Lecture 2
The Schrodinger Equation

Quantum mechanics incorporates three classes of phenomena that classical physics cannot account for:

(i)   the quantization (discretization) of certain physical quantities,

(ii)   wave-particle duality—de Broglie wavelength $\lambda = \dfrac{h}{p}$, &

(iii)   the uncertainty principle: $\Delta x . \Delta p \geq \dfrac{\hbar}{2}$

In classical mechanics, coordinates and momenta defines the classical state. Following Heisenberg Uncertainty principle, it is clear to us that the same will not work for a microscopic system like electrons. Wave particle duality means there exists matter wave which in turn implies that there is an amplitude associated with the wave, first introduced by Erwin Schrodinger "ψ" → wave function "psi" and an associated wave Equation of Motion (EOM). In quantum mechanics, the state of a system is defined by its wave function; say for a system containing one particle and in one dimension (say x), the wave function is denoted by ψ(x). Here ψ is some function of the coordinate x.

Uncertainty Principle $\Rightarrow$ abandon classical notion of a trajectory, i.e., [$x(t)$, $p_x(t)$].
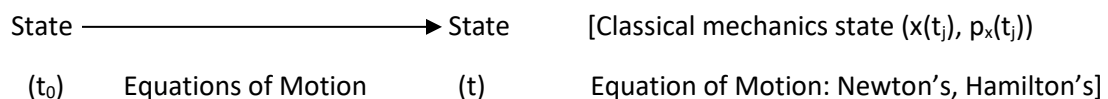For example: Uncertainty in position is important when it is $\gtrsim$ order of system size

In 1927, Paul Dirac gave the mathematical formulation of quantum mechanics which unifies and generalizes the two earliest formulations of quantum mechanics, matrix mechanics (invented by Werner Heisenberg) and wave mechanics (invented by Erwin Schrödinger).

In this formulation, the instantaneous state of a quantum system encodes the probabilities of its measurable properties, or "observables". Examples of observables include energy, position, momentum, and angular momentum. Observables can be either continuous (e.g., the position of a particle) or discrete (e.g., the energy of an electron bound to a hydrogen atom).

So, we cannot both {x(t), p$_x$(t)} but can pick one of these and measure with arbitrary precision.

Since we are interested in structure, let us pick position, *x* (could have as well picked momentum).

If we simply specify quantum state by *x*(t), we have no information on p$_x$. However, physical properties usually are functions of both *x* and p$_x$.

State ⎯⎯⎯⎯⎯⎯⎯⎯⎯⎯→ State   [Classical mechanics state (x(t$_j$), p$_x$(t$_j$))

(t$_0$)   Equations of Motion   (t)   Equation of Motion: Newton's, Hamilton's]

With *x* alone obtaining EOM is not possible: both *x* and *t* are important. So, we can start with ψ(x,t).

The key part of this theoretical development relies critically on the final connections to the observations in the physical world, which are characterized by measurements. Thus, to measure the 'position', which is the observable connected to 'x' in the quantum world; we would proceed as follows:

If the quantum system is in state Ψ, we "operate" on Ψ with an appropriate "operator", so, for example, $\hat{x}\Psi \rightarrow$ yields information about position.

We crown the "operator" with a Hat to make sure that we can distinguish it from the operant (function) or the resulting value, e.g. $\hat{x}$ as the position operator to give the position result 'x'.

"Operator" may be a strange notion at first, so it can be better understood with examples below:

Differentiation $\quad \dfrac{"d"}{dx}$ is an operator

$\dfrac{\hat{d}}{dx} f(x) \quad \rightarrow$ yields information on the slope of the function *f(x)*

Integration $\qquad\qquad \int_a^{"b"} dx \quad$ is an operator

$\int_a^b dx f(x) \quad \rightarrow$ yields information on area enclosed by the function *f(x)*

Simple operators, such as,

Addition: $\qquad\qquad$ 5 + 4 = 9 $\qquad$ Subtraction: 5 − 4 = 1, etc. also exist.

We can also construct our own operator; for example, consider the following: e.g., define an operator $\hat{M}$ denoting modulus and square, which will always result in a real value for any input!

Similarly, subtraction, division, division, multiplication, exponentiation, log, … all are operators.

In general, one associates any observable ω (i.e., measurable quantity) with an operator, $\hat{\Omega}$.

If we want to measure position and momentum, then there are two options:

$\quad$ First measure position & then momentum: $\hat{x}\hat{p}_x\Psi$

$\quad$ Or the other way around: $\qquad\qquad\qquad \hat{p}_x\hat{x}\Psi$

Now, we can state uncertainty in the operator Language.

$$\hat{x}\hat{p}_x\Psi \neq \hat{p}_x\hat{x}\Psi$$

But it may be also possible that the state changes!

For example, $x\Psi \rightarrow \phi$. (State changes & no measurement possible)

It is important to look for cases like:

$$\hat{\Omega}\Psi = \omega\,\Psi$$

Operator   value corresponding to observable represented by operator $\hat{\Omega}$

Such relations are Eigenvalue Equations or Characteristic Equations (In German, Eigen means Characteristic)
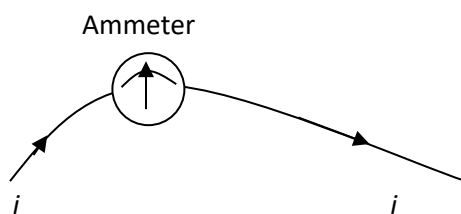
$$\hat{\Omega}\,\Psi = \omega\,\Psi$$

Eigenfunction   Eigenvalue

$\Rightarrow$ If the quantum system is in state Ψ, then we know for certainty that observable $\hat{\Omega}$ has value ω.

Link to Physical Macroscopic World:

You may consider a similar but not the same situation: e.g., Measurement of current i with "Ammeter"

Ammeter

i i

If you think of this as a current operator!

$$\hat{I}(wire\ state) = i(wire\ state)$$

Note: In true sense of measurement: measurement with an ammeter as shown above does not change the current "i" flowing before and after…

Important operator/observation for us is the Hamiltonian operator ($\hat{H}$) corresponding to Energy

So, this brings us back to the eigen functions of Ψ of $\hat{H}$

i.e. $\hat{H}\Psi = E\Psi$ 1926 Schrodinger Eqn.

Thus, if quantum state is in Ψ then applying $\hat{H}$ measures the total energy of the system, E (certain or fixed values). This means we have a Time Independent case.

So, how to arrive at this Hamiltonian Operator? Now Energy is composed of Kinetic & Potential energy parts.
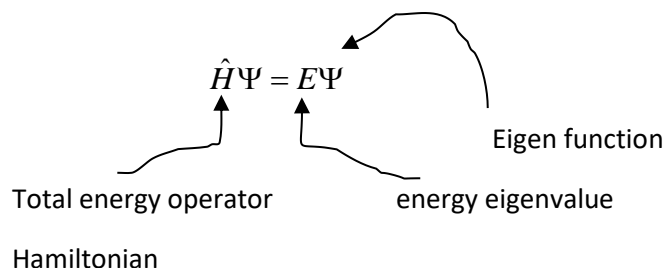
So, $\hat{H} = \hat{T} + \hat{V}$, where $\hat{T}$ is the KE operator & $\hat{V}$ is the PE operator.

Key point in QM: Every observable has a corresponding operator.

Some fundamental operators are for: position & momentum, etc.

Most operators with the exception of spin can be written in terms of x and $\hat{p}_x$.

Thus:
$$\hat{H}\Psi = E\Psi$$

Total energy operator   energy eigenvalue

Hamiltonian

Eigen function

We have the state function: $\Psi = \Psi(x)$ in 1-dimension.

Where is the time? We had started with $\Psi(x,t)$!

The interpretation of $\hat{H}\Psi = E\Psi$ is that the quantum state is in an eigenstate or energy with specific E (certain).

Thus, there is no uncertainty in Energy, i.e., $\Delta E \equiv 0$ and state does not change either.

$$\Rightarrow \Delta t = \frac{\hbar}{\Delta E} \to \infty \text{ (interpret as lifetime i.e., stationary state or eigenstate)}$$

Thus, such a quantum state is in a stationary state and time dependence is "redundant" & so we can drop the "t" dependence in $\Psi(x,t)$.

Classically: Stationary states (total energy is conserved)

What if Ψ is not an Eigenstate of $\hat{H}$?

In that case, $\Psi(x,t)$ has nontrivial t-dependence and we have dynamics.

Thus, equation of Motion in QM:

$$\hat{H}\Psi = i\hbar \frac{d}{dt}\Psi; \quad i = \sqrt{-1}$$

Time dependent Schrodinger equation.

Heisenberg and Schrödinger have independently developed theories that looked very different, but correctly account for the wave like properties of microscopic systems. Here we considered here only the Schrödinger equation. The general form of this equation contains time as a variable, but we will be concerned only with the time-independent form of the Schrödinger wave equation (because most of the chemical applications that we are interested only requires time independent states).

Schrödinger wave equation is a fundamental postulate of quantum mechanics (like $f = ma$ in classical mechanics), which cannot be derived. By using analogy, however, one can arrive at the Schrödinger equation from classical wave equation.

For structural and bonding issues in "chemistry" there is no dynamics and we will mostly be dealing with the time-independent one: $\hat{H}\Psi = E\Psi$.

Now we come to the question: What are x and $\hat{p}_x$?

To be consistent with the Heisenberg principle, i.e., $\hat{x}(\hat{p}_x\Psi) - \hat{p}_x(\hat{x}\Psi) \neq 0$, we have to choose:

x: position operation action is multiplication by x → the usual classical mechanics position functions

$\hat{p}_x : -i\hbar\dfrac{d}{dx}$ → a differential operator.

This was chosen in this form by Dirac—could choose other forms but this will do for us in this course.

The action of these operators (for example) can be understood in terms of their effect on a function:

$$xf(x) = xf(x) \qquad\qquad \text{If } f(x) = x+1, \text{ then } xf(x) = x^2 + x$$

$$\hat{p}_x f(x) = -i\hbar\dfrac{d}{dx}f(x) = -i\hbar$$