Formalism of quantum mechanics

After getting exposed to basic wave mechanics in 1D let us recast the knowledge we have accumulated in a more general form.

Like any theory the quantum theory deals with two kind of things: objects and actions on those objects. In our case objects are wave functions (or state vectors) and actions are defined by operators. Since the fundamental equations that lie at the heart of quantum mechanics (e.g. the Schrödinger equation) are linear, the natural language of it is linear algebra.

Any fundamental theory is based on a set of postulates. Postulate is a basic principle or property that is not derived from something.

The foundation of quantum mechanics are several postulates. They can be cast in somewhat different forms, but the essence remains the same. How do we know if those postulates are correct and consistent. The proof comes from the experiment and so far QM has been found to be capable of describing the phenomena within its area of applicability very well.

Now let us list the postulates of QM:

__Postulate 1__ The dynamical state of a QM system is completely described by a wave function.

The wave function can be complex and it contains all that can be known about the system.

In order to be physically admissible the wave function must satisfy several conditions:

a) It must be normalizable

b) Single valued

c) continuous

__Postulate 2__ For every measurable property of the system there exists a corresponding operator

The operators ~~co~~rresponding to most common observables are listed below:

observable	operator	symbol
Position	x	$\hat{X}$
Momentum	$-i\hbar\frac{\partial}{\partial x}$	$\hat{P}_x$
Kinetic energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, $\frac{p_x^2}{2m}$	$\hat{T}$, $\frac{\hat{P}_x^2}{2m}$
Potential energy	$V(x)$	$\hat{V}(x)$
Total energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$	$\hat{H}$
& Angular momentum	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$	$\hat{L}_x$
	$-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$	$\hat{L}_y$
	$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$	$\hat{L}_z$

Physically observed quantities are real (i.e. not complex). This ~~restr~~ puts a restriction on the operators that are associated with them. They must be Hermitian (we will give a definition of a Hermitian operator a bit later).

Action of operators is generally order dependent

$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$$

When written, operators are assumed to operate from left to right:

$\hat{A}\hat{B}f(x)$: $\hat{B}$ is applied first, then $\hat{A}$

<u>Postulate 3</u> For any measurement involving an observable corresponding to an operator, the only values that will be measured will be eigenvalues of the operator.

Eigenvalues of an operator : $\hat{A}\varphi_i(x) = a_i \varphi_i(x)$

the number of eigenvalues and eigenfunctions ~~may~~ depends on the operator/system.

The eigenvalues of Hermitian operators are known to be always real (no exceptions)

Postulate 4   If the system is in a state described by a wave function and the value of the observable "a" is measured once each on many identically prepared systems, the average (or expectation value of all measurements will be

$$\langle a \rangle = \frac{\int \psi^*_{(x)} \hat{A} \psi(x)\, dx}{\int \psi^*_{(x)} \psi_{(x)} dx} = \int \psi^* A \psi \, dx \quad \text{(if normalized)}$$

If the wave function happens to be an eigenfunction of $\hat{A}$ then

$$\langle a \rangle = \int \psi^* \hat{A} \psi = \int \varphi_j^* A \varphi_j \, dx = a_j \int \varphi_j^* \varphi_j \, dx =$$

$$= a_j$$

The fourth postulate states what will happen when a large number of identical systems are interrogated one time.

What happens for an individual measurement? You will get an aswer corresponding to one of the eigenvalues. Eeach eigenvalue may occur with a different frequency (probability) as it depends on the wave function. But there is no way to know in advance which outcome will be produced in a particular measurement.

After a large number of measurements the result will converge to $\langle a \rangle$

In QM, the act of the measurement is believed to cause the system to "collapse" into a single eigenstate and in the absence of an external perturbation it will remain in that eigenstate

<u>Postulate 5</u> The time evolution of the wave function is described by the Schrödinger equation:

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

For the particular case of time-independent potential $V = V(x)$ the above equation is separable, leading to the time-independent (stationary) Schrödinger equation:

$$H\psi_n(x) = E_n \psi_n(x)$$

The n-th particular solution is then

$$\Psi_n(x,t) = \psi_n(x)\, e^{-\frac{iE_n t}{\hbar}}$$

Utilizing the superposition principle, the general solution can be represented as an expansion

$$\Psi(x,t) = \sum_n c_n \psi_n(x)\, e^{-\frac{iE_n t}{\hbar}}$$

The sufficient condition for this expansion to be valid for a general wave function $\Psi(x,t)$ is that the function $\psi_n(x)$ form a complete set of functions.

Hilbert space

It is a generalization of the notion of Euclidean space to the case of any finite or infinite number of dimensions.

In Hilbert space we define

a) vectors (points)

b) addition operation on vectors

c) the inner product (dot product)

Illustrative examples:

$$|\alpha\rangle \to \vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \\ a_N \end{pmatrix}$$

N can be infinite

inner product:

$$\langle\alpha|\beta\rangle = a_1^* b_1 + a_2^* b_2 + \dots + a_N^* b_N$$

Compare:

$$\langle f|g\rangle = \int f(x)^* g(x)\, dx$$

if in some basis $\{\phi_i\}$ $f(x) = \sum_i a_i \phi_i$ $g(x) = \sum_j b_j \phi_j$

then (assuming $\int \phi_i^* \phi_j \, dx = \delta_{ij}$)

$$\langle f|g\rangle = \int \left(\sum_i a_i^* \phi_i^*\right)\left(\sum_j b_j \phi_j\right) dx = \sum_{ij} a_i^* b_j \int \phi_i^* \phi_j \, dx =$$

$$= \sum_{ij} a_i^* b_j \delta_{ij} = \sum_i a_i^* b_i = a_1^* b_1 + a_2^* b_2 + a_3^* b_3 + \dots$$

Normalized wave functions (state vectors) are possible only when $\sum_i a_i^* b_i$ is finite. When N is infinite the series $\sum_{i=1}^{\infty} a_i^* b_i$ must be converging

Linear operators can be represented by matrices (which may be infinitely large)

$$|\beta\rangle = M|\alpha\rangle = \begin{pmatrix} m_{11} & m_{12} & \cdots & m_{1N} \\ m_{21} & m_{22} & \cdots & m_{2N} \\ \vdots & & \ddots & \vdots \\ m_{N1} & m_{N2} & \cdots & m_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \\ a_N \end{pmatrix} =$$

$$= (b_1, b_2, b_3 \ldots b_N)$$

Elements of the matrices may be complex. However, since the eigenvalues of the matrices that correspond to observables must be real it puts a constraint on those matrices. They have to be Hermitian.

Hermitian matrix: $M_{ij} = M_{ji}^*$

$\langle\alpha|M|\alpha\rangle$ is real for any $|\alpha\rangle$

$$\langle\alpha|M|\alpha\rangle \equiv \sum_{ij} a_i^* M_{ij} a_j$$

Compare:

$$\int \psi^*(x)\, \hat{M}\, \psi(x)\, dx = \int \Big(\sum_i a_i^* \phi_i\Big) \hat{M} \Big(\sum_j a_j \phi_j\Big) dx =$$

$$= \sum_{ij} a_i^* a_j M_{ij} \qquad M_{ij} = \int \phi_i^* \hat{M} \phi_j\, dx$$

Eigenvalues of Hermitian matrices are known to be real, while their eigenvectors corresponding to different eigenvalues are orthogonal:

$$M|\mu_i\rangle = \lambda_i|\mu_i\rangle \qquad \langle\mu_i|\mu_j\rangle = \delta_{ij}$$

The eigenvectors corresponding to the same (degenerate) eigenvalue can always be rearranged and made orthogonal

An operator is called Hermitian if

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$$

A related concept is the adjoint operator (or hermitian conjugate):

$$\langle f | \hat{A} g \rangle = \langle \hat{A}^{+} f | g \rangle \qquad \hat{A}^{+} \text{ is adjount of } \hat{A}$$

if $\hat{A}^{+} = \hat{A}$ then $\hat{A}$ is Hermitian (or self-adjoint)

Example: momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$

$$\langle f | \hat{p} g \rangle = \int_{-\infty}^{+\infty} f^{*} \left(-i\hbar \frac{dg}{dx} \right) dx \overset{\text{integrate}}{\underset{\text{by parts}}{=\!=\!=}} \underbrace{-i\hbar f^{*} g \Big|_{-\infty}^{+\infty}}_{0} +$$

$$+ \int_{-\infty}^{+\infty} (-i\hbar) \frac{df^{*}}{dx} g \, dx = + \int_{-\infty}^{+\infty} \left(-i\hbar \frac{d}{dx} f \right)^{*} g \, dx$$

As we just verified, $\hat{p}$ is a hermitian operator. Its eigenvalues are real.