Quantum Mechanics: Principles

Reading: Atkins, ch. 8 (p. 260)

- Information in wavefunction: probability density, eigenfunction & eigenvalue, operator, expectation value
- The uncertainty principle
- Postulates of quantum mechanics

The information in a wavefunction

mass m particle, **free to move** parallel to x-axis with zero potential energy

(a) **The probability density**

if $B = 0$, $\Psi = Ae^{ikx}$

where is the particle? $\rightarrow$ Probability of finding the particle

$$|\Psi|^2 = (Ae^{ikx})^*(Ae^{ikx}) = (A^*e^{-ikx})(Ae^{ikx}) = |A|^2$$

equal probability of finding the particle

$\rightarrow$ cannot predict where we will find the particle

same if $A = 0$, $|\Psi|^2 = |B|^2$

if $A = B$, $\Psi = A(e^{-ikx} + e^{ikx}) = 2A\cos kx$

$$|\Psi|^2 = 4|A|^2\cos^2 kx$$

(b) **eigenvalues and eigenfunctions**

total energy: $k^2 \hbar^2/2m = E = E_k + V(= 0) = E_k = p^2/2m$

$\Rightarrow p = k\hbar = (2\pi/\lambda)(h/2\pi) = h/\lambda$: de Broglie's law

k: wave vector (= $2\pi / \lambda$), independent of A, B

Schrödinger equation

$$\mathbf{H\psi = E\psi}$$

1-D, H =

H: Hamiltonian operator: carried out a mathematical operation on the function ψ

$\rightarrow$ correspondence between hamiltonian operator and energy

$\rightarrow$correspondence of operators and classical mechanical variables are fundamental to the quantum mechanics

cf. 19 century mathematician William Hamilton

Mathematical operation on the function ψ

(operator)(function) = (constant factor) x (same function)

$$\Omega\Psi = \omega\Psi$$

Ψ: **eigenfunction**

ω: **eigenvalue** of the operator Ω

e.g., $H\psi = E\psi$; eigenvalue is the energy, eigenfunction is wavefunction

$\Rightarrow$ “solve the Schrodinger equation” = “find the eigenvalues and eigenfunctions of the hamiltonian operator for the system” e.g., show that e^{ax} is an eigenfunction of the operator d/dx, find eigenvalue

e^{ax2} ?

(operator)Ψ = (value of observable) x Ψ

observables: energy, momentum, dipole moment

(c) **operators**
Ω: operator (Ω carat)

Position operator:
Momentum operator:

(d) **Superpositions and expectation values**

The uncertainty principle

if $\Psi = Ae^{ikx}$, $p_x = +k\hbar$: travelling to the right, but we cannot predict the position of the particle ($|\Psi|^2 = |A|^2$)

if the momentum is specified precisely, it is impossible to predict the location of the particle

Heisenberg uncertainty principle

"It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle"

if we know a definite location, Ψ must be large there and zero everywhere else. To do so, an infinite number of linear combinations of wavefunctions is needed

$\rightarrow$ perfect localization $\rightarrow$ lost all information about its momentum; completely unpredictable quantitatively,

$$\Delta p \Delta q \geq \tfrac{1}{2}\hbar$$

(and $\Delta t \Delta E \geq \tfrac{1}{2}\hbar$)

Δp: uncertainty in position along that axis
Δq: uncertainty in the linear momentum parallel to the axis q

if $\Delta q = 0$ (exact position) $\rightarrow \Delta p = \infty$
$\Delta p = 0 \rightarrow \Delta q = \infty$

e.g., 1g particle, speed 1×10^{-6} m/s, minimum position uncertainty?

Electron in $2a_0$

General uncertainty principle: the Heisenberg uncertainty principle applies to any pair of observables called “**complementary observables**”

e.g., position & momentum

C.M.: position & momentum of a particle could be specified simultaneously with arbitrary precision
Q.M.: position and momentum are complementary

The postulates of quantum mechanics (1-D)

(1) Physical state of a particle at time t is fully described by a wavefunction $\Psi(x,t)$

(2) $\Psi(x,t)$, $\partial\Psi(x,t)/\partial x$, $\partial^2\Psi(x,t)/\partial x^2$ must be continuous, finite and single valued for all values of x

(3) Any quantity that is physically observable can be represented by a Hermitian operator. Hermitian operator is a linear operator F that satisfies

(4)

Ψ_i: eigenfunction of F with eigenvalue f_i

(5) average or expectation value $<F>$

(6) Quantum mechanical operator is constructed by the classical expression of x, p_x, t, E and converting the expression to an operator by means of following rules,

(7) $\Psi(x,t)$ is a solution of time-dependent Schrödinger equation

Operator: fundamental in Q.M.

(1) commute $\rightarrow$ in Q.M., many operators do not commute
cf: uncertainty principle

(2) linear operation $\rightarrow$ Q.M: deal with linear operators

(3) Hermitian operator: Q.M. operators must be hermitian operators: Operators generally are complex quantities but certainly the eigenvalues must be real quantities (experimental measurement)

(4) orthogonal: the eigenfunctions of hermitian operators are orthogonal

Summary

(1) The Schrödinger equation is the equation for the wavefunction of a particle
(2) The Schrödinger equation can be formulated as an eigenvalue problem
(3) C.M. quantities are represented by linear operators in Q.M.
(4) Wavefunctions have a probabilistic interpretation
(5) Wavefunctions are normalized
(6) Average value, expectation is given by