

I. Schrödinger Wave Mechanics

1.2. The Postulates

In order to elucidate the wave-particle duality of matter as suggested by the de Broglie hypothesis further, Schrödinger associated a function of space and time, the wavefunction (whose interpretation we shall discuss later), with a free particle ($E = \frac{\vec{p}^2}{2m}$) of the form

$$\psi(\vec{r}, t) = A e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et)}$$

where A is a constant and \vec{p} is the momentum and E the energy of the free, non-relativistic particle, $E = \frac{\vec{p}^2}{2m}$.

Since $i\hbar \frac{\partial \psi}{\partial t} = E\psi$ and

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \frac{\vec{p}^2}{2m} \psi, \text{ the wavefunction}$$

for a free particle obeys the partial differential equation

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

which has the form of a complex diffusion equation.

If the particle is moving under the influence of a potential $V(\vec{r})$, Schrödinger replaced the free equation with

$$E \psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t).$$

Heuristically we have made the identification
kinetic energy $T = \frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m} \nabla^2$

potential energy $V = V(\vec{r})$

total energy $E \rightarrow i\hbar \frac{\partial}{\partial t}$

with $E = T + V$.

Further, if $V = V(\vec{r}, t)$, Schrödinger hypothesized that the wave function of a particle of mass m moving under its influence obeys the partial differential equation (Schrödinger's Equation)

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t),$$

and quantum (wave) mechanics was born.

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Contemporaneously with Schrödinger, Heisenberg developed his matrix mechanics version of quantum theory. Eventually, it was shown by Dirac to be completely equivalent to Schrödinger's wave mechanics. Further, in the years shortly after the pioneering work of Schrödinger and Heisenberg, many physicists struggled to make the foundations of quantum theory and its interpretation clear and concise. Consequently, all the properties of quantum theory can be shown to follow from a few postulates. For simplicity, the postulates are stated for a single particle of mass m . Later in the course they will be generalized to include multi-particle systems.

The Postulates of Wave Mechanics

- 1) Postulate 1: 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.

2) Postulate 2: The wavefunction $\psi(\vec{r}, t)$

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

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

where N is a constant of normalization. Since the probability of finding the particle somewhere in space at time t is 1,

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

The normalization constant is simply

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

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

Thus

$$dP(\vec{r}, t) = \frac{|\psi(\vec{r}, t)|^2 d^3r}{\int |\psi(\vec{r}, t)|^2 d^3r}$$

with $|\psi(\vec{r}, t)|^2$ interpreted as a probability density. Note $|\psi(\vec{r}, t)|^2$ is unchanged if $\psi \rightarrow e^{i\omega} \psi$ with $\omega \in \mathbb{R}$. Thus $\psi(\vec{r}, t)$ itself is unobservable and all ψ differing only in phase represent the same state of the particle.

3.) Postulate 3: Every observable property \mathcal{O} of the system corresponds to a hermitian operator A acting on the wavefunction.

A hermitian operator A is defined so that if $\psi_1(\vec{r}, t)$ and $\psi_2(\vec{r}, t)$ are wavefunctions (functions which vanish sufficiently fast as $|\vec{r}| \rightarrow \infty$) then

$$\int d^3r [A\psi_1(\vec{r},t)]^* \psi_2(\vec{r},t) = \int d^3r \psi_1^*(\vec{r},t) [A\psi_2(\vec{r},t)].$$

Some familiar Hermitian operators are the position operator $\hat{X}\psi(\vec{r},t) = \vec{r}\psi(\vec{r},t)$, i.e. $\hat{X} = \vec{r}$, the momentum operator

$\vec{P} = -i\hbar\vec{\nabla}$ and the energy operator

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

The principle of spectral decomposition applies to the measurement of physical quantities \hat{A}

- 1) The result of a measurement of observable \hat{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_i of A is associated an eigenfunction $\psi_{a_i}(\vec{r})$ such that

$$A\psi_{a_i}(\vec{r}) = a_i\psi_{a_i}(\vec{r}).$$

(If the eigenvalue a is N -fold degenerate, there are N linearly independent eigenfunctions.) The eigenfunctions of the hermitian operator corresponding to any observable are assumed to form a complete set, that is any wavefunction at time t , $\psi(\vec{r}, t)$, can be expanded in terms of them.

3. For any state of the system $\psi(\vec{r}, t)$, $P_a(t)$,

The probability of obtaining the eigenvalue a of A during a measurement of A at time t , is found by expanding $\psi(\vec{r}, t)$ in terms of the complete set of eigenfunctions $\psi_a(\vec{r})$,

$$\psi(\vec{r}, t) = \sum_a c_a(t) \psi_a(\vec{r}) .$$

The probability is then given by

$$P_a(t) = \frac{|c_a(t)|^2}{\sum_a |c_a(t)|^2} .$$

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Note that $\sum_a P_a(t) = 1$, as required.

4. If the measurement of A at time t yields the value a , then the wave function of the particle immediately after the measurement is $\psi(\vec{r}, t) \equiv \psi_a(\vec{r})$. If a is a degenerate eigenvalue of A ,

then $\psi(\vec{r}, t)$ is a linear combination of the eigenfunctions of A with eigenvalue a , i.e. $\psi(\vec{r}, t) = \sum_{\alpha_a} C_{\alpha_a}(t) \psi_{\alpha_a}(\vec{r})$
where $\psi(\vec{r}, t) = \sum_a \sum_{\alpha_a} C_{\alpha_a}(t) \psi_{\alpha_a}(\vec{r})$.

4.) Postulate 4: The time evolution of the state described by the wavefunction $\psi(\vec{r}, t)$ is given by the Schrödinger equation

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

Note that the Schrödinger equation is linear and homogeneous in ψ . Thus it satisfies the principle of (linear) superposition. That is, if both ψ_1 and ψ_2 individually satisfy the Schrödinger equation, then so does

$$\psi = \psi_1 + \lambda \psi_2$$

with $\lambda \in \mathbb{C}$. Further, since

$|\psi|^2 = |\psi_1 + \lambda \psi_2|^2$ has the interpretation of a position probability density, one can see how wave-like effects such as interference can occur from the cross-terms.

Also, note the equation is first order in $\frac{\partial}{\partial t}$. Thus knowledge of the state of the system at time t_0 , $\psi(\vec{r}, t_0)$, determines the state $\psi(\vec{r}, t)$, at all other times via Schrödinger's equation.

We are now in a position to deduce the consequences of quantum mechanics from the above postulates. At the same time this will help us to fine tune even further the underlying principles of the theory.