# APPLICATIONS OF QUANTUM MECHANICS

An important problem in Quantum Mechanics is how to use the time independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + U(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$

to determine the possible energy levels and the corresponding wave functions of various systems. The fundamental problem is then the following: for a given potential energy $U(x)$ what are the possible stationary-state wave functions $\psi(x)$ and what are the corresponding energies $E$.

## 1) Free particle

$U(x) = 0$

the particle is moving along a line, freely

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

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

wave vector $\in \mathbb{R}$

$$\left(E = \frac{p^2}{2m} \quad p = \hbar k\right)$$

The solution of that equation

$$\boxed{\psi = Ae^{ikx}} + Be^{-ikx}$$

$\longrightarrow$ propagative plane wave along $+x$

$$\Rightarrow \boxed{\psi(x) = Ae^{ikx}}$$

free particle described as a plane wave.

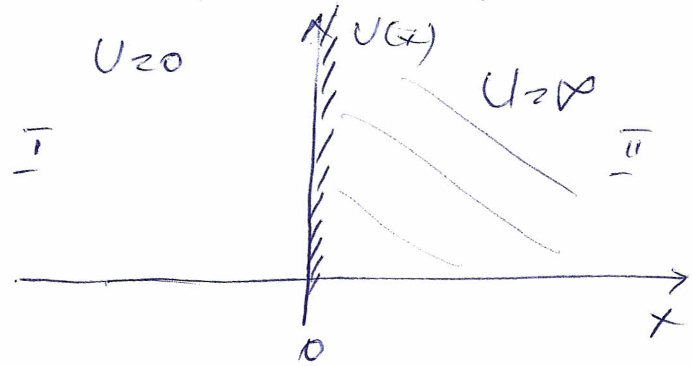
and $E = \dfrac{\hbar^2 k^2}{2m}$ can have any value from zero to infinity

Furthermore, the particle can be found with equal probability at any value $x$ from $-\infty$ to $+\infty$

$$|\psi(x)|^2 = \psi^*(x)\,\psi(x) = A^* e^{-ikx} A e^{ikx} = |A|^2$$

## (2) The infinite step

$\Longleftrightarrow$ stationary waves on a string




$$U(x) = \begin{cases} 0 & x<0 \quad (\mathrm{I}) \\ \infty & x>0 \quad (\mathrm{II}) \end{cases}$$

The particle propagates along $+x$ and is completely reflected by an infinite potential wall at $x=0$

We write the Schrödinger equation for the regions $\underline{\mathrm{I}}$ and $\underline{\mathrm{II}}$

$(\underline{\mathrm{I}})$ $U(x)=0$ $\Rightarrow -\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} = E\psi$

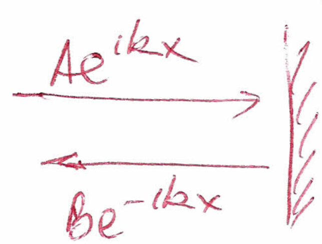
has the general form: $\dfrac{d^2\psi}{dx^2} + k^2\psi = 0$

with $k = \sqrt{\dfrac{2mE}{\hbar^2}}$

$\Rightarrow$ general solution $\boxed{\psi(x) = \underbrace{Ae^{ikx}}_{\text{incident}} + \underbrace{Be^{-ikx}}_{\text{reflected}}}$

incident plane wave propagating along $+x$

reflected wave propagating along $-x$




$\psi(x)$ = superposition of two waves (incident and reflected) $\Rightarrow$ stationary wave. (see analogy with wave on a string)

In region (II) $\quad U(x) = \infty$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right)\psi = E\psi$$ possible only if $\psi(x) = 0$

$\Rightarrow |\psi(x)|^2 = 0$ for $x > 0$

$\Rightarrow$ the particle is fully reflected in $x = 0$, it does not exist for $x > 0$

For $x < 0$ we can calculate $A, B$ from the condition:

$\psi(x)\big|_{x=0} = 0$ (continuity of the wave function)

$\Rightarrow \quad A + B = 0 \quad \Rightarrow A = -B$

$\Rightarrow \boxed{\psi(x) = A\left(e^{ikx} - e^{-ikx}\right)}$ stationary wave.

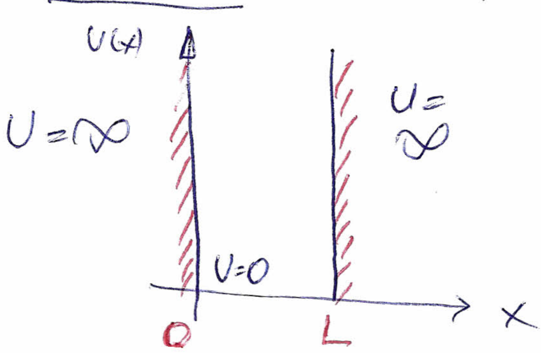
and energy $\boxed{E = \frac{\hbar^2 k^2}{2m}}$

## ③ Particle in a 1D box

$\Leftrightarrow$ standing waves in a string

Let's look to a simple model in which a particle is bound, so it cannot escape to infinity but is rather constricted in a certain region of space (e.g. simplified model for an $e^-$ surrounding the nucleus)

Model $\quad U(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x < 0 \text{ and } x > L \end{cases}$



We write the Schrödinger equation for <u>outside</u> and <u>inside</u> regions:

outside: $U(x) = \infty$ $\quad \hat{H}\psi = E\psi$ possible only if $\psi(x) = 0$

inside: $U(x) = 0$ $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \Leftrightarrow$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0}$$

$$k^2 = \frac{2m}{\hbar^2}E$$

has the general solution:

$$\psi(x) = \underset{\longrightarrow}{Ae^{ikx}} + \underset{\longleftarrow}{Be^{-ikx}}$$

superposition of 2 waves travelling along $+x$ and $-x$
$\Rightarrow$ standing wave

$x = 0 \quad \psi(x) = 0 \Rightarrow A = -B$

$x = L \quad \psi(x) = 0 \Rightarrow A(e^{ikL} - e^{-ikL}) = 0$

$2iA \sin kL = 0 \quad \Rightarrow \sin kL = 0$

$\Leftrightarrow kL = n\pi$

$n = 1, 2, \ldots$

$$\Rightarrow \boxed{k_n = \frac{n\pi}{L}}$$

quantification for the wave number
$\Rightarrow$ energy quantification

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

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

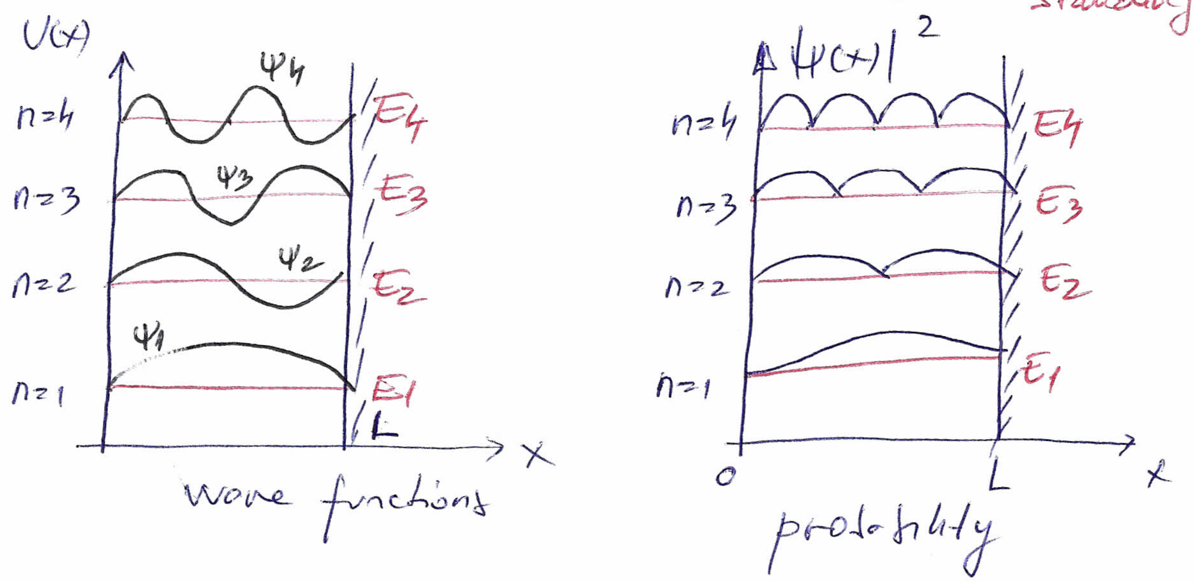
energy levels for the particle in the box

The wave functions:

$$\psi_n(x) = \underbrace{2iA}_{C} \sin k_n x = C \sin k_n x$$

$$\Rightarrow \boxed{\psi_n(x) = C \sin \frac{n\pi x}{L}}$$

bounded particle $\Leftrightarrow$ particle in a box described as a standing wave.




## Probability and normalization

$$|\psi(x)|^2 dx = C^2 \sin^2 \frac{n\pi x}{L} dx$$

The particle has to be somewhere between $-\infty$ and $+\infty$

$\Rightarrow$ the normalization condition:

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

Since $\psi(x) = 0$ for $x < 0$ and $x > L$

$$\Rightarrow \int_0^L C^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

we use $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

$$\Rightarrow C^2 \frac{L}{2} = 1 \Rightarrow C = \sqrt{\frac{2}{L}} \Rightarrow$$

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

$n = 1, 2, \ldots$

normalized wave function for particle in the box.

## Time dependence

If we know the stationary solution $\Psi(x)$, one can write the time-dependent solution (stationary state)

$$\boxed{\Psi_n(x,t) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) e^{-\frac{iE_n t}{\hbar}}}$$

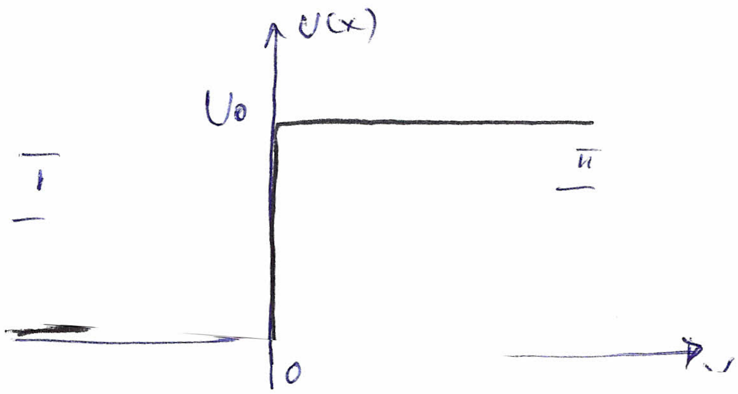
$$\underbrace{\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)}_{\text{time independent solution}} \times \underbrace{e^{-\frac{iE_n t}{\hbar}}}_{\text{phase factor}}$$

→ oscillates in time with frequency $\omega_n = \frac{E_n}{\hbar}$

since $|\Psi(x,t)|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)\underbrace{\left|e^{-\frac{iE_n t}{\hbar}}\right|^2}_{1}$

$= \Psi(x)$ independent on time and does not oscillate in time ⇒ Stationary state.

## ④ Finite potential step




$$U(x) = \begin{cases} 0 & x < 0 \\ U_0 & x > 0 \end{cases}$$

The Schrödinger eq for the two regions is:

$$\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi & (\mathrm{I}) \\ -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + U_0\Psi = E\Psi & (\mathrm{II}) \end{cases}$$

$$\Rightarrow \begin{cases} \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 & (\underline{i}) \quad x < 0 \\ \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U_0)\psi = 0 & (\underline{ii}) \quad x > 0 \end{cases}$$

(1) If $E < U_0$ ; the eq become:

$$\begin{cases} \frac{d^2\psi}{dx^2} + k_1^2\psi = 0 & k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad x < 0 \\ \frac{d^2\psi}{dx^2} + k_2\psi = 0 & k_2 = \sqrt{\frac{2m}{\hbar^2}(E - U_0)} \in \mathbb{C} \\ & = iK \end{cases}$$

The ~~solution~~ are:

$$\boxed{\psi_{\underline{I}}(x) = \underbrace{Ae^{ik_1x}}_{\text{incident wave}} + \underbrace{Be^{-ik_1x}}_{\text{reflected wave}}} \quad x < 0$$

$\Rightarrow$ standing wave

$$\psi_{\underline{II}}(x) = Ce^{Kx} + De^{-Kx}$$

cannot be zero in $x = +\infty$ otherwise the norm $|\psi(x)|^2$ diverges $\Rightarrow C = 0$

$$\Rightarrow \boxed{\psi_{\underline{II}}(x) = De^{-Kx}}$$

evanescent wave

Obs: The constants $A, B, D$ can be deduced from the continuities of wave function and its derivatives in $x = 0$ + the normalization condition.

$$\begin{cases} \psi_{I}(x)\Big|_{x=0} = \psi_{II}(x)\Big|_{x=0} \\ \dfrac{d\psi_I}{dx}\Big|_{x=0} = \dfrac{d\psi_{II}(x)}{dx}\Big|_{x=0} \end{cases}$$

$$\Rightarrow \begin{cases} A+B=D \\ ik(A-B) = -KD \end{cases} \Rightarrow \begin{cases} A = \dfrac{D}{2k_1}(k_1+iK) \\ B = \dfrac{D}{2k_1}(k_1-iK) \end{cases}$$

$$\Rightarrow \begin{cases} \psi_I(x) = \underbrace{\dfrac{D}{2k_1}(k_1+ik)\,e^{ik_1x}}_{\text{incident}} + \underbrace{\dfrac{D}{2k_1}(k_1-iK)\,e^{-ik_1x}}_{\text{reflected wave}} \\ \psi_{II}(x) = De^{-Kx} \quad \text{evanescent wave} \end{cases}$$

<u>obs</u>: In the region II the probability to find the particle

$\boxed{|\psi_{II}(x)|^2 = D^2e^{-2Kx} \neq 0}$ and decays exponentially with $x$

has no classical analogy because classically if $E<U_0$ the particle should be fully reflected.

## Reflexion and transmission coefficients

The <u>transmission coefficient</u> T and <u>the reflexion coeff. R</u> are used to describe the behavior of waves incident to a barier.

$$\begin{cases} T = \dfrac{\vec{j}_{trans} \cdot \vec{n}}{\vec{j}_{inc} \cdot \vec{n}} \\ R = \dfrac{\vec{j}_{refl}\,(-\vec{n})}{\vec{j}_{inc} \cdot \vec{n}} = \dfrac{|j_{refl}|}{|j_{inc}|} \end{cases}$$

$\vec{n}$ = unit normal vector on the barrier

Probability conservation implicates $R + T = 1$

$j_{inc}$, $j_{refl}$, $j_{transm}$ = probability flux of - incident wave, - reflected, - refracted

$$j(x,t) = -\frac{i\hbar}{2m}\psi^* \frac{d\psi}{dx} \Rightarrow$$

$$\begin{cases} j_{inc} = |A|^2 \dfrac{\hbar k_1}{m} \\ j_{refl} = |B|^2 \dfrac{\hbar k_1}{m} \\ j_{transm} = |D|^2 \dfrac{\hbar k_2}{m} = |D|^2 \dfrac{\hbar i k}{m} \end{cases}$$

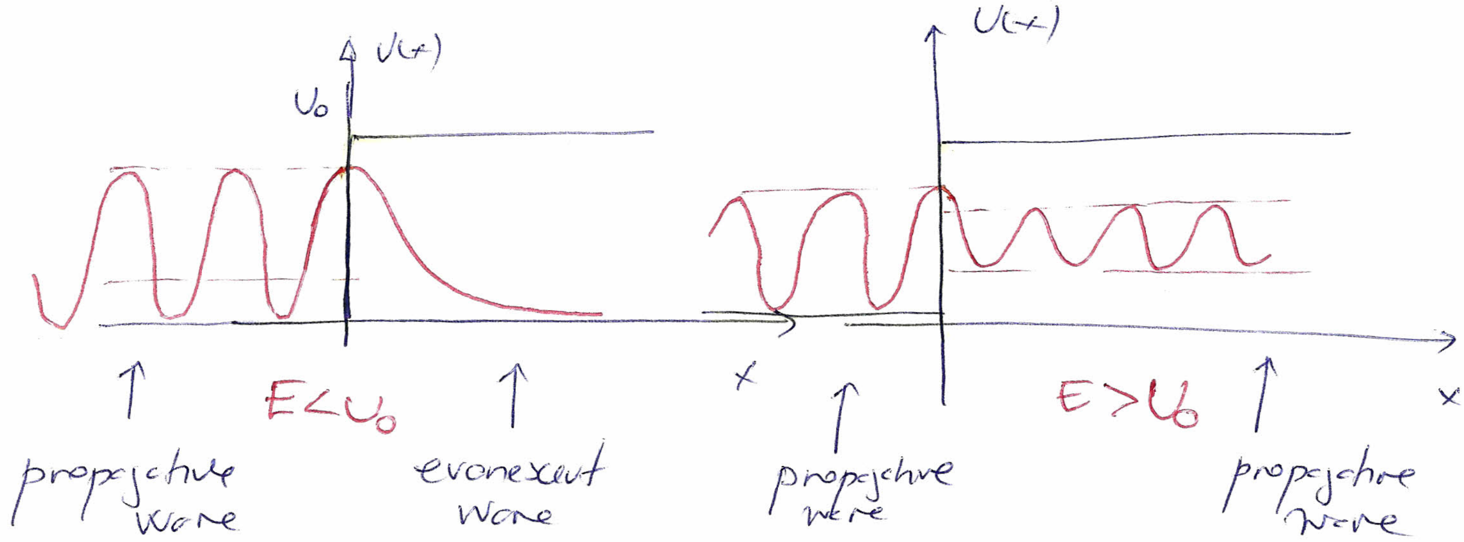
$$\Rightarrow \begin{cases} R = \dfrac{|B|^2}{|A|^2} = \left|\dfrac{k_1 - ik}{k_1 + ik}\right|^2 \\ T = 1 - R = \dfrac{4 k_1 k}{|k_1 + ik|^2} \end{cases}$$

② If $E > U_0$

$$\begin{cases} \dfrac{d^2\psi}{dx^2} + k_1^2 \psi = 0 & k_1 = \sqrt{\dfrac{2mE}{\hbar^2}} \in \mathbb{R} \quad x < 0 \\ \dfrac{d^2\psi}{dx^2} + k_2^2 \psi = 0 & k_2 = \sqrt{\dfrac{2m(E-U_0)}{\hbar^2}} \in \mathbb{R} \quad x > 0 \end{cases}$$

$$\Rightarrow \begin{cases} \psi_I(x) = \underset{\longrightarrow}{A e^{ik_1x}} + \underset{\longleftarrow}{B e^{-ik_1x}} \\ \psi_{II}(x) = \underset{\longrightarrow}{C e^{ik_2x}} + \cancel{\underset{\longleftarrow}{D e^{-ik_2x}}} \end{cases}$$

no reflexion in $+\infty$



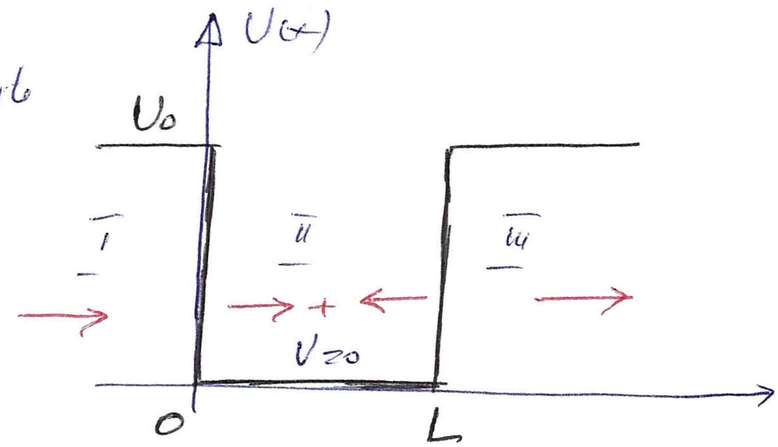

Obs: • In case when $E > U_0$ the incident wave will have a reflexion in $x=0$ and continue as propagative wave in region II.

• One can similarly calculate the reflexion and the transmitted coefficients $R$, $T$.

## (5) Potential wells (finite)

A potential well is a potential energy function that has a minimum

rectangular finite well




$$U(x) = \begin{cases} U_0 & x<0,\ x>L \\ 0 & 0<x<L \end{cases}$$

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

has to be solved in the three regions (2 outside + 1 inside)

### $E < U_0$

Following the calculations performed for the infinite well and finite step we get:

$$\begin{cases} \psi_I(x) = \underbrace{Ae^{Kx}}_{\text{incident evanescent wave}} + \cancel{Be^{-Kx}} \\ \psi_{II}(x) = \underbrace{Ce^{ikx}}_{\text{incident plane wave}} + \underbrace{De^{-ikx}}_{\text{reflected plane wave}} \\ \psi_{III}(x) = \cancel{Ee^{Kx}} + \underbrace{Fe^{-Kx}}_{\text{evanescent wave}} \end{cases}$$

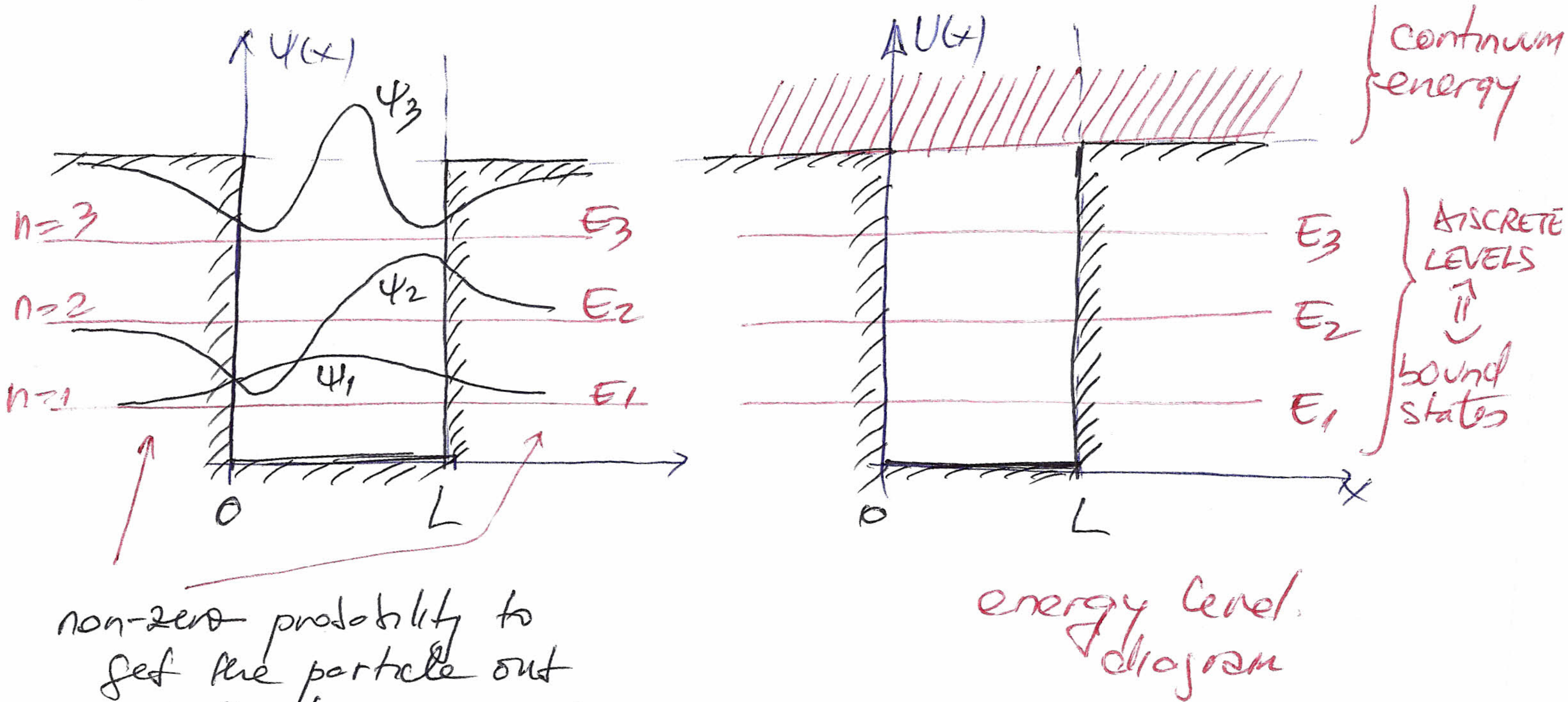
zero to avoid divergence in $-\infty$

$\Rightarrow$ standing wave

zero to avoid divergence in $+\infty$

Obs ① The constants A, C, D, F are deduced from the continuity conditions of $\psi(x)$ and its derivative $\frac{d\psi}{dx}$ in $x=0$ and $x=L$ ⟹ complex math pb. usually solved numerically for more complex situations.

Wave function for the three bound states for the particle in the finite potential well.




non-zero probability to get the particle out of the box even for $E < U_0$

↳ classically not possible; forbidden by the Newtonian mechanics because here the particle would have negative kinetic energy.

If $E > U_0$ free particle states (sinusoidal standing waves) with all possible energies ⟹ continuum of energy

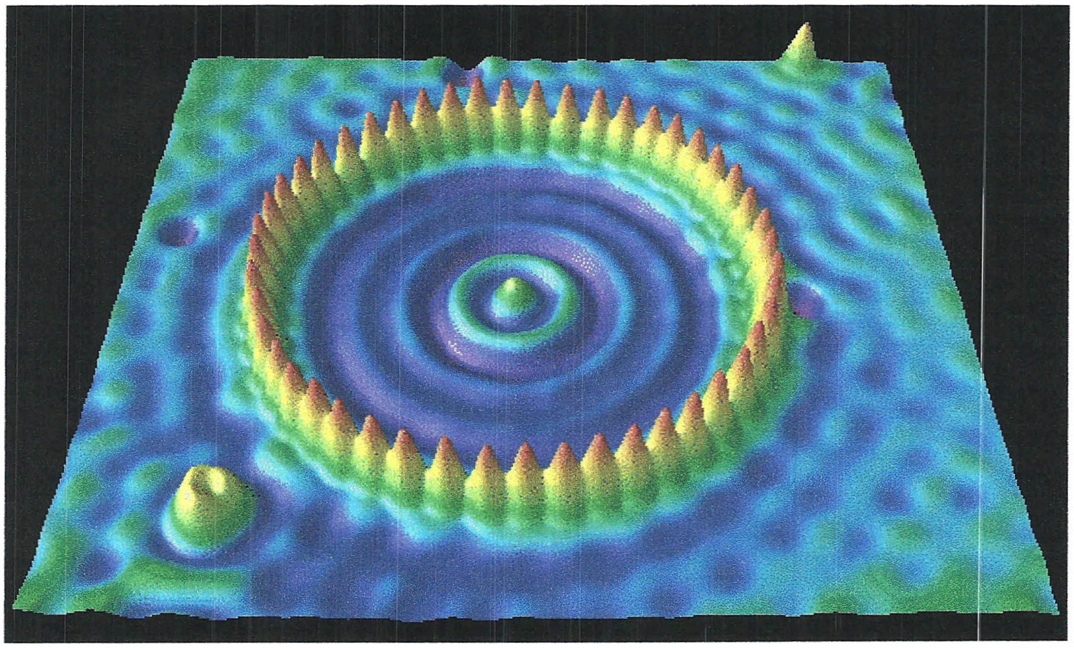
Obs ② Matching the sinusoidal and exponential waves functions at the boundary points is possible only for certain values of the total energy E, so this determines the possible energy levels for the finite square well.

## 2D finite potential well =» **QUANTUM CORAL**

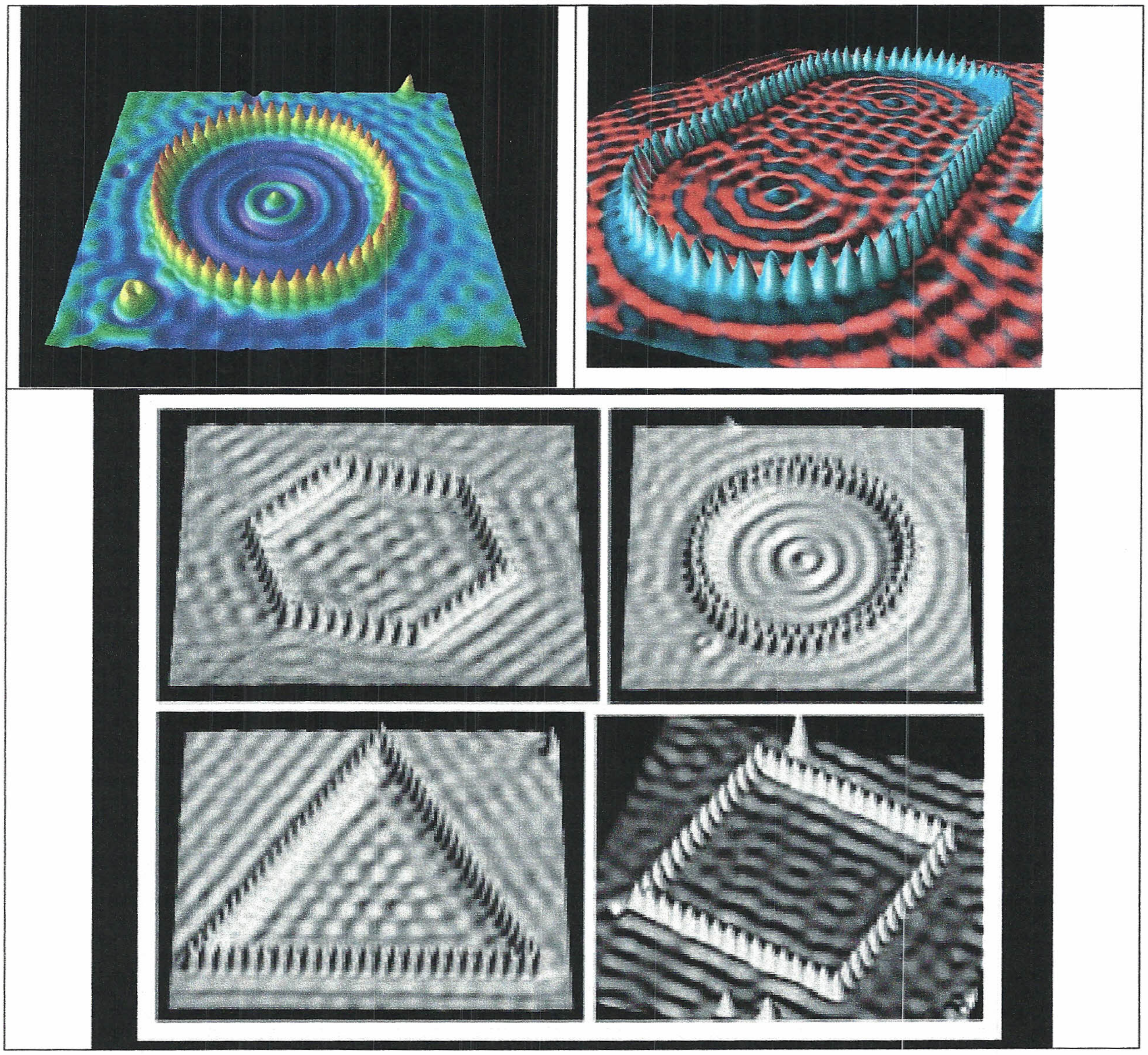
To make this image, 48 iron atoms (shown as yellow peaks) were placed in a circle on a copper surface. The “elevation” at each point inside the circle indicates the electron density within the circle. The standing-wave pattern is very similar to the probability distribution function for a particle in a one-dimensional finite potential well: $e\left|\Psi(x,y)\right|^2$.

*(This image was made with a scanning tunneling microscope, discussed in the next paragraph).*

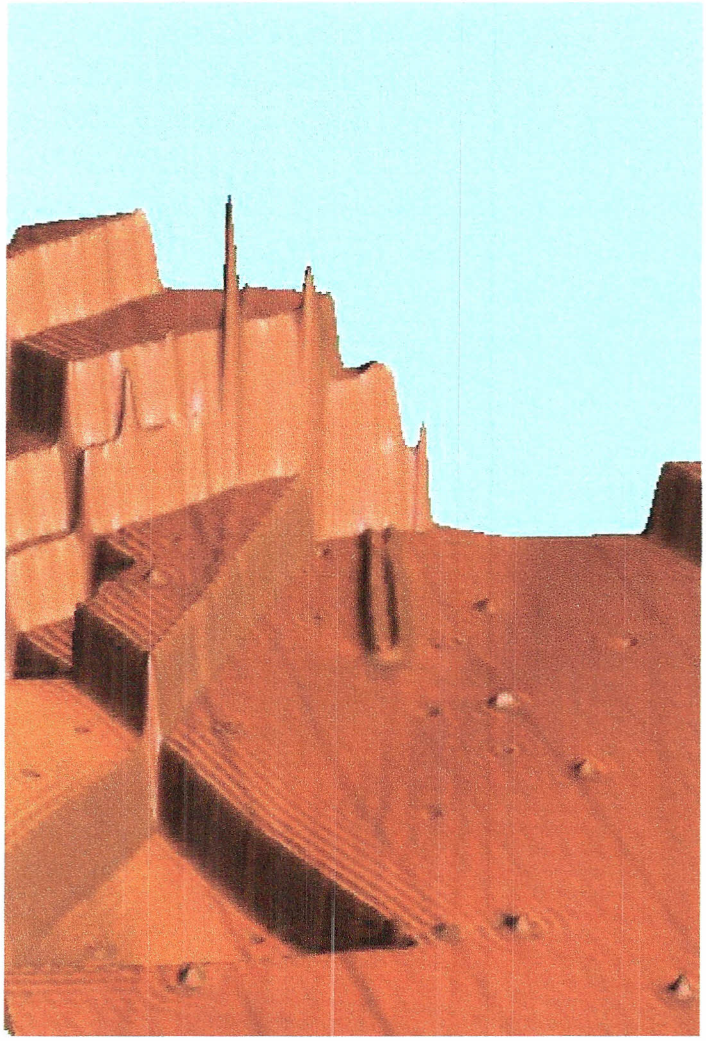
2D electron gas on Cu surface confined into a circular 2D box.



**IBM-** *M.F. Crommie, C.P. Lutz, D.M. Eigler, Science 262, 218-220 (1993).*



We see from this collection of different shaped corrals (including one with a double wall) some evidence that the artists went through a period of infatuation with their creations. Despite having achieved structures of considerably greater complexity, it can be argued that they never surpassed the beauty of the original 48 atom circular shaped corral.



*Reminiscent of formal Japanese rock gardens*, here we see ripples surrounding features on the copper (111) surface.
The artists' fortunes took a major turn upward when they determined that the ripples were due to "surface state electrons." These electrons are free to roam about the surface but not to penetrate into the solid. When one of these electrons encounters an obstacle like a step edge, it is partially reflected.
The ripples extending away from the step edges and the various defects in the crystal surface are just the standing waves that are created whenever a wave scatters off of something. The standing waves are about 15 Angstroms (roughly 10 atomic diameters) from crest to crest. The amplitude is largest adjacent to the step edge where it is about 0.04 Angstroms from crest to trough.