Scrödinger’s Equation

• The equation for total energy in quantum mechanics is known as the time independent Scrödinger’s Equation

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

• \( r \) is a vector containing the positions of all electrons and nuclei in your system.
• \( E \) is total energy
• \( \psi \) is the wavefunction
• Where the H-operator represents total energy. In the case of an Hydrogen atom that is:

\[ \hat{H} = \hat{T}_e + \hat{T}_p + \hat{V} \]
Scrödinger’s Equation

• The equation for total energy in quantum mechanics is known as the time independent Scrödinger’s Equation

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

• Scrodinger solved this equation for hydrogen and its results matched experimental results for hydrogen exactly!
Where did Scrödinger’s Equation come from?

• To answer this we will review a few topics from physics
Physics Review
Classical Mechanics
• Issac Newton wrote a book in 1687 called *Mathematical Principles of Natural Sciences* where he outlined the laws of Classical Mechanics:
  • Newton’s Laws of Motion
    • 1\textsuperscript{st}: if F=0 then acceleration = 0 (e.g. an object is at rest or moving at a constant velocity when no force is acting on the object)
    • 2\textsuperscript{nd}: F=ma
    • 3\textsuperscript{rd}: To every action there is an equal and opposite reaction; \(F_{12}=-F_{21}\)
  • Gravity
  • Energy is continuous
  • Describes objects with mass
Physics Review: Electromagnetic Radiation

**Photons** are waves that are electromagnetic fields that move at the speed of light and carry energy.

Examples: UV and visible light is produced by the sun.

Photons come in packets of energy. The energy of one photon is,

\[ E = hv \]

- \( h \) = plank’s constant
- \( v \) = frequency of electromagnetic wave

The energy of Photons is not continuous.

Photons have no mass.
Quantum Mechanics

<table>
<thead>
<tr>
<th>Classical Mechanics</th>
<th>Wave-Particle Duality</th>
<th>Electromagnetic Radiation</th>
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<tbody>
<tr>
<td>• Describes particles with <strong>mass</strong></td>
<td>Through a series of experiments scientist found the small particles, like electrons, can behave like waves and photons can behave like a particle with mass.</td>
<td>• Describes “energy waves” with <strong>no mass</strong></td>
</tr>
<tr>
<td>• Energy is <strong>continuous</strong></td>
<td></td>
<td>• Energy is not continuous or <strong>quantized</strong></td>
</tr>
</tbody>
</table>

Here are key words to look up if you want to learn about these experiments:

• Photoelectric effect
• Double Split Experiment
• Black body radiation
Where did Scrödinger’s Equation come from?

- Scrödinger was inspired by Wave-Particle Duality
- So much so that he gave particles with mass a wave function and applied equations used to describe electromagnetic radiation to hydrogen
- And the equations worked!
What is the total energy for $H_2$?

$$E_{total} = V + T$$

**Kinetic Energy ($T$):**

$$T = \frac{1}{2} m_e (v_{e_1}^2 + v_{e_2}^2) + \frac{1}{2} m_p (v_{p_1}^2 + v_{p_2}^2)$$

**Potential Energy ($V$):**

$$V = k_e \frac{e_1 e_2}{r} + k_e \frac{p_1 p_2}{r} + k_e \frac{p_1 e_1}{r} + k_e \frac{p_1 e_2}{r} + k_e \frac{p_2 e_1}{r} + k_e \frac{p_2 e_2}{r}$$
Electronic Structure Methods

• As we raise dimension, the complexity of the potential energy will increase dramatically
• We will deal with dimensionality today.
What is the total energy for H$_2$?

\[ E_{\text{total}} = V + T \]

**Kinetic Energy (T):**

\[ T = \frac{1}{2} m_e (v_{e_1}^2 + v_{e_2}^2) + \frac{1}{2} m_p (v_{p_1}^2 + v_{p_2}^2) \]

**Potential Energy (V):**

\[ V = k_e \frac{e_1 e_2}{r} + k_e \frac{p_1 p_2}{r} + k_e \frac{p_1 e_1}{r} + k_e \frac{p_1 e_2}{r} + k_e \frac{p_2 e_1}{r} + k_e \frac{p_2 e_2}{r} \]

And in quantum mechanics we can write the total energy as...

\[ (\hat{T}_{e_1} + \hat{T}_{e_2} + \hat{T}_{p_1} + \hat{T}_{p_2} + \hat{V}_{e_1 e_2} + \hat{V}_{e_1 p_1} + \hat{V}_{e_1 p_2} + \hat{V}_{e_2 p_1} + \hat{V}_{e_2 p_2} + \hat{V}_{p_1 p_2})\psi(\vec{r}) = E_{\text{total}} \psi(\vec{r}) \]

And then simplify this expression by using summation notation

\[ \left( \sum_{e=1}^{2} \hat{T}_e + \sum_{e=1}^{2} \hat{T}_e + \hat{V}_{ee} + \sum_{e=1}^{2} \sum_{n=1}^{2} \hat{V}_{ne} \right) \psi(\vec{r}) = E_{\text{total}} \psi(\vec{r}) \]
What is the total energy for H$_2$?

Total energy with quantum mechanics

\[
(\hat{T}_{e1} + \hat{T}_{e2} + \hat{T}_{p1} + \hat{T}_{p2} + \hat{V}_{e1e2} + \hat{V}_{e1p1} + \hat{V}_{e1p2} + \hat{V}_{e2p1} + \hat{V}_{e2p2} + \hat{V}_{p1p2})\psi(\vec{r}) = E_{total}\psi(\vec{r})
\]

To shorten equations we will use summation notation

\[
\left(\sum_{e=1}^{2} \hat{T}_e + \sum_{e=1}^{2} \hat{V}_{ee} + \hat{V}_{nn} + \sum_{e=1}^{2} \sum_{n=1}^{2} \hat{V}_{ne}\right)\psi(\vec{r}) = E_{total}\psi(\vec{r})
\]
Increasing dimensionality

Here is a general equation for a chemical system with $N$ nuclei and $E$ total electrons:

$\left( \sum_{e=1}^{E} \hat{T}_e \right) + \left( \sum_{n=1}^{N} \hat{T}_n \right) + \left( \sum_{e=1}^{E} \sum_{e>1}^{E} \hat{V}_{ee} \right) + \left( \sum_{n=1}^{N} \sum_{n>1}^{N} \hat{V}_{nn} \right) + \left( \sum_{n=1}^{N} \sum_{e=1}^{E} \hat{V}_{en} \right) \Psi(\vec{r}) = E_{total} \Psi(\vec{r})$

- **Kinetic energy**
- **Electrons**
- **Nuclei**
- **Potential Energy:**
  - **Electron-electron interactions**
  - **Nuclei-nuclei interactions**
- **Potential Energy:**
  - **Nuclei-nuclei interactions**
  - **Electron-nuclei interactions**

$E + N \approx 0.5(E^2) + 0.5(N^2) + NE = \text{total # of terms in Hamiltonian!}$
Increasing dimensionality

A 38 atom Platinum nanoparticle has 38 nuclei, N, and 78*38=2964 electrons

\[
\Psi(\vec{r}) = E_{\text{total}} \Psi(\vec{r})
\]

\[
\left( \sum_{e=1}^{E} \hat{T}_e + \sum_{n=1}^{N} \hat{T}_n + \sum_{e_1=1}^{E} \sum_{e_2=e_1}^{E} \hat{V}_{e_1 e_2} + \sum_{n_1=1}^{N} \sum_{n_2=n_1}^{N} \hat{V}_{n_1 n_2} + \sum_{n=1}^{N} \sum_{e=1}^{E} \hat{V}_{en} \right) \Psi(\vec{r}) = E_{\text{total}} \Psi(\vec{r})
\]

- Kinetic energy
  - Electrons
  - Nuclei
- Potential energy
  - Electron-electron interactions
  - Nuclei-nuclei interactions
  - Electron-nuclei interactions

\[
E + N + \sim0.5(E^2) + \sim0.5(N^2) + NE = \text{total # of terms in Hamiltonian!}
\]

\[
2964 \quad 38 \quad \sim4.4M \quad 722 \quad \sim0.1M \quad = \sim4.5M
\]
Fun Fact about Scrädinger’s Equation

• The only neutral chemical system that can be solved exactly for is the hydrogen atom!

• So when we move up to larger chemical systems we will need to make some approximations to solve this equation.

• All these approximations will be used to find the lowest energy state of the system or the ground state.
Common Approximations: Born Oppenheimer Approximation

- All atoms are composed of electrons and protons. How does the mass of an electron compare to the mass of a proton?

\[
\frac{m_p}{m_e} \approx 1800
\]

- Should higher mass objects move faster or slower than lower mass objects?
  - The large difference in mass allows us to assume that electrons can respond almost instantaneously to the motion of the nuclei.
Common Approximations:
Born Oppenheimer Approximation

• Instead of trying to solve Scrodinger’s equation while relaxing all degrees of freedom (electrons and nuclei), we will
  • Fix the nuclei in place → solve for the location of the electrons
  • From this use energy and forces on the nuclei to move the nuclei
Example: Born Oppenheimer Approximation used in local optimization

**Geometry Optimization**

*Finding a critical point or local minima on the PES*
Example: Born Oppenheimer Approximation used in local optimization

Geometry Optimization
Finding a critical point or local minima on the PES

Start at an initial starting structure and calculate the force the atoms feel at this configuration.
Example: Born Oppenheimer Approximation used in local optimization

**Geometry Optimization**

*Finding a critical point or local minima on the PES*

Check to see if the forces are near zero.

If forces near zero: STOP.

Else:

Example: Born Oppenheimer Approximation used in local optimization

**Geometry Optimization**

*Finding a critical point or local minima on the PES*

Move down hill to a new configuration
Example: Born Oppenheimer Approximation used in local optimization

Geometry Optimization
Finding a critical point or local minima on the PES

Potential Energy
Bond length

Repeat
Example: Born Oppenheimer Approximation used in local optimization

Continue moving down hill until the force the atoms feel is close to zero

Geometry Optimization
Finding a critical point or local minima on the PES
Algorithm for Local Optimization

The general procedure for numerical geometry optimization is as follows:

1. Calculate the force on all atoms for some configuration of an atomic system.
2. If the magnitude of the force is less than threshold, you have found a critical point! STOP.
3. If not, move the atoms such that they go down hill towards a local minimum
4. Repeat.
Algorithm for local optimization with an electronic structure method

The general procedure for numerical geometry optimization is as follows:

1. Calculate the force on all atoms for some configuration of an atomic system.
   
   1. To calculate the force on all the atoms (at fixed nuclei) we will need to optimize the wave function for all the electrons in your chemical system. This means find the lowest energy state of the electron on ground state

2. If the magnitude of the force is less than threshold, you have found a critical point! STOP.

3. If not, move the atoms such that they go towards a critical points

4. Repeat.
Example: Born Oppenheimer Approximation used in local optimization

Start at an initial starting structure

Geometry Optimization
Finding a critical point or local minima on the PES
Example: Born Oppenheimer Approximation used in local optimization.

To calculate the forces, I will solve for the most likely location of the electrons given the fixed nuclei.

**Geometry Optimization**

*Finding a critical point or local minima on the PES*
Example: Born Oppenheimer Approximation used in local optimization

Move down hill to a new configuration

Geometry Optimization

Finding a critical point or local minima on the PES
Example: Born Oppenheimer Approximation used in local optimization

Geometry Optimization
Finding a critical point or local minima on the PES
Example: Born Oppenheimer Approximation used in local optimization

Geometry Optimization

Finding a critical point or local minima on the PES

Continue moving down hill until the force the atoms feel is close to zero
Increasing dimensionality

A 38 atom Platinum nanoparticle has 38 nuclei, $N$, and $78 \times 38 = 2964$ electrons.

$$\hat{T}_e = \sum_{e=1}^{E} \hat{T}_e$$

$$\hat{T}_n = \sum_{n=1}^{N} \hat{T}_n$$

$$\hat{V}_{e1e2} = \sum_{e1=1}^{E} \sum_{e2 > e1}^{E} \hat{V}_e$$

$$\hat{V}_{n1n2} = \sum_{n1=1}^{N} \sum_{n2 > n1}^{N} \hat{V}_n$$

$$\hat{V}_{en} = \sum_{n=1}^{N} \sum_{e=1}^{E} \hat{V}_e$$

$$\Psi(\vec{r}) = E_{total} \Psi(\vec{r})$$

$$E + N + \sim 0.5(E^2) + \sim 0.5(N^2) + NE = \text{total # of terms in Hamiltonian!}$$

$$2964 \quad 38 \quad \sim 4.4M \quad 722 \quad \sim 0.1M = \sim 4.5M$$
Increasing dimensionality

A 38 atom Platinum nanoparticle has 38 nuclei, N, and 78*38=2964 electrons

\[
\Psi(\vec{r}) = E_{total} \Psi(\vec{r})
\]

Can we lower the dimensionality of the wavefunction?

\[
\begin{align*}
E &+ N &+ \sim 0.5(E^2) &+ \sim 0.5(N^2) &+ NE &= \text{total # of terms in Hamiltonian!} \\
2964 & 38 & \sim 4.4M & 722 & \sim 0.1M &= \sim 4.5M
\end{align*}
\]
Electron Density

• Recall the following property of the wavefunction:
  • The probability that N electrons are at a particular set of coordinates $r_1, r_2, ... r_E$ is proportional to $|\Psi(r_1, r_2, ... r_E)|^2$

• Another way of describing this is the density of electrons at a particular positions in space:

$$n(x, y, z) = |\psi(\vec{r})|^2$$

• So, we can write the electron density with only 3 degrees of freedom.
Density Functional Theory

• Density Functional Theory (DFT) is an approximate method for solving Scrödinger’s equation that we will use in this class.
• Three scientist, Kohn, Hohenburg, and Sham, rewrote Scrödinger’s equation in terms of the electron density, n(x,y,z).
• This lowers the dimensionality of solving the location of the electrons in your system drastically.
Density Functional Theory

• Why use it?
  • Cheap, efficient
  • Does a good job for ground state energy calculations of materials

• When does it fail?
  • Excited electronic states
  • Some band gap calculations
Algorithm for Gradient Descent while using Density Functional Theory

The general procedure for numerical geometry optimization is as follows:

1. Calculate the force on all atoms for some configuration of an atomic system.

   1. To calculate the force on all the atoms (fixed nuclei fixed) we will need to optimize the electron density for all the electrons in your chemical system.

2. If the magnitude of the force is less than threshold, you have found a critical point! STOP.

3. If not, move the atoms such that they go towards a local minimum.

4. Repeat.
Summary

• Quantum mechanics > Classical mechanics

• We introduced **Scrödinger’s Equation** which is used to calculate the total energy of physical system with quantum mechanics

• Scrödinger’s Equation is complicated for high dimensional system; so much so that we can not solve it for chemical systems larger than Hydrogen!

• To approximately solve this equation we will use these two approximations:
  • Born Oppenheimer approximation
  • Solve for the electron density instead of the wavefunction → Density Functional Theory
Summary

• In practice this means we will separate the optimization of the electron density and the positions of the nuclei:
  • Selecting initial positions
  • Finding the electron density at fixed nuclei
  • Based on this information, we move the nuclei so that the energy of the atomic configuration is lowered
  • Repeat
If you want to learn more

• Here are a few text books where you can learn more. Both of these books are available electronically via UT library:

1) If you are looking for a practical introduction to DFT check out:
   1) Density Functional Theory: a practical introduction by David Sholl and Janice Steckell
   2) Chapter 1

2) If you are looking for more information on the foundations of quantum mechanics check out:
   1) Introduction to Quantum Mechanics : In Chemistry, Materials Science, and Biology by S. M. Blinder
   2) Chapter 1-3