QUANTUM MECHANICS

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•The time-dependent Schrödinger equation

Free particle

Particle in a potential

• Interpretation of the wave function

Probability

Normalization

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•Boundary conditions on the wave function

• Derivation of the time-independent Schrödinger equation

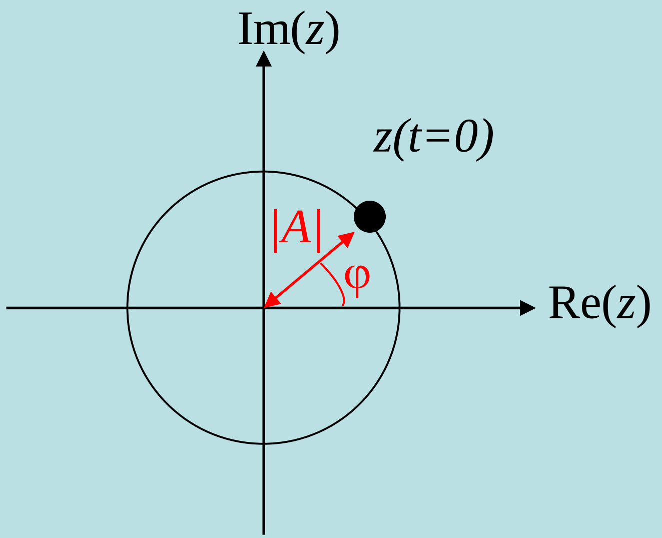
Separation of variables

Complex numbers in classical physics

Often *convenient* to use complex numbers in classical physics, especially in description of wave motion or vibration

$$z = A\mathrm{e}^{\mathrm{i}\omega \mathrm{t}} \qquad A = |A|e^{i\phi}$$

$$\Rightarrow z = |A|\mathrm{e}^{\mathrm{i}(\omega \mathrm{t}+\phi)}$$



Displacement

Velocity

Acceleration

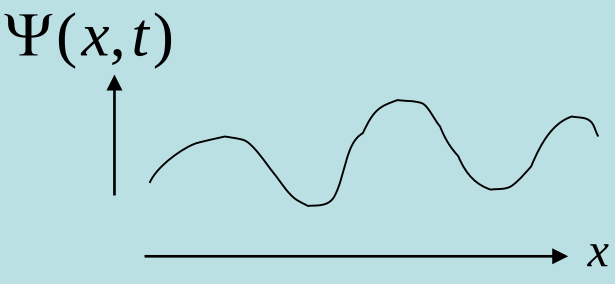
Can take real *or* imaginary part as physical solution.
Complex numbers are a mathematical convenience.

An equation for matter waves: the time-dependent Schrödinger equation

Classical 1D wave equation

e.g. waves on a string:

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



$\Psi(x,t) =$ wave displacement

$v =$ wave velocity

Can we use this to describe matter waves in free space?

Try solution $\boxed{\Psi\left(x,t\right) = e^{i\left(kx-\omega t\right)}}$

But this isn't correct! For free particles we know that $E = \dfrac{p^2}{2m}$

An equation for matter waves (2)

Seem to need an equation that involves the *first derivative* in time, but the *second derivative* in space

$$\text{Try } \alpha \frac{\partial \Psi}{\partial t} = \frac{\partial^2 \Psi}{\partial x^2}$$

$\Psi(x,t)$ is "wave function" associated with matter wave

As before try solution $\boxed{\Psi\left(x,t\right) = e^{i\left(kx-\omega t\right)}}$

So equation for matter waves in free space is (free particle Schrödinger equation)

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2}$$

An equation for matter waves (3)

What about particles that are not free?

Substitute $\Psi\left(x,t\right)=e^{i\left(kx-\omega t\right)}$ into free particle equation $i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}$

gives $$\boxed{\hbar\omega\psi\left(x,t\right)=\frac{\hbar^2k^2}{2m}\psi\left(x,t\right)}$$

Has form (Total Energy)*(wavefunction) = (KE)*(wavefunction) $\boxed{E=\frac{p^2}{2m}}$

For particle in a potential *V(x,t)* $E=\frac{p^2}{2m}+V\left(x,t\right)$ Total energy = KE + PE

Suggests modification to Schrödinger equation:

(Total Energy)*(wavefunction) = (KE+PE)*(wavefunction)

Schrödinger

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

Time-dependent Schrödinger equation

The Schrödinger equation: notes

- This was a plausibility argument, *not* a derivation. We believe the Schrödinger equation not because of this argument, but because its predictions agree with experiment.
- There are limits to its validity. In this form it applies only to a single, non-relativistic particle (i.e. one with non-zero rest mass and speed much less than c)
- The Schrödinger equation is a partial differential equation in x and t (like classical wave equation). Unlike the classical wave equation it is first order in time.
- The Schrödinger equation contains the complex number i. Therefore its solutions are *essentially* complex (unlike classical waves, where the use of complex numbers is just a mathematical convenience).
- Note the +ve sign of i in the Schrödinger equation. This came from our looking for plane waves of the form $\Psi \sim e^{-i\omega t}$

We could equally well have looked for solutions of the form $\Psi \sim e^{+i\omega t}$

Then we would have got a –ve sign.

This is a matter of convention (now very well established).

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

The Hamiltonian operator

Time-dependent Schrödinger equation

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

Can think of the RHS of the Schrödinger equation as a *differential operator that represents the energy of the particle*.

This operator is called the *Hamiltonian* of the particle, and usually given the symbol $\hat{H}$

$$\Bigg[\underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\text{Kinetic energy operator}} + \underbrace{V(x,t)}_{\text{Potential energy operator}}\Bigg]\Psi \equiv \hat{H}\Psi$$

Hence there is an alternative (shorthand) form for the time-dependent Schrödinger equation:

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

Hamiltonian is a linear differential operator.
Schrödinger equation is a linear homogeneous partial differential equation

Interpretation of the wave function

Ψ is a complex quantity, so how can it correspond to real physical measurements on a system?

Remember photons: number of photons per unit volume is proportional to the electromagnetic energy per unit volume, hence to *square* of electromagnetic field strength.

Postulate (Born interpretation): probability of finding particle in a small length δx at position x and time t is equal to

$$\left|\Psi(x,t)\right|^2 \delta x$$

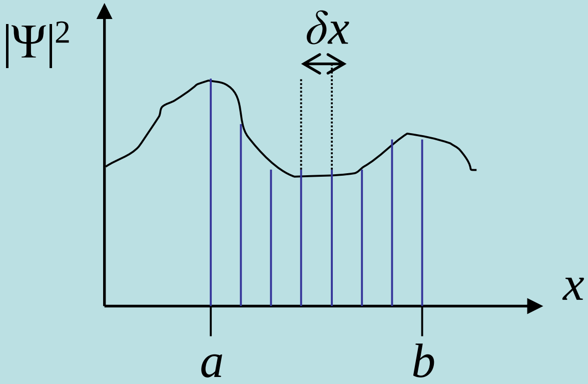
$$\boxed{\left|\Psi\right|^2 = \Psi^*\Psi}$$

Note: $|\Psi(x,t)|^2$ is the probability *per unit length*. It is real as required for a probability distribution.

Born

Total probability of finding particle between positions a and b is

$$\sum_{x=a}^{b}\left|\Psi(x,t)\right|^2 \delta x \xrightarrow[\delta x \to 0]{} \int_a^b \left|\Psi(x,t)\right|^2 \mathrm{d}x$$



Example

Suppose that at some instant of time a particle's wavefunction at t=0 is

$$\boxed{\Psi(x,0) = 2x}$$

The picture can't be displayed.

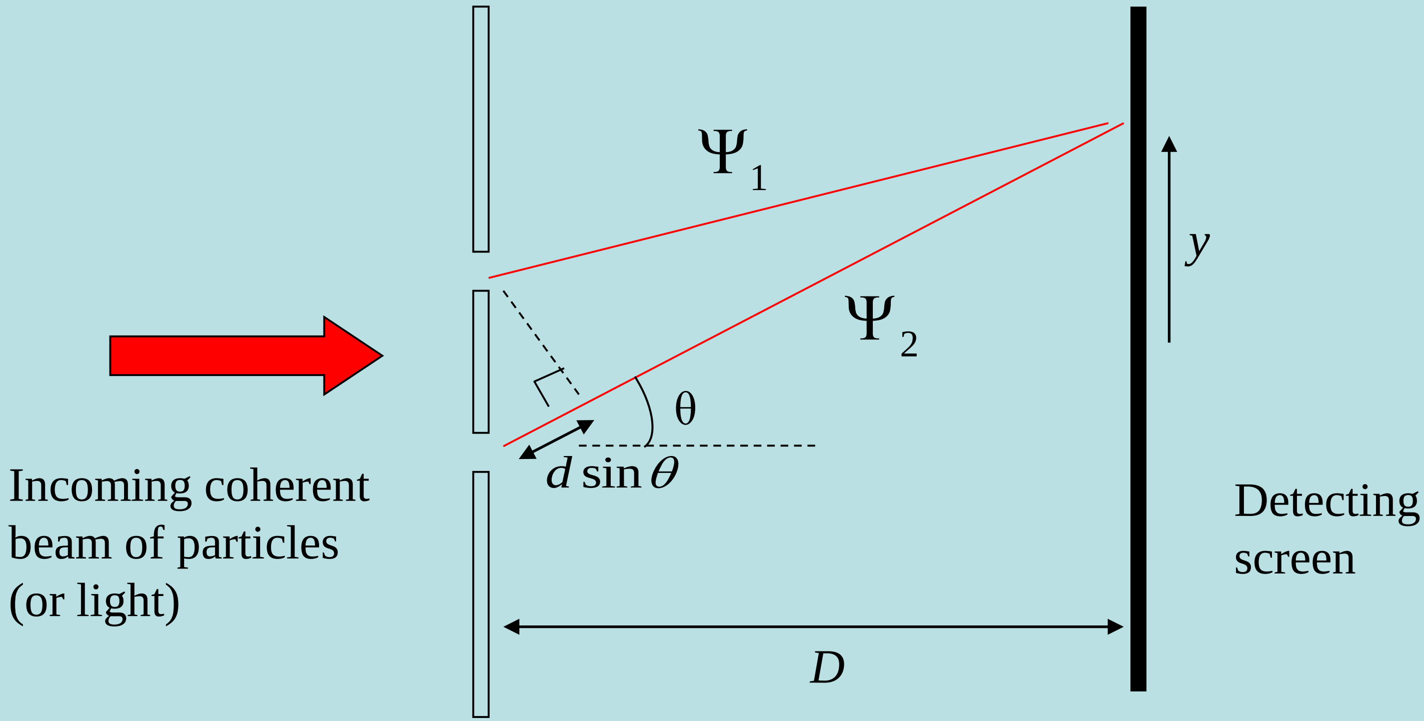
What is:

(a) The probability of finding the particle between *x*=1.0 and *x*=1.001?

(b) The probability per unit length of finding the particle at *x*=1?

(c) The probability of finding the particle between *x*=0 and *x*=0.5?

DOUBLE-SLIT EXPERIMENT REVISITED



Schrödinger equation is linear: solution with both slits open is $\boxed{\Psi = \Psi_1 + \Psi_2}$

Observation is nonlinear $$|\Psi|^2 = \underbrace{|\Psi_1|^2 + |\Psi_2|^2}_{\text{Usual “particle” part}} + \underbrace{\Psi_1^* \Psi_2 + \Psi_1 \Psi_2^*}_{\text{Interference term gives fringes}}$$

Normalization

Total probability for particle to be *somewhere* should always be one

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, \mathrm{d}x = 1$$

Normalization condition

A wavefunction which obeys this condition is said to be normalized

Suppose we have a solution to the Schrödinger equation that is not normalized. Then we can

•Calculate the *normalization integral*

$$N = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, \mathrm{d}x$$

•*Re-scale* the wave function as

$$\psi(x,t) \to \frac{1}{\sqrt{N}} \psi(x,t)$$

(This works because any solution to the SE multiplied by a constant remains a solution, because the SE is LINEAR and HOMOGENEOUS)

New wavefunction is normalized to 1

Normalizing a wavefunction - example

Particle with un-normalized wavefunction at some instant of time t

$$\boxed{\begin{aligned} \Psi(x,t) &= a^2 - x^2, \quad && -a \le x \le a \\ \Psi(x,t) &= 0, && |x| > a \end{aligned}}$$

Conservation of probability

If the Born interpretation of the wavefunction is correct then the normalization integral must be independent of time (and can always be chosen to be 1 by normalizing the wavefunction)

$$\boxed{\int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 \mathrm{d}x = \text{constant}}$$

Total probability for particle to be *somewhere* should ALWAYS be one

We can prove that this is true for physically relevant wavefunctions using the Schrödinger equation. This is a very important check on the consistency of the Born interpretation.

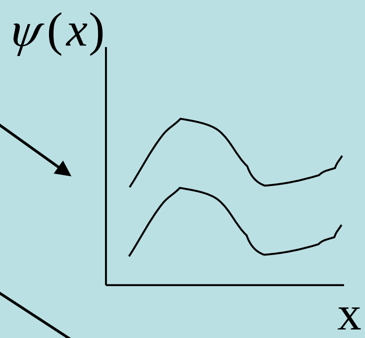
$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x,t)\Psi} \quad \Rightarrow \quad \boxed{\int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 \mathrm{d}x = \text{constant}}$$

Boundary conditions for the wavefunction

The wavefunction must:

Examples of unsuitable wavefunctions

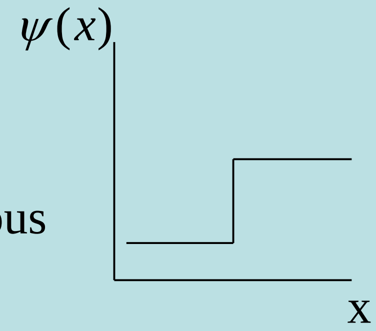
1. Be a continuous and single-valued function of both *x* and *t* (in order that the probability density is uniquely defined)



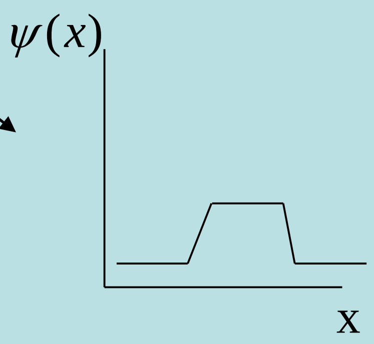
Not single valued

2. Have a continuous first derivative (except at points where the potential is infinite)

Discontinuous



3. Have a finite normalization integral (so we can define a normalized probability)



Gradient discontinuous

Time-independent Schrödinger equation

Suppose potential is independent of time

$$V\left(x,t\right)=V\left(x\right)$$

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

LHS involves only variation of Ψ with t

RHS involves only variation of Ψ with x (i.e. Hamiltonian operator does not depend on t)

Look for a *separated* solution

$$\Psi(x,t)=\psi(x)T(t)$$

Substitute:

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

$$\frac{\partial^2}{\partial x^2}\left[\psi(x)T(t)\right]=T(t)\frac{d^2\psi}{dx^2}$$ etc

N.B. **Total** not partial derivatives now

$$\boxed{-\frac{\hbar^2}{2m}T\frac{d^2\psi}{dx^2}+V(x)\psi T=i\hbar\psi\frac{dT}{dt}}$$

$$-\frac{\hbar^2}{2m}T\frac{d^2\psi}{dx^2}+V(x)\psi T=i\hbar\psi\frac{dT}{dt}$$

Divide by ψT

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}+V(x)=i\hbar\frac{1}{T}\frac{dT}{dt}$$

LHS depends only on x, RHS depends only on t.
True for all x and t so both sides must be a constant, A (A = separation constant)

This gives

$$i\hbar\frac{1}{T}\frac{dT}{dt}=A$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}+V(x)=A$$

So we have two equations, one for the time dependence of the wavefunction and one for the space dependence. We also have to determine the separation constant.

SOLVING THE TIME EQUATION

$$\boxed{i\hbar \frac{1}{T}\frac{dT}{dt} = A}$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = A}$$

$$i\hbar \frac{1}{T}\frac{dT}{dt} = A$$

$$\downarrow$$

$$\frac{dT}{dt} = \left(\frac{-iA}{\hbar}\right)T$$

$$\downarrow$$

$$T(t) = ae^{-iAt/\hbar}$$

This is like a wave $e^{-i\omega t}$ with $\omega = A/\hbar$. So $A = E$.

$$\boxed{T(t) = ae^{-iEt/\hbar}}$$

- This only tells us that *T(t)* depends on the energy E.
 It doesn't tell us what the energy actually is. For that we have to solve the space part.

- *T(t)* does not depend explicitly on the potential *V(x)*. But there is an implicit dependence because the potential affects the possible values for the energy E.

Time-independent Schrödinger equation

With A = E, the space equation becomes:

$$\boxed{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi}$$

or

$$\boxed{\hat{H}\psi=E\psi}$$

This is the time-independent Schrödinger equation

Solution to full TDSE is $\boxed{\Psi(x,t)=\psi(x)T(t)=\psi(x)e^{-iEt/\hbar}}$

Even though the potential is independent of time the wavefunction still oscillates in time

But probability distribution is static

$$P(x,t)=\left|\psi(x,t)\right|^2=\psi^*(x)e^{+iEt/\hbar}\psi(x)e^{-iEt/\hbar}$$

$$=\psi^*(x)\psi(x)=\left|\psi(x)\right|^2$$

For this reason a solution of the TISE is known as a stationary state

Solving the space equation = rest of course!

Notes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi$$

- In one space dimension, the time-independent Schrödinger equation is an *ordinary* differential equation (not a partial differential equation)

- The time-independent Schrödinger equation is an *eigenvalue equation* for the Hamiltonian operator:

Operator × function = number × function

(Compare Matrix × vector = number × vector)

$$\boxed{\hat{H}\psi = E\psi}$$

- We will consistently use uppercase Ψ(*x,t*) for the full wavefunction (TDSE), and lowercase ψ(*x*) for the spatial part of the wavefunction when time and space have been separated (TISE)

SE in three dimensions

To apply the Schrödinger equation in the real (3D) world we keep the same basic structure:

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi} \qquad \boxed{\hat{H}\psi = E\psi}$$

BUT

Wavefunction and potential energy are now functions of *three* spatial coordinates:

$$\begin{aligned} \psi(x) &\to \psi(\mathbf{r}) = \psi(x,y,z) \\ V(x) &\to V(\mathbf{r}) = V(x,y,z) \end{aligned}$$

Kinetic energy now involves *three* components of momentum

$$\frac{p_x^2}{2m} \to \frac{\mathbf{p}^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \to -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

Interpretation of wavefunction:

$$\boxed{d^3\mathbf{r}\left|\psi(\mathbf{r},t)\right|^2} \qquad \boxed{\left|\psi(\mathbf{r},t)\right|^2}$$

probability of finding particle in a volume element centred on **r**

probability density at **r**
i.e. probability *per unit volume*

SE in three dimensions

So 3D Hamiltonian is

$$\boxed{\hat{H}\left(\mathbf{r}\right) = -\frac{\hbar^2}{2m}\nabla^2 + V\left(\mathbf{r}\right)}$$

Time-dependent Schrödinger equation is

$$\boxed{\mathrm{i}\hbar\frac{\partial\Psi\left(\mathbf{r},t\right)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi\left(\mathbf{r},t\right) + V\left(\mathbf{r},t\right)\Psi\left(\mathbf{r},t\right)}$$

Time-independent Schrödinger equation is

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

This is a linear homogeneous *partial* differential equation

Puzzle

The requirement that a plane wave

$$\Psi(x,t) = \mathrm{e}^{i(kx-\omega t)}$$

plus the energy-momentum relationship for free-non-relativistic particles

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

led us to the free-particle Schrödinger equation.

Can you use a similar argument to suggest an equation for free *relativistic* particles, with energy-momentum relationship:

$$E^2 = p^2c^2 + m_0{}^2c^4$$

SUMMARY

Time-dependent Schrödinger equation

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

Probability interpretation and normalization

$$\boxed{P(x,t)\,dx=\left|\Psi(x,t)\right|^2 dx=\Psi^*(x,t)\Psi(x,t)\,dx}$$

$$\boxed{\int_{-\infty}^{+\infty} dx\,P(x,t)=\int_{-\infty}^{+\infty} dx\left|\Psi(x,t)\right|^2=1}$$

Time-independent Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi(x)=E\psi(x)}$$

$$\boxed{\Psi(x,t)=\psi(x)T(t)=\psi(x)e^{-iEt/\hbar}}$$

Conditions on wavefunction

single-valued, continuous, normalizable,
continuous first derivative

$$\boxed{\psi(x,t)=U(x)T(t)=U(x)e^{-iEt/\hbar}}$$


THANK YOU