Need a new theory to understand (dynamics of) electrons and atoms

- **<u>Wavelike equation</u>** for describing sub-atomic systems

NO ONE TOLD ME THAT I WAS GOING TO HAVE TO WORK WITH HER!
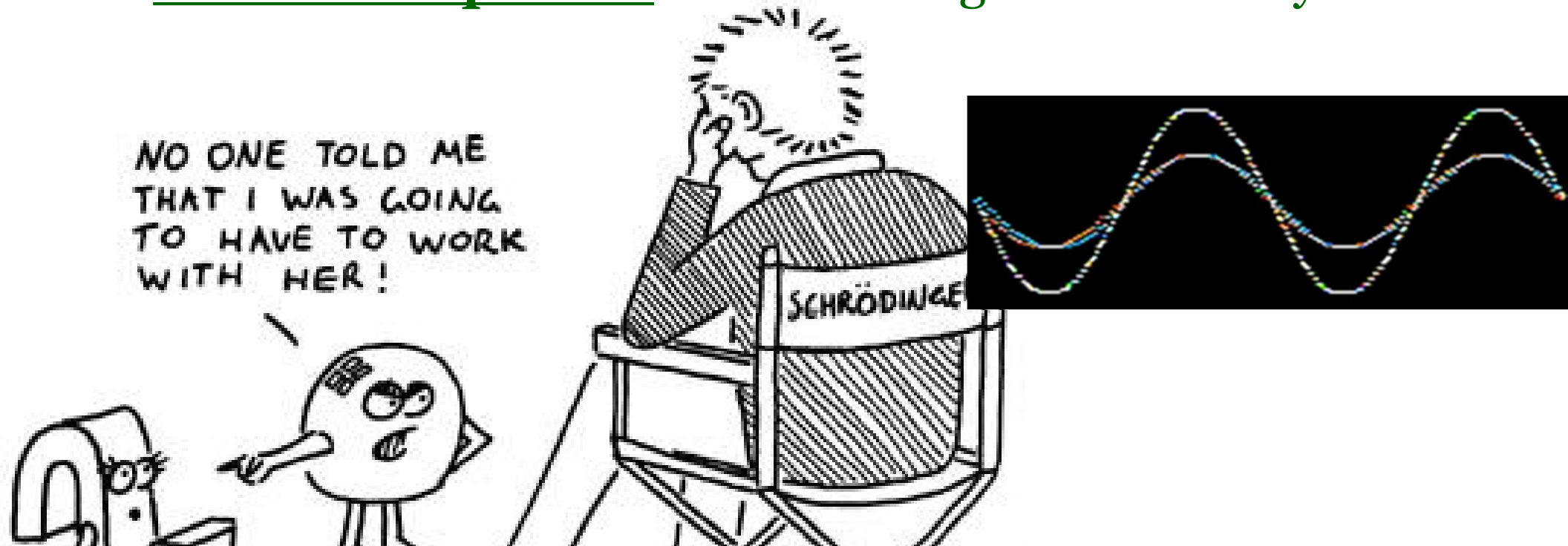
SCHRÖDINGER

"Where did we get that (equation) from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrödinger."

- Richard Feynman

Schrodinger's philosophy

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2}$$ Classical Wave Equation

$\Psi(x,t) =$ Amplitude

$\Psi(x,t) = Ce^{i\alpha}$; Where $\alpha = 2\pi\left(\frac{x}{\lambda} - vt\right)$ is the phase

Remember!

$$E = h\nu = \hbar\omega$$

$$\lambda = \frac{h}{p} = \frac{2\pi}{k}$$

$$\alpha = 2\pi\left(\frac{x}{\lambda} - vt\right) = \frac{x \cdot p - E \cdot t}{\hbar}$$

Schrodinger Equation

In classical mechanics $\hat{H}$ represents total energy

We can therefore write

$$\hat{H}\psi = W\psi \qquad \text{as} \qquad \hat{H}\psi = E\psi$$

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

Time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\cdot\Psi(x,t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(x) \right]\Psi(x,t)$$

Schrodinger equation is an eigenvalue equation

There can be many solutions $\psi_n(x)$ each corresponding to different energy E_n

Why believe in Schrodinger's Eq.?

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

Why believe in Newton's LAWs?

Did you ever question their validity?

__Laws__ → **Based on Postulates or Axioms**
Not been proven wrong experimentally

Laws of Quantum Mechanics

1. The state of a system is _completely specified_ by a wave- function Ψ(r,t). Square of "wavefunction" →probability density

2. To every observable in classical mechanics, there corresponds a linear operator in quantum mechanics

3. In measurement of observable associated with operator **A**, _only values that will be observed_ are the (real) _eigenvalues of A, which satisfy the eigenvalue eq._

$$\hat{A} \cdot \Psi_n = a_n \cdot \Psi_n$$

$\boldsymbol{\Psi_n}$ are the eigenfunctions of the system and $\boldsymbol{a_n}$ are corresponding eigenvalues

If the system is in state $\boldsymbol{\Psi_k}$, a measurement on the system will yield an eigenvalue $\boldsymbol{a_k}$

Laws of Quantum Mechanics

Only real eigenvalues will be observed, which will specify a number corresponding to the classical variable

If $\quad \Psi(x) = Sin(cx)$

$$\frac{d}{dx}\Psi(x) = c \cdot Cos(cx)$$

$$\frac{d^2}{dx^2}\Psi(x) = -c^2 \cdot Sin(cx) = -c^2 \cdot \Psi(x)$$

There may be, and typically are, many eigenfunctions for the same QM operator!

If $\quad \Psi(x) = e^{\alpha x}$

$$\frac{d}{dx}\Psi(x) = \alpha \cdot e^{\alpha x}$$

$$\frac{d^2}{dx^2}\Psi(x) = \alpha^2 \cdot e^{\alpha x} = \alpha^2 \cdot \Psi(x)$$

Operators

$$\frac{-h}{i}\frac{\partial \Psi(x,t)}{\partial t} = E \times \Psi(x,t) \qquad \frac{h}{i}\frac{\partial \Psi(x,t)}{\partial x} = p_x \times \Psi(x,t)$$

$$\frac{-h}{i}\frac{\partial}{\partial t}\Psi(x,t) = E \times \Psi(x,t) \qquad \frac{h}{i}\frac{\partial}{\partial x}\Psi(x,t) = p_x \times \Psi(x,t)$$

$$\frac{-h}{i}\frac{\partial}{\partial t} = ih\frac{\partial}{\partial t} = \cancel{E} \qquad \frac{h}{i}\frac{\partial}{\partial x} = -ih\frac{\partial}{\partial x} = \cancel{p}_x \qquad \text{Operators}$$

Operator

A symbol that tells you to do something to whatever follows it

Operators can be real or complex,

Operators can also be represented as matrices

Schrodinger Equation

Time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \widehat{H}\cdot\Psi(x,t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(x)\right]\Psi(x,t)$$

$$\widehat{H}\cdot\Psi(x,y,z,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t) \; ; \quad \widehat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(x,y,z)$$

Schrodinger equation in 3-dimensions

Schrodinger Equation

Time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \widehat{H}\cdot\Psi(x,t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(x)\right]\Psi(x,t)$$

$$\widehat{H}\cdot\Psi(x,y,z,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t) \; ; \quad \widehat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(x,y,z)$$

$$\Psi(x,y,z,t) = \psi(x,y,z)\cdot\phi(t) \implies \Psi = \psi\cdot\phi$$

$$\widehat{H}\cdot\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

$$\widehat{H}(\psi\cdot\phi) = i\hbar\frac{\partial}{\partial t}(\psi\cdot\phi)$$

Schrodinger Equation

$$\widehat{H}(\psi \cdot \phi) = i\hbar \frac{\partial}{\partial t}(\psi \cdot \phi)$$

$\widehat{H}$ operates only on ψ and $\frac{\partial}{\partial t}$ operates only on ϕ

$$\phi \cdot \widehat{H}\psi = \psi \left(i\hbar \frac{\partial}{\partial t} \phi \right)$$

Divide by $\psi \cdot \phi$

$$\frac{\widehat{H}\psi}{\psi} = \frac{1}{\phi} \left(i\hbar \frac{\partial}{\partial t} \phi \right)$$

LHS is a function of co-ordinates and RHS is function of time. If these two have to be equal then both functions must be equal to constant, say W

Schrodinger Equation

$$\frac{\widehat{H}\psi}{\psi} = \frac{1}{\phi}\left(i\hbar\frac{\partial}{\partial t}\phi\right) = W$$

$$\frac{\widehat{H}\cdot\psi}{\psi} = W \qquad\qquad \widehat{H}\psi = W\psi$$

$$\frac{1}{\phi}\left(i\hbar\frac{\partial}{\partial t}\phi\right) = W \qquad\qquad i\hbar\frac{\partial}{\partial t}\phi = W\phi$$

Separation of variables

The solution of the differential equation

$$i\hbar\frac{\partial}{\partial t}\phi = W\phi \qquad \text{is} \qquad \phi(t) = e^{-iWt/\hbar}$$

Schrodinger Equation

In classical mechanics $\hat{H}$ represents total energy

We can therefore write

$$\widehat{H}\psi = W\psi \qquad \text{as} \qquad \widehat{H}\psi = E\psi$$

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

Schrodinger equation is an eigenvalue equation

There can be many solutions $\psi_n(x)$ each corresponding to different energy E_n

Laws of Quantum Mechanics

4. All the eigenfunctions of Quantum Mechanical operators are "Orthogonal"

$$\int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x)dx = \langle \psi_m | \psi_n \rangle = 0 \quad \text{for} \quad m \neq n$$

Laws of Quantum Mechanics

5. The average value of the observable corresponding to operator Â is

$$\langle a \rangle = \int \Psi * \hat{A} \Psi \, d\upsilon$$

From classical correspondence we can define average values for a distribution function **P(x)**

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) \cdot dx \text{ and } \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \cdot dx$$

<a> corresponds to the average value of a classical physical quantity or observable , and Â represents the corresponding Quantum mechanical operator

$$\langle a \rangle = \int_{-\infty}^{+\infty} \hat{A} . P(x) \, dx = \int_{-\infty}^{+\infty} \hat{A} . |\Psi|^2 \, dx \approx \int_{all \; space} \Psi^* \hat{A} \Psi \, dx = \left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle$$

Math-3. Probability Distributions: Expectation (Average/Mean value) and Most-Probable Value
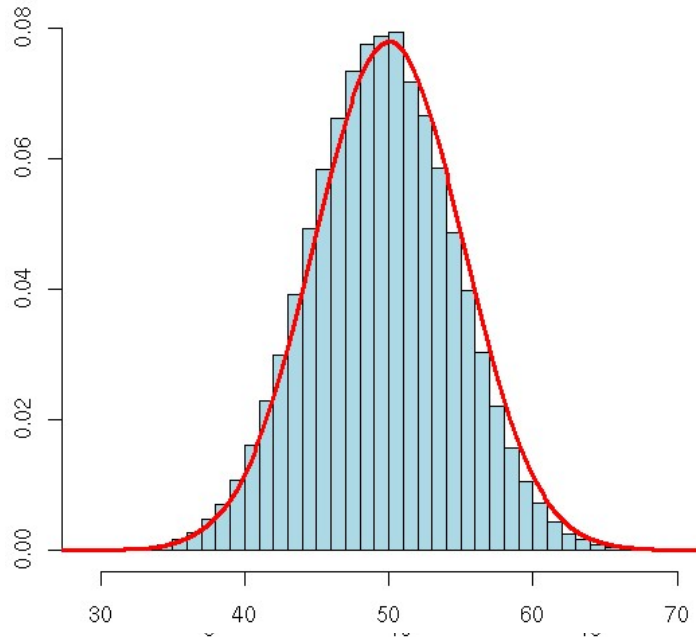
If P(x) is the probability distribution

Most Probable (Modal) value at $Maxima \rightarrow \dfrac{dP(x)}{dx} = 0$

$$Mean: E(x) = \langle x \rangle = \sum_{j=1}^{n} x_j P_j(x_j) \text{ and } E(x^2) = \langle x^2 \rangle = \sum_{j=1}^{n} x_j^2 P_j(x_j)$$

What can you get from solving the Schrodinger Equation?

Ψ

x

$p = \hbar k$
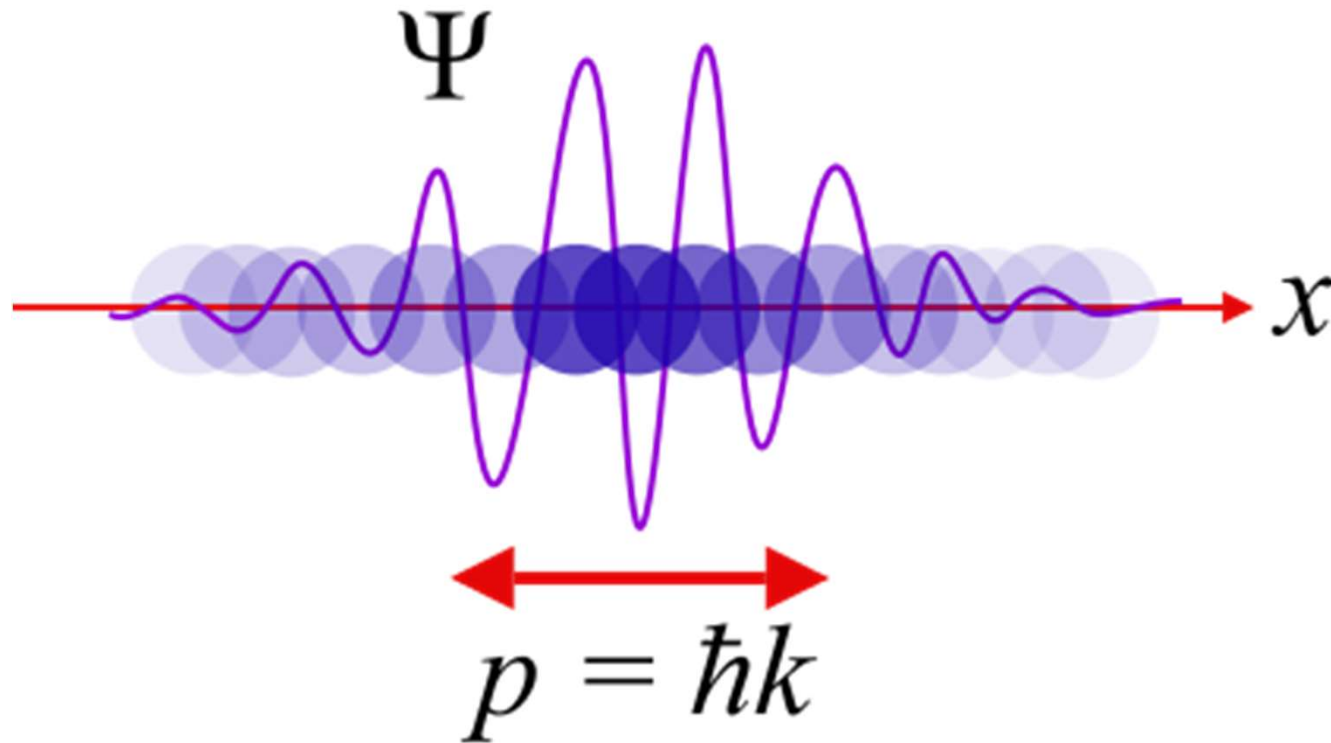
Ψ is a mathematical function; real or complex

What is the meaning of ψ(x,t)?

Born Interpretation

Classical wave equation:
$\Psi(x,t)$ = Amplitude and $|\Psi(x,t)|^2$ = Intensity

Quantum mechanical system:

- The state is completely specified by a wavefunction $\Psi(x,t)$, which can be complex

- All possible information can be derived from $\Psi(x,t)$

- Intensity is equivalent to Probability.

- $|\Psi(x,t)|^2 = P(x)$

Born Interpretation

Probability density

$$P(x) = \left| \Psi(x,t) \right|^2 = \Psi^*(x,t) \cdot \Psi(x,t)$$

Probability

$$P(x_a \leq x \leq x_a + dx) = \left| \Psi(x,t) \right|^2 dx = \Psi^*(x_a,t) \cdot \Psi(x_a,t)dx$$

Probability in 3-dimensions
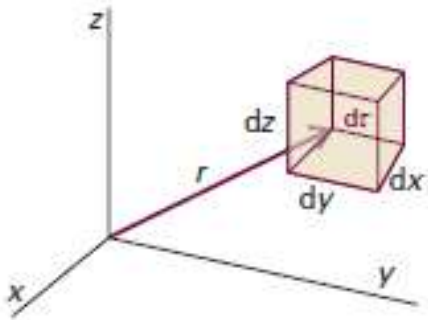
$$\mathrm{P}(x_a \leq x \leq x_a + dx, y_a \leq y \leq y_a + dy, z_a \leq z \leq z_a + dz)$$

$$= \Psi^*(x_a, y_a, z_a, t') . \Psi(x_a, y_a, z_a, t')dxdydz$$

$$= \left| \Psi(x_a, y_a, z_a, t') \right|^2 d\tau$$

6. Normalization of Wavefunction

Since $\Psi^*\Psi d\tau$ is the probability, the total probability of finding the particle somewhere in space has to be unity
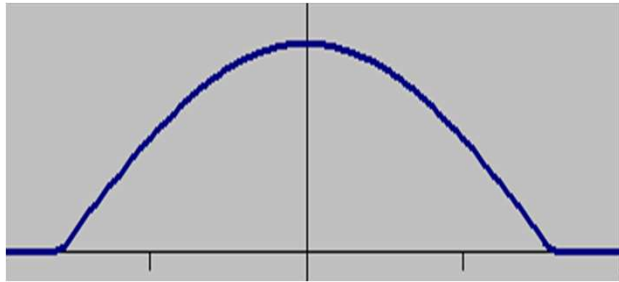
$$\iiint_{all\ space} \Psi^*(x,y,z).\Psi(x,y,z)dxdydz$$

$$= \int_{all\ space} \Psi^*\Psi d\tau = \langle \Psi | \Psi \rangle = 1$$

If function diverges, i.e. $\rightarrow \infty$: Ψ can not be normalized, and therefore is NOT an acceptable wave function.
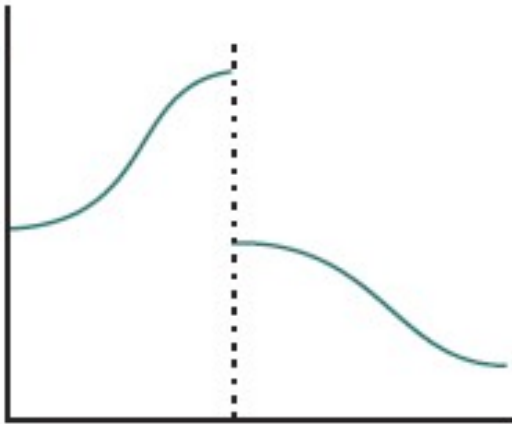

Unacceptable wavefunction
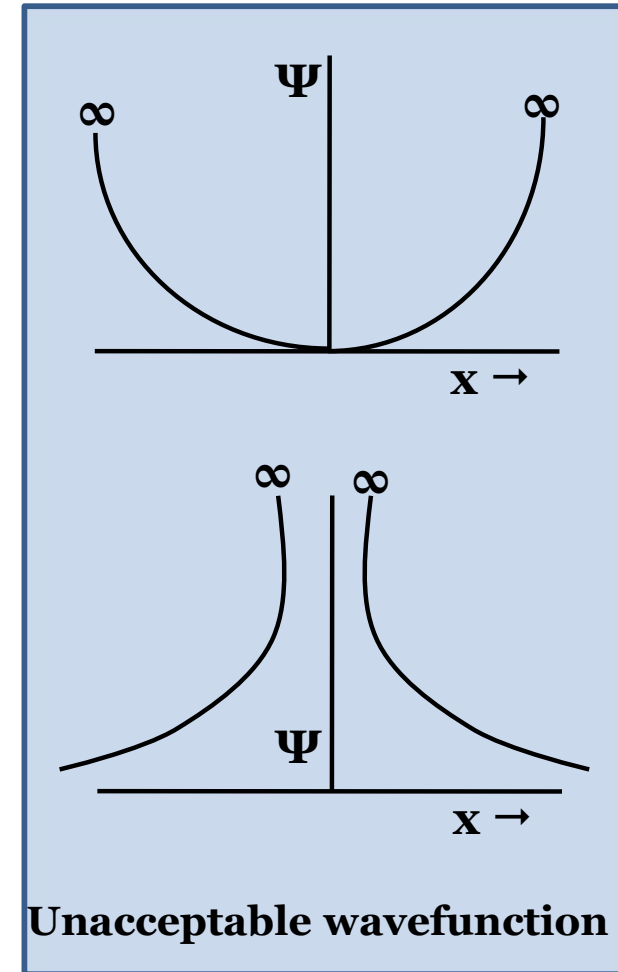
Ψ must vanish at $\pm\infty$, or more appropriately at the boundaries and Ψ must be finite
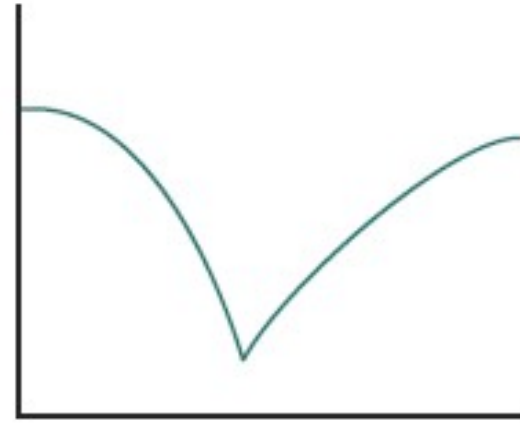
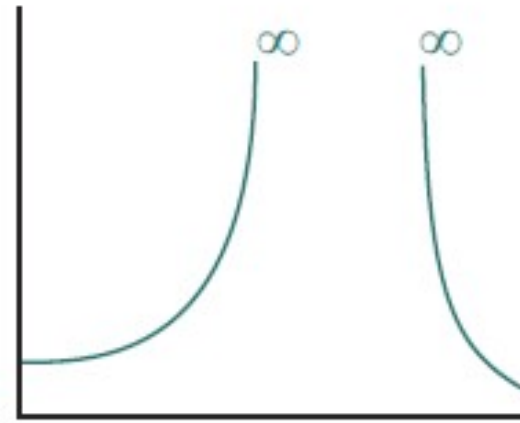# Acceptable wavefunctions
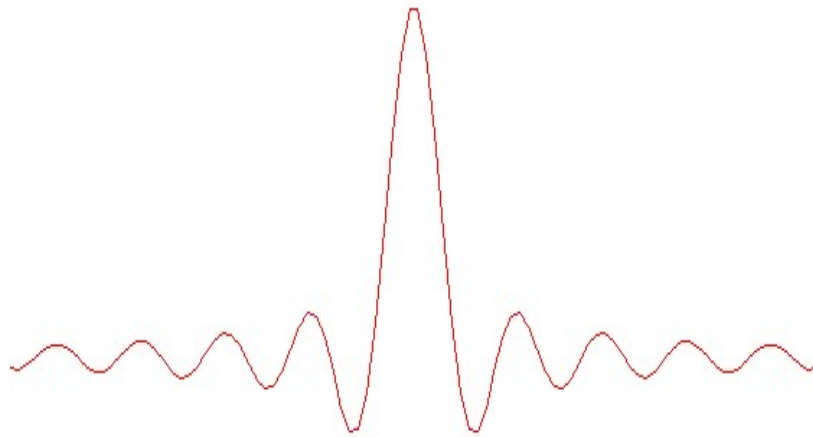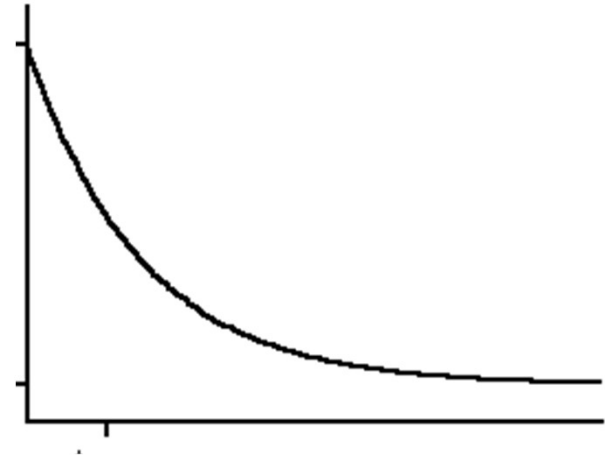
Restrictions on wavefunction

Unacceptable because ψ is not continuous

Unacceptable because dψ/dq is not continuous

Unacceptable because ψ is not single-valued

Unacceptable because ψ goes to infinity

Restrictions on wavefunction

$\boldsymbol{\psi}$ must be a solution of the Schrodinger equation

$\boldsymbol{\psi}$ must be normalizable: $\boldsymbol{\psi}$ must be finite and $\rightarrow$0 at boundaries/ ±∞

$\boldsymbol{\Psi}$ must be a continuous function of x,y,z

d$\boldsymbol{\Psi}$/dq must be must be continuous in x,y,z

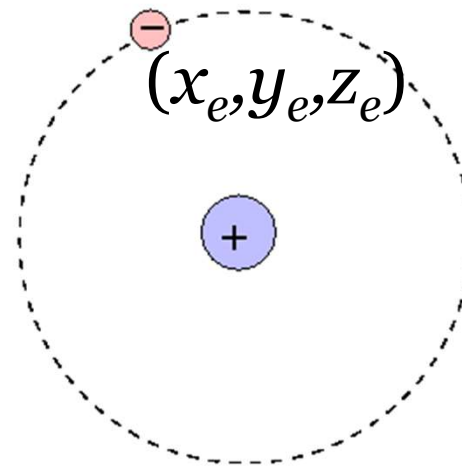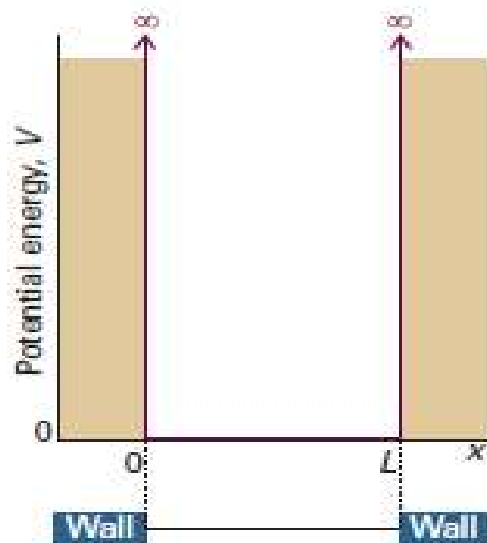$\boldsymbol{\Psi}$ must be single-valued

$\boldsymbol{\Psi}$ must be quadratically-intergrable
    (square of the wavefunction should be integrable)

Boundary conditions: Quantization

Quantum Mechanics

Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential
3. Hydrogen Atom

(x_e, y_e, z_e)

Free Particle

Time-independent Schrodinger equation

$$\widehat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right]\psi(x) = E \cdot \psi(x)$$
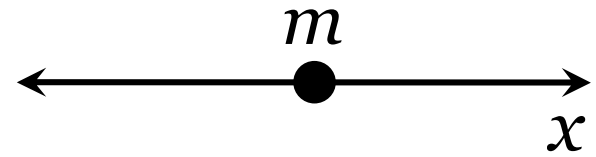
For a free particle $V(x)=0$
There are no external forces acting

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E \cdot \psi(x)$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E \cdot \psi(x)$$

Second-order linear differential equation

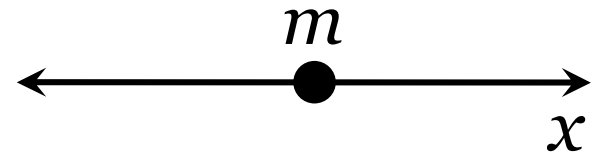Let us assume

$$\psi(x) = A\sin kx + B\cos kx$$

Trial Solution

$$\psi(x) = A\sin kx + B\cos kx$$

$$\frac{\partial}{dx}\psi(x) = \frac{\partial}{dx}\left(A\sin kx + B\cos kx\right) = k\left(A\cos kx - B\sin kx\right)$$

$$\frac{\partial^2}{dx^2}\psi(x) = -k^2\left(A\sin kx + B\cos kx\right) = -k^2\psi(x)$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$

m

x

Second-order linear differential equation

Let us assume

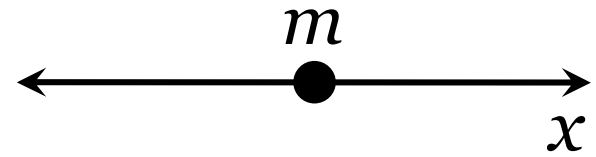$\psi(x) = A\sin kx + B\cos kx$

Trial Solution

$$\psi(x) = A\sin kx + B\cos kx$$

$$\frac{\partial}{dx}\psi(x) = \frac{\partial}{dx}\left(A\sin kx + B\cos kx\right) = k\left(A\cos kx - B\sin kx\right)$$

$$\frac{\partial^2}{dx^2}\psi(x) = -k^2\left(A\sin kx + B\cos kx\right) = -k^2\psi(x)$$

Free Particle
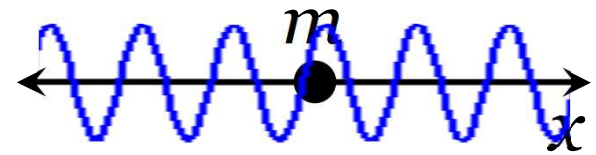
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E \cdot \psi(x)$$

$$\frac{\hbar^2}{2m}k^2\psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E \cdot \psi(x)$$

de Broglie wave

$$\frac{\hbar^2}{2m}k^2\psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

$$E = \frac{\hbar^2 k^2}{2m}$$

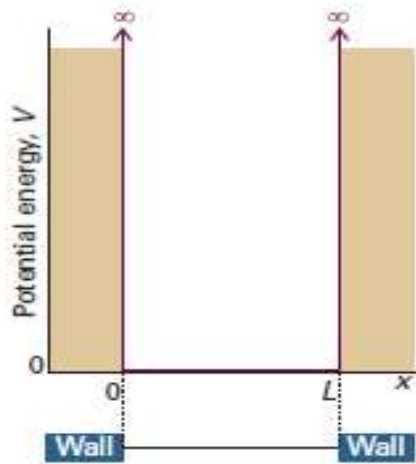There are no restrictions on k
E can have any value
Energies of free particles are continuous

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

No Quantization   **All energies are allowed**

Particle in 1-D Square-Well Potential

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

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

For regions in the space $x < 0$ and $x > L \Rightarrow V = \infty$

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

Normalization condition not satisfied $\Rightarrow$

$$\psi(x < 0) = 0 \quad \text{and} \quad \psi(x > L) = 0$$

Particle in 1-D Square-Well Potential

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

For regions in the space $0\leq x\leq L\Rightarrow V=0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\cdot\psi(x)$$

This equation is similar to free particle Schrodinger
However, boundary conditions are present

Let is assume

$$\psi(x)=A\sin kx+B\cos kx$$ Trial Solution

$$E=\frac{\hbar^2 k^2}{2m}$$ Energy

Particle in 1-D Square-Well Potential

$$\psi(x) = A\sin kx + B\cos kx$$

Boundary Condition $x = 0 \implies \psi(x) = 0$

$$\psi(x) = A\sin kx \qquad \cos 0 = 1$$

Boundary Condition $x = L \implies \psi(L) = 0$

$$\psi(L) = 0 \implies A\sin kL = 0 \implies A = 0 \;\; \text{or} \;\; \sin kL = 0$$

But the wavefunction $\psi(x)$ CANNOT be ZERO everywhere

$$\sin kL = 0 \implies kL = n\pi \;\; \text{n=1,2,3,4...}$$
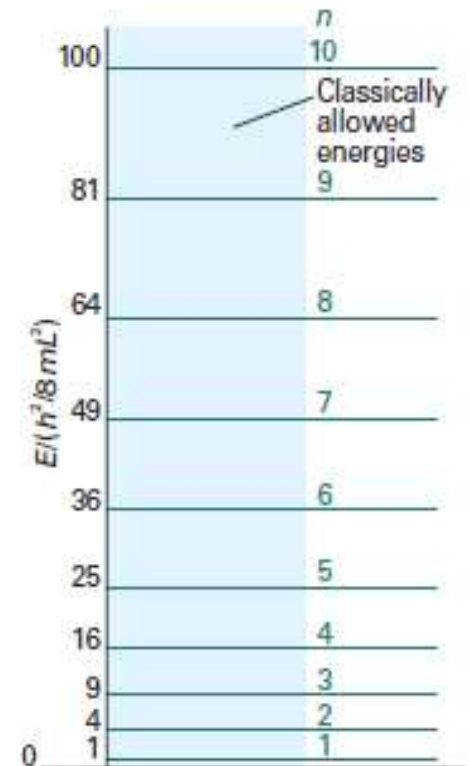
Wavefunction is $\psi(x) = A\sin kx$

Particle in 1-D Square-Well Potential

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad k = \frac{n\pi}{L}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \quad \text{n=1,2,3,4...}$$

Energy is no longer continues but has discrete values; Quantization of energy

Energy separation increases with increasing values of *n*

The lowest allowed energy level is for *n=1*

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \quad \text{has a non zero value} \Rightarrow \text{Zero Point Energy}$$