Schrödinger Equation

For nonconservative forces,

\[
\begin{align*}
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x) \Psi(x, t) \hbar \frac{\partial \Psi(x, t)}{\partial t} &= \frac{\partial \Psi(x, t)}{\partial t} \\
\text{Turns out to be K.E.} \\
\text{term} &= \frac{-\hbar^2}{2m} \frac{\partial \Psi(x, t)}{\partial x^2} \\
\text{Turns out to be E.E.} \\
\text{term} &= U(x) \Psi(x, t) \\
\end{align*}
\]

Essentially stipulates conservation of energy for \( \Psi(x, t) \),

To get, must solve this Eq. given a particular \( U(x) \)
Time-Independent Schrödinger Eq.

Usually, the potential isn't going to change with time.
- If so, can factorize

$$\Psi(x, z) = \Phi(x) \phi(z)$$

- Use "separation of variables" technique to create two independent wave equations
  → temporal part
  → spatial part

Plugging in gives,

$$\frac{-\hbar^2}{2m} \phi(z) \frac{d^2 \Phi(x)}{dx^2} + U(x) \Phi(x) \phi(z) = i\hbar \Phi(x) \frac{d \phi(z)}{dz}$$

Convert to full derivatives + divide by $$\Phi(x) \phi(z)$$:

$$\frac{-\hbar^2}{2m} \frac{1}{\Phi(x)} \frac{d^2 \Phi(x)}{dx^2} + U(x) = i\hbar \frac{1}{\phi(z)} \frac{d \phi(z)}{dz}$$

1. Depends only on \(x\)
2. Depends only on \(z\)
For both sides to be equal, each must equal a constant.

Right side, temporal part:

\[ i \hbar \frac{\phi(x)}{2 \hbar} = C \]

\[ \frac{d\phi(x)}{dx} \cdot \frac{C}{\hbar} = \frac{\phi(x)}{\hbar} \]

\[ \text{Soln. } \phi(x) = e^{-i \omega x} \]

So, \( c/\hbar = \omega = \frac{E}{\hbar} \)

\[ E = \hbar \omega \]

Time-dependence of wave function

Time-independent Schrödinger

Left side of Eq. now, Ex.

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

Effort will be to find \( \phi(x) \).
Interpretation of time-independent Schröd. eq.

We have

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

Calculate probability density as

$$\Psi^* \Psi = e^{i\omega t} \Psi^* \Psi = \Psi^2(x)$$

This means the probability density is constant in time.

Classical waves: standing waves

Quantum Mech.: stationary states

This is fundamentally why Bohn was wrong

- $e^-$ is not a particle orbiting nucleus with $n\lambda = \text{orbit circumference}$
- $e^-$ is standing wave of probability density in confines of electric potential set up by change in nucleus
Normalization

Consider probabilistic interpretation of $\Psi$: (complex conjugate of $\Psi$

$$P(x) \, dx = (\Psi^*)^2 (x, z) \, \Psi(x, z) \, dx$$

$\Rightarrow$ probability of a particle to be in region $x \rightarrow x + dx$ ($\Rightarrow \Psi^* \text{ is complex conjugate of } \Psi$)

The total probability of a particle wave-function must $= 1$:

$$\int_{-\infty}^{\infty} \Psi^* (x, z) \, \Psi(x, z) \, dx = 1$$

Normalization condition

This provides an important constraint because generally wave functions have unknown constants to determine,

e.g. $\Psi(x, z) = Ae^{-\alpha x} e^{-i\beta}$

what is $A$?
\[ \psi(x) = A e^{-\alpha |x|} \]

A symmetric, localized wave function.

Normalizing this gives

\[ \int_{-\infty}^{\infty} \psi^* \psi \, dx = \int_{-\infty}^{\infty} A^2 e^{-2\alpha |x|} \, dx = 1 \]

By symmetry, we have

\[ 2A^2 \int_{0}^{\infty} e^{-2\alpha x} \, dx = 1 \]

\[ 2A^2 \left[ -\frac{1}{2\alpha} e^{-2\alpha x} \right]_0^{\infty} = \frac{2A^2}{2\alpha} (0 - 1) = 1 \]

\[ A^2/\alpha = 1 \Rightarrow A = \sqrt{\alpha} \]

So normalized wave function is

\[ \phi(x, z) = \sqrt{\alpha} e^{-\alpha |x|} \]
Consider a non-localized wave function instead:

\[ \Psi(x, t) = Ae^{i(kx - \omega t)} \]

The normalization condition would give

\[ 1 = \int_{-\infty}^{\infty} |\Psi|^2 dx = \int_{-\infty}^{\infty} A^2 e^{-i(kx - \omega t)} e^{i(kx - \omega t)} dx = 1 \]

\[ A^2 \int_{-\infty}^{\infty} 1 \, dx = 1 \]

\[ A \left[ x \right]_{-\infty}^{\infty} = 1 \]

variable \( \neq \) constant

\[ \text{cannot normalize this} \]

unphysical wave-particle
Properties of Valid Wave Functions

These provide "boundary conditions" for physically meaningful situations.

1) \( \psi \) must be finite everywhere (avoids \( \infty \) probabilities)

2) \( \psi \) must be single valued

3) \( \psi + \frac{d\psi}{dx} \) must be continuous for finite potentials
   \( \Rightarrow \) second order derivative in Schrödinger Eq. must be single valued

4) For normalization to work, \( \psi \) must \( \rightarrow 0 \) as \( |x| \rightarrow \infty \)
Infinite Square Well Potential

We want to consider increasingly realistic potentials to extract information from Schrödinger Eq.

\[ V(x) = \begin{cases} \infty & x \leq 0, x \geq L \\ 0 & 0 < x < L \end{cases} \]

In Regions I + III: \( \psi(x) = 0 \) to keep terms in Schrödinger Eq. finite

For region II:

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

\[ \Rightarrow \frac{d^2 \psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x) \]

\[ = -k^2 \psi(x) \]

A Solution: \( \psi(x) = A \sin kx + B \cos kx \)
Constraining Wave Function

Since \( f(x) = 0 \) @ \( x = 0 \) and \( x = L \)

\[ B = 0 \]

Since \( f(x) = 0 \) @ \( x = L \)

\[ A \sin(kL) = 0 \]

\[ \therefore kL = n\pi \Rightarrow k = \frac{n\pi}{L} \quad n = 1, 2, 3, \ldots \]

\[ f(x) = A \sin\left(\frac{n\pi}{L}x\right) \]

Normalizing, we have

\[ \int_{-\infty}^{\infty} f^2(x) \, dx = 1 \]

All probability in the well

\[ A^2 \int_{0}^{L} \sin^2\left(\frac{m\pi}{L}x\right) \, dx = 1 \]

\[ \frac{L}{2} \Rightarrow A = \sqrt{\frac{2}{L}} \]

So the wave function is

\[ f(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \]
What kind of system is this?

\[ kn = \frac{\sqrt{2mE}}{\hbar} \]

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

Energy levels quantized!

Flat probability classically
Expectation Values

How do we extract position, $\hat{x}$?

- An 'expectation value' is $\langle x \rangle$
- obtained from many measurements
- each measurement is different
- The average has some relation to physical observable

Since physically observable quantities are real (not complex) quantities
- Expectation values must be real

Classically, averages are

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \ldots}{N_1 + N_2 + N_3 \ldots} = \frac{\Sigma N_i x_i}{\Sigma N_i}$$

Discrete Measurements: $N_i$ are # times find particle @ $x_i$.

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x P(x) \, dx}{\int_{-\infty}^{\infty} P(x) \, dx}$$

Continuous Probability $P(x)$
Quantum Expectation Values

Probability distribution given by,

\[ P(x) \, dx = \overline{\Phi(x, z_2) \overline{\Phi(x, z_2)} \, dx} \]

So that

\[ <x> = \frac{\int_{-\infty}^{\infty} x \, \overline{\Phi(x, z_2)} \times \overline{\Phi(x, z_2)} \, dx}{\int_{-\infty}^{\infty} \overline{\Phi(x, z_2)} \times \overline{\Phi(x, z_2)} \, dx} \]

This is a general approach. Take any function \( \xi(x) \), then

\[ <\xi(x)> = \int_{-\infty}^{\infty} \overline{\Phi(x, z_2)} \xi(x) \overline{\Phi(x, z_2)} \, dx \]

placement important!

some \( \xi(x) \) are differential operators on \( \overline{\Psi} \),

not \( \overline{\Phi} \).
Operators

Consider the derivative
\[ \frac{\partial}{\partial x} \Phi(x, t) = \frac{\partial}{\partial x} \left[ e^{ikx - \omega t} \right] = ike^{ikx - \omega t} \]
\[ = ik \Phi(x, t) = i \frac{\partial}{\partial x} \Phi(x, t) \]

\[ \langle \rho = \hbar \frac{\partial}{\partial x} \rangle \]

can be written,
\[ \rho \frac{\partial}{\partial x} \phi(x, t) = \frac{i\hbar}{\partial x} \phi(x, t) \]

Define 'operators' as mathematical operations transforming wave functions,
\[ \hat{\rho} = -i \hbar \frac{\partial}{\partial x} \]

Momentum operator

Obtaining expectation values,
- use corresponding operator
\[ \langle \rho \rangle = \int_{-\infty}^{\infty} \rho \phi^* \frac{\partial}{\partial x} \phi \, dx \]
\[ (= \int_{-\infty}^{\infty} \phi \phi^* \frac{\partial}{\partial x} \phi \, dx ) \]

Other operators:
\[ \hat{x} = x \]
\[ \hat{\rho} = \hbar \frac{\partial}{\partial t} \]
\[ \hat{\rho} = \frac{\partial}{\partial t} \]
Example

What is $\langle x \rangle$, $\langle p \rangle$ for infinite potential well for 1st excited state?

$n = 2$

$$\frac{\psi}{2} \langle x \rangle = \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi n x}{L} \right)$$

$$\langle x \rangle \bigg|_{n=2} = \frac{2}{L} \int_0^L x \sin^2 \left( \frac{2\pi n x}{L} \right) dx$$

$$= \frac{2}{L} \left[ \frac{x^2}{4} - \frac{L x}{8\pi} \sin \left( \frac{2\pi n x}{L} \right) - \frac{L^2}{32\pi^2} \cos \left( \frac{2\pi n x}{L} \right) \right]_0^L$$

$$= \frac{L}{2}$$

For momentum,

$$\langle p \rangle = (-i\hbar) \frac{2}{L} \int_0^L \sin \left( \frac{2\pi n x}{L} \right) \frac{d}{dx} \sin \left( \frac{2\pi n x}{L} \right) dx$$

$$= -\frac{i\hbar}{L^2} \left[ \sin \left( \frac{2\pi n x}{L} \right) \cos \left( \frac{2\pi n x}{L} \right) \right]_0^L$$

$$= 0$$

Value is zero since wave has backward and forward components equally.
Eigenvectors

In most wavefunctions, observables have finite uncertainties.

For an operator \( \hat{A} \):

- \( \psi(x, s) \) is an eigenfunction of \( \hat{A} \) if \( \hat{A} \psi(x, s) = \text{constant} \times \psi(x, s) \).

This means a well-defined observable with no uncertainty.

Pure wave \( \psi(x) = e^{i k x} \) is an eigenfunction of \( \hat{p} \):

\[ \hat{p} \psi = -i \hbar \frac{\partial}{\partial x} e^{i k x} = i \hbar k e^{i k x} = \hat{p} \psi \]

\( \Delta k = 0 \), \( \Delta p = 0 \).

Pure wave \( \psi = e^{-i \omega t} \) is an eigenfunction of \( \hat{E} \):

\[ \hat{E} \psi = i \hbar \frac{\partial}{\partial t} e^{-i \omega t} = i \hbar \omega e^{-i \omega t} \]

\( \Delta \omega = 0 \), \( \Delta E = 0 \).
Finite Square Well Potential

\[ V(x) = \begin{cases} 
  V_0 & x \leq 0 \\
  0 & 0 < x < L \\
  V_0 & x \geq L 
\end{cases} \]

\[ E < V_0 \text{ case} \]

Outside the well:

\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = (E - V_0) \psi \]

\[ \frac{d^2 \psi}{dx^2} = \left( \frac{2m}{\hbar^2} (V_0 - E) \right) \psi = \lambda^2 \psi \quad (\lambda > 0) \]

Solutions are:

\[ \psi(x) = C e^{\pm \lambda x} \]

Avoid \[ \psi \to \infty \text{ when } x \to \pm \infty \]:

\[ \psi_I(x) = Ce^{\lambda x} \quad (x \leq 0) \]

\[ \psi_III(x) = De^{-\lambda x} \quad (x \geq L) \]
Inside the Finite Potential Well

$V=0$:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = -\frac{2m \epsilon}{\hbar^2} \psi = -k^2 \psi \quad (k > 0)$$

We've seen this before. Solutions are:

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

So how to proceed? Enforce continuity.

@ $x = 0$:

$\psi$ contin.

$$C e^{+x0} - A \sin(k0) + B \cos(k0) \rightarrow \boxed{C = B}$$

$$\psi(0) = \psi'(0)$$

$$\frac{d \psi}{dx} \text{ contin.} \quad \alpha C e^{+x0} = k A \cos(k0) - k B \sin(k0)$$

$$\Rightarrow \alpha C = kA$$

So,

$$C = B = \frac{kA}{\alpha}$$
More Continuity

\[ @ x = L \]

4 contin.:

\[ A \sin kL + B \cos kL = \delta e^{-\alpha L} \]

\[ \frac{d4}{dx} \text{ contin.} : \quad kA \cos kL - kB \sin kL = \alpha \delta e^{-\alpha L} \]

Since we know \( \delta = kA/\alpha \), these 2 Eqs. in 2 unknowns \((A + B)\) can be solved.

\[ \psi(x) \rightarrow V(x) \]

\[ V_0 \rightarrow <V_0 \]

\( n = 2 \)

\( n = 1 \)

\( x = 0 \quad x = L \quad x \)

Prohibited classically

Penetration distance into walls of well

\[ \delta x = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \]
Simple Harmonic Oscillator

Classical Spring potential

\[ F = -k(x-x_0) \]
\[ V(x) = k(x-x_0)^2/2 \]

Take \( x_0 = 0 \) \( \implies V = kx^2/2 \)

This has relevance for atoms in crystals.

V(r) is a strong repulsive potential at small r

V=0 weak attractive potential

Region of good approximation

So, for atoms near the preferred position \( x_0 \), can use this potential in Schrödinger Eq.
Solutions to Schrödinger Eq.

Using $V(x) = kx^2/2$, we get

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = \left( \epsilon - \frac{kx^2}{2} \right) \psi$$

If we take $\alpha = \frac{mk}{\hbar^2} + \beta = \frac{2m \epsilon}{\hbar^2}$

$$\frac{d^2 \psi}{dx^2} = -\frac{2m}{\hbar^2} \left( \epsilon - \frac{kx^2}{2} \right) \psi$$

$$= \left( \beta - \alpha^2 x^2 \right) \psi$$

More complicated differential equation.

Solutions:

$$\psi_n(x) = H_n(x) e^{-\alpha^2 x^2/2}$$

Hermite polynomials

$n = 0 \rightarrow $ see next page

$n = 1 \rightarrow \quad H_1(x) = \left( \frac{x}{\sqrt{\alpha}} \right)^1 \sqrt{\frac{2}{\alpha}} \times$

$n = 2 \rightarrow \quad H_2(x) = \left( \frac{x}{\sqrt{\alpha}} \right)^2 \sqrt{\frac{1}{2\alpha}} (2\alpha x^2 - 1)$
Normalizing the Ground State

Harmonic Oscillator

\[ \psi(x) = A e^{-\alpha x^2/2} \]

Normalization condition gives

\[ \int_{-\infty}^{\infty} A^2 e^{-\alpha x^2} \, dx = 1 \]

\[ A^2 \left( \frac{\pi}{\alpha} \right) = 1 \Rightarrow A = \left( \frac{\alpha}{\pi} \right)^{1/4} \]

Classically, a particle with \( E < V_a \) is confined to \( |x| < a \).

Quantum mechanically, like finite potential well

\[ E_n = (n + \frac{1}{2}) \frac{\hbar \omega}{m} \]

\[ E_n = (n + \frac{1}{2}) \frac{\hbar \omega}{2} \]

\[ E_0 = \frac{\hbar \omega}{2} \]

From uncertainty principle