Density of states

1 allowed $\vec{k}$ in volume $(2\pi/L)^3$ in k-space

$\Rightarrow$ 2 allowed states ——————"—————— (since $g_s = 2$)

$\Rightarrow D(\vec{k}) = 2/(2\pi/L)^3 = V/4\pi^3$ = density of states in k-space

states with |wave vector| < k:

$$N(k) = D(\vec{k}) \cdot V_k = \frac{V}{4\pi^3} \cdot \frac{4}{3}\pi k^3 = \frac{V}{3\pi^2} \cdot k^3$$

states with energy < E:

$$N(E) = \frac{V}{3\pi^2} \cdot \left\{\sqrt{2mE/\hbar^2}\right\}^3 = \frac{V}{3\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot E^{3/2}$$

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$D(E)$ = density of states = # states per unit energy $= \lim_{\Delta E \to 0} \frac{\Delta N}{\Delta E} = \frac{dN}{dE}$

$\Rightarrow$ # states in $(\varepsilon, \varepsilon + d\varepsilon) = D(\varepsilon)\, d\varepsilon$

$\Rightarrow$ ——"—— $(0, E)$: $N(E) = \int_0^E D(\varepsilon)\, d\varepsilon$

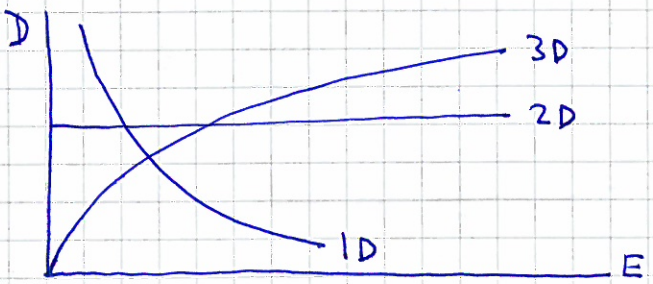
$\Rightarrow \frac{dN}{dE} = \frac{d}{dE} \int_0^E D(\varepsilon)\, d\varepsilon =$ [illegible] $D(E)$

in 3D system: $D_3(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot E^{1/2}$

(Exercise 1) in 2D: $D_2(E) \sim E^0$ (i.e. constant)

in 1D: $D_1(E) \sim E^{-1/2}$

(in 0D: $D_0(E) \sim \sum_i \delta(E - E_i)$)



Fermi energy E_F and chemical potential μ

Ground state, N electrons: N lowest-energy states occupied, $E \leq E_F$

Fermi energy: E_F = max energy of occupied states

From page 10: $N = \frac{V}{3\pi^2} k_F^3 \Rightarrow k_F = (3\pi^2 n)^{1/3}$ = Fermi wave vector

Density of electrons: $n = N/V$

$\Rightarrow E_F(n) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

Fermi temp: $T_F = E_F / k_B$

— " — momentum: $p_F = \hbar k_F$

— " — velocity: $v_F = p_F / m$

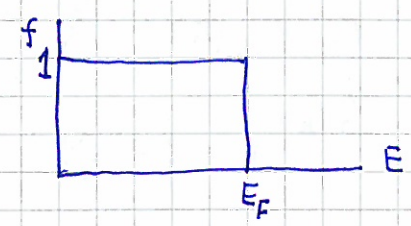
Electrons are <u>fermions</u> and obey Fermi-Dirac statistics:

$f(E) = \left\{ \exp\left[\frac{E-\mu}{k_B T} \right] + 1 \right\}^{-1}$ = prob. of finding electron in given state with energy E at temp. T

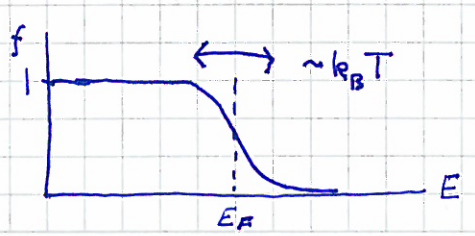
Chemical potential: μ

$f(\mu) = \{ e^0 + 1 \}^{-1} = 1/2$

$T = 0$: $f(E < \mu) = 1$, $f(E > \mu) = 0$ $\Rightarrow \mu(0) = E_F$



$T > 0$: $\mu(T) = E_F \left(1 - \frac{\pi^2}{12} \frac{T^2}{T_F^2}\right) < E_F$ (see e.g. Hemmer, Appendix)



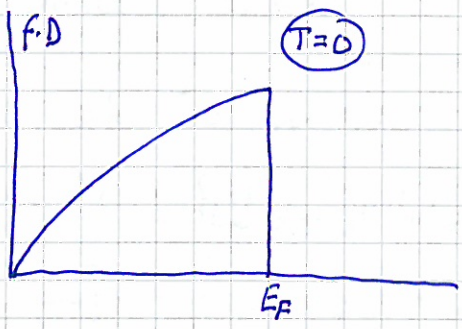
Since $D(E)\,dE$ = # states in $(E, E+dE)$,

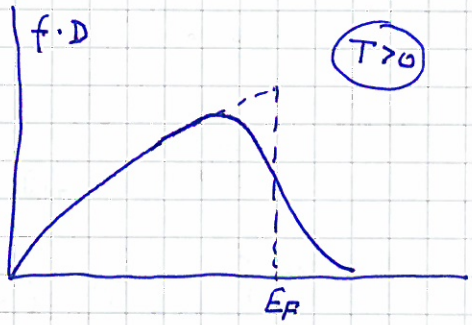
occupied states in $(E, E+dE)$ = $f(E)\,D(E)\,dE$

$$\left[\Rightarrow N = \int_0^\infty f(E)D(E)\,dE\right]$$

$\Rightarrow$ # electrons pr unit energy = $f(E)\cdot D(E)$

In 3D:





electrons excited to states above E_F ~ $k_BT\cdot D(E_F)$

For high energies $(E-\mu \gg k_BT)$: $f(E) \approx e^{\mu/k_BT}\cdot e^{-E/k_BT}$

$\gg$ Boltzmann distribution

Electrons in periodic potential

Need periodic potential, $V(\vec{r}+\vec{R}) = V(\vec{r})$, to explain the presence of energy bandgap:

$$H\Psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r}) = E\Psi(\vec{r})$$

Bloch's theorem: $\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\,u_{\vec{k}}(\vec{r})$

(=Bloch states)

$$u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$$

Bloch functions are periodic in reciprocal space:

$$\psi_{\vec{k}+\vec{K}}(\vec{r}) = \psi_{\vec{k}}(\vec{r})$$

$$\Rightarrow E(\vec{k}+\vec{K}) = E(\vec{k})$$

$\Rightarrow \vec{k}+\vec{K}$ and $\vec{k}$ are equivalent wave vectors

$\Rightarrow$ can use a single unit cell in reciprocal space, natural choice: 1. BZ

Bloch state into S.E. yields:

$$\nabla\left\{u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}\right\} = \left\{i\vec{k}\, u_{\vec{k}}(\vec{r}) + (\nabla u_{\vec{k}}(\vec{r}))\right\} e^{i\vec{k}\cdot\vec{r}}$$

$$\Rightarrow \nabla^2\{\text{---}''\text{---}\} = \left\{-k^2 u_{\vec{k}}(\vec{r}) + 2i\vec{k}\cdot(\nabla u_{\vec{k}}(\vec{r})) + (\nabla^2 u_{\vec{k}}(\vec{r}))\right\} e^{i\vec{k}\cdot\vec{r}}$$

$$= e^{i\vec{k}\cdot\vec{r}} \left(\nabla + i\vec{k}\right)^2 u_{\vec{k}}(\vec{r})$$

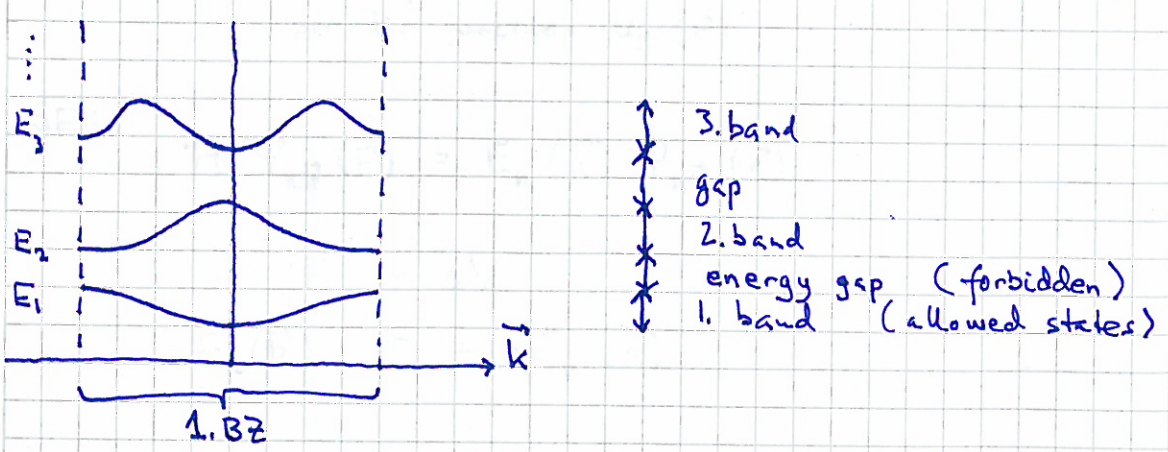
$$\Rightarrow \left[-\frac{\hbar^2}{2m}\left(\nabla + i\vec{k}\right)^2 + V(\vec{r})\right] u_{\vec{k}}(\vec{r}) = E(\vec{k})\, u_{\vec{k}}(\vec{r})$$

V and $u_{\vec{k}}$ periodic [in real space] [$\vec{k}$ enters as <u>parameter</u>]

$\Rightarrow$ may use one primitive cell and PBC

$\Rightarrow$ eigenvalues $E_1(\vec{k}), E_2(\vec{k}), \ldots, E_n(\vec{k}), \ldots$ for given $\vec{k}$

$\Rightarrow$ energy <u>bands</u> $E_n(\vec{k})$; $n = 1, 2, \ldots$ (band index)



N primitive cells $\Rightarrow$ N allowed $\vec{k}$-values in 1. BZ

$\Rightarrow$ 2N allowed states in each band

$$E_n(-\vec{k}) = E_n(\vec{k})$$

Tight binding approximation

SE for single atom (in $\vec{R}=0$): $H_a \chi_n(\vec{r}) = E_n \chi_n(\vec{r})$ ← orthonormal set

$$H_a = -\frac{\hbar^2}{2m}\nabla^2 + V_a(\vec{r})$$

← potential from atom in $\vec{R}=0$

Real crystal: $H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$

$$V(\vec{r}) = V_a(\vec{r}) + \Delta V$$
$$= V_a(\vec{r}) + \sum_{\vec{R}\neq 0} V_a(\vec{r}-\vec{R})$$

I.e: potential felt by electron near origin (in atom in $\vec{R}=0$) equals atomic (ionic) potential, $V_a(\vec{r})$ + small perturbation due to other atoms (ions), $\Delta V = \sum_{\vec{R}\neq 0} V_a(\vec{r}-\vec{R})$

⇒ atomic level E_n is perturbed: $E_n + \Delta E_n$

and eigenstate $\chi_n(\vec{r})$ must be replaced by

Bloch function $\psi_{n\vec{k}}(\vec{r})$

Natural choice: $\psi_{n\vec{k}}(\vec{r}) \overset{(*)}{=} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi_n(\vec{r}-\vec{R})$ ("LCAO")

$$\left(= e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_{\vec{R}} e^{-i\vec{k}\cdot(\vec{r}-\vec{R})} \chi_n(\vec{r}-\vec{R})}_{\text{periodic function } u_{n\vec{k}}(\vec{r})} = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \text{ ; Bloch Function !}\right)$$

SE:

$$H\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n\vec{k}}(\vec{r})$$

$$H = H_a + \Delta V$$

$$E_n(\vec{k}) = E_n + \Delta E_n(\vec{k})$$

Multiply SE with $\chi_n^*(\vec{r})$ and $\int d^3r$

$$\Rightarrow \int d^3r\, \chi_n^*(\vec{r})\left[H_a + \Delta V\right]\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) \int d^3r\, \chi_n^*(\vec{r})\psi_{n\vec{k}}(\vec{r})$$

H_a is <u>hermitian</u> operator $\Rightarrow$

$$\int \chi_n^* H_a \Psi \, d^3r = \int \Psi \left(H_a \chi_n\right)^* d^3r$$

$$= \int \Psi \left(E_n \chi_n\right)^* d^3r$$

$$= E_n \int \chi_n^* \Psi \, d^3r$$

$$\Rightarrow E_n(\vec{k}) = E_n + \frac{\int d^3r \, \chi_n^*(\vec{r}) \, \Delta V \, \Psi_{n\vec{k}}(\vec{r})}{\int d^3r \, \chi_n^*(\vec{r}) \, \Psi_{n\vec{k}}(\vec{r})}$$

$$= E_n + \frac{\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \int d^3r \, \chi_n^*(\vec{r}) \, \Delta V \, \chi_n(\vec{r}-\vec{R})}{\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \int d^3r \, \chi_n^*(\vec{r}) \chi_n(\vec{r}-\vec{R})}$$

Overlap integrals:

$$\int d^3r \, \chi_n^*(\vec{r}) \, \chi_n(\vec{r}-\vec{R}) \approx \delta_{\vec{R},0} \quad \left(\Rightarrow \text{denominator} = 1\right)$$

Transfer integrals:

$$\gamma(\vec{R}) = \int d^3r \, \chi_n^*(\vec{r}) \, \Delta V \, \chi_n(\vec{r}-\vec{R}) = \sum_{\vec{R}' \neq 0} \int d^3r \, \chi_n^*(\vec{r}) \, V_a(\vec{r}-\vec{R}') \, \chi_n(\vec{r}-\vec{R})$$

$$\Rightarrow E_n(\vec{k}) = E_n + \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \, \gamma(\vec{R})$$

Keep $\vec{R} = 0$ and $\vec{R}_{nn}$ = nearest neighbour to origin :

$$\gamma(0) = \sum_{\vec{R}' \neq 0} \int d^3r \, \chi_n^*(\vec{r}) \, V_a(\vec{r}-\vec{R}') \, \chi_n(\vec{r}) \qquad \text{(small)}$$

($\Rightarrow$ a <u>constant</u> contribution to $E_n(\vec{k})$)

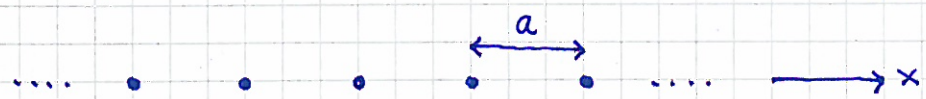
$$\gamma(\vec{R}_{n.n.}) \approx \int d^3r \, \chi_n^*(\vec{r}) \, V_a(\vec{r}-\vec{R}_{nn}) \, \chi_n(\vec{r}-\vec{R}_{nn}) \qquad \text{(small)}$$

$$\Rightarrow E_n(\vec{k}) \approx E_n + \gamma(0) + \sum_{nn} e^{i\vec{k}\cdot\vec{R}} \, \gamma(\vec{R})$$

Example: 1D lattice

$\vec{R} = ja\hat{x}$, $\vec{K} = \ell \cdot \frac{2\pi}{a}\hat{x}$

$\Rightarrow$ 1. BZ : $[-\frac{\pi}{a}, \frac{\pi}{a}]$



$$\left.\begin{aligned} E_n + \gamma(0) &= E_0 \\ \gamma_{n.n.} &= \gamma \end{aligned}\right\} \Rightarrow E(k) = E_0 + \gamma \sum_{n.n.} e^{ikX}$$

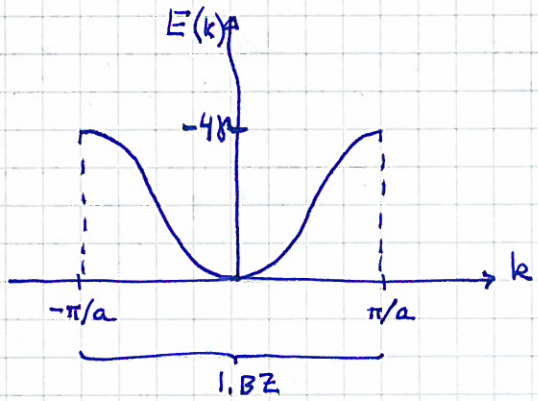
$$= E_0 + \gamma\left(e^{ika} + e^{-ika}\right)$$

$$= E_0 + 2\gamma \cos ka$$

Choose $E_0 = -2\gamma$ and $\gamma < 0$

$\Rightarrow E(k) = -2\gamma(1 - \cos ka)$

$\Rightarrow E(0) = 0$



Small k:

$1 - \cos ka \approx \frac{1}{2}k^2a^2$

$\Rightarrow$ if $\gamma = -\hbar^2/2ma^2$, we have $E(k) \approx \frac{\hbar^2k^2}{2m}$ near $k = 0$

More generally: $\left((\partial E/\partial k)_{k=0} = 0\right)$

$$E(k) = E(0) + \frac{1}{2}\left(\frac{\partial^2 E}{\partial k^2}\right)_{k=0} \cdot k^2 + \ldots \quad \text{(Taylor expansion)}$$

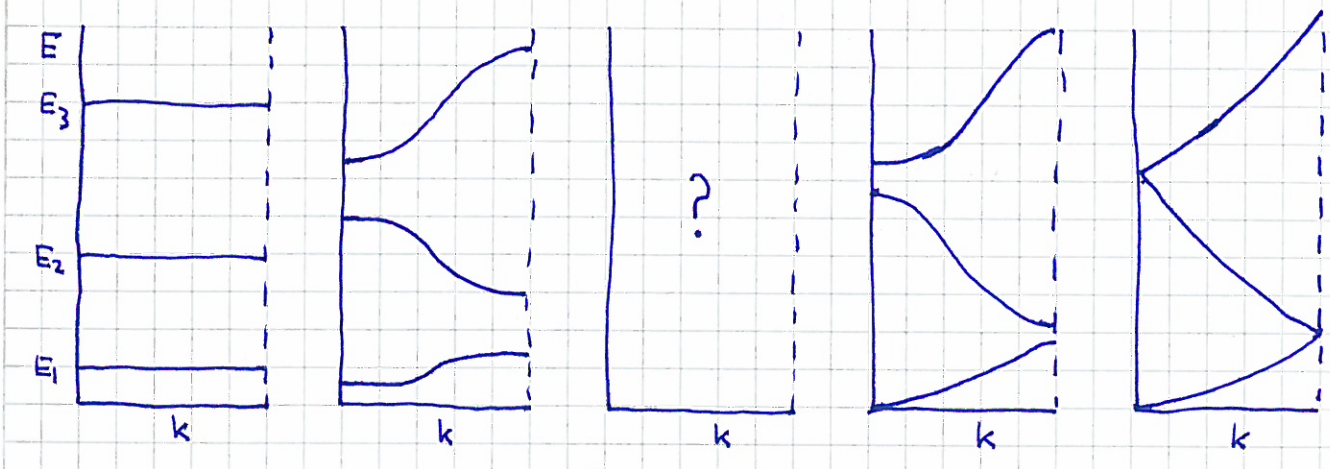
$\Rightarrow$ from $E(k)$ near $k = 0$, we can derive an <u>effective mass</u> m^* for the electrons:

$$m^* = \hbar^2 \left[\left(\frac{\partial^2 E}{\partial k^2}\right)_{k=0}\right]^{-1}$$

Various generalizations:

- 1D $\rightarrow$ 2D or 3D
- 1 atomic state $\rightarrow$ several atomic states

From isolated atoms to free electrons: (1D, half of 1BZ) 17



isolated atoms | tight binding | reality | weak potential | free electrons

← increasing strength of periodic potential