EEE 3396

Note Title 8/29/2017

First Things First:

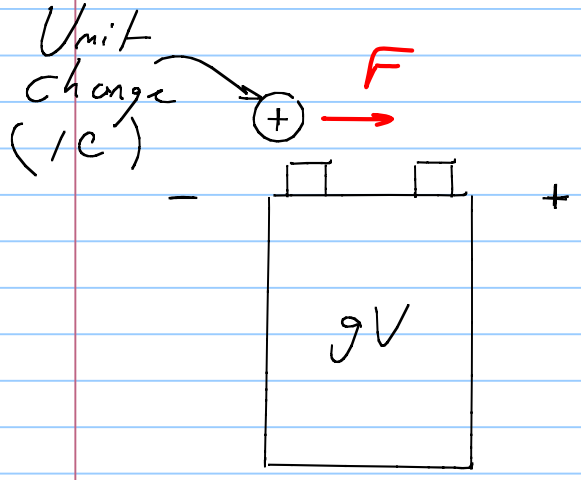
- The Electron-Volt
- Boltzmann Constant
- Avogadro's number

① The Electron-Volt (symbol: eV)

It is a unit of energy that is equal to $1.6 * 10^{-19}$ Joules.

It is frequently used as a measure of energy in atomic processes.

Recall: the definition of the "volt"



If we move a charge of +1 Coulomb from the negative electrode to the positive electrode of a 9V battery, the work done in moving the charge will be exactly 9 Joules.

Hence, voltage is a measure of energy, specifically, the energy required in moving a unit charge.

Now, if we we move an electron between the two terminals of the battery, the work done will be equal to

$$9 \text{ Joules} * \underbrace{(1.6 * 10^{-19})}_{\text{charge of electron}}$$

$$= \underbrace{(9 * 1.6 * 10^{-19})}_{\text{"eV"}} \text{ Joules}$$

$$\equiv 9 \text{ "Electron Volts"}$$

$$\text{or } 9 \text{ eV}$$

(2) Boltzmann's Constant (symbol: k)

The energy content in many random atomic processes is related to the ambient temperature by a simple constant: Boltzmann's constant.

Examples are: Molecular processes, noise in electrical circuits, etc.

Noise (or energy in a molecular process) $= kT$

k : Boltzman Constant

T : Ampient temperature

$\left(k = 1.3806 * 10^{-23} \text{ Joule}/^{\circ}K \right)$

③ Avogadro's Number (Symbol : N_A or A)

Recall : the "Mole" of any element is that element's atomic mass expressed in grams.

Example : . Atomic mass of Hydrogen $= 1$

∴ One mole of Hydrogen is 1 gram of that element.

• Atomic mass of Carbon (C_{12}) = 12

Avogadro's conclusion: a quantity equal to 1 mole of any element will always contain the same number of atoms. That number is

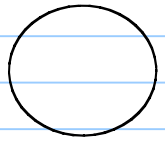
$$N_A = 6.022 \times 10^{23}$$

Why?

1 atom of hydrogen

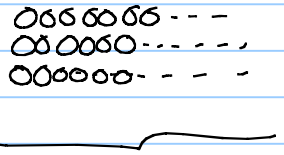
(mass = 1)

1 atom of Carbon



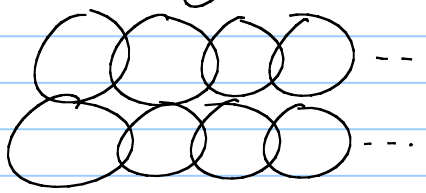
(mass = 12)

N_A atoms of Hydrogen



mass = 1 gram
(mole)

N_A atoms of Carbon



mass = 12 grams
(mole)

Planck's Law and the discovery of the "Quantum":

In 1900, Max Planck discovered the very important principle that the energy content in radiation is always an integral multiple of a "quantum" that is given by the product hV, where h is Planck's constant and V is the frequency of the radiation.

Planck's law: $\boxed{E = hV}$

(Energy in Joules or eV of a quantum of radiation, or "photon")

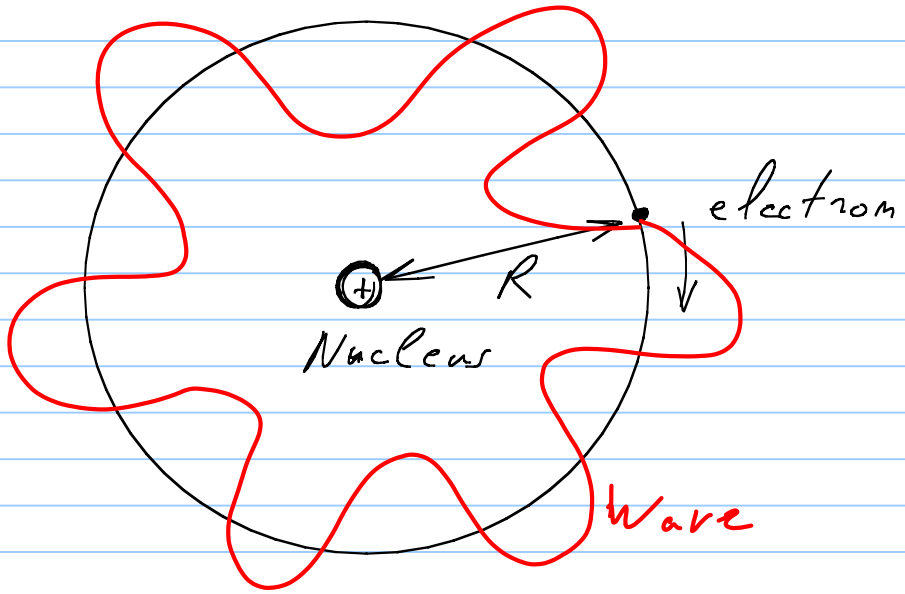
$h = 6.6256 * 10^{-34}$ Joule.sec.

The atomic model of Rutherford and Bohr:

In a series of important experiments, E. Rutherford discovered in 1911 that the atom must be composed of a heavy, positive "nucleus" that contains most of the mass of the atom. The nucleus is surrounded by a cloud of negatively charged electrons.

Using Rutherford's model, Niels Bohr succeeded in 1913 to formulate a theory for the atom that explained the atomic spectrum of Hydrogen.

Bohr's atomic model:



Bohr's postulate: the electron forms a "standing wave" around the nucleus.

Hence $n\lambda = 2\pi R$

(λ: Wavelength)

If the particle is treated as a wave, an important relationship that holds is:

$$\lambda = \frac{h}{p} = \frac{\text{Planck's Constant}}{\text{Particle's momentum}}$$

De Broglie's Formula

Hence, $2\pi R = n\lambda$

$= n\left(\frac{h}{p}\right)$

$= n\left(\frac{h}{mv}\right)$

m : electron's mass

v : electron's velocity

n : integer

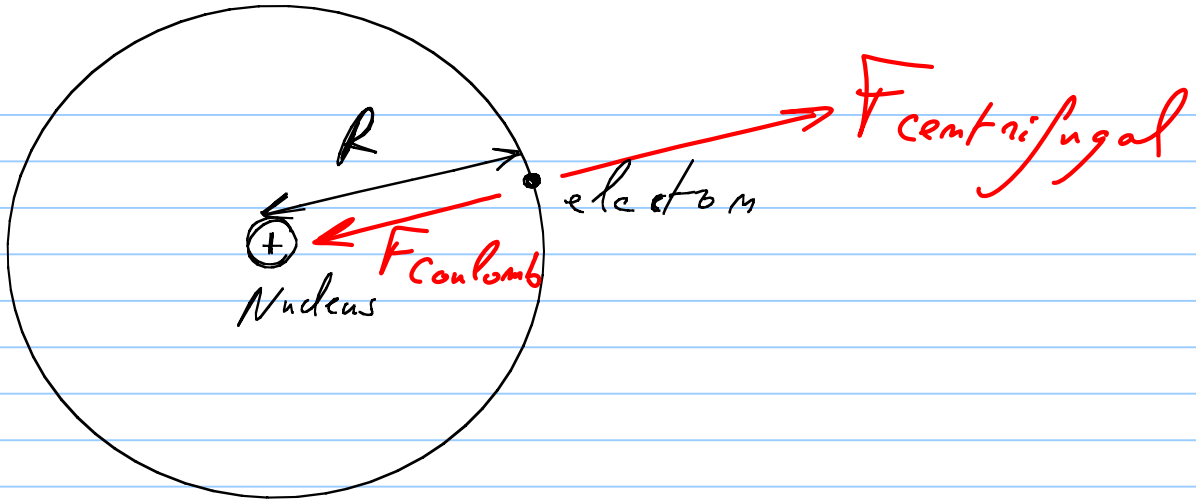
Hence, R (Radius of the orbit)

$= \frac{nh}{mv} \cdot \frac{1}{2\pi}$

$= \frac{n\hbar}{mv}$ ---- (1)

where $\boxed{\hbar = h/2\pi}$

Treating the electron as a material particle :



Since the electron is in a stable orbit,

$$F_{Coulomb} = F_{centrifugal}$$

$$\frac{1}{4\pi\varepsilon_0}\,\frac{(q)(q)}{R^2} = \frac{mv^2}{R}$$

ε_0 ← permittivity of free space

$\left(\varepsilon_0 = 8.85 * 10^{-12}\ C^2/N.m^2\right)$

The quantity $q^2/4\pi\varepsilon_0$, where q is the electron's charge, appears a lot in physics equations, and is often abbreviated by the symbol "e^2".

Hence, $\dfrac{e^2}{R} = mv^2$ ..... (2)

From eqs. ① and ②:

$$R = \frac{e^2}{m v^2} = \frac{n\hbar}{m v}$$

$$\therefore \boxed{v = \frac{e^2}{n\hbar} \quad \text{(velocity of the electron)}}$$

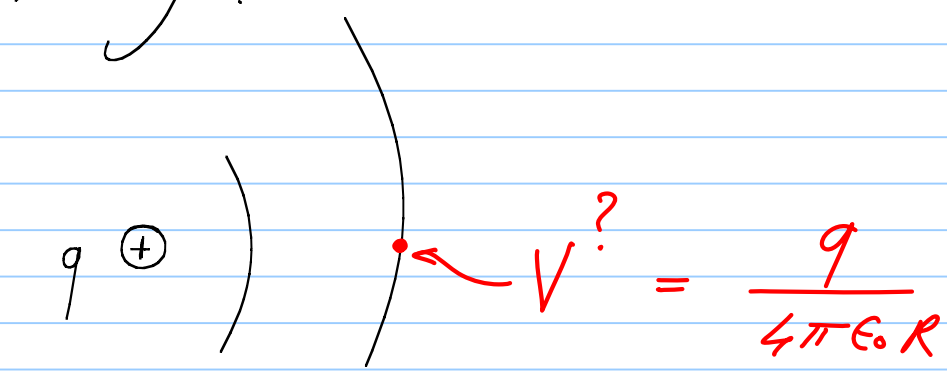
and

$$\boxed{R = \frac{n\hbar}{mv} = \frac{n\hbar}{m\left(\frac{e^2}{n\hbar}\right)} = \frac{n^2\hbar^2}{me^2}}$$

(radius of the orbit)

Electron's total energy:

First, the electrostatic potential due to the field of the nucleus is given by:



(Work done in moving a unit charge from infinity up to that specific point)

The quantity of energy required in moving one electron will be

$$\frac{q}{4\pi\epsilon_0 R} * \underbrace{(-q)}_{\text{electron's charge}}$$

$$= \frac{-q^2}{4\pi\epsilon_0 R}$$

$$= -\frac{e^2}{R}$$

(Electrostatic potential of electron)

$$= W_p$$

Secondly, the kinetic energy of the electron, W_K, is given by:

$$W_K = \frac{1}{2} m v^2$$

$$= \frac{1}{2} m \left(\frac{e^2}{nh}\right)^2$$

$$= \frac{1}{2} m \frac{e^4}{n^2 \hbar^2}$$

The total energy of the electron is therefore:

$$W = W_p + W_k$$

$$= -\frac{e^2}{R} + \frac{1}{2} m \frac{e^4}{n^2 \hbar^2}$$

$$= -\frac{e^2}{\left(\frac{n^2 \hbar^2}{m e^2}\right)} + \frac{1}{2} m \frac{e^4}{n^2 \hbar^2}$$

$$= -\frac{m e^4}{n^2 \hbar^2} + \frac{1}{2} \frac{m e^4}{n^2 \hbar^2}$$

$$= \boxed{-\frac{1}{2} \frac{m e^4}{n^2 \hbar^2}}$$

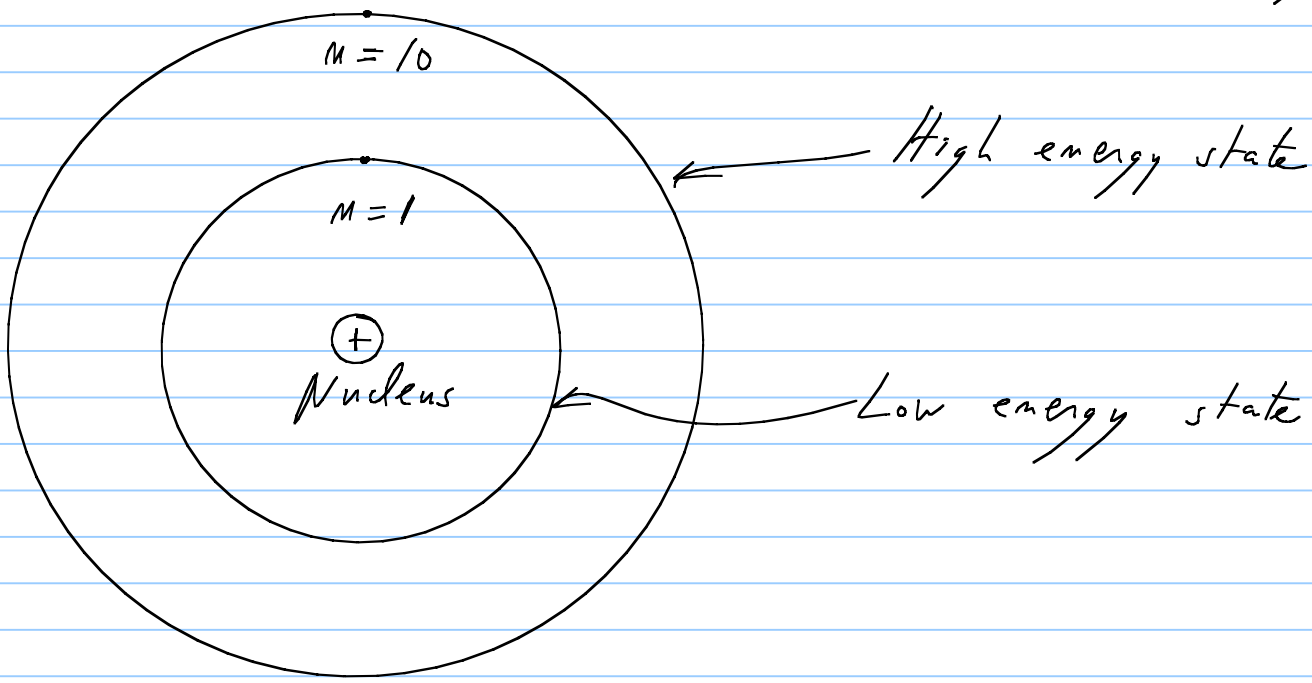
Bohr's total energy formula

The negative sign indicates that the electron doesn't have net energy on its own. It takes external energy to liberate the electron from the atom.

- The integer n is called the "principal" quantum number. It takes the values

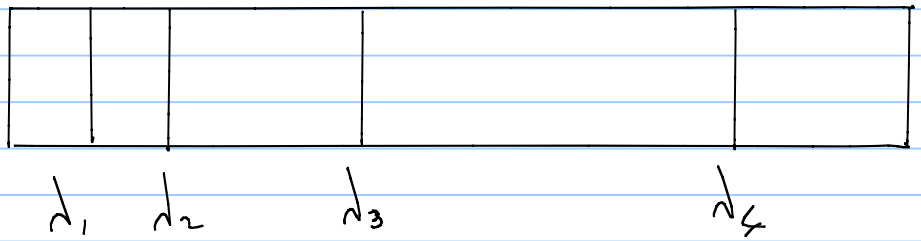
$$1, 2, 3, 4, \ldots$$

- The larger the value of n the larger the radius R (and the smaller the velocity v). Also, as n grows, the larger the total energy W. ($W \to 0$ as $n \to \infty$)

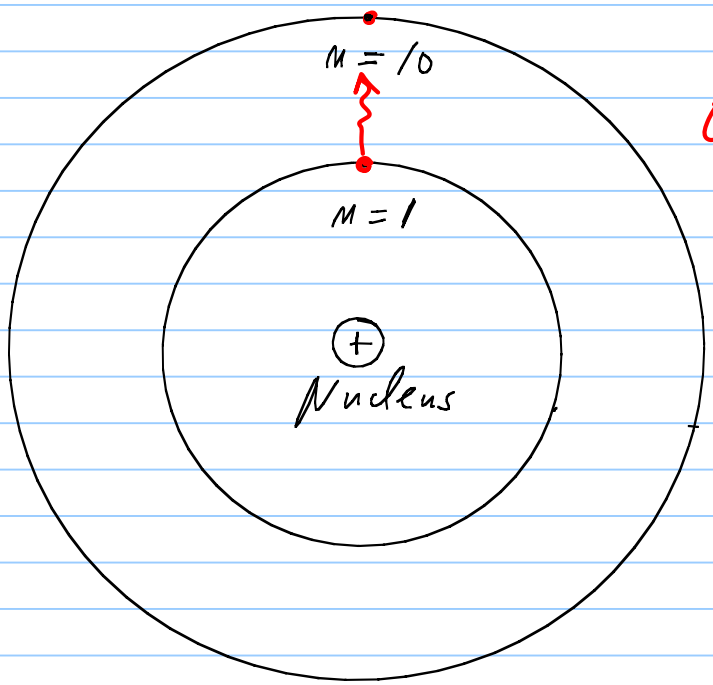


- Atomic spectra and Bohr's explanation of the Hydrogen spectrum:

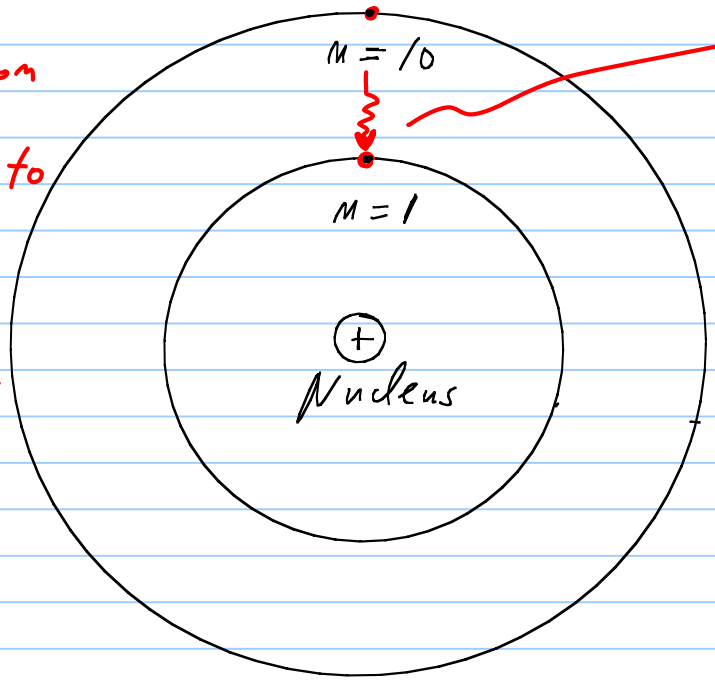
  - Any element when heated emits a very distinctive set of visible (or invisible) electromagnetic frequencies. Those frequencies, when separated with a diffraction grating or a prism, produce a distinct "spectrum" that identifies the element.



  - Bohr suggested that an atom emits radiation when the electron falls from a higher energy state to a lower energy state.



Energy is supplied to the atom



Electron falls back to the low energy state

Photon or quantum of radiation

- The energy of the emitted photon will be given by:

$$E_{n_2} - E_{n_1} = h\nu$$

(ν = photon's frequency)

$$= -\frac{1}{2}\frac{me^4}{n_2^2\hbar^2} - \left(-\frac{1}{2}\frac{me^4}{n_1^2\hbar^2}\right)$$

$$= \frac{1}{2}\frac{me^4}{\hbar^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= h\nu$$

(Recall: $\nu\lambda = c$)

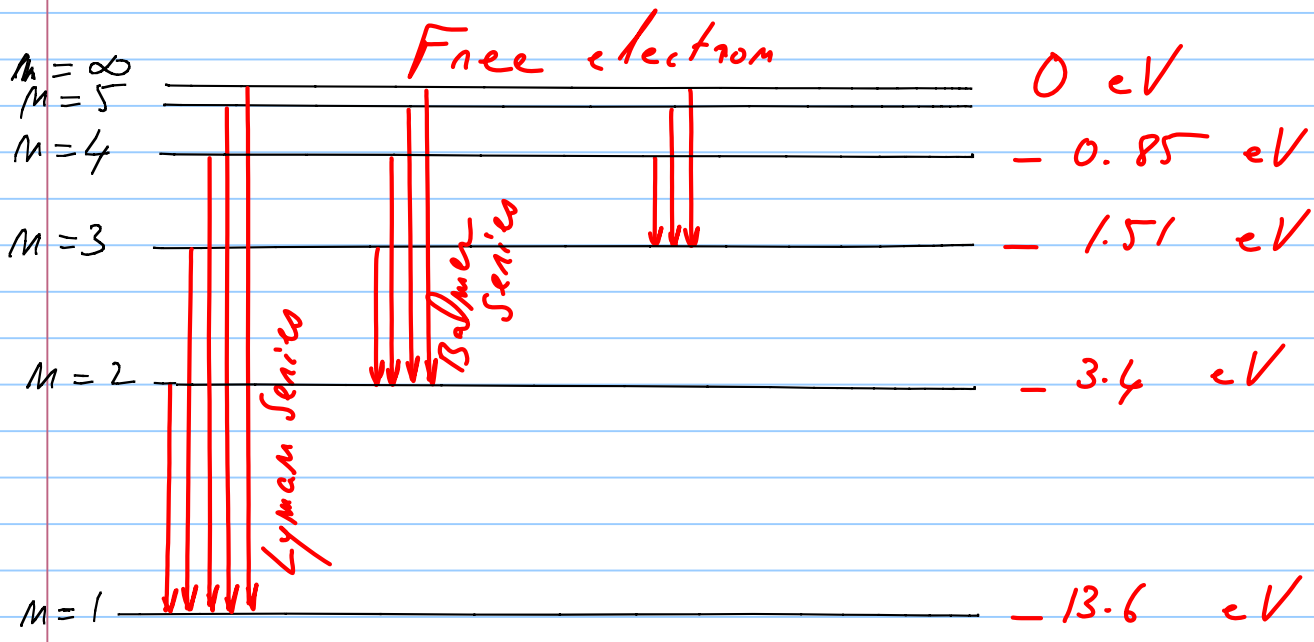
(ν: freq., λ: wavelength, c: speed of light)

Hence, the wavelength $\lambda = \frac{c}{\nu}$.

- Different transitions in Bohr's model:

n_1	n_2	Series discovered by
1	2, 3, 4, 5,	Lyman (1916)
2	3, 4, 5, 6,	Balmer (1884)
3	4, 5, 6, 7,	Paschen (1908)
4	5, 6, 7, 8,	Brackett (1922)
5	6, 7, 8, 9, ...	Pfund (1924)

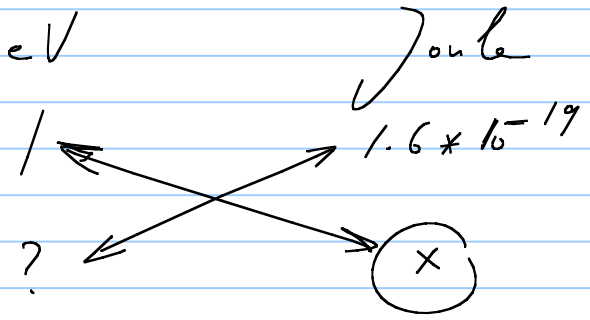
Energy level diagram for the Hydrogen atom:



$$= \boxed{-\frac{1}{2}\frac{m e^4}{n^2 \hbar^2}}$$

Bohr's total energy formula (in Joules)

How to convert from Joule to eV and vice versa?



- For $n = 1$, the atom is said to be in the "ground state". This is the lowest possible energy state. The atom can be "excited" by supplying energy to it. The electron absorbs the energy and moves to a higher energy level. Only 13.6 eV of energy is sufficient to liberate the electron from

the atom. An atom that has lost one or more electrons is said to be "ionized".

- The electron eventually "drops" from a higher energy state to a lower energy state, emitting the difference of energy in the form of a quantum of radiation (photon).

Example:

A free electron falls to a bound state where $n = 2$. Calculate the energy and the frequency of the emitted photon. Is the photon in the visible spectrum?

$$W = 0 - (-3.4\ eV) = +3.4\ eV$$

$$= 3.4 * 1.6 * 10^{-19}\ \text{Joule}$$

$$\therefore \nu\ (\text{frequency}) = \frac{W}{h} = \frac{3.4 * 1.6 * 10^{-19}}{6.626 * 10^{-34}}$$

$= 8.21 * 10^{14}\ Hz$

$\therefore \lambda\ (\text{wavelength}) = \dfrac{c}{\nu} = \dfrac{3 * 10^{8}\ m/s}{8.21 * 10^{14}}$

$= 3.65 * 10^{-7}\ m$

$= 365 * 10^{-9}$

$= 365\ nm$

Visible light has wavelengths in the range of 400 – 700 nm.

Ultraviolet ← (400 – 700 nm) → Infrared

Checks on the predictions of Bohr's theory:

In the visible spectrum of Hydrogen:

$\lambda_{red} = 657.7\ nm$

$\lambda_{green} = 487\ nm$

Check the transition 3 → 2:

$$= \frac{1}{2} \frac{m e^4}{\hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= 13.6\ eV \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= h\nu$$

$$= 13.6 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$= 1.89\ eV$$

$$= 1.89 * 1.6 * 10^{-19}\ J$$

$$\therefore \nu (\text{frequency}) = \frac{1.89 * 1.6 * 10^{-19}}{h}$$

$$\therefore \lambda (\text{wavelength}) = \frac{c}{\nu} = \frac{(3 * 10^8)}{\nu}$$

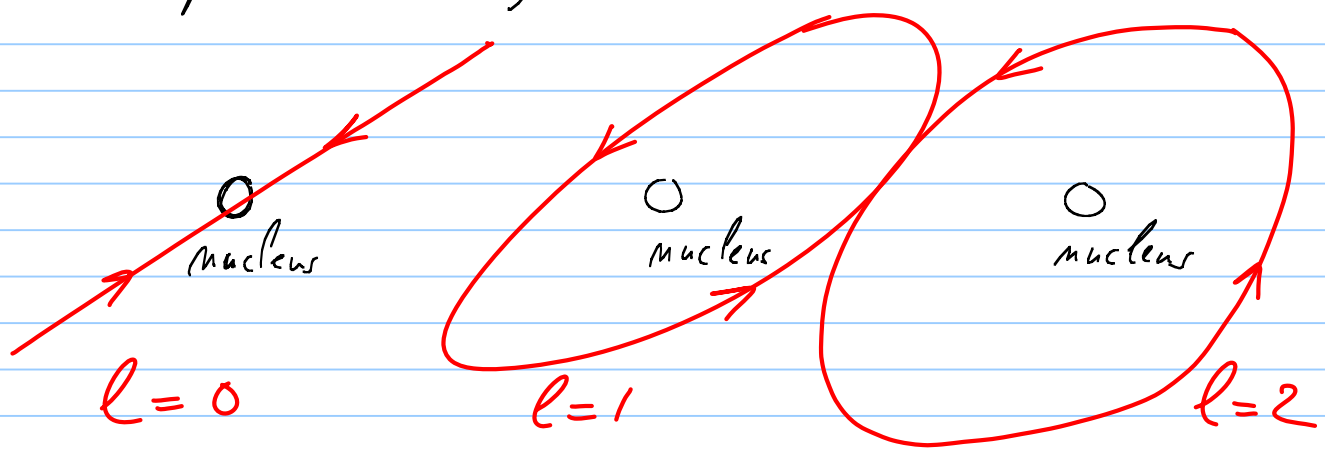
$$= 657.7\ nm$$

(Check the λ for the photon emitted in the transition $4 \rightarrow 2$.)

The Fine Structure of Hydrogen and the Discovery of the Quantum Numbers:

- Further high precision spectroscopic measurements showed that the energy levels of Hydrogen can be subdivided into finer levels (the so-called "doublets").

- It quickly became apparent that the basic theory of Bohr cannot explain the fine structure of Hydrogen. In 1915, Sommerfeld postulated that the orbit of the electron is not circular but rather elliptical, and succeeded in deriving a formula that explained the fine structure.



All these orbits share the same principal quantum number n.

- Sommerfeld introduced a second quantum number, "ℓ", called the "orbital quantum number", to account for the eccentricity of the orbit.

- Sommerfeld deduced theoretically that "ℓ" can have values ranging from 0 to $(n-1)$. For example, if $n = 3$, then $\ell = 0$, 1, or 2.

- Sommerfeld's formula for the total energy W of the electron:

$$W = -\frac{1}{2} \frac{m e^4}{\hbar^2 \left(n - \ell + \sqrt{\ell^2 - \alpha^2} \right)^2}$$

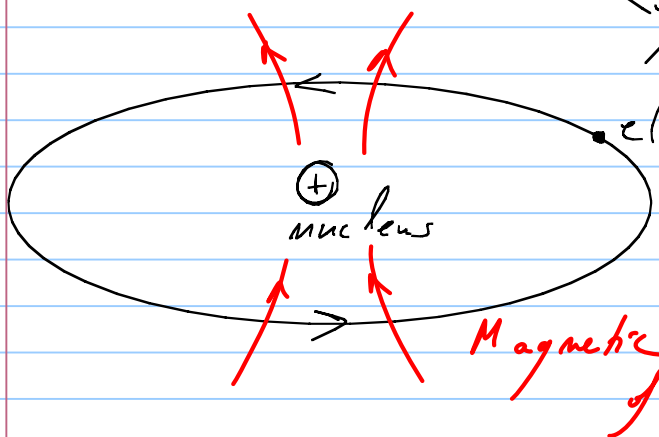
$$= \boxed{-\frac{1}{2}\frac{m e^4}{n^2 \hbar^2}}$$

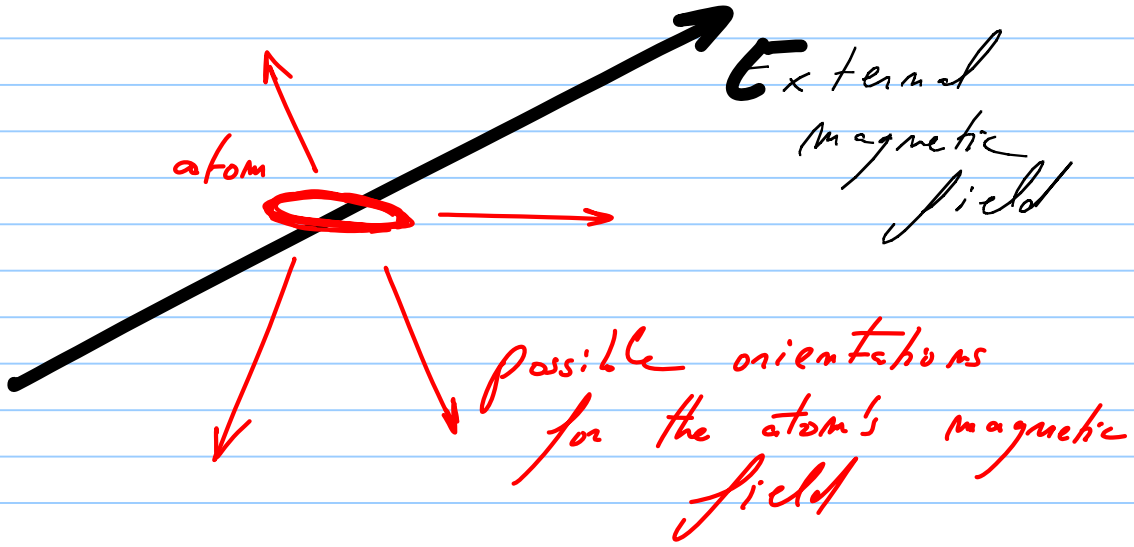
Bohr's total energy formula (in Joules)

The "α" is Sommerfeld's equation is a new constant known as the "Fine Structure Constant"

- Additional experiments with atoms placed in magnetic fields showed that two more quantum numbers must exist:

#3: The "orbital magnetic" quantum number (symbol: m_ℓ)



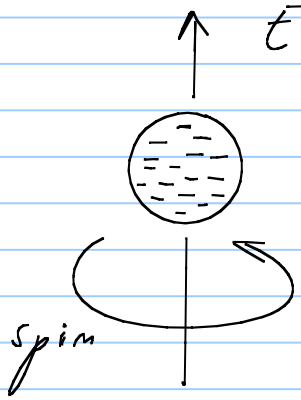


It was found that the alignment of the atom's magnetic field occurs in only a set of specific, discrete directions in space. m_ℓ is the quantum number that describes those different alignments. m_ℓ can have an integer value ranging from $-\ell$ to $+\ell$. For example, if $\ell = 2$, then $m_\ell = -2, -1, 0, +1, +2$.

Hence, there are 5 possible orientations for the electron's magnetic field.

#4 : The "Spin" quantum number (symbol : S)

The "space quantization" of the atom's magnetic field can only occur if the electron has a property called "Spin".



Electron rotates around itself, creating a second, local magnetic field.

Due to spin, the electron has a "magnetic moment", μ, given by:

$$\mu = \pm \frac{1}{2} \frac{q\hbar}{m}$$

Summary: the 4 Quantum Numbers

1. n (principal): $1, 2, 3, 4, \ldots \infty$
2. ℓ (orbital): $0, 1, 2, \ldots (n-1)$
3. m_ℓ (orbital magnetic): $-\ell, \ldots +\ell$
4. s (spin) $\pm \frac{1}{2}$

More about spectral transitions:

Transitions to the different "ℓ" states are given the following names:

Transitions to	Name of Series
$\ell = 0$	"Sharp" series, or "s"
$\ell = 1$	"Principal" series, or "p"
$\ell = 2$	"Diffuse" series, or "d"
$\ell = 3$	"Fundamental" series, or "f"
$\ell = 4$	"g"
$\ell = 5$	"h"
⋮	

Based on those definitions, electron configurations in atoms are described in the following manner: if an atom has 6 electrons for which $n = 3$ and $\ell = 2$, then the atom is said to have $3d^6$ electrons.

The Pauli Exclusion Principle:

(introduced by Wolfgang Pauli)

> In any one atom, no two electrons can have the same set of quantum numbers!

Examples:

- Let $n = 1$, then $\ell = 0$

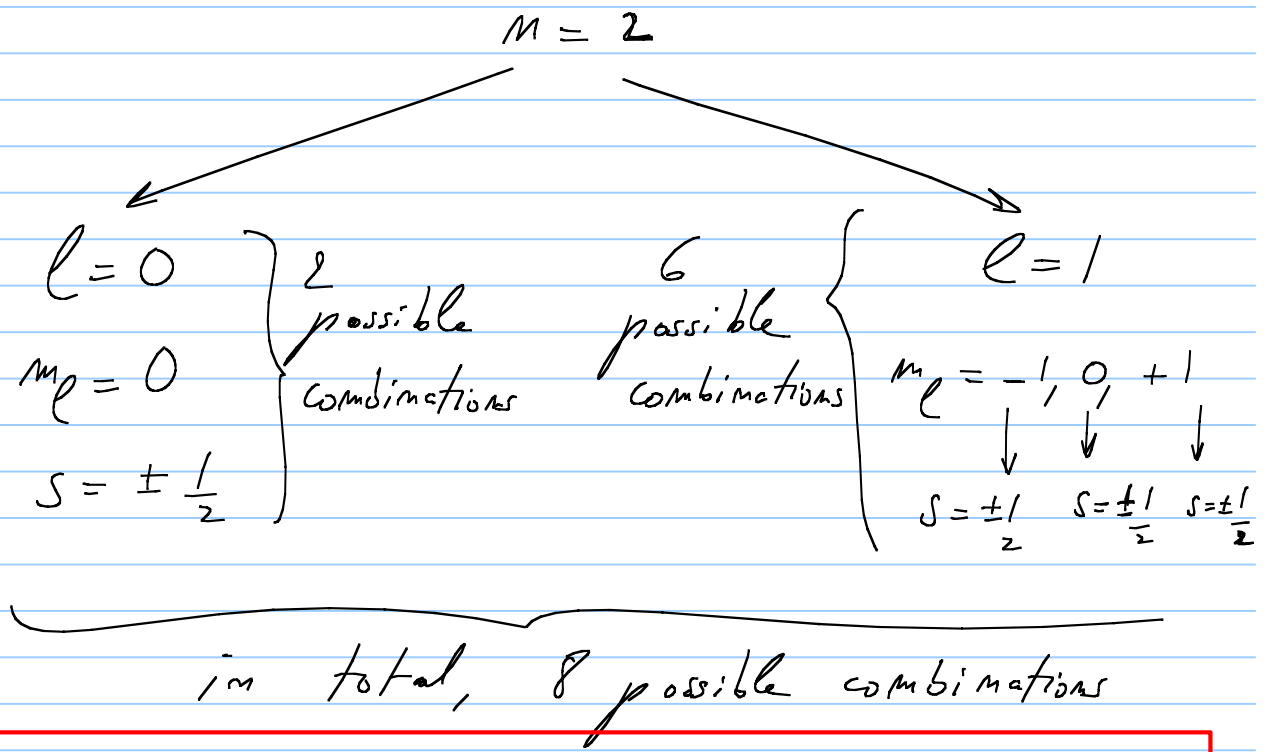
$$m_\ell = 0$$

Hence, the possible quantum numbers are:

$$\begin{cases} n = 1 \\ \ell = 0 \\ m_\ell = 0 \\ s = \pm \frac{1}{2} \end{cases}$$

Only 2 electrons can occupy the $n = 1$ level!

- Let $n = 2$, then we have:



As a result of Pauli's exclusion principle, we can have a maximum of $2n^2$ electrons in any given shell.

The electrons in the outermost shell of any element are known as the "valence" electrons. Those electrons are responsible for the chemical reactions of the element.

Elements that have fully populated (complete) outer shells are known as

the "inert" or "noble" gases
(helium, neon, argon, ...)

-- please do homework #1 --

Quantum Mechanics

De Broglie's hypothesis and the development of the Schrödinger equation:

- In 1924, Louis De Broglie hypothesized that every material particle is inherently a wave, and can be described by an equation that relates its mechanical properties to its wave properties:

$$\lambda = \frac{h}{p} = \frac{\text{Planck's Constant}}{\text{Particle's momentum}}$$

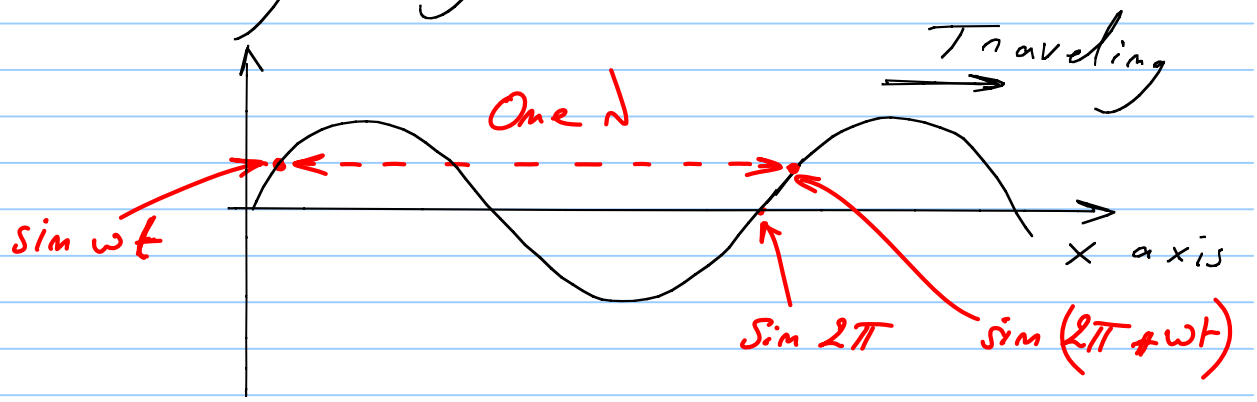
De Broglie's Formula

λ : Particle's wavelength

The equation was confirmed experimentally in 1927.

The Traveling Wave Equation:

Assume that a sinusoidal wave is traveling along the x-axis:



Equation of a stationary wave:

$$V = A \sin \omega t$$

Let us define $k = \frac{2\pi}{\lambda}$

as a "propagation constant".

Then, the equation of a traveling wave will be:

$$V = A \sin(kx + \omega t)$$

$$= A \sin\left(\frac{2\pi}{\lambda} x + \omega t\right)$$

at $x = \lambda$ (one wavelength), we have

$$V = A \sin\left(\frac{2\pi}{\lambda} \cdot \lambda + \omega t\right)$$

$$= A \sin(2\pi + \omega t)$$

By convention,

$$V = A \sin(kx - \omega t)$$

by choice

Schrödinger's derivations:

- The De-Broglie "Wave function", ψ

$$\psi(x,t) = \underbrace{A}_{\text{magnitude}} \underbrace{e^{i(kx-\omega t)}}_{\text{pure phase}}$$

We use the exponential function (rather than sine or cosine) to be able to represent phase information, in addition to magnitude.

$e^{i\theta} = \cos\theta + i\sin\theta$ Euler's eq.

$= \sqrt{\cos^2\theta + \sin^2\theta}\ \angle\theta$

$= 1\ \angle\theta$

= pure phase

Since $k = \frac{2\pi}{\lambda}$, and

Since $\omega = 2\pi\nu$

Then $\omega = (k\lambda)\nu$

But the product $\lambda\nu$ is well known: it is the speed of propagation of the wave (if the wave is electromagnetic, the speed is equal to c)

For a wave that is not electromagnetic (i.e, not a photon),

$$\lambda\nu = \text{"}u\text{"}$$

speed of propagation,

where $u < c$

$$\therefore \boxed{\omega = k u}$$

Now, the De Broglie wave function becomes

$$\psi(x,t) = A e^{i(kx - \omega t)}$$

$$= A e^{i(kx - kut)}$$

$$= A e^{ik(x - ut)}$$

Now,

$$\frac{\partial \psi}{\partial t} = A e^{ik(x-ut)} \cdot (-iku)$$

$$= -iku\psi$$

$$= -i\omega\psi$$

Multiplying by $i\hbar$, we get

$$i\hbar \frac{\partial \psi}{\partial t} = -(i^2)\hbar\omega\psi$$

$$= +\hbar\omega\psi$$

$$= \frac{h}{2\pi} \cdot 2\pi\nu \cdot \psi$$

$$= (h\nu)\cdot\psi$$

Total energy according to planck!

Let $h\nu \triangleq H$

(total energy of the particle)

Hence

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = H\psi}$$

The Schrödinger Equation

More about the total energy H of the particle:

Since $\nu = \frac{h}{p} = \frac{u}{\gamma}$ ← speed of propagation

Hence, $h\nu = pu = H$ (total energy)

Since $p = mv$ (momentum), now, we let $u = v$ (velocity of particle), then

$$H = pu = (mv)(v) = mv^2$$

The "wave mechanical" formulation of the total energy of a particle

A special case is when the velocity v approaches c, or the speed of light, i.e, $v \longrightarrow c$: we get

$$H = mc^2$$

Einstein's mass-energy equivalence equation

The Quantum Mechanical "Operators":

$$\psi = A e^{i(kx - \omega t)}$$

Now, $k = \frac{2\pi}{\lambda}$, and $\omega = 2\pi\nu$

Hence,

$$\psi = A e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)}$$

$$= A e^{2\pi i\left(\frac{x}{\lambda} - \nu t\right)}$$

Multiply and divide the exponent by h, getting:

$$\psi = A e^{\frac{2\pi i}{h}\left(\frac{h}{\lambda}x - h\nu t\right)}$$

but $h\nu = H$ (total energy)

$$\text{also, } \frac{h}{\lambda} = p \quad \text{(momentum)}$$

$$\text{Hence, } \psi = A e^{\frac{2\pi i}{h}(px - Ht)}$$

$$= A e^{\frac{i}{\hbar}(px - Ht)}$$

$$\frac{\partial \psi}{\partial x} = \psi \left(\frac{i}{\hbar} p\right)$$

or,

$$-i\hbar \frac{\partial \psi}{\partial x} = p\psi \leftarrow \text{The "companion" Eq.}$$

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \leftarrow \text{Schrödinger's Eq.}$$

What the equations mean physically?

$$\text{Energy } (H) \equiv i\hbar \frac{\partial}{\partial t}$$

$$\text{Momentum } (p) \equiv -i\hbar \frac{\partial}{\partial x}$$

The "Quantum Mechanical Operators"

In three dimensions, $p \equiv -i\hbar \nabla$

↑ del operator

$$\left(\nabla = \frac{\partial}{\partial x}\hat{x}, \frac{\partial}{\partial y}\hat{y}, \frac{\partial}{\partial z}\hat{z} \right)$$

The practical form of the Schrödinger Equation:

The total observable energy of a particle, H, will be given by

$$H = \text{kinetic energy} + \text{potential energy}$$

$$= \frac{1}{2} m v^2 + V$$

$$= \frac{1}{2m} m^2 v^2 + V$$

$$= \frac{p^2}{2m} + V$$

but $p \equiv -i\hbar \nabla$, hence $p^2 \equiv -\hbar^2 \nabla^2$

$$\therefore \quad H = -\frac{\hbar^2 \nabla^2}{2m} + V$$

but $H\psi = i\hbar \frac{\partial \psi}{\partial t}$ (Schrödinger's eq.)

Hence, $\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar \frac{\partial \psi}{\partial t}}$

Practical form of the Schrödinger Eq.

Applications of the Schrödinger Eq:

Application #1:

The problem of the Hydrogen atom

$$\psi = A e^{\frac{2\pi i}{h}(px - Ht)}$$

$$= A e^{\frac{i}{\hbar}(px - Ht)}$$

$$= A \underbrace{e^{\frac{ip}{\hbar}x}}_{\text{function of } x \text{ only}} \cdot \underbrace{e^{\frac{-iH}{\hbar}t}}_{\text{function of } t \text{ only}}$$

Hence, any solution or expression for ψ must be a product of two functions:

$$\psi(x, y, z), \text{ and } \psi(t).$$

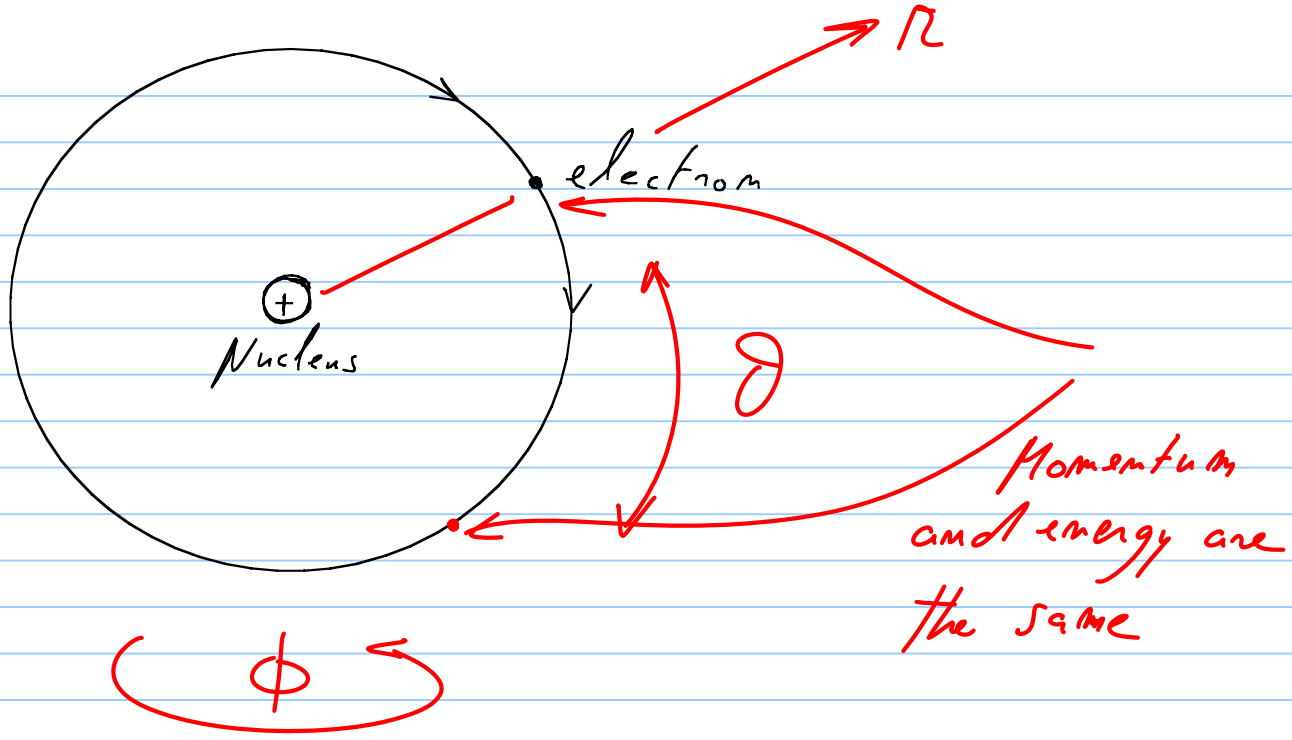
We shall use the spherical coordinate system, in which the operator ∇^2 is expressed as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

(spherical coordinate system : r, θ, ϕ)

Since ψ can be separated into a product of functions (i.e, is well behaved),

then $\psi = \underbrace{\psi(r, \theta, \phi)}_{\psi(r)\cdot\psi(\theta)\cdot\psi(\phi)} \cdot \psi(t)$



The wave function is dependent on the energy and the momentum of the electron, which are functions of the distance r only. Hence, ψ cannot be a function of θ or ϕ, but only r!

i.e, $\psi = \psi(r)$ only!

Hence,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

Hence,

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right)$$

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)$$

verify yourself

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t}}$$

Practical form of the Schrödinger Eq.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Operator acting on ψ — product

Substituting for $\nabla^2\psi$,

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)\right) + V\psi = i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

Multiplying by r, we get

$$-\frac{\hbar^2}{2m}\cdot\frac{d^2}{dr^2}(r\psi)+V(r\psi)=H(r\psi)$$

Now, let $r\psi=\Gamma$ (new function)

Hence,

$$-\frac{\hbar^2}{2m}\cdot\frac{d^2\Gamma}{dr^2}+V\Gamma=H\Gamma$$

V ? $\left(\frac{-e^2}{r}\right)$ ← This is not the exponential function

Hence,

$$-\frac{\hbar^2}{2m}\cdot\frac{d^2\Gamma}{dr^2}-\frac{e^2}{r}\Gamma=H\Gamma$$

Solving for Γ (unknown function)

- Solution for large r:

$$\frac{e^2}{r}\longrightarrow 0$$

Hence, $$-\frac{\hbar^2}{2m}\frac{d^2\Gamma}{dr^2}\approx H\Gamma$$

The solution is a function of the form

$$f(r) = e^{-Cr}$$

where C is a constant

Substituting in the equation, we get

$$-\frac{\hbar^2}{2m}\left(+C^2 e^{-Cr}\right) \approx H\, e^{-Cr}$$

Hence, H (total energy) $= \frac{-\hbar^2}{2m} C^2$ ← unknown

$$\therefore C^2 = -\frac{2mH}{\hbar^2}$$

$$\text{or } C = \sqrt{\frac{-2mH}{\hbar^2}}$$

- Solution for small r:

At the origin (where $r = 0$), we must assume that $f(0) = 0$, since the electron cannot exist

where the proton is located.

Hence, the solution must rather be of the form

$$f(r) = r e^{-cr}$$

Hence,

$$f(r) = r\, e^{-\sqrt{\frac{-2mH}{\hbar^2}}\, r}$$

Substituting in the full eq:

$$\frac{-\hbar^2}{2m} \cdot \frac{d^2 f}{dr^2} - \frac{e^2}{r} f = H f$$

→ we get (verify yourself)

$$\frac{-\hbar^2}{2m}\left(-\frac{2mH}{\hbar^2} \cdot r - \frac{2\sqrt{-2mH}}{\hbar}\right) - e^2 = Hr$$

$\left(\frac{q^2}{4\pi\epsilon_0}\right)$

$$\therefore \cancel{Hr} + \frac{\hbar}{m}\sqrt{-2mH} - e^2 = \cancel{Hr}$$

$$e^2 = \frac{\hbar}{m}\sqrt{-2mH}$$

$$e^4 = \frac{\hbar^2}{m^2}\left(-2mH\right)$$

Hence,

$$\boxed{H = -\frac{1}{2}\frac{me^4}{\hbar^2}}$$

$$= \boxed{-\frac{1}{2}\frac{me^4}{m^2\hbar^2}}$$

Bohr's total energy formula (in Joules)

Homework #1 :

(1) $R = 0.53 * 10^{-10} m = 0.53 \text{ Å}$

$V = 2.2 * 10^6 m/s$

② $W = -2.16 * 10^{-18}\ J$

$= -13.6\ eV$

③ $\lambda = 487\ nm$

④ $\alpha = 0 \quad \left(\frac{1}{137}\right)$

⑤

$$\Delta W = \frac{1}{2}\frac{m e^4}{\hbar^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 13.6\ eV\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$= h\nu$

n_1: 2 $\quad$ n_2: ?

λ (visible radiation) $= 400 - 700\ nm$

↳ calculate ν (frequency) $= 7.5 * 10^{14}\ Hz$

$\longrightarrow 4.29 * 10^{14}\ Hz$

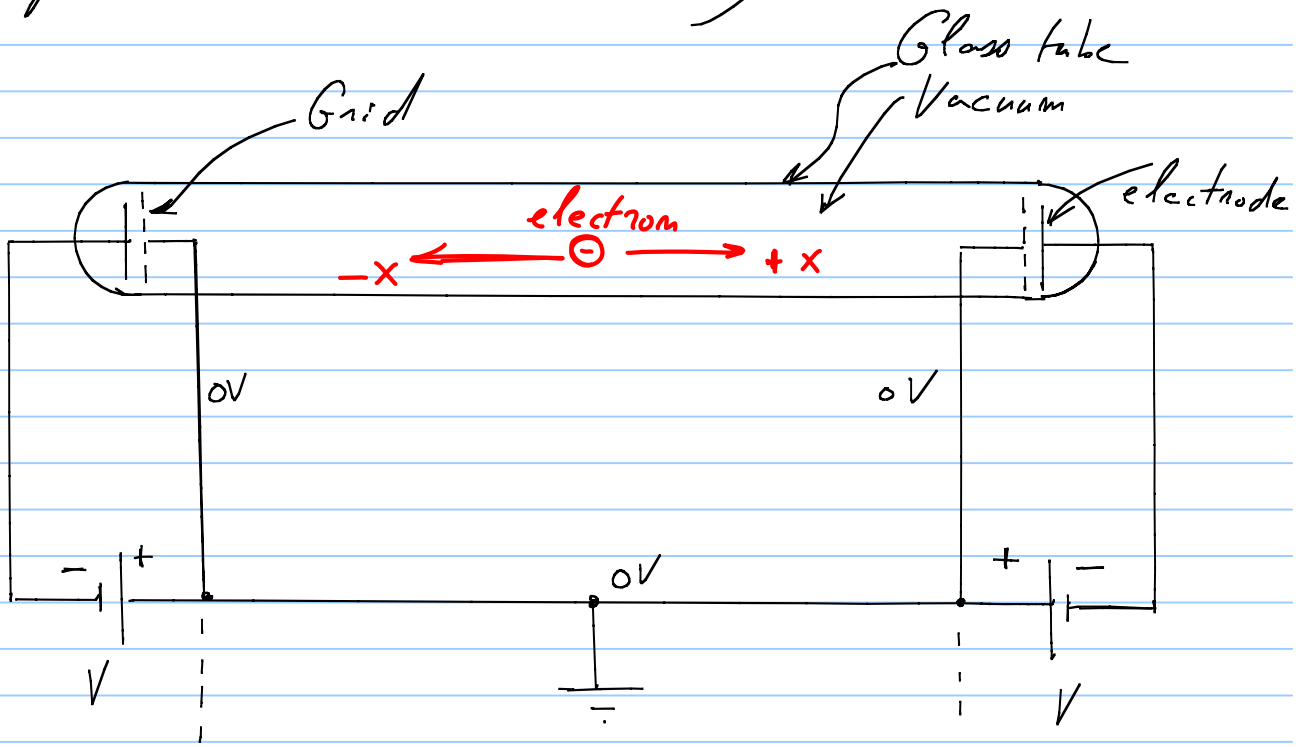
n_2 : 2.89 ⟷ 6.9

3, 4, 5, 6

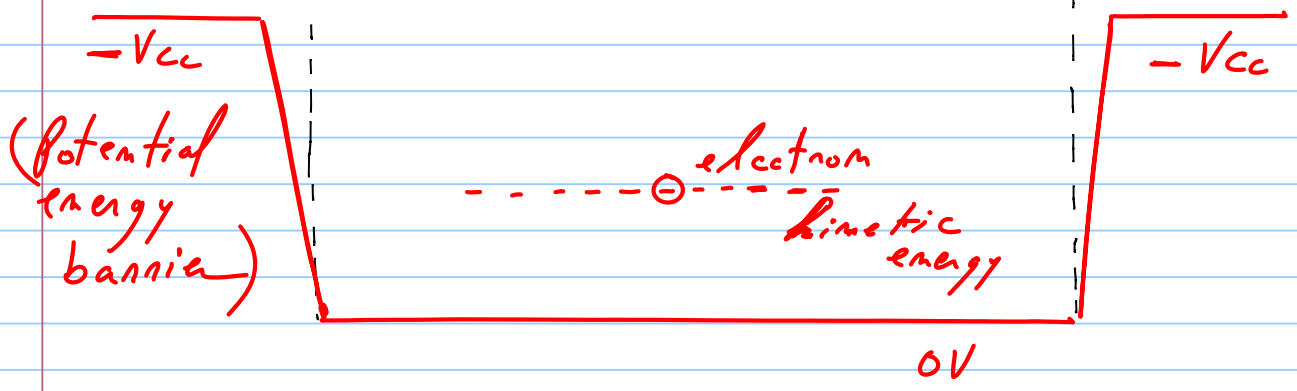
Application # 2:

The problem of the electron inside a potential well.

Assume that an electron exists inside a vacuum tube, with negative potentials on both sides of the tube.



Energy level diagram:



If the electron's kinetic energy (E_k) is higher than the potential energy (V_{cc}), then the electron will be able to penetrate the potential barrier and reach the electrode. Otherwise, the electron will remain trapped inside the tube.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Practical form of the Schrödinger Eq.

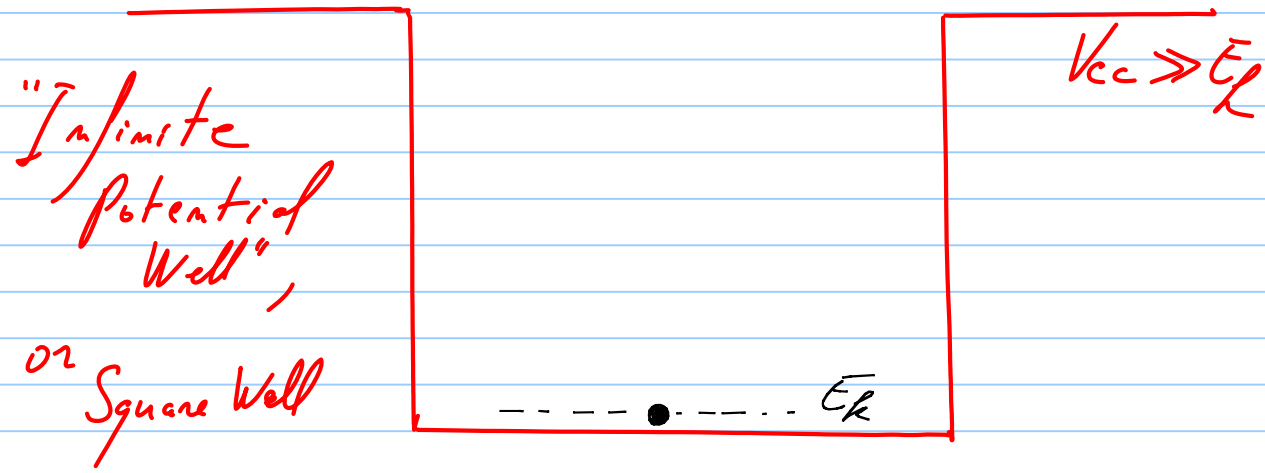
In one dimension, the eq. is:

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\psi = H\psi$$

V = 0 everywhere inside the tube

The total energy H of the electron is just the kinetic energy E_k.

We also assume that the applied potential $V_{cc} \gg E_k$ (hence, the electron will remain trapped inside the tube).



$$E_k = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

We saw that $k = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar}$

k: propagation constant

$$\boxed{p = \hbar k}$$

Hence,

Hence, $E_k = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

Now, the Schrödinger eq. is

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

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

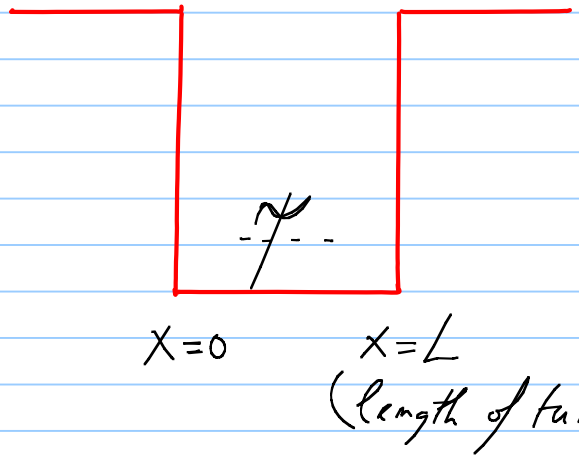
$$\therefore \frac{d^2\psi}{dx^2} = -k^2\psi$$

Diff. eq. that describes the electron inside the infinite potential well.

The solution is

$$\psi(x) = \underbrace{C_1 e^{ikx}}_{\text{electron is moving along } +x \text{ axis}} + \underbrace{C_2 e^{-ikx}}_{\text{electron moving along } -x \text{ axis}}$$

Applying the initial conditions to find the unknown constants C_1 and C_2:



$\psi = 0$ at $x = 0$ and $x = L$

(Also $\psi = 0$ outside the well)

$$\psi(0) = 0 = C_1 + C_2$$

Hence, $C_1 = -C_2$

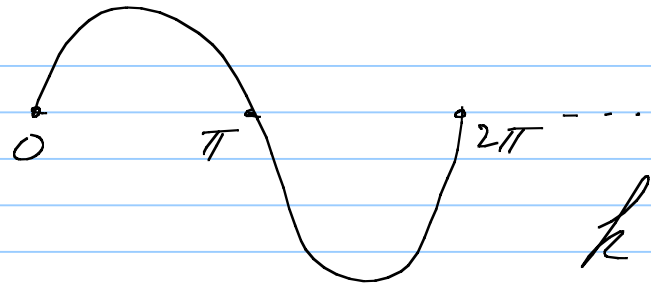
Hence, $$\psi(x) = C_1 \underbrace{\left(e^{ikx} - e^{-ikx}\right)}_{\sin kx}$$

$$= A \sin kx$$

A: New constant

$$\psi(L) = 0 = A \sin \underbrace{kL}_{\text{angle}}$$

?



$$kL = n\pi$$

or $$\boxed{k = \frac{n\pi}{L}}$$

The kinetic energy now can be written as follows:

$$\bar{t}_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{L^2}\right)$$

$$= \frac{1}{2m}\left(\frac{\hbar^2}{4\pi^2}\right)\left(\frac{n^2\pi^2}{L^2}\right)$$

$$= \boxed{\frac{n^2\hbar^2}{8mL^2}}$$

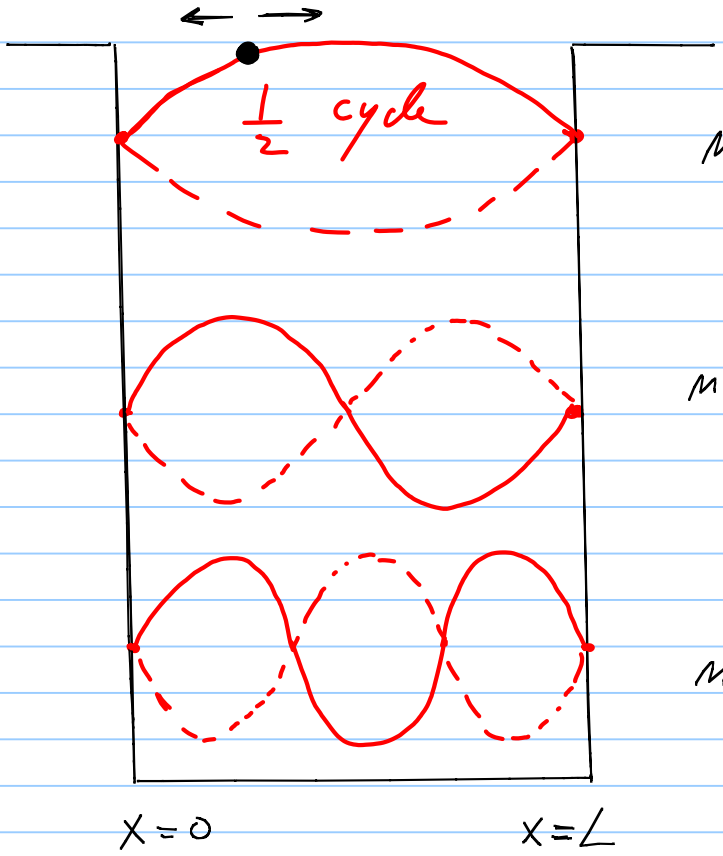
The complete solution:

$$\psi(x) = A\sin kx = A\sin\frac{n\pi}{L}x$$

$$\bar{t}_k = \frac{n^2\hbar^2}{8mL^2}$$

where $0 \leq x \leq L$

and n = integer $(1, 2, 3, \ldots)$



$n = 1, \quad \psi(L) = A \sin \pi$

$n = 2, \quad \psi(L) = A \sin 2\pi$

$n = 3, \quad \psi(L) = A \sin 3\pi$

The electron is a "standing wave" between the points $x = 0$ and $x = L$. The values on n represent the different "modes" of vibration.

The Heisenberg Uncertainty Principle:

Heisenberg's conclusion: there is uncertainty in the position x of the particle!

Since $p \equiv -i\hbar \frac{\partial}{\partial x}$, what is the product $\Delta p \, \Delta x$, where Δp is a small change in momentum?

$$\Delta p \, \Delta x \equiv -i\hbar \frac{\Delta x}{\Delta x} = -i\hbar$$

From statistics, the "expected" value of this product (a random variable) is

$$\langle \Delta p \, \Delta x \rangle = \sqrt{(\Delta p \, \Delta x)(\Delta p \, \Delta x)^*}$$

$$= \sqrt{(-i\hbar)(+i\hbar)}$$

$$= \sqrt{\hbar^2}$$

$$= \hbar$$

or $\langle \Delta p \, \Delta x \rangle = \hbar$

Also, since $H \equiv i\hbar \frac{\partial}{\partial t}$

we can show that

$$\langle \Delta H \, \Delta t \rangle = \hbar$$

Summary:

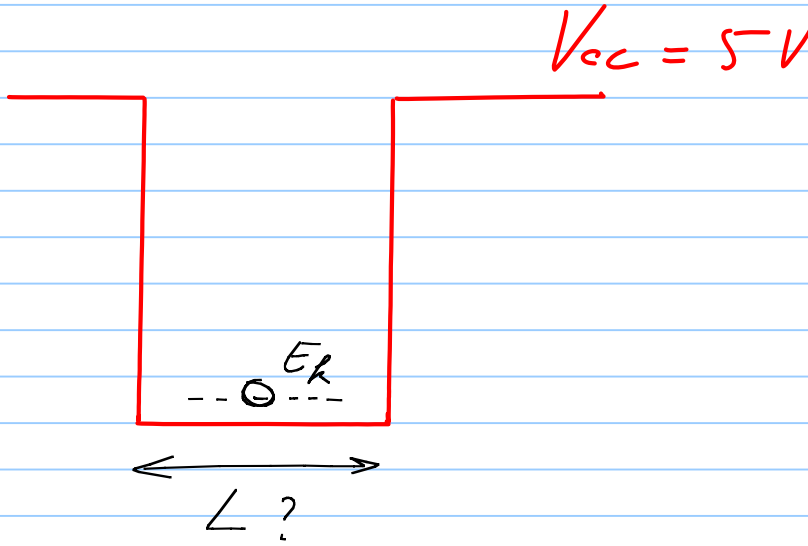
$$\langle \Delta p \, \Delta x \rangle = \hbar$$

$$\langle \Delta H \, \Delta t \rangle = \hbar$$

The Heisenberg Uncertainty Relations

Homework #2

(1)



5 eV of energy will be needed for the electron to escape from the well.

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{(in Joule)}$$

$$= \frac{n^2 h^2}{8mL^2} * \frac{1}{1.6 * 10^{-19}} \quad eV$$

$$= 5$$

$$5 = \frac{n^2}{L^2} * \frac{(6.6256 * 10^{-34})^2}{8(9.11 * 10^{-31})} * \frac{1}{1.6 * 10^{-19}}$$

$$= \frac{n^2}{L^2} * 3.77 * 10^{-19}$$

$$L = n \sqrt{\frac{3.77 * 10^{-19}}{5}}$$

$$= n * 2.74 * 10^{-10} \text{ meter}$$

$$= n * 2.74 \text{ Angstrom}$$

typical distance between atoms inside solid materials

(2) Normalization condition:

$$\int_{-\infty}^{+\infty} \psi^* \cdot \psi \, dx = 1$$

This is an expression that "the sum of probabilities must be equal to 1"

$$\psi(x) = A \sin kx$$

$$\psi^*(x) = A \sin kx$$

Hence,

$$\int_{-\infty}^{+\infty} \psi^* \cdot \psi \, dx = \int_{-\infty}^{\infty} \psi^2 dx = 1$$

$$= \int_{-\infty}^{\infty} A^2 \sin^2 kx \, dx = 1$$

$$\left(\sin^2\theta = \frac{1}{2} - \frac{1}{2} \cos 2\theta \right)$$

Hence,

$$\int_{-\infty}^{+\infty} A^2 \left(\frac{1}{2} - \frac{1}{2} \cos 2kx \right) dx = 1$$

$$\frac{1}{2}\int_{-\infty}^{+\infty} A^2\,dx - \frac{1}{2}\int_{-\infty}^{+\infty} \cos 2kx\,dx = 1$$

$$\frac{1}{2}\int_{0}^{L} A^2\,dx - \frac{1}{2}\int_{0}^{L} \cos 2\frac{n\pi}{L}x\,dx = 1$$

0 by inspection
(multiple of a full cycle cosine wave)

Hence,

$$\frac{1}{2}\int_{0}^{L} A^2\,dx = 1$$

$$\frac{1}{2}A^2(L) = 1$$

$$A = \sqrt{\frac{2}{L}}$$

③ Solve

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

$$\int \frac{1}{\psi}\,d\psi = \int \frac{-i}{\hbar} H\,dt$$

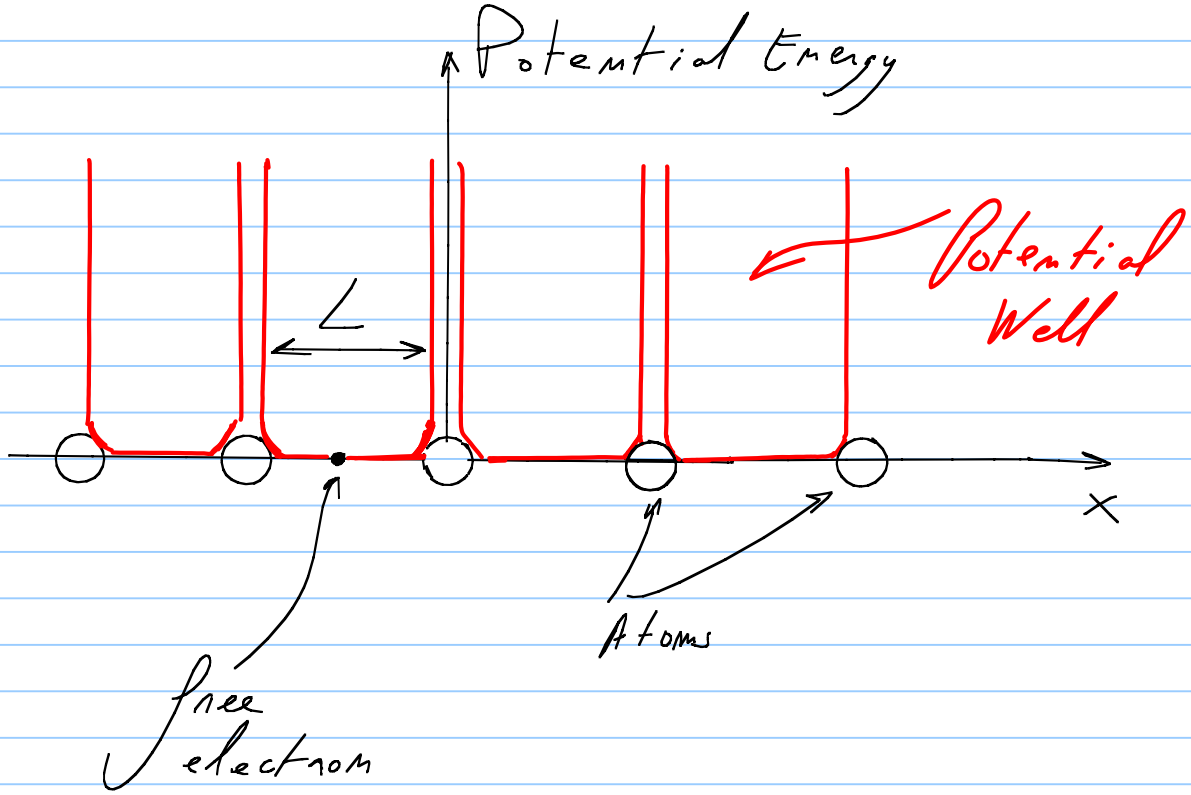
$$\ln \psi + \text{Const.} = \frac{-i}{\hbar} H t + \text{Const.}$$

$$\ln \psi = \frac{-i}{\hbar} H t + \text{Const.}$$

$$\psi = e^{\left(\frac{-i}{\hbar} H t + \text{Const.}\right)}$$

$$= \underbrace{e^{\text{Const.}}}_{\text{fn. of } (x,y,z)} \cdot \underbrace{e^{-i/\hbar H t}}_{\text{fn. of time only}}$$

Electrons in Solids



- Electrostatic potentials acting on electrons inside solids give rise to the boundary conditions of the square-well problem.

The energies of free electrons inside solids will be given by

$$E_k(n) = \frac{n^2 h^2}{8 m L^2}$$

- The probability of a certain energy level (or n-level) to be occupied is given by the Fermi-Dirac distribution function

$$P\left(E_{k(n)}\right) = \frac{1}{1 + e^{\left(E_{k(n)} - \mu\right)/kT}}$$

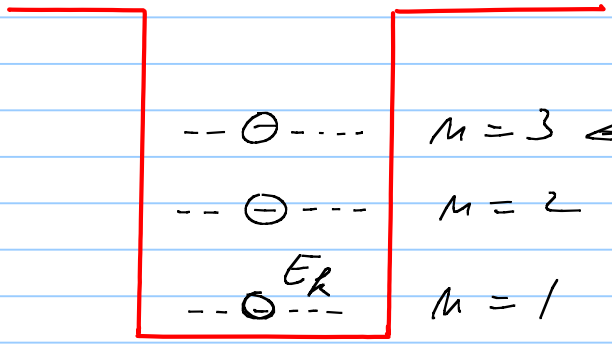
where:

k : Boltzmann's constant

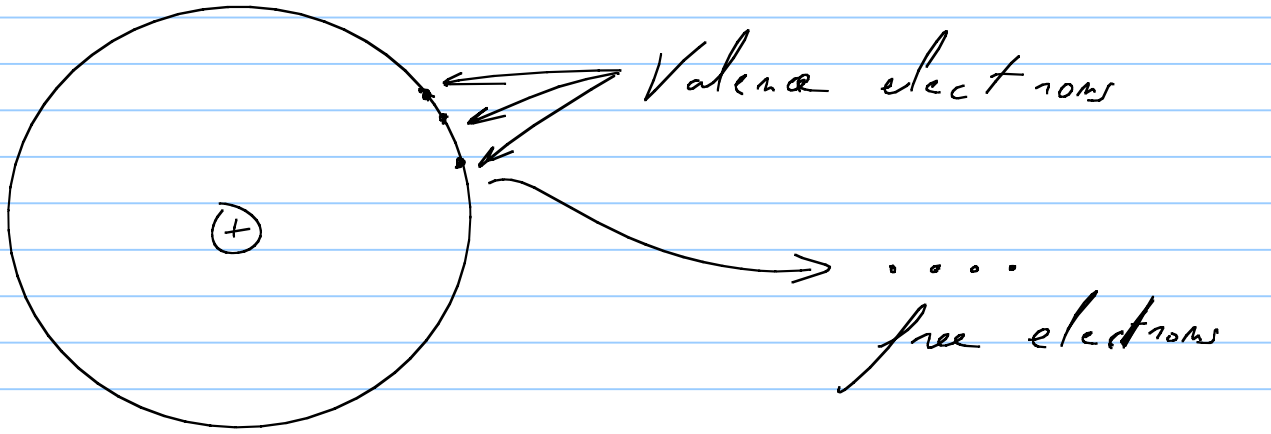
T : Temperature ($^\circ K$)

μ : Chemical Potential of the element.

- The various energy levels $E_{k(n)}$ can be filled with electrons. The highest energy level that is occupied by free electrons is called the "Fermi level".



- The "Energy Gap" in a material:



The energy gap in a material is the amount of energy that is needed for a valence electron to escape and become a free electron. It is also the <u>same</u> amount of energy that is needed for a free electron to overcome the repulsive potential and move inside the solid.

Conductors

Conduction band

free

Energy Gap $\approx 10^{-19}$ V

Valence band

Semi-Conductors

Conduction band

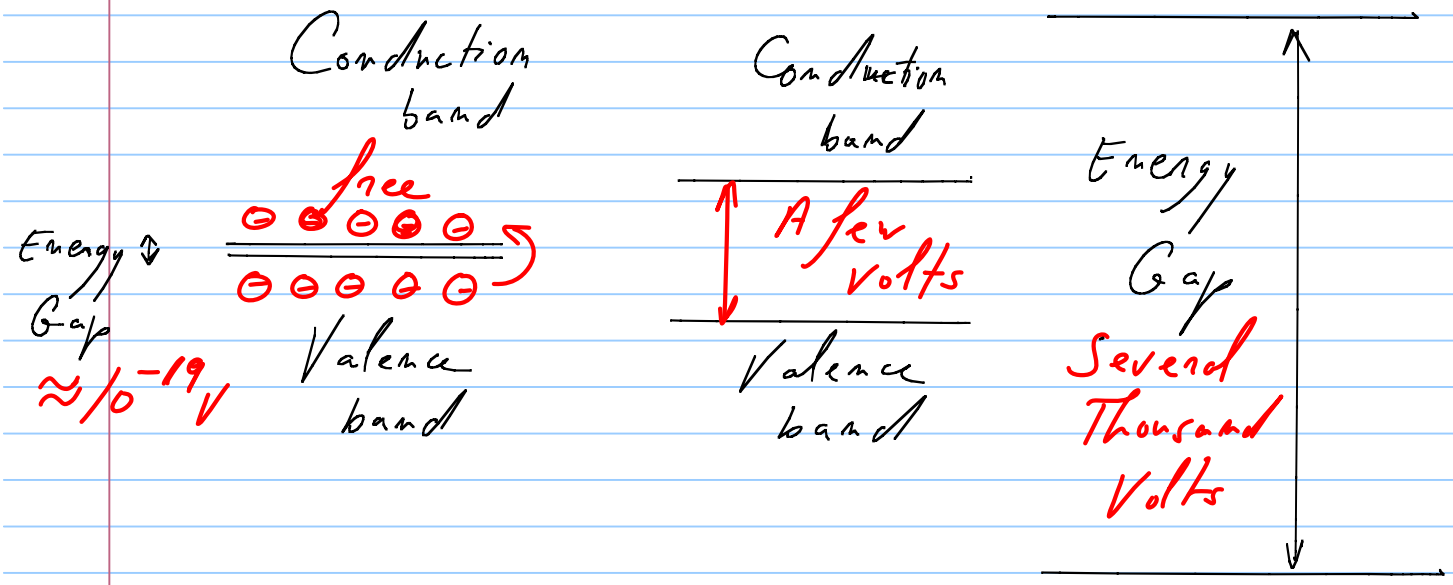
A few volts

Valence band

Insulators

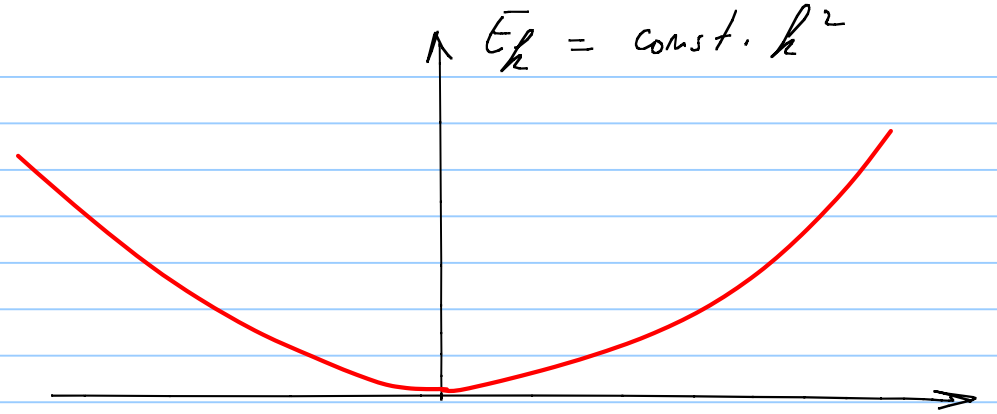
Energy Gap

Several Thousand Volts

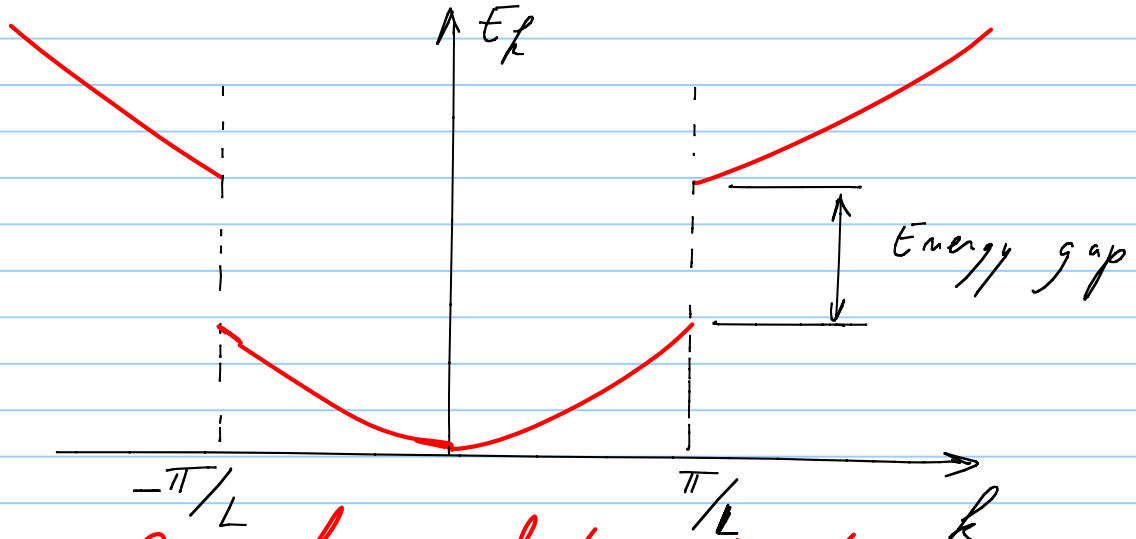


- In semi-conductors, the Fermi level lies approximately in the middle of the energy gap. For insulators, the Fermi level is very close to the valence band; and for conductors it is very close to the conduction band.

- Plot of $E_k = \frac{\hbar^2 k^2}{2m}$ versus the propagation constant k:



(a) Case of a totally free electron

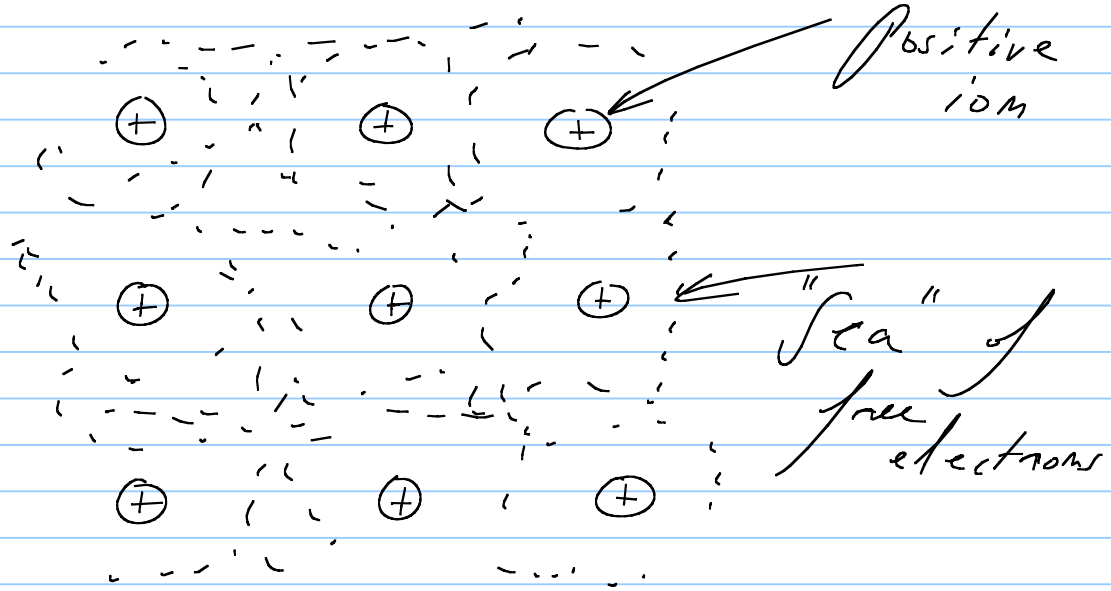


(b) Case of an electron inside a linear atomic lattice with lattice constant L

- The solution of the Schrödinger equation for the periodic well structure (inside a solid) is of the form

$$\psi(x) = \underbrace{U(x)}_{\text{Periodic function}} \underbrace{\left(A e^{ikx} + B e^{-ikx}\right)}_{\text{one well}}$$

Electrons in Metals

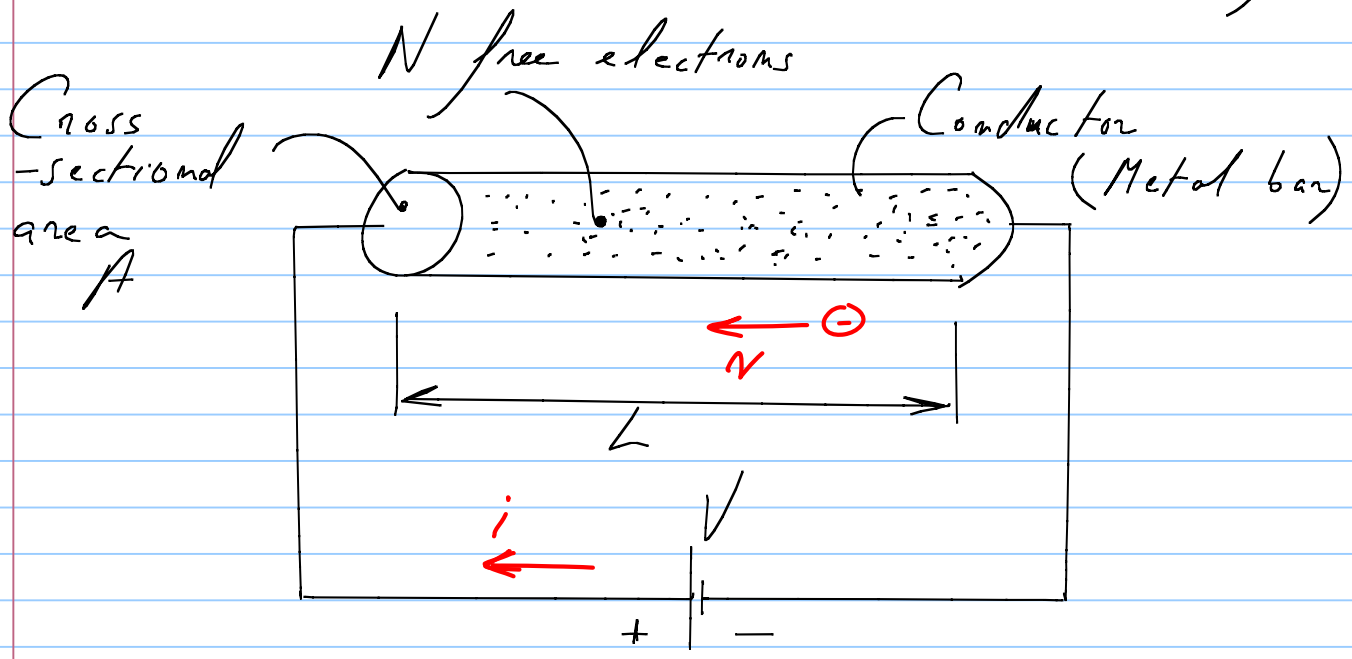


If we apply an external voltage across the metal, the free electrons move, and their speed is given by the following equation:

$$V = \mu E$$

- V: Velocity of electrons
- μ: Mobility of electrons (constant)
- E: Applied electric field intensity

(this velocity is only a few centimeters per second inside metals)



- The time needed for an electron to travel through the bar is

$$t = \frac{L}{v}$$

- The magnitude of the current I through the bar is

$$I \triangleq \frac{\text{Charge}}{\text{Time}}$$

$$= \frac{Nq}{t}, \quad \text{where } q \text{ is the electron's charge}$$

$$= \frac{Nq}{L/v}$$

$$= \frac{Nqv}{L}$$

- The "Current Density", J, is defined as:

$$J \triangleq \frac{I}{A} = \frac{\text{Current}}{\text{Cross-sectional area}}$$

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dx = 1$$

$$\int_0^L (Ae^{i\theta})(Ae^{-i\theta}) \, dx = 1$$

$$A^2 \int_0^L e^0 \, dx = 1$$

$$A^2 L = 1$$

$$A = 1/\sqrt{L}$$

$$= \frac{Nqv}{LA}$$

$$= \frac{Nqv}{\text{Volume of bar}}$$

But $\frac{N}{\text{Volume of bar}}$ = Free electron density (n)

Hence, $J = n q v$

$= n q (\mu E)$

free electron density; charge; mobility

Definition: the product $n q \mu$ is known as the "conductivity" of the material ($n q \mu \triangleq \sigma$)

(Unit of σ is $1/\Omega\,m$)

$\therefore \boxed{J = \sigma E}$

J: Current density; σ: Conductivity of material; E: Electric field intensity

Definition: the reciprocal of σ, "ρ", is called the "resistivity" of the material.

Typical values for n (free electron density):

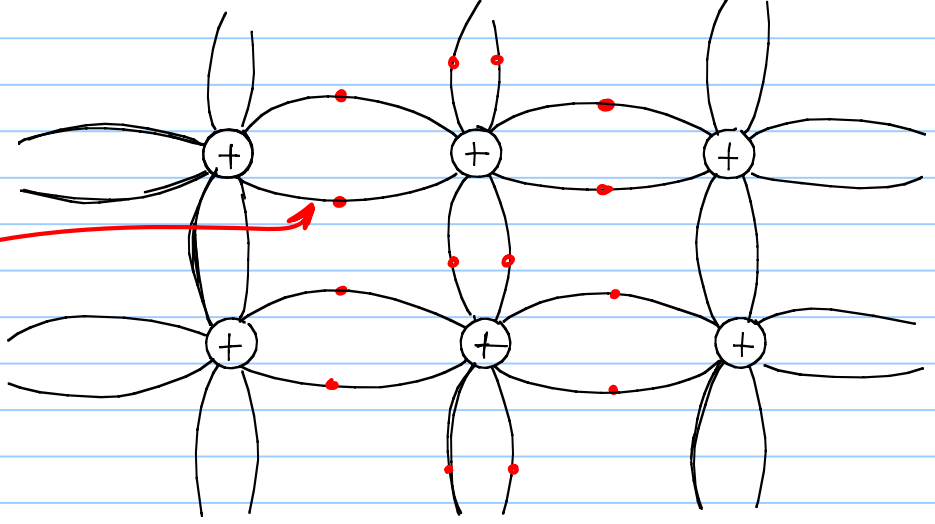
Copper : $n \approx 10^{28}$ electrons $/m^3$

Semi-conductors:
- Silicon : $n \approx 1.5 * 10^{16}$ electrons $/m^3$
- Germanium : $n \approx 2.5 * 10^{19}$ "

Wood : $n \approx 10^{7}$ electrons $/m^3$

Electrons in Semi Conductors:

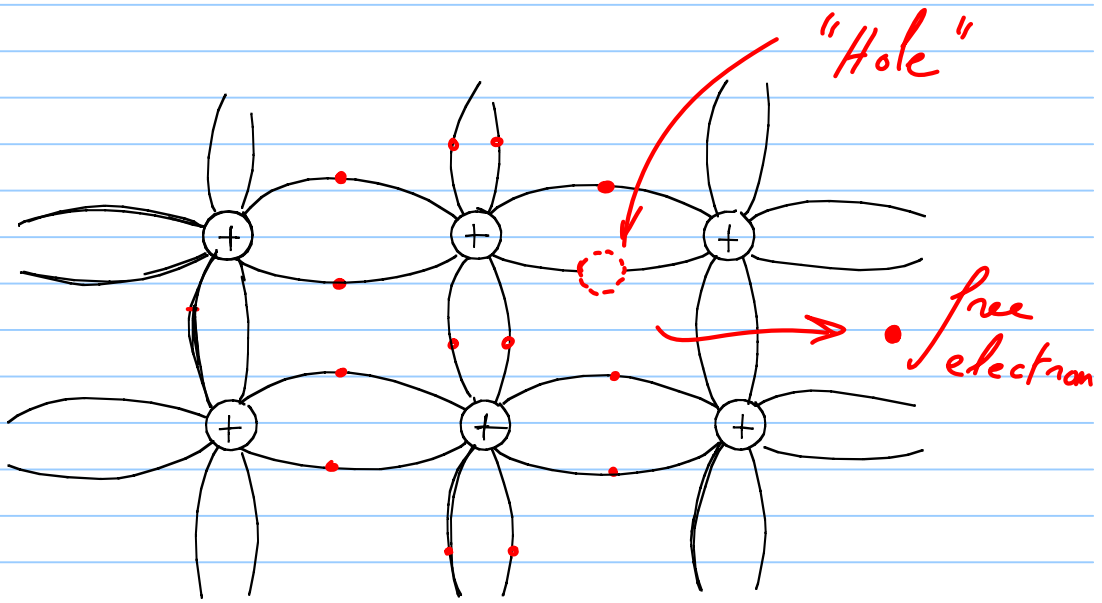
- In Semiconductors, the valence electrons are shared between adjacent atoms and form what is known as "covalent bonds".



Si and Ge atoms have 4 valence electrons.

They need 8 valence electrons to have complete outer shells.

- At room temperature and above, thermal energy can break some of the covalent bonds, which results in "holes".



- It takes an energy of a few electron-volts to free an electron (i.e, break the bond) at room temperature.

- Once a hole has been created, another free electron can move in to fill that hole. This process can continue, giving the effect of a "hole in motion".

- In a pure semiconductor, the free-electron density, n, is equal to the hole density, p, i.e,

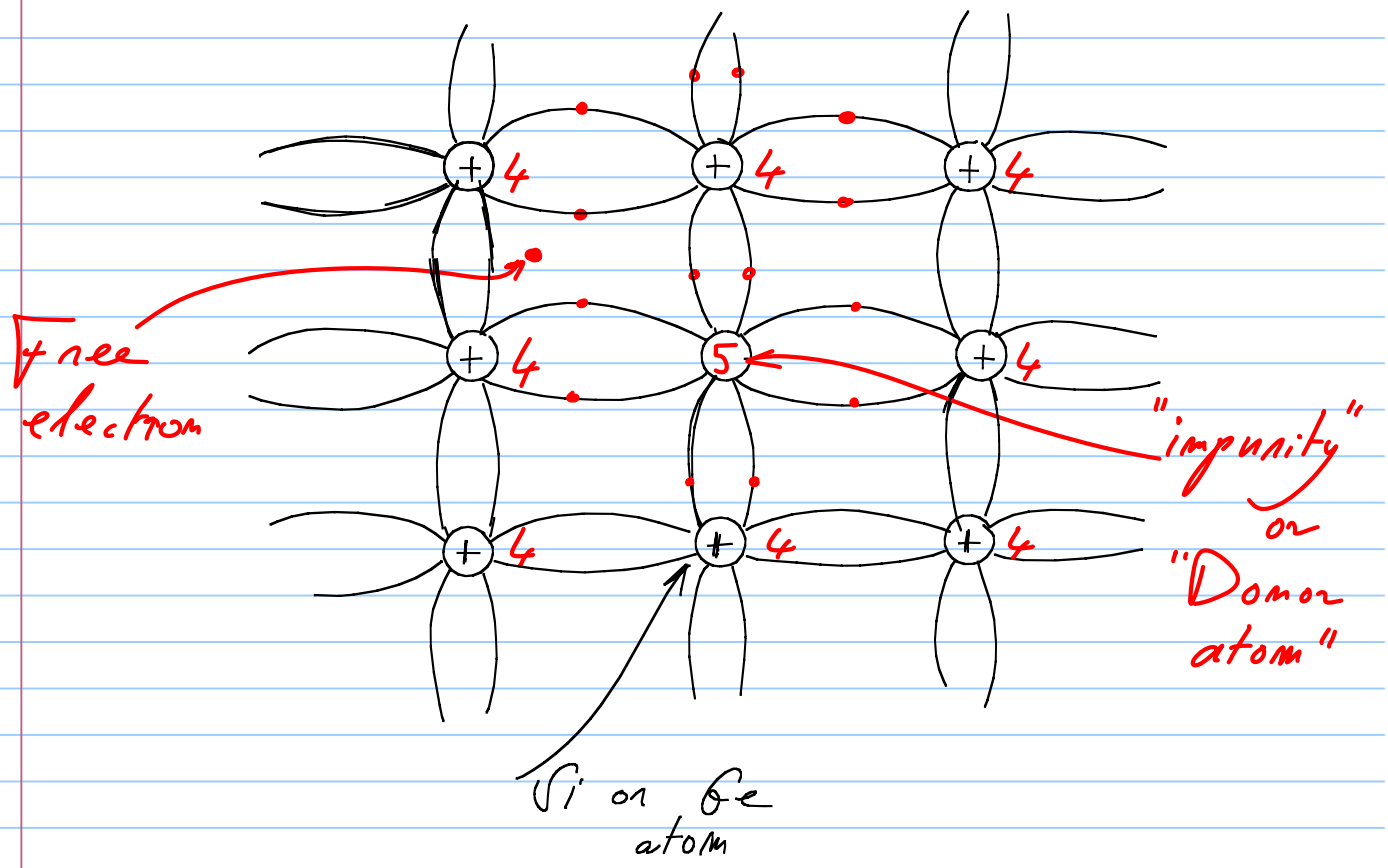
$$\boxed{n = p \triangleq n_i}$$

(intrinsic density)

- "Doped" Semiconductor:

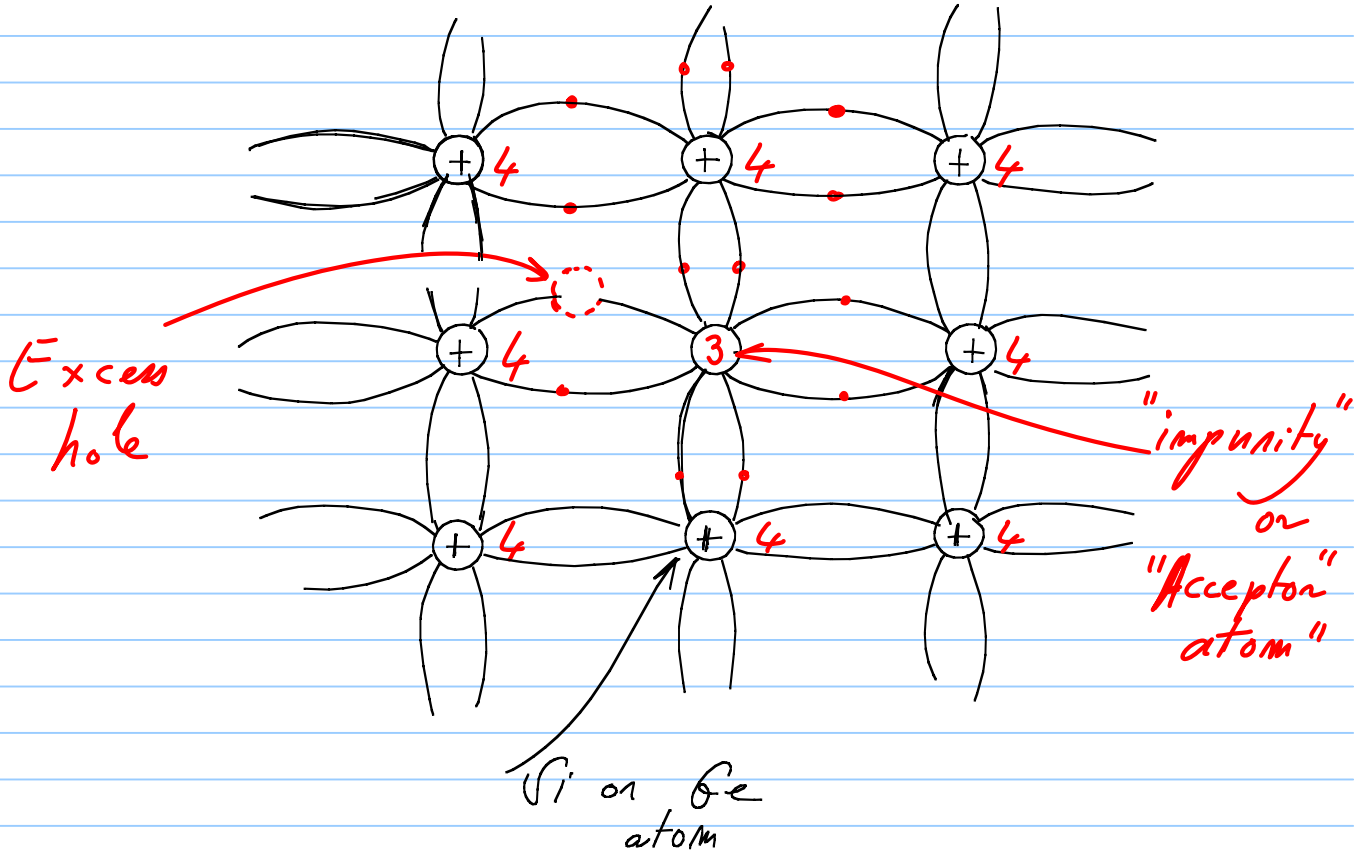
  - The conductivity of a semiconductor can be increased or decreased substantially by adding small amounts of impurities to it. Such a process is referred to as "doping".

- Elements like Phosphorus or Arsenic have 5 valence electrons. If added to Silicon or Germanium (4 valence electrons), the result will be one free electron.



This material is called an "n-type" semiconductor. (n for "negative" or "donor")

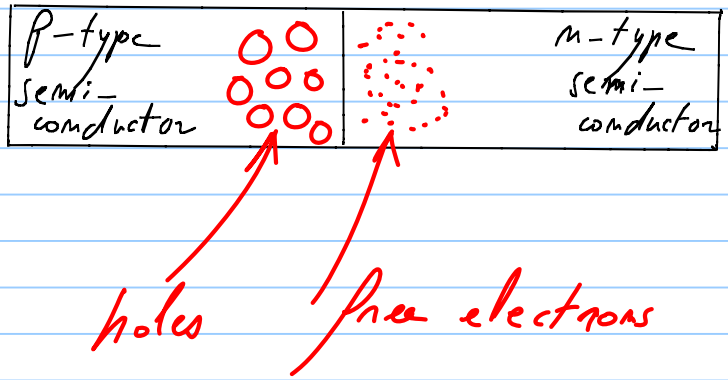
- Elements like Boron or Gallium have only 3 valence electrons. If added to an intrinsic semiconductor, the result will be an excess hole.



This material is called an "p-type" semiconductor. (p for "positive" or "acceptor")

- In a p-type semiconductor, the holes are the majority carriers and the free electrons are the minority carriers (i.e, current is carried predominantly by holes). The opposite is true for n-type semiconductors.

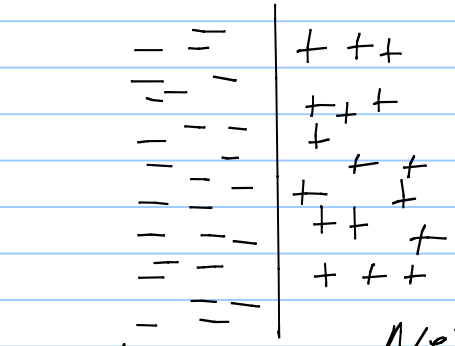
The P-N Junction



- The electrons will flow from the n-type material to the p-type material to fill the holes close to the interface.

Since any material is electrically neutral, the p-type semiconductor

will become negatively charged, and the n-type semiconductor will become positively charged.



Net negative charge

Net positive Charge

E (electric field)

Voltage build up

This process of electron migration is called "diffusion".

Bardeen's derivation of the Contact Potential (voltage buildup):

- The Diffusion current density is given by

$$J = \sigma E$$

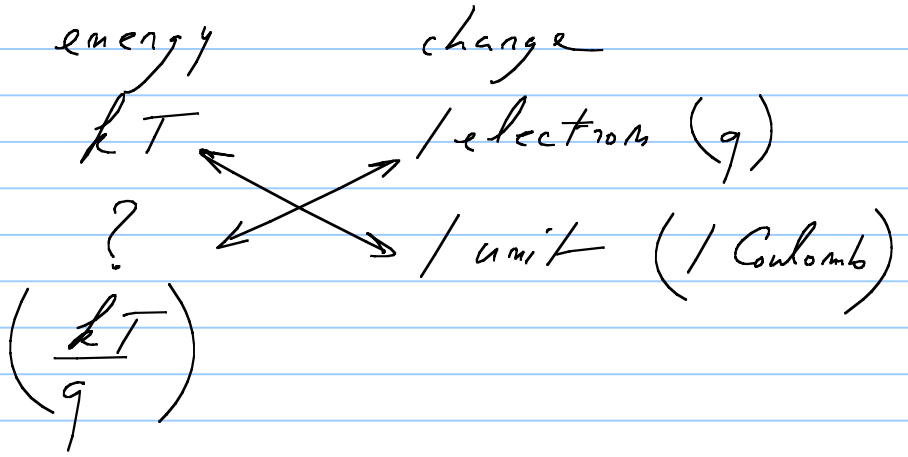
$$= (nq\mu)\left(\frac{dV}{dx}\right)$$

voltage gradient

$$= \left(\frac{\Delta n}{\Delta x}\right) \cdot \Delta V \cdot q\mu$$

This is because the voltage gradient is the result of a "concentration gradient", or rate of change of free electron density.

- But voltage is the work done in moving a unit charge. The work in moving a particle (here, an electron) according to Boltzmann's law is equal to kT.



Hence, ΔV, or the work done in moving a unit charge, is

$$\Delta V = \frac{kT}{q} \triangleq V_t$$

Hence,

$$J = \left(\frac{dn}{dx}\right) \cdot \left(\frac{kT}{q}\right) \cdot q\mu$$

- Definition: Let $D \triangleq \mu \frac{kT}{q}$ be the "Diffusion Constant" of the material.

Hence, $J = qD \cdot \frac{dn}{dx}$

(Diffusion current density)

- The quantity $V_t = \frac{kT}{q}$ is called the "Volt equivalent of temperature" (measured is Volts).

$$\boxed{V_t = \frac{T}{11,586}}$$

- The electric field that builds up at the interface of the P-N junction "pulls" the electrons in the opposite direction; i.e, back toward the n-material.

When the current finally stops, we must have

Diffusion Current = (Current in the opposite direction)

"Drift Current"

$$\cancel{q} D \frac{dn}{dx} = (n \cancel{q} \mu) \underline{\underline{E}}$$

Hence, the internal electric field E will be given by

$$E = \frac{D}{n\mu} \frac{dn}{dx}$$

But $$\frac{D}{\mu} = \frac{kT}{q} = V_t$$

Hence, $$\boxed{E = \frac{V_t}{n} \frac{dn}{dx}}$$

- Since $$E = -\text{grad } V = -\frac{dV}{dx}$$

then, $$E = -\frac{dV}{dx} = \frac{V_t}{n} \frac{dn}{dx}$$

Integrating both sides of the eq., we get

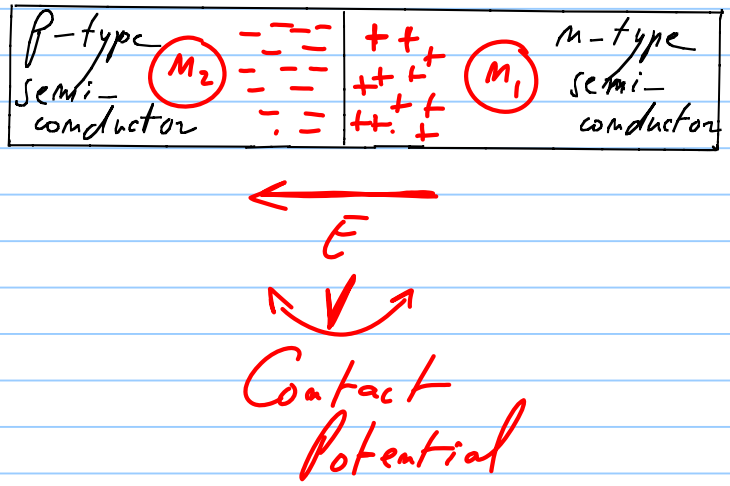
$$\int_{n_1}^{n_2} -dV = V_t \int_{n_1}^{n_2} \frac{1}{n} dn$$

$$-V = V_t \left| \ln n \right|_{n_1}^{n_2}$$

$$= V_t \left(\ln n_2 - \ln n_1 \right)$$

or $$V = V_t \left(\ln n_1 - \ln n_2 \right)$$

$$= \boxed{V_t \ln \frac{n_1}{n_2}}$$



. For the n-type semiconductor, the free electron density, n, is approximately equal to the number of Donor atoms, i.e,

$$n \simeq N_D$$

where N_D is the number of donor atoms per unit volume.

Similarly, for the p-type semiconductor, the hole density is approximately equal to the number of acceptor atoms per unit volume, i.e,

$$p \simeq N_A$$

(N_A = no. of acceptor atoms per unit volume)

- We saw that

$$n = p = n_i$$

(for an intrinsic semiconductor)

For a doped semiconductor, $n \neq p$, however, we must have

$$\boxed{n \uparrow p \downarrow = n_i^2}$$

The mass-action law

Hence, n_2 (on the p-side) must be equal to

$$n_2 = \frac{n_i^2}{p}$$

$$= \boxed{\frac{n_i^2}{N_A}}$$

- Finally,

$$V_{contact} = \boxed{V_t \ln \frac{n_1}{n_2}}$$

$$= V_t \ln \frac{N_D}{n_i^2 / N_A}$$

$$\boxed{= V_t \ln \frac{N_A N_D}{n_i^2}}$$

Bardeen's Equation

Detailed Calculation:

Find the contact potential for a Silicon PN junction at room temperature

Room temperature : 300°K

Physical properties of Silicon :

- Atomic mass = 28.0855
- Density = 2329 Kg/m^3
- Electrical Conductivity (σ) = $3.24 * 10^{-4}$ $\Omega^{-1} m^{-1}$
- Electron mobility (μ) = 0.135 $m^2/V.s.$

Doping of Silicon :

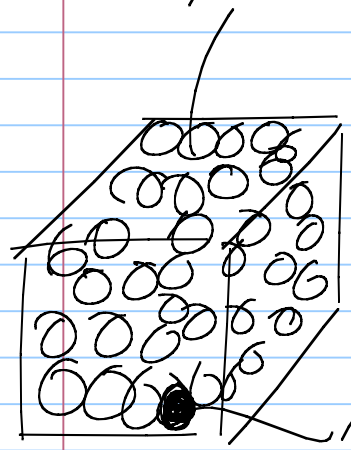
- P-side is typically doped with one part per 10^8 of an acceptor impurity.
- N-side is typically doped with 2 parts per 10^7 of a donor impurity.

Calculation of N_A and N_D:

① Determine the number of atoms per unit volume of the intrinsic (pure) element.

One mole of Si weighs 28.0855 grams.

Hence, one cubic meter of the element contains:



2329 Kg

$$\frac{2329\ Kg}{28.0855 * 10^{-3}\ Kg} = 8.3 * 10^4 \text{ moles}$$

Now, one mole of any element contains a number of atoms equal to Avogadro's number. Hence, one cubic meter contains

$$(8.3 * 10^4)(6.022 * 10^{23}) = 5 * 10^{28} \text{ atoms}$$

Avogadro's No.

(2) Calculate N_A and N_D from the given mixing ratios:

$$N_A = \left(\frac{1}{10^8}\right) 5 * 10^{28}$$

$$= 5 * 10^{20} \text{ acceptor atoms/m}^3$$

$$N_D = \left(\frac{2}{10^7}\right) 5 * 10^{28}$$

$$= 1 * 10^{22} \text{ donor atoms/m}^3$$

(3) Calculate n_i (intrinsic free electron density)

$$\sigma = n_i q \mu$$

$$n_i = \frac{\sigma}{q\mu} = \frac{3.24 * 10^{-4}}{(1.6 * 10^{-19})(0.135)}$$

$$= 1.5 * 10^{16} \text{ electrons/m}^3$$

④ Calculate the Contact Potential from Bardeen's equation:

$$V_{contact} = V_t \ln \frac{N_A N_D}{n_i^2}$$

Bardeen's Equation

$$= \frac{(300\ K)}{11,586} \ln \frac{(5 * 10^{20})(10^{22})}{(1.5 * 10^{16})^2}$$

$$= 0.6\ Volts!$$

Home work #3:

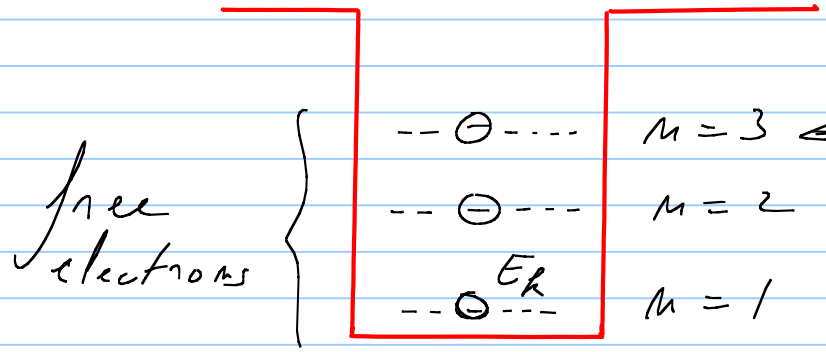
①

$$P\left(\bar{E}_{k(m)}\right) = \frac{1}{1 + e^{(E_{k(m)} - \mu)/kT}}$$

Probability that a certain energy level $E_{k(m)}$ be occupied by free electrons.

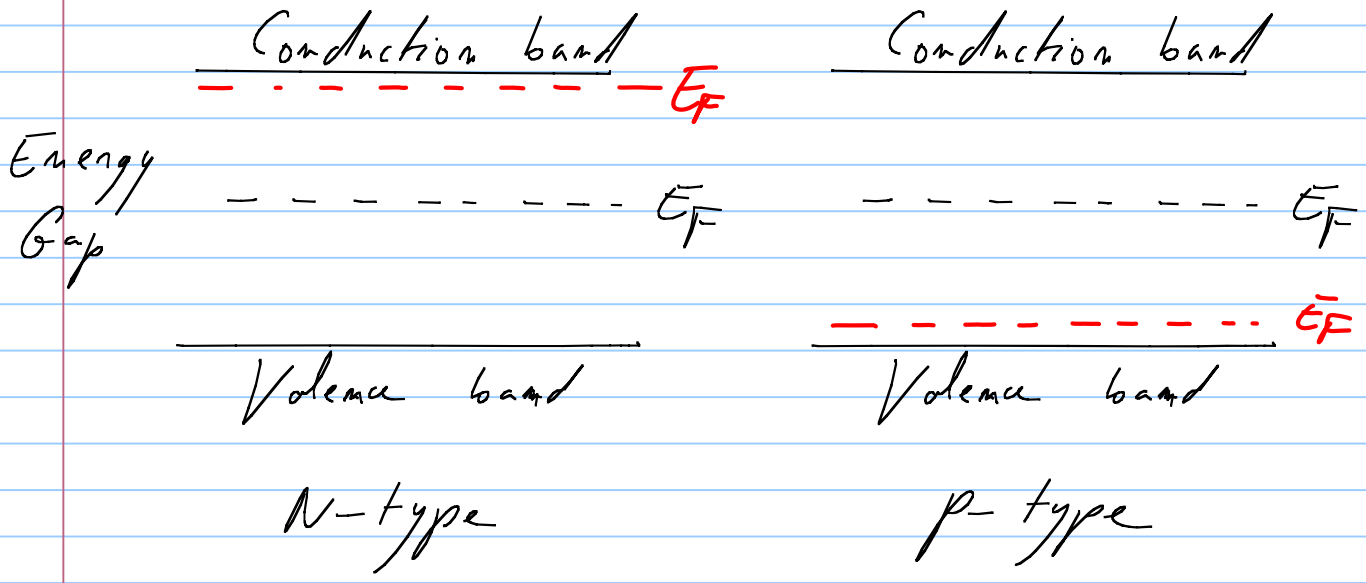
μ $\quad$ $e^{(E_k(n)-\mu)/kT}$ $\quad$ Probability

N – doping	increases	decreases	increases
P – doping	decreases	increases	decreases



Hence, E_F increases or decreases along with μ.

Doped semiconductor:



Material becomes almost a conductor

Material becomes almost an insulator

② Current density

$$J = \sigma E$$

σ: conductivity

$$= (3.24 * 10^{-4})(100\ V/m)$$

$$= 3.24 * 10^{-2}\ Amp/m^2$$

$$\text{Current} = J * \underbrace{A}_{\text{Cross-sectional area}}$$

Doping: $N_A = 10^{20}$ atoms $/m^3$

σ_{new} (after doping)

$$= n_{(new)}\, q\, \mu$$

q: electron's charge

μ: electron's mobility

n (new), on the new free electron density

$$= \frac{n_i^2}{N_A} = \frac{(1.5 * 10^{16})^2}{10^{20}}$$

$$= 2.25 * 10^{12} \text{ electrons/m}^3$$

$$\sigma (\text{new}) = n q \mu$$

$$= \left(\frac{n}{n_i}\right) \underbrace{n_i q \mu}_{\sigma_{old}}$$

$$\text{Current ratio} = \frac{J_{old} \cdot A}{J_{new} \cdot A} = \frac{\sigma_{old} \cdot E}{\sigma_{new} \cdot E}$$

$$= \frac{n_i}{n} = \frac{1.5 * 10^{16}}{2.25 * 10^{12}}$$

$$\simeq 10,000$$