

# In-Course Assessment



- The ICA test for this course will take place next Monday at 10am (NOT 11am!)
- There are ***two groups***. Check your online timetable for times and locations.
- ICA tests are under ***exam conditions***
- Please bring:
  - Pen, (spare pen!) and **Paper**
  - An ***allowed*** calculator (CASIO FX83GT+, CASIO FX85GT+).
- Please arrive ***on time***. ICAs start at 10:05 prompt and there will be no extensions for latecomers.
- If you are entitled to ***extra time*** in exams, your mark will be modified - please make sure that ***Stan Z.*** is aware of this.
- The ICA for this half term will be based on PST 1 and PST 2.

- To help your exam preparation, I will upload an extra Practise Problem Sheet to Moodle.
- This will cover material not covered by the PSTs.
- Solutions will also be uploaded to Moodle.
- These extra problems are not covered in the ICA.

# Summary of Part 5a

- We introduced the **Time-Independent Schrödinger Equation.**

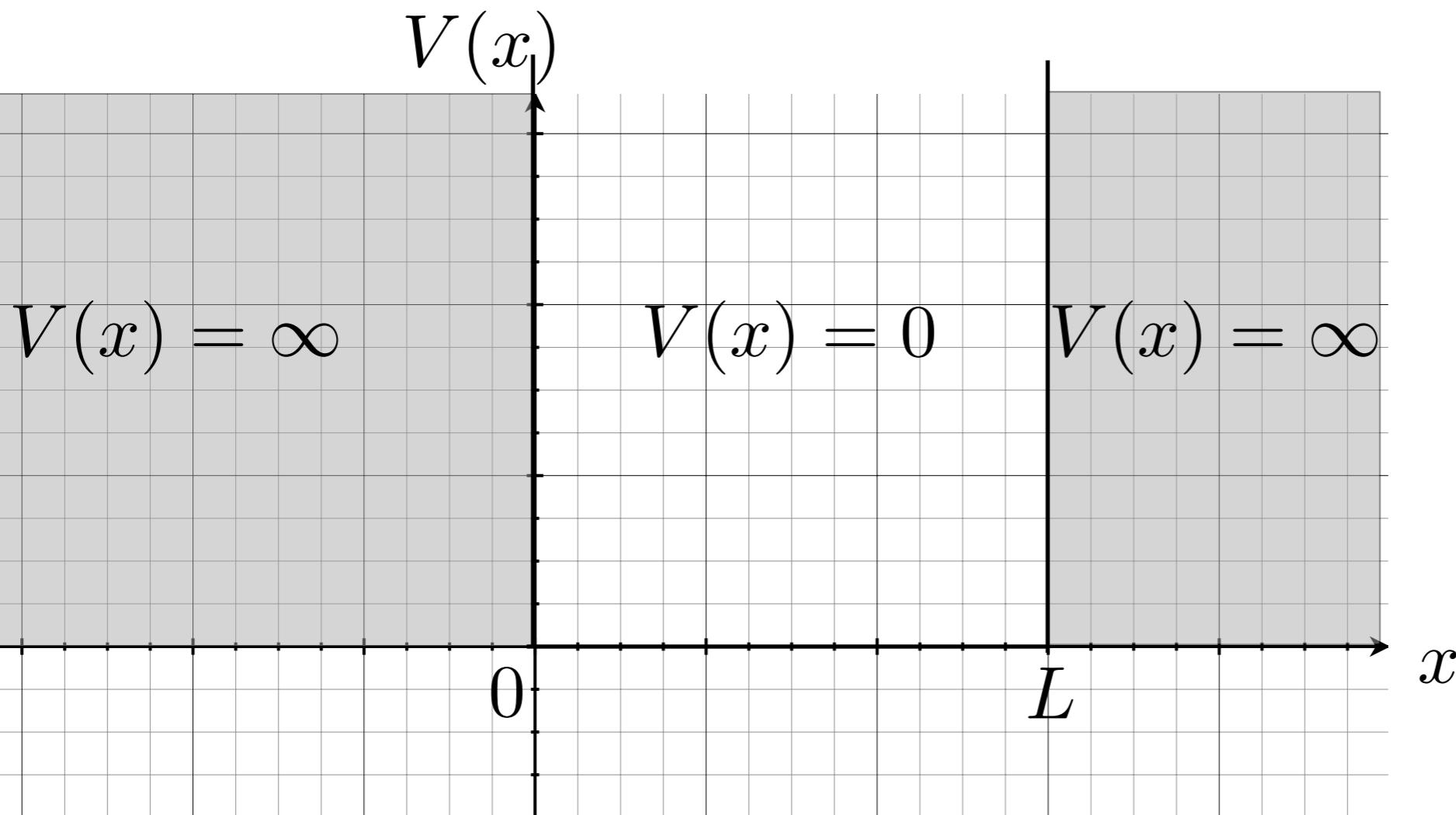
$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

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

# Infinite square well

- The **infinite** square well:

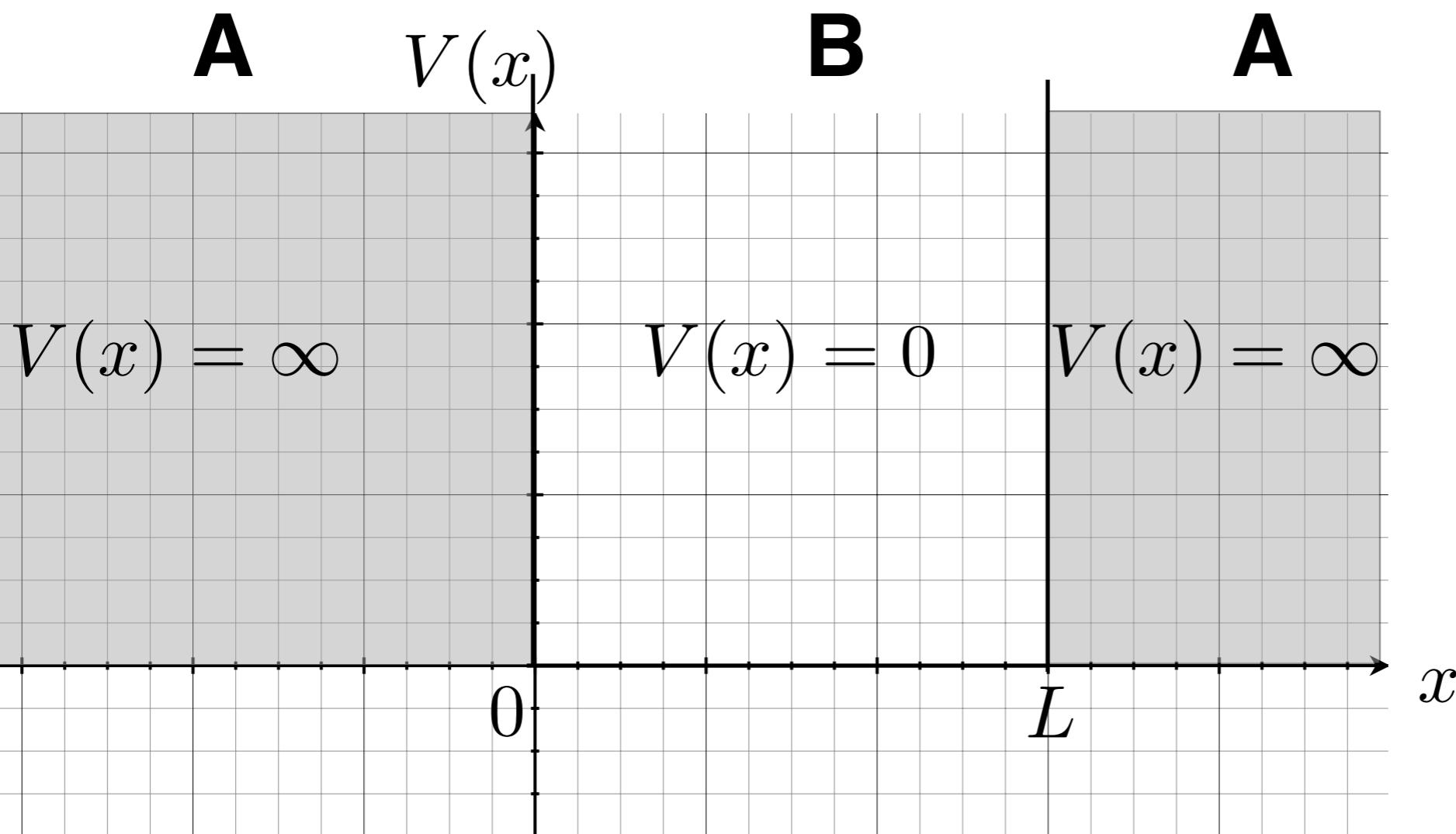
$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{elsewhere} \end{cases}$$



# Infinite square well

- Two regions to consider:
  - **B) Zero potential -**
  - Solutions take the form:

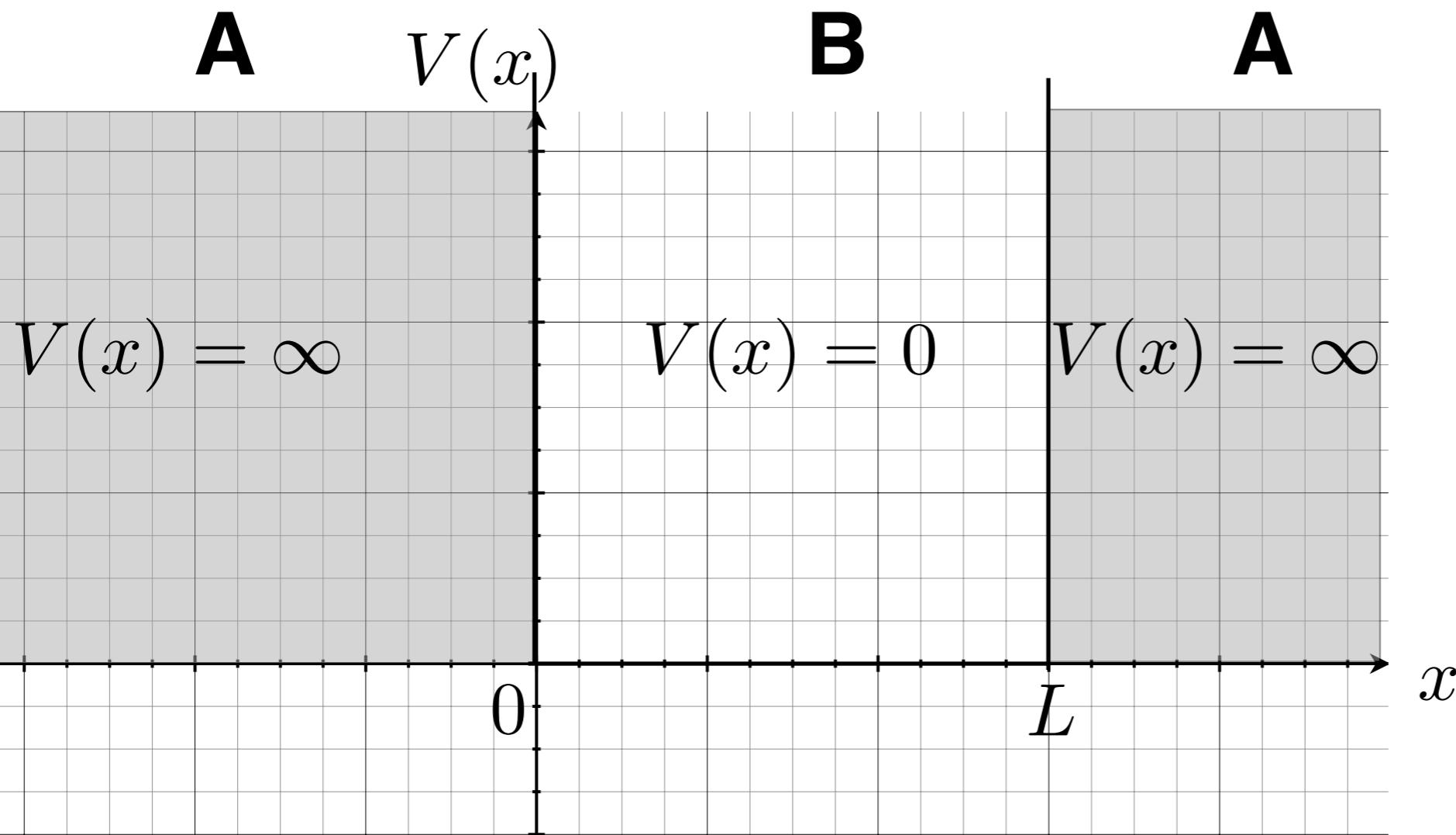
$$\psi_B(x) = a \sin\left(\frac{px}{\hbar} + c\right) \quad E = \frac{p^2}{2m}$$



# 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:

$$\psi_A(x) = 0$$



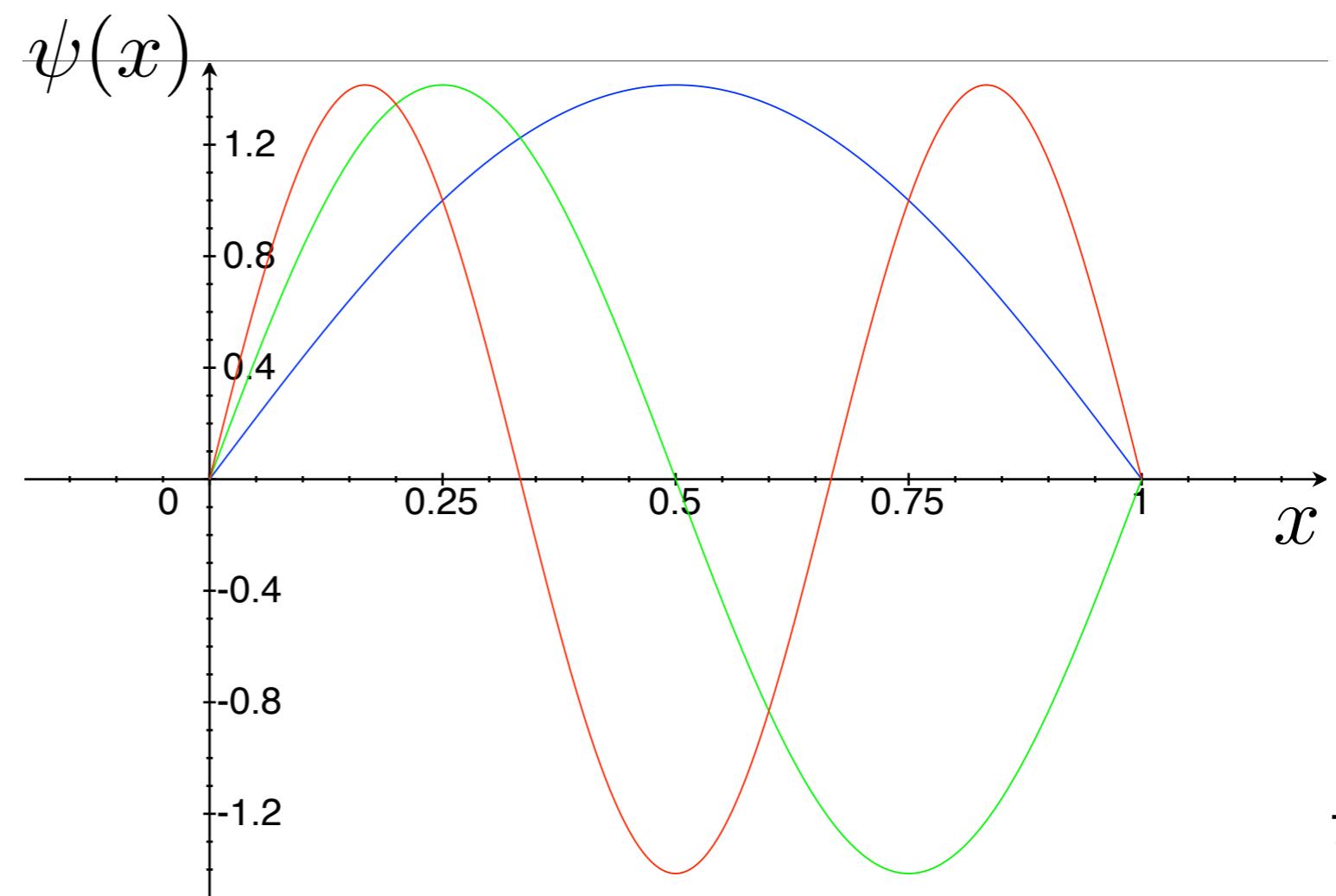
# Infinite square well

- Applying **boundary conditions** and **normalising**:

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

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

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

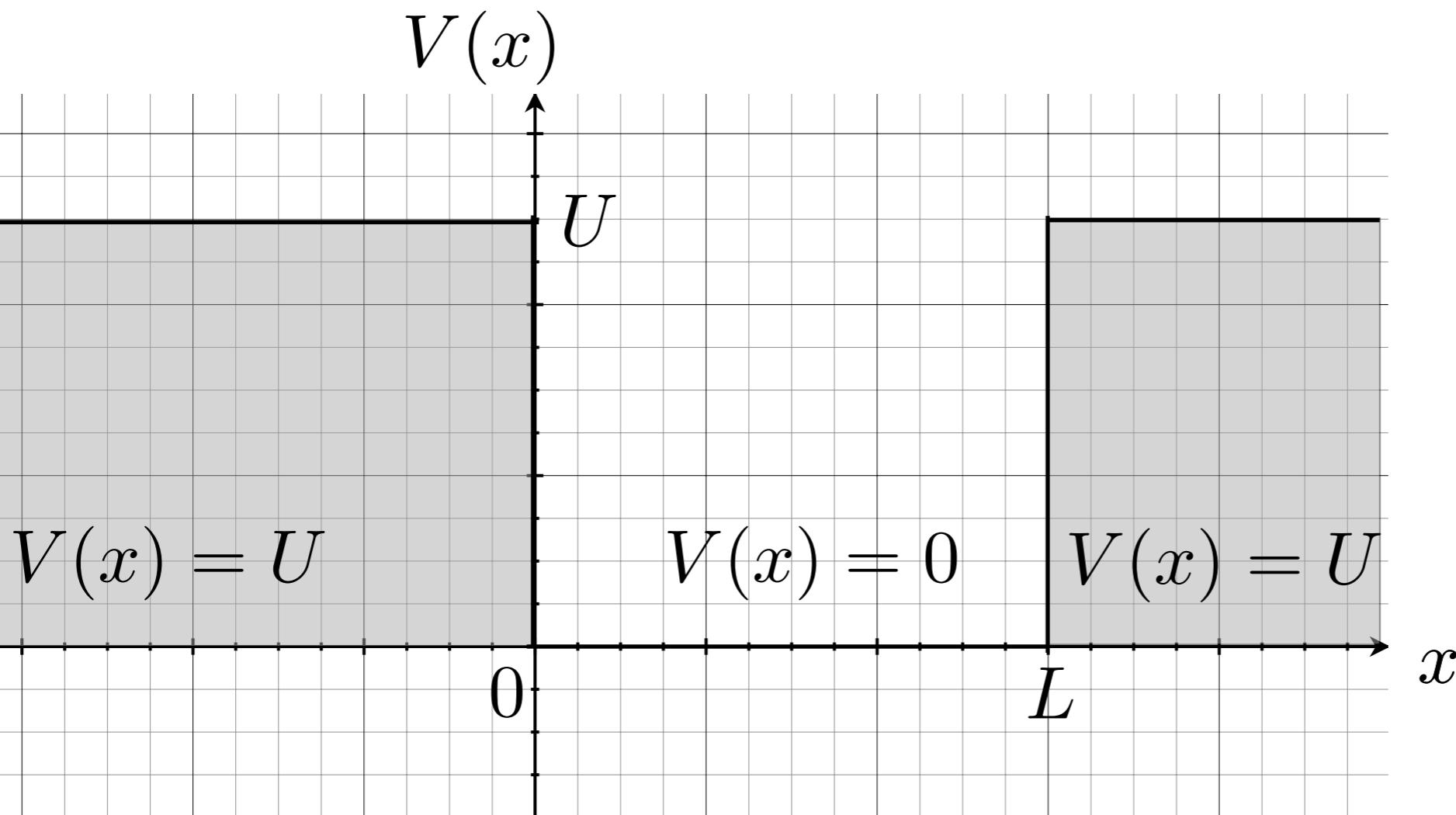


# Finite square well

- 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**.

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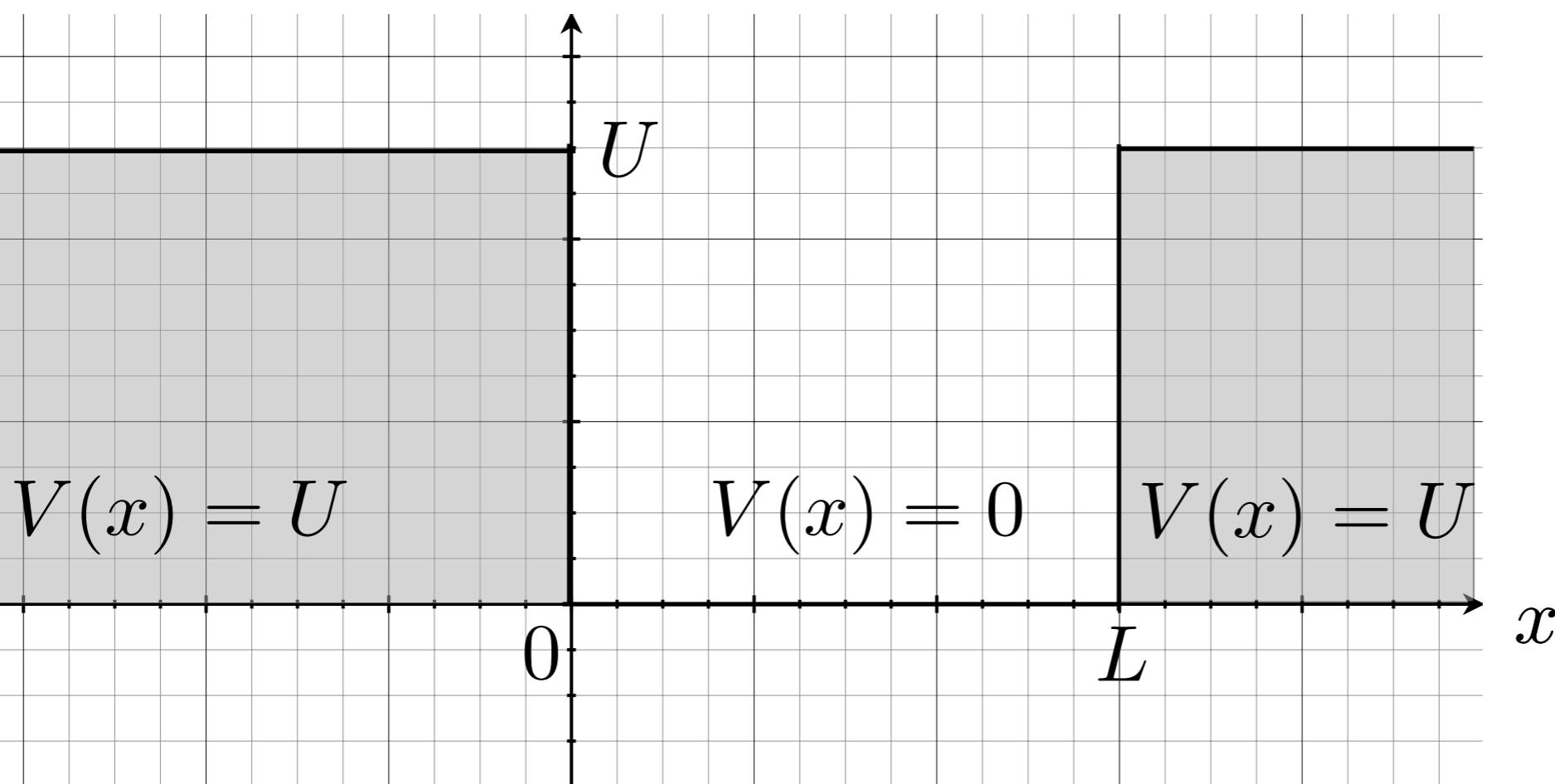


# Finite square well

- The potential function for the finite square well is:

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

$$V(x) \quad U > 0$$



$$V(x) = U$$

$$V(x) = 0$$

$$V(x) = U$$

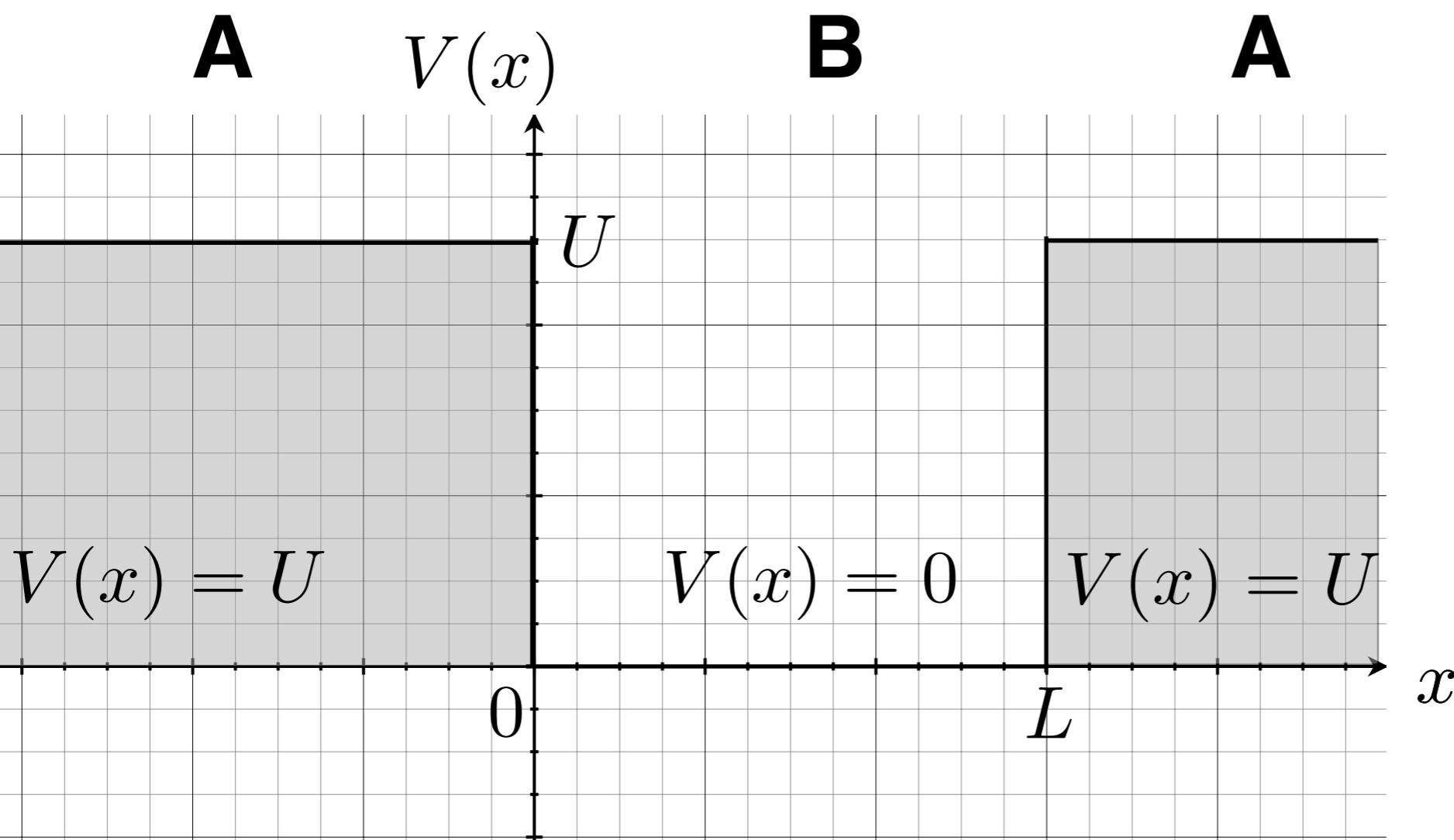
0

$L$

$x$

# 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

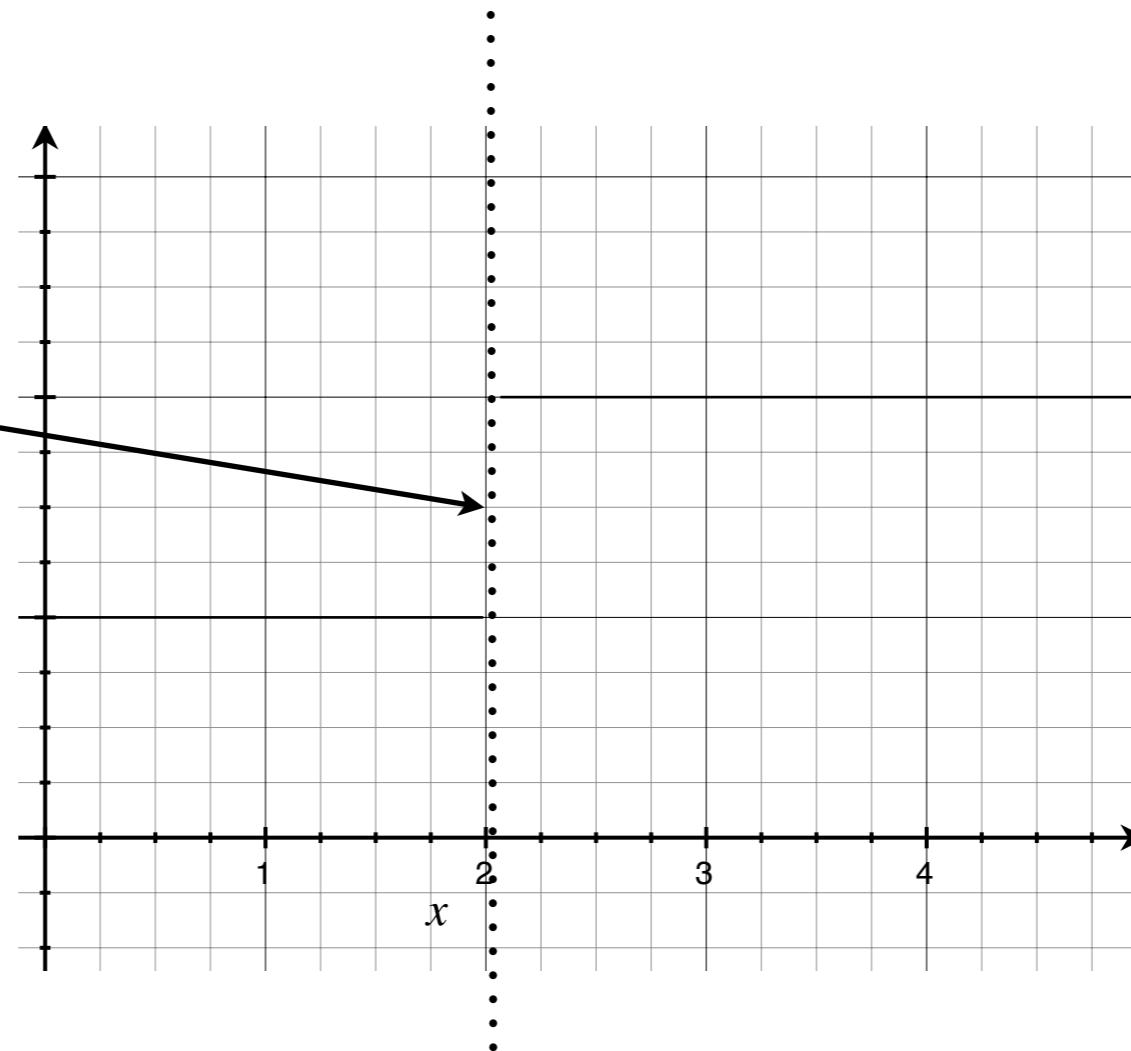
- We have seen that wavefunctions must be **continuous**.
- The reason for this is that in a **discontinuous** function, the **gradient**, or **first derivative** is **infinite**.

# Boundary conditions

- We have seen that wavefunctions must be **continuous**.
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**Infinite  
gradient**

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



$f(x)$  **discontinuous** →  $\frac{df(x)}{dx}$  **infinite**

# Boundary conditions

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

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

similar to

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

# Boundary Conditions

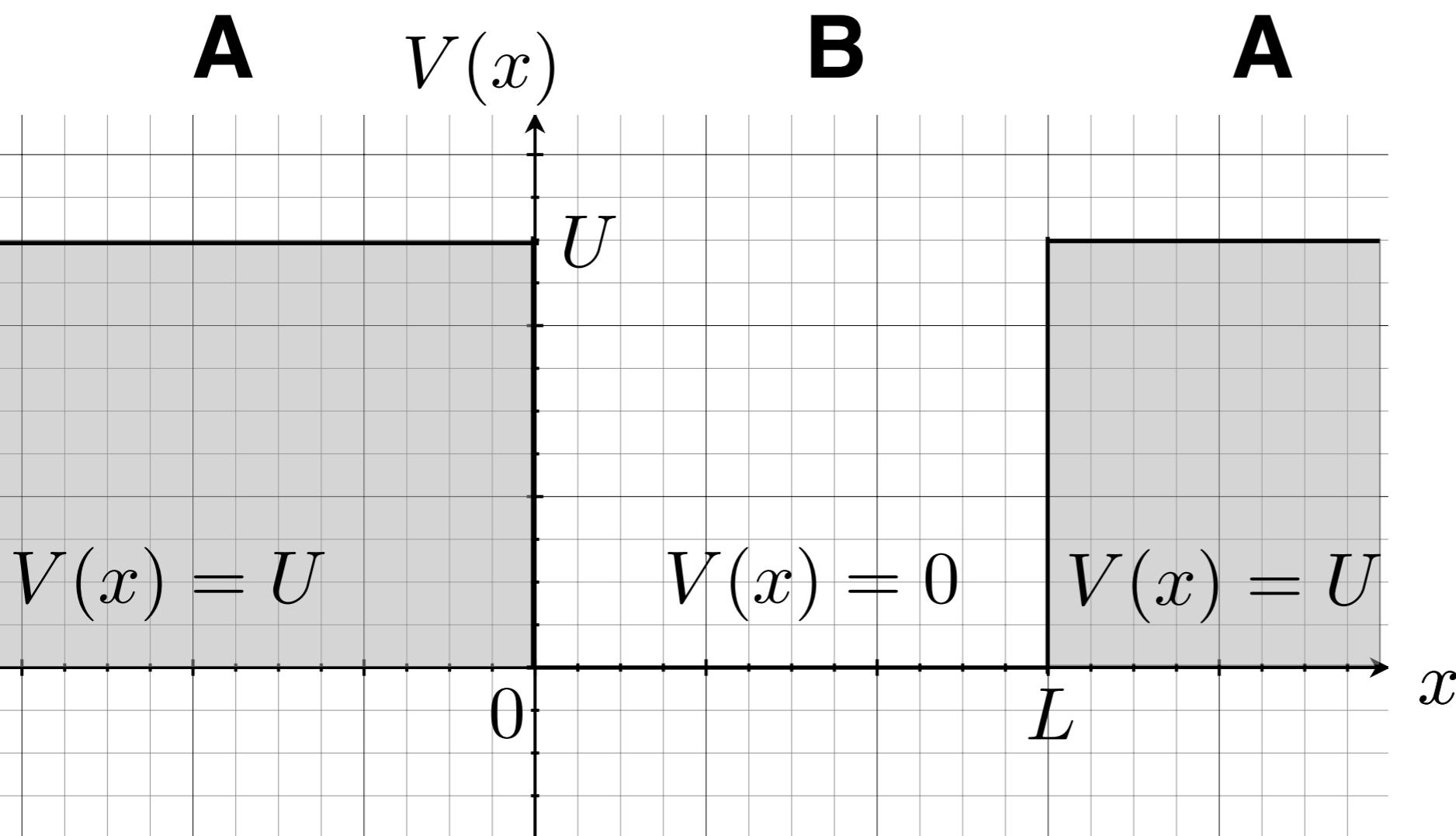
- The TISE contains the second derivative of  $\psi(x)$ :

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

- 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:
  - $\psi(x)$  must be **continuous**
  - $d\psi(x)/dx$  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  $V(x) = 0$ .

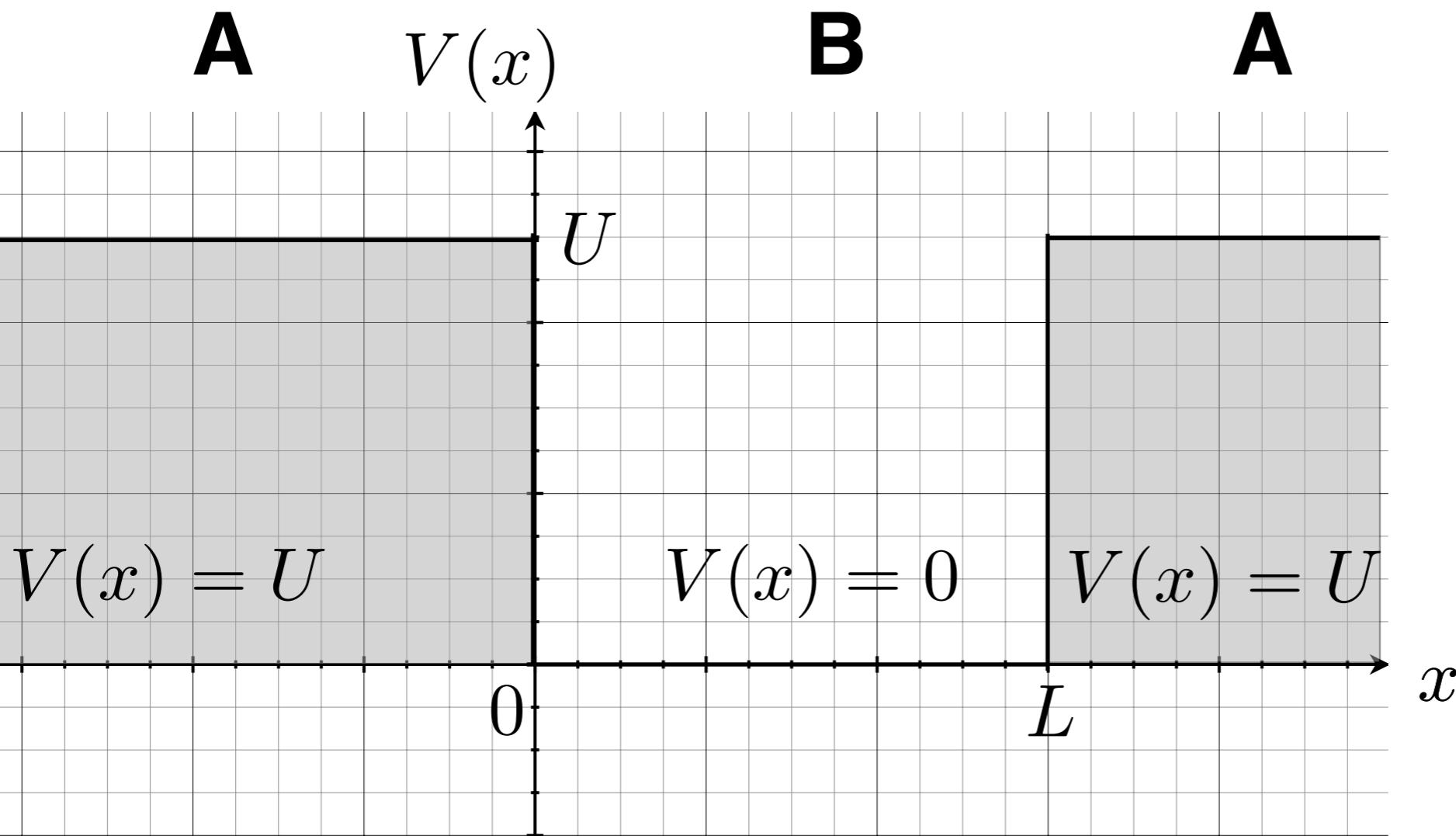


# Finite square well

–Region B - where  $V(x) = 0$ .

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

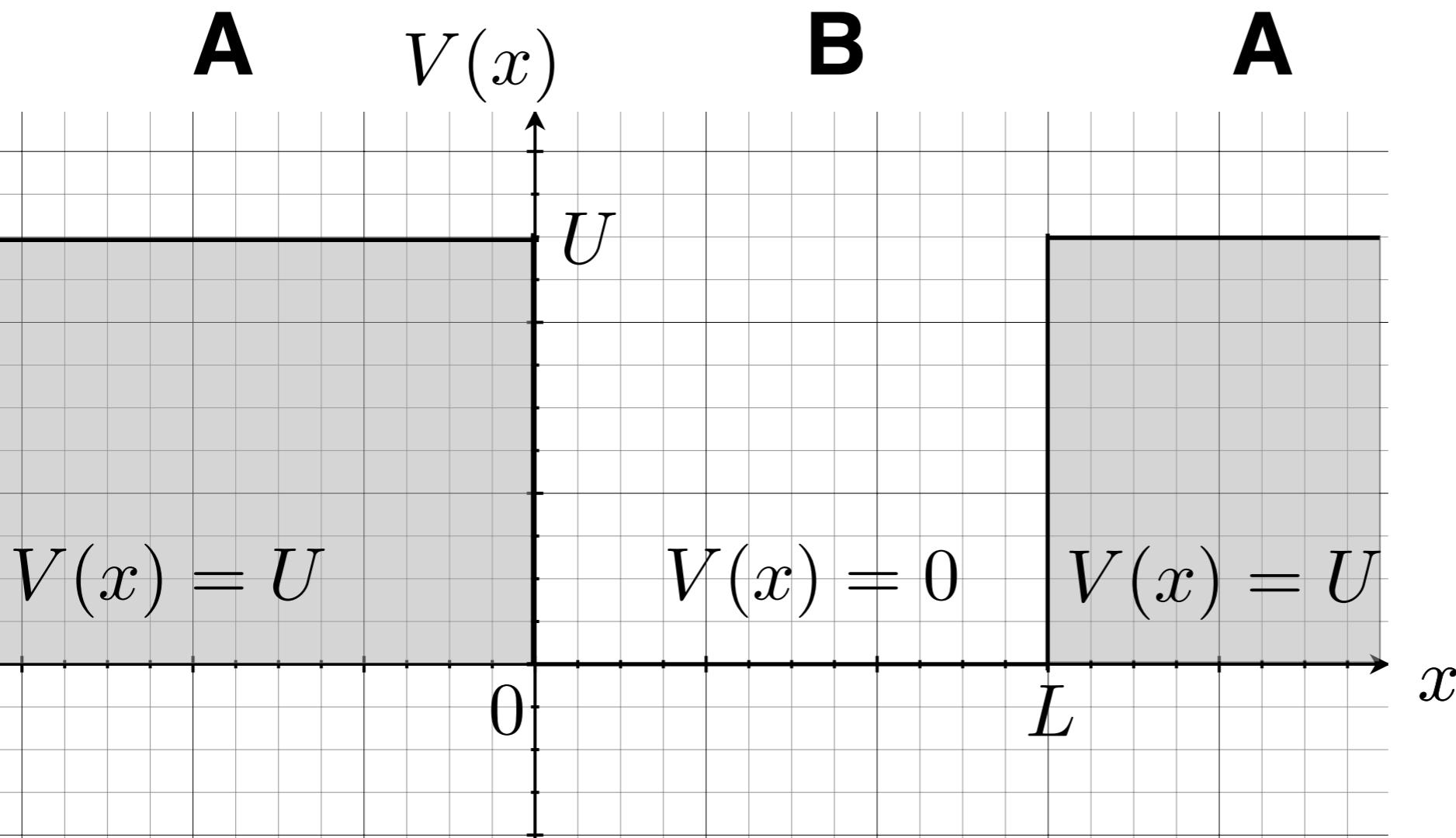
$$\psi_B(x) = a \sin \left( \frac{px}{\hbar} + c \right)$$



# Finite square well

–Region A - where  $V(x) = U$ .

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

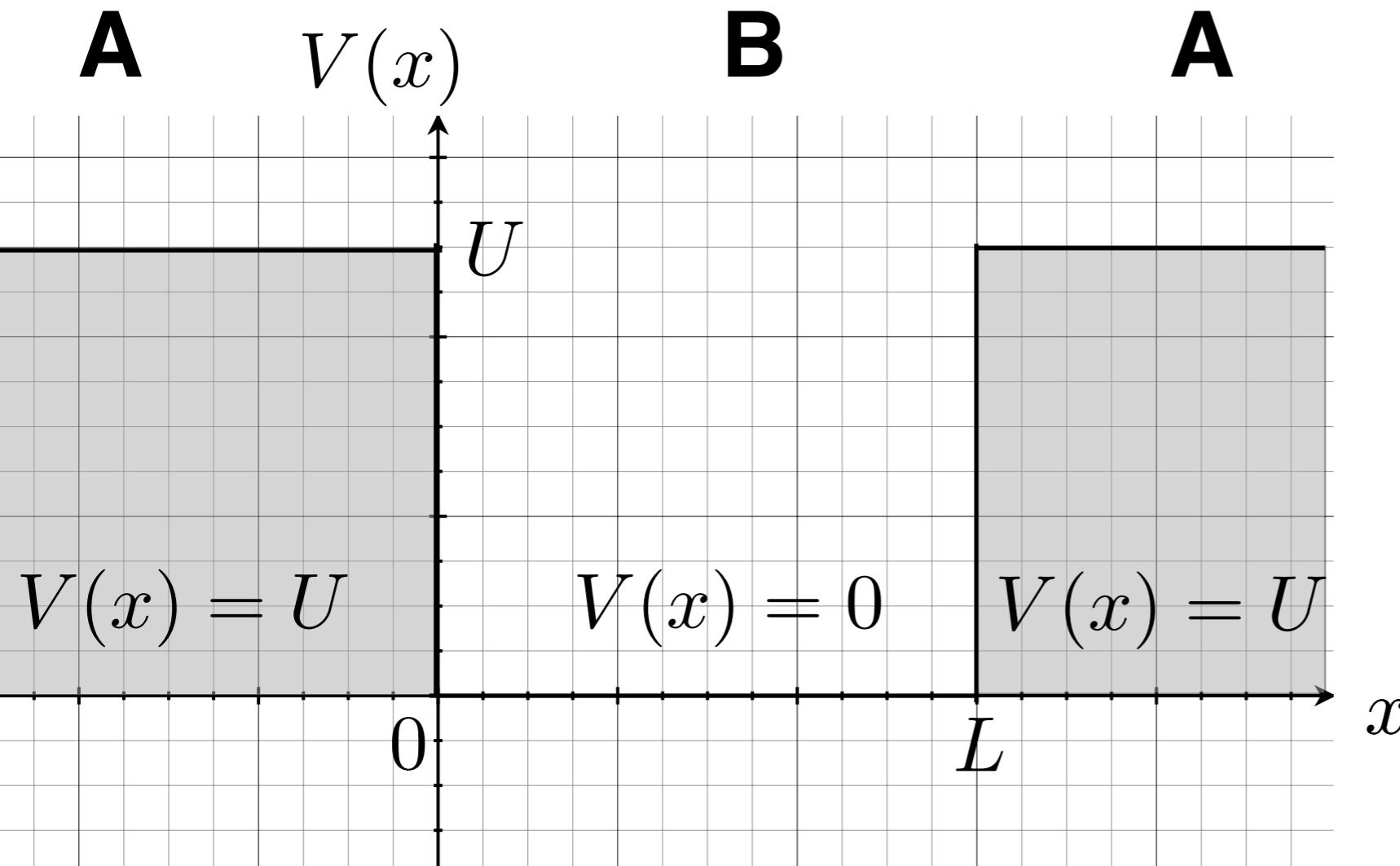


# Finite square well

–When  $E < U$ , the solutions to the TISE have the form.

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

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



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

$$p = \sqrt{E2m}$$

# Finite square well

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–We can find the allowed values for  $A$ ,  $K$ ,  $C$ ,  $a$ ,  $p$  and  $c$  by imposing the boundary conditions:

- $\Psi(x)$  must be **continuous**
- $d\Psi(x)/dx$  must be **continuous**
- $\Psi(x)$  must be **normalised**

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

$$p = \sqrt{E2m}$$

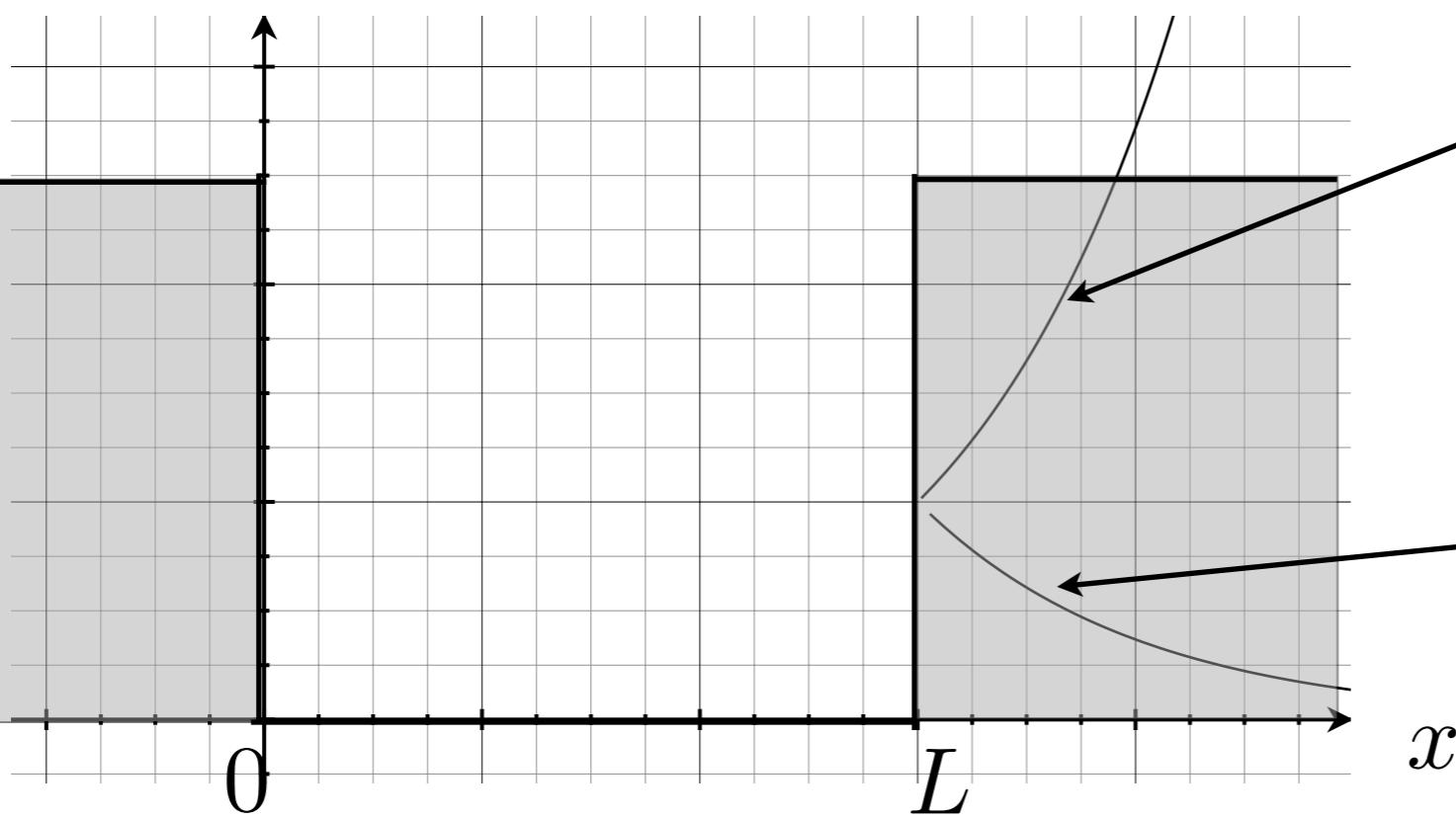
# Finite square well

- 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.

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

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

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

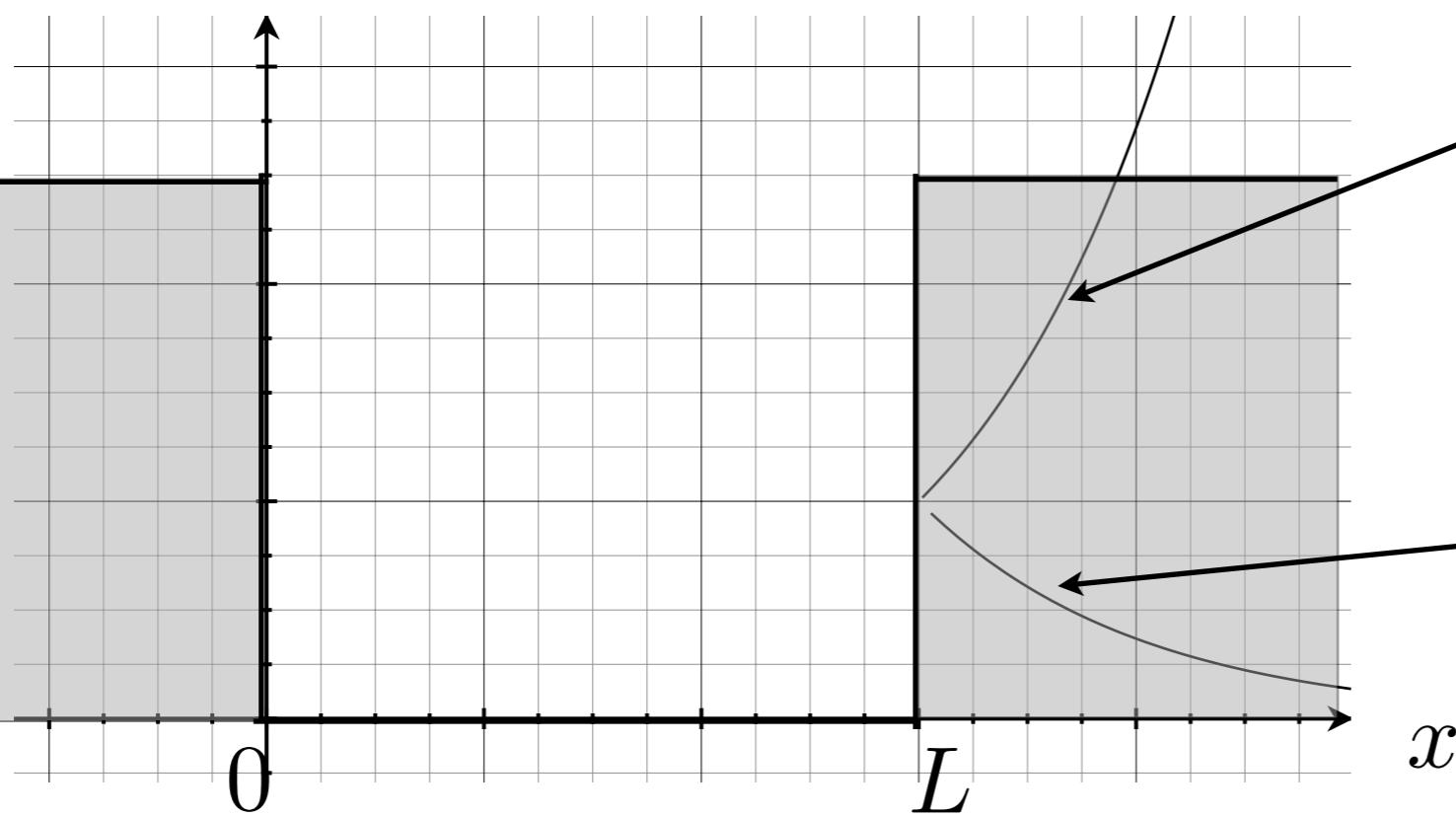


# Finite square well

- 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:

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

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



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

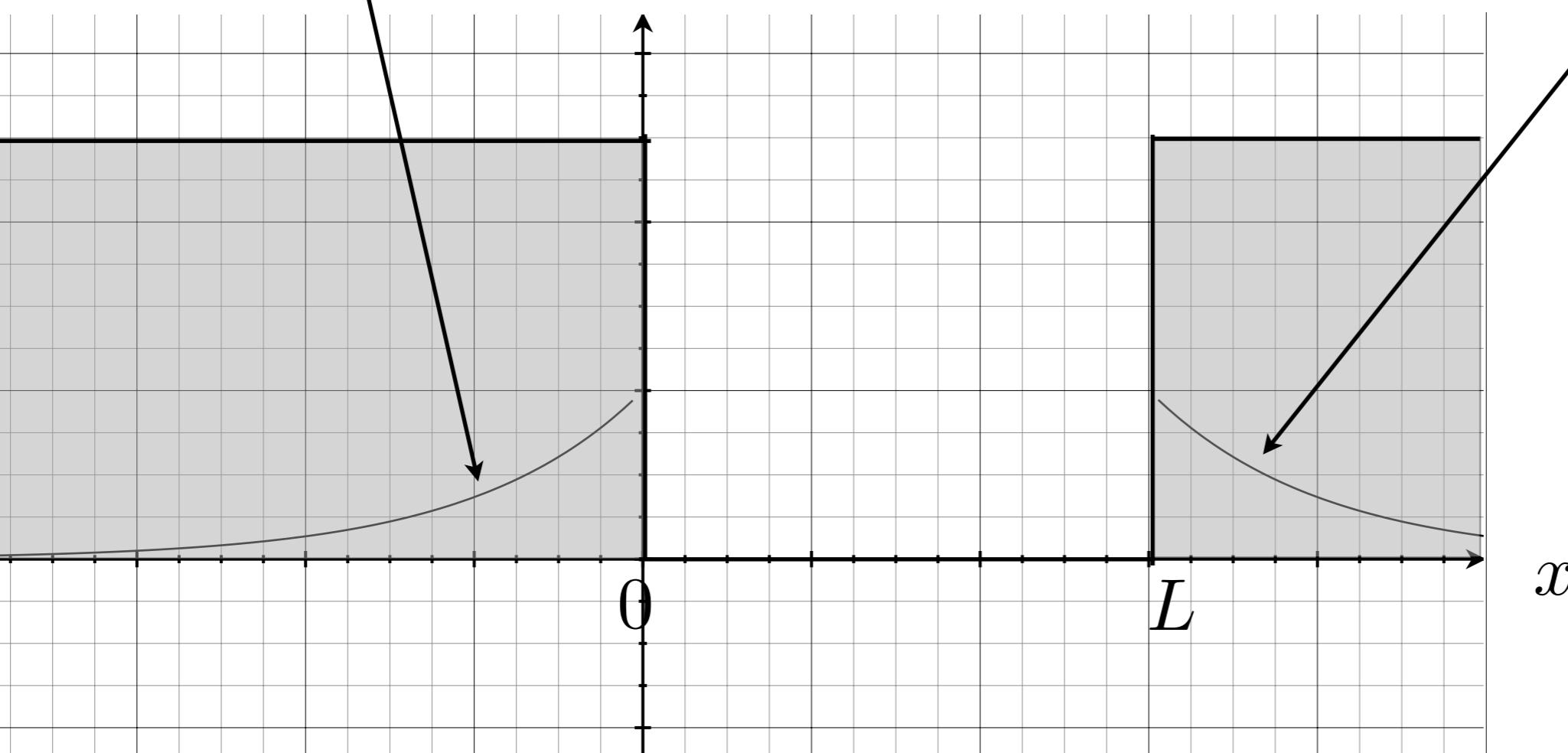
# Finite square well

- Similarly, in the region,  $x < 0$  the wavefunction must be of the form:
- NB A classical particle would **never** leave the well, but we see a **finite probability** of measuring the particle **outside the well!**

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

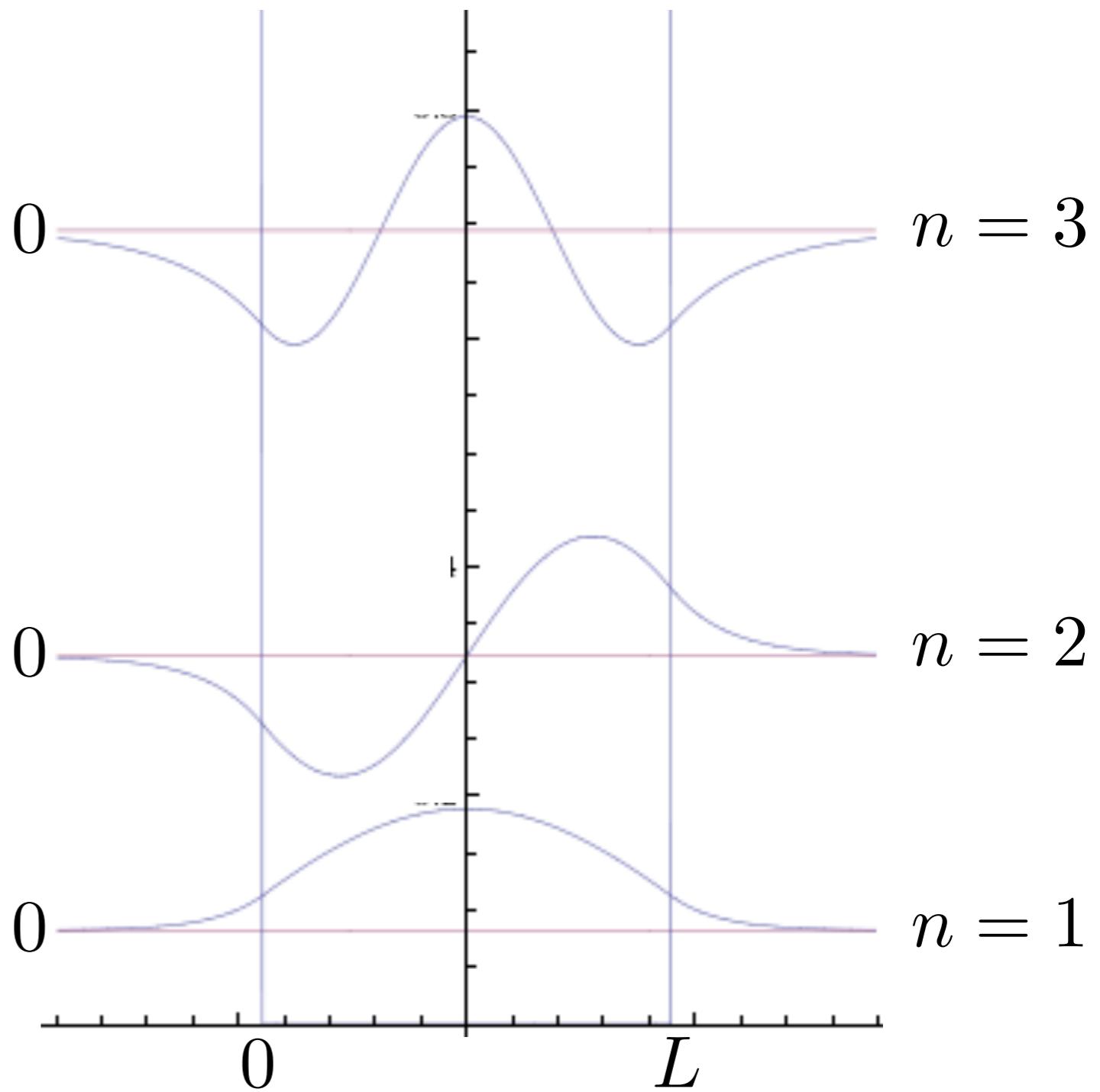
$$\psi_{x<0}(x) = Ae^{Kx+C}$$

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



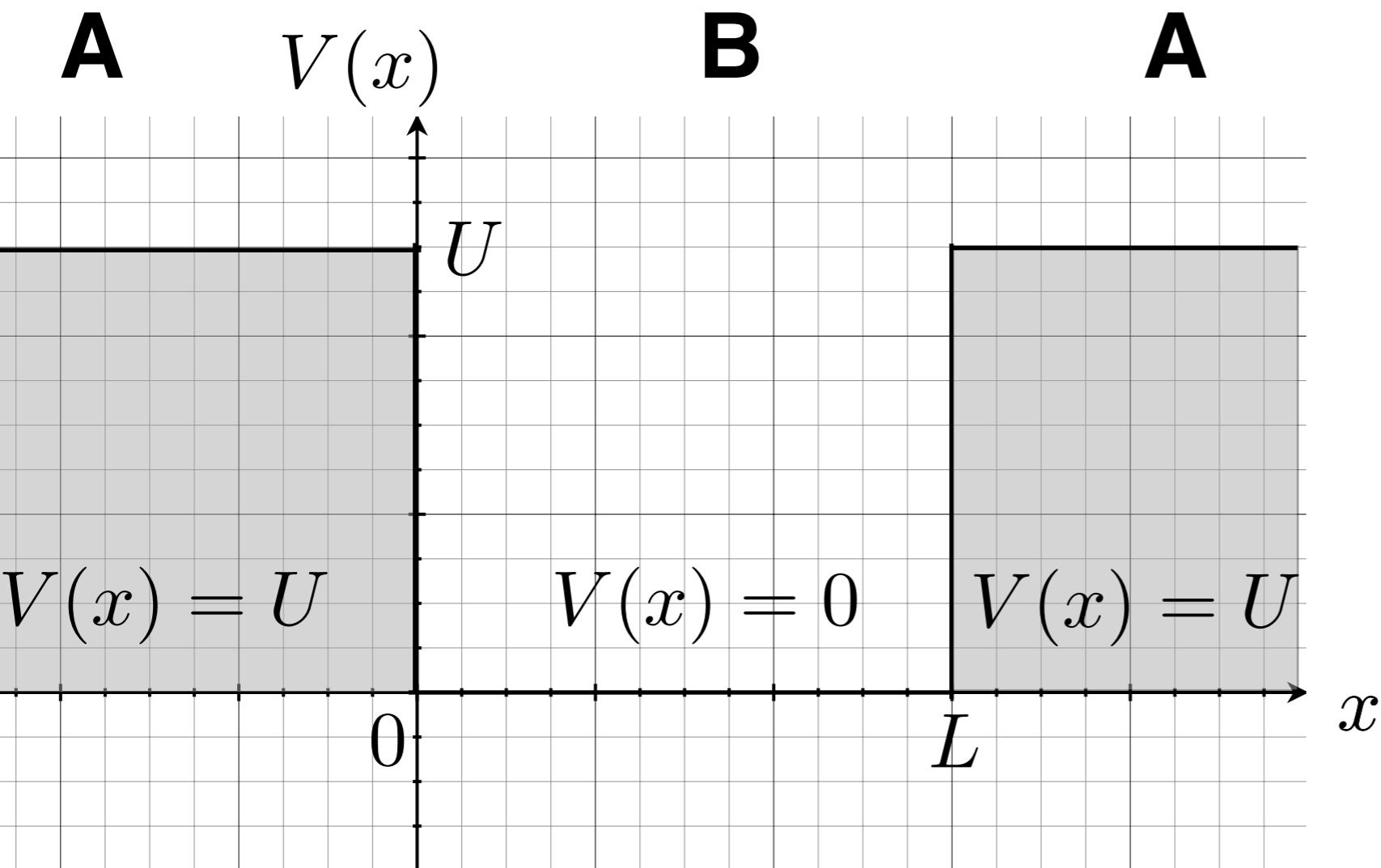
# Finite square well

- 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.



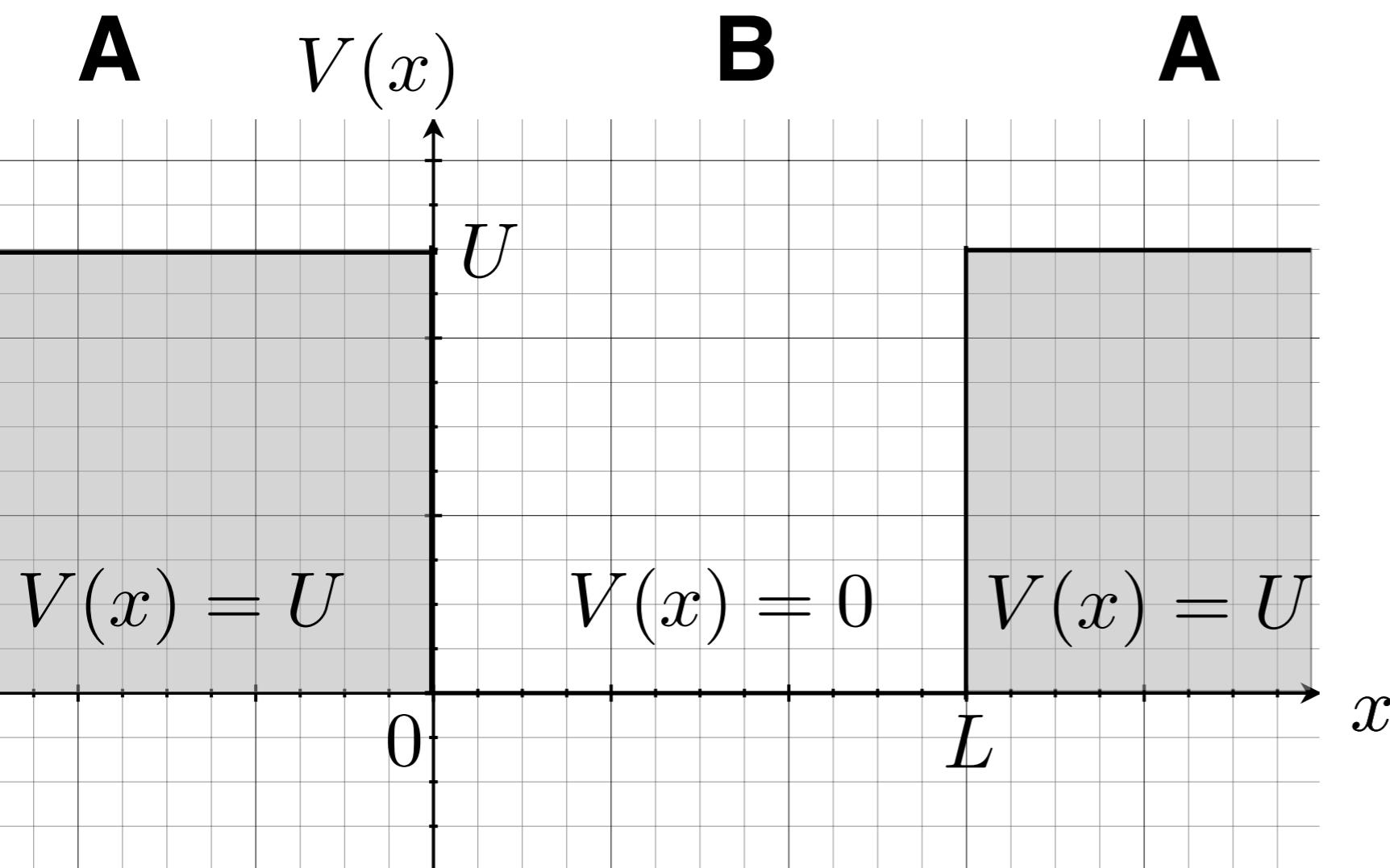
# Finite square well

- 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.

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

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

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

–which we can rewrite:

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

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

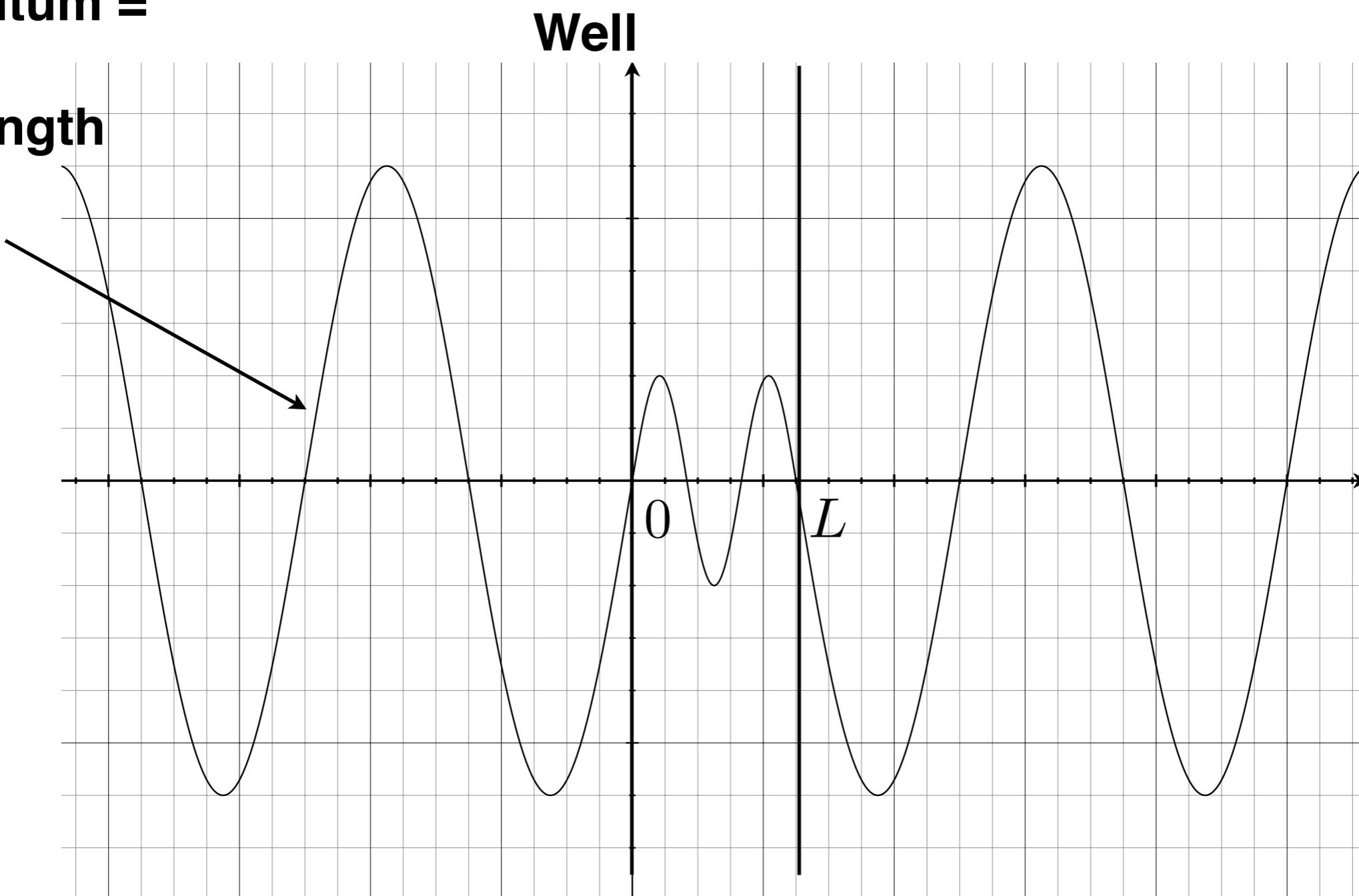
–These equations **match the energy equation** for a **classical particle!**

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

# Finite square well

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

**Lower momentum =  
longer wavelength**



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

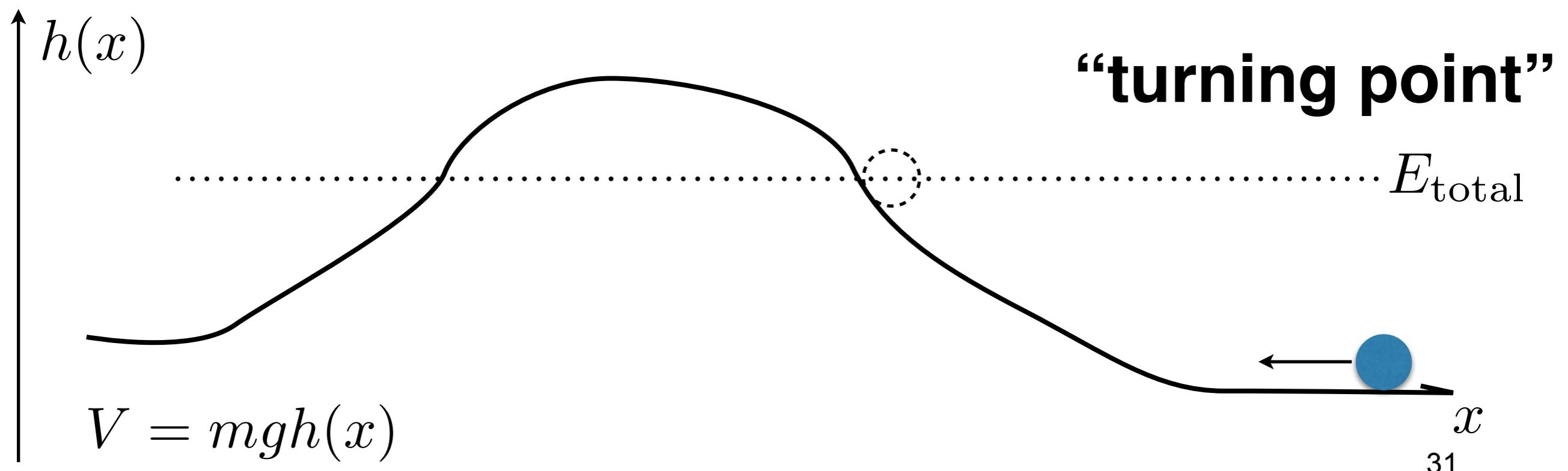
# Finite square well - summary

- 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

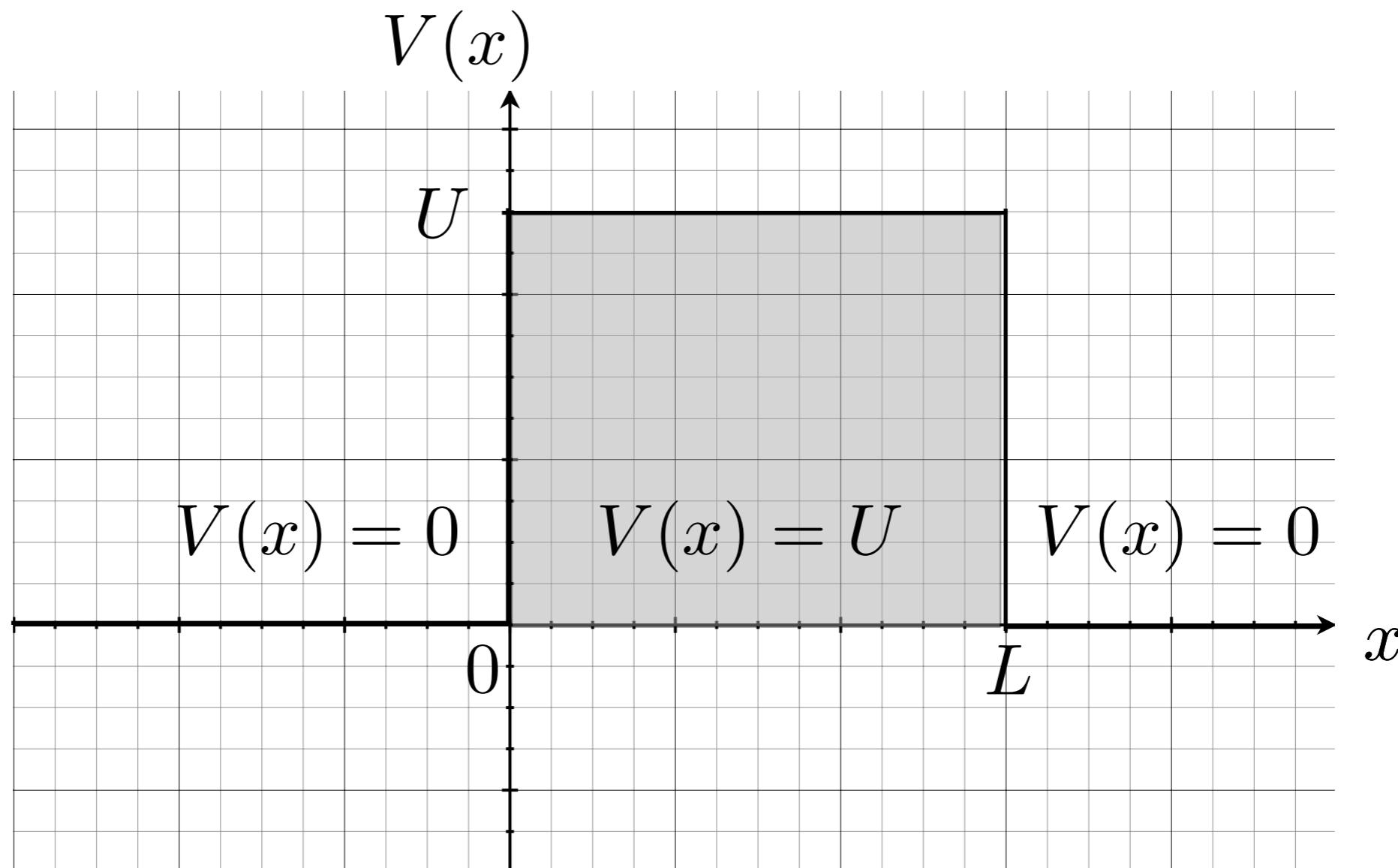
- In classical physics, potential energy can form a barrier.

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



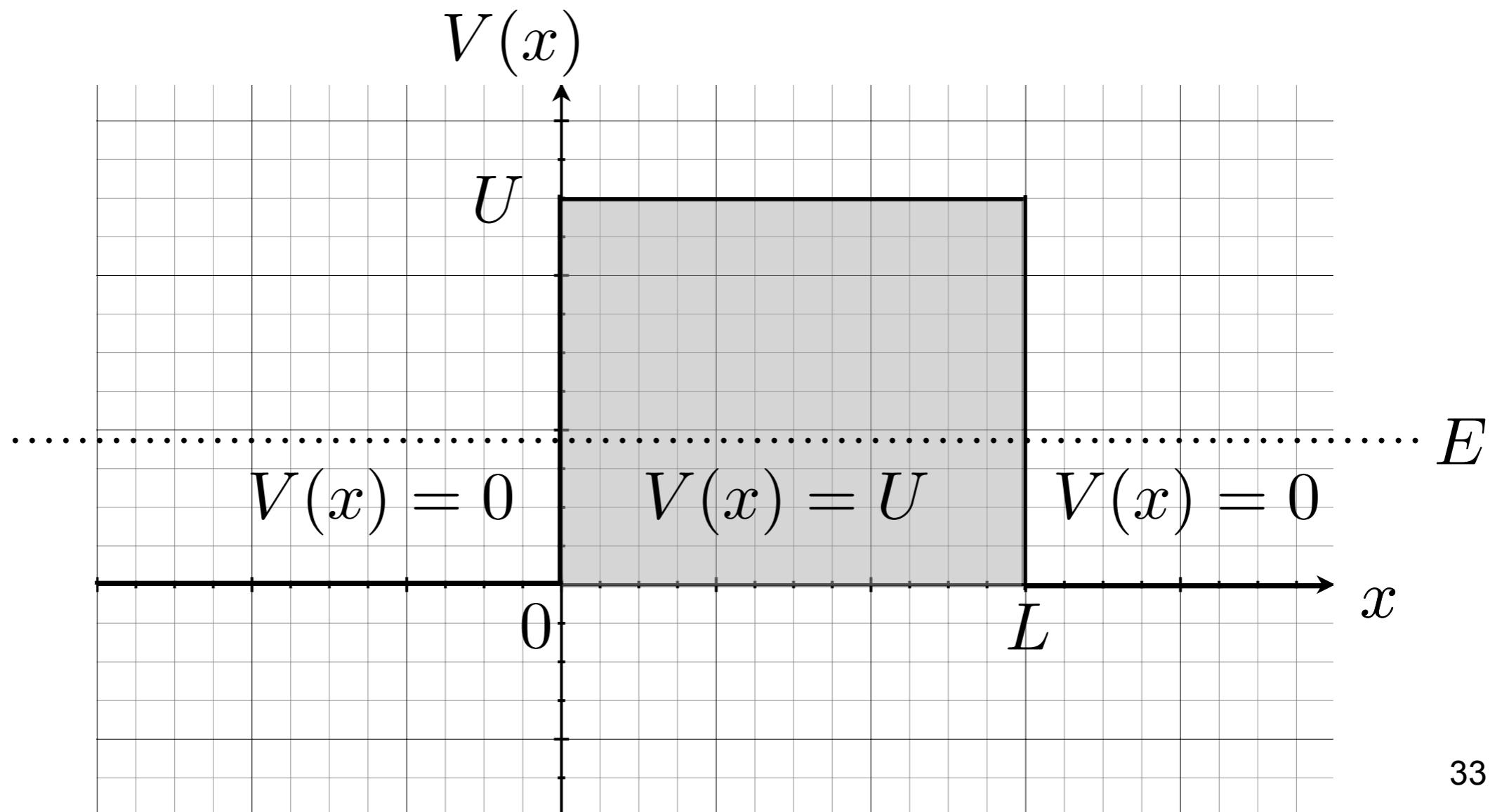
# Quantum Tunnelling

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



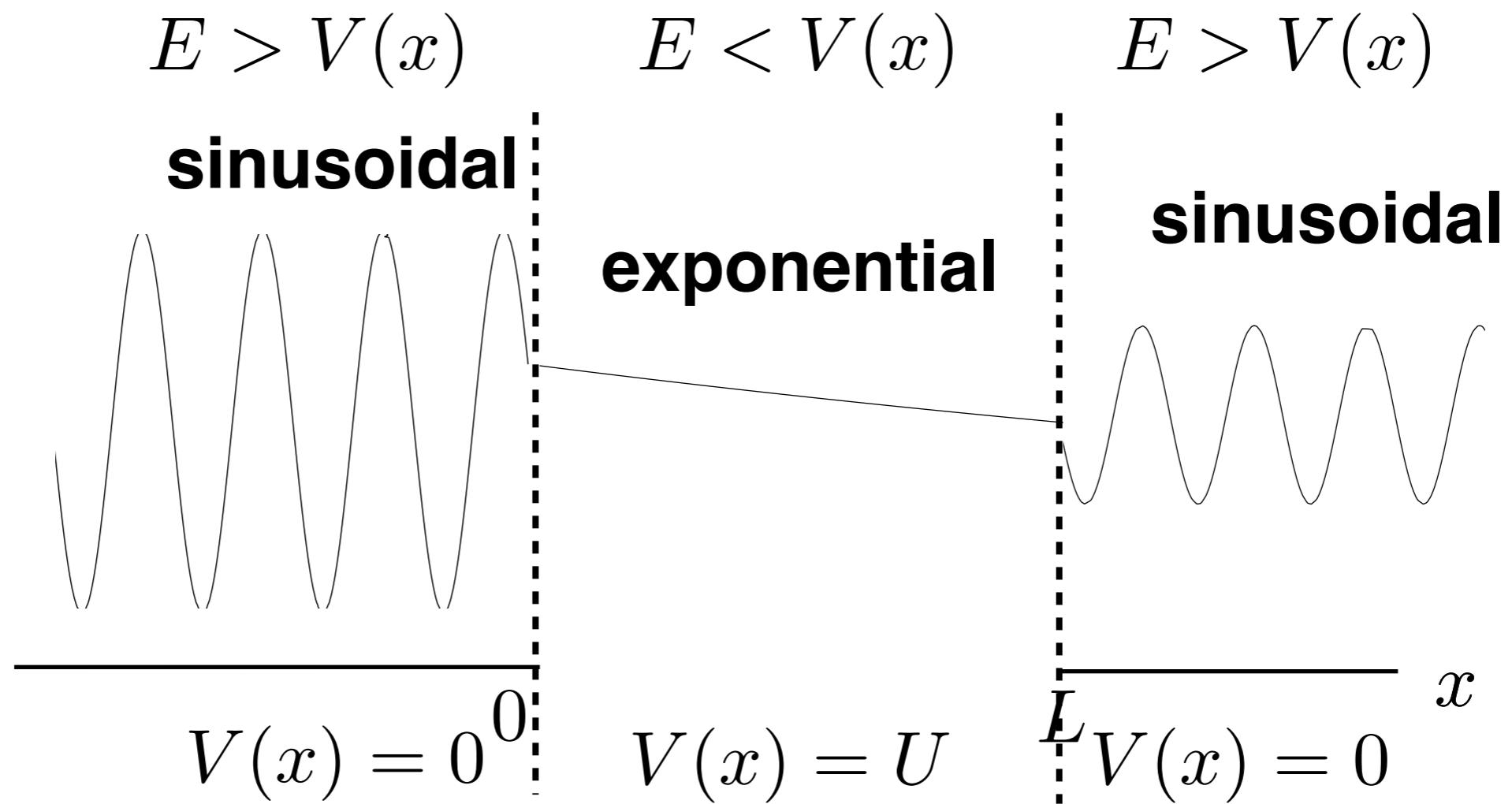
# Quantum Tunnelling

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



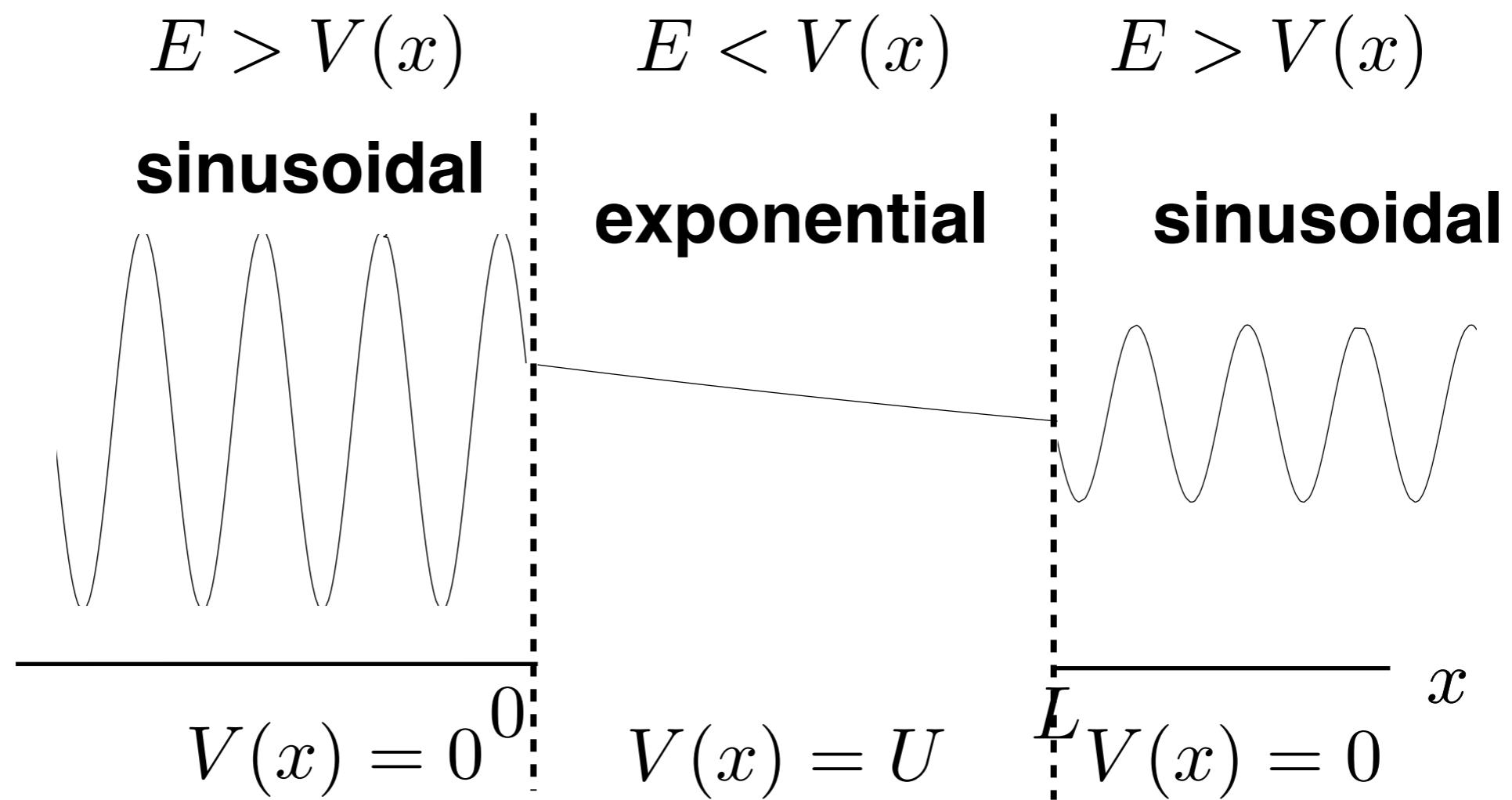
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# Quantum Tunnelling

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

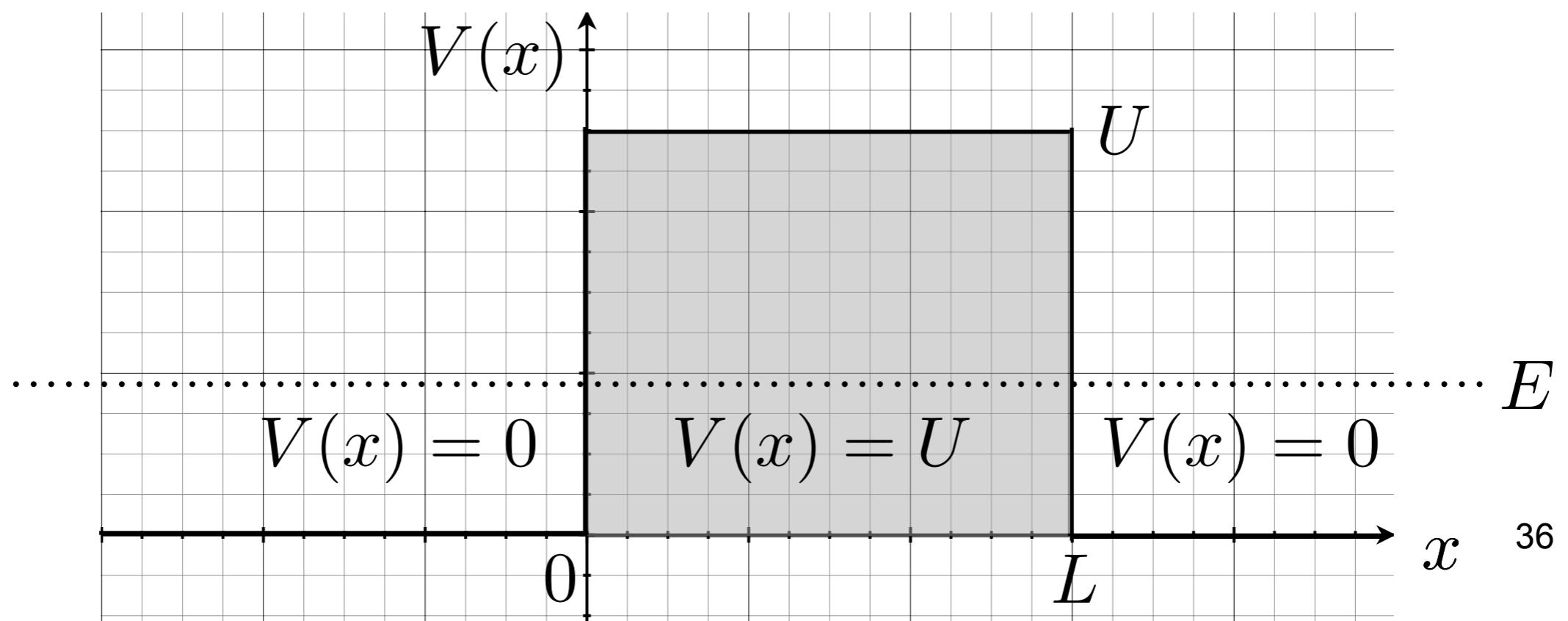


# Quantum Tunnelling

- If a quantum particle (wavepacket) approaches the barrier, there is a finite probability that it will tunnel through.
- If the barrier is high ( $E \ll U$ ), the probability of tunnelling is given by:
- where

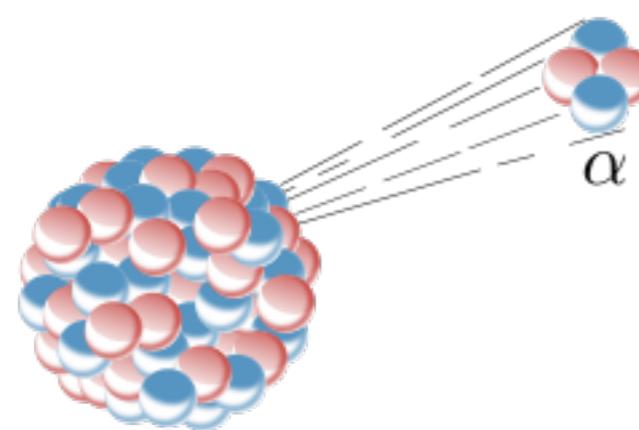
$$P = e^{-2CL}$$

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



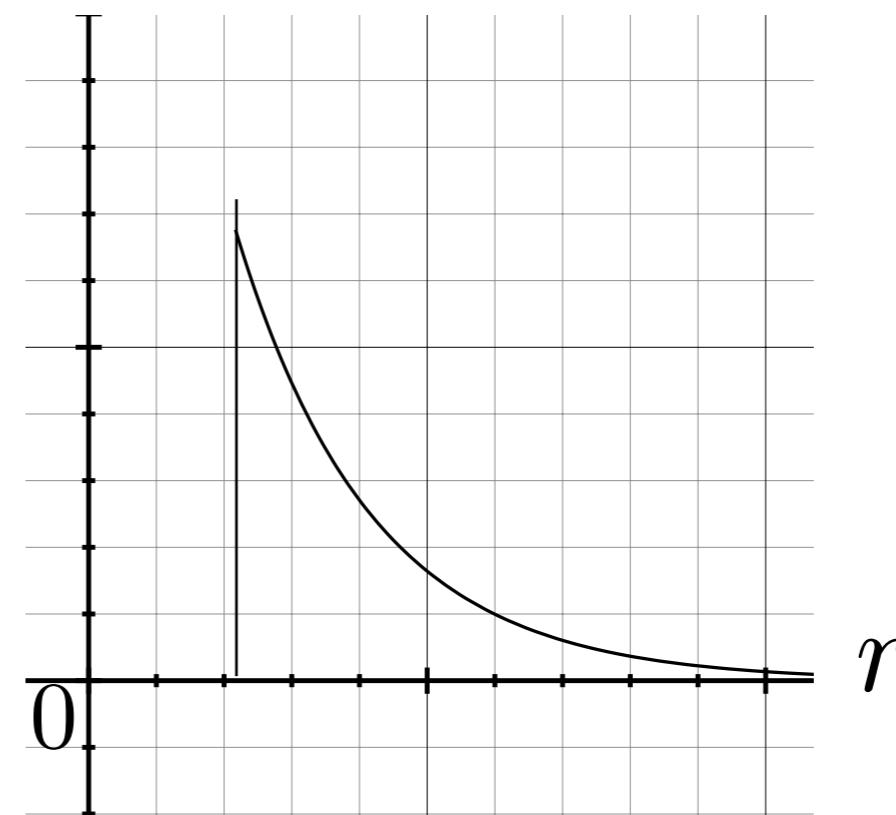
# Quantum Tunnelling

- 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.



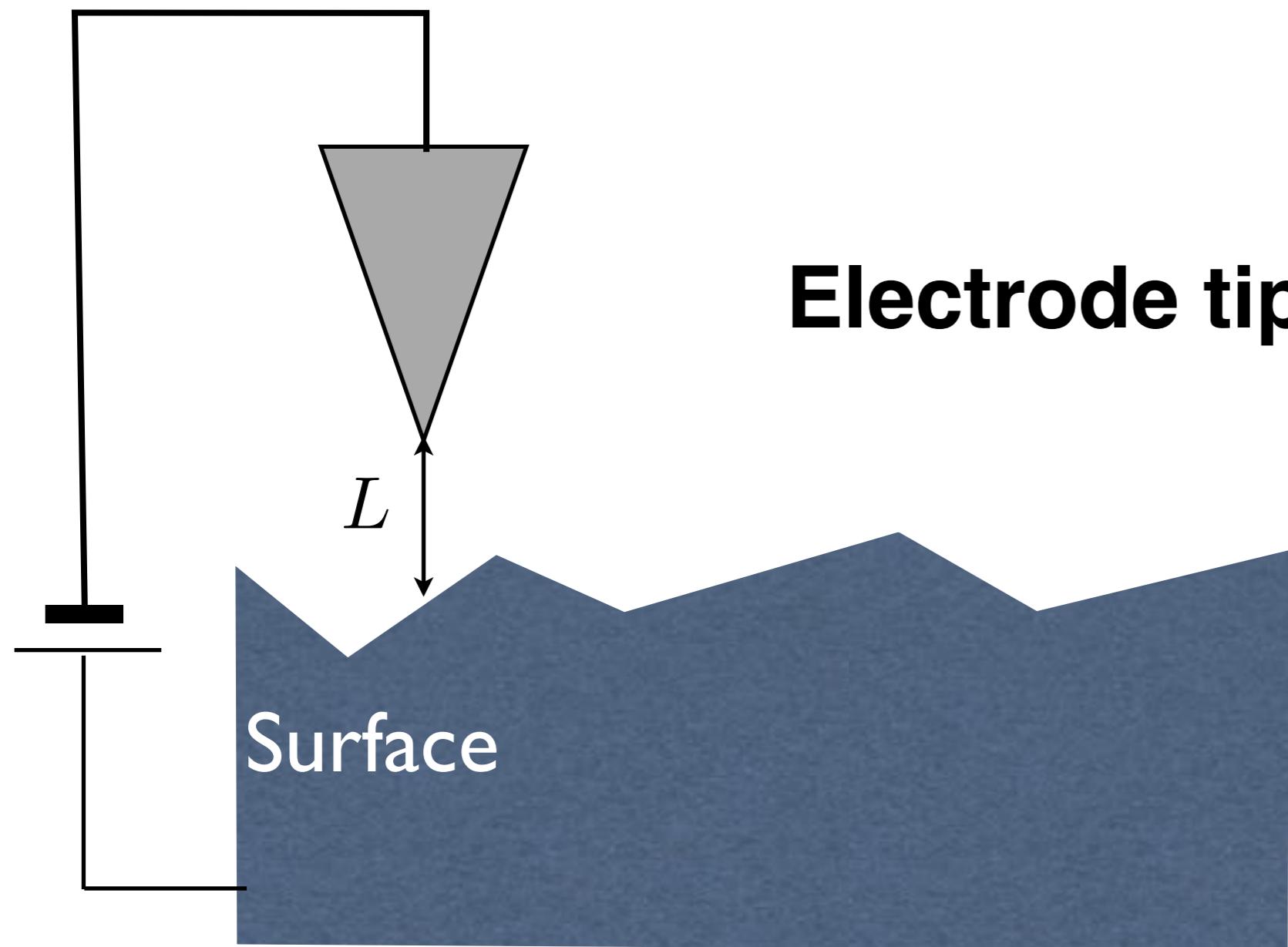
$V(r)$

**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.

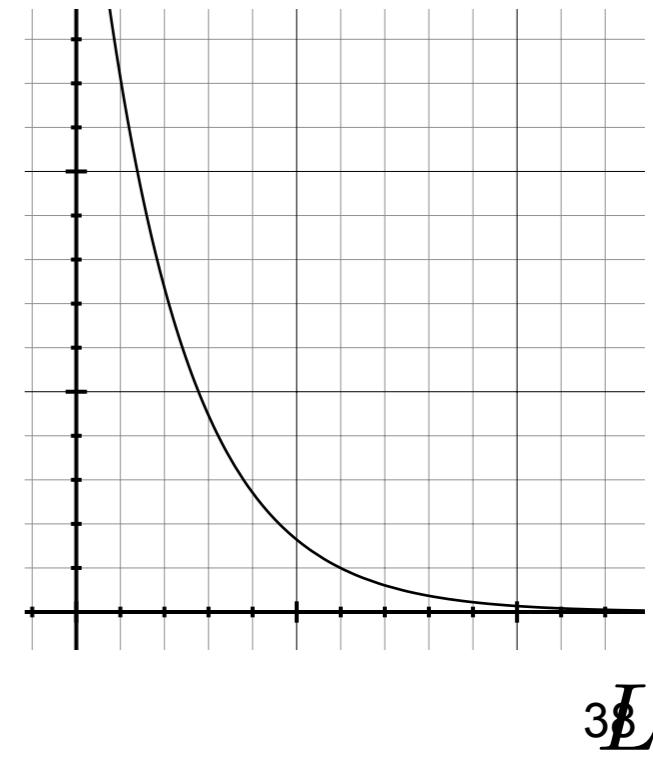


$$P = e^{-2CL}$$

**Electrode tip**

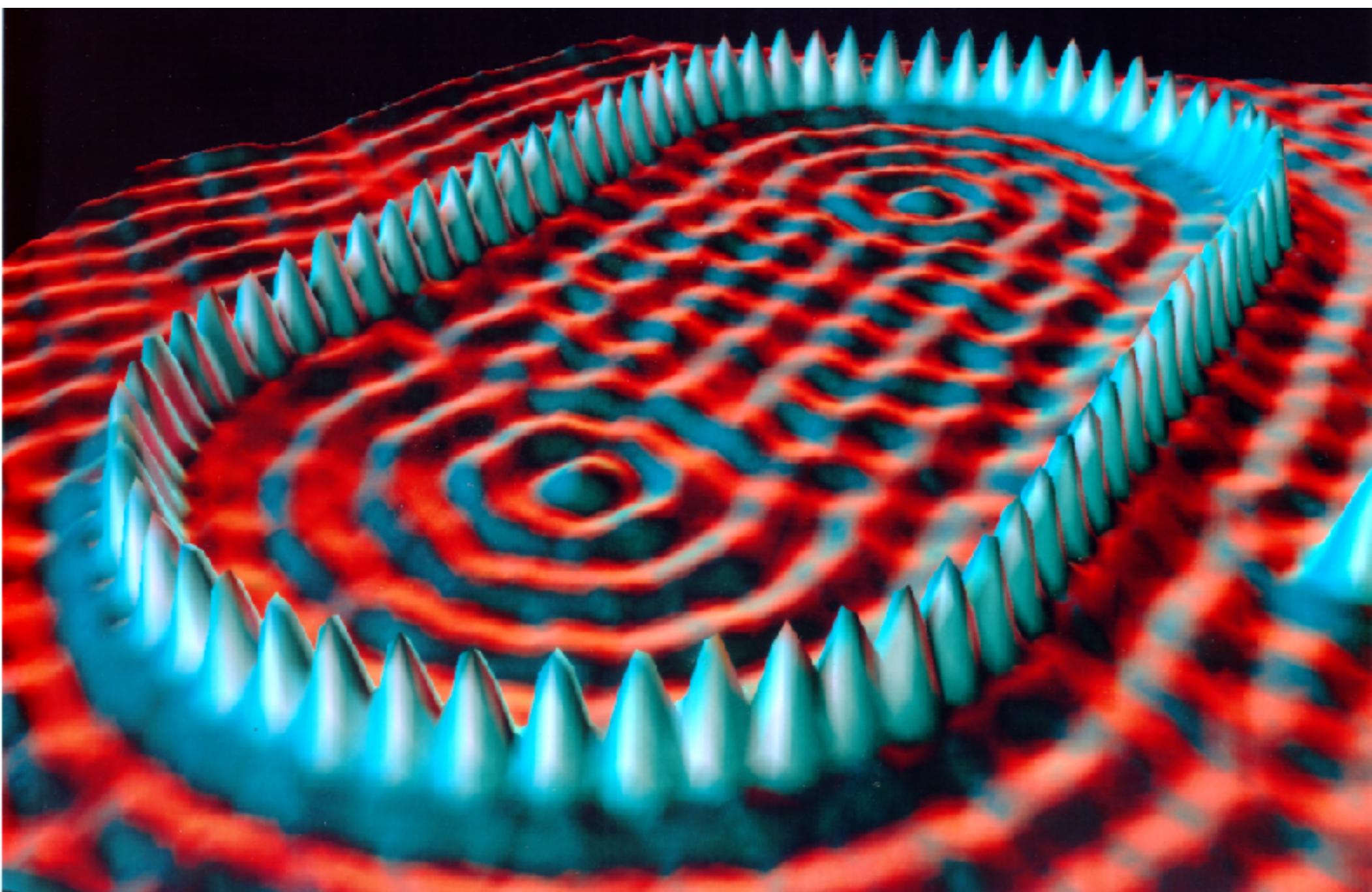
**Surface**

**Current**



# 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.
- Now, we apply these tools to develop a **quantum model** of the **atom**.

# Towards a Quantum Atomic Model

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

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



# Towards a Quantum Atomic Model

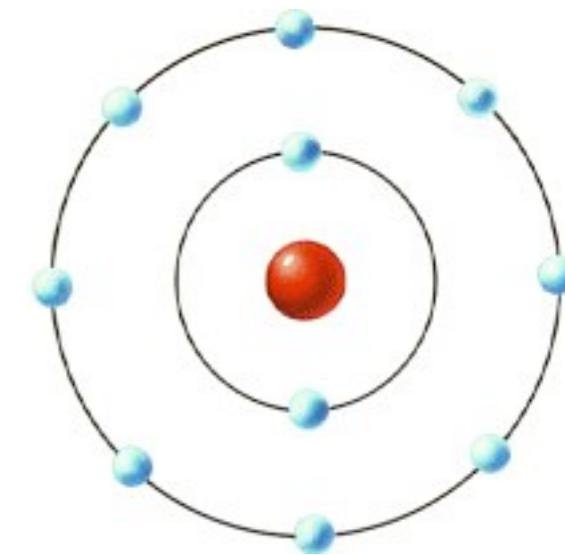
- Clue from Chemistry
  - Structure of the periodic table.

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																2 He	
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

- Have you studied **A-level Chemistry** or equivalent?
  - » 1. Yes
  - » 2. No

# Towards a Quantum Atomic Model

- A-level Chemistry **Energy Shell** picture -
  - Essentially the Bohr atom generalised by Sommerfeld (pre-quantum).
    - Element with **atomic number  $n$** .
    - Nucleus containing  $n$  protons
    - Orbited by  $n$  electrons
- Electrons inhabit “**shells**”
  - Electrons in each shell have a fixed energy.
  - Each shell can contain **up to a maximum number** of electrons.
  - Shells “**fill up**” from the lowest energy shell.



increasing energy ↓

	Number of electrons
K-shell	2
L-shell	8
M-shell	18
N-shell	32

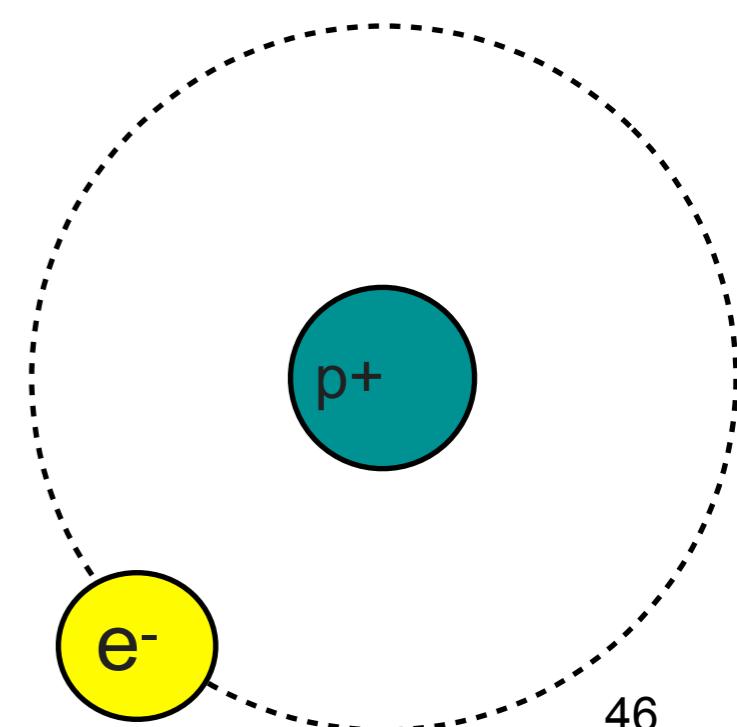
# Towards a Quantum Atomic Model

- Structure of periodic table provides evidence for this **shell picture**.

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																2 He	
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

# The quantum Hydrogen Atom

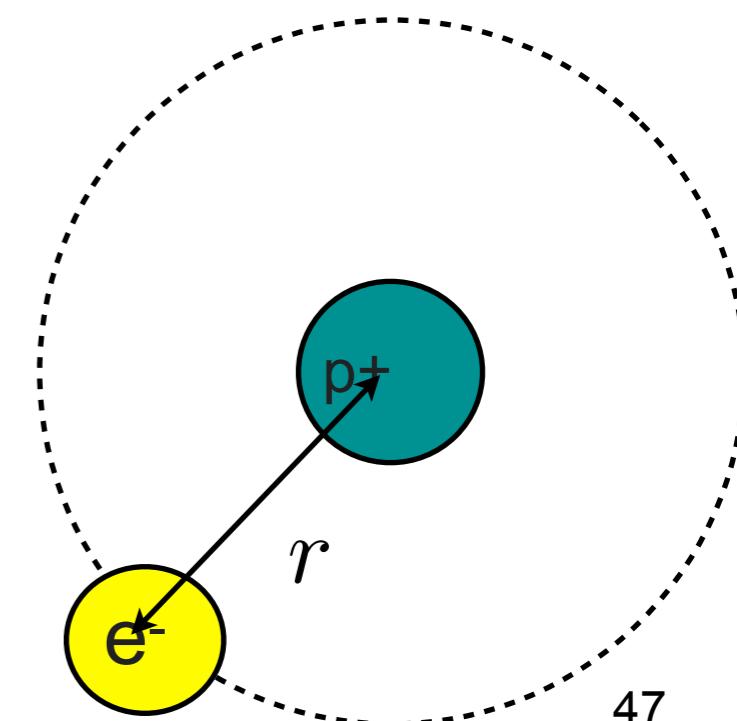
- The Hydrogen atom consists of
  - **1 proton** (mass  $2 \times 10^{-27}$  kg).
  - **1 electron** (mass  $10^{-30}$  kg).
- Proton is **2000 times** more massive than electron.
- For **external properties** of atom,
  - Atomic position and momentum
- we can **ignore** electron mass.



# The quantum Hydrogen Atom

- Internal properties of atom,
  - E.g. internal energy
- depends on motion of **electron** relative to **nucleus**.
- We work in the **centre-of-mass** frame of the atom, and treat the **nucleus** as **stationary**.
  - This is called the **Born-Oppenheimer** approximation.
- The electron experiences a **Coulomb force** due to the positive nucleus, described by Coulomb potential:

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$

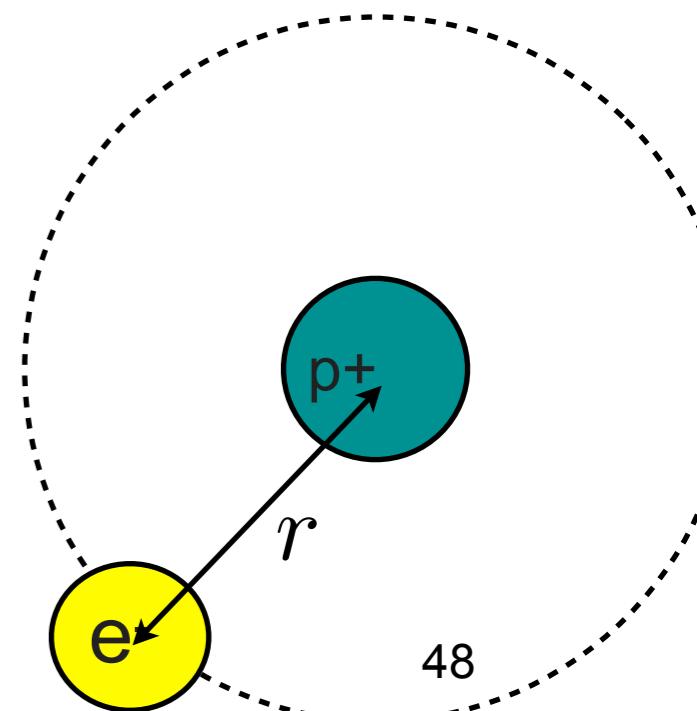


# The quantum Hydrogen Atom

- For a quantum model of the Hydrogen atom, we treat the **electron** as a **quantum particle**.
- To compute its allowed **energies** and associated **wavefunctions**, we solve the **TISE** with a **Coulomb potential**:

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$

- But, the **Hydrogen atom** is a **three-dimensional** object!
- We thus need to solve the **three-dimensional TISE** to calculate the **allowed wave-functions** of the electron and hence a **quantum model** for Hydrogen.



- In one-dimension, the TISE is:

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

- In three-dimensions:

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2\psi(x, y, z)}{\partial x^2} + \frac{\partial^2\psi(x, y, z)}{\partial y^2} + \frac{\partial^2\psi(x, y, z)}{\partial z^2} \right] + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

- Have you studied **partial differentials** in your Mathematics courses yet?
  - » 1. Yes
  - » 2. No

- Normally, when we differentiate (e.g. by  $x$ ), we need to worry about how **other variables** (e.g.  $y$ ,  $z$ ) **depend** on  $x$  and use the **chain rule**:

$$\begin{aligned}\frac{d}{dx} (x + y^2) &= 1 + \frac{d(y^2)}{dx} \\ &= 1 + \frac{d(y^2)}{dy} \frac{dy}{dx} \\ &= 1 + 2y \frac{dy}{dx}\end{aligned}$$

- Partial differentials are **easier**.
- When we **partially differentiate** (e.g. by x), we treat **other variables** (e.g. y,z) as **constants**.

$$\frac{\partial}{\partial x} (x + y^2) = 1 + 0 = 1$$

$$\frac{\partial}{\partial y} (x + y^2) = 0 + 2y = 2y$$

- Apart from this, the rules of differentiation are the same.
- Partial differentials are indicated by the symbol  $\partial$ .
- **Most** of the **key equations** in Physics are partial differential equations.

- We often rewrite the TISE in 3-D using **differential operators**:

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(x, y, z) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

–and use the short hand:

$$\nabla^2 = \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$$

–where is called “**del-squared**” or “**nabla-squared**”.

- to write the **3-D TISE** in its most famous form:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

# Quantum Model for Hydrogen

- In the **Quantum Model for Hydrogen**,
  - the allowed **energies** and **wave-functions** for the electron,
- are given by the **3D TISE**

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(x, y, z) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

- with Coulomb potential

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$

$$V(x, y, z) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{\sqrt{x^2 + y^2 + z^2}}$$

# Quantum Model for Hydrogen

- **Solving the 3D TISE for Hydrogen involves several advanced techniques:**
  - Spherical polar coordinates
  - Separation of Variables
  - Quantum Angular Momentum
  - Laguerre Polynomials

# Quantum Model for Hydrogen

- Solving the 3D TISE for Hydrogen involves several advanced techniques:
    - Spherical polar coordinates
    - ~~Separation of Variables~~
    - ~~Quantum Angular Momentum~~
    - ~~Laguerre Polynomials~~
  - In this course, we will instead study some properties of the **solutions** of the 3D TISE for Hydrogen.
- }
- Second-year course**

# Solutions of the TISE for H

- Energies from the TISE
  - Solving the **3D-TISE** and applying appropriate **boundary conditions**, we find the **energies** have to satisfy:

$$\begin{aligned} E_n &= - \left( \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{a_0} \right) \frac{1}{n^2} \\ &= - \frac{2.2 \times 10^{-18}}{n^2} \text{ Joules} \\ &= - \frac{13.6}{n^2} \text{ eV} \end{aligned}$$

- where  **$n=1,2,3\dots$**  We call  **$n$**  the **principle quantum number**.
- Energies are **discrete** - electron is in a **bound state** similar to the square well.
- Energies are **identical** to those of the **Bohr model**, and hence match precisely the **Rydberg formula!**

# Solutions of the TISE for H

- What are the **wave-functions** which correspond to these energies?
- Due to the spherical symmetry of the Hydrogen atom, these are best expressed in **spherical polar coordinates**.
- I.e. instead of

$$\psi(x, y, z)$$

- we write

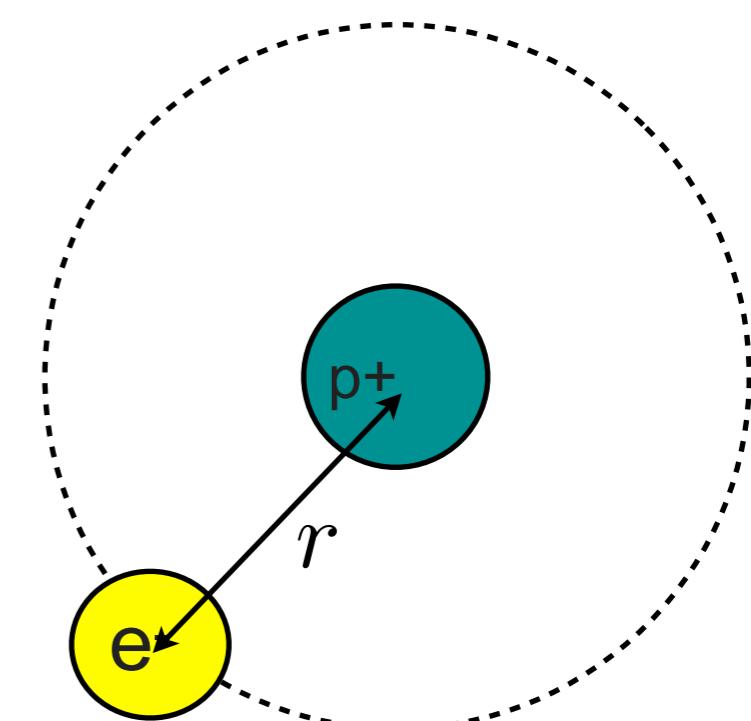
$$\psi(r, \theta, \phi)$$

- Have you studied Spherical Polar coordinates before?
  - » 1. Yes
  - » 2. No

# Spherical polar coordinates

- It is usually convenient (i.e. it makes calculations easier) to work with a **coordinate system** which shares the **symmetries** of the problem.
- The **Coulomb potential** is **spherically symmetric**.

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$



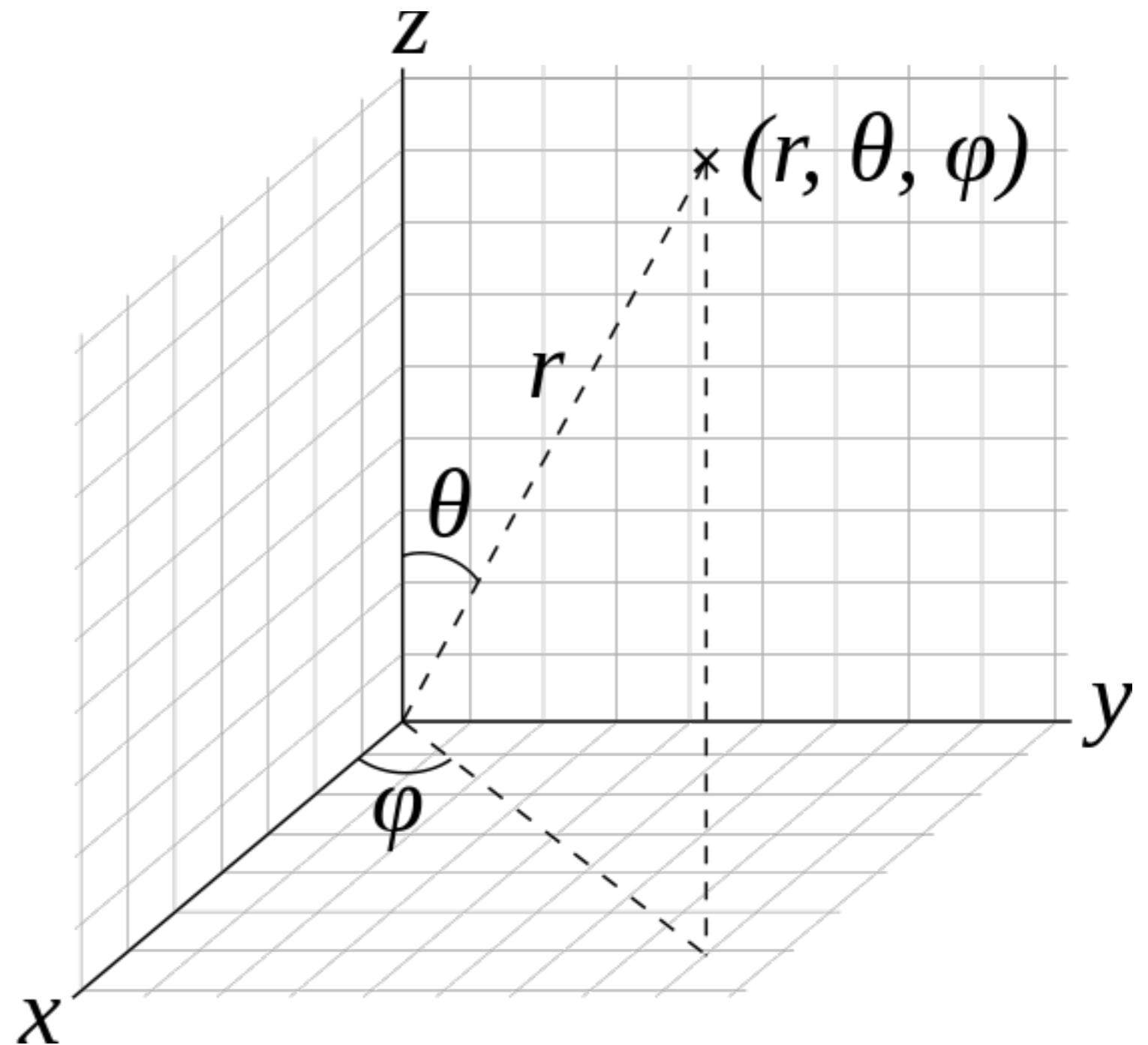
# Spherical polar coordinates

- Instead of  $x$ ,  $y$ , and  $z$ , we work with  $r$ ,  $\theta$  and  $\phi$ .

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \arccos\left(\frac{z}{r}\right)$$

$$\phi = \arctan\left(\frac{y}{x}\right)$$



# Solutions of the TISE for H

- The spherical symmetry of TISE for H is reflected in the form of the **wave-function solutions**.
- These have the factorised form:

$$\psi(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\phi, \theta)$$

- where  $R_{n,l}(r)$  is called the **radial wave-function**
  - It is dependent on coordinate  $r$ , not  $\theta$  and  $\phi$
  - It also depends on integers  $n$  and  $l$  (ell).
- and  $Y_{n,l}(r)$  is called the angular wave-function
  - It is dependent on coordinate  $\theta$  and  $\phi$ , not  $r$ .
  - It depends on integers  $l$  (ell) and  $m$ .

# Quantum Numbers

- Integers  $n$ ,  $l$  (ell) and  $m$  are called **Quantum Numbers**.
- They are **integers** which index the **wave-functions**.
  - Solving the TISE shows they take the following values.
- **$n$  - Principle Quantum Number**
  - $n = 1, 2, 3, 4, \dots$  (any non-zero non-negative integer)
- **$l$  - Orbital Quantum Number**
  - $l = 0, 1, 2, \dots, n-1$  (any non-negative integer less than  $n$ )
- **$m$  - Magnetic Quantum Number**
- $m = -l \text{ (ell)}, -l+1, \dots, -1, 0, +1, \dots, l-1, l$   
(any integer with modulus less than  $l$ )

# Quantum Numbers

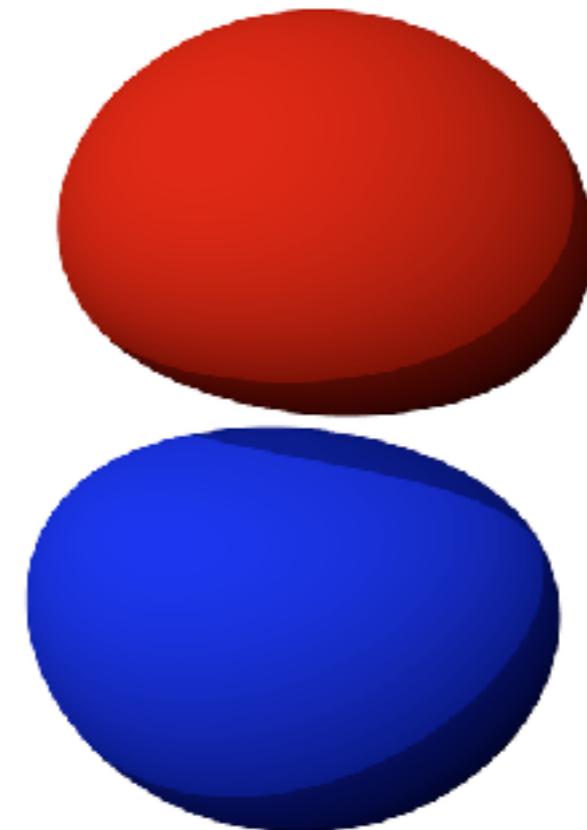
- Energy depends only on the **principle quantum number -  $n$** .

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

- The other quantum numbers  $l$  and  $m$  help determine the **shape** of the wave-function, but do not effect energy.
- There can be **different** wave-functions (with different values of  $l$  and  $m$ ) for the **same  $n$** , and hence the **same energy**.
- Different wave-functions with the same energy are called **degenerate**.

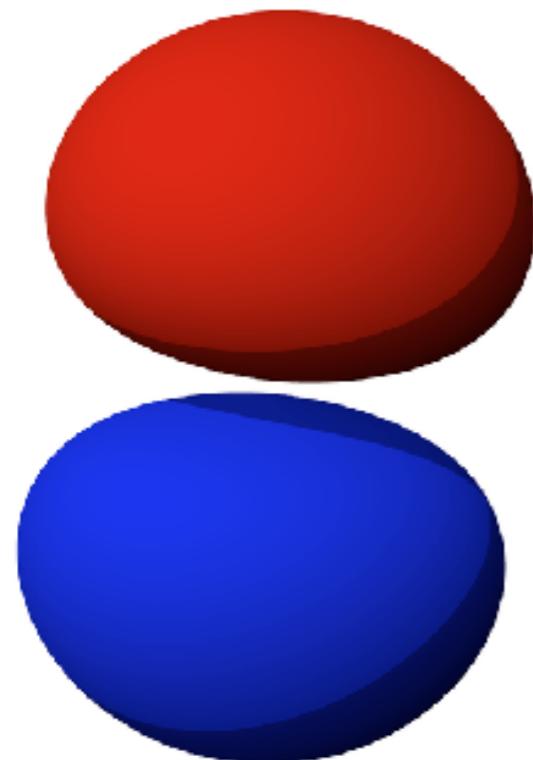
# Quantum Numbers

- We can **visualise** 3-D wavefunctions with a wavefunction contour map.
- The electron is likely to be found in coloured region with **90% certainty**.
- **Red** indicates **negative wave function**, blue indicates a **positive wave function**.
- Example:  $n=2$
- $l = 1, m = 0$

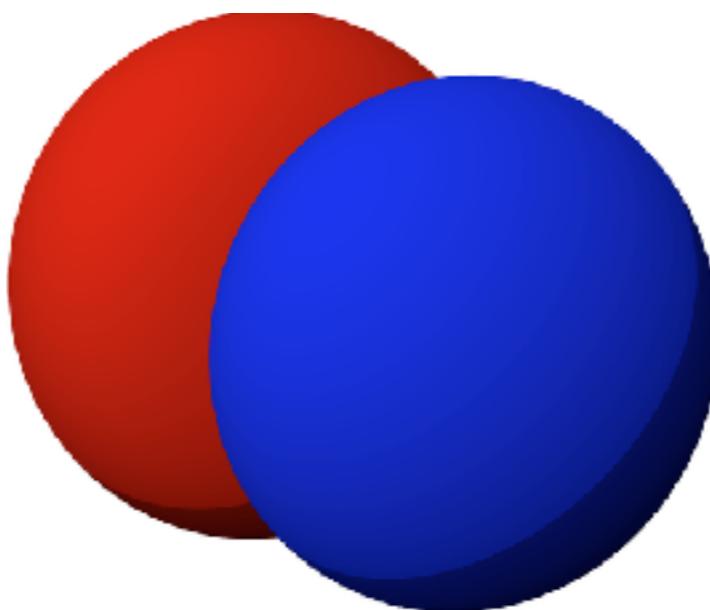


# Quantum Numbers

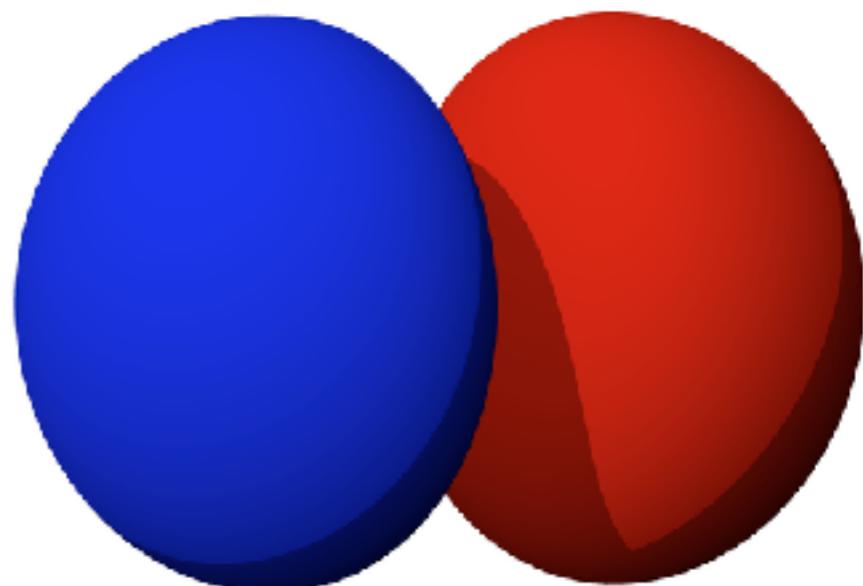
- Example:  $n=2$
- $l = 1, m = 0$



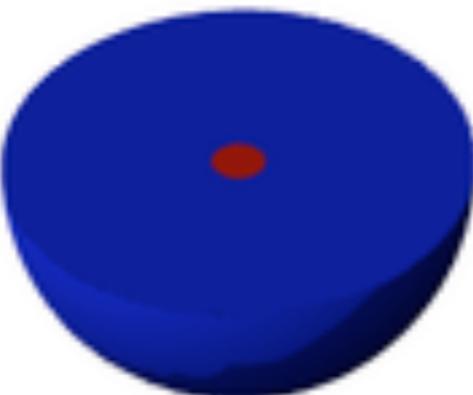
- $l = 1, m = -1$



- $l = 1, m = 1$



- $l = 0, m = 0$



- All 4 wave-functions have the same energy.

**$l=0$  wavefunction is always spherical. This is a section to show internal structure.**

# Quantum Numbers

## - $n=1$

- $l = 0, m = 0$
- Only 1 wave-function for  $n=1$ .

## - $n=2$

- $l = 0, m = 0$
- or  $l = 1, m = -1, 0, 1$
- $1+3 = 4$  wave-functions

## - $n=3$

- $l = 0, m = 0$
- or  $l = 1, m = -1, 0, 1$
- or  $l = 2, m = -2, -1, 0, 1, 2$
- $1 + 3 + 5 = 9$  wave-functions

- In general (see practice problem sheet) for given  $n$ , there are  $n^2$  wavefunctions.

# Quantum Numbers

- For historical reasons, wave-functions with a given orbital quantum number  $l$ , are referred to by a **letter**.

$l=0$	s
$l=1$	p
$l=2$	d
$l=3$	f
$l=4$	g
$l=5$	h

- Choose your own mnemonic - e.g. **Sticky Paint Dries Fast**.

# Hydrogen Ground State

## –Example

- The **ground state** of Hydrogen is the state of lowest energy, the  **$n = 1, l = 0$**  state.
  - It is called the **1s** state (**1** from  **$n=1$** , **s** from  **$l = 0$** ).
- Its wave-function does not depend on  $\theta$  and  $\phi$  and hence is **spherically symmetric**:

$$\psi_{1s}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

–where  **$a_0$**  is the **Bohr radius**.

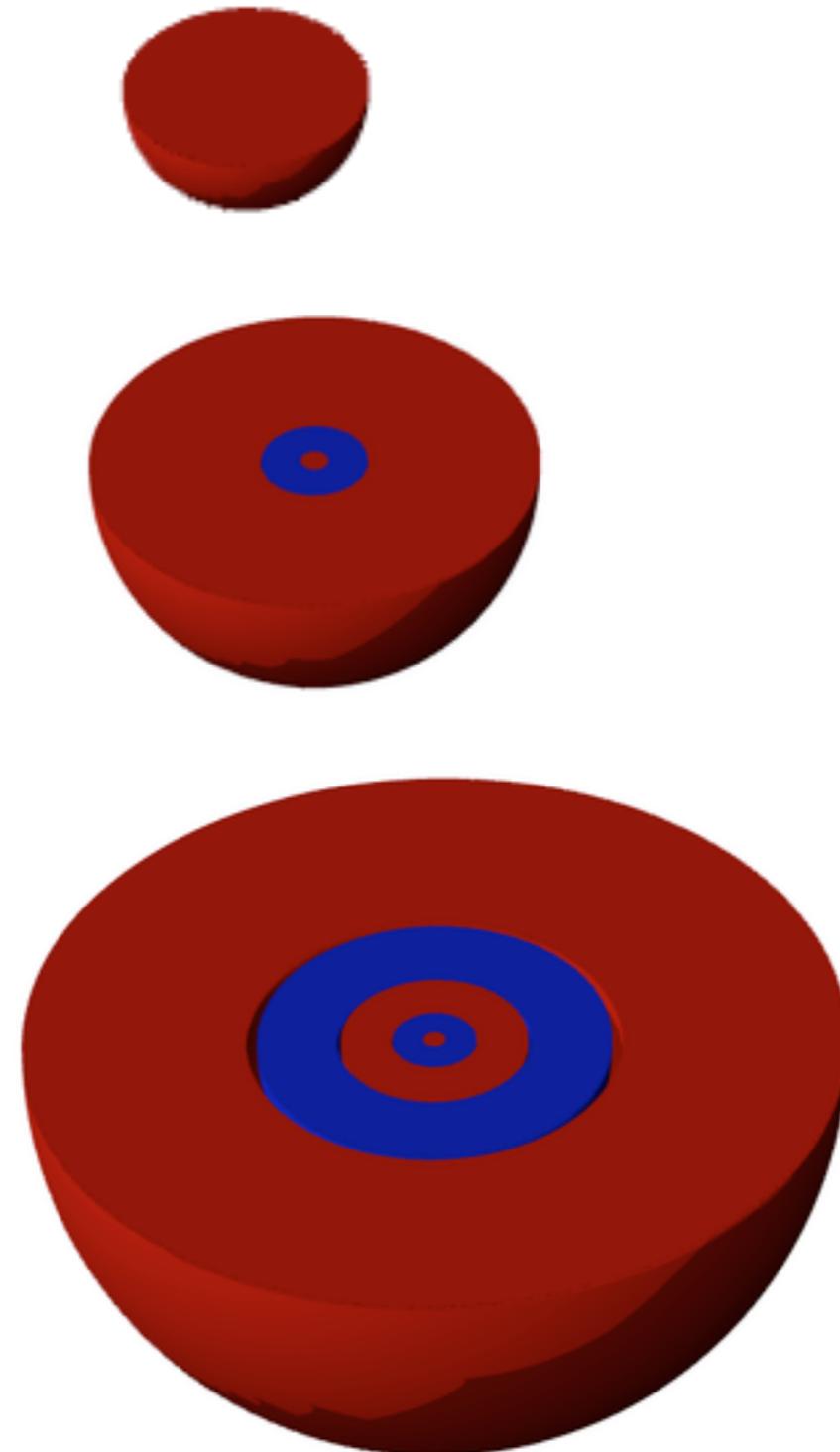
# Hydrogen s States

– In general, all **s-states** are spherically symmetric.

- E.g.  $n=1$

- $n=3$

- $n=5$



**larger  $n$**

**more oscillations**

**expectation  
values  
of radius  
larger**

*Sections through half of  
the sphere to show  
internal structure.*

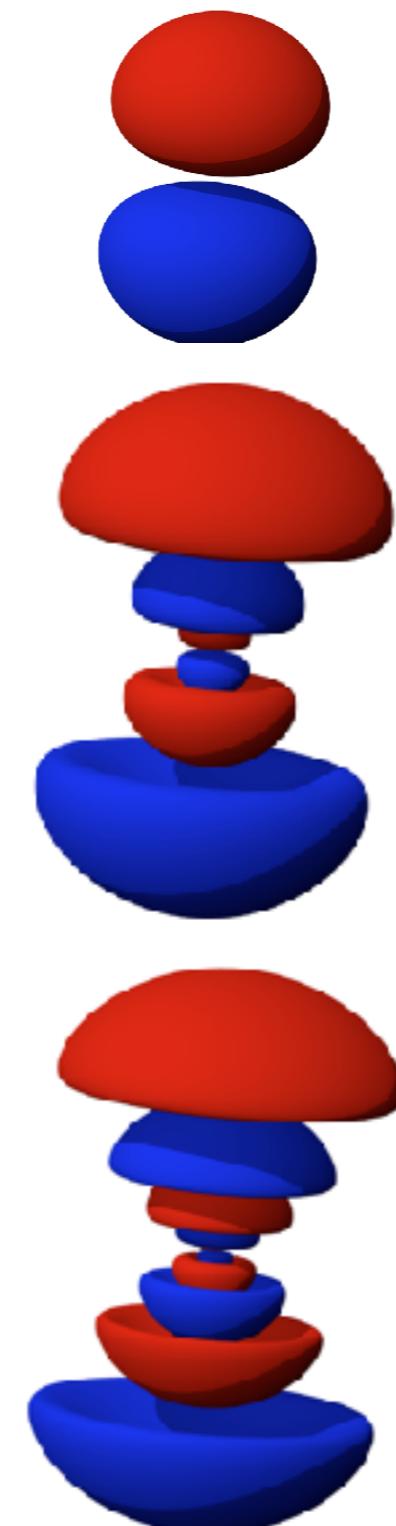
# Hydrogen p States

– P-states are dumbbell shaped

- E.g. n=2

- n=4

- n=6



larger n

more oscillations

expectation  
values  
of radius  
larger

# Quantum Model for Hydrogen

- To summarise, the solutions to the TISE for the Hydrogen atom have energy

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

- and wave-functions of the form

$$\psi(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\phi, \theta)$$

- where  $R_{n,l}(r)$  is called the **radial wave-function**
- and  $Y_{n,l}(r)$  is called the angular wave-function
  - You will study the exact form of these wave-functions in Y2.
- The **energy** depends only on principle **quantum number  $n$** , but the **shape** of the wavefunction depends on  **$n$ ,  $l$  and  $m$** .

- In the Chemistry A-level model of multi-electron atoms, the electrons lie in shells, up to a maximum number in each shell.

	Number of electrons
K-shell	2
L-shell	8
M-shell	18
N-shell	32

- We just saw, that for the Hydrogen atom, that for a given energy, there are multiple wavefunctions:

	Number of wavefunctions
$n=1$	1
$n=2$	4
$n=3$	9
$n=4$	16

- In the Chemistry A-level model of multi-electron atoms, the electrons lie in shells, up to a maximum number in each shell.

	Number of electrons
K-shell	$2 = 1 \times 2$
L-shell	$8 = 4 \times 2$
M-shell	$18 = 9 \times 2$
N-shell	$32 = 16 \times 2$

- We just saw, that for the Hydrogen atom, that for a given energy, there are multiple wavefunctions:

	Number of wavefunctions
$n=1$	1
$n=2$	4
$n=3$	9
$n=4$	16

- Is this a coincidence? No! To understand the connection, we must study spin.



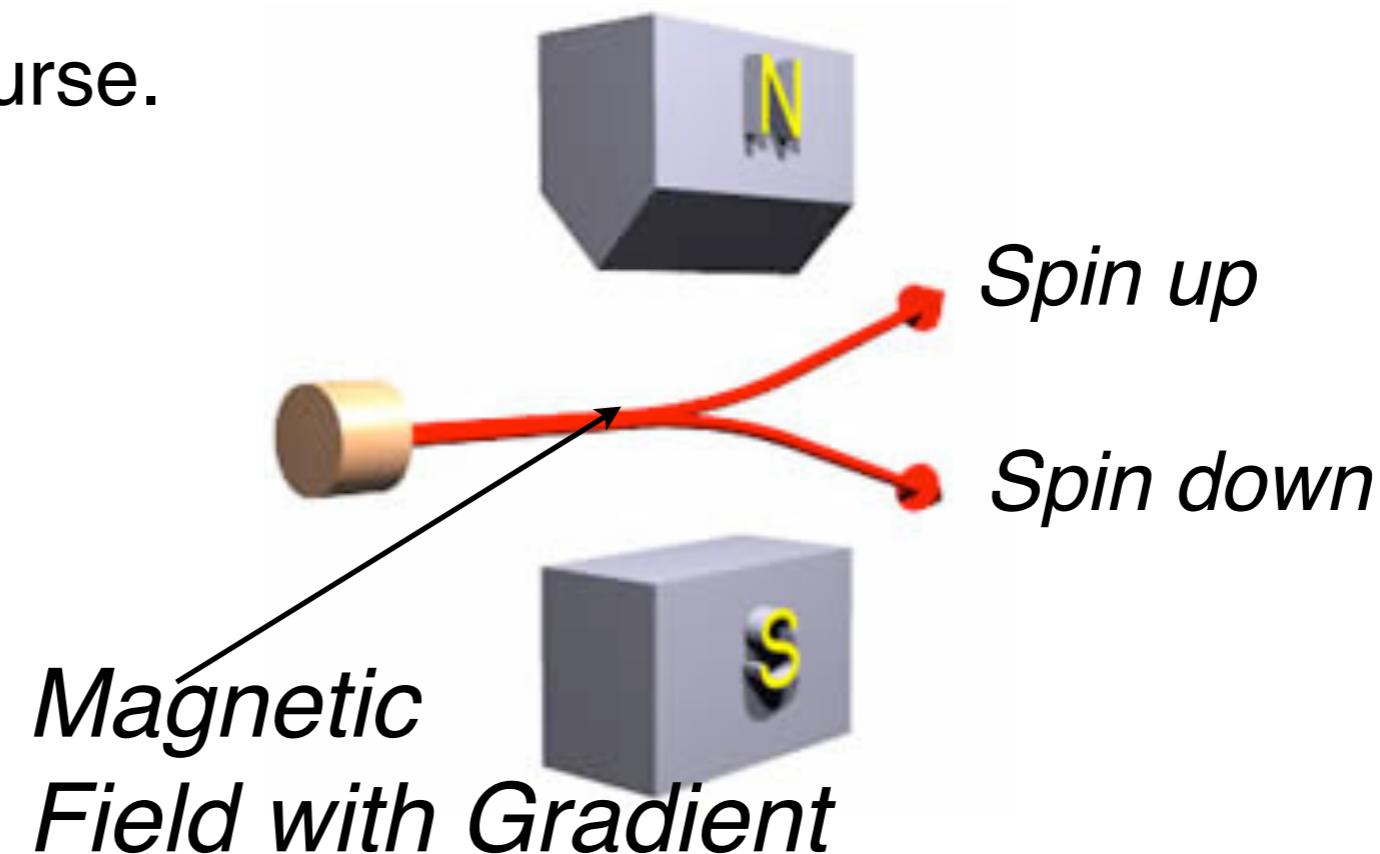
Satyendra  
Nath Bose



Enrico  
Fermi

- **Spin** is an **intrinsic** property of all **quantum** particles.
- It is similar to **angular momentum** mathematically (hence the name), but is an internal property of particles.
- **Spin** takes **integer** or **half-integer** values.
  - Particles with **integer** spin are called **Bosons**.
  - Particles with **half-integer** spin are called **Fermions**.
- The **electron** is a **Fermion** - with spin **1/2**.
- The **photon** is a **Boson** - with spin **0**.

- We can measure **spin** in a **Stern Gerlach** device.
  - Details in Y2 course.



- A **spin**  $s$  particle can inhabit one of  $2s + 1$  different **spin** states.
- Thus an **electron** has 2 possible spin states - we call these “**spin up**” and “**spin down**”.
- In the Hydrogen atom spin is an extra quantum number which must be included to fully specify the state of the electron.

- Shell model:

	Number of electrons
K-shell	2
L-shell	8
M-shell	18
N-shell	32

- Number of wave-functions for H **including spin**

	Number of wavefunctions
n=1	2
n=2	8
n=3	18
n=4	32

- This holds the key for us to start to understand the Shell model of atoms in quantum mechanical terms.

# Pauli exclusion principle

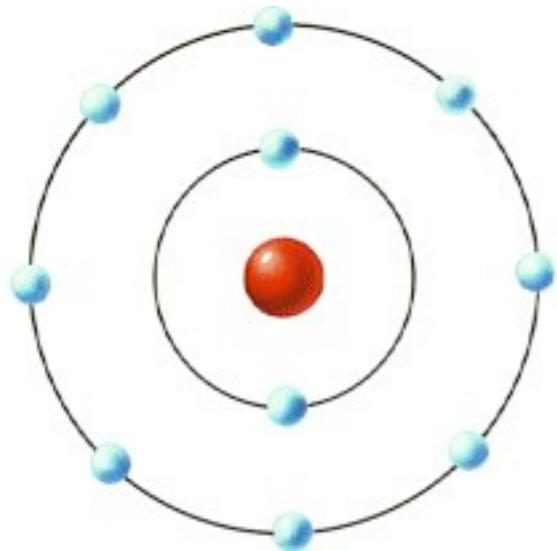


**Wolfgang  
Pauli**

- Fermions and Bosons have very different properties.
- One of the most important is the **Pauli Exclusion Principle** first stated by Wolfgang Pauli in 1925.
- Pauli Exclusion Principle
  - **No two Fermions** may inhabit the **same** quantum state.

# Pauli exclusion principle

- Explanation for the “shell model”
  - **Electrons are fermions** - every electron in the atom must occupy a **different state**.
  - Shells “fill up” from lowest energy



- There is **no such exclusion principle for Bosons**,
  - e.g. in a laser beam, **billions** of photons may be in the **same state** (frequency, polarisation, path etc.)



# Quantum Model for Multi-electron Atoms

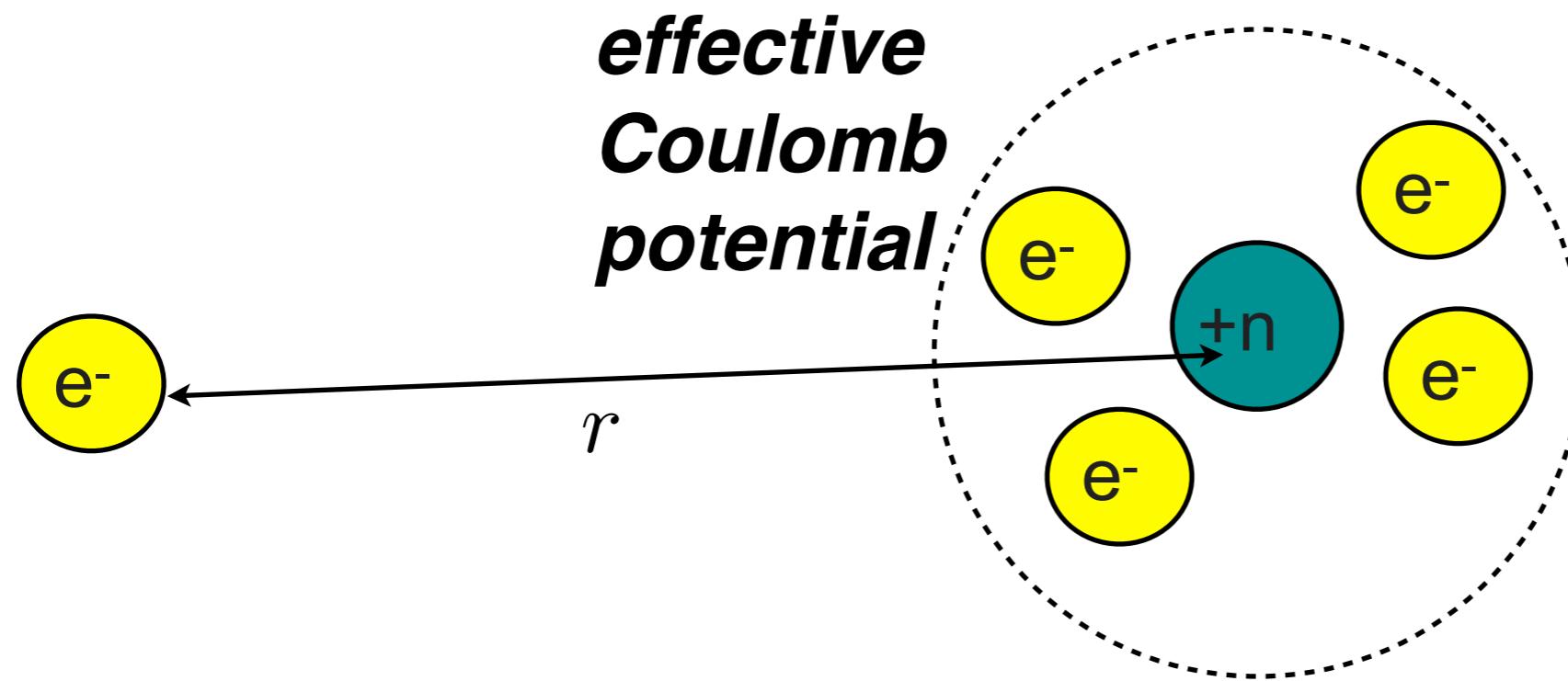


- Every other atom apart from Hydrogen has **more than 1 electron**.
- We work in the Born-Oppenheimer approximation, so we neglect the motion of the nucleus, and work in centre-of-mass-frame of the atom.
- We can write down a **TISE** for **all n electrons**.
- The potential will contain:
  - Electrostatic **attraction** of the **nucleus**
  - Electrostatic **repulsion** between **each electron**
- This will be an extremely complicated potential - hard to solve!

# Quantum Model for Multi-electron Atoms



- To a first approximation, we can assume that each electron “sees” the other electrons + nucleus as a single object.



- We recover a TISE for **each electron** which is **very similar** to the Hydrogen TISE.
  - The solutions we recover are then **very similar** to the Hydrogen wave-functions.
  - Just like Hydrogen they are described with **quantum numbers l, m, n** and **electron spin**.

# Quantum Model for Multi-electron Atoms



- However, as electrons are Fermions
  - the **Pauli Exclusion principle** comes into play.
- **No two electrons** can occupy the **same quantum state**,
  - e.g. **no two electrons** can have the **same quantum numbers**.
- In the lowest energy state for the atom (**ground state**), the electrons will occupy the **lowest energy states** that they can.
- The shell model can be explained by this principle:
- Shell model:
  - Electrons inhabit “**shells**”
    - Electrons in each shell have a fixed energy.
    - Each shell can contain **up to a maximum number** of electrons.
    - Shells “**fill up**” from the lowest energy shell.

# Quantum Model for Multi-electron Atoms



- Thus, the shell model can be understood in quantum mechanical terms!

	Number of electrons
K-shell	2
L-shell	8
M-shell	18
N-shell	32

- Number of wave-functions for H **including spin**:

	Number of wavefunctions
$n=1$	2
$n=2$	8
$n=3$	18
$n=4$	32

# Quantum Model for Multi-electron Atoms



- Thus, the shell model can be understood in quantum mechanical terms!

		Number of
$n=1$	K-shell	2
$n=2$	L-shell	8
$n=3$	M-shell	18
$n=4$	N-shell	32

- Each “shell” represents a set of wavefunctions with the **same principle quantum number**.
- This Hydrogen-like model is only an **approximation**,
  - and many-electron atomic spectra have a **more complicated structure** than Hydrogen
  - due to **electron-electron interactions** and **other effects** (e.g. interaction with the spin of the nucleus).

# Quantum Model for Multi-electron Atoms



- But the Hydrogen wave-functions are an **excellent first approximation** - as seen by the **Periodic table**, whose structure reflects the **quantum numbers** of Hydrogen.

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H															He		2
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Tl	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	31	32	33	34	35	36
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49	50	51	52	53	54
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	81	82	83	84	85	86
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	113	114	115	116	117	118
<b>20=18+2</b>																		
Lanthanides		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

- Quantum mechanics works!

- 1 - Waves as particles - the Photon [3 hours]
- 2 - Atomic theory from 400 BC to 1913 [2 hours]
- 3 - Particles as Waves [1 hour]
- 4 - Elements of Quantum Mechanics I -  
The wave-function [3 hours]
- 5 - Elements of Quantum Mechanics II -  
Energy in quantum mechanics [6 hours]

# Atoms, Stars and the Universe



image: wikipedia



image: nationalgeographic.com

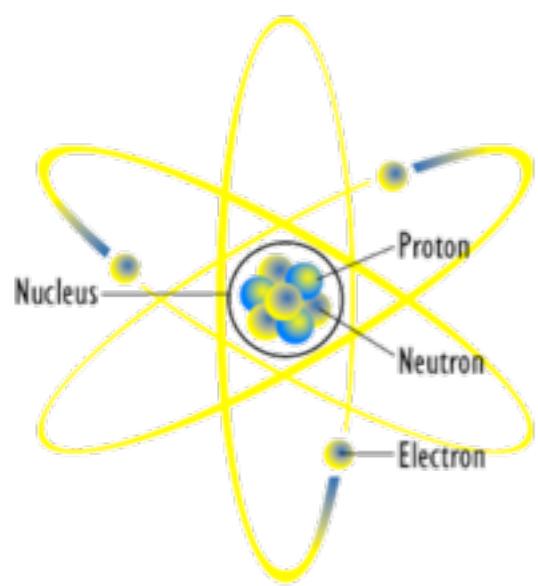


image: wikipedia

# Atoms, Stars and the Universe

- This concludes **Part 1** of Atoms, Stars and the Universe.
  - We saw that **wave-particle duality** of light and matter forces us to move **beyond** the deterministic world of classical physics.
  - We saw that **quantum particles** may be described by wave-functions with **wave-like evolution**, and **probabilistic measurement**.
  - And that wave-functions and energy are linked by the **Time-Independent Schrödinger Equation**, which allows us to develop a quantum atomic model based on Coulomb forces.
- This was just a taste of quantum physics, but you encountered many of the key quantum concepts and techniques.
- In **Part 2**, lectured by **Prof. Raman Prinja**, you will see how our **understanding of atoms and photons** allows us to study and understand objects millions of light years away - **Stars and the Universe**.

