2-4 The Schrödinger equation

$$\boxed{\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int dp \; \Phi(p)\, e^{i(px - Et)/\hbar}} \leftarrow \text{Fourier transform}$$

$\omega = \frac{E}{\hbar}$ ← Planck's relation

$k = \frac{p}{\hbar}$ ← de Broglie relation

For free particle : $E(p) = \frac{p^2}{2m}$, $v_g = \frac{\partial \omega}{\partial k} = \frac{\partial E}{\partial p} = \frac{p}{m}$

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp\, \Phi(p)\, \frac{p^2}{2m}\, e^{i(px-Et)/\hbar}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p)\, p\, e^{i(px-Et)/\hbar}\, dp$$

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 \Psi(x,t) = \frac{1}{\sqrt{2m\hbar}} \int_{-\infty}^{\infty} \Phi(p)\, p^2\, e^{i(px-Et)/\hbar}\, dp$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = i\hbar\frac{\partial\Psi}{\partial t}} \leftarrow \text{SE for a plane wave}$$

If $E = \frac{p^2}{2m} + V(x)$, one can guess the solution

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

SE for a particle in the potential $V(x)$

Even though $\Psi(x,t)$ is a "wave amplitude", the equation is different from the classical wave eq:

$$\frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2} = \frac{\partial^2\Psi}{\partial x^2}$$

SE is a first-order differential equation in t, therefore the initial value at $t = t_0$, $\Psi(x, t_0)$, is sufficient for a solution

* Initial value:

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

this is a Fourier integral, therefore

$$\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x,0) \, e^{-ipx/\hbar} \, dx \, .$$

2-5. The Heisenberg uncertainty relation

From the package propagation: $\Delta k \, \Delta x > 1/2 \rightarrow$

$\rightarrow \boxed{\Delta p \, \Delta x \geq \hbar/2}$ Heisenberg uncertainty relation

What does it mean?

If $\Psi(x)$ fully describes the state of the system, then

$$\Delta x = \left[\int \Psi^*(x) \, x^2 \, \Psi(x) \, dx - \left(\int \Psi^*(x) \, x \, \Psi(x) \, dx \right)^2 \right]^{1/2}$$

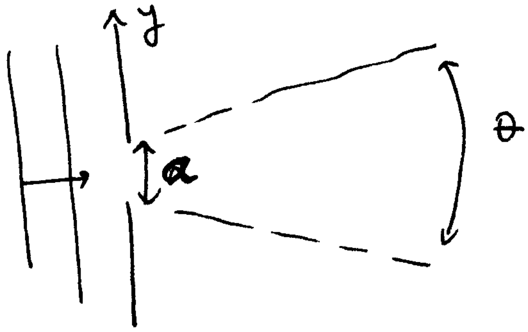
and

$$\Delta p = \left[\int \Psi^*(x) \, p^2 \, \Psi(x) \, dx - \left(\int \Psi^*(x) \, p \, \Psi(x) \, dx \right)^2 \right]^{1/2}$$

cannot be zero and their product is of the order of $\hbar$. Variables connected by uncertainty relations are called complementary. They also do not commute in the operator representation.

Examples of uncertainty relations

Beam of photons



$$\theta \approx \frac{\lambda}{a}$$

$$\Delta y \approx a$$

$$\Delta p_y \approx \frac{h}{\Delta y} = \frac{h}{a}$$

$$\theta = \frac{\Delta p_y}{p_x} = \frac{h}{a\, h/\lambda} = \frac{\lambda}{a}$$

Bohr orbits

$\lambda \ll r_{n+1} - r_n$ ← condition to distinguish between Bohr orbits with light

$$\frac{\hbar}{m_e c \alpha}\left((n+1)^2 - n^2\right) \approx \frac{h}{m_e c \alpha} n$$

$$p_\gamma = \frac{h}{\lambda} \gg \frac{m_e c \alpha}{n}$$

$$\Delta E = \frac{p \Delta p}{m_e} \gg \frac{m_e (c\alpha)^2}{n^2} \leftarrow$$

an attempt to see an electron on the orbit requires uncontrollable transfer of momentum

what cannot be measured does not exsist → there are <u>no</u> Bohr orbits in atoms

Energy – lifetime uncertainty:

$$\Delta E\ \Delta t > h$$

ΔE: uncertainty in energy

Δt: lifetime of a quantum state

2-6. Quantum probability

Normalization condition:

for any $\psi(x,t)$ that satisfies the SE eq., $A\psi(x,t)$ also satisfies the same equation. The factor A can be chosen to satisfy the normalization condition:

$$A^2 \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1$$

Phase: $\psi = Re^{i\theta}$, $R = [(\psi')^2 + (\psi'')^2]^{1/2}$

$\theta = \tan^{-1}(\psi''/\psi')$ real part, imaginary part

the phase θ does not affect $|\psi| = R$.

However, when ψ is not an eigenstate,

$$|\psi_1 + \psi_2|^2 = |R_1 e^{i\theta_1} + R_2 e^{i\theta_2}|^2 = R_1^2 + R_2^2 + \underbrace{2R_1 R_2 \cos(\theta_1 - \theta_2)}_{\text{interference}}$$

The probability current:

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

real potential

$$\frac{\partial P}{\partial t} = \frac{\partial |\psi|^2}{\partial t} = \frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} = \frac{\hbar}{2mi}\left(\psi\frac{\partial^2 \psi^*}{\partial x^2} - \psi^*\frac{\partial^2 \psi}{\partial x^2}\right) =$$

$$= -\frac{\partial}{\partial x}\left[\frac{\hbar}{2mi}\left(\psi^*\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right)\right]$$

Conservation equation (similar to mass conservation)

$$\boxed{\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} j(x,t), \qquad j(x,t) = \frac{\hbar}{2mi}\left(\psi^*\frac{\partial \psi}{\partial x} - \psi\frac{\partial \psi^*}{\partial x}\right)}$$

2-7. Expectation values and the momentum

Expectation values are observables of experimental measurements, we need some rules of how to connect the quantum equations to measurements

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} P(x,t)\, f(x)\, dx \quad \xrightarrow{\text{correct implication}}$$

probability density, $P(x,t) = |\psi(x,t)|^2$

$$\longrightarrow \int_{-\infty}^{\infty} \psi^*(x,t)\, f(x)\, \psi(x,t)\, dx$$

observable varible

flanked by wave function on two sides

Momentum observation

$$p = m \frac{dx}{dt}$$

$$\langle p \rangle = m \frac{d}{dt} \int dx\, \psi^*(x,t)\, x\, \psi(x,t) = m \int dx\, x \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) =$$

$$= \frac{\hbar}{2i} \int dx \left(x\psi \frac{\partial^2 \psi^*}{\partial x^2} - x\psi^* \frac{\partial^2 \psi}{\partial x^2} \right)$$

SE

$$x\psi \frac{\partial^2 \psi^*}{\partial x^2} = \frac{\partial}{\partial x}\left(x\psi \frac{\partial \psi^*}{\partial x} \right) - \psi \frac{\partial \psi^*}{\partial x} - x \frac{\partial \psi}{\partial x} \frac{\partial \psi^*}{\partial x}$$

$$= \frac{\hbar}{2i} \int dx \left[\frac{\partial}{\partial x} \left(x\psi \frac{\partial \psi^*}{\partial x} - x\psi^* \frac{\partial \psi}{\partial x} \right) - \psi \frac{\partial \psi^*}{\partial x} + \psi^* \frac{\partial \psi}{\partial x} \right]$$

$$= \frac{\hbar}{i} \int dx\, \psi^* \frac{\partial \psi}{\partial x} = \int dx\, \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi$$

Finally,

$$\boxed{\langle p \rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t) \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi(x,t)}$$

In order to calculate the expectation value of a function of p, one needs to replace p with the operator:

$$\boxed{\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}}$$

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \underline{\underline{f\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)}}\, \Psi(x,t)\, dx$$

the operator function goes in between Ψ^* and Ψ

! Show that $\langle p \rangle = \langle p \rangle^*$, i.e. physical observables are real numbers. Hermition operator has real expectation values!

Hamiltonian operator is obtained from the Hamiltonian of classical mechanics by replacing

$p \rightarrow \hat{p}$

Classical:

$$H(p,x) = \frac{p^2}{2m} + V(x)$$

Quantum:

$$H = \frac{\hat{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

Wave function in the momentum space

Fourier transformation suggests that, mathematically, representations in terms of $\psi(x)$ and $\Phi(p)$ are equivalent. What is the physical meaning of that

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

$$\int_{-\infty}^{\infty} dp\, \Phi^*(p)\Phi(p) = \int_{-\infty}^{\infty} \frac{dx}{2\pi\hbar}\, \psi(x) \int_{-\infty}^{\infty} dy\, \psi^*(y) \int_{-\infty}^{\infty} dp\, e^{ip(y-x)/\hbar} =$$

$$= \iint_{-\infty}^{\infty} dx\, dy\, \psi(x)\psi^*(y)\delta(x-y) = \int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1$$

if $\psi(x)$ is normalized, $\Phi(p)$ is normalized as well

$$\langle p \rangle = \int_{-\infty}^{\infty} dx\, \psi^* \frac{\hbar}{i}\frac{\partial \psi}{\partial x} = \int_{-\infty}^{\infty} dx\, \psi^*(x) \frac{\hbar}{i}\frac{\partial}{\partial x} \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p)\, e^{ipx/\hbar}\, dp$$

$$= \int_{-\infty}^{\infty} dp\, \Phi(p)\, p\, \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi^*(x)\, e^{ipx/\hbar}\, dx = \int_{-\infty}^{\infty} dp\, \Phi^*(p)\, p\, \Phi(p)$$

Since $\Phi(p)$ is sufficient to calculate the observables, one concludes that $\Phi(p)$ is <u>the wave function in the momentum space</u>

In this space, $\hat{x}$ becomes a non-local differential operator

$$\hat{x} = i\hbar \frac{\partial}{\partial p}$$

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} dp\, \Phi^*(p)\, f\!\left(i\hbar\frac{\partial}{\partial p}\right) \Phi(p)$$

Example

$$\psi(x) = 2\alpha\sqrt{\alpha}\, e^{-\alpha x}, \qquad x > 0$$

$$= 0, \qquad x < 0$$

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

$$= \frac{2\alpha\sqrt{\alpha}}{\sqrt{2\pi\hbar}} \int_0^{\infty} x\, e^{-(\alpha + \frac{ip}{\hbar})x}\, dx = \underbrace{-\sqrt{\frac{2\alpha^3}{\pi\hbar}}\, \frac{1}{(\alpha + ip/\hbar)^2}}_{\phi(p) \text{ is complex!}}$$

even function

$$\langle p \rangle = \int_{-\infty}^{\infty} dp\, p\, |\phi(p)|^2 = 0$$

odd function

$$\langle p^2 \rangle = \frac{2\alpha^3}{\pi\hbar} \int_{-\infty}^{\infty} dp\, \frac{p^2}{(\alpha^2 + p^2/\hbar^2)^2} =$$

$$= \frac{2\alpha^3\hbar^3}{\pi} \int_{-\infty}^{\infty} dp\, \frac{p^2}{(p^2 + (\alpha\hbar)^2)^2} =$$

$$= \frac{2\alpha^3\hbar^3}{\pi}\, 2\pi i\, \frac{d}{dp} \frac{p^2}{(p + i\alpha\hbar)^2} \Bigg|_{p = i\alpha\hbar} =$$

$$= \frac{2\alpha^3\hbar^3}{\pi}\, 2\pi i \left[\frac{2i\alpha\hbar}{-4\alpha^2\hbar^2} - \frac{2\alpha^2\hbar^2}{8\alpha^3\hbar^3 i} \right] =$$

$$= \alpha^2\hbar^2$$

Operators and commutators

Once we introduce operators, we need to be concerned about their order in the product

acts on the right

$$\underbrace{x\ p}_{\text{product of operators}}\quad \underbrace{\psi(x)}_{\text{wave function}}$$

Product of operators acts on a wave function

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

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

$$(\hat{p}x - x\hat{p})\psi = -i\hbar\,\psi(x)$$

taking the operators separately,

$$\hat{p}x - x\hat{p} = -i\hbar = [\hat{p}, x]$$

commutation relation

Commutation relations is a mathematical representation of the Heisenberg uncertainty principle.