Computational Materials Research

**Applications**
- Use existing computational tools to explore problems relevant in society
- Finding new materials for catalysis in alternative energy

**Methods**
- Alter existing computational tools to improve accuracy and efficiency
- Global Optimization

**Question**
- How do we predict the catalytic ability of material using a computer?
- How do we create a potential energy surface using a computer?
Predicting Catalytic Activity
Introduction to Fuel Cells

Anode (oxidation—loss of electrons): \( 2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^- \)

Cathode (reduction—gain of electrons) \( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \)

Overall reaction (redox): \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \)

We will particularly interested in the oxygen reduction reaction (ORR) in this class
Platinum is currently the best catalyst for ORR, but it costs \textbf{\$1,000.00 per ounce.}
Arrhenius Rates

- Arrhenius Equation – an empirical expression for rate constants which has been shown to be accurate for chemical reactions that we care about in this stream

\[ k = Ae^{-\frac{\Delta E}{kT}} \]
Catalyst and Reaction Rates: Arrhenius Rates

Arrhenius Equation – an empirical expression for rate constants which has been shown to be accurate for chemical reactions that we care about in this stream

\[ k = A e^{-\frac{\Delta E}{kT}} \]

Where k is the rate constant (measure of how quickly the reaction occurs)
\( \Delta E \) is the activation energy
kT is a measure of the temperature
A is a prefactor (we will discuss this later)

This means that if we lower the activation energy – the reaction rate increases exponentially! And vice versa!
Explore mechanisms: ORR toy example

The steps highlighted in blue tend to be rate limiting steps in ORR— that is we need oxygen to form a bond with the catalyst and we need to break the oxygen catalyst bond.
Sabatier Principles

Interaction between a substrate and a catalyst needs to be “just right.” Too strong of binding means you cannot remove the substrate from the material. Too weak means it is difficult to bind the substrate to the material.

Strong binding case

In this case the **rate limiting step** is removing H2O from the catalyst.

Recall:

\[ k = e^{-\frac{\Delta E}{kT}} \]
Weak binding case

In this case the rate limiting step is binding O2 to the catalyst.
Ideally we find middle ground!
Volcano Plot

Previous research shows that binding energies of reaction intermediates are good predictors of catalytic activity

![Volcano Plot](image)

We will calculate binding energies and use a volcano plot to predict catalytic activity!

Binding Energies

- Binding energy: energy required to separate a system into two parts

\[ E_{\text{binding-oxygen}} = E - (E + 0.5E) \]

- In the case of oxygen binding energies, the two parts will be the material and \( O_2 \)
- We use \( O_2 \), the most stable form of oxygen.
Cohesive Energies

• Cohesive Energy: Energy difference between the energy of a nanoparticle or solid with the energy of the individual atoms not interacting (free atoms)

\[ E_{\text{cohesive}} = - \]

• Another way to think about cohesive energy is how much energy are you gaining from creating a molecular structure

• You can also think of it as a measure of stability
Cohesive Energies

We will calculate cohesive energy by calculating the potential energy of a nanoparticle and an individual atom with the following equation where $N$ is the number of atoms in the nanoparticle:

$$E_{\text{cohesive}} = \text{nanoparticle} - N$$
Cohesive Energies

• Let’s say I want to compare the stability of a 38 atom and a 55 atom nanoparticle using the equation given. Can I directly compare cohesive energies?

\[ E_{\text{cohesive}} = \]
Cohesive Energies

- Yes, if I calculate the cohesive energy per atom

\[ E_{\text{cohesive-per-atom}} = \frac{-N}{N} \]