Why Study Quantum Chemistry?

**Molecules**

**MACROSCOPIC BEHAVIOR**

Chemistry is a molecular science. The goal of chemists is to understand macroscopic behavior in terms of the properties of individual molecules.
- Electron transport
- Chemical Bonding
- Laser in your CD player
- Integrated circuit in your computer

**Spectroscopy**

- Identify chemical Compounds
- Provide images of surfaces, tissues etc

**Quantum Theory**

*not Classical Theory*

Recently used for biomolecules

- Proteins, DNA
Classical Theory

Classical Mechanics + Maxwell's Electromagnetic Theory

Electricity, Magnetism & Waves

In Early 20th Century

⇒ New Experiments ⇒ New Theory

* Energy in atomic domain is not continuous, but discrete
* Wave-particle duality
A Brief Look at Classical Mechanics

Newton’s Laws

\[ F = m \cdot a \]  

\( (\text{Newton’s 2}^{\text{nd}} \text{ Law}) \)

- Consider a particle in 1-Dimension

\[
\begin{array}{c}
\text{Force: } F = m \frac{d^2 x}{dt^2} \\
\text{Position: } x(t) \\
\text{Velocity: } v(t) = \frac{dx}{dt} \\
\text{Acceleration: } a(t) = \frac{d^2 x}{dt^2}
\end{array}
\]

If we solve \((*)\) and determine \(x(t)\) we know everything. We can calculate \(v(t)\), \(a(t)\), \(p = m \cdot v\), \(T = 1/2mv^2\) etc.
• Hamiltonian Formalism

\[ H = T + V \]

- Classical Hamiltonian
- Kinetic Energy
- Potential Energy

Hamilton’s Equations

\[ \dot{x} = \frac{dx}{dt} = \frac{\partial H}{\partial p} \]

\[ \dot{p} = \frac{dp}{dt} = -\frac{\partial H}{\partial x} \quad \Rightarrow \text{gives equation of motion} \]
Classical Theory

• Electrons, Protons ➞ Point particles obeying Newton’s Laws

• Electromagnetic Radiation ➞ Waves described by Maxwell’s Equations
  e.g. light, X-rays
• The reflections ensure that the radiation is in thermal equilibrium with the solid.
\[ f(v, T) \, dv = \frac{8\pi v^2}{c^3} \overline{E_{osc}} \, dv \]

\( f \): Spectral density
\( T \): Temperature
\( v \): Frequency
\( \overline{E_{osc}} \): Ave. energy of an oscillating dipole

\[ \overline{E_{osc}} = k \cdot T \]

Boltzmann Constant

Energy, Volume, Freq

Energy for that freq. range
Total energy goes to infinity any $T > 0$ K in classical theory.

\[ p(v, T) \, dv = \frac{8 \pi k T \cdot v^2}{c^3} \, dv \]

High freq. oscillators do not emit at low $T$. 

Area = Total Energy
Max Planck

\[ E \propto v \]

\[ E = n \hbar v \]

\[ n = 0, 1, 2, \ldots \]

• Energy is net continuous but **discrete**!

• Energy is quantized.
\[ \bar{E}_{osc} = \frac{\hbar \nu}{e^{\hbar \nu / k \cdot T} - 1} \]

- **High temperatures T:**
  \[ \frac{\hbar \nu}{k \cdot T} \ll 1 \]
  Taylor –Maclaurin series
  \[ \Rightarrow \bar{E}_{osc} = \frac{\hbar \nu}{(1 + \frac{\hbar \nu}{k \cdot T} + \ldots) - 1} \]

- **Low temperatures T:**
  \[ \frac{\hbar \nu}{k \cdot T} \gg 1 \]
  \( \bar{E}_{osc} \) becomes low for high \( \nu \).
  They do not emit.
Quantum Theory:

\[ P(v, t) \, dv = \frac{8\pi \hbar v^3}{c^3} \frac{1}{e^{\hbar v/kT} - 1} \, dv \]

\( h \): single fitting parameter

\( h = 6.6260755 \times 10^{-34} \text{ J.s} \)

Still not many believed Planck!
Conservation of Energy:

\[
\text{absorbed light of energy} = \text{energy to eject } e^- + \text{kinetic energy of } e^-
\]
CLASSICAL THEORY

• Light is a plane wave on the whole cupper plate
  → Any electron get fraction of light energy

• For all light frequencies, electrons should be emitted.
• Kinetic energy of electron increases with light intensity.

EXPERIMENTS

• Number of electrons is proportional to the light intensity but kinetic energy is independent

• No electrons emitted unless a threshold freq.
• Electrons are emitted at Such low intensities that they are barely enough to eject a single electron on whole cupper plate.
• Specific kinetic energy behavior.
In 1905, Albert Einstein:

Energy of light:

\[ E = \beta \nu \]

Energy of electrons:

“Kinetic energy of photoelectron”

\[ E_e = \beta \nu - \Phi \]

\( \beta = h \) ! \[ E = h \nu \]

\[ E_e = h \nu - \Phi \]

h: universal constant

Einstein won Nobel Prize!
“photon” a spatially localized pocket of light

⇒ “particle” like behavior

experiments

Wave nature

particle nature

“Wave–particle duality”