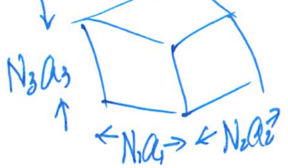
VII. Density of States

A. Density of Electronic States

- Uniform density of allowed $\vec{k}$-values in $\vec{k}$-space (within 1st B.Z.)



Crystal (Volume V)

$\underbrace{N}_{\gg 1} = N_1 \cdot N_2 \cdot N_3$ unit cells ($\sim 10^{23}$ for 1 cm^3 crystal)

Periodic Boundary Conditions $\Rightarrow$ N (densely and uniformly spaced) $\vec{k}$-values in 1st B.Z.

Key Concept for understanding many topics in solid state physics $\rightarrow$

$$\boxed{\text{Every } \vec{k}\text{-values occupies a "volume" of } \frac{(2\pi)^3}{V} \ \vec{k}\text{-space in 1st B.Z.}} \quad (1)$$

Crystal Volume

$$\Omega_c \cdot \Omega_R = (2\pi)^3 \Rightarrow \underbrace{\Omega_R = \frac{(2\pi)^3}{\Omega_c} \text{ has } N \ \vec{k}\text{-values}}_{\text{Each } \vec{k}\text{-value occupies } \frac{\Omega_R}{N} = \frac{(2\pi)^3}{N \cdot \Omega_c} = \frac{(2\pi)^3}{V} \ \vec{k}\text{-space}}$$

Ω_c: primitive cell volume $|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$

Ω_R: BZ volume $|\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)|$

Q: What is it in $\underbrace{2D}_{\frac{(2\pi)^2}{A}}$ and $\underbrace{1D}_{\frac{2\pi}{L}}$? [Quantum Wells, Quantum Wires]

$A \leftarrow$ Area of system, $L \leftarrow$ Length of system

- Because $\frac{(2\pi)^3}{V}$ is a constant (does not depend on where in B.Z), for a volume d^3k, there are

$$\frac{d^3k}{\frac{(2\pi)^3}{V}} = \frac{V}{(2\pi)^3} \underbrace{d^3k}_{\text{some volume in } k\text{-space}} \text{ allowed } \vec{k}\text{-values} \quad (2)$$

Question: (On the energy axis) In the interval of energy from $E=\varepsilon$ to $E=\varepsilon+d\varepsilon$, how many electronic states $g(\varepsilon)\,d\varepsilon$ are there?

- Digest the question:
  - $g(\varepsilon)\,d\varepsilon$ may have contributions from more than one band (e.g. bands overlap at ε)
  - can analyze band by band
  - there are spin↑ and spin↓ for electron (be careful with spin-degeneracy)
  - see $\frac{V}{(2\pi)^3} \propto V$, answer will $\propto V$, DOS/Volume useful for comparing different materials

Take-Home Message

- When you see some expressions of DOS, check careful if it is given as per spin (?), or per unit volume (?), or just per unit volume but with a factor "2" for spin degeneracy.

Strategy of getting DOS

- Take a band n, thus knowing $E_n(\vec{k})$ ← in B.Z.
- Make a "cut" at a constant energy ε ⇒ Constant energy surface at ε

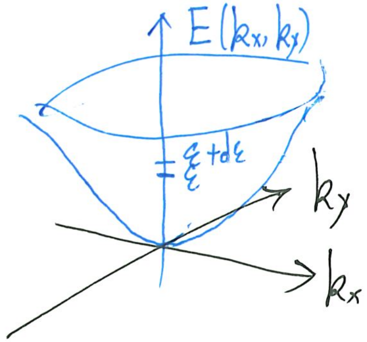
  Make a "cut" at a constant energy $\varepsilon + d\varepsilon$ ⇒ another constant energy surface at $\varepsilon + d\varepsilon$

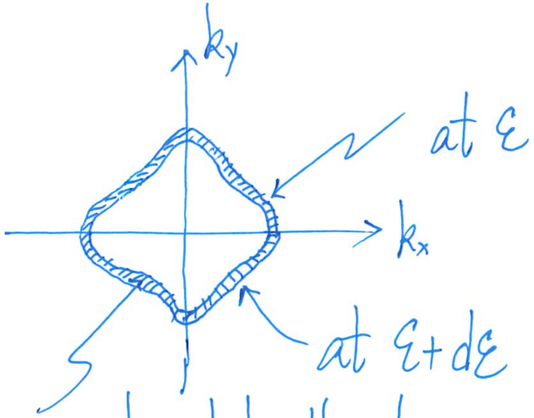
$$\left(\begin{array}{l}\text{Volume of } \vec{k}\text{-space enclosed between}\\ \text{the surfaces}\end{array}\right) \times \frac{V}{(2\pi)^3}$$

$= \#$ $\vec{k}$-values with energy ε to $\varepsilon + d\varepsilon$

(Done!)

2D Example





$$\underbrace{\frac{A}{(2\pi)^2}}_{\text{2D system}} \times (\text{Area}) = \#\ \text{electronic states (per spin) in } \varepsilon \text{ to } \varepsilon + d\varepsilon$$

Area enclosed by the two surfaces ($\propto d\varepsilon$)

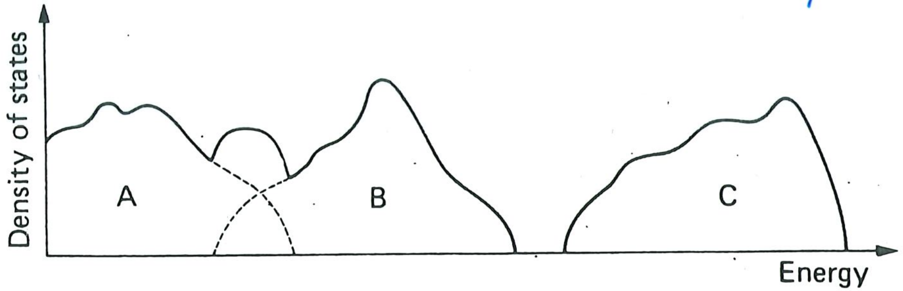
The general formula in 3D is: $$\frac{V}{(2\pi)^3} \int_{\substack{\text{over} \\ \text{constant energy surface at } \varepsilon}} \frac{dS}{|\nabla_{\vec{k}} E_n(\vec{k})|} \quad \text{(per spin)}$$

$$g_{\underset{\substack{\uparrow \\ \text{due to} \\ n^{\text{th}} \text{ band}}}{n}}(\varepsilon) = \quad \text{both are useful} \begin{cases} \dfrac{1}{(2\pi)^3} \displaystyle\int \dfrac{dS}{|\nabla_{\vec{k}} E_n(\vec{k})|} & \text{(per spin per unit volume of crystal)} \\[2ex] \dfrac{2}{(2\pi)^3} \displaystyle\int \dfrac{dS}{|\nabla_{\vec{k}} E_n(\vec{k})|} & \text{(per unit volume)} \end{cases} \tag{3}$$

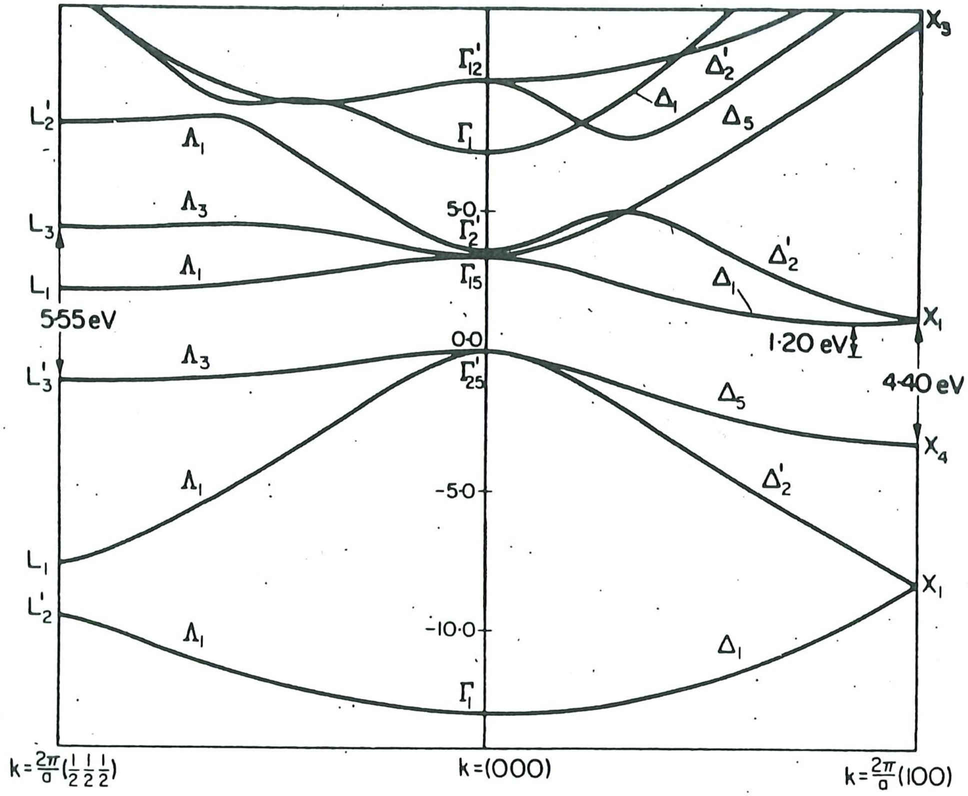
This provides a way to numerically compute $g(\varepsilon)$ from complicated band structures

Bands A & B overlap

Band C is separated from Bands A&B

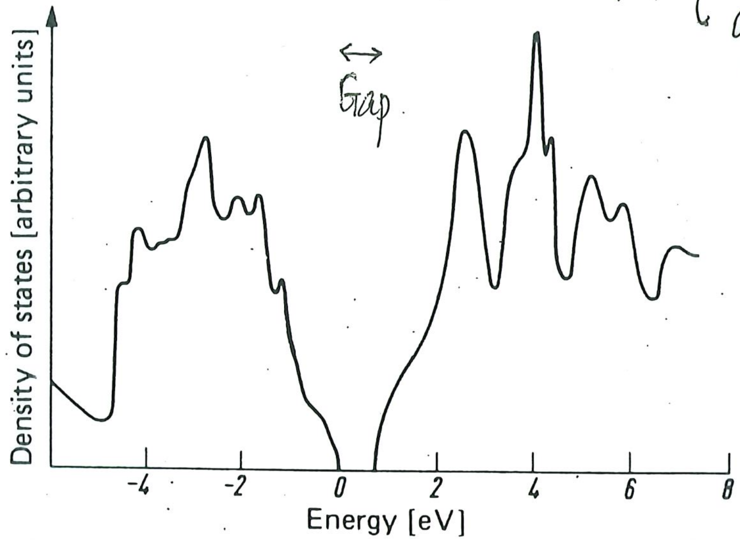


Density of states (schematic) with overlapping bands and with a band separated from the others by an energy gap.



Band structure of silicon along the most important axes of symmetry in the Brillouin zone.

structures related to { overlapping bands / flatter region of a band



Density of states in silicon

Taken from Madelung, "Solid State Theory"

B. DOS near band edges

- Simple forms due to description using effective masses

(a) Isotropic parabolic band

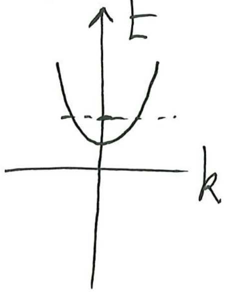
quadratic

$$E_c(\vec{k}) = E_c(0) + \frac{\hbar^2 k^2}{2m_e^*}$$

(one m_e^* works for all directions)

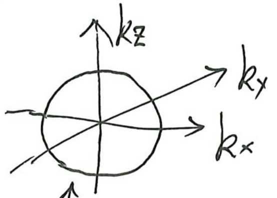
(e.g. GaAs CB)

- For $\varepsilon > E_0 \equiv E_c(0)$, constant energy surface is a spherical surface of radius



$$k_\varepsilon = \sqrt{\varepsilon - E_0} \cdot \left(\frac{2m_e^*}{\hbar^2}\right)^{1/2}$$

depends on ε

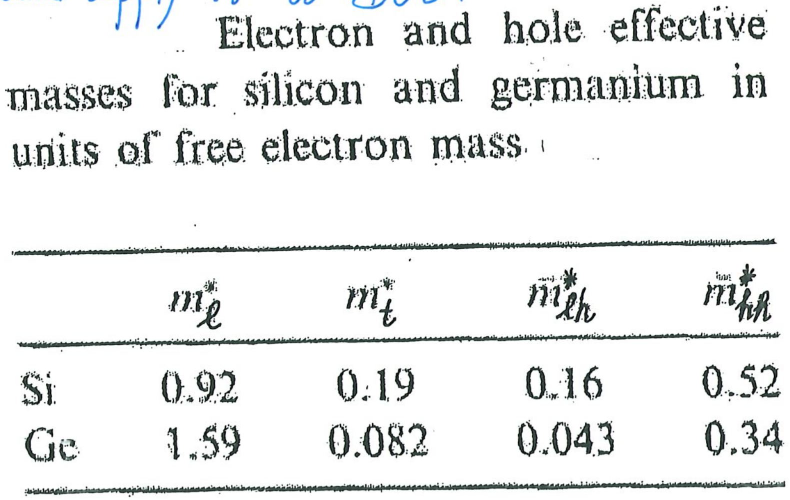


constant energy surface

$$g^<(\varepsilon) = [\#\ \vec{k}\text{-values (electronic states per spin) of energy} \leq \varepsilon]$$

$$= \frac{V}{(2\pi)^3} \times \underbrace{\left(\frac{4\pi}{3} k_\varepsilon^3\right)}_{\text{Volume enclosed by constant energy surface}} = \frac{V}{(2\pi)^3} \cdot \frac{4\pi}{3} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} (\varepsilon - E_0)^{3/2} \qquad (4)$$

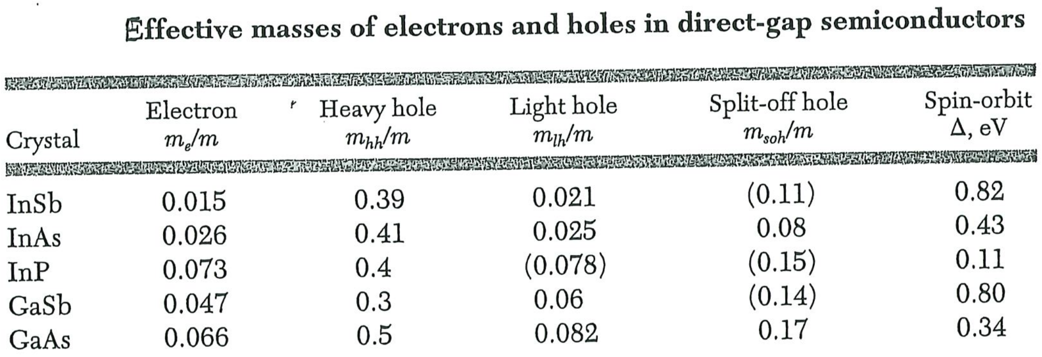
The idea is to make use of the simple description of CB and VB near band edges and apply it to DOS.



Electron and hole effective masses for silicon and germanium in units of free electron mass.

	m_l^*	m_t^*	m_{lh}^*	m_{hh}^*
Si	0.92	0.19	0.16	0.52
Ge	1.59	0.082	0.043	0.34

From Kittel, "Introduction to Solid State Physics"



Effective masses of electrons and holes in direct-gap semiconductors

Crystal	Electron m_e/m	Heavy hole m_{hh}/m	Light hole m_{lh}/m	Split-off hole m_{soh}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34

$g(\varepsilon)\,d\varepsilon = g^{<}(\varepsilon+d\varepsilon) - g^{<}(\varepsilon) = \#\ \vec{k}$-values of energies in $\varepsilon \to \varepsilon+d\varepsilon$

$$\Rightarrow g(\varepsilon) = \frac{g^{<}(\varepsilon+d\varepsilon) - g^{<}(\varepsilon)}{d\varepsilon} = \frac{dg^{<}(\varepsilon)}{d\varepsilon} \qquad (5)$$

$$\therefore\ g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_0} \qquad \text{(per spin)} \qquad (6a)$$

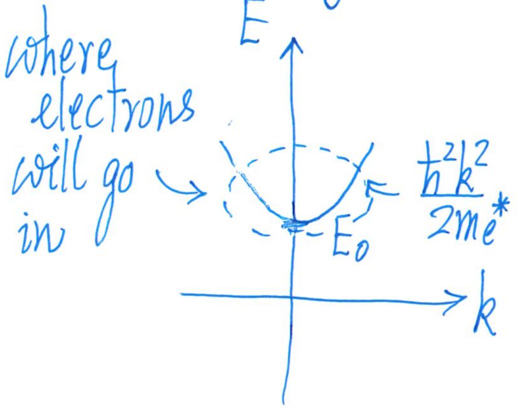
OR

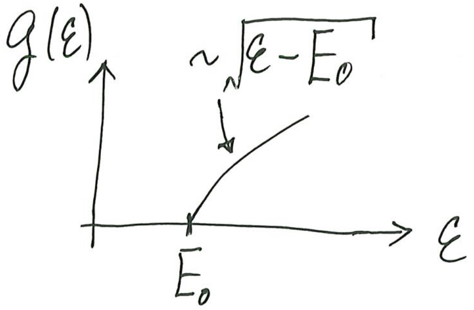
$$\boxed{g(\varepsilon) = \frac{1}{4\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_0}} \qquad \text{(per spin, per unit volume)} \qquad (6b)$$

OR

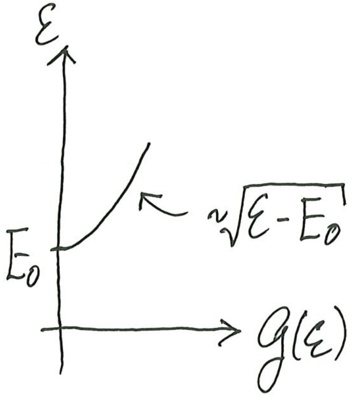
$$\boxed{g(\varepsilon) = 2\cdot\frac{1}{4\pi^2}\underbrace{\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}}_{\sim m_e^{*\,3/2}}\sqrt{\varepsilon - E_0}} \qquad \text{(per unit volume)} \qquad (6c)$$

often used





OR (rotate it)



Key Result

For one parabolic band $E(\mathbf{k}) = E_0 + \frac{\hbar^2 k^2}{2m^*}$,

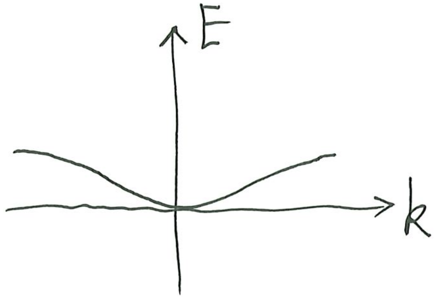
the Density of (electronic) States per unit volume (including spin degeneracy) is

$$g(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_0} \qquad \text{for } \varepsilon > E_0 \qquad (6)$$

- Often simply called Density of States
- Often wanted to keep the form of Eq.(6) even for more complicated (still quadratic) band structures [e.g. m_1^*, m_2^*, m_3^*] by replacing m^* by some m^*_{DOS}

Physical Sense

- flatter band has higher DOS (∵ Same # (2N states) in a band)



↓ all 2N states in narrow range of energy ↑

⇓

High DOS

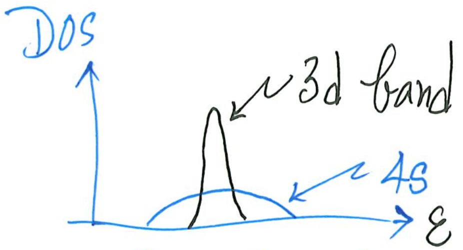
- flatter part of band ⇒ higher DOS in that range of energies

[Consequence: Transition metals' d-band (LCAO $\underbrace{\text{d-orbitals}}_{\text{not the outer most}}$) is narrow

⇒ hopping integral smaller

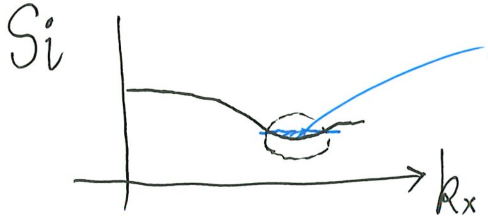
⇒ narrower band

⇒ High DOS in range of band energies]



(gives color of material)

(b) Ellipsoidal Energy bands



fill electrons to some energy ε above minimum, constant energy surface is 

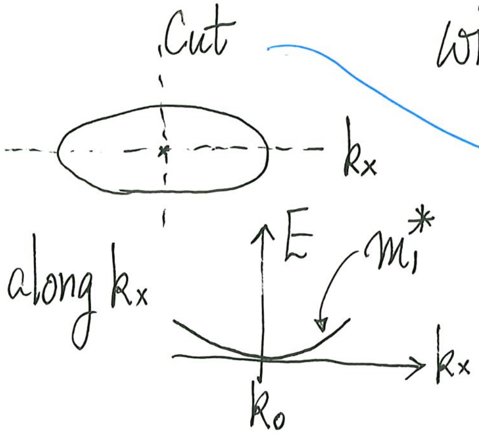
$$\underbrace{\text{(there are 6 such minima)}}_{\text{study } g(\varepsilon) \text{ around one minimum and multiply result by } \eta = 6}$$

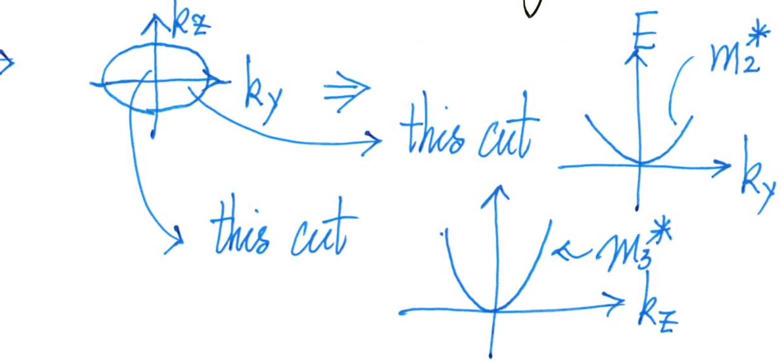
Let's consider a more general case

$$E(\vec{k}) = E_0 + \frac{\hbar^2 k_x^2}{2m_1^*} + \frac{\hbar^2}{2m_2^*} k_y^2 + \frac{\hbar^2}{2m_3^*} k_z^2 \qquad (7)$$

align k_x, k_y, k_z with principal axes

with k_x, k_y, k_z counted from band minimum (e.g. $(k_0, 0, 0)$)





For Si,

$$\underset{(m_l^*)}{m_1^*} > \underset{(m_t^*)}{m_2^*} = m_3^*$$

For energy ε above minimum E_0, the highest k_i $(i = x, y, z)$ is given by

$$k_{i,\varepsilon} = \left(\frac{2m_i^*}{\hbar^2}\right)^{1/2}(\varepsilon - E_0)^{1/2} \quad ; \quad i = x, y, z$$

longer for bigger m^*

Volume Enclosed by constant energy surface

= Volume of ellipsoid with main semiaxes k_x, k_y, k_z

$$= \frac{4\pi}{3}\left(\frac{2}{\hbar^2}\right)^{3/2}(m_1^* m_2^* m_3^*)^{1/2}(\varepsilon - E_0)^{3/2} \tag{8}$$

$$\therefore\ g^<(\varepsilon) = \frac{V}{(2\pi)^3}\cdot\frac{4\pi}{3}\left(\frac{2}{\hbar^2}\right)^{3/2}(m_1^* m_2^* m_3^*)^{1/2}(\varepsilon - E_0)^{3/2}$$

$$\therefore\ g(\varepsilon) = \frac{dg^<(\varepsilon)}{d\varepsilon} = \frac{\sqrt{2}\,V}{2\pi^2\hbar^3}(m_1^* m_2^* m_3^*)^{1/2}\sqrt{\varepsilon - E_0} \qquad (\varepsilon > E_0) \tag{9a}$$

(per spin)

(for one valley)

OR $$g(\varepsilon) = \frac{\sqrt{2}}{2\pi^2\hbar^3}\left(m_1^* m_2^* m_3^*\right)^{1/2}\sqrt{\varepsilon - E_0} \qquad (9b)$$ (per spin per unit volume)

OR $$g(\varepsilon) = \frac{\sqrt{2}}{\pi^2\hbar^3}\underbrace{\left(m_1^* m_2^* m_3^*\right)^{1/2}}_{\text{see how } m_1^*, m_2^*, m_3^* \text{ enter}}\underbrace{\sqrt{\varepsilon - E_0}}_{\leftarrow\ \sim\sqrt{\varepsilon - E_0}\ (3D)\ \text{as for isotropic bands}} \qquad (9c)$$ (per unit volume)

The appearance of $m_1^* m_2^* m_3^*$ is good. It is the Determinant of $\begin{pmatrix} m_1^* & 0 & 0 \\ 0 & m_2^* & 0 \\ 0 & 0 & m_3^* \end{pmatrix}$. Thus, this factor (value) remains even for other choices of axes.

$g(\varepsilon)\cdot d\varepsilon$ = number per unit volume

$g(\varepsilon)$ has units of $\dfrac{1}{\text{energy}\cdot\text{Volume}}$

For silicon, $m_1^* = m_\ell^*$; $m_2^* = m_3^* = m_t^*$

$$g(\mathcal{E}) = \frac{\sqrt{2}}{\pi^2\hbar^3}\left(m_\ell^* m_t^2\right)^{1/2}\sqrt{\mathcal{E}-E_0}\cdot \overset{=6 \text{ valleys}}{\eta} = \frac{\sqrt{2}}{\pi^2\hbar^3}\left(m_\ell^* m_t^2\right)^{1/2}\cdot 6\cdot\sqrt{\mathcal{E}-E_0} \quad (10)$$

Sometimes, $g(\mathcal{E})$ is written in the form

$$g(\mathcal{E}) = \frac{1}{2\pi^2}\left(\frac{2m_{DOS}^*}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}-E_0}\cdot\eta \quad (11)$$

as if it is an isotropic band

with $m_{DOS}^{*3} = m_\ell^* m_t^2$ OR $m_{DOS}^* = \left(m_\ell^* m_t^2\right)^{1/3}$ as a weighted effective mass

- Similar for Ge, $\eta = 4$

Remark:

- For m_1^*, m_2^*, m_3^*,

$$m^*_{DOS} = \left(m_1^* m_2^* m_3^*\right)^{1/3} \quad \text{(can be evaluated from data)} \quad (12a)$$

- In some literature/books, absorbs $\eta \leftarrow$ # minima into m^*_{DOS} as

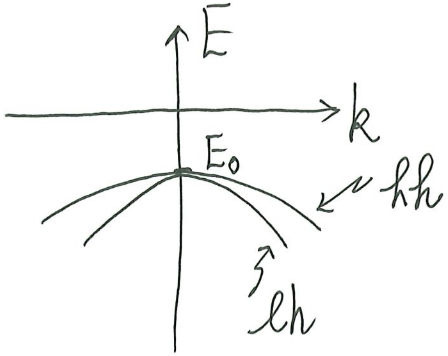
$$m^*_{DOS} = \left(\eta^2 m_1^* m_2^* m_3^*\right)^{1/3} \quad \text{(can be evaluated from data)} \quad (12b)$$

so that

$$g(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m^*_{DOS}}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_0}$$

remains valid

Valence Bands



"Heavy hole" (actually in electron viewpoint)

$$E_{hh}(\vec{k}) = E_0 - \frac{\hbar^2 k^2}{2\underbrace{m_{hh}^*}}$$

(this is electron band)

positive ($m_e^* = -m_{hh}^*$ near top of VB)
(heavy hole mass)

$$g_{hh}(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_{hh}^*}{\hbar^2}\right)^{3/2}\sqrt{\underbrace{E_0-\varepsilon}_{\text{positive}}}$$

for $\underset{\substack{\uparrow \\ \text{below top of VB}}}{\varepsilon} < E_0 \leftarrow$ top of VB

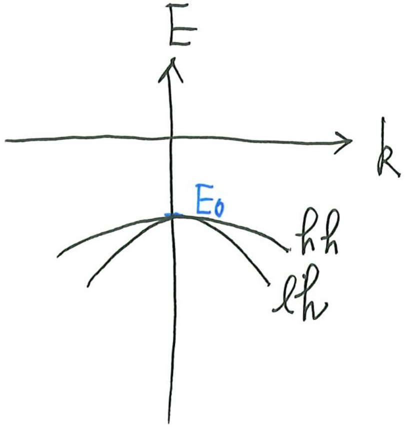
(per unit volume)

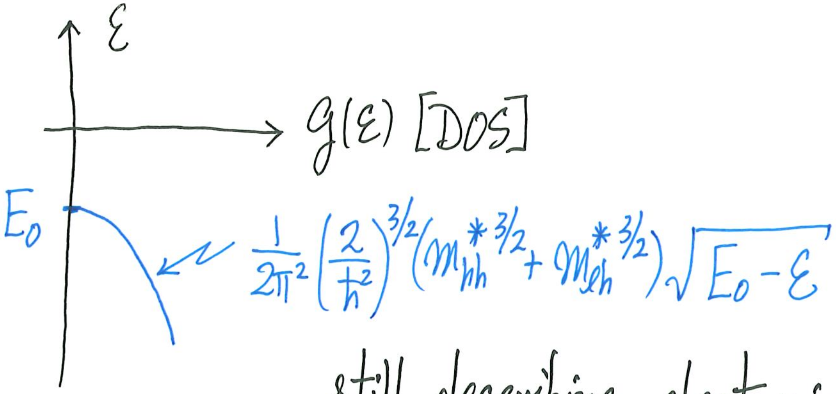
Similarly,

$$g_{lh}(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_{lh}^*}{\hbar^2}\right)^{3/2}\sqrt{E_0-\varepsilon}$$

$$g(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2}{\hbar^2}\right)^{3/2}\underbrace{\left(m_{hh}^{*\,3/2} + m_{lh}^{*\,3/2}\right)}_{\text{like a } \underbrace{(m_{VB}^{DOS})^{3/2}}_{\text{to keep standard form working}}}\underbrace{\sqrt{E_0-\varepsilon}}_{\text{Good for not too far away from top of VB}} \qquad (13)$$

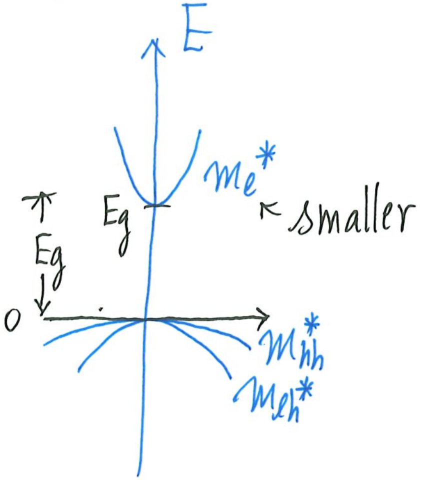
(per unit volume)

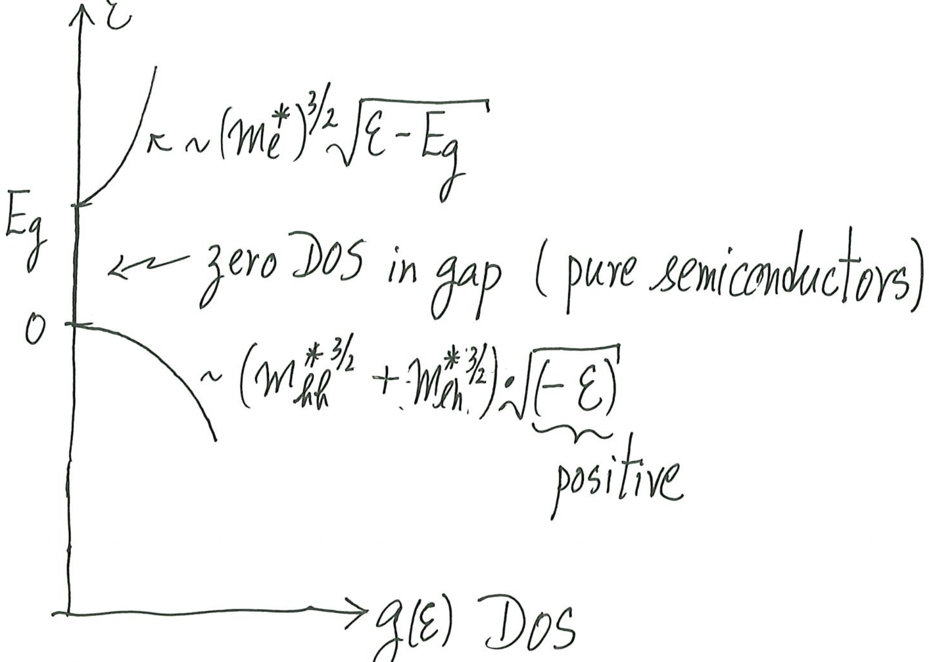




still describing electronic DOS

Putting CB and VB together





Electrons are to be filled into these electronic states

What's next?

- Fill in the electrons
- Where are the impurity states?
- Number of electrons in CB and number of unoccupied states in VB at temperature T?

Refs

- Balkanski and Wallis, Sec. 6.1
- Blackmore, "Semiconductor Statistics"