Crystal Lattice

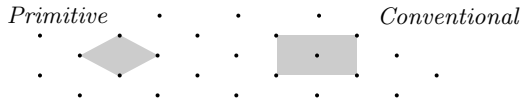
Lattices:

A lattice is an infinite set of points defined by integer sums of a set of linearly independent primitive lattice vectors. A Bravais lattice looks the same at all points.

$$\vec{\mathbf{R}} = u_1\underline{\mathbf{a}}_1 + u_2\underline{\mathbf{a}}_2 + u_3\underline{\mathbf{a}}_3$$

Unit Cells:

A unit cell is the repeated motif which is the elementary building lock of the period structure, containing all symmetries.

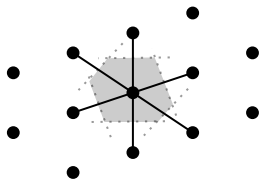


Primitive Unit Cells:

Primitive unit cells contain exactly one lattice point...

$$A = |\underline{\mathbf{a}}_1 \times \underline{\mathbf{a}}_2| \qquad V = |\underline{\mathbf{a}}_1 \cdot \underline{\mathbf{a}}_2 \times \underline{\mathbf{a}}_3|$$

Wigner-Seitz Cell:



Basis:

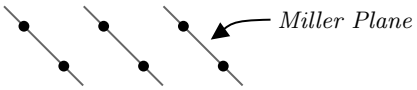
A basis is the description of the objects (atoms) within a unit cell with respect to the reference lattice point of the unit cell.

$$\textsc{Crystal} = \textsc{Lattice} + \textsc{Basis}$$

The Miller System

Miller Planes:

Miller Planes are planes that contain at least three non-collinear points of a lattice...



Miller Indices:

$$\frac{|\underline{\mathbf{a}}_1|}{x} : \frac{|\underline{\mathbf{a}}_2|}{y} : \frac{|\underline{\mathbf{a}}_3|}{z} = h : k : l$$

Direction: $[uvw]$ *Plane:* (hkl)

Plane Spacing:

$$d_{(hkl)} = \frac{2\pi}{|\underline{\mathbf{G}}|} = \frac{2\pi}{\sqrt{h^2|\underline{\mathbf{b}}_1|^2 + k^2|\underline{\mathbf{b}}_2|^2 + l^2|\underline{\mathbf{b}}_3|^2}}$$

$$d^{\text{cubic}}_{(hkl)} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

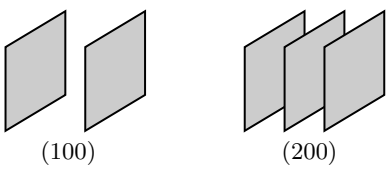
Reciprocal Space

Bragg's Law:

$$2d\sin(\theta) = n\lambda \quad \lambda \leq 2d$$

Wave Vector:

$$\underline{\mathbf{k}} = \frac{2\pi}{\lambda}\widehat{\mathbf{k}}$$



Reciprocal Lattice:

The reciprocal lattice is the set of all wave vectors $\underline{\mathbf{k}}$ *that yield plane waves with the periodicity of the real lattice.*

$$\vec{\mathbf{G}} = v_1\underline{\mathbf{b}}_1 + v_2\underline{\mathbf{b}}_2 + v_3\underline{\mathbf{b}}_3$$

$$\underline{\mathbf{a}}_i \cdot \underline{\mathbf{b}}_j = 2\pi\delta_{ij} \qquad \underline{\mathbf{b}}_i = 2\pi\frac{\underline{\mathbf{a}}_j \times \underline{\mathbf{a}}_k}{\underline{\mathbf{a}}_i \cdot \underline{\mathbf{a}}_j \times \underline{\mathbf{a}}_k}$$

Diffraction

The Laue Condition for Diffraction:

$$e^{i\vec{\mathbf{R}}\cdot\vec{\mathbf{G}}} = 1$$

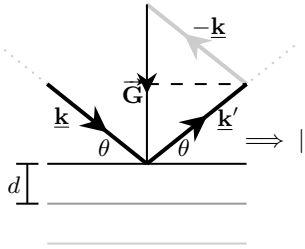
$$\vec{\mathbf{G}} = \underline{\mathbf{k}}' - \underline{\mathbf{k}} = \Delta\underline{\mathbf{k}} \qquad \underline{\mathbf{k}} \cdot \frac{\vec{\mathbf{G}}}{|\underline{\mathbf{G}}|} = \frac{1}{2}|\vec{\mathbf{G}}|$$

Laue Diffraction:

Consider two wavevectors $\underline{\mathbf{k}}$ *and* $\underline{\mathbf{k}}'$ *that satisfy the Laue condition for diffraction...*

$$\implies \vec{\mathbf{G}} = \underline{\mathbf{k}}' - \underline{\mathbf{k}}$$

If the reflection off the plane is elastic, $|\underline{\mathbf{k}}| = |\underline{\mathbf{k}}'|$ *and the angles are the same...*



$$\implies |\vec{\mathbf{G}}| = 2|\underline{\mathbf{k}}|\sin(\theta)$$

To maintain the Bragg condition, $|\underline{\mathbf{G}}_0| = 2\pi/d$*...*

$$\vec{\mathbf{G}} = n\vec{\mathbf{G}}_0 \implies |\underline{\mathbf{G}}| = 2|\underline{\mathbf{k}}|\sin(\theta) = n|\vec{\mathbf{G}}_0| = \frac{2\pi n}{d}$$

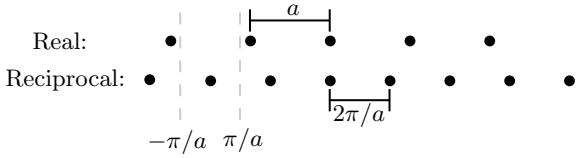
$$2d\sin(\theta) = n\lambda$$

"For higher order, there are more wave planes between the lattice planes"

The Brillouin Zone

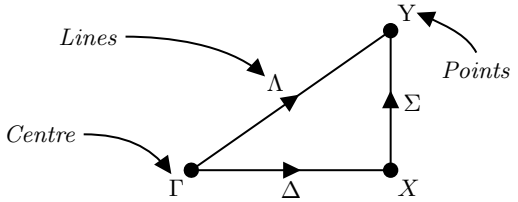
Constructing the Brillouin Zone:

The 1^{st} *Brillouin zone is the Wigner-Seitz cell of the reciprocal space.*



"If $\underline{\mathbf{k}}$ *touches the* BZ $\implies$ *Diffraction"*

Brillouin Zone Points:

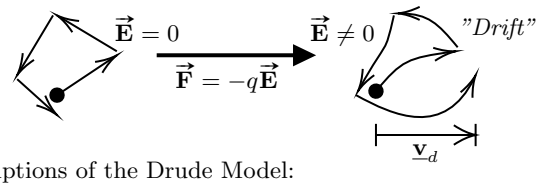


The Classic Drude Model

The Classical Free Electron Gas:

$$\mathrm{v_{rms}} = \sqrt{\frac{3k_BT}{m_e}} \approx 10^6 \ \mathrm{m \cdot s^{-1}}$$

Theory of Metallic Conduction:



Assumptions of the Drude Model:

- *Between collisions there are no interactions.*
- *Collisions happen "just because" every τ unit time.*
- *Each collision happens with probability $1/\tau$ per unit time.*
- *Electrons are in thermal equilibrium* $\implies$ Boltzmann Statistics

The Drude Model with the Lorentz Force:

$$\frac{\mathrm{d}\underline{\mathbf{p}}}{\mathrm{d}t} = \vec{\mathbf{F}} - \frac{\underline{\mathbf{p}}}{\tau} = -e(\vec{\mathbf{E}} + \underline{\mathbf{v}} \times \underline{\mathbf{B}}) - \frac{\underline{\mathbf{p}}}{\tau}$$

Current Density:

$$\underline{\mathbf{j}} = \frac{\vec{\mathbf{I}}}{\text{Area}} = -ne\underline{\mathbf{v}}_d$$

Conduction in the Drude Model:

For electrons at drift velocity in a conductor with $\vec{\mathbf{B}} = 0$...

$$\frac{\mathrm{d}\underline{\mathbf{p}}}{\mathrm{d}t} = -e\vec{\mathbf{E}} - \frac{\underline{\mathbf{p}}}{\tau} = 0 \implies \underline{\mathbf{p}} = -e\vec{\mathbf{E}}\tau = m\underline{\mathbf{v}}_d$$

The current density can then be used to determine the Drude conductivity...

$$\underline{\mathbf{j}} = -ne\underline{\mathbf{v}}_d = -ne\frac{-e\vec{\mathbf{E}}\tau}{m} = \frac{ne^2\tau}{m}\vec{\mathbf{E}} = \sigma\vec{\mathbf{E}}$$

Ohm's Law: $\underline{\mathbf{j}} = \sigma\vec{\mathbf{E}}$ Drude Conductivity: $\sigma = \frac{ne^2\tau}{m}$

The Hall Effect:

"Deflection of the current by an external magnetic field"

Hall Resistance: $R_H = \frac{\rho_{yx}}{|\vec{\mathbf{B}}|} = -\frac{1}{ne}$

Matthiesson's Rule

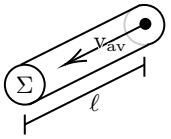
The Empirical Matthiesson's Rule:

$$\rho(T) = \rho_{\mathrm{imp}} + \rho_{\mathrm{vib}}(T)$$

Impurity — *Material* $\rho(T \gtrsim 60\mathrm{K}) \propto T$

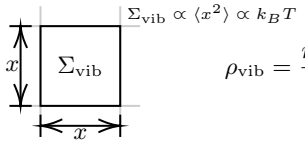
$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} = \frac{m}{ne^2}\left[\frac{1}{\tau_{\mathrm{imp}}} + \frac{1}{\tau_{\mathrm{vib}}}\right]$$

Impurity Scattering:



$$\rho_{\mathrm{imp}} = \frac{m\mathrm{v_{av}}}{ne^2} n_{\mathrm{imp}} \Sigma_{\mathrm{imp}}$$

Vibrational Scattering: *"Drude Model"*



$$\rho_{\mathrm{vib}} = \frac{m\mathrm{v_{av}}}{ne^2} n_{\mathrm{vib}} k_B T$$

Drude Resistivity:

$$\mathrm{v_{av}} = \sqrt{\frac{3k_BT}{m_e}} \propto T^{1/2} \implies \rho(T) \equiv C_1T^{1/2} + C_2T^{3/2}$$

"The Drude model is okay for simple metals, limited for Hall effect and wrong for Matthiessen's rule"

Drude-Sommerfeld Model

Fermi-Dirac Statistics:

"A fermion is not a billiard ball"

$$f_{\mathrm{FD}}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_{\mathrm{F}}}{k_BT}\right) + 1}$$

The Schrödinger Equation:

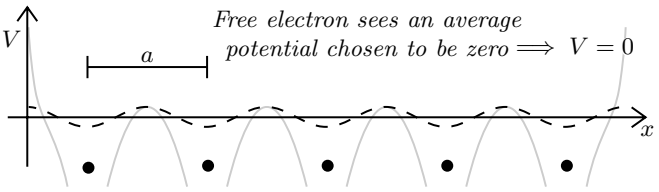
$$\widehat{H}\psi = E\psi$$

The Born-Oppenheimer Approximation: *"Adiabatic"*

- *Ion motion is ignored.*
- *Electron-electron interactions ignored due to single electron.*
- *Ion-ion interactions ignored.*

$$\implies \widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ele-ion}}$$

Free Electron Model:



Free electron sees an average potential chosen to be zero $\implies V = 0$

$$\implies \widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 \implies -\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

Fixed Boundary Conditions:

$$\psi_n(x) = C\sin\left(\frac{n\pi}{L}x\right) \qquad k = \frac{n\pi}{L}$$

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

Periodic Boundary Conditions: $\psi(x) = \psi(x + L)$

$$\psi_k(x) = A\mathrm{e}^{\mathrm{i}kx} \qquad k = \pm\frac{2\pi n}{L}$$

$$E_n = \frac{\hbar^2}{2m}|k|^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2$$

Free electron Momentum:

$$m\underline{\mathbf{v}} = \hbar\underline{\mathbf{k}}$$

Filling States:

For the number of electron states, find the ratio of the k-state and the fermi-volume ...

$$N_e = 2 \times N_0 = 2 \times \frac{V_{\text{fermi}}}{V_{\text{state}}} \qquad V_{\text{state}} = \frac{2\pi}{L}\cdots$$

Spin Degeneracy

$$N_e = \frac{k_{\mathrm{F}}^3}{3\pi^2}V$$

Fermi Vector: $k_{\mathrm{F}} = \left(\frac{3\pi^2N}{V}\right)^{1/3}$ Fermi Velocity: $\mathrm{v_F} = \frac{\hbar k_{\mathrm{F}}}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2N}{V}\right)^{1/3}$

At $T = 0$...

Fermi Energy: $\varepsilon_{\mathrm{F}} = \frac{\hbar^2}{2m}k_{\mathrm{F}}^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3}$ Fermi Temp: $T_{\mathrm{F}} = \frac{\varepsilon_{\mathrm{F}}}{k_B}$

Ground State Energy:

$$\frac{E}{V} = \frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m} \qquad \frac{E}{N} = \frac{3}{5}k_B T_f < \frac{3}{2}k_B T_f$$

Less than classical energy per electron

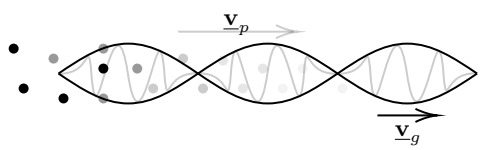
Density of States:

$$g(\varepsilon) = \frac{\mathrm{d}N}{\mathrm{d}\varepsilon}$$

3D Electron System: $g(\varepsilon) = \dfrac{V}{2\pi^2}\dfrac{(2m)^{3/2}}{\hbar^3}\varepsilon^{1/2}$

Electronic Transport:

What does this mean for the Drude model?... Wave Packets



$$\omega = \frac{\varepsilon}{\hbar}$$

Group Velocity: $\underline{\mathbf{v}}_g = \dfrac{\mathrm{d}\omega}{\mathrm{d}\underline{\mathbf{k}}} = \dfrac{1}{\hbar}\dfrac{\mathrm{d}\varepsilon}{\mathrm{d}\underline{\mathbf{k}}} \to \dfrac{\hbar\underline{\mathbf{k}}}{m} = \dfrac{\underline{\mathbf{p}}}{m}$

Quantum Drude Model: $\hbar\left(\dfrac{\mathrm{d}\underline{\mathbf{k}}}{\mathrm{d}t} + \dfrac{\underline{\mathbf{k}}}{\tau}\right) = -e\vec{\mathbf{E}} - e\underline{\mathbf{v}} \times \vec{\mathbf{B}}$

"The presence of an $\vec{\mathbf{E}}$ field shifts the fermi surface by $\Delta k = -eE\tau/\hbar$, which allows surface electrons to freely transition between states and conduct a current."

Matthiesson's Rule:

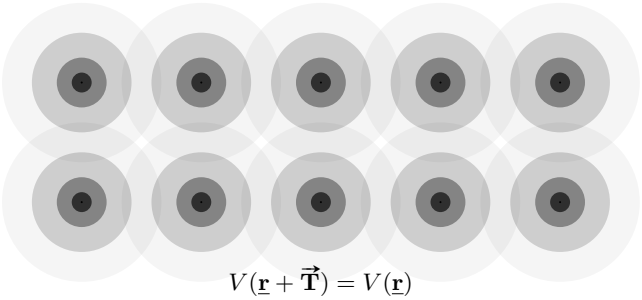
$$\rho(T) \equiv C_1' + C_2' T$$

"The free electron model successfully explains electrical/thermal conductivity and its Matthiesson temperature dependence. It fails to explain positive Hall coefficients and conductors/semiconductors/insulators."

The Nearly Free Electron Model

The Central Potential:

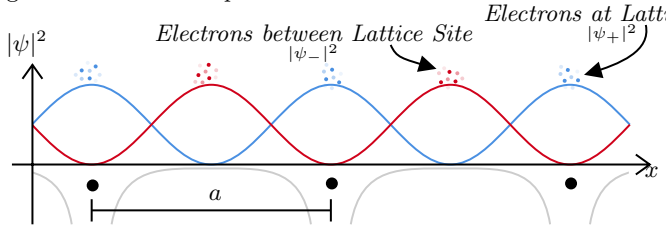
$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\underline{\mathbf{r}}) = -\frac{\hbar^2}{2m}\nabla^2 + \sum_n \frac{-qe^2}{4\pi\varepsilon_0|\underline{\mathbf{r}} - n\underline{\mathbf{R}}|}$$



$$V(\underline{\mathbf{r}} + \vec{\mathbf{T}}) = V(\underline{\mathbf{r}})$$

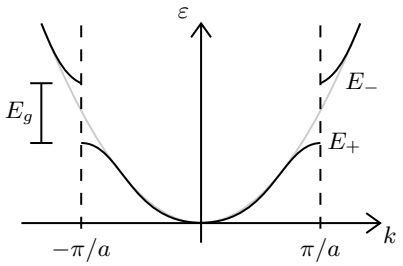
"Potential is periodic with lattice, whereas wavefunction is periodic with whole system"

Origins of the Band Gap:



$$|\psi_+|^2 \propto \cos^2\left(\frac{\pi x}{a}\right) \qquad |\psi_-|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$$

These different wavefunctions produce band gaps at the BZ's...



"Different representations are the extended, repeated and reduced zones"

Bloch and The Central Equation

Bloch Theorem:

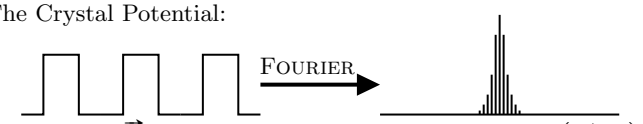
An electron passing through any periodic potential can be described generally...

$$\psi_{nk}(\underline{\mathbf{r}}) = u_{nk}(\underline{\mathbf{r}})\ \mathrm{e}^{\mathrm{i}\underline{\mathbf{k}}\cdot\underline{\mathbf{r}}} \qquad u_{nk}(\underline{\mathbf{r}}) = u_{nk}(\underline{\mathbf{r}} + \vec{\mathbf{T}})$$

Born-von Kármán Boundary Conditions: "$L = Na$"

$$\psi(\underline{\mathbf{r}} + N_i\underline{\mathbf{a}}_i) = \psi(\underline{\mathbf{r}}) \implies \mathrm{e}^{\mathrm{i}kNa} = 1 \implies k = \frac{2\pi}{Na}m$$

The Crystal Potential:



The Central Equation:

$$\left(\frac{\hbar^2 k^2}{2m} - E\right)c_k + \sum_g V_g c_{k-g} = 0$$

"This can be mapped to an eigenvalue problem"

Weak Lattice Approximation:

By assuming the lattice is weak, V_g is very small and the central equation can be truncated to 2×2...

$$\begin{bmatrix} \frac{\hbar^2}{2m}k^2 - E & V_g \\ v_{-g} & \frac{\hbar^2}{2m}(k-g)^2 - E \end{bmatrix}\begin{bmatrix} c_k \\ c_{k-g} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\implies \begin{vmatrix} E_0^k - E & |V_g| \\ |V_g| & E_0^{k-g} - E \end{vmatrix} = 0$$

"Bands split near boundaries"

Empty Lattice Approximation:

$$V_g = 0 \implies E(\underline{\mathbf{k}}) = \frac{\hbar^2}{2m}|\underline{\mathbf{k}} - \vec{\mathbf{G}}|^2$$

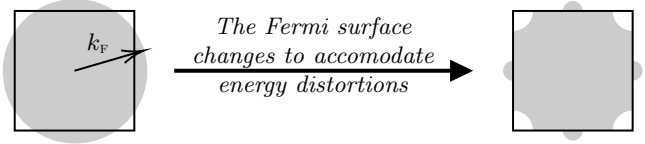
By moving across the BZ in different directions $\underline{\mathbf{G}}$ and plotting energy ε, the bands slowly start to appear. Eventually, degenerate direction bands appear. Where the bands cross, a band gap would open and distort if the weak lattice is introduced.

The Fermi Surface and Metals

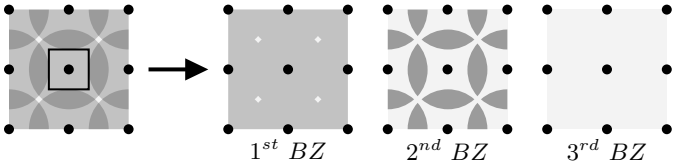
Band Filling:

Metals are a solid with a fermi surface. Bands fill from the lowest energy level to the fermi energy, defining the fermi surface.

Fermi Surface:



Harrison Construction:



Fermi Surface Conduction:

From the Drude-Sommerfeld Model, an $\underline{\mathbf{E}}$ *field shifts the fermi surface. A new prediction for conductivity can now be given...*

$$\sigma_{\text{eff}} = \frac{|\mathbf{j}|}{|\vec{\mathbf{E}}|} = \frac{e^2 \ell_{\text{eff}}}{4\pi^3 \hbar} S_{\text{F}}$$

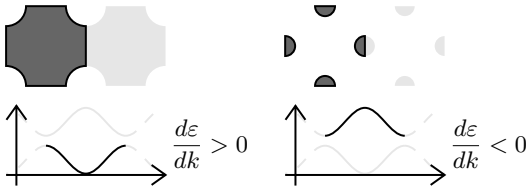
Free Area
Key Factor of Conductivity

The Hall Effect:

$$\hbar \frac{\mathrm{d}\underline{\mathbf{k}}}{\mathrm{d}t} = -e\underline{\mathbf{v}}_{\text{F}} \times \vec{\mathbf{B}} \implies \frac{\mathrm{d}k}{\mathrm{d}t} = -\frac{e}{\hbar^2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}k} B$$

Group Velocity: $\underline{\mathbf{v}}_{\text{F}} = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial \underline{\mathbf{k}}}$

In the nearly free electron model, the gradient of the dispersion relation can either be positive or negative, allowing for different sign Hall coefficients...



Hole-like and Electron-like Pockets:

"The dispersion relation of Electron-like pockets are cups, whereas Hole-like pockets are hats"

Semiconductors

Effective Mass:

The effect of the lattice on an electron wave packet can be taken into account using an effective mass...

$$m^* = \frac{\hbar^2}{\left(\frac{\mathrm{d}^2\varepsilon}{\mathrm{d}k^2}\right)} \implies m_e^* \frac{\mathrm{d}\underline{\mathbf{v}}}{\mathrm{d}t} = -e\vec{\mathbf{E}}$$

Newton's 2^{nd} *Law*

Charge Carriers:

Electrons:

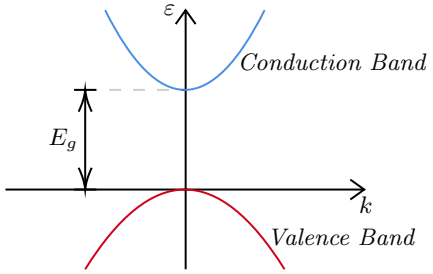
$$m_e^* = \frac{\hbar^2}{(\mathrm{d}^2\varepsilon / \mathrm{d}k^2)} \qquad m_e^* \frac{\mathrm{d}\underline{\mathbf{v}}_e}{\mathrm{d}t} = -e\vec{\mathbf{E}}$$

Holes:

$$m_h^* = -\frac{\hbar^2}{(\mathrm{d}^2\varepsilon / \mathrm{d}k^2)} \qquad m_h^* \frac{\mathrm{d}\underline{\mathbf{v}}_h}{\mathrm{d}t} = +e\vec{\mathbf{E}}$$

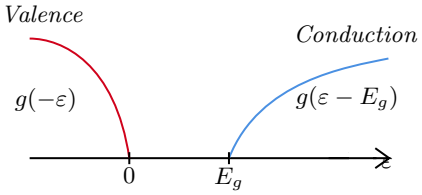
"The hole is an empty state, with positive energy and negative momentum. To encapsulate a negative effective mass, the charge is positive."

Parabolic Band Model:



Conduction: $\varepsilon = E_G + \dfrac{\hbar^2 k^2}{2m_e^*}$ Valence: $\varepsilon = -\dfrac{\hbar^2 k^2}{2m_h^*}$

Carrier Populations:



Charge carriers follow Boltzmann, explaining why the Drude model worked so well...

$$f_{\text{FD}}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1} \to \exp\left(\frac{\mu - \varepsilon}{k_B T}\right)$$

Density of Free Electrons:

$$n = \frac{1}{V}\int_{E_g}^{\infty} g(\varepsilon - E_g) \exp\left(\frac{\mu - \varepsilon}{k_B T}\right) \mathrm{d}\varepsilon = N_c \exp\left(\frac{\mu - E_g}{k_B T}\right)$$

$$\textit{Effective DOS Conduction Band} \; : \; N_c = 2\left(\frac{2\pi m_e^* k_B T}{\hbar^2}\right)^{3/2}$$

Density of Free Holes:

$$p = \frac{1}{V}\int_{-\infty}^{0} g(-\varepsilon)\left[1 - \exp\left(\frac{\mu - \varepsilon}{k_B T}\right)\right] \mathrm{d}\varepsilon = N_v \exp\left(\frac{-\mu}{k_B T}\right)$$

$$\textit{Effective DOS Valence Band} \; : N_v = 2\left(\frac{2\pi m_h^* k_B T}{\hbar^2}\right)^{3/2}$$

Law of Mass Action:

$$np = N_c N_v \mathrm{e}^{-E_g / k_B T}$$

Intrinsic Semiconductors:

$$n_i = p_i = \sqrt{N_c N_v}\, \mathrm{e}^{-E_g / 2k_B T}$$

$$n = p \implies \exp\left(\frac{2\mu - E_g}{k_B T}\right) = \frac{N_v}{N_c}$$

$$\implies \mu = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln\left(\frac{m_h^*}{m_e^*}\right)$$

$$\textit{At } T\text{=}0\ldots \; \mu = \frac{1}{2}E_g$$

Extrinsic Semiconductors:

"An intrinsic semiconductor is a pure semiconductor, while an extrinsic semiconductor is doped with impurities."

Doping:

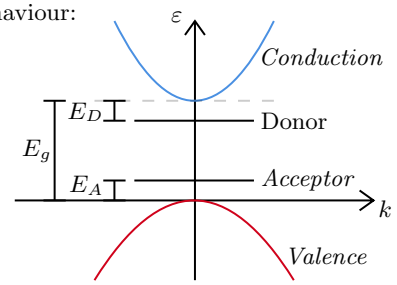
Doping adds impurities to introduce new charge carriers to the system. If sparse, they can be considered as delocalised electrons. An extra electron near the condition band is a donor (n-type), whereas an extra hole near the valence band is an acceptor (p-type). Adding impurities is like adding a proton and electron (hydrogen atom)...

$$E_n = \frac{-m_e^* e^4}{2\epsilon^2 \hbar^2 n^2 (4\pi\epsilon_0)^2} \qquad r_n = \frac{\epsilon n^2 \hbar^2}{m_e^* e^2} 4\pi\epsilon_0$$

$$E_0 = -13.6 \text{ eV} \qquad r_0 = 0.53 \text{ Å}$$

Drift and Diffusion

Extrinsic Behaviour:



$$n + N_A^- = p + N_D^+$$

$$N_A^- = N_A f(E_A) \qquad N_D^+ = N_D\left[1 - f(E_g - E_D)\right]$$

N-Type Materials:

"Acceptors and donors present with more donors than acceptors at $T = 0$."

The fermi level μ is at the highest occupied state (donor)...

$$\implies \mu = E_g - E_D \implies n = N_c \mathrm{e}^{-E_D/k_B T}$$

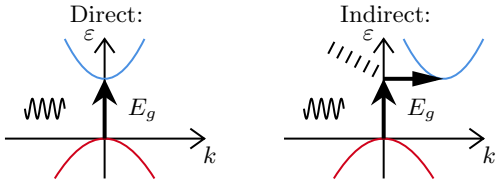
P-Type Materials:

"Acceptors and donors present with more acceptors than donors at $T = 0$."

The fermi level μ is at the highest occupied state (acceptor)...

$$\implies \mu = E_A \implies p = N_v \mathrm{e}^{-E_A/k_B T}$$

Photon Absorption:



Carrier Drift Mobility:

"How quickly a carrier moves through a material"

$$\underline{\mathbf{v}}_e = -\frac{e\tau_e}{m_e^*}\vec{\mathbf{E}} = -\mu_e \vec{\mathbf{E}} \qquad \mu_e = \frac{e\tau_e}{m_e^*}$$

Combined Conductivity:

$$\underline{\mathbf{j}} = -ne\underline{\mathbf{v}}_e + pe\underline{\mathbf{v}}_h = (ne\mu_e + pe\mu_h)\,\vec{\mathbf{E}} = \sigma\vec{\mathbf{E}}$$

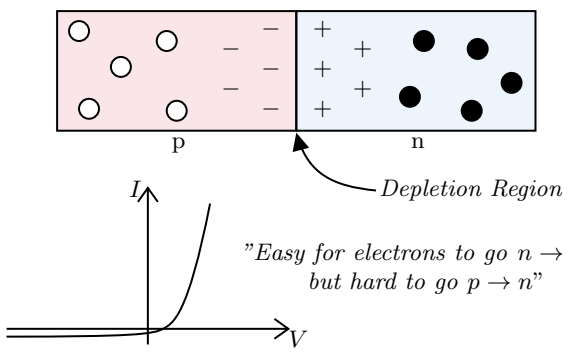
Charge Carrier Continuity:

Carriers move through drift and diffusion.

$$\vec{\mathbf{J}}_e = -n\mu_e\vec{\mathbf{E}} \qquad \vec{\mathbf{J}}_h = p\mu_h\vec{\mathbf{E}}$$

The P-N Junction:

"The electrons recombine with the holes, creating a depletion region leaving behind ions."



"Easy for electrons to go $n \to p$ but hard to go $p \to n$"