WHY STUDY QUANTUM CHEMISTRY?

Physical Chemisty can be divided into three parts:

- Matter in equilibrium
  - Thermodynamics - concepts of heat & internal energy, entropy, equilibrium
    - Applications to gases, liquids & solids
    - Macroscopic behavior
  - Statistical mechanics - relates macroscopic behavior to microscopic states of atoms & molecules
- Physical & chemical kinetics
  - Collisions - gases, liquids
  - Reactions between molecules due to collisions

Structure of matter - study of the microscopic world of atoms & molecules that can't be perceived directly with our senses. Rather, we need special techniques and eqiuipment (spectroscopy, computer technology) to observe & understand it.

Quantum chemistry - study of atomic & molecular structure & reactivity

Quantum mechanics - mathematical framework used in quantum chemistry

We will study:

Examples of quantum-like behavior that lead scientists to the idea that the classical description of nature could not describe all phenomena

Photoelectric Effect

Blackbody radiation

Model systems

Harmonic oscillator (model for molecular vibration)

Rigid Rotor (model for molecular rotation)

Atoms

Molecules

Light and the Electromagnetic Spectrum

Light - common term for electromagnetic radiation

It is oscillating force field that has both direction of propagation & magnitude

It oscillates in time with frequency, ν (period $\tau = 1/\nu$)

At any time, t, the magnitude of the time-dependent part of the force field

$$\text{Force} \propto \sin(2\pi\nu t + \text{constant})$$

If the direction of propagation is along the x-axis, then the magnitude of the spatial part of the force field is proportional to

$$F(x) \propto \sin(x/\lambda + \text{constant}),$$

where λ is the wavelength (the distance between two consecutive wave crests.

In a vacuum, the speed of the electromagnetic radiation of *any* wavelength is c, the speed of light

$$c = 3.00 \times 10^8 \text{ m/s} = \nu\,\lambda$$

One can probe the electronic structure of atoms and molecules by using radiation of wavelength which corresponds to energy level spacing

Wave-Particle Nature of Light and Electrons

As experimental techniques became more sophisticated, scientists noticed that in some cases light behaved as a wave, in other cases as a particle

Wave: light passing through a slit gives a diffraction pattern typical of waves

Particle:

Blackbody radiation
Photoelectric effect
Spectrum of hydrogen atom

Wave nature of the electron:
de Broglie
Davisson & Germer

Blackbody Radiation

A blackbody is a sealed container with a pinhole through which radiation can be absorbed. The blackbody absorbs essentially all radiation the radiation that falls on it. When it is heated, it emits radiation of all frequencies, allowing study of the energy distribution and its temperature dependence. Many attempts were made to come up with a mathematical formula that would describe the experimentally-observed temperature dependence of the energy distribution at low and high frequency, assumimg that the electromagnetic field could be described as a collection of classical oscillators.

Nothing worked until Plank suggested that *each oscillator could take on only certain discrete energies:*

$$E = nh\nu,$$

where n = 0, 1, 2, 3,... and h is a constant that came to be known as Plank's constant. This means that light energy is absorbed or emitted in finite (quantized) units of $h\nu$. This was a revolutionary idea, since in classical physics, light can be absorbed or emitted in continuous amounts.

The Spectrum of the Hydrogen Atom

When hydrogen atoms were excited electrically in a sodium vapor lamp, they emitted radiation that could be observed in the visible region of the electromagnetic spectrum. The result was a “line spectrum” of hydrogen in which lines appeared at certain values of the frequency (or wavelength)

By trial & error, Balmer came up with a formula that related all the wavelengths in the series (which became known as the Balmer series):

$$1/\lambda = R\ (1/2^2 - 1/n^2),$$

where $n = 3, 4, \ldots$ and $R = 109{,}677\ \text{cm}^{-1}$

Bohr was able to derive this relationship from physical principles using a classical picture of an electron moving around a proton like a planet around the sun. He assumed that:

the system obeyed Newton’s Law’s of Motion, and

the attraction between electron and proton was due to Coulomb’s Law’s of electricity

But he applied a quantum condition on the angular momentum of the electon (i.e. the momentum due to its circular motion):

the angular momentum could only take on certain values (not a continuous range of values as in classical physics)

By combining this quantum condition with the classical physical picture above, Bohr was able to "derive" a general expression which incorporated Balmer's formula ($n_1=2$):

$$1/\lambda = R\,(1/n_1^2 - 1/n_2^2),$$

where $n_1 = 1,2,3,\ldots$ and $n_2 = 2, 3, 4\ldots$ Using this formula, Bohr was able to correctly predict the lines in the Paschen series ($n_1=3$) found in the IR region and in the Lyman series ($n_1=1$) found in the UV region.

However, Bohr's approach was an odd mixture of classical mechanics and quantum hypotheses. It was not rigorously derived from first principles. It was only accurate for one-electron atoms or ions (5% in error for helium)

THE FORMULATION OF QUANTUM MECHANICS

1926 - Schrödinger formulated quantum (or wave) mechanics to describe wavelike behavior & energy quantization

It was called wave mechanics because it was based on differential equations similar to those that describe wave motion or a vibrating string. It was shown to be equivalent to a matrix mechanics method developed by Heisenberg, Born, and Jordan at the same time.

The state of a classical system (i.e. made up of macroscopic particles) is defined by specifying all the forces acting on the system, as well as all the positions & velocities. Knowledge of the present state of the system leads to prediction of the future state

But, for a *microscopic* (i.e. quantum mechanical) system, it is impossible to know both the position & momentum of the particles (Heisenberg's Uncertainty Principle)

The state of a quantum mechanical system is defined by

Ψ - state function

Ψ is a time-dependent wavefunction which is a function of the particle coordinates & time. For a two-particle system,

$$\Psi(x_1,y_1,z_1,x_2,y_2,z_2,t)$$

where the (x,y,z) are cartesian coordinates and t is the time. Ψ is an abstract quantity, but can be related to a physically measurable quantity (observable). Ψ is a complex number, $\Psi = x + iy$.

Schrödinger postulated the eqn. that describes how Ψ changes with time. Since it explains physical phenomena, the postulate must be correct. For an n-particle system:

$$-(\underline{h}/i)(\partial\Psi/\partial t) = -(\underline{h}^2/2m_1)(\partial^2\Psi/\partial x_1{}^2+\partial^2\Psi/\partial y_1{}^2+\partial^2\Psi/\partial z_1{}^2)$$

$$+ \ldots -(\underline{h}^2/2m_n)(\partial^2\Psi/\partial x_n{}^2+\partial^2\Psi/\partial y_n{}^2+\partial^2\Psi/\partial z_n{}^2) + V\Psi$$

where m_i is the mass, (x_i, y_i, z_i) are the Cartesian coordinates of particle i, and $\underline{h} = h/(2\pi)$. The first n terms on the right-hand side are kinetic energy terms, the last is a potential energy term.

$$V = V(x_1, y_1, z_1, \ldots x_n, y_n, z_n)$$

is derived from the forces on the system:

$-\partial V/\partial x = F_x$ = magnitude of force in x-direction

Analogous to classical mechanics, knowledge of the present state can lead to prediction of the future state of the system. But knowledge in the quantum mechanical case is only probability. If one knows Ψ at time t_o, i.e.

$$\Psi(x_1, y_1, z_1, \ldots x_n, y_n, z_n, t_o),$$

one can predict Ψ at a later time since the Schrödinger eqn. is given in terms of the first derivative of Ψ with respect to t. Integration of the eqn. with respect to t leads to Ψ at a later time (with a constant of integration).

Quantum & classical mechanics are related by taking the limit of an eqn. as

$\underline{h} \rightarrow 0$ (classical limit)

Ψ itself has no physical interpretation. But

$$|\Psi|^2$$

is the probability density for finding the particle in a given region of space. $|\Psi|^2$ is non-negative, real, & normalizable. Ψ contains all the information needed to calculate the probability of position, momentum or other properties of a system (such as dipole moment, polarizability, etc. of molecules)

MATHEMATICAL PRELIMINARIES

Probability - gives the likelihood of occurance of a particular event

If an experiment has n equally probable outcomes with m of them favorable to the occurrence of event A, then the probability that A occurs is m/n.

If one performs an experiment n times & A occurs m times, then the probability of A occuring is

$$\lim_{n \to \infty} m/n.$$

Example: Coin toss--the fraction of times "heads" comes up approaches 1/2 as the number of tosses increases.

Example: Playing cards--A deck has 52 cards. This means 52 equally probable outcomes (13 hearts, 13 spades, 13 clubs, 13 diamonds). Draw a card from the deck. What is the probability that it will be a heart?

$$m/n = 13/52 = 1/4$$

Related events: What is the probability of drawing two hearts from the deck consecutively (if you don't replace the first)?

First draw: 52 equally probable outcomes
Second draw: 51 equally probable outcomes

Total number of equally probable outcomes = 52x51

It is possible to get a heart in the first draw in 13 different ways; In the second draw, 12 different ways.

Total number of ways = 13x12

Probability = 13x12/(52x51) = 1/17

The probability that A & B both occur is the probability of A times the probability of B, calculated assuming A occured

The *Heisenberg Uncertainty Principle* states that the position & momentum of a quantum mechanical particle cannot both be specified exactly.

For example, the probability of finding a particle at *exactly* x = 0.500 is zero.

One can only talk of the *probability* of finding a particle in a region of space

For a 1-dimensional system, dx is an infinitesimal element of length along the x-axis.

The probability of finding the particle will vary at different points along the x-axis

$|\Psi|^2$ is the probability density (i.e. the probability/unit length). It describes the probability of finding the particle at different points on the x-axis.

Since $| \Psi |^2$ has physical meaning, it must be:

real
non-negative

Ψ describes the spatial & temporal behavior of the quantum mechanical partical. It is not a physical observable. It can be negative or complex.

What is the probability that the particle lies between a & b on the x-axis?

$$\int_a^b | \Psi |^2 \, dx$$

A probability of 1 equals a certainty. So in a 1-dimensional problem, the particle must be *somewhere* on the x-axis. So the probability of finding it somewhere on the x-axis is equal to 1:

$$\int_{-\infty}^{\infty} | \Psi |^2 \, dx = 1.$$

If this holds for Ψ, then Ψ is said to be *normalized.*

If $\int_{-\infty}^{\infty} | \Psi |^2 \, dx$ is not equal to 1, then Ψ be normalized by multiplying by a constant so that the integral equals 1.

For example, what if

$$\int_{-\infty}^{\infty} | \Psi_1 |^2 \, dx = 4 \text{ ?}$$

Define $\Psi_2 = c \, \Psi_1$. Find c such that $\int_{-\infty}^{\infty} | \Psi_2 |^2 \, dx = 1$.

$\int_{-\infty}^{\infty} | \Psi_2 |^2 dx = c^2 \int_{-\infty}^{\infty} | \Psi_1 |^2 dx = c^2\, 4 = 1.$

So $c^2 = 1/4$ & $c = 1/2$.

The normalized wavefunction is

$\Psi_2 = (1/2)\, \Psi_1$

Complex Numbers

z is a complex number: $z = x + i\, y$,

where x & y are real & $i = \sqrt{-1}$.

x = Real part of z = Re (z) = $r \cos \theta$

y = Imaginary part of z = Im (z) = $r \sin \theta$

$|z|$ = r = absolute value or modulus of z = $(x^2 + y^2)^{1/2}$

θ = phase, argument; $\tan \theta = x/y$

Complex Plane:

y z

r

θ

x

$z = x + i y = r \cos\theta + i r \sin\theta = r(\cos\theta + i \sin\theta) = r e^{i\theta}$

Complex Conjugate: replace i by - i:

$z^* = x - i y = r \cos\theta - i r \sin\theta = r(\cos\theta - i \sin\theta) = r e^{-i\theta}$

$|z|^2 = z z^* = r e^{i\theta} r e^{-i\theta} = r^2$.

For a real number, $y = 0$ & $z = z^*$.

Time-Independent Schrödinger Eqn.:

Function of only Cartesian coordinates

Example: 1 particle in 1 dimension $\Psi = \Psi(x,t)$

Assume V depends only on x: $V = V(x)$

$$-(\underline{h}/i)\partial\Psi(x,t)/\partial t = -(\underline{h}^2/2m)\,\partial^2\Psi(x,t)/\partial x^2 + V(x)\Psi(x,t)$$

USE THE METHOD OF SEPARATION OF VARIABLES TO OBTAIN AN EQN. FOR $\psi(x)$:

Assume $\Psi(x,t) = f(t)\,\psi(x)$ since V depends only on x, not x & t.

$$\partial\Psi(x,t)/\partial t = \psi(x)\, df(t)/dt$$

$$\partial^2\Psi(x,t)/\partial x^2 = f(t)\, d^2\psi(x)/dx^2$$

So

$$-(\underline{h}/i)\ (df/dt)\ \psi(x) = -\ (\underline{h}^2/2m)\ f(t)\ d^2\psi(x)/dx^2 + V(x)\psi(x)\ f(t)$$

Divide by $f(t)\psi(x)$ to get all terms in t on one side & all terms in x on the other:

$$-(\underline{h}/i)\ (df/dt)(1/f(t)) = -\ (\underline{h}^2/2m)\ (1/\psi(x))\ \ d^2\psi(x)/dx^2 + V(x)$$

Since the left side depends only on t & the right side depends only on x & the two sides are equal to each other, then they must be equal to a constant, let's call it E.

$$-(\underline{h}/i)\ (df/dt)(1/f(t)) = E$$

Rearrange & integrate:

$$\int df(t)/f(t) = -(i/\underline{h})\ E \int dt$$

Or $\quad \ln f(t) = -(i/\underline{h})\ E\ t + C$

$$f(t) = e^{-(i/\underline{h})\ Et + C} = A\ e^{-(i/\underline{h})\ Et}$$

Since $\Psi(x,t) = f(t)\ \psi\ (x)$, the arbitrary constant A could be included in $\psi\ (x)$ instead so that

$$f(t) = e^{-(i/\underline{h})\ E\ t}$$

Also

$$-\ (\underline{h}^2/2m)\ (1/\psi(x))\ d^2\psi(x)/dx^2 + V(x) = E$$

This leads to the time-independent Schrödinger Eqn. for a particle of mass m moving in a potential V:

$$d^2\psi(x)/dx^2 + (2m/\underline{h}^2)\,(E - V(x))\,\psi(x) = 0$$

where E has dimensions of energy & is a real number. (In order to solve this eqn. with two unknowns (ψ & E) must impose *boundary conditions* in order to get another eqn. We will see how this is done when we study the model systems.)

So, $\Psi(x,t) = e^{-(i/\underline{h})\,E\,t}\,\psi(x)$

where Ψ is complex & $|\Psi|^2$ is the probability density.

$$|\Psi|^2 = \Psi(x,t)\,\Psi^*(x,t) = e^{-(i/\underline{h})\,E\,t}\,\psi(x)\,e^{(i/\underline{h})\,E\,t}\,\psi^*(x)$$

$$= \psi(x)\,\psi^*(x) = |\psi|^2$$

ψ is the wavefunction for a *stationary state*, one that doesn't change with time. The particle moves, but $|\psi|^2$ is stationary

Conditions on ψ:

ψ must be

(1) single-valued
(2) continuous
(3) quadratically integrable.

(1) ψ must have only one value for each value of the variable

Multivalued ψ

Single-valued ψ

(2) There must be no sudden jumps in value

Discontinuous: $\psi = \tan x$

Continuous: $\psi = \sin x$

(3) $\int |\psi|^2 \, d\tau$ = finite number

If $\psi = x^2$, then $\int_{-\infty}^{\infty} |\psi|^2\, dx = \int_{-\infty}^{\infty} x^4\, dx = \infty$

ψ is not an acceptable wavefunction