The Postulates of Quantum Mechanics

The Postulates of QM

-QM is based on 6 postulates

-Postulates can’t be proved; validity can be tested by experiments

-No violation of the postulates has been found in the ~70 years since their formulation.

Quantum mechanics is a highly successful theory providing us with insight into the world of atoms and molecules. Its foundations are a set of postulates, which we state and comment on below. The only justification for them is quite simply that they work. In order to understand and do quantum mechanical computations and make interpretations, some level of mastery of these postulates is essential. The main objectives of this dry lab (computing) is to have you use the postulates to set up quantum mechanical equations for physical systems and to examine the properties of operators. Interpretation of quantum theory is another matter. Indeed, there are a number of interpretations, but none appear to be completely. The so-called ‘Copenhagen interpretation’ - quantum theory is a probabilistic theory and there is no deep reality - is widely used, but is not without its flaws. Probabilities enter into our discussion of wave functions and they are mentioned in comments of Postulate 1, but otherwise interpretations are not important in this course.

Definition : To begin, assume a 3-dimensional Cartesian coordinate system and denote the coordinates of a point by the 3-tuple of numbers (x,y,z). We shall use the notation

r = (x,y,z). The symbol **r** also denotes the vector

r = xe1 + ye2 +ze3 Such a coordinate system is referred to as ***configuration space*.**

Postulate 1. (1st postulate addresses the meaning of Ψ(x,t). The state of a quantum system is described by a function, Ψ(x,y,z,t) or Ψ(r,t) of the configuration space variables and time. This function is referred to as the **state function** or as the wave function. It contains all the information that can be determined about the system. Furthermore, we require that Ψ(x,y,z,t) be single-valued, continuous, differentiable to all orders, and quadratically integrable, i.e.

I-(a) The state of a dynamical particle cab be describe by a wave function Ψ which is a function of coordinates and time , i.e. Ψ(x,y,z,t)

(b) If the function Ψ describes the state of a particle, then the quantity $\Psi^*\Psi d\tau$ gives the probability of finding the particle in the volume element $d\tau$ at some specific coordinates and time t. This is the born of interpretation of the wave function.

If Ψ included the time explicitly, it is called a time-dependent wave function but if the desirable properties of the system do not change with time (stationary state system), Ψ will be time-independent.

Part (b) of the postulate which gives a physical interpretation of Ψ as a probability function necessitate that Ψ:

1- Must be every where finite.

2- Must be single valued.

3- Must have an integrable squares

More about Ψ(x,t)

-All Knowable about system contained in Ψ(x,t)

-Tie to physical reality is $\Psi^*(x_0,t_0)\ \Psi(x_0,t_0)$

-Magnitude of Ψ(x,t) always >0

-Two Ψ(x,t) of same magnitude not distinguishable

-Link to probability means that

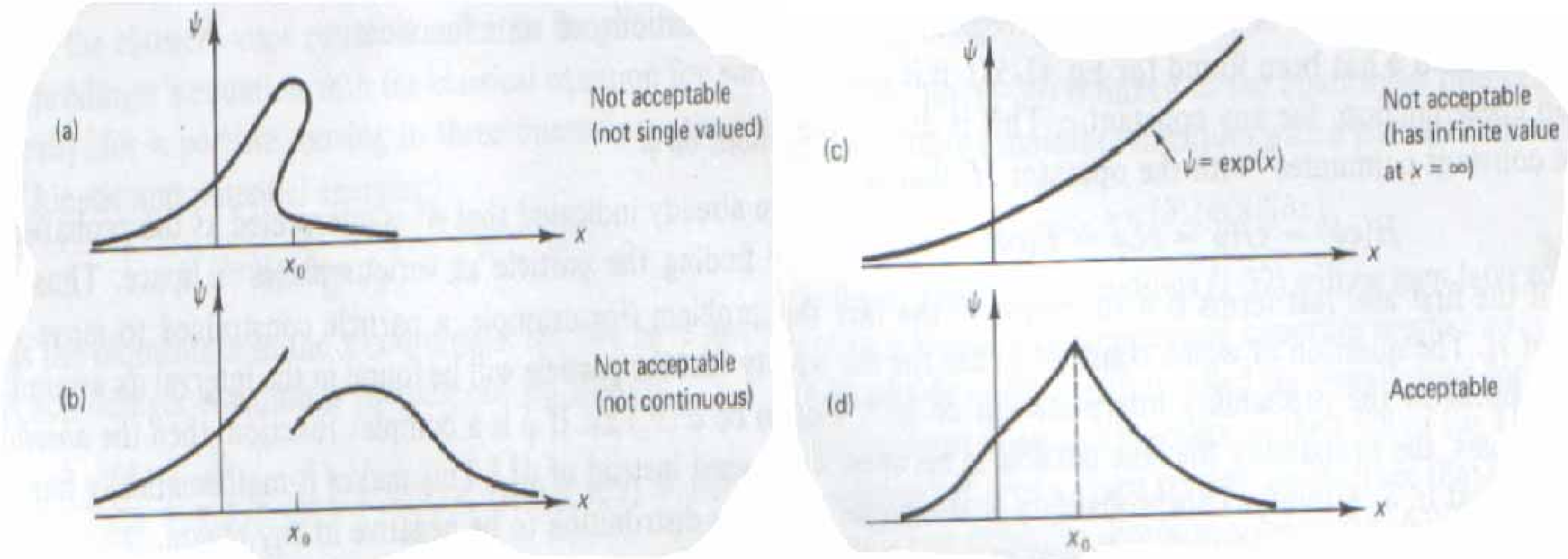
$$\int_{-\infty}^{\infty} \Psi(x,t)*\Psi(x,t)dx = 1$$

This is the normalization condition.

Condition on $\Psi(x,t)$

$\Psi(x,t)$ must be single valued

Otherwise two different probability for x



(α) Ψ is triple valued at x_0. (b) Ψ is discontinuous at x_0. (c) Ψ grows without limit at x approaches $+\infty$ (i.e. Ψ “blows up,” or “explodes” . (d) Ψ is continuous and has a “cusp” at x_0. Hence, first derivative of Ψ is discontinuous at x_0 and is only piecewise continuous. This does not prevent Ψ from being acceptable.

In order for HΨ to be defined everywhere, it is necessary that the second derivative of Ψ be defined everywhere. This requires that the first derivative of Ψ be *piecewise continuous* and that Ψ Itself be *continuous.* (We shall see an example of this shortly.)

Functions that are single-valued, continuous, nowhere infinite, and have piecewise continuous first derivatives will be referred to as *acceptable* functions.

The meanings of these terms are illustrated by some sample functions above namely (a) , (b), (c) and (d).

In most cases, there is one more general restriction we place on Y namely, that it be a normalizable function. This means that the integral of $\left|\Psi\right|^2$ over all space must not be equal to zero or infinity. A function satisfying this condition is said to be *square-integrable.*

The restriction of integrable squares arises from the requirement that the probability of finding the particle in all space must be finite. A special case in when

$$\int_{allspace} \Psi^* \Psi d\tau = 1$$

which means that

The probability of finding the particle in all space is 1 such a wave function is said to be normalized All wave functions have to be normalized.

<u>Postulate II</u> Every observable property of a system has a linear Hermitain operator. The Hermitian property of the operator ensure that the calculated values of the observable will always be real. The following procedure is followed to obtain the operator of any observable.

i.e. Postulate 2: stated that for every measurable property of the system in classical mechanics such as position, momentum and energy, there exists a corresponding operator in quantum mechanics. An experiment in the laboratory to measure a value for such an observable is simulated in the theory by operating on the wave function of the system with the corresponding operator.

1- The classical expression for te observable is written in thus of coordinate, momentum and time.

2- time and all coordinates are left as they are.

3- Momentum , p_q are replaced by the differential operator where q represents a general coordinate e.g. x,y,z , r,θ,ϕ.

Example-1 Find the operator for the kinetic energy?

Kinetic Energy $T = \frac{1}{2} m v^2$

$$= \frac{m}{2}\left(v^2 x + v^2 y + v^2 z\right)$$

Multiply by $\frac{m}{m}$

$$T = \frac{m^2}{2m}\left(v^2{}_x + v^2{}_y + v^2{}_z\right)$$

$$T = \frac{1}{2m}\left(m^2 v^2{}_x + m^2 v^2{}_y + m^2 v^2{}_z\right)$$

$$= \frac{1}{2m}\left(p^2{}_x + p^2{}_y + p^2{}_z\right)$$

Step 2 Not applicable

Step 3

$$\hat{T} = \frac{1}{2m}\left[\left(-i\hbar\frac{d}{dx}\right)^2 + \left(-i\hbar\frac{d}{dy}\right)^2 + \left(-i\hbar\frac{d}{dz}\right)^2\right]$$

$$\hat{T} = \frac{1}{2m}\left[-\hbar^2\frac{d^2}{dx^2} - \hbar^2\frac{d^2}{dy^2} - \hbar^2\frac{d^2}{dz^2}\right]$$

$$\hat{T} = \frac{-\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)$$

$$\hat{T} = \frac{-\hbar^2}{2m}\nabla^2 \text{ Kinetic energy operator is called Laplacian}$$

The Del squared ∇^2 (3D) is the laplacian.

$$1D = Tx = \frac{p^2 x}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$3D = T = \frac{p^2 x + p^2 y + p^2 z}{2m}$$

So, to Constructing operators

The steps are:

1. Write out the classical expression in terms of *r* (*x,y,z*)and *p*.
2. Replace *r* and *p* with the operators.

$$r \to \left(r \text{ multiply by r}\right)$$

$$p \to \frac{\hbar}{i}\left(\frac{d}{dx} + \frac{d}{dy} + \frac{d}{dz}\right)$$

The potential energy operator V

The potential energy will depend on the specifics of a given system. As an example, consider an electron in the field of an atomic nucleus of charge *Z.* The potential energy then comes from the Coulomb potential:

$$V(r) = -\frac{Ze2}{4\pi\varepsilon_0 r}$$

Where –*e* is the charge on an electron (or +*e* for a proton), and *r* is the separation distance, which is a function of *x,y,z*.

Example 2- Write down the Hamiltonian which is the operator of total energy of a system?

Total Energy H is equal the sum of Kinetic energy T, and the potential energy V

$$\therefore \hat{H} = \hat{T} + \hat{V}$$

For a conservative system i.e. a system where T+V remains constant with time.

Because the operator of the kinetic energy was derived previously, the potential energy V is a function of coordinates only therefore it remains as it is:

$$\therefore \hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(q)$$

The total energy operator, H

The total energy is the sum of the kinetic and potential energy:

H =T + V

The Hamiltonian →

$$1D = H_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \quad \text{And For 3D is :}$$

$$3D = H = \frac{-\hbar^2}{2m}\nabla^2 + V(r)$$

For an electron moving in a coulomb potential with Z=1 the Hamiltonian is

$$H = \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$