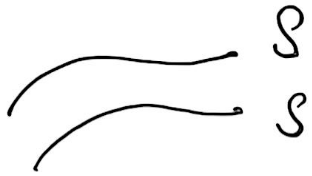
Lect 4 Wave mechanics

§ De Broglie's matter wave

§ Wave equation for matter wave.

Hint from Hamilton - Jacobi Eq



$$\psi(r,t) = e^{iS/K}$$

$$= e^{i(W(r)-Et)/K}$$

$$S = -i\hbar \ln \psi(r) - Et$$

Complex number "i" $\leftarrow$ $i\hbar \frac{\partial}{\partial t}\psi = H\psi$

§ unification wave and ~~me~~ matrix mechanics

$$[p, x] = \hbar/i \quad \longrightarrow \quad p = i\hbar \frac{d}{dx} \qquad H\psi_n = E_n \psi_n$$

$$\langle \psi_1 | \hat{O} | \psi_2 \rangle$$

$$= \int dx \, \psi_1 \, \hat{O} \, \psi_2$$

De Broglie : Matter wave

Einstein's photon hypothesis $E = \hbar\omega$

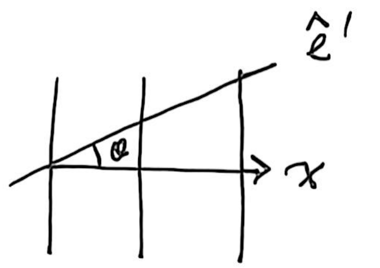
De Broglie's: Can we generalize this idea to material particles, say, electrons?

The question is how the frequency, i.e, osc(i)lation associate with the particle? If we view the particle has certain internal oscillation, there would be time dilation according to relativity. Hence, for a moving particle, the frequency would be lower, which is in contradictory to $E = \sqrt{p^2+m^2}$.

How to slove this problem? This frequency is not the frequency of a clock fixed to the electron. But a wave in accompanied with the particle, say, an electron. For a wave, what is invariance under frame transformation?

It is the number of periods, or, the phase is invarient.

$$\boxed{\vec{k}\cdot\vec{x} - \omega t = \text{const}}$$



wavevector λ multiplied with a direction, say $\lambda\hat{x}$. This is not a vector, because the wave vector along the direction of $\hat{e}'$ is longer. Rather, if we define $\vec{k} = \frac{2\pi}{\lambda}\hat{x}$, then

$\vec{k}\cdot\hat{e}' = k\cos\theta \Rightarrow \lambda_{e'} = \lambda/\cos\theta$. Hence $\vec{k}$ is a 3-vector

Similarly, for the relativitic case $\vec{k}\cdot\vec{x} - \omega t$ = scalar

and $(\vec{x}, t)$ transforms according to Lorentz transformation.

So does $(\vec{k}, \omega)$.

De Broglie assumed the group velocity $v_g = \frac{d\omega}{dk}$ as particle's velocity

relativistic particle $E = \sqrt{p^2c^2 + m_0^2 c^4} = mc^2$

$$v = \frac{p}{m} = \frac{pc^2}{E}$$

wave $v_g = \frac{d\omega}{dk} = v = \frac{pc^2}{E}$

$$\Rightarrow \left.\begin{aligned} \frac{\hbar d\omega}{\hbar dk} &= \frac{pc^2}{E} \\ E &= \hbar\omega \end{aligned}\right\} \Rightarrow \begin{aligned} &\tfrac{1}{2} dE^2 = \hbar c^2 p\, dk \\ &c^2 p\, dp = \hbar c^2 p\, dk \Rightarrow dp = \hbar dk \end{aligned}$$

or $p = h/\lambda$

$p \to 0$ take $\lambda \to \infty$ $\longrightarrow$

$$v_g v = \frac{\omega}{k}\frac{d\omega}{dk} = \frac{d\omega^2}{dk^2} = c^2$$

Debye's comment: if it is a wave, there should be a wave equation. — classical wave $\underline{(\nabla^2 + k^2)\psi(x) = 0}$

In fact De Broglie's picture is also valid in terms of non-relativistic physics — no-relativity is needed!

$\vec{k}\cdot\vec{x} - \omega t$ is also invariant under Galiean transform:

$$\begin{cases} x' = x - vt \\ t' = t \end{cases} \qquad \begin{cases} k' = k \\ \omega' = \omega - vk \end{cases} \Rightarrow \boxed{\vec{k}'\cdot\vec{x}' - \omega' t' = \vec{k}\cdot\vec{x} - \omega t}$$

non-relative particle $\begin{cases} E = \dfrac{p^2}{2m} \\ v = \dfrac{p}{m} \end{cases} \Rightarrow dE = \dfrac{p}{m}dp$, $\quad \dfrac{dE}{dp} = v$

wave $\quad v_g = \dfrac{d\omega}{dk}$

energy quantum $\quad E = \hbar\omega$

$$\Rightarrow v_g = \frac{1}{\hbar}\frac{dE}{dk} = v \text{ (identify } v = v_g)$$

$$\Rightarrow \frac{1}{\hbar}\frac{dE}{dk} = \frac{dE}{dp}$$

$$\Rightarrow \boxed{p = \hbar k}$$

Schröding Eq from Hamiton - Jacobi Eq.

$$S = S(x, p\, t ; x_0, p_0)$$

$$\begin{cases} \frac{\partial S}{\partial t} + H(x, p, t) = 0 \\ p = \frac{\partial S}{\partial x} \end{cases} \Rightarrow \frac{\partial S}{\partial t} + H\left(x, \frac{\partial S}{\partial x}\right) = 0$$

say. $\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 + V(x) = 0 \leftarrow \left(\frac{\partial}{\partial x} S\right)^2 \to (\nabla S)^2$ in 3d

Set $S = W(r) - Et \Rightarrow \boxed{(\nabla S)^2 = 2m(E - V(r))}$

Define the equal potentian surface

$$S(x, y, z, t) = \text{Const}$$

$S = c_1$

$$\frac{dS}{dt} = \frac{\partial S}{\partial t} + \nabla S \cdot \frac{d\vec{r}}{dt} = 0 \leftarrow$$ the equal vaule (phase) surface's motion

$$-E + \nabla S \cdot \frac{d\vec{r}}{dt} = 0$$

$$\vec{u} = \left|\frac{d\vec{r}}{dt}\right| = \frac{E}{|\nabla S|} = \frac{E}{\sqrt{2m(E-V)}}$$

$$P_x^2 + \cdots P_z^2 = \left(\frac{\partial}{\partial x} S\right)^2 + \cdots \left(\frac{\partial}{\partial z} S\right)^2$$

$\vec{u} \perp \nabla S$ this is the phase velocity, not the group velocity we set $\psi(r,t) = e^{iS/k} = e^{i(W(r)-Et)/k} = \psi(r)\, e^{-iEt/k}$

$E = \hbar\omega \Rightarrow k = \hbar \Rightarrow S = -i\hbar \ln\psi(r) - Et$

plug in $(\nabla S)^2 = 2m(E - V(r))$

$$\left.\begin{aligned}&(\nabla S)^2 = 2m(E-V(r))\\ &\nabla S = \frac{-i\hbar}{\psi(r)}\nabla\psi(r)\end{aligned}\right\} \Rightarrow -\hbar^2\left(\frac{1}{\psi(r)}\nabla\psi(r)\right)^2 = 2m(E - V(r))$$

$$\frac{\hbar^2}{2m}(\nabla\psi(r))^2 + (E - V(r))(\psi(r))^2 = 0$$

But as a wave equation, it should be linear, we linearize it

test

$$\boxed{\begin{aligned}&\psi = e^{ikr}\\ &\nabla\psi = ik\psi\\ &\nabla^2\psi = (ik)^2\psi\\ &\quad = (\nabla\psi)^2/\psi\end{aligned}}$$

$$\nabla\psi = \psi\cdot\frac{i}{\hbar}\nabla S$$

$$\nabla^2\psi = \nabla\psi\cdot\frac{i}{\hbar}\nabla S + \psi\frac{i}{\hbar}\nabla^2 S$$

$$= \cdots\ \psi\left(\frac{-1}{\hbar^2}\right)(\nabla S)^2 + \psi\frac{i}{\hbar}\nabla^2 S$$

$\hbar \to 0$ $\quad \nabla^2\psi = \psi\left(\frac{-1}{\hbar^2}\right)\left(\frac{\hbar}{i}\right)^2\left(\frac{\nabla\psi}{\psi}\right)^2 = (\nabla\psi)^2/\psi$

Then $\frac{\hbar^2}{2m}(\nabla\psi)^2 \sim \psi\frac{\hbar^2}{2m}\nabla^2\psi$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi - (E - V(r))\psi(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi(r) = E\psi(r)$$

§ time-dependence

The ordinary wave Eq. $\left(\frac{1}{v^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right)\psi(x,t) = 0$

$$\psi(x,t) = \psi_\omega(x)\, e^{-i\omega t} \Rightarrow \left(k^2 + \frac{\partial^2}{\partial x^2}\right)\psi_\omega(x) = 0, \quad k^2 = \frac{\omega^2}{v^2}.$$

But now:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi = E\psi$$

$$\psi \sim e^{-i\omega t} = e^{-iE/\hbar\, t}, \quad E \to i\hbar\frac{\partial}{\partial t}\psi$$

This is in consistent with the choice of $e^{-i\omega t}$

The appearance of "i" turns out to be important.

And there's no way to remove it from the equation

Complex numbers are essential quantum mechanics

under time evolution, the real and imaginary part of ψ mixes.

§ unification of wavemechanics and matrix mechanics.

Compare $H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$ (in matrix mechanics)

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \underset{\cdots}{\tfrac{1}{2} m\omega^2 x^2}\right)\psi = E\psi$$ (wave mechanics)

* Hermitian matrix $\longleftrightarrow$ self-adjoint operator

$$p^2 = -\hbar^2 \frac{d^2}{dx^2}$$

Check the canonical commutation law $\boxed{p = -i\hbar \frac{d}{dx}}$

$$[p, x]\,\psi(x) = -i\hbar \frac{d}{dx}(x\psi) + i\hbar\, x \frac{d}{dx}\psi = -i\hbar\,\psi(x)$$

$\Rightarrow$ $[p, x] = \hbar/i$

$\therefore$ $\psi(x)$ is called wavefunction.

under a given boundary condition, i.e. $\psi(x \to \pm\infty) = 0$,

the eigenstates $|\psi_n\rangle$ of $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$, span a linear

$\therefore$ space of infinite dimensions. — Hilbert space

☆ linear functional space $\rightarrow$ Normed vector space

$\rightarrow$ Banach space $\longrightarrow$ Hilbert space (inner product!)

Hilbert space: $|\psi_n\rangle \to \psi_n(x)$ satisfying

$$\int dx\, \psi_n^*(x)\, \psi_n(x) = 1, \qquad L^2\text{- space}$$

$$\psi = \sum_{n=1}^{\infty} a_n |\psi_n\rangle .$$

inner product $\langle \psi_1 | \psi_2 \rangle = \int dx\, \psi_1^* \psi_2$

$$\langle \psi_2 | \psi_1 \rangle = \langle \psi_1 | \psi_2 \rangle^*$$

2. operator $\langle \psi_1 | O(x, \frac{d}{dx}) | \psi_2 \rangle = \int dx\, \psi_1^* \hat{O} \psi_2$

$$\langle \psi_1 | O^\dagger | \psi_2 \rangle = \langle \psi_2 | O | \psi_1 \rangle^* = \langle O\psi_1 | \psi_2 \rangle$$

$$\langle \psi_1 | \hat{p} | \psi_2 \rangle = \int dx\, \psi_1^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi_2$$

$$= \underbrace{\int dx\, (-i\hbar) \frac{d}{dx} (\psi_1^* \psi_2)}_{=0} + i\hbar \int dx \left(\frac{d}{dx} \psi_1^*\right) \psi_2$$

$$= \left(-i\hbar \int dx\, \psi_2^* \frac{d}{dx} \psi_1 \right)^* = \langle \psi_2 | \hat{p} | \psi_1 \rangle^*$$

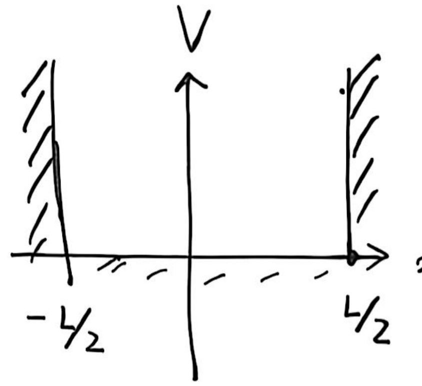
hence $\hat{p}^\dagger = p$, this is called Hermitian (self-adjoint operator)

3° For any Hermitian operator $\hat{O}$, ~~its eigenvalue much be real.~~ ~~$\hat{O}\, \psi(x) = \sum \hat{O}\, a_n \psi$~~

we define $\bar{O} = \dfrac{\langle\psi|O|\psi\rangle}{\langle\psi|\psi\rangle} = \dfrac{\int dx\, \psi^*(x)\,\hat{O}\,\psi(x)}{\int dx\, \psi^*(x)\,\psi(x)}$

(A) Simple examples:

infinitely deep potential well



$$\begin{cases} -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \\ \psi(-L/2) = \psi(L/2) = 0 \end{cases}$$

V has the reflection symmetry.

$P\psi(x) = \psi(-x)$, $P^{-1} = P$. $P^2 = 1 \Rightarrow$ eigenvalues of $P = \pm 1$.

$PV\psi = V(-x)\psi(-x) = \underline{PVP^{-1}}(P\psi)$

$\Rightarrow PV(x)P^{-1} = V(-x)$, if $PV(x)P^{-1} = V(x)$

then, we say V is reflectionally invariant.

we can classify $\psi(x)$ according to its even and oddness under reflection. Since $PHP^{-1} = -\frac{\hbar^2}{2m}\nabla^2 + V = H$,

we can find the common eigenstates of H.

$$\begin{cases} H\psi_n = E_n\psi \\ P\psi_n = \pm\psi_n \end{cases}$$

① even parity solution

$$\psi^e_n(x) = A\cos k_n x \quad \Rightarrow \quad \frac{k^e_n L}{2} = n\pi + \frac{\pi}{2}$$

$$= A\cos\frac{(2n+1)\pi}{L}x \qquad k_n = \frac{(2n+1)\pi}{L}$$

$n = 0, 1, 2, \ldots$

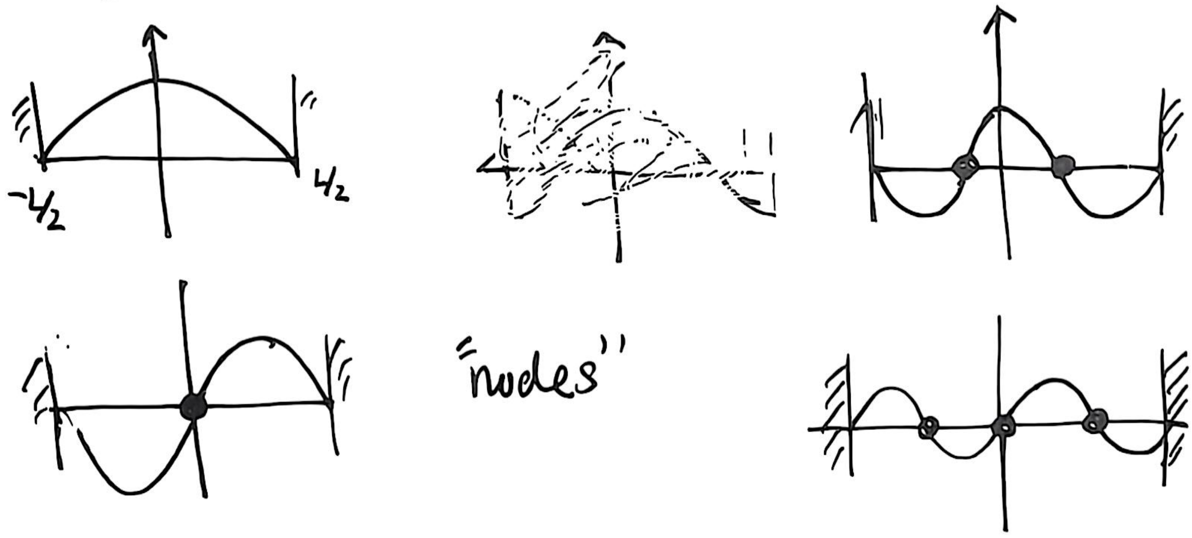
② odd parity solution

$$\psi^o_n(x) = A\sin k_n x \qquad \frac{k^o_n L}{2} = \pi n$$

$$= A\sin\frac{2\pi}{L}n\,x \qquad k^o_n = \frac{2\pi n}{L}$$

$n = 1, 2$

$$A^2\int_{-L/2}^{L/2} dx\,|\psi|^2 = 1 \Rightarrow \frac{1}{2}\cdot L A^2 = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$



$$\Rightarrow \quad E_K = \frac{\hbar^2 k^2}{2m} \Rightarrow \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \begin{cases} (2n)^2, & n = 1, 2\ldots \quad \text{odd} \\ (2n+1)^2 & n = 0, 1, 2\ldots \quad \text{even parity} \end{cases}$$

The ground state $\psi^e(x) = A\cos\frac{\pi}{L}x$.