Non-collinear Spin Characterization of Platinum Catalyst Clusters from Computer Simulations

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Introduction

Catalysts are central to many present and future technologies used in pollution control and energy conservation. The chemical mechanisms of such catalysts however remains largely unknown. A fundamental understanding of these catalytic mechanisms is imperative for optimization of their use in such technologies as in fuel cells of future cars.

The effects of the magnetic properties of catalysts on their catalytic effectiveness remains largely unstudied, though the effects of magnetism on catalytic chemistry has long been reported (Cohn and Hedvall, et al.). The effects of spin in homogeneous catalysis have recently been reviewed (Minaev and Agren).

The Halley research group has developed a self consistent tight-binding (SCTB) code that has been shown calculate band structures, lattice coefficients , and cohesive energies of platinum catalyst clusters consistent with the most accurate and widely used first-principles simulation package, the Vienna Ab-initio Simulation Package (VASP). The ability to calculate spin structures has recently been added to the SCTB code, and its results must be must be verified against VASP calculations before further development can be made to the SCTB code. In the future, the SCTB code will allow simulated catalytic reactions to be studied on a larger scale that is allowed by first principles calculations.

This research has studied the collinear and non-collinear spin structure of 13 atom platinum clusters, as calculated from first principles simulations using VASP.

Methods

The VASP code used was accessed through the Minnesota Supercomputing Institute (MSI). Using the Calhoun computer cluster at the MSI, simulations were run to calculate both collinear and non-collinear spin structures for Pt_{13} clusters with cuboctohedron geometries. No geometric relaxation was performed.

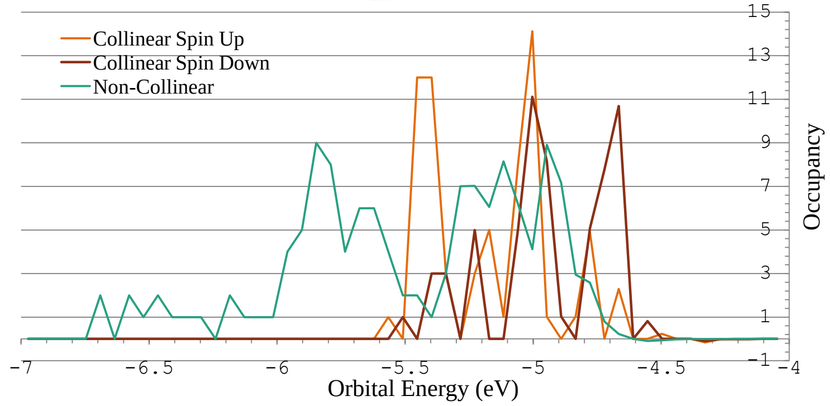
The energy densities of these calculations were extracted and plotted. These plots give the occupancies of the Kohn-Sham orbitals for the Pt_{13} clusters as calculated from the density functional theory based VASP code.

As a preliminary means of analyzing the non-collinear spin structure calculated, the VASP calculated structure was compared to spin structures calculated from a primitive Heisenberg Model. The Heisenberg Model spin structures were calculated via a minimization of the function:

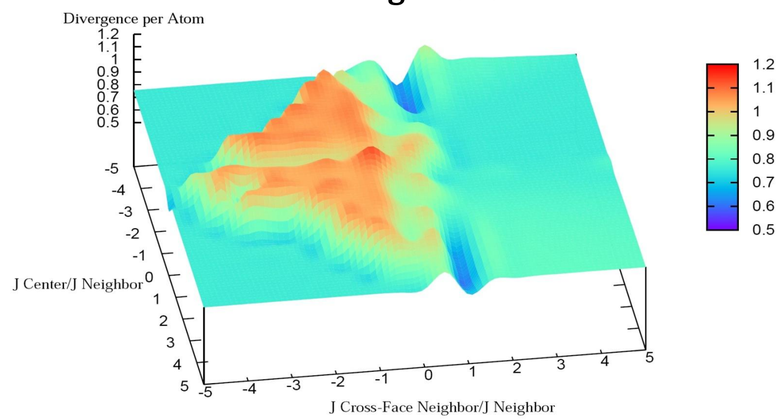
$$E = \frac{1}{2}\sum_{i=1}^{12}\vec{S}_{i,Surface}\cdot\left(\sum_{j=1}^{4}\vec{S}_{j,Neighbor}\right) + J_1\sum_{i=1}^{12}\vec{S}_i\cdot\vec{S}_{Center} + \frac{1}{2}J_2\sum_{i=1}^{12}\vec{S}_{i,Surface}\cdot\left(\sum_{j=1}^{2}\vec{S}_{j,Cross-Face\ Neighbor}\right)$$

where J_1 and J_2 represent variable weights for each of the dot product sums, and S_i is the normalized spin at site i on the cluster surface. The normalized VASP non-collinear result was aligned to Heisenberg Model structure by a Monte Carlo random walk, minimizing the deviation between the two structures. The values of J_1 and J_2 that minimized this deviation were determined, and, using these values, the final aligned spin structures were plotted.

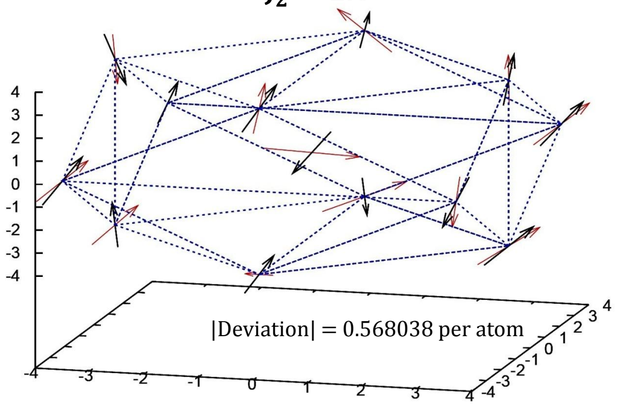
VASP Energy Density in both Collinear and Non-Collinear Calculations (Cuboctohedron Pt_{13} cluster)



Deviation of VASP Non-Collinear Spin Structure vs. Heisenberg Model for Various J Values after Alignment



Heisenberg Spin Structure (Black Arrows) with Aligned VASP Spin Structure (Red Arrows); $J_1 = 4.0$, $J_2 = 1.0$



Results

• The total free energy of the Pt13 cluster in the collinear VASP calculation was -7.957 eV. The total magnetic moment of the cluster was calculated to be ($23.87\mu_B$).

• The total free energy of the Pt13 cluster in the non-collinear VASP calculation was -9.115 eV. The calculated total magnetic moment of the cluster was ($5.00\mu_B$, $6.77\mu_B$, $8.95\mu_B$)

• The Heisenberg Model spin structure showed the greatest correspondence to the calculated VASP non-collinear spin structure when $J_1 = 4.0$ and $J_2 = 1.0$; the average deviation between the two spin structures at these J values was 0.568038 per atom.

Conclusions

Though the current non-collinear VASP calculation of cuboctohedron Pt_{13} clusters is still only partially complete, it has still yielded lower total free energy values, and greater occupation of lower energy Kohn-Sham orbitals, than those of the collinear VASP calculation. The non-collinear calculation also resulted in a smaller (though still non-zero) total magnetic moment than that of the collinear calculation. These observations are consistent with previous studies demonstrating such platinum clusters have intrinsic, non-zero magnetic moments.

The comparison between the VASP non-collinear spin structure and those from the Heisenberg Model exhibited clear minima with varying J_1 and J_2. Again, with partially converged calculations, this suggests a promising correlation between the two models.

The VASP non-collinear calculation for the cuboctohedron Pt13 cluster must reach convergence before firm conclusions can be reached. Once converged, the results will be compared to the SCTB results. Further VASP calculations will be performed on platinum clusters of different geometries and compositions, allowing a thorough review of the SCTB code's current accuracy.

References

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