The Postulates Of Wave Mechanics

The postulates of wave mechanics for a single particle of mass m are:

Postulate 1: The State of the System

The quantum state of a particle is characterized by a wave function, a complex function of space and time, $\psi(\vec{r}, t)$, which contains all the information it is possible to obtain about the particle.

Postulate 2: Statistical Interpretation

The wave function $\psi(\vec{r}, t)$ is the probability amplitude for the particle's presence. That is the probability, $d\mathcal{P}(\vec{r}, t)$, of observing the particle at time t in the volume element d^3r about the position $\vec{r}$ is

$$d\mathcal{P}(\vec{r}, t) = \frac{1}{N}|\psi(\vec{r}, t)|^2 d^3r \ , \tag{1}$$

where N is a constant of normalization.

Since the probability of finding the particle somewhere in space at time t is 1,

$$1 = \int_{\text{all space}} d\mathcal{P} = \frac{1}{N}\int_{\text{all space}} d^3r|\psi(\vec{r}, t)|^2 \ , \tag{2}$$

the normalization constant is simply

$$N = \int_{\text{all space}} d^3r|\psi(\vec{r}, t)|^2 \ . \tag{3}$$

Hence $\psi(\vec{r}, t)$ must be square-integrable. Thus

$$d\mathcal{P}(\vec{r}, t) = \frac{|\psi(\vec{r}, t)|^2 d^3r}{\int_{\text{all space}} d^3r|\psi(\vec{r}, t)|^2} \ , \tag{4}$$

with $|\psi(\vec{r}, t)|^2$ interpreted as a probability density and $\psi(\vec{r}, t)$ as a probability amplitude. Note that $|\psi(\vec{r}, t)|^2$ is unchanged if $\psi \longrightarrow e^{i\omega}\psi$ with $\omega \in \mathcal{R}$. The overall phase of ψ is unobservable, hence all ψ differing only in phase represent the same state of the particle.

Postulate 3: Measurement and the Principle of Spectral Decomposition

Every observable property $\mathcal{A}$ of the system corresponds to a hermitian operator A acting on the wave function.

The principle of spectral decomposition applies to the measurement of physical quantities $\mathcal{A}$:

1. The result of a measurement of observable $\mathcal{A}$ is one of the eigenvalues of the hermitian operator A. The set of eigenvalues of A is denoted by $\{a\}$.

2. To each eigenvalue a of A is associated an eigenfunction $\varphi_a(\vec{r})$ such that

$$A\varphi_a(\vec{r}) = a\varphi_a(\vec{r}) \ . \tag{5}$$

(If the eigenvalue a is N_a-fold degenerate, there are N_a linearly independent eigenfunctions.)

The eigenfunctions of the hermitian operator corresponding to any observable are assumed to form a complete set, that is any wave function at time t, $\psi(\vec{r},t)$, can be expanded in terms of them.

3. For any state of the system $\psi(\vec{r},t)$, $\mathcal{P}_a(t)$, the probability of obtaining the eigenvalue a of A during a measurement of $\mathcal{A}$ at time t, is found by expanding $\psi(\vec{r},t)$ in terms of the complete set of eigenfunctions $\varphi_a(\vec{r})$,

$$\psi(\vec{r},t) = \sum_{\{a\}} c_a(t)\varphi_a(\vec{r}) \ . \tag{6}$$

The probability is then given by

$$\mathcal{P}_a(t) = \frac{|c_a(t)|^2}{\sum_{\{a\}} |c_a(t)|^2} \ . \tag{7}$$

Note that $\sum_{\{a\}} \mathcal{P}_a(t) = 1$, as required since a measurement of $\mathcal{A}$ must yield one of the eigenvalues of A. This has been written for the case that the eigenvalues are discrete, so the completeness of the orthonormal eigenfunctions, $\int d^3r\varphi_a^*(\vec{r})\varphi_b(\vec{r}) = \delta_{ab}$, is expressed as

$$\sum_{\{a\}} \varphi_a^*(\vec{r}\,')\varphi_a(\vec{r}) = \delta^3(\vec{r}\,' - \vec{r}) \ . \tag{8}$$

If the eigenvalue spectrum is continuous then $\psi(\vec{r},t)$ is represented by an integral over the set of continuous eigenvalues

$$\psi(\vec{r},t) = \int_{\{a\}} \frac{da}{N^2(a)} c(a,t)\varphi_a(\vec{r}) \ , \tag{9}$$

with the expansion coefficient $c(a,t)$ a function of the eigenvalue a and time t. The eigenfunctions $\varphi_a(\vec{r})$ now obey the continuum normalization conditions

$$\int d^3r \varphi_a^*(\vec{r})\varphi_b(\vec{r}) = N^2(a)\delta(a-b) \ , \tag{10}$$

with $N^2(a)$ an arbitrary normalization factor. Hence, completeness is expressed as

$$\int_{\{a\}} \frac{da}{N^2(a)} \varphi_a^*(\vec{r}\,')\varphi_a(\vec{r}) = \delta^3(\vec{r}\,' - \vec{r}) \ . \tag{11}$$

The probability, $d\mathcal{P}(a,t)$, of obtaining a result between a and $a + da$ when measuring property $\mathcal{A}$ at time t is

$$d\mathcal{P}(a,t) = \frac{|c(a,t)|^2 \frac{da}{N^2(a)}}{\int_{\{a\}} \frac{da}{N^2(a)} |c(a,t)|^2} \ . \tag{12}$$

As required of a probability $\int_{\{a\}} d\mathcal{P}(a,t) = 1$.

4. In the case of a discrete eigenvalue spectrum, if the measurement of $\mathcal{A}$ at time t yields the value a, then the wave function of the particle immediately after the measurement, $t = t^+$, is $\psi(\vec{r},t^+) = \varphi_a(\vec{r})$. This is known as the collapse of the wave function. (If a is a degenerate discrete eigenvalue of A, then $\psi(\vec{r},t)$ is a linear combination of the eigenfunctions of A with eigenvalue a. The general the spectral decomposition of the (normalized) wave function $\psi(\vec{r},t)$ is given by a sum over all the (normalized) eigenfunctions $\varphi_a^{(\alpha_a)}(\vec{r})$ where $\alpha_a = 1, 2, \ldots, N_a$ labels the N_a linearly independent eigenfunctions with eigenvalue a

$$\psi(\vec{r},t) = \sum_{\{a\}} \sum_{\alpha_a=1}^{N_a} c_a^{(\alpha_a)}(t)\varphi_a^{(\alpha_a)}(\vec{r}) \ . \tag{13}$$

Immediately after the measurement of $\mathcal{A}$ at time $t = t^+$ the normalized wave function becomes

$$\psi(\vec{r},t^+) = \frac{1}{\sqrt{\sum_{\alpha_a=1}^{N_a} |c_a^{(\alpha_a)}(t)|^2}} \sum_{\alpha_a=1}^{N_a} c_a^{(\alpha_a)}(t)\varphi_a^{(\alpha_a)} \ , \tag{14}$$

the wave function has collapsed to this eigenstate of A.

In the case of a continuous spectrum of eigenvalues of A, if a measurement of $\mathcal{A}$ at time t yields the value of a to within a range Δa, then the wavefunction immediately after the measurement collapses to that part of the wavefunction that was within the Δa range of a at time t

$$\psi(\vec{r}, t^+) = \frac{1}{\sqrt{\int_{a-\frac{\Delta a}{2}}^{a+\frac{\Delta a}{2}} \frac{da}{N^2(a)} |c(a,t)|^2}} \int_{a-\frac{\Delta a}{2}}^{a+\frac{\Delta a}{2}} \frac{da}{N^2(a)} c(a,t)\varphi_a(\vec{r}) \ , \tag{15}$$

where the wavefunction has been normalized once again.

Postulate 4: Time Evolution and The Schrödinger Equation

The time evolution of the state described by the wave function $\psi(\vec{r}, t)$ is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(\vec{r}, t) = \frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}, t) + V(\vec{r}, t)\psi(\vec{r}, t) \ . \tag{16}$$