CHAPTER 3

The Schrödinger Equation

The Wavefunction Postulate

It is one of the postulates of quantum mechanics that for a physical system consisting of a particle there is an associated wavefunction. This wavefunction determines everything that can be known about the system. The wavefunction is assumed here to be a single-valued function of position and time, since that is sufficient to gaurantee an unambiguous value of probability of finding the particle at a particular position and time. The wavefunction may be a complex function, since it is its product with its complex conjugate which specifies the real physical probability of finding the particle in a particular state.

$\Psi(x,t)$ = single-valued probability amplitude at (x,t)

$\Psi^*(x,t)\Psi(x,t)$ = probability of finding particle at x at time t provided wavefunction is normalized.

The Wavefunction

Each "particle" is represented by a wavefunction Ψ(position, time) such that $\Psi^*\Psi$ = the probability of finding the particle at that position at that time.

The wavefunction is used in the Schrodinger equation. The Schrodinger equation plays the role of Newton's laws and conservation of energy in classical mechanics - i.e., it predicts the future behavior of a dynamic system. It predicts analytically and precisely the probability of events or outcome. The detailed outcome depends on chance, but given a large number of events, the Schrodinger equation will predict the distribution of results.

Wavefunction Properties

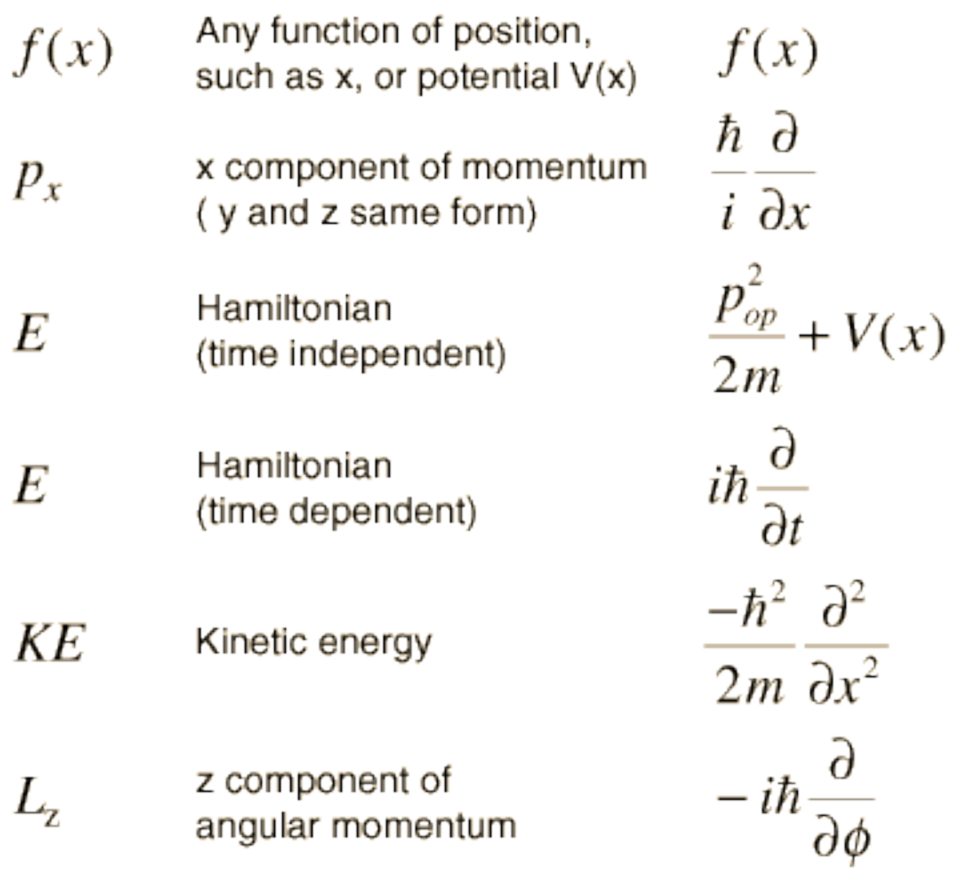
- Ψ contains all the measurable information about the particle
- $\Psi^*\Psi$ summed over all space = 1, (if particle exists, probability of finding it somewhere must be one)
- Ψ is continuous
- Ψ allows energy calculations via the Schrodinger equation
- Ψ establishes the probability distribution in three dimensions
- Ψ permits calculation of most probable value (expectation value) of a given variable
- Ψ for a free particle is a sine wave, implying a precisely determined momentum and totally uncertain position (uncertainty principle).

$$\boxed{\Psi(x,t) = Ae^{ikx - i\omega t}}$$

Plane wave

Operators in Quantum Mechanics

Associated with each measurable parameter in a physical system is a quantum mechanical operator. Such operators arise because in quantum mechanics you are describing nature with waves (the wavefunction) rather than with discrete particles whose motion and dymamics can be described with the deterministic equations of Newtonian physics. Part of the development of quantum mechanics is the establishment of the operators associated with the parameters needed to describe the system. Some of those operators are listed below.



$f(x)$	Any function of position, such as x, or potential V(x)	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m}+V(x)$
E	Hamiltonian (time dependent)	$i\hbar\frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar\frac{\partial}{\partial \phi}$

It is part of the basic structure of quantum mechanics that functions of position are unchanged in the Schrodinger equation, while momenta take the form of spatial derivatives. The Hamiltonian operator contains both time and space derivatives.

Classical Mechanics vs Quantum Mechanics

Kinetics Energy+ Potential=Total Energy

Classical Mechanics $(1/2)mv^2+ (1/2)kX^2=E$

Newton's Law $F=ma$ momentum $p=mv$

$$(p^2/2m)+ (1/2)kX^2=E$$

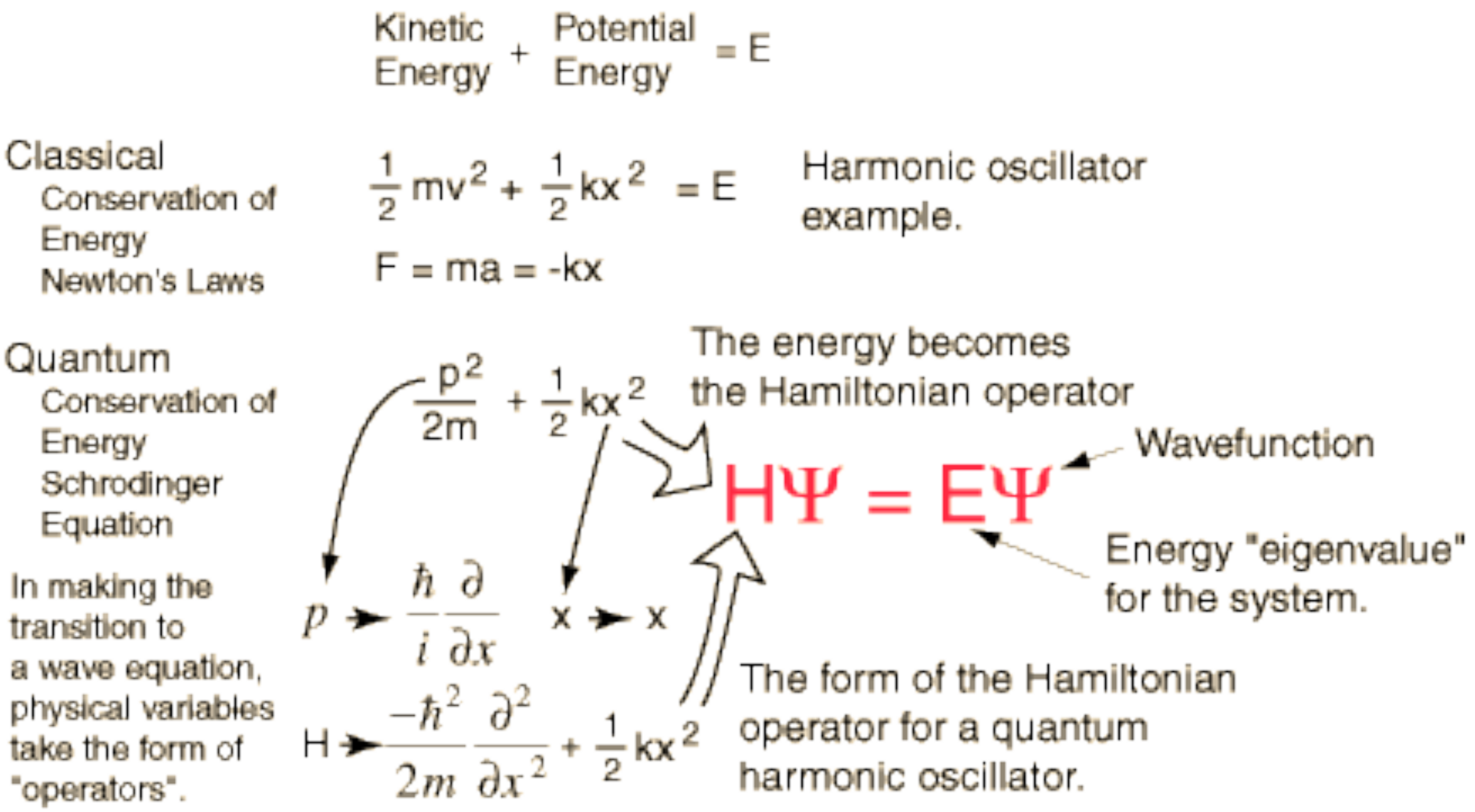
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i}\frac{\partial}{\partial x}$	E	Hamiltonian (time dependent)	$i\hbar\frac{\partial}{\partial t}$

$$H \rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

KE	Kinetic energy	$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

Schrodinger Equation

The Schrodinger equation plays the role of Newton's laws and conservation of energy in classical mechanics - i.e., it predicts the future behavior of a dynamic system. It is a wave equation in terms of the wavefunction which predicts analytically and precisely the probability of events or outcome. The detailed outcome is not strictly determined, but given a large number of events, the Schrodinger equation will predict the distribution of results.



Kinetic Energy + Potential Energy = E

Classical
Conservation of Energy
Newton's Laws

$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2 = E$$

$$F = ma = -kx$$

Harmonic oscillator example.

Quantum
Conservation of Energy
Schrodinger Equation

$$\frac{p^2}{2m} + \frac{1}{2}kx^2$$

The energy becomes the Hamiltonian operator

$$H\Psi = E\Psi$$

Wavefunction

Energy "eigenvalue" for the system.

In making the transition to a wave equation, physical variables take the form of "operators".

$$p \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad x \rightarrow x$$

$$H \rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

The form of the Hamiltonian operator for a quantum harmonic oscillator.

The kinetic and potential energies are transformed into the Hamiltonian which acts upon the wavefunction to generate the evolution of the wavefunction in time and space. The Schrodinger equation gives the quantized energies of the system and gives the form of the wavefunction so that other properties may be calculated.

Time Dependent Schrodinger Equation

The time dependent Schrodinger equation for one spatial dimension is of the form

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

For a free particle where $V(x)$ =0 the wavefunction solution can be put in the form of a plane wave

$$\Psi(x,t) = Ae^{ikx-i\omega t}$$

For other problems, the potential $V(x)$ serves to set boundary conditions on the spatial part of the wavefunction and it is helpful to separate the equation into the time-independent Schrodinger equation and the relationship for time evolution of the wavefunction

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Time Evolution

$$\frac{-\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$

Time Independent Schrodinger Equation

3-D Schrodinger Equation

In three dimensions, the time-independent Schrodinger equation takes the form

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right]+U(x,y,z)\Psi(x,y,z)=E\Psi(x,y,z)$$

for cartesian coordinates. This can be written in a more compact form by making use of the Laplacian operator

$$\nabla^2 f=\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}$$

The Schrodinger equation can then be written:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi+U(x,y,z)\Psi(x,y,z)=E\Psi(x,y,z)$$