Part IV

The Quantum formalism

Previous lecture

- Matrix elements of X matrix

$$\boldsymbol{x_{mn} = \int_{-\infty}^{\infty} \psi_m^*(x)\, x\, \psi_n(x)\, dx}$$

- Expectation value of $f(x)$

$$\boldsymbol{\langle f(x)\rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, f(x)\, \psi_n(x)\, dx}$$

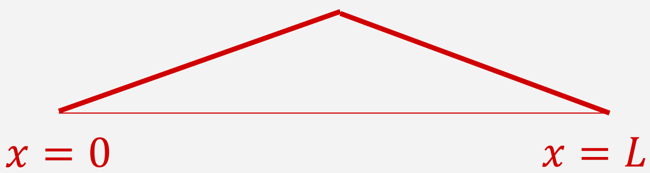
- Time-dependent Schrödinger equation

$$\boldsymbol{i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t)}$$

- For stationary-states $V(x,t) = V(x)$ and the eigenfunctions have the time-dependence

$$\boldsymbol{\psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}}$$

How does a wavefunction which is not an eigenfunction evolve with time?



Imagine a string pulled at time $t = 0$ in an arbitrary shape $f(x)$, which is not of the form of an eigenfunction. Then $\boldsymbol{f(x, t = 0) = \sum_n C_n \sin\left(\frac{n\pi}{L}x\right)}$.

Its time evolution is given as $\boldsymbol{f(x, t) = \sum_n C_n \sin\left(\frac{n\pi}{L}x\right) \cos \omega_n t}$

Similarly, if a system is out in a superposition of its eigenstates at time $t = 0$, its time evolution is obtained in exactly the same manner. Thus (*you will show this by solving an Assignment problem*)

$$\boldsymbol{f(x, t = 0) = \sum_n C_n \psi_n(x)} \text{ and } \boldsymbol{f(x, t) = \sum_n C_n \psi_n(x) e^{-iE_n t/\hbar}}$$

Previous lecture

- Time-dependent matrix elements of X matrix

$$x_{\alpha\beta}(t) = \int_{-\infty}^{\infty} \psi_\alpha^*(x)\, x\, \psi_\beta(x)\, dx \;\; e^{i\omega_{\alpha\beta}t} \;\; ; \;\; \omega_{\alpha\beta} = \frac{E_\alpha - E_\beta}{\hbar}$$

- Matrix elements of velocity matrix

$$v_{\alpha\beta} = \frac{dx_{\alpha\beta}}{dt} = i\omega_{\alpha\beta}x_{\alpha\beta}$$

- Matrix elements of momentum matrix p

$$p_{\alpha\beta} = mv_{\alpha\beta} = im\omega_{\alpha\beta}x_{\alpha\beta}$$

Lecture 22

Momentum operator;

Equivalence of Heisenberg and Schrödinger formulations;

The uncertainty principle

The momentum operator

How to get $\boldsymbol{p_{\alpha\beta}}$ from the wavefunction directly without taking the time-derivative of $\boldsymbol{x_{\alpha\beta}}$

$$x_{\alpha\beta}(t) = \int_{-\infty}^{\infty} \psi_\alpha^*(x,t)\, x\, \psi_\beta(x,t)\, dx$$

$$\frac{dx_{\alpha\beta}(t)}{dt} = \int_{-\infty}^{\infty} \frac{\partial \psi_\alpha^*(x,t)}{\partial t}\, x\, \psi_\beta(x,t)\, dx + \int_{-\infty}^{\infty} \psi_\alpha^*(x,t)\, x\, \frac{\partial \psi_\beta(x,t)}{\partial t} dx$$

$$\frac{\partial \psi_\alpha^*(x,t)}{\partial t} = \frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2 \psi_\alpha^*(x,t)}{\partial x^2} + V(x)\psi_\alpha^*(x,t)\right]$$

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

$$\frac{dx_{\alpha\beta}(t)}{dt} = \frac{i}{\hbar}\int_{-\infty}^{\infty}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi_\alpha^*(x,t)}{\partial x^2} + \cancel{V(x)\psi_\alpha^*(x,t)}\right] x\,\psi_\beta(x,t)\,dx$$

$$-\frac{i}{\hbar}\int_{-\infty}^{\infty}\psi_\alpha^*(x,t)\,x\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi_\beta(x,t)}{\partial x^2} + \cancel{V(x)\psi_\beta(x,t)}\right]dx$$

$$\frac{dx_{\alpha\beta}(t)}{dt} = \frac{\hbar}{2im}\int_{-\infty}^{\infty}\left[\frac{\partial^2\psi_\alpha^*(x,t)}{\partial x^2}\,x\,\psi_\beta(x,t) - \psi_\alpha^*(x,t)\,x\,\frac{\partial^2\psi_\beta(x,t)}{\partial x^2}\right]dx$$

$$\frac{\partial^2 \psi_\alpha^*(x,t)}{\partial x^2}\, x\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, x\, \frac{\partial^2 \psi_\beta(x,t)}{\partial x^2} = \frac{\partial}{\partial x}\left[\frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, x\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, x\, \frac{\partial \psi_\beta(x,t)}{\partial x}\right]$$

$$-\left[\frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, \frac{\partial \psi_\beta(x,t)}{\partial x}\right] - \cancel{\left[\frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, x\, \frac{\partial \psi_\beta(x,t)}{\partial x} - \frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, x\, \frac{\partial \psi_\beta(x,t)}{\partial x}\right]}$$

0

$$\int_{-\infty}^{\infty}\left[\frac{\partial^2 \psi_\alpha^*(x,t)}{\partial x^2}\, x\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, x\, \frac{\partial^2 \psi_\beta(x,t)}{\partial x^2}\right] dx$$

The integral is 0

$$= \cancel{\int_{-\infty}^{\infty} \frac{\partial}{\partial x}\left[\frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, x\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, x\, \frac{\partial \psi_\beta(x,t)}{\partial x}\right] dx}$$

$$-\int_{-\infty}^{\infty}\left[\frac{\partial \psi_\alpha^*(x,t)}{\partial x}\, \psi_\beta(x,t) - \psi_\alpha^*(x,t)\, \frac{\partial \psi_\beta(x,t)}{\partial x}\right] dx$$

$$\int_{-\infty}^{\infty}\left[\frac{\partial^2\psi_\alpha^*(x,t)}{\partial x^2}x\,\psi_\beta(x,t)-\psi_\alpha^*(x,t)\,x\,\frac{\partial^2\psi_\beta(x,t)}{\partial x^2}\right]dx$$

$$=-\int_{-\infty}^{\infty}\left[\frac{\partial\psi_\alpha^*(x,t)}{\partial x}\,\psi_\beta(x,t)-\psi_\alpha^*(x,t)\,\frac{\partial\psi_\beta(x,t)}{\partial x}\right]dx$$

Integration by parts gives

$$\int_{-\infty}^{\infty}\frac{\partial\psi_\alpha^*(x,t)}{\partial x}\,\psi_\beta(x,t)dx=-\int_{-\infty}^{\infty}\psi_\alpha^*(x,t)\,\frac{\partial\psi_\beta(x,t)}{\partial x}dx$$

Therefore

$$\boldsymbol{p_{\alpha\beta}}=m\frac{dx_{\alpha\beta}(t)}{dt}=\frac{\hbar}{2i}\int_{-\infty}^{\infty}\left[\frac{\partial^2\psi_\alpha^*(x,t)}{\partial x^2}x\,\psi_\beta(x,t)-\psi_\alpha^*(x,t)\,x\,\frac{\partial^2\psi_\beta(x,t)}{\partial x^2}\right]dx$$

$$=\int_{-\infty}^{\infty}\boldsymbol{\psi_\alpha^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi_\beta(x,t)dx}$$

Momentum operator and calculating momentum using the wavefunction

- Momentum operator and its matrix elements

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad\qquad p_{mn} = \int \psi_m^*(x)\,\frac{\hbar}{i}\frac{\partial \psi_n(x)}{\partial x}$$

- Expectation value of momentum

$$\langle p_x \rangle = \int \psi^*(x)\,\frac{\hbar}{i}\frac{\partial \psi(x)}{\partial x}$$

Operators for other quantities related to momentum

- Operator for square of momentum and its expectation value

$$\hat{p}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2} \qquad \langle p_x^2 \rangle = -\hbar^2 \int \psi^*(x) \frac{\partial^2 \psi(x)}{\partial x^2}$$

- Kinetic energy (KE) operator and its expectation value

$$\frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \langle KE \rangle = -\frac{\hbar^2}{2m} \int \psi^*(x) \frac{\partial^2 \psi(x)}{\partial x^2}$$

Energy operator (Hamiltonian) and the Schrödinger equation

- Energy operator, called Hamiltonian, and denoted by $\widehat{H}$

$$\widehat{H} = KE + PE = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

- Schrödinger equation

$$\widehat{H}\psi = E\psi$$

Does the operator form lead to the Quantum condition?

- Operator for position

$$\hat{x}\psi(x) = x\psi(x)$$

- Operator for momentum

$$\hat{p}_x\psi(x) = \frac{\hbar}{i}\frac{\partial\psi(x)}{\partial x}$$

- Quantum condition

$$(\hat{\boldsymbol{x}}\hat{\boldsymbol{p}}_x - \hat{\boldsymbol{p}}_x\hat{\boldsymbol{x}})\boldsymbol{\psi}(\boldsymbol{x}) = \boldsymbol{x}\frac{\hbar}{\boldsymbol{i}}\frac{\boldsymbol{\partial\psi}(\boldsymbol{x})}{\boldsymbol{\partial x}} - \frac{\hbar}{\boldsymbol{i}}\frac{\boldsymbol{\partial}\left(\boldsymbol{x\psi}(\boldsymbol{x})\right)}{\boldsymbol{\partial x}} = \boldsymbol{i}\hbar\boldsymbol{\psi}(\boldsymbol{x})$$

$$\Rightarrow \boldsymbol{x}\boldsymbol{p}_x - \boldsymbol{p}_x\boldsymbol{x} = \boldsymbol{i}\hbar$$

Complete equivalence between the Heisenberg and the Schrödinger formalisms established

Heisenberg	Schrödinger
ω_{mn}	$\dfrac{E_m - E_n}{\hbar}$
x_{mn}	$\int \psi_m^*(x,t)\, x\, \psi_n(x,t) dx$
p_{mn}	$\int \psi_m^*(x,t) \dfrac{\hbar}{i} \dfrac{\partial \psi_n(x,t)}{\partial x} dx$
Quantum condition $xp_x - p_x x = i\hbar I$	$\int \psi_m^*(x,t) \left(x \dfrac{\hbar}{i} \dfrac{\partial \psi_n(x,t)}{\partial x} - \dfrac{\hbar}{i} \dfrac{\partial}{\partial x} x \psi_n(x,t) \right) dx = i\hbar \delta_{mn}$
Equation of motion $\dot{p} = F(x)$	$i\hbar \dfrac{\partial \psi(x,t)}{\partial t} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t)$

A fundamental principle followed by nature:
The uncertainty principle

Some questions raised by discovery of quantum nature of the world:

- In interference experiment with electrons, which slit does the electron pass from?
- When an electron makes a jump from one quantum-state to another, where is it during the transition?
- Where is the electron when an electron moving in a Wilson cloud chamber leaves makes a trail (reference: Cloud chamber – Wikipedia)?

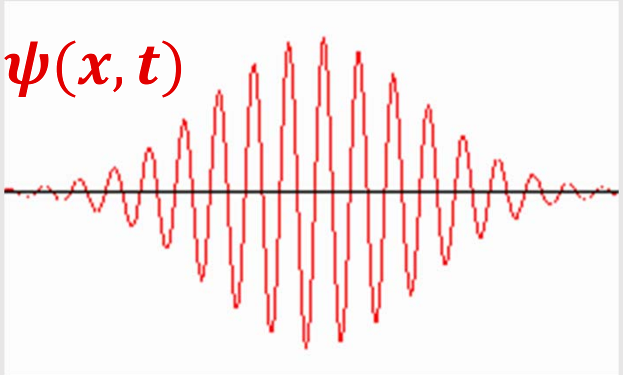
The uncertainty principle

One cannot determine **(nature does not allow it)** both the position and the momentum of a particle in a given direction with arbitrary accuracy simultaneously.

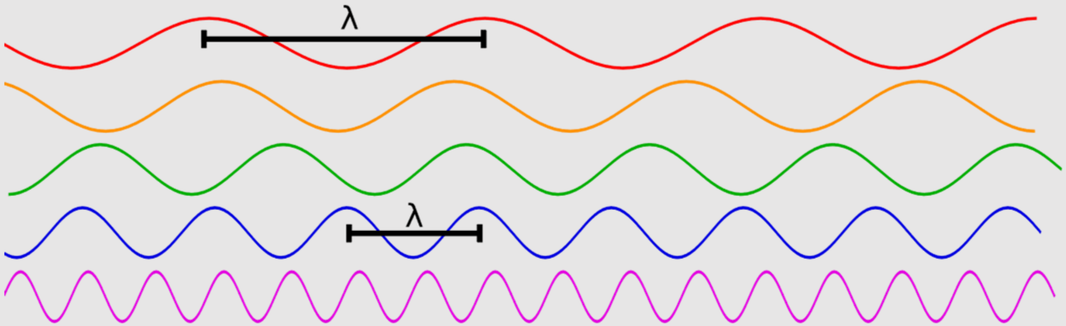
Bohr's complementarity principle: one cannot see both the particle nature (position) and the wave nature (momentum or, equivalently, the wavelength) simultaneously. Both are, however, required and complement each other for a complete description.

Both these principles manifest themselves beautifully in the interference experiments with electrons. **HOW SO?** is left for you to think.

Position and momentum of a particle



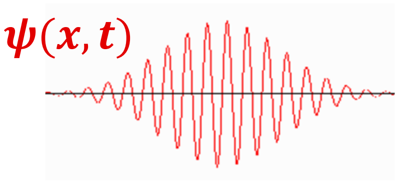
=



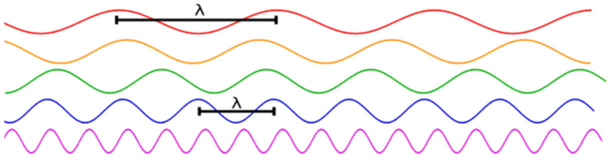
Where in this wavepacket is the particle?

What is the momentum of the particle?

Mathematical representation

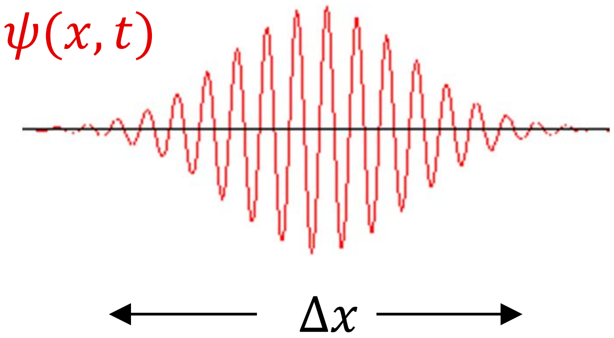


$=$

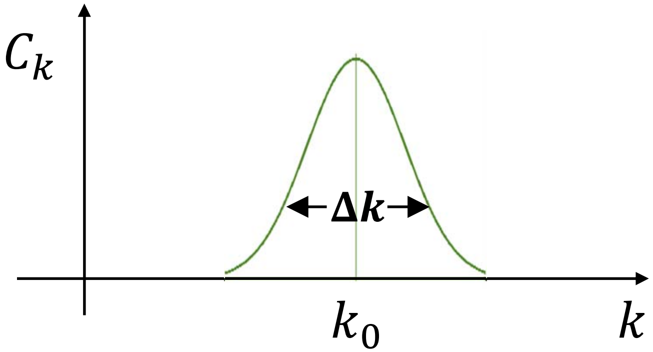


$$\psi(x,t) = \sum_k C_k e^{i(kx-\omega t)}$$

To be consistent with the time-dependence in quantum theory given by $e^{-i\omega t}$, we expand the function $\psi(x,t)$ in terms of $e^{i(kx-\omega t)}$ rather than in terms of $\sin(kx - \omega t + \phi)$.



$\equiv$



Definition of uncertainty and the resulting uncertainty product

Uncertainty in $x = \boldsymbol{\Delta x} = \sqrt{\langle(\boldsymbol{x^2} - \langle \boldsymbol{x} \rangle^2)\rangle} = \sqrt{\langle(\boldsymbol{x} - \langle \boldsymbol{x} \rangle)^2\rangle}$

Uncertainty in $p_x = \boldsymbol{\Delta p_x} = \sqrt{\left\langle\left(\boldsymbol{p_x^2} - \langle \boldsymbol{p_x} \rangle^2\right)\right\rangle} = \sqrt{\langle(\boldsymbol{p_x} - \langle \boldsymbol{p_x} \rangle)^2\rangle}$

Uncertainty product $\boldsymbol{\Delta x \Delta p_x} = \sqrt{\langle(\boldsymbol{p_x} - \langle \boldsymbol{p_x} \rangle)^2\rangle\langle(\boldsymbol{x} - \langle \boldsymbol{x} \rangle)^2\rangle}$

An inequality (Cauchy-Schwarz)

- Cauchy-Schwarz inequality for vectors

$$|\vec{a}|\left|\vec{b}\right| \geq \left|\vec{a}\cdot\vec{b}\right| = |\vec{a}|\left|\vec{b}\right|\cos\theta$$

- In the current case

This is like $|\vec{a}|\left|\vec{b}\right|$

$$\boldsymbol{\Delta x \Delta p_x} = \sqrt{\langle(p_x - \langle p_x\rangle)^2\rangle\langle(x - \langle x\rangle)^2\rangle}$$

$$\geq \sqrt{\langle(p_x - \langle p_x\rangle)(x - \langle x\rangle)\rangle^2}$$

$$= |\langle(\boldsymbol{p_x} - \langle\boldsymbol{p_x}\rangle)(\boldsymbol{x} - \langle\boldsymbol{x}\rangle)\rangle|$$

This is like $\left|\vec{a}\cdot\vec{b}\right|$

A bit of mathematical manipulation and using the quantum condition

$$|\langle(p_x - \langle p_x\rangle)(x - \langle x\rangle)\rangle| = \left|\langle p_x x - p_x\langle x\rangle - \langle p_x\rangle x + \langle p_x\rangle\langle x\rangle\rangle\right|$$

$$\left\langle p_x x - p_x\langle x\rangle - \langle p_x\rangle x + \langle p_x\rangle\langle x\rangle\right\rangle = \left\langle p_x x - \langle p_x\rangle\langle x\rangle\right\rangle$$

$$\left\langle p_x x - \langle p_x\rangle\langle x\rangle\right\rangle = \left\langle\frac{p_x x + x p_x}{2} - \langle p_x\rangle\langle x\rangle + \frac{p_x x - x p_x}{2}\right\rangle$$

$$|\langle(p_x - \langle p_x\rangle)(x - \langle x\rangle)\rangle| = \left|\left\langle\frac{p_x x + x p_x}{2}\right\rangle - \langle p_x\rangle\langle x\rangle - \frac{i\hbar}{2}\right|$$

Uncertainty relation follows from the quantum condition

$$|\langle (p_x - \langle p_x \rangle)(x - \langle x \rangle) \rangle| = \left| \left\langle \frac{p_x x + x p_x}{2} \right\rangle - \langle p_x \rangle \langle x \rangle - \frac{i\hbar}{2} \right|$$

$\left\langle \frac{p_x x + x p_x}{2} \right\rangle$, $\langle p_x \rangle$ and $\langle x \rangle$ are all real numbers

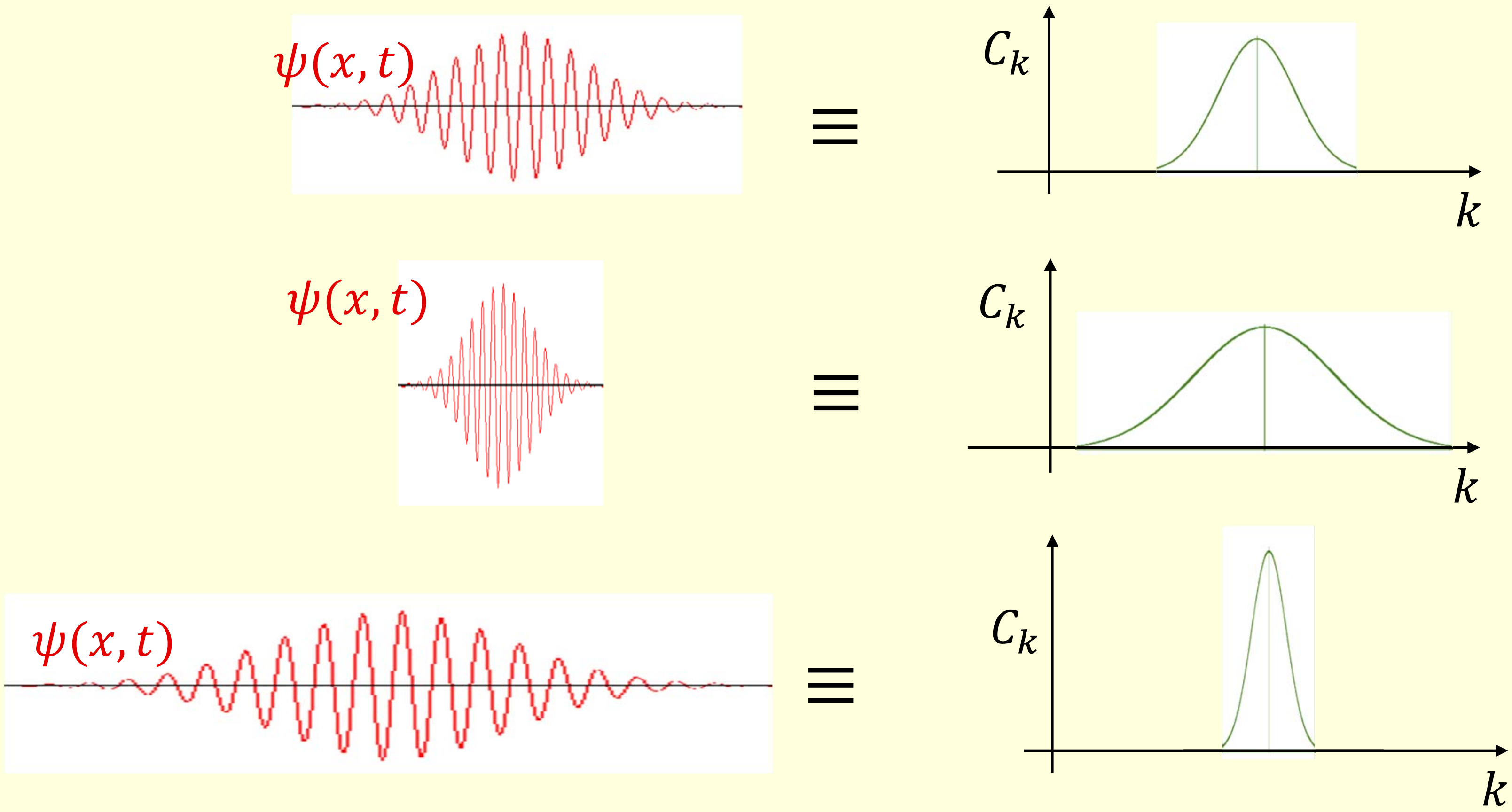
$$\boldsymbol{\Delta x \Delta p_x \geq |\langle (p_x - \langle p_x \rangle)(x - \langle x \rangle) \rangle| = \sqrt{R^2 + \frac{\hbar^2}{4}} \geq \frac{\hbar}{2}}$$

This inequality is a result of the quantum condition

The uncertainty relation

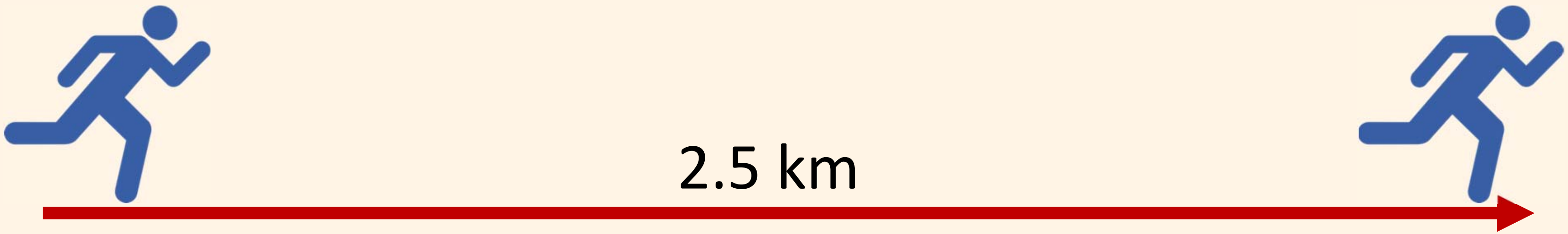
$$\boldsymbol{\Delta x \Delta p_x \geq \frac{\hbar}{2}}$$

Pictorial representation



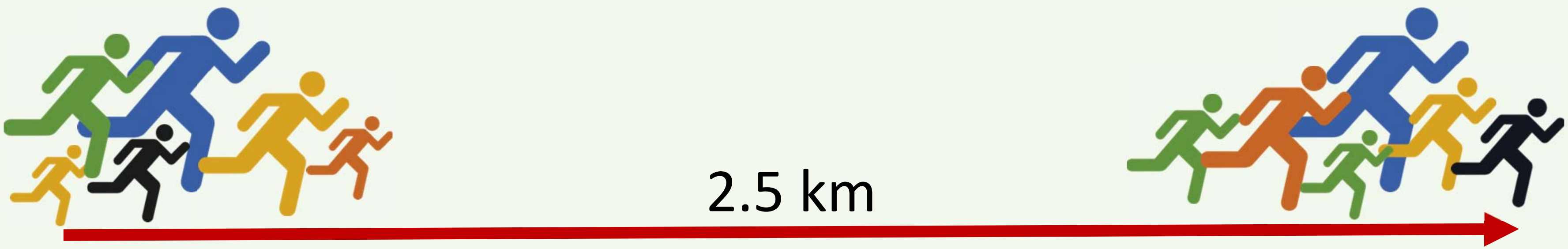
<u>Classical statement</u>:

"A person at the origin is running along the x-axis with a speed of 5 km per hour and will be at x = 2.5 km in half an hour"



<u>Quantum mechanical statement</u>:

"A person around the origin is walking along the x-axis with a speed of about 5 km per hour and will be around x = 2.5 km in half an hour"



In the figure above, the same person is shown to be at different places around the origin and around x = 2.5 km with the probability proportional to the size of the figure. The speed at each point is also different and has been shown by different colours.

Energy-Time uncertainty relationship

A related uncertainty relation is between the energy and the time of observation of a system. It states if a system is observed for time Δt, its energy will have an uncertainty ΔE such that

$$\boldsymbol{\Delta E \Delta t \geq \frac{\hbar}{2}}$$

For example, consider an excited state of an atom that has life time $\tau = \frac{1}{A}$, where A is the coefficient for spontaneous emission. Thus, on the average we will be able to observe the state for a maximum time of τ. This makes the energy of the excited state uncertain by $\Delta E = \frac{\hbar}{2\tau}$. Therefore, the frequency of emission has a spread $\Delta\nu \sim \frac{1}{\tau} = A$, which is roughly equal to $\frac{1}{\tau}$ or equivalently equal to coefficient of spontaneous emission.

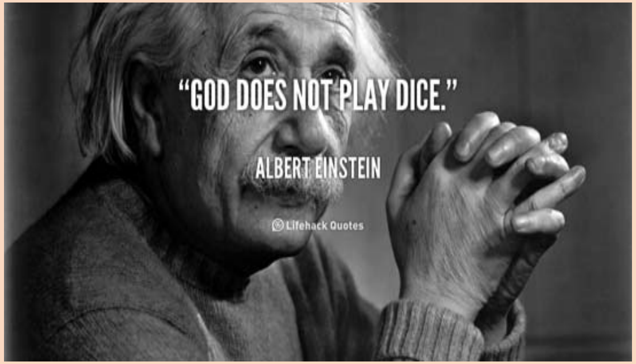
Some consequences of the uncertainty principle

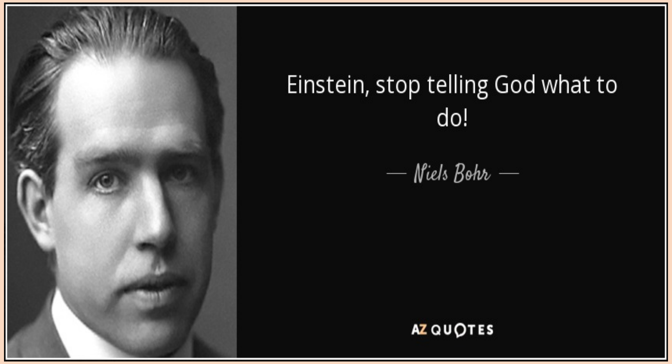
- If a particle is more (less) confined, it has higher (lower) kinetic energy.
- A covalent bond is formed when an electron is shared between two or more nuclei.
- Lowest energy of a particle in box or a harmonic oscillator is not zero.
- Force between nucleons in an nucleus is mediated by a particle called $\pi - \mathrm{meson}$ with a mass of about 200 to 300 times the mass of an electron.

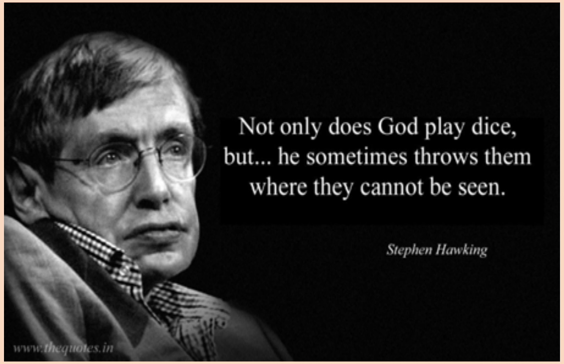
Concluding remarks

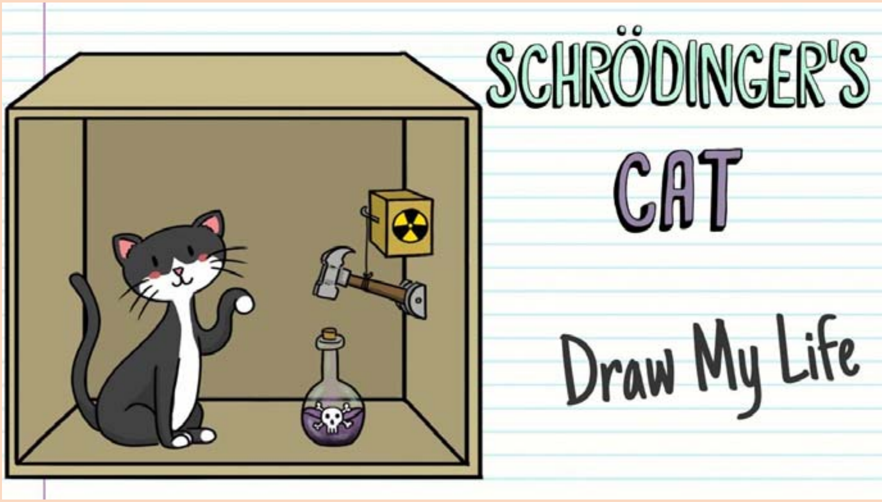
The uncertainty principle and the complementarity principle are results of the quantum nature – the quantum condition and probability interpretation of wavefunction – of the world. All these together form the basis of the **Copenhagen interpretation of quantum mechanics** with Bohr and Heisenberg being its main proponents.

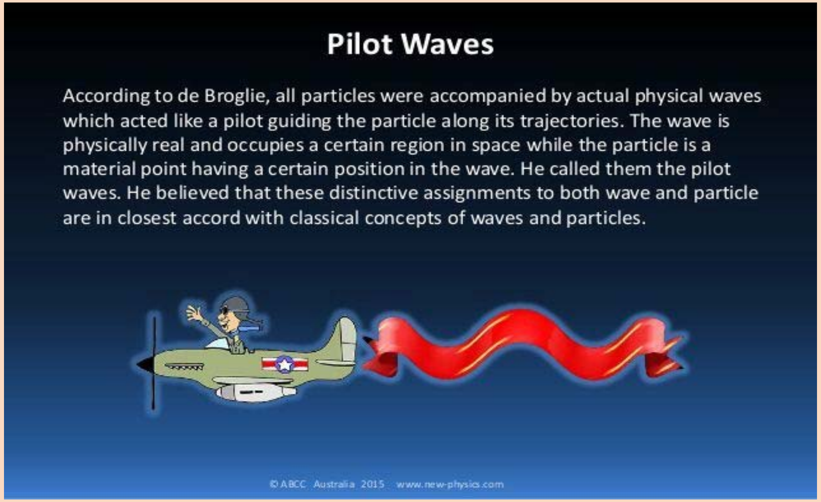
Einstein, Schrödinger and de Broglie never accepted this interpretation. Their critical ways of finding loopholes in it resulted in many excellent debates, suggested new experiments and led to further advancement of the field. Nobel prize for the year 2022 is the latest in that series.



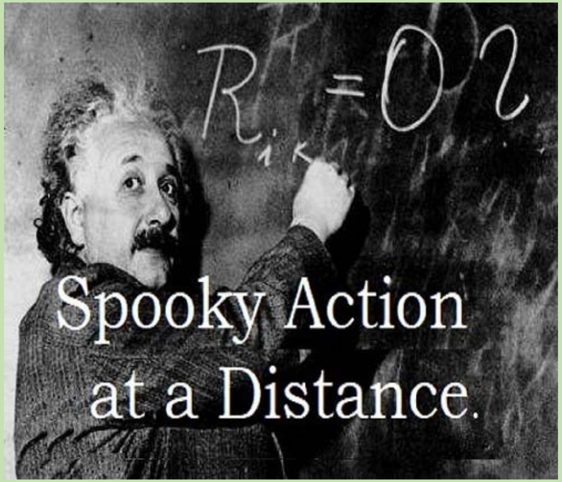


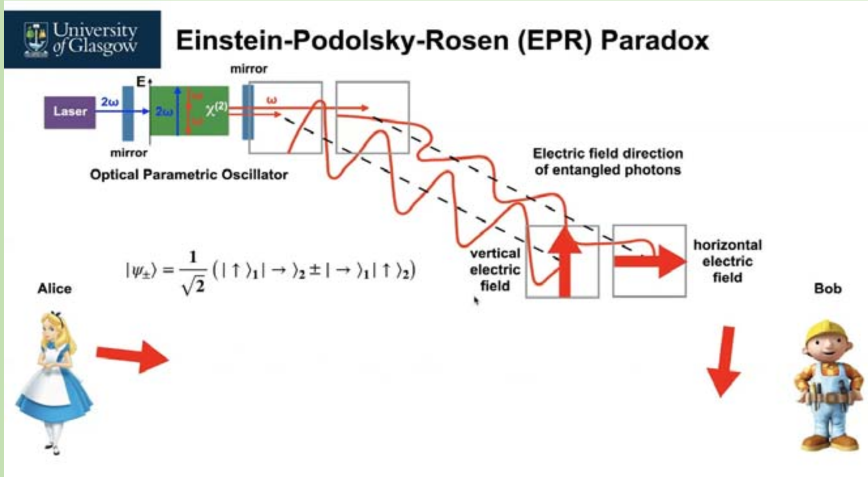


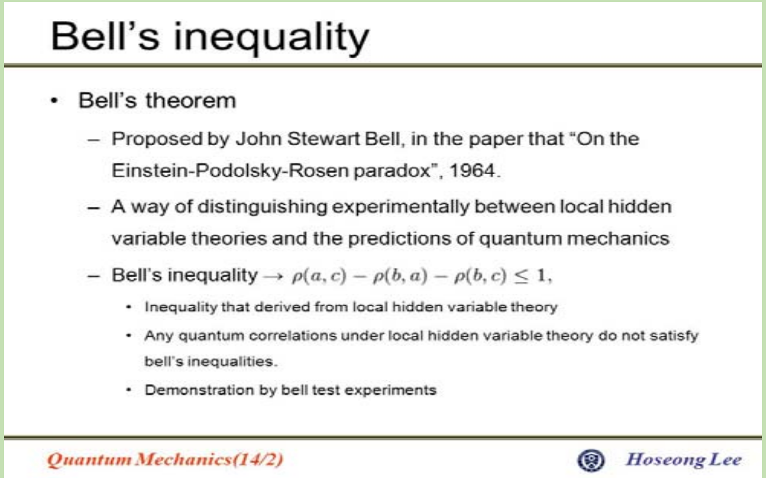


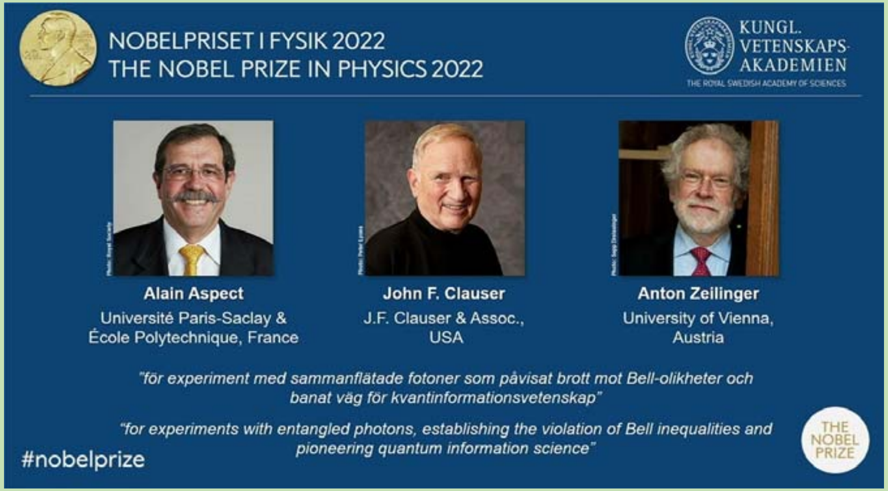


Source: Images on the internet









Source: Images on the internet