Basis Set Postulate

The set of functions $\psi_j$ which are eigenfunctions of the eigenvalue equation

$$Q \Psi_j = q_j \Psi_j$$

form a complete set of linearly independent functions. They can be said to form a basis set in terms of which any wavefunction representing the system can be expressed:

$$\Psi = \sum c_j \Psi_j$$

This implies that any wavefunction $\psi$ representing a physical system can be expressed as a linear combination of the eigenfunctions of any physical observable of the system.
WAVE FUNCTION IN MOMENTUM SPACE

\[ \phi(p) = \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{\infty} dx \psi(x,0) e^{-ipx/\hbar} \]

\[ \psi(x,t) = \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p,0) dp \]

\[ \int_{-\infty}^{\infty} dp \phi^*(p) \phi(p) = 1 \]

\[ \langle p \rangle = \int_{-\infty}^{\infty} dp \phi^*(p) p \phi(p) \]

In momentum space

\[ x = i\hbar \frac{\partial}{\partial p} \]
Hermitian Property Postulate

The quantum mechanical operator \( Q \) associated with a measurable property \( q \) must be Hermitian. Mathematically this property is defined by

\[
\int \Psi_a^* Q \Psi_b \, dr = \int (Q \Psi_a)^* \Psi_b \, dr
\]

where \( \Psi_a \) and \( \Psi_b \) are arbitrary normalizable functions and the integration is over all of space. Physically, the Hermitian property is necessary in order for the measured values (eigenvalues) to be constrained to real numbers.
Hermitian Operator

Example:  \[ \langle p \rangle - \langle p \rangle^* = \int_{-\infty}^{\infty} dx \psi^* \left( \frac{\hbar}{i} \right) \frac{\partial \psi}{\partial x} - \psi \left( - \frac{\hbar}{i} \right) \frac{\partial \psi^*}{\partial x} \]

\[ = \frac{\hbar}{i} \int_{-\infty}^{\infty} dx \left[ \psi^* \frac{\partial \psi}{\partial x} + \psi \frac{\partial \psi^*}{\partial x} \right] = \frac{\hbar}{i} \int_{-\infty}^{\infty} dx \frac{\partial}{\partial x} \left( \psi \psi^* \right) = 0 \]

If \( \psi(x) = \psi(x + L) \)

\[ \langle p \rangle - \langle p \rangle^* = \int_{0}^{L} dx \psi^* \left( \frac{\hbar}{i} \right) \frac{\partial \psi}{\partial x} - \psi \left( - \frac{\hbar}{i} \right) \frac{\partial \psi^*}{\partial x} \]

\[ = \frac{\hbar}{i} \int_{0}^{L} dx \left[ \psi^* \frac{\partial \psi}{\partial x} + \psi \frac{\partial \psi^*}{\partial x} \right] = \frac{\hbar}{i} \int_{0}^{L} dx \frac{\partial}{\partial x} \left( \psi \psi^* \right) = 0 = \frac{\hbar}{i} \left( |\psi(L)|^2 - |\psi(0)|^2 \right) = 0 \]

\( \langle p \rangle \) is real, Therefore \( \langle p \rangle \) is a Hermitian operator.
Wavepackets and the Uncertainty Principle

Wavepackets are the best way of describing a quantum system with both particle-like and wave-like characteristics.

We cannot have absolute certainty of both position and momentum. But we can construct a wavepacket which is localized in both position and momentum.

E.g. real space probability density

\[ \psi(x) \propto e^{ikx} \exp\left(-\frac{x^2}{4\sigma^2}\right) \]

\[ |\psi(x)|^2 \propto \exp\left(-\frac{x^2}{2\sigma^2}\right) \]

Write this as a Fourier transform (expansion in momentum eigenstates)

\[ \psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk A(k) e^{ikx} \]

\[ |A(k)|^2 \propto e^{-2\sigma^2(k-k_0)^2} \]

\[ A(k) \propto e^{-\sigma^2(k-k_0)^2} \]
Wavepackets and the Uncertainty Principle (2)

Rough uncertainty in position given from the point where the Gaussian falls to 1/e of its peak value:

\[ \Delta x = \sqrt{2\sigma^2} \]

Similarly, rough uncertainty in momentum:

\[ \Delta k = \sqrt{\frac{1}{2\sigma^2}} \Rightarrow \Delta p = \hbar \Delta k = \hbar \sqrt{\frac{1}{2\sigma^2}} \]

Hence the product of uncertainties is a constant, independent of \( \sigma \):

\[ \Delta p \Delta x = \hbar \sqrt{\frac{1}{2\sigma^2}} \sqrt{2\sigma^2} = \hbar \]

NB: The Uncertainty relation is usually evaluated using rms widths rather than our 1/e estimate. In that case we get

\[ \Delta p \Delta x = \frac{\hbar}{2} \]

So the Gaussian is actually a minimum uncertainty wavepacket.
Time Dependent Schrödinger Equation

The time dependent Schrödinger equation for one spatial dimension is of the form

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}\]

For a free particle where \(U(x) = 0\) the wavefunction solution can be put in the form of a plane wave

\[\Psi(x,t) = Ae^{ikx - i\omega t}\]

or other problems, the potential \(U(x)\) serves to set boundary conditions on the spatial part of the wavefunction and it is helpful to separate the equation into the time-independent Schrödinger equation and the relationship for time evolution of the wavefunction

\[H\Psi = i\hbar \frac{\partial \Psi}{\partial t}\]

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + U(x)\Psi(x) = E\Psi(x)\]

Time evolution

Time independent equation
This gives a plane wave solution:

\[ \Psi(x,t) = Ae^{i \frac{2\pi}{\lambda} - \omega t} = Ae^{ikx - i\omega t} \]

Free particle approach to the Schrödinger equation
Time-Independent Schroedinger Equation

\[
- \frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V(x) \Psi = E \Psi
\]

\[
V(x) = 0 \quad \frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi \quad \frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + E \Psi = 0
\]

Solution of DE:
\[
\Psi(x) = A e^{ikx} + B e^{-ikx}
\]

Standard time dependence:
\[
\exp(-iEt / \hbar)
\]

\[
\Psi(x) = A e^{ik(x - \frac{\hbar k}{2m} t)} + B e^{-ik(x - \frac{\hbar k}{2m} t)}
\]

\[
\Psi(x) = A e^{ik(x - \frac{\hbar k}{2m} t)}
\]

\[
k \equiv \pm \sqrt{2mE / \hbar}, \quad \text{with} \begin{cases} 
    k > 0 \Rightarrow \text{travelling to the right} \\
    k < 0 \Rightarrow \text{travelling to the left}
\end{cases}
\]
Free Particle Waves
The general free-particle wavefunction is of the form
\[
\Psi(x,t) = A e^{i \frac{2\pi}{\lambda} \cdot k x - \omega t} = A e^{i k x - i \omega t}
\]
which as a complex function can be expanded in the form
\[
\Psi(x,t) = A \cos(k x - \omega t) + i A \sin(k x - \omega t)
\]
Euler relationship.

Either the real or imaginary part of this function could be appropriate for a given application. In general, one is interested in particles which are free within some kind of boundary, but have boundary conditions set by some kind of potential. The free particle wavefunction is associated with a precisely known momentum:
\[
p = \frac{h}{\lambda} = \frac{\hbar k}{2\pi} = \hbar k
\]
but the requirement for normalization makes the wave amplitude approach zero as the wave extends to infinity (uncertainty principle).
WAVEFUNCTION PROPERTIES

\[ \psi^* \psi \] summed over all space = 1, (if particle exists, probability of finding it somewhere must be one)

is continuous

allows energy calculations via the Schrodinger equation

establishes the probability distribution in three dimensions

permits calculation of most probable value (expectation value) of a given variable

for a free particle is a sine wave, implying a precisely determined momentum and totally uncertain position (uncertainty principle).
What are the mathematical restrictions on a function so that it can be the wavefunction of a physical system?

It must be continuous, single-valued, finite, and its squared magnitude must be integrable over all space.
What is the significance of the set of eigenvalues of an operator corresponding to an observable quantity? What is the significance of the corresponding eigenfunctions of the operator?

The eigenvalues constitute the set of allowed values, and any measurement must yield one of these values. The eigenfunctions are wavefunctions for a system having the corresponding eigenvalue as the value of the observable.
Why are operators that commute with the Hamiltonian of special interest?

Operators that commute with $H$ correspond to observables that are “constants of the motion”. Their value can be known simultaneously with the energy, and their probability distributions are independent of time.
Argue that a particle of mass $m$ confined in a one-dimensional region of size $a$ must have kinetic energy at least of order $\frac{\hbar^2}{2ma^2}$.

Take the Uncertainty Principle and use $\Delta x = a$. Then $\Delta p \approx \hbar / a$. But $(\Delta p)^2 = \langle p^2 \rangle^2 - \langle p \rangle^2$, and the average momentum is of order zero. (The particle has roughly equal probability of going either direction with the same speed.) Thus the average kinetic energy is

$$\left\langle \frac{p^2}{2m} \right\rangle \approx \frac{\hbar^2}{2ma^2}.$$
A particle is confined to the region $0 \leq x \leq a$ and has the wavefunction

$$\Phi(x) = \begin{cases} 
A\sqrt{x(x-a)} & \text{for } 0 \leq x \leq a, \\
0 & \text{elsewhere.}
\end{cases}$$

(a) Sketch the probability distribution for finding the particle at various values of $x$.

(b) What is the average value of $x$? [You must first find $A$.]

(c) What is the average value of $x^2$?

(d) What is $\Delta x$?

(e) Estimate the average kinetic energy for this state.
(a) Plot $\Phi^2$. It is a parabola with a peak at $a/2$ and going to zero at 0 and a.

(b) Require $\int_0^a \Phi^2(x)\,dx = 1$. This gives $A = \sqrt{6/\ a^3}$. Then

$$\langle x \rangle = (6/\ a^3)\int_0^a x^2 (a - x)\,dx = a/2.$$  

(c) Now

$$\langle x^2 \rangle = (6/\ a^3)\int_0^a x^3 (a - x)\,dx = 3a^2/10.$$  

(d) $(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2/20$, so $\Delta x = a/\sqrt{20}$.

(e) Following the procedure in Question 8 above, we have

$$\langle E_k \rangle \approx \frac{\hbar^2}{2m(\Delta x)^2} = \frac{10\hbar^2}{ma^2}.$$
Consider the function \( f(\theta, \phi) = A \sin \theta \cdot \sin \phi \). This is an eigenfunction of \( L^2 \) with quantum number \( l = 1 \).

(a) Show that it is not an eigenfunction of \( L_z = -i\hbar \frac{\partial}{\partial \phi} \).

(b) What is the average value of \( L_z \) in this state?

(c) What is the probability that a measurement of \( L_z \) will yield the result \( \hbar \)?
(a) Operation with $L_z$ does not give the same function times a number, so it is not an eigenfunction.

(b) The average value is

$$\langle L_z \rangle = \frac{\int f^* L_z f \, d\Omega}{\int f^* f \, d\Omega} = \frac{\int_0^{2\pi} \int_0^{2\pi} \sin \phi \cdot \cos \phi \, d\phi}{\int_0^{2\pi} \sin ^2 \phi \, d\phi} = 0.$$ 

(c) The eigenfunctions of $L_z$ are $1$, $e^{\pm i \phi}$, corresponding to eigenvalues $0$, $\pm \hbar$. The given function is a superposition of $e^{\pm i \phi}$, since

$$\sin \phi = \frac{e^{i \phi} - e^{-i \phi}}{2i}.$$ 

Since the coefficients of these terms have the same magnitude, the two eigenvalues are equally probable. Thus the probability that a measurement will give $\hbar$ as result is $1/2$. 
A particle is confined to the region \( 0 \leq x \leq a \) and has the wavefunction

\[
\Phi(x) = \begin{cases} 
    A\sqrt{x(x-a)} & \text{for } 0 \leq x \leq a, \\
    0 & \text{elsewhere.}
\end{cases}
\]

(b) What is the average value of \( x \)? [You must first find \( A \).]

(c) What is the average value of \( x^2 \)?

(d) What is \( \Delta x \)?