



Western Washington University
Western CEDAR

WWU Honors Program Senior Projects

WWU Graduate and Undergraduate Scholarship

Spring 2006

A DFT Study of Iron-Oxide Nanoparticle Ground-State Geometries

Danielle McDermott
Western Washington University

Follow this and additional works at: https://cedar.wwu.edu/wwu_honors

 Part of the [Physics Commons](#)

Recommended Citation

McDermott, Danielle, "A DFT Study of Iron-Oxide Nanoparticle Ground-State Geometries" (2006). *WWU Honors Program Senior Projects*. 229.
https://cedar.wwu.edu/wwu_honors/229

This Project is brought to you for free and open access by the WWU Graduate and Undergraduate Scholarship at Western CEDAR. It has been accepted for inclusion in WWU Honors Program Senior Projects by an authorized administrator of Western CEDAR. For more information, please contact westerncedar@wwu.edu.



HONORS THESIS

In presenting this Honors paper in partial requirements for a bachelor's degree at Western Washington University, I agree that the Library shall make its copies freely available for inspection. I further agree that extensive copying of this thesis is allowable only for scholarly purposes. It is understood that any publication of this thesis for commercial purposes or for financial gain shall not be allowed without my written permission.

Signature _____

Date 6/17/06

A DFT Study of Iron-Oxide Nanoparticle Ground-State Geometries

Danielle Marie McDermott

Advisor Brad L. Johnson

WWU Department of Physics and Astronomy

Senior Project – Spring 2006

Density Functional Theory was used to construct a ground state configuration for Fe₂O₃, or maghemite. The bipyramidal structure that resulted from a numerical optimization scheme was computationally stable with a lower energy than individual (free) components of the molecule. These stable bipyramids form a basic building block to generate iron-oxide nanoparticles. The primary focus of the study is understanding appropriate input geometries and using proper basis sets to model the real system, and to approximate possible reaction kinetics with other compounds.

I. Introduction

It is impossible to solve any quantum mechanical system beyond the hydrogen atom exactly. Instead there are career making approximation schemes to understand the qualitative behavior of molecular systems at the quantum level. The general Hamiltonian for a molecule is:

$$\hat{H} = V_{Kinetic} + V_{Nucleus-Electron} + V_{Electron-Electron} + V_{Nucleus-Nucleus}$$

Which can be expressed mathematically as:

$$\hat{H} = \sum_i \left\{ -\frac{1}{2} \nabla_i^2 \right\} + \sum_{iA} \left\{ -\frac{Z_A}{r_{iA}} \right\} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

The simplest case of the many body problem is the Helium atom:

$$\hat{H}_{Helium} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

But unfortunately, while the potential energy landscape of a system can be written, these are insoluble. To get around this difficulty, physicists often use the variational principle solve for the ground state energy of a system. The variational principle says for some Hamiltonian, we can pick a wavefunction, any wavefunction, and use it to solve for an energy. We know that for whatever energy comes out...

$$E_{GS} \leq E$$

If we put a dimensionless parameter λ in our wavefunction (we pick out of the sky anyway), we can minimize whatever energy we get:

$\frac{dE}{d\lambda}$, to find the λ that gives us a minima. This will take us closer to the ground state.

This is a fine start, but to implement this method, various solution schemes are necessary.

Generally, we can solve for the energy of the system

$$E = \int \psi^*(x_1, x_2, \dots, x_N) \hat{H} \psi(x_1, x_2, \dots, x_N) dx_1 dx_2 \dots dx_N$$

The Hartree-Fock or Self Consistent field method takes this notion and states that

$$E = \sum_a I_a + \frac{1}{2} \sum_{a,b} (J_{ab} - K_{ab})$$

Where the Kinetic and Nucleus-Electron piece is rolled into

$$I_a = \int \phi_a(x) \left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right\} \phi_a(x) dx,$$

The electron-electron pairs are described by

$$J_a = \iint \phi_a(x_1)^2 \frac{1}{r_{12}} \phi_b(x_2)^2 dx_1 dx_2 \quad (\text{direct})$$

$$K_a = \iint \phi_a(x_1) \phi_b(x_1) \frac{1}{r_{12}} \phi_a(x_2) \phi_b(x_2) dx_1 dx_2 \quad (\text{exchange})$$

This amounts to the square terms and the cross/exchange terms for a generalized wavefunction of two identical fermions

$$\phi(x_1, x_2) = \frac{1}{\sqrt{2}} [\phi_a(x_1) \phi_b(x_2) - \phi_b(x_1) \phi_a(x_2)]$$

This wave function can be expressed generally as an N body Slater determinant:

$$\phi(x_1, x_2, \dots, x_N) = \begin{vmatrix} \phi_a(x_1) & \phi_b(x_1) & \dots & \phi_N(x_1) \\ \phi_a(x_2) & \dots & \dots & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_a(x_N) & \dots & \dots & \phi_N(x_N) \end{vmatrix}$$

Kohn-Sham is Hartree-Fock with the exchange correlation piece. XC is the black magic that allows us to obtain accurate answers with these methods.

Density Functional Theory comes out of the first theorem of the Hohenberg-Kohn. The idea is that if the density of a given system is known, then we know what the probability DENSITY amplitude is!

$$\rho(\vec{r}) = N \iint \dots \iint |\psi(\vec{r}, \vec{r}_1, \dots, \vec{r}_N)|^2 ds dx_2 \dots dx_N$$

The wavefunction is a unique functional of the density. The energy of a system, is the energy, is the energy. So, instead of guessing a wavefunction and crunching out an energy to minimize, find the energy based on the electron density, and minimize that:

$$E_{GS} \leq E(\rho) ,$$

And just as the Hamiltonian can be broken into the different potentials:

$$E(\rho) = E^K(\rho) + E^V(\rho) + E^J(\rho) + E^{XC}(\rho)$$

Nucleus-Electron and Nucleus-Nucleus:

$$E^V(\rho) = -\sum_A Z_A \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_A|} d\tau + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

Electron-Electron:

$$E^J(\rho) = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\tau_1 d\tau_2$$

Kinetic Energy Functional—first approximation based on Thomas-Fermi Method – like the first year type model of the motion of a particular wandering through a gas

$$E^K(\rho) = \frac{3}{10} (3\pi^2)^{2/3} \int [\rho(\vec{r})]^{5/3} d\tau$$

Exchange-Correlational Black Magic – comes out of the Paul Exclusion principle and electron correlation

$$E^X(\rho) = -\frac{9}{8} \alpha \left(\frac{3}{\pi}\right)^{1/3} \int [\rho(\vec{r})]^{4/3} d\tau$$

Kohn-Sham – hybrid of DFT and HF

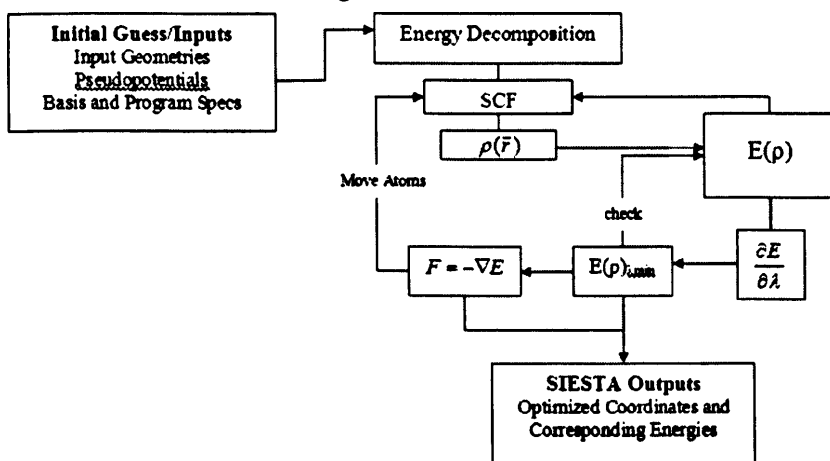
$$\left\{ -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|\vec{r} - \vec{R}_A|} + V^J(\rho) + V^{XC}(\rho) \right\} \psi_a(\vec{r}) = E_a \psi_a(\vec{r})$$

The SIESTA Code:

So, this is great... if we know the wavefunction, we can get the density, so we can get the energy, so we can... find the energy without finding the wavefunction???

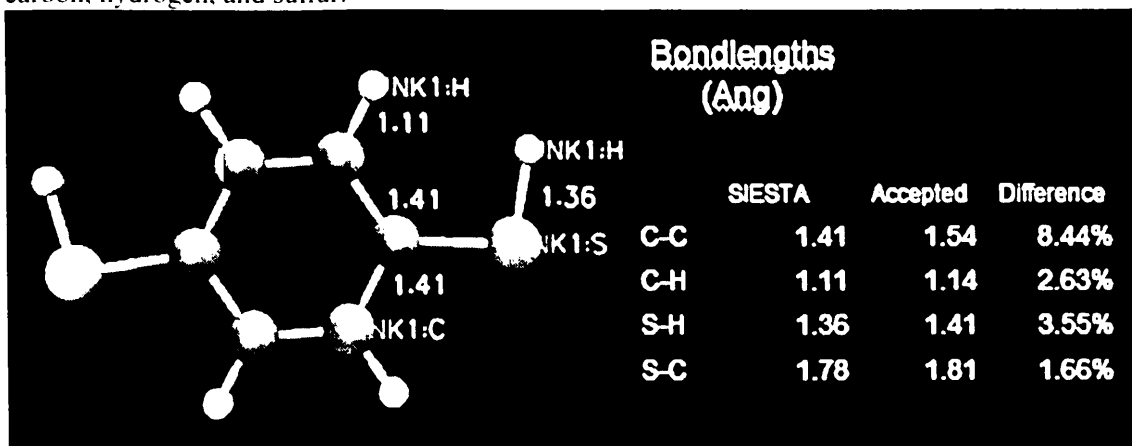
The problem with all this, is that we can get energies based on the electronic density of a system, BUT we have to start with a guess of the wavefunction – using Slater Determinants to describe the wavefunctions of the electrons. We will also use pseudopotentials to describe the wavefunctions of the nucleus and core electron system.

To implement this for any number of atoms, it is necessary to use a computer code. To look at the iron-oxide system, we used the SIESTA code, or the Spanish Initiative for Stimulating Thousands of Atoms. The algorithm of the code is below:

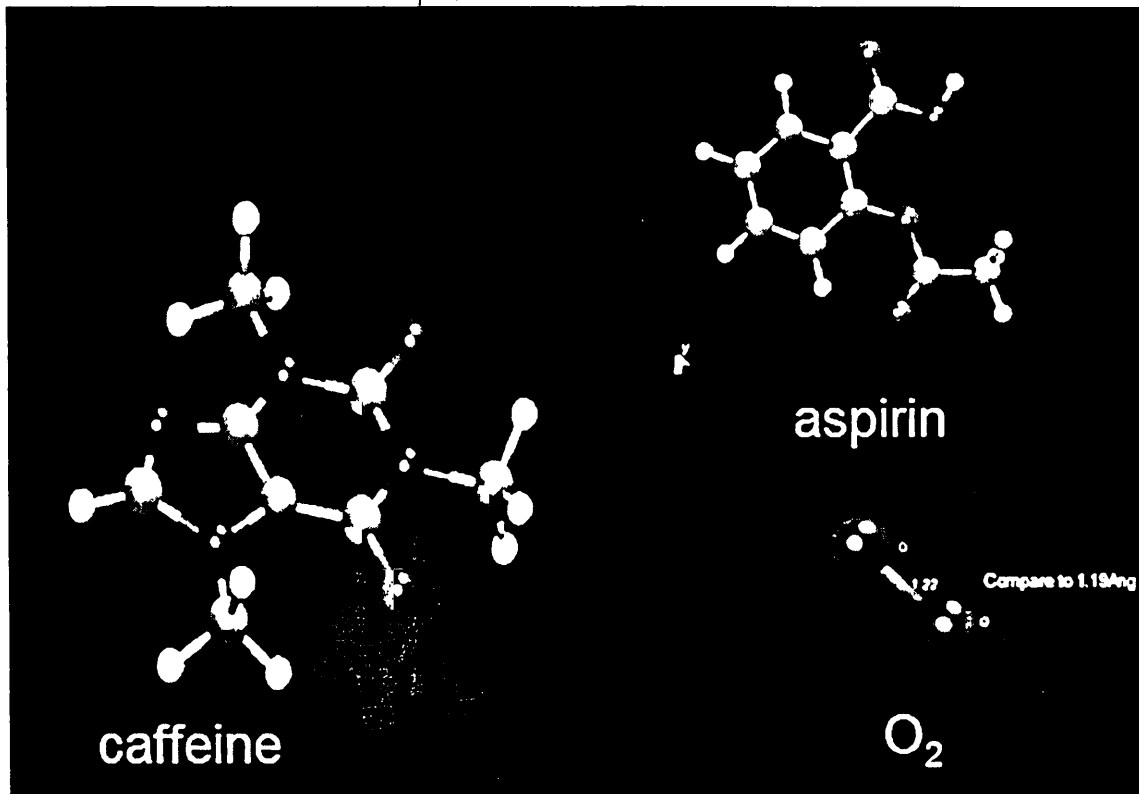


So the general scheme is to feed SIESTA a geometry with the guesses at the various wavefunctions (both basis sets and pseudopotentials) and use the Self Consistent Fields method to get out the electron density. Use this to find the energy, and minimize. Once this energy stops changing, the system is in the groundstate.

Before using the code to look at the geometries of iron-oxide nanoparticles, it was necessary to use well understood systems to understand SIESTA. The first system examined was benzenedithiol. It was necessary to use the ATOM program to generate pseudopotentials for carbon, hydrogen, and sulfur.



Covalent bonds in SIESTA are simple, here are some basic molecules:

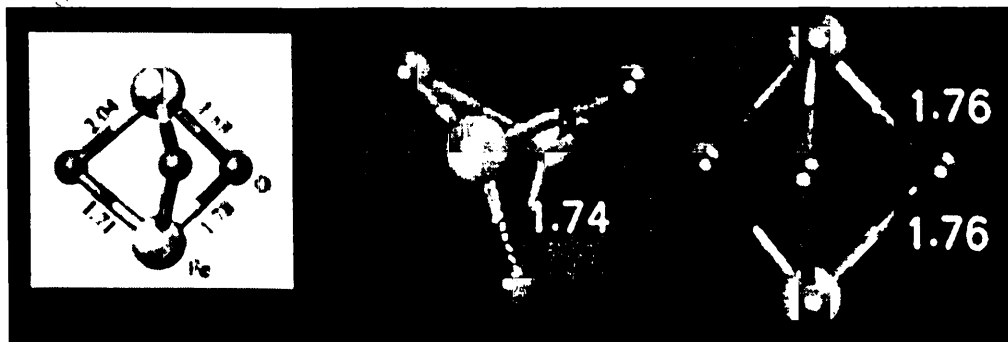


Ionic Bonds are harder. It turns out that it is possible to strip electrons off an atom and make a positively charged pseudopotential, but it is not possible to add electrons to make a negatively charged ion. To set the charge of the atoms so that a bond will form, SIESTA requires an explicit basis set with charge defined.

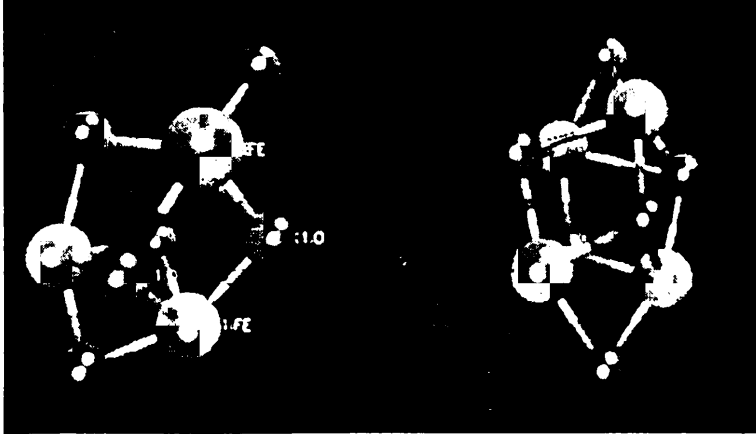
Iron-Oxide Nanoparticles:

The choice to examine iron-oxide nanoparticles stems from the hydrogen fuel cell problem. Obtaining and storing pure hydrogen requires as much energy as the output of any fuel cell. To make this process cleaner, it is highly desirable to desulfurize fuel so that it will burn clean. Chemists are searching around for a catalyst that will perform this reaction.

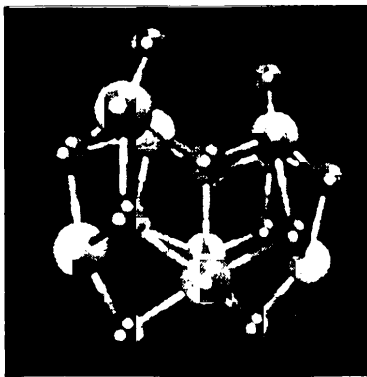
Since it has been shown that iron-oxide nanoparticles will catalyze such reactions, it is interesting to examine their geometries and use SIESTA to model such catalysis. After much pain and deliberation, the bipyramidal structure found by Reddy and Khanna¹ was reproduced using SIESTA:



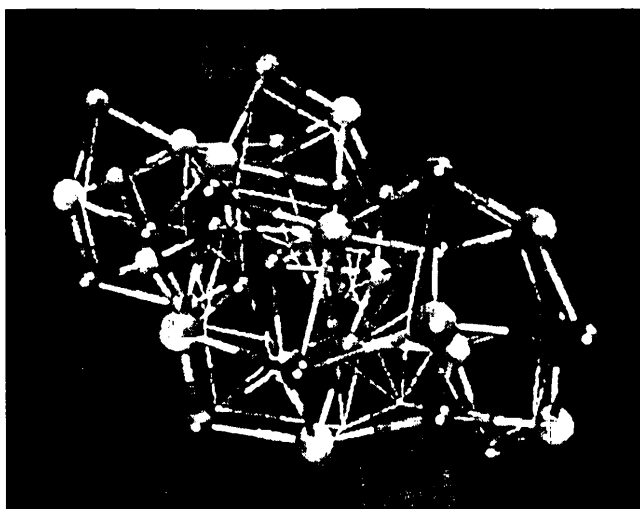
Once this basic unit was formed, it was a simple matter of placing multiple bipyramids close together and looking for more stable structures. The resulting geometry was considered a nanoparticle: larger than a single molecule, but lacking the properties of a crystal.



Once this was achieved, we could easily double our size:



And double that:



Conclusion:

This project has really become interesting now that I have run out of time. Given the computational time required to optimize these large systems, further results are out of the question. It would be interesting to look for a crystalline structure with enough atoms. Because density functional theory is really effective at looking at geometries, it would be extremely useful to perform extended Huckel theory to these nanoparticles to examine the nature of the bonds. Obviously the catalysis reaction that was to follow will be left for the next student.

¹ Reddy, B.V., Khanna, S.N., *Self-Stimulated NO Reduction and CO Oxidation by Iron Oxide Clusters*. Physical Review Letters. Vol 93, Num 6.