

Chapter 3

Hermitian linear operator

**Real dynamical variable –
represents observable quantity**

Eigenvector

**A state associated with an
observable**

Eigenvalue

**Value of observable associated
with a particular linear operator
and eigenvector**

Momentum of a Free Particle

Free particle – particle with no forces acting on it.

The simplest particle in classical and quantum mechanics.

classical



rock in interstellar space

**Know momentum, p , and position, x ,
can predict exact location at any subsequent time.**

Solve Newton's equations of motion.

$$p = mV$$

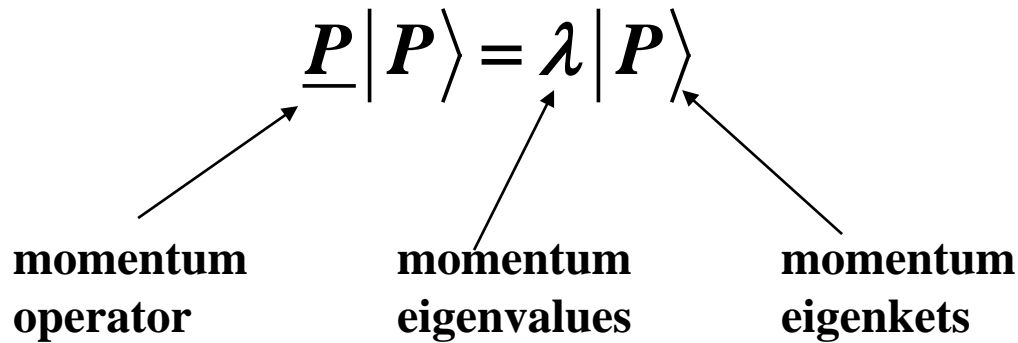
What is the quantum mechanical description?

Should be able to describe photons, electrons, and rocks.

Momentum eigenvalue problem for Free Particle

$$\underline{P} |P\rangle = \lambda |P\rangle$$

momentum operator momentum eigenvalues momentum eigenkets



Know operator \longrightarrow want: eigenvectors
eigenvalues

Schrödinger Representation – momentum operator

$$\underline{P} = -i\hbar \frac{\partial}{\partial x}$$

Later – Dirac's Quantum Condition shows how to select operators
Different sets of operators form different representations of Q. M.

Have
$$\underline{P}|P\rangle = -i\hbar \frac{\partial}{\partial x} |P\rangle = \lambda |P\rangle$$

Try solution

$$|P\rangle \equiv ce^{i\lambda x/\hbar}$$

eigenvalue

Eigenvalue – observable.

Proved that must be real number.

Function representing state of system in a particular representation and coordinate system called wave function.

$$\underline{P} = -i\hbar \frac{\partial}{\partial x}$$

**Schrödinger Representation
momentum operator**

$$|P\rangle \equiv ce^{i\lambda x/\hbar}$$

Proposed solution

Check

$$\begin{aligned} -i\hbar \frac{\partial}{\partial x} [ce^{i\lambda x/\hbar}] &= -i\hbar i\lambda/\hbar [ce^{i\lambda x/\hbar}] \\ &= \lambda [ce^{i\lambda x/\hbar}] \end{aligned}$$

**Operating on function gives
identical function back
times a constant.**

$$\underline{P}|P\rangle = \lambda|P\rangle$$

**Continuous range of eigenvalues.
Momentum of a free particle can take on
any value (non-relativistic).**

$$|P\rangle = \Psi_p = ce^{ipx/\hbar} = ce^{ikx}$$

momentum
eigenkets

momentum
wave functions

Have called eigenvalues $\lambda = p$

$$p = \hbar k \quad k \text{ is the "wave vector."}$$

c is the normalization constant.

c doesn't influence eigenvalues

—————> direction not length of vector matters.

Show later that normalization constant $c = \frac{1}{\sqrt{2\pi}}$

The momentum eigenfunction are

$$\Psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$$

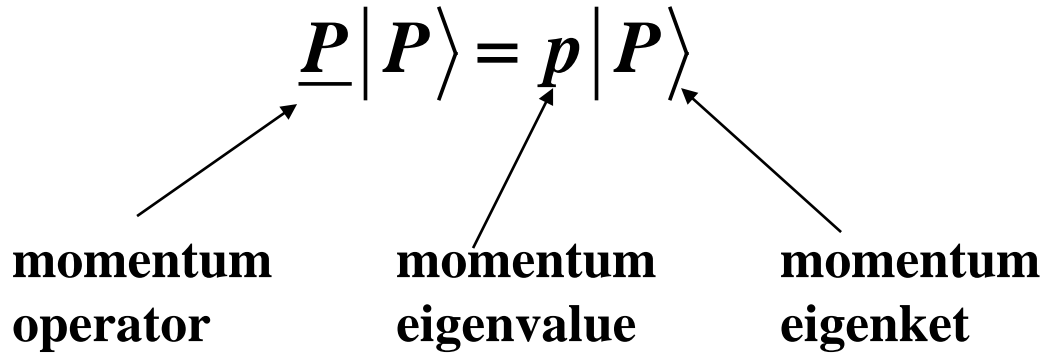
$$\hbar k = p$$

momentum eigenvalue

Momentum eigenstates are delocalized.

$$\underline{P} |P\rangle = p |P\rangle$$

momentum operator momentum eigenvalue momentum eigenket



Free particle wavefunction in the Schrödinger Representation

$$|P\rangle = \Psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} = \frac{1}{\sqrt{2\pi}} (\cos kx + i \sin kx) \quad \hbar k = p \quad k = \frac{2\pi}{\lambda}$$

State of definite momentum

wavelength



Born Interpretation of Wavefunction

Schrödinger **Concept of Wavefunction**
Solution to Schrödinger Eq.
Eigenvalue problem (see later).

Thought represented “Matter Waves” – real entities.

Born put forward

Like E field of light – amplitude of classical E & M wavefunction proportional to E field, $\psi \propto E$.

Absolute value square of E field \longrightarrow Intensity.

$$|E|^2 = E^* E \propto I$$

Born Interpretation – absolute value square of Q. M. wavefunction proportional to probability.

Probability of finding particle in the region $x + \Delta x$ given by

$$\text{Prob}(x, x + \Delta x) = \int_x^{x+\Delta x} \Psi^*(x) \Psi(x) dx$$

Q. M. Wavefunction \longrightarrow **Probability Amplitude.**

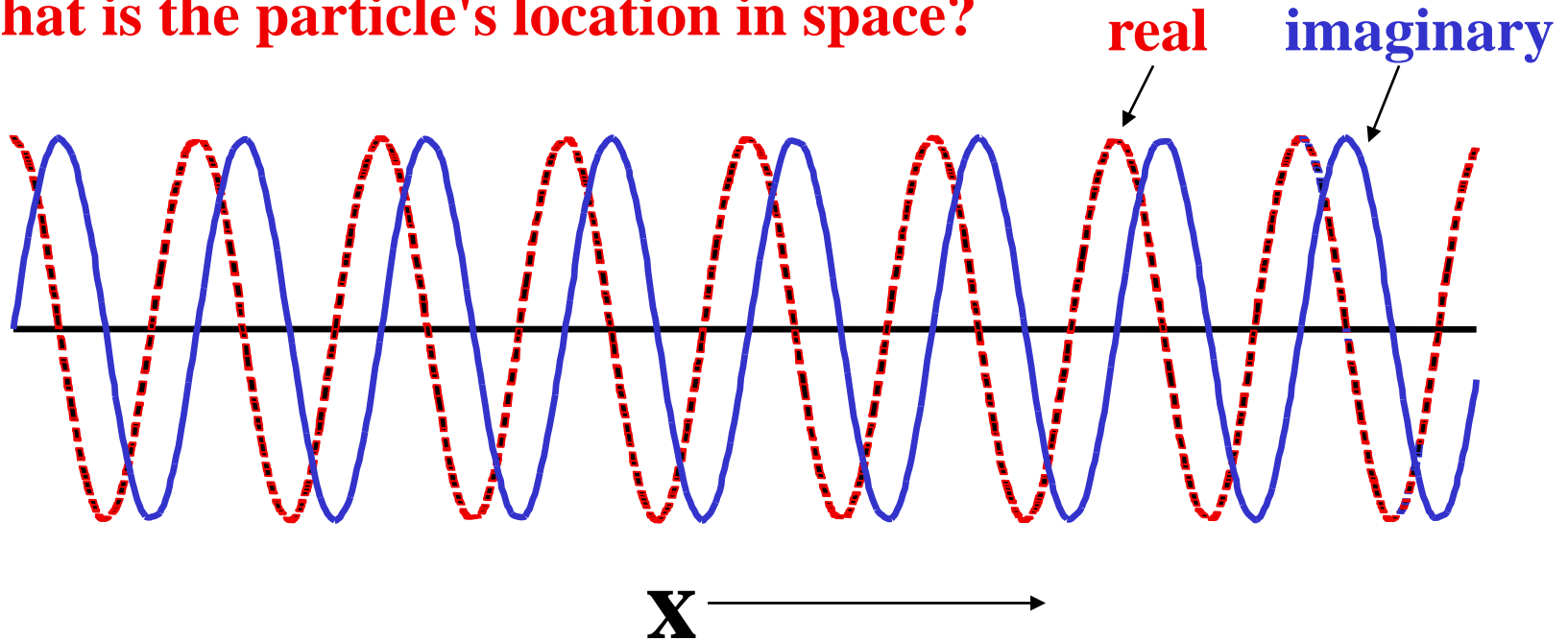
Wavefunctions complex.

Probabilities always real.

Free Particle

$$|P\rangle = \Psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} = \frac{1}{\sqrt{2\pi}} (\cos kx + i \sin kx) \quad \hbar k = p$$

What is the particle's location in space?



Not localized \longrightarrow Spread out over all space.

Equal probability of finding particle from $-\infty$ to $+\infty$.

Know momentum exactly \longrightarrow No knowledge of position.

Not Like Classical Particle!

Plane wave  spread out over all space.

Perfectly defined momentum – no knowledge of position.

Wave Packets

What does a superposition of states of definite momentum look like?

$$\Psi_{\Delta p}(x) = \int_p c(p) \Psi_p(x) dp$$

must integrate because continuous range of momentum eigenkets

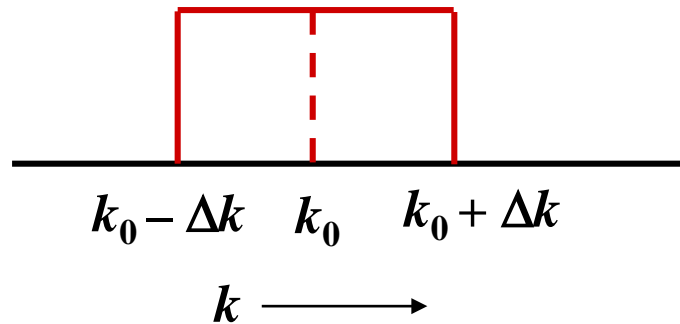
coefficient – how much of each eigenket is in the superposition

indicates that wavefunction is composed of a superposition of momentum eigenkets

First Example

Work with wave vectors -

$$k = p/\hbar$$



Wave vectors in the range

$$k_0 - \Delta k \text{ to } k_0 + \Delta k.$$

In this range, equal amplitude of each state.

Out side this range, amplitude = 0.

$$\Delta k \ll k_0$$

Then

$$\Psi_{\Delta k} = \int_{k_0 - \Delta k}^{k_0 + \Delta k} e^{ikx} dk$$

Superposition of
momentum eigenfunctions.

Integrate over k about k_0 .

$$\Psi_{\Delta k}(x) = \frac{2 \sin \Delta k x}{x} e^{ik_0 x}$$

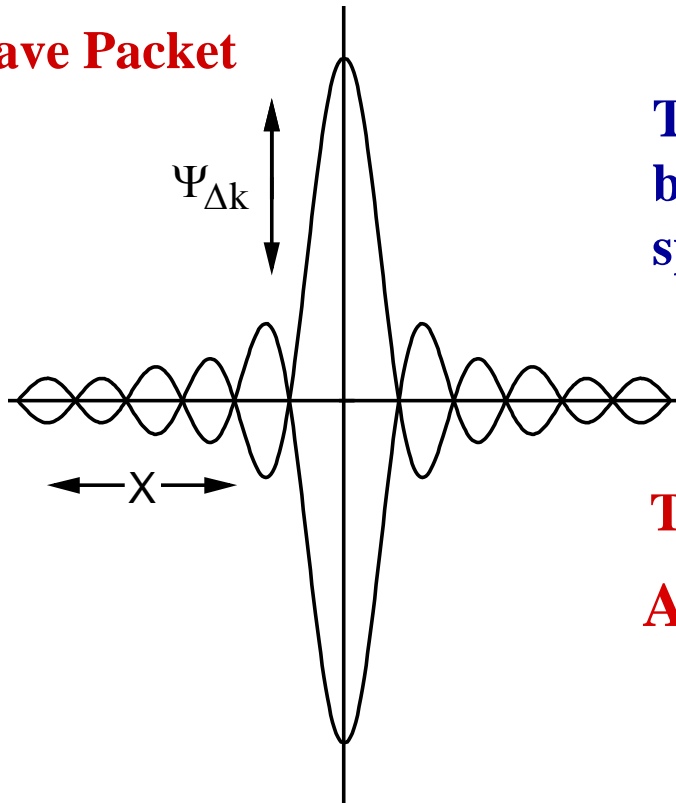
Rapid oscillations in envelope of
slow, decaying oscillations.

$$\text{At } x = 0 \text{ have } \lim_{x \rightarrow 0} \frac{2 \sin(\Delta k x)}{x} = 2\Delta k$$

Writing out the e^{ik_0x}

$$\Psi_{\Delta k} = \frac{2 \sin(\Delta k x)}{x} [\cos k_0 x + i \sin k_0 x] \quad \Delta k \ll k_0$$

Wave Packet



This is the “envelope.” It is “filled in” by the rapid real and imaginary spatial oscillations at frequency k_0 .

The wave packet is now “localized” in space.

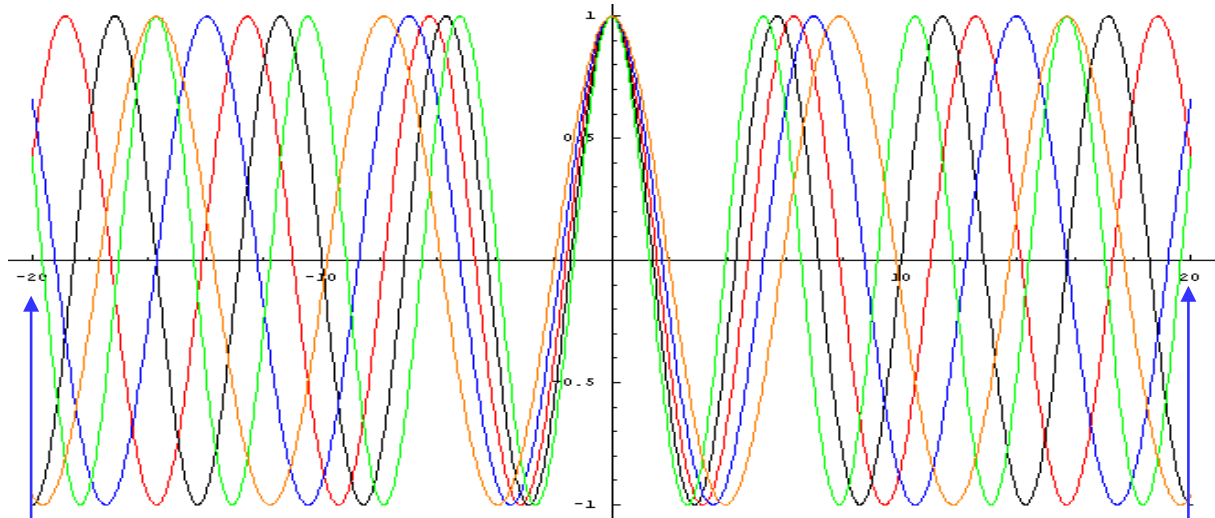
As $|x| \rightarrow$ large, $\Psi_{\Delta k} \rightarrow$ small.

Greater $\Delta k \longrightarrow$ more localized.

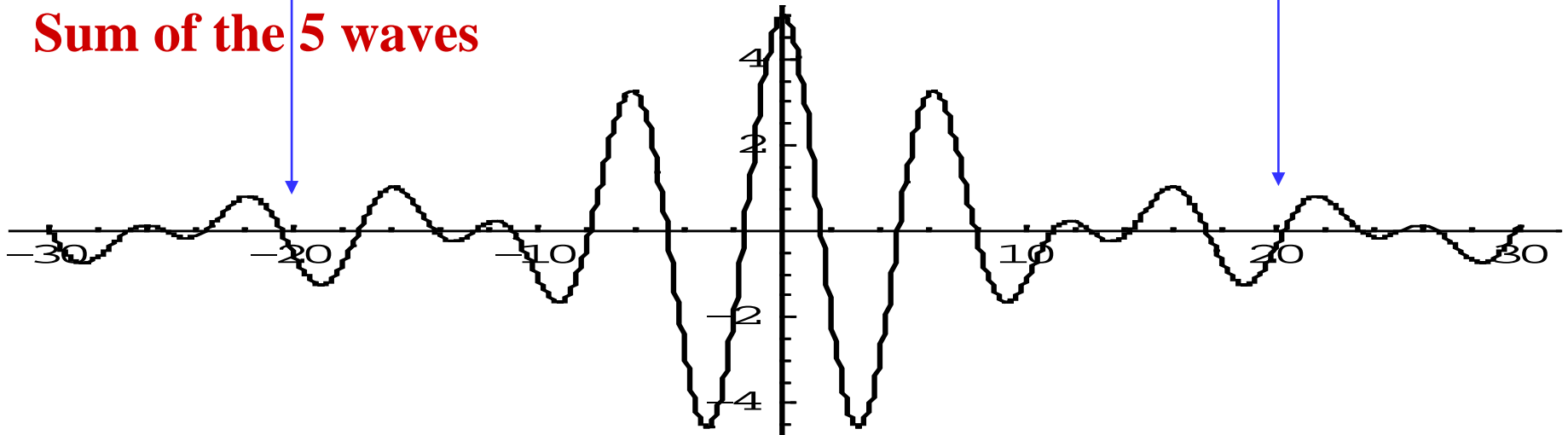
Large uncertainty in $p \longrightarrow$ small uncertainty in x .

Localization caused by regions of constructive and destructive interference.

5 waves \longrightarrow $\text{Cos}(ax)$ $a = 1.2, 1.1, 1.0, 0.9, 0.8$



Sum of the 5 waves



Wave Packet – region of constructive interference

Combining different $|P\rangle$,
free particle momentum eigenstates
→ wave packet.

Concentrate probability of finding particle in some region of space.

Get wave packet from

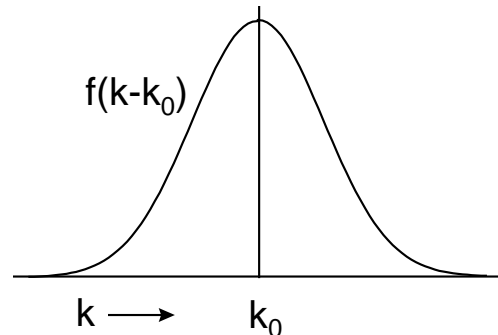
$$\Psi_{\Delta k}(x) = \int_{-\infty}^{\infty} f(k - k_0) e^{ik(x - x_0)} dk$$

$f(k - k_0) \Rightarrow$ weighting function

Wave packet centered around
 $x = x_0$,
made up of k -states centered around
 $k = k_0$.

Tells how much of each k -state is in superposition.

Nicely behaved → dies out rapidly away from k_0 .



$f(k - k_0) \Rightarrow$ weighting function Only have k -states near $k = k_0$.

At $x = x_0$ $e^{ik(x - x_0)} = e^0 = 1$

All k -states in superposition in phase.

Interfere constructively \longrightarrow add up.

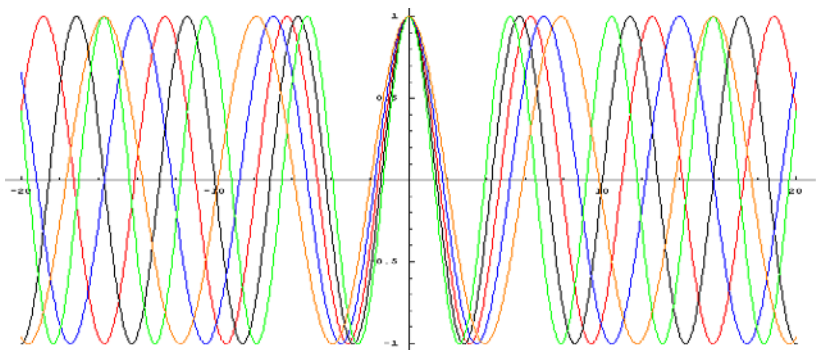
All contributions to integral add.

For large $(x - x_0)$ $e^{ik(x - x_0)} = \cos k(x - x_0) + i \sin k(x - x_0)$

Oscillates wildly with changing k .

Contributions from different k -states \longrightarrow destructive interference.

$|x| \gg x_0$ $\Psi_{\Delta k} \rightarrow 0$ Probability of finding particle $\longrightarrow 0$



$$k = \frac{2\pi}{\lambda} \longleftarrow \text{wavelength}$$

Gaussian Wave Packet

$$G(y) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp[-(y - y_0)^2 / 2\sigma^2] \quad \text{Gaussian Function}$$

$\sigma \equiv$ standard deviation

Gaussian distribution of k -states

$$f(k) = \frac{1}{\sqrt{2\pi\Delta k^2}} \exp\left[-\frac{(k - k_0)^2}{2(\Delta k)^2}\right] \quad \text{Gaussian in } k, \text{ with } \Delta k = \sigma \quad \text{normalized}$$

Gaussian Wave Packet

$$\Psi_{\Delta k}(x) = \frac{1}{\sqrt{2\pi\Delta k^2}} \int_{-\infty}^{\infty} e^{-\frac{(k - k_0)^2}{2(\Delta k)^2}} e^{ik(x - x_0)} dk$$

$f(k - k_0) e^{ik(x - x_0)}$

Written in terms of $x - x_0$ \longrightarrow Packet centered around x_0 .

Gaussian Wave Packet

$$\Psi_{\Delta k}(x) = e^{-\frac{1}{2}(x-x_0)^2(\Delta k)^2} e^{ik_0(x-x_0)} \quad (\text{Have left out normalization})$$

Looks like momentum eigenket at $k = k_0$
times Gaussian in real space.

Width of Gaussian (standard deviation)

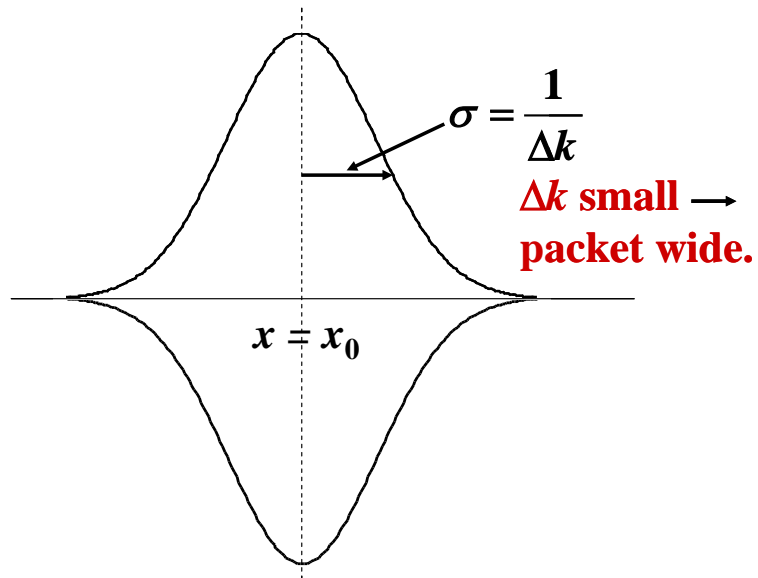
$$\frac{1}{\Delta k} = \sigma$$

The bigger Δk , the narrower the wave packet.

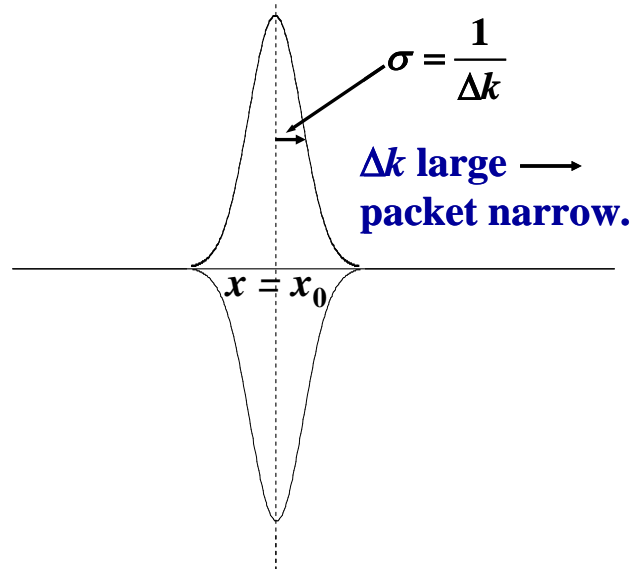
When $x = x_0$, $\exp = 1$.

For large $|x - x_0|$, real exp term $\ll 1$.

Gaussian Wave Packets



$$\Psi_{\Delta k}(x) = e^{-\frac{1}{2}(x-x_0)^2(\Delta k)^2} e^{ik_0(x-x_0)}$$



To get narrow packet (more well defined position) must superimpose broad distribution of k states.

Brief Introduction to Uncertainty Relation

Probability of finding particle
between x & $x + \Delta x$

$$\text{Prob}(x) = \int_x^{x+\Delta x} \psi^*(x)\psi(x)dx$$

Written approximately as

$$\psi^*(x)\psi(x)$$

For Gaussian Wave Packet

$$\Psi_{\Delta k}(x) = e^{-\frac{1}{2}(x-x_0)^2(\Delta k)^2} e^{ik_0(x-x_0)}$$

$$\Psi_{\Delta k}^* \Psi_{\Delta k} \propto \exp\left[-(x-x_0)^2(\Delta k)^2\right]$$

(note – Probabilities are real.)

This becomes small when

$$(x-x_0)^2(\Delta k)^2 \geq 1$$

Call $x-x_0 \equiv \Delta x$, then

$$\Delta x \Delta k \cong 1$$

$$\Delta x \Delta k \cong 1$$

$$\hbar k = p \quad \text{momentum}$$

$$\hbar \Delta k = \Delta p \quad \text{spread or "uncertainty" in momentum}$$

$$\Delta k = \frac{\Delta p}{\hbar}$$

$$\Delta x \frac{\Delta p}{\hbar} \cong 1$$

$$\therefore \Delta x \Delta p \cong \hbar$$

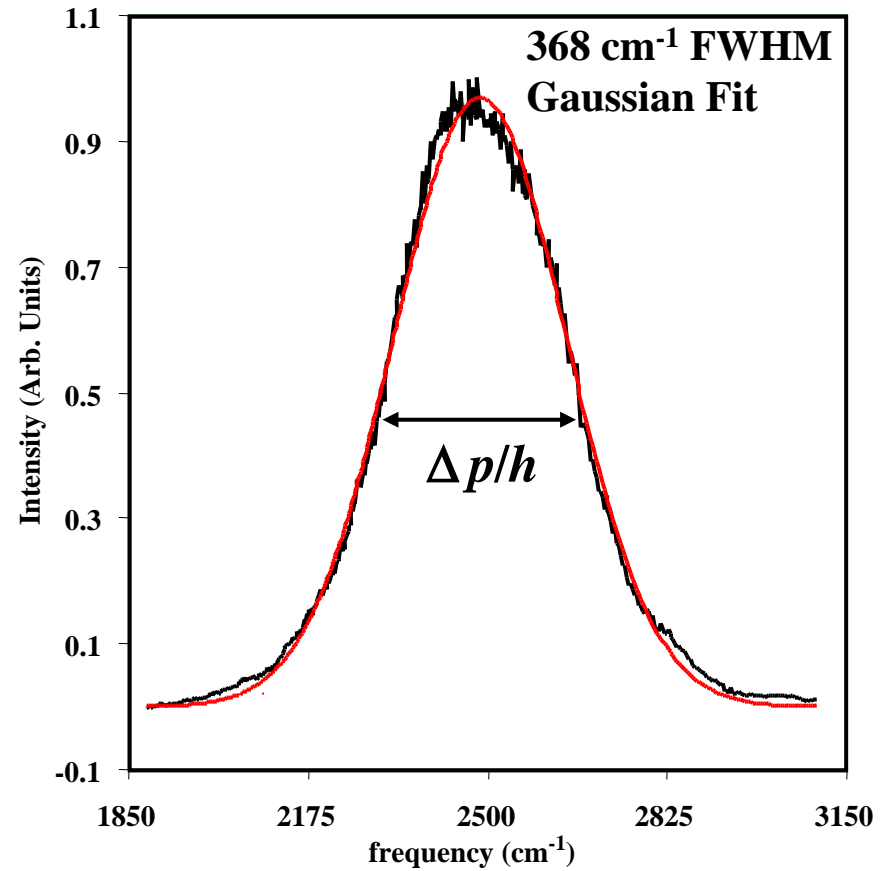
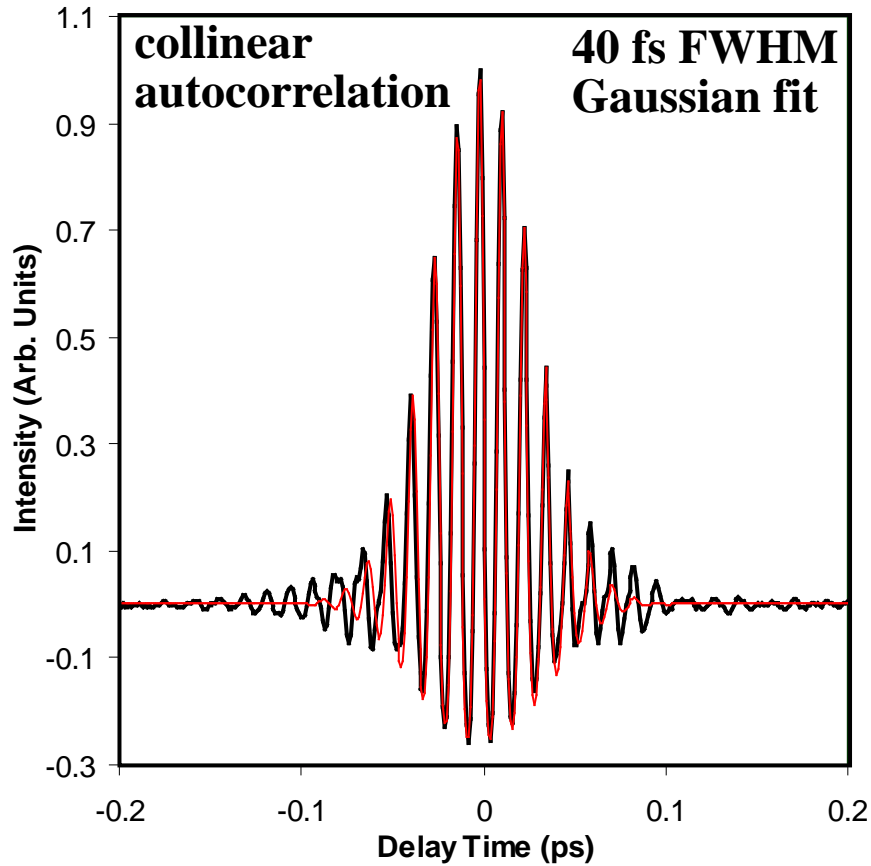
Superposition of states leads to uncertainty relationship.

Large uncertainty in x , small uncertainty in p , and vis versa.

(See later that $\Delta x \Delta p \geq \hbar/2$
differences from choice of 1/e point instead of σ)

Observing Photon Wave Packets

Ultrashort mid-infrared optical pulses



$$\Delta t = 40 \text{ fs} = 40 \times 10^{-15} \text{ s}$$

$$\Delta x = c \Delta t$$

$$\Delta x = 1.2 \times 10^{-5} \text{ m} = 12 \mu\text{m} \text{ (FWHM)}$$

$$p = h/\lambda \quad \lambda^{-1} = p/h$$

$$\Delta p = 2.4 \times 10^{-29} \text{ kg-m/s} \text{ (FWHM, 14\%)}$$

$$p_0 = 1.7 \times 10^{-28} \text{ kg-m/s}$$

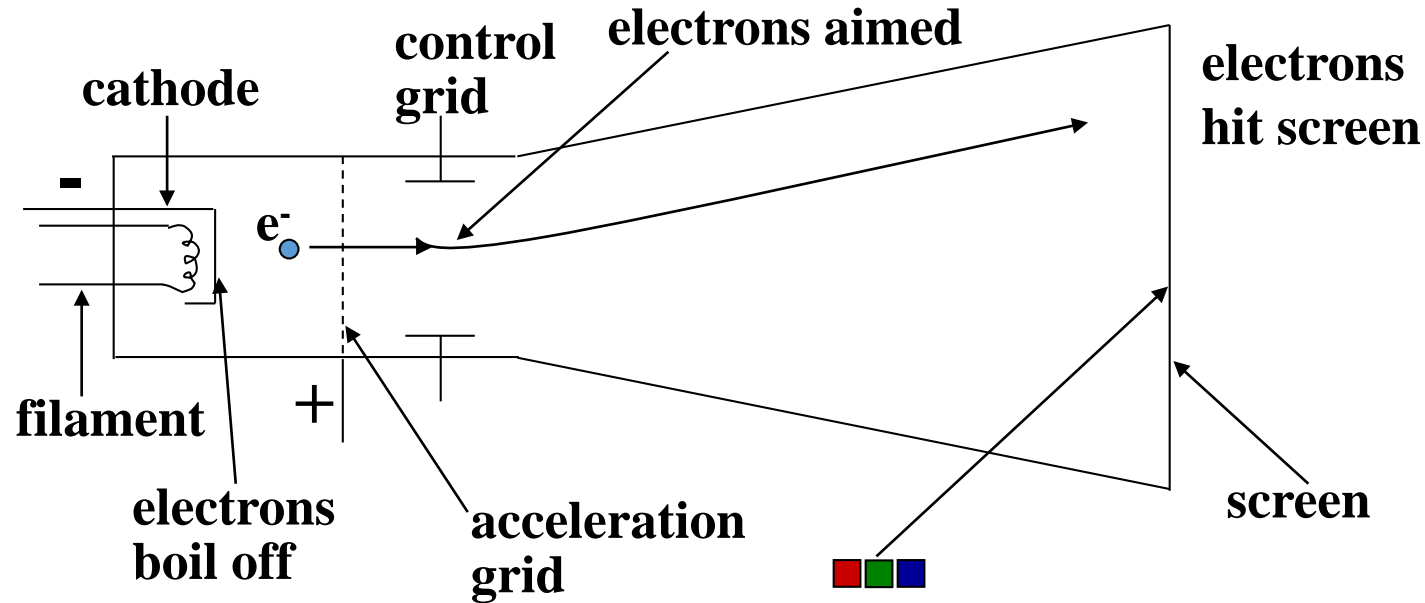
$$\Delta x \Delta p = \hbar / 2 = 5.3 \times 10^{-35} \text{ Js} = (1.2 \times 10^{-5} \text{ m}) / 2.35 \times (2.4 \times 10^{-29} \text{ kg-m/s}) / 2.35 = 5.2 \times 10^{-35} \text{ Js}$$

? ← FWHM to σ →

Electrons can act as “particle” or “waves” – wave packets.

CRT - cathode ray tube

Old style TV or computer monitor



Electron beam in CRT.

Electron wave packets like bullets.

Hit specific points on screen to give colors.

Measurement localizes wave packet.

Electron diffraction

in coming electron "wave"

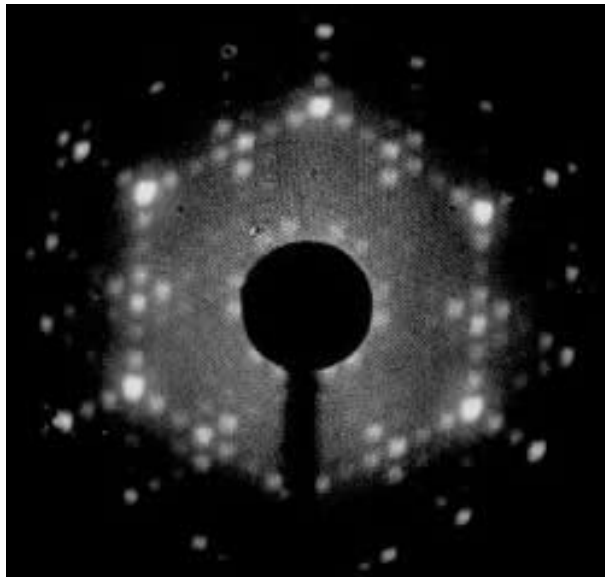
crystal surface

Electron beam impinges on surface of a crystal
low energy electron diffraction diffracts from surface.
Acts as wave.
Measurement determines momentum eigenstates.

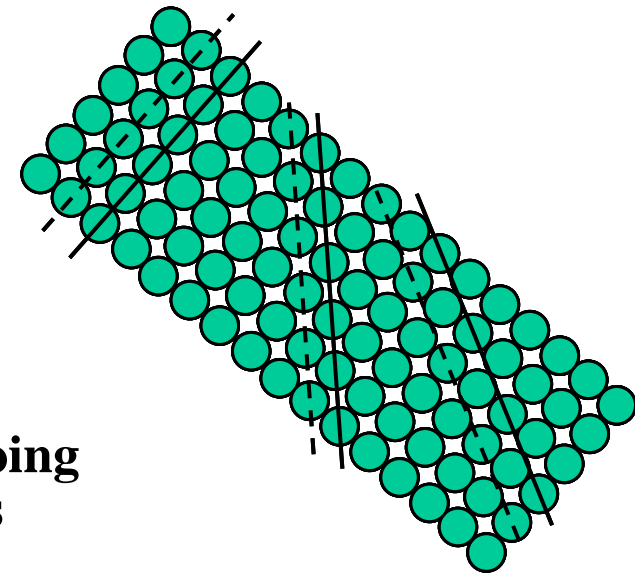
out going waves

Peaks line up.
Constructive interference.

many grating
different directions
different spacings



Low Energy Electron Diffraction (LEED)
from crystal surface



Group Velocities

Time independent momentum eigenket

$$|P\rangle = \Psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \quad p = \hbar k$$

Direction and normalization \longrightarrow ket still not completely defined.

Can multiply by phase factor $e^{i\varphi}$ φ real

Ket still normalized.

Direction unchanged.

For time independent Energy
In the Schrödinger Representation (will prove later)

Time dependence of the wavefunction is given by

$$e^{-i E t / \hbar} = e^{-i \omega t} \quad \hbar \omega = E$$

Time dependent phase factor.

$$e^{-i \omega t} e^{i \omega t} = 1, \quad \text{Still normalized}$$

The time dependent eigenfunctions of the momentum operator are

$$\Psi_k(x, t) = e^{i \left[k(x - x_0) - \omega(k)t \right]}$$

Time dependent Wave Packet

$$\Psi_{\Delta k}(x, t) = \int_{-\infty}^{\infty} f(k) \exp \left[i \left(k(x - x_0) - \omega(k)t \right) \right] dk$$

time dependent phase factor

Photon Wave Packet in a vacuum

Superposition of photon plane waves.

Need ω

$$\omega = ck = c \frac{2\pi}{\lambda}$$

$$c = \lambda \nu$$

$$2\pi\nu = \omega$$

Using $\omega = ck$

$$\Psi_{\Delta k}(x, t) = \int_{-\infty}^{\infty} f(k) \exp[ik(x - x_0 - ct)] dk$$

At $t = 0$,

Packet centered at $x = x_0$.

Argument of exp. = 0. \longrightarrow Max constructive interference.

At later times,

Peak at $x = x_0 + ct$.

Point where argument of exp = 0 \longrightarrow Max constructive interference.

Packet moves with speed of light.

Each plane wave (k -state) moves at same rate, c .

Packet maintains shape.

Motion due to changing regions of constructive and destructive interference of delocalized planes waves

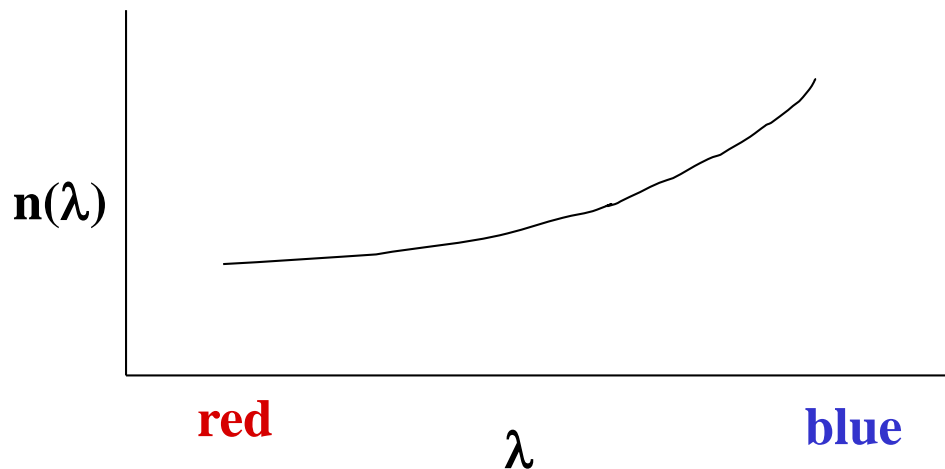
Localization and motion due to superposition of momentum eigenstates.

Photons in a Dispersive Medium

Photon enters glass, liquid, crystal, etc.

Velocity of light depends on wavelength.

$n(\lambda)$ → Index of refraction – wavelength dependent.



glass – middle of visible
 $n \sim 1.5$

$$\omega(k) = 2\pi c / \lambda n(\lambda) = kc / n(k)$$

$$V = \frac{c}{n(\lambda)} \quad \frac{\omega}{2\pi} = v \quad v\lambda = V \quad k = 2\pi/\lambda$$

Dispersion, $\omega(k)$ no longer linear in k .

Wave Packet

$$\Psi_{\Delta k}(x, t) = \int_{-\infty}^{\infty} f(k) \exp[i(k(x-x_0) - \omega(k)t)] dk$$

Still looks like wave packet.

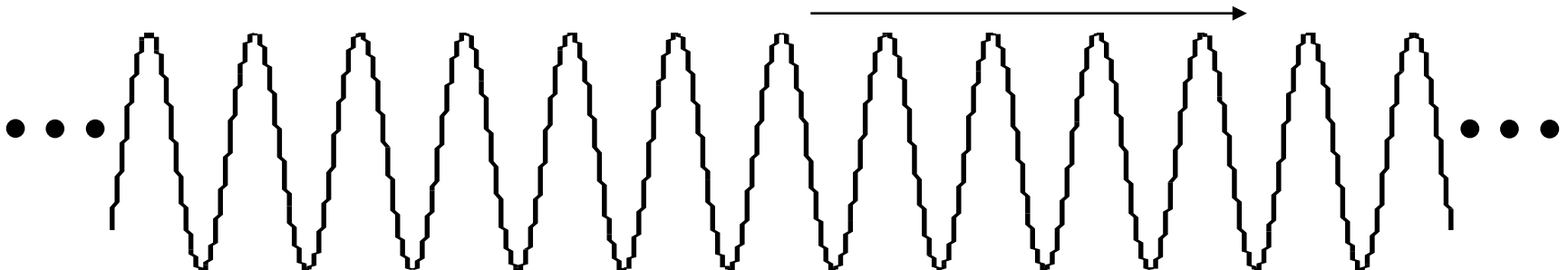
At $t = 0$, the peak is at $x = x_0$

Moves, but not with velocity of light.

Different states move with different velocities;
in glass blue waves move slower than red waves.

Velocity of a single state in superposition

→ Phase Velocity.



Velocity – velocity of center of packet.

$$\phi = k(x - x_0) - \omega(k)t$$

$t = 0, \quad x = x_0$ **max constructive interference**

Argument of exp. zero for all k -states at $x = x_0, t = 0$.

The argument of the exp. at later times

$$\phi = k(x - x_0) - \omega(k)t$$

$\omega(k)$ does not change linearly with k , can't factor out k .

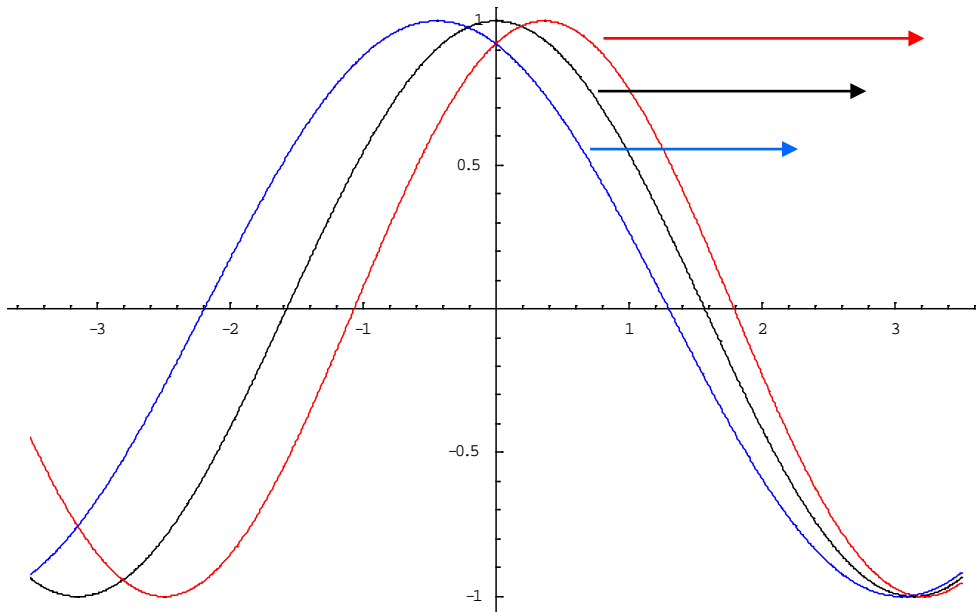
**Argument will never again be zero
for all k in packet simultaneously.**

**Most constructive interference when argument changes with k
as slowly as possible.**

 **This produces slow oscillations as k changes.**

 **k -states add constructively, but not perfectly.**

No longer perfect constructive interference at peak.



In glass

Red waves get ahead.

Blue waves fall behind.

The argument of the exp. is $\phi = k(x - x_0) - \omega(k)t$

When ϕ changes slowly as a function of k within range of k determined by $f(k)$

→ Constructive interference.

Find point of max constructive interference.

ϕ changes as slowly as possible with k .

$$\frac{\partial \phi}{\partial k} = 0 = (x - x_0) - t \left(\frac{\partial \omega(k)}{\partial k} \right)_{k_0}$$

max of packet
at time, t.

$$x = x_0 + t \left(\frac{\partial \omega(k)}{\partial k} \right)_{k_0}$$

Distance Packet has moved at time t

$$d = (x - x_0) = \left(\frac{\partial \omega(k)}{\partial k} \right)_{k_0} t = Vt$$

Point of maximum constructive interference (packet peak) moves at

$$V_g = \left(\frac{\partial \omega(k)}{\partial k} \right)_{k_0} \Rightarrow \text{Group Velocity}$$

V_g \Rightarrow speed of photon in dispersive medium.

V_p \Rightarrow phase velocity = $\lambda v = \omega/k$
only same when $\omega(k) = ck \longrightarrow$

vacuum (approx. true in
low pressure gasses)

Electron Wave Packet

de Broglie wavelength

$$p = h / \lambda = \hbar k \quad (1922 \text{ Ph.D. thesis})$$

A wavelength associated with a particle

—————→ unifies theories of light and matter.

$$E = \hbar \omega$$

$$\omega(k) = E / \hbar = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m}$$

Used $p = \hbar k$

Non-relativistic free particle
energy divided by \hbar (will show later).

V_g – Free non-zero rest mass particle

$$V_g = \frac{\partial \omega(k)}{\partial k} = \frac{\hbar}{2m} \frac{\partial k^2}{\partial k} = \frac{\hbar k}{m} = p/m$$

$$p/m = mV/m = V$$

Group velocity of electron wave packet \Rightarrow same as classical velocity.

However, description very different. Localization and motion due to changing regions of constructive and destructive interference.

Can explain electron motion and electron diffraction.

Correspondence Principle – Q. M. gives same results as classical mechanics when in “classical regime.”

$$|P\rangle = \Psi_p = ce^{ipx/\hbar} = ce^{ikx}$$

momentum
eigenkets

momentum
wave functions

Have called eigenvalues $\lambda = p$

$$p = \hbar k \quad k \text{ is the "wave vector."}$$

c is the normalization constant.

c doesn't influence eigenvalues \longrightarrow

direction not length of vector matters.

Normalization

$\langle a | b \rangle$ scalar product

$\langle a | a \rangle$ scalar product of a vector with itself

$$(\langle a | a \rangle)^{1/2} = 1 \quad \longrightarrow \quad \text{normalized}$$

Normalization of the Momentum Eigenfunctions – the Dirac Delta Function

$$\langle b | a \rangle = \int \psi_b^* \psi_a d\tau \quad \text{scalar product of vector functions (linear algebra)}$$

$$\langle a | a \rangle = \int \phi_a^* \phi_a d\tau. \quad \text{scalar product of vector function with itself}$$

$$\langle P' | P \rangle = \int_{-\infty}^{\infty} \psi_{P'}^* \psi_P dx = \begin{cases} 1 & \text{if } P' = P \\ 0 & \text{if } P' \neq P \end{cases} \quad \begin{array}{l} \text{normalization } P' = P \\ \text{orthogonality } P' \neq P \end{array}$$

Using $p = \hbar k$

$$c^2 \int_{-\infty}^{\infty} e^{-ik'x} e^{ikx} dx = c^2 \int_{-\infty}^{\infty} e^{i(k-k')x} dx \quad \text{Want to adjust } c \text{ so the integral times } c^2 = 1.$$

Can't do this integral with normal methods – oscillates.

$$\int_{-\infty}^{\infty} e^{i(k-k')x} dx = \int_{-\infty}^{\infty} [\cos(k-k')x + i \sin(k-k')x] dx.$$

Dirac δ function

Definition

$$\delta(x) = 0 \quad \text{if } x \neq 0$$

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

For function $f(x)$ continuous at $x = 0$,

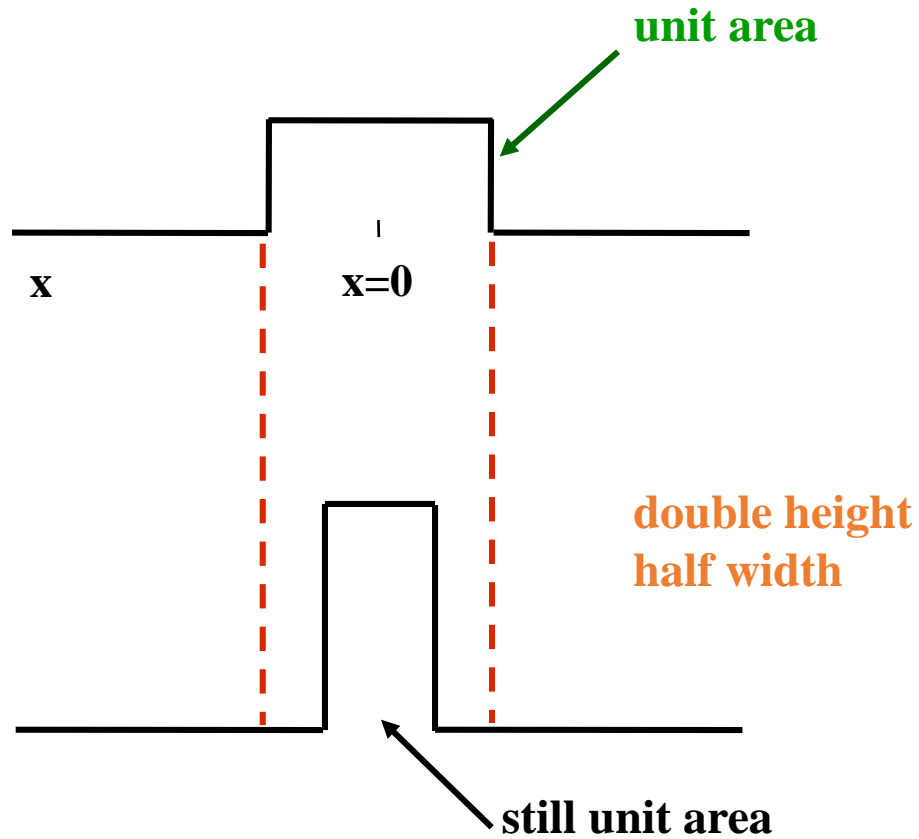
$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = f(0)$$

or

$$\delta(x - a) = 0 \quad \text{if } x \neq a$$

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) dx = f(a)$$

Physical illustration



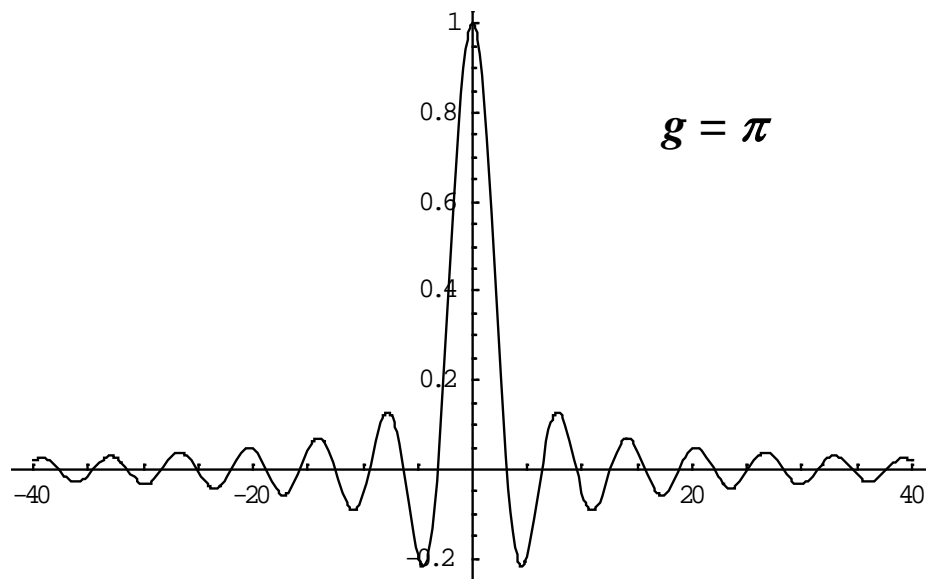
Limit width $\rightarrow 0$, height $\rightarrow \infty$
area remains 1

Mathematical representation of δ function

$$\frac{\sin(g x)}{\pi x} \quad g \text{ any real number}$$

πx

zeroth order spherical
Bessel function



Has value g/π at $x = 0$.

Decreasing oscillations for increasing $|x|$.

Has unit area independent of the choice of g .

As $g \rightarrow \infty \rightarrow \delta$

$$\delta(x) = \lim_{g \rightarrow \infty} \frac{\sin gx}{\pi x}$$

1. Has unit integral

2. Only non-zero at point $x = 0$,

because oscillations infinitely fast, over
finite interval yield zero area.

Use $\delta(x)$ in normalization and orthogonality of momentum eigenfunctions.

Want $\langle \mathbf{p} | \mathbf{p} \rangle = 1$
 $\langle \mathbf{p} | \mathbf{p}' \rangle = 0$

$$c^2 \int_{-\infty}^{\infty} e^{-ik'x} e^{ikx} dx = \begin{cases} 1 & \text{if } k = k' \\ 0 & \text{if } k \neq k' \end{cases} \quad \text{Adjust } c \text{ to make equal to 1.}$$

Evaluate

$$\int_{-\infty}^{\infty} e^{i(k-k')x} dx = \int_{-\infty}^{\infty} [\cos(k-k')x + i \sin(k-k')x] dx$$

Rewrite

$$= \lim_{g \rightarrow \infty} \int_{-g}^g [\cos(k-k')x + i \sin(k-k')x] dx$$

$$= \lim_{g \rightarrow \infty} \left\{ \frac{[\sin(k-k')x]}{(k-k')} - \frac{[i \cos(k-k')x]}{(k-k')} \right\} \Bigg|_{-g}^g$$

$$\lim_{g \rightarrow \infty} \left\{ \frac{[\sin(k - k')x]}{(k - k')} - \frac{[i \cos(k - k')x]}{(k - k')} \right\} \Bigg|_{-g}^g = \lim_{g \rightarrow \infty} \frac{2 \sin g(k - k')}{(k - k')}$$

δ function multiplied by 2π .

$$= 2\pi \delta(k - k')$$

$$2\pi \delta(k - k') = 0 \quad \text{if } k \neq k'$$

δ function

The momentum eigenfunctions are orthogonal. We knew this already. Proved eigenkets belonging to different eigenvalues are orthogonal.

To find out what happens for $k = k'$ must evaluate $2\pi \delta(k - k')$.

But, whenever you have a continuous range in the variable of a vector function (Hilbert Space), can't define function at a point. Must do integral about point.

$$\int_{k'=k-\varepsilon}^{k'=k+\varepsilon} \delta(k - k') dk' = 1 \quad \text{if } k = k'$$

Therefore

$$\frac{1}{c^2} \langle P' | P \rangle = \begin{cases} 2\pi & \text{if } P' = P \\ 0 & \text{if } P' \neq P \end{cases}$$

$|P\rangle$ are orthogonal and the normalization constant is

$$c^2 = \frac{1}{2\pi}$$

$$c = \frac{1}{\sqrt{2\pi}}$$

The momentum eigenfunction are

$$\Psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$$

$$\hbar k = p$$

momentum eigenvalue