Chapter 2: Schrödinger Equation, Wave Packets, and Uncertaintly Principle

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How to mathematically describe quantum behavior?

- We know that the dynamics of material particles at macroscopic level (i.e. large scales) is described by Newton's equations
- The solutions of Newton's equations provide the trajectories of particles as functions of time, i.e., $\vec{r}(t)$
- In the previous chapter we learned that the particles behave very differently at the microscopic level
- We called that behavior "quantum behavior"
- But, what exactly is quantum behavior?
- What are the mathematical quantities relevant to describe the quantum behavior?
- What are the mathematical equations that govern quantum behavior?

Wave function

- Consistent with the wave-particle duality of de Broglie, we argue that instead of a trajectory, at the microscopic levels, a particle is described by a wave function $\psi(\vec{r}, t)$, which depends on its position and time, and, in general, is complex.
- We assign a probabilistic interpretation to $\psi(\vec{r}, t)$ in that it denotes the probability amplitude of a particle's presence at position $\vec{r}$ and time t
- This amplitude is same as that discussed in the context of the Young's double-slit experiment done with particles
- If $dP(\vec{r}, t)$ denotes the probability of finding the particle at time t in an infinitesimal volume $d^3\vec{r} = dxdydz$, located at point $\vec{r}$, we have

$$dP(\vec{r}, t) = |\psi(\vec{r}, t)|^2 d^3\vec{r} \tag{1}$$

this is called the Born interpretation of the wave function, proposed by originally by Max Born

Schrödinger Equation

- If a particle of mass m is in a region where it experiences a potential energy $V(\vec{r},t)$ (henceforth we will call potential energy simply as "potential"), its wave function $\psi(\vec{r},t)$ is the solution of the Schrödinger Equation

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t), \qquad (2)$$

  where, $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ denotes the Laplacian operator

- Note that Eq. 2 above is a partial differential equation which admits multiple solutions for a given potential $V(\vec{r},t)$ depending on the boundary and initial conditions satisfied by $\psi(\vec{r},t)$
- However, Eq. 2 is linear, therefore, its solutions will follow the principle of linear superposition

Principle of Linear Superposition

- This means that if $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$ are two solutions of Eq. 2
- A linear combination $\psi'(\vec{r},t) = c_1\psi_1(\vec{r},t) + c_2\psi_2(\vec{r},t)$ (c_1, c_2 are constants) is also its solution
- Let us verify it by plugging $\psi'(\vec{r},t)$ on the LHS of Eq. 2

$$i\hbar\frac{\partial\psi'(\vec{r},t)}{\partial t} = c_1 i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t} + c_2 i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t} \tag{3}$$

- But $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$ are solutions of Eq. 2, therefore

$$i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_1(\vec{r},t) + V(\vec{r},t)\psi_1(\vec{r},t)$$
$$i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_2(\vec{r},t) + V(\vec{r},t)\psi_2(\vec{r},t)$$

Verification of the principle of Linear Superposition

- Substituting these on the RHS of Eq. 3, we obtain

$$
\begin{aligned}
i\hbar\frac{\partial\psi'(\vec{r},t)}{\partial t} &= -\frac{c_1\hbar^2}{2m}\nabla^2\psi_1(\vec{r},t) + c_1V(\vec{r},t)\psi_1(\vec{r},t) \\
&- \frac{c_2\hbar^2}{2m}\nabla^2\psi_2(\vec{r},t) + c_2V(\vec{r},t)\psi_2(\vec{r},t) \\
&= -\frac{\hbar^2}{2m}\nabla^2\{c_1\psi_1(\vec{r},t) + c_2\psi_2(\vec{r},t)\} \\
&+ V(\vec{r},t)\{c_1\psi_1(\vec{r},t) + c_2\psi_2(\vec{r},t)\} \\
&= -\frac{\hbar^2}{2m}\nabla^2\psi'(\vec{r},t) + V(\vec{r},t)\psi'(\vec{r},t)
\end{aligned}
$$

- Clearly, the principle of linear superposition has been verified

Normalizability of wave function

- We know that the total probability of finding a particle somewhere in the entire space must be unity, i.e.,

$$\int dP(\vec{r},t) = 1$$

- Above equation implies

$$\int |\psi(\vec{r},t)|^2 d^3\vec{r} = 1, \tag{4}$$

  where the integrals above are over entire space
- Eq. 4 implies that the wave function $\psi(\vec{r},t)$ of any system must be square integrable (or normalizable).
- Square integrability of wave function is a very important concept in quantum mechanics, and is not satisfied in some cases
- A free particle is one such case which we will investigate later on

Time-Independent Schrödinger Equation (TISE)

- We saw that the Schödinger equation is a partial differential equation in both space and time coordinates
- Next, we consider an important case in which the particle moves in a time-independent potential

$$V = V(\vec{r})$$

- Note that the potential above depends on the spatial coordinates $\vec{r}$, but not on time t
- Thus, the Schrödinger equation for this system is

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t). \tag{5}$$

- Note that the differential operator has time dependence on the LHS, but no time dependence on the RHS

TISE...

- Such partial differential equations (PDEs) are called separable, on which the method of separation of variables can be employed
- According to which, the solution of the PDE can be written as a product of functions which are functions of different variables
- In this case, we write the solution as a product of a function $\phi(\vec{r})$, which is a function only of the spatial coordinates
- and a function $\chi(t)$, a function only of time

$$\psi(\vec{r},t) = \phi(\vec{r})\chi(t). \tag{6}$$

- On substituting Eq. 6 in Eq. 5, we obtain

$$i\hbar\phi(\vec{r})\frac{d\chi(t)}{dt} = -\frac{\hbar^2}{2m}\chi(t)\nabla^2\phi(\vec{r}) + \chi(t)V(\vec{r})\phi(\vec{r}). \tag{7}$$

TISE...

- Note that on the LHS of Eq. 7, the time derivative is a total derivative and not a partial one
- On dividing Eq. 7 by $\psi(\vec{r},t) = \phi(\vec{r})\chi(t)$ on both the sides, we have

$$i\hbar \frac{1}{\chi(t)} \frac{d\chi(t)}{dt} = \frac{1}{\phi(\vec{r})} \left\{ -\frac{\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + V(\vec{r})\phi(\vec{r}) \right\}.$$

- Note that the LHS is a function only of time variable t, while the RHS is a function only of the space coordinates $\vec{r}$, yet both are equal!
- Such an equality is mathematically possible only if both the sides are equal to the same constant, which we call E

- This leads to two differential equations

$$\frac{i\hbar}{\chi(t)}\frac{d\chi(t)}{dt} = E \tag{8}$$

$$\frac{1}{\phi(\vec{r})}\left\{-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r}) + V(\vec{r})\phi(\vec{r})\right\} = E \tag{9}$$

- The first one (Eq. 8) is a first-order ordinary differential equation which we can solve as follows

$$\begin{aligned}
\frac{d\chi(t)}{dt} &= -\frac{i}{\hbar}E\chi(t) \\
\implies \int \frac{d\chi(t)}{\chi(t)} &= -\frac{i}{\hbar}E\int dt \\
\implies \ln\chi(t) &= -\frac{i}{\hbar}Et + A \text{ (constant)} \\
\implies \chi(t) &= Ce^{-\frac{iEt}{\hbar}}, \qquad (10)
\end{aligned}$$

where C is another constant

TISE...

- The second equation above (Eq. 9) can be rearranged as

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r}) + V(\vec{r})\phi(\vec{r}) = E\phi(\vec{r}). \tag{11}$$

- This is the famous time-independent Schrödinger equation, or TISE for short
- If we define an operator called H as

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{12}$$

- Then Eq. 11 can be written as

$$H\phi = E\phi, \tag{13}$$

  which is clearly an eigenvalue problem.
- Operator H is called the Hamiltonian, and its eigenvalue E is nothing but the energy of the system

- Now, we can write the final solution of the original time-dependent Schrödinger equation (TDSE) by substituting Eq. 10 in Eq. 6

$$\psi(\vec{r},t) = C\phi(\vec{r})e^{-\frac{iEt}{\hbar}} \tag{14}$$

- Assuming that the initially ($t = 0$) the wave function is known

$$\psi(\vec{r},t=0) \equiv \psi(\vec{r},0).$$

- Then from Eq.14, we have

$$\psi(\vec{r},0) = C\phi(\vec{r}),$$

So that our final solution becomes

$$\psi(\vec{r},t) = \psi(r,0)e^{-\frac{iEt}{\hbar}} \tag{15}$$

TISE...

- Eq. 15 is a famous form of the general solution of TDSE, when the particle is moving in a time-independent potential
- Note that the time part of the solution is oscillatory in nature
- And the space part of the solution will depend on the nature of the potential $V(\vec{r})$, and can be obtained by solving the corresponding TISE
- As it turns out that solving TISE exactly is possible only in a very few cases such as a free particle ($V = 0$), particle in various potential wells and barriers, simple harmonic oscillator, hydrogen atom, etc.
- For all other more complicated cases, one has to use numerical methods
- Next, let us consider the simplest case of the solution of TISE for a free particle

The case of a free particle

- As stated earlier, the free particle is one which experiences no potential, i.e.,

$$V(\vec{r}, t) = 0$$

- It is called a "free particle" in the classical sense because when there is no potential energy, there will be no forces
- And the particle will move freely in the space
- Clearly, the TISE for a free particle will be

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r}) = E\phi(\vec{r}). \tag{16}$$

- The solution for Eq. 16 can be obtained very easily using the method of separation of variables
- But, let us first consider a free particle moving in one space dimension (1D, for short), say x

Free particle in 1D

- Now

$$\phi(\vec{r}) \equiv \phi(x)$$
$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} \equiv \frac{d^2}{dx^2}$$

- Note that the partial derivative has been converted to total derivative because we have only one variable (x) leading to TISE in 1D

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} = E\phi$$
$$\Longrightarrow \frac{d^2\phi}{dx^2} + k^2\phi = 0, \tag{17}$$

where in Eq. 16, wave number k is defined as

$$k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{18}$$

1D free particle...

- In Eq. 18, k will be real if $E \geq 0$, but for $E < 0$, k will be imaginary
- We saw earlier for a free particle mass m, the momentum $\vec{p}$ is related to the kinetic energy K by

$$p = \sqrt{2mK}$$

- If in Eq. 18 we consider E to be the kinetic energy of the particle, we obtain

$$k = \frac{p}{\hbar}$$
$$\implies p = \hbar k.$$

- Remember that earlier this is the way we defined the momentum of a photon of wave length λ, with $k = \dfrac{2\pi}{\lambda}$ being the wave number
- But, here we are dealing with a material particle of mass m

TISE for a 1D free particle

- If we write $k = \dfrac{2\pi}{\lambda}$ for this case too, with $k = \frac{p}{\hbar}$, we obtain the de Broglie formula
$$\lambda = \frac{h}{p}$$
- Thus, TISE for a free particle represents a wave of de Broglie wave length!
- This means that the Schrödinger equation has wave-particle duality built into it
- Let us solve Eq. 17 for $E > 0$, for which $k^2 > 0$
- Then TISE
$$\frac{d^2\phi}{dx^2} + k^2\phi = 0, \tag{19}$$
is of the same form as that of a simple harmonic oscillator (SHO) with t replaced by x, ω replaced by k, and x replaced by ϕ.

1D free particle

- Recall that for the SHO, the differential equation is

$$\frac{d^2x}{dt^2} + \omega^2 x = 0,$$

- Whose possible solutions for $\omega^2 > 0$ are

$$x(t) = A \sin \omega t + B \cos \omega t$$
$$\text{OR}$$
$$x(t) = Ae^{i\omega t} + Be^{-i\omega t}$$

- Therefore, by analogy, the solutions of Eq. 19 will be

$$\phi(x) = A \sin kx + B \cos kx$$
$$\text{OR}$$
$$\phi(x) = Ae^{ikx} + Be^{-ikx}$$

with $k > 0$.

1D Free particle...

- Solution of the form $e^{\pm ikx}$ denote a particle of momentum $p = \hbar k$, moving towards $\pm$ve x directions for $k > 0$
- But we can combine two solutions into one if we allow k to be negative as well
- Thus, for $-\infty \leq k \leq \infty$, we consider the solution, or the energy eigenfunction of TISE

$$\phi(x) = Ae^{ikx},$$

with the energy eigenvalue obtained from Eq. 18.

$$E(k) = \frac{\hbar^2 k^2}{2m}. \tag{20}$$

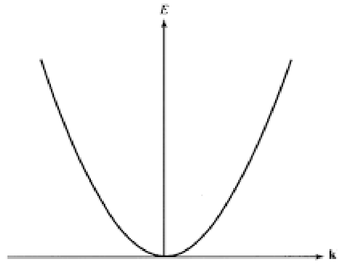
- Solutions of the form $e^{\pm ikx}$ are called plane-wave solutions
- Note that according to this equation $-\infty \leq k \leq \infty$, $0 \leq E(k) \leq \infty$

Degeneracy of 1D free-particle energy levels

- Also, each energy eigenvalue is two-fold degenerate

$$E(k) = E(-k) = \frac{\hbar^2 k^2}{2m}$$

- Energy levels are said to be degenerate when different eigenfunctions have the same eigenvalue
- If we plot $E(k)$ vs k, we get a parabolic curve



Energy–momentum relationship for a free particle.

- This curve is called a "band diagram", and from it also $E(k) = E(-k)$ degeneracy is obvious

Degeneracy of energy levels...

- Clearly, $\phi(x) = Ae^{\pm ikx}$ denote different eigenfunctions (left moving vs. right moving) with the same eigenvalues
- This degeneracy exists because space is perfectly homogeneous in the absence of any forces
- Therefore, left/right moving particles have the same energy, although different momenta
- Let us now try to solve the TISE for a free particle in 3D

TISE for a free-particle in 3D

- There are several ways obtaining the solution of TISE in 3D (see Eq. 16)
$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r}) = E\phi(\vec{r}).$$
- The first approach is by generalizing the solution of 1D TISE to 3D TISE by defining it is a product of three functions corresponding to 3 dimensions
$$\begin{aligned}\phi(\vec{r}) &= Ae^{ik_x x}e^{ik_y y}e^{ik_z z}\\ &= Ae^{i\vec{k}\cdot\vec{r}},\end{aligned} \tag{21}$$
with
$$\begin{aligned}\vec{k} &= k_x\hat{i} + k_y\hat{j} + k_z\hat{i}\\ \vec{r} &= x\hat{i} + y\hat{j} + z\hat{k},\end{aligned}$$
and if we substitute Eq. 21 in the TISE above, we have
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)Ae^{ik_x x}e^{ik_y y}e^{ik_z z} = E\phi(\vec{r})$$

TISE for a particle in 3D...

- Using the fact that partial derivatives with respect to a given variable act only on the functions of that variable, we get on the LHS

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)Ae^{ik_x x}e^{ik_y y}e^{ik_z z}$$
$$=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)Ae^{ik_x x}e^{ik_y y}e^{ik_z z}$$
$$=\frac{\hbar^2\vec{k}^2}{2m}\phi(\vec{r}),$$

  where $\vec{k}^2 = k_x^2 + k_y^2 + k_z^2$.

- On substituting this result on the LHS of the TISE, we conclude that the eigenvalue problem is satisfied with the given wave function $\phi(\vec{r})$, and the energy eigenvalues are

$$E(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) \tag{22}$$

3D Free-particle TISE by separation of variables

- We can also obtain the same result by applying the method of separation of variables to the 3D TISE

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}\right\}=E\phi$$

- We assume that $\phi(\vec{r})$ can be written in the product form

$$\phi(\vec{r})=\phi(x,y,z)=X(x)Y(y)Z(z), \tag{23}$$

where $X(x)$, $Y(y)$, and $Z(z)$ are exclusive functions of x, y, and z, respectively

- On substituting Eq. 23 in the TISE above, we obtain

$$-\frac{\hbar^2}{2m}\left\{YZ\frac{d^2X}{dx^2}+ZX\frac{d^2Y}{dy^2}+XY\frac{d^2Z}{dz^2}\right\}=EX(x)Y(y)Z(z)$$

3D Free particle

- We divide the previous equation by $X(x)Y(y)Z(z)$ on both the sides, and then take all the y and z dependent parts on the RHS, we obtain

$$-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2} = E + \frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2} + \frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}$$

- LHS is a function of x, while RHS is a function of y and z, therefore, they must be equal to the same constant, say $\hbar^2 k_x^2/2m$ which leads to two differential equations

$$\begin{aligned} -\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2} &= \frac{\hbar^2 k_x^2}{2m} \\ \implies \frac{d^2X}{dx^2} + k_x^2 X &= 0 \end{aligned}$$

- And

$$E + \frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2} + \frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2} = \frac{\hbar^2 k_x^2}{2m}$$

- Which can be rearranged as

$$-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2} = E + \frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2} - \frac{\hbar^2 k_x^2}{2m}$$

- On again using the separation of variable argument, and equating the LHS and RHS to the same constant $\hbar^2 k_y^2/2m$, we obtain the separate equations for y and z variables

$$\frac{d^2Y}{dy^2} + k_y^2 Y = 0$$

$$\frac{d^2Z}{dz^2} + k_z^2 Z = 0,$$

where

$$\frac{\hbar^2 k_z^2}{2m} = E - \frac{\hbar^2 k_x^2}{2m} - \frac{\hbar^2 k_y^2}{2m}$$

$$\implies E(k_x, k_y, k_z) = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}$$

$$= E_x(k_x) + E_y(k_y) + E_z(k_z)$$

3D Free particle

- Thus, by using the method of separation of variables we have reduced the 3D TISE for a free particle into three separate 1D TISEs for the three directions

$$\frac{d^2X}{dx^2} + k_x^2 X = 0$$
$$\frac{d^2Y}{dy^2} + k_y^2 Y = 0$$
$$\frac{d^2Z}{dz^2} + k_z^2 Z = 0$$

- Using the results of the 1D case, we clearly will have

$$\phi(x,y,z) = X(x)Y(y)Z(z) = Ae^{ik_x x}e^{ik_y y}e^{ik_z z} = Ae^{i\vec{k}\cdot\vec{r}}$$

- With the energy eigenvalues given by

$$E(k_x,k_y,k_z) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2\vec{k}^2}{2m}$$

we obtained the same results earlier by just generalizing the 1D results to 3D

Square Integrability of the Free-Particle Wave Function

- Using Eqs. 21 and 22, we obtain the solution of the TDSE for the free particle in 3D
- $$\psi(\vec{r},t) = Ae^{i\left(\vec{k}\cdot\vec{r}-\frac{\hbar k^2}{2m}t\right)} \tag{24}$$
- Let us try to normalize it using the condition
$$\int |\psi(\vec{r},t)|^2 d^3\vec{r} = 1$$
- But
$$\left| e^{i\left(\vec{k}\cdot\vec{r}-\frac{\hbar k^2}{2m}t\right)} \right| = 1$$
- Therefore
$$\int |\psi(\vec{r},t)|^2 d^3\vec{r} = |A|^2 \int d^3\vec{r} = |A|^2 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz = \infty \tag{25}$$
- Which means that the probability of finding the particle anywhere in space is infinite!

Normalizability of Free-particle wave function

- In other words, the free-particle wave function is NOT square integrable!
- Let us try to understand why that is the case?
- Actually, this result is fully consistent with the Heisenberg uncertainty principle
- A wave function of the form of Eq. 24 means that the particle has a precise momentum $\vec{p} = \hbar\vec{k}$
- Thus, according to Heisenberg uncertainty principle, its position must become completely uncertain!
- This is exactly what Eq. 25 is telling us.
- Then the question arises what is the correct quantum mechanical description of a free particle wave function?

How to normalize the free-particle wave function

- There are two approaches to normalize a free-particle wave function: (a) box normalization, and (b) wave packet construction
- In box normalization, one doesn't normalize over the whole space
- Instead one normalizes over a box of volume V
- That is

$$\int |\psi(\vec{r},t)|^2 d^3\vec{r} = |A|^2 \int d^3\vec{r} = AV = 1$$

$$\implies |A| = \frac{1}{\sqrt{V}}$$

$$\implies \psi(\vec{r},t) = \frac{1}{\sqrt{V}} e^{i\left(\vec{k}\cdot\vec{r} - \frac{\hbar k^2}{2m}t\right)}, \tag{26}$$

- Above we assumed that A is a real quantity so that $A = |A| = \dfrac{1}{\sqrt{V}}$
- Later on, the limit $V \to \infty$ can be taken, and in many cases V cancels out leading to satisfactory results

Phase velocity

- It is obvious that the maximum of the plane wave (Eq. 26) is given by the condition

$$\vec{k} \cdot \vec{r} - \omega(k)t = 0,$$

where $\omega(k) = \hbar k^2/2m$.

- Clearly, the maximum condition implies

$$\vec{r}(t) = \frac{\omega}{k} t\hat{k} = v_p t\hat{k}$$

- This clearly implies that the maximum moves through the space with a velocity v_p, called the phase velocity

$$v_p = \frac{\omega}{k}. \tag{27}$$

Construction of wave packets

- Above we saw that a free-particle wave function with a single momentum leads to a completely delocalized wave function in space
- Therefore, we should construct a wave function which has multiple values of the momentum
- That is a wave function with momentum values exhibiting a distribution about some mean value
- And those momentum values are within a spread (say $\Delta\vec{k}$) around some mean value $\vec{k}_0$
- We use the principle of superposition and try a wave function of the form

$$\psi(\vec{r},t) = \sum_i C_i(\vec{k}_i) e^{i(\vec{k}_i\cdot\vec{r}-\omega(\vec{k}_i)t)}, \tag{28}$$

where $\omega(\vec{k}_i) = \dfrac{\hbar k_i^2}{2m}$ with $|\vec{k}_0 - \Delta\vec{k}| \leq |\vec{k}_i| \leq |\vec{k}_0 + \Delta\vec{k}|$

Wave packets

- A solution of this form, which is a linear combination of several solutions of TDSE, each with momentum $\hbar\vec{k}_i$, is called a wave packet
- But, if in Eq. 28, allowed $\vec{k}$ values form a continuous distribution, we can convert the discrete sum into an integral of the form

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}} \int g(\vec{k}) e^{i(\vec{k}\cdot\vec{r}-\omega(\vec{k})t)} d^3\vec{k}, \tag{29}$$

above it is assumed that $g(\vec{k})$ is a function of $\vec{k}$ (and hence momentum $\vec{p}$) which peaks at some value $\vec{k}_0$, and decays sharply away from it .

Wave packet solutions...

- A Gaussian distribution function $g(\vec{k}) = Ce^{-(\vec{k}-\vec{k}_0)^2/\Delta k^2}$ is one possibility which we will study in detail later on
- A mathematical equation of the form of Eq. 29 is called a Fourier Transform (FT) or Fourier Integral.
- $\psi(\vec{r},0)$ and $g(\vec{k})$ are related to each other by the inverse Fourier transform

$$g(\vec{k}) = \frac{1}{(2\pi)^{3/2}} \int \psi(\vec{r},0) e^{-i\vec{k}\cdot\vec{r}} d^3\vec{r}$$

- The variables over which integrals in FT and inverse FT are carried out are said to be canonically conjugate
- In this case, $\vec{k}$ and $\vec{r}$ are canonically conjugate
- Another set of canonically conjugate variables are time t and frequency ω

Wave packets in 1D

- Henceforth, for the sake of simplicity we will analyze the wave packets assuming 1D motion in the x direction

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int g(k) e^{i(kx - \omega(k)t)} dk. \tag{30}$$

- So that at $t = 0$,

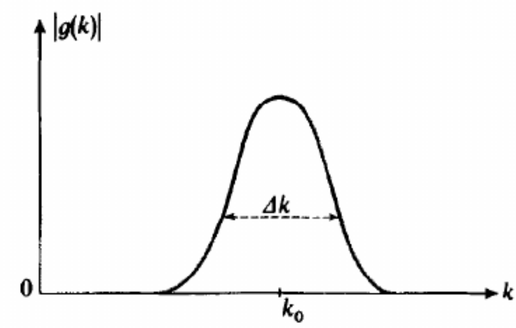
$$\psi(x,0) = \frac{1}{\sqrt{2\pi}} \int g(k) e^{ikx} dk, \tag{31}$$

with the inverse FT given by

$$g(k) = \frac{1}{\sqrt{2\pi}} \int \psi(x,0) e^{-ikx} dx. \tag{32}$$

1D wave packets

- An example of $g(k)$ is the Gaussian type distribution shown below



- Let us start our analysis by considering a simple case (taken from the textbook by Cohen-Tannoudji et al.) in which the wave packet is formed by a linear superposition of just three plane waves

A simple wave packet

- We consider a discrete wave packet at $t = 0$, using the notation $\psi(x) \equiv \psi(x, 0)$

$$\psi(x) = \sum_{i=1}^{3} C(k_i) e^{ik_i x},$$

and assume

$$\begin{aligned} k_1 &= k_0 - \frac{\Delta k}{2} \\ k_2 &= k_0 \\ k_3 &= k_0 + \frac{\Delta k}{2} \end{aligned}$$

where k_0 and Δk have been arbitrarily chosen subject to the condition $\Delta k \ll k_0$

A discrete wave packet...

- Further, the linear combination coefficients are chosen to be

$$C(k_1) = C(k_3) = \frac{g(k_0)}{2\sqrt{2\pi}}$$
$$C(k_2) = \frac{g(k_0)}{\sqrt{2\pi}},$$

  where $g(k_0)$

- Clearly, this denotes a discrete wave packet peaked at $k = k_0$
- This is because the coefficients at $k = k_0 \pm \Delta k/2$ are half of that at $k = k_0$. Now

$$\begin{aligned}\psi(x) &= \frac{g(k_0)}{\sqrt{2\pi}}\left(e^{ik_0x} + \frac{1}{2}e^{i(k_0-\Delta k/2)x} + \frac{1}{2}e^{i(k_0+\Delta k/2)x}\right) \\ &= \frac{g(k_0)}{\sqrt{2\pi}}e^{ik_0x}\left(1+\cos\frac{\Delta kx}{2}\right) \qquad (33)\end{aligned}$$

A 1D discrete wave packet...

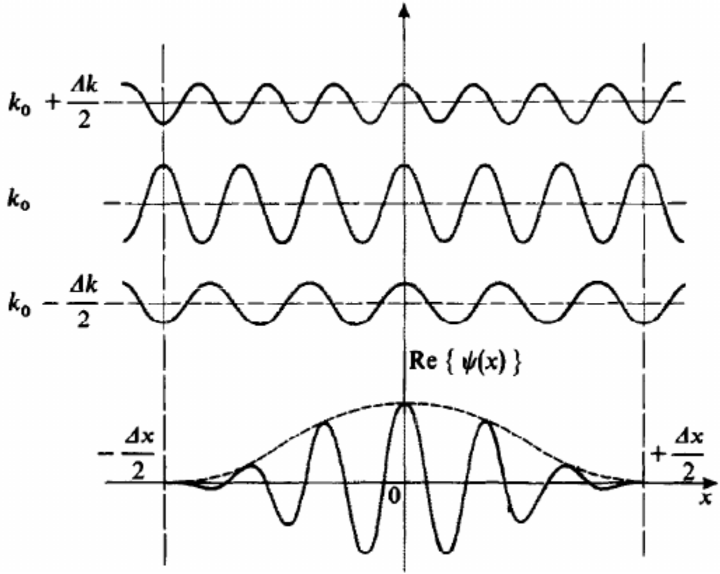
- From the previous equation, it is obvious that

$$
\begin{aligned}
|\psi(x)| &= \frac{g(k_0)}{\sqrt{2\pi}}\left(1+\cos\frac{\Delta k x}{2}\right) \\
\mathrm{Re}(\psi(x)) &= \frac{g(k_0)}{\sqrt{2\pi}}\cos k_0 x\left(1+\cos\frac{\Delta k x}{2}\right)
\end{aligned}
$$

- Clearly, $|\psi(x)|$ will be maximum at $x = 0$
- This is because all the three waves are in phase there

1D wave packet of discrete waves...

- Thus, they interfere constructively at $x = 0$ as shown in the figure below



- As we move away from $x = 0$, waves become more and more out of phase leading to destructive interference
- and decreasing amplitude
- Finally, at $x = \pm\Delta x/2$, $\psi(x) = 0$, where Δx is defined by the condition

$$\frac{\Delta k}{2}\frac{\Delta x}{2} = \pi$$
$$\implies \Delta x \Delta k = 4\pi$$

- This means that smaller the width Δk of the wave packet, larger its width Δx in the space
- This is something like Heisenberg uncertainty principle because the width Δk is related to the uncertainty in momentum by $\Delta p = \hbar \Delta k$
- But, we note that we achieved a more localized wave packet by using three k values, as compared to just one

Time-dependent discrete wave packet

- Having examined the properties of $\psi(x)$ for this case, let us consider the fully time dependent wave packet $\psi(x,t)$ next
- We use the notation

$$\omega_0 = \omega(k_0) = \frac{\hbar k_0^2}{2m}$$
$$\omega_0 \pm \frac{\Delta\omega}{2} = \omega(k_0 \pm \frac{\Delta k}{2})$$

- From above it is obvious that to the first order in Δk

$$\frac{\Delta\omega}{2} \approx \frac{\hbar k_0 \Delta k}{2m}$$

- So that

$$\psi(x,t) = \frac{g(k_0)}{\sqrt{2\pi}} \left(e^{i(k_0 x - \omega_0 t)} + \frac{1}{2} e^{i(k_0 - \Delta k/2)x - (\omega_0 - \Delta\omega/2)t)} + \frac{1}{2} e^{i(k_0 + \Delta k/2)x - (\omega_0 + \Delta\omega/2)t)} \right)$$

Time-dependent wave packets

- which leads to

$$\psi(x,t) = \frac{g(k_0)}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \left(1 + \cos\frac{1}{2}(\Delta k x - \Delta\omega t)\right)$$

- Clearly above $|\psi(x,t)|$ is maximum not when $x = 0$, but when

$$\Delta k x - \Delta\omega t = 0$$
$$\implies x = v_g t$$

- This implies that now the maximum moves with a velocity called group velocity v_g given by

$$v_g = \frac{\Delta\omega}{\Delta k}. \tag{34}$$

- Thus phase velocity $v_p = \omega/k$ denotes the velocity of the individual waves forming the wave packet, while the group velocity is the collective velocity of the wave packet.

Phase and group velocities...

- The result that the group velocity is different from phase velocity can be understood as follows
- In a single plane wave there is a single momentum leading to a single velocity called phase velocity
- However, in a wave packet, we have plane waves of several momenta each of which moves with a different phase velocity
- Therefore, they will interfere constructively at different places, location of which is given by the group velocity.

A general one-dimensional wave packet

- Let us discuss a 1D wave packet given by a general distribution function $g(k)$
- We will first discuss the case at $t = 0$, followed by the time-dependent case
- We assume it to be a complex function, in general, which can be written as

$$g(k) = e^{i\alpha(k)}|g(k)|. \tag{35}$$

- As before, $g(k)$ is assumed to be peaked at $k = k_0$, with appreciable values in the interval $k \in (k_0 - \frac{\Delta k}{2}, k_0 + \frac{\Delta k}{2})$
- Furthermore, we assume that the phase $\alpha(k)$ varies smoothly in the same interval

A 1D wave packet...

- Therefore, we Taylor expand it around k_0, retaining the terms up to first order

$$\alpha(k) = \alpha(k_0) + (k - k_0)\left(\frac{d\alpha}{dk}\right)_{k=k_0} + \cdots$$

- Substituting this in Eq. 31, we obtain

$$\psi(x,0) \approx \frac{1}{\sqrt{2\pi}} \int |g(k)| e^{i\alpha(k_0)} e^{i(k-k_0)\alpha'(k_0)} e^{ikx} dk,$$

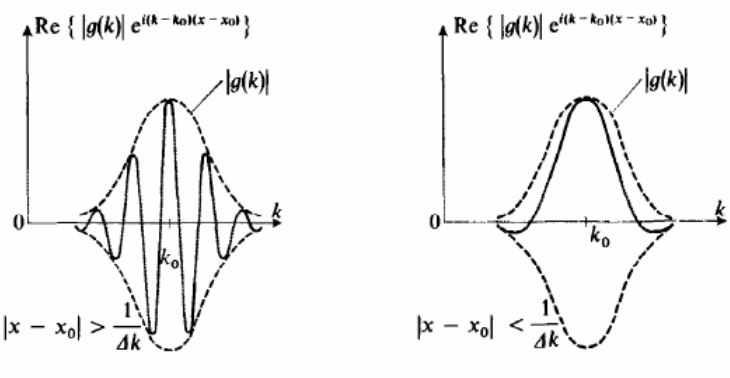
where $\alpha'(k_0) = \left(\frac{d\alpha}{dk}\right)_{k=k_0}$

- Defining $\alpha'(k_0) = -x_0$, the previous equation can be written as

$$\psi(x,0) \approx \frac{e^{i\alpha(k_0)+ik_0x}}{\sqrt{2\pi}} \int |g(k)| e^{i(k-k_0)(x-x_0)} dk \qquad (36)$$

1D Wave packet...

- From Eq. 36 it is obvious that for $|x - x_0| \gg 0$, the integrand will undergo rapid oscillations when $k \in (k_0 - \frac{\Delta k}{2}, k_0 + \frac{\Delta k}{2})$, leading to destructive interference of waves
- While, for $|x - x_0| \approx 0$, we will clearly get a large contribution due to constructive interference as shown below



- Thus, we conclude that that the maximum of the wave packet at time $t = 0$ is located at $x = x_0$

$$x_M(0) = x_0 = -\left(\frac{d\alpha}{dk}\right)_{k=k_0}$$

- As discussed above, when x moves away from x_0, due to rapid oscillations $|\psi(x,0)|$ decays
- Thus, width of the wave packet can be estimated by the condition

$$\Delta k(x - x_0) \approx 1$$

- $|x - x_0|$ is a measure of the width of the wave packet in real space
- Thus, we conclude

$$\Delta k \Delta x \geq 1$$
$$\implies \Delta p \Delta x \geq \hbar$$

- Which is the Heisenberg uncertainty principle for the wave packet

Time evolution of a general 1D wave packet

- A general 1D time-dependent wave packet was given in Eq. 30

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int g(k) e^{i(kx-\omega(k)t)} dk$$

- Following steps similar to in Eq. 35, we have

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int |g(k)| e^{i(\alpha(k)+kx-\omega(k)t)} dk$$

- Taylor expanding both $\alpha(k)$ and $\omega(k)$ around k_0, and retaining up to the first-order terms

$$\begin{aligned} \alpha(k) &= \alpha(k_0) + (k-k_0)\alpha'(k_0) + \cdots \\ \omega(k) &= \omega_0 + (k-k_0)\omega'(k_0) + \cdots, \end{aligned} \tag{37}$$

where $\omega_0 = \omega(k_0)$, $\alpha'(k_0) = \left.\dfrac{d\alpha}{dk}\right|_{k=k_0}$ and $\omega'(k_0) = \left.\dfrac{d\omega}{dk}\right|_{k=k_0}$

Time evolution of a wave packet

- We define

$$x_M(t) = \omega'(k_0)t - \alpha'(k_0) = \omega'(k_0)t + x_0. \qquad (38)$$

- On substituting Eqs. 38 and 37 in Eq. 36, we obtain

$$\psi(x,t) = \frac{e^{i\alpha(k_0)-(ik_0x-i\omega_0t)}}{\sqrt{2\pi}} \int |g(k)| e^{i(k-k_0)(x-x_M(t))} dk$$

- From above it is obvious that $|\psi(x,t)|$ is maximum when

$$\begin{aligned} x - x_M(t) &= 0 \\ \implies x(t) &= x_0 + \omega'(k_0)t \\ &= x_0 + V_g t \end{aligned}$$

Time evolution of a 1D wave packet

- Note that above $\omega'(k_0) = \left.\dfrac{d\omega}{dk}\right|_{k=k_0}$ is nothing but the group velocity V_g
- But, for the free particle case $\omega(k) = \dfrac{\hbar k^2}{2m}$, therefore

$$V_g = \left.\frac{d\omega}{dk}\right|_{k=k_0} = \frac{hk_0}{m} = \frac{p_0}{m}$$

- Thus the given wave packet has the group velocity corresponding to a classical particle of momentum p_0

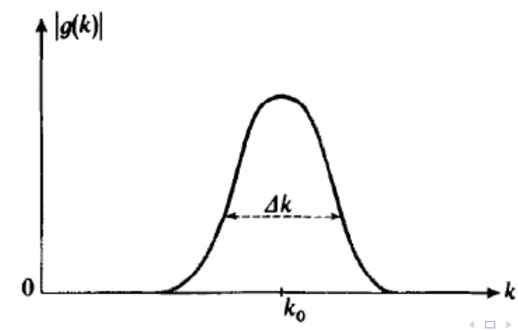
An Example: 1D Gaussian Wave Packet

- Suppose at time $t = 0$, a free particle wave packet is described by a Gaussian momentum distribution

$$g(k) = \frac{\sqrt{a}}{(2\pi)^{1/4}} \exp(-\frac{a^2}{4}(k - k_0)^2),$$

where a and k_0 are constants.

- Such a wave packet is called a Gaussian wave packet
- We plotted this wave packet earlier



1D Gaussian wave packet...

- We want to obtain the corresponding initial wave packet $\psi(x, t=0)$ and determine whether it is localized in the space or not.
- Does it satisfy the uncertainty principle?
- Then, we want to describe the time evolution of this system by obtaining and analyzing $\psi(x, t)$.
- We use Eq. 31 to first compute $\psi(x, 0)$

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx} dk$$

- Which for the present case is

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}} \frac{\sqrt{a}}{(2\pi)^{1/4}} \int_{-\infty}^{\infty} e^{-\frac{a^2}{4}(k-k_0)^2 + ikx} dk$$

1D Gaussian wave packet...

- Let us change the integration variable to $k' = k - k_0$, so that

$$\psi(x,0) = \frac{e^{ik_0 x}}{\sqrt{2\pi}} \frac{\sqrt{a}}{(2\pi)^{1/4}} \int_{-\infty}^{\infty} e^{-\frac{a^2 k'^2}{4} + ik'x} dk'$$

- Next we write the exponent in the integral in the form of a perfect square

$$\begin{aligned} -\frac{a^2 k'^2}{4} + ik'x &= -\frac{a^2}{4}\left(k'^2 - \frac{4ik'x}{a^2} - \frac{4x^2}{a^4} + \frac{4x^2}{a^4}\right) \\ &= -\frac{a^2}{4}\left(k' - \frac{2ix}{a^2}\right)^2 - \frac{x^2}{a^2} \end{aligned}$$

- Substituting this above, we have

$$\psi(x,0) = \frac{e^{ik_0 x - x^2/a^2}\sqrt{a}}{(2\pi)^{3/4}} \int_{-\infty}^{\infty} e^{-\frac{a^2}{4}\left(k' - \frac{2ix}{a^2}\right)^2} dk'$$

1D Gaussian wave packet...

- We make another change of integration variables to $z = \frac{a}{2}\left(k' - \frac{2ix}{a^2}\right)$, leading to

$$\psi(x,0) = \frac{2e^{ik_0x - x^2/a^2}}{(2\pi)^{3/4}\sqrt{a}} \int_{-\infty}^{\infty} e^{-z^2}\,dz$$

- The integral above is quite famous, and is called Gaussian integral, whose value is $\sqrt{\pi}$

$$\int_{-\infty}^{\infty} e^{-z^2}\,dz = \sqrt{\pi}$$

- Using this we obtain

$$\psi(x,0) = \left(\frac{2}{\pi a^2}\right)^{1/4} e^{ik_0x - x^2/a^2} \tag{39}$$

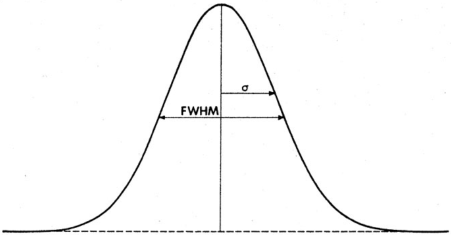
- This clearly is a plane wave of momentum $\hbar k_0$, whose amplitude decays as we move away from $x = 0$

1D Gaussian wave packet...

- From which we obtain

$$|\psi(x,0)|^2 = \left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2x^2/a^2}$$

- Which is also a Gaussian function, but centered at $x = 0$, and the plot will look like



The function plotted above is

$$f(x) = \frac{1}{\sigma\sqrt{\pi}} e^{-x^2/2\sigma^2}$$

1D Gaussian wave packet...

- For a Gaussian function of the form $e^{-(x-x_0)^2/b^2}$, the width is defined as $\Delta x = b/\sqrt{2}$
- Therefore, for $|\psi(x,0)|^2$ it will be

$$\Delta x = \frac{a}{\sqrt{2}\sqrt{2}} = \frac{a}{2}$$

- And for $|g(k)|^2$ the width will be

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

- Therefore,

$$\Delta x \Delta k = \frac{1}{2} \implies \Delta p \Delta x = \frac{\hbar}{2}$$

- Which is minimum allowed uncertainty as per Heisenberg uncertainty principle
- That is why a Gaussian wave packet is also called a minimum uncertainty wave packet

Time-dependent 1D Gaussian Wave packet

- We know that the time-dependence of a general 1D wave packet is (Eq. 30)

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx-\omega(k)t)} dk$$

- For, the Gaussian wave packet we have

$$\psi(x,t) = \frac{\sqrt{a}}{(2\pi)^{3/4}} \int_{-\infty}^{\infty} e^{-\frac{a^2}{4}(k-k_0)^2 + ikx - i\frac{\hbar k^2}{2m}t} dk,$$

above we used $\omega(k) = \dfrac{\hbar k^2}{2m}$.

Time-dependent 1D Gaussian wave packet

- By substituting $k' = k - k_0$, and on simplification, we obtain

$$\psi(x,t) = \frac{\sqrt{a}e^{-i\hbar k_0^2 t/2m + ik_0 x}}{(2\pi)^{3/4}} \int_{-\infty}^{\infty} dk' e^{-\left(\frac{a^2}{4}+\frac{i\hbar t}{2m}\right)k'^2 + ik'(x - v_g t)} dk'$$

where $v_g = \left.\frac{d\omega}{dk}\right|_{k=k_0} = \frac{\hbar k_0}{m}$ is the group velocity of the wave packet.

- Next, by making the substitution

$$k'' = \left(\frac{a^2}{4}+\frac{i\hbar t}{2m}\right)^{1/2}\left(k' - \frac{i(x - v_g t)}{\left(\frac{a^2}{4}+\frac{i\hbar t}{2m}\right)}\right)$$

and completing the perfect square in the exponent and using the Gaussian integral as before, we obtain

$$\psi(x,t) = \frac{\sqrt{a\pi}e^{i(k_0 x - \omega(k_0)t)}}{\left(\frac{a^2}{4}+\frac{i\hbar t}{2m}\right)^{1/2}} \exp - \left(\frac{(x - v_g t)^2}{a^2 + \frac{2i\hbar t}{m}}\right)$$

1D time-dependent wave packet...

- The previous expression can be further rationalized

$$\psi(x,t) = \left(\frac{2a^2}{\pi}\right)^{1/4} \frac{e^{i(k_0 x - \omega(k_0)t) - i\theta(t)}}{\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)^{1/4}} \exp - \left(\frac{(x - v_g t)^2}{a^2 + \frac{2i\hbar t}{m}}\right)$$

  above θ is determined by $\tan 2\theta = \frac{2\hbar t}{ma^2}$

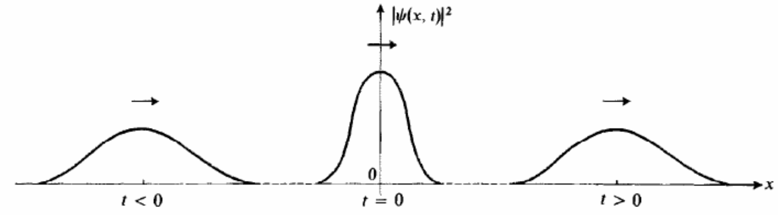
- The previous expression is quite tedious
- But, we get a somewhat simpler expression for the probability density

$$|\psi(x,t)|^2 = \sqrt{\frac{2}{\pi a^2}} \frac{1}{\sqrt{1 + \frac{4\hbar^2 t^2}{m^2 a^4}}} \exp\left\{ - \frac{2a^2 (x - v_g t)^2}{a^4 + \frac{4\hbar^2 t^2}{m^2}} \right\}$$

- However, one can show that the total probability associated with the wave packet $\int_{-\infty}^{\infty} dx |\psi(x,t)|^2 = 1$, i.e., it is time independent as it should be.

Time evolution of 1D Gaussian Wave Packet

- The plot of $|\psi(x,t)|^2$ as a function of time looks like



- Clearly, the wave packed moves with the group velocity $v_g = \dfrac{\hbar k_0}{m}$
- As it moves, it undergoes deformation
- From the figure it is clear that in the past ($t < 0$) the width of the wave packet, $\Delta x(t)$ was larger than at $t = 0$, where it is minimum
- For $t > 0$ also the wave packet width is larger than at $t = 0$

Time evolution of Gaussian Wave packet...

- It is clear that $\Delta x(-t) = \Delta x(t)$
- Thus, for $t \in (-\infty, 0)$, the width increases with the increasing time
- But, for $t \in (0, \infty)$, the width decreases with the increasing time
- For $t \to \infty$, the wave packet becomes completely delocalized