



Development of a Force Field for Iron Oxide Catalysts

By Josh Slocum

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Outline



Disclaimer: No force field has been developed yet!

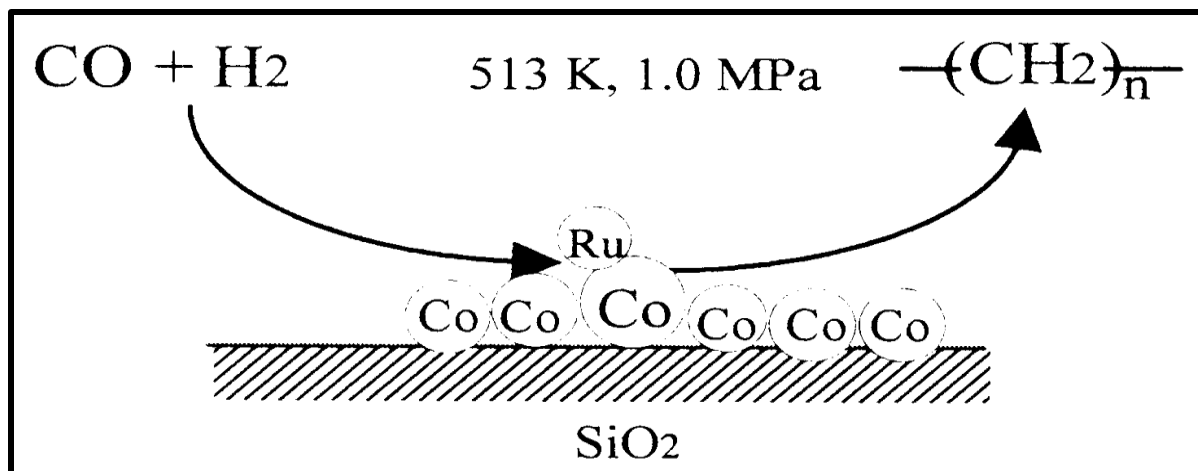
I will provide you with...

- 1) Background
- 2) Force field game plan
- 3) How I followed the game plan
- 4) What comes next

Why Iron Oxide?



- Several transition-metal oxides are useful as catalysts in the Fischer-Tropsch process, where coal, natural gas, and biomass are converted to useable petroleum.
- We are studying Fe and Al to construct a force field that will help us understand the catalysis process and hopefully be transferable to other metal oxides.



What is a force field?



- All of the parameters and equations that describe the potential energy of a system
- Types of equations and parameters depend on the system at hand
- In this case the types of interactions are: bonded, non-bonded, van der Waals, electrostatic, and polarizable.



Why do we want a force field?



- Previous *Ab initio* calculations have explained certain processes very well for small systems.
- Material defects on catalyst surfaces often give rise to high catalytic activity, a process that is very unlikely seen with small systems in *ab initio* methods.
- We think a force field approach with higher time scale *ab initio* can provide more insight into the catalytic process of metal oxides.



Process to Develop Force Field

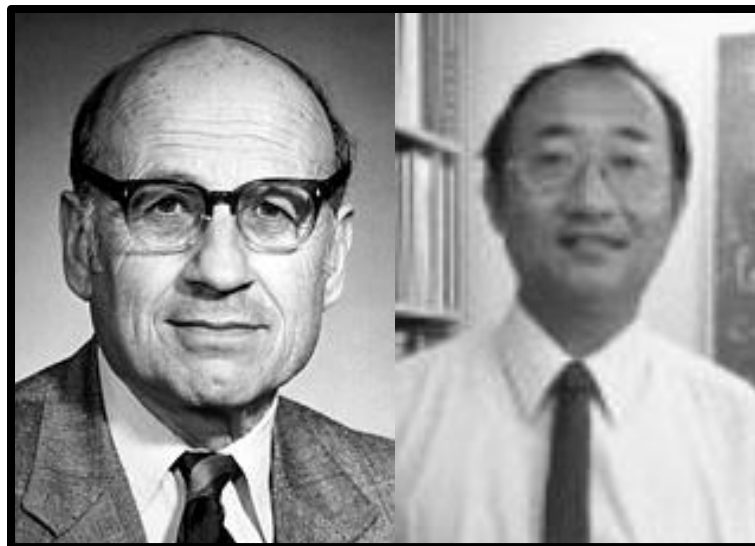


- Optimize geometry of small molecules to reproduce crystal structure
- Run relaxed potential scans on optimized geometries
- Calculate force constants from potential scans
- Calculate charge densities
- Pull together all parameters for force field
- Test the force field

Geometry Optimizations Using Gaussian



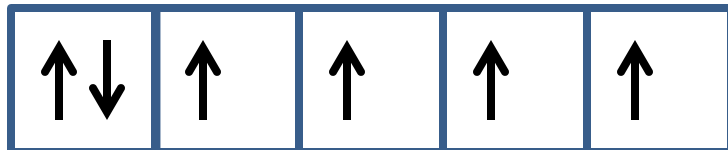
- Build a molecule using GaussView interface
- Gaussian uses density functional theory (DFT) to find the 'preferred' geometry.
- For calculations on Iron we used the m06-l functional with the 6-311+G(d,p) basis (*large*) and sometimes the LANL2dz basis (*small*).



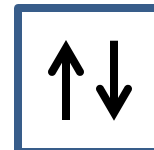
Predicting the Ground State Spin State



Fe



3d



4s

$$2S + 1 =$$
$$2(4/2) + 1 = 5$$

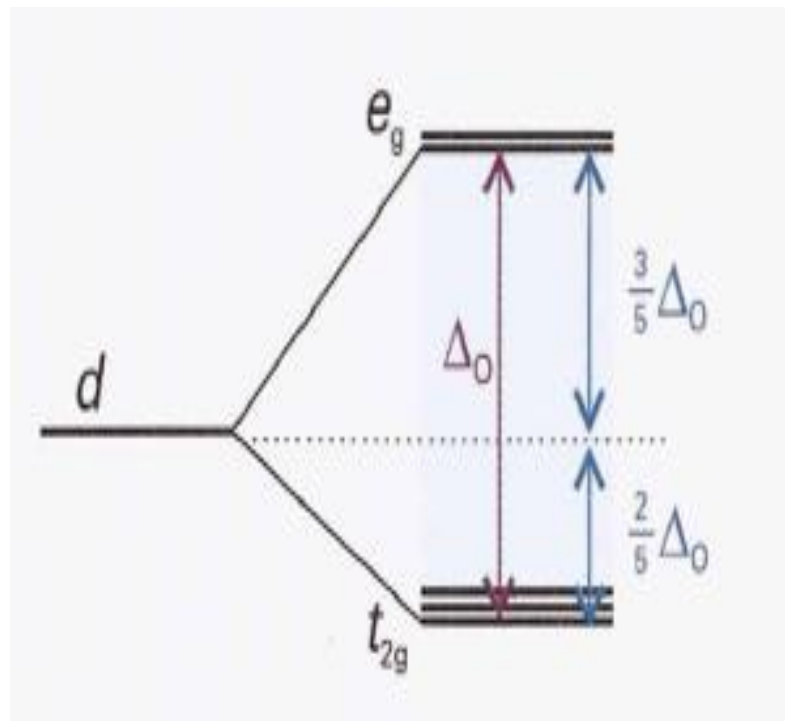
$$2S + 1 =$$
$$2(4/2) + 1 = 5$$

$$2S + 1 =$$
$$2(5/2) + 1 = 6$$

Ligand Field Splitting



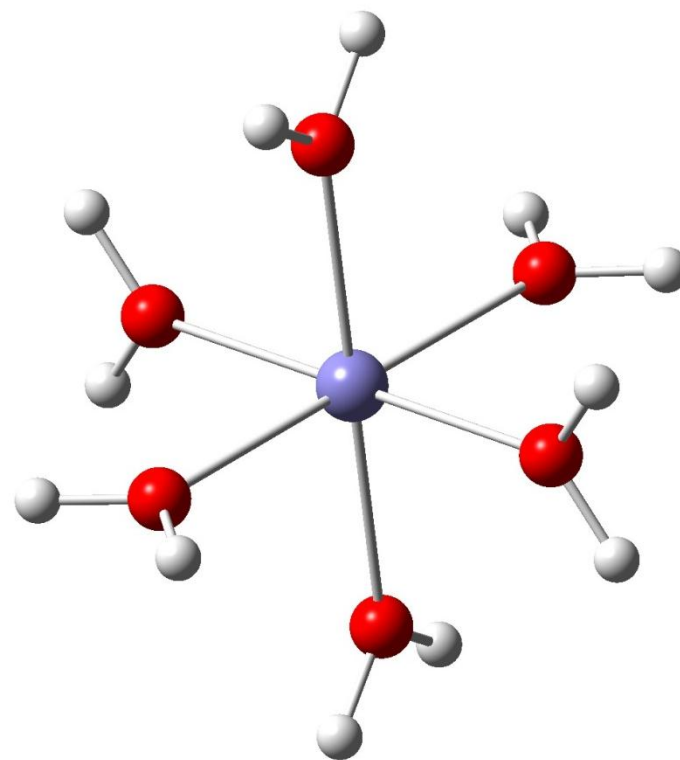
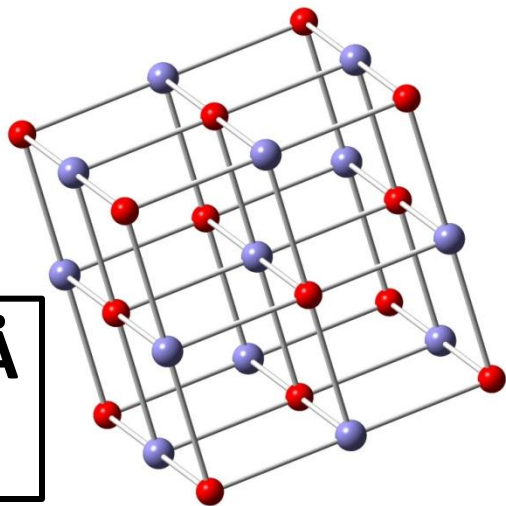
- The electron configurations and spin states from the previous slide were for single Iron atoms/ions.
- Octahedral complexes should show ligand field splitting.
- We didn't observe this.



Optimization of $[\text{Fe}(\text{OH}_2)_6]^{2+}$



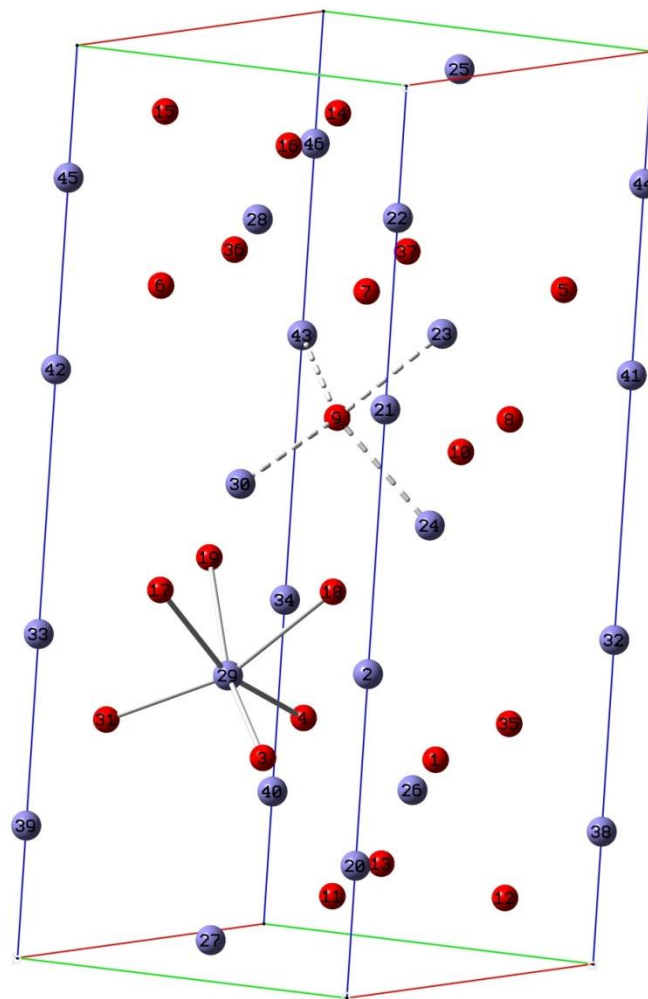
- We wanted to build a complex of Fe^{2+} that would mimic the crystal structure of FeO .



Optimization of $\text{Fe}(\text{OH}_2)_3(\text{OH})_3$

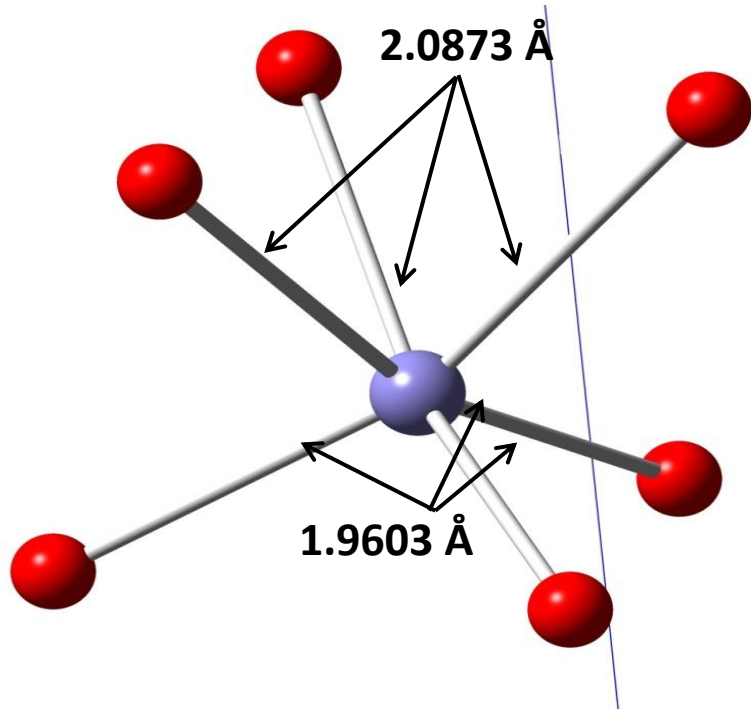


- Iron 3+ proved to be more troublesome than Iron 2+.
- Tried several different geometries before deciding on $\text{Fe}(\text{OH}_2)_3(\text{OH})_3$.
- Reproduced important features of crystal structure, but with less accuracy than desired.

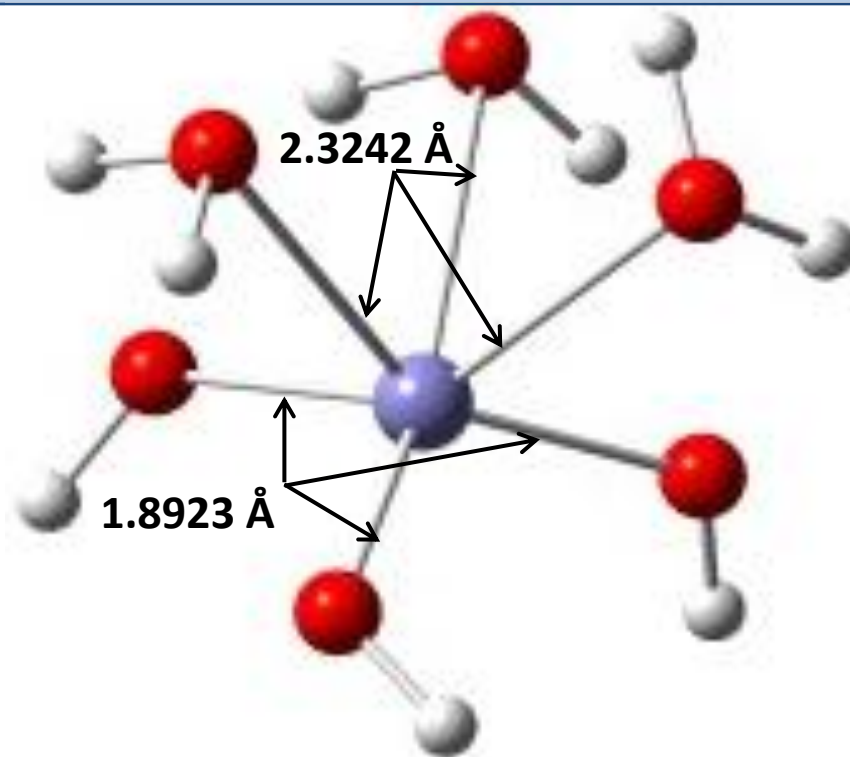


Crystal Structure

Geometry from Gaussian calc.



The angles between the shorter bonds are greater ($\sim 103^\circ$). Those between the longer bonds are smaller (77.6°).



The angles between the shorter bonds are greater ($\sim 111^\circ$) while those between the longer bonds are smaller ($\sim 77^\circ$).

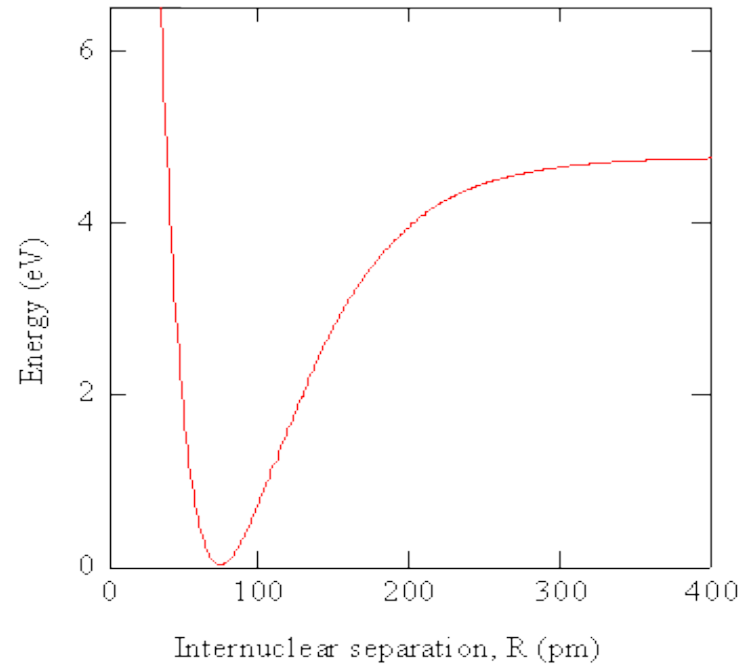
Relaxed Potential Energy Scans



- From optimized geometries, scan a variable (bond or angle). The geometry of the molecule is allowed to 'relax', and an energy calculation is performed.
- Bonds are treated as harmonic oscillators. Force constants can be calculated from the scans.

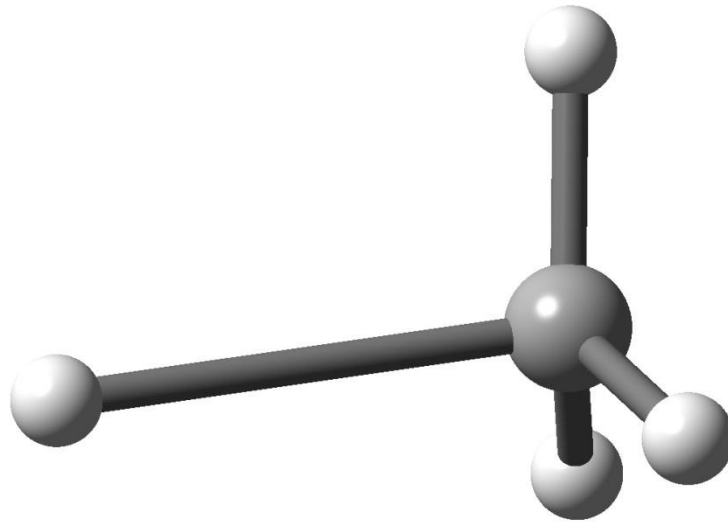


Getting Force Constants from Scans

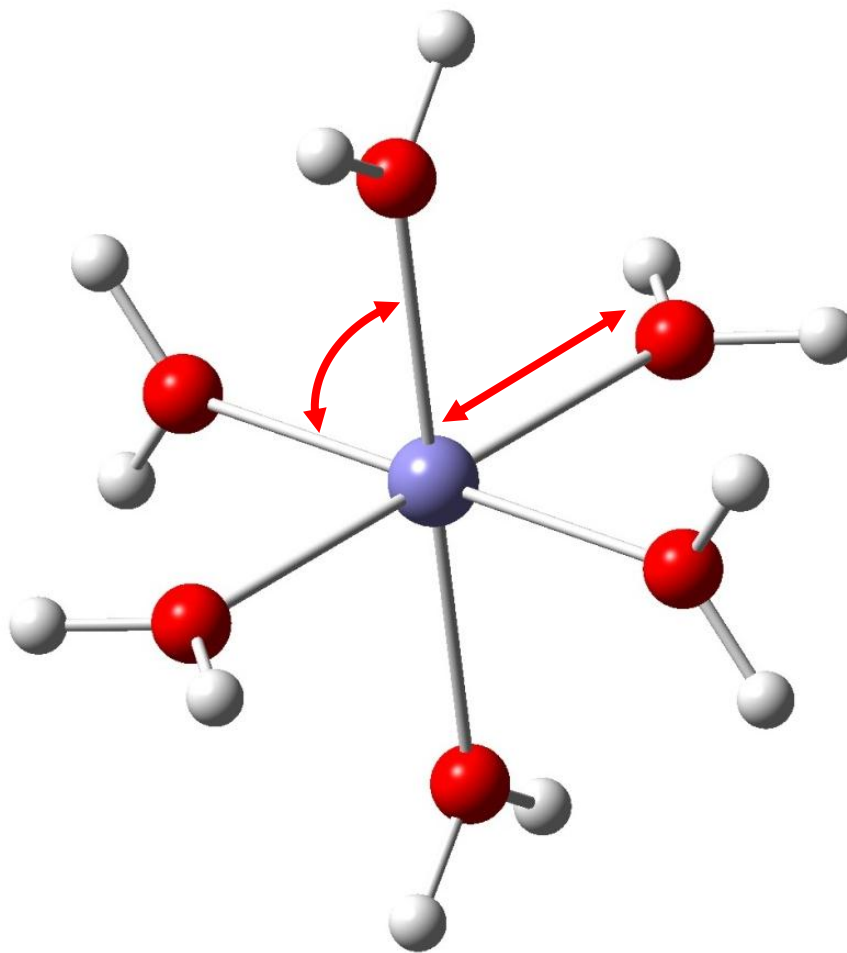


$$\left(\frac{\partial^2 V}{\partial r^2}\right) = k$$

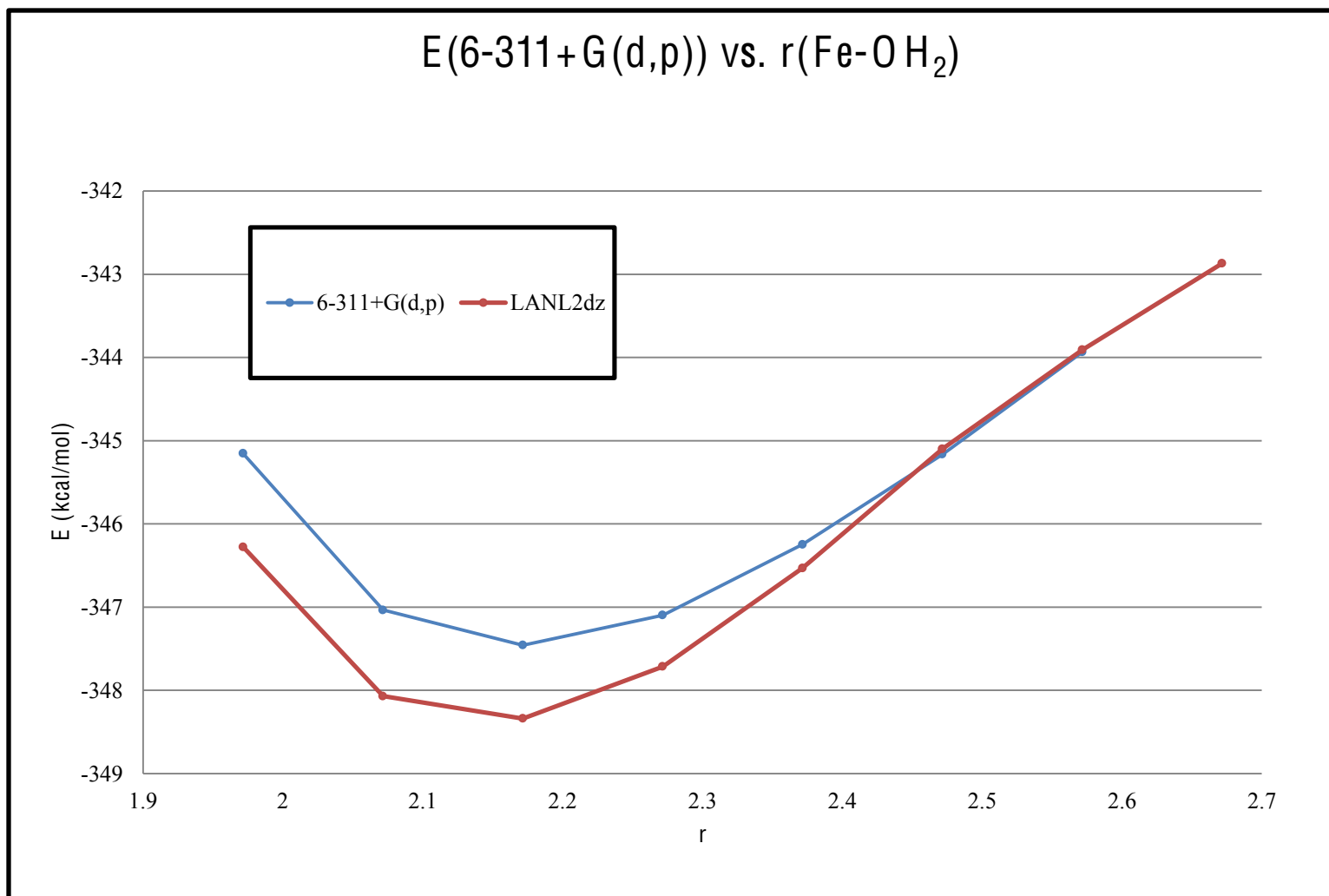
Example Relaxed Potential Scan



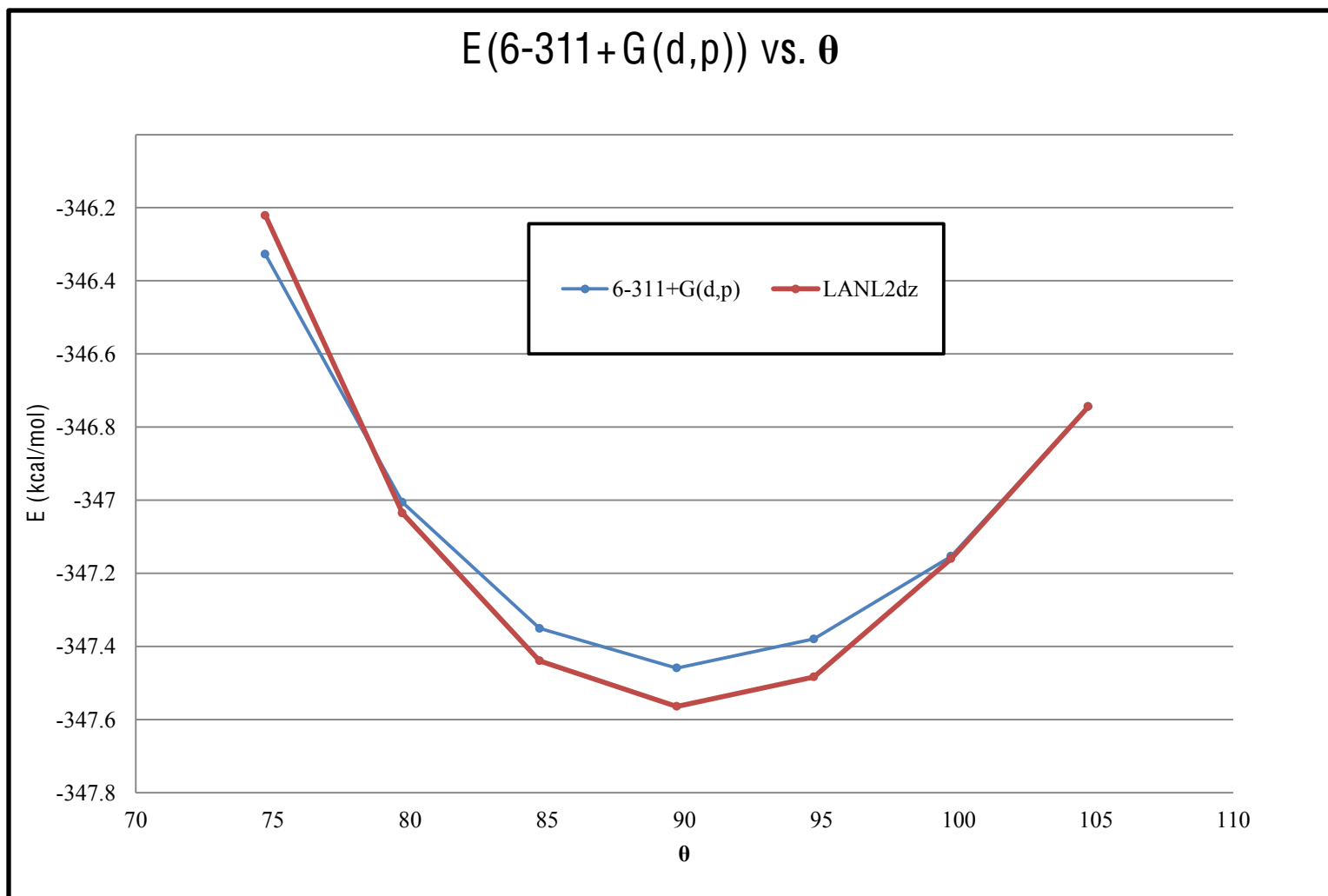
Potential Scans for $[\text{Fe}(\text{OH}_2)_6]^{2+}$



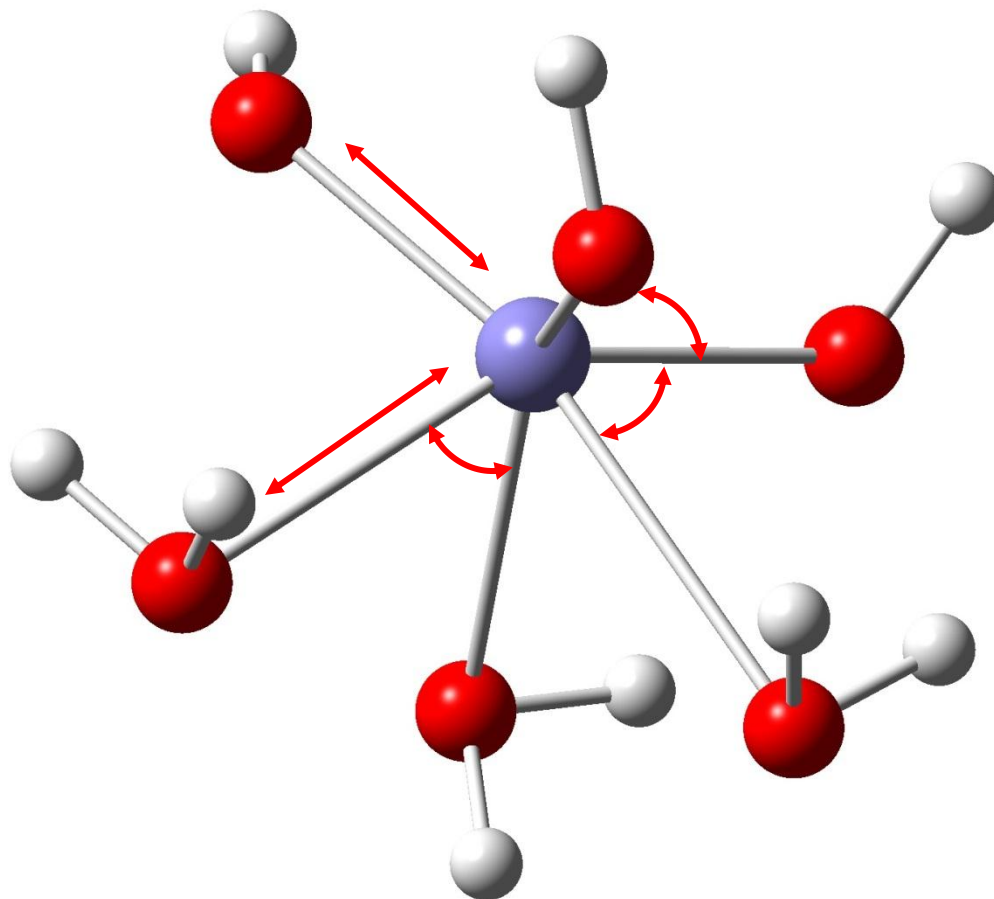
Potential Scans for $[\text{Fe}(\text{OH}_2)_6]^{2+}$



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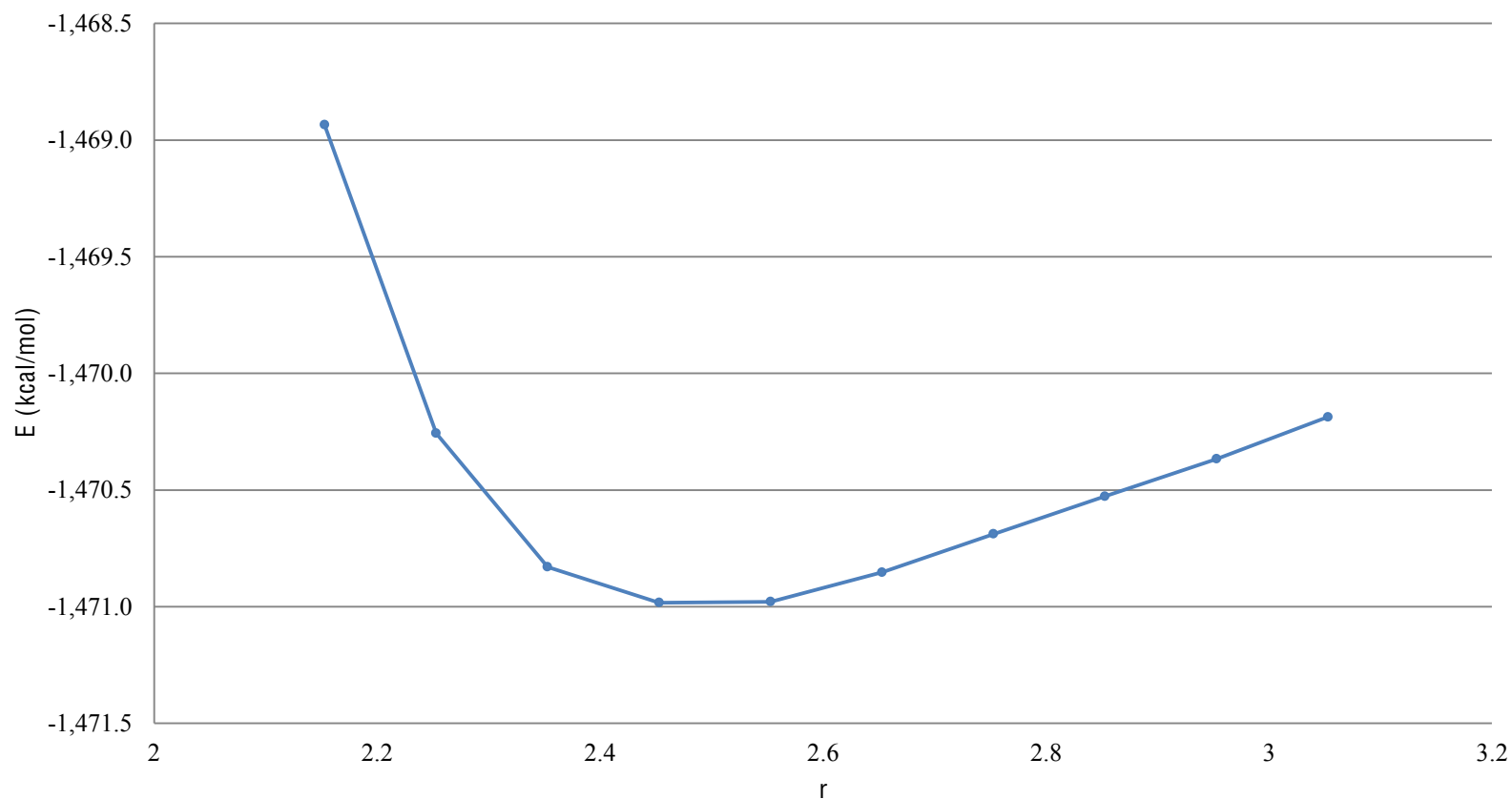
Potential Scans for $\text{Fe}(\text{OH}_2)_3(\text{OH})_3$



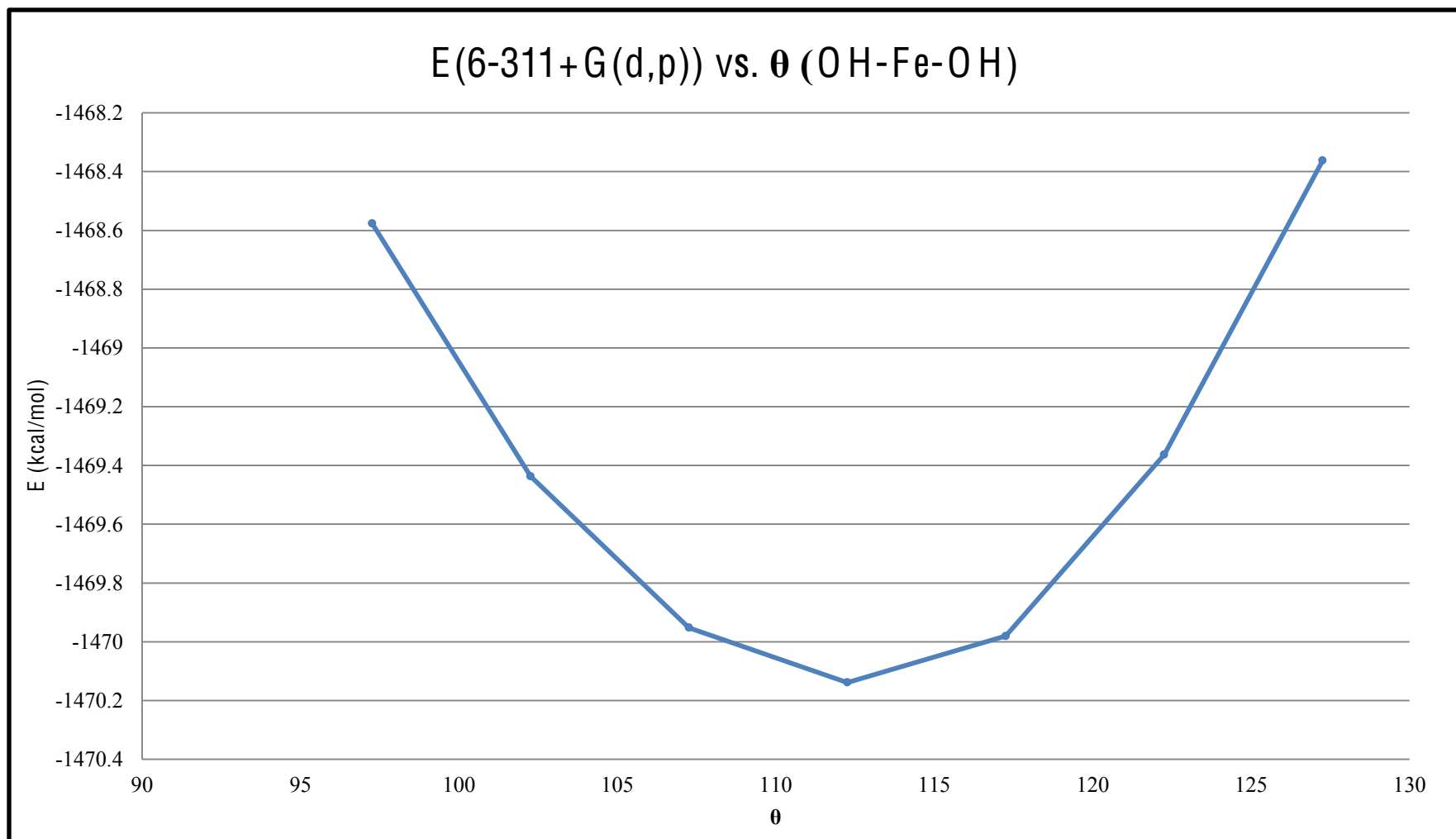
Potential Scans for $\text{Fe}(\text{OH}_2)_3(\text{OH})_3$



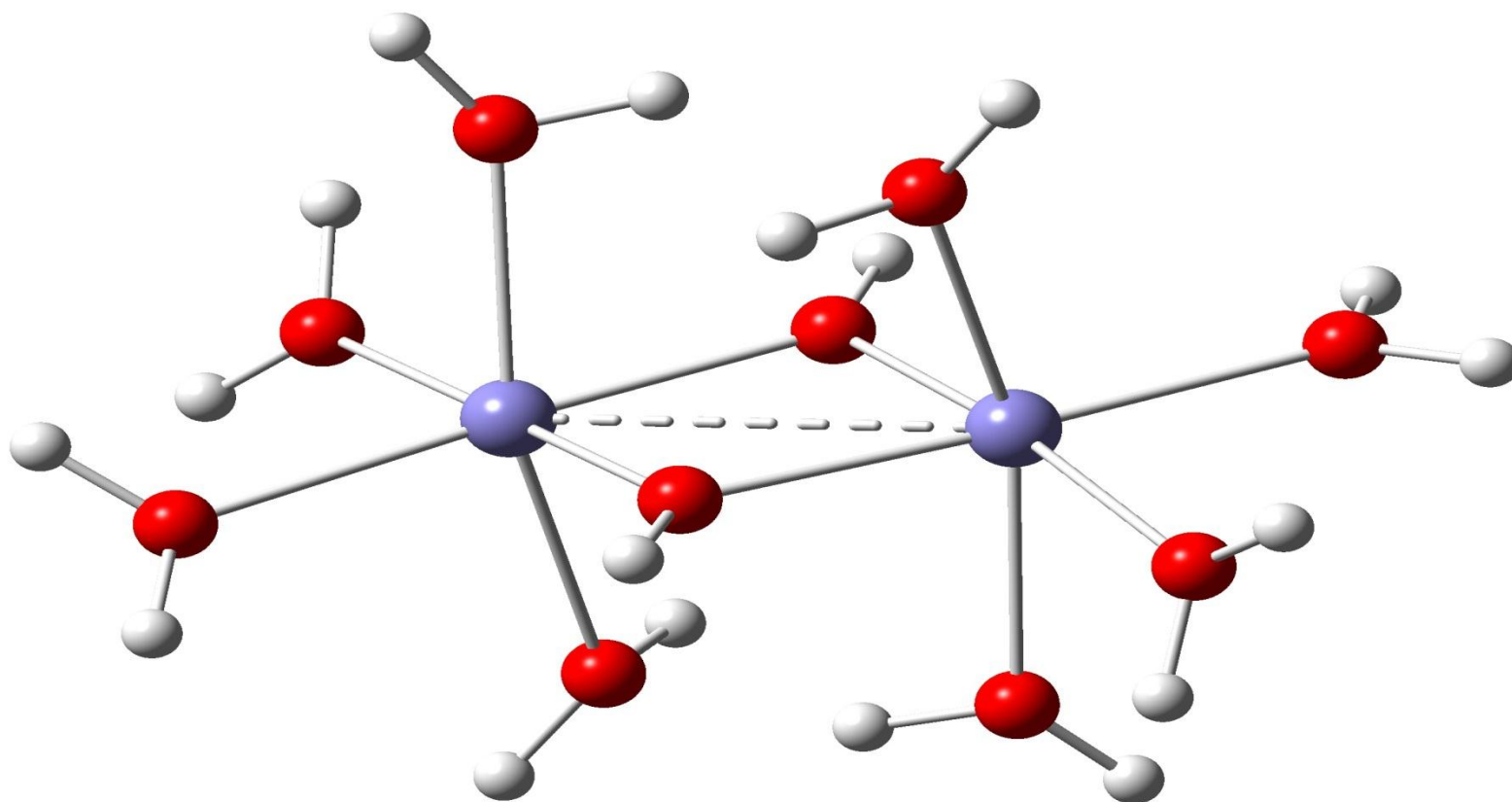
E(6-311+G(d,p) vs. r(Fe-OH₂)



Potential Scans for $\text{Fe}(\text{OH}_2)_3(\text{OH})_3$



Fe-Fe non-bonded interactions



What is left to do?



- Solve problem with Fe_2O_3 scans
- Quantum Espresso?
- Pull together parameters for force field
- Test the model

Thanks to everyone involved with this research



- Dr. Ramu
- Dr. Wick
- Shuo Yao
- NSF
- LA-SiGMA