CHAPTER 4

# Solution of the Schrödinger Equation for Four Specific Problems

# 4.1. Free Electrons

it is assumed

that no "wall," i.e., no potential barrier ($V$), restricts the propagation of the electron wave.

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

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

and given the dependence upon both position and time, we try a wavefunction of the form

$$\Psi = Ae^{ax}e^{bt}$$

Presuming that the wavefunction represents a state of definite energy E, the equation can be separated by the requirement,

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

# Time independent Equation

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

$$\psi = Ae^{ax}$$

$$\frac{-\hbar^2}{2m}a^2\Psi = E\Psi$$

$$a^2 = \frac{-2mE}{\hbar^2}$$

$$a = i\sqrt{\frac{2mE}{\hbar^2}}$$

Treating the system as a particle where

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad a = i\frac{p}{\hbar}$$

Now using the De Broglie relationship and the wave relationship:

$$a = i\frac{h}{\hbar\lambda} = i\frac{2\pi}{\lambda}$$

# a=iα

$$\alpha = \sqrt{\frac{2m}{\hbar^2}E}.$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} = k,$$

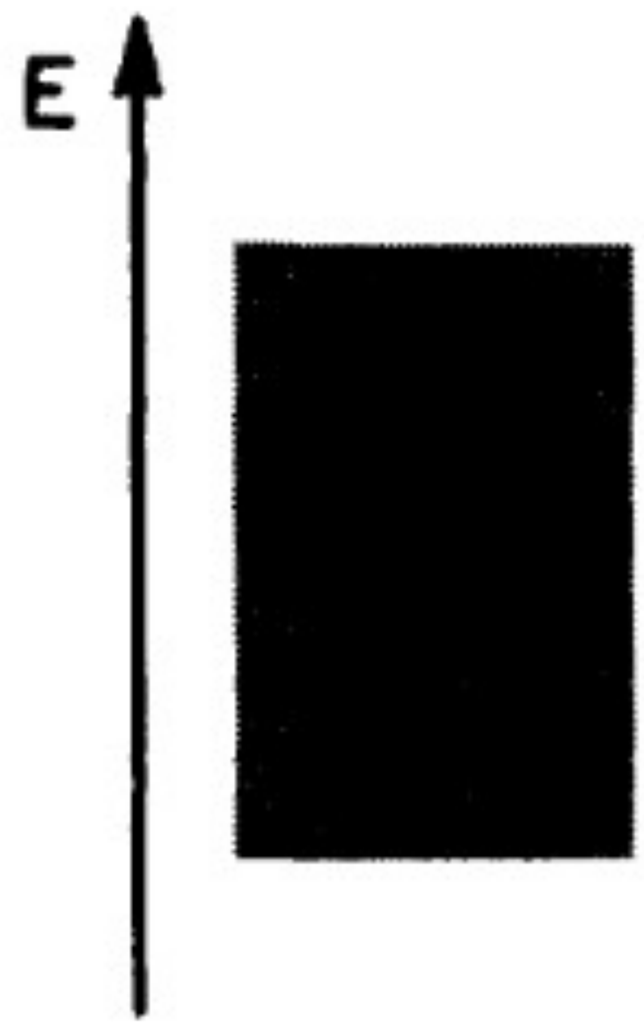
$$\boxed{E = \frac{\hbar^2}{2m}\alpha^2.}$$

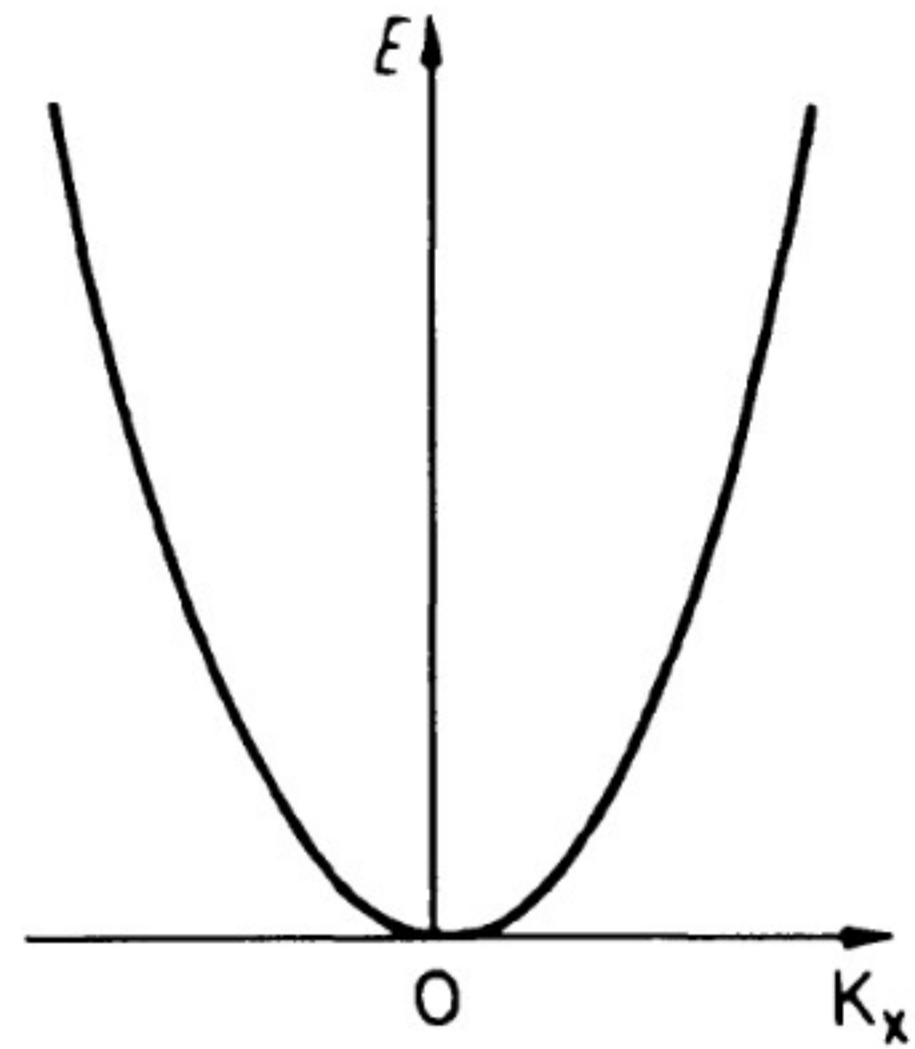
$$\boxed{E = \frac{\hbar^2}{2m}k^2.}$$

Since **k** is inversely proportional to the wavelength, $\lambda$, it is also called the "wave vector."

$$|\mathbf{k}| = \frac{2\pi}{\lambda}$$

# Energy continuum of a free electron




Since no boundary condition had to be considered for the calculation of the free-flying electron, all values of the energy are "allowed," i.e., one obtains an **energy continuum**

# Time dependent Equation

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

$$\Psi = Ae^{ax}e^{bt}$$

$$E\Psi = i\hbar b\Psi$$

$$b = \frac{-iE}{\hbar}$$

Treating the system as a wave packet, or photon-like entity where the Planck hypothesis gives

$$E = \hbar\omega$$

we can evaluate the constant b

$$b = -i\omega$$

This gives a plane wave solution:

$$\Psi(x,t) = Ae^{i\frac{2\pi}{\lambda} - \omega t} = Ae^{ikx - i\omega t}$$

# Free Particle Waves

The general free-particle wavefunction is of the form

$$\Psi(x,t) = Ae^{i\frac{2\pi}{\lambda} - \omega t} = Ae^{ikx - i\omega t}$$

which as a complex function can be expanded in the form

$$\Psi(x,t) = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$$

Either the real or imaginary part of this function could be appropriate for a given application. In general, one is interested in particles which are free within some kind of boundary, but have boundary conditions set by some kind of potential. The particle in a box problem is the simplest example.

The free particle wavefunction is associated with a precisely known momentum:

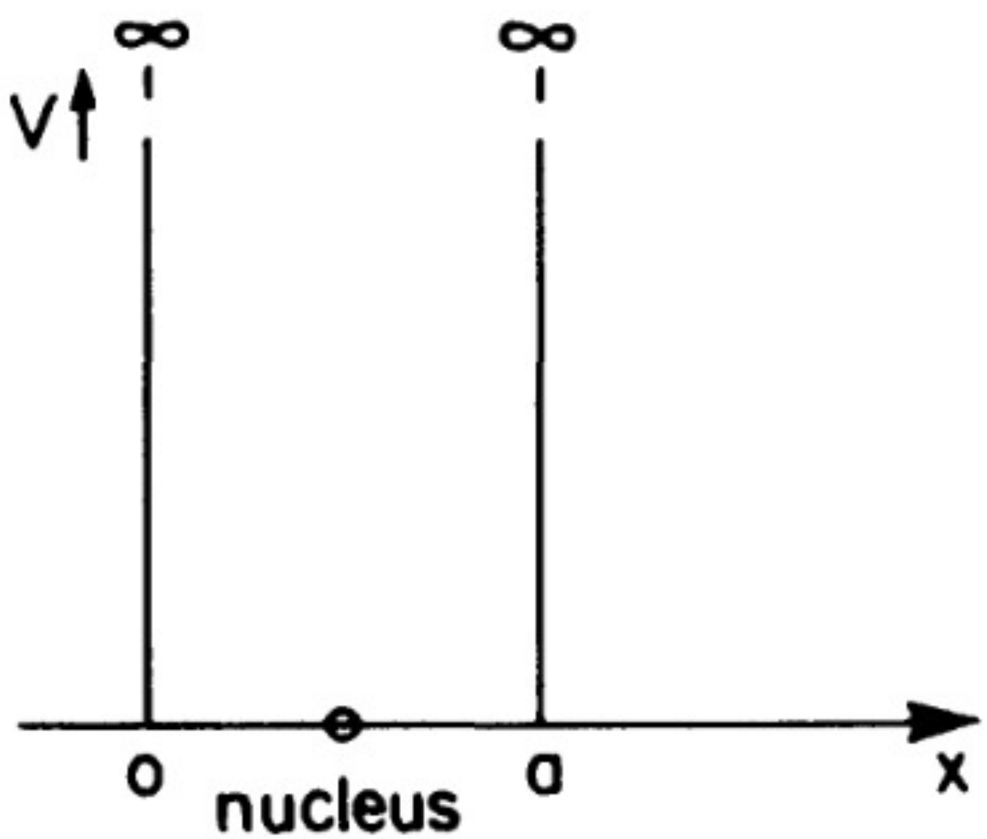
$$p = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k$$

but the requirement for normalization makes the wave amplitude approach zero as the wave extends to infinity (uncertainty principle).

## 4.2. Electron in a Potential Well (Bound Electron)

we assume that the electron can move freely between two infinitely high potential barriers

The potential barriers do not allow the electron to escape from this potential well




$$\psi = 0 \text{ for } x \leqq 0$$

$$\text{and } x \geqq a$$

The potential energy inside the well is zero

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

Because of the two propagation directions of the electron, the solution of

$$\psi = Ae^{i\alpha x} + Be^{-i\alpha x}$$

$$\alpha = \sqrt{\frac{2m}{\hbar^2}E}. \qquad \alpha = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} = k,$$

$\psi = 0$ for $x = 0$ $\qquad B = -A$

$\psi = 0$ for $x = a$ $\qquad 0 = Ae^{i\alpha a} + Be^{-i\alpha a} = A(e^{i\alpha a} - e^{-i\alpha a})$

Euler equation

$$\sin \rho = \frac{1}{2i}(e^{i\rho} - e^{-i\rho})$$

$$A[e^{i\alpha a} - e^{-i\alpha a}] = 2Ai \cdot \sin \alpha a = 0$$

$$\alpha a = n\pi, \qquad n = 0, 1, 2, 3, \ldots.$$

$$\boxed{E_n = \frac{\hbar^2}{2m}\alpha^2 = \frac{\hbar^2 \pi^2}{2ma^2} n^2,} \qquad n = 1, 2, 3, \ldots.$$

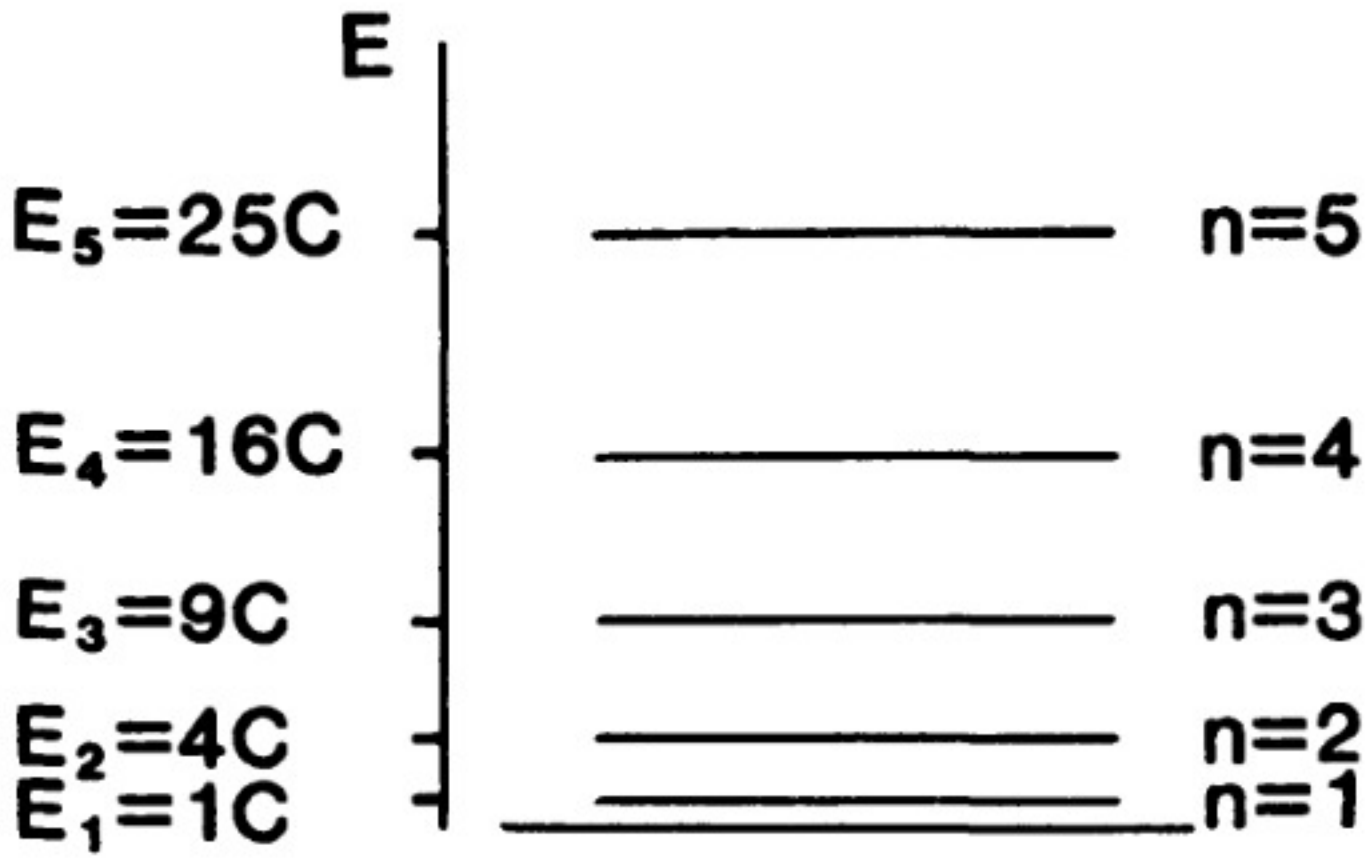
We exclude $n = 0$, which would yield $\psi = 0$, that is, no electron wave

Because of the boundary conditions, only certain solutions of the Schrödinger equation exist

The allowed values are called "**energy levels**."

~ discrete energy level

# Discrete Energy Level "**energy quantization.**"




Allowed energy values of an electron that is bound to its atomic nucleus

$E$ is the excitation energy in the present case. $C = \hbar^2\pi^2/2ma^2$

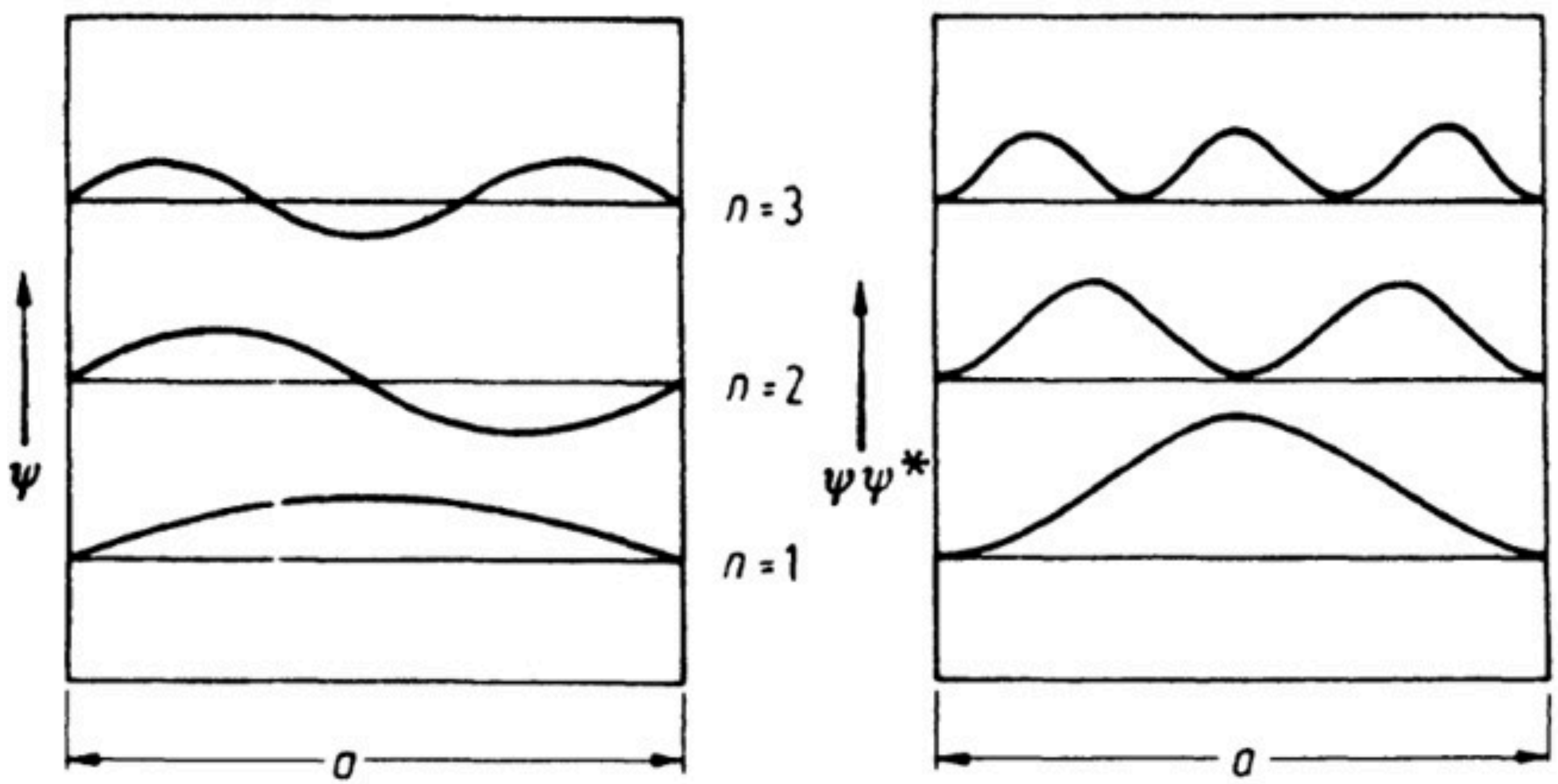
$E_1$ is the "**zero-point energy**"

the lowest allowed energy

# Probability of Finding Electrons

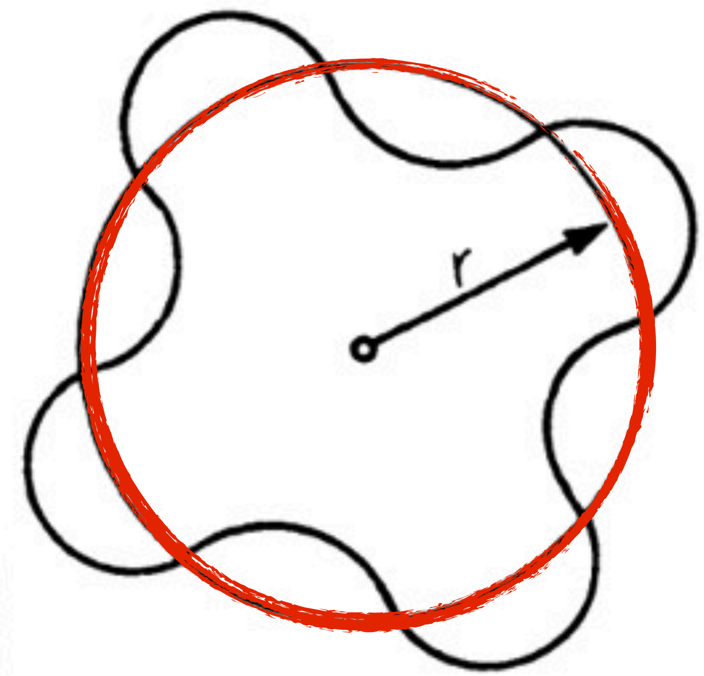
$$\psi = 2Ai \cdot \sin \alpha x \qquad \psi^* = -2Ai \sin \alpha x$$

$$\psi\psi^* = 4A^2 \sin^2 \alpha x$$




(a) (b)

Bohr radius

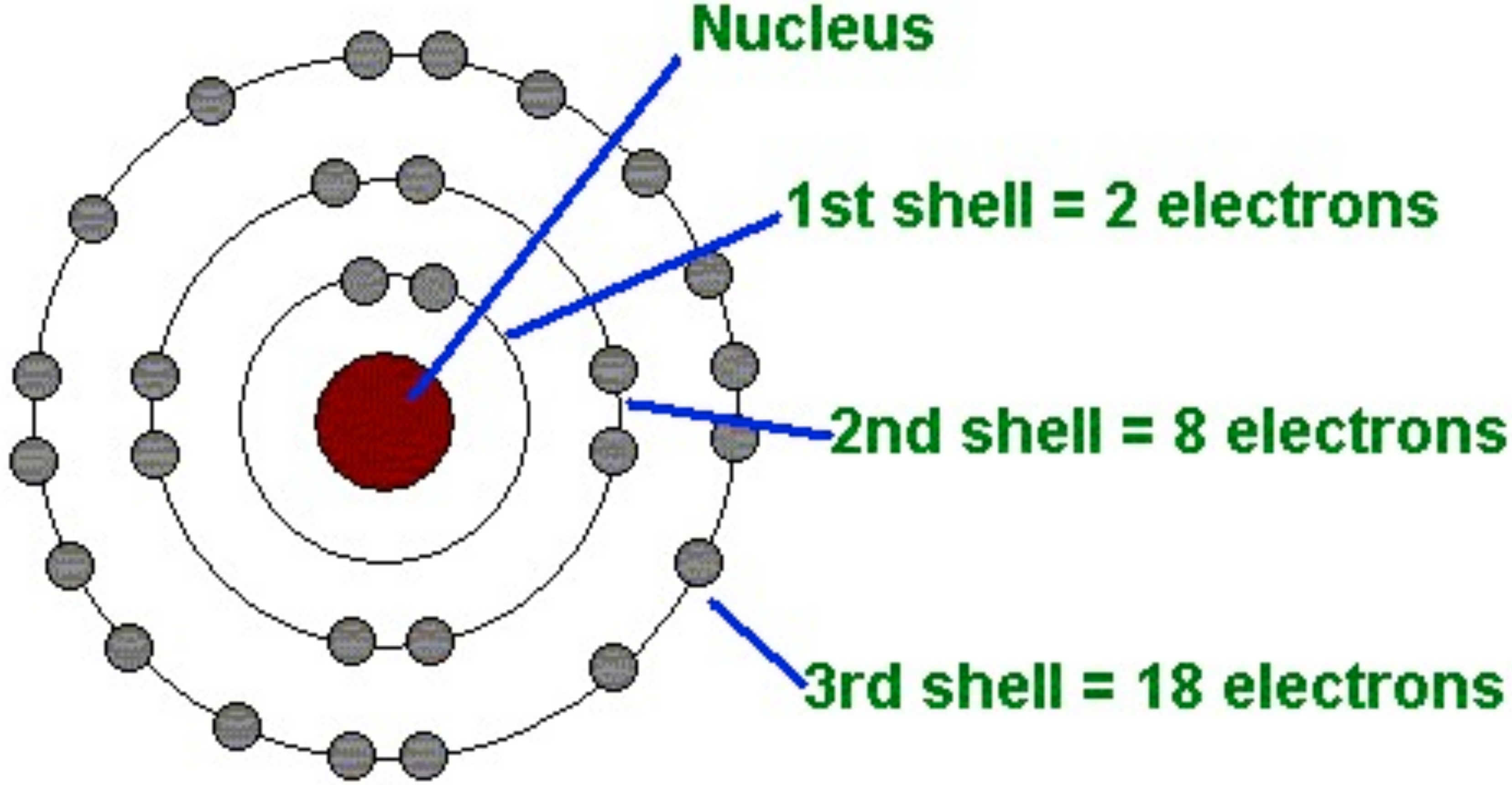



$$2\pi r = n\lambda,$$

$$r = \frac{\lambda}{2\pi} n.$$

the electron waves associated with an orbiting electron have to be standing waves.

# Rutherford Bohr model




$$\int_0^a \psi\psi^* \, dx = 4A^2 \int_0^a \sin^2(\alpha x) \, dx = \frac{4A^2}{\alpha}\left[-\frac{1}{2}\sin\alpha x\cos\alpha x + \frac{\alpha x}{2}\right]_0^a = 1$$

$$A = \sqrt{\frac{1}{2a}}.$$

- Classical mechanics

The electron is held in a circular orbit by electrostatic attraction. The centripetal force is equal to the Coulomb force.

$$\frac{m_e v^2}{r} = \frac{Z k_e e^2}{r^2}$$

where $m_e$ is the mass, $e$ is the charge of the electron and $k_e$ is Coulomb's constant. This determines the speed at any radius:

$$v = \sqrt{\frac{Z k_e e^2}{m_e r}}$$

It also determines the total energy at any radius:

$$E = \frac{1}{2} m_e v^2 - \frac{k_e e^2}{r} = -\frac{k_e e^2}{2r}$$

$$k_e = 1/(4\pi\varepsilon_o)$$

- Quantum rule

The angular momentum $L = m_e v r$ is an integer multiple of $\hbar$:

$$m_e v r = n\hbar$$

Substituting the expression for the velocity gives an equation for $r$ in terms of n:

$$\sqrt{Z k_e e^2 m_e r} = n\hbar$$

so that the allowed orbit radius at any n is:

$$r_n = \frac{n^2\hbar^2}{Z k_e e^2 m_e}$$

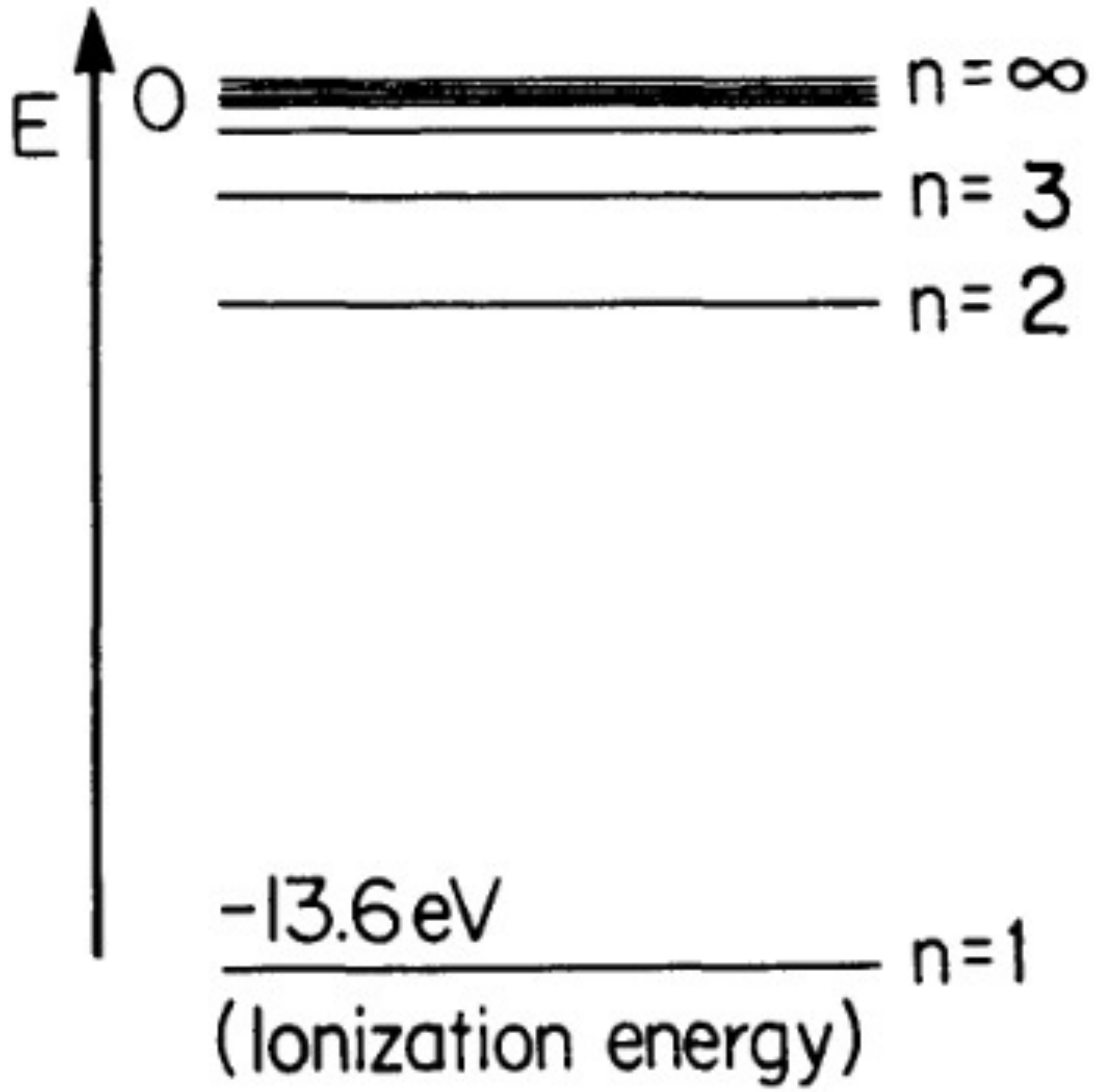
The smallest possible value of $r$ in the hydrogen atom is called the Bohr radius and is equal to:

$$r_1 = \frac{\hbar^2}{k_e e^2 m_e} = 0.529 \times 10^{-10}\mathrm{m}$$

The energy of the $n$-th level is determined by the radius:

$$E = -\frac{k_e e^2}{2r_n} = -\frac{(k_e e^2)^2 m_e}{2\hbar^2 n^2} = \frac{-13.6\mathrm{eV}}{n^2}$$

$$E = \frac{me^4}{2(4\pi\varepsilon_0\hbar)^2}\frac{1}{n^2} = -13.6 \cdot \frac{1}{n^2}(\mathrm{eV})$$




Energy levels of atomic hydrogen. *E* is the binding energy.

three-dimensional potential well

**"electron in a box"**

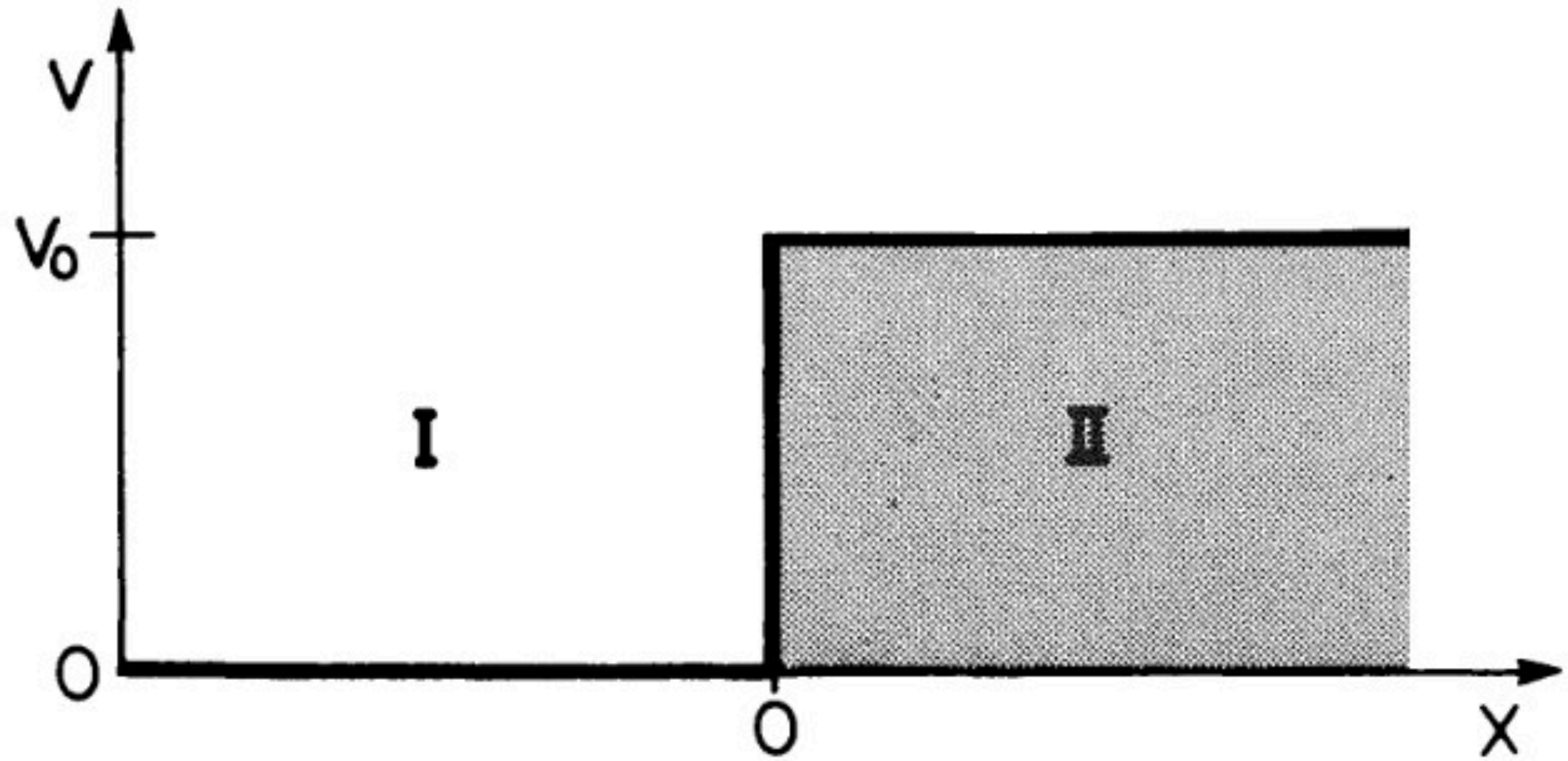
$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)$$

The smallest allowed energy in a three-dimensional potential well is occupied by an electron if $n_x = n_y = n_z = 1$

For the next higher energy there are three different possibilities for combining the *n*-values $(n_x, n_y, n_z) =$ (1, 1, 2), (1, 2, 1), or (2, 1, 1).

One calls the states which have the same energy but different quantum numbers "**degenerate**" **states**.

# 4.3. Finite Potential Barrier (Tunnel Effect)




Finite potential barrier

$$(\mathrm{I}) \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0.$$

$$\psi_{\mathrm{I}} = Ae^{i\alpha x} + Be^{-i\alpha x},$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}},$$

$$(\mathrm{II}) \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0.$$

$$\psi_{\mathrm{II}} = Ce^{i\beta x} + De^{-i\beta x},$$

$$\beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}.$$

$$\beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}.$$

$V_o > E$

$\beta$ becomes imaginary

$$\gamma = i\beta.$$

$\psi_{II} = Ce^{i\beta x} + De^{-i\beta x}$, -------> $\psi_{II} = Ce^{\gamma x} + De^{-\gamma x}$.

For $x \to \infty$

$$\psi_{II} = C \cdot \infty + D \cdot 0.$$

$\psi_{II}\psi_{II}^*$ are infinity

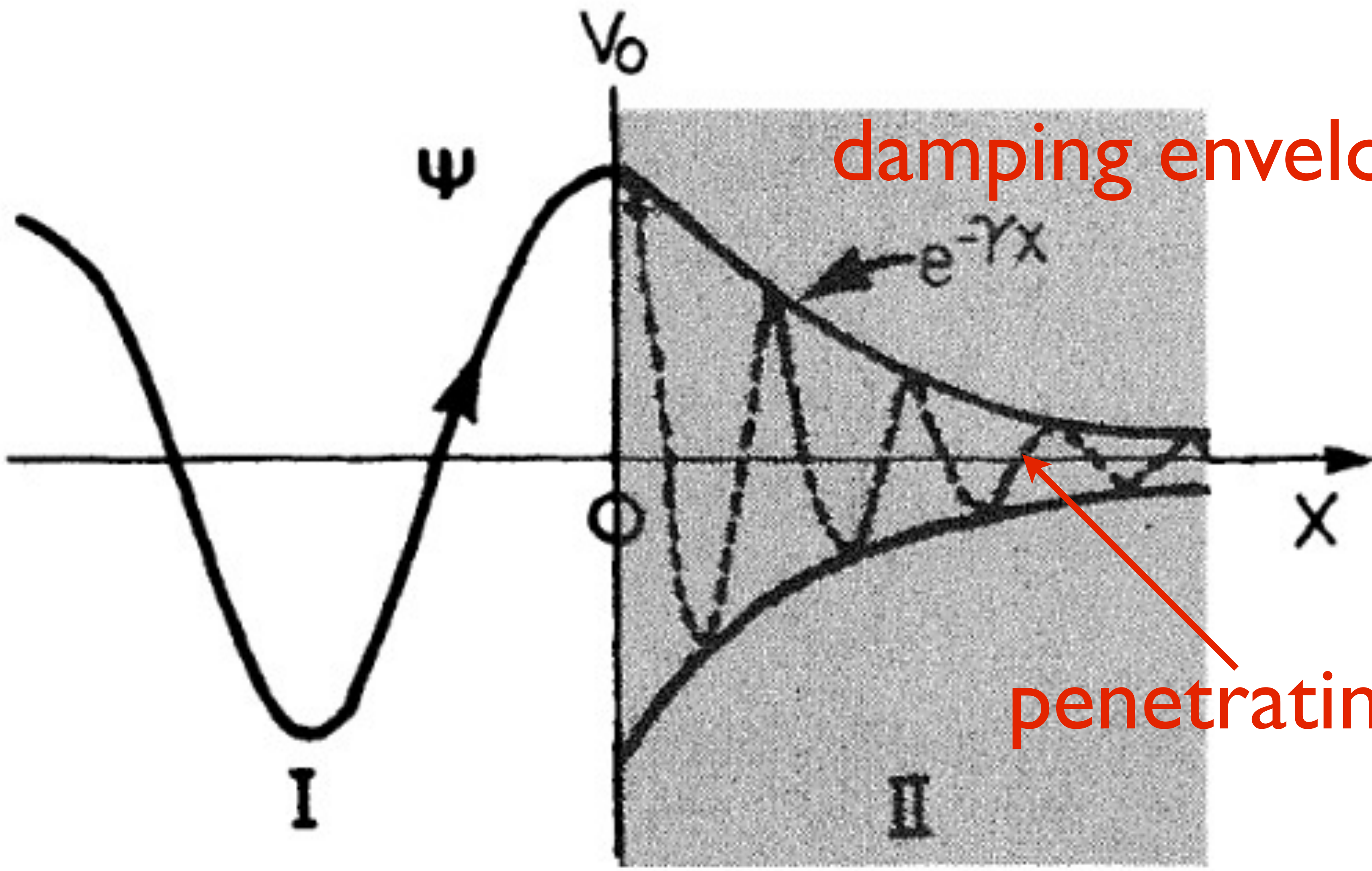
To avoid this, $C$ has to go to zero: $C \to 0$.

$$\psi_{II} = De^{-\gamma x},$$

The electron wave $\Psi(x,t)$ is

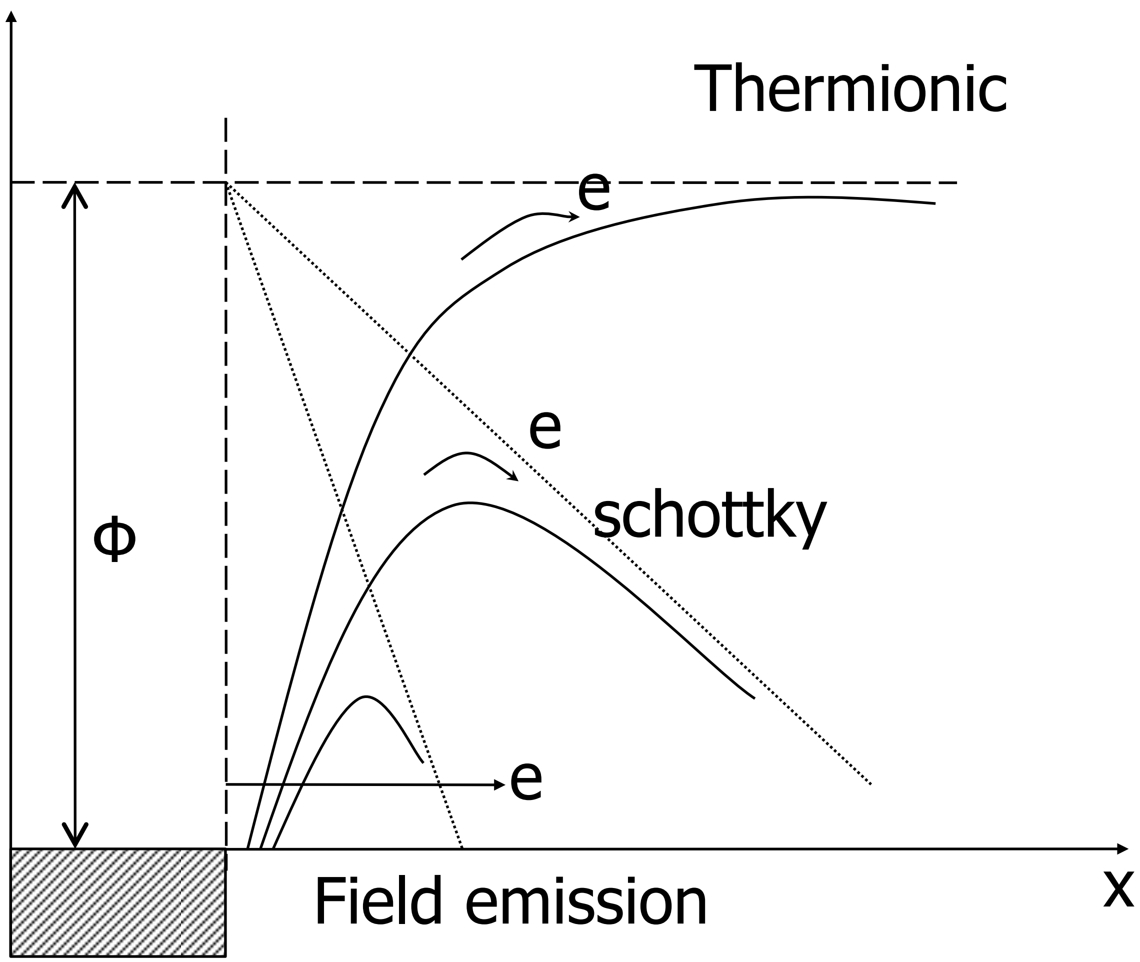
$$\boxed{\Psi = De^{-\gamma x} \cdot e^{i(\omega t - kx)}}$$

II I

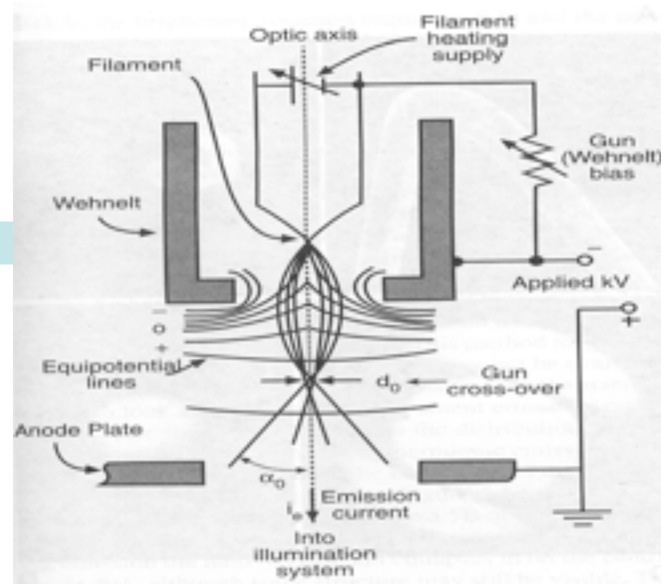


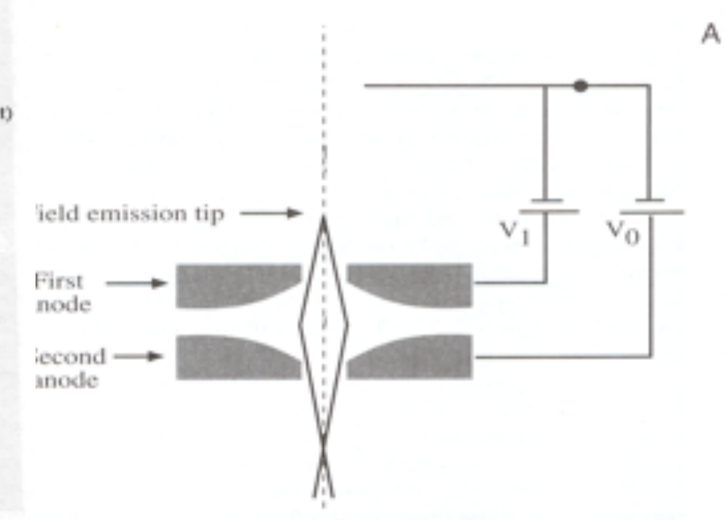

a light wave, which likewise penetrates to a certain degree into a material and whose amplitude also decreases exponentially

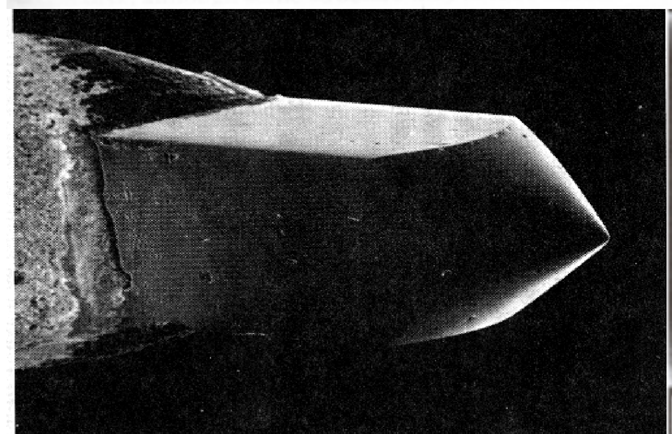
# Thermionic Source vs. Field Emission Source

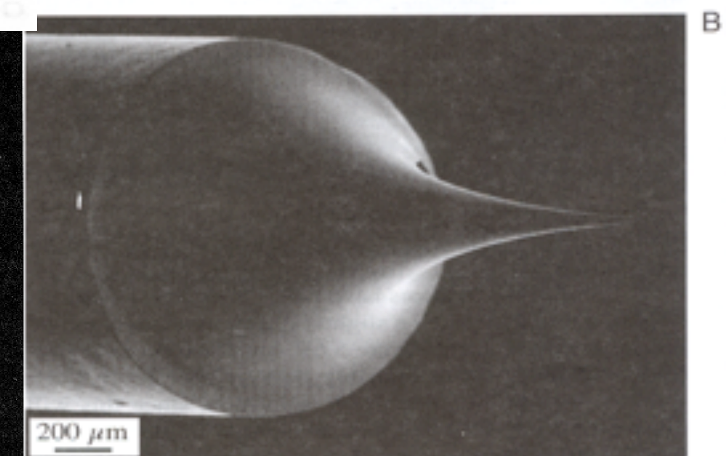


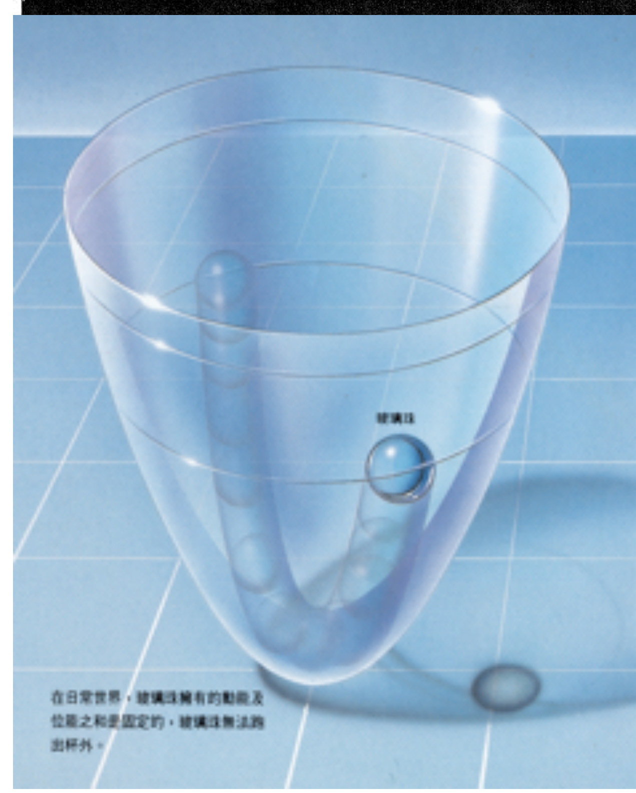

$$E = \frac{V}{r}$$

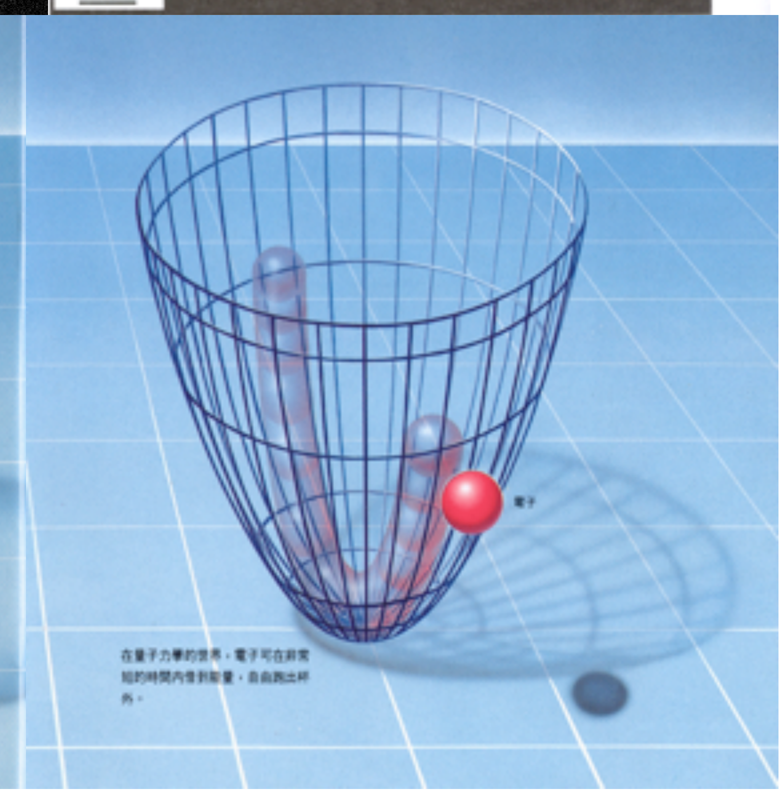




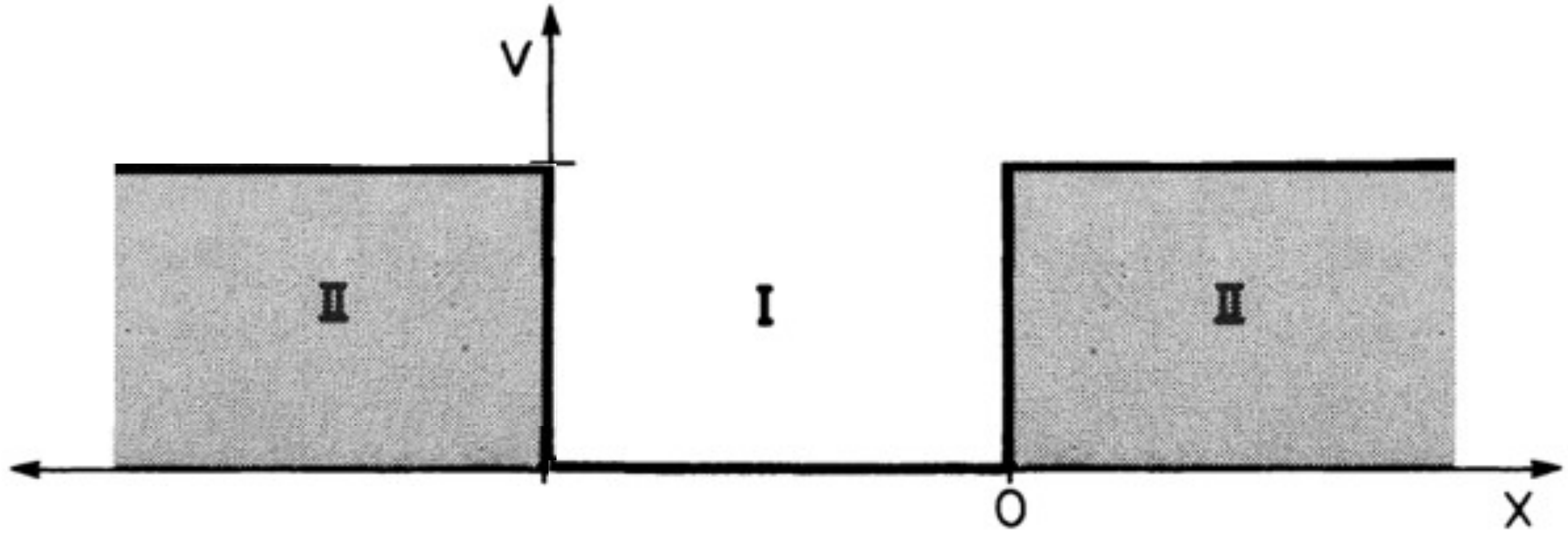


# Quantum Tunneling

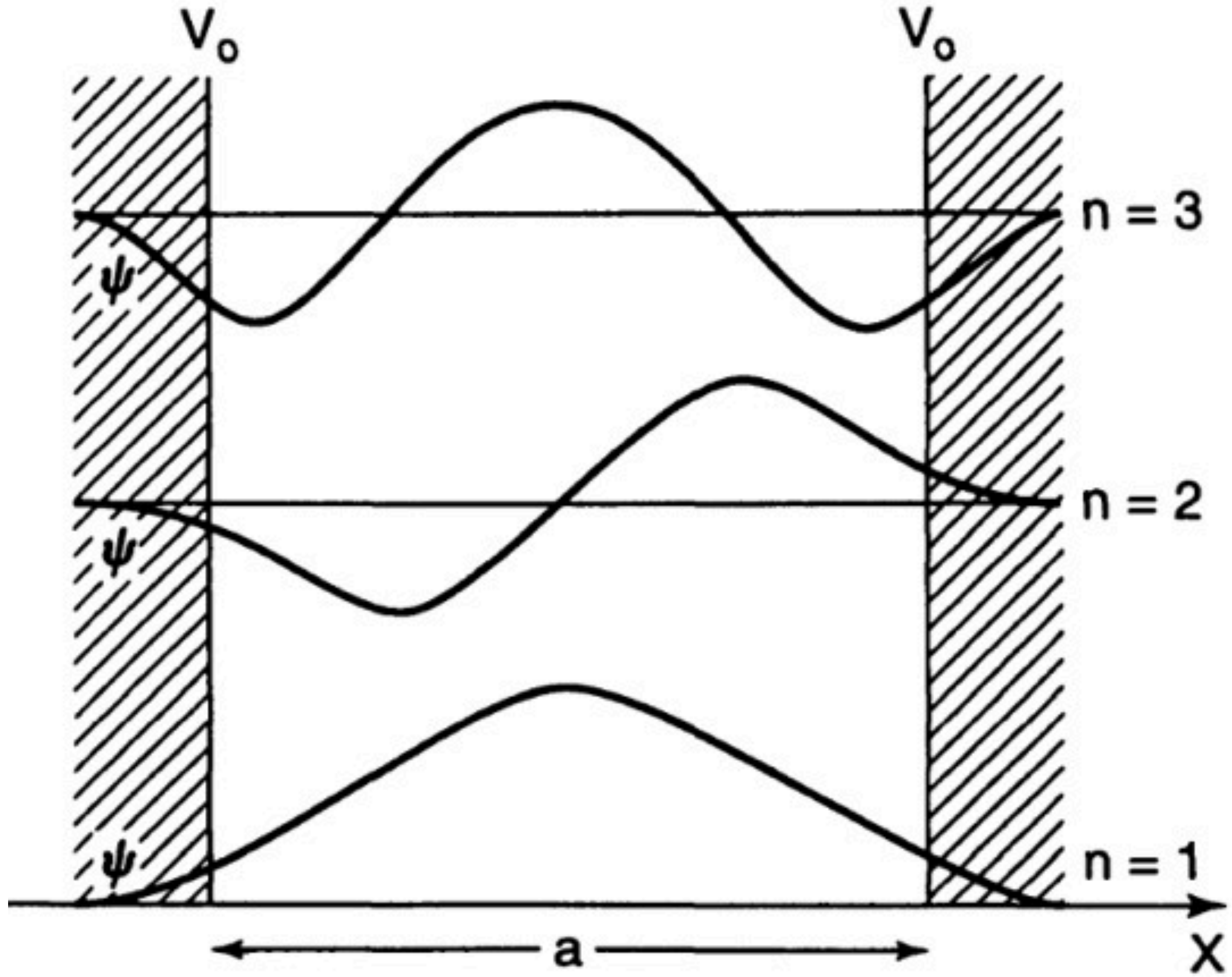
The penetration of a potential barrier by an electron wave is called "**tunneling**"

~ tunnel diode, tunnel electron microscope, field ion microscope

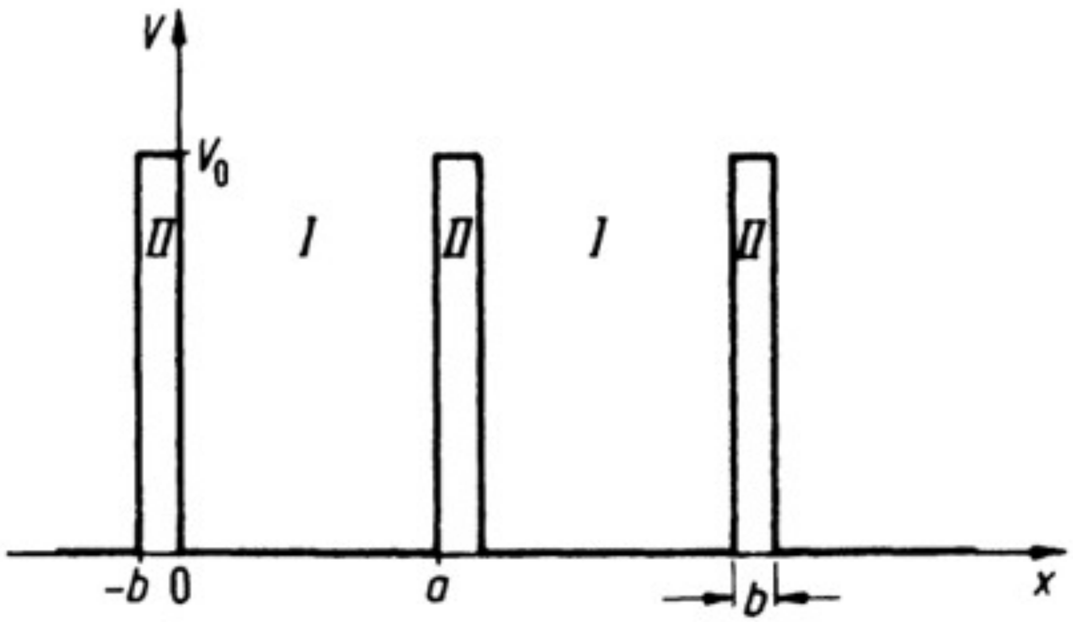
In classical physics, the electron (particle) would be described to be entirely reflected back from the barrier (at $x = 0$) if its kinetic energy is smaller than $V_0$.




Square well with finite potential barriers.

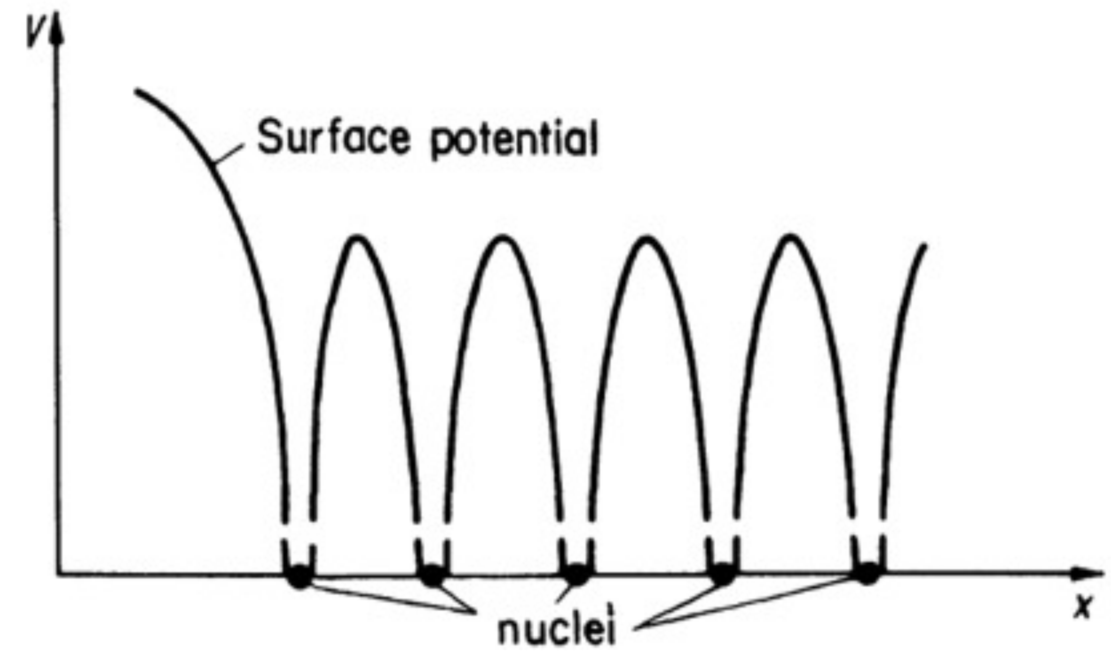


# 4.4. Electron in a Periodic Field of a Crystal




One-dimensional periodic potential distribution (simplified)

Kroning-Penny Model




One-dimensional periodic potential distribution for a crystal

Muffin-Tin Potential

$$\text{(I)} \qquad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0, \qquad \alpha^2 = \frac{2m}{\hbar^2}E,$$

$$\text{(II)} \qquad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0. \qquad \gamma^2 = \frac{2m}{\hbar^2}(V_0 - E).$$

# Bloch function

Bloch showed
that the solution of this type of equation has the following form:

$$\boxed{\psi(x) = u(x) \cdot e^{ikx}}$$

$u(x)$ is a periodic function which possesses the periodicity of the lattice in the $x$-direction

$u(x)$ is no longer a constant (amplitude $A$)
but changes periodically with increasing $x$ (modulated amplitude)

$u(x)$ is different for various directions in the crystal lattice.

Differentiating the Bloch function twice

$$\frac{d^2\psi}{dx^2} = \left(\frac{d^2u}{dx^2} + \frac{du}{dx}2ik - k^2u\right)e^{ikx}.$$

$$\text{(I)} \quad \frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 - \alpha^2)u = 0,$$

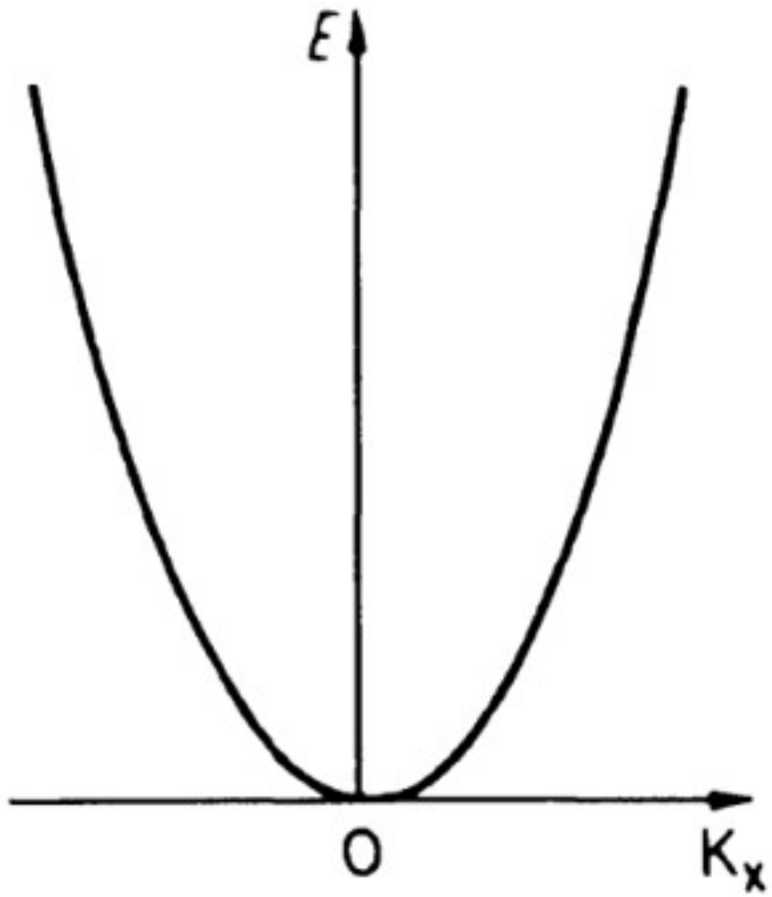
$$\text{(II)} \quad \frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 + \gamma^2)u = 0.$$

$$\text{(I)} \quad u = e^{-ikx}(Ae^{i\alpha x} + Be^{-i\alpha x}),$$

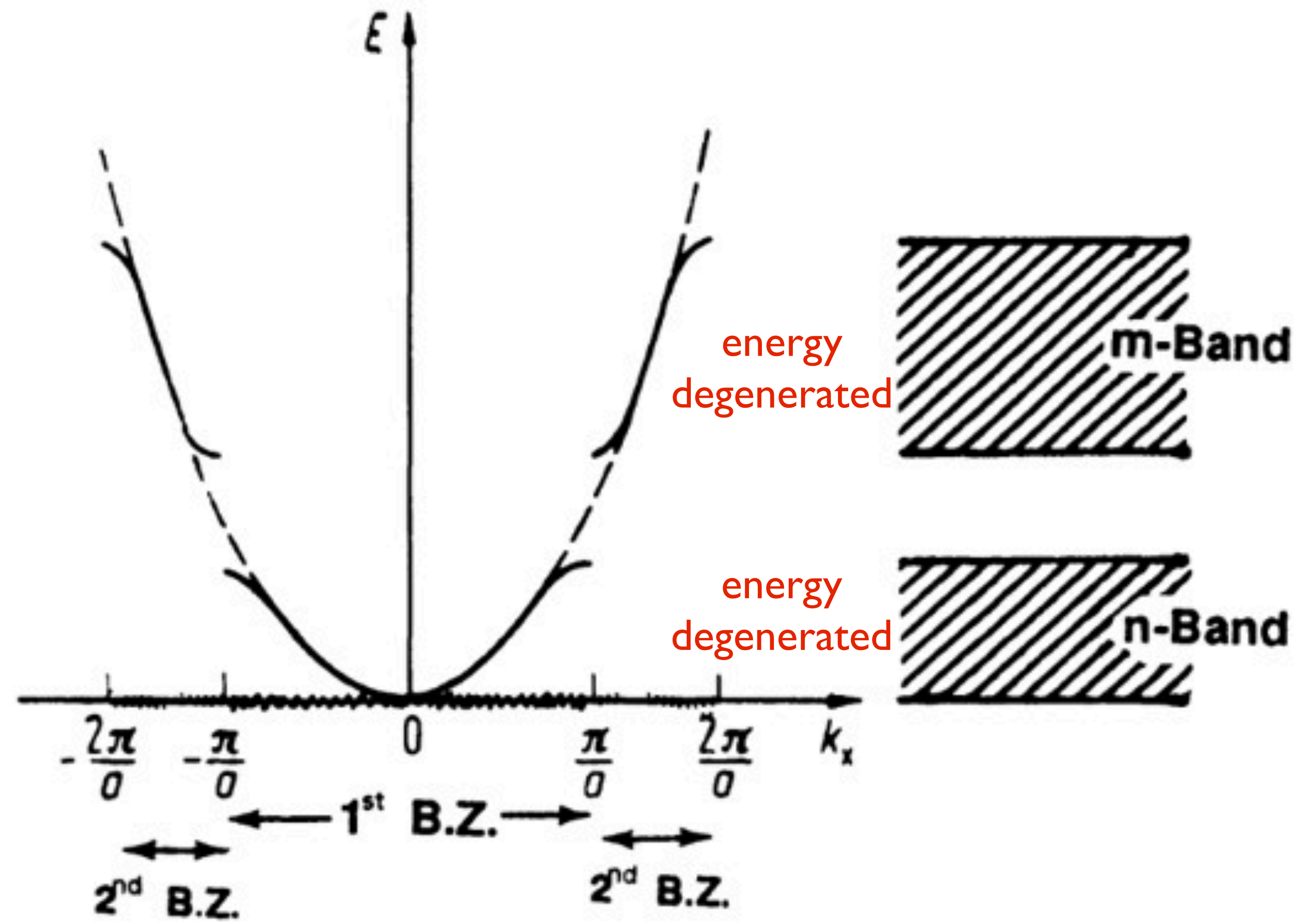
$$\text{(II)} \quad u = e^{-ikx}(Ce^{-\gamma x} + De^{\gamma x}).$$

The derivation of band gap/ structure is out of scope in this lecture

# Band Gap Theory for Crystal



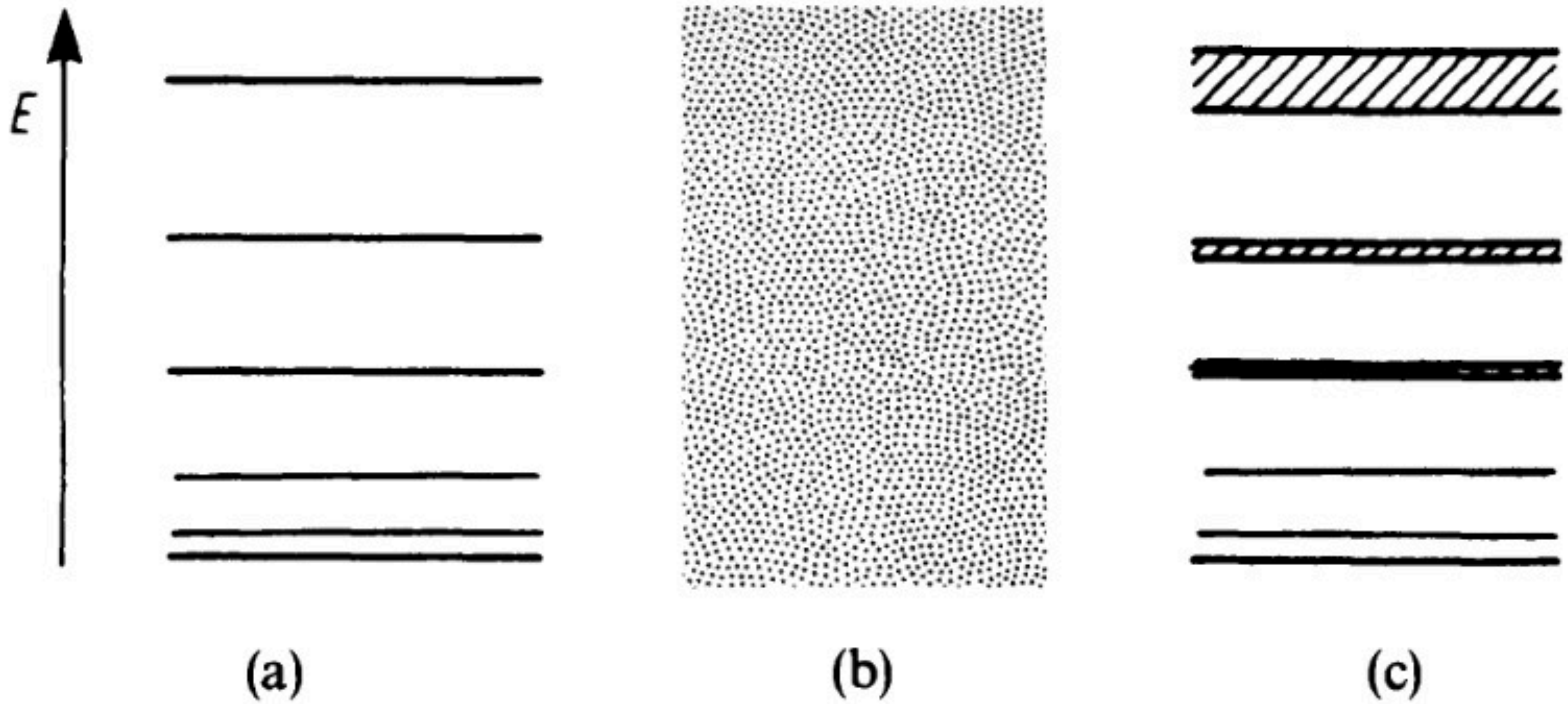

Electron energy $E$ versus the wave vector $k_x$ for free electrons.




energy band for crystalline

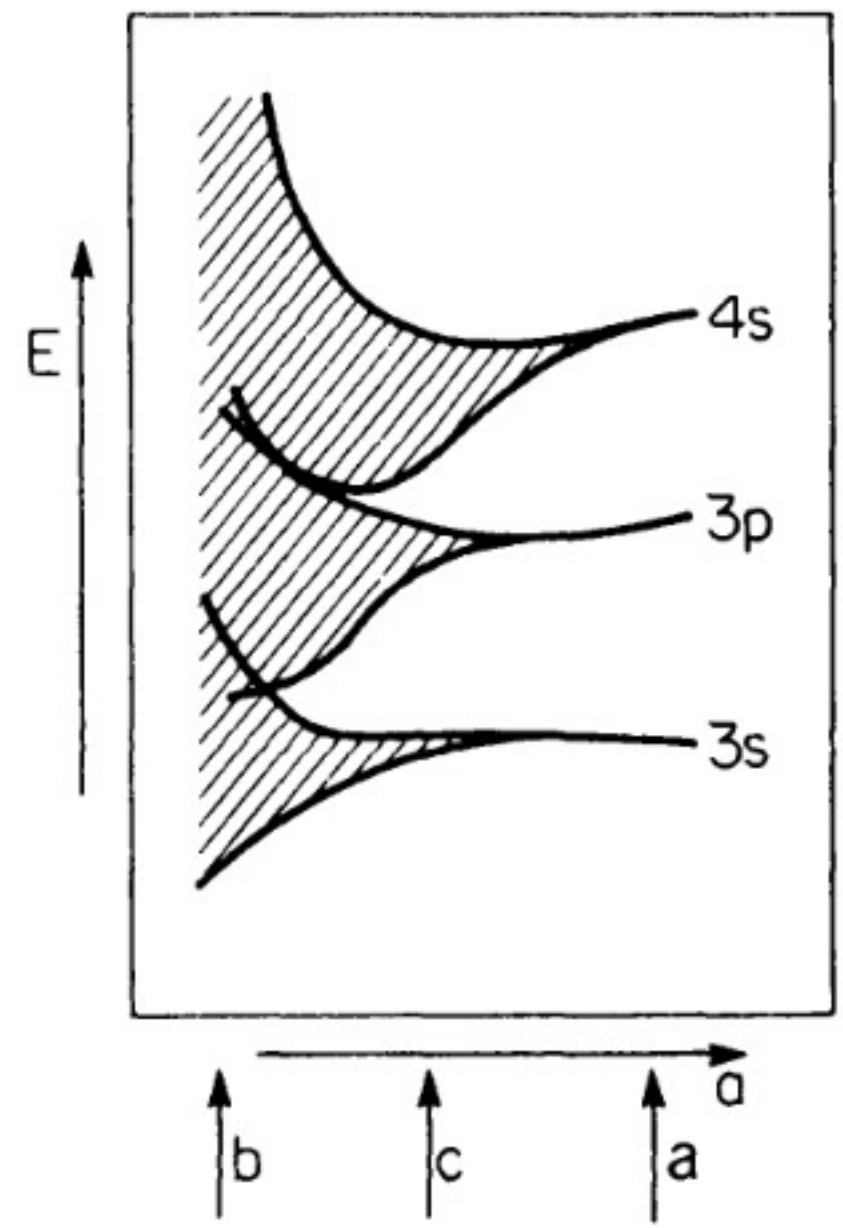
only certain special energy is allowed for
electron propagates inside the crystal

electrons in a crystal behave, for most $k_x$ values, like free electrons, except when $k_x$ approaches the value $n \cdot \pi/a$.




Allowed energy levels for (a) bound electrons, (b) free electrons, and (c) electrons in a solid.

If the electrons are strongly bound, i.e., if the potential barrier is very large, one obtains sharp energy levels (electron in the potential field of *one* ion). If the electron is not bound, one obtains a continuous energy region (free electrons). If the electron moves in a periodic potential field, one receives energy bands (solid).




Widening of the sharp energy levels into bands and finally into a quasi-continuous energy region with decreasing interatomic distance, *a*, for a metal (after calculations of Slater).