Electrons in crystals

First: free and non-interacting electrons

Later: include effects of periodic potential, $V(\vec{r}+\vec{R}) = V(\vec{r})$

(Neglect real-world complications: e-e interaction, lattice vibrations (= phonons), impurities, spin-orbit coupling etc)

$$V=0 \Rightarrow H = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 = -\frac{\hbar^2}{2m}\nabla^2$$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

Pauli principle: 0 or 1 electron in given single-particle state

Assume system is cubic box, $L\cdot L\cdot L$, potential $V=0$ inside and $V=\infty$ outside box, periodic boundary conditions (PBC) $\psi(x+L) = \psi(x)$ etc.

$\Rightarrow \psi(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}}$ with $\vec{k} = \frac{2\pi}{L}\left(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}\right)$ $(n_i = 0, \pm1, \pm2, \cdots)$

Spin degeneracy: $s = 1/2 \Rightarrow |\vec{S}| = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$

$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar$$

$\Rightarrow g_s = 2$ spin states for each <u>orbital</u> state $\psi(\vec{r})$

Energy eigenvalues: $\nabla^2 e^{i\vec{k}\cdot\vec{r}} = -k^2 e^{i\vec{k}\cdot\vec{r}}$

$$\Rightarrow E(\vec{k}) = \frac{\hbar^2k^2}{2m} = \frac{p^2}{2m}, \quad \text{with momentum } \vec{p} = \hbar\vec{k}$$

<u>Macroscopic system</u>: $L\to\infty$ $\Rightarrow$ continuous $E(\vec{k})$

(dispersion relation, band structure)

Density of states (DOS)

$D(E)$ = # states pr unit energy (# : "number of")

$g(E) = D(E)/V$ = DOS pr unit volume (in 2D: $g_2(E) = D_2(E)/A$)

DOS depends on system <u>dimensionality</u>:

0D (quantum dot, atom): $D_0(E) = 2 \sum_i \delta(E - E_i)$ ($2 \uparrow g_s = 2$, $\uparrow$ eigenvalues)

1D (quantum wire): $D_1(E) = \sqrt{2m}\, L / \pi\hbar \sqrt{E} \sim E^{-1/2}$

2D (— " — well): $D_2(E) = m A / \pi\hbar^2 \sim E^0$

} Exercise 1

3D:

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

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

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

states with magnitude of wave vector smaller than k:

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

$\Rightarrow$ # states with energy less than $E = \hbar^2 k^2/2m$:

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

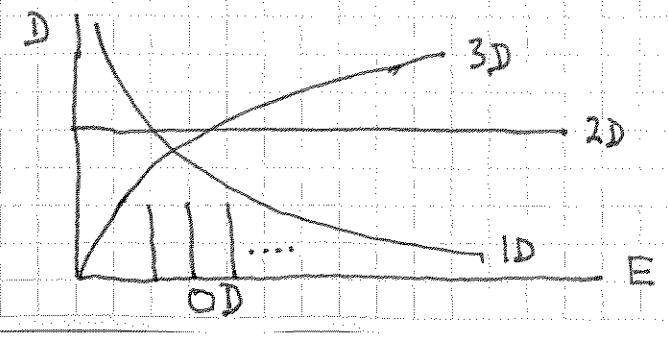
$$D(E) = \lim_{\Delta E \to 0} \frac{\Delta N}{\Delta E} = \frac{dN}{dE}$$

[Alternative argument: # states in $(\varepsilon, \varepsilon + d\varepsilon)$ is $D(\varepsilon) \cdot d\varepsilon$

$\Rightarrow$ # states in $(0, E)$ is $N(E) = \int_0^E D(\varepsilon)\, d\varepsilon$

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

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



Fermi energy E_F and chemical potential μ

At $T=0$, system is in <u>ground state</u>, with the N electrons occupying the N states with <u>lowest energy</u>.

Fermi energy: E_F = max. energy of occupied states (at $T=0$)

$N = \frac{V}{3\pi^2} \cdot k_F^3 \Rightarrow k_F = (3\pi^2 n)^{1/3}$ = Fermi wave number

$n = N/V$ = electron density

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

Fermi temperature : $T_F = E_F / k_B$

— " — momentum : $p_F = \hbar k_F$

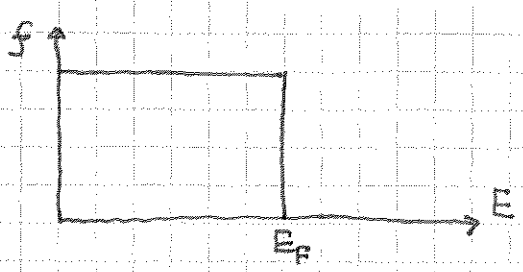
— " — velocity : $v_F = p_F / m$

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

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$ = probability of finding electron in state with energy E at temperature T

μ = chemical potential; $f(\mu) = 1/2$

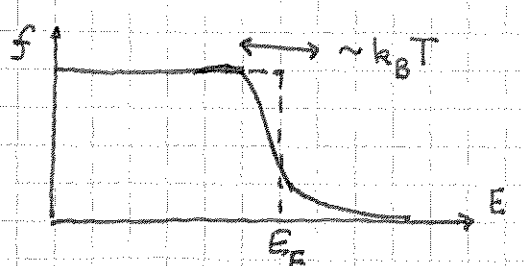
$T=0$:



$f(E<\mu) = 1$, $f(E>\mu) = 0$

$\mu = E_F$ at $T=0$

$T>0$:



$\mu(T) \approx E_F \left(1 - \frac{\pi^2}{12} \frac{T^2}{T_F^2}\right) < E_F$

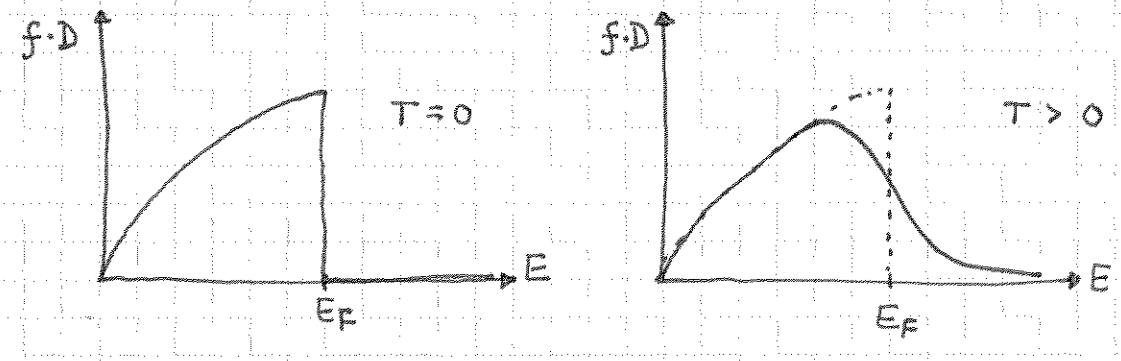
$D(E)\,dE$ = # states in $(E, E+dE)$

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

$\Rightarrow N = \int_0^\infty f(E)D(E)\,dE$ = # electrons (determines $\mu(T)$)

i.e. $f(E)D(E)$ = # electrons pr unit energy

In 3D system:



thermally excited electrons $\approx k_B T \cdot D(E_F)$

High-energy tail, $E-\mu \gg k_B T$:

$f(E) \approx e^{\mu/k_BT}\, e^{-E/k_BT}$ Boltzmann distribution

Electrons in periodic potential

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

with $V(\vec{r}+\vec{R}) = V(\vec{r})$; $\vec{R}$ = Bravais lattice vector

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

$u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$ (periodic in direct space)

(See any SSP book for proof of Bloch's theorem)

Simplify notation, $\vec{k} \to k$, $\vec{r} \to r$ etc

$H\psi_k = E\psi_k$; $\psi_k = e^{ikr} u_k$

Introduce $k_o = k + K$, i.e., $k = k_o - K$

$$\Rightarrow H e^{ik_o r} \underbrace{e^{-iKr}}_{\text{periodic}} \underbrace{u_k}_{\text{periodic}} = E e^{ik_o r} e^{-iKr} u_k$$

$\Rightarrow e^{-iKr} u_k$ is periodic

$\Rightarrow e^{ik_o r} \cdot e^{-iKr} u_k$ is a Bloch function, ψ_{k_o}

$\Rightarrow H\psi_{k_o} = E\psi_{k_o}$

$\Rightarrow \vec{k}$ and $\vec{k}_o = \vec{k} + \vec{K}$ correspond to <u>equivalent</u> eigenstates and eigenvalues:

$$\left.\begin{aligned} \psi_{\vec{k}+\vec{K}}(\vec{r}) &= \psi_{\vec{k}}(\vec{r}) \\ E(\vec{k}+\vec{K}) &= E(\vec{k}) \end{aligned}\right\} \text{ periodic in k-space}$$

$\Rightarrow$ we may use a single unit cell in k-space, e.g., 1BZ

From S.E. [≡ Schrödinger Eqn.] for ψ_k we find eqn. for u_k:

$$\nabla^2 \psi_k = \nabla^2 \{ e^{ikr} u_k \} = \nabla \{ e^{ikr} [iku_k + \nabla u_k] \}$$

$$= e^{ikr} \{ -k^2 u_k + 2ik \nabla u_k + \nabla^2 u_k \}$$

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

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

($i\vec{k}$: parameter)

⇒ we may use a single primitive cell in direct space

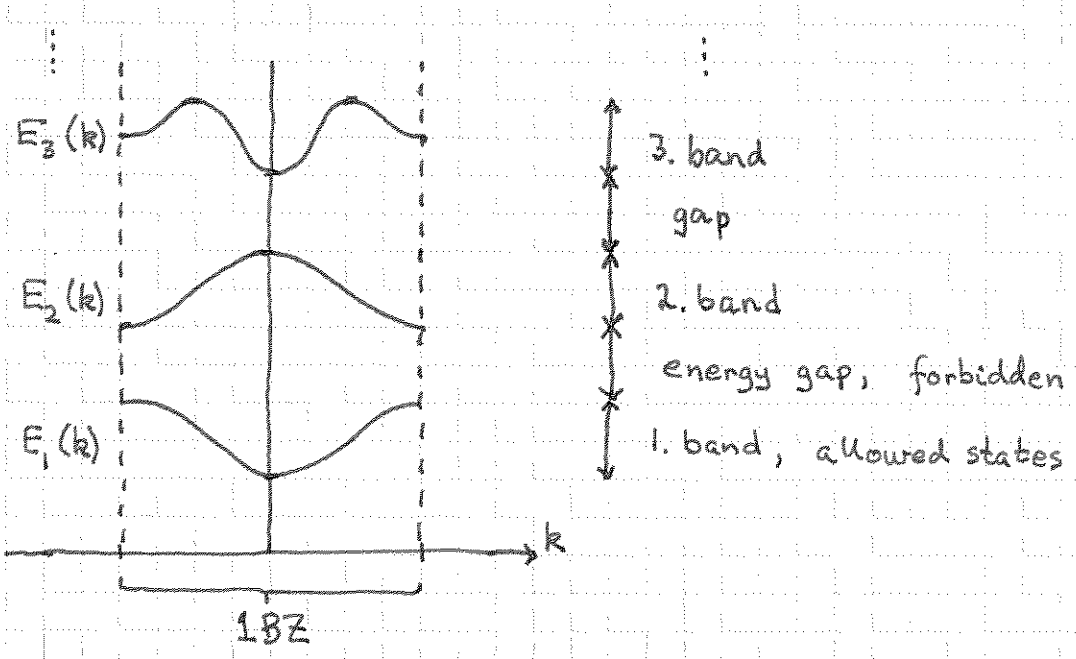
(+ periodic boundary conditions, "PBC")

For each $\vec{k}$ in 1BZ, we have eigenvalues $E_1(\vec{k}), E_2(\vec{k}), \ldots$

Many primitive cells, $N \sim 10^{23} \approx \infty$ ⇒ $\Delta k \to 0$

⇒ continuous energy bands $E_n(\vec{k})$; $n = 1, 2, \ldots$ = band index

N allowed $\vec{k}$-values in 1BZ ⇒ 2N allowed states in each band ($g_s = 2$); $E_n(-\vec{k}) = E_n(\vec{k})$ (inversion symmetry)



Various methods to calculate $E_n(\vec{k})$:

- Nearly free electron approximation
- → Tight binding approx.
- $\vec{k} \cdot \vec{p}$ method (perturbation theory around $\vec{k} = 0$ or some other point in k-space)
- Density functional theory (efficient ab initio many body theory, "DFT")

etc. etc.

Tight Binding Approximation

S.E. for single atom in $\vec{R}=0$: $H_a \chi_n(\vec{r}) = \varepsilon_n \chi_n(\vec{r})$

$H_a = -\frac{\hbar^2}{2m}\nabla^2 + V_a(\vec{r})$; $V_a(\vec{r})$ = atomic potential for atom in $\vec{R}=0$

ε_n = atomic energy levels

χ_n = orthonormal set of atomic states

} $n = 1, 2, \ldots$

Rest of real crystal represents potential $\Delta V = \sum_{\vec{R}\neq 0} V_a(\vec{r}-\vec{R})$

assumed to be small perturbation:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{\vec{R}} V_a(\vec{r}-\vec{R})$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + V_a(\vec{r}) + \sum_{\vec{R}\neq 0} V_a(\vec{r}-\vec{R})$$

$$= H_a + \Delta V$$

Then, atomic states $\chi_n(\vec{r}) \rightarrow$ Bloch functions $\psi_{n\vec{k}}(\vec{r})$

and atomic levels $\varepsilon_n \rightarrow$ bands $\varepsilon_n + \Delta\varepsilon_n(\vec{k}) = E_n(\vec{k})$

Natural choice: construct $\psi_{n\vec{k}}(\vec{r})$ as linear combination of atomic orbitals (LCAO) χ_n, i.e.,

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\, \chi_n(\vec{r}-\vec{R})$$

May write $\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\, \chi_n(\vec{r}-\vec{R}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_{\vec{R}} e^{-i\vec{k}\cdot(\vec{r}-\vec{R})}\, \chi_n(\vec{r}-\vec{R})}_{\text{periodic}}$

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

End 17.01.12