Two research areas were introduced on the first day of class. What were these two research areas? What were the research problems?

Find catalyst to replace Platinum in alternative energy

Oxygen Reduction Reaction:
Cathode (reduction—gain of electrons)
\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

Platinum is currently the best catalyst for ORR, but it cost \(~\$1,000.00\) per ounce.

Improve efficiency and accuracy of global optimization methods

For a 55 atom cluster there are \(~10^{21}\) local minima!
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**
- How do we predict the catalytic ability of material using a computer?
- How do we create a potential energy surface using a computer?
Potential Energy Surface

• Describes the potential energy of an atomic system, or collections of atoms, in terms of the positions (or relative positions) of the atoms.
Potential Energy Surface: a diatomic (H₂, O₂, N₂, etc.)
Potential Energy Surface (PES): What would the PES of Ar₂ look like?
How can we generate a PES of a chemical system on a computer?

- There are several ways to generate a PES.
- The methods for generating the PES come in two classes:

<table>
<thead>
<tr>
<th>Electronic Structure Methods</th>
<th>Empirical Potentials (Force Fields)</th>
</tr>
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<tbody>
<tr>
<td>accurate, slow</td>
<td>not as accurate, Fast</td>
</tr>
</tbody>
</table>
Empirical Potentials

Assumes a functional form of the PES and then uses free parameters to fit the potential to have a desired properties known from either experiment or electronic structure calculations
Empirical Potentials

Example:
*Morse Potential* for a diatomic molecule

\[ V(r) = D_e \left( 1 - e^{-a(r-r_e)} \right)^2 \]

- \(D_e\) is the well depth or energy to break a bond
- \(r_e\) is the equilibrium bond length
- \(a\) controls the width of the potential

Diagram showing the Morse potential with labels for \(D_e\), \(r_e\), and \(a\).
Lennard-Jones

\[ V(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) \]

In Lab 2, you will explore this empirical potential!
### Generating PES

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**Cases when used:**

1. Get away with less accuracy
2. Can not afford electronic structure calculations
3. When exploring computational methods and want to explore a well studied system
Electronic Structure Methods

• *Electronic Structure Methods* take into account all electrons and nuclei in an atomic system.
What equation from physics do we need to calculate the total energy of a hydrogen atom?

Potential Energy (V): Coulomb’s Law

\[ V = k_e \frac{q_1 q_2}{r} \]

Kinetic Energy (T):

\[ T = \frac{1}{2} m_e v_e^2 + \frac{1}{2} m_p v_p^2 \]

Total Energy (T):

\[ E_{\text{total}} = \frac{1}{2} m_e v_e^2 + \frac{1}{2} m_p v_p^2 + k_e \frac{q_1 q_2}{r} \]
Electronic Structure Methods

- What is the total energy $H_2$ using classical physics?

**Potential Energy (V):**

$$V = k_e \frac{e_1 e_2}{r} + k_e \frac{p_1 p_2}{r} - k_e \frac{p_1 e_1}{r} - k_e \frac{p_1 e_2}{r} - k_e \frac{p_2 e_1}{r} - k_e \frac{p_2 e_2}{r}$$

**Kinetic Energy (T):**

$$T = \frac{1}{2} m_e v_{e1}^2 + \frac{1}{2} m_e v_{e2}^2 + \frac{1}{2} m_{p1} v_{p1}^2 + \frac{1}{2} m_{p2} v_{p2}^2$$

**Total Energy (T):**

$$E_{total} = V + T$$
Electronic Structure Methods

• As we raise dimension, the complexity of the potential energy will increase dramatically
• We will deal with dimensionality next week!
Quantum mechanics > Classical mechanics

- We will need to use quantum mechanics to accurately model electrons
- A superior theory to classical mechanics is quantum mechanics
- Quantum mechanics has a different way of calculating properties like kinetic energy, potential energy, momentum, etc.
- I will first introduce you to the “new world” of quantum mechanics. This will include some assumptions that are made.
Quantum Mechanics Postulates

• The state of a physical system is described by a wave function, \( \Psi(r) \), where \( r \) represents the position of the physical system. This function and its space derivative are continuous, finite and single valued.

• You can think of the wave function is a function which holds all information about your system.
What does the wave function represent?

• There isn’t a great way to explain the meaning of $\Psi(r)$; scientists do not agree other than the fact that quantum mechanics works!
• The wave function has the important property that the probability that a particle lies in a volume $d\tau$ is proportional to $|\Psi(r)|^2$. This is also known as the probability density or a particle $r$. 
Quantum Mechanics (QM) Postulates

In quantum mechanics, there are operators which are applied to wavefunctions and allow us to calculate properties we see in classical physics (kinetic energy, potential energy, momentum, etc.)

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<th>Observable</th>
<th>Classical variable</th>
<th>Operator symbol</th>
<th>operator</th>
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</thead>
<tbody>
<tr>
<td>Kinetic Energy</td>
<td>T</td>
<td>$\hat{T}$</td>
<td>$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2}$</td>
</tr>
</tbody>
</table>

**Classical**

$$T = \frac{1}{2} mv^2$$

**Quantum**

$$\hat{T}\Psi_n (r) = T_n \Psi_n (r)$$ where $n=1,2,3...$

In QM, you solve for both $T$ and $\Psi$. I will show you in a few slides that you have actually seen this before!
Quantum Mechanics Postulates

In quantum mechanics, there are **operators** which are applied to wavefunctions and allow us to calculate properties we see in classical physics (kinetic energy, potential energy, momentum, etc.)

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<td>Potential Energy</td>
<td>V</td>
<td>( \hat{V} )</td>
<td>(-k \frac{q_1 q_2}{r})</td>
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</table>

**Classical**

\[
V = k_e \frac{q_1 q_2}{r}
\]

**Quantum**

\[
\hat{V} \Psi(r) = V \Psi(r)
\]
Hydrogen Atom

Equation for total energy with classical physics

\[ E_{total} = \frac{1}{2} m_e v_e^2 + \frac{1}{2} m_p v_p^2 + k_e \frac{q_1 q_2}{r} \]

Equation for total energy with quantum mechanics

\[ (\hat{T}_e + \hat{T}_p + \hat{V}) \Psi(r) = E_{total} \Psi(r) \]

Kinetic energy electron
Kinetic energy proton
Potential Energy
Total Energy
Wave Function

electrons
protons
Total Energy of Hydrogen Atom using Quantum mechanics

$$E_{total} = E(n, l, m_l)$$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>n = 1</td>
<td>l = 0</td>
</tr>
<tr>
<td>n = 2</td>
<td>l = 0</td>
</tr>
<tr>
<td></td>
<td>l = 1</td>
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From General chemistry you may recall learning about quantum numbers which describe allowable energy states of electrons:

- n is the principle quantum number
- l is the orbital quantum number
- m is the magnetic quantum number
Total Energy of Hydrogen Atom using Quantum mechanics

\[ E_{\text{total}} = E(n,l,m_l) \]

From General chemistry you may recall learning about quantum numbers which describe allowable energy states of electrons:

- **n** is the principle quantum number
- **l** is the orbital quantum number
- **m** is the magnetic quantum number
Solutions for the Hydrogen Atom

\[ E_{total} = E(n,l,m_l) \]
\[ \Psi_{nlm_l}(r), \Psi_{nlm_l}(r)^2 \]

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<td></td>
<td>l = 2</td>
<td>d orbital</td>
</tr>
<tr>
<td></td>
<td>l = 3</td>
<td>complex shape</td>
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[Diagram showing electron orbitals and energy levels]
Scrödinger’s Equation

• The equation we have just introduced and the equation for total energy in quantum mechanics is known as **Scrödinger’s Equation**: 

\[ \hat{H}\Psi(r) = E\Psi(r) \]

• Where the H-operator represents total energy. In the case of an Hydrogen atom that is:

\[ \hat{H} = \hat{T}_e + \hat{T}_p + \hat{V} \]
Electronic Structure Methods

• Next week, we will continue to discuss Schrödinger’s Equation and how we can solve this equation for systems more complicated than hydrogen.
## Generating PES

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**Cases when used:**
1. Get away with less accuracy
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3. When exploring computational methods and want to explore a well studied system

**Cases when used:**
1. When the accuracy is required
2. When we can afford it
3. Application projects – discovering new materials or comparing computational results with experimental results