Quantum Mechanics Revision

Let's start with some definitions we will be using a lot in this module.

Operators: All physically measureable quantities (called observables) can be mathematically represented by a linear operator. An operator acts on a wavefunction to produce another wavefunction.

Eigenfunctions & Eigenvalues: For any particular operator, there exists certain functions which, when the operator is applied on them, only changes the magnitude of the function, and not the function itself. eg. for operator $\hat{O}$:

$$\hat{O}\psi(x) = \lambda\psi(x)$$ ψ is eigenfunction, λ is eigenvalue

In QM, the only values an observable can take are the eigenvalues of the operator that represents it.

Degeneracy: Multiple eigenfunctions can produce the same eigenvalue. This is called degeneracy. For a particular eigenvalue, the degeneracy is the number of eigenfunctions with that eigenvalue.

Expectation value: Although a single measurement of an observable gives us a eigenvalue, the average value of the eigenvalue is obtained from the wave function. This is called the expectation value.

$$\langle\hat{O}\rangle = \int_{-\infty}^{\infty} \psi^*(x)\,\hat{O}\,\psi(x)\,dx$$

This can be written in ket-bra notation:

$$\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle$$

Matrix Elements: The matrix element is an integral represented by

$$\langle \psi_i | \hat{O} | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i^*(x)\, \hat{O}\, \psi_j(x)\, dx$$

It should be clear that the expectation value is itself a matrix element. i and j denote the member number of a set of wavefunctions. All possible forms of the integral form a matrix.

Hermitian operators: All physical observables have to be real numbers with no imaginary components. This means all operators that represent these observables must be hermitian, meaning:

$$\int_{-\infty}^{\infty} f^*(x)\, \hat{O}\, g(x)\, dx = \int_{-\infty}^{\infty} [\hat{O} f(x)]^* g(x)\, dx = \int_{-\infty}^{\infty} g(x)\, \hat{O}^*\, f^*(x)\, dx$$

i.e the eigenvalues of the operator are real.

Orthogonality: The eigenfunctions of hermitian operators form a set which is orthogonal. So:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

where δ_{ij} is the kronecker delta $\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$

Although the proof for this orthogonality only works for non-degenerate wavefunctions, any linear superposition of degenerate eigenfunctions is itself a wavefunction. So it is always possible to choose a set of degenerate eigenfunctions which are orthonormal.

Expansion Theorem: The eigenfunctions of a Hermitian operator form a complete set. Any possible wavefunction of the system can be written as the superposition of the eigenfunctions of the hermitian operator.

$$\psi(x) = \sum_i a_i\, \psi_i(x)$$

where a_i is obtained by using orthonormality properties:

$$\langle \psi_i | \psi \rangle = \sum_j a_j \langle \psi_i | \psi_j \rangle = \sum_j a_j\, \delta_{ij} = a_i \quad \text{so:} \quad a_i = \langle \psi_i | \psi \rangle$$

Commuting and Non-commuting operators

The order of two operators indicates which one operates first. eg. in the case of $\hat{O}\hat{M}\psi(x)$, $\hat{M}$ operates first, and $\hat{O}\hat{M}\psi$ may not equal $\hat{M}\hat{O}\psi$. The commutator of two operators is:

$$[\hat{O}, \hat{M}] = \hat{O}\hat{M} - \hat{M}\hat{O}$$

If the commutator is 0, the two operators are said to commute. Then it can be shown that all eigenfunctions of one operator are also eigenfunctions of the other. We can prove this:

Let ψ_i^M be the eigenfunction of $\hat{M}$ with eigenvalue λ_i^M

if λ_i^M is not degenerate, then $\hat{O}\psi_i^M = \lambda_i^O \psi_i^M$.

if λ_i^M is degenerate, then it is possible to produce a new set of eigenfunctions of $\hat{M}$, which when operated on by $\hat{O}$ give themselves multiplied by a constant. Therefore, all eigenfunctions of $\hat{M}$ are also eigenfunctions of $\hat{O}$.

Since the eigenfunctions of two commuting operators are the eigenfunctions of both operators, it is possible for the system to exist in a state which has a precisely defined value for both observables associated with the operators. i.e, there is no uncertainty in either observable.

If the operators do not commute, we can't precisely know the value of both operators. This is heiserberg's uncertainty principle:

$$\Delta O \, \Delta M \geq \frac{1}{2} \left| \langle [\hat{O}, \hat{M}] \rangle \right|$$

we will prove this on the next page

Let's start by defining the variance of an operator:

$$\Delta O^2 = \langle O^2 \rangle - \langle O \rangle^2$$
$$= \langle \psi | \hat{O}^2 | \psi \rangle - \langle \psi | \hat{O} | \psi \rangle^2$$

Let's define $|\psi_0\rangle$, a state for a generic operator:

$$|\psi_0\rangle = (\hat{O} - \langle \psi | \hat{O} | \psi \rangle) |\psi\rangle$$

so $|\psi_0\rangle = \hat{O}|\psi\rangle - \langle \psi | \hat{O} | \psi \rangle |\psi\rangle$

$\Rightarrow \langle \psi_0 | \psi_0 \rangle = \langle \psi | \hat{O}^2 | \psi \rangle - \langle \psi | \hat{O} | \psi \rangle \langle \psi | \hat{O} | \psi \rangle$

so $\langle \psi_0 | \psi_0 \rangle = \Delta O^2$

$\therefore \Delta O^2 \Delta M^2 = \langle \psi_0 | \psi_0 \rangle \langle \psi_M | \psi_M \rangle \geq |\langle \psi_0 | \psi_M \rangle|^2$

here, we have made use of the Cauchy Schwartz inequality

in general $\langle \psi_0 | \psi_M \rangle$ is some complex number $\alpha + i\beta$

so $|\langle \psi_0 | \psi_M \rangle|^2 = \alpha^2 + i(-i)\beta^2 = \alpha^2 + \beta^2 \geq \beta^2$

with $\beta^2 = \dfrac{\langle \psi_0 | \psi_M \rangle - \langle \psi_M | \psi_0 \rangle}{2i} = \frac{1}{2i} \langle \psi | [\hat{O}, \hat{M}] | \psi \rangle$

Therefore $\Delta O \, \Delta M \geq \frac{1}{2} |\langle [\hat{O}, \hat{M}] \rangle|$

Thus, we have proven the general form of the uncertainty principle.

Schrödinger's Equation

Schrödinger's equation can be expressed as:

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t}\Psi$$

where $\hat{H} = \frac{\hat{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

$$\Rightarrow \boxed{i\hbar \frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi}$$

if Ψ_E is an eigenfunction of $\hat{H}$ with eigenvalue energy E:

$$\hat{H}\Psi_E = E\Psi_E$$

so if the wavefunction is in this state at $t=0$, then $\Psi(0) = \Psi_E$

so $i\hbar \frac{\partial}{\partial t}\Psi(t) = E\Psi(t)$ which has solution:

$$\Psi(t) = \Psi_E e^{-iEt/\hbar}$$

So we can determine the time dependence of the wavefunction relatively easily.

If the energy eigenfunctions Ψ_E are given as a set by:

$$\Psi_E = \sum_j a_j \Psi_j^E = \sum_j \langle \Psi_j^E | \Psi(t=0) \rangle \Psi_j^E$$

so: $$\Psi(t) = \sum_j \langle \Psi_j^E | \Psi(t=0) \rangle \Psi_j^E e^{-iE_j t/\hbar}$$

Conserved Quantities (Good Quantum Numbers)

A consequence of the SE lets us know the time evolution of the expectation values of time independent operators. This is given by:

$$i\hbar \frac{\partial}{\partial t} \langle \hat{O} \rangle = \langle [\hat{O}, \hat{H}] \rangle$$

so if the operator commutes with $\hat{H}$, then there is no time evolution. The observable is conserved!

Since it is often tedious to write out the whole wavefunction, we will label the wavefunction in terms of eigenvalues. We might initially think to label them in terms of the energy eigenvalue, but this is often degenerate. So, we want to use multiple eigenvalues. We call these quantum numbers.

In situations where the operators we use to provide labels no longer commute with the hamiltonian, we call these quantum numbers: bad quantum numbers.

This happens when, although $\hat{O}$ commutes with the unperturbed Hamiltonian, we can no longer ignore the perturbations. $\hat{O}$ will not commute with the perturbations. Since $\langle O \rangle$ now changes with time, labels based on it no longer effectively describe the system.

In situations where the operators commute with both the Hamiltonian and its perturbation, the observable is conserved and we call these quantum numbers:

good quantum numbers.

Linear Momentum

The momentum operator in 1D is:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

This commutes with the kinetic part of the Hamiltonian:

$$\left[-i\hbar \frac{\partial}{\partial x}, -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] = (-i\hbar)(-\frac{\hbar^2}{2m}) \frac{\partial}{\partial x}\left(\frac{\partial^2}{\partial x^2}\right) - (-i\hbar)(-\frac{\hbar^2}{2m}) \left(\frac{\partial^2}{\partial x^2}\right)\left(\frac{\partial}{\partial x}\right)$$

$$= \underline{0}$$

But we also need it to commute with the potential term. For this, for a potential $V(r)$ and for all $\psi(r)$:

$$\left[-i\hbar \frac{\partial}{\partial x}, V \right]\psi = -i\hbar \frac{\partial}{\partial x} V\psi + V i\hbar \frac{\partial}{\partial x} \psi$$

$$= -i\hbar \left\{ \frac{\partial V}{\partial x} \psi + V \frac{\partial \psi}{\partial x} \right\} + V i\hbar \frac{\partial \psi}{\partial x}$$

$$= -i\hbar \psi \frac{\partial V}{\partial x} - i\hbar V \frac{\partial \psi}{\partial x} + i\hbar V \frac{\partial \psi}{\partial x}$$

$$= 0$$

$\Rightarrow \frac{\partial V}{\partial x} = 0$ which means there must be no forces on the body described by the hamiltonian. This also means the derivative of the potential is 0 everywhere, so an observer should see no difference in potential from one point to another. i.e the system has translational symmetry.

So if there is no external force on the body, momentum is conserved.