Quantum Mechanics

Definitions and Results (L1-15)

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1 Postulates

1.1 Postulate 1

The wavefunction $\psi(\mathbf{x}, t)$ of a particle is normalisable.

$$\int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)\,\mathrm{d}V = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2\,\mathrm{d}V = N < \infty$$

1.2 Postulate 2

Writing the normalised wavefunction as $\bar{\psi}(\mathbf{x}, t) = \psi(\mathbf{x}, t)/\sqrt{N}$, the probability density function for finding the particle within a certain volume is

$$\rho(\mathbf{x}, t) = |\bar{\psi}(\mathbf{x}, t)|^2.$$

1.3 Postulate 3

The wavefunction of a particle of mass m in a potential $U(\mathbf{x})$ satisfies the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(\mathbf{x}, t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{x}, t) + U(\mathbf{x})\psi(\mathbf{x}, t).$$

2 Operators

2.1 Important Operators

For a quantity z, if the corresponding operator is $\hat{z}$ then we can find the expectation value using

$$\langle z \rangle = \int_{-\infty}^{\infty} \psi^* (\hat{z}\psi)\, \mathrm{d}x.$$

Quantity	Operator
$\hat{x}$	x
$\hat{p}$	$-i\hbar\nabla$
$\hat{T}$	$-\frac{\hbar^2}{2m}\nabla^2$
$\hat{U}$	$U(\hat{x})$
$\hat{H}$	$\hat{T} + \hat{U}$

2.2 Hermitian Operators

If $\hat{A}$ is an operator, the Hermitian conjugate $\hat{A}^\dagger$ is the operator that satisfies

$$(\hat{A}^\dagger \psi_1, \psi_2) = (\psi_1, \hat{A}\psi_2).$$

$\hat{A}$ is Hermitian if $\hat{A} = \hat{A}^\dagger$.

3 Time-Independent Schrödinger Equation

Using the Hamiltonian operator $\hat{H}$ we can rewrite the time-dependent Schrödinger equation in the following time-independent form

$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}\psi)(\mathbf{x}, t).$$

Trying the solution $\psi(\mathbf{x}, t) = \chi(\mathbf{x})T(t)$, plugging into the TDSE and separating variables we get

$$i\hbar \frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = \frac{\hat{H}\chi(\mathbf{x})}{\chi(\mathbf{x})} := E$$

which must be constant (depends both only on t and only on $\mathbf{x}$). Solving gives $T(t) = e^{-iEt/\hbar}$.
So we get a solution of the form

$$\psi(\mathbf{x}, t) = \chi(\mathbf{x})e^{-iEt/\hbar}$$

and these solutions are called stationary states. The probability density ρ for stationary states is time-independent. Every solution of the TDSE can be written as a superposition of stationary states.
The TISE also gives the following by which we solve for $\chi(\mathbf{x})$:

$$\hat{H}\chi(x) = E\chi(x) \implies -\frac{\hbar^2}{2m}\chi''(x) + U(x)\chi(x) = E\chi(x).$$

If $U(x) = U(-x)$ and the energy spectrum is non-degenerate, then eigenfunctions χ are either even or odd.

3.1 Bound and Non-bound Systems

Bound (discrete eigenfunctions, normalisable) and non-bound (continuous) system superpositions.

$$\psi(\mathbf{x}, t) = \sum_{n=1}^{\infty} a_n \chi_n(\mathbf{x}) e^{-iE_n t/\hbar} \qquad \psi(\mathbf{x}, t) = \int_{\Delta} A(\alpha)\chi_\alpha(\mathbf{x}) e^{-iE_\alpha t/\hbar}\, \mathrm{d}\alpha$$

3.2 Free Particle

We take a linear superposition (here Gaussian) of $\psi_k(x,t) = e^{ikx - i\hbar k^2 t/2m}$ since χ is not normalisable. Sometimes we write $k = \sqrt{2mE/\hbar^2}$.

$$\psi(x,t) = \int_{-\infty}^{\infty} \exp\left(-\frac{\sigma}{2}(k-k_0)^2 + ikx - \frac{i\hbar k^2 t}{2m}\right) \mathrm{d}k \implies \psi(x,t) = \sqrt{\frac{2\pi}{\alpha}} \exp\left(-\frac{\sigma(x - \frac{\hbar k_0}{m}t)^2}{2(\sigma^2 + \frac{\hbar^2 t^2}{m^2})}\right)$$

3.3 Harmonic Oscillator

For the harmonic oscillator, the potential is $U(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$ so the corresponding TISE is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\chi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 \chi = E\chi.$$

We can rescale variables, writing $\eta^2 = m\omega x^2/\hbar$ and $\varepsilon = 2E/\hbar\omega$, and find a particular solution $\chi_0(\eta) = Ae^{-\eta^2/2}$ corresponding to $\varepsilon = 1$. To generalise this, we write $\chi(\eta) = f(\eta)e^{-\eta^2/2}$, plug this into the TISE, and use power series methods to find $f(\eta)$. The series must in fact terminate, in order for $\chi(\eta)$ to be normalisable.

4 Expectation and Uncertainty

4.1 Expectation

Given an observable o on a state ψ, the corresponding eigenvalues give the possible measurements for o. Hence

$$\langle o \rangle = \sum_i p_i \lambda_i = \sum_i |(\psi, \psi_i)|^2 \lambda_i = \left(\sum_i (\psi, \psi_i)\psi_i, \sum_j \lambda_j (\psi, \psi_j)\psi_j\right).$$

We define $\langle \hat{o} \rangle_\psi$ as

$$\langle \hat{o} \rangle_\psi = (\psi, \hat{o}\psi) = \int_{\mathbb{R}^{\not\models}} \psi^*(\mathbf{x})\hat{o}\psi(\mathbf{x}) \, \mathrm{d}V.$$

4.2 Commutators

The commutator of the two operators $\hat{A}$ and $\hat{B}$ is

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

Two Hermitian operators are simultaneously diagonalisable (have a shared spanning basis of eigenfunctions) if and only if their commutator is zero.

4.3 Uncertainty

The uncertainty in the measurement of A on a state ψ is given by

$$(\Delta_\psi A)^2 = \langle (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \rangle_\psi = \langle \hat{A}^2 \rangle_\psi - \langle \hat{A} \rangle_\psi^2.$$

The uncertainty is zero if and only if ψ is an eigenfunction of A.

4.4 Generalised Uncertainty Theorem

Let A and B be observables and ψ be a state. Then

$$(\Delta_\psi A)(\Delta_\psi B) \geq \frac{1}{2}|(\psi, [\hat{A}, \hat{B}]\psi)|.$$

The Heisenberg uncertainty principle follows from this by using $[\hat{x}, \hat{p}] = i\hbar\hat{I}$.
If $\hat{x}\psi = ia\hat{p}\psi$ for some $a \in \mathbb{R}$, then ψ is a state of minimal uncertainty.

4.5 Ehrenfest Theorem

The expectation value of an operator $\langle \hat{A} \rangle$ on a state ψ evolves according to

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \hat{A} \rangle_\psi = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle_\psi + \langle \frac{\partial \hat{A}}{\partial t} \rangle_\psi .$$

5 Schrödinger Equation in 3D

In 3D, the TISE is

$$-\frac{\hbar^2}{2m} \nabla^2 \chi(\mathbf{x}) + U(\mathbf{x})\chi(\mathbf{x}) = E\chi(\mathbf{x}).$$

In Cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and in spherical coordinates

$$\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2 \sin^2 \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) - \frac{\partial^2}{\partial \phi^2} \right).$$

For a spherically symmetric potential, the TISE becomes

$$-\frac{\hbar^2}{2mr} \frac{\mathrm{d}^2}{\mathrm{d}r^2} (r\chi(r)) + U(r)\chi(r) = E\chi(r).$$

To solve this, define $\sigma(r) = r\chi(r)$ to get

$$-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2 \sigma(r)}{\mathrm{d}r^2} + U(r)\sigma(r) = E\sigma(r)$$

and solve this over all of $\mathbb{R}$ by using $U(r) = U(-r)$ and look for odd solutions with $\sigma(-r) = -\sigma(r)$.

6 Angular Momentum

Define $\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = -i\hbar \mathbf{x} \times \nabla$ which gives

$$L_i = -i\hbar \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}$$

and generally $[\hat{L_i}, \hat{L_j}] = i\hbar \varepsilon_{ijk} \hat{L_k}$. We can also check that for $\hat{L}^2 := \hat{L_1}^2 + \hat{L_2}^2 + \hat{L_3}^2$, we have e.g. $[\hat{L}^2, \hat{L}_1] = 0$. In fact, $\{\hat{H}, \hat{L}^2, \hat{L}_i\}$ is a set of three mutually commuting operators.