fe-O	2.05	2.05	0.00	2.17	0.12	2.10	0.05
Fe(H ₂ O) ₆ ²⁺	Fe-O	2.07	1.99	-0.08	2.01	-0.06	2.15	0.08
	Fe-O	2.15	2.08	-0.07	2.53	0.38	2.22	0.07
Fe(H ₂ O) ₆ ³⁺	Fe-O	2.06	2.01	-0.05	2.05	-0.01	2.08	0.02
FeCH ₅ O ₂ (methyl iron(III)dihydroxide)	Fe-O	1.75	1.83	0.08	1.75	0.00	1.71	-0.04
	Fe-C	1.93	1.92	-0.01	1.64	-0.29	1.93	0.00
Fe(CO)	Fe-C	1.72	1.80	0.08	1.63	-0.09	1.76	0.04
Fe(CO) ⁻	Fe-C	1.79	1.85	0.06	1.80	0.01	1.19	-0.60
Fe(CO) ₂	Fe-C	1.84	1.88	0.04	1.76	-0.08	1.84	0.00
Fe(CO) ₂ ⁻	Fe-C	1.79	1.85	0.06	1.75	-0.04	1.82	0.03
Fe(CO) ₃	Fe-C	1.67	1.82	0.15	1.67	-0.01	1.82	0.14
Fe(CO) ₃ ⁻	Fe-C	1.82	1.88	0.06	1.40	-0.42	1.92	0.09
Fe(CO) ₄	Fe-C	1.78	1.89	0.11	1.71	-0.07	1.84	0.05
	Fe-C	1.82	1.89	0.08	1.80	-0.02	1.84	0.02
Fe(CO) ₄ ⁻	Fe-C	1.78	1.88	0.10	1.66	-0.13	1.84	0.06
Fe(CO) ₄ ²⁻	Fe-C	1.75	1.84	0.09	1.46	-0.29	1.78	0.03
Fe(CO) ₄ H ₂	Fe-C	1.81	1.89	0.09	1.81	0.00	1.84	0.03
	Fe-H	1.56	1.58	0.02	1.36	-0.20	1.62	0.06
	H-Fe-C	89.9	89.9	0.0	56.9	-33.0	90.0	0.1
Fe(CO) ₅	Fe-C(eq)	1.81	1.92	0.11	1.77	-0.04	1.82	0.01
	Fe-C(ax)	1.81	1.92	0.11	1.83	0.02	1.85	0.04
Fe(CO) ₄ C ₂ H ₄	Fe-C	1.81	1.89	0.08	1.75	-0.06	1.84	0.03
	Fe-C	2.13	1.98	-0.15	2.33	0.20	2.00	-0.13
FeC ₆ O ₁₂ ³⁻ (Fe(III)(Ox) ₃)	Fe-O	1.97	1.97	0.00	1.99	0.02	2.04	0.07
	O-Fe-O	83.2	80.8	-2.4	99.8	16.6	82.1	-1.1
FeC ₆ H ₃ O ₁₂ (H ₃ Fe(III)(Ox) ₃)	Fe-O	1.92	1.93	0.01	1.89	-0.03	2.02	0.10
	Fe-O	2.03	2.02	-0.01	1.98	-0.05	2.22	0.19
FeC ₇ H ₄ O ₃ (cyclobutadiene iron tricarbonyl)	Fe-C(C=O)	1.79	1.92	0.13	1.74	-0.05	1.78	-0.01
	Fe-C(C ₄ H ₄)	2.06	2.00	-0.06	2.08	0.02	2.34	0.28
	C-Fe-C	99.3	83.0	-16.3	88.5	-10.8	97.6	-1.7
FeC ₈ H ₂ O ₆ (FCPEN0)	Fe-C	1.81	1.90	0.09	1.82	0.01	1.86	0.05
	Fe-C	2.02	1.95	-0.07	1.83	-0.19	2.02	0.00
FeC ₉ H ₁₂ O (BUDFEC01)	Fe-C(O)	1.77	2.05	0.28	1.67	-0.10	1.82	0.05
	Fe-C	2.06	2.05	-0.01	2.08	0.02	2.13	0.07
	C-Fe-C	125.6	117.9	-7.7	109.5	-16.2	118.4	-7.2
FeC ₉ H ₁₂ O (FeCO(1,3-C ₄ H ₆) ₂)	Fe-C	2.11	2.00	-0.11	2.20	0.09	2.07	-0.04
	C-Fe-C	88.8	83.3	-5.5	79.2	-9.5	82.9	-5.9
Fe ₂ (CO) ₉	Fe-C	1.83	1.94	0.11	1.80	-0.03	1.85	0.02
	Fe-C	1.98	1.96	-0.02	2.02	0.04	2.03	0.05
	Fe-C#O	180.0	175.2	-4.8	177.0	-3.0	179.9	-0.1
	Fe-C#O	140.7	138.9	-1.8	141.8	1.1	139.1	-1.7

Table 7 (continued)

Compound	Variable	Target	AM1*		PM6		PM5	
				Error		Error		Error
FeC ₁₀ H ₁₄ O ₄ (Fe(II)(Acac) ₂)	Fe-O	1.90	1.91	0.01	1.92	0.02	1.94	0.04
	O-Fe-O	93.9	90.9	-3.0	73.4	-20.6	92.4	-1.5
FeC ₁₅ H ₂₁ O ₆ ⁻ (Fe(II)(Acac) ₃)	Fe-O	1.97	1.98	0.01	2.03	0.06	2.02	0.05
	O-Fe-O	95.1	90.2	-4.9	91.3	-3.7	94.7	-0.4
FeN	Fe-N	1.56	1.72	0.16	1.33	-0.23	1.62	0.06
FeN ⁺	Fe-N	1.58	1.66	0.08	1.36	-0.22	1.54	-0.04
FeN ⁻	Fe-N	1.58	1.80	0.22	1.36	-0.22	1.71	0.13
Fe(NH ₃) ₆ ²⁺	Fe-N	2.10	2.07	-0.03	2.04	-0.06	2.19	0.09
Fe(CN) ₄ ⁴⁻	Fe-C	1.99	1.98	-0.01	1.98	-0.01	1.95	-0.04
	C-Fe-C	180.0	179.9	-0.1	179.9	-0.1	180.0	0.0
	Fe-C	1.82	1.97	0.15	1.78	-0.04	1.88	0.05
	Fe-N	1.68	1.79	0.11	1.66	-0.02	1.69	0.01
Fe(CO) ₂ (NO) ₂	C-Fe-C	98.7	83.8	-14.9	90.5	-8.2	86.8	-11.9
	N-Fe-N	109.0	146.7	37.8	92.5	-16.5	118.7	9.7
	Fe-N	2.13	2.00	-0.14	2.13	0.00	2.19	0.06
	Fe-C	1.79	1.89	0.10	1.93	0.14	1.82	0.03
FeC ₆ N ₆ H ₂₄ ²⁺ (Fe(II)en) ₃	Fe-C	2.09	2.06	-0.03	2.07	-0.02	2.27	0.18
	Fe-O	1.97	1.97	0.00	1.84	-0.13	2.06	0.09
FeC ₇ NH ₅ O ₅ (CNOFEA)	Fe-C	1.91	1.90	-0.01	1.92	0.01	1.96	0.05
	Fe-C	1.78	1.90	0.12	1.76	-0.02	1.81	0.03
	Fe-C	2.19	2.11	-0.08	2.07	-0.12	2.23	0.04
	C-Fe-C	89.2	83.0	-6.2	74.2	-15.0	89.2	0.0
FeC ₉ NH ₈ O ₂ ⁺ (CPACFE)	Fe-N	1.91	1.95	0.04	1.83	-0.08	2.04	0.13
	Fe-C	1.77	1.91	0.14	1.78	0.01	1.84	0.07
FeC ₁₀ N ₄ H ₁₀ O ₆ (Diaqua-bis(pyrazinecarboxylato)-iron)	Fe-O	2.11	1.93	-0.18	1.99	-0.12	2.08	-0.03
	Fe-N	2.12	1.95	-0.17	1.92	-0.20	2.08	-0.04
	Fe-OH ₂	2.14	2.14	0.00	2.07	-0.07	2.09	-0.05
	O-Fe-N	78.1	83.4	5.3	76.5	-1.6	79.7	1.6
FeC ₁₀ N ₂ H ₁₂ O ₈ ⁻ (Iron(III)EDTA)	Fe-N	2.03	2.21	0.18	2.19	0.16	2.32	0.29
	Fe-O	2.12	2.60	0.48	2.08	-0.04	2.26	0.14
FeC ₁₆ N ₅ H ₁₁ O ₄	Fe-O	1.92	1.87	-0.05	1.95	0.03	2.01	0.09
	Fe-N	1.89	1.83	-0.06	1.88	-0.01	2.02	0.13
	O-Fe-O	81.4	78.8	-2.6	73.4	-8.0	77.9	-3.5
	Fe-N	1.90	1.84	-0.06	1.86	-0.04	1.90	0.00
FeC ₁₇ N ₂ H ₁₆ (Toluene-(2,2'-bipyridine)-iron)	Fe-C	2.11	2.07	-0.04	2.07	-0.04	2.28	0.17
	N-Fe-N	81.9	86.3	4.4	76.5	-5.4	82.7	0.8
	N-Fe-C	122.8	114.7	-8.1	107.3	-15.5	128.2	5.4
	Fe-N	1.97	1.93	-0.04	1.92	-0.05	2.02	0.05
FeC ₂₀ H ₁₂ N ₄ (iron porphyrin)	Fe-N	2.05	1.97	-0.08	1.95	-0.10	2.14	0.09
FeC ₃₆ N ₆ H ₂₄ ⁺ (ferrous tris(ortophenantholine))	Fe-F	1.76	1.80	0.04	1.75	-0.01	1.77	0.01
FeF	Fe-F	1.89	1.70	-0.19	1.82	-0.07	1.90	0.01
	Fe-O	2.05	2.04	-0.01	2.15	0.10	2.10	0.05
FeF ₂	Fe-F	1.77	1.71	-0.06	1.76	-0.01	1.79	0.02
FeO ₂ F ₂ (iron(VI)difluoride dioxide)	Fe-F	1.74	1.71	-0.03	1.74	0.00	1.81	0.07
	Fe=O	1.58	1.85	0.27	1.55	-0.03	1.66	0.08
FeF ₃	Fe-F	1.78	1.75	-0.03	1.73	-0.05	1.77	-0.01
FeF ₆ ³⁻	Fe-F	2.06	1.85	-0.21	1.94	-0.12	2.02	-0.04
FeAl	Fe-Al	2.30	2.27	-0.03	2.65	0.35	2.28	-0.03
Fe(AlH ₂) ₂	Fe-Al	2.47	2.39	-0.08	3.06	0.59	2.69	0.22
FeSiH	Fe-Si	2.30	2.30	0.00	3.96	1.66	2.48	0.18
FeSiH ₂	Fe-Si	2.26	2.31	0.05	4.24	1.98	2.48	0.22
Fe(SiH ₃) ₂	Fe-Si	2.52	2.52	0.00	4.47	1.95	2.52	0.00
FeP	Fe-P	2.23	2.20	-0.03	1.85	-0.38	2.30	0.06
FePH	Fe-P	2.20	2.30	0.10	2.05	-0.15	2.35	0.15
FeC ₁₂ P ₄ H ₃₄ S ₂ (JIYFAY)	Fe-S	2.35	2.33	-0.02	2.10	-0.25	2.33	-0.02
	Fe-P	2.23	2.64	0.41	2.26	0.03	2.49	0.26
	P-Fe-S	89.4	90.8	1.4	83.1	-6.4	70.5	-18.9
FeS	Fe-S	2.04	2.10	0.06	1.99	-0.05	2.06	0.02
Fe(SH) ₂	Fe-S	2.25	2.26	0.02	1.82	-0.43	2.26	0.01
FeC ₉ H ₁₀ SO ₂ (CEYTFE)	Fe-S	2.30	2.32	0.02	2.00	-0.30	2.34	0.04

Table 7 (continued)

Compound	Variable	Target	AM1*		PM6		PM5	
				Error		Error		Error
	Fe-C(O)	1.75	1.89	0.14	1.74	-0.01	1.80	0.05
	Fe-C(C ₄)	2.12	2.12	0.00	2.04	-0.08	2.25	0.13
	C-Fe-S	90.7	85.0	-5.7	102.3	11.6	91.9	1.2
FeC ₁₆ N ₂ H ₁₈ S ₂ O ₂ (dicarbonyl ethylenediamine bis(phenylthiolato)iron)	Fe-S	2.33	2.37	0.04	2.26	-0.07	2.38	0.05
	Fe-S	2.34	2.37	0.03	2.13	-0.21	2.39	0.04
	Fe-N	2.04	1.96	-0.08	2.15	0.11	2.15	0.11
	Fe-N	2.03	1.97	-0.06	1.95	-0.08	2.15	0.12
	Fe-C	1.76	1.88	0.12	1.73	-0.03	1.79	0.03
	N-Fe-S	86.8	88.2	1.4	80.1	-6.7	82.0	-4.8
	C-Fe-S	93.2	84.9	-8.3	96.1	2.9	98.0	4.8
FeC ₉ N ₃ H ₁₈ S ₃ O ₃ (tris(N,N-dimethylthiocarbamato)iron(III))	Fe-S	2.43	2.44	0.01	2.49	0.06	2.52	0.09
	Fe-O	2.09	1.99	-0.10	1.88	-0.21	2.07	-0.02
	S-Fe-O	68.9	70.5	1.6	72.1	3.2	66.9	-2.0
	S-Fe-S	103.1	96.0	-7.1	98.0	-5.1	101.5	-1.6
Fe ₄ S ₄	Fe-S	2.27	2.27	0.00	2.28	0.01	2.37	0.10
FeC ₁₂ H ₁₄ S ₄ O ₂ (CIBGAV10)	Fe-S	2.31	2.35	0.04	2.23	-0.08	2.36	0.05
	Fe-C	1.80	1.89	0.09	1.73	-0.07	1.81	0.01
	S-Fe-S	85.2	85.7	0.4	108.8	23.6	87.8	2.6
	C-Fe-S	90.1	89.4	-0.7	83.1	-7.0	90.7	0.6
FeC ₁₄ N ₆ H ₁₆ S ₆ (diisothiocyanato-bisthiazoline iron(II))	Fe-N	2.19	2.09	-0.10	1.87	-0.32	2.06	-0.13
	Fe-N(CS)	2.08	1.87	-0.21	1.84	-0.24	1.98	-0.10
	N-Fe-N	73.9	81.3	7.4	101.9	28.0	78.1	4.2
	SCN-Fe-NCS	97.4	94.3	-3.1	99.8	2.4	89.0	-8.4
FeCl	Fe-Cl	2.13	2.23	0.10	1.55	-0.58	2.16	0.02
Fe(II)(H ₂ O) ₅ Cl ⁺	Fe-Cl	2.29	2.17	-0.12	2.45	0.16	2.29	0.00
	Fe-O	2.06	2.06	0.00	2.07	0.01	2.10	0.04
FeCl ₂	Fe-Cl	2.16	2.17	0.01	1.94	-0.22	2.15	-0.01
FeCl ₃	Fe-Cl	2.16	2.17	0.02	2.18	0.03	2.17	0.02
FeC ₆ N ₂ H ₁₈ Cl ₃ (FINJIV)	Fe-Cl	2.23	2.35	0.12	2.34	0.11	2.25	0.02
	Fe-N	2.27	1.93	-0.34	1.96	-0.31	2.28	0.01
	Cl-Fe-Cl	121.0	120.1	-0.9	119.4	-1.6	119.8	-1.3
FeCl ₄ ⁻	Fe-Cl	2.19	2.22	0.03	2.11	-0.08	2.18	-0.01
FeCl ₄ ²⁻ (GOXLUA)	Fe-Cl	2.34	2.33	-0.01	2.35	0.01	2.36	0.02
FeCl ₆ ³⁻	Fe-Cl	2.53	2.54	0.01	2.51	-0.02	2.41	-0.12
FeTi	Fe-Ti	2.54	2.54	0.00	3.67	1.13	-	-
FeV	Fe-V	2.31	2.31	0.00	3.50	1.19	2.04	-0.27
FeCr	Fe-Cr	2.27	2.06	-0.21	3.65	1.38	1.60	-0.67
FeMn	Fe-Mn	2.40	2.40	0.00	5.21	2.81	-	-
FeCo	Fe-Co	2.31	2.30	-0.01	4.68	2.38	1.70	-0.61
FeNi	Fe-Ni	2.33	2.21	-0.12	4.69	2.36	2.05	-0.29
FeCu	Fe-Cu	2.31	2.31	0.00	7.36	5.05	2.05	-0.26
FeZn	Fe-Zn	2.53	2.37	-0.16	2.98	0.45	2.63	0.10
FeBr	Fe-Br	2.23	2.16	-0.07	2.17	-0.06	2.31	0.08
FeBr ₂	Fe-Br	2.31	2.13	-0.18	2.13	-0.18	2.31	0.00
FeC ₆ H ₉ BrO ₃ (ALCFEA)	Fe-Br	2.50	2.20	-0.30	2.46	-0.04	2.43	-0.07
	Fe-C(C ₂)	2.13	2.03	-0.10	2.14	0.01	2.13	0.00
	Fe-C(O)	1.79	1.91	0.12	1.83	0.04	1.85	0.06
	C-Fe-Br	88.6	87.6	-1.0	108.9	20.3	84.9	-3.7
Fe(H ₂ O) ₅ Br ⁺	Fe-Br	2.42	2.14	-0.28	2.47	0.05	2.38	-0.04
	Fe-O	2.06	2.10	0.04	2.07	0.01	2.24	0.18
Fe(H ₂ O) ₄ Br ₂	Fe-O	2.07	1.99	-0.08	2.15	0.08	2.09	0.02
	Fe-Br	2.50	2.20	-0.30	2.71	0.21	2.48	-0.02
FeC ₄ H ₈ BrO ₇ (Diaquabromo(oxydiacetato-O,O',O'')-iron(III))	Fe-Br	2.37	2.17	-0.20	2.38	0.01	2.36	-0.02
	Fe-O	2.00	2.07	0.07	1.85	-0.15	1.98	-0.02
	Br-Fe-O	105.6	94.5	-11.1	98.6	-7.0	111.5	5.9
FeBr ₂ O ₂	Fe-Br	2.27	2.15	-0.12	2.56	0.29	2.38	0.11

Table 7 (continued)

Compound	Variable	Target	AM1*		PM6		PM5	
				Error		Error		Error
	Fe=O	1.58	1.74	0.16	1.55	-0.03	1.52	-0.06
	Br-Br-Fe	110.6	110.0	-0.6	129.6	19.0	98.1	-12.5
FeZr	Fe-Zr	2.59	2.59	0.00	2.84	0.25	3.04	0.46
FeMo	Fe-Mo	2.21	2.14	-0.07	3.29	1.08	11.58	9.37
Fel	Fe-I	2.44	2.46	0.02	2.70	0.26	2.38	-0.06
Fe(CO) ₃ (C ₃ H ₅)I	Fe-I	2.75	2.61	-0.14	2.80	0.05	2.48	-0.27
	Fe-C(O)	1.80	1.96	0.16	1.73	-0.07	1.84	0.04
	C-Fe-I	81.6	81.7	0.1	75.3	-6.3	76.2	-5.4
Fe(CO) ₃ (C ₃ H ₅)I (ALCOFE10)	Fe-I	2.75	2.59	-0.16	2.80	0.05	2.59	-0.16
	Fe-C	1.80	1.95	0.15	1.73	-0.07	1.83	0.03
	C-Fe-I	81.6	96.5	14.9	75.3	-6.3	81.8	0.2
Fel ₂	Fe-I	2.50	2.49	-0.01	2.55	0.05	2.43	-0.07
			AM1*		PM6		PM5	
N=153								
MSE bond length			0.00		0.12		0.08	
MUE bond length			0.09		0.27		0.15	
N=33								
MSE bond angle			-1.3		-2.6		-1.7	
MUE bond angle			5.8		10.4		4.0	

parameterizations [5, 6]. Generally, large errors in AM1* for iron are given by compounds that contain original AM1 elements or AM1 elements with chlorine, bromine or iodine. We attribute this to a weakness in the AM1* parameterization for the halogens and also a general weakness of the original AM1 parameterization.

Ionization potentials and dipole moments

A comparison of the calculated and experimental ionization potentials and dipole moments of iron-containing compounds for AM1*, PM6 and PM5 is shown in Table 6.

AM1* and PM5 overestimate Koopmans' theorem ionization potentials of iron-containing compounds with MSEs of 0.42 and 0.52 eV, respectively, for the dataset used, whereas PM6 underestimates them by 0.63 eV. AM1* with an MUE of 0.93 eV performs better than both PM5 (MUE=1.03 eV) and PM6 (1.29 eV) for ionization potentials of iron compounds. The large errors for AM1* are found mainly for iron-carbonyl compounds, which is once again an indirect result of using original AM1 parameters for carbon and oxygen.

Both AM1* and PM5 tend to give positive systematic errors for dipole moments of iron-containing compounds with MSEs of 0.31 and 0.34 Debye, respectively, whereas PM6 underestimates by 0.35 Debye. AM1* with an MUE of 0.96 Debye performs slightly better than PM5 (MUE=1.01 Debye) and far better PM6 (1.79 Debye) for dipole moments of iron-containing compounds. The large errors for AM1* are obtained mainly from the compounds containing hydrogen, carbon, oxygen and nitrogen. This is not unexpected because AM1* uses the original AM1 parameters for these elements.

Geometries

The geometrical variables used to parameterize AM1* for iron and a comparison of the AM1*, PM6 and PM5 results are shown in Table 7.

AM1* shows no systematic error trend for bond lengths in iron compounds, whereas both PM5 and PM6 overestimate them by 0.08 Å and 0.12 Å, respectively. AM1* with MUE of 0.09 Å performs better than PM5 (MUE=0.15 Å) and far better than PM6 (MUE=0.27 Å) for bond lengths. Here once again we note that the large PM6 errors for bond lengths resulted from iron-transition metal diatomic model compounds, and that these compounds are not covered by PM6 parameterization dataset.

All three available methods produce negative systematic errors for bond angles of iron-containing compounds. While AM1* underestimates them by 1.3°, PM5 and PM6 also underestimate by 1.7° and 2.6°, respectively. The performance of AM1* for bond angles in iron-containing compounds is comparable to PM5 and better than PM6. The MUEs for AM1* and PM5 are 5.8° and 4.0°, respectively, and 10.4° for PM6. Here, perhaps surprisingly, the relatively old method PM5 performs similarly to, or better than, more modern methods.

Discussion

In this work, we have presented our new AM1* parameters for manganese and iron, providing important additional elements for the chemistry of organometallic and biological catalysts and for biochemical systems especially in the active sites of enzymes. Since experimental data for compounds of

these two metals are relatively sparse and sometimes of poor quality, we have extended the range of the parameterization dataset and made it more reliable in checking experimental data by including results from DFT calculations. We aim to produce a parameter set that is more robust and generally more applicable than those trained only using experimental data. For the extended training set used here, AM1* parameterizations for manganese and iron give very good energetic and electronic results and also performed very well for structural properties. Both AM1* and PM6 extend the range of applicability of NDDO-based MNDO-like techniques and provide good starting points for reaction-specific local parameterizations and comparison calculations.

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