

Lecture 1- Free electron theory -Drude Model

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Early Days of Solid State Physics- Drude Model(1900)

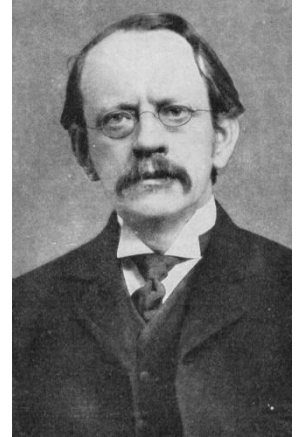
Modern Condensed Matter Physics was boosted with the discovery of the electron by J.J. Thompson in 1897

Electrical Conductivity of Metals (electrons) – Drude Theory

What do we learn here?:

- Understand how to apply the Drude model
- Determine the density of conduction electrons
- Calculate the electrical conductivity of a metal
- Discuss the classical Hall effect and why the Drude model doesn't perfectly explain the results

For more on Drude Model, see Ashcroft ch. 1-3 and Ch 3-4 of Steven H. Simon



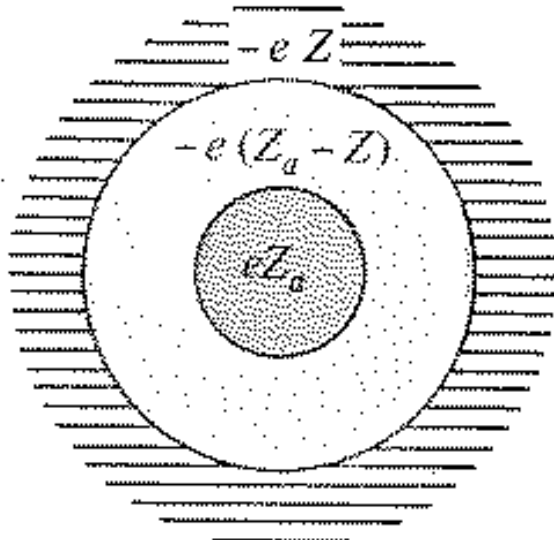
Sir Joseph John Thomson
(18 December 1856 – 30 August 1940)
Nobel Prize (1906) for discovery of
electrons



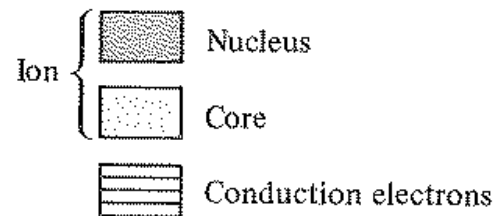
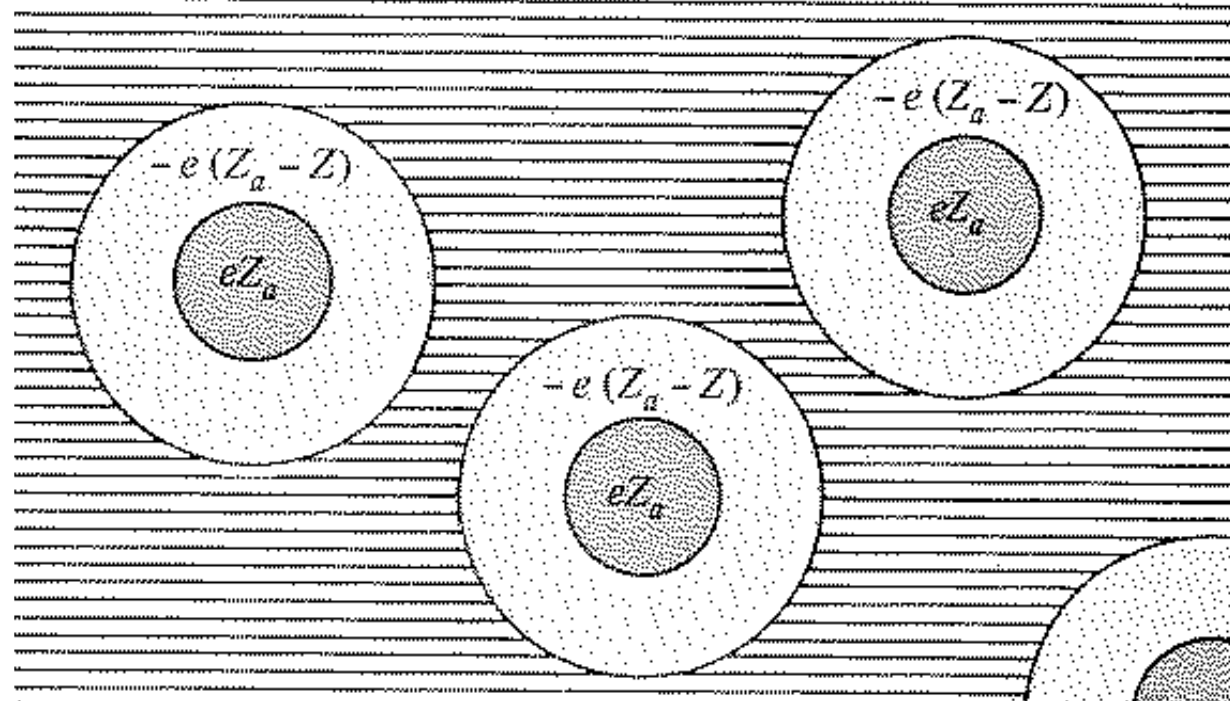
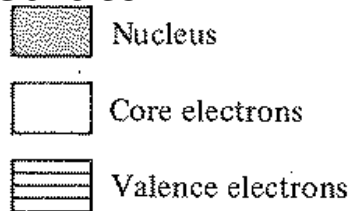
Paul Drude
12 July 1863
5 July 1906

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Z_a = atomic number
= # of electrons



isolated atom



in a metal

In a metal, the core electrons remain bound to the nucleus to form the metallic ion

Valence electrons wander away from their parent atoms, called conduction electrons

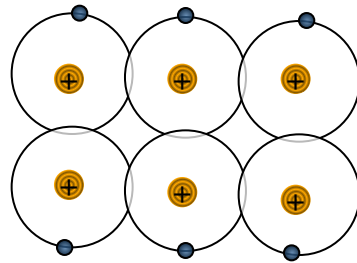
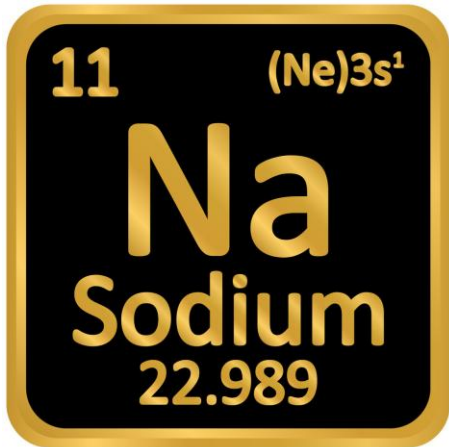
Z valence electrons - weakly bound to the nucleus (participate in reactions)

$Z_a - Z$ core electrons - tightly bound to the nucleus (less of a role)

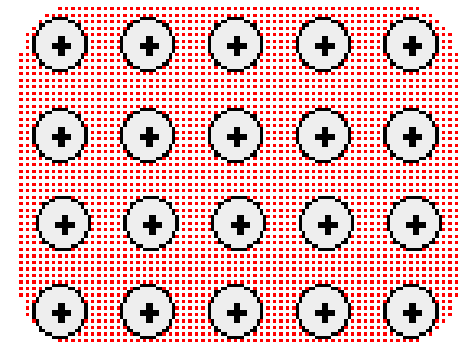
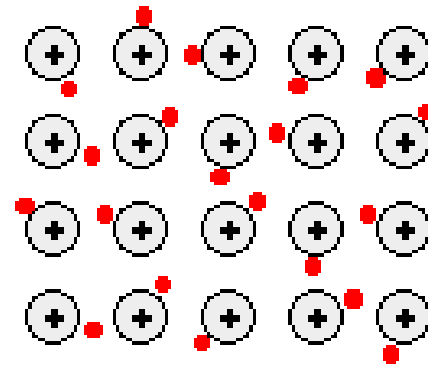
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How the mobile electrons become mobile

- When we bring Na atoms together to form a Na metal, the orbitals overlap slightly and the valance electrons become no longer attached to a particular ion, but belong to all.



Metal (classical picture)



↑
delocalised electrons

A valance electron really belongs to the whole crystal, **since it can move readily from one ion to its neighbour and so on.**

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For Drude model, we will need to know the conduction electron density $n = N/V$

- 6.022×10^{23} atoms per mole (N)
- Multiply by number of valence electrons (Z) : Each atom gives Z electrons
- Convert from g/cm^3 to mole/cm^3 (using mass density ρ_m (g/cm^3) and atomic mass A (g/mol)) : $\frac{\rho_m}{A}$
- Total # of electrons/ cm^3 (n): $n = N/V = (6.022 \times 10^{23} \text{ Z-electrons/mole}) \times (\frac{\rho_m}{A}) \text{ mole/cm}^3$
- Density of conduction electrons in metals $\sim 10^{22} - 10^{23} \text{ cm}^{-3}$

Another useful quantity is the measure of electronic density in terms of radius of free electron sphere whose volume is equal to the volume per conduction electron defined below

$$\frac{\text{Total Volume for all electrons}}{N} = \frac{N \frac{4\pi r_s^3}{3}}{N} = \frac{4\pi r_s^3}{3} = \frac{V}{N} = \frac{1}{n} \quad \Rightarrow \quad r_s = \left(\frac{3}{4\pi n} \right)^{1/3} = \left(\frac{3A}{6.022 \times 10^{23} Z \rho_m} \right)^{1/3}$$

r_s = radius of a sphere whose volume is equal to the volume per electron

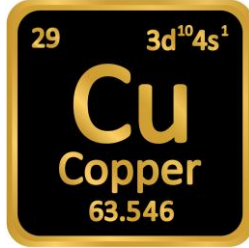
In metals $r_s \sim 1 - 3 \text{ \AA}$

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FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS^a

ELEMENT	Z	n ($10^{22}/\text{cm}^3$)	$r_s(\text{\AA})$	r_s/a_0
Li (78 K)	1	4.70		
Na (5 K)	1	2.65		
K (5 K)	1	1.40		
Rb (5 K)	1	1.15		
Cs (5 K)	1	0.91		
Cu	1	8.47		
Ag	1	5.86		
Au	1	5.90		
Be	2	24.7		
Mg	2*	8.61		
Ca	2	4.61		
Sr	2	3.55		
Ba	2	3.15		
Nb	1	5.56		
Fe	2	17.0		
Mn (α)	2	16.5		
Zn	2	13.2		
Cd	2	9.27		
Hg (78 K)	2	8.65		
Al	3	18.1		
Ga	3	15.4		
In	3	11.5		
Tl	3	10.5		
Sn	4	14.8		
Pb	4	13.2		
Bi	5	14.1		
Sb	5	16.5		

^a At room temperature (about 300 K) and atmospheric pressure, unless otherwise noted. The radius r_s of the free electron sphere is defined in Eq. (1.2). We have arbitrarily selected one value of Z for those elements that display more than one chemical valence. The Drude model gives no theoretical basis for the choice. Values of n are based on data from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963.



Calculate radius of the free electrons in Cu, Ag, & Be

Hint:

Density (ρ_m) in g/cm^3 = Cu: 8.96, Ag: 10.49, Be: 1.85

Z = Valence Electrons = 1 (Cu, Ag), 2 (Be);

A (Atomic Mass Number) = 63.546 (Cu), 107.68 (Ag), 9.3227 (Be)

Bohr radius (a_0) is a measure of radius of a hydrogen atom in its GND state: $\hbar^2 / me^2 = 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ \AA}$

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} = \left(\frac{3A}{6.022 \times 10^{23} Z \rho_m} \right)^{1/3}$$

$$n = N/V = 6.022 \times 10^{23} Z \rho_m / A = 8.47 \times 10^{22} / \text{cm}^3$$

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} = 1.41 \times 10^{-8} \text{ cm} = 1.41 \text{ \AA} = 2.67 a_0$$

The densities of electrons in metals are typically 1000 times greater than the densities of classical gas atoms at normal temperatures (T) and pressures (P)

In spite of this and the strong electron-electron and electron-ion electromagnetic Interaction, Drude treats the dense electrons in metals through Boltzmann's kinetic theory of dilute gas with some modification as in the following assumptions

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Assumptions of Drude Model

0. Electrons don't have a ballistic transport, instead there is some kind of Scattering/collisions 

1. Between Collisions, the interaction of a given electron, both with the other electrons and with ions, is neglected.

Neglect of the electron-electron interactions is **the independent electron approximation**.

Neglect of the electron-ion interactions is the **free electron approximation**.

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2. In the KE of gases, one can estimate the scattering time based on the velocity, density and scattering cross section.

But, here estimate of scattering time is given by τ and it is **purely phenomenological** as we can not be sure of what causes the scattering.

i.e,

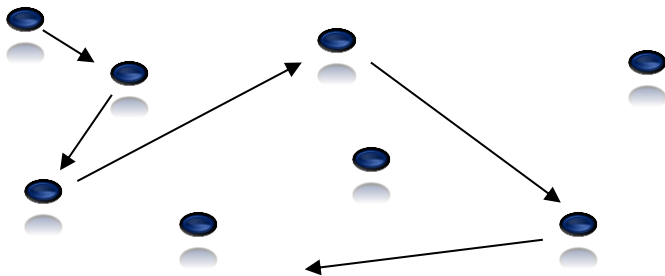
1. Electrons interact through long range Coulomb interaction, so it is hard to define the scattering cross section.
2. There can be many other things like defects that can distract before it scatters with another electron.

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3. **Collisions of electrons** in Drude model (like kinetic theory of gas), are **instantaneous** events that abruptly alter the velocity of an electron randomly.

So the average momentum (as the final momentum is in all directions) is zero, $P_f = 0$.

The collisions are assumed to maintain the local thermal equilibrium. i.e immediately after each collision, an electron will emerge in random direction with a speed appropriate to the temperature prevailing at that place where collision occurred.



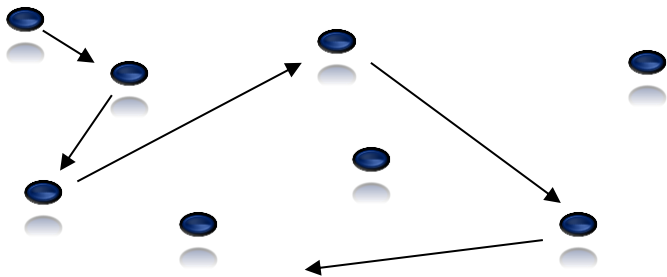
Trajectory of conduction electrons scattering, according to native picture of Drude's theory

4. In between scattering events, the electrons, which are charge $-e$ particles, respond to the externally applied electric field \mathbf{E} and magnetic field \mathbf{B} .

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Assumptions of Drude Model

1. Between Collisions, the interaction of a given electron, both with the other electrons and with ions, is neglected. Neglect of the electron-electron interactions is **the independent electron approximation**. Neglect of the electron-ion interactions is the **free electron approximation**.
2. In the KE of gases, one can estimate the scattering time based on the velocity, density and scattering cross section. But, here estimate of scattering time is given by τ and it is **phenomenological** as we can not be sure of what causes the scattering (1. Electrons interact through long range Coulomb interaction, so it is hard to define the scattering cross section. 2. There can be many other things like defects that can distract before it scatters with another electron).
3. **Collisions of electrons** in Drude model (like kinetic theory of gas), **are instantaneous** events that abruptly alter the velocity of an electron randomly. So the average momentum (as the final momentum is in all directions) is zero, $P_f = 0$. The collisions are assumed to maintain the local thermal equilibrium. i.e immediately after each collision, an electron will emerge in random direction with a speed appropriate to the temperature prevailing at that place where collision occurred.



Trajectory of conduction electrons undergoing scattering, according to native picture of Drude's theory

4. In between scattering events, the electrons, which are charge $-e$ particles, respond to the externally applied electric field \mathbf{E} and magnetic field \mathbf{B} .

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DC Electrical conductivity of a metal

Ohm's Law:

$$\underline{I = V/R}$$

R depends on the dimensions of the wire

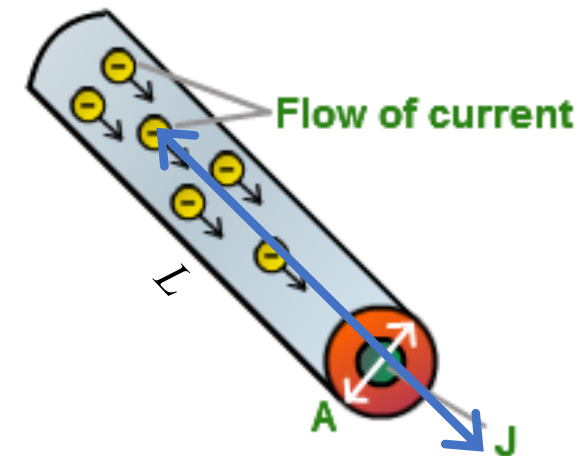
The current I flowing through a wire is proportional to the potential drop along the wire

Here $R = \rho L/A$ (ρ - resistivity (Ohm-m), L – length of the wire, A – Cross sectional area of the wire)

Current Density: $\vec{J} = \vec{I}/A$ and E – Electric field

In terms of the current density vector, \vec{J} , $\vec{E} = \rho \vec{J}$ where ρ is the resistivity (does not depend on the dimensions of the wire), $\vec{V} = \vec{E} L = \rho \vec{J} * L = \frac{\rho L}{A} \vec{I}$

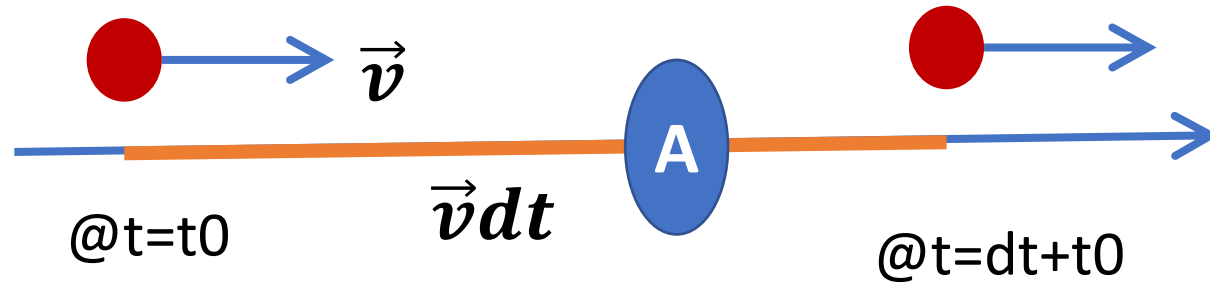
Here, $R = \frac{\rho L}{A}$ (ρ - resistivity (Ohm-m), L – length of the wire, A – Cross sectional area of the wire)



**J = The flow of current over
Cross Section area "A"**

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Now, if 'n' electrons/unit volume move with velocity, \vec{v} , then in a time 'dt', the electron would travel a distance of vdt in the direction of \vec{v} ,



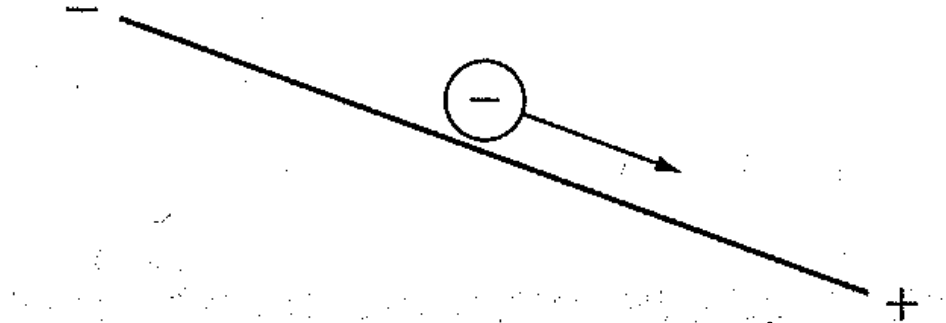
so that $n\vec{v}.dt.A$ will be the # of electrons that will cross an area of A perpendicular to the direction of flow.

Hence the total charge crossing A in time 'dt' will be $-nevdtA$, thus current density

$$\vec{J} = \vec{I}/A = (dQ/dt)*(1/A) = -nev dtA/(dtA) = -nev$$

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Determining Velocity When Applying an Electric Field E to a Metal

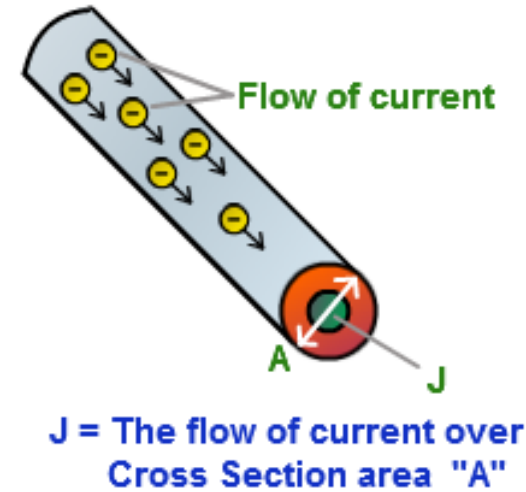


$$F = ma = -eE, \text{ so acceleration } a = -eE / m$$

$$\text{Integrating gives } v = -eEt / m$$

So the average $v_{\text{avg}} = -eE\tau / m$, where τ is “relaxation time” or time between collisions

$v_{\text{avg}} = \Delta x / \tau$, we can find the Δx_{avg} or mean free path



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$$v_{\text{avg}} = - e E \tau / m$$

$$\vec{J} = \vec{I}/A = -nev = -n e * (- e \vec{E} \tau / m) = \frac{n \tau e^2}{m} \vec{E}$$

linear dependence of \vec{J} and \vec{E} - Ohm's Law

Above result is normally written in terms of inverse of the resistivity, called conductivity

$$\sigma = 1/\rho \qquad \vec{J} = (1/\rho) \vec{E}$$

Then conductivity $\sigma = n e^2 \tau / m$ ($\sigma = 1/\rho$)

Only scattering time is unknown and can be estimated from measured values
i.e $\tau = m / (\rho n e^2) \sim 10^{-15} - 10^{-14} \text{ s} \sim 1-10 \text{ fs} (10^{-15} \text{ s})$

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- Often, instead of a scattering time τ , it's useful to formulate a theory of conductivity in terms of

An average distance between collisions (*The mean free path*).

- To do this, we have to consider the average electron velocity. This should not be v_{drift} , which is the electron velocity due to the electric field.
- Instead, it should be $v_{\text{random}} / v_{\text{avg}}$, the velocity associated with the intrinsic thermal energy of the electrons.

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- Estimate \mathbf{v}_{avg} by treating the electrons as a classical ideal gas & using the result from classical statistical physics:

The Equipartition Theorem:

$$(\frac{1}{2})m(\mathbf{v}_{random})^2 = (\frac{3}{2})(k_B)T$$

- Results: The mean free path is $\ell = \mathbf{v}_{avg} \tau \approx 1-10 \text{ \AA}$
- This is of the order of interatomic distances, *so it is reasonable!*

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Group Exercise

$$\tau = m / (\rho n e^2)$$

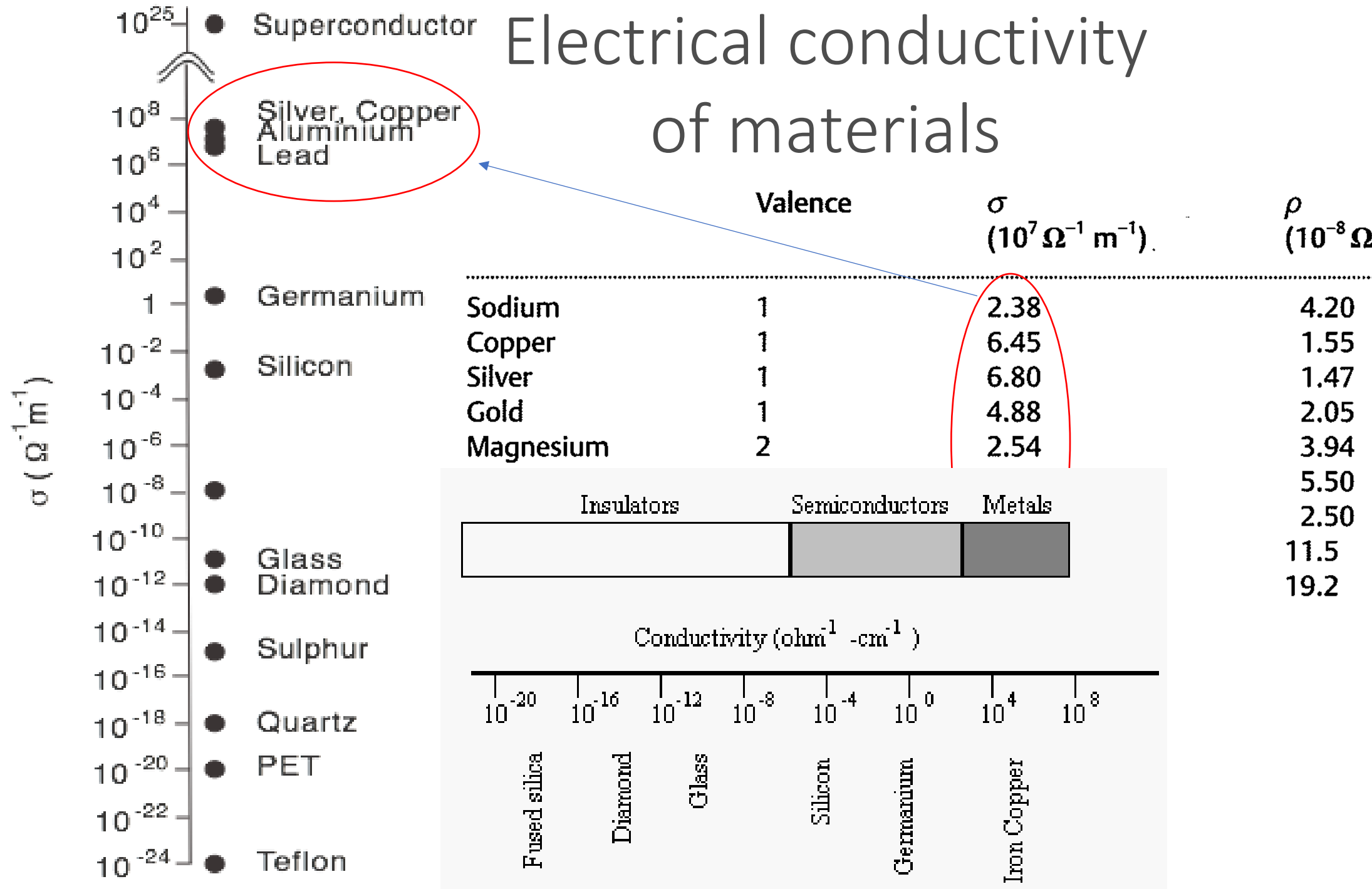
Calculate the average time between collisions τ for electrons in copper at 273 K.

	Valence	σ ($10^7 \Omega^{-1} \text{ m}^{-1}$)	ρ ($10^{-8} \Omega \text{ m}$)	n (10^{28} m^{-3})
Sodium	1	2.38	4.20	2.65
Copper	1	6.45	1.55	8.50
Silver	1	6.80	1.47	5.86
Gold	1	4.88	2.05	5.90
Magnesium	2	2.54	3.94	8.60
Zinc	2	1.82	5.50	13.2
Aluminium	3	4.00	2.50	18.1
Tin	4	0.87	11.5	14.5
Lead	4	0.52	19.2	13.2

Assuming that the average speed for free electrons in copper is $1.6 \times 10^6 \text{ m/s}$ calculate their mean free path (ℓ).

$$v_{\text{avg}} = \ell / \tau$$

Electrical conductivity of materials



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Equation of motion/Drude Transport Equation of electrons in metals

At any given time, t , the average electron velocity $\vec{v}(t) = \vec{p}(t)/m$

- Momentum, $\vec{p}(t) = m \vec{v}(t)$ @ time, t
- So $\vec{j} = n e \vec{p}(t) / m$
- Probability of collision/scattering during time, dt is dt/τ , thus prob of not scattering will be $(1 - dt/\tau)$

Momentum of the electron @ ' $t+dt$ ' is

$$\vec{p}(t+dt) = (1-dt/\tau) * [\vec{p}(t) + \vec{F}.dt] + (dt/\tau) * \vec{0} \quad \longrightarrow$$

Momentum acquired due to scattering
(Zero avg momentum as velocity is random)

(Here \vec{F} is the force ($e\vec{E}$ or $e \vec{v}(t) \times \vec{B}$ or both together) that acts on the electron in between the scattering)

$$= \vec{p}(t) - \vec{p}(t) dt/\tau + \vec{F}.dt$$

$$\frac{\vec{p}(t+dt) - \vec{p}(t)}{dt} = -\vec{p}(t)/\tau + \vec{F} \quad \text{Or} \quad \frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau + \vec{F}$$

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$$\frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau + \vec{F}$$

Drude Transport Equation (DTE)
of electrons in metals

Here $\vec{F} = -e (\vec{E} + \vec{v} \times \vec{B})$ – Lorentz Force

Case1: No field ($\vec{B} = 0, \vec{E} = 0$, i.e $\vec{F} = 0$)

$$\frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau \quad \text{i.e. } \vec{p}(t) = \vec{p}_0 e^{-\frac{t}{\tau}}$$

i.e the Initial Momentum decays exponentially by scattering. This means $-\vec{p}(t)/\tau$ is just the drag force on the electron.

Case2: Electrons in an electric field ($E \neq 0, B = 0$)

$$\frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau - e\vec{E}$$

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$$\frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau - e\vec{E}$$

In a steady state, $\frac{d\vec{p}(t)}{dt} = 0$, hence we have

$$m\vec{v} = \vec{p}(t) = -e\tau\vec{E}$$

m – mass of the electron

\vec{v} – velocity of the electron

If the density of electrons ($Q = -e$) in the metal is 'n' and all of them are moving with a velocity \vec{v} , then the electrical current is

$$\begin{aligned}\vec{J} &= -ne\vec{v} = -ne * (-e\tau\vec{E} / m) \\ &= \frac{n\tau e^2}{m} \vec{E} = \sigma \vec{E}\end{aligned}$$

(Q_T) crossing area 'A' in time 'dt' will be ' $-nevdtA$ ' (vdt is the distance travelled)
 $\vec{J} = \vec{I}/A = (dQ/dt)*(1/A) = -ne\vec{v}$

Here, Drude DC conductivity is $\sigma = \frac{n\tau e^2}{m} = ne\mu$ Also, $\vec{v} = \mu \vec{E}$ with $\mu = \frac{e\tau}{m}$: **Drude Mobility**
 (We will look in details in semiconductors)

By measuring the conductivity of the metal (with 'm' and 'Q' of electron known), we can determine the product of electron density (n) and the scattering time, τ .

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Case3: Electrons in both electric and magnetic fields ($E \neq 0, B \neq 0$)

$$\frac{d\vec{p}(t)}{dt} = -\vec{p}(t)/\tau - e\vec{E} - e\vec{v} \times \vec{B}$$

Now in a steady state, $\frac{d\vec{p}(t)}{dt} = 0$, and using $\vec{J} = -ne\vec{v}$, we get the steady state current equation

$$0 = -\frac{m}{ne} \frac{\vec{J}}{\tau} - e\vec{E} - e \frac{-\vec{J} \times \vec{B}}{ne} \quad \vec{p} = m\vec{v} \quad \vec{v} = \frac{-\vec{J}}{ne} \quad \text{Set } \sigma_0 = \frac{ne^2\tau}{m}$$

$$\Rightarrow \vec{E} = \frac{\vec{J} \times \vec{B}}{ne} + \frac{m}{ne^2\tau} \vec{J} \quad \text{Applying } \vec{B} = B \hat{z} \text{ and define sigma as } 3 \times 3 \text{ matrix}$$

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} 1 \\ ne \end{bmatrix} * \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ J_x & J_y & J_z \\ 0 & 0 & B \end{vmatrix} + \frac{1}{\left(\frac{ne^2\tau}{m}\right)} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = \begin{bmatrix} \frac{J_y B}{ne} \\ \frac{J_x B}{ne} \\ 0 \end{bmatrix} + \frac{1}{\sigma_0} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = \begin{bmatrix} \frac{1}{\sigma_0} & \frac{B}{ne} & 0 \\ \frac{-B}{ne} & \frac{1}{\sigma_0} & 0 \\ 0 & 0 & \frac{1}{\sigma_0} \end{bmatrix} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}$$

Lecture 2- Drude Theory of electrons (Continuation)

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This equation is same as we had seen little earlier, $\vec{E} = \rho \vec{J}$
where ρ is the resistivity (Here it is a 3x3 matrix) and

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} \frac{1}{\sigma_0} & \frac{B}{ne} & 0 \\ \frac{-B}{ne} & \frac{1}{\sigma_0} & 0 \\ 0 & 0 & \frac{1}{\sigma_0} \end{bmatrix} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}$$

$$\sigma = 1/\rho$$

$$\rho = \begin{bmatrix} \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zx} & \rho_{zy} & \rho_{zz} \end{bmatrix} = \begin{bmatrix} \frac{1}{\sigma_0} & \frac{B}{ne} & 0 \\ \frac{-B}{ne} & \frac{1}{\sigma_0} & 0 \\ 0 & 0 & \frac{1}{\sigma_0} \end{bmatrix}$$

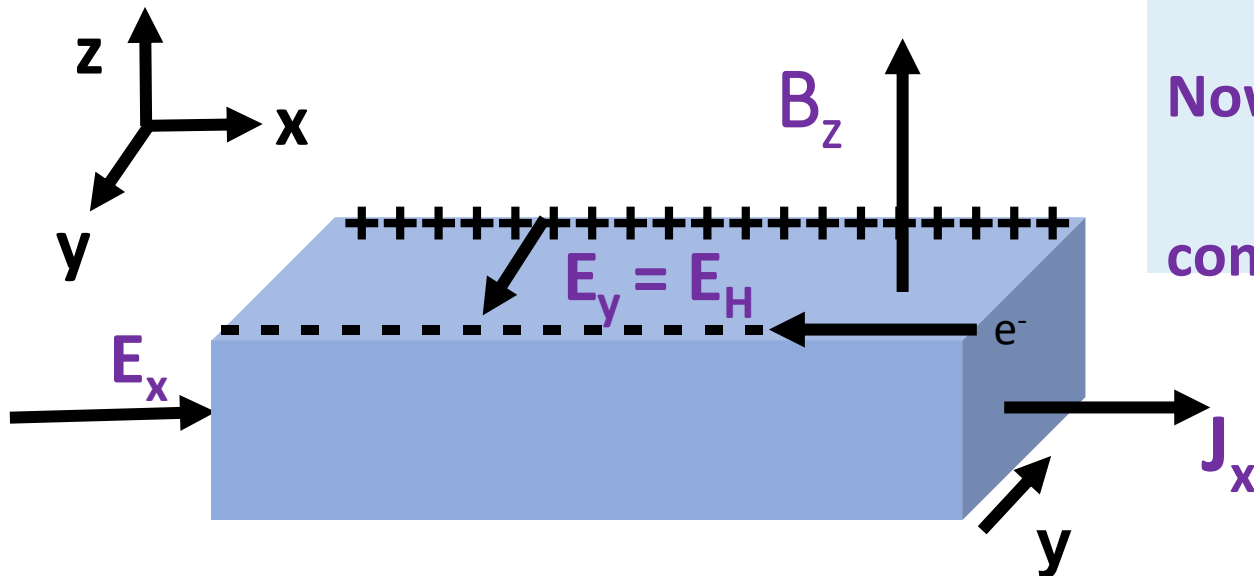
$$\rho_{xx} = \rho_{yy} = \rho_{zz} = \frac{1}{\sigma_0} = \frac{n\tau e^2}{m}$$

DC Resistivity

$$\rho_{xy} = -\rho_{yx} = \frac{B}{ne} = R_H B$$

Hall Resistivity (1879)

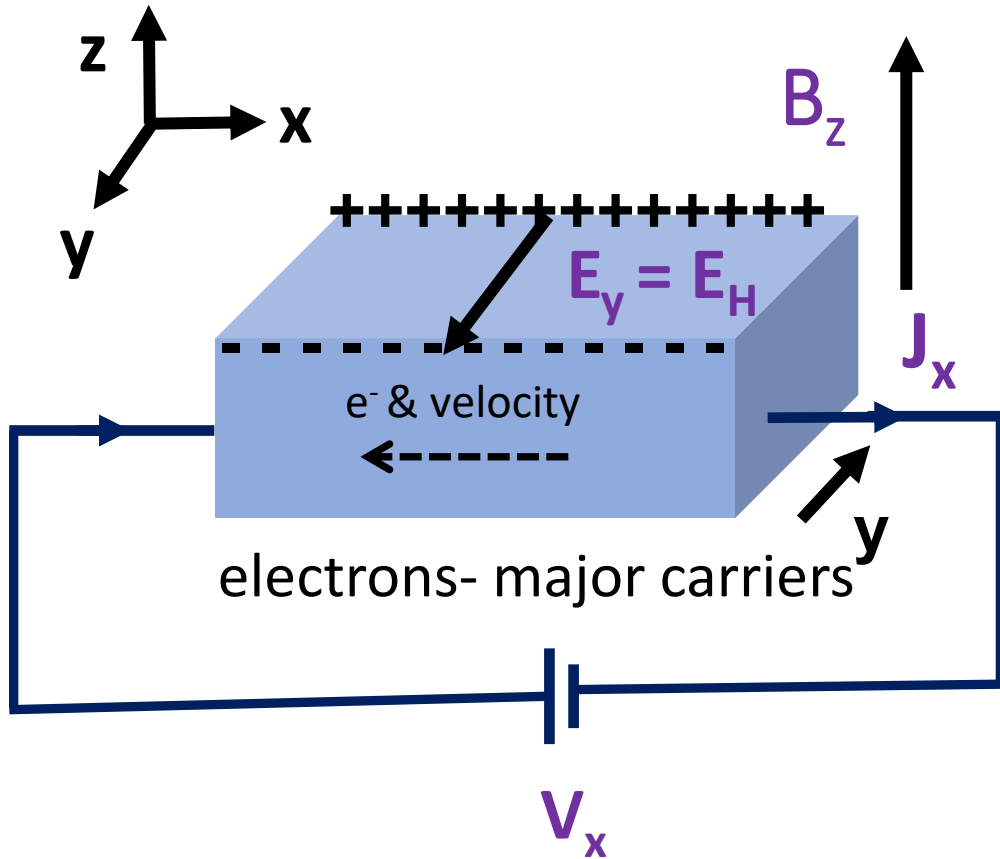
Now, calculate $\begin{bmatrix} \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zx} & \rho_{zy} & \rho_{zz} \end{bmatrix}^{-1}$ and hence the conductivity tensor (HW)



Hall Coefficient

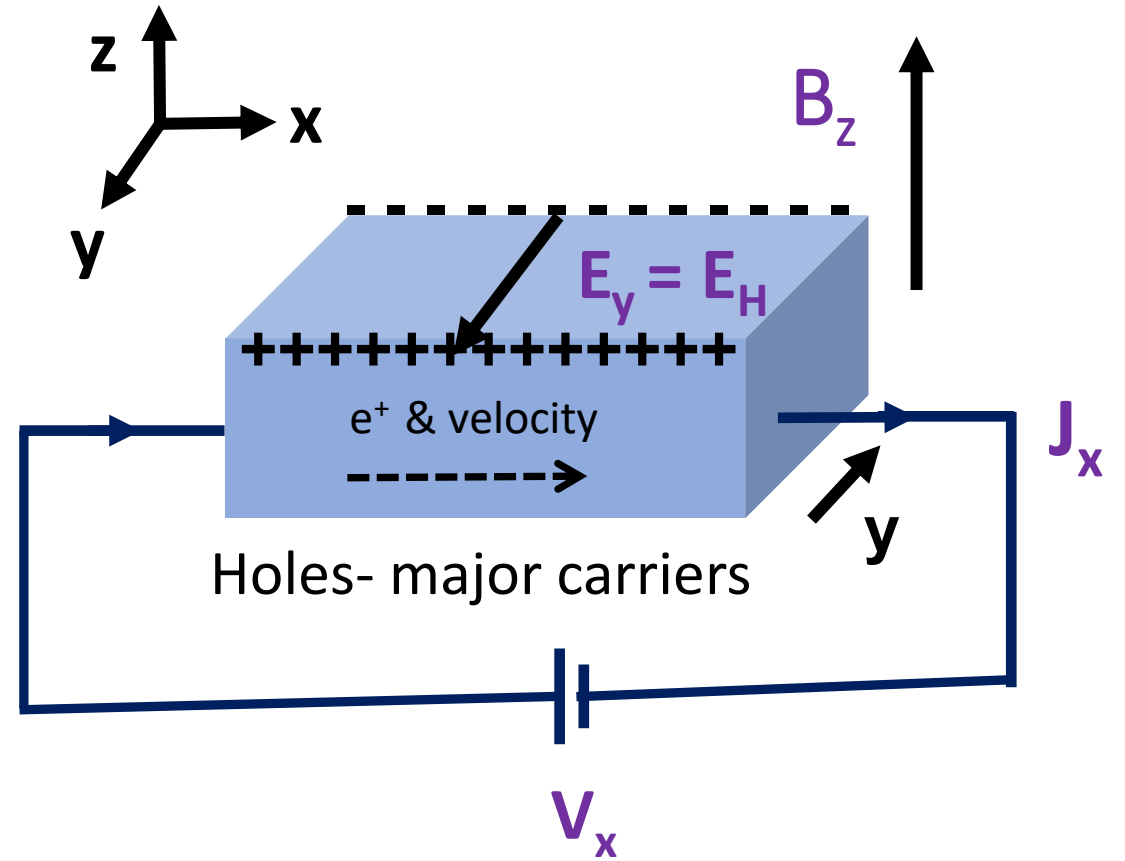
$$R_H = \frac{\rho_{yx}}{|B|} = \frac{-1}{ne}$$

$V \times B$ is in $-y$ direction & $-eV \times B$ is the y direction



Case 1: For negative carriers

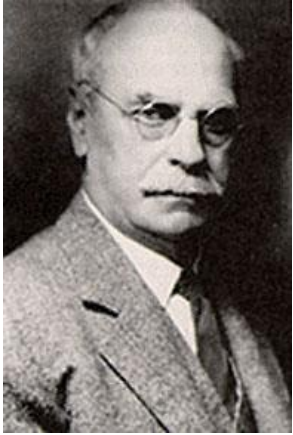
$V \times B$ is in $-y$ direction & $-eV \times B$ is the y direction



Case 2: For +ve carriers/holes

See that E_y for case 1 (electrons) is negative of E_y of case 2 (holes)

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Edwin Herbert Hall
(1855 –1938)

Say we know 'n, e, J' and we measure E_H get B

Hall
Probe/Sensor

In general, $E_H = \frac{-B}{ne} J_x = B * R_H J_x$

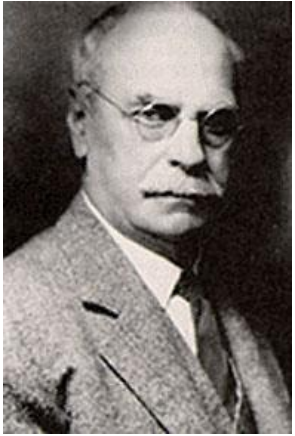
$$R_H = \frac{-1}{ne}$$

Thus, if we want to have a good Hall sensor, we need to have a BIG R_H thereby measuring large E_H / V_H

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} == \begin{bmatrix} \frac{1}{\sigma_0} & \frac{B}{ne} & 0 \\ \frac{-B}{ne} & \frac{1}{\sigma_0} & 0 \\ 0 & 0 & \frac{1}{\sigma_0} \end{bmatrix} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}$$

i.e we need to select materials with low carrier density (n). Hence semiconductors are normally preferred in Hall Probes

Early Days of Solid State Physics- Drude Model(1900)



Edwin Herbert Hall
(1855 –1938)

Say we know 'n, e, J' and we measure E_H --- We can get B

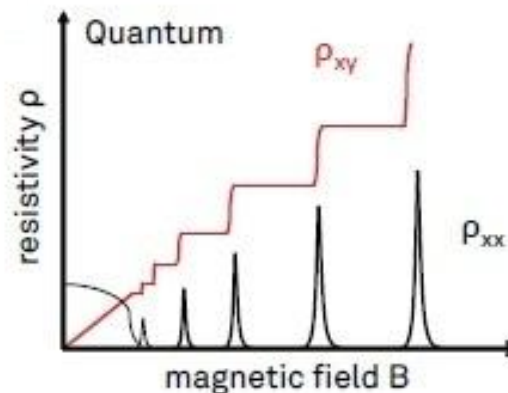
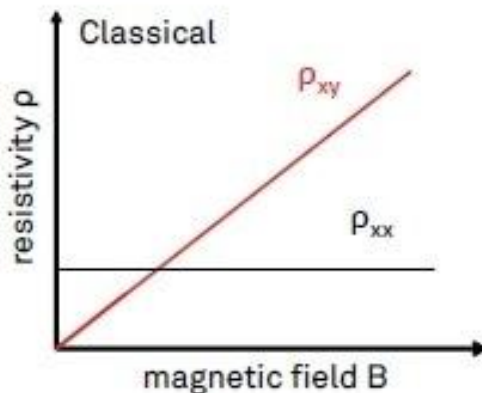
Hall
Probe/Sensor

In general, $E_H = \frac{-B}{ne} J_x = B * R_H J_x$

$$R_H = \frac{-1}{ne}$$

Thus, if we want to have a good Hall sensor, we need to have a BIG R_H thereby measuring large E_H / V_H

i.e we need to select materials with low carrier density (n). Hence semiconductors are normally preferred in Hall Probes



Why?

Cyclotron frequencies are quantized

Early Days of Solid State Physics- Drude Model(1900)

Hall
Probe/Sensor

Say we know 'n, e, J' and we measure E_H get B

In general, $E_H = \frac{-B}{ne} J_x = B * R_H J_x$ (Assuming scattering time is small (1-10 fs))

$$R_H = \frac{-1}{ne}$$

Thus, if we want to have a good Hall sensor, we need to have a BIG R_H thereby measuring large E_H / V_H

Drude was able to calculate the electron density normalized to the density of atoms, once R_H is measured, i.e $n/n_{\text{atom}} = (\frac{-1}{R_H e}) * (\frac{1}{n_{\text{atom}}}) = \text{free/valence electrons per atom}$

Table 3.1 Comparison of the valence of various atoms to the valence predicted from the measured Hall coefficient.

Material	$\frac{1}{-e R_H n_{\text{atomic}}}$	Valence
Li	.8	1
Na	1.2	1
K	1.1	1
Cu	1.5	1
Be	-0.2*	2
Mg	-0.4	2
Ca	1.5	2

Drude theory with so much approximations, still able to match up to actual valence electrons for materials with VE (Valence electrons) =1

But for some materials where VE=2, we can see that the sign of R_H is reversed and the calculated electrons per atom do not come close at all !!!

Drude's theory does not have any clue why R_H is positive

$$R_H = \frac{1}{n(-e)}$$

For +ve R_H , Either n (electron density) has to be -ve (absurd)/ charge of the carriers is +ve (possible if holes are carriers...though this was not a possibility by Drude)

Even with these exceptions, Drude theory explained many things !!!



Edwin Herbert Hall
(1855 –1938)

What Drude can not explain?

However, Drude's model cannot explain:

- The positive Hall coefficient observed for some metals.
- The later observed dependence of the Hall coefficient on the temperature, magnetic field and the care by which the conducting sample was prepared.
- The additional magnetoresistance that was observed in later experiments.

Reference

For more on Drude Model, see Ashcroft ch. 1-3 and Ch 3-4 of Steven H. Simon

For AC Field Drude model – optical reflectivity...etc, see Kittel 8th ed, Ch 14. and Ch 15 (10th ed) and Ch10 (5th ed)

Marder, Ch 20

Extra Reading:

Paul Drude (1863–1906), Ann. Phys. (Leipzig) **15**, No. 7 – 8, 449 – 460 (2006) / **DOI** 10.1002/andp.200610210