The Schrödinger equation

DISCLAIMER

At the very beginning, it must be stated that
Erwin Schrödinger
GUESSED
the form of the differential equation governing
quantum dynamics.

Any attempt to “derive” it is only hand-wavy. Its
success will be judged by its ability to explain
observed phenomena

What are components that went into the GUESS?

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right)\psi = 0 \quad \rightarrow \quad \left(\frac{m_0 c}{\hbar}\right)^2 \psi$$ ..... modified classical wave eqn

Klein, Gordon, Schrödinger, Fock and few other tried it (1925-26).....
Does not work for electrons in an atom

A generic wave ~ $e^{i(kx-\omega t)}$ But $p \Leftrightarrow k$ and $E \Leftrightarrow t$

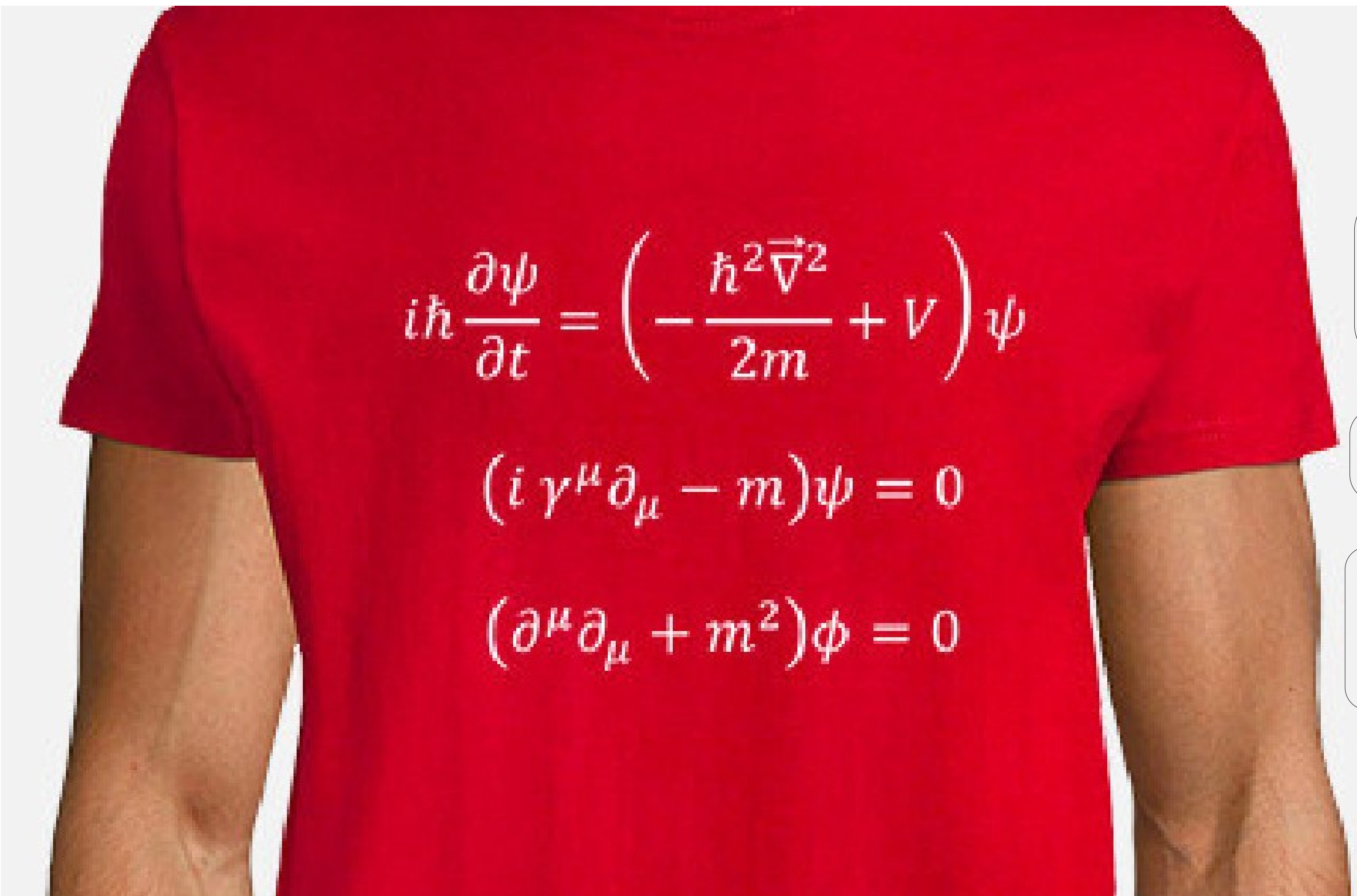
Is there a correspondence ? $\begin{cases} \text{spatial derivative} \Leftrightarrow \text{momentum} \\ \text{time derivative} \Leftrightarrow \text{energy} \end{cases}$

Hamiltonian formulation of classical mechanics gives a certain correspondence between x and p and a few others quantitities ......

Special relativity : $E^2 = p^2 c^2 + m_0^2 c^4 \Rightarrow$ a relation between E, p etc.
Note : Schrödinger eqn is NOT relativistic at the end.

What MUST the end product be able to explain ?

Extensive data on atomic spectra, splitting of lines of H-atom...
Discrete levels from something more than just standing waves
Essentially : The systematic step beyond Bohr-Sommerfeld



Schrödinger (1926)

Dirac (1928)

Klein & Gordon (1926)

What did Schrödinger find a way to do?

Quantization as an eigenvalue problem

E. Schrödinger, *Annalen der Physik,* **4**, 79 (1926)

An undulatory theory of the mechanics of atoms and molecules

E. Schrödinger, *Physical Review,* **28**(6), 1049 (1926)

Atomic spectra is discrete → some robust formalism is necessary to generate this sequence of the allowed values.

[Operator][Some function] = [constant] [Same function]

Only works for some specific values characteristic of the operator.

Schrödinger made this connection.
[Some function] → wavefunction of "matter waves".
[constant] → the eigenvalue (eigen = own).
These eigenvalues are the desired energy values.

Justifying the form of Schrödinger equation : after knowing the answer!

Consider a matter wave : $\Psi(x,t) = Ae^{i(kx-\omega t)} \equiv \psi(x)\phi(t)$

$$\frac{d^2}{dx^2}\psi(x) = -k^2\psi(x) = -\frac{p^2}{\hbar^2}\psi(x)$$ ...de Broglie

$$\frac{d}{dt}\phi(t) = -i\omega\phi(t) = -i\frac{E}{\hbar}\phi(t)$$

non-relativistic $E = \frac{p^2}{2m} + V(x) \Rightarrow p^2 = 2m(E - V(x))$

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

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

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

But where is the eigenvalue in this ?

Now let us start from the final form :

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\Psi=i\hbar\frac{\partial}{\partial t}\Psi \quad \text{\& write} \quad \Psi(x,t)=\psi(x)e^{-iEt/\hbar}$$

The spatial part would give the Eigenvalue form →

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

generalise $\frac{d^2}{dx^2}\to\nabla^2$ in 3D & put $V(r)=-\frac{e^2}{4\pi\epsilon_0 r}$

A non-trivial eignevalue problem : solved by Schrödinger and Weyl
With correct boundary conditions gives the H-atom spectra correctly !

Note : like any differential equation...
You cannot solve it unless you know/justify the boundary conditions

Interpretation of $\Psi(x,t)$ and measurement of a physical quantity

Max Born provided the correct interpretation

$|\Psi(x,t)|^2 dx$ is the *probability* of locating the particle in $x, x+dx$

This assumes Ψ is normalised $\Rightarrow \int_{\substack{all\\space}} |\Psi(x,t)|^2 dx = 1$

Once $\Psi(x,t)$ is computed, how do we get things other than energy ?

Corresponding to every physical quantity there is an operator $\hat{O}$

Any measurement of that quantity can only yield an eigenvalue of $\hat{O}$

The average of MANY such measurement is the expectation value

$$\langle \hat{O} \rangle \equiv \frac{\int \Psi^* \left(\hat{O}\, \Psi \right) dx}{\int \Psi^* \Psi \, dx}$$

The wavefunction is in general complex. The operators corresponding to phsyical quantities will always have REAL *expectation* values.

Problem 1 : The wavefunction for a free particle

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad \begin{cases} V=0 \\ \text{everywhere} \end{cases}$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2}\right)\psi = 0$$

$$\text{introduce wavevector :} \quad k^2 = \frac{2mE}{\hbar^2} \qquad \begin{cases} \text{assume} \\ E>0 \end{cases}$$

$$\text{wavelike solution :} \quad \psi(x) = A\,e^{ikx} + B\,e^{-ikx}$$

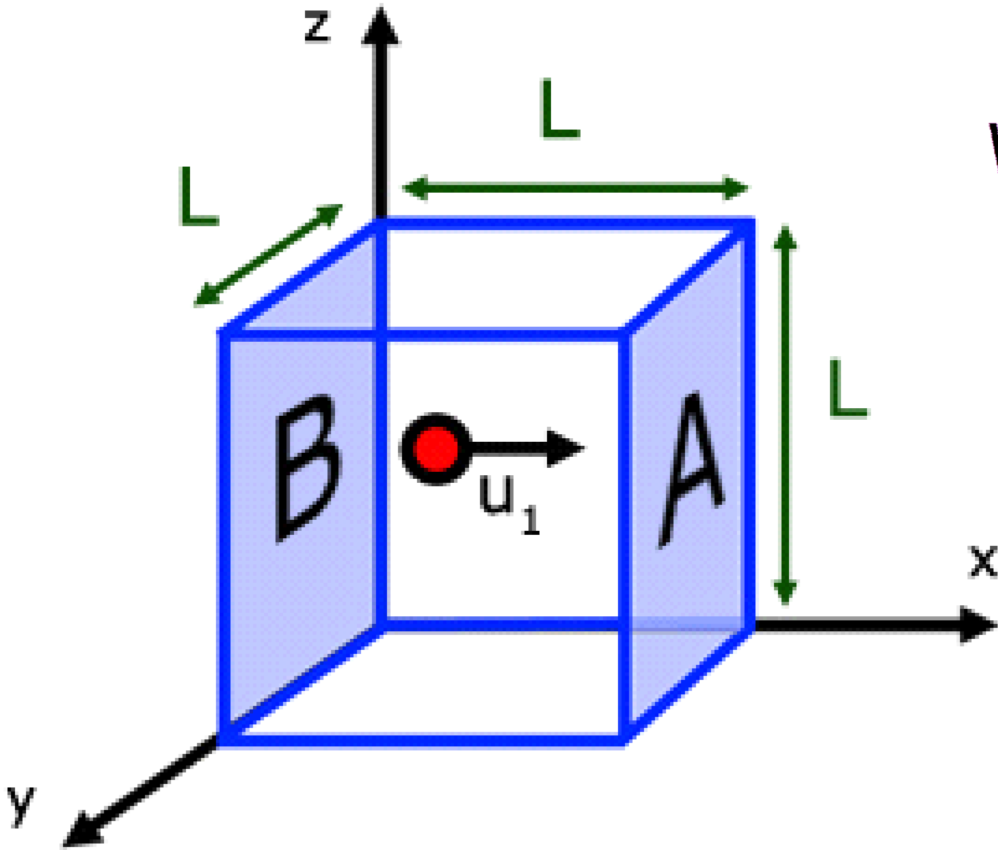
Note : $\psi = A\cos kx + B\sin kx$ are special choices only

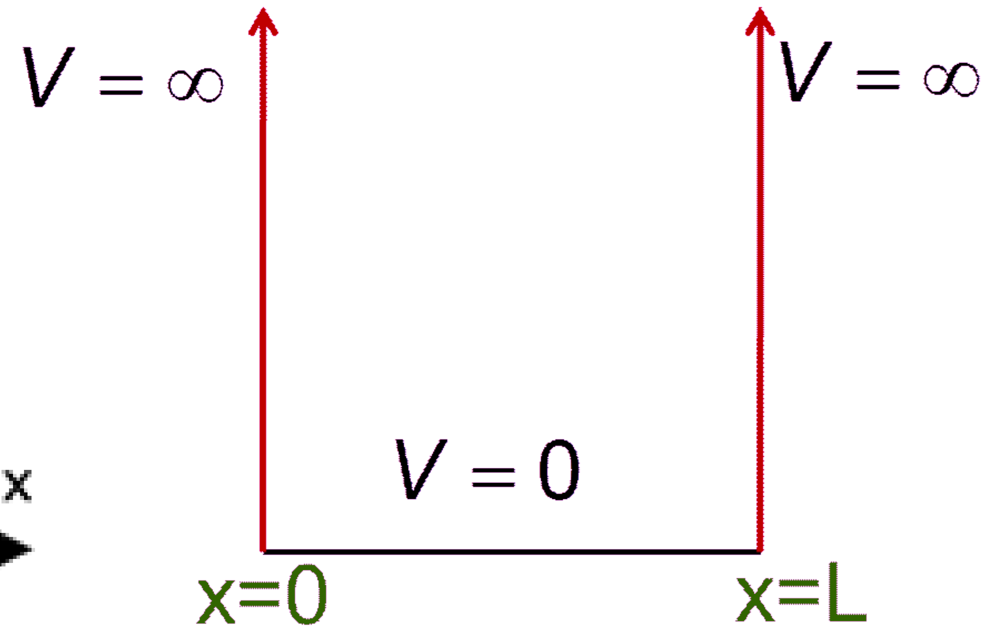
In this case the energy eigenvalues are continuous

Try calculating the momentum expectation $\langle \hat{p} \rangle$

Problem 2 : a particle in the box ....for the N^{th} time

Pic Courtesy: http://www.a-levelphysicstutor.com/therm-kin-theory.php



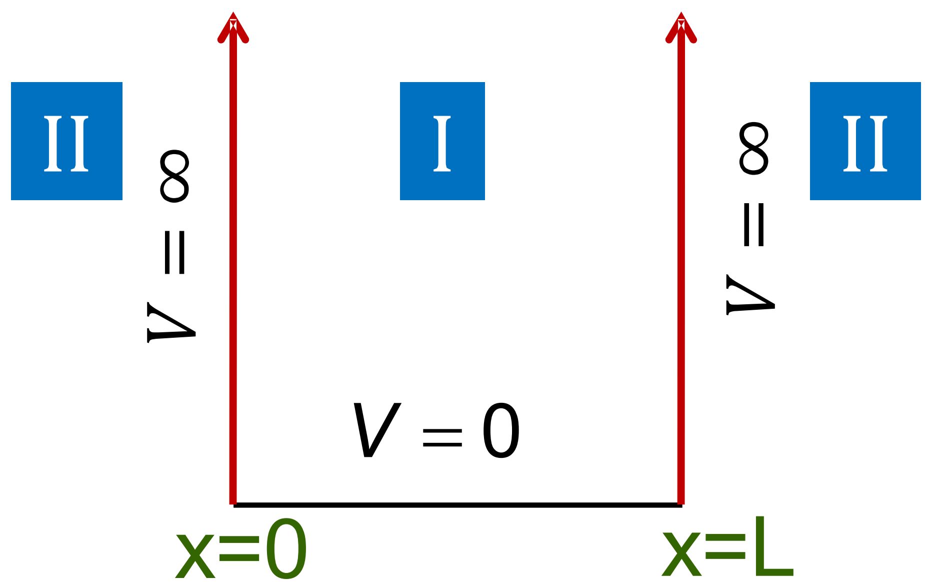


$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad \begin{cases} V = 0 & \text{for } 0 < x < L \\ V = \infty & \text{otherwise} \end{cases}$$

$V = \infty \Rightarrow$ particle cannot exist there $\Rightarrow \psi = 0$ there

Problem 2 : a particle in the box ....for the N^{th} time

Divide the required interval into regions. In this case we only need the solution for region I



We need to know what the wavefunction will do at the boundaries.

The wavefunction MUST be continuous. So in this case it needs to vanish at both boundaries

Unless the discontinuity of the potential is *infinite* , (as in this case), the derivative of the wavefunction should also be continuous. In this case it will be so.

Problem 2 : a particle in the box ....for the N^{th} time : Energy eigenvalues

For Region I : $\quad \ldots k^2 = \dfrac{2mE}{\hbar^2}$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \Rightarrow \psi = A e^{ikx} + B e^{-ikx}$$

Boundary conditions
$$\begin{cases} \psi(0) = 0 \Rightarrow A + B = 0 \\ \psi(L) = 0 \Rightarrow A e^{ikL} + B e^{-ikL} = 0 \end{cases}$$

$$\Rightarrow A\left(e^{ikL} - e^{-ikL}\right) = 0 \Rightarrow \begin{cases} \text{either } A, B = 0 \\ \text{or} \quad \sin kL = 0 \end{cases}$$

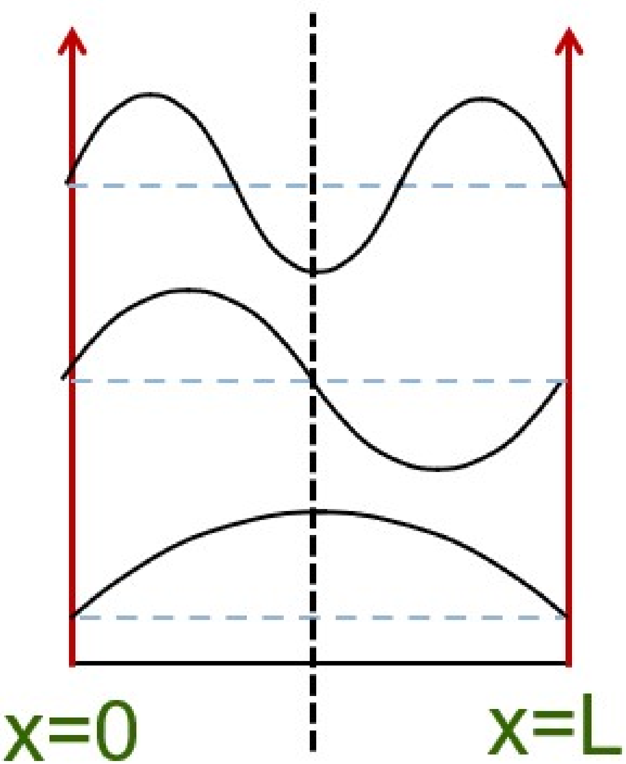
$$\sin kL = 0 \quad \Rightarrow k_n = \frac{n\pi}{L} \quad \Rightarrow E_n = \frac{\hbar^2\pi^2}{2mL^2} n^2$$

Problem 2 : a particle in the box ....for the N^{th} time : Wavefunctions

$$A+B=0 \;\Rightarrow\; \psi(x)=C_n \sin k_n x \Rightarrow |C_n|^2 \int_0^L (\sin k_n x)^2 dx = 1$$

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \;\Rightarrow\; \int_0^L \psi_n(x)\psi_m(x)\,dx = \delta_{mn}$$

in this case normalisation is n independent



$\psi_n(x)$ are alternately odd or even w.r.t to the centre of the box

As n increases, the number of nodes of $\psi_n(x)$ increases

Calculate $\langle \hat{p} \rangle$ for any $\psi_n(x)$

Does the result surprise you ?