재료의 전자기적 성질

PART I.
FUNDAMENTALS OF ELECTRON THEORY

0 Introduction: Wave & Particle

0.1 Introduction

The understanding of the behavior of electrons in solids is one of the key elements to understand the properties of materials such as electrical, optical, magnetic, and thermal properties.

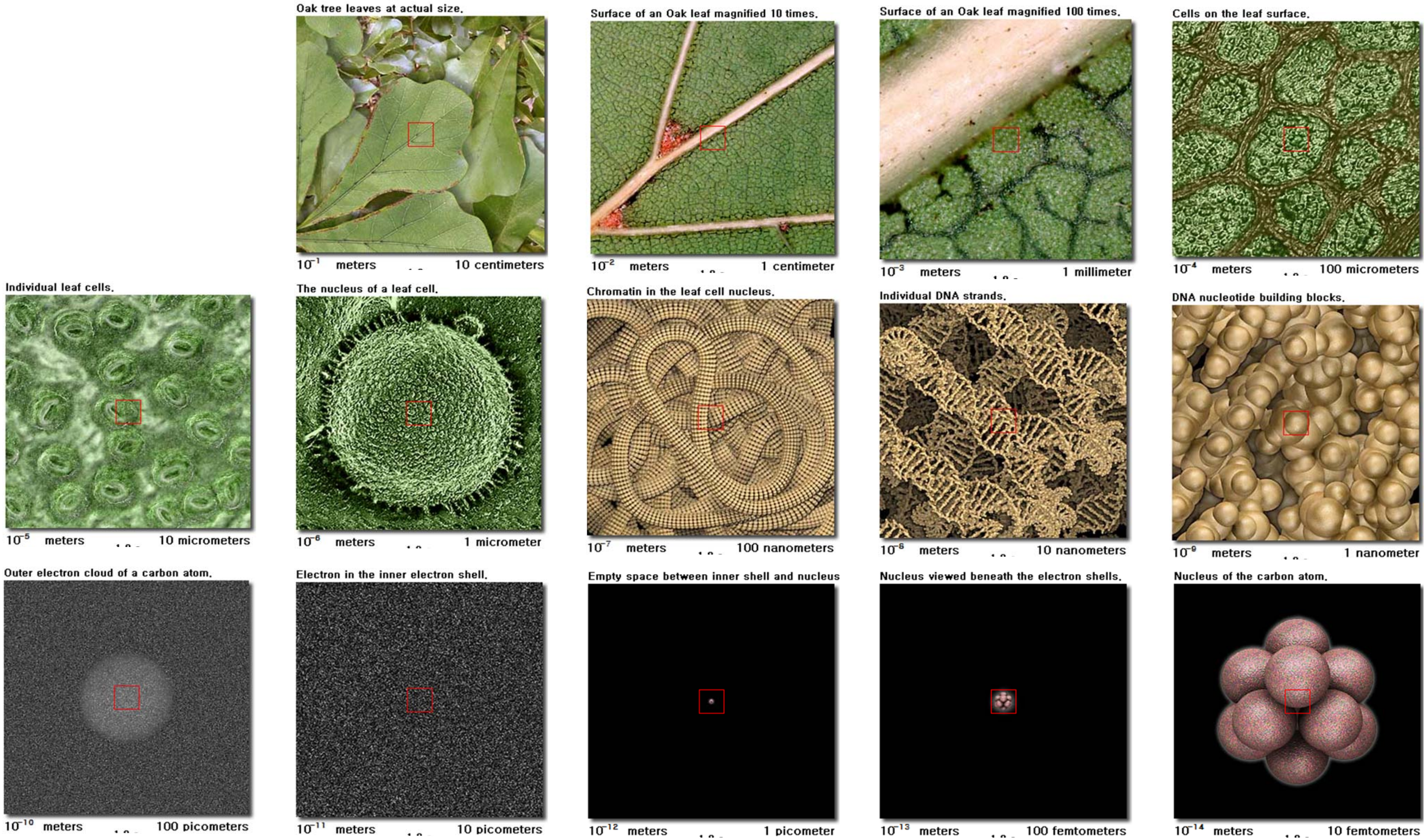
There have been several approaches for the understanding of the electronic properties of materials.

(a) **Continuum Theory –** phenomenological description of the experimental observation
ex. **Ohm's law, Maxwell equation Hagen-Rubens equation etc.**

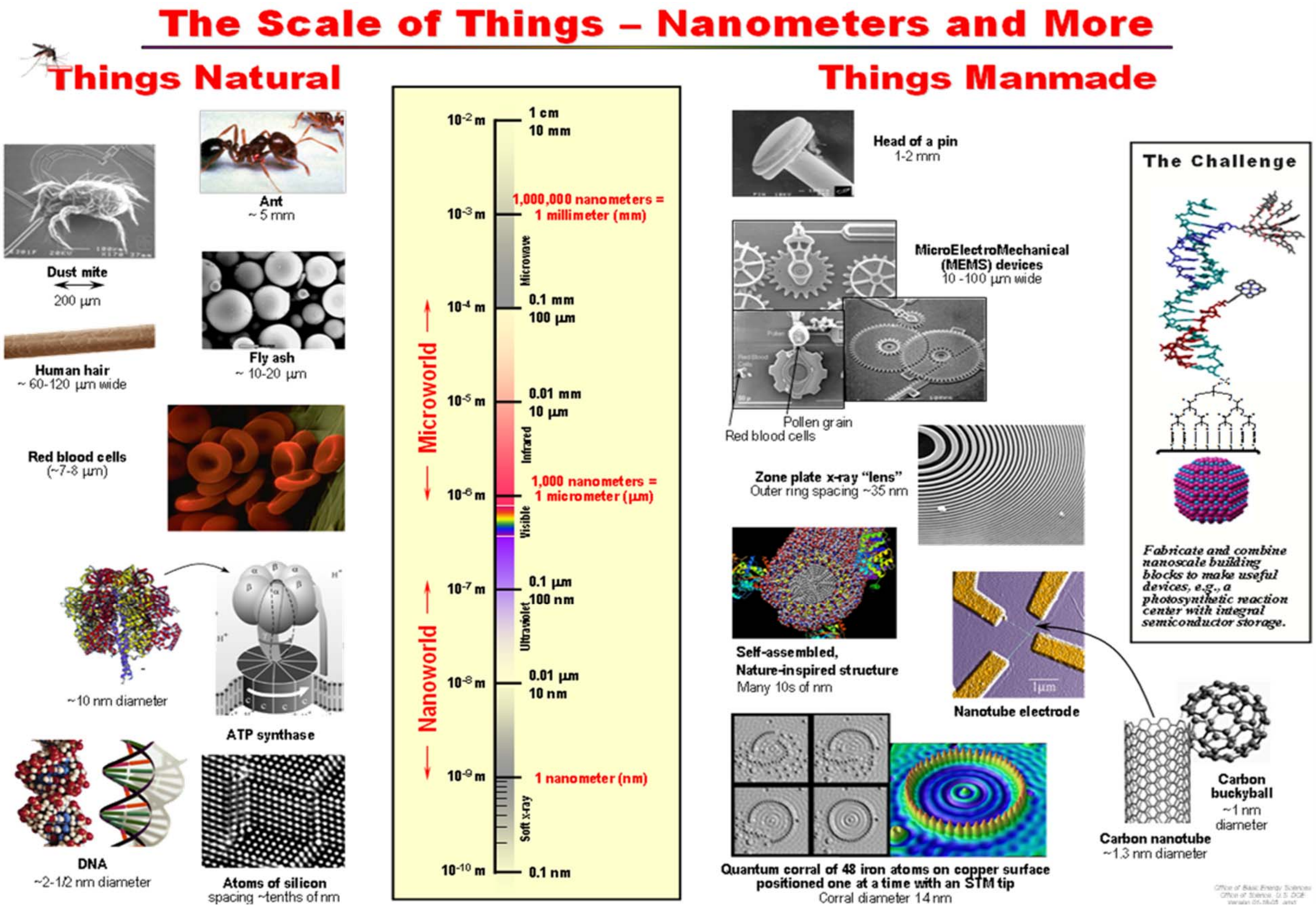
(b) **Classical Electron Theory –** introducing atomistic principles into the description of matter
ex. Drude equation (free electron in metals)

(c) **Quantum Theory –** explain the interaction of electrons with solids which could not explain by the classical Newtonian mechanics

Structure of Materials



Ref. *http://micro.magnet.fsu.edu*


The Scale of Things – Nanometers and More
Things Natural
Things Manmade
Dust mite
200 µm
Ant
~ 5 mm
Human hair
~ 60-120 µm wide
Fly ash
~ 10-20 µm
Red blood cells
(~7-8 µm)
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing ~tenths of nm
10^{-2} m
1 cm
10 mm
10^{-3} m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10^{-4} m
0.1 mm
100 µm
10^{-5} m
0.01 mm
10 µm
Infrared
10^{-6} m
1,000 nanometers =
1 micrometer (µm)
Visible
10^{-7} m
0.1 µm
100 nm
Ultraviolet
10^{-8} m
0.01 µm
10 nm
10^{-9} m
1 nanometer (nm)
Soft x-ray
10^{-10} m
0.1 nm
Microworld
Nanoworld
Head of a pin
1-2 mm
MicroElectroMechanical
(MEMS) devices
10 -100 µm wide
Pollen grain
Red blood cells
Zone plate x-ray "lens"
Outer ring spacing ~35 nm
Self-assembled,
Nature-inspired structure
Many 10s of nm
Nanotube electrode
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm
Carbon nanotube
~1.3 nm diameter
Carbon
buckyball
~1 nm
diameter
The Challenge
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

Wave- Particle Duality

What is an electron? – we experience merely the actions of electrons, e.g., television screen or in an electron microscope, showing particle-like and wave-like behavior of electrons, respectively.

Similar discussion to discuss the property of light.

We perceive light intuitively as a wave – electromagnatic wave
-as the color of light is related to its waverlength λ, or to its frequency ν.
-Diffraction, interference, dispersion

We also know that the light also has a particle nature.
-Photoelectric effect (1905, Einstein)

Newton's Law:

$$F = ma$$

$$E_{kin.} = \frac{1}{2} m v^2$$

$$p = mv$$

$$thus, E_{kin.} = \frac{p^2}{2m}$$

Light:

speed of light: $c = \nu\lambda$

energy quanta (photon): $E = h\nu = \hbar\omega$

$$(\hbar = \frac{h}{2\pi},\ \omega = 2\pi\nu)$$

Planck constant: h=6.626 x 10^{-34} J sec
=4.136 x 10^{-16} eV sec

Wave- Particle Duality of Electron

In 1897, particle like property of electrons was discovered by J.J. Thompson at the Cavendish Lab.

Charge: 1.6X10^{-19}C, Mass: ~1/2000 of the mass of hydrogen atom

In 1924 de Broglie postulated that the electrons should also possess wave-particle duality and suggested the wave-nature of electrons.

From the equations of the light, such as:

$$E = h\nu$$

$$E = mc^2$$

$$p = mc$$

$$c = \nu\lambda$$

$$\Rightarrow$$

$$E = h\nu = h\frac{c}{\lambda} = mc^2$$

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

$$E = h\nu = \hbar\omega$$

$$p = h\frac{1}{\lambda} = \hbar k$$

$$(\hbar = \frac{h}{2\pi},\ \omega = 2\pi\nu,\ k = \frac{2\pi}{\lambda})$$

In 1926, Schrodinger provide a mathmatical Form of this idea. – Schrodinger equation

What is a wave?

A wave is a "disturbance" which is periodic in position and time.

Waves are characterized by a velocity, v, a frequency, ν, and a wavelength, λ, which are interrelated by,

$$v = \lambda \nu = \frac{\omega}{k}$$

Simplest waveform is mathematically expressed by a sine (or a cosine) function – "harmonic wave".

$$\Psi = \sin(kx - wt)$$

The wave-particle duality may be better understood by realizing that the electron can be represented by a combination of several wave trains having slightly different frequencies, for example, ω and ω+Δω, and different wave numbers, k and k+Δk.

$$\Psi_1 = \sin(kx - \omega t)$$
$$\Psi_2 = \sin[(k + \Delta k)x - (\omega + \Delta\omega)t]$$

$$\Psi = \Psi_1 + \Psi_2 = 2\cos(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x) \cdot \sin[(k + \frac{\Delta k}{2})x - (\omega + \frac{\Delta\omega}{2})t]$$

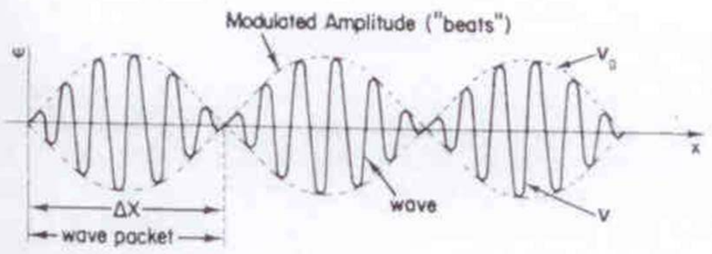
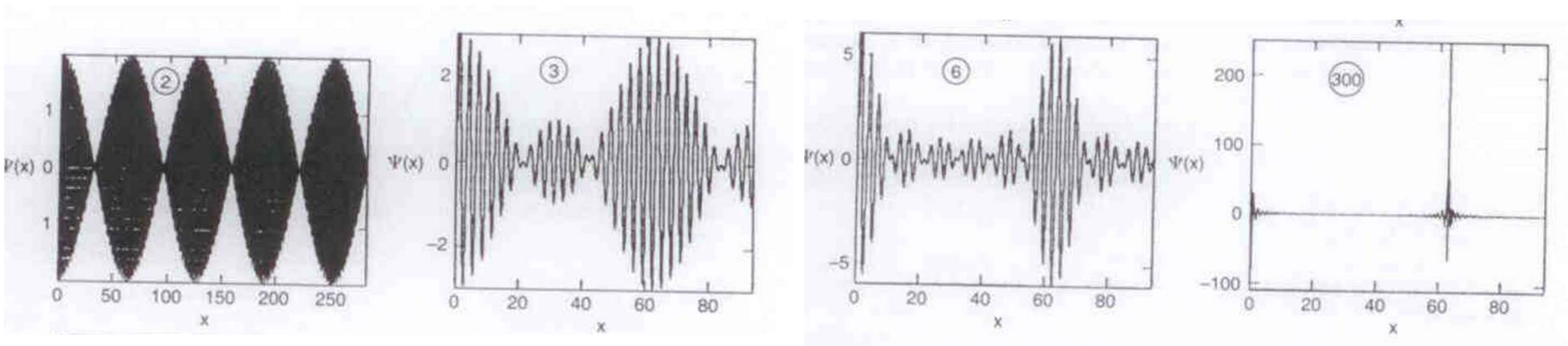


Figure 2.1. Combination of two waves of slightly different frequencies. ΔX is the distance over which the particle can be found.

Two extreme cases:

(α) $\Delta\omega$ and Δk=0, "infinitely long" wave packet – monochromatic wave
(β) $\Delta\omega$ and Δk assumed to be very large – short wave packet
if a large number of different waves are combined, having frequencies $\omega + n\Delta\omega$ (where n= 1, 2, 3,…), then the string of wave packets reduces to one wave packet only. The electron is then represented as a particle.



Different velocities:

(1) The velocity of "matter wave" is called the wave velocity or "phase velocity".

- stream of particles of equal velocity whose frequency, wavelength, momentum, or energy can be exactly determined.
- the location of particles, however, is undetermined.
- the phase velocity varies for different wavelength.

$$v = \frac{x}{t} = \frac{\omega + \Delta\omega}{k + \Delta k} = \frac{\omega'}{k'}$$

(2) Particle can be understood as a "wave packet" where, the velocity of a particle is called "group velocity", vg.

- the velocity of a "modulated amplitude" is expressed as

$$v_g = \frac{x}{t} = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk}$$

- the location x of a particle is known precisely, whereas the frequency is not.
- the better the location, Δx, of a particle can be determined, the wider is the frequency range, $\Delta\omega$
- one form of Heisenberg's uncertainty principle

$$\Delta p \cdot \Delta X \geq h$$

TABLE 1.1 Particle and Wave Properties[a]

Particlelike	Wavelike	Correlation
Has a position in space; its location can be specified by giving spatial coordinates.	Is extended in space; spatial characteristics are specified by a wavelength λ.	Heisenberg indeterminacy principle: $\Delta x \cdot \Delta(1/\lambda) \geq 1/2\pi$
		Totally particlelike: $\Delta x = 0$, $\Delta(1/\lambda) = \infty$ Totally wavelike: $\Delta(1/\lambda) = 0$, $\Delta x = \infty$.
Has a momentum given by $p = mv$.	Momentum is described in terms of a wave number $k = 2\pi/\lambda$	If particlelike momentum is mv, wavelike wavelength is $\lambda = h/mv$ where v is the group velocity of the corresponding waves.
Has kinetic and potential energy given by $E = \frac{1}{2}mv^2 + V$	Has an angular frequency $\omega = 2\pi\nu$.	If particlelike energy is E, wavelike frequency is $\omega = E/\hbar$.
Can take on all values of energy $E \geq 0$.	Can exhibit all frequencies ω if the wave is effectively infinite, i.e., unconfined.	Can exhibit all energies $E = \hbar\omega \geq 0$ if the "wave" is effectively infinite, i.e., a free particle" with $V = 0$.
	Can exhibit only a set of discrete frequencies ω_i if the wave is finite, i.e., confined to a specific region of space.	Can exhibit only a set of discrete energies $E_i = \hbar\omega_i$ if the "wave" is confined, i.e., if the "particle" is constrained by $V \neq 0$.

[a] A comparison of particlelike and wavelike properties and the correlation between them when both are used in appropriate circumstances to describe the behavior of entities with particlelike and wavelike properties, e.g., an electron.

1

Solution of Schrödinger Equation for Four Specific Problems

Derivation of Schrodinger Equation:

Matter wave equation is expressed as a harmonic wave form:

$$\Psi = A\exp[i(kx - \omega t)]$$

	Energy(E)	**Momentum(p)**
Particle:	$\dfrac{p^2}{2m} + V$	mv
Wave:	$\hbar\omega$	$\hbar k$
	$\dfrac{\partial \Psi}{\partial t} = -i\omega\Psi$	$\dfrac{\partial^2 \Psi}{\partial x^2} = -k^2\Psi$
	$E = \dfrac{i\hbar}{\Psi}\dfrac{\partial \Psi}{\partial t}$	$p^2 = -\dfrac{\hbar^2}{\Psi}\dfrac{\partial^2 \Psi}{\partial x^2}$

Since, E= $\dfrac{p^2}{2m} + V$

$$\frac{i\hbar}{\Psi}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\Psi}\frac{\partial^2 \Psi}{\partial x^2} + V$$

$$\boxed{i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi}$$ (time-dependent Schrodinger equation)

Derivation of Schrodinger Equation:

At stationary state – time independent state
We are asking what energy states are allowed.

We can write, $\Psi = \psi(x) \cdot \exp(-i\omega t)$

Then,

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) \quad \text{(time-independent Schrodinger equation)}$$

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

Solution:

1. Choose desired potential energy V(x, y, z)
2. Get the general solution of ψ(x, y, z)
3. Retain only mathematically well behaved terms

   single valued
   not=0
   continuous and continuous derivatives
   finite

4. Apply boundary condition - E_n

1.1 Free Electrons

Time-Independent Schrödinger Equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0.$$

We consider electrons which propagate freely with no potential barrier(V), namely, in a potential-free space in the positive x-direction.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0.$$

$$\psi(x) = Ae^{i\alpha x}, \qquad \alpha = \sqrt{\frac{2m}{\hbar^2}E}$$

$u = Ae^{ikx} + Be^{-ikx}$, Taking on the standard time dependence $e^{i\omega x}$

$$u = \underline{Ae^{i(kx-\omega t)}} + \underline{Be^{-i(kx+\omega t)}},$$

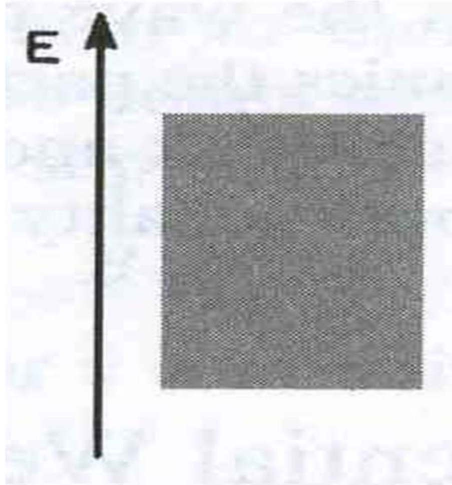
Traveling in the -x direction

Traveling in the x direction

When we concern about wave traveling in the x-direction

$$\Psi(x) = Ae^{i\alpha x} \cdot e^{i\omega t}$$

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



Energy continuum of a free

Because there are no boundary conditions, we can obtain an energy continnum

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

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

$$\left|\vec{\mathrm{k}}\right| = \frac{2\pi}{\lambda}.$$ **(Wave vector)**

$$\vec{k} \propto \vec{p}$$

k-vector describes the wave properties of an electron, just as one describes in classical mechanics the particle property of an electron with the momentum

1.2 Electron in a Potential Well (Bound Electron)

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

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0.$$ **(In side of potential well V=0)**

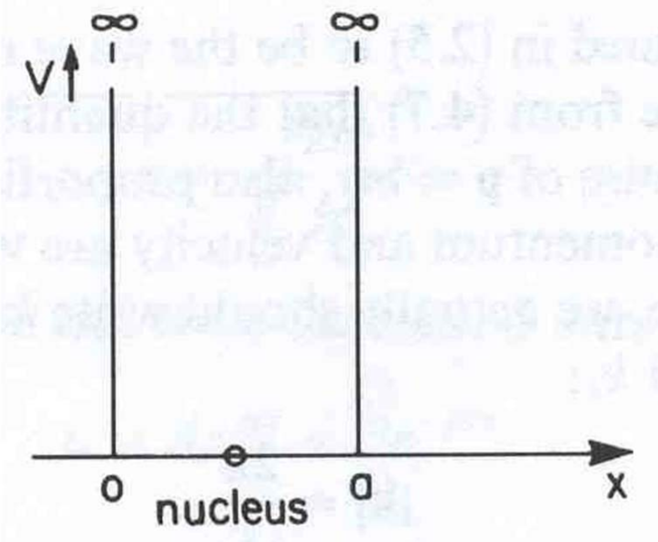
$$\psi = Ae^{i\alpha x} + Be^{-i\alpha x} \quad ,\alpha = \sqrt{\frac{2m}{\hbar^2}E}$$

Boundary condition

$$\psi = 0 \quad (\,for\; x \leq 0, x \geq a)$$

$$B = -A.$$

$$0 = Ae^{i\alpha a} + Be^{-i\alpha a} = A(e^{i\alpha a} - e^{-i\alpha a}).$$



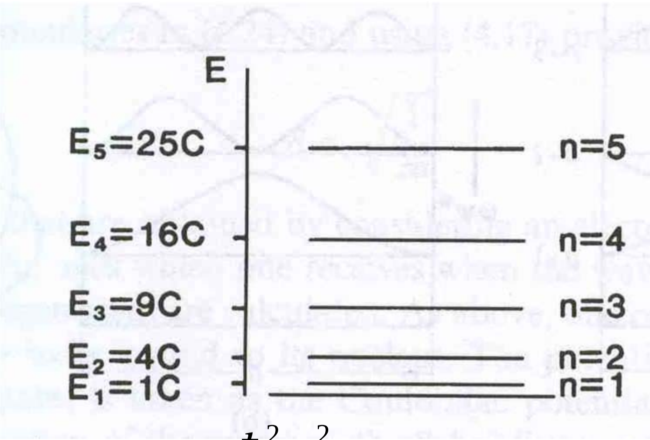
One-dimensional potential well.

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

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

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

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



$$C = \frac{\hbar^2\pi^2}{2ma^2}$$

This result is called "Energy Quantization"

Now, since

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

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

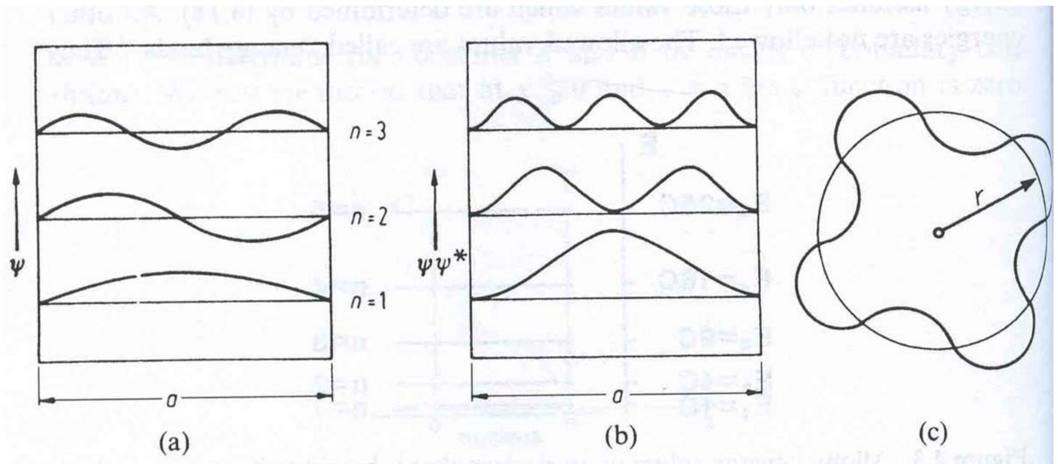
Normalization

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

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

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

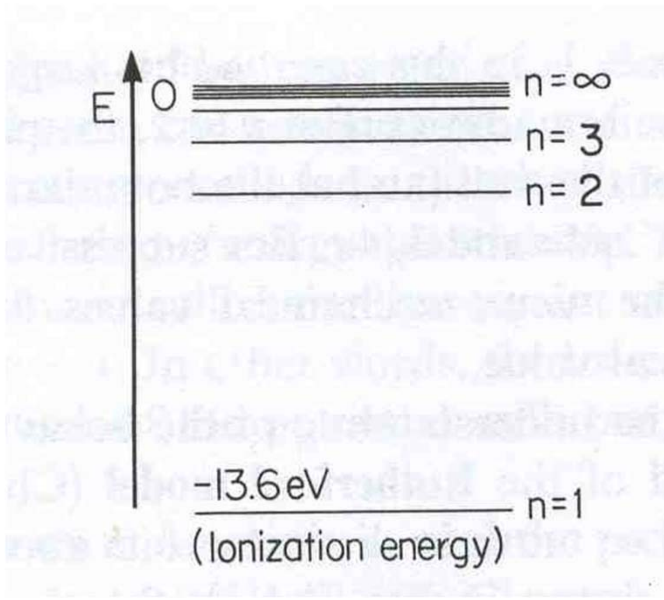
n	E_n
1	$\frac{\hbar^2 \pi^2}{2ma^2}$
2	$4\frac{\hbar^2 \pi^2}{2ma^2}$
3	$9\frac{\hbar^2 \pi^2}{2ma^2}$



For hydrogen model

The potential ,V, is taken as the Coulombic potential $V = -e^2 / 4\pi\varepsilon_0 r$, *and solve Schrodinger equation by setting the polar coordinates.*

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



For electron in a box (3-D)

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2). \qquad (n_x, n_y, n_z : \textit{ Integer })$$

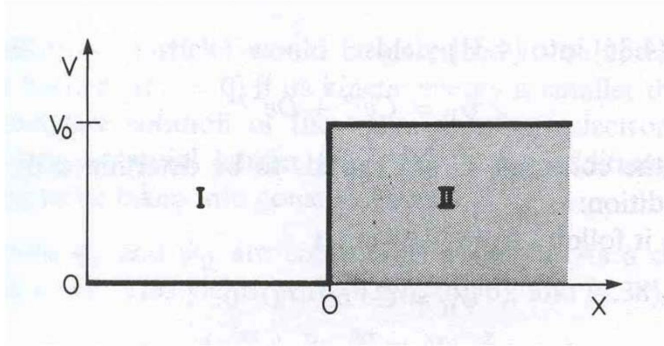
The smallest allowed energy is when $n_x=n_y=n_z=1$
For the next higher energy,
$(n_x, n_y, n_z) = (1, 1, 2), (1, 2, 1), (2, 1, 1)$

"Degenerate States":
have the same energy but different quantum numbers

1.3 Finite Potential Barrier (Tunnel Effect)

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

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



(I) $$\psi_{\mathrm{I}} = Ae^{i\alpha x} + Be^{-i\alpha x}, \alpha = \sqrt{\frac{2mE}{\hbar^2}},$$

(II) $$\psi_{\mathrm{II}} = Ce^{i\beta x} + De^{-i\beta x}, \ \beta = \sqrt{\frac{2m}{h^2}(E - V_0)}.$$

$$\gamma = i\beta. \quad \Rightarrow \quad \gamma = \sqrt{\frac{2m}{h^2}(V_0 - E)}. \quad (\because V_0 > E)$$

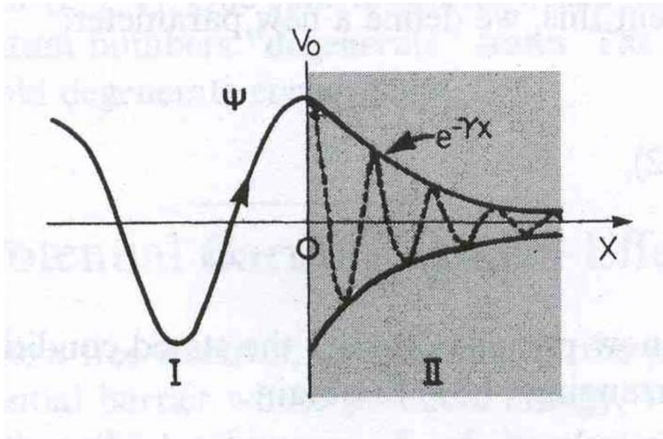
$$\psi_{\mathrm{II}} = Ce^{\gamma x} + De^{-\gamma x}.$$

$$\psi_{\mathrm{II}} = C \cdot \infty + D \cdot 0. \ (x \to \infty, \ \psi \to 0 \ \ for \ \ bound \ \ state)$$

Thus, $C \to 0.$

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

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



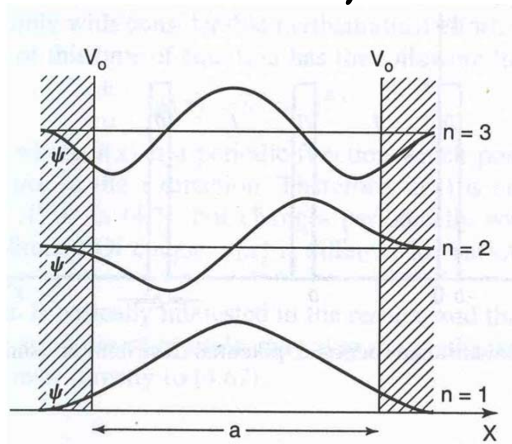
(1) The function ψ_{I} and ψ_{II} are continuous at x=0. As a consquence, at x=0.

$$Ae^{i\alpha x} + Be^{-i\alpha x} = De^{-\gamma x} \xrightarrow[x=0]{} A + B = D.$$

(2) The slopes of the wave functions in Regions I and II are continuous at x=0, i.e. $(d\psi_{\mathrm{I}}/dx) \equiv (d\psi_{\mathrm{II}}/dx)$

$$Ai\alpha e^{i\alpha x} + Bi\alpha e^{-i\alpha x} = -\gamma De^{-\gamma x}. \xrightarrow[x=0]{} Ai\alpha - Bi\alpha = -\gamma D.$$

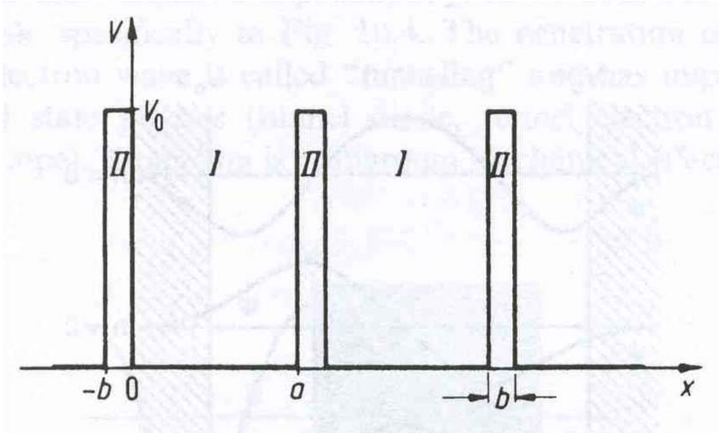
$$A = \frac{D}{2}\left(1 + i\frac{\gamma}{\alpha}\right), B = \frac{D}{2}\left(1 - i\frac{\gamma}{\alpha}\right).$$



1.4 Electron in a Periodic Field of a Crystal (The Solid State)

The goal of this section is to study the behavior of an electron in a crystal-periodic potential.

<u>Kronig-Penney Model</u>

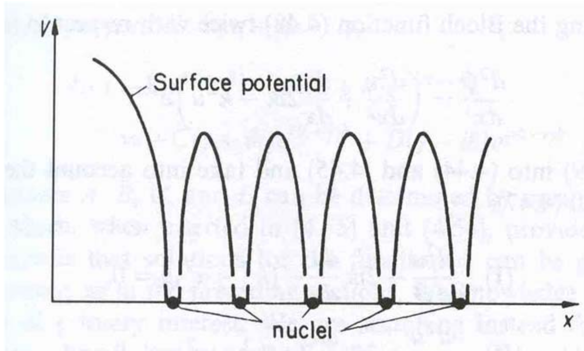


(I) $$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0,$$

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

$$\alpha^2 = \frac{2m}{\hbar^2}E, \quad \gamma^2 = \frac{2m}{\hbar^2}(V_0 - E).$$

$$\psi(x) = u(x)\cdot e^{ikx}$$ **(Bloch function)**



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

Put it to equation (I) , (II) then

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

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

(I) $$u=e^{-ikx}(Ae^{iax}+Be^{-iax}),$$

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

Boundary condition

$$\psi_{\mathrm{I}}=\psi_{\mathrm{II}}$$

$$\left(d\psi/dx\right)_{\mathrm{I}}=\left(d\psi/dx\right)_{\mathrm{II}}$$

(1) **At x=0**

$$A + B = C + D.$$

$$A(i\alpha - ik) + B(-i\alpha - ik) = C(-\gamma - ik) + D(\gamma - ik).$$

(2) **For periodicity , Eq I = Eq II (at x=0,x=a+b)**

$$Ae^{(i\alpha - ik)a} + Be^{(-i\alpha - ik)a} = Ce^{(ik+\gamma)b} + De^{(ik-\gamma)b}.$$

$$Ai(\alpha - k)e^{ia(\alpha - k)} - Bi(\alpha + k)e^{-ia(\alpha + k)}$$
$$= -C(\gamma + ik)e^{(ik+\gamma)b} + D(\gamma - ik)e^{(ik-\gamma)b}.$$

➡ **From this 4 equations we can determine unknowns A,B,C,D and the conditions which tells us where solutions to the Schrödinger equations exist.**

$$\therefore \frac{\gamma^2 - \alpha^2}{2\alpha\gamma} \sinh(\gamma b) \cdot \sin(\alpha a) + \cosh(\gamma b) \cos(\alpha a) = \cos k(a+b).$$

The potential barrier will be of a kind that b is very small and V_0 is very large. It is further assumed that the product bV_0 remains finite.

$$V_0 b \equiv \textit{Potential Barrier Strength}(\textit{finite}) \ \textit{and} \ \ b \to 0$$

If V_0 is very large, then E is considered to be small and can be neglected,

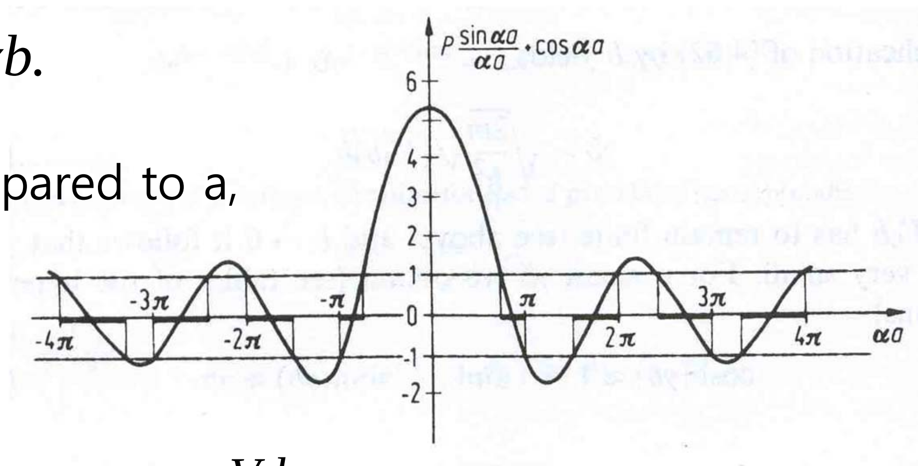
$$\gamma = \sqrt{\frac{2m}{\hbar^2}} \sqrt{V_0}, \qquad \gamma b = \sqrt{\frac{2m}{\hbar^2}} \sqrt{(V_0 b) b}.$$

And since b ~ 0

$$\cosh(\gamma b) \approx 1 \quad \text{and} \quad \sinh(\gamma b) \approx \gamma b.$$

Neglect α^2 compared to γ^2 and b compared to a,

$$\frac{m}{\alpha \hbar^2} V_0 b \sin \alpha a + \cos \alpha a = \cos ka.$$



$$\boxed{P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka.}$$

$$P = \frac{m a V_0 b}{\hbar^2}$$

Because of $-1 \leq \cos ka \leq 1$

$P\dfrac{\sin \alpha a}{\alpha a} + \cos \alpha a$ are allowed at specific region of αa

It means that Energy of electron is forbidden at specific regions

Because of $\alpha^2 = \dfrac{2m}{h^2}E,$ this forbidden regions are called by

"Energy band gap".

Special cases of this system

(a) Potential barrier strength $V_0 b$ is large,

Curve in Fig 4.11 proceeds more steeply
-> The allowed bands are narrow

(b) Potential barrier strength $V_0 b$ is small,

The allowed bands become wider

(c) Potential barrier strength $V_0 b$ goes to 0

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

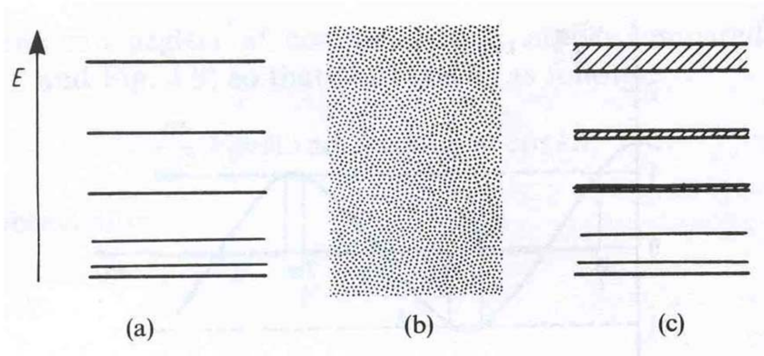
(Free electron like)

(d) Potential barrier strength $V_0 b$ is large, $P \rightarrow \infty$

$$\frac{\sin \alpha a}{\alpha a} \rightarrow 0 \quad \Rightarrow \sin \alpha a \rightarrow 0 \,, \alpha a = n\pi$$

$$\boxed{\therefore \; E = \frac{\pi^2 \hbar^2}{2ma^2} n^2}$$

(Bound electron like)



(a) bound electrons (b) free electrons (c) electrons in a solid