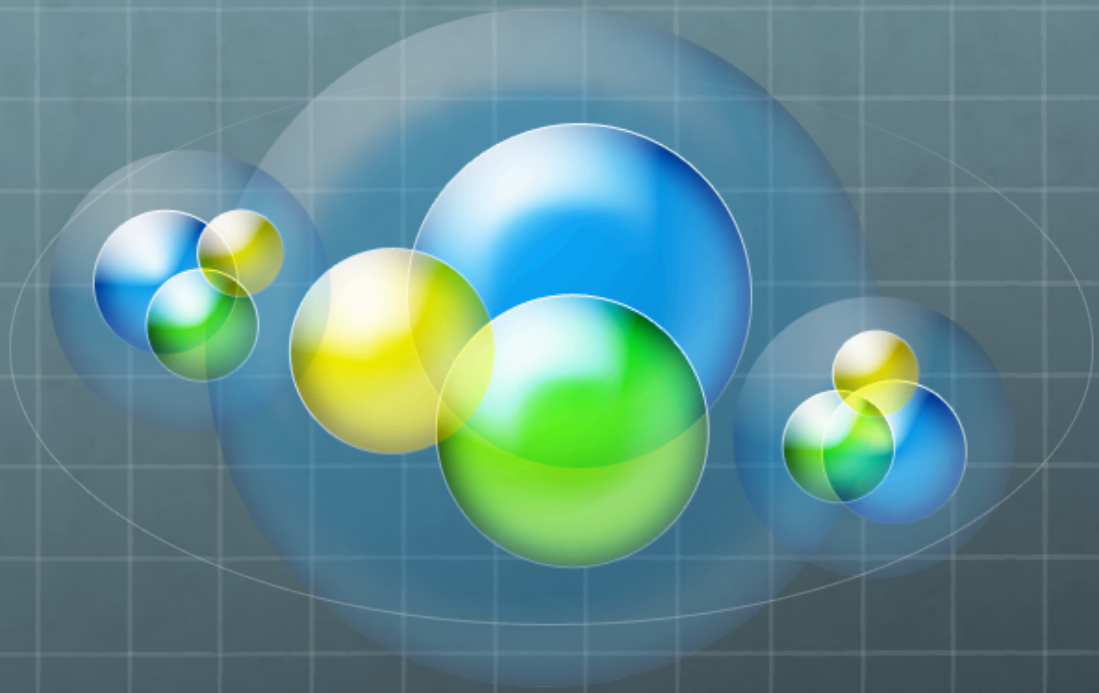
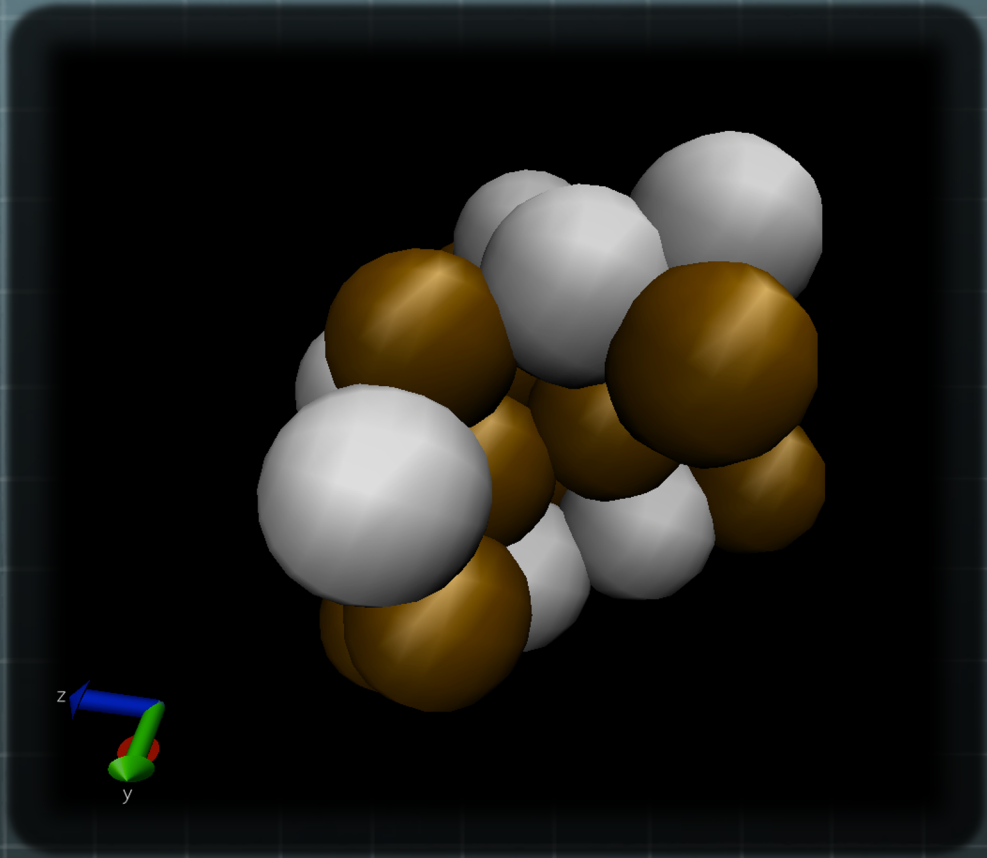


Using Simulation to Investigate the Contribution of Graphene to Pt & Pd Based Catalysts

Jason Castaneda, Oregon State University

Overview

- Background
- Objectives
- Methods
- Results & Discussion
- Conclusions
- Future Works
- Acknowledgements
- References
- Time for Questions



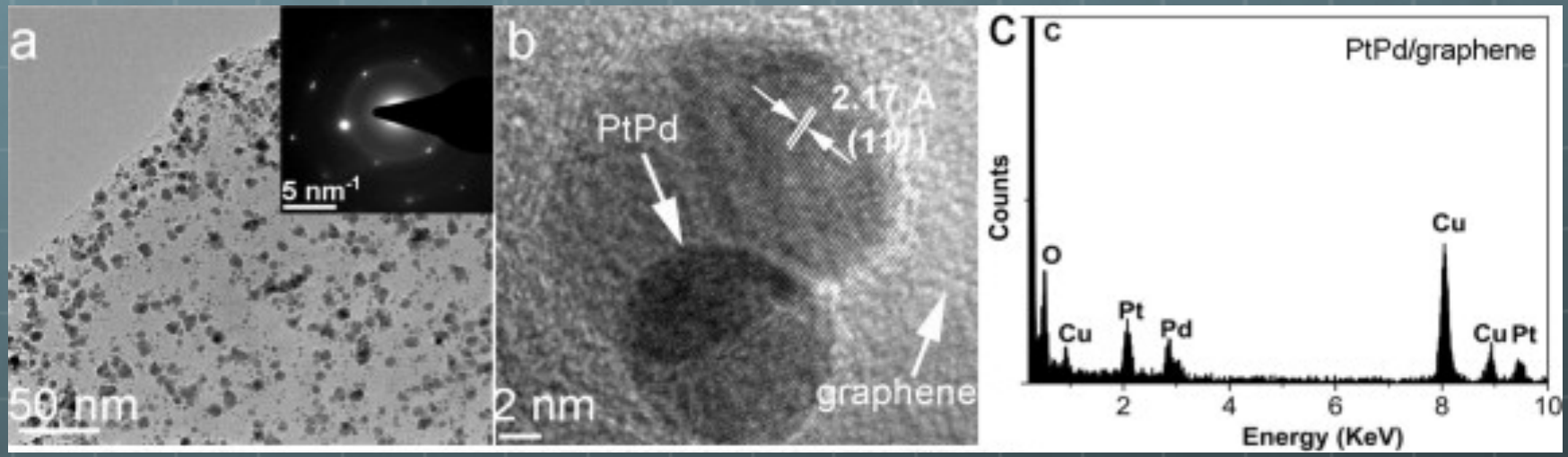
24-atom Pt-Pd Alloy Rendered in VMD

Background

- Pt based catalysts
- Current research on various catalysts in presence of graphene
- Introduction to molecular dynamics simulation
  - Classical mechanics simulations
  - Ab initio simulations

Pt-based Catalysts

- Pt-based catalysts important to advancing new technologies
  - Oxidation and hydrogenation reactions
  - Pt/C catalysts used in methanol oxidation for direct methanol fuel cells
- Pt catalysts suffer from significant limitations
  - Pt atoms become poisoned by carbon monoxide
  - One-time use
  - Relatively short lifetime
  - Pt is expensive
- Either Pt's potency or lifetime can be improved



TEM images of graphene decorated with PtPd from Qian et al. (2013)

Catalysts & Graphene

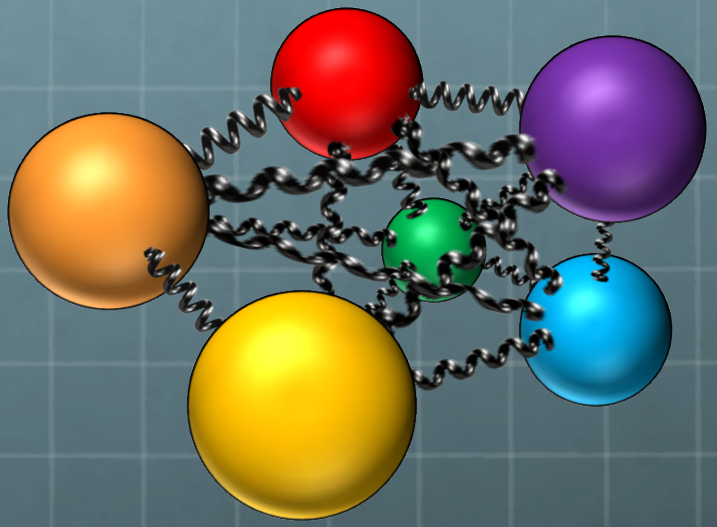
- **Current research has investigated catalysts adsorbed onto graphene**
  - **Pt-Pd on graphene had a four times larger chemically active site compared to Pt/C**
  - Au-Pd on graphene many times more effective for water purification than Au-Pd alone
- Presence of graphene significantly improves potency of catalysts
- Pt-Pd alloy raises Pt's tolerance to poisoning

Molecular Dynamics Simulation

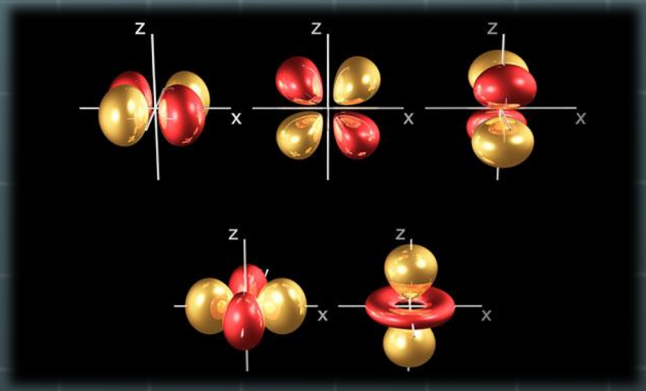
- Simulations governed by classical mechanics
  - Forces on atomic systems are computed using Newton's laws
  - Atoms modeled like marbles attached by magic springs
  - Assumptions made to make atoms behave "naturally"
- Ab initio simulation
  - Cutting edge method for molecular simulation
  - Incorporates Newtonian physics and wave functions (Schrodinger Equation)
  - Simulates the exact theoretical behavior of atoms
  - Very little assumption

$$F = ma$$

Newton's 2nd Law



Resistance (2013). Retrieved 08/06/13, from: http://www.javaworld.com/javaworld/jw-02-2013/130213-smart-shops-know-when-resistance-is-fertile.html



Quantum Mechanics. (2013). Retrieved 08/06/13, from: http://www.bbc.co.uk/science/space/universe/questions_and_ideas/quantum_mechanics

$$E\psi(r) = \frac{-h^2}{2m}\nabla^2\psi(r) + V(r)\psi(r)$$

The Schrodinger Equation

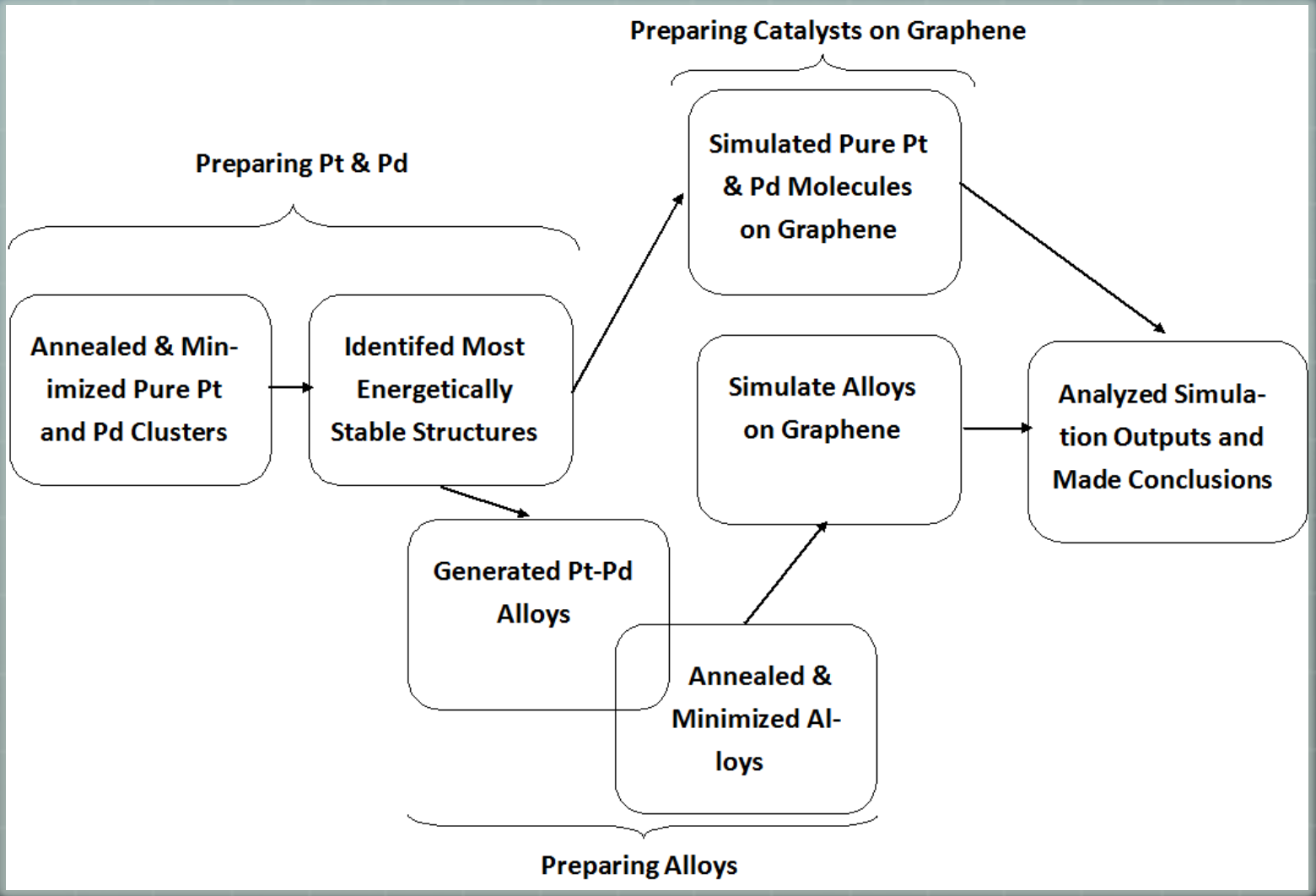
Objectives

- What does the graphene do to the Pt that causes improved catalysis
- Characterize the observed electronic interaction between graphene and adsorbed metals
  - Simulate Pt, Pd, and Pt-Pd alloys deposited on graphene
  - Charge transfer, band alignment, projected density of states

Key Research Tools

- SIESTA Computer Program (Spanish Initiative for Electronic Simulation of Thousands of Atoms)
- MATLAB
- VMD (Visual Molecular Dynamics)
- TACC (Texas Advanced Computing Center)
  - An NSF user facility operated by the Extreme Science and Engineering Discovery Environment (XSEDE)

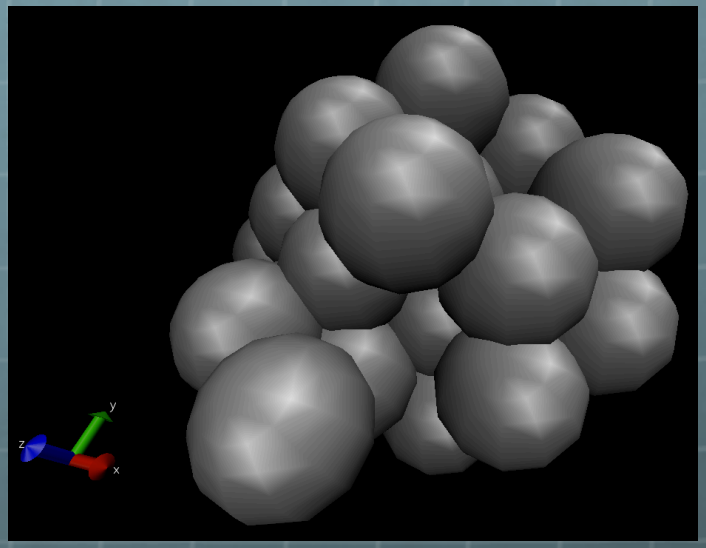
Key Research Steps



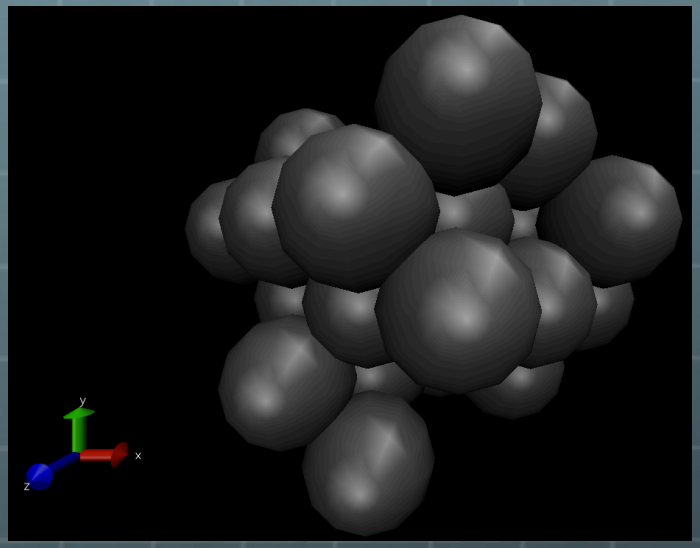
Creating Stable Molecules

- Simulated molecules of pure Pt & Pd from 8 to 40 atoms
- Initial minimization simulation
- Annealing simulation
- Second minimization simulation
- Plot molecule energies for each simulation
- Identify especially stable molecules

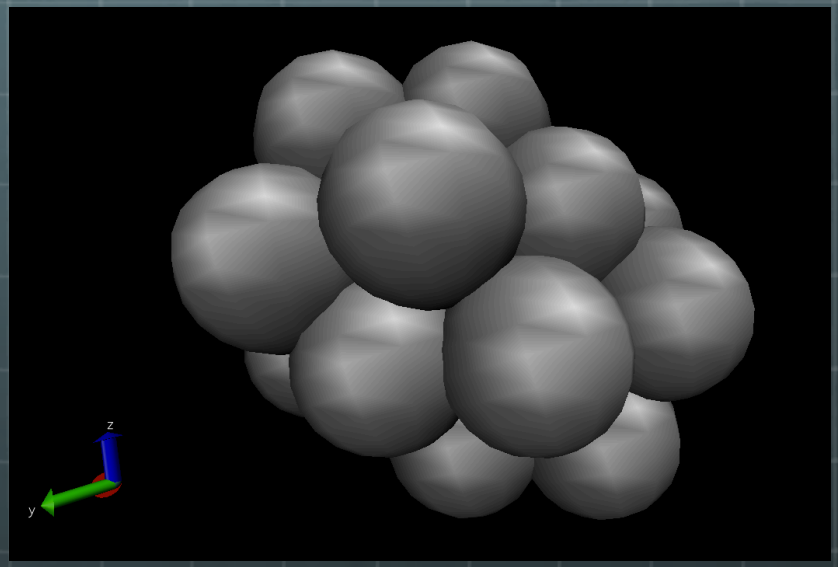
Pt molecule before annealing



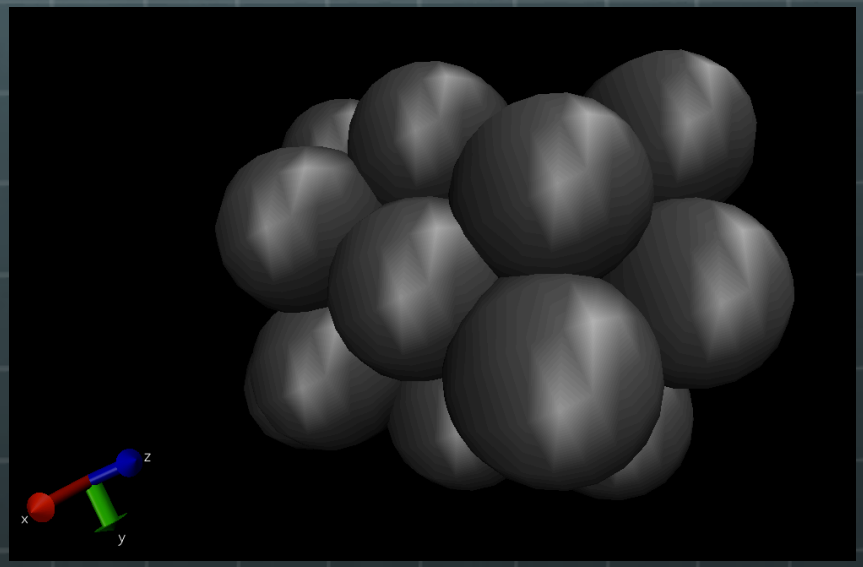
Pt molecule before annealing

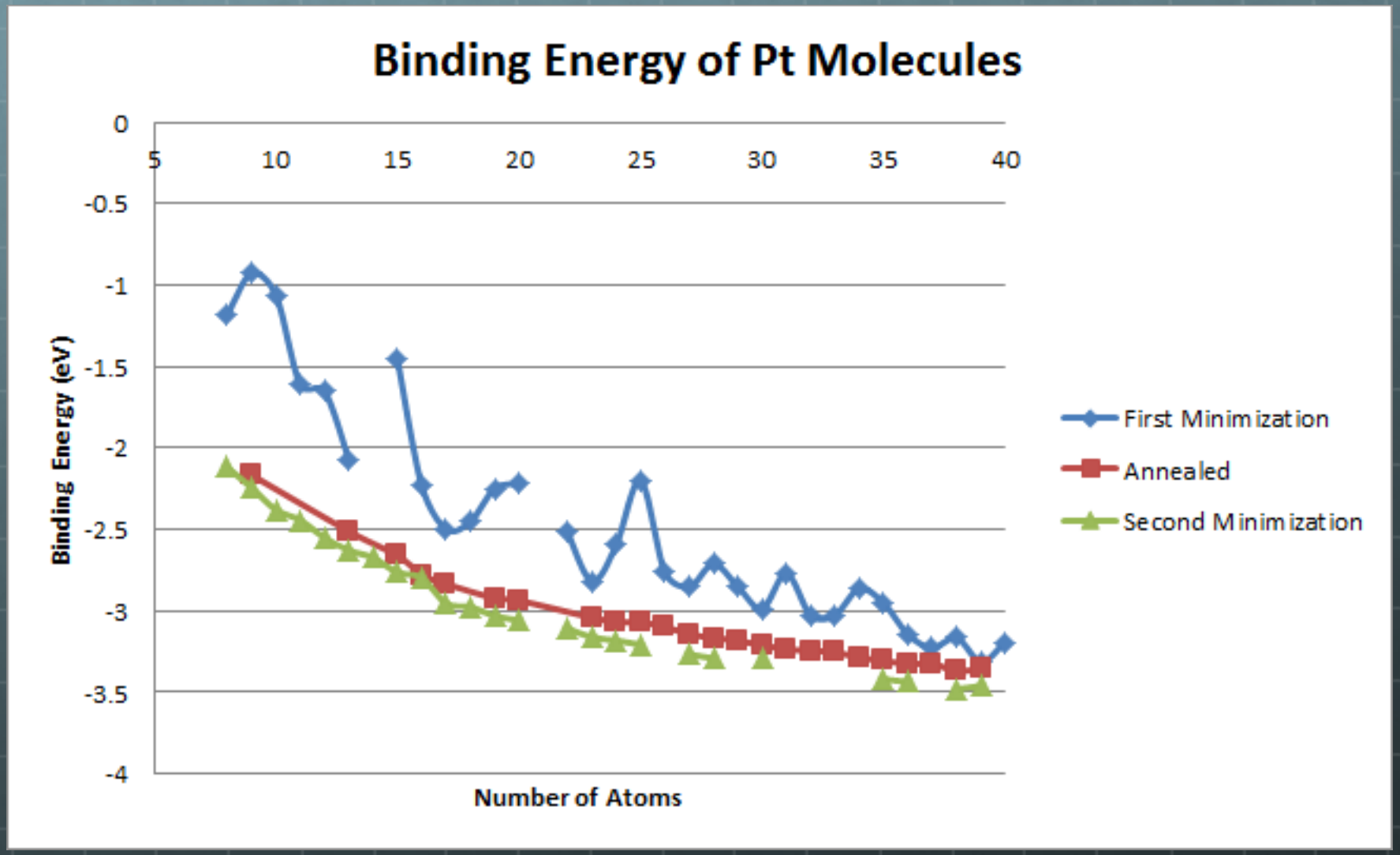


Annealed & minimized Pt molecule



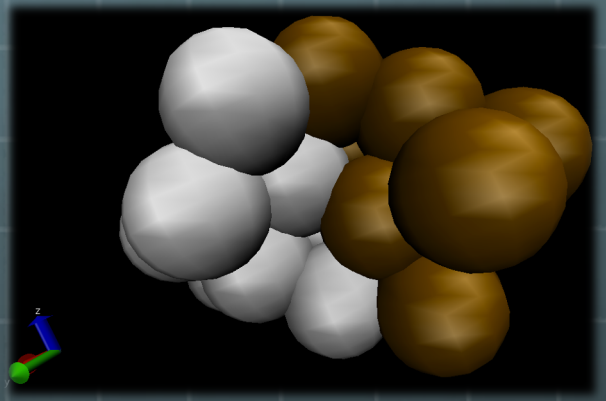
Annealed & minimized Pd molecule

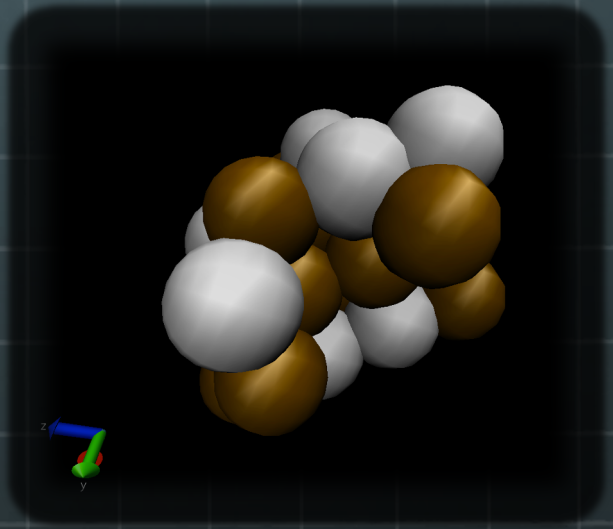



Binding Energy of Pt Molecules
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
5
10
15
20
25
30
35
40
Binding Energy (eV)
Number of Atoms
First Minimization
Annealed
Second Minimization

Alloy Generation

- PtPd Janus Particle
- Random alloy
  - Random number generator in MATLAB
  - Roughly 50/50
- Repeat min/anneal for alloys





Catalysts on Graphene

- Created graphene structure in SIESTA
- Added catalysts
  - Pt/graphene
  - Pd/graphene
- Ran minimization simulations

Results & Discussion

- What we have learned from the annealing
  - Pt molecules seem to be amorphous shaped
  - Pd molecules seem to fit into a crystalline structure
  - The alloys and Janus particles may have either characteristic
  - They will certainly have interesting behavior which is promising

Near Results & Discussion

- Prediction of the relative potency of catalysts by examining several quantities
  - Projected density of states at the Fermi energy
  - Charge transfer
  - Binding affinity for O (introduce oxygen to the system and observe how the catalysts bind)
- We are currently in the midst of these processes

Preliminary Conclusions

- The alloy structures will have interesting characteristics
- Anneal/Minimization effectively stabilized the Pt and Pd molecules
- What will this mean for catalysis?
- I have become much more proficient in various simulation techniques and code writing

Future Work

- Finish graphene simulations
- Perform the same graphene simulations with alloys
- Explore the difference between Pt alone and PtPd
- Investigate how graphene affects Au and Au-Pd alloys

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Questions