PH 107: Quantum Physics and applications

Distribution Function and Schrodinger Equation

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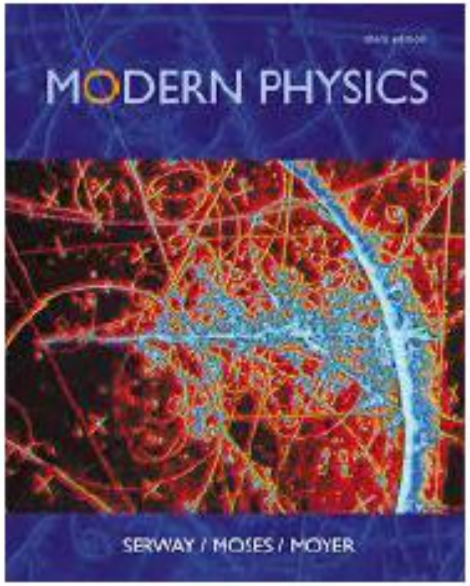
Lecture08: 30-12-2021

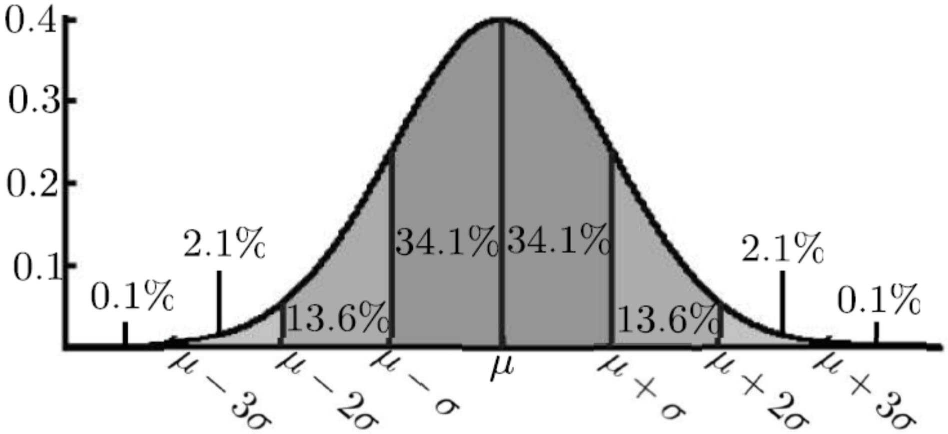
Recommended Readings

Schroedinger equation, sections 6.1, 6.2 and 6.3.



Fourier Integral : The Gaussian Function

$$f(x) = A\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$



***μ** specifies the position of the bell curve's central maximum, **σ** specifies the standard deviation (**a measure of uncertainty**)*

Normalization

Normalization of *probability distribution function* *P(x)* means

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

$$f(x) = A\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$\int_{-\infty}^{\infty} Ae^{-(x-\mu)^2/2\sigma^2}dx = 1$$

Find A

$$\boxed{\int_{-\infty}^{\infty} e^{-\alpha x^2}dx = \left(\frac{\pi}{\alpha}\right)^{1/2} \qquad \alpha = \frac{1}{2\sigma^2}}$$

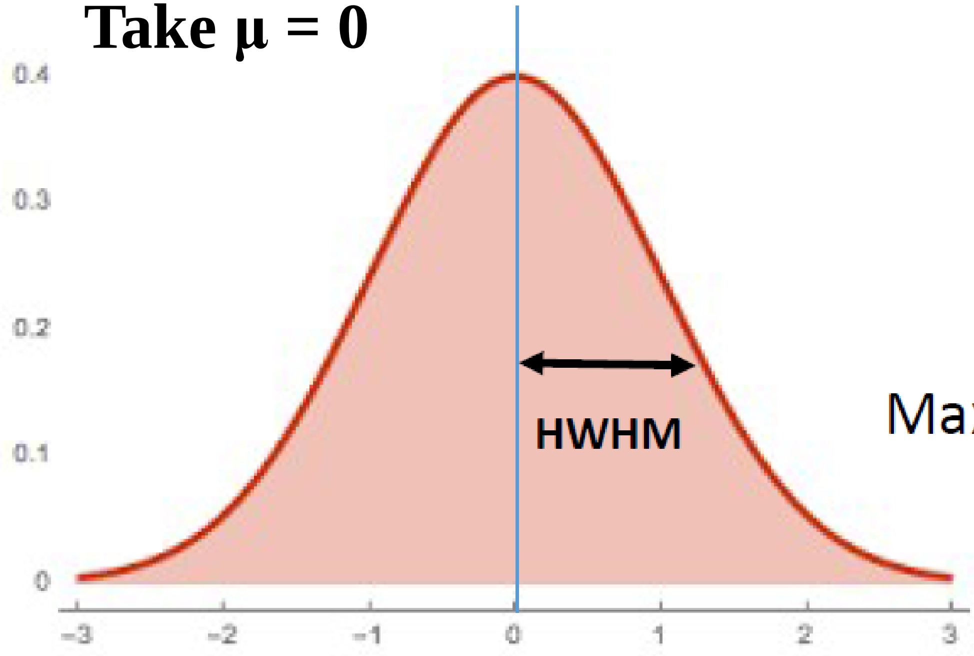
$$\int_{-\infty}^{\infty} Ae^{-(x-\mu)^2/2\sigma^2}dx = A\int_{-\infty}^{\infty} e^{-y^2/2\sigma^2}dy \qquad y = x-\mu$$

$$= A(2\sigma^2\pi)^{1/2} = 1$$

$$\therefore A = \frac{1}{\sqrt{2\pi}\sigma} \qquad f(x) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$ is normalized.

$$i.e.\ \int_{-\infty}^{\infty} f(x)dx = 1$$

Take μ = 0



$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2} \right)$$

Maximum value $f(0) = \frac{1}{\sqrt{2\pi}\sigma}$

What is the value of x where f(x) becomes f(0)/2?

$$\frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2} \right) = \frac{1}{2}\frac{1}{\sqrt{2\pi}\sigma} \quad \Rightarrow \quad x = \sigma\sqrt{2\ln 2}$$

Half width at half maximum $= \sigma\sqrt{2\ln 2}$

Full width at half maximum $= 2\sigma\sqrt{2\ln 2}$

$$\boxed{\textbf{Width} \propto \sigma}$$

What is uncertainty ?

For large number of measurements on the system

Average $\langle x \rangle = \bar{x}$

Standard deviation σ_x = Uncertainty in measurement Δx

$$\sigma^2 = \langle (x - \bar{x})^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

To get the uncertainty relation, we need to calculate

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$(\Delta k)^2 = \langle k^2 \rangle - \langle k \rangle^2$$

Uncertainty is the square root of the variance

Note the following examples

$$f(x) = A\exp\left(-\frac{x^2}{2\sigma^2}\right)$$

Is a Gaussian with <x>=0 and standard deviation σ

$$f(x) = A\exp\left(-\frac{x^2}{4\sigma^2}\right)$$

Is a Gaussian with <x>=0 and standard deviation $\sqrt{2}\sigma$

$$f(x) = A\exp\left(-\frac{(x-2)^2}{\sigma^2}\right)$$

Is a Gaussian with <x>=2 and standard deviation $\sigma/\sqrt{2}$

$$f(x) = A\exp\left(-\frac{\sigma x^2}{2}\right)$$

Is a Gaussian with <x>=0 and standard deviation $1/\sqrt{\sigma}$

Fourier Transform of a Gaussian Function

$$f(x) = 1.\, exp\left[-\frac{x^2}{2\sigma^2}\right]$$

$$-\frac{x^2}{2\sigma^2} - ikx + \frac{k^2\sigma^2}{2} - \frac{k^2\sigma^2}{2}$$

$$-\left(\frac{x}{\sqrt{2}\sigma} + \frac{ik\sigma}{\sqrt{2}}\right)^2 - \frac{k^2\sigma^2}{2}$$

$$g(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)\, e^{-ikx}\, dx$$

$$g(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} exp\left[-\frac{x^2}{2\sigma^2}\right] e^{-ikx}\, dx$$

$$g(k) = \frac{1}{\sqrt{2\pi}} exp\left[-\frac{k^2\sigma^2}{2}\right]\sqrt{2}\sigma \int_{-\infty}^{\infty} exp[-y^2]\, dy$$

$$g(k) = \sigma exp\left[-\frac{k^2\sigma^2}{2}\right] \qquad since \int_{-\infty}^{\infty} exp[-y^2]\, dy = \sqrt{\pi}$$

FT of Gaussian is Gaussian with different width

Reciprocity Relation

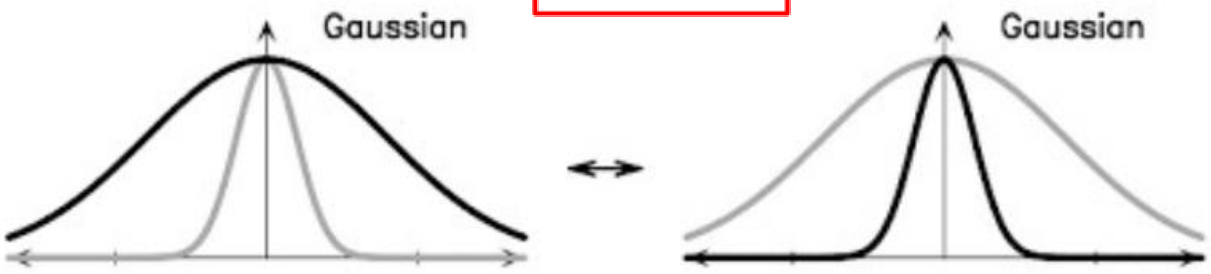
$$f(x) = exp\left[-\frac{x^2}{2\sigma^2}\right] \longrightarrow g(k) = \sigma exp\left[-\frac{k^2\sigma^2}{2}\right]$$

Standard deviation $\Delta x = \boldsymbol{\sigma}_x$

Standard deviation $\Delta k = 1/\ \boldsymbol{\sigma}_k$

$$\boxed{\sigma_k = \frac{1}{\sigma_x}}$$

$f(x)$ $\quad$ $g(k)$



The reciprocal relation is at the origin of uncertainty relation, $\boldsymbol{\sigma}_x\boldsymbol{\sigma}_k = 1$

For the Gaussian function $\Delta k \Delta x$ attains the minimum value, i.e. $\Delta k \Delta x \approx 1$

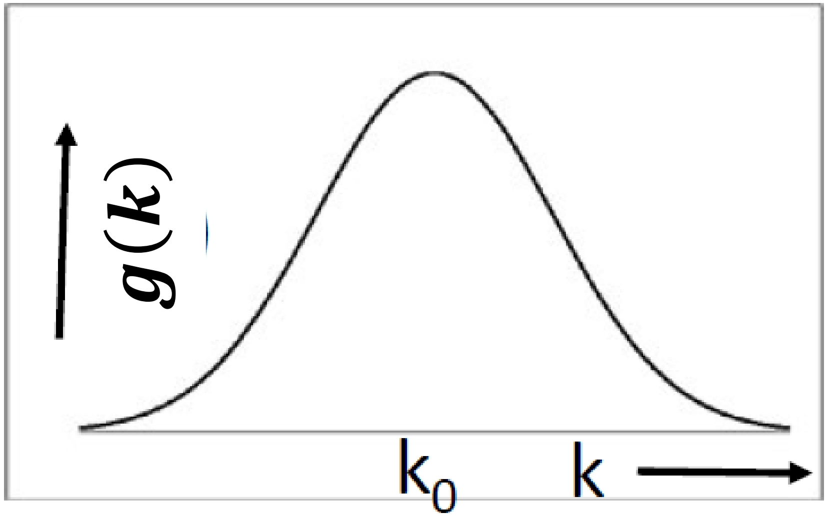
or minimum uncertainity in $\quad \Delta k \Delta x \geq 1$

$$\Delta p \Delta x \geq \hbar$$

Gaussian Wave Packet

$$\boldsymbol{g(k) = Aexp\left[-\frac{(k-k_o)^2}{2\sigma_k^2}\right]} \xrightarrow{\text{FT}} \boldsymbol{f(x)} = \int_{-\infty}^{\infty} \boldsymbol{g(k)\, e^{ikx}}\, dk$$

$\boldsymbol{g(k)}$ is Gaussian $\xrightarrow{\text{FT}}$ $\boldsymbol{f(x)}$ is Gaussian



$\xrightarrow{\text{FT}}$??

Gaussian Wave Packet

$$\boldsymbol{f}(\boldsymbol{x}) = A\int_{-\infty}^{\infty}\exp\left[-\frac{(k-k_0)^2}{2\sigma_k^2}\right]\exp(ikx)dk$$

$$= A\int_{-\infty}^{\infty}\exp\left[-\frac{(k-k_0)^2}{2\sigma_k^2}\right]\exp[i(k-k_0)x]\exp(ik_0x)dk$$

$$\kappa = k - k_0$$

$$= A\exp(ik_0x)\int_{-\infty}^{\infty}\exp\left[-\frac{\kappa^2}{2\sigma_k^2}+i\kappa x\right]d\kappa$$

Note:

$$-\frac{\kappa^2}{2\sigma_k^2}+i\kappa x = -\frac{\kappa^2}{2\sigma_k^2}+i\kappa x+\frac{\sigma_k^2x^2}{2}-\frac{\sigma_k^2x^2}{2} = -\left(\frac{\kappa}{\sqrt{2}\sigma_k}-\frac{i\sigma_k x}{\sqrt{2}}\right)^2-\frac{\sigma_k^2x^2}{2}$$

We have

$$\psi(x) = A\exp(ik_0 x)\int_{-\infty}^{\infty}\exp\left[-\frac{\kappa^2}{2\sigma_k^2} + i\kappa x\right]d\kappa$$

$$-\frac{\kappa^2}{2\sigma_k^2} + i\kappa x = -\left(\frac{\kappa}{\sqrt{2}\sigma_k} - \frac{i\sigma_k x}{\sqrt{2}}\right)^2 - \frac{\sigma_k^2 x^2}{2}$$

$$\therefore \psi(x) = A\exp(ik_0 x)\exp\left(-\frac{\sigma_k^2 x^2}{2}\right)\int_{-\infty}^{\infty}\exp\left[-\underbrace{\left(\frac{\kappa}{\sqrt{2}\sigma_k} - \frac{i\sigma_k x}{\sqrt{2}}\right)}_{\text{y}}^2\right]d\kappa$$

$$\psi(x) = A\exp(ik_0 x)\exp\left(-\frac{\sigma_k^2 x^2}{2}\right)\sqrt{2}\sigma_k\int_{-\infty}^{\infty}\exp\left(-y^2\right)dy$$

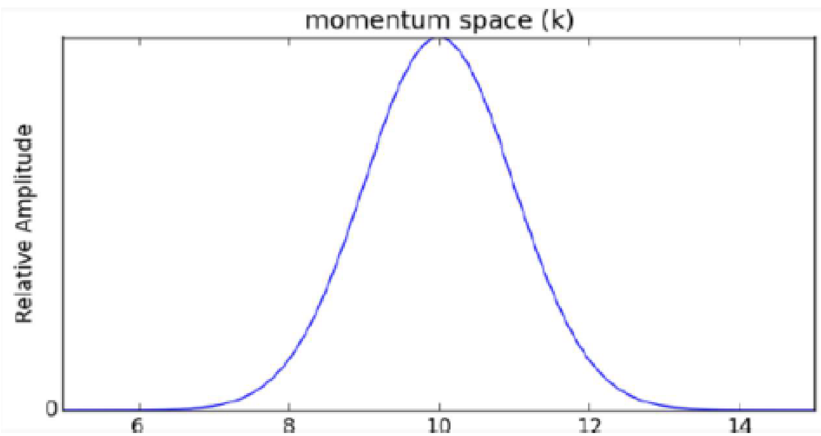
$$\boxed{\psi(x) = A\sqrt{2\pi}\sigma_k\exp(ik_0 x)\exp\left(-\sigma_k^2 x^2/2\right)}$$

Gaussian Wave Packet

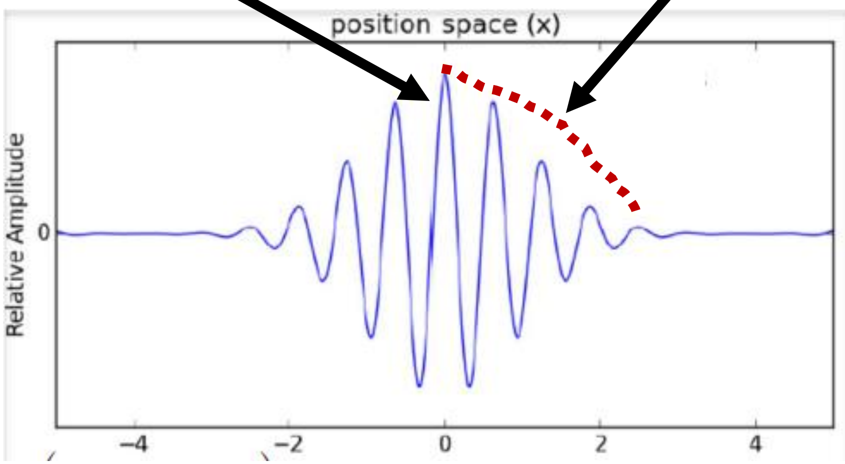
$$g(k) = A exp\left[-\frac{(k-k_o)^2}{2\sigma_k^2}\right] \xrightarrow{\text{FT}} f(x) = A\sqrt{2\pi}\sigma_k \; e^{ik_o x} e^{-\sigma_k^2 x^2/2}$$

Oscillatory part

Envelop



FT



$g(k)$ is Gaussian $\xrightarrow{\text{FT}}$ $f(x)$ is Gaussian

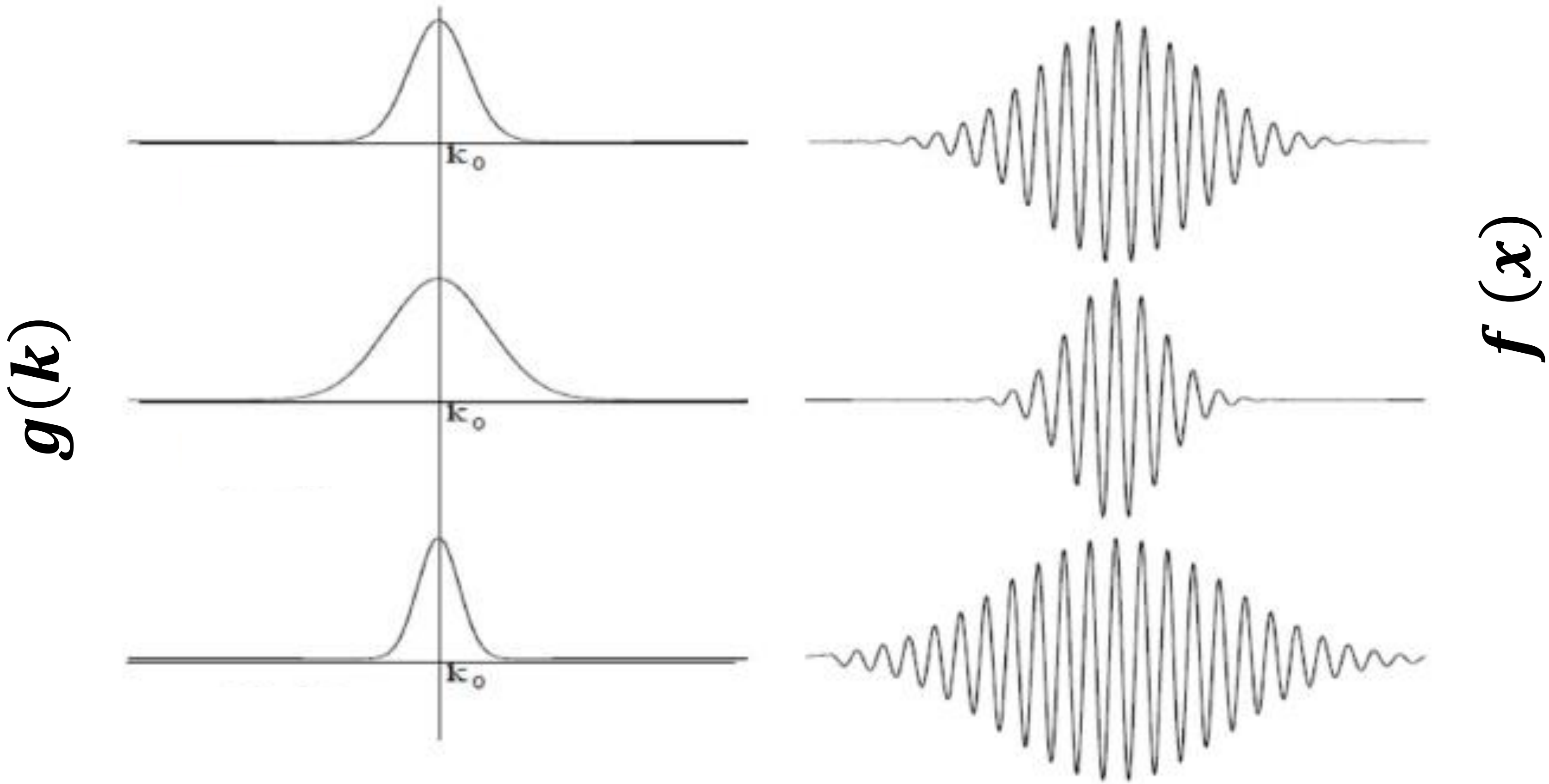
Gaussian Wave Packet

$$g(k) = Aexp\left[-\frac{(k-k_o)^2}{2\sigma_k^2}\right]$$

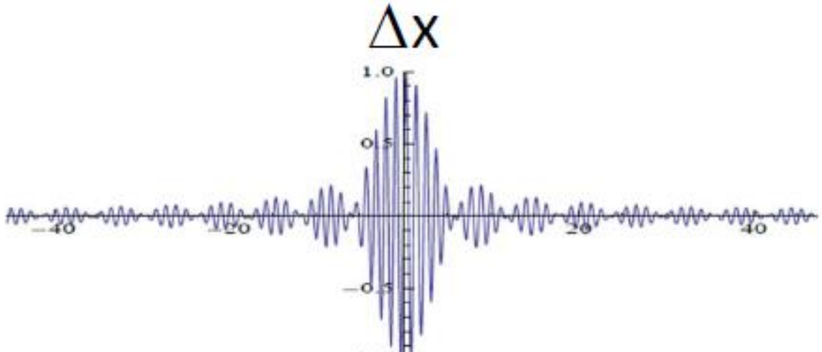
Variance: $= \sigma_k^2$

$$f(x) = A\sqrt{2\pi}\sigma_k \; e^{ik_o x} e^{-\sigma_k^2 x^2/2}$$

Variance: $= 1/\sigma_k^2$



Wave Packet and Fourier Integrals



$$\psi(\mathrm{x}) = \sum_{i=1}^{n} g_i(Sink_i x)$$

For a non-periodic function $\psi(\boldsymbol{x}) = \int_{-\infty}^{\infty} \boldsymbol{g}(\boldsymbol{k})\, \boldsymbol{e}^{\boldsymbol{ikx}}\, dk$

In Real Space; x

In Reciprocal Space; k

$$\boldsymbol{f}(\boldsymbol{x}) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}\boldsymbol{\pi}}} \int_{-\infty}^{\infty} \boldsymbol{g}(\boldsymbol{k})\, \boldsymbol{e}^{\boldsymbol{ikx}}\, dk$$

$$\boldsymbol{g}(\boldsymbol{k}) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}\boldsymbol{\pi}}} \int_{-\infty}^{\infty} \boldsymbol{f}(\boldsymbol{x})\, \boldsymbol{e}^{-\boldsymbol{ikx}}\, dk$$

$\psi(x)$ if IFT of g(k) and g(k) is FT of $\psi(x)$ Since k = p/ħ, $\psi(x)$ if IFT of g(p) and g(p) is FT of $\psi(x)$

In Time Domain; t

In Frequency Domain; $\boldsymbol{\omega}$

$$\boldsymbol{f}(\boldsymbol{t}) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}\boldsymbol{\pi}}} \int_{-\infty}^{\infty} \boldsymbol{g}(\boldsymbol{\omega})\boldsymbol{e}^{\boldsymbol{i\omega t}}\, \boldsymbol{d\omega}$$

$$\boldsymbol{g}(\omega) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}\boldsymbol{\pi}}} \int_{-\infty}^{\infty} \boldsymbol{f}(\boldsymbol{t})\boldsymbol{e}^{-\boldsymbol{i\omega t}}\, \boldsymbol{d\omega}$$

Such relation is valid for t and ω or t and E (E=ħω)

Summary

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx}\, dk \qquad g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx}\, dx$$

Reciprocity relations

- For non periodic symmetric box $\Delta x \Delta p = 4\pi\, \hbar$.
- For Gaussian distribution function, $\Delta x \Delta p = \hbar$

(**we will recalculate using operator form and show it to be $\boldsymbol{\hbar/2}$**)

- Probability to observe particles $\propto |\, de\ Broglie\ wave\ amplitude\ |^2$

Heisenberg Uncertainty Relation and Principle

- The Heisenberg Uncertainty Relations consequence of the intrinsic wave packet construct of de Broglie wave.
- The statement of Uncertainty Principle is necessarily associated with a *distribution.*

$$\Delta \boldsymbol{x} \Delta p_x \geq \frac{\hbar}{\mathbf{2}} \qquad \Delta \boldsymbol{E} \Delta t \geq \frac{\hbar}{\mathbf{2}}$$

Measurement on a classical vs quantum “object”

In classical mechanics, the future of a particle is completely determined by its initial position and momentum (together with the forces that act upon it.)

In QM, we arrive at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic scale.

For example in classical picture the radius of the electron’s orbit in a ground – state hydrogen atom is always exactly $5.3X10^{-11}m$, however quantum mechanics states that this is the “most probable radius “

From Newtonian (*Classical*) to New (*Quantum*) world

- Firstly, because the "object" is not a **particle** in the Newtonian sense. **It is not a wave either**.

- Is the wave packet the "object" ?

- **NO**: It is a function which carries the information about the "state" of the object.

- And that too…not in a **deterministic** way but in a **probabilistic** way (due to Heisenberg uncertainty principle).

From Newtonian (*Classical*) to New (*Quantum*) world

In case of classical waves, we know :

For EM waves, the mutually perpendicular electric and magnetic fields are oscillating.

In case of elastic waves in a stretched string, one (or two) of the spatial co-ordinates is(are) oscillating.

Now that we have associated a wave packet with subatomic particle.

Lets ask again "what is oscillating in a de-Broglie wave ?

Probability Amplitude

In de Broglie waves, the oscillating variable is known as the **probability amplitude**.

If $\Psi(x,t)$ represents the state of the object, then

$|\Psi(x,t)|^2 \, dx$ give the probability of finding the particle between

x and $x + dx$, at time t.

In other words:

$$\int_a^b |\Psi(x,t)|^2 \, dx$$

Probability of finding the particle between ***a*** and ***b*** at time ***t***.

Born Interpretation

This is Born's statistical interpretation of $\Psi(x,t)$, which we will now onwards call the wave function.

Now if you ask me, "where is the particle ?" **Everywhere**

"Is the particle at $x = x_0$ now $(t = t_0)$?"

Yes

but with a probability of $|\Psi(x_0, t_0)|^2$

(Very strictly, the correct answer is that the particle can be found in the region $x = x_0 \pm \delta x$ with a probability of

$$\int_{x_0-\delta x}^{x_0+\delta x} |\Psi(x, t_0)|^2 \, dx$$

Key Points

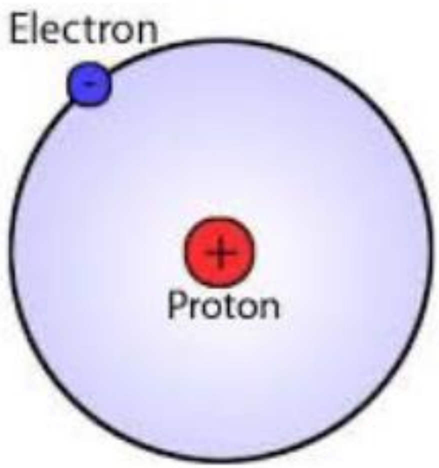
Wave function $\psi(x,t)$

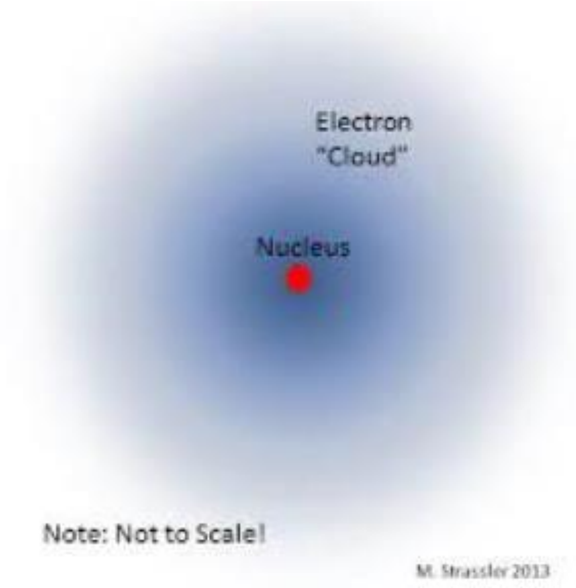
Probability $|\psi(x,t)|^2 = \psi^*(x,t)\psi(x,t)$

Probability of finding a particle at x at time t.

Normalization $\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx = 1$

From *Classical* to *Quantum* world





Classical Motion vs motion in atomic systems

- In classical world, macroscopic objects are described as **particles**. The "**state**" of particle (in simple words, position, momentum) is *exactly* known.

- **HOW ?**

- If we know the forces acting on the particle, **Newton's second law** allows us to find the state of a particle at some time t, provided the state is specified at some other time t'.

- **Newton's second law !!**

Newton's second law

- Mathematically, it is a second order differential equation in time, with spatial coordinates as dependent variables:

$$\vec{F} = ma = m\frac{d^2\vec{r}}{dt^2}$$

This is the dynamical equation governing the evolution of the state of a classical particle

So, if $\vec{r}$ (position) and $\frac{d\vec{r}}{dt}$ (velocity) are given for $t = t$, we can find the trajectory ($\vec{r}(t)$) and the state ($\vec{r}, \frac{d\vec{r}}{dt}$) at another time $t = t'$.

Equation to find "state" of matter wave

$\Psi(x, t)$ provide an information (though probabilistic) about the position (state, in general) of the particle.

Can we construct an equivalent of Newton's second law : i.e. a dynamical equation governing the evolution of the state of the object ?

We know for classical object

$$\vec{F} = m\frac{d^2\vec{r}}{dt^2}$$

BUT, it does not imply any wave-like solution at all !!

Now what ? How about classical wave equation ? LETS SEE !!

Wave Equation

The equation governing classical wave dynamics

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \varphi}{\partial t^2}$$

Possible solution are

$$\varphi(x,t) = A\cos(kx - \omega t)$$
$$\varphi(x,t) = A\sin(kx - \omega t)$$
$$\varphi(x,t) = Ae^{i(kx-\omega t)}$$
$$\varphi(x,t) = Ae^{-i(kx-\omega t)}$$

Solutions of this equation must superimpose.

Solutions of the wave Equation

Considering superposition property of waves, if $\varphi_1(x,t)$ and $\varphi_2(x,t)$ are solutions of the eqn.

$$\frac{\partial^2\varphi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2}$$

then

$$\varphi(x,t) = a\varphi_1(x,t) + b\varphi_2(x,t)$$

must also be a solution. Lets verify:

$$\frac{\partial^2\varphi}{\partial x^2} = \frac{\partial^2(a\varphi_1 + b\varphi_2)}{\partial x^2} = a\frac{\partial^2\varphi_1}{\partial x^2} + b\frac{\partial^2\varphi_2}{\partial x^2}$$

$$= a\frac{1}{c^2}\frac{\partial^2\varphi_1}{\partial t^2} + b\frac{1}{c^2}\frac{\partial^2\varphi_2}{\partial t^2}$$

Wave Equation

Since $\varphi_1$and φ_2 are solutions of the wave equation.

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 (a\varphi_1 + b\varphi_2)}{\partial t^2} = \frac{1}{c^2}\frac{\partial^2 \varphi}{\partial t^2}$$

We see that $a\varphi_1 + b\varphi_2$ is also a solution of the wave equation. But note that here $\boldsymbol{c}$ is same for both the waves.

φ would not be a solution of the wave equation if φ_1 and φ_2 had different velocities.

But to form a wave packet, we need waves travelling at different speeds to superimpose. The dynamical equation should also govern the evolution of the wave packet.

So, the standard wave equation cannot be used for de Broglie waves. We need something different .

The Schrödinger Equation: “Derivation”

DISCLAIMER

At the very beginning, it must be state that Erwin Rudolf Josef Alexander Schoedinger GUESSED the form go the differential equation governing quantum dynamics.

Any attempt to “derive”, it is only hand-wavy. Its success will be judged by its ability to explain observed phenomena.

The Schrödinger Equation

The differential equation whose solution gives us the wave behavior of particle is called the **Schrödinger Equation.**

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \mathbf{U}(\mathbf{x})\,\Psi(\mathbf{x}) = \mathbf{E}\,\Psi(\mathbf{x})$$

E is the total energy ; U is the potential energy.

This is the time-independent Schrödinger Equation for 1D motion.

Have you derived Newtons law ?? **NO**

Newton's laws of motion were not derived from any other principles.

Lets consider the motion of a free particle and justify the form of the SE.

The Schrödinger Equation: "Derivation"

Lets consider the motion of a free particle (*which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed*) to be given by

$$\Psi(x) = A\,Sinkx$$

A is the amplitude of the wave and *k* is the wave number = $\frac{2\pi}{\lambda}$

Differentiating $\Psi(x,t)$ w.r.t. to x ⟹ $\frac{\partial\Psi}{\partial x} = kACoskx$

Differentiating $\Psi(x,t)$ twice w.r.t. to x ⟹ $\frac{\partial^2\Psi}{\partial x^2} = -k^2\Psi$

Since Kinetic energy, $\mathrm{K} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

$$\Longrightarrow \quad \frac{\partial^2\Psi}{\partial x^2} = -k^2\Psi(x) = -\frac{2mK}{\hbar^2}\Psi(x)$$

The Schrödinger Equation: “Derivation”

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{2mK}{\hbar^2}\Psi(x)$$

$$\Longrightarrow \quad \frac{\partial^2 \Psi}{\partial x^2} = -\frac{2m(E-U)}{\hbar^2}\Psi(x)$$

E = U+K is the nonrelativistic total energy of the particle.
U is the potential energy.

For a free particle, U=0 so E=K $\Longrightarrow$ $-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = E\,\Psi(x)$

$$\Longrightarrow \quad \boxed{-\frac{\hbar^2}{2m}\frac{\partial^2 \boldsymbol{\Psi}}{\partial x^2} + \mathbf{U}(\mathbf{x})\,\boldsymbol{\Psi}(\mathbf{x}) = \mathbf{E}\,\boldsymbol{\Psi}(\mathbf{x})}$$

The time independent Schrodinger equation is a wave equation in terms of the wavefunction which plays the same role as of **Newton's laws** and **conservation of energy** in classical mechanics - i.e., it predicts the future behavior of a dynamic system.