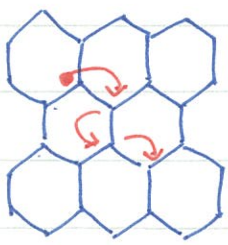
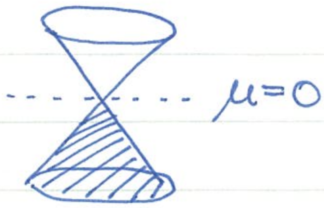
HH0040 Electrons and Holes in Semiconductors

Let us start with the Nobel-Prize-winning material: graphene.

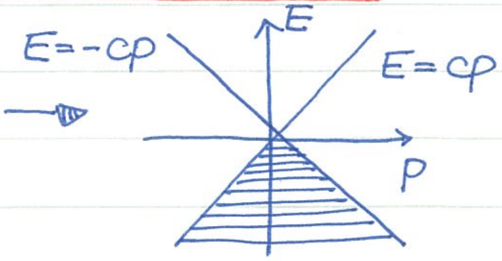


It consists of carbon atoms arranged in 2D honeycomb lattice. Electrons hop (quantum!) on the lattice with relativistic kinetic energy:

$$\boxed{E(p_x, p_y) = \pm c\,|\vec{p}\,|} \quad \text{where } |\vec{p}\,| = \sqrt{p_x^2 + p_y^2}$$



2D Dirac



1D Dirac

The effective Hamiltonian

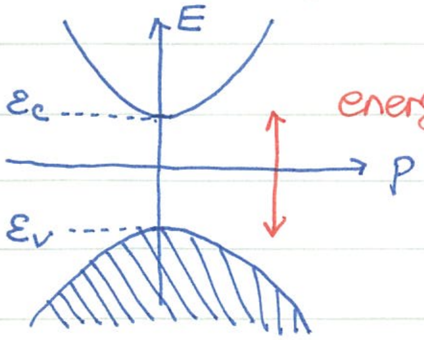
$$H_{eff}^{(0)} = \begin{pmatrix} cp & 0 \\ 0 & -cp \end{pmatrix}$$

(similar to photons. 😊)

If the right and left movers are coupled together,

$$H_{eff} = \begin{pmatrix} cp & \Delta \\ \Delta & -cp \end{pmatrix} \longrightarrow \boxed{E = \pm\sqrt{c^2p^2 + \Delta^2}}$$

relativistic w/ non-zero mass!!. $\Delta = m_0 c^2$.



energy gap 2Δ.

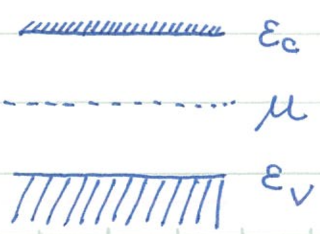
The upper branch (particle) is called conduction band with dispersion

$$\boxed{\varepsilon_c(p) \approx \varepsilon_c + \frac{1}{2m_e^*}p^2 + \cdots\cdots}$$

The lower branch (antiparticle) is called valence band with dispersion

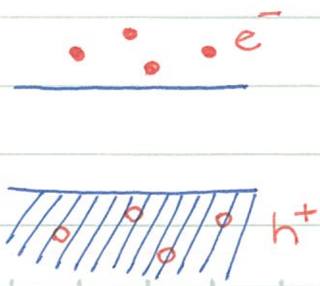
$$\boxed{\varepsilon_v(p) \approx \varepsilon_v - \frac{1}{2m_h^*}p^2 + \cdots\cdots}$$

Sometimes it is convenient to ignore the p-dependence and plot the band diagram.



$\varepsilon_g = \varepsilon_c - \varepsilon_v$

The low-energy excitations are electrons + holes



Let's derive an important relation between electron and hole concentrations, often referred as Law of Mass Action ö'''

$$\boxed{\begin{aligned} N_e &= \sum_{CB} f_e(\varepsilon) = \sum_{CB} \frac{1}{e^{(\varepsilon-\mu)/\tau}+1} \\ N_h &= \sum_{VB} 1-f_e(\varepsilon) = \sum_{VB} \frac{1}{e^{(\mu-\varepsilon)/\tau}+1} \end{aligned}}$$

For holes, it's almost like reverse the signs of μ and ε !

For most semiconductors at room temperature, they are non-degenerate

$$\boxed{e^{-(\varepsilon_c-\mu)/\tau} \ll 1 \quad \text{and} \quad e^{-(\mu-\varepsilon_v)/\tau} \ll 1} \longrightarrow \text{in class regime.}$$

The electron number in the conduction band is approximately

$$N_e \approx \sum_{CB} e^{-(\varepsilon-\mu)/\tau} = e^{-(\varepsilon_c-\mu)/\tau} \times \left[\sum_{CB} e^{-(\varepsilon-\varepsilon_c)/\tau}\right]$$

Because $\varepsilon-\varepsilon_c \approx \frac{1}{2m_e^*}p^2$, the sum is the same as the ideal gas discussed before.

$$\sum_{CB} e^{-(\varepsilon-\varepsilon_c)/\tau} = \underset{\text{from spin}}{2} n_Q V = 2\underbrace{\left(\frac{m_e^*\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}}_{n_c} \cdot V$$

The electron concentration in the conduction band is

$$\boxed{n_e \equiv \frac{N_e}{V} = n_c\, e^{-(\varepsilon_c-\mu)/\tau}} \longrightarrow \mu = \varepsilon_c - \tau \log\left(\frac{n_c}{n_e}\right)$$

similar to the ideal gas

The derivation for hole concentration in valence band follows a similar logic.

$$N_h \approx \sum_{VB} e^{-(\mu-\varepsilon)/\tau} = e^{-(\mu-\varepsilon_v)/\tau} \times \underbrace{\left[\sum_{VB} e^{-(\varepsilon_v-\varepsilon)/\tau}\right]}_{n_v \cdot V}$$

$$\longrightarrow \boxed{n_h \equiv \frac{N_h}{V} = n_v\, e^{-(\mu-\varepsilon_v)/\tau}} \longrightarrow \mu = \varepsilon_v + \tau \log\left(\frac{n_v}{n_h}\right)$$

Combine both results together :

$$n_e n_h = n_c n_v\, e^{-(\varepsilon_c-\varepsilon_v)/\tau}$$

Note that the band gap is $\varepsilon_g = \varepsilon_c - \varepsilon_v$. The product of electron and hole concentrations is

$$\boxed{n_e n_h = n_c n_v e^{-\varepsilon_g/\tau}}$$

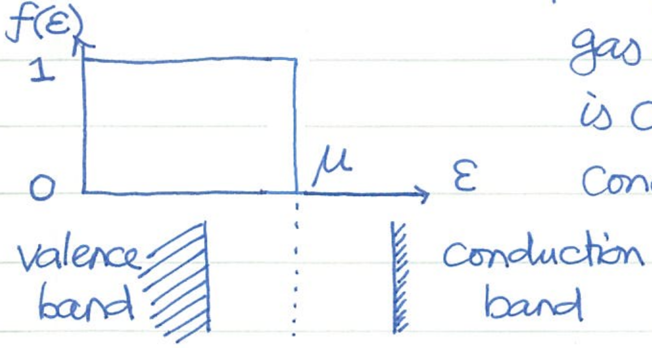
Law of Mass Action.

Compare the relation with electron-positron pair production $e^+ + e^- \rightleftarrows$ photons.

$$n_{e^+} n_{e^-} = n_Q^2 e^{-2m_0c^2/\tau}$$

$\longrightarrow$ $\hat{\phi}$ electrons and $\hat{\phi}$ holes in semiconductor are "antiparticles" to each other! CUTE :-)

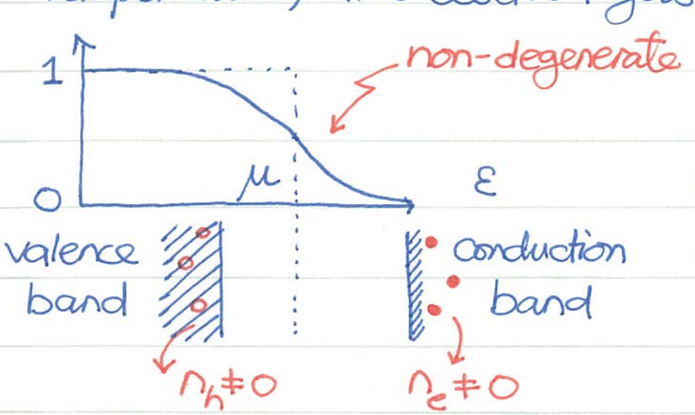
① Intrinsic Semiconductor: Suppose the semiconductor is pure without any impurities. What are the concentrations of electrons and holes? For simplicity, take $\tau = 0$ limit first. The electron gas is degenerate so that the valence band is completely filled (no holes) and the conduction band is completely empty (no electrons).



$\varepsilon_v < \mu < \varepsilon_c$

$$\boxed{\tau \to 0 \implies n_e = 0 \text{ and } n_h = 0}$$

However, the situation changes at room temperature, the electron gas is non-degenerate. Let's estimate the non-vanishing n_e, n_h due to thermal fluctuations.



(1) mass action law: $n_e n_h = n_c n_v e^{-\varepsilon_g/\tau}$

(2) charge neutrality: $n_+ = n_-$.

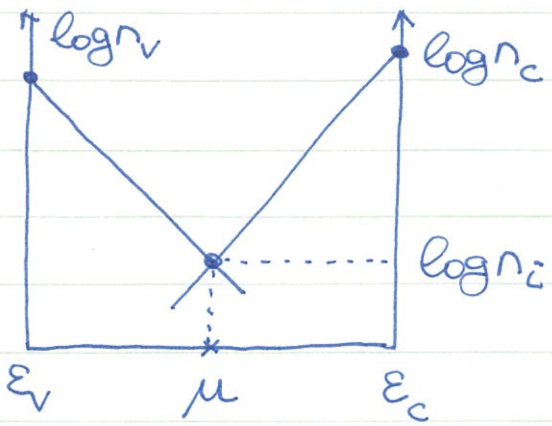
Since there is no external impurities, $n_+ = n_h$ and $n_- = n_e$

$$\begin{cases} n_e n_h = n_c n_v e^{-\varepsilon_g/\tau} \\ n_e = n_h \end{cases} \longrightarrow \text{intrinsic concentration } n_i = n_e = n_h$$

$$\boxed{n_i = \sqrt{n_c n_v}\, e^{-\varepsilon_g/2\tau}}$$

It is also insightful to plot $\log n_+$, $\log n_-$ to find the intrinsic concentration n_i and the chemical potential μ.

$$n_e = n_c\, e^{-(\varepsilon_c-\mu)/\tau} \qquad n_h = n_v\, e^{-(\mu-\varepsilon_v)/\tau} \longrightarrow \boxed{\begin{aligned}\log n_e &= \log n_c - \tfrac{1}{\tau}(\varepsilon_c-\mu)\\ \log n_h &= \log n_v - \tfrac{1}{\tau}(\mu-\varepsilon_v)\end{aligned}}$$



It's rather easy to solve for μ —

$$\log n_e - \log n_h = (\log n_c - \log n_v) + \frac{1}{\tau}(2\mu - \varepsilon_c - \varepsilon_v)$$

with $\log n_e - \log n_h \to 0$

$$\longrightarrow \boxed{\begin{aligned}\mu &= \tfrac{1}{2}(\varepsilon_c+\varepsilon_v) + \tfrac{\tau}{2}\log(n_v/n_c)\\ &= \tfrac{1}{2}(\varepsilon_c+\varepsilon_v) + \tfrac{3}{4}\tau\log(m_h^*/m_e^*)\end{aligned}}$$

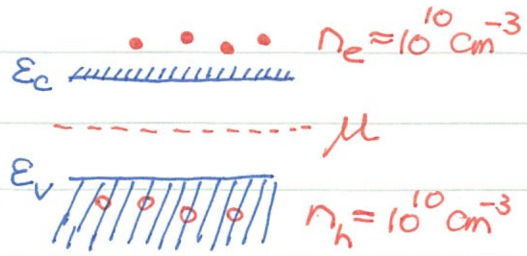
For Si, $\varepsilon_g = 1.14\ \text{eV}$.

$n_c \approx n_v \approx 10^{19}\ \text{cm}^{-3}$

$m_e^* = 1.06\, m_e$, $m_h^* = 0.58\, m_e$ $\longrightarrow$ intrinsic concentration $n_i \sim 10^{10}\ \text{cm}^{-3}$.

Since $m_h^*/m_e^* \sim O(1)$, the chemical potential is $\mu \approx \frac{1}{2}(\varepsilon_v + \varepsilon_c)$

Therefore, at room temperature, the semiconductor without external impurities contains intrinsic concentrations of electrons and holes $n_e = n_h = n_i$ and the chemical potential is in the middle of the gap.



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