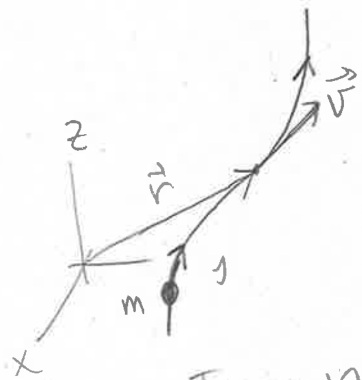
QUESTION: WHERE DOES THE wave function go?

In classical mechanics, at each time t, a particle at position

$$\vec{r}(t) = \vec{e}_x x(t) + \vec{e}_y y(t) + \vec{e}_z z(t)$$

is DIRECTED along the TANGENT vector

$$\vec{v}(t) = \frac{d\vec{r}}{dt} = \vec{e}_x \dot{x}(t) + \vec{e}_y \dot{y}(t) + \vec{e}_z \dot{z}(t)$$



What about a quantum particle? Is there any way to calculate where the probability density function

$$P(\underline{r}, t)\, d^3r = |\Psi(\underline{r}, t)|^2 d^3r$$

goes?

To answer this question, let:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{\underline{r}}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{\underline{r}})$$

with (This is important!) $V(\hat{\underline{r}}) \in \mathbb{R}$.

Then, the Schr. eq. is..

$$+i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \qquad (1.2)$$

The COMPLEX CONJUGATE of This expression is..

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* \qquad (2.2)$$

Now, multiply from left (1.2) by ψ^* and (2.2) by ψ. Then, subtract each side of the equations:

$$\left.\begin{aligned} +i\hbar\psi^*\frac{\partial\psi}{\partial t} &= -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V|\psi|^2 \\ -i\hbar\psi\frac{\partial\psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + V|\psi|^2 \end{aligned}\right\}$$

Now subtract the second from the first.

$$+i\hbar\underbrace{\left(\psi^*\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^*}{\partial t}\right)}_{=\frac{\partial}{\partial t}|\psi|^2} = -\frac{\hbar^2}{2m}\underbrace{\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right)}_{\text{use the identity}} + 0$$

use the identity: $\vec\nabla\cdot(\phi\nabla\psi) = \phi\nabla^2\psi + \vec{\nabla\phi}\cdot\vec{\nabla\psi}$

where

$$\vec\nabla(\psi^*\vec{\nabla\psi} - \psi\vec{\nabla\psi^*}) = \psi^*\nabla^2\psi + \cancel{\vec{\nabla\psi^*}\cdot\vec{\nabla\psi}} + \\ - \cancel{\vec{\nabla\psi}\cdot\vec{\nabla\psi^*}} - \psi\nabla^2\psi^*$$

$$= \psi^*\nabla^2\psi - \psi\nabla^2\psi^*$$

Therefore, we have obtained:

$$-i\cancel{\hbar}\frac{\partial}{\partial t}|\psi(\underline{r},t)|^2 = -\frac{\hbar^{\cancel{2}}}{2m}\vec{\nabla}\cdot\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right)$$

$$\frac{\partial}{\partial t}|\psi|^2 + \frac{\hbar}{2m}\vec{\nabla}\cdot\underbrace{\frac{\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*}{i}}_{=2\,\mathrm{Im}\left(\psi^*\vec{\nabla}\psi\right)} = 0$$

This is usually written as:

$$\rho(\underline{r},t) \equiv |\psi(\underline{r},t)|^2 \quad \leftarrow \text{Probability density}$$

$$\vec{J}(\underline{r},t) = \frac{\hbar}{2mi}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right) \leftarrow \text{Prob. current}$$

and

$$\boxed{\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0} \leftarrow \text{continuity equation}$$

— HOMEWORK —

Calculate the probability current $\vec{J}(\underline{r},t)$ for

$$\psi(\vec{r},t) = A\,e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar} - iE\frac{t}{\hbar}} + B\,e^{-i\frac{\vec{p}\cdot\vec{x}}{\hbar} - iE\frac{t}{\hbar}}$$

where $E = \frac{\vec{p}\cdot\vec{p}}{2m}$

Gives an interpretation of the result.

A complex number $z = x + iy$ can always be written in "polar form" as:

$$z = x + iy = |z| e^{i \arg z}$$

where $|z| = \sqrt{x^2 + y^2}$ and $\tan(\arg z) = \frac{y}{x}$

Similarly we write:

$$\psi(\underline{r}, t) = |\psi(\underline{r}, t)| e^{i \arg[\psi(\underline{r}, t)]}$$

For simplicity, define the phase $S(\underline{r}, t)$ as:

$$S(\underline{r}, t) \equiv \hbar \arg[\psi(\underline{r}, t)]$$

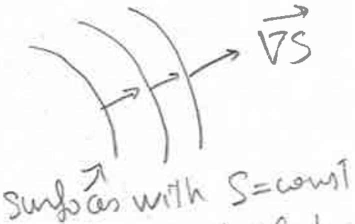
Moreover, by def: $|\psi(\underline{r}, t)| = \sqrt{\rho(\underline{r}, t)}$

Therefore we can write:

$$\psi(\underline{r}, t) = \sqrt{\rho(\underline{r}, t)} \exp\left[i \frac{S(\underline{r}, t)}{\hbar}\right]$$

Then, if we calculate $\vec{J}(\underline{r}, t) = \frac{\hbar}{m} \mathrm{Im}(\psi^* \vec{\nabla} \psi)$ we get:

$$\boxed{\vec{J}(\underline{r}, t) = \rho(\underline{r}, t) \frac{\vec{\nabla} S(\underline{r}, t)}{m}}$$



So, the gradient of the phase give the "flow" of probability.

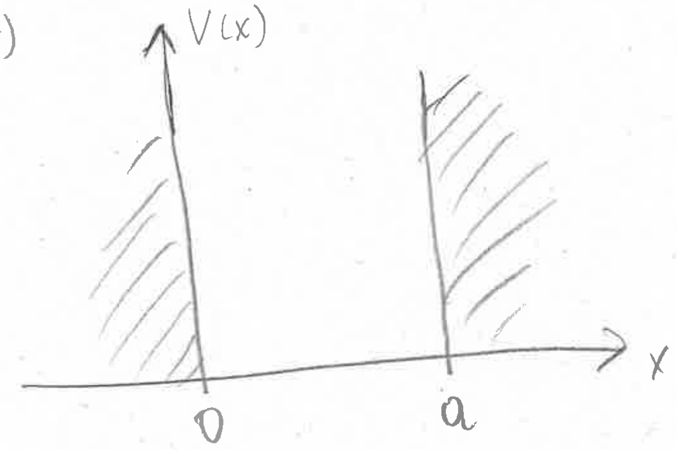
For a plane wave $\phi(\underline{x}, \underline{p}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \exp\left(i \frac{\underline{p} \cdot \underline{x}}{\hbar} - i \frac{Et}{\hbar}\right)$

we find $\vec{\nabla} S = \underline{p}$ and a "velocity" $\underline{v}$ can be defined as:

$$\underline{v} = \frac{\vec{\nabla} S}{m} \Rightarrow \vec{J}(\underline{r}, t) = \rho(\underline{r}, t) \underline{v}(\underline{r}, t)$$

– Anoter solution of Sch eq: a 1D particle in a box –

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



$$V(x) = \begin{cases} \infty, & x<0 \\ 0, & 0<x<a \\ \infty, & a<x \end{cases}$$

Let E a real constant and look for a solution of the form:

$$\psi(x,t) = u(x)\exp\left(-iE\frac{t}{\hbar}\right) \qquad \omega \equiv \frac{E}{\hbar}$$

Then Sch. eq. becomes:

$$i\cancel{\hbar}\left(-i\frac{E}{\cancel{\hbar}}\right)u(x)\cancel{e^{-i\omega t}} = -\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2}\cancel{e^{-i\omega t}} + V\cancel{e^{-i\omega t}}$$

$$\Leftrightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2 u}{dx^2} = E\,u(x) \qquad \text{for} \quad 0<x<a \quad (\text{because } V=0)$$

with the boundary conditions:

$$u(x) = 0 \qquad x<0 \ \text{ and } \ x>a$$

We can rewrite as:

$$\boxed{\frac{d^2u(x)}{dx^2} + \frac{2mE}{\hbar^2}u(x) = 0}$$

If $E<0$ then

$$\frac{2mE}{\hbar^2} \equiv -k^2 \quad \text{with } k \in \mathbb{R}$$

Then the solutions of

$$\frac{d^2u}{dx^2} - k^2 u = 0$$

are $\quad u(x) = A e^{+kx} + B e^{-kx}$

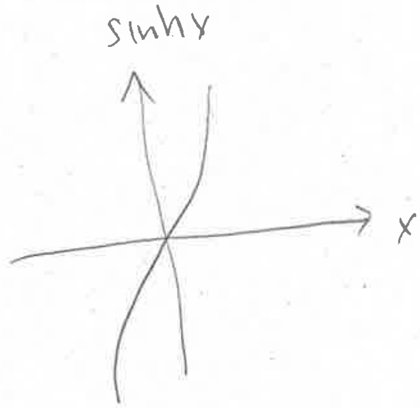
at $x=0$: $\quad u(0) = A + B = 0 \Rightarrow B = -A$

therefore $\quad u(x) = A\left(e^{kx} - e^{-kx}\right)$

then $\quad u(a) = A\left(e^{ka} - e^{-ka}\right)$

$$= 2A \sinh ka$$

$$\neq 0 \text{ for } a \neq 0$$



So, $E<0$ is NOT acceptable!

Therefore, let $E>0$ and def:

$$\frac{2mE}{\hbar^2} \equiv k^2 > 0$$

The eq is:

$$\boxed{\frac{d^2u}{dx^2} + k^2 u = 0}$$

whose solution is:

$$u(x) = A e^{ikx} + B e^{-ikx}$$

because: $u'(x) = ik\left(A e^{ikx} - B e^{-ikx}\right)$

$$u''(x) = \underbrace{(ik)^2}_{=-k^2}\left(A e^{ikx} + B e^{-ikx}\right) = -k^2 u \Rightarrow$$

$$\Rightarrow u''(x) + k^2 u = 0 \quad \checkmark$$

Then $u(0) = A + B = 0 \Rightarrow B = -A \Rightarrow$

$$\Rightarrow u(x) = C \sin kx$$

New proportionality constant. It will be fixed by the normalization

Then $u(a) = 0 \Leftrightarrow \sin(ka) = 0 \Rightarrow$

$$\Rightarrow ka = n\pi \qquad n = 1, 2, 3, \ldots$$

or $\boxed{k = \frac{n\pi}{a}}$ QUANTIZATION!!!

Therefore $E = \frac{\hbar^2 k^2}{2m} \rightarrow \boxed{E_n = \frac{\hbar^2 \pi^2 n^2}{2 m a^2}}$

The normalization is easily found.

$$C^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = C^2 \frac{a}{\pi} \int_0^\pi \sin^2(ny)\, dy \qquad y = \frac{\pi x}{a}$$

but: $\int_0^{\pi} \sin^2(\alpha x)\,dx = \frac{\pi}{2} - \frac{\sin(2\pi\alpha)}{4\alpha}$

In our case $\alpha = n \Rightarrow$ the second Term is null, and

$$C^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx = C^2 \frac{a}{\cancel{\pi}}\frac{\cancel{\pi}}{2} = 1 \Rightarrow C = \sqrt{\frac{2}{a}}$$

imposed by normalization

Therefore: $\boxed{u_n(x) = \sqrt{\frac{2}{a}} \sin\left(n\pi \frac{x}{a}\right)}$

It is easy to check that:

$$I_1 = \int_0^a u_n^*(x)\, u_m(x)\,dx = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

but $\cos(\alpha \pm \beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta \Rightarrow$

$$\Rightarrow \frac{\cos(\alpha-\beta) - \cos(\alpha+\beta)}{2} = \sin\alpha\sin\beta \Rightarrow$$

$$\Rightarrow I_1 = \frac{\cancel{2}}{a}\frac{1}{\cancel{2}}\int_0^a \left[\cos\left((n-m)\frac{x\pi}{a}\right) - \cos\left((n+m)\frac{\pi x}{a}\right)\right]dx$$

but $\int \cos(\alpha x)\,dx = \frac{\sin(\alpha x)}{\alpha} + C \Rightarrow$

$$\Rightarrow I_1 = \frac{1}{\cancel{a}}\left\{\frac{\sin[(n-m)\pi]}{(n-m)\frac{\pi}{\cancel{a}}} - \frac{\sin[(n+m)\pi]}{(n+m)\frac{\pi}{\cancel{a}}}\right\} \Leftrightarrow$$

$$\Leftrightarrow I_1 = \begin{cases} 1, & n=m \\ 0, & n\neq m \end{cases}$$

So: $$\boxed{\int_0^a u_n^*(x)\, u_m(x)\, dx = \delta_{nm}}$$

– Things to notice –

1) The lowest energy level, attained for $n=1$, is called the GROUND STATE:

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

For a classical particle, it would be $P=0 \Rightarrow E=0$ so the particle is at the bottom and it does not move. Instead here, if we identify:

$$\text{"ground state momentum"} = P_1 = \frac{\pi}{a}\hbar \equiv k_1\hbar \neq 0$$

minimum momentum

Then $$E_1 = \frac{P_1^2}{2m}$$

So why it cannot be $P_1=0$? Because the particle is localized in the interval $0<x<a$!

Let us calculate for these eigenfunctions:

mean:

$$\langle \hat{x} \rangle_n = \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$= \frac{a}{2}$ This means that, on average, the particle is at the center of the box.

variance:

$$\left\langle \left(\hat{x} - \frac{a}{2}\right)^2 \right\rangle_n = \frac{2}{a}\int_0^a \left(x - \frac{a}{2}\right)^2 \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{a^2}{12}\left(1 - \frac{6}{n^2\pi^2}\right) = \frac{a^2}{12} - \frac{1}{2}\frac{1}{\frac{n^2\pi^2}{a^2}}$$

mean:

$$\langle \hat{p} \rangle_n = -i\hbar \int_0^a \sin\left(\frac{n\pi x}{a}\right)\left[\frac{d}{dx}\sin\left(\frac{n\pi x}{a}\right)\right]\frac{2}{a}\,dx$$

$= 0$

Also because, being $u_n(x) \in \mathbb{R}$, we have:

$$\langle \hat{p} \rangle_n = -i\hbar \int_0^a u_n \frac{d}{dx} u_n \, dx = -\frac{i\hbar}{2}\int_0^a \frac{d}{dx}\left(u_n^2(x)\right) dx$$

$$= -\frac{i\hbar}{2}\left[u_n^2(a) - u_n^2(0)\right] = 0 \quad \text{because of BC}$$

Finally:

variance:

$$\langle \hat{p}^2 \rangle_n = -\hbar^2 \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\underbrace{\left[\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{a}\right)\right]}_{= -\left(\frac{n\pi}{a}\right)^2 \sin\left(\frac{n\pi x}{a}\right)} dx$$

$$= -\hbar^2\left(-\frac{n^2\pi^2}{a^2}\right) \leftarrow \text{because of normalization}$$

So $\langle \hat{P}^2 \rangle_n = \dfrac{n^2 \pi^2 \hbar^2}{a^2}$

Then, it is clear that $E_n = \dfrac{\langle \hat{P}^2 \rangle_n}{2m}$

Therefore

$$\widehat{\Delta X}_n = \hat{X} - \langle \hat{X} \rangle_n = \hat{X} - \frac{a}{2}$$

$$\widehat{\Delta P}_n = \hat{P} - \langle \hat{P} \rangle_n = \hat{P}$$

$$\langle u_n | \widehat{\Delta X}_n^2 | u_n \rangle = \frac{a^2}{12}\left(1 - \frac{6}{n^2\pi^2}\right)$$

$$= \frac{a^2}{12} - \frac{1}{2\left(\frac{n^2\pi^2}{a^2}\right)} \equiv (\Delta X_n)^2$$

$$\langle u_n | \widehat{\Delta P}_n^2 | u_n \rangle = \frac{n^2\pi^2}{a^2}\hbar^2 \equiv (\Delta P_n)^2$$

$$\Rightarrow (\Delta X_n \, \Delta P_n)^2 = \frac{n^2\pi^2}{a^2}\hbar^2\left(\frac{a^2}{12} - \frac{1}{2\frac{n^2\pi^2}{a^2}}\right)$$

$$= \frac{n^2\pi^2}{12}\hbar^2 - \frac{\hbar^2}{2}$$

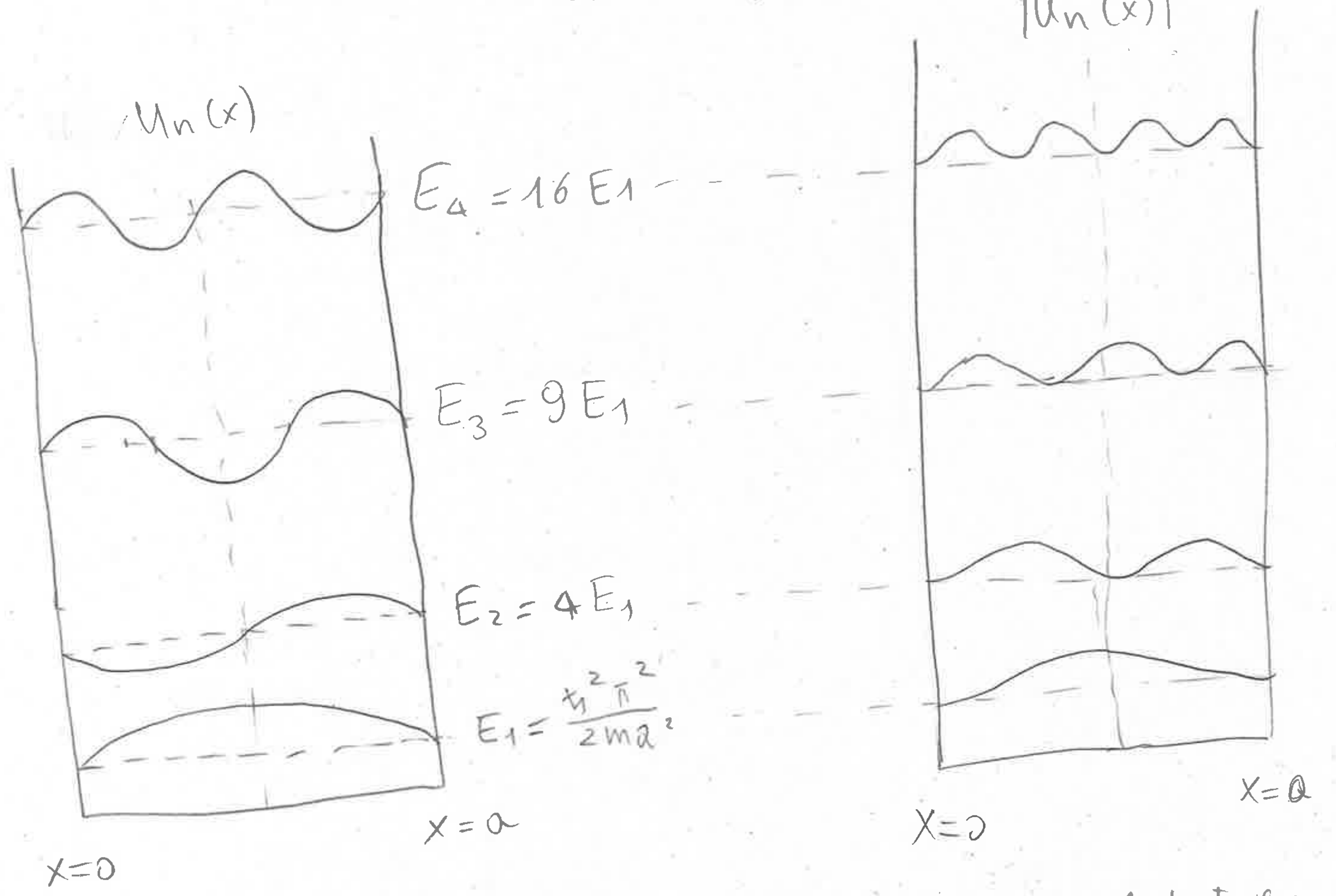
$$= \frac{\hbar^2}{4}\left(\frac{n^2\pi^2}{3} - 2\right)$$

$$\Rightarrow \Delta X_n \Delta P_n = \frac{\hbar}{2}\underbrace{\sqrt{\frac{n^2\pi^2}{3} - 2}}_{>1} > \frac{\hbar}{2}$$ c.v.d

The probability to find at time t the particle between x and $x+dx$ is:

$$|\psi(x,t)|^2 = \left| u_n(x)\, e^{-\frac{iE_n t}{\hbar}} \right|^2$$

$$= |u_n(x)|^2 = \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right)$$



– Homework –
Calculate the CLASSICAL probability to find a particle between x and $x+dx$ at a randomly picked time

– Homework –
Consider a particle of mass $m = \frac{1}{10}g$ moving at constant speed $v = 1\frac{m}{s}$ in a box of width $a = 1mm$. Calculate the approximate value of n corresponding to this energy.

– Homework – At time $t=0$, the particle in the box has: $\psi(x) = \begin{cases} A(x/a), & 0<x<\frac{a}{2} \\ A(1-\frac{x}{a}), & \frac{a}{2}<x<a \end{cases}$
a) Normalize ψ; b) Calculate the probability to find the particle in a state with energy E_n.

– EHRENFEST THEOREM –

Consider a single particle in a potential (time-independent)

$$V(\underline{r})$$

The Hamiltonian is:

$$\hat{H} = \frac{\hat{\underline{p}}^2}{2m} + V(\hat{\underline{r}}) \quad \leftarrow \text{Time independent}$$

Suppose that the particle is described by $\psi(\underline{r},t)$. We want to calculate:

$$\frac{d^2}{dt^2}\langle \hat{\underline{r}} \rangle_\psi = ?$$

where, as usual,

$$\langle \hat{\underline{r}} \rangle_\psi = \int \psi^*(\underline{r},t)\, \underline{r}\, \psi(\underline{r},t)\, d^3r$$

We have already demonstrated that:

$$\boxed{\frac{d}{dt}\langle \hat{f} \rangle_\psi = \frac{i}{\hbar}\langle [\hat{H}, \hat{f}] \rangle_\psi} \qquad (1.12)$$

In our case:

$$[\hat{H}, \hat{r}_i] = \frac{1}{2m}\sum_{j=1}^{3} \underbrace{[\hat{p}_j^2, \hat{r}_i]}$$

$$= [\hat{p}_j, \hat{r}_i]\hat{p}_j + \hat{p}_j[\hat{p}_j, \hat{r}_i]$$

$$= -2i\hbar\, \delta_{ij}\, \hat{p}_j$$

$$= -\frac{i\hbar}{m}\hat{p}_i$$

Therefore:

$$\frac{d}{dt}\langle \hat{\underline{r}} \rangle_\psi = \frac{i}{\hbar}\left(-\frac{i\hbar}{m}\right)\langle \hat{\underline{p}} \rangle_\psi = \frac{1}{m}\langle \hat{\underline{p}} \rangle_\psi$$

This is the quantum analogous of: $\underline{v}_\alpha = \underline{p}_\alpha \frac{1}{m}$

Now, we derive again:

$$\frac{d^2}{dt^2}\langle \hat{\underline{r}} \rangle_\psi = \frac{1}{m}\frac{d}{dt}\langle \hat{\underline{p}} \rangle_\psi$$ use (1.12)

$$= \frac{1}{m}\frac{i}{\hbar}\langle [\hat{H}, \hat{\underline{p}}] \rangle_\psi$$

$$= \frac{i}{m\hbar}\langle [V(\hat{\underline{r}}), \hat{\underline{p}}] \rangle_\psi$$

Now, we know that:

$$[G(\hat{\underline{r}}), \hat{p}_i] = i\hbar \frac{\partial G}{\partial r_i} \Rightarrow$$

$$\Rightarrow [V(\hat{\underline{r}}), \hat{\underline{p}}] = i\hbar \vec{\nabla} V$$

Therefore:

$$\frac{d^2}{dt^2}\langle \hat{\underline{r}} \rangle_\psi = \frac{i}{m\cancel{\hbar}} i\cancel{\hbar} \langle \vec{\nabla} V \rangle_\psi$$

$$= -\frac{1}{m}\langle \vec{\nabla} V \rangle_\psi \Leftrightarrow$$

$$\Leftrightarrow \boxed{m\frac{d^2}{dt^2}\langle \hat{\underline{r}} \rangle_\psi = -\langle \vec{\nabla} V \rangle_\psi} \quad (1.13)$$

In classical mechanics we have:

$$m\frac{d^2}{dt^2}\underline{r}(t) = -\vec{\nabla} V(\underline{r}(t)) \quad (2.13)$$

However, now: $\langle \vec{\nabla} V(\hat{\underline{r}}) \rangle_\psi \neq \vec{\nabla} V(\langle \hat{\underline{r}} \rangle_\psi)$

Therefore (1.13) is NOT completely analogous to the classical equation (2.13).

The difference is in the quantum fluctuations.

For example, in 1D:

$$V(x) = V(0) + x V'(0) + \frac{x^2}{2} V''(0) + \frac{x^3}{3!} V'''(0) + \dots$$

$$V' = \frac{dV}{dx} = 0 + V'(0) + x V''(0) + \frac{x^2}{2} V'''(0) + \dots$$

and $\langle V' \rangle_\psi = V'(0) + \langle x \rangle_\psi V''(0) + \frac{1}{2} \langle x^2 \rangle_\psi V'''(0) + \dots$

If ψ is NOT an eigenstate of position, then

$$\langle x^2 \rangle_\psi \neq \langle x \rangle_\psi^2 \Rightarrow$$

$$\Rightarrow \langle V'(x) \rangle_\psi \neq V'(\langle x \rangle_\psi)$$