Part 5: Elements of Quantum Mechanics II
Energy in Quantum Mechanics

Towards a Quantum Atomic Model

- **Atomic spectra**
    - A **clue** to atomic structure
    - **Discrete frequencies** imply discrete (i.e. non-continuous) energy states of atom.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

Towards a Quantum Atomic Model

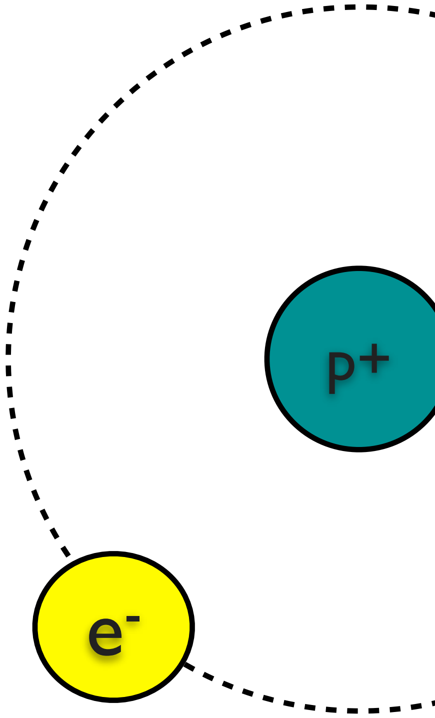
- **The Bohr model**
  - **Discrete energies** put in "by hand" via angular momentum rule.

$$l = mvr = \hbar n = \frac{h}{2\pi} n$$

  - **Energies** match **Rydberg formula**

$$E_n = -\left(\frac{1}{2}\frac{1}{4\pi\epsilon_0}\frac{e^2}{a_0}\right)\frac{1}{n^2} = -\frac{hcR_H}{n^2}$$

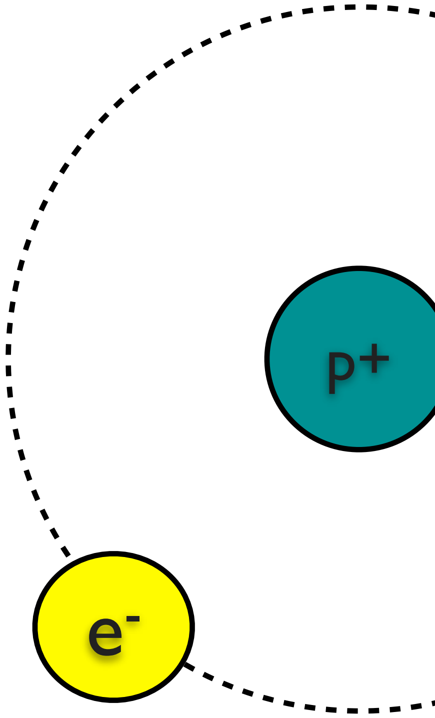
Niels Bohr



Towards a Quantum Atomic Model

- **Problems with the Bohr model**
  - No underlying **physical theory** (incompatible with classical E-M.)
  - Not able to predict **finer details** of spectra for more complicated atoms (even with modifications).
  - Does not include **wave-like** properties of the electron.
  - We know electrons must be represented by **wavefunctions**, not classical orbits.

Niels Bohr



Wavefunctions - Summary of properties

- A **wavefunction** is a function of position which:
  - is a **positive** and / or **negative** (and/or complex) number for all values of x (can be zero).
  - ψ(x) is **normalised**.
  - ψ(x) is **continuous**.
  - Probability of position measurement via the **Born rule**:

$$\mathrm{Prob}(a \leq x \leq b) = \int_a^b |\psi(x)|^2 dx$$

Outline - Part 5 - Energy in Quantum Mechanics

Erwin Schrödinger

- In this part we will
  - Introduce the **Time-independent Schrödinger Equation**
  - which governs **states of fixed energy** in quantum mechanics.
  - Study examples (**free-particle**, **infinite square well**, **finite well**, **barriers**, **tunnelling**).
  - See quantitatively how the TISE predicts the **spectrum** of **Hydrogen** and other atoms.

Today's lecture

- Today we will
  - Introduce the **Time-independent Schrödinger Equation**
  - which governs **states of fixed energy** in quantum mechanics.
  - Introduce two very important examples (**free-particle**, **infinite square well**)

Erwin Schrödinger

Time-independent Schrödinger Equation

Erwin Schrödinger

- What **properties** will determine the wave-functions of the electron in the Hydrogen atom?
- Schrödinger convinced that **energy** was the key.
- 1925 - He proposed an equation - the **Time-independent Schrödinger Equation (TISE).**
- The **TISE** predicts
    - allowed **energies**,
    - and the **wavefunctions** associated with those energies,
- for a **very wide range** of physical settings.

Time-independent Schrödinger Equation

Erwin Schrödinger

- The **TISE** in 1-dimension:

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

- where
  - **m**: mass of the particle
  - **E**: energy of the particle
  - **V(x)**: The potential energy at position ***x***.

Time-independent Schrödinger Equation

Erwin Schrödinger

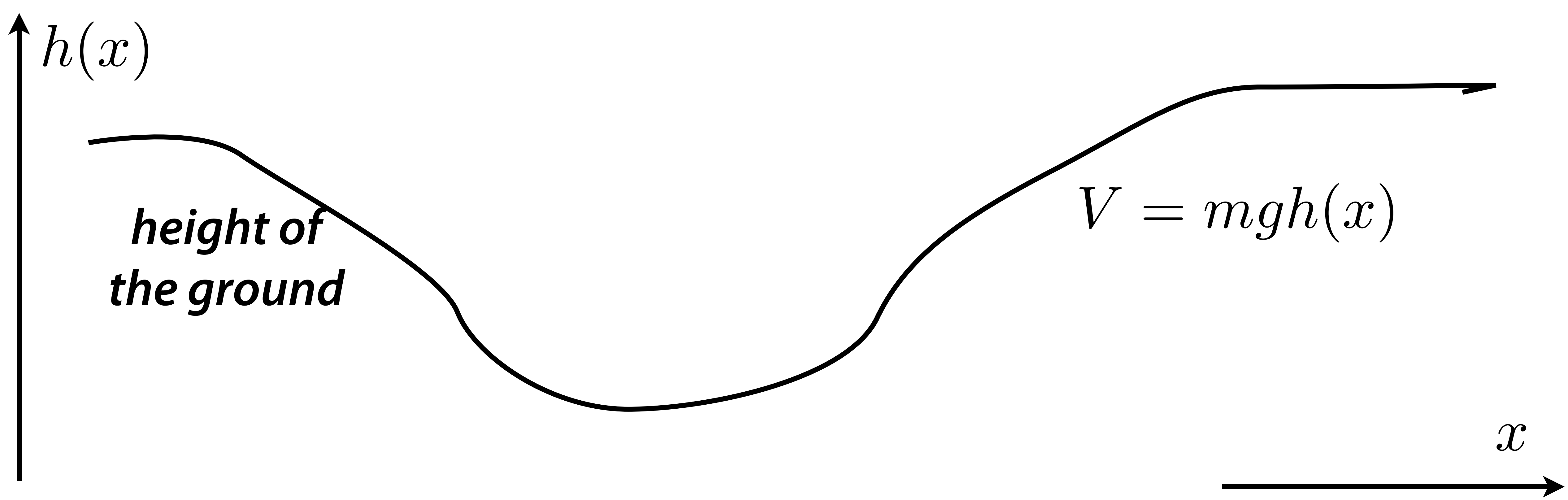
- The **TISE** in 1-dimension:

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

  - This is a **2nd order differential equation**.
  - When we **solve** it, we recover
    - the allowed **energies E**,
    - and the corresponding **wavefunctions ψ(x).**
- We will solve this equation in several contexts in this course.

Potential Energy

- The term V(x) is **potential energy** (or just **potential).**
- This makes the **TISE extremely flexible.**
- **Many** physical situations can be described in terms of **potential energy**.
- E.g. **gravitational potential**



Poll

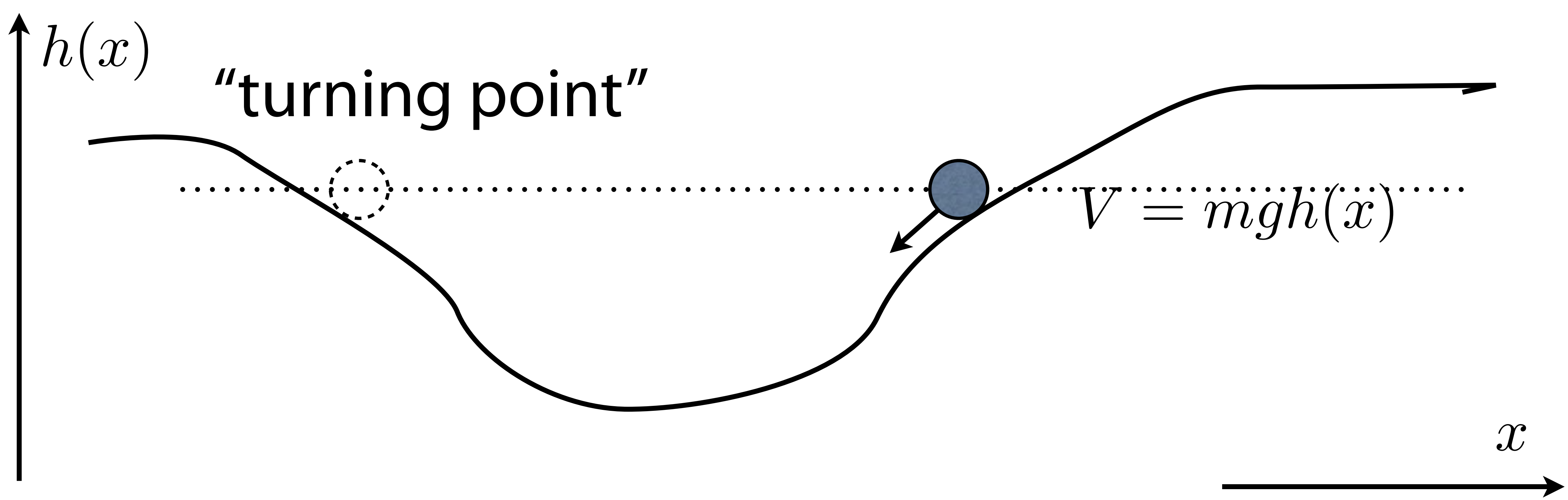
- Have you studied **potential energy** before in classical mechanics?
  - 1. Yes
  - 2. No

Potential Energy

- In classical mechanics we can compute a particles evolution, from **initial conditions** and the **potential**.

- E.g. if we **release** a stationary particle in a potential we can compute its motion (neglecting friction) via energy conservation.

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



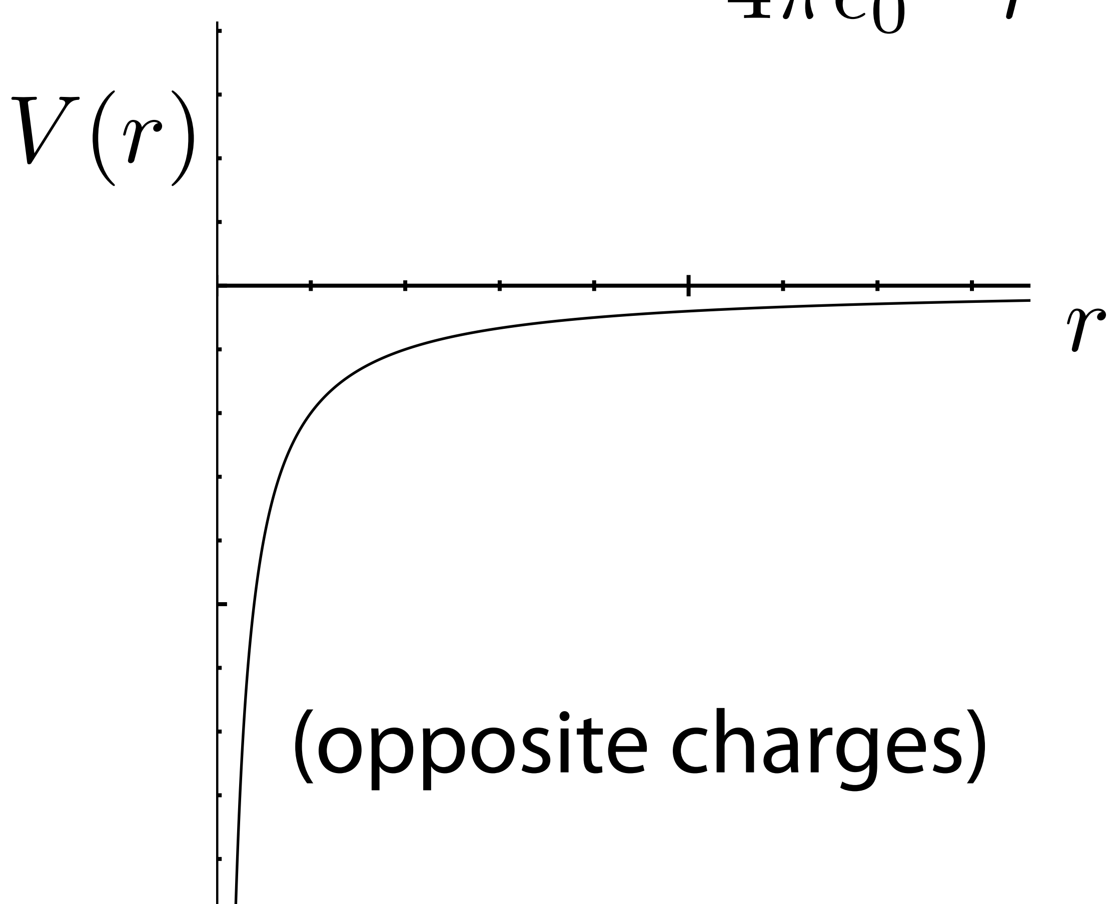
Coulomb Potential

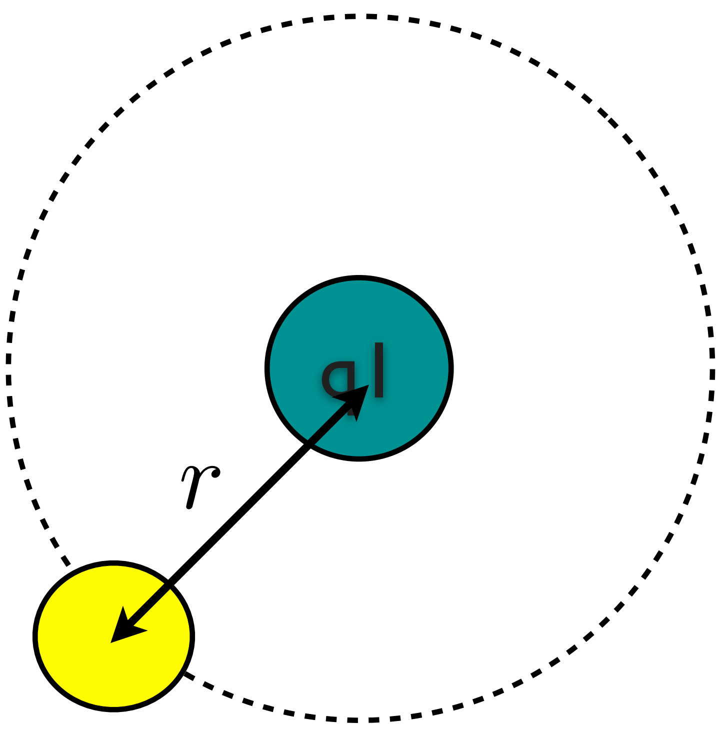
- Potential can be used to describe any conservative **force**.
- Coulomb's law:

$$|F(r)| = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r^2}$$

can be formulated in terms of potential energy

$$V(r) = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r} \qquad |F(r)| = \left|\frac{dV}{dr}\right|$$





Time-independent Schrödinger Equation

Erwin Schrödinger

- The **TISE** in 1-dimension:

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

- The TISE may be used for to study any **potential energy** problem.
- Hence it has wide applicability.
- Notice the similarity in structure between the TISE and the classical mechanics equation:

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

Solving the TISE - Free particle

- When there is no potential (**V(x)=0**) we say that the particle is "**free**".
- The **TISE** for a **free particle** is

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

- This equation should look familiar!
- Same form as **simple harmonic motion** in classical mechanics.

$$m\frac{d^2x}{dt^2} = -kx$$

- We solve it in the same way:

Poll

- Have you studied **simple harmonic motion** before in classical mechanics?
    - 1. Yes
    - 2. No

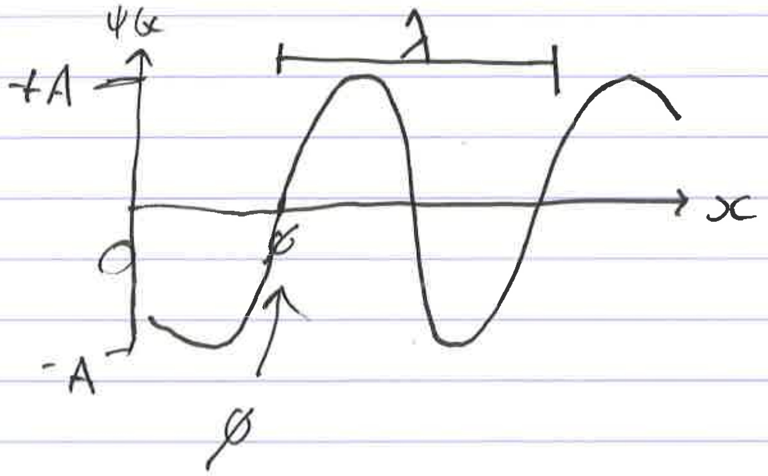
TISE for a free particle.

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

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

<u>Trial solution</u> (general sinusoidal function).

$$\psi(x) = A\sin\left(\frac{2\pi(x-\phi)}{\lambda}\right)$$



Calculate $d^2\psi/dx^2$

$$\frac{d\psi}{dx} = A\cos\left(\frac{2\pi(x-\phi)}{\lambda}\right)\frac{2\pi}{\lambda}$$

$$\frac{d^2\psi}{dx^2} = A\left(-\sin\left(\frac{2\pi(x-\phi)}{\lambda}\right)\right)\left(\frac{2\pi}{\lambda}\right)^2$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \underbrace{A\sin\left(\frac{2\pi(x-\phi)}{\lambda}\right)}_{\psi(x)} = -\left(\frac{2\pi}{\lambda}\right)^2\psi(x)$$

$$\boxed{\frac{1}{\lambda} = \frac{p}{h}}$$

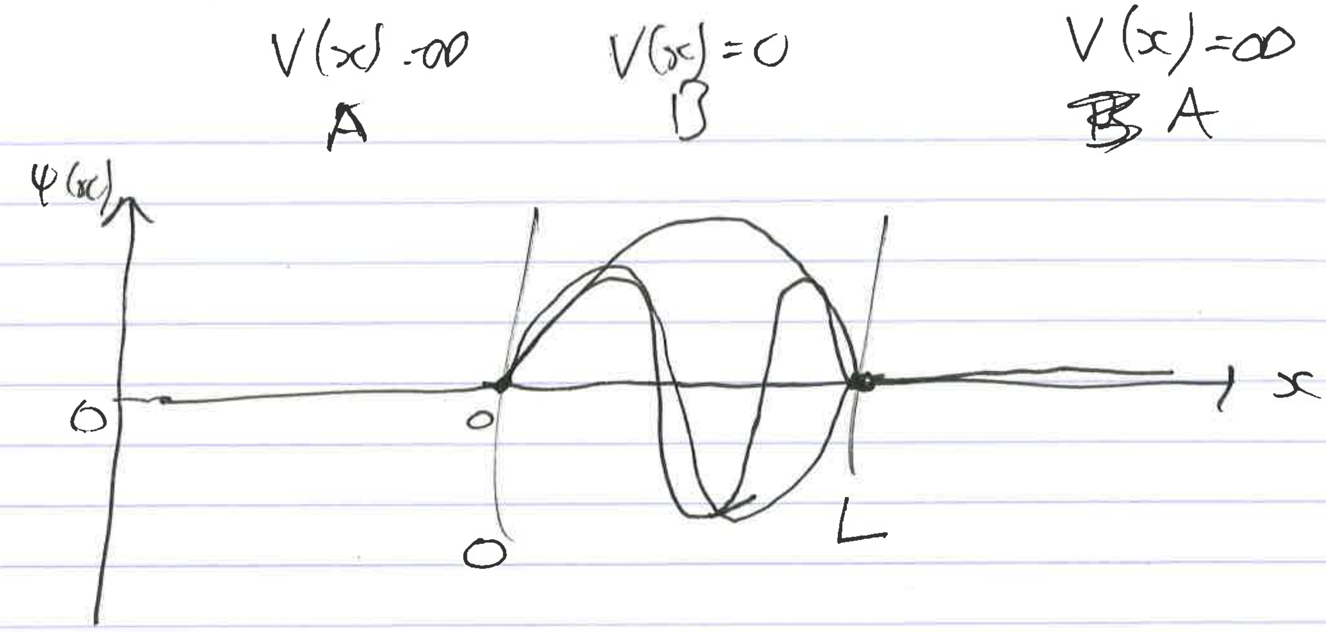
subst into TISE:

$$\cancel{-}\left(\frac{2\pi}{\lambda}\right)^2\cancel{\psi(x)} = \cancel{-}\left(\frac{2mE}{\hbar^2}\right)\cancel{\psi(x)}$$

$$\frac{1}{\lambda} = \frac{\sqrt{2mE}}{h}$$

$$\left(\frac{2\pi}{\lambda}\right)^2 = \left(\frac{2mE}{\hbar^2}\right)$$

$$\frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar}$$

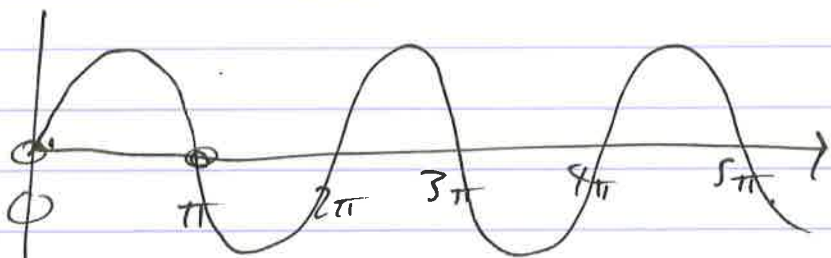


$\psi_A(x) = 0$ $\qquad$ $\psi_B(x) = A\sin\left(\frac{px}{\hbar} + c\right)$

$\psi_A(0) = 0 = \psi_B(0) = A\sin\left(\cancel{\frac{p0}{\hbar}} + c\right) = A\sin(c)$

Can't have $A = 0$ (no particle) hence to solve this:

$$\sin(c) = 0$$

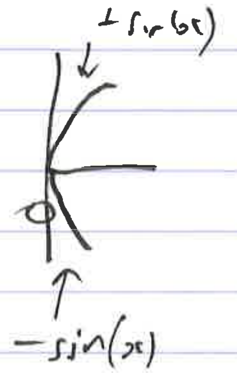


$c = n\pi$ where n is an integer.

$\psi_B(x) = A\sin\left(\frac{px}{\hbar} + n\pi\right)$ for any integer n.

$\sin(f(x) + 2\pi) = \sin(f(x))$ $\qquad$ $\sin(f(x) + \pi) = -\cancel{A}\sin(f(x))$

$$A \sin\left(\frac{px}{\hbar} + n\pi\right) = \pm A \sin\left(\frac{px}{\hbar}\right)$$



Will see later $\psi(x) = f(x)$ and $\psi(x) = -f(x)$ have same physical properties.

Hence, ignore -1 solution for now.

Let: $\psi_B(x) = A \sin\left(\frac{px}{\hbar}\right)$

<u>Second B.C.:</u> is $\psi_A(L) = \psi_B(L)$.

$$A \sin\left(\frac{pL}{\hbar}\right) = 0$$

By same reasoning $A \neq 0$ hence.

$$\sin\left(\frac{pL}{\hbar}\right) = 0 \quad \text{hence} \quad \frac{pL}{\hbar} = n\pi$$

for any integer n.

$n = 0$ not allowed since $\sin(0) = 0$ is not a physical wavefunction "No particle"

$$\Psi_B(x) = \sin\left(\frac{px}{\hbar}\right) \quad \text{where} \quad \frac{pL}{\hbar} = n\pi$$

$$\text{Set} \quad \frac{pL}{\hbar} = n\pi \qquad p = \frac{n\pi\hbar}{L}$$

$$\Psi_B(x) = \sin\left(\cancel{\frac{n\pi\hbar}{L}\,\frac{x}{\hbar}}\right)$$

$$= \sin\left(\frac{x}{\cancel{\hbar}}\,\frac{n\pi\cancel{\hbar}}{L}\right) = \sin\left(\frac{n\pi x}{L}\right)$$

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

Since $\sin(-x) = -\sin(x)$

Since "global" minus signs on a wavefunction have no physical effect, ignore -ve values of n.

→ Wavefunctions for a particle in an ∞ square well

$$\psi(x) = A\sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \ldots$$

Hand-written Calculations

Solving the TISE - Free particle

- We saw that **solutions** to the TISE for a free particle:

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

- are the **de Broglie-like wavefunctions** we studied before:

$$\psi(x) = A\sin\left(\frac{px}{\hbar}\right)$$

- or more generally:

$$\psi(x) = A\sin\left(\frac{px}{\hbar} + c\right)$$

- where:

$$E = \frac{p^2}{2m}$$

Solving the TISE - Free particle

- This is **consistent** with classical **mechanics**
  - where for a **free particle** (no potential energy) all energy is kinetic energy.

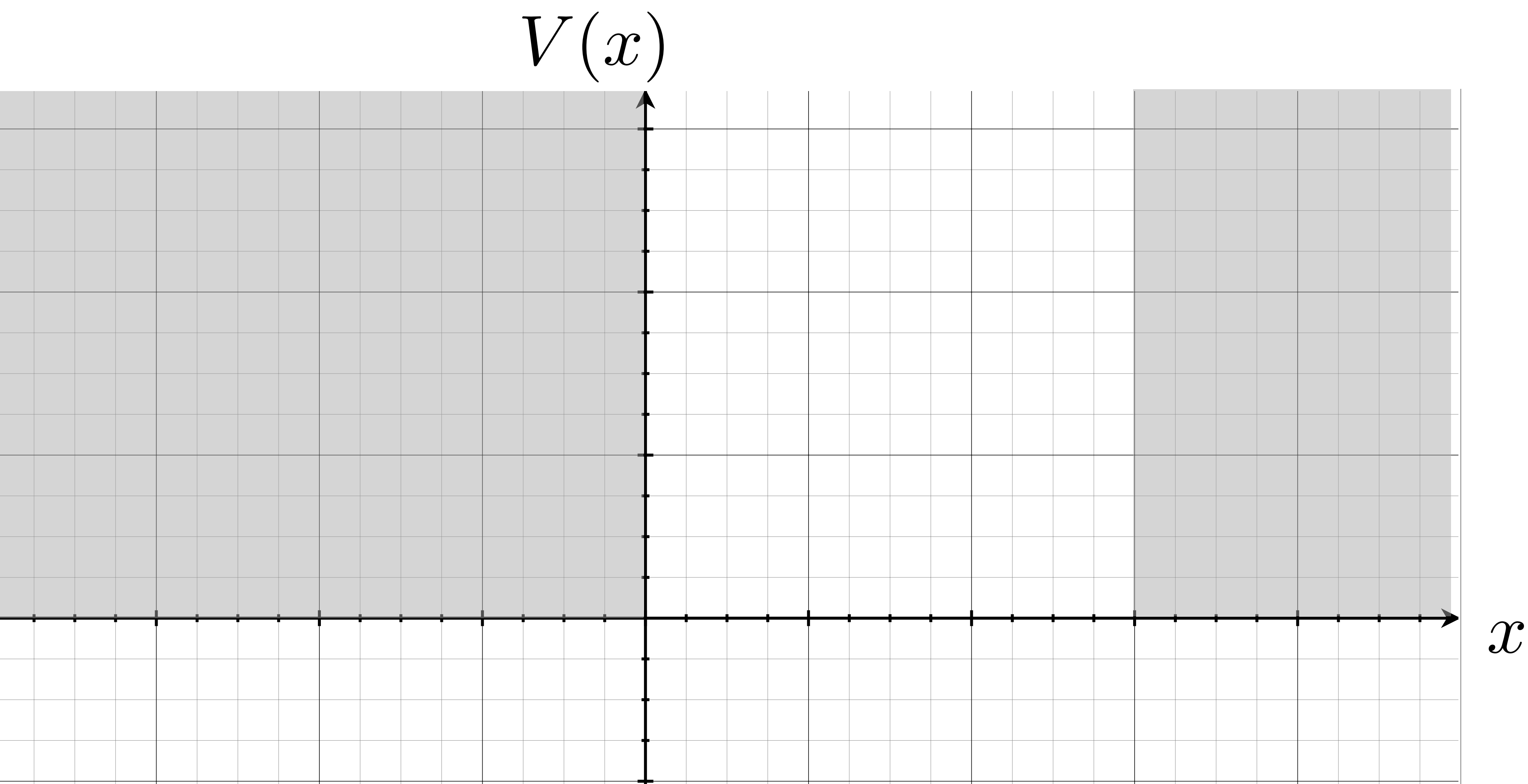
$$E = \frac{p^2}{2m}$$

- The **TISE** thus tells us that **these sinusoidal wave-functions** represent states with energy **E=p²/2m**.

$$\psi(x) = A \sin\left(\frac{px}{\hbar} + c\right)$$

Infinite square well

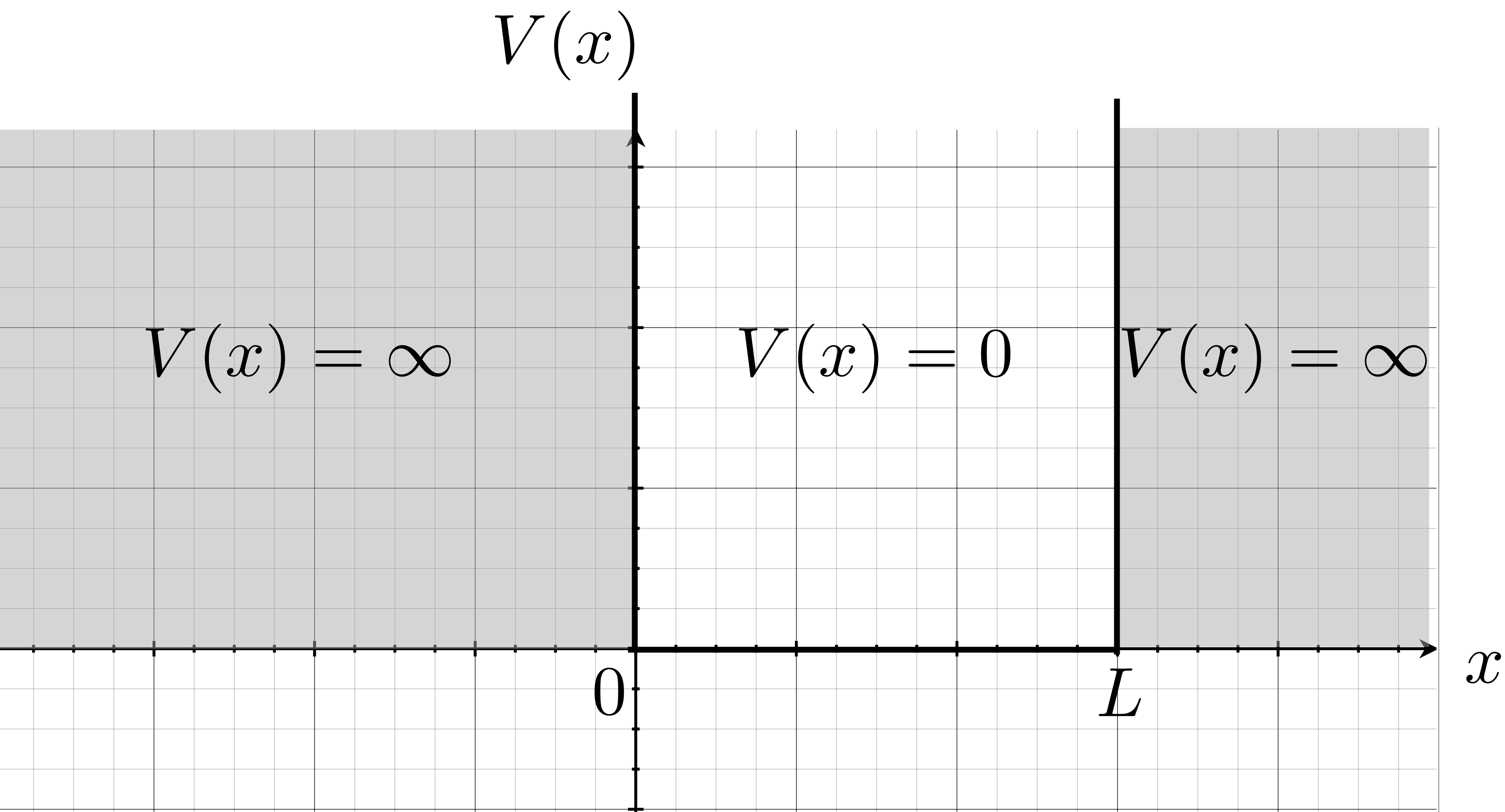
- We have seen that for **free particles** (when V(x)=0) the TISE has **de Broglie-like** wavefunctions as solutions.
- Now we will study our first case with a **non-trivial potential**.
- The **infinite** square well.



Infinite square well

- The **infinite** square well:

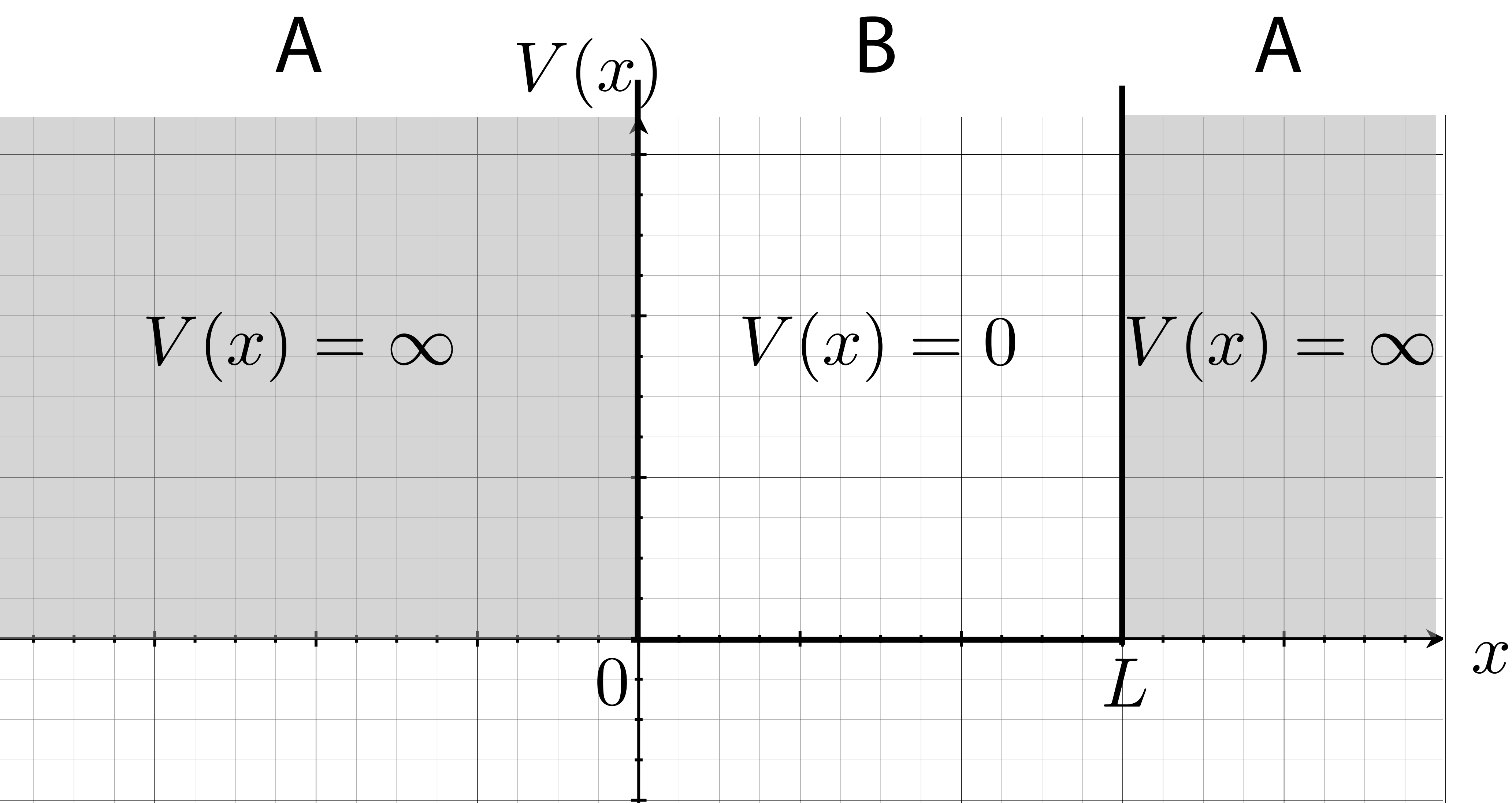
$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & \text{elsewhere} \end{cases}$$



Infinite square well

- Two regions to consider:
  - **A) Infinite potential** - any particle found in this region would have **infinite potential energy** - impossible!
  - Hence, in this region:

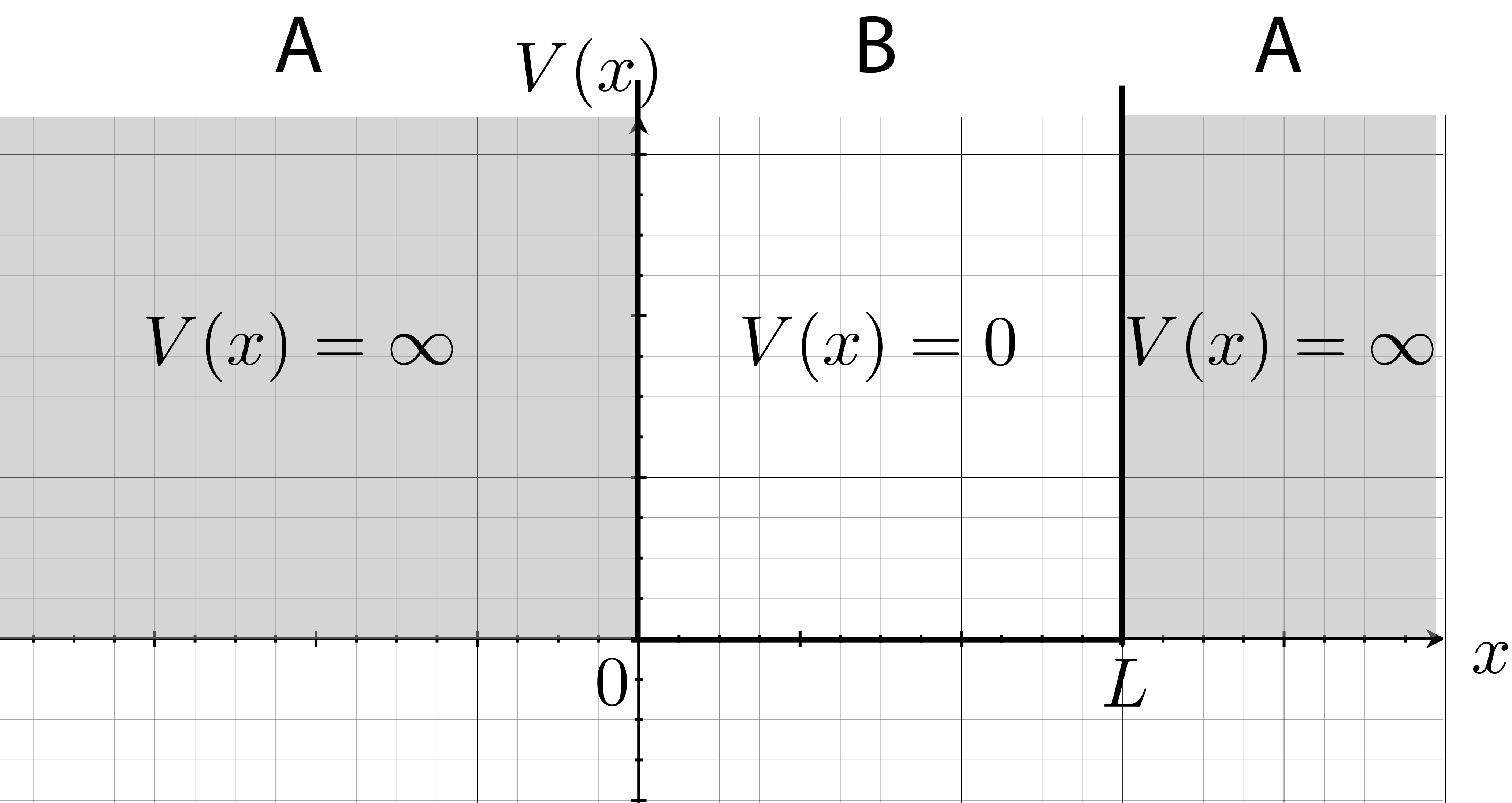
$$\psi_A(x) = 0$$



Infinite square well

- Two regions to consider:
  - **B) Zero potential -** We have already solved TISE with **V(x)=0**.
  - Solutions take the form:

$$\psi_B(x) = a\sin\left(\frac{px}{\hbar} + c\right) \qquad E = \frac{p^2}{2m}$$

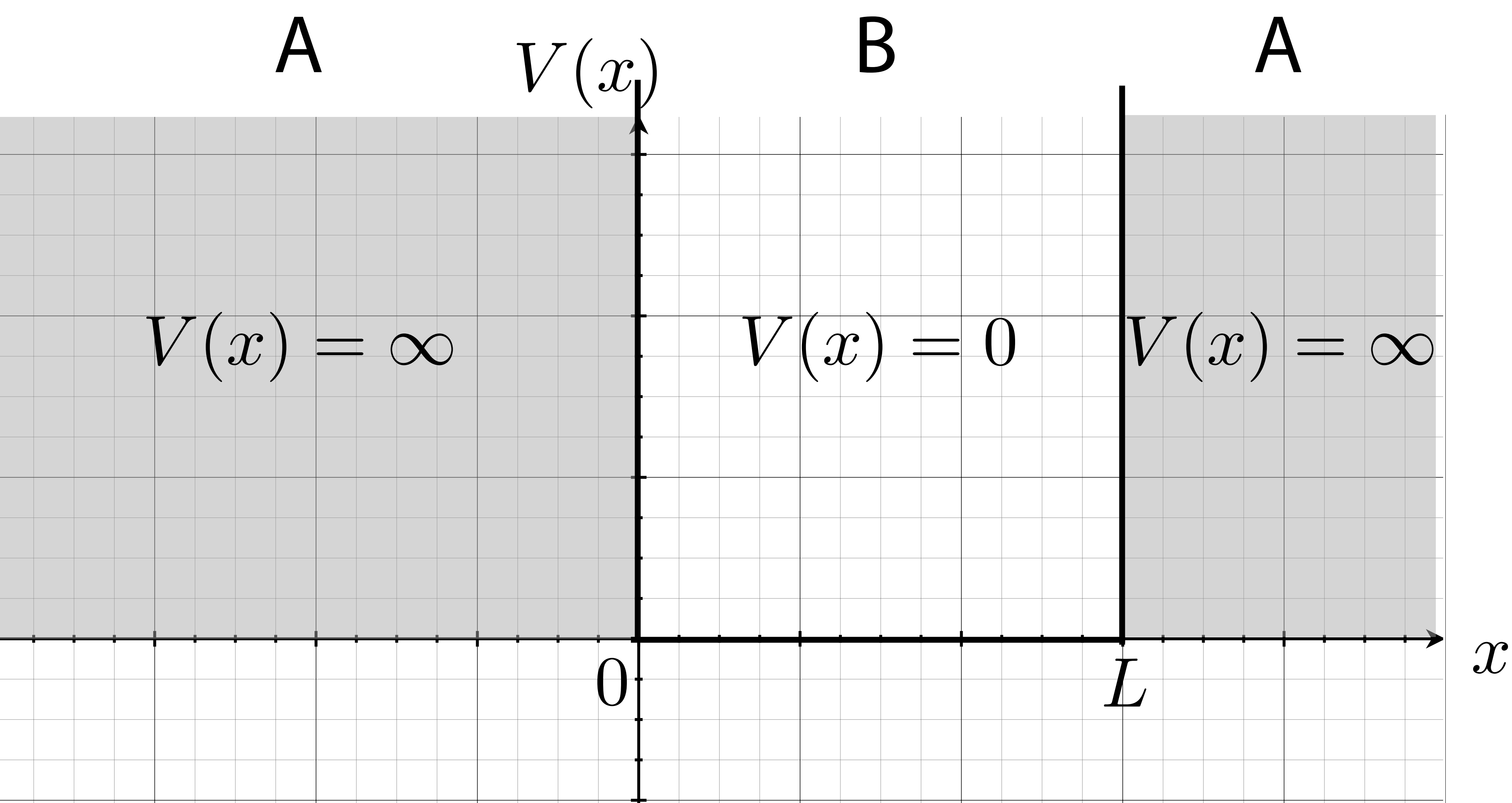


Infinite square well

- Hence we have

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a\sin\left(\frac{px}{\hbar} + c\right) \qquad 0 \leq x \leq L$$



Infinite square well

- Hence we have

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a \sin\left(\frac{px}{\hbar} + c\right) \qquad 0 \leq x \leq L$$

- Recall that wavefunctions must be **continuous**.
  - Thus the wavefunctions above must match at the **boundaries.**
- I.e. the following **boundary conditions** must be satisfied:

$$\psi_A(0) = \psi_B(0) \qquad\qquad \psi_A(L) = \psi_B(L)$$

Hand-written Calculations

Infinite square well

- Imposing the boundary conditions leads to the following wave-function in region B.

$$\psi_B(x) = a \sin\left(\frac{n\pi x}{L}\right)$$

- where **n** is an integer.
- If **n = 0, ψ(x)=0** everywhere, so we will discount the **n = 0** solution.
- We can also discount negative integers, since

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

and we can absorb this minus sign in the, yet to be determined, constant **a**.

Infinite square well

- So the wave-functions in region B for the infinite square well take the form:

$$\psi_B(x) = a \sin\left(\frac{n\pi x}{L}\right)$$

- where **n** = 1, 2, 3, 4…

- We can now use the **TISE** to calculate the **energies** of these wave-functions.

$$\frac{\cancel{2\pi}}{\lambda} = \left(\frac{\cancel{2\pi}}{h}\right)\sqrt{2mE} \rightarrow \frac{1}{\lambda} = \frac{\sqrt{2mE}}{h}$$

Let $\frac{1}{\lambda} = \frac{p}{h}$ $\qquad \frac{p}{\cancel{h}} = \frac{\sqrt{2mE}}{\cancel{h}}$

$$\frac{p^2}{2m} = E$$

Replace λ by $\frac{h}{p}$

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

$$\psi(x) = A\sin\left(\frac{2\pi(x-\phi)}{\lambda}\right) = A\sin\left(\frac{2\pi p}{h}(x-\phi)\right)$$

$$= A\sin\left(\frac{px}{\hbar} - \frac{\phi p}{\hbar}\right)$$

$$c = -\frac{\phi p}{\hbar}$$

$$= A\sin\left(\frac{px}{\hbar} + c\right)$$

$$\psi(x) = A \sin\left(\frac{2\pi\,(x - \phi)}{\lambda}\right)$$

$$\frac{1}{\lambda} = \frac{p}{h} \qquad \frac{p^2}{2m} = E$$

$$\psi(x) = A \sin\left(\frac{2\pi}{h}\,p\,x - \frac{2\pi\phi\,p}{h}\right)$$

$\frac{1}{\hbar}$

$+ C.$

Energies in the ∞-square well.

Subst. $\psi(x) = a \sin\left(\frac{n\pi x}{L}\right)$ $n = 1, 2, 3, \ldots$

into TISE.: $\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x)$.

$$\frac{d\psi}{dx} = a\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right) \quad \Bigg| \quad \frac{d^2\psi}{dx^2} = a\left(-\sin\left(\frac{n\pi x}{L}\right)\right)\left(\frac{n\pi}{L}\right)^2$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{n\pi}{L}\right)^2 \underbrace{a\sin\left(\frac{n\pi x}{L}\right)}_{\psi(x)} = -\left(\frac{n\pi}{L}\right)^2\psi(x)$$

subst. into TISE:

$$\left(\cancel{-}\frac{\hbar^2}{2m}\right)\left(\cancel{-}\left(\frac{n\pi}{L}\right)^2\right)\cancel{\psi(x)} = E\cancel{\psi(x)}$$

$$E = \frac{\hbar^2 n^2\pi^2}{2mL^2} = \frac{h^2}{4\cancel{\pi^2}}\frac{n^2\cancel{\pi^2}}{2mL^2} = \frac{h^2 n^2}{8mL^2}$$

We want: $\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$

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

Use: $\sin^2(x) = \frac{1-\cos(2x)}{2}$

$$= a^2 \int_0^L \frac{1 - \cos\left(\frac{2n\pi x}{L}\right)}{2} dx$$

$$= \frac{a^2}{2}\left[\int_0^L 1 \, dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right) dx\right] = \frac{a^2}{2}(L-0) - \left[\frac{\sin\left(\frac{2n\pi x}{L}\right)}{\left(\frac{2n\pi}{L}\right)}\right]_{x=0}^{x=L}$$

$$= \frac{a^2}{2}\left((L-0) - (0-0)\right) = \frac{a^2 L}{2}$$

Set $\frac{a^2 L}{2} = 1$ $\quad a^2 = \frac{2}{L}$ $\quad \boxed{a = \sqrt{\frac{2}{L}}}$ (ignore -ve solution)

Hand-written Calculations

Infinite square well

- So the wave-functions in region B for the infinite square well take the form:

$$\psi_B(x) = a \sin\left(\frac{n\pi x}{L}\right)$$

- where **n** = 1, 2, 3, 4…
- We can now use the **TISE** to calculate the **energies** of these wave-functions and find:

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

- The energies only take **discrete values** - the energy is **quantised**.
- Unlike in the Bohr model, where quantisation was put in by hand, this **quantisation** has **emerged** from the requirement of a **continuous** wavefunction - the **boundary conditions**.

Infinite square well

- We have not yet checked whether the wavefunctions are normalisable or normalised.

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a \sin\left(\frac{n\pi x}{L}\right) \qquad\qquad 0 \leq x \leq L$$

- Recall, all physical wavefunctions must satisfy:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

- Let us verify that our wave-functions can be **normalised**.

Hand-written Calculations

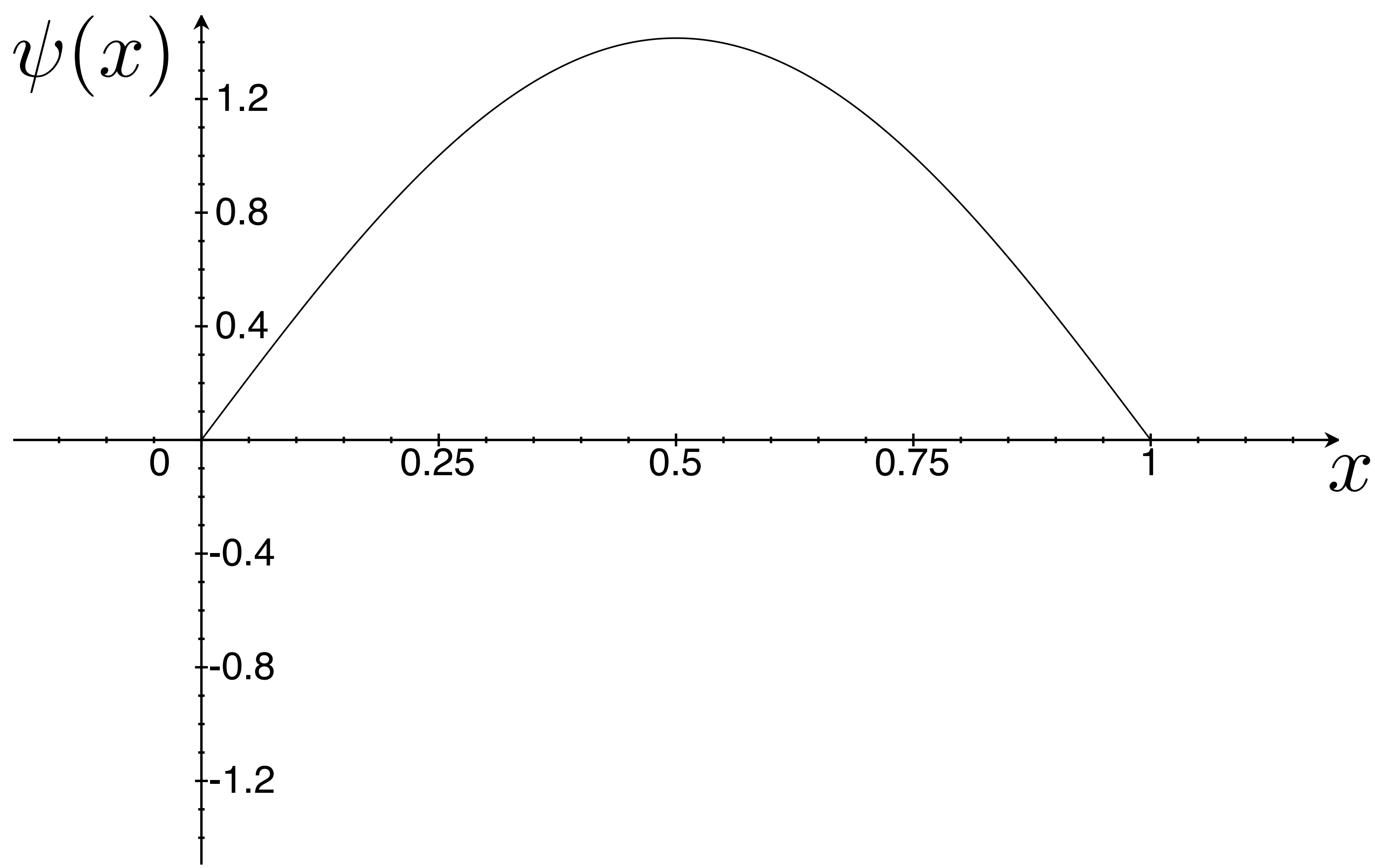
Infinite square well

- The normalised wave-functions are:

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 \leq x \leq L$$

- E.g. **n=1 L=1,**



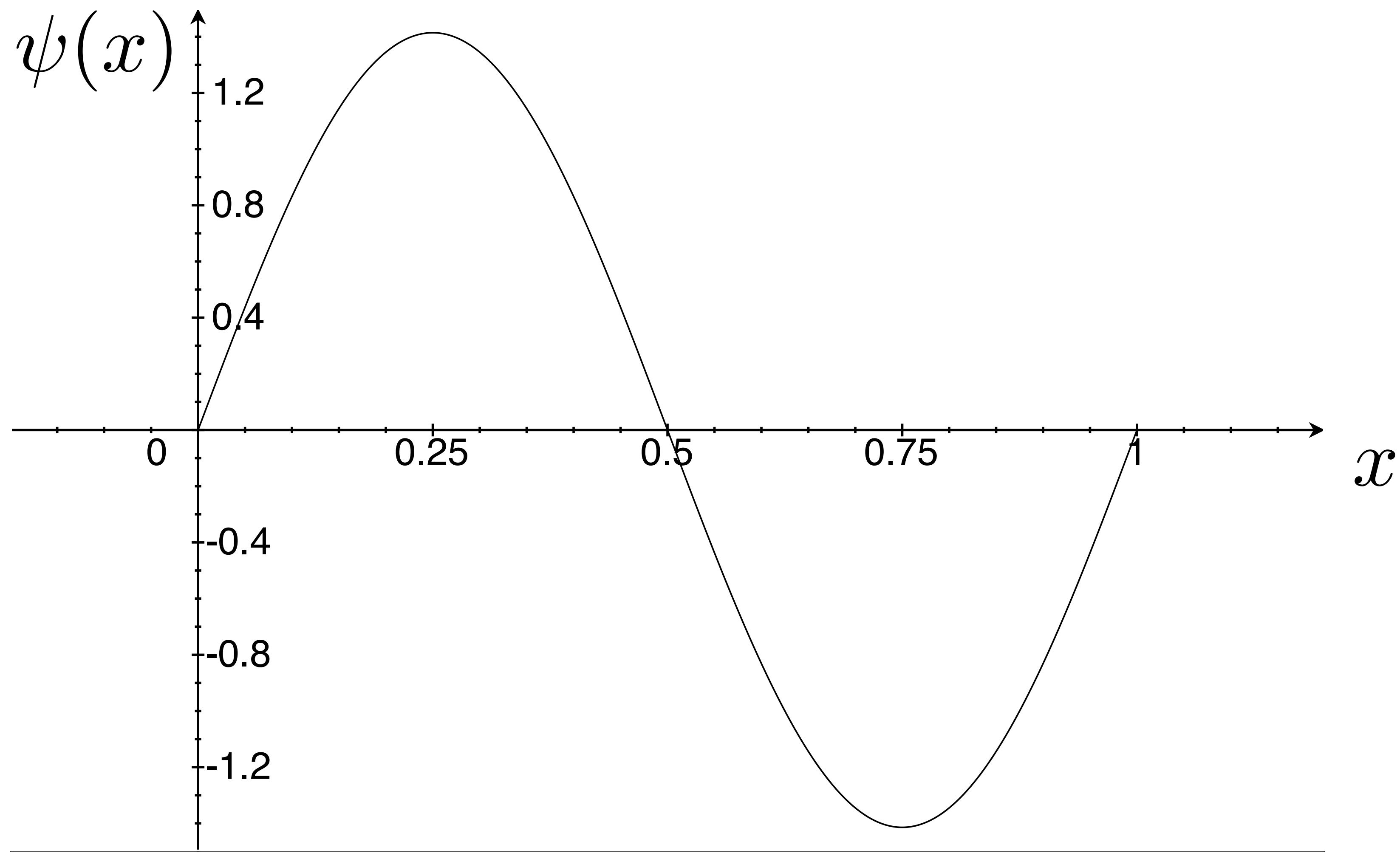
Infinite square well

- The normalised wave-functions are:

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \quad x \geq L$$

$$\psi_B(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 \leq x \leq L$$

- E.g. **n=2, L=1**



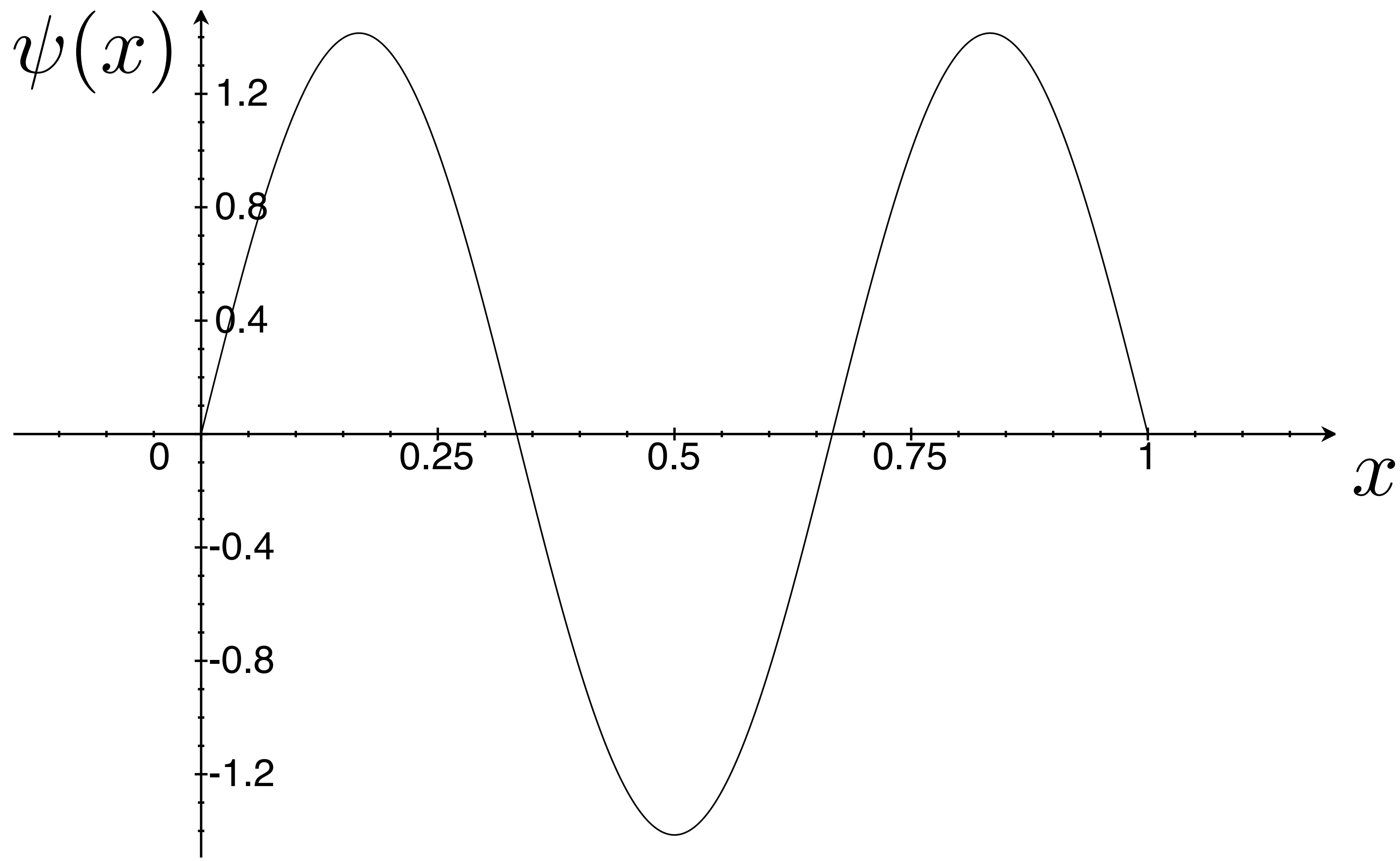
Infinite square well

- The normalised wave-functions are:

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 \leq x \leq L$$

- E.g. **n=3, L=1**



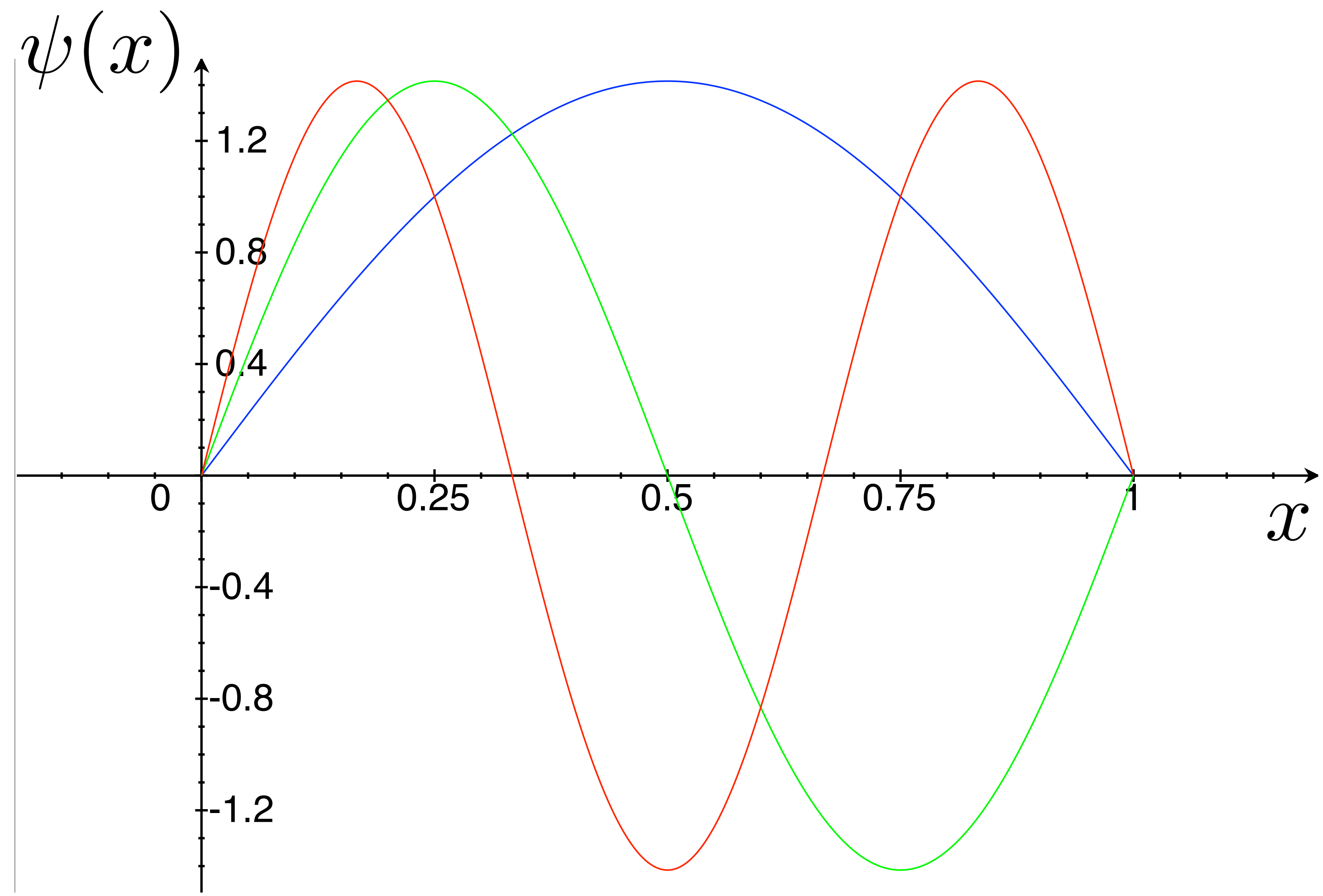
Infinite square well

- The normalised wave-functions are:

$$\psi_A(x) = 0 \qquad\qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 \leq x \leq L$$

- E.g. **n=1,2,3**
L=1



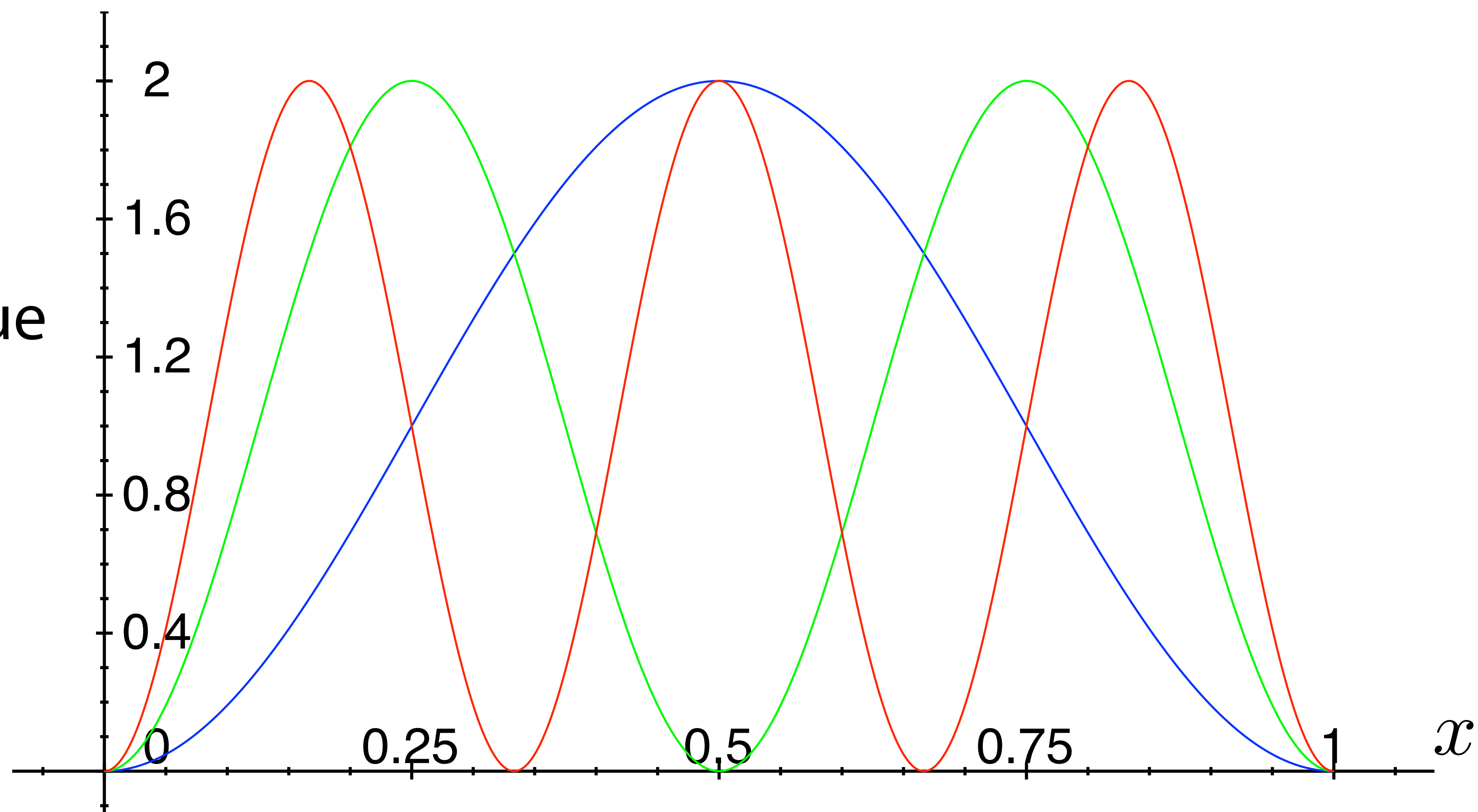
Infinite square well

- The corresponding **probability density** for position:

$$\rho(x) = 0 \qquad\qquad x \le 0 \quad x \ge L$$

$$\rho(x) = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right) \qquad\qquad 0 \le x \le L$$

- E.g. **n=1,2,3**
L=1,



- For all values of n, the expectation value of x is:

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

Infinite square well

- **Summary**
  - By solving the TISE and applying boundary conditions, we find that the **only allowed energies** for the **infinite square well** are:

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

  - and the corresponding wave-functions:

$$\psi_A(x) = 0 \qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad 0 \leq x \leq L$$

Infinite square well

- **Our solution strategy**
  - Solve the TISE in **separate regions** of **constant potential.**
  - Use continuity of wavefunction between region to give us **boundary conditions**.
- This is a **general technique** which we will use often in solving the TISE.
- Before we consider some other examples, we will take a closer look at the **structure** of the TISE.

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

Structure of the TISE

- Let us take another look at the **time-independent Schrödinger equation.**

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

- The wavefunction **ψ(x)** appears in every term of the equation.

- As already noted, it has a similar structure to:

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

Differential operators

Differential operators

- You are familiar with writing **derivatives**.
  - E.g. First derivative of $f(x)$: $\dfrac{df(x)}{dx}$
- The mathematical object:

$$\frac{d}{dx}$$

  is called a **differential operator**.

- It acts as follows: $$\frac{d}{dx} f(x) = \frac{df(x)}{dx}$$
- Examples of differential operators:

$$\frac{d}{dx} \qquad \frac{d^2}{dt^2} \qquad \frac{d^2}{dxdy}$$

Structure of the TISE

- We can rewrite the TISE in terms of differential operators:

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

$$\downarrow$$

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

- Equations in the form

$$\hat{D}\psi(x) = E\psi(x)$$

are called **eigenvalue equations**.

- where ***E*** is called the **eigenvalue**
- **ψ(x)** is called the **eigenfunction**
- and $\hat{D}$ is any sum of differential operators and functions of ***x***.

Structure of the TISE

- The **Time-independent Schrödinger equation** is an example of an **eigenvalue equation**,
  - where energy **E** is the **eigenvalue**
  - and wavefunction **ψ(x)** is the **eigenfunction**

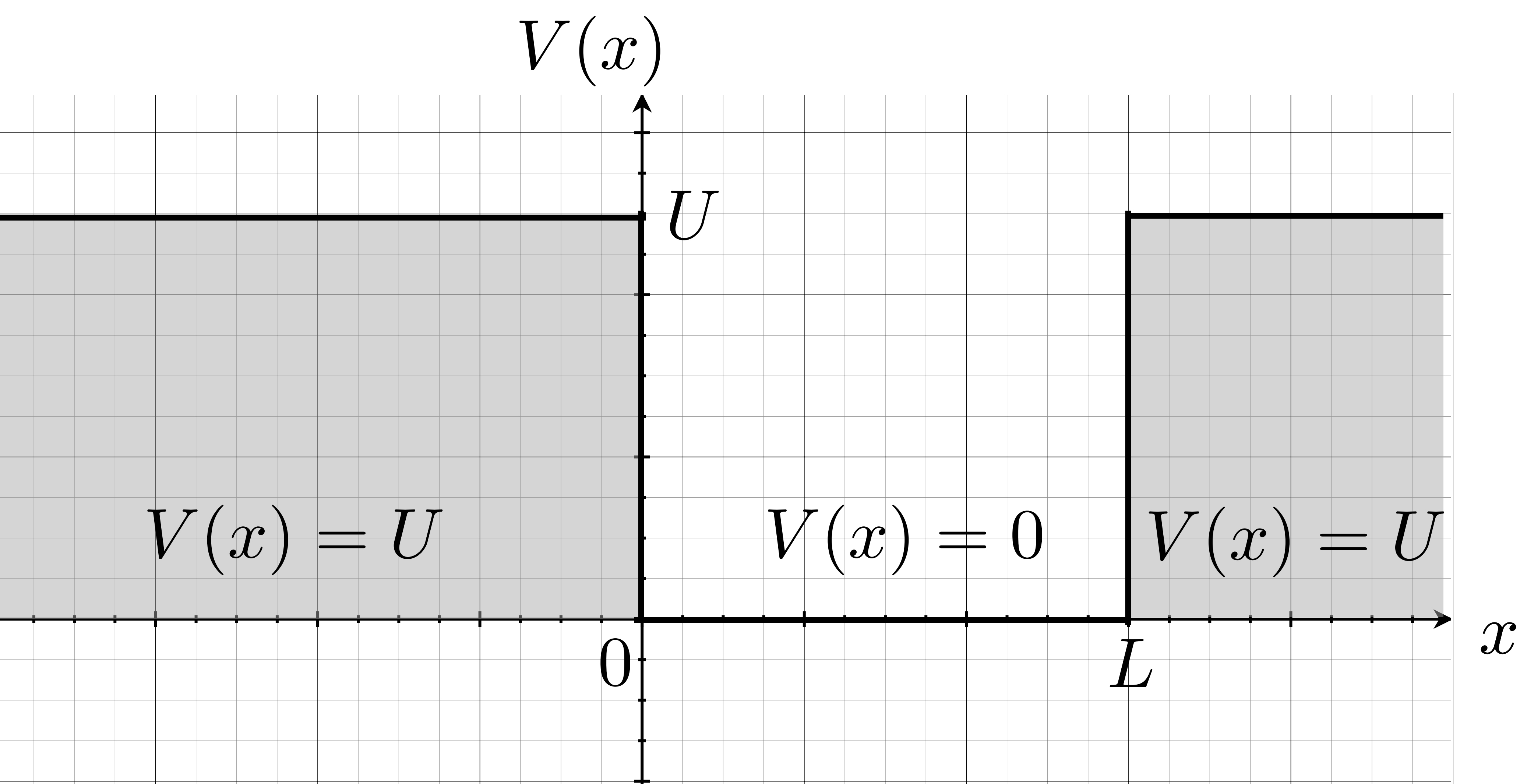
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x)=E\psi(x)$$

- As we have seen, the TISE can have **multiple eigenvalues** (the allowed energies), and for each eigenvalue a **different eigenfunction** (the wavefunction for that energy).
- **Eigenvalue equations** play a **central role** in quantum mechanics and you will study them in great detail in your future courses.

Finite square well

Finite square well

- The **infinite square well** is an important first example of solving the TISE.
- In nature, potential energy is usually **finite**.
- We will study the **finite square well**.

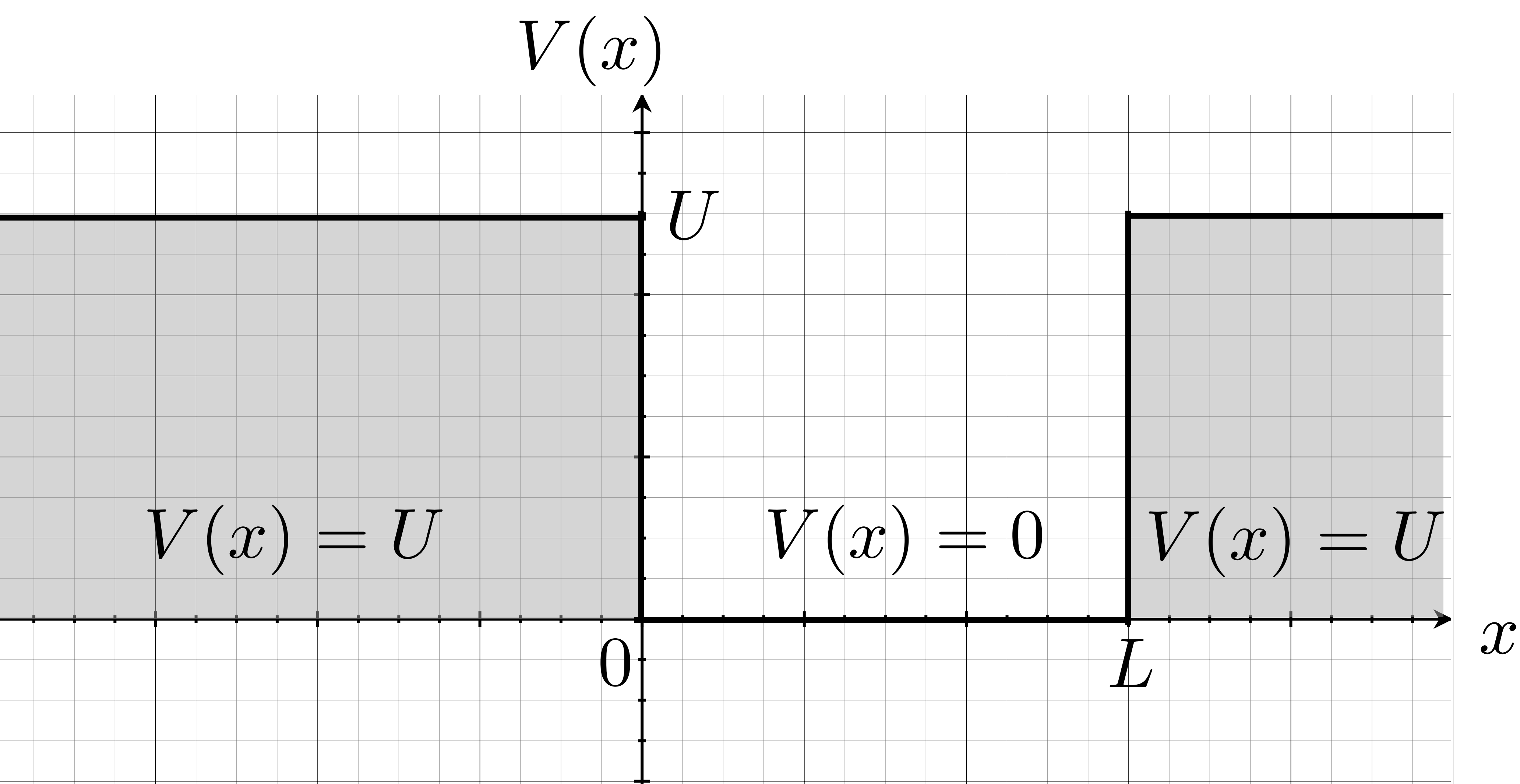


Finite square well

- The potential function for the finite square well is:

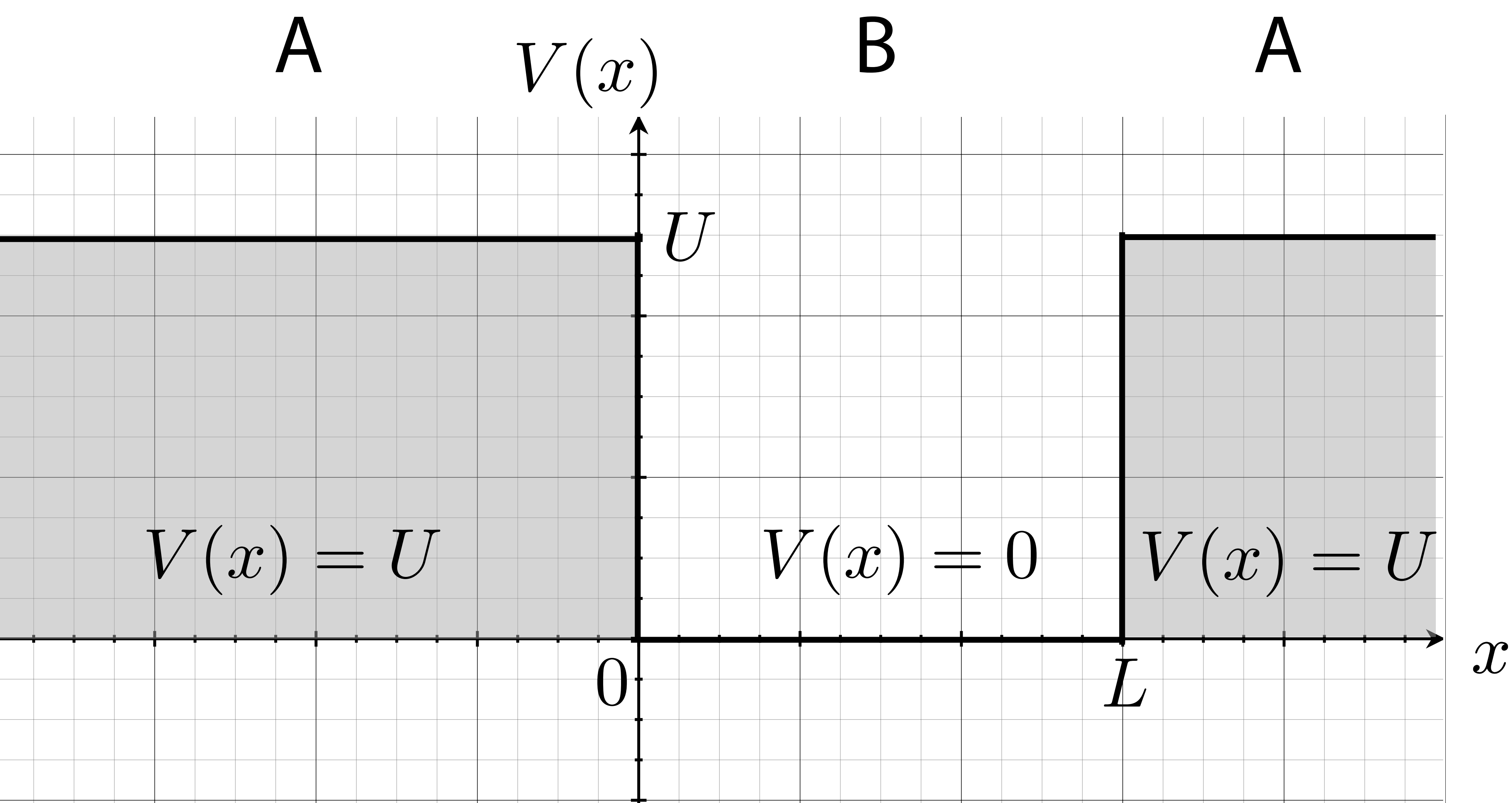
$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ U & \text{elsewhere} \end{cases}$$

- where $U > 0$.



Finite square well

- To solve the **TISE**, we again split the problem up into **regions**, and then apply **boundary conditions**.
    - **Region A)** where **V(x) = U.**
    - **Region B)** where **V(x) = 0.**



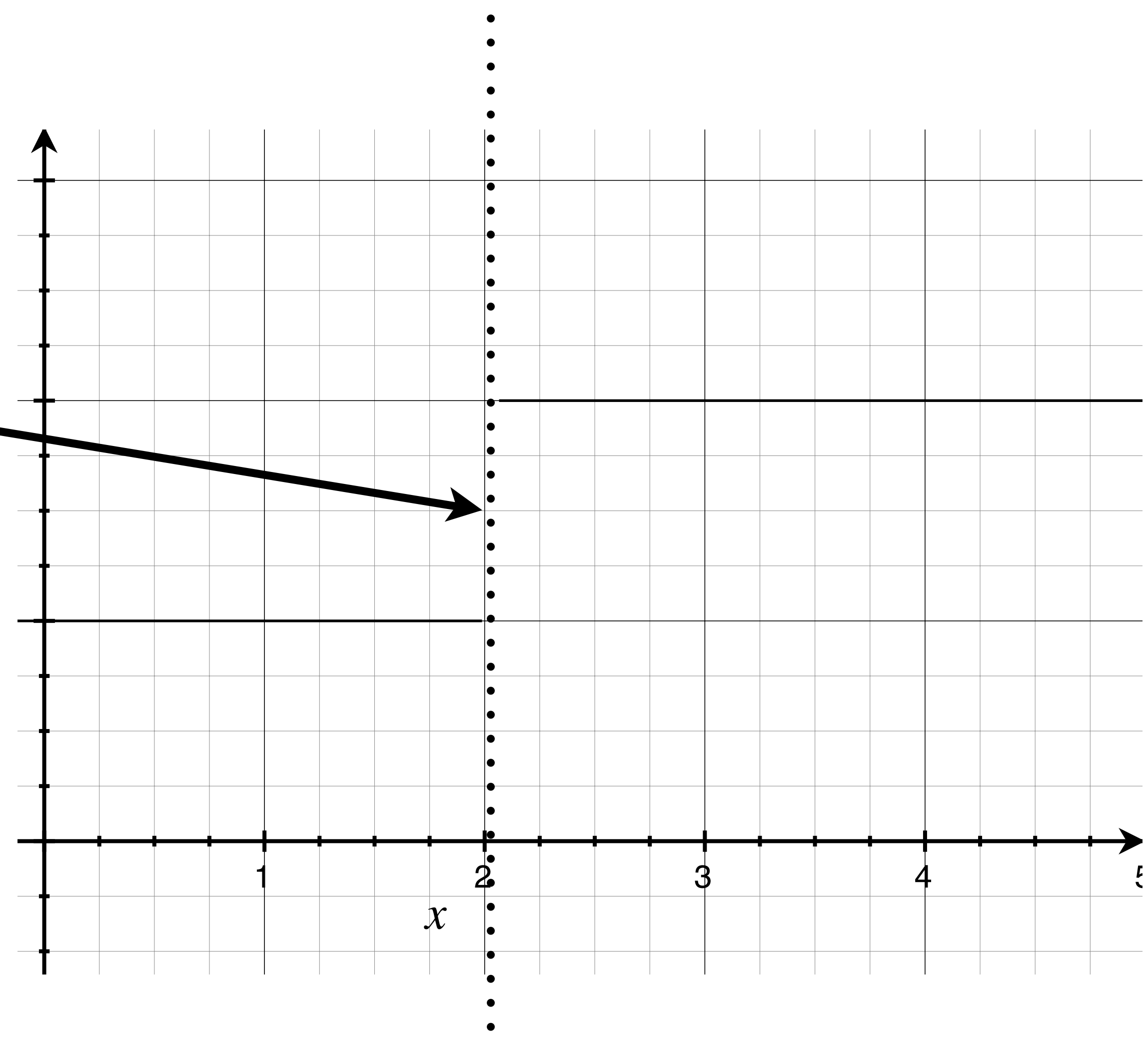
Boundary conditions

Boundary conditions

- We have seen that wavefunctions must be **continuous**.
- The reason for this is that in a **discontinuous** function, the **gradient**, or **first derivative** is **infinite**.

Infinite gradient

$$\frac{\Delta y}{\Delta x}$$



$$f(x) \text{ discontinuous} \longrightarrow \frac{df(x)}{dx} \text{ infinite}$$

Boundary conditions

- Similarly $\dfrac{d^2 f(x)}{dx^2}$ is the gradient of $\dfrac{df(x)}{dx}$
- So

$$\frac{df(x)}{dx} \text{ discontinuous } \longrightarrow \frac{d^2 f(x)}{dx^2} \text{ infinite}$$

similar to

$$f(x) \text{ discontinuous } \longrightarrow \frac{df(x)}{dx} \text{ infinite}$$

Boundary Conditions

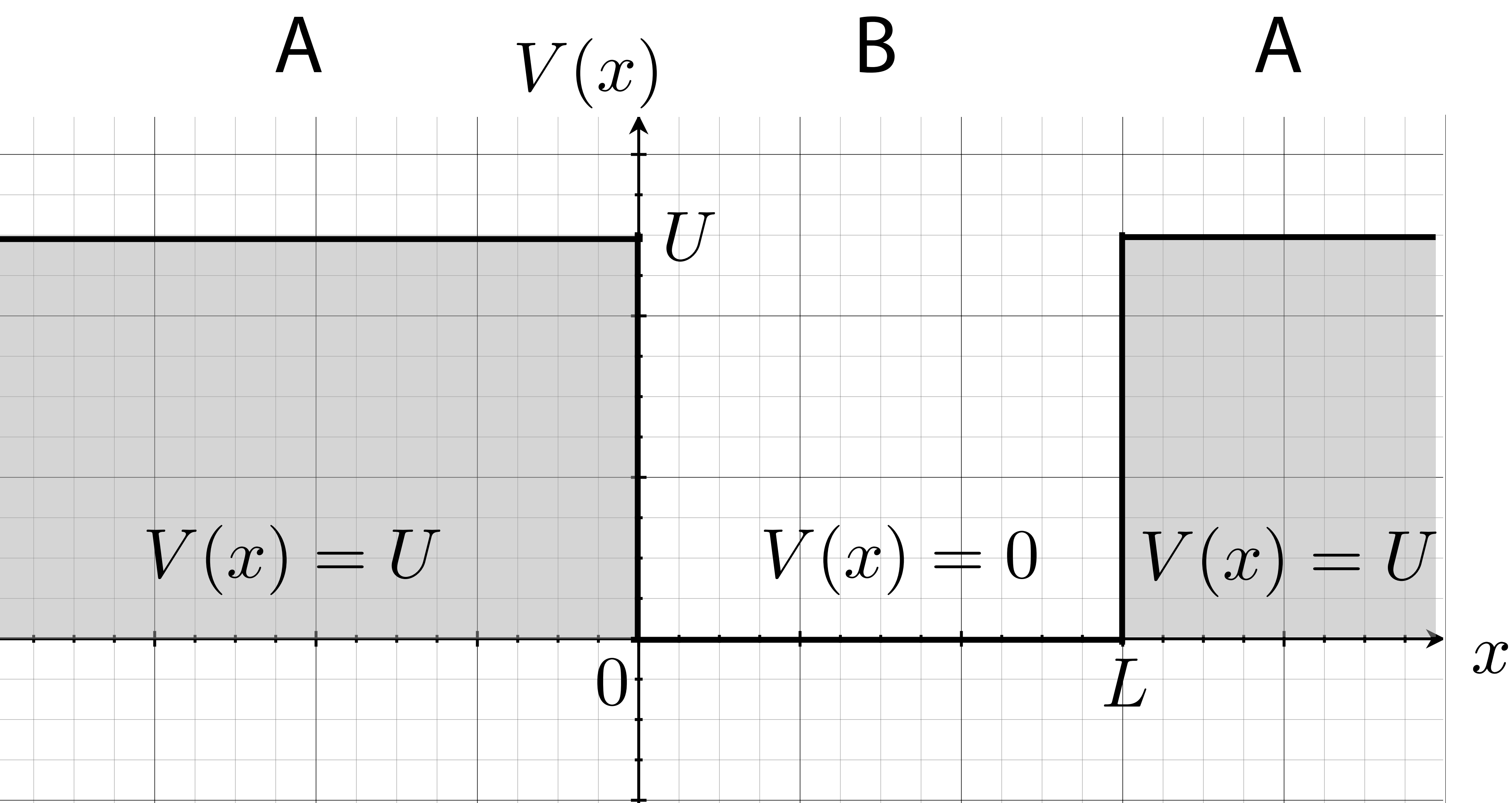
- The TISE contains the second derivative of ψ(x):

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

- If **energy E** is **finite**, the second derivative cannot be infinite, hence the first derivative of the wave-function must be continuous.
- This gives us an extra continuity condition:
  - **ψ(x)** must be **continuous**
  - **dψ(x)/dx** must be **continuous**
- This contributes an **additional boundary condition** which **TISE solutions** must satisfy.

Finite square well

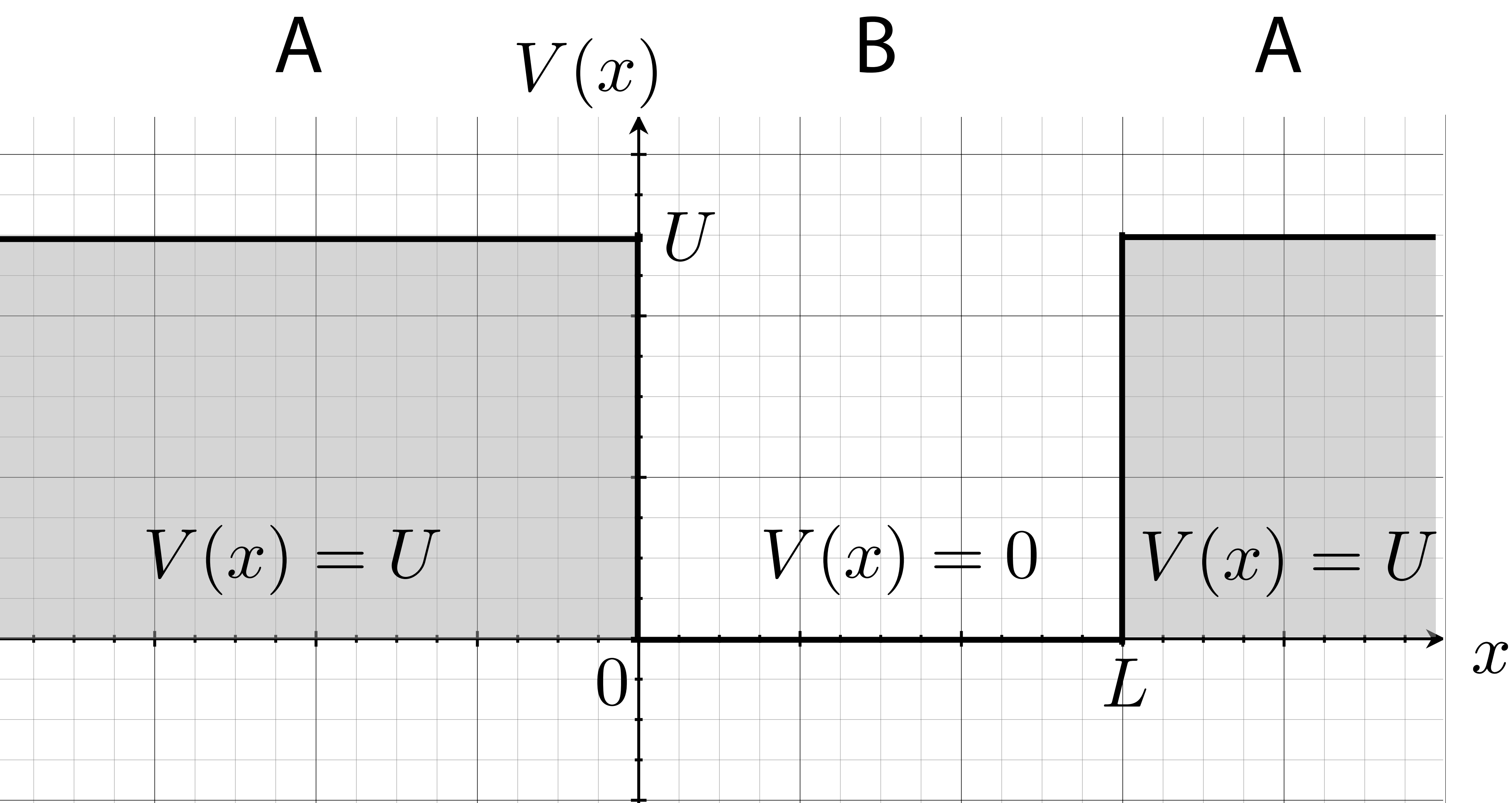
- To solve the **TISE**, we again split the problem up into **regions**, and then apply **boundary conditions**.
    - **Region A**) where **V(x) = U.**
    - **Region B**) where **V(x) = 0.**



Finite square well

- **Region B -** where **V(x) = 0.**
  - We have already solved the **TISE** for **V(x) = 0.**
  - Solutions:

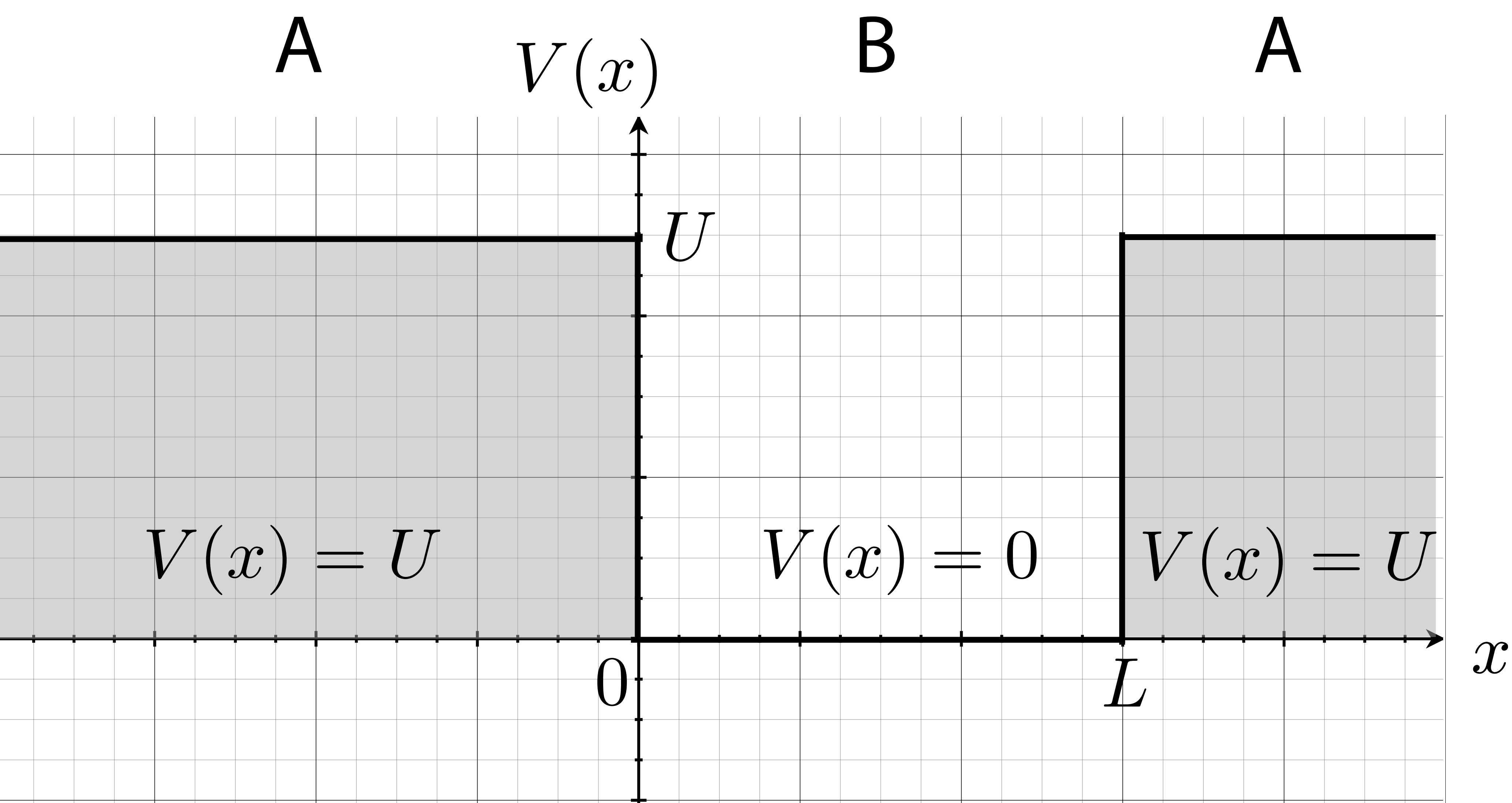
$$\psi_B(x) = a \sin\left(\frac{px}{\hbar} + c\right)$$



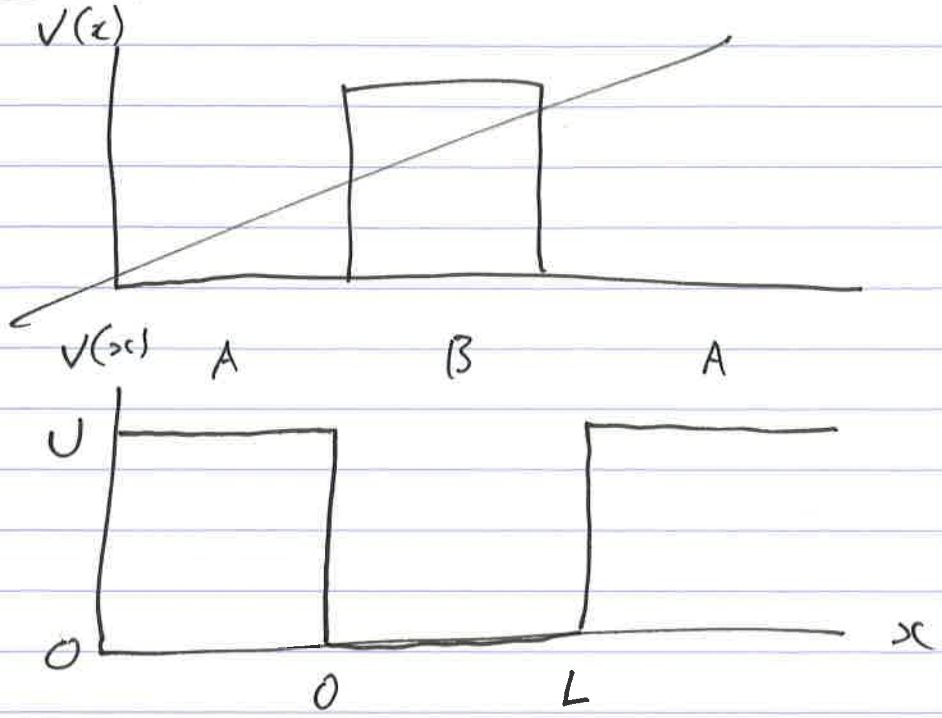
Finite square well

- **Region A -** where **V(x) = U.**

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



Finite well



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

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

$$\frac{d^2\psi(x)}{dx^2} = \frac{-2m}{\hbar^2}(E-U)\psi(x) \quad (*)$$

Two cases:

i) $E > U$	ii) $E < U$
$(E-U) > 0$	$(E-U) < 0$
RHS of $*$ is $-$ve	RHS of $*$ is $+$ve.

Use trial solution:

$$\psi(x) = Ae^{(Bx+C)}$$

$$\frac{d\psi(x)}{dx} = ABe^{(Bx+C)} \qquad \frac{d^2\psi}{dx^2} = AB^2 e^{(Bx+C)}$$

$$= B^2 \psi(x)$$

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

$$\rightarrow \quad B^2 = \frac{-2m(E-U)}{\hbar^2} = \frac{2m}{\hbar^2}(U-E)$$

$$B = \pm\sqrt{\frac{2m}{\hbar^2}(U-E)}$$

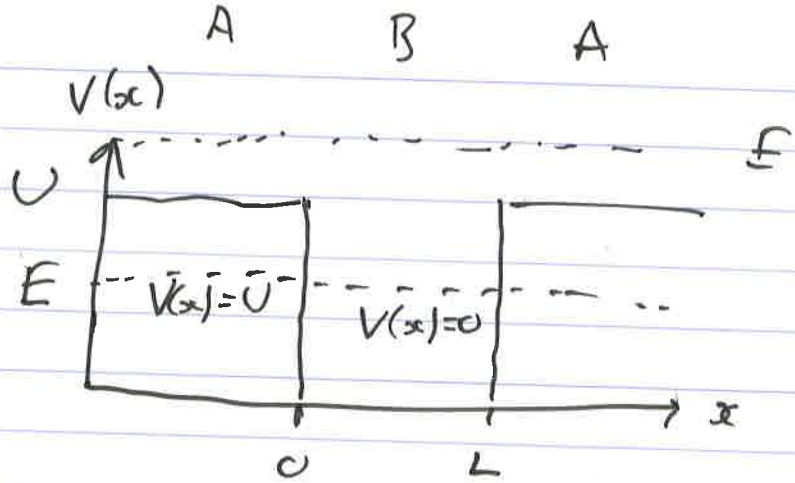
$$\text{Let } K = \sqrt{\frac{2m}{\hbar^2}(U-E)}$$

$$B = \pm K$$

Hence solns of TISE for $E<U$ are:

$$\psi(x) = Ae^{\pm kx+c}$$

Finite Square Well



In region A: $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi(x) = E\psi(x)$$

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

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

Two cases:

i) $E > U$ or ii) $E < U$

$(E-U) > 0$ $\quad$ $(E-U) < 0$

$\downarrow$ $\quad$ $\downarrow$

RHS: $-$ve $\quad$ RHS: $+$ve

Case ii) Recall: $$\frac{d^2}{dx^2}e^x = e^x$$

Use trial solution: $$\psi(x) = Ae^{Bx+C}$$

$$\frac{d\psi}{dx} = ABe^{Bx+C} \qquad \frac{d^2\psi}{dx^2} = AB^2e^{Bx+C}$$

$$= B^2\psi(x)$$

$$\psi(x) = A e^{Bx + C} \qquad \frac{d^2\psi}{dx^2} = B^2 \psi(x)$$

$$B^2 \cancel{\psi(x)} = \frac{d^2}{dx^2}\psi(x) = \frac{-2m}{\hbar^2}(E-U)\,\cancel{\psi(x)}$$

$$B^2 = \frac{-2m(E-U)}{\hbar^2}$$

Recall $\underline{\underline{E < U}}$

$$B^2 = \frac{2m(U-E)}{\hbar^2} \qquad B = \pm\sqrt{\frac{2m(U-E)}{\hbar^2}}$$

Let $K = \sqrt{\frac{2m(U-E)}{\hbar^2}}$

Hence $B = \pm k$

Subst into trial solution: $\boxed{\psi(x) = Ae^{\pm kx + C}}$

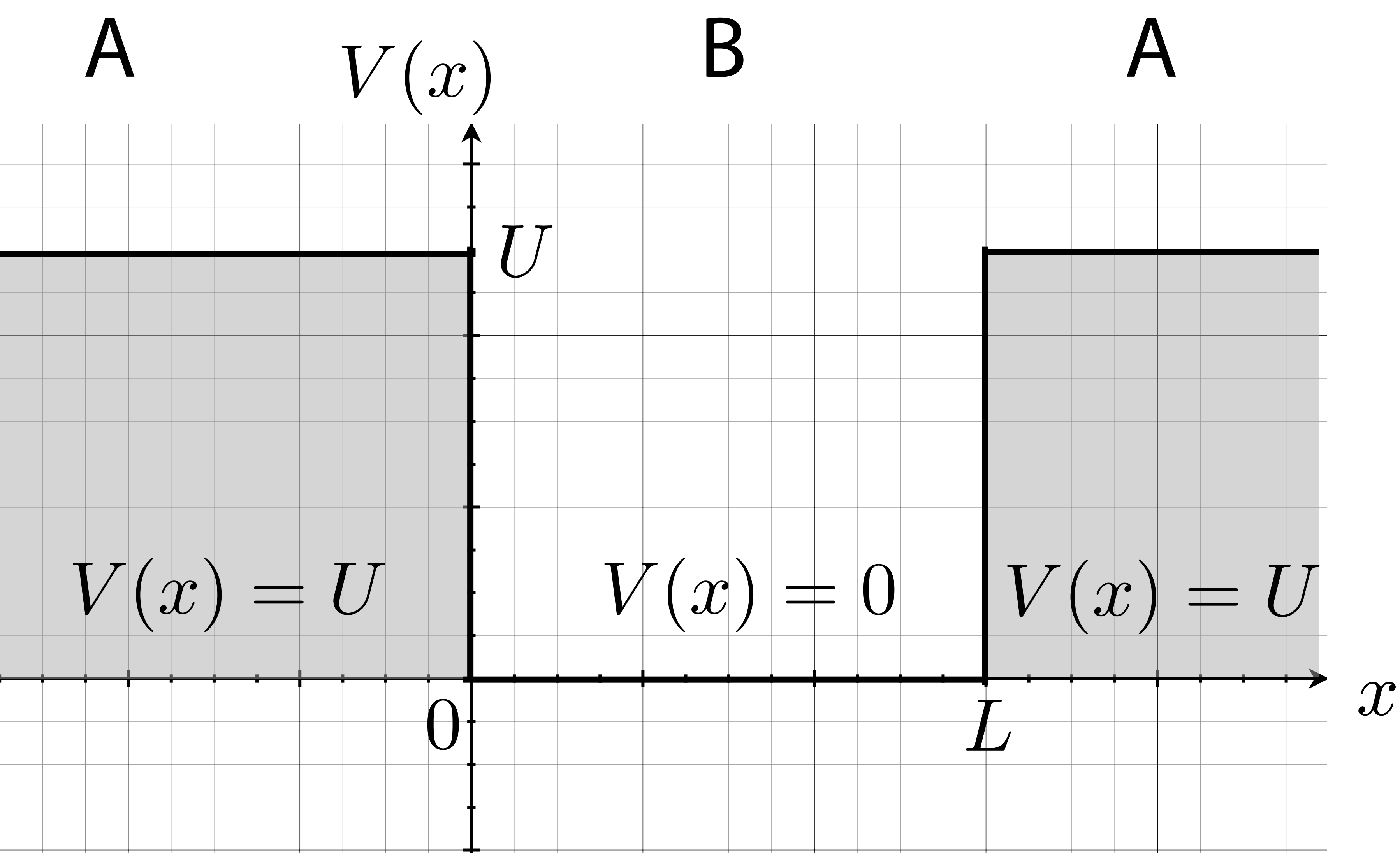
Hand-written Calculations

Finite square well

- When **E < U**, the solutions to the TISE have the form.

$$\psi_A(x) = Ae^{\pm Kx + C} \qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a\sin\left(\frac{px}{\hbar} + c\right) \qquad 0 \leq x \leq L$$



$$K = \frac{\sqrt{|E-U|2m}}{\hbar}$$

$$p = \sqrt{E2m}$$

Finite square well

- When **E < U**, the solutions to the TISE have the form.

$$\psi_A(x) = Ae^{\pm Kx + C} \qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a\sin\left(\frac{px}{\hbar} + c\right) \qquad 0 \leq x \leq L$$

- We can find the allowed values for ***A***, ***K***, ***C***, ***a***, ***p*** and ***c*** by imposing the boundary conditions:
  - **ψ(x)** must be **continuous**
  - **dψ(x)/dx** must be **continuous**
  - **ψ(x)** must be **normalised**

$$K = \frac{\sqrt{|E - U|2m}}{\hbar}$$

$$p = \sqrt{E2m}$$

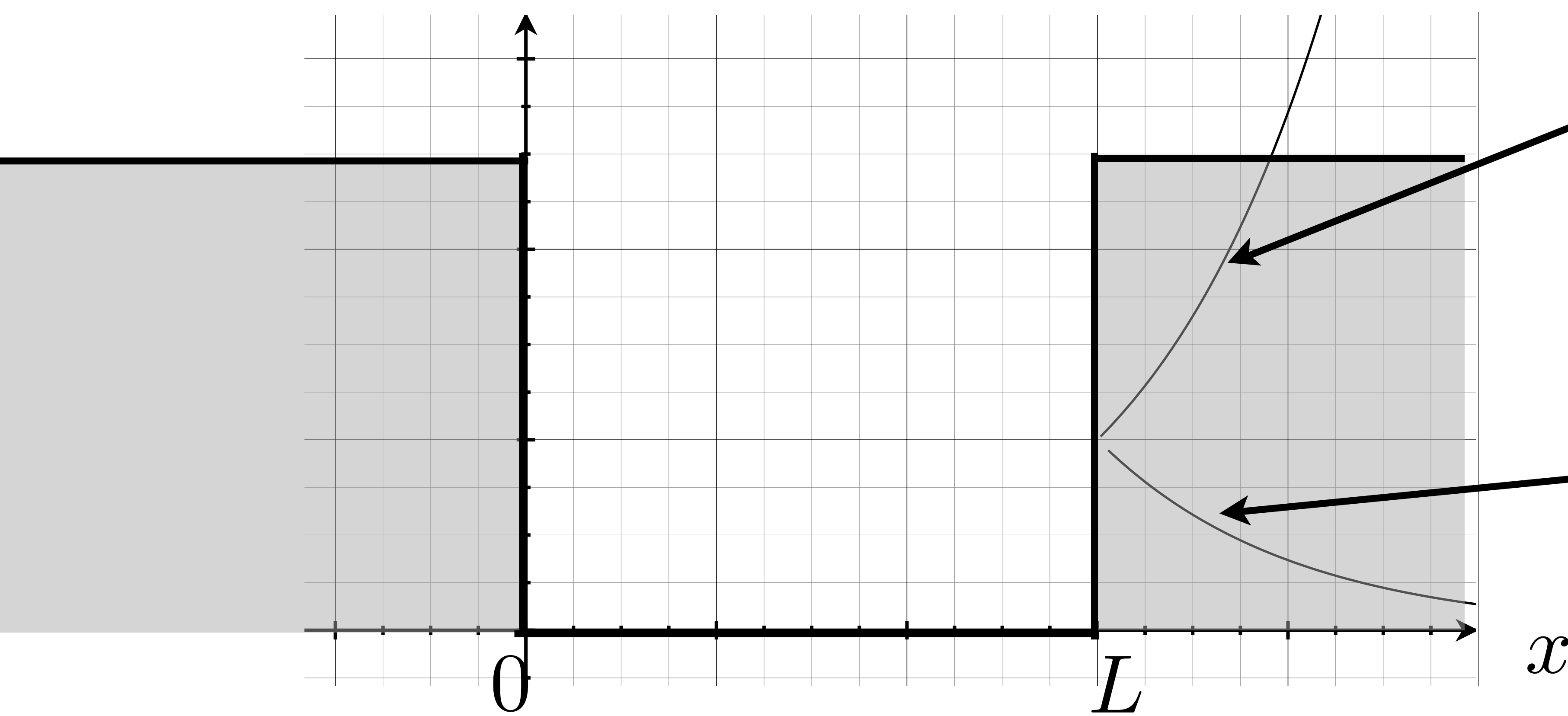
Finite square well

- We will **not** perform the detailed calculation here (2nd year course) but let us see what this solution should look like.

- First, let's consider region A.

$$\psi_A(x) = Ae^{\pm Kx+C}$$

$$\psi_A(x) = Ae^{+Kx+C}$$

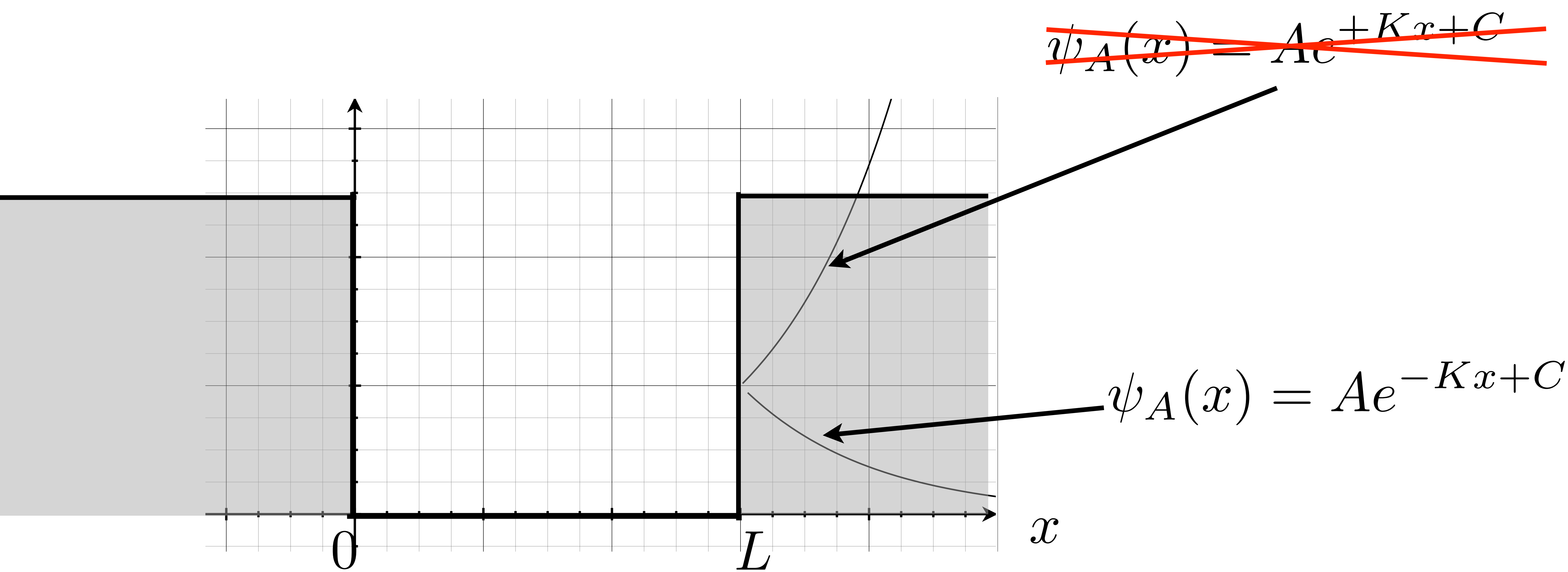


$$\psi_A(x) = Ae^{-Kx+C}$$

Finite square well

- One of these solutions **blows up** to infinity, as **x** tends to **infinity**.
- The **wavefunction** must **not** be infinite.
- Therefore in the region **x > L**, the wavefunction must be:

$$\psi_{x>L}(x) = Ae^{-Kx+C}$$

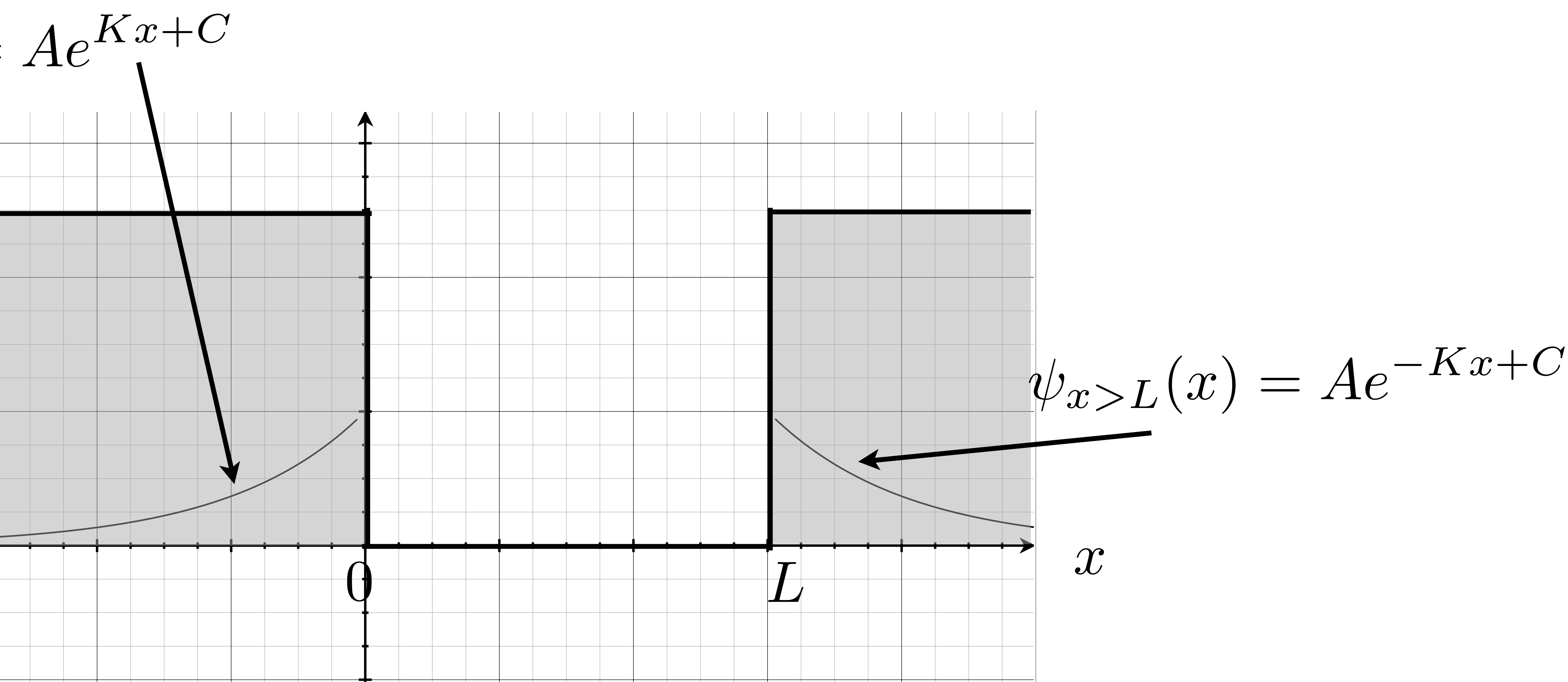


Finite square well

- Similarly, in the region, **x < 0** the wavefunction must be of the form:

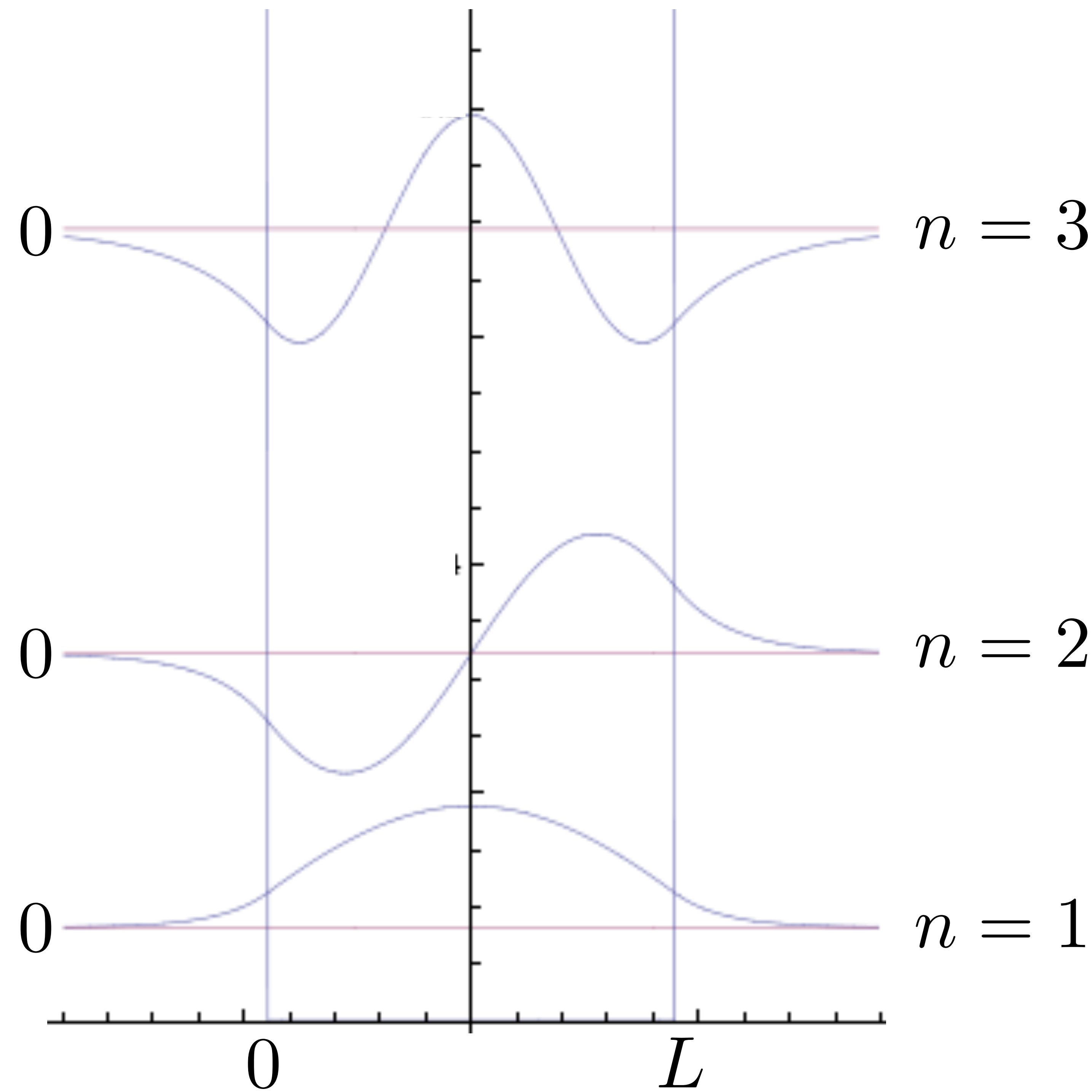
$$\psi_{x<0}(x) = Ae^{Kx+C}$$

- NB A classical particle would **never** leave the well, but we see a **finite probability** of measuring the particle **outside the well**!



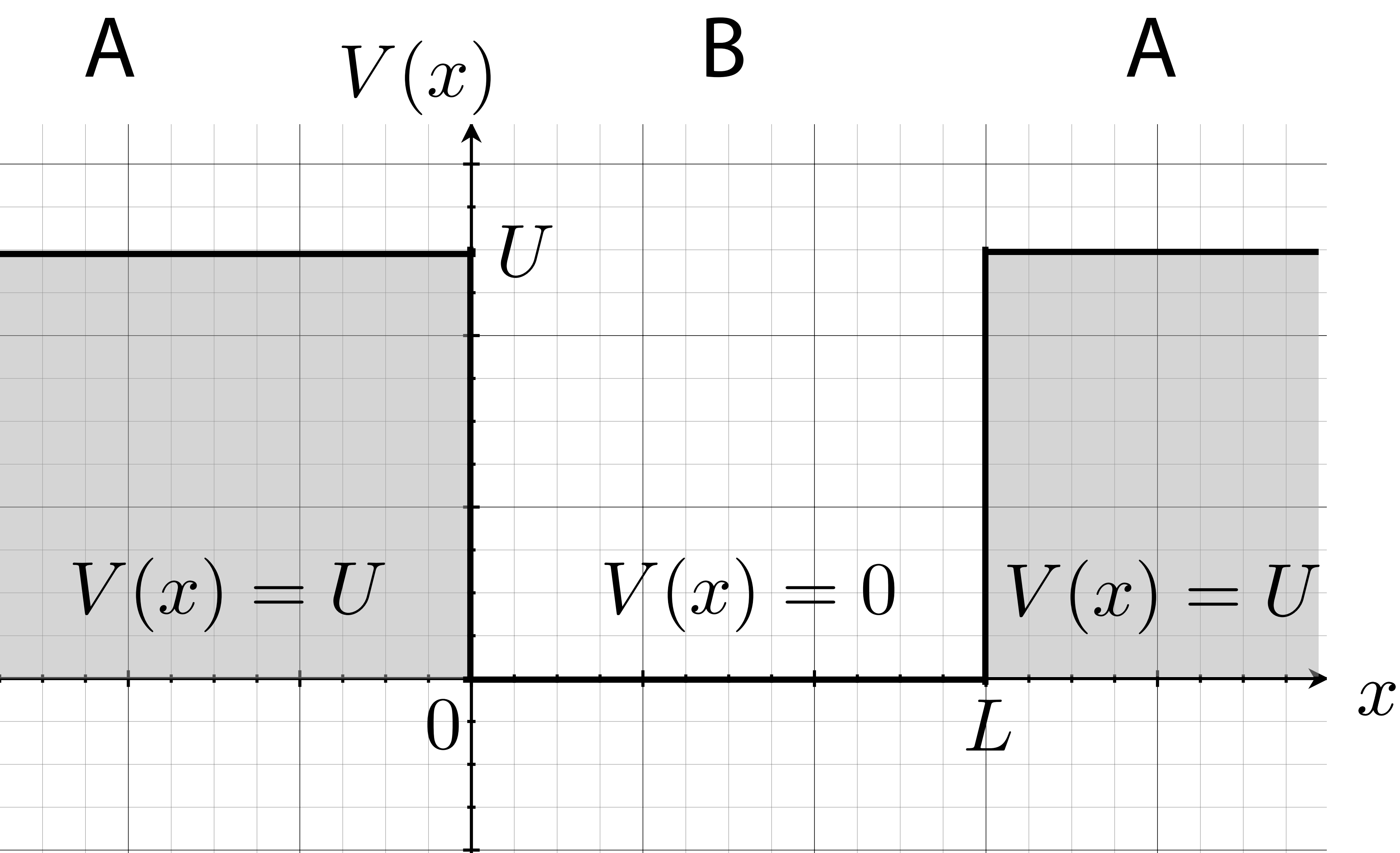
Finite square well

- Applying **boundary conditions** we can calculate the **wavefunctions** and allowed **energies**.
- The **energy** is still **quantised**.
- Wavefunction is :
  - **sinusoidal** inside well
  - **exponentially decaying** outside well
- All **wavefunctions** have a **non-zero** region **outside** the well.



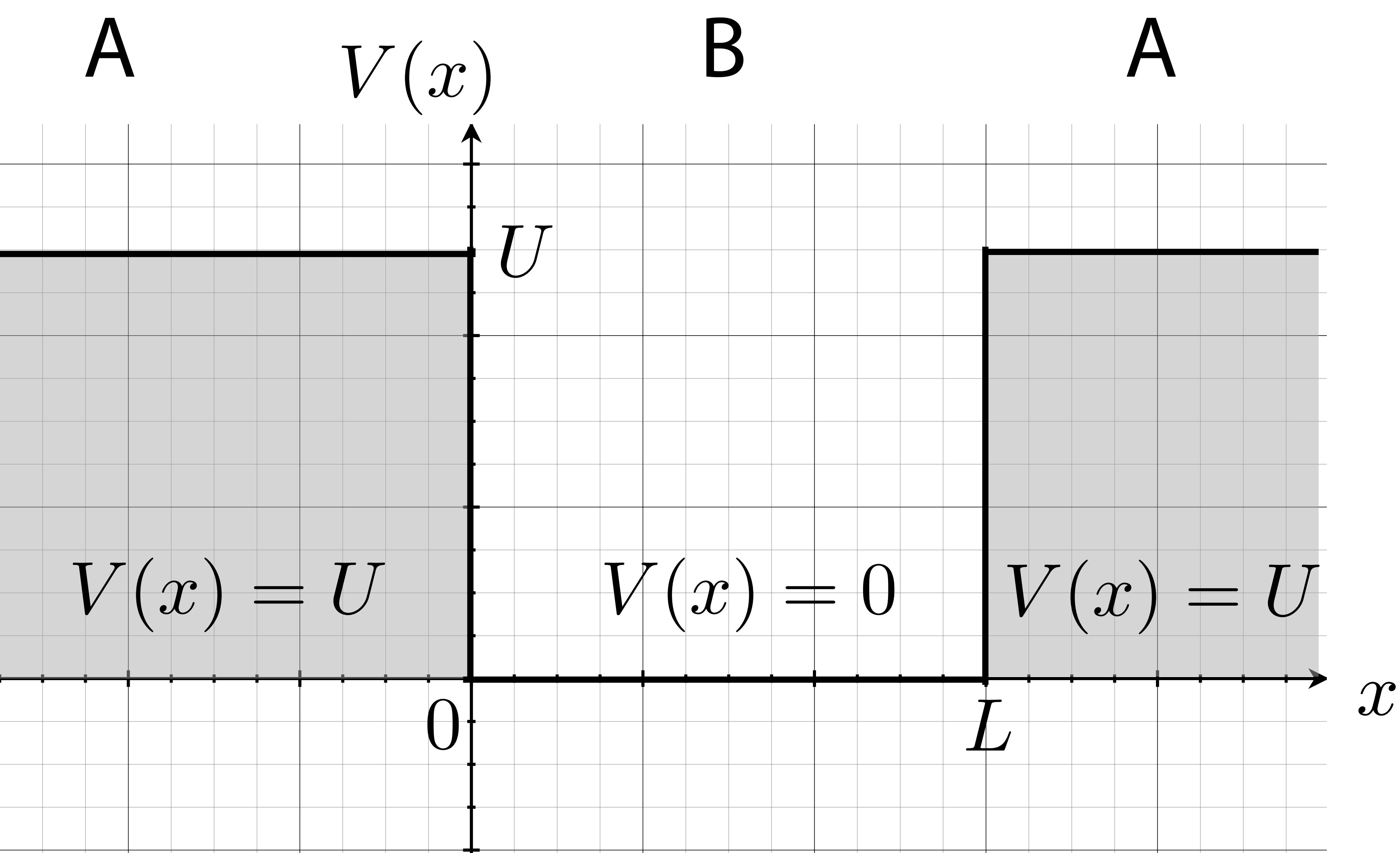
Finite square well

- So far we have assumed **E < U**, where a **classical particle** would **not** have **enough energy** to leave the well.
- We found the quantum particles have wavefunctions **mostly**, but **not entirely, inside** the well.
- We call these **bound states.**



Finite square well

- What happens when **E > U?**
- Where a **classical particle** would have **enough energy** to leave the well?



Hand-written Calculations

Finite square well

- When **E > U**, the solutions to the TISE have the form.

$$\psi_A(x) = a\sin\left(\frac{\tilde{p}x}{\hbar} + c\right) \qquad x \leq 0 \;\; x \geq L$$

$$\psi_B(x) = a\sin\left(\frac{px}{\hbar} + c\right) \qquad 0 \leq x \leq L$$

- where

$$p = \sqrt{E2m} \qquad \tilde{p} = \sqrt{(E-U)2m}$$

- which we can rewrite:

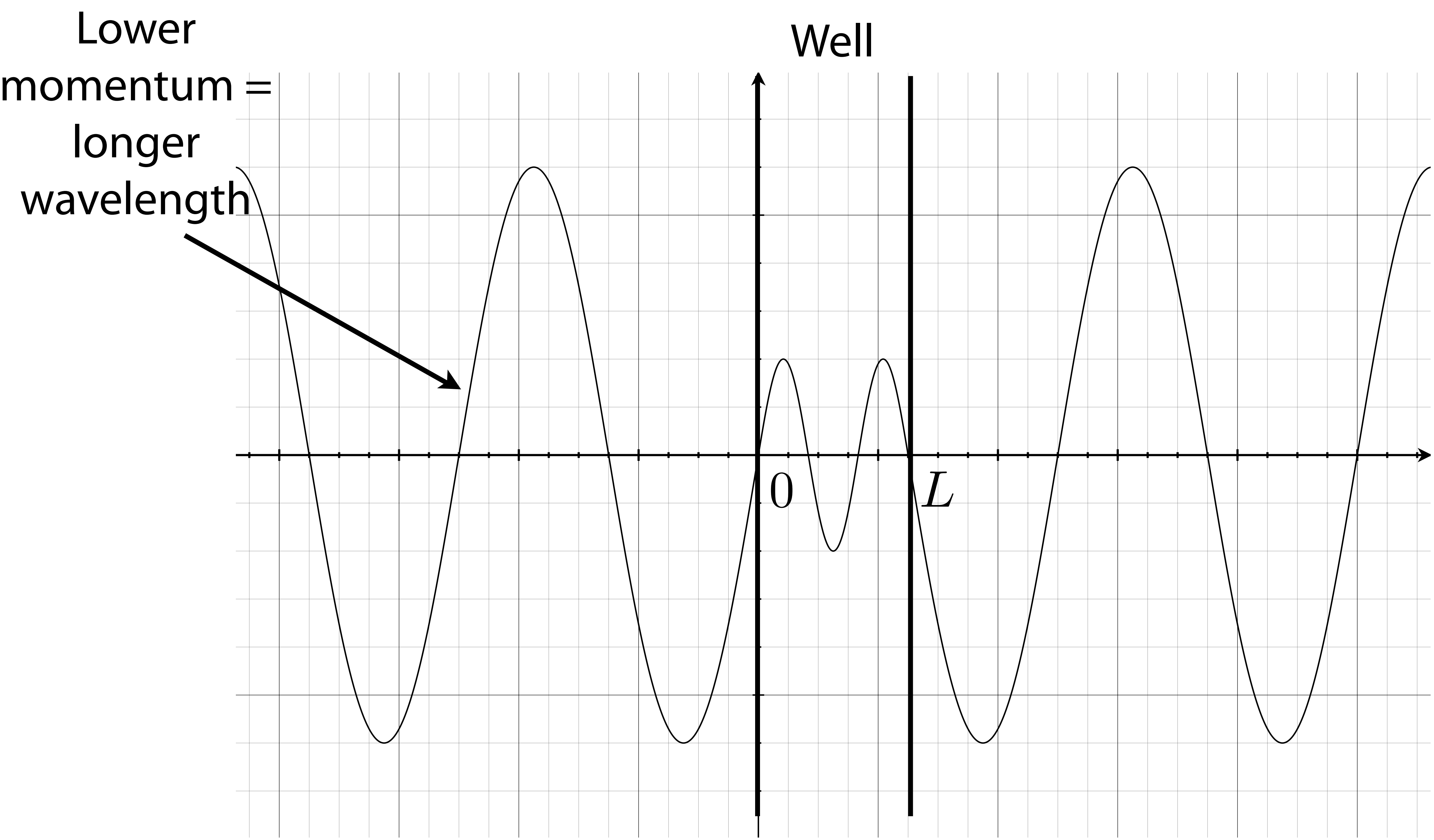
$$E = \frac{p^2}{2m} \qquad E = \frac{\tilde{p}^2}{2m} + U$$

- These equations **match** the **energy equation** for a **classical particle**!

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

Finite square well

- Applying **boundary conditions**, we find **continuous sinusoidal** solutions:



- We find solutions for **all** values of **E > U**, the **energy** in this case is **not quantised**.

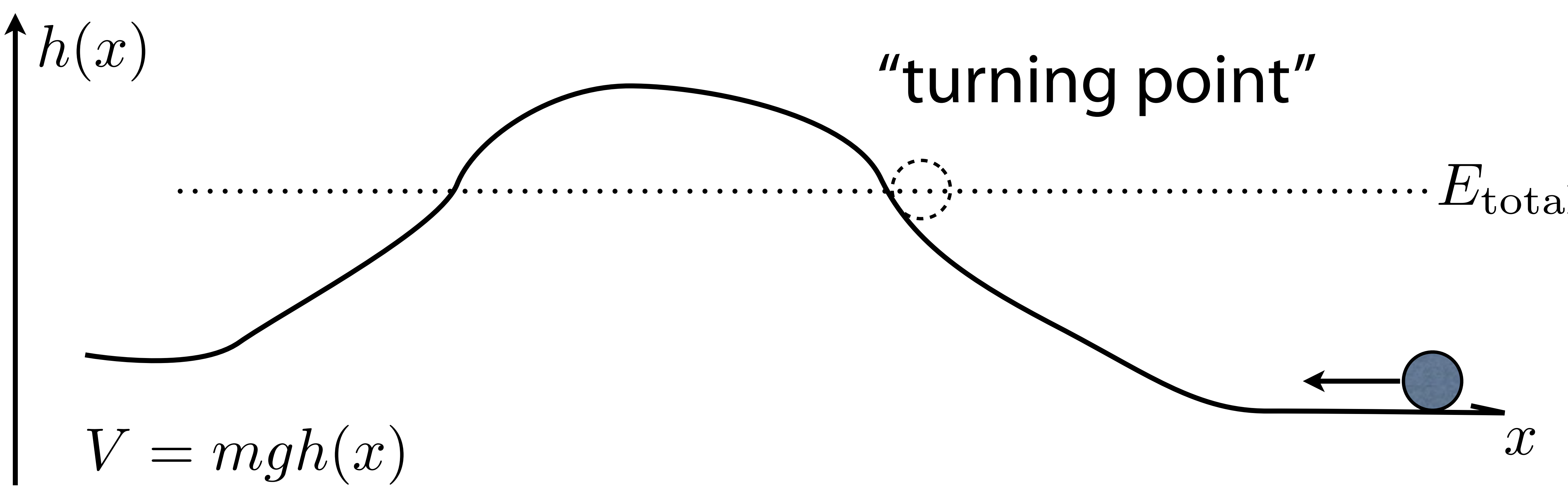
Finite square well - summary

- **Two** different types of behaviour:
  - **Bound states:** If **$E < U$** (classically particle trapped in well)
    - **Quantised** energies, **wavefunctions** largely (but not entirely) **localised** in well.
    - **Exponentially decay** outside well.
  - **Free states:** If $E > U$ (classically particle not trapped)
    - Energy **not quantised**
    - Wavefunction **sinusoidal everywhere** (wavelength consistent with classical momentum).
- That the particle can be found **outside** the well, even if classically its **energy wouldn't allow it**, is a uniquely quantum behaviour, and related to the next topic - **quantum tunnelling**!

Quantum Tunnelling

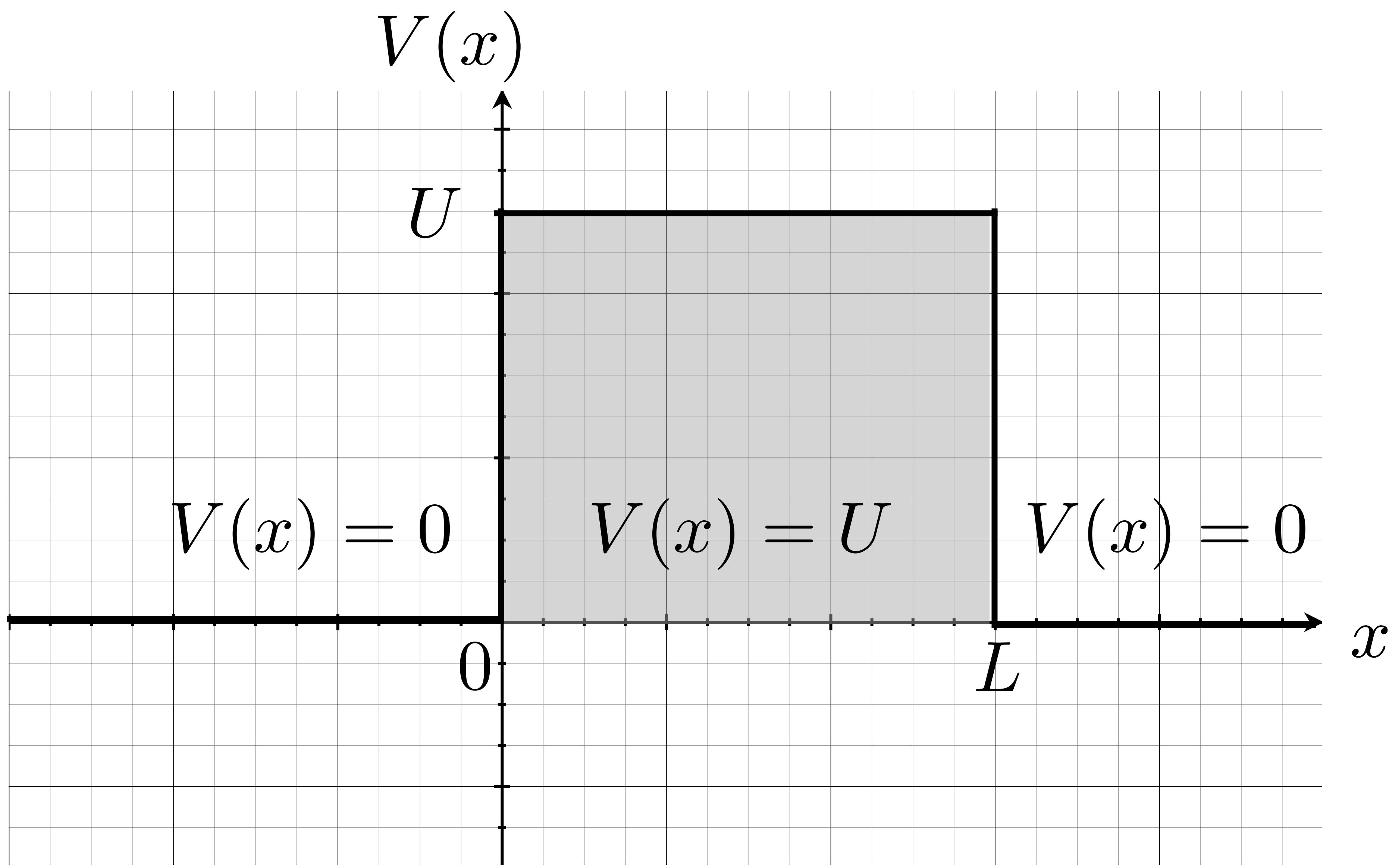
- In classical physics, potential energy can form a **barrier**.

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



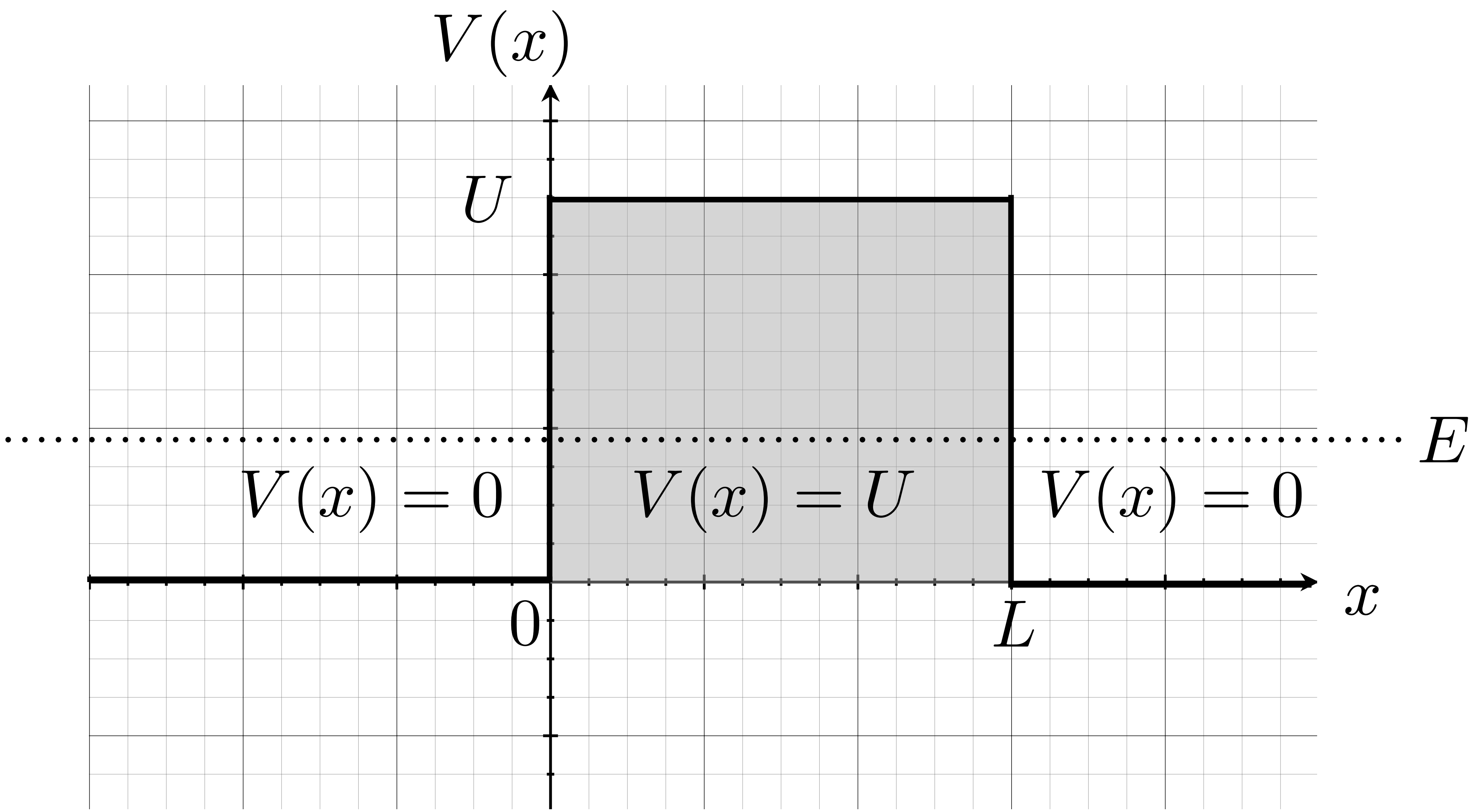
Quantum Tunnelling

- We can study a **quantum potential barrier** via the time-independent Schrödinger equation.



Quantum Tunnelling

- You will solve this in detail in **future courses**.
- However, the **finite well** gives us an insight.



Quantum Tunnelling

- You will solve this in detail in **future courses**.
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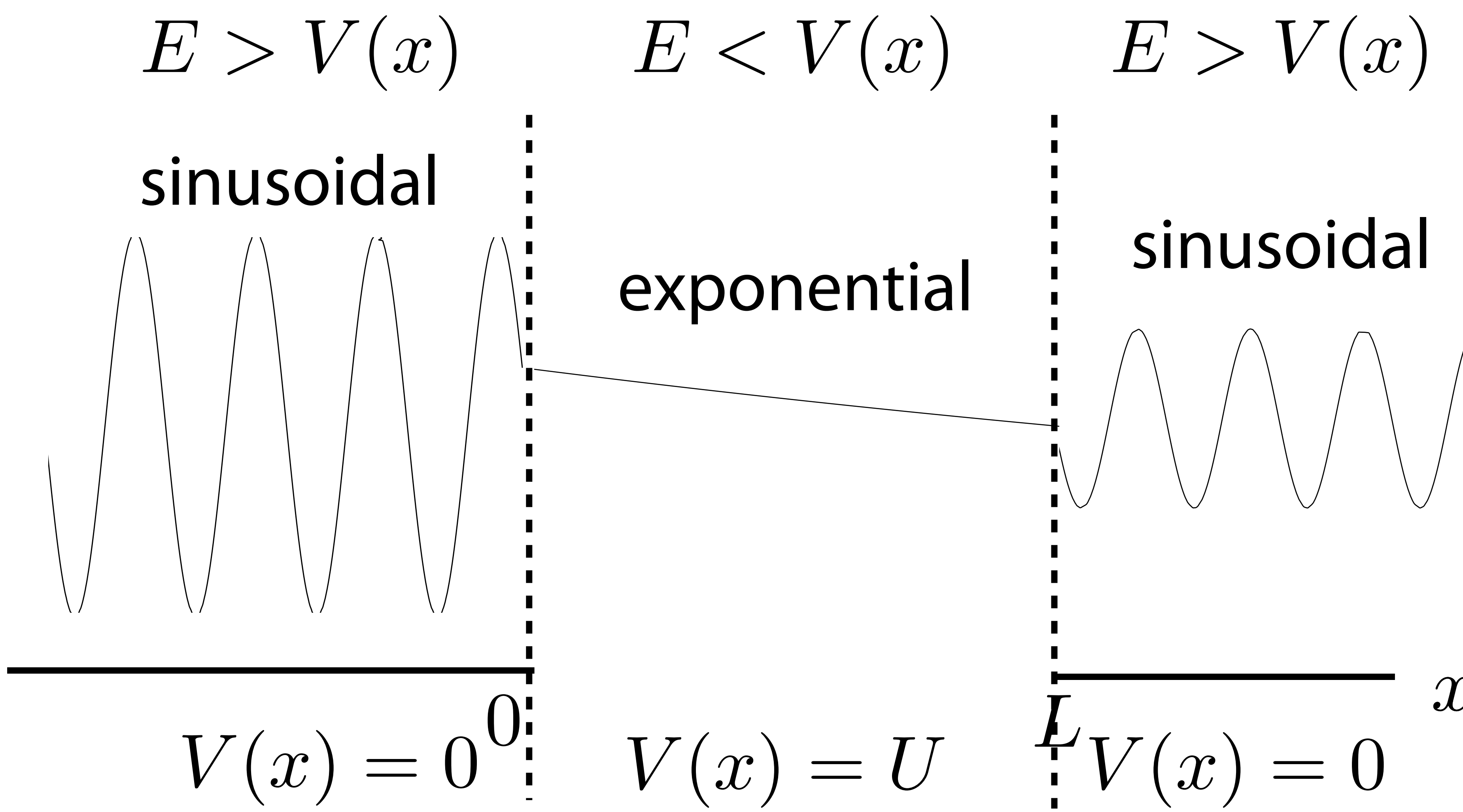
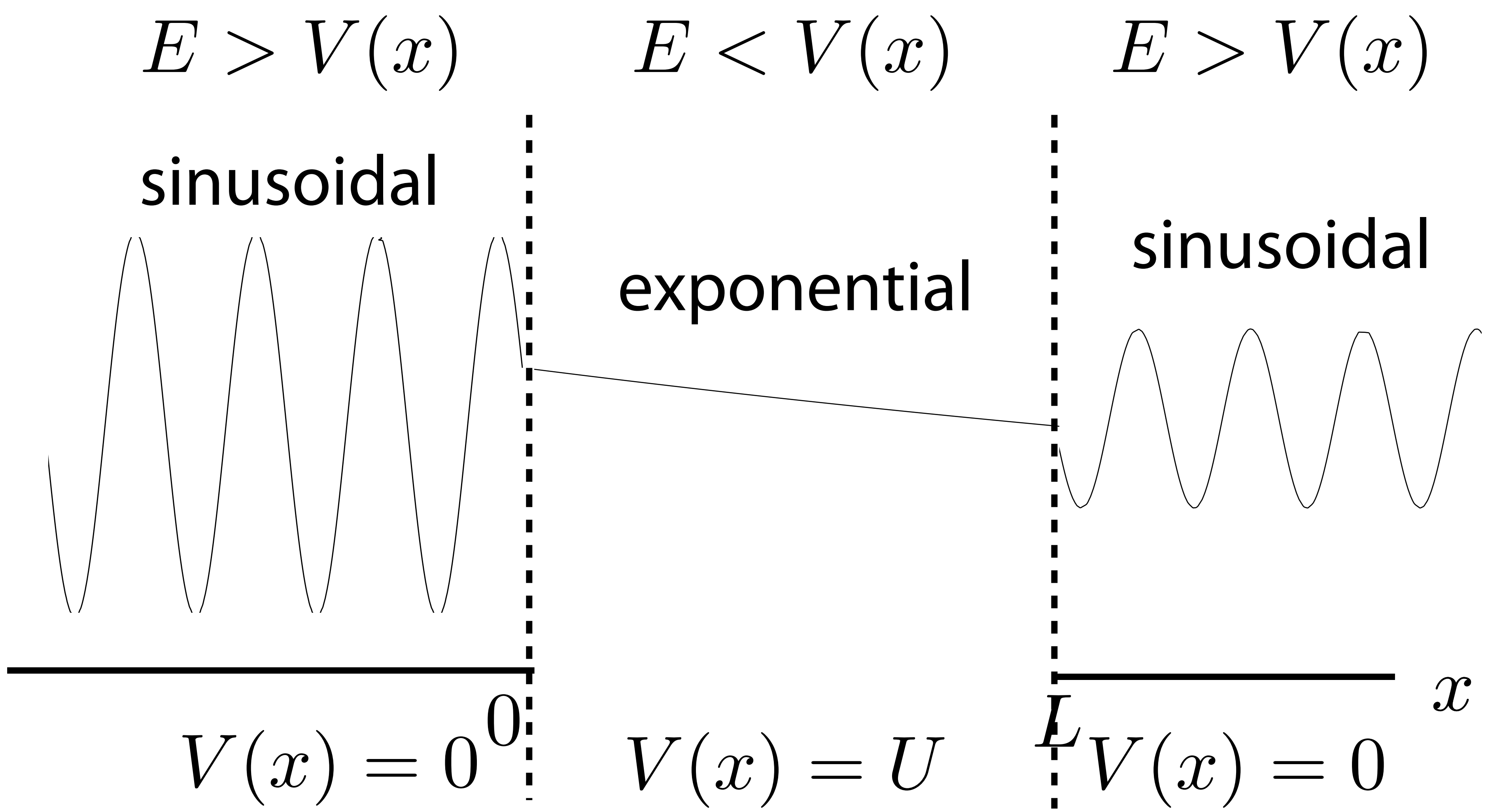


Quantum Tunnelling

- If a quantum particle (wavepacket) approaches the barrier, there is a finite probability that it will **tunnel through**.



Quantum Tunnelling

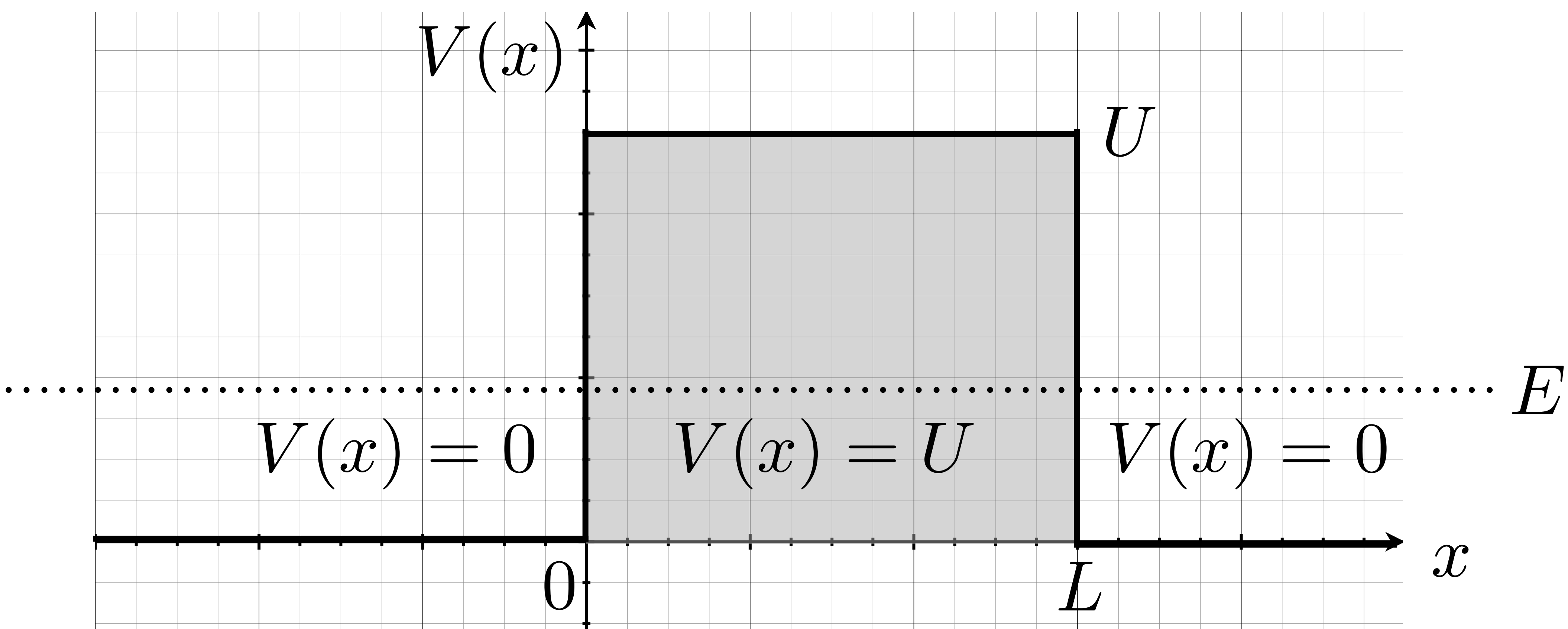
- If a quantum particle (wavepacket) approaches the barrier, there is a finite probability that it will **tunnel through**.

- If the barrier is high **(E<<U),** the probability of tunnelling is given by:

$$P = e^{-2CL}$$

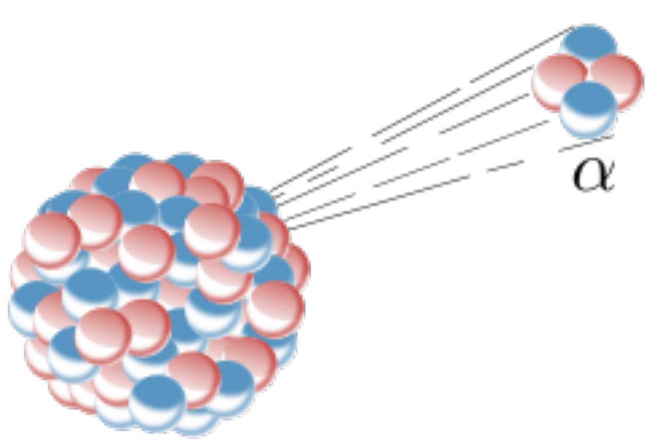
- where

$$C = \frac{\sqrt{2m(U-E)}}{\hbar}$$

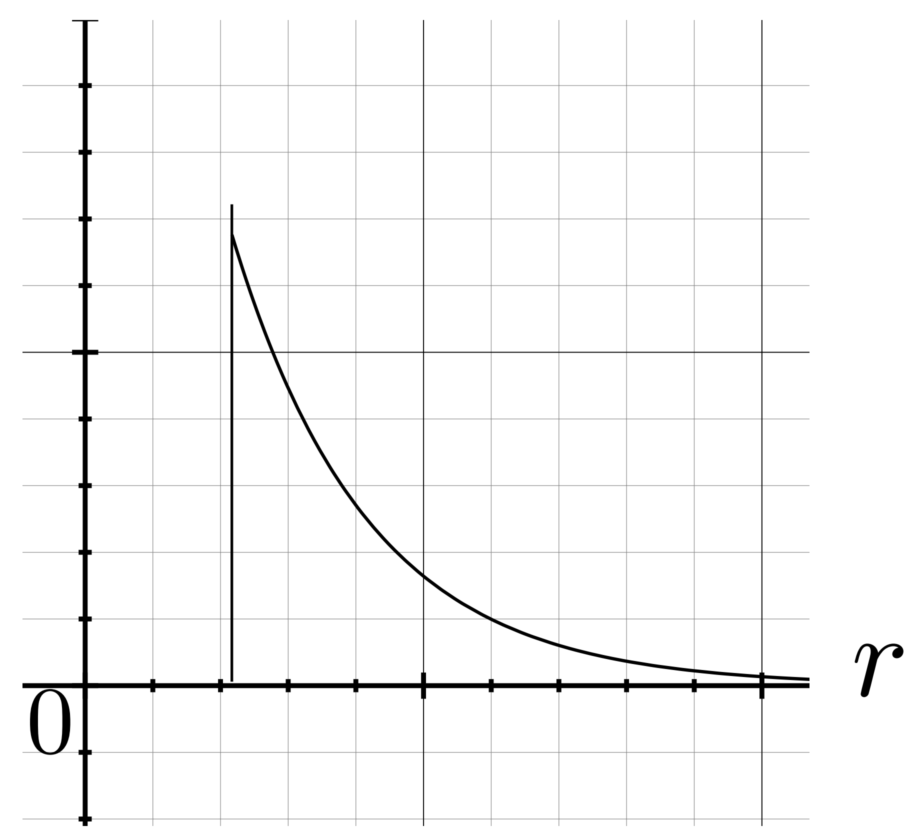


Quantum Tunnelling

- Quantum tunnelling is important in a number of physical processes.
- In **radioactive decay** (alpha decay), alpha particles tunnel through a potential barrier.
- This gives rise to the probabilistic nature of radioactive decay.

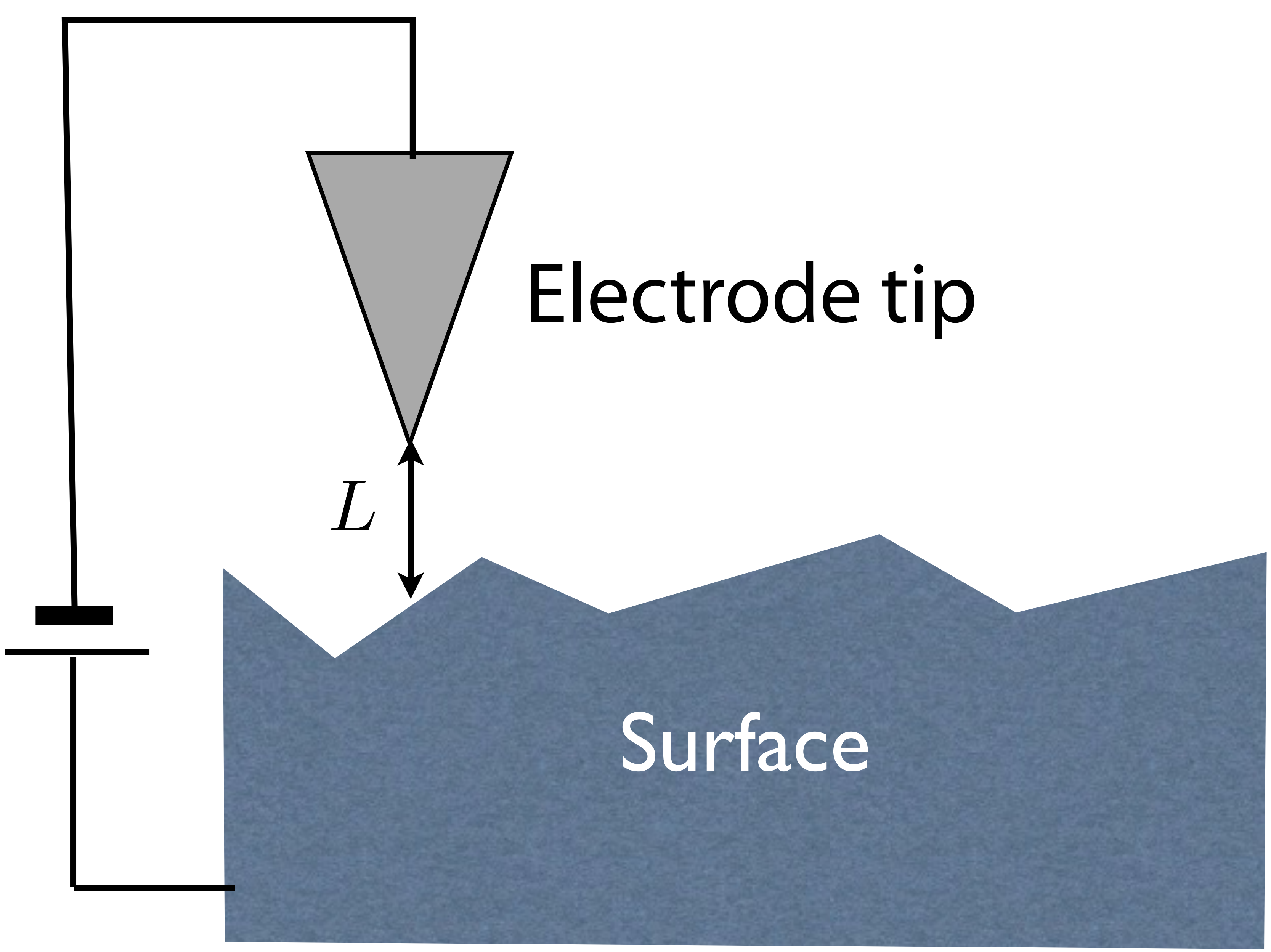


$V(r)$ nuclear potential

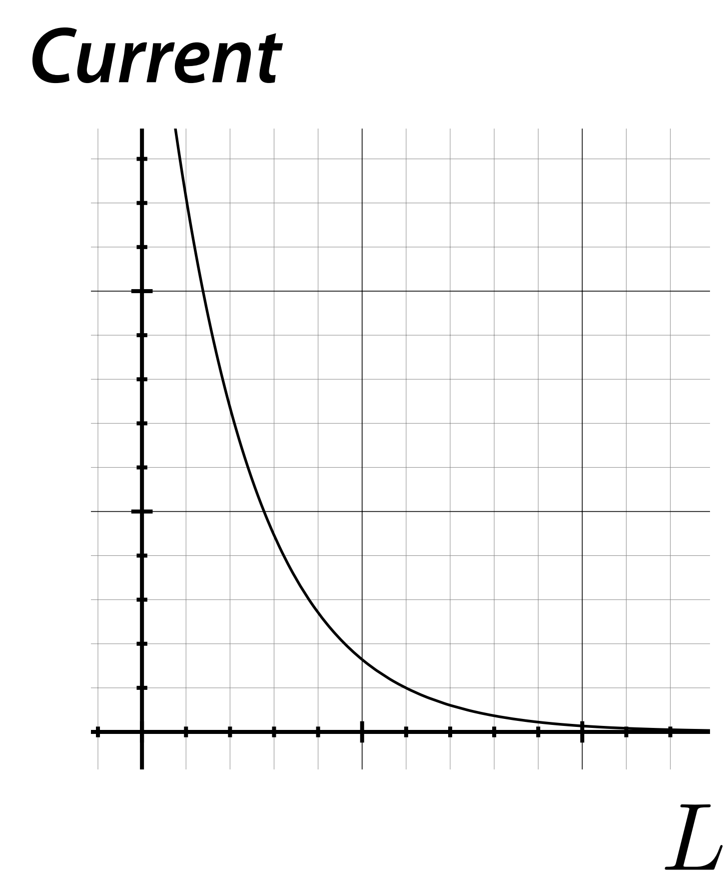


Quantum Tunnelling

- A **scanning tunnelling microscope** is one of our most precise tools for **measuring surfaces**.
- The rate of current is proportional to tunnelling probability.

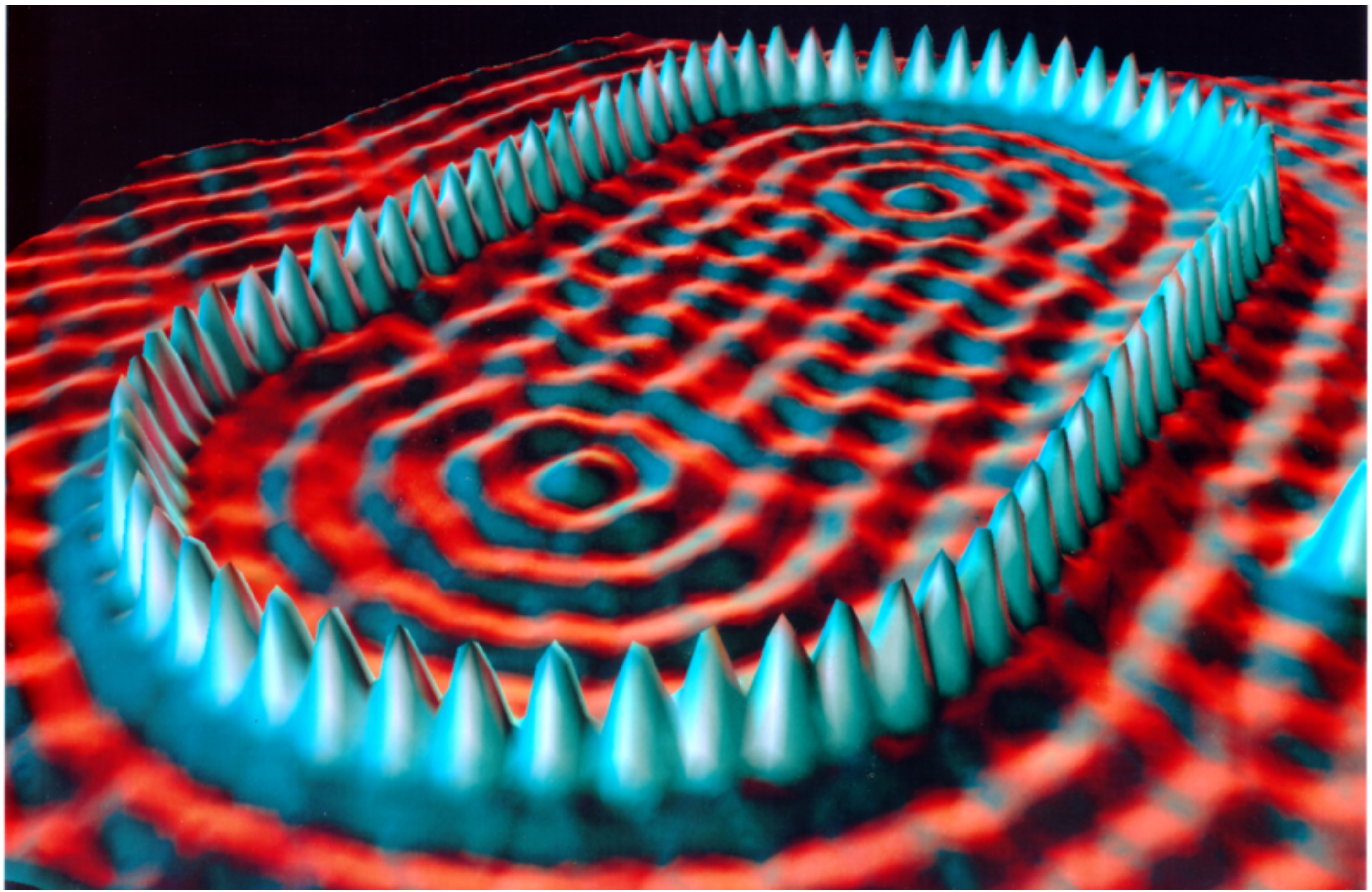


$$P = e^{-2CL}$$



Quantum Tunnelling

- This is a STM image taken by IBM.
- Individual atomic sites, and wave-behaviour can be resolved!



Part 5: Summary so far...

- We introduced the Time-independent Schrödinger Equation, which connects **energies** and **wave-functions**.

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

- And saw how to **solve it** to study the physics of **potential wells** (infinite and finite).
- We also used it to study **quantum tunnelling** and its applications.
- Next week, we apply these tools to develop a **quantum model** of the **atom**.