Quantum Mechanics

Dr Mohammad Abdur Rashid

The Wave Function

The Wave Function

The configuration or state of a quantum object is completely specified by the wave function.

The wave function of a particle, at a particular time, contains all the information that anybody at that time can have about the particle (e.g. position, momentum, and energy).

The wave function, in general, is not a real quantity, but a complex-valued functions of space and time.

The Wave Function

In one dimension the wave function is denoted by $\Psi(x,t)$, while in three dimension it is $\Psi(x,y,z,t)$.

How do we get the wave function?

The wave function is derived by solving Schrödinger equation.

The Wave Function

The Schrödinger equation of the particle moving in the potential $V(x)$ is written as

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2}+V(x)\Psi(x)=E\Psi(x)$$

The Wave Function

The wave function itself has no physical interpretation.
It is not measurable.

The square of the absolute value of the wave function has a physical interpretation.

In one dimension, we interpret $|\Psi(x,t)|^2$ as a probability density, a probability per unit length of finding the particle at a time *t* at position x.

The Wave Function

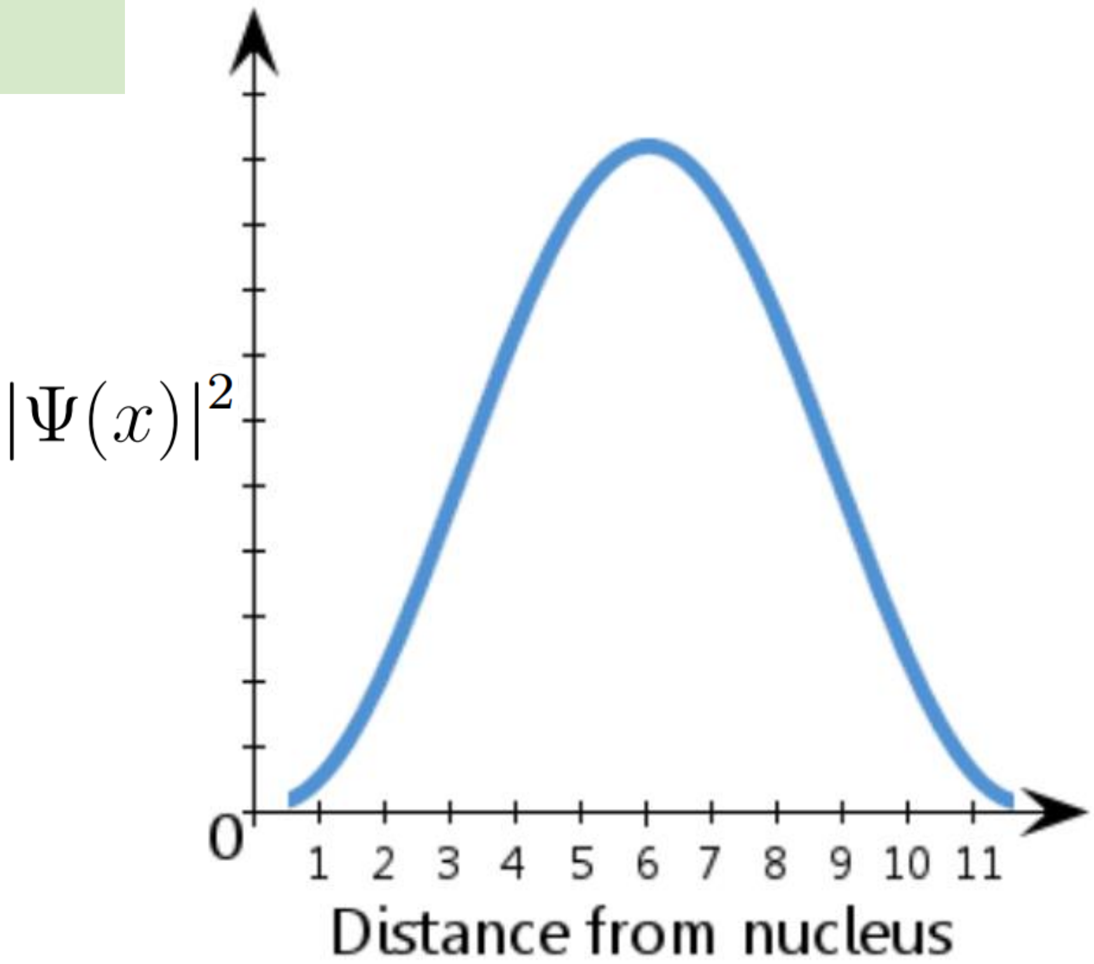
Since the wave function, in general, is a complex function we write

$$\boxed{|\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)}$$

$$|\Psi(x,t)|^2\mathrm{d}x = \left\{ \begin{array}{l} \text{probability of finding the particle} \\ \text{between } x \text{ and } (x+\mathrm{d}x)\text{, at time } t \end{array} \right\}$$

The Wave Function

A (fictitious) schematic diagram showing $|\Psi(x)|^2$ against distance from nucleus, in arbitrary unit.



There is a 100% probability that the electron is somewhere - in other words a probability of 1.

The Wave Function

The normalization condition of the wave function

$$\boxed{\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \mathrm{d}x = 1}$$

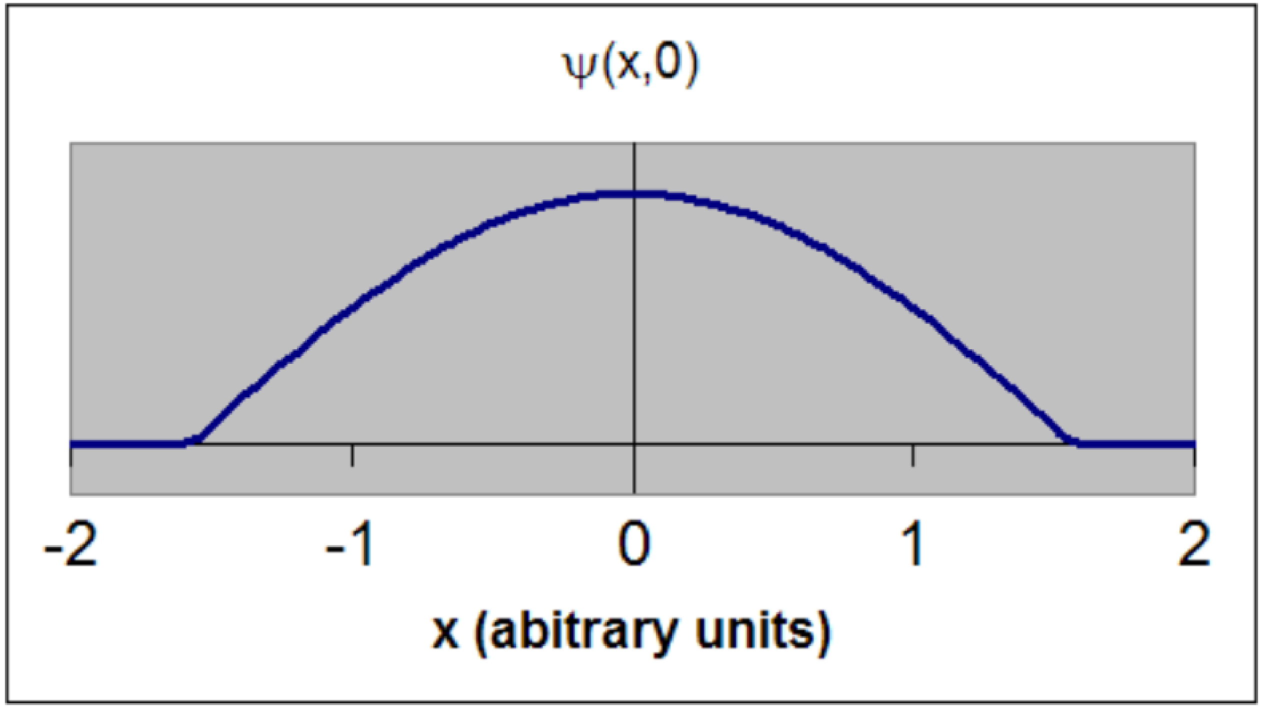
The wave function must be single valued and continuous.

The Wave Function

Single-valued wave function: $\Psi(x) = x^2$

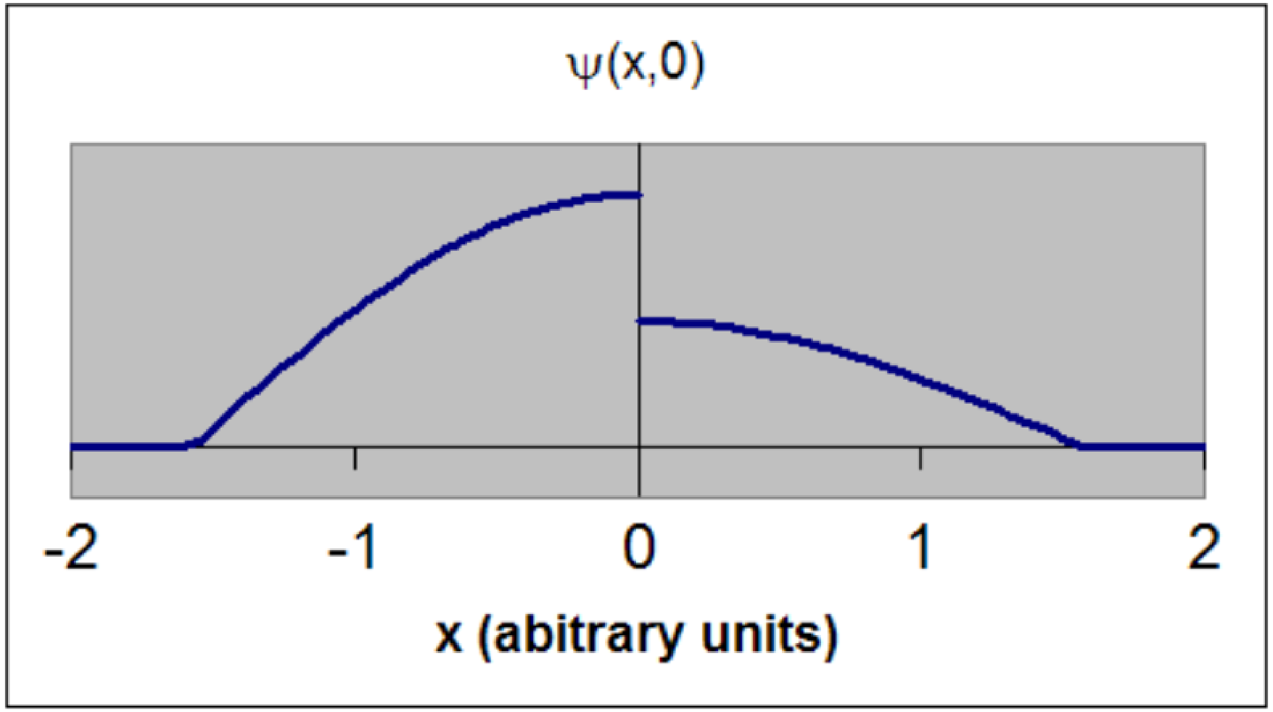
Multi-valued wave function: $\Psi(x) = \pm\sqrt{x}$

The Wave Function



This is an acceptable wave function.
It is single valued and continuous.

The Wave Function



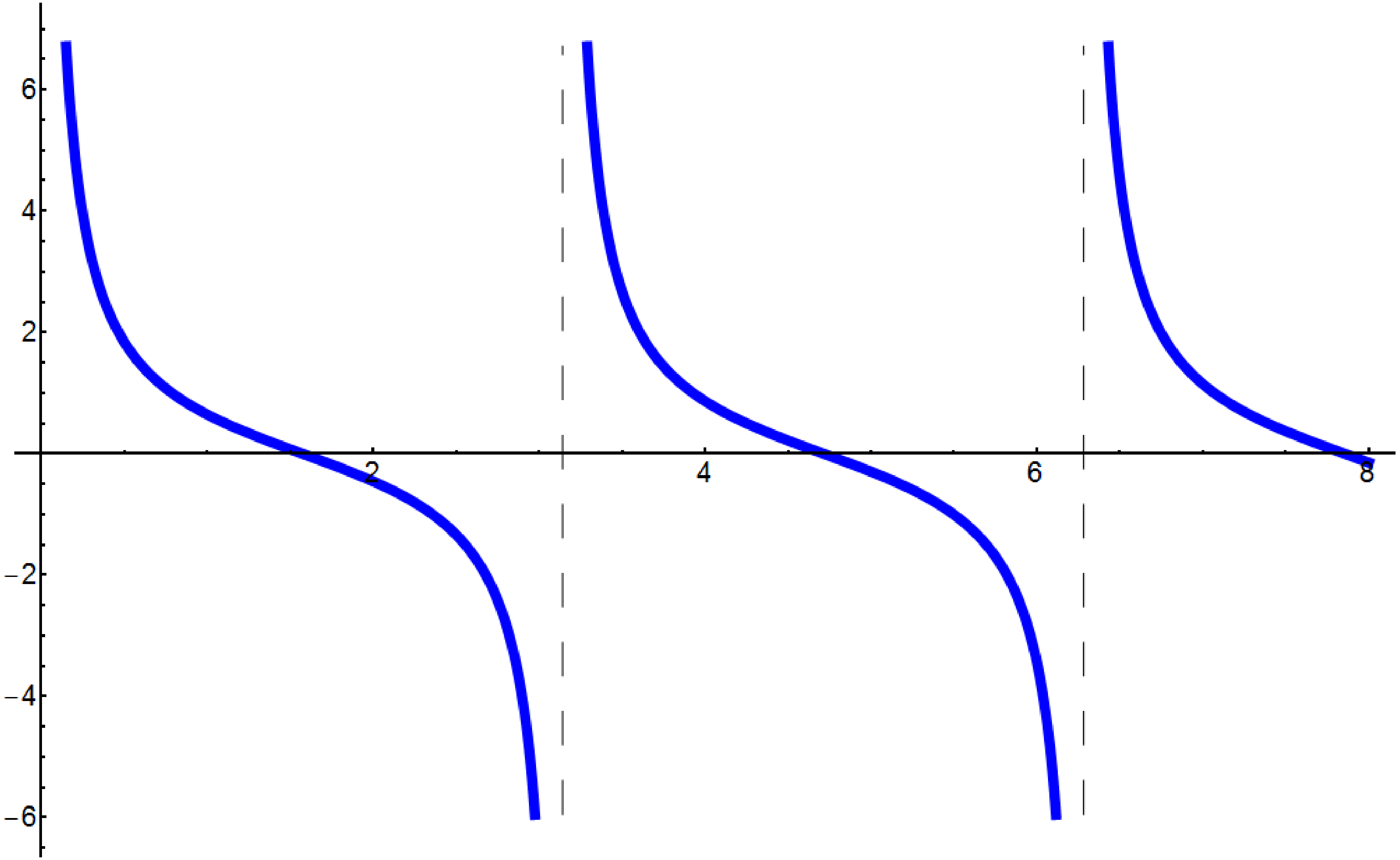
This is an unacceptable wave function. $\Psi(x,0)$ does not have a unique single value at $x = 0$. The wave function is not continuous.

The Wave Function

1. In order to avoid infinite probabilities, Ψ must be finite everywhere.
2. In order to avoid multiple values of the probability, Ψ must be single valued.
3. For finite potentials, Ψ and $\partial\Psi/\partial x$ must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when V is infinite.)
4. In order to normalize the wave functions, Ψ must approach zero as x approaches $\pm\infty$.

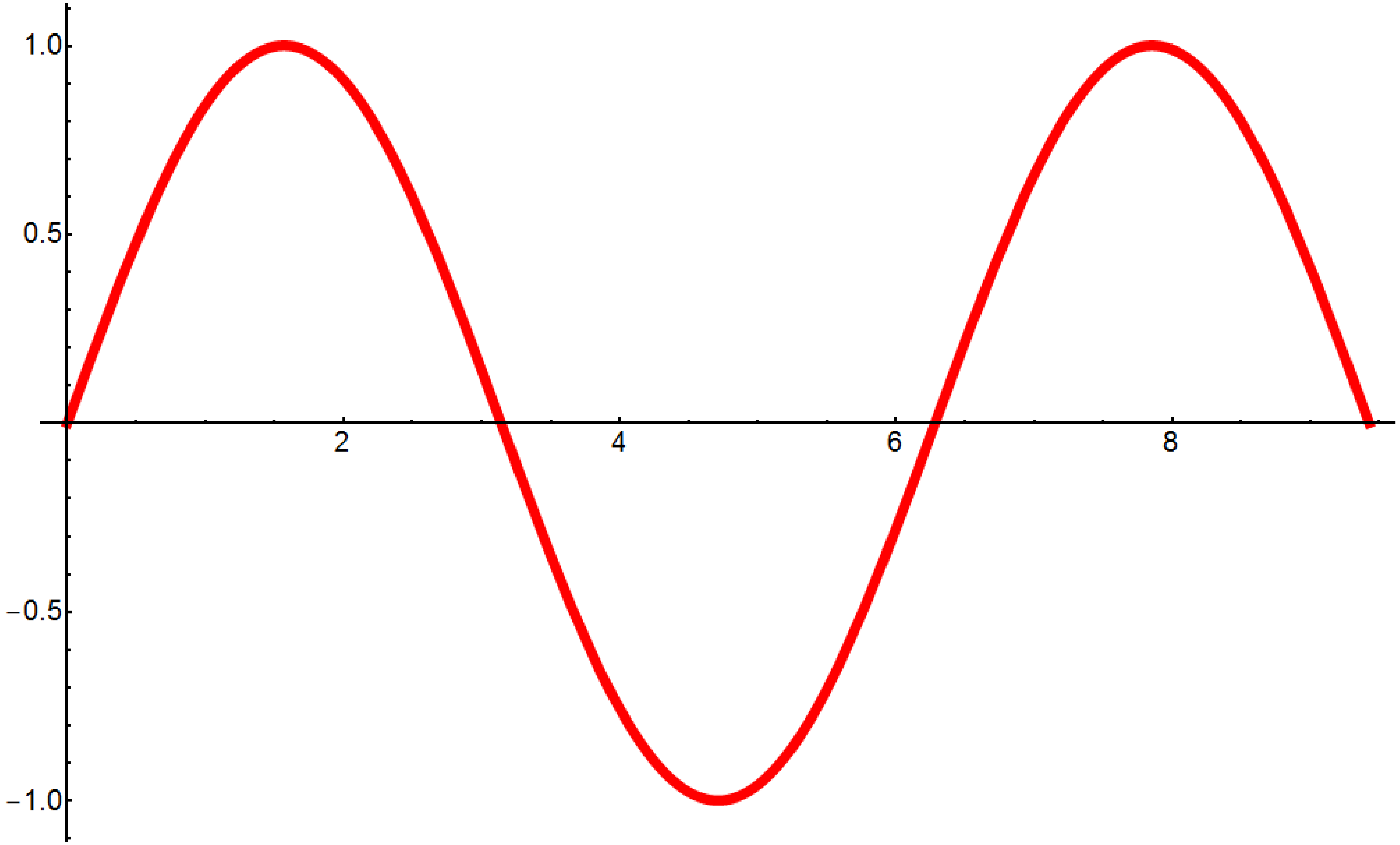
The Wave Function

$$\Psi(x) = A\cot x$$



The Wave Function

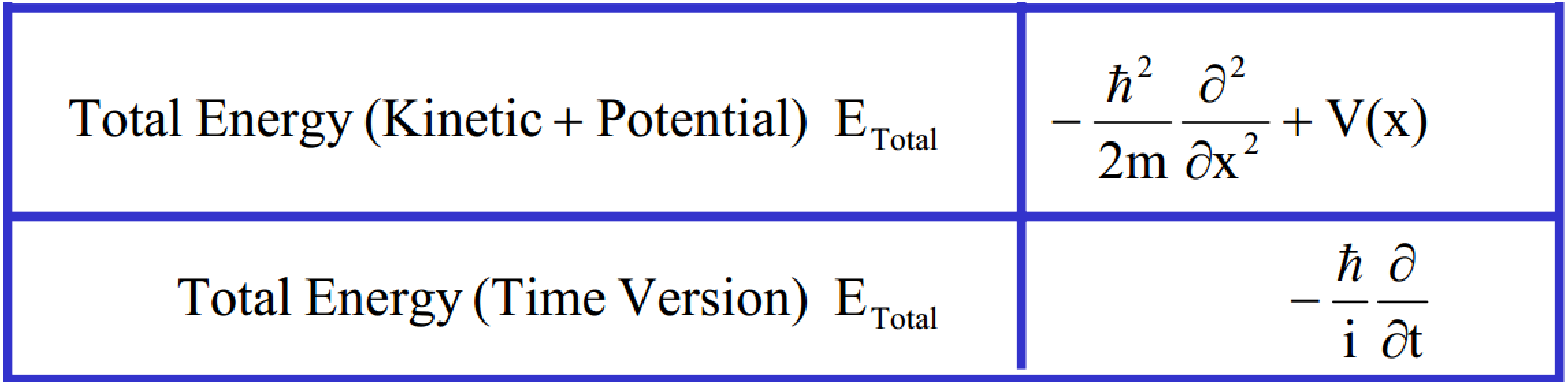
$$\Psi(x) = A\sin x$$



Operators in QM

Position x	x
Potential Energy $V(x)$	$V(x)$
Momentum p_x	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Kinetic Energy $\frac{p_x^2}{2m}$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

Operators in QM



Total Energy (Kinetic + Potential) E_{Total}	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)$
Total Energy (Time Version) E_{Total}	$-\frac{\hbar}{i}\frac{\partial}{\partial t}$

Heisenberg's Uncertainty Principle

Heisenberg’s Uncertainty Principle

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2}$$

$$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J s}$$

Heisenberg’s Uncertainty Principle

The uncertainty principle restricts the precision with which complementary observables may be specified and measured simultaneously.

$$\Delta x \propto \frac{1}{\Delta p_x}$$

Heisenberg's Uncertainty Principle

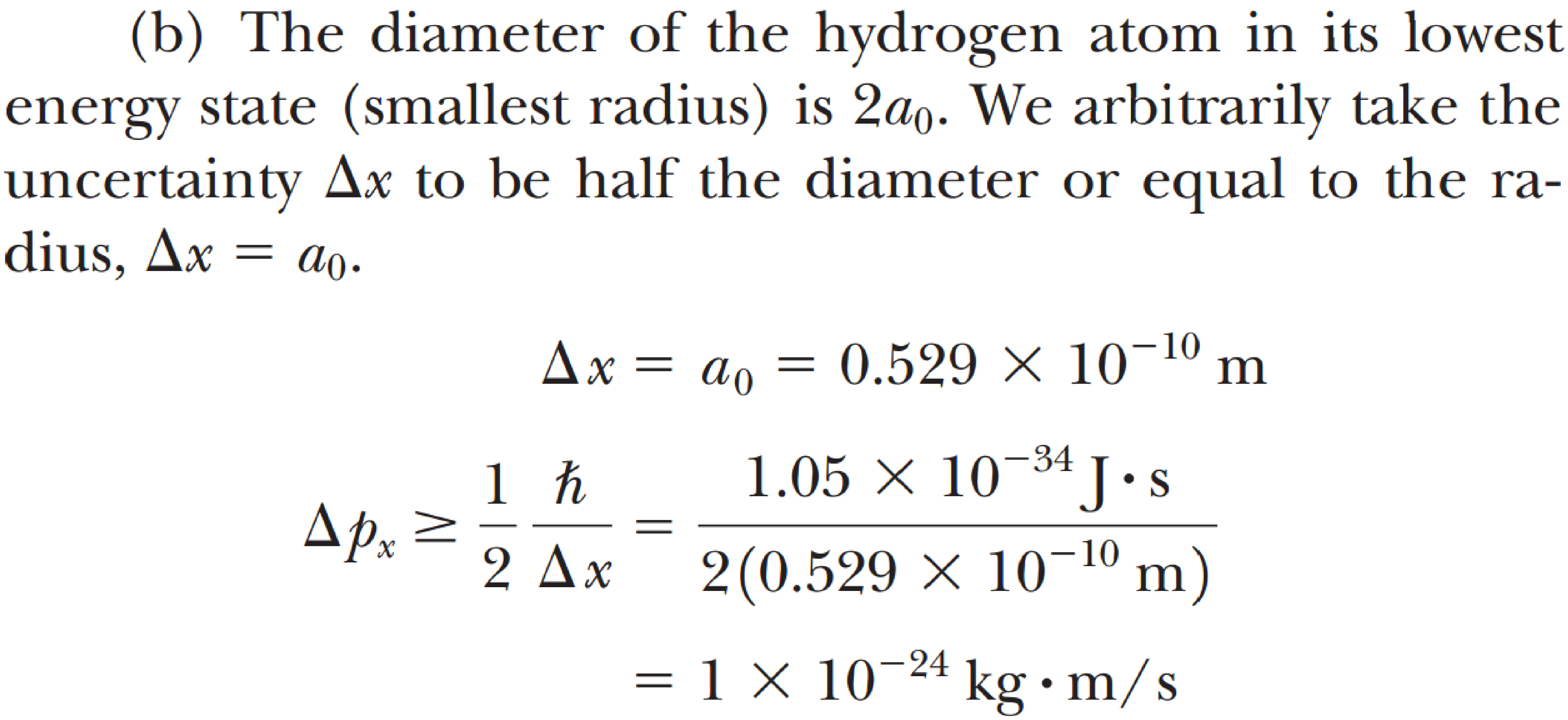
Calculate the momentum uncertainty of (a) a tennis ball constrained to be in a fence enclosure of length 35 m surrounding the court and (b) an electron within the smallest diameter of a hydrogen atom.

Uncertainty Principle

Solution (a) If we insert the uncertainty of the location of the tennis ball, $\Delta x = (35\ \text{m})/2$, into $\Delta p_x \Delta x \geq \hbar/2$, we have

$$\Delta p_x \geq \frac{1}{2}\frac{\hbar}{\Delta x} = \frac{1.05 \times 10^{-34}\ \text{J}\cdot\text{s}}{2(35\ \text{m})/2} = 3 \times 10^{-36}\ \text{kg}\cdot\text{m/s}$$

Uncertainty Principle



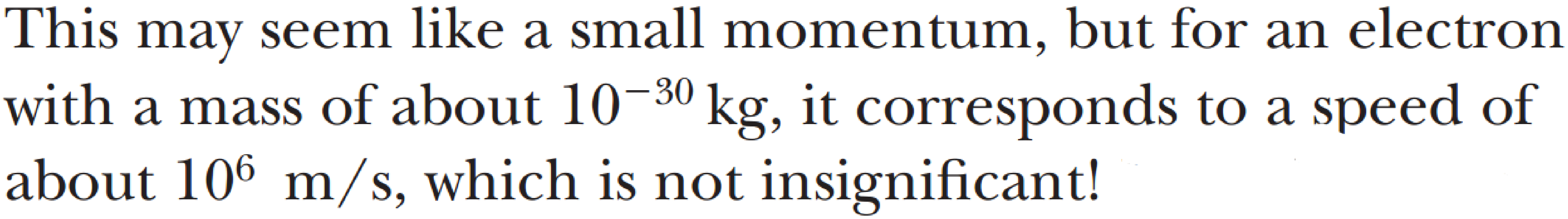
(b) The diameter of the hydrogen atom in its lowest energy state (smallest radius) is $2a_0$. We arbitrarily take the uncertainty Δx to be half the diameter or equal to the radius, $\Delta x = a_0$.

$$\Delta x = a_0 = 0.529 \times 10^{-10}\ \mathrm{m}$$

$$\Delta p_x \geq \frac{1}{2}\frac{\hbar}{\Delta x} = \frac{1.05 \times 10^{-34}\ \mathrm{J \cdot s}}{2(0.529 \times 10^{-10}\ \mathrm{m})}$$

$$= 1 \times 10^{-24}\ \mathrm{kg \cdot m/s}$$

Uncertainty Principle

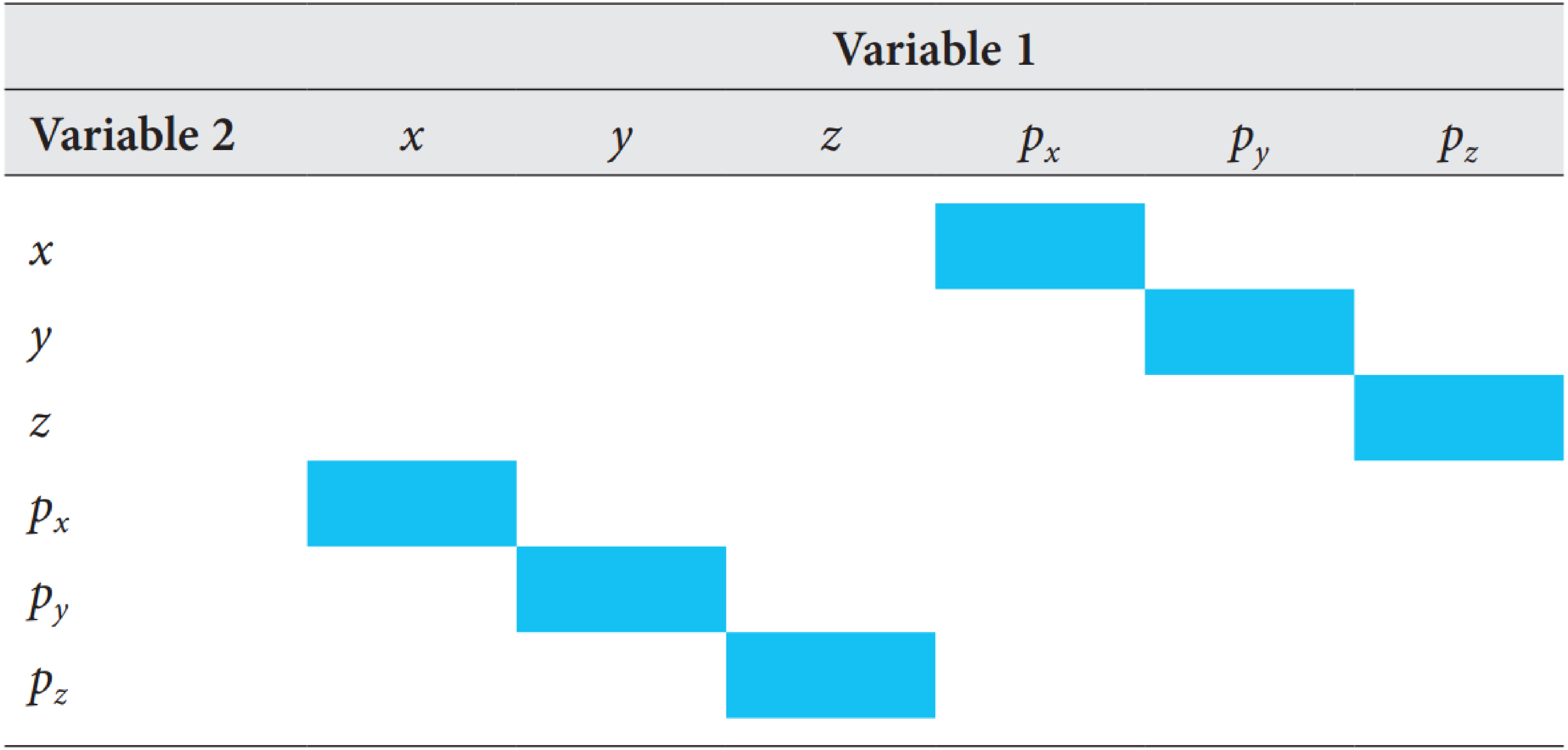


This may seem like a small momentum, but for an electron with a mass of about 10^{-30} kg, it corresponds to a speed of about 10^{6} m/s, which is not insignificant!

Heisenberg’s Uncertainty Principle

$$\boxed{\Delta x\,\Delta p_x \geq \frac{\hbar}{2}, \qquad \Delta y\,\Delta p_y \geq \frac{\hbar}{2}, \qquad \Delta z\,\Delta p_z \geq \frac{\hbar}{2}.}$$

Constraints of the uncertainty principle



	Variable 1					
Variable 2	x	y	z	p_x	p_y	p_z
x				🟦		
y					🟦	
z						🟦
p_x	🟦					
p_y		🟦				
p_z			🟦			

Energy-Time Uncertainty Principle

$$\boxed{\Delta E\,\Delta t \geq \frac{\hbar}{2}}$$

Uncertainty Principle

This relation states that if we make two measurements of the energy of a system and if these measurements are separated by a time interval Δt the measured energies will differ by an mount ΔE which can in no way be smaller than $\hbar / \Delta t$ If the time interval between the two measurements is large, the energy difference will be small.

Uncertainty Principle

We must emphasize that the uncertainties are intrinsic. They are not due to our inability to construct better measuring equipment. No matter how well we can measure, no matter how accurate an instrument we build, and no matter how long we measure, we can never do any better than the uncertainty principle allows.

The Postulates of Quantum Mechanics

The Postulates of QM

Postulate 1. The state of a quantum-mechanical system is completely specified by a wavefunction Ψ that depends on the coordinates and time. The square of this function $\Psi^*\Psi$ gives the probability density for finding the system with a specified set of coordinate values.

The wavefunction must be single-valued, finite and continuous.

$$\int \Psi^* \Psi \, d\tau = 1$$

The Postulates of QM

Postulate 2. Every observable in quantum mechanics is represented by a linear, hermitian operator.

A linear operator is one which satisfies the identity $\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\hat{A}\psi_1 + c_2\hat{A}\psi_2$

Postulate 3. In any measurement of an observable A, associated with an operator $\hat{A}$, the only possible results are the eigenvalues a_n, which satisfy an eigenvalue equation

$$\hat{A}\psi_n = a_n\,\psi_n$$

The Postulates of QM

Postulate 4. For a system in a state described by a normalized wave function Ψ , the average or expectation value of the observable corresponding to A is given by

$$\langle A \rangle = \int \Psi^* \, \hat{A} \, \Psi \, d\tau$$

Postulate 5. The wavefunction of a system evolves in time in accordance with the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \, \Psi$$

Time-dependent Schrödinger wave equation

$$i\hbar\frac{\partial\Psi(x,\,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,\,t)}{\partial x^2} + V\Psi(x,\,t)$$

Time-independent Schrödinger wave equation

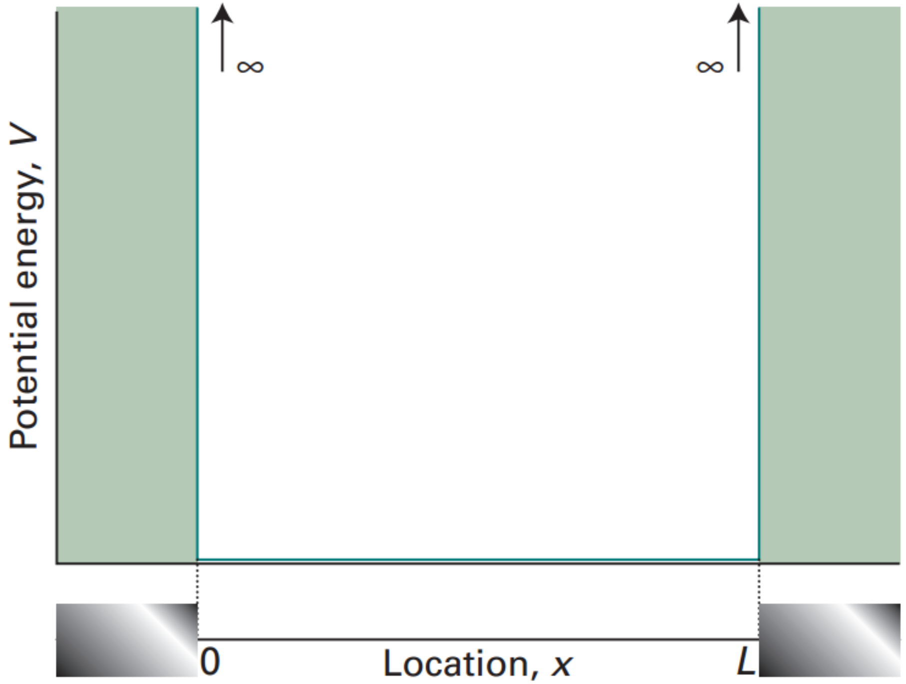
$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Infinite Square-Well Potential

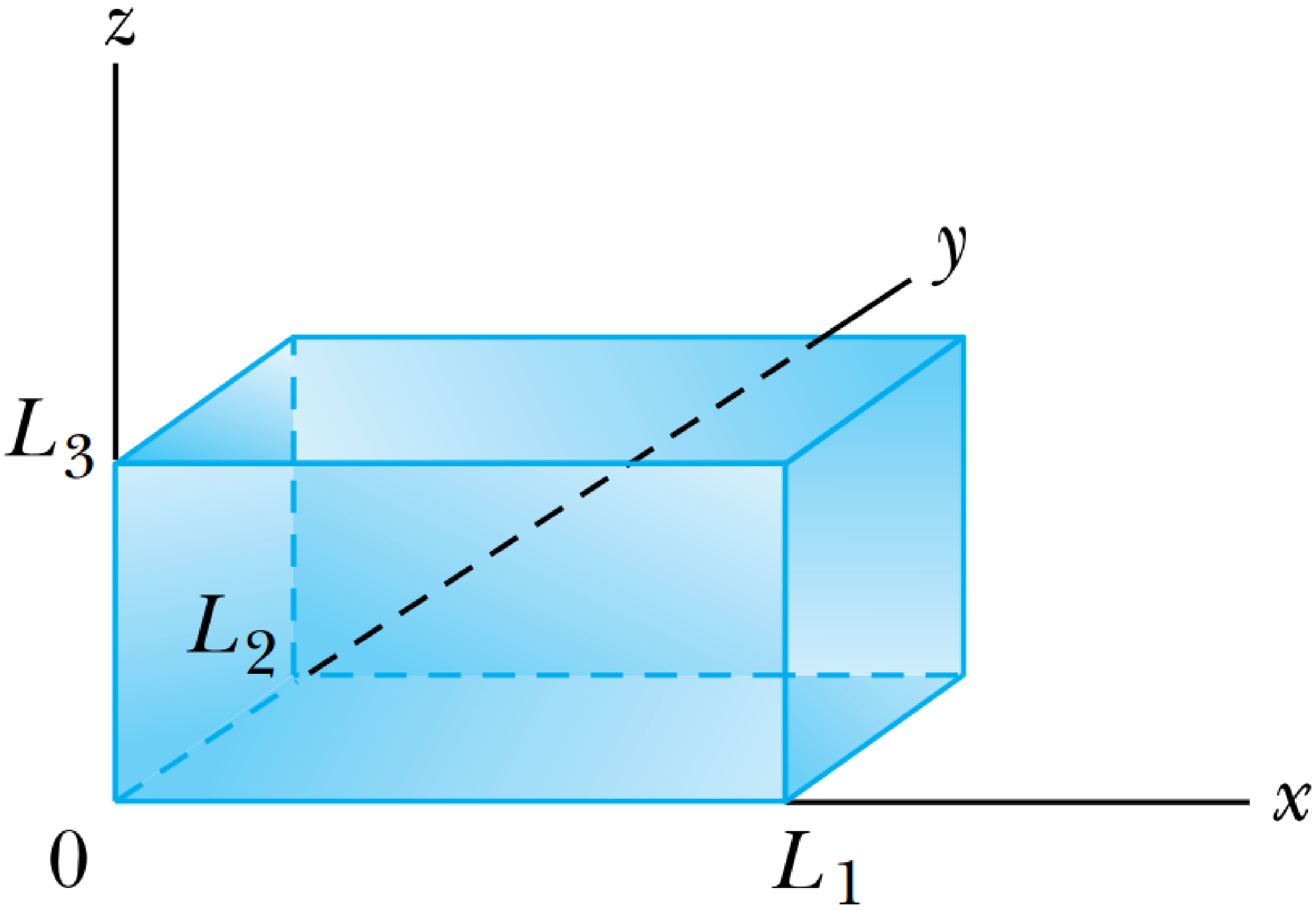
Particle in a Box in 1D

Infinite Square-Well Potential

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



Particle in a Box

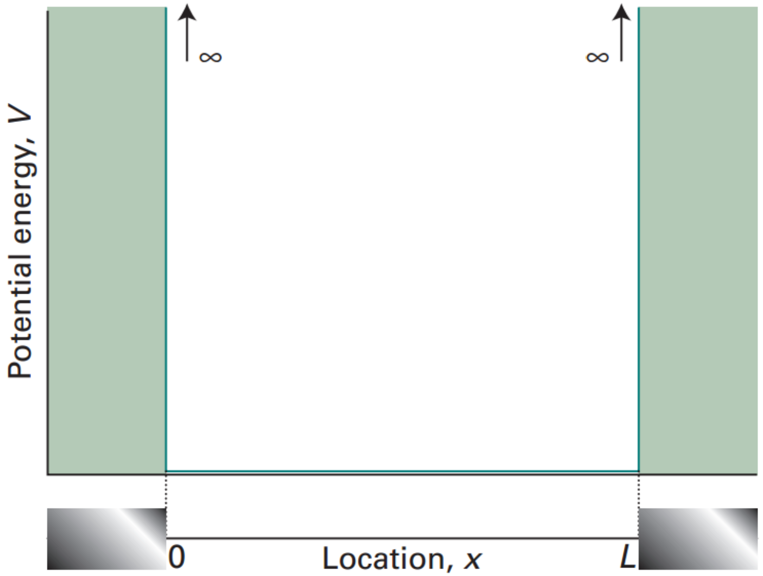


Infinite Square-Well Potential

One dimensional time-independent Schrödinger Equation

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

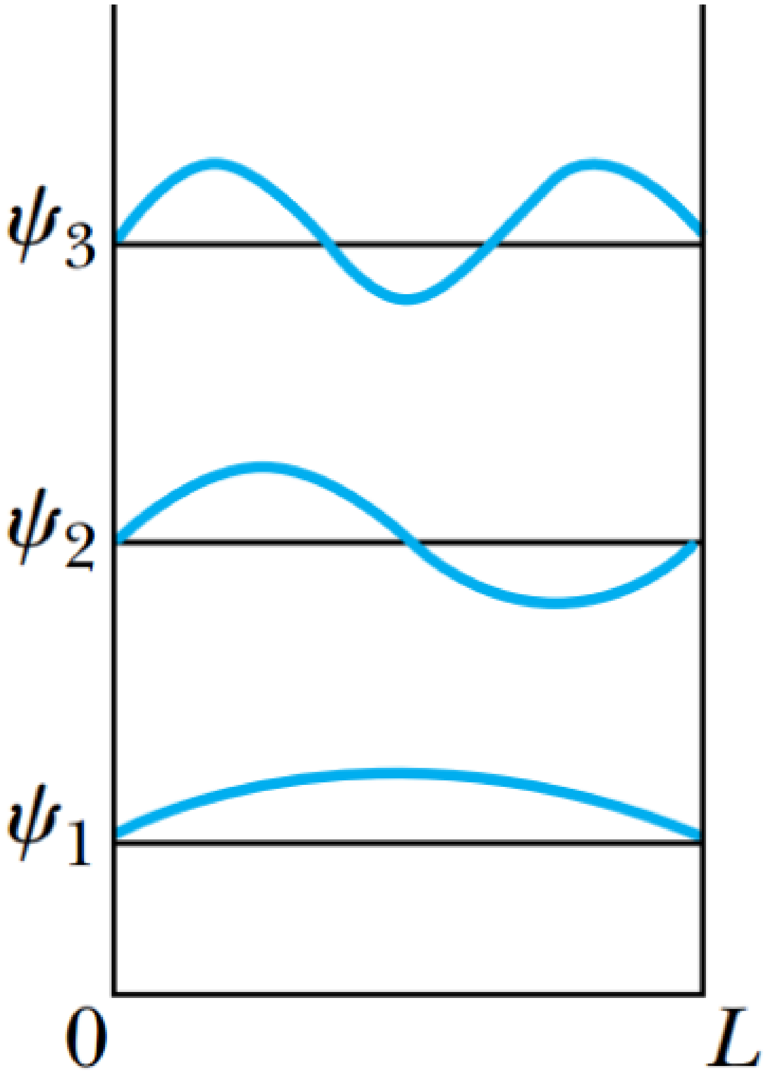
$$\boxed{-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x)}$$



Infinite Square-Well Potential

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

$$(n = 1, 2, 3, 4, \ldots)$$

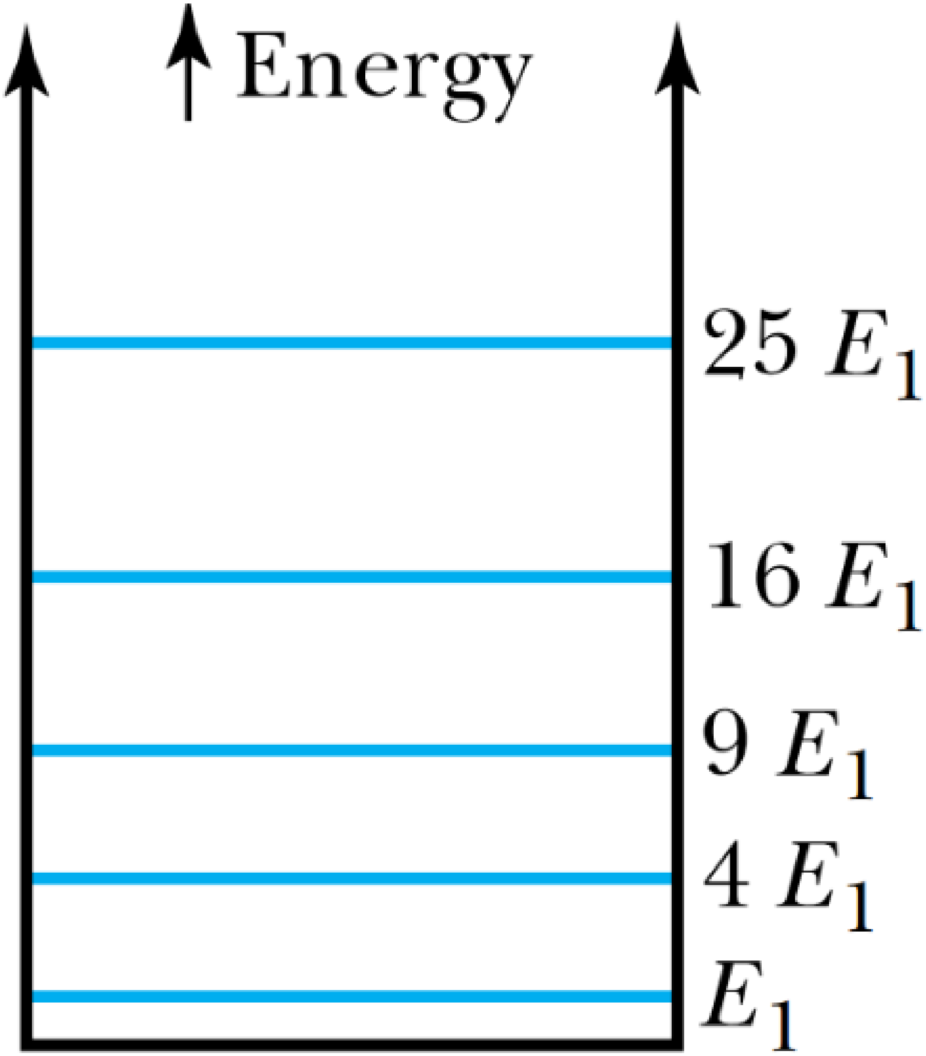


Infinite Square-Well Potential

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

$$(n = 1, 2, 3, 4, \ldots)$$

Quantized energy levels



Infinite Square-Well Potential

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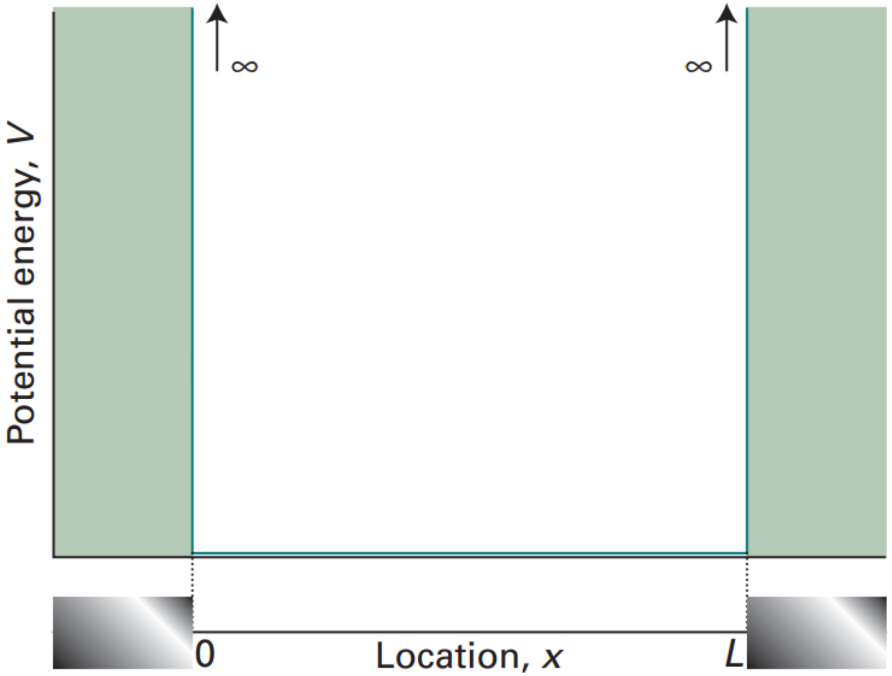

Three-Dimensional Infinite-Potential Well

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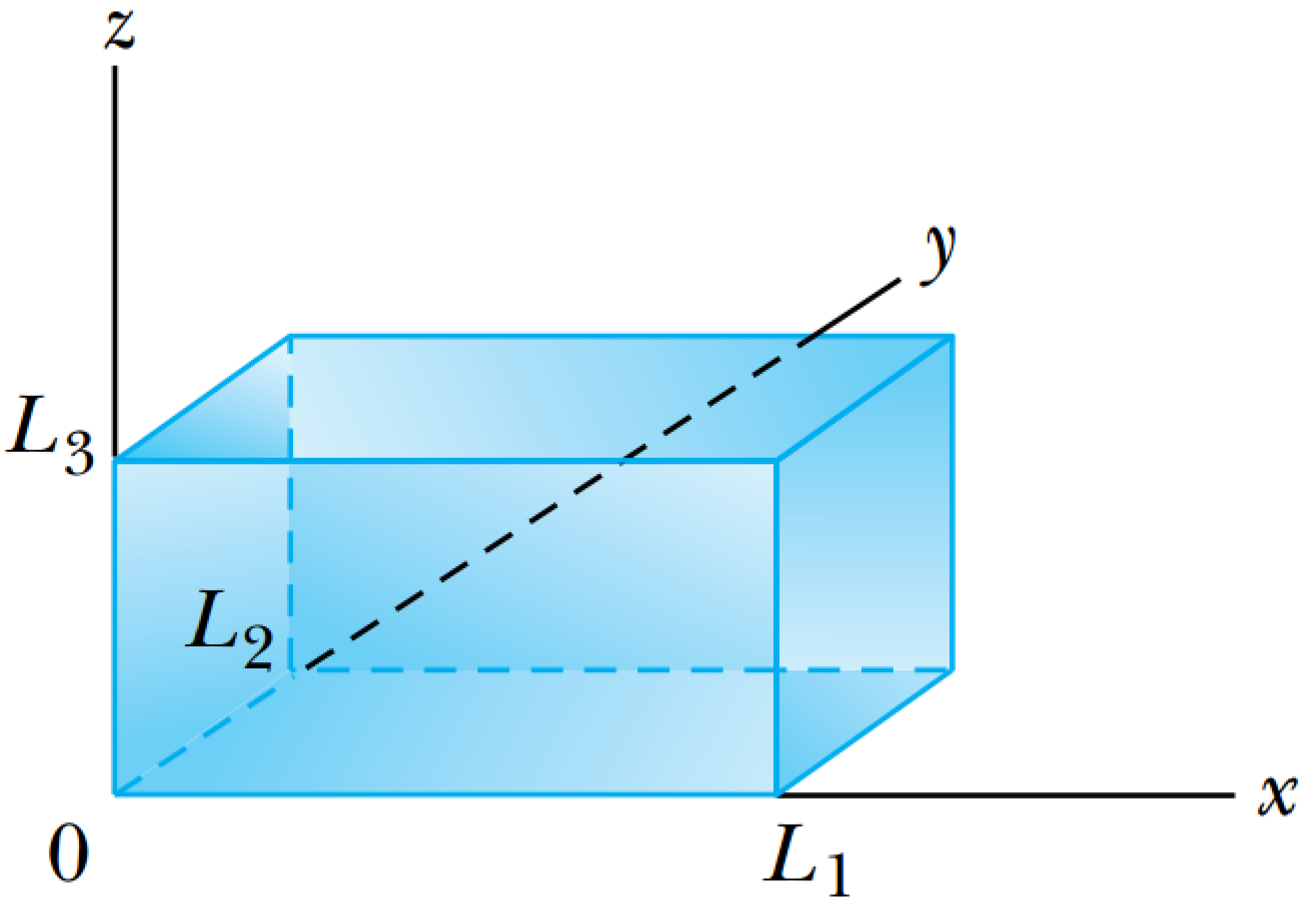
3D Infinite-Potential Well



Inside the box

$$V = 0$$

3D Infinite-Potential Well

$$\boxed{E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)}$$

For the *cubical* box, with $L_1 = L_2 = L_3 = L$.

$$\boxed{E = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)}$$

The allowed energy values depend on the values of the three quantum numbers n_1, n_2, and n_3.

3D Infinite-Potential Well

$$n_1 = n_2 = n_3 = 1$$

$$E_{\mathrm{gs}} = \frac{3\pi^2\hbar^2}{2mL^2}$$

$$\psi_{\mathrm{gs}} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

3D Infinite-Potential Well

What is the energy of the first excited state?

$$\boxed{E = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)}$$

$$E_{1\text{st}} = \frac{\pi^2\hbar^2}{2mL^2}(2^2 + 1^2 + 1^2) = \frac{3\pi^2\hbar^2}{mL^2}$$

3D Infinite-Potential Well

n_1	n_2	n_3	E
1	1	1	E_{gs}
2	1	1	$2E_{\text{gs}}$
1	2	1	$2E_{\text{gs}}$
1	1	2	$2E_{\text{gs}}$
2	2	1	$3E_{\text{gs}}$
2	2	2	$4E_{\text{gs}}$

$$E = \frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

$$\boxed{E_{\text{gs}} = \frac{3\pi^2\hbar^2}{2mL^2}}$$

Degenerate State

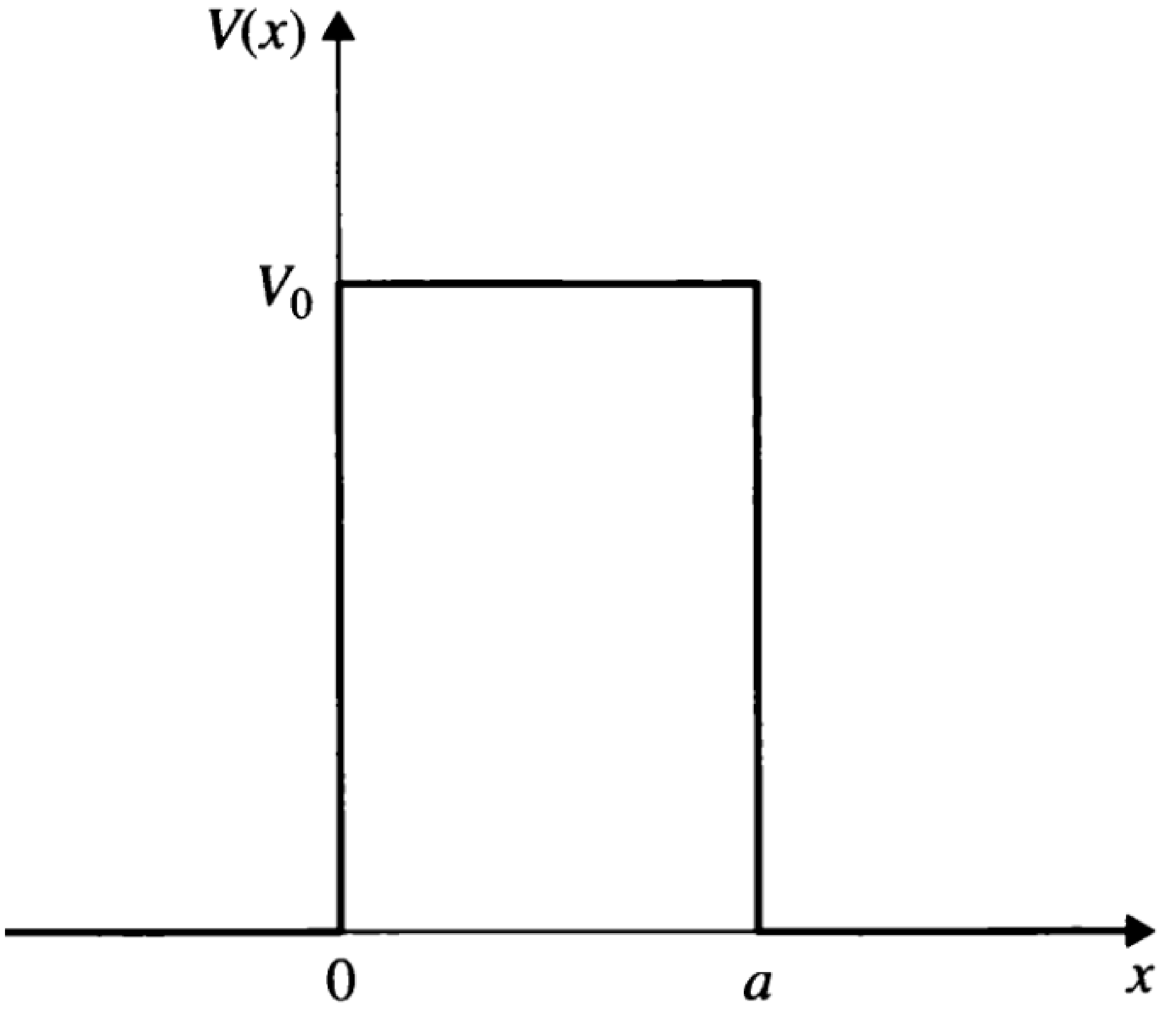
In physics we say that a given state is degenerate when there is more than one wave function for a given energy.

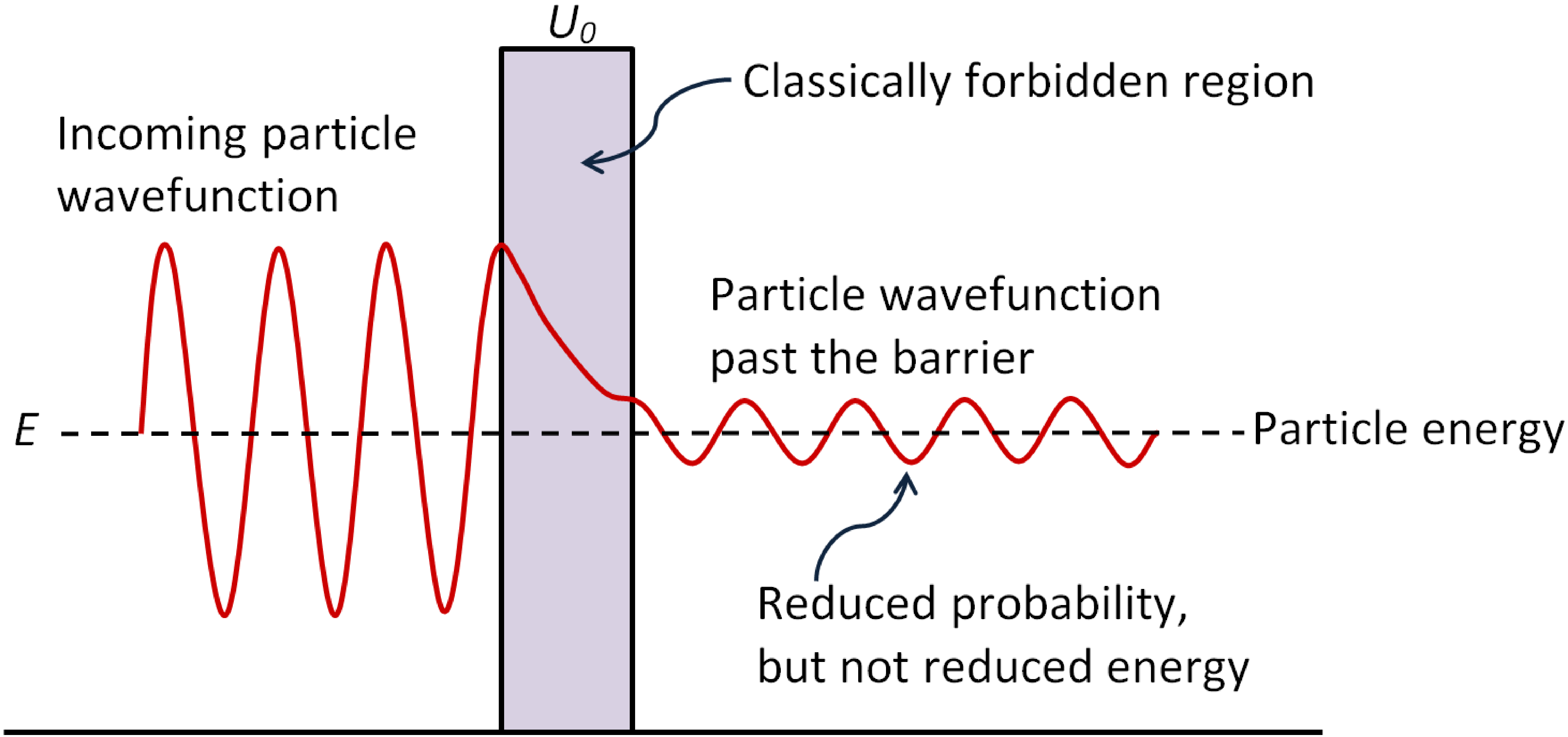
In our case all three possible wave functions for the first excited state have the same energy. The degeneracy in this case is a result of the symmetry of the cube.

If the box had sides of three different lengths, we say the degeneracy is removed, because the three quantum numbers in different orders (211, 121, 112) would result in three different energies.

The potential barrier

$$V(x) = \begin{cases} 0, & x < 0, \\ V_0, & 0 \leq x \leq a, \\ 0, & x > a. \end{cases}$$





U_0

Classically forbidden region

Incoming particle wavefunction

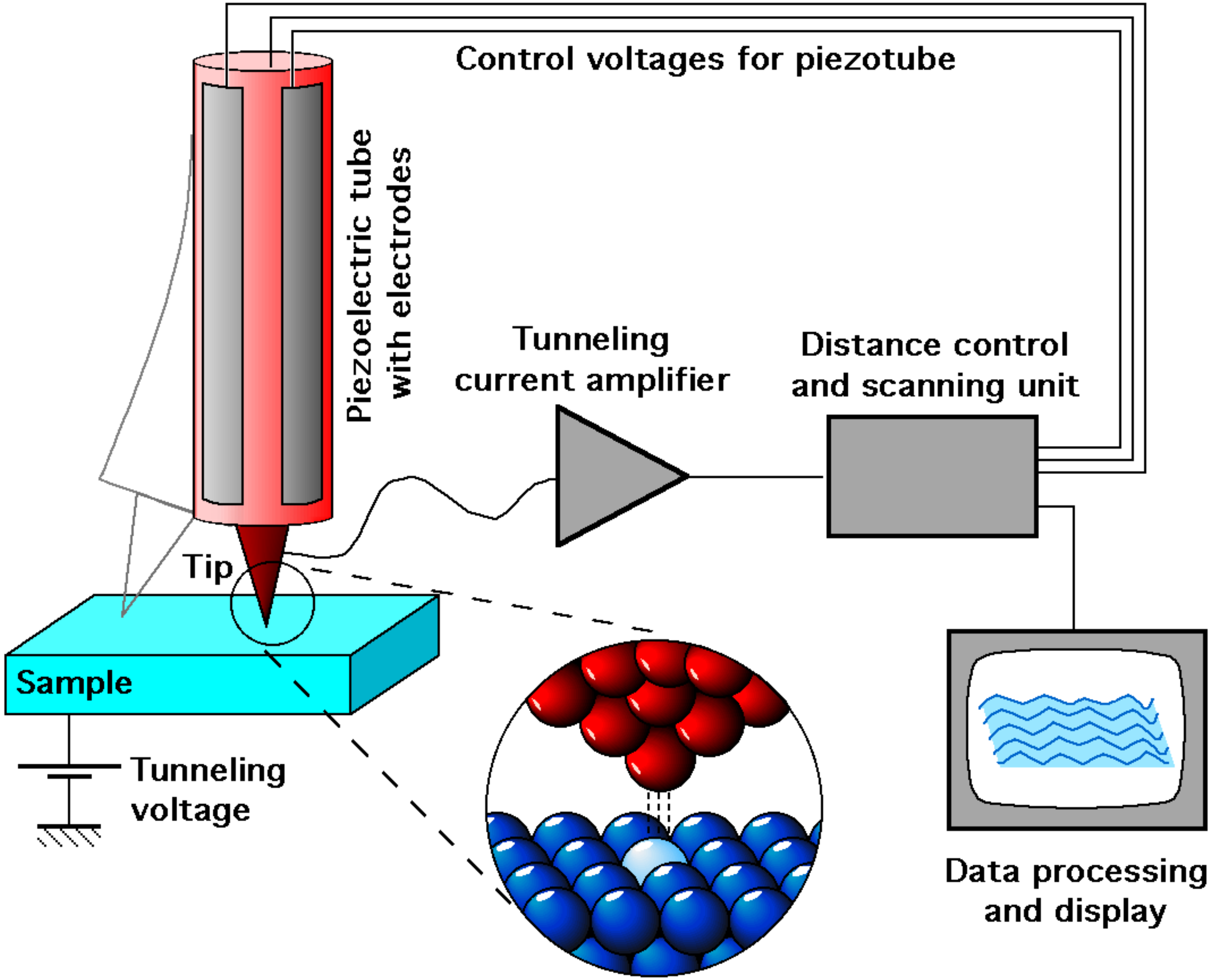
Particle wavefunction past the barrier

E

Particle energy

Reduced probability, but not reduced energy

Scanning tunnelling microscopy (STM)



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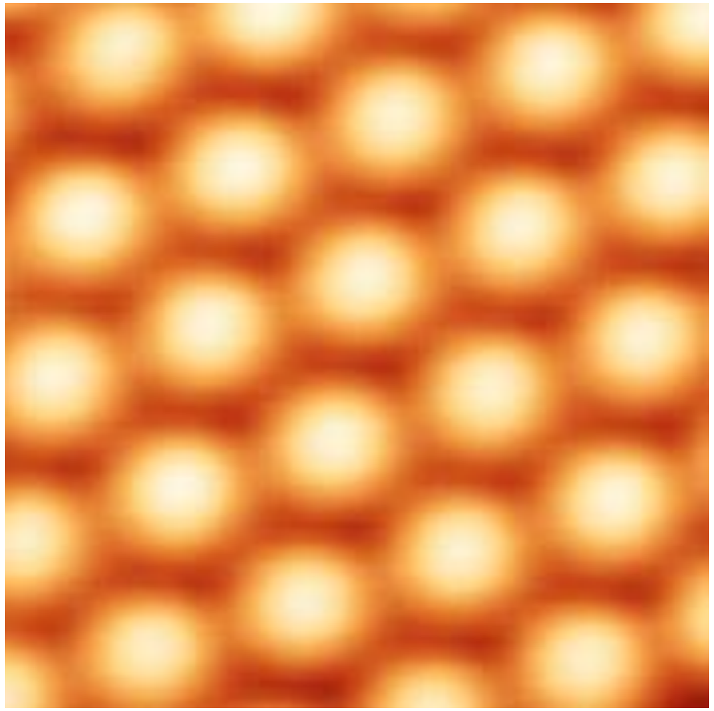
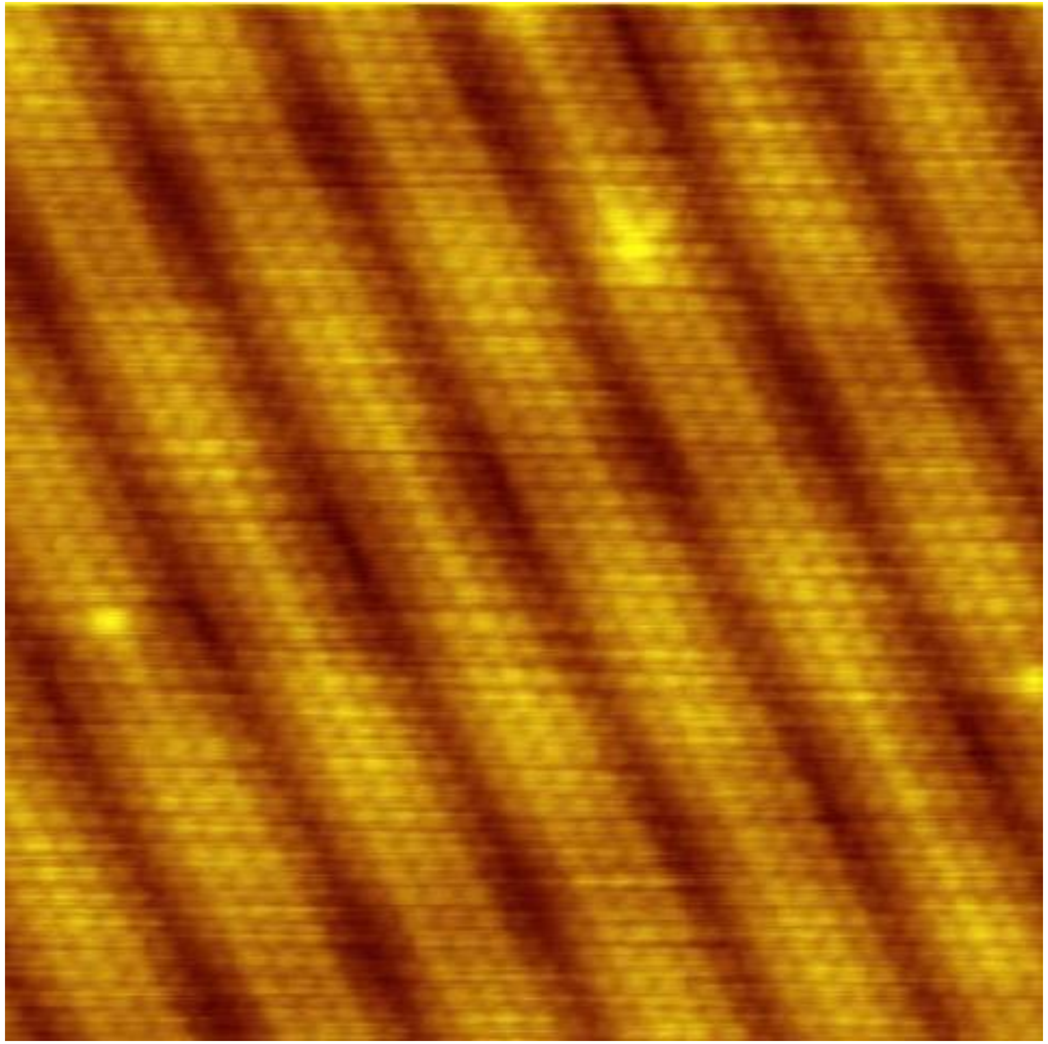
Si & Au as seen in STM





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