Quantum Mechanics - Summary

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1 Physical background

1.1 Electromagnetic Waves

Light / EM waves consist of quanta called *photons* with energy

$$E = h\nu = \hbar\omega$$

and momentum

$$p = h/\lambda = \hbar k$$

where $\omega = 2\pi\nu$ is the frequency of the wave, λ the wavelength and $k = 2\pi/\lambda$ the wavenumber.

The speed is $c = \omega/k = \nu\lambda$, and $E = cp$.

1.2 Bohr model of the atom

Hydrogen atom: an electron with charge $-e$ and mass m orbits a proton of charge $+e$ stationary at the origin. The potential for the electron is

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}.$$

The total energy of the electron is

$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r}.$$

For a circular orbit,

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}.$$

Bohr's postulate is that angular momentum is *quantised* with $L = mrv = n\hbar$ for $n = 1, 2, \ldots$. Then

$$\begin{aligned} r_n &= \frac{4\pi\epsilon_0}{me^2}\hbar^2 n^2 \\ v_n &= \frac{e^2}{4\pi\epsilon_0 \hbar n} \\ E_n &= -\frac{1}{2}m\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2 \frac{1}{n^2}. \end{aligned}$$

If the electron makes a transition between levels n and n', accompanied by emission or absorption of a photon of frequency ω then

$$\hbar\omega = E_{n'} - E_n = \frac{1}{2}m\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2\left(\frac{1}{n^2} - \frac{1}{n'^2}\right).$$

2 Schrödinger equation and solutions

2.1 Wavefunctions

In QM a particle has a *state* at each time, specified by a complex-valued *wavefunction* $\psi(x)$. A measurement of position gives a result x with probability density $|\psi(x)|^2$, i.e. $|\psi(x)|^2\delta x$ is the probability that a measurement finds a particle in the interval x to $x+\delta x$, and $\int_a^b |\psi(x)|^2 dx$ for the interval $a \leq x \leq b$.

This probability interpretation relies on the normalisation $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$, and we say $\psi(x)$ is *normalisable* if this integral is finite.

2.2 Particle beams

If $\psi(x)$ is not normalisable, it can still be given meaning. Consider the plane wave $\psi(x) = Ce^{ikx}$ which has $|\psi(x)|^2 = |C|^2$ independent of x. We can interpret this to represent a *beam* of individual particles on the entire line with $|C^2|$ the number of particles per unit length.

3 Operators

The quantum state given by $\psi(x)$ contains information about physical quantities of *observables* which are represented by an *operator* acting on ψ.

- Position: $\hat{x} = x \qquad (\hat{x}\psi)(x) = x\psi(x)$
- Momentum: $\hat{p} = -i\hbar\frac{d}{dx} \qquad (\hat{p}\psi)(x) = -i\hbar\psi'(x)$
- Energy: $H = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$ for a particle in a potential $V(x)$, where H is called the *Hamiltonian*.

If ψ is an *eigenstate* or *eigenfunction* of the operator, we get a definite result (probability 1), i.e.

$\hat{p}\psi = p\psi$ if and only if ψ is a state of definite momentum p.

$H\psi = E\psi$ if and only if ψ is a state of definite energy E.

In general, if an observable Q is measured when the system is in a *normalised* state ψ then the outcome is some eigenvalue λ_n of Q and is obtained with probability $P_n = |\alpha_n|^2$ where $\alpha_n = (\chi_n, \psi)$ is the *amplitude*. This measurement is instantaneous and it forces the system into the state χ_n (wavefunction collapse).

3.1 Time-independent Schödinger equation

The energy eigenvalue equation $H\psi = E\psi$ or

$$-\frac{\hbar^2}{2m}\psi'' + V\psi = E\psi$$

is the time-independent Schrödinger equation. The possible values for E are the allowed energy levels of the quantum particle in a potential $V(x)$.

3.2 Expectation & Uncertainty

The expectation value of an operator Q in state ψ is

$$\langle Q\rangle_\psi = (\psi, Q\psi) = \sum_n \lambda_n P_n.$$

The uncertaintly of Q in state ψ is $(\Delta Q)_\psi$ where

$$(\Delta Q)^2_\psi = \langle (Q - \langle Q\rangle_\psi)^2\rangle_\psi = \langle Q^2\rangle_\psi - \langle Q\rangle^2_\psi$$

3.3 Ehrenfest's Theorem

If Q is any operator with no explicit time dependence then

$$i\hbar\frac{d}{dt}\langle Q\rangle_\Psi = \langle [Q, H]\rangle_\Psi$$

where $[Q, H] = QH - HQ$ is the commutator.

4 Time-dependent Schrödinger equation

In general, the state can depend on time too, giving a wavefunction $\Psi(x, t)$ which obeys the time-dependent Schrödinger equation

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

where H is the Hamiltonian for a particle in a potential $V(x)$.

4.1 Stationary states

A wavefunction of the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t}$$

with definite frequency ω which satisfies the time-dependent SE is a *stationary state.*

In this case, ψ is an energy eigenstate with eigenvalue $E = \hbar\omega$, and $|\Psi(x, t)|^2 = |\psi(x)|^2$ independent of t.

4.2 Conservation of probability

For a wavefunction $\Psi(x,t)$ obeying the time-dependent SE with real potential $V(x)$, the probability

$$P(x,t) = |\Psi(x,t)|^2$$

obeys a conservation equation

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x}$$

where

$$j(x,t) = -\frac{i\hbar}{2m}\left(\Psi^*\Psi' - \Psi^{*\prime}\Psi\right)$$

is the *probability current.*

This implies that

$$\frac{d}{dt}\int_a^b |\Psi(x,t)|^2 dt = j(a,t) - j(b,t).$$

If Ψ is normalisable with $\Psi, \Psi', j \to 0$ as $x \to \pm\infty$ (for fixed t) then taking $a \to -\infty$ and $b \to \infty$ we get

$$\frac{d}{dt}\int_a^b |\Psi(x,t)|^2 dt \equiv 0$$

i.e. if $\Psi(x,0)$ is normalised then $\Psi(x,t)$ is normalised for all t.

For a stationary state, the probability current j is independent of t and the conservation equation implies $\frac{\partial j}{\partial x} = 0$ since the probability density is independent of t.

4.2.1 Particle beams

For a free particle, the wavefunction $\psi(x) = Ce^{ikx}$ is a momentum eigenstate with eigenvalue $p = \hbar k$, and an energy eigenstate with eigenvalue $E = \frac{\hbar^2 k^2}{2m}$. This gives rise to a stationary state

$$\Psi(x,t) = Ce^{ikx}e^{-iEt/\hbar}.$$

We interpret $|\Psi(x,t)|^2 = |C^2|$ as the number of particles per unit length in a beam, each with momentum p and energy E. The corresponding interpretation of current is that $j(x) = |C|^2\frac{\hbar k}{m}$ is the particle *flux* at x, i.e. the number of passing particles at x per unit time.

4.2.2 Transmission and Reflection

For particles incident on a potential step / barrier / well etc., we find a probability current

5 Quantum Mechanics in 3d

The quantum state of a particle in 3d is given by a wavefunction $\psi(\mathbf{x})$ for fixed t or $\Psi(\mathbf{x},t)$ as t varies.

The inner product is

$$(\phi,\psi) = \int \phi(\mathbf{x})^*\psi(\mathbf{x})d^3\mathbf{x}$$

with ψ normalised if $(\psi,\psi) = 1$. Then $|\psi(\mathbf{x})|^2\delta V$ is the probability of measuring the particle to be in a small region δV about $\mathbf{x}$.

5.1 Operators

Position and momentum are Hermitian operators

$$
\begin{aligned}
\hat{\mathbf{x}} &= (\hat{x}_1, \hat{x}_2, \hat{x}_3) \quad \text{ where } \hat{x}_i \psi = x_i \psi \\
\hat{\mathbf{p}} &= (\hat{p}_1, \hat{p}_2, \hat{p}_3) \quad \text{ where } \hat{p}_i \psi = -i\hbar \frac{\partial \psi}{\partial x_i} \\
&= -i\hbar \boldsymbol{\nabla} = -i\hbar \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right)
\end{aligned}
$$

The Uncertainty Principle applies to position and momentum in the same direction

$$
(\Delta x_i)_\psi (\Delta p_i)_\psi \geq \frac{\hbar}{2}
$$