Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

$$\hat{H} = H(\hat{q}, \hat{p}, t)$$

$$\psi = \psi(q, t)$$

Assume that $\frac{\partial H}{\partial t} = 0$

$$\psi(q,t) = u(q) f(t)$$

PARTICULAR SOLUTION

GENERAL SOLUTION

$$\psi = \sum_n c_n u_n(q) f_n(t)$$

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar\, u(q) \frac{df}{dt}$$

$$\hat{H}\psi = \hat{H}\big(u(q) f(t)\big)$$

$$= f(t) \hat{H} u(q)$$

$$i\hbar\, u(q)\frac{df}{dt} = f(t)\,\hat{H}u(q)$$

$$\times \frac{1}{uf}$$

$$\underbrace{i\hbar\,\frac{\frac{df}{dt}}{f(t)}}_{\text{depends only on } t} = \underbrace{\frac{\hat{H}u(q)}{u(q)}}_{\text{depends only on } q} = \underset{\text{constant}}{E}$$

$$\begin{cases} i\hbar\dfrac{df}{dt} = E f(t) \\ \hat{H}u(q) = E u(q) \end{cases}$$

$$\int \frac{df}{f} = \int \frac{E}{i\hbar}\, dt + C'$$

$$\ln|f| = \frac{E}{i\hbar} t + C'$$

$$f(t) = A e^{-\frac{iEt}{\hbar}}$$

$$\psi(q,t) = u(q)\, e^{-\frac{iEt}{\hbar}}$$

where $\hat{H} u = E u$

time-indep. Schrödinger eqn.

For a single particle,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]u(\vec{r}) = E\,u(\vec{r})$$

$\hat{H}u = Eu$ is an example of an eigenvalue problem

$$\hat{F} = F(\hat{q}, \hat{p}, t)$$

eigenvalue

$$\hat{F}u_k = \omega_k u_k$$

eigenfunction

Interpretation of the wave function

$$\psi^*(q_1, \ldots, q_f, t)\,\psi(q_1, \ldots q_f, t)$$

$$= |\psi(q_1, \ldots, q_f, t)|^2$$

$$\boxed{\text{Max Born}} \quad = P(q_1, \ldots, q_f, t)$$

$$= P(q, t)$$

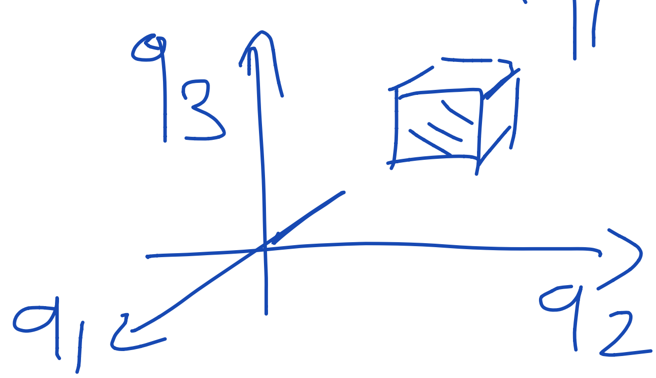
position probability density

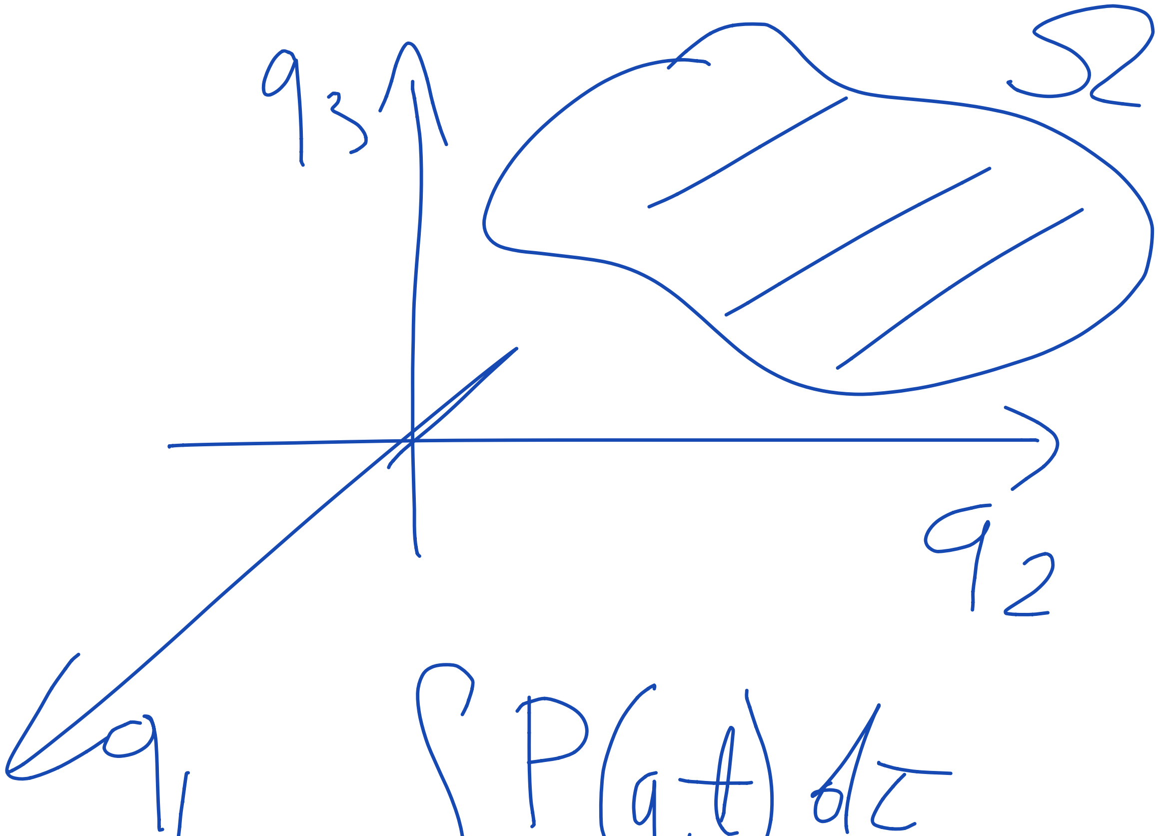
$P(q,t)\,d\tau \to$ probability of finding the QM-cal system in

infinitesimal volume element

$[q_1, q_1+dq_1] \times \ldots \times [q_f, q_f+dq_f]$

$d\tau \sim dq_1 \ldots dq_f$



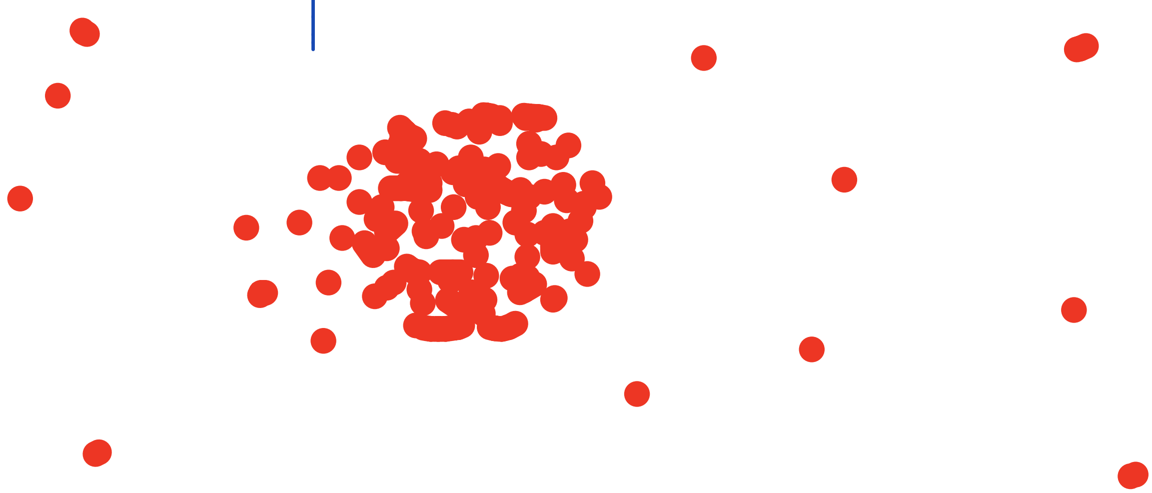


$$\int_{\Omega} P(q,t)\, d\tau$$

= probability of finding the (QM-cal system in $\Omega \subset \Gamma$

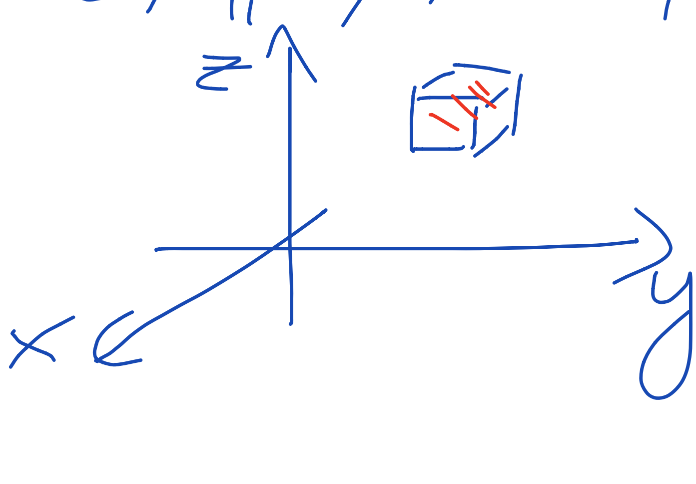
coordinate space

$$\int_{\Gamma} P(q,t)\, d\tau = 1$$



$\overline{\text{Single}}$ particle

$$P(x,y,z,t) = |\psi(x,y,z,t)|^2$$



$$[x, x+dx] \times [y, y+dy] \times [z, z+dz]$$

$$d\tau = dx\,dy\,dz$$

$$q_1, q_2, q_3$$

$$x = x(q_1, q_2, q_3)$$
$$y = y(q_1, q_2, q_3)$$
$$z = z(q_1, q_2, q_3)$$

$$dP = P\,d\tau = |\psi(x, y, z, t)|^2$$
$$\times\, dx\,dy\,dz =$$

$$= \underbrace{\left|\psi\big(x(q_1,q_2,q_3),\, y(q_1,q_2,q_3),\, z(q_1,q_2,q_3)\big)\right|^2 \times \left|\frac{\partial(x,y,z)}{\partial(q_1,q_2,q_3)}\right| dq_1\, dq_2\, dq_3}_{dx\,dy\,dz}$$

$$\left|\frac{\partial(x,y,z)}{\partial(q_1,q_2,q_3)}\right| = \begin{vmatrix} \frac{\partial x}{\partial q_1} & \frac{\partial x}{\partial q_2} & \frac{\partial x}{\partial q_3} \\ \frac{\partial y}{\partial q_1} & \frac{\partial y}{\partial q_2} & \frac{\partial y}{\partial q_3} \\ \frac{\partial z}{\partial q_1} & \frac{\partial z}{\partial q_2} & \frac{\partial z}{\partial q_3} \end{vmatrix}$$

Jacobian

$$q_1 = r,\ q_2 = \vartheta,\ q_3 = \varphi$$

$$dx\,dy\,dz = \underline{r^2 \sin\vartheta}\, dr\, d\vartheta\, d\varphi$$

$$dP = P\,dx\,dy\,dz$$

$$= |\psi(x(r,\vartheta,\varphi), y(r,\vartheta,\varphi), z(r,\vartheta,\varphi))|^2\ \underline{r^2 \sin\vartheta}$$

$$\times \underline{dr\, d\vartheta\, d\varphi}$$

$$\int_\Gamma |\psi|^2 d\tau = 1$$

What if

$$\int_{\Gamma} |\psi|^2 d\tau = N ?$$

$$\psi' = \frac{1}{\sqrt{N}} \psi$$

$$\int_{\Gamma} |\psi'|^2 d\tau = 1$$

In 1D:

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 < \infty \quad (N)$$

$\cancel{e^{x^2}}$ $\sin x$

$e^{-\alpha x^2}$

BOUND STATES

$$\int |\psi|^2 dx < \infty$$

Γ

ψ must vanish at infinities

$\psi \in L^2(\Gamma)$

(square integrable)

Stationary states

$$\frac{\partial P}{\partial t} = 0$$

$$P = P(q)$$

Example,

$$\psi(q,t) = u(q)e^{-\frac{iEt}{\hbar}}$$

$$|\psi|^2 = |u(q)|^2$$

Equation of continuity

$$\int_{\Gamma} |\psi|^2 \, d\tau = 1$$

independent of t

$$\frac{d}{dt} \int_{\Gamma} |\psi|^2 \, d\tau = 0$$

What about

where $\Omega \subset \Gamma$?

Single particle

$$\frac{d}{dt}\int_{\Omega} \psi^*(x,y,z,t)\,\psi(x,y,z,t) \times \underbrace{dx\,dy\,dz}_{d\tau}$$

$$\boxed{\Omega \subseteq \Gamma} \to \mathbb{R}^3$$

$$= \int_{\Omega} \frac{\partial}{\partial t}(\psi^*\psi)\, d\tau$$

$$= \int_{\Omega} \left[\frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t}\right] d\tau$$

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi$$

$$\frac{\partial\psi}{\partial t}=\frac{i\hbar}{2m}\nabla^2\psi+\frac{1}{i\hbar}V\psi$$

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

$$(V=V^*)$$

$$\frac{\partial\psi^*}{\partial t}=-\frac{i\hbar}{2m}\nabla^2\psi^*-\frac{1}{i\hbar}V\psi^*$$

$$\frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t}$$

$$= -\frac{i\hbar}{2m}\left(\nabla^2 \psi^*\right)\psi$$

$$-\frac{1}{i\hbar}\left(V\psi^*\right)\psi \qquad \leftarrow V\psi^*\psi$$

$$+\frac{i\hbar}{2m}\psi^* \nabla^2 \psi$$

$$+\frac{1}{i\hbar}\left(V\psi\right)\psi^*$$

$$\frac{d}{dt}\int_{\Omega}\psi^*\psi\,d\tau$$

$$= \frac{i\hbar}{2m}\int_{\Omega}\left[\psi^*\nabla^2\psi - (\nabla^2\psi^*)\psi\right] \times d\tau$$

$x_1 = x$
$x_2 = y$
$x_3 = z$

$$\psi^*\nabla^2\psi - (\nabla^2\psi^*)\psi$$

$$= \sum_{j=1}^{3}\left[\psi^*\frac{\partial^2\psi}{\partial x_j^2} - \frac{\partial^2\psi^*}{\partial x_j^2}\psi\right]$$

$$= \sum_{j=1}^{3}\frac{\partial}{\partial x_j}\left[\psi^*\frac{\partial\psi}{\partial x_j} - \frac{\partial\psi^*}{\partial x_j}\psi\right]$$

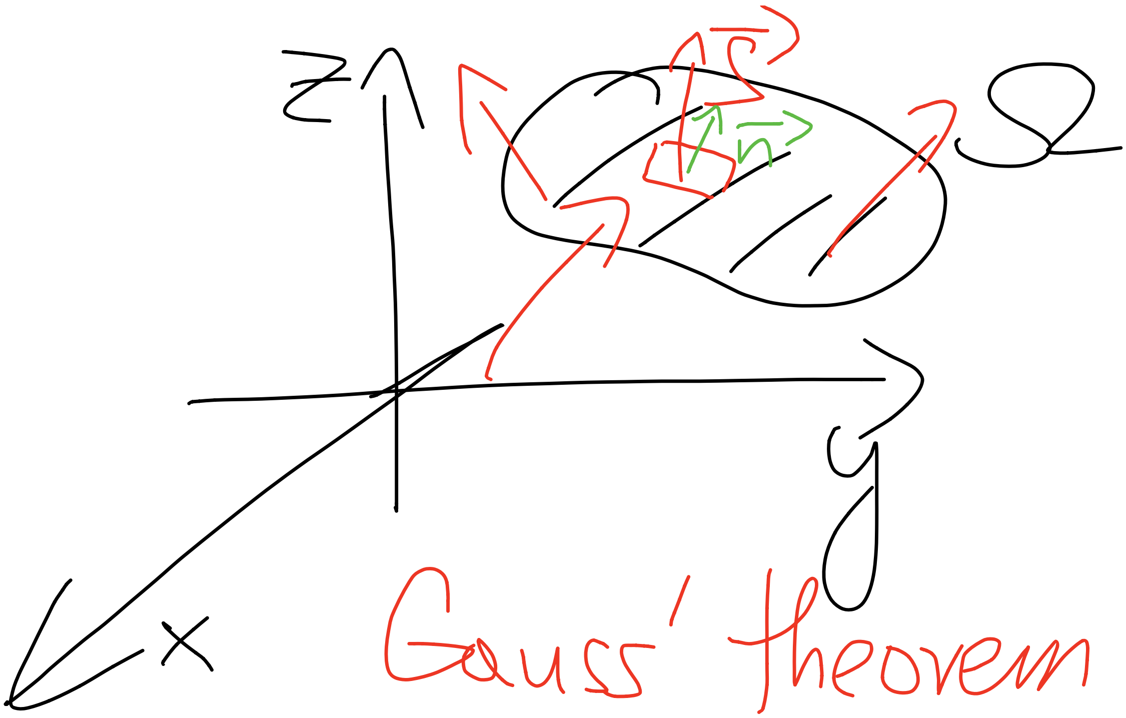
$$= \vec{\nabla} \cdot \left[\psi^* \vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$

$$\frac{d}{dt}\int_{\Omega} (\psi^* \psi)\, d\tau =$$

$$= - \int_{\Omega} \vec{\nabla} \cdot \vec{S}\, d\tau$$

$$\vec{S} = -\frac{i\hbar}{2m}\left[\psi^* \vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$

$$= \frac{\hbar}{2im}\left[\psi^* \vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$



Gauss' theorem

$$\int_{\Omega} \vec{\nabla} \cdot \vec{S} \, d\tau = \int_{A=\partial\Omega} (\vec{S} \cdot \vec{n}) \, dA$$

boundary surface ($\partial\Omega$)

$$\frac{d}{dt} \int_{\Omega} \psi^* \psi \, d\tau = - \int_{A \in \partial\Omega} \vec{S} \cdot \vec{n} \, dA$$

$$\vec{S} = \frac{\hbar}{2im}\left[\psi^* \vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$

Observations :

A. $\Omega = \mathbb{R}^3$, ψ is square integrable

$\Longrightarrow$ ψ vanishes at $\pm\infty$ for x, y, z

$$\int_A \vec{S}\cdot\vec{n}\, dA = 0$$

$$\Rightarrow \quad \frac{d}{dt}\int_{\mathbb{R}^3} \psi^* \psi \, d\tau = 0$$

$$\int_{\mathbb{R}^3} \psi^* \psi \, d\tau = \text{const.}$$

$$(= N, 1)$$

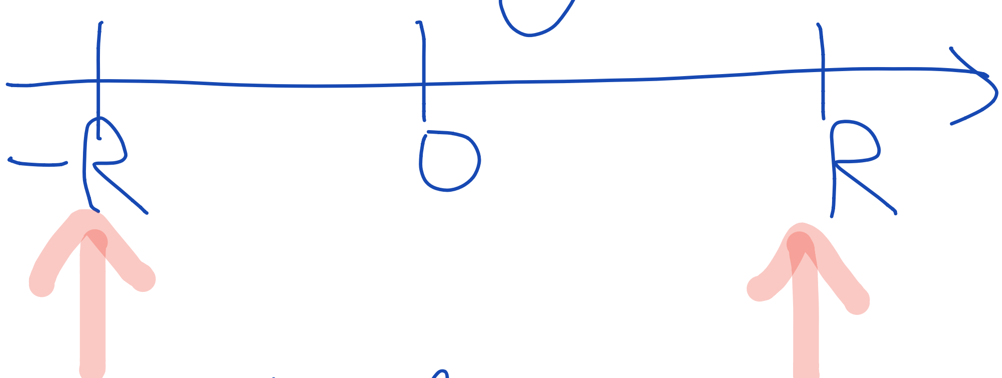
B. ψ does not vanish at infinities, remains finite at $\pm\infty$ (x, y, z)

(e.g., $e^{i(\vec{k}\cdot\vec{r} - \omega t)}$)

We can always make

$$\int_A \vec{S}\cdot\vec{n}\, dA = 0$$

by introducing periodic boundary conditions.



so that

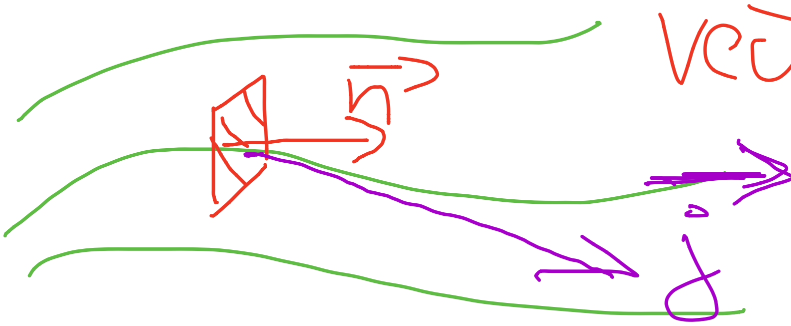
$$\frac{d}{dt}\int_{\text{"huge box"}} \cancel{\eta^* \eta}\, dx = 0$$

In hydrodynamics,

$$\frac{d}{dt}\int_\Omega \rho \, d\tau = -\oint_{A(=\partial\Omega)} (\vec{j}\cdot\vec{n})\, dA$$

density of fluid

current density (mass flow vector)



$$\boxed{\begin{array}{l} \rho(x,y,z,t) \\ \vec{j}(x,y,z,t) \end{array}}$$

Gauss th.

$$\frac{d}{dt}\int_\Omega \rho \, d\tau = -\int_\Omega (\nabla\cdot\vec{j})\, d\tau$$

$$\int_{\Omega}\left[\frac{\partial \rho}{\partial t}+\vec{\nabla}\cdot\vec{j}\right]d\tau=0$$

[eqn. of continuity]

$$\frac{\partial \rho}{\partial t}+\vec{\nabla}\cdot\vec{j}=0$$

$$\frac{d}{dt}\int_{\Omega}\underbrace{\psi^{*}\psi}_{\rho}\,d\tau=-\int_{A}(\underbrace{\vec{S}}_{\vec{j}}\cdot\vec{n})\,dA$$

$$=-\int_{\Omega}(\vec{\nabla}\cdot\vec{S})\,d\tau$$

$$\boxed{\frac{\partial P}{\partial t}+\vec{\nabla}\cdot\vec{S}=0,\ P=\psi^{*}\psi}$$

equation of continuity

$P = \psi^* \psi$ = position probability density

$\vec{S}$ = probability current density

In fluid dynamics,

$$\vec{j} = \rho \vec{v}$$

In QM, $\rho \to P = \psi^* \psi$

Is $\vec{S}$ analogous to $\vec{j}$?

$$\vec{j} = \rho \vec{v} \xrightarrow{QM} \psi^* \hat{\vec{v}} \psi$$

"velocity operator"

$$= \psi^* \frac{\hat{\vec{p}}}{m} \psi$$

$$= \frac{\hbar}{im} \left(\psi^* \vec{\nabla} \psi \right)$$

$$\vec{S} \sim \frac{\hbar}{im} \left(\psi^* \vec{\nabla} \psi \right)$$

$$\vec{S} = \frac{\hbar}{2im} \left[\overbrace{\psi^* \vec{\nabla} \psi}^{a+bi} - (\vec{\nabla} \psi^*) \psi \right]$$

$$\vec{S} = \frac{\hbar}{2im}\left[(\cancel{a}+bi)-(\cancel{a}-bi)\right]$$

$$= \frac{\hbar}{\cancel{2}\cancel{i}m}\,\cancel{2}b\cancel{i} = \frac{\hbar}{m}b$$

$$= \frac{\hbar}{m}\,\mathrm{Im}\left(\psi^* \nabla \psi\right)$$

$$\vec{S} = \mathrm{Re}\left(\frac{\hbar}{mi}\psi^* \vec{\nabla}\psi\right)$$