At the Limits of Isolobal Bonding: π -Based Covalent Magnetism in Mn_2Hg_5

Vincent J. Yannello, Erdong Lu, and Daniel C. Fredrickson*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison WI, 53706, United States *email: <u>danny@chem.wisc.edu</u>

SUPPORTING INFORMATION

S1. Computational Details

Parameters used in the GGA-DFT calculations are shown in Table S1, with optimized cell parameters obtained from the calculations being listed in Table S2. Tables S3-4 give the optimized atomic positions and total energies for $CrGa_4$ and Mn_2Hg_5 . The initial polarization on the Mn atoms for the spin-polarized calculation was set with alternating +5 and -5 for the Mn atoms along the *c* axis, with the final integrated values being +3.563 and -3.563. In addition, Tables S5 and S6 give the optimized geometries of the antiferromagnetic and ferromagnetic models used for the purpose of calculating the energetics of the spin-polarization. The supercell of the conventional cell used in the Hückel raMO calculations for $CrGa_4$ and Mn_2Hg_5 were 4×4×4 and 2×2×6, respectively. Table S7 gives the optimized Hückel parameters used for the Hückel-raMO calculations.

For the DFT-raMO calculations in this work, individual wavefunctions from the DFT output were treated as either unoccupied or occupied, which leads to some difficulties for states very close to the Fermi energy. A cutoff of 49% was used to approach the correct number of electrons. For example, in Mn_2Hg_5 , the total number of electrons in sum over the raMO functions was 74.0625 electrons/formula unit, compared to the actual number of 74 electrons/formula unit. For the DFT-raMO calculations, coarser k-point grids sampling the full Brillouin zones (rather than irreducible wedges) were used: $5 \times 5 \times 5$ for CrGa₄ and $2 \times 2 \times 4$ for Mn_2Hg_5 (with $1 \times 1 \times 2$ supercell to allow for its antiferromagnetic superstructure).

For the exploration of spin-orbit coupling with ABINIT, the Mn_2Hg_5 crystal structure was first optimized (without spin-orbit coupling or spin-polarization) in a two-step method: an optimization of atomic coordinates with fixed unit cell parameters followed by another optimization where all structural parameters were relaxed, yielding the geometry given in Table S8. The k-point mesh for the calculation was specified by the kptrlatt in ABINIT as a 3×3 matrix: [4 0 0; 0 4 0; 0 0 14] with shiftk [0.5 0.5 0.5]. The LDA HGH pseudopotentials were used, and specifically, the Mn atoms were modeled with the valence only pseudopotential (with 7 electrons in the valence set) and Hg atoms were modeled with the semi-core pseudopotential (treating 12 electrons as part of the valence set). Table S7 gives the structure parameters obtained from the ABINIT geometry optimization. Afterwards, the electronic DOS of Mn_2Hg_5 both with spin-orbit coupling and without spin-orbit coupling were calculated based on this optimized geometry. The in-house program ExtractDOS_ABINIT was then used to reformat the outcomes from ABINIT into files readable by VIEWKEL, where the electronic DOS were finally plotted.

Structure	Geo Optimized	Spin Polarization	Pseudopotentials	Energy Cut-off	k-point mesh ^a
CrGa ₄	Yes	No	PAW GGA	283.9 eV	15×15×15, Γ-centered
Mn_2Hg_5	Yes	No	PAW GGA	337.4 eV	6×6×19, Г-centered
Mn ₂ Hg ₅	Yes ^b	Yes	PAW GGA	337.4 eV	6×6×10, Г-centered

Table S1. Details of GGA-DFT calculations on structures serving as bases for the parameterization of Hückel models.

^aAll k-point grids were converged to a total energy of <1meV/atom

^bSame geometry as for the non-spin-polarized calculation.

Table S2.	Cell	parameters for all	GGA-DFT	optimized	compounds
	0011	parameters for an		opullinded	compoundo

i		1	. 1			
	a (Å)	b (Å)	c (Å)	a (°)	β (°)	γ(°)
CrGa ₄	4.8844	4.8844	4.8844	109.47	109.47	109.47
Mn_2Hg_5	9.7044	9.7044	2.8475	90	90	90
Mn ₂ Hg ₅ (spin polarized) ^a	9.7044	9.7044	5.6950	90	90	90

^aGeometry derived as 1×1×2 supercell of non-spin-polarized structure without further optimization.

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Element	x	Y	Ζ		
Cr	0.000000	0.000000	0.500000		
Ga	0.500000	0.000000	0.000000		
Ga	0.000000	0.500000	0.000000		
Ga	0.500000	0.500000	0.500000		
Ga	0.000000	0.000000	0.000000		
Total Energy:	-22.085999 eV/cell				

Table 34. Atomic coordinates for the GGA-DFT optimized Mil2rigs-type compound Mil2rigs

Element	x	Y	Ζ
Mn	0.178964	0.678964	0.500000
Mn	0.821036	0.321036	0.500000
Mn	0.321036	0.178964	0.500000
Mn	0.678964	0.821036	0.500000
Hg	0.000000	0.500000	0.000000
Hg	0.500000	0.000000	0.000000
Hg	0.066968	0.206806	0.000000
Hg	0.933032	0.793194	0.000000
Hg	0.793194	0.066968	0.000000
Hg	0.206806	0.933032	0.000000
Hg	0.433032	0.706806	0.000000
Hg	0.566968	0.293194	0.000000
Hg	0.706806	0.566968	0.000000
Hg	0.293194	0.433032	0.000000
Total Energy:	-30.150678 eV/cell		

Cell vector	x	у	z
a	9.879267	0.000000	0.000000
b	0.000000	9.879267	0.000000
с	0.000000	0.000000	3.003893
Element	x	у	\boldsymbol{z}
Mn	0.179851	0.679851	0.500000
Mn	0.820149	0.320149	0.500000
Mn	0.320149	0.179851	0.500000
Mn	0.679851	0.820149	0.500000
Hg	0.000000	0.500000	0.000000
Hg	0.500000	0.000000	0.000000
Hg	0.064602	0.204648	0.000000
Hg	0.935398	0.795352	0.000000
Hg	0.795352	0.064602	0.000000
Hg	0.204648	0.935398	0.000000
Hg	0.435398	0.704648	0.000000
Hg	0.564602	0.295352	0.000000
Hg	0.704648	0.564602	0.000000
Hg	0.295352	0.435398	0.000000
Total Energy:	-34.425738 eV/cell		

Table S5. GGA-DFT optimized structure of Mn_2Hg_5 with antiferromagnetic order

Table S6.	GGA-DFT o	ptimized	structure	of Mn ₂ H	g ₅ with	ferromagne	etic order
					n ³ · · · - · · - ·		

Cell vector	x	у	
a	9.937695	0.000000	0.000000
b	0.000000	9.937695	0.000000
c	0.000000	0.000000	2.992252
Element	x	у	\boldsymbol{z}
Mn	0.180701	0.680701	0.500000
Mn	0.819299	0.319299	0.500000
Mn	0.319299	0.180701	0.500000
Mn	0.680701	0.819299	0.500000
Hg	0.000000	0.500000	0.000000
Hg	0.500000	0.000000	0.000000
Hg	0.064106	0.203565	0.000000
Hg	0.935894	0.796435	0.000000
Hg	0.796434	0.064106	0.000000
Hg	0.203565	0.935894	0.000000
Hg	0.435894	0.703565	0.000000
Hg	0.564106	0.296435	0.000000
Hg	0.703565	0.564106	0.000000
Hg	0.296434	0.435894	0.000000
Total Energy:	-33.917021 eV/cell		

Compound, RMS deviation (for bands up to 1 eV above the $E_{\rm F}$).	Element	Orbital	H _{ii} (eV)	c ₁	$\zeta_1 \left(a_o^{-1} \right)$	c ₂	$\zeta_2\left(\mathrm{a_o}^{-1}\right)$
CrGa4, 0.115201 eV	Cr	Cr 4s	-4.177		2.5016		
		Cr 4p	0.410		1.7355		
		Cr 3d	-7.360	0.9618	8.4896	0.2387	1.0658
	Ga	Ga 4s	-9.271		2.3958		
		Ga 4p	-5.118		2.3367		
Mn ₂ Hg ₅ , 0.071454 eV	Mn	Mn 4s	-4.1970		2.2834		
		Mn 4p	-1.4590		2.0225		
		Mn 3d	-4.7640	0.3058	4.7617	0.8034	2.0095
	Hg	Hg 6s	-6.5700		2.9217		
		Hg 6p	-1.8440		2.4786		
		Hg 5d	-11.4480	0.7747	9.3971	0.5265	2.8084

Table S7. DFT-calibrated Hückel parameters used in this work

Table S8. LDA-DFT optimized Mn₂Hg₅-type compound Mn₂Hg₅ used for the spin-orbit coupling test

Cell vector	x	У	z
a	9.428996	0.000000	0.000000
Ь	0.000000	9.428996	0.000000
c	0.000000	0.000000	2.769974
Element	x	у	z
Mn	0.179875	0.679875	0.500000
Mn	0.820125	0.320125	0.500000
Mn	0.320125	0.179875	0.500000
Mn	0.679875	0.820125	0.500000
Hg	0.000000	0.500000	0.000000
Hg	0.500000	0.000000	0.000000
Hg	0.065152	0.206727	0.000000
Hg	0.934848	0.793273	0.000000
Hg	0.793273	0.065152	0.000000
Hg	0.206727	0.934848	0.000000
Hg	0.434848	0.706727	0.000000
Hg	0.565152	0.293273	0.000000
Hg	0.706727	0.565152	0.000000
Hg	0.293273	0.434848	0.000000
Total Energy (spin-orbit coup	oling): -470.290201 Ha/cell		

Total Energy (non spin-orbit coupling): -470.088386 Ha/cell

S2. Determination of the appropriate ζ values used in the raMO calculations

In determining the appropriate ζ value used for the Slater-Type Orbitals used in the DFT-raMO analyses, least-squares fittings were performed against the pseudowavefunctions for the valence states in the core region (provided by the VASP PAW-GGA potential files). As the grid used is not evenly spaced (having more data points closer to the core), a pure least-squares fitting would put extra emphasis on reproducing the core region of these pseudowavefunctions, whereas we are much more concerned with the behavior at longer distances. As such, an additional weight factor was used which emphasizes data points that are more sparsely spaced. Mathematically, this sparsity is quantified as the distance between the current grid point and the previous one, called *Diff* for future reference. This value is then scaled even further, as the fit continued to put too large of an emphasis on core reproduction, by raising it to the power of 10. Though this weighting may seem extreme, it guaranteed a reasonable reproduction of the outer regions of the pseudowavefunction, which is desirable in a raMO calculation. Lastly, an additional normalization parameter was allowed to be relaxed alongside the ζ parameter to most accurately reproduce the *shape* of the curve rather than emphasizing its exact values. These features are encoded in the following fit parameter equation, which was minimized in MATLAB using the fminsearch function:

$$f(N,\zeta) = \sum_{all \ grid \ points} \left[[N * STO(n,\zeta) - PW] \times \text{Diff}^{10} \right]^2$$
(S1)

Here, PW represents the input pseudowavefunction values, and STO refers to the appropriate Slater-Type Orbital. Graphical representations of the fits for the valence orbitals of Mn, Cr, and Hg used in the raMO reproductions are shown in Figures S1-7, along with the end value of the fitting function $f(N,\zeta)$ for each case.

Importantly, we have found that the overall results of the DFT-raMO analysis are not strongly dependent on the quality of these fits, as the main goal of using these Slater-Type Orbitals in the first place is merely to template the shape and symmetry of the target orbitals. Even moderate changes in ζ values will not alter the conclusions of the calculation.



Figure S1. Pseudowavefunction (PW) for the Cr 4s orbital and best-fit Slater-Type Orbital.



Figure S2. Pseudowavefunction (PW) for the Cr 3d orbital and best-fit Slater-Type Orbital.



Figure S3. Pseudowavefunction (PW) for the Cr 4p orbital and best-fit Slater-Type Orbital.



Figure S4. Pseudowavefunction (PW) for the Mn 4s orbital and best-fit Slater-Type Orbital.



Figure S5. Pseudowavefunction (PW) for the Cr 3d orbital and best-fit Slater-Type Orbital.



Figure S6. Pseudowavefunction (PW) for the Mn 4p orbital and best-fit Slater-Type Orbital.



Figure S7. Pseudowavefunction (PW) for the Hg 5d orbital and best-fit Slater-Type Orbital.

S3. Exploration of potential role of spin-orbit coupling in Mn₂Hg₅



Figure S8. Comparison of non-spin-polarized LDA-DFT DOS distributions calculated for Mn_2Hg_5 (a) without and (b) with spin-orbit coupling included.

S3. Isosurfaces of the Spin-Polarized DFT-raMO Results



Figure S9. Results of the DFT-raMO spin polarized analysis on Mn_2Hg_5 after orthogonalizing out the Hg d orbitals. (a) raMO results for the majority spin states. The Mn d orbitals appear here are quite localized, with the cross-sections providing a better view of their spread toward neighboring atoms. (b) raMO results for the minority spin states.

Of all of the isosurfaces, the most information can be gleaned from the minority spin d_{xy} and d_{x2-y2} states (those oriented for Mn-Mn δ interactions). In these states, the localization of electrons focuses on the Hg-Hg contacts along the *c* direction of the pentagonal prism. The lack of symmetry in the lobes surronding in these pictures further supports this claim, as the majority of the density is coming from the pentagonal symmetry of Hg dimers. As we are concerned with electrons templated by the Mn atom, not requiring them to reside mainly on the Mn atoms, these states are still considered filled from the viewpoint of the 18-*n* rule.



S4. Mn-Mn π Interactions Over the Course of Dialing-in Spin-Polarization

Figure S10. DOS curves, and slices of the d_{xz} raMOs for Mn in Mn_2Hg_5 gradually including spin polarization. Nonself-consistent calculations were performed with charge densities interpolated between those of the non-spinpolarized and spin-polarized ground states. A gradual opening of the pseudogap near the Fermi energy is apparent across the series.