The Birth of Quantum Mechanics

Louis de Broglie 1892-1987
Erwin Schrödinger 1887-1961
Paul Dirac 1902-1984
Werner Heisenberg 1901-1976

New Wave Rock Stars
Blackbody radiation: Light energy is quantized.

\[ E = h \nu = \frac{hc}{\lambda} \]

\[ h = \text{Planck's constant} \]

\[ 6.626 \times 10^{-34} \text{ Joule sec} \]

Max Planck
1858-1947
The Photoelectric Effect (1905)

The energy of a photon, $E_{\text{photon}}$, is given by $h\nu$

$E_{\text{photon}} = h\nu$

- $v_{\text{max}} = 6.22 \times 10^5$ m/s
- $550 \text{ nm } 2.25 \text{ eV}$
- $400 \text{ nm } 3.1 \text{ eV}$
- $700 \text{ nm } 1.77 \text{ eV}$

No electrons emitted for wavelengths below the threshold frequency.

Potassium - 2.0 eV needed to eject electron

Photoelectric effect

$h\nu = E_{\text{kinetic}} + \phi_{\text{metal}}$

Wavelength dependence must be explained by the existence of quantized light.

Nobel Prize (his only one) awarded in 1921.

Albert Einstein 1879-1955
De Broglie Wavelength (1924)

All particles have a wave nature, just as electromagnetic waves have a particle nature.

\[ \lambda = \frac{h}{p} \]

Electron diffraction is observed, even when the flux of electrons is so low, that consecutive electrons encounter these slits one at a time.

Louis de Broglie
1892-1987

Clearly, we need a way to predict the bizarre behavior of these particles. Enter the New Wave Stars: Schrödinger, Heisenburg and Dirac!
The Birth of Quantum Mechanics

Erwin Schrödinger
1887-1961
Schrödinger Equation
Wave Mechanics

Werner Heisenberg
1901-1976
Heisenberg Representation
Matrix Mechanics

Paul Dirac
1902-1984
Dirac Equation
Relativistic Quantum Mechanics

Plus: Max Born, Wolfgang Pauli, Enrico Fermi, Freeman Dyson, Richard Feynman...
A psi for everything -- what a state!

\[ |\Psi(t)\rangle \]

State Vectors (most general)
Dirac bra-ket notation
Spins, Photons, SHO

\[ \Psi(x,t) \]

One-Dimensional
Wavefunction
PIAB

\[ \Psi(r,t) \]

Three Dimensional
Wavefunction
Hydrogen Atom
The Schrödinger Equation

\[ i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \]

\[ i^2 = -1 \]

\[ \hbar = \frac{h}{2\pi} \]

The Full Time Dependent Schrödinger Equation. The real deal. $H$ is the "Hamiltonian Operator".
The Time Independent Schrödinger Equation

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \]

or \[ E = \langle \Psi | \hat{H} |\Psi\rangle \]

The wavevector \( \Psi \) is now time independent.
The Hamiltonian Operator

\[ \hat{H} = \frac{\hat{p}^2}{2m} + V(x) \]

\[ \hat{p} = -i\hbar \frac{d}{dx} \]

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \]

H is the Hamiltonian operator. In classical physics, \( H \) for a particle is the sum of its kinetic and potential energy: \( p^2/2m + V(x) \). Schrödinger replaced \( p \) with a differential operator.

Hamiltonian for one-dimensional problems
The Hamiltonian Operator

\[ \hat{H} = \frac{\hat{p}^2}{2m} + V(\mathbf{r}) \]

\[ \hat{p} = -i\hbar \nabla \]

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \]

H is the Hamiltonian operator. In classical physics, \( H \) for a particle is the sum of its kinetic and potential energy: \( p^2/2m + V(r) \). Schrödinger replaced \( p \) with a differential operator.

Hamiltonian for three-dimensional problems

\[ \mathbf{r} = \hat{i}x + \hat{j}y + \hat{k}z \]
\[ \nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \]
Energy eigenvectors/eigenstates

\[ \hat{H} |\Psi_n\rangle = E_n |\Psi_n\rangle \]

or

\[ E_n = \langle \Psi_n | \hat{H} | \Psi_n \rangle \]

Energy eigenstates are wavevectors that fulfill this equation. There can be many possible solutions, either finite or infinite in number. The eigenvalues \( E_n \) are the only possible observable energies.
Energy eigenvectors/eigenstates

\[ |\Psi_n \rangle \]
State Vectors
Dirac bra-ket notation
Spins, Photons, SHO

\[ \Psi_n (x) \]
One-Dimensional
Wavefunction
PIAB

\[ \Psi_{n_{\ell m}} (r) \]
Three Dimensional
Wavefunction
Hydrogen Atom
An example: Particle in a Box (PIAB)

\[ \hat{H} |\Psi_n \rangle = E_n |\Psi_n \rangle \]

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x) \]

The one dimensional Schrödinger Equation.
An example: Particle in a Box (PIAB)

The eigenstate wavefunction

\[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n\psi_n(x)\]
An example: Particle in a Box (PIAB)

the kinetic energy “operator”

\[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x)\]

the total energy of the particle in this eigenstate
An example: Particle in a Box (PIAB)

the potential energy “operator”

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x) \]

\(V(x)\) is the potential energy of the particle as a function of its position.
An example: Particle in a Box (PIAB)

V(x) for the PIAB.

V(x ≤ 0) = ∞
V(0 < x < L) = 0
V(x ≥ L) = ∞
WHEN we solve the Schrödinger equation, we always obtain two things:

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n\psi_n(x) \]
WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate wavefunctions, $\psi_n(x)$.

\[
\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x)
\]

\[
\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)
\]

$n = 1, 2, 3, \ldots$
WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate wavefunctions, $\psi_n(x)$.
2. a set of eigenstate energies, $E_n$ (that is, a set of allowed values for the energy).

$$\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, 3 ...$$

$$E_n = \frac{n^2 \hbar^2}{8mL^2}$$
Can we derive the Newton's second law? No.

\[ F = ma \]

Newton’s second law.
Can we explain why Schrödinger chose this operator for $p$? No.

$\hat{p} = -i\hbar \frac{d}{dx}$

$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x)$

The one dimensional Schrödinger Equation.
But for particles in one dimension, we can follow Schrödinger's logic:

Classically...

\[ E_{\text{total}} = E_{\text{kinetic}} + V(x) \]

\[ E_{\text{total}} = \frac{1}{2} mv^2 + V(x) \]

\[ E_{\text{total}} = \frac{p^2}{2m} + V(x) \]

\[ p = \left[ 2m \left( E - V(x) \right) \right]^{\frac{1}{2}} \]

Drop the “total” subscript.
But for particles in one dimension, we can follow Schrödinger's logic:

\[ p = \left[ 2m(E - V(x)) \right]^{\frac{1}{2}} \]

use the de Broglie Eq.

now... \[ \lambda = \frac{h}{p} = \frac{h}{\left[ 2m(E - V(x)) \right]^{\frac{1}{2}}} \]
Now use lambda in the classical wave equation:

\[
\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0
\]

\[
f(x) = \sin\left(\frac{2\pi x}{\lambda}\right)
\]

The exact form of f(x) depends upon the boundary conditions.
Now use lambda in the classical wave equation:

\[
\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0
\]

substituting from the de Broglie wavelength

\[
\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2 2m(E - V(x))}{h^2} f(x) = 0
\]

\[
\hbar = \frac{h}{2\pi}
\]

using \( \hbar \)

\[
\frac{d^2 f(x)}{dx^2} + \frac{2m(E - V(x))}{\hbar^2} f(x) = 0
\]
Now use lambda in the the classical wave equation:

\[
\frac{d^2 f(x)}{dx^2} + \frac{2m(E - V(x))}{\hbar^2} f(x) = 0
\]

divide by: \( \frac{-\hbar^2}{2m} \), move E to the RHS...

give \( f(x) \) a new name: \( \psi(x) \)

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

Voila! The one dimensional Schrödinger Equation.
We can use the wave equation to get the PIAB energies

\[ \frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0 \]

L = \lambda/2

L = n\lambda/2 \quad n = 1, 2, 3...

OR

\lambda = 2L/n \quad n = 1, 2, 3...

Only certain wavelengths will fit in the box.
We can use the wave equation to get the PIA energies

\[ \frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0 \]

\[ \lambda = \frac{2L}{n} \quad n = 1, 2, 3, \ldots \]

\[ \lambda = \left( \frac{\hbar^2}{2mE} \right)^{1/2} \]

from the de Broglie \( \lambda \) (with \( V=0 \))
We can use the wave equation to get the PIAB energies

\[
\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0
\]

\[
\lambda = \frac{2L}{n} \quad n = 1, 2, 3, \ldots
\]

\[
\lambda^2 = \frac{h^2}{2mE}
\]

\[
E = \frac{h^2}{2m\lambda^2} = \frac{n^2h^2}{8mL^2}
\]

PIAB energies
PIAB Energies and Wavefunctions

Energy eigenstates:

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

Energy eigenstate wavefunctions:

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) \]

\[ n = 1, 2, 3, \ldots \]
what is the **position**, and **energy**, of a particle located within a one-dimensional box?
classical mechanics says the following:

1. This particle can have any energy.
classical mechanics says the following:

1. This particle can have **any energy**.
2. It can be located **anywhere, with equal probability**.
classical mechanics says the following:

1. This particle can have **any energy**...
2. It can be located **anywhere, with equal probability**.
3. At any instant in time, this particle will have a particular position that can be specified with arbitrarily high precision.
quantum mechanics makes a completely different set of predictions:

\[ E_n = \frac{n^2 h^2}{8mL^2} \]

1. This particle can only have certain “allowed” values of energy. For PIAB, E=0 is NOT allowed!
quantum mechanics makes a completely different set of predictions:

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

I. The particle can only have certain “allowed” values of energy. For PIAB, \( E=0 \) is NOT allowed!

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) \]

\( n = 1,2,3... \)

II. We cannot know the exact trajectory and location of the particle in a given energy eigenstate. Only probabilities.
PIAB Energies and Wavefunctions

Energy eigenstates:

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

Energy eigenstate wavefunctions:

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) \]

\[ n = 1, 2, 3, \ldots \]
The wavefunctions for PIAB.

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) \]

\[ n = 1,2,3,... \]

Note that \( \Psi(0)=0 \) and \( \Psi(L)=0 \). This is a property of standing waves in general (e.g., guitar or violin strings,).

\[ \Psi(x)=0 \text{ for } x<0 \text{ and } x>L \]
What IS $\psi(x)$?

The one dimensional eigenstate wavefunction has no direct physical significance itself.

However, $\psi^2(x)$ is the probability of finding our particle in the interval from $x$ to $x + dx$. "Born interpretation" (From Max Born, 1926).

$\psi^2(x)$ is called the "probability density."

example: the probability of finding the particle in the region, say, from 0 to L (inside the box) is:

$$\langle \Psi_n \| \Psi_n \rangle = \int_{-\infty}^{+\infty} \psi_n^2(x) dx = \frac{2}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

for all $n = 1, 2, 3...$
\( \psi^2(x) \) is the probability density...

...here is what \( \psi^2(x) \) looks like for \( n=2 \) (left) and \( n=1 \) (right)...

E.g., for \( n=1 \), the particle "prefers" the center of the box!
classical mechanics says the following:

1. This particle can have **any energy**...
2. It can be located **anywhere, with equal probability**.
3. At any instant in time, this particle will have a particular position that can be specified with arbitrarily high precision.
quantum mechanics makes a completely different set of predictions:

1. The particle can only have certain “allowed” values of energy.

2. We cannot know the exact trajectory and location of the particle in a given energy eigenstate. Only probabilities.

3. There is an inherent uncertainty in the position and momentum of the particle:

\[ \Delta p \Delta x \geq \frac{\hbar}{2} \]

Heisenberg uncertainty principle
Heisenberg uncertainty principle

There are many Heisenberg pairs of observables. The two most important are:

\[ \Delta p \Delta x \geq \frac{\hbar}{2} \]

\[ \Delta E \Delta t \geq \frac{\hbar}{2} \]
\[ \lambda = \frac{h}{p} \]

\( \Delta p = 0; \Delta x? \)

\( p \) is exactly defined, but \( x \) is completely indeterminate.
\[ \lambda = \frac{h}{p} \]

the summation of five sine waves, varying in momentum by 2%

\[ \Delta x \]
\[ \Delta p = 2\% \]

“wavepacket” for a free particle.
the summation of five sine waves, varying in momentum by 5%

and here are the five sine waves that were added.

the greater the range of $p$, the higher the degree of localization...

$$\lambda = \frac{h}{p}$$

$\Delta p = 5\%$
Some nomenclature:

States are sometimes just labelled with their quantum numbers.

\[ |n = 5 \rangle \]

\[ |n = 1 \rangle \]

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right) \]

\[ n = 1, 2, 3 \ldots \]

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]
Absorption and Emission Spectroscopy

\[ \Delta E_{51} = E_5 - E_1 = h\nu \]

Light will be absorbed or emitted only if \( \Delta E = h\nu \)

The spectrum is QUANTIZED!

\[ \Delta E_{51} = 24G \]
\[ \Delta E_{41} = 15G \]
\[ \Delta E_{31} = 8G \]
\[ \Delta E_{21} = 3G \]

\[ G = \frac{h^2}{8mL^2} \]
Atomic Emission Spectroscopy

The atomic emission spectrum is the result of many atoms emitting light simultaneously.
The emission spectra of H, He and Hg are all quantized!
Atomic Emission Spectroscopy

Therefore, AES tells us that the electron energy levels in atoms are quantized.

Next up: the quantum mechanical calculation of the electron energy levels in a Hydrogen atom.

Grotrian diagram for Hydrogen