Schrödinger Equation

For nonconservative forces,

$$\boxed{\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}}_{\text{turns out to be K.E. term } = \frac{p^2}{2m}\Psi(x,t)} + U(x)\,\Psi(x,t) = \underbrace{i\hbar\frac{\partial \Psi(x,t)}{\partial t}}_{\text{turns out to be tot. E term } = E}}$$

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

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

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

Plugging in gives:

$$\frac{-\hbar^2}{2m}\phi(t)\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\psi(x)\phi(t) = i\hbar\,\psi(x)\frac{\partial}{\partial t}\phi(t)$$

Convert to full derivatives + divide by $\psi(x)\phi(t)$:

$$① \quad \underbrace{\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x)}_{\text{depends only on 'x'}} = \underbrace{i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}}_{\text{depends only on 't'}}$$

For both sides to be equal, each must equal a constant.

Right side, temporal part:

$$i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = C$$

$$\boxed{\frac{d\phi(t)}{dt} = -\frac{iC}{\hbar}\,\phi(t)}$$

Soln. $\phi(t) = e^{-i(C/\hbar)t}$ a frequency

So, $C/\hbar = \omega = E/\hbar$

$$\boxed{C = E}$$

Time-dependence of wave function: $\boxed{\phi(t) = e^{-i\omega t}}$

Time-Independent Schrödinger Eq.

Left side of ① now,

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

Effort will be to find $\psi(x)$.

Interpretation of Time-Independent Schröd. Eq.

We have

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

Calculate probability density as

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

This means the probability density is constant in time.

Classical waves: standing waves

Quantum Mech.: stationary states

This is fundamentally why Bohr wrong

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

Normalization

Consider probabilistic interpretation of Ψ: ("complex conjugate" of Ψ)

$$\underline{P(x)\,dx} = \Psi^*(x,t)\,\Psi(x,t)\,dx$$

→ probability of a particle to be in region $x \to x+dx$

($\hookrightarrow \Psi^*$ is complex conjugate of Ψ)

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

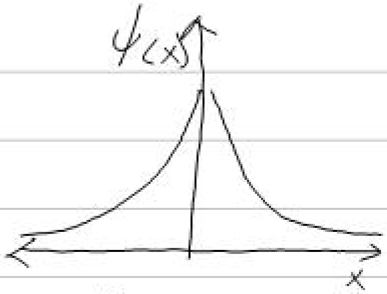
$$\boxed{P = \int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx = 1}$$

Normalization condition

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

e.g. $\underline{\Psi(x,t) = Ae^{-\alpha|x|}}$

what is A?



A symmetric, localized wave function.

$$\psi(x) = A e^{-\alpha|x|}$$

Normalizing this gives

$$\int_{-\infty}^{\infty} \Psi^* \Psi \, dx = \int_{-\infty}^{\infty} A^2 e^{-2\alpha|x|} dx = 1$$

By symmetry, we have

$$2A^2 \int_0^{\infty} e^{-2\alpha x} dx = 1$$

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

$$A^2/\alpha = 1 \Rightarrow \boxed{A = \sqrt{\alpha}}$$

So normalized wave-function is

$$\boxed{\Psi(x,t) = \sqrt{\alpha}\, e^{-\alpha|x|}}$$

Consider a non-localized wave function instead:

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

The normalization condition would give

$$1 = \int_{-\infty}^{\infty} \Psi^* \Psi \, dx = \int_{-\infty}^{\infty} Ae^{-i(kx-\omega t)} \times Ae^{i(kx-\omega t)} dx$$

$$A^2 \int_{-\infty}^{\infty} \underbrace{e^{-i(kx-\omega t)+i(kx-\omega t)}}_{1} dx = 1$$

$$\underbrace{A[x]_{-\infty}^{\infty} = 1}_{\text{variable} \neq \text{constant}}$$

∴ cannot normalize this!

unphysical

wave-particle

Properties of Valid Wave Functions

These provide "boundary conditions" for physically meaningful situations

1) ψ must be finite everywhere (avoids ∞ probabilities)

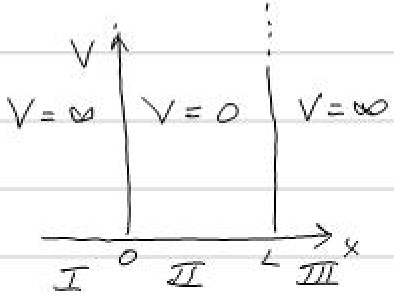
2) ψ must be single valued

3) ψ + $\partial\psi/\partial x$ must be continuous for finite potentials
   → second order derivative in Schrödinger Eq. must be single valued

4) For normalization to work, ψ must $\to 0$ as $|x| \to \infty$

Infinite Square Well Potential

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



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

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

For region II:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + 0 = E\,\psi(x)$$

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

$$= -k^2\psi(x)$$

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

Constraining Wave function

Since $\psi(x) = 0$ @ $x = 0$ and $x = L$

$$B = 0$$

Since $\psi(x) = 0$ @ $x = L$

$$A \sin kL = 0$$

$$\therefore kL = n\pi \rightarrow \boxed{k = \frac{n\pi}{L}} \quad n = 1, 2, 3, \ldots$$

$$\psi(x) = A \sin\left(\frac{n\pi}{L} x\right)$$

Normalizing, we have

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

All probability in thy well

$$\int_0^L A \sin\left(\frac{n\pi x}{L}\right) A \sin\left(\frac{n\pi x}{L}\right) dx = 1$$

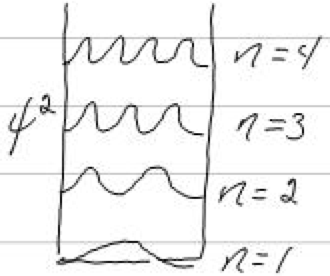
$$A^2 \underbrace{\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx}_{L/2} = 1$$

$$\Rightarrow A = \sqrt{2/L}$$

So the wave-function is

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

What kind of system is this?

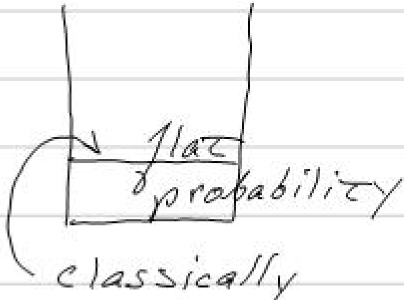


$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{L^2 2m}}$$

$n = 1, 2, 3, \ldots$



Energy levels quantized!

Expectation Values

How do we extract position, E+p?

- 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

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

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,

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

So that

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^*(x,t)\; x\; \Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^* \Psi\, dx}$$

$\rightarrow 1$ (after normalization)

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

This is a general approach. Take any function $g(x)$, then

$$\boxed{\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, g(x)\, \Psi(x,t)\,dx}$$

placement important! some $g(x)$ are differential 'operators' on $\Psi(x,t)$, not Ψ^*.

Operators

Consider the derivative

$$\frac{\partial}{\partial x}\Psi(x,t) = \frac{\partial}{\partial x}\left[e^{i(kx-\omega t)}\right] = ik\, e^{i(kx-\omega t)}$$

$$= ik\,\Psi(x,t) = i\frac{p}{\hbar}\Psi(x,t)$$

$$(p = \hbar k)$$

can be written,

$$p\,\Psi(x,t) = -i\hbar\frac{\partial}{\partial x}\Psi(x,t)$$

Define 'operators' as mathematical operations transforming wave function

$$\boxed{\hat{p} = -i\hbar\frac{\partial}{\partial x}}$$ Momentum Operator

Obtaining expectation values:
- use corresponding operator

$$\langle p\rangle = \int_{-\infty}^{\infty}\Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)\,dx$$

$$\left(= \int_{-\infty}^{\infty}\Psi^*\,\hat{p}\,\Psi\,dx\right)$$

Other operators:

$$\hat{x} = x \qquad \hat{E} = i\hbar\frac{\partial}{\partial t}$$

$$\hat{t} = t$$

Example

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

$n=2$

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

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

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{Lx}{8\pi}\underbrace{\sin\left(\frac{2\pi x}{L}\right)}_{\to \phi} - \frac{L^2}{32\pi^2}\underbrace{\cos\left(\frac{2\pi x}{L}\right)}_{\to \phi}\right]$$

$$\langle x \rangle = \boxed{\frac{L}{2}}$$

For momentum,

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

$$= -\frac{4i\pi\hbar}{L^2}\underbrace{\int_0^L \sin\left(\frac{2\pi x}{L}\right)\cos\left(\frac{2\pi x}{L}\right)dx}_{\frac{1}{2a}\sin^2 ax \quad \left(a = \frac{2\pi}{L}\right)}$$

$$= \underline{0}$$

Value is zero since wave has backward + forward components equally

Eigenvalues

In most wavefunctions, observables have finite uncertainties

For an operator $\hat{Q}$:

$\psi(x)$ is an 'eigenfunction' of $\hat{Q}$ if

'eigenvalue'

$$\boxed{\hat{Q}\,\psi(x) = \text{const}\;\psi(x)}$$

Means a well-defined observable with no uncertainty

Pure wave $\psi(x) = e^{ikx}$ is eigenfunction of $\hat{p}$:

$$\hat{p}\,\psi = -i\hbar\frac{\partial}{\partial x}e^{ikx} = \hbar k e^{ikx} = \underline{\underline{p\,\psi}}$$

$\rightarrow$ pure wave, $\Delta k = 0$, $\Delta p = 0$

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

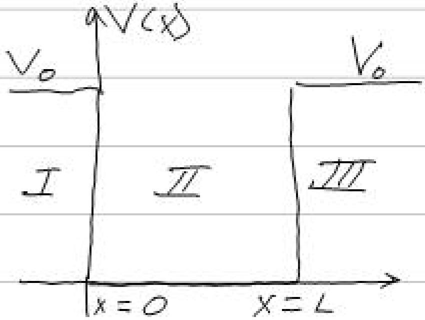
$$\hat{E}\,\psi = i\hbar\frac{\partial}{\partial t}e^{-i\omega t} = \hbar\omega\, e^{-i\omega t} = \underline{\underline{E\,\psi}}$$

$\rightarrow$ again,

$\Delta\omega = 0$, $\Delta E = 0$.

Finite Square-Well Potential

$$V(x) = \begin{cases} V_0 & x \le 0 \\ 0 & 0 < x < L \\ V_0 & x \ge L \end{cases}$$



$E < V_0$ case

Outside the well:

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

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

$(\alpha > 0)$

Solutions are: $\psi(x) = c' e^{\pm\alpha x}$

Avoid $\psi \to \infty$ when $x \to \pm\infty$:

$$\boxed{\psi_I(x) = C e^{+\alpha x}} \quad (x \le 0)$$

$$\boxed{\psi_{III}(x) = D e^{-\alpha x}} \quad (x \ge L)$$

Inside the Finite Potential Well

$V=0$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = -\left(\frac{2mE}{\hbar^2}\right)\psi = -k^2\psi$$

$(k>0)$

We've seen this before. Solutions are:

$$\boxed{\psi_{II}(x) = A\sin kx + B\cos kx}$$

So how to proceed? Enforce continuity

@ $x=0$:

ψ contin.: $Ce^{+\alpha 0} = A\sin(k0) + B\cos(k0) \rightarrow \boxed{C=B}$

$$\psi_I(0) = \psi_{II}(0)$$

$\frac{d\psi}{dx}$ contin.: $\alpha Ce^{+\alpha 0} = kA\cos(k0) - kB\sin(k0)$

$$\Rightarrow \alpha C = kA$$

So, $\boxed{C = B = \frac{kA}{\alpha}}$

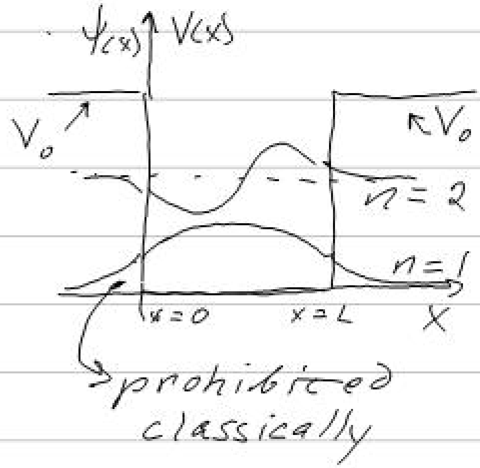
More Continuity

@ $x = L$

ψ contin.: $\boxed{A \sin kL + B \cos kL = \delta e^{-\alpha L}}$

$\frac{d\psi}{dx}$ contin.: $\boxed{kA \cos kL - kB \sin kL = -\alpha \delta e^{-\alpha L}}$

Since know $B = kA/\alpha$, these 2 Eq.'s in 2 unknowns ($A + \delta$) can be solved.



ψ extends beyond well, so λ's longer than ∞ well case.

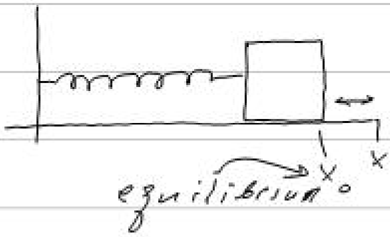
$\therefore$ lower Energy levels

Penetration distance into walls of well

$$\boxed{\delta x = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}}$$

Simple Harmonic Oscillator

Classical Spring potential



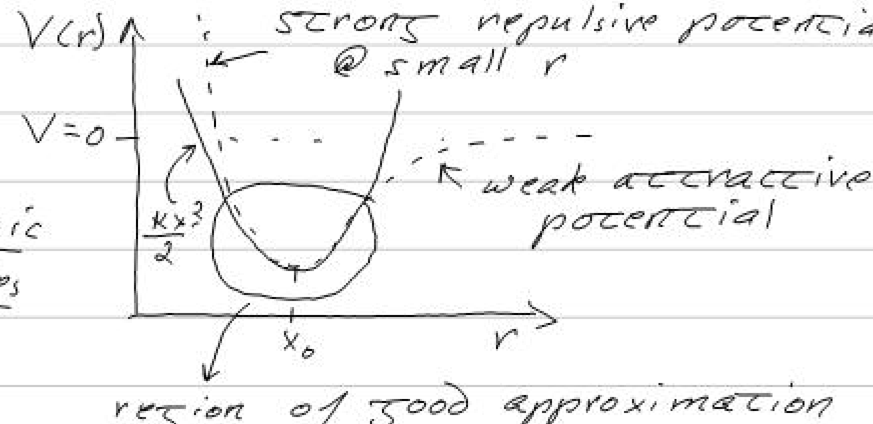
$$F = -k(x - x_0)$$

$$V(x) = k(x - x_0)^2/2$$

Take $x_0 = 0 \rightarrow \boxed{V = kx^2/2}$

This has relevance for atoms in crystals.

Diatomic Molecules



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

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

If take $\alpha = \frac{mK}{\hbar^2}$ + $\beta = \frac{2mE}{\hbar^2}$

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

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

More complicated differential equation.

Solutions!

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

Hermite polynomials

$n = 0 \rightarrow$ see next page

$n = 1 \longrightarrow \quad H_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{2\alpha}\; x$

$n = 2 \longrightarrow \quad H_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{2}}\left(2\alpha x^2 - 1\right)$

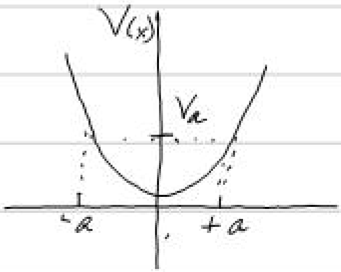
Normalizing the Ground State
Harmonic Oscillator

$$\psi_{n=0}(x) = A e^{-\alpha x^2/2}$$

Normalization condition gives

$$\int_{-\infty}^{\infty} A^2 e^{-\alpha x^2} dx = 1$$

$$A^2 \left(\sqrt{\frac{\pi}{\alpha}}\right) = 1 \Rightarrow \boxed{A = \left(\frac{\alpha}{\pi}\right)^{1/4}}$$



Classically, a particle with $E < V_a$ is confined to $|x| < a$.

Quantum mechanically, like finite potential well

$$E_n = (n + \tfrac{1}{2})\hbar\sqrt{\frac{k}{m}}$$

$$\boxed{E_n = (n + \tfrac{1}{2})\hbar\omega}$$

$$E_0 = \hbar\omega/2$$

from uncertainty principle