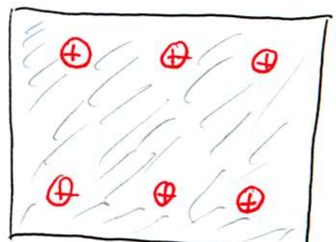
Model prostih e^-

Na$^+$



e^- se prosto gibljejo med $^+$ioni

Valentni: Li, Na, K, Rb, Cs

Na$^+$ ima 10 el. vezanih v lupinah: 1s, 2s, 2p

e^- v 3s pa je "prost"   Na$^+$ zavzema le 15% prostora Na kristala

Alkalni elementi kristalizirajo v BCC strukturi:

– Prevodniške e^- v kovini ima pri nizki temp. povprečna prosta pot $\sim$ 1 cm

a.) Rešitve enodelčne Schröd. enačbe v periodičnem kristalu so ravni valovi, modulirani z periodično funkcijo ~ stanja niso lokalizirana.

b.) Sipanje med e^- je majhno zaradi Paulijevega izkl. principa.

Schrödingerjeva enačba za sistem prostih e^-:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$$

Rešitev: $\psi_k(\vec{r}) = A e^{i\vec{k}\vec{r}}$

Periodični R.P.

$$\psi_k(x+L, y, z) = \psi_k(x, y, z)$$
$$\psi_k(x, y+L, z) = \psi_k(x, y, z)$$
$$\vdots$$

$$e^{i[k_x(x+L)+k_y(y+L)+k_z(z+L)]} = e^{i[k_x x + k_y y + k_z z]}$$

$$k_{n_1,n_2,n_3} = \left(n_1\frac{2\pi}{L}, n_2\frac{2\pi}{L}, n_3\frac{2\pi}{L}\right);\ n_i\in\mathbb{Z}$$

Energija:

$$\varepsilon_{\vec k} = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) \; ; \; k=\frac{2\pi}{\lambda}$$

$\vec k = (k_x, k_y, k_z)$ določa stanje e^-. (n_1, n_2, n_3) ter orientacija spina m_s
(ORBITALA)

$\psi_{\vec k}(\vec r)$ je lastna funkcija operatorja za gibalno količino:

$\vec p = -i\hbar\vec\nabla$:

$$\vec p\,\psi_{\vec k}(\vec r) = A\hbar\vec k\, e^{i\vec k\vec r} = \hbar\vec k\,\psi_{\vec k}(\vec r)$$

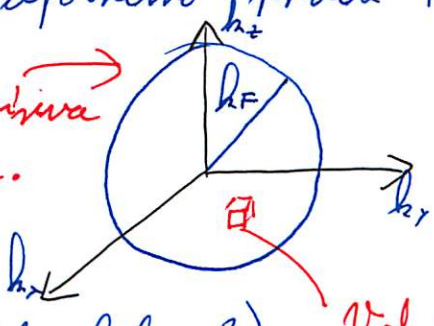
z lastno vrednostjo $\hbar\vec k$. $\vec v = \frac{\hbar\vec k}{m}$ hitrost delca v orbitali $\vec k$

Prvih nekaj najnižjih stanj (orbital)

n_1	n_2	n_3	$\varepsilon_{\vec k}\left[\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\right]$	m_s	deg.
0	0	0	0	↑, ↓	2
±1	0	0	1	↑↓	12
0	±1	0			
0	0	±1			
±1	±1	0	2	↑↓	24
±1	0	±1			
0	±1	±1			
±1	±1	±1	3	↑↓	16

Osnovno stanje z N e^- pri $T=0$: zapolnimo prvih N orbital do energije ε_F

Fermijeva sfera.



$$\varepsilon_F = \frac{\hbar^2}{2m}k_F^2$$

Kako je k_F odvisen od števila (gostote delcev?)

Vol. element v $\vec k$ prostoru $d^3k = \left(\frac{2\pi}{L}\right)^3$

Število stanj: najnižji ležečih

$$2\,\frac{V\ \text{Ferm. krogle}}{\text{Vol. element v } k\text{-prostoru}} = N$$

spin

$$\left(\frac{2\pi}{L}\right)^3$$

V (kristala)

$$2\,\frac{4\pi k_F^3\, L^3}{3\cdot(2\pi)^3} = N$$

$$k_F = \left(3\pi^2\frac{N}{V}\right)^{\frac{1}{3}}$$

vol. gostota št. delcev

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{\frac{2}{3}} \quad ; \quad \varepsilon_F = k_B T_F$$

(Fermi temperature!)

Fermijeva energija je odvisna le od št. gostote delcev!

Fermijeva hitrost:

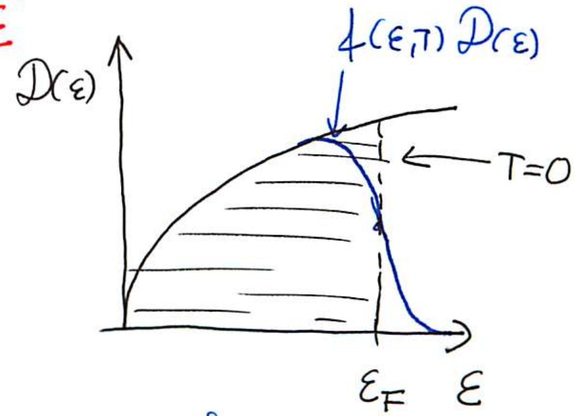
$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(3\pi^2\frac{N}{V}\right)^{\frac{1}{3}}$$

Definicija gostote stanj:

$$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}}$$

Št. stanj! Ali št. elektronov z (stanj) energijo $\leq \varepsilon$!

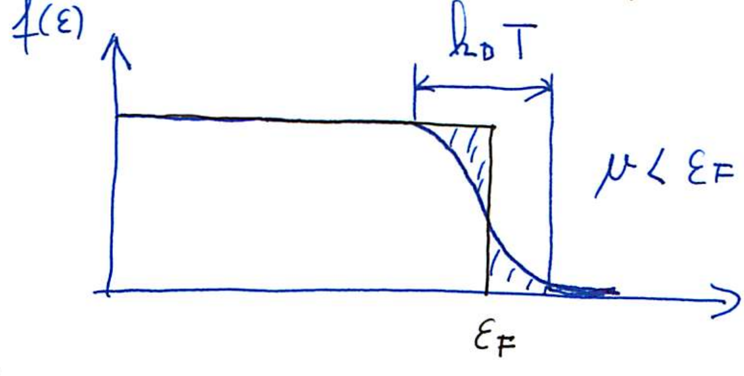
$$D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}$$



Končna T!

Fermijeva (Fermi-Dirac) funkcija

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\mu}{k_B T}}+1}$$



Pri $T=0$; $\mu = \varepsilon_F$

Gostota stanj na volumsko enoto:

$$g(\varepsilon) = \frac{\mathcal{D}(\varepsilon)}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}$$

$$n = \frac{N}{V}\ ; \qquad \varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}}$$

$$\varepsilon_F^{\frac{3}{2}} = 3\pi^2 n\left(\frac{\hbar^2}{2m}\right)^{\frac{3}{2}}$$

$$g(\varepsilon)\,\varepsilon_F^{\frac{3}{2}} = \frac{3}{2}\, n\,\sqrt{\varepsilon}$$

$$g(\varepsilon) = \frac{3}{2}\frac{n}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}\ ; \quad g(\varepsilon_F) = \frac{3}{2}\frac{n}{\varepsilon_F}$$

$$\mathcal{D}(\varepsilon) = \frac{3}{2}\frac{N}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

Termične lastnosti plina prost. elektronov:

$$f_{\mathbf{k},\sigma} = \frac{1}{e^{\frac{\varepsilon_{\mathbf{k},\sigma}-\mu}{k_BT}}+1} \quad \text{ali:} \quad f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\mu}{k_BT}}+1}$$

$$T=0:\ f_{\mathbf{k},\sigma} = \begin{cases} 1; & \varepsilon(\mathbf{k}) < \varepsilon_F \\ 0; & \varepsilon(\mathbf{k}) > \varepsilon_F \end{cases} \qquad \lim_{T\to 0}\mu = \varepsilon_F$$

$c_V = ?$

$$c_V = \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V\ ; \quad u = \frac{U}{V}$$

U: notranja energija

po vseh $\mathbf{k}$!

$$U = 2\sum_{\mathbf{k}}\varepsilon(\mathbf{k})\, f(\varepsilon(\mathbf{k}))$$

f je odvisna od $\mathbf{k}$ <u>le</u> skozi $\varepsilon(\mathbf{k})$

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{(2\pi)^3}\int d\mathbf{k}\, F(\mathbf{k})$$

; Velja v $V\to\infty$ limiti.

$$\parallel$$

$$\sum_{\mathbf{k}} F(\mathbf{k})\,\frac{\Delta \mathbf{k}}{\frac{(2\pi)^3}{V}}$$

$\Delta \mathbf{k} = \frac{8\pi^3}{V}$ volumen v $\mathbf{k}$-prostoru, ki ustreza eni orbitali

$$u = \frac{U}{V} = \int \frac{d\mathbf{k}}{4\pi^3}\,\varepsilon(\mathbf{k})\, f(\mathbf{k})$$ Gostota notranje energije

$$n = \int \frac{d\mathbf{k}}{4\pi^3}\, f(\mathbf{k})$$ Gostota št. delcev

$$\int \frac{d\mathbf{k}}{4\pi^3}\, F(\mathbf{k}) = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, F(\varepsilon)$$

Velja: $$\frac{d\mathbf{k}}{4\pi^3} = \frac{4\pi k^2\, dk}{4\pi^3} = g(\varepsilon)\, d\varepsilon \quad = \frac{1}{g(\varepsilon)} = \pi^2 \frac{d\varepsilon}{k^2\, dk}$$

$$\varepsilon = \frac{\hbar^2 k^2}{2m}\ ; \quad \frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m}\ ; \quad k = \sqrt{\frac{2m}{\hbar^2}\varepsilon}$$

$$\frac{1}{g(\varepsilon)} = \pi^2 \frac{\hbar^2 k}{m k^2} = 2\pi^2 \sqrt{\left(\frac{\hbar^2}{2m}\right)^3}\, \frac{1}{\sqrt{\varepsilon}}$$

$$g(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon}$$

$$u = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, \varepsilon\, f(\varepsilon)\ ; \quad n = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, f(\varepsilon)$$

Sommerfeldov razvoj: Dodatek C (ASHCROFT)

$$\int_{-\infty}^{\infty} H(\varepsilon) f(\varepsilon)\, d\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) + O(T^4)$$

$$u = \int_{-\infty}^{\mu} d\varepsilon\, \varepsilon\, g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \left[\mu g'(\mu) + g(\mu)\right] + O(T^4)$$

$$n = \int_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) + O(T^4)$$

Pozor: $\mu \neq \varepsilon_F$

a.) $$\int_{-\infty}^{\mu} d\varepsilon\, H(\varepsilon) = \int_{-\infty}^{\varepsilon_F} d\varepsilon\, H(\varepsilon) + (\mu - \varepsilon_F) H(\varepsilon_F)$$

b.) v vseh členih reda T^2 nadomestimo $\mu \to \varepsilon_F$

$$u = \int_{-\infty}^{\varepsilon_F} d\varepsilon\, \varepsilon\, g(\varepsilon) + (\mu - \varepsilon_F)\varepsilon_F g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 \left[\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)\right]$$

$$n = \underbrace{\int_{-\infty}^{\varepsilon_F} d\varepsilon\, g(\varepsilon)}_{\parallel} + (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F)$$

Pozor: n ! $\Rightarrow$ $$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}$$

$$\left.\begin{aligned} g(\varepsilon) &= A\sqrt{\varepsilon} \\ g'(\varepsilon) &= \frac{A}{2}\varepsilon^{-\frac{1}{2}} \end{aligned}\right\} \quad \frac{g'(\varepsilon)}{g(\varepsilon)} = 2\varepsilon^{-1}$$

$$\mu = \varepsilon_F \left[1 - \frac{1}{2}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right]$$

vstavimo v izraz za u:

$$u = u_0 + \left(-\frac{\pi^2}{6}\right)(k_B T)^2 \varepsilon_F g'(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 \left[\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)\right]$$

$$U = U_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F)$$

Sledi iz $c_V = \left(\frac{\partial u}{\partial T}\right)_n$:

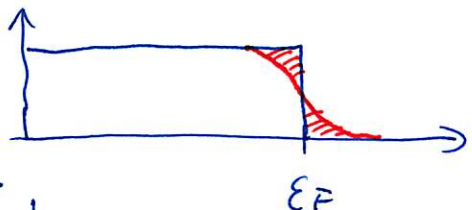
$$g(\varepsilon_F) = \frac{3}{2}\frac{n}{\varepsilon_F}$$

Velja za sistem prostih e^-!

$$c_V = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F)$$

$$c_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right) n k_B$$

- K el. specifični toploti prispeva le "majhen" delež e^- okoli Ferm. energ.
- Klasični rezultat idealnega plina: $c_V = \frac{3}{2} n k_B$. Vpliv FD porazdelitve je torej v faktorju: $\frac{\pi^2}{3}\left(\frac{k_B T}{\varepsilon_F}\right)$! Ta faktor je reda pri sobni T le okoli 10^{-2}!

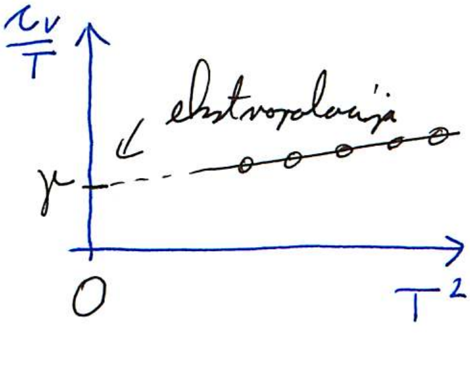


Ocena za c_V: $u \sim \underbrace{(k_B T)\cdot g(\varepsilon_F)}_{\text{delež term. vzb. } e^-}\cdot \underbrace{k_B T}_{\text{energija}}$

Eksperimentalno: $c_V = \underbrace{\gamma T}_{\text{pri nizkih } T \text{ prevlada}} + AT^3$; A prispevek mrežnih nihanj

γT: $\boxed{\text{el. prispevek zanemarljiv pri 300 K!}}$

Določitev γ: $\frac{c_V}{T} = \gamma + AT^2$



Običajno se navaja $C = \frac{Z N_A}{n}\cdot c_V$

Toplotna kapaciteta na mol; Z = valenca; $Z N_A$ št. e^- v enem molu. $\frac{Z N_A}{n}$ je volumen enega mola $= Z N_A \frac{V}{N}$ volumen, ki pripada enemu prev. e^-

$$C = \frac{\pi^2}{3} \frac{z N_A k_B^2}{n} T g(\varepsilon_F); \quad N_A \cdot k_B = R$$

$$C = \frac{\pi^2}{3} z R \frac{k_B T}{n} g(\varepsilon_F) = \underbrace{\frac{\pi^2}{2} R \frac{z}{T_F}}_{\gamma} T$$

$\Rightarrow \gamma \propto \varepsilon_F^{-1} \propto m$

Element	γ_e $\frac{mJ}{mol\,K^2}$	γ_{free}	$\frac{m^*}{m} = \frac{\gamma_e}{\gamma_{free}}$
Li	1,63	0,749	2,18
Na	1,38	1,094	1,26
Cu	0,695	0,505	1,38
Fe	1,5	20	12 ← !

Kittel

Še nekaj zvez:

$$n = \frac{k_F^3}{3\pi^2} \; ; \quad \frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}$$

r_s: radij sfere, katere V je enak volumnu, ki pripada enemu elektronu.

$$k_F = \frac{\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}}{r_s}$$

$$k_F = \frac{3{,}63}{r_s / a_0} \cdot 10^{-1}\, nm^{-1} = \frac{0{,}363}{r_s a_0}\, nm^{-1} \; ; \quad a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e_0^2}$$

$$a_0 = 5{,}3 \cdot 10^{-11}\, m$$

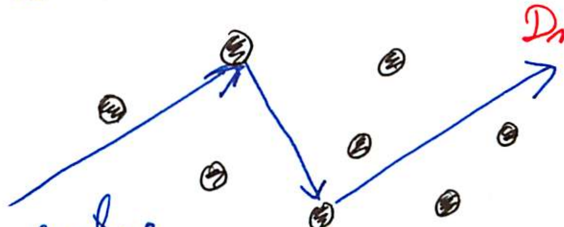
Drudejev model el. upornosti: P. Drude 1900

– Osnovne predpostavke: Z elektronov na atom kovine se prosto giblje po kristalu. Ostalih $Z_A - Z$ so vezani. Z_A je vrstno število.

Dodatne predpostavke:

1) Med trki so e^- prosti. Zanemari interakcije z drugimi e^- ter tudi z ioni. e^- se prosto giblje, seveda pod vplivom zun. polj.

2.) Trki so "trenutni" (kratki). Predpostavil je, da so trki predvsem z drugimi ioni. Zanemari trke z e^- (napačno!)



Drudejeva slika

3.) Verjetnost za trk na čas. enoto:

$$1/\tau \quad ; \quad \tau \text{ relaksacijski čas}$$

τ: neodvisen od lege $\vec{r}$ ter hitrosti $\vec{v}$.

4.) e^- vzpostavijo termično ravnovesje izključno preko trkov z ioni, ki se nahajajo v term. ravnovesju z okolico. Takoj po trku je hitrost e^- popolnoma neodvisna od njegove hitrosti pred trkom. Njena smer je naključna, velikost pa ustreza lokalni termični porazdelitvi.

$$\vec{E} = \rho \vec{j}$$: ρ: el. upornost

$\vec{j}$: gostota el. toka

$$\vec{j} = -ne\vec{v}$$

(−) zaradi negativnega naboja

$\vec{v}$: povprečna hitrost e^-

Če ni $\vec{E}$ polja, je $\langle \vec{j} \rangle = 0$

Končno $\vec{E}$ polje:

Uklenimo: sila dušenja

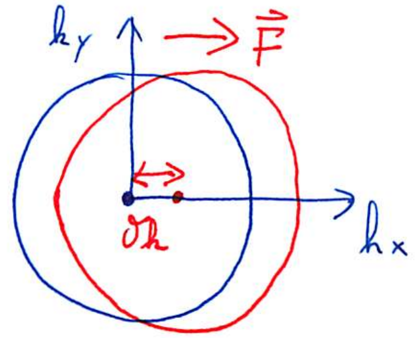
$$m\vec{a} = -e\vec{E} - \frac{m\vec{v}}{\tau} \Rightarrow \vec{v}_{avg} = -\frac{e\vec{E}\tau}{m}$$

$$\vec{j} = \frac{ne^2\tau}{m}\vec{E} \; ; \; \vec{j} = \sigma\vec{E}$$

$$\Rightarrow \sigma = \frac{ne^2\tau}{m} \; ; \; \tau: \text{relaksacijski čas}$$

Vpliv $\vec{E}$ polja na FD kroglo:

$$\vec{F} = m\frac{d\vec{v}}{dt} = \hbar\frac{d\vec{k}}{dt} = -e\vec{E} \Rightarrow \vec{k}(t) - \vec{k}(0) = -\frac{e\vec{E}t}{\hbar}$$



$$\delta k = -\frac{e\vec{E}t}{\hbar}$$ FDS se premakne

zaradi sipanj

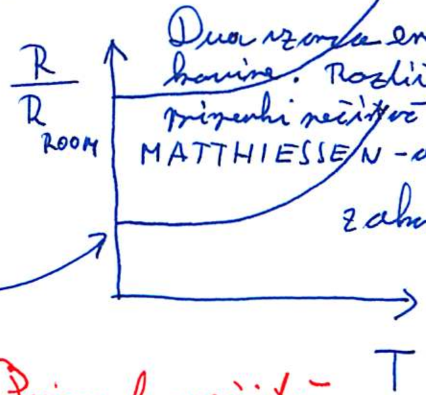
$$\delta k = -\frac{e\vec{E}\tau}{\hbar}$$ premik FDS je konstanten!

Ocene Cu:

$$l = \tau \cdot v_F$$

$$v_F = 1{,}57 \cdot 10^{6}\ \tfrac{m}{s}$$

T	τ	l (povprečna prosta pot)
4 K	$2\cdot10^{-9}$ s	0,3 cm
300 K	$2\cdot10^{-14}$ s	$3\cdot10^{-6}$ cm



Izvor sipanja

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i}$$

fononski prispevek — Prevladuje pri sobni T

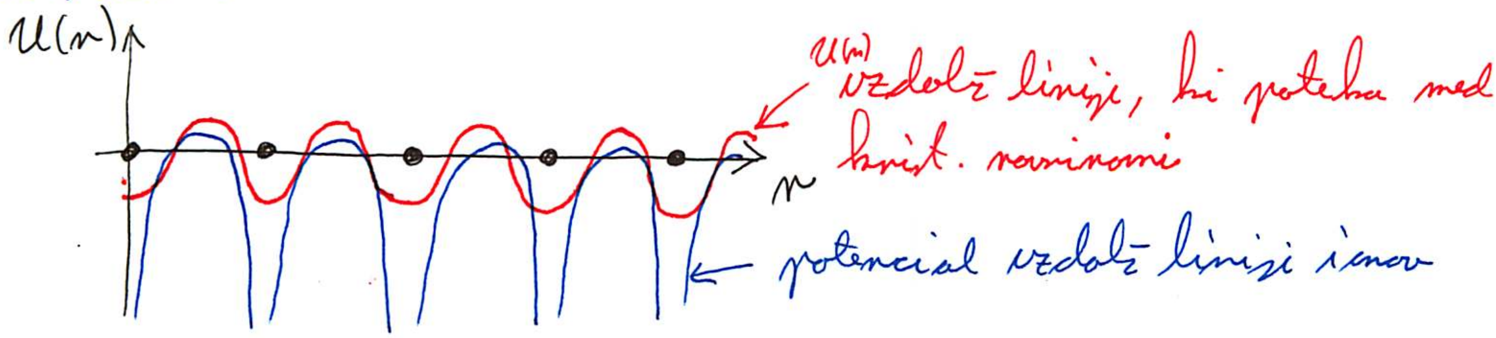
Prispevek nečistoč — Prevladuje pri nizkih T. Neodvisen od T

Elektronska stanja v periodičnem potencialu

Osnovno dejstvo: $\boxed{U(\vec{r} + \vec{R}) = U(\vec{r})}$

e^- se gibljejo v potencialu, ki ima periodo B.R.

- V principu je problem več-delčen, upoštevati bi morali interakcije med e^-. Obravnavamo le enodelčni problem!
- $U(\vec{r})$ ne predstavlja le eno-elektronskega potenciala zaradi vpliva ionov, temveč tudi efektivni povprečni potencial, ki opisuje sklopitev $e^- - e^-$.



$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi = \varepsilon\psi$$

Lastna stanja enodelčne Schröd. enačbe v $U(\vec{r})$ imenujemo Blochova stanja

Blochov teorem:

Če velja $U(\vec{r} + \vec{R}) = U(\vec{r}) \Rightarrow$

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{n\vec{k}}(\vec{r})$$

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

n: indeks pasu. $\forall \vec{k}$ obstaja več rešitev $\Rightarrow n$

Velja tudi:

$$\psi_{nk}(\vec{r}+\vec{R}) = e^{ik\vec{R}}\,\psi_{nk}(\vec{r})$$

<u>Prvi</u> dokaz B.T.

$$T_{\vec{R}}\, f(\vec{r}) = f(\vec{r}+\vec{R}) \qquad \text{Operator translacije}$$

$$T_{\vec{R}}\, H\psi = H(\vec{r}+\vec{R})\,\psi(\vec{r}+\vec{R}) = H(\vec{r})\,\psi(\vec{r}+\vec{R}) = H T_{\vec{R}}\,\psi$$

H in $T_{\vec{R}}$ komutirata: $\quad T_{\vec{R}} H - H T_{\vec{R}} = 0$!

Velja tudi

$$T_{\vec{R}}\, T_{\vec{R}'}\, \psi(\vec{r}) = T_{\vec{R}'}\, T_{\vec{R}}\, \psi(\vec{r}) = \psi(\vec{r}+\vec{R}+\vec{R}')$$

Torej:
$$T_{\vec{R}}\, T_{\vec{R}'} = T_{\vec{R}'}\, T_{\vec{R}} = T_{\vec{R}+\vec{R}'}$$

Lastna stanja H morajo biti tudi lastna stanja $T_{\vec{R}}$

$$H\psi = \varepsilon\psi$$
$$T_{\vec{R}}\,\psi = c(\vec{R})\,\psi$$

Veljati mora še:

$$T_{\vec{R}'}\, T_{\vec{R}}\,\psi = c(\vec{R})\, T_{\vec{R}'}\,\psi = c(\vec{R})\, c(\vec{R}')\,\psi$$

ter

$$T_{\vec{R}'}\, T_{\vec{R}}\,\psi = T_{\vec{R}+\vec{R}'}\,\psi = c(\vec{R}+\vec{R}')\,\psi$$

$$c(\vec{R}+\vec{R}') = c(\vec{R})\, c(\vec{R}')$$

Naj bodo $\vec{a}_i$ ($\vec{a}, \vec{b}, \vec{c}$) trije primitivni vektorji B.R.

$$c(\vec{a}_i) = e^{2\pi i x_i}$$

$\vec{a} \equiv \vec{a}_1$
$\vec{b} \equiv \vec{a}_2$
$\vec{c} \equiv \vec{a}_3$

Za poljuben vektor B.R.

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$c(\vec{R}) = c(\vec{a}_1)^{n_1} c(\vec{a}_2)^{n_2} c(\vec{a}_3)^{n_3}$$

To pa lahko zapišemo tudi kot:

$$c(\vec{R}) = e^{i \vec{k} \vec{R}}, \text{ za}$$

$\vec{b}_i$ so primitivni vekt. rec. mreže

$$\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$$

$\vec{A} \equiv \vec{b}_1$
$\vec{B} \equiv \vec{b}_2$
$\vec{C} \equiv \vec{b}_3$

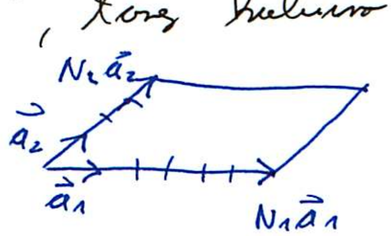
$$\vec{a}_i \vec{b}_j = 2\pi \delta_{ij}$$

$$\vec{k} \vec{R} = 2\pi (n_1 x_1 + n_2 x_2 + n_3 x_3)$$

$$\Rightarrow \underline{T_{\vec{R}} \psi} = \psi(\vec{r} + \vec{R}) = c(\vec{R}) \psi(\vec{r}) = \underline{e^{i \vec{k} \vec{R}} \psi(\vec{r})}$$

Born - von Karmanovi R.P.

V primeru prostih e^- smo za V vzeli kar L^3, torej kubično
str. V splošnem:



$$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r}); \quad i = 1, 2, 3$$

$\vec{a}_i$ primit. vektorji:

Uporabimo B.T.:

$$\psi_{n\vec{k}}(\vec{r} + N_i\vec{a}_i) = e^{iN_i\vec{a}_i\vec{k}}\,\psi_{n\vec{k}}(\vec{r})$$

R.P. zadostimo, če velja: $\quad \vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$

$$e^{iN_i\vec{a}_i\vec{k}} = 1 \quad ; \; i = 1, 2, 3$$

$$\Rightarrow \; e^{i2\pi N_i x_i} = 1 \;\Rightarrow\; x_i = \frac{m_i}{N_i} \quad ; \; m_i \in \mathbb{Z}$$

$\vec{k}$ ni več poljuben, temveč: $\quad \vec{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\underline{\vec{b}_i}$ primit. vekt. rec. mreže.

$\Delta\vec{k}$, ki pripada dovoljenemu $\vec{k}$:

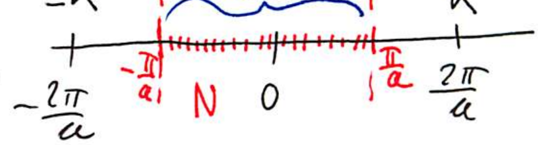
$$\Delta\vec{k} = \left(\frac{b_1}{N_1}, \frac{b_2}{N_2}, \frac{b_3}{N_3}\right) = \frac{\overbrace{(b_1, b_2, b_3)}^{\text{vol. 1. B.C.}}}{N} \quad ; \; N = N_1 \cdot N_2 \cdot N_3$$

v 1. B.C. je toliko dov. $\vec{k}$, kot N!

(Brillouinova cona!!)

Število dovoljenih $\vec{k}$ v primitivni celici recipročne mreže $\equiv$ številu točk B.R. v kristalu (št. prim. celic v kristalu)

$$V_B = \frac{(2\pi)^3}{V_C} \qquad \Delta\vec{k} = \frac{(2\pi)^3}{V} = \frac{(2\pi)^3}{V_C \cdot N}$$



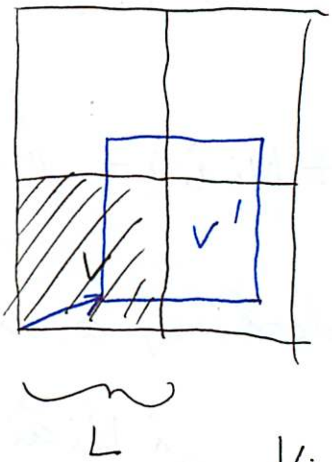
Drugi dokaz B.T. $\quad \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$

$$\psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\vec{r}} \qquad ; \; \vec{q} \text{ ustrezajo BK RP}$$

$U(\vec{r})$ je periodičen s periodo $\vec{R}$

$$U(\vec{r}) = \sum_{\vec{K}} U_{\vec{K}}\, e^{i\vec{K}\vec{r}}$$

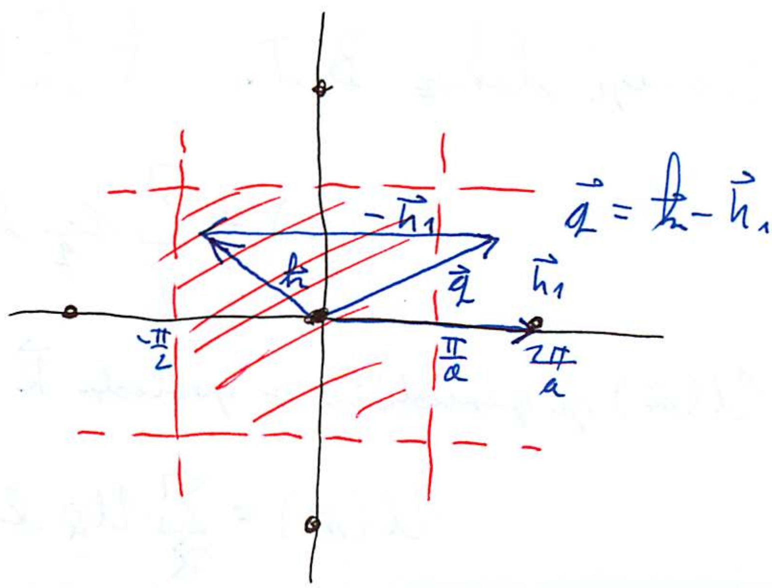
$$\int_V e^{i\vec{k}\vec{r}}\,d\vec{r} = \underbrace{\int_{V'} e^{i\vec{k}(\vec{r}+\vec{d})}\,d\vec{r}}_{\substack{\text{premik funk. ter} \\ \text{premik } V \to V'}} =$$



$$= \underbrace{\int_V e^{i\vec{k}(\vec{r}+\vec{d})}\,d\vec{r}}_{\text{zaradi periodičnosti}} \;;\; \text{velja za } \forall\, \vec{d}$$

V: vol. krožnih
+ BvK R.R.

$$\Rightarrow \left(e^{i\vec{k}\vec{d}} - 1\right) \underbrace{\int_V e^{i\vec{k}\vec{r}}\,d\vec{r}}_{0\ \forall\, \vec{k} \neq 0} = 0 \;;\; \text{to mora veljati za } \forall\, \vec{d},$$



$U_{\vec{k}}$ predstavlja Fourierovo komponento

$$U_{\vec{k}} = \frac{1}{v}\int_{cel} d\vec{r}\, e^{-i\vec{k}\vec{r}}\, U(\vec{r})$$

Dodatno zahtevamo, da velja: $U_0 = \frac{1}{v}\int_{cel} d\vec{r}\, U(\vec{r}) = 0$

$U(\vec{r})$ je tako določen do konstante.

Velja tudi $U_{-\vec{k}} = U_{\vec{k}}^*$, ker je $U(\vec{r})$ realen

Velja še: $U_{-\vec{k}} = U_{\vec{k}} = U_{\vec{k}}^*$ če velja $U(\vec{r}) = U(-\vec{r})$

– center inverzije!

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \sum_{\vec{q}} \frac{\hbar^2}{2m} q^2 c_{\vec{q}}\, e^{i\vec{q}\vec{r}}$$

$$U\psi = \sum_{\vec{k}\vec{q}} c_{\vec{q}} U_{\vec{k}}\, e^{i\underbrace{(\vec{q}+\vec{k})}_{\vec{q}\,'}\vec{r}} = \sum_{\vec{k}\vec{q}\,'} U_{\vec{k}}\, c_{\vec{q}\,'-\vec{k}}\, e^{i\vec{q}\,'\vec{r}}$$

$$\sum_{\vec{q}} e^{i\vec{q}\vec{r}} \left\{ \left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_{\vec{q}} + \sum_{\vec{k}'} U_{\vec{k}'}\, c_{\vec{q}-\vec{k}'} \right\} = 0$$

Ravni valovi, ki ustrezajo B.v.K. rob. pogojem so ortogonalni $\Rightarrow$

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_{\vec{q}} + \sum_{\vec{k}'} U_{\vec{k}'}\, c_{\vec{q}-\vec{k}'} = 0$$

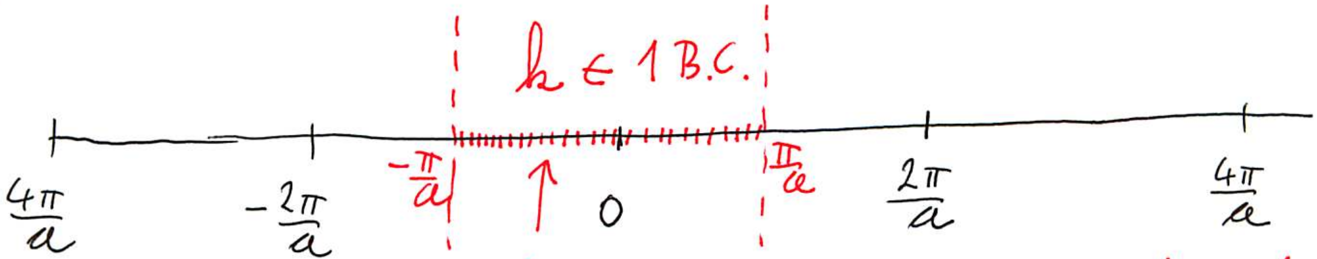
Transformacija: $\vec{q} = \vec{k} - \vec{K}$ tako, da je k znotraj prve Brillouinove c.

$$\left(\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2-\varepsilon\right)c_{\vec{k}-\vec{K}}+\sum_{\vec{K}'}U_{\vec{K}'}\,c_{\vec{k}-\vec{K}-\vec{K}'}=0$$

$$\vec{K}'\to\vec{K}'-\vec{K}$$

$$\left(\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2-\varepsilon\right)c_{\vec{k}-\vec{K}}+\sum_{\vec{K}'}U_{\vec{K}'-\vec{K}}\,c_{\vec{k}-\vec{K}'}=0$$

- Enačba je ~~f~~ enodelčna Schröd. enačba za primer, ko je $U(\vec{r})$ periodičen ⇒ Ima neničelne Fourierove komponente le pri $\vec{K}$ (vekt. rec. mreže!)
- za izbrani $\vec{k}$, obstaja set lin. enač. za $c_{\vec{k}-\vec{K}}$, ki se razlikujejo le za vektorji rec. mreže! Problem je razpadel na N neodvisnih problemov, saj v 1 B.C. obstaja le N različnih $\vec{k}$



vsled BvK periodičnih R.P., je vseh različnih k le N!

$$\psi_{\vec{k}}=\sum_{\vec{K}}c_{\vec{k}-\vec{K}}\,e^{i(\vec{k}-\vec{K})\vec{r}}=e^{i\vec{k}\vec{r}}\underbrace{\sum_{\vec{K}}c_{\vec{k}-\vec{K}}\,e^{-i\vec{K}\vec{r}}}_{u_{\vec{k}}(\vec{r})}$$

Periodična funkcija

$$\Downarrow$$

$$\psi_{\vec{k}}=e^{i\vec{k}\vec{r}}\sum_{\vec{K}}c_{\vec{k}-\vec{K}}\,e^{-i\vec{K}\vec{r}}=e^{i\vec{k}\vec{r}}\,u_{\vec{k}}(\vec{r})$$

Obravnava: $\left(\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2-\varepsilon\right)c_{\vec{k}-\vec{K}}+\sum_{\vec{K}'}U_{\vec{K}'-\vec{K}}\,c_{\vec{k}-\vec{K}'}=0$

a.) Primer prostih elektronov:

$U_{\vec{K}}=0$; ni pogoji, da bi moral biti $\vec{k}$ omejen na 1BC $\Rightarrow$

$$\left(\varepsilon^0_{\vec{k}-\vec{K}}-\varepsilon\right)c_{\vec{k}-\vec{K}}=0 \quad ; \quad \varepsilon^0_{\vec{q}}=\frac{\hbar^2 q^2}{2m}$$

Rešitev: $c_{\vec{k}-\vec{K}}=0$ ali $(\varepsilon_{\vec{k}-\vec{K}}-\varepsilon)=0\Rightarrow$

$$\varepsilon=\varepsilon_{\vec{k}-\vec{K}} \text{ ter } \psi_{\vec{k}}\propto e^{i(\vec{k}-\vec{K})\vec{r}}$$

b.) $U_{\vec{K}}$ je majhen $|U_{\vec{K}}|\ll\varepsilon^0_{\frac{\vec{K}}{2}}$; Nedegeneriran primer:

izberemo $\vec{k}$ in vzemimo $\vec{K}_1$ tak, da velja:

$$\left|\varepsilon^0_{\vec{k}-\vec{K}_1}-\varepsilon^0_{\vec{k}-\vec{K}}\right| \gg !! \ U \quad \text{za izbran } \vec{k} \text{ ter } \vec{K}\neq\vec{K}_1$$

Zanima nas vpliv U na el. stanje

$$\varepsilon\cong\varepsilon^0_{\vec{k}-\vec{K}_1}\ ; \ \text{ter } c_{\vec{k}-\vec{K}}=0 \text{ za } \vec{K}\neq\vec{K}_1$$

$$\text{ter } c_{\vec{k}-\vec{K}_1}\sim 1$$

$$\left(\varepsilon^0_{\vec{k}-\vec{K}_1}-\varepsilon\right)c_{\vec{k}-\vec{K}_1}+\sum_{\vec{K}}U_{\vec{K}-\vec{K}_1}\,c_{\vec{k}-\vec{K}}=0$$

Člen z $\vec{K}=\vec{K}_1$ je 0 ker $U_0=0$!

obdržimo le člen z $\vec{K}'=\vec{K}_1$!

$$\left(\varepsilon_{\vec{k}-\vec{K}}-\varepsilon\right)c_{\vec{k}-\vec{K}}+\sum_{\vec{K}'}U_{\vec{K}'-\vec{K}}\,c_{\vec{k}-\vec{K}'}=0$$

U in $c_{\vec{k}-\vec{K}'}$ sta oba majhna člena (za $\vec{K}'\neq\vec{K}_1$)

$$(\varepsilon - \varepsilon^0_{\vec k - \vec h_1})\, c_{\vec k - \vec h_1} = \sum_{\vec h} \frac{U_{\vec h - \vec h_1} U_{\vec h_1 - \vec h}}{(\varepsilon - \varepsilon^0_{\vec k - \vec h})}\, c_{\vec k - \vec h_1}$$

nadomestimo z $\varepsilon^0_{\vec k - \vec h_1}$

$$\varepsilon = \varepsilon^0_{\vec k - \vec h_1} + \sum_{\vec h} \frac{|U_{\vec h - \vec h_1}|^2}{\varepsilon^0_{\vec k - \vec h_1} - \varepsilon^0_{\vec k - \vec h}}$$ (popravek v II redu v U)

a.) Popravki reda U^2

b.) Predznak je odvisen od lege nivoja 0. $\vec k - \vec h$ glede na $\vec k - \vec h_1$

$\varepsilon^0_{\vec k - \vec h} < \varepsilon^0_{\vec k - \vec h_1} \Rightarrow O(U^2) > 0$ in obratno!

Degeneriran primer

$$|\varepsilon^0_{\vec k - \vec h_1} - \varepsilon^0_{\vec k - \vec h_2}| \sim U_{\vec h_1 - \vec h_2}$$

$$(\varepsilon^0_{\vec k - \vec h_1} - \varepsilon)\, c_{\vec k - \vec h_1} + U_{\vec h_2 - \vec h_1}\, c_{\vec k - \vec h_2} = 0$$

$$(\varepsilon^0_{\vec k - \vec h_2} - \varepsilon)\, c_{\vec k - \vec h_2} + U_{\vec h_1 - \vec h_2}\, c_{\vec k - \vec h_1} = 0$$

Nazaj na $\boxed{\vec q = \vec k - \vec h_1 \text{ ter } \vec h = \vec K_2 - \vec h_1}$!

$$(\varepsilon - \varepsilon^0_{\vec q})\, c_{\vec q} - U_{\vec h}\, c_{\vec q - \vec h} = 0$$

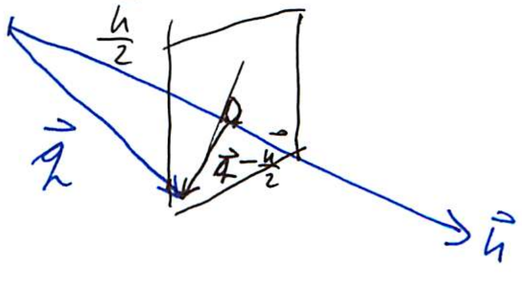
$$(\varepsilon - \varepsilon^0_{\vec q - \vec h})\, c_{\vec q - \vec h} - U_{-\vec h}\, c_{\vec q} = 0$$

Ta pomeni pogoj $\varepsilon^0_{\vec q} \sim \varepsilon^0_{\vec q - \vec h} \Rightarrow q = |\vec q - \vec h| \Rightarrow$

$\vec q$ leži na Braggovi ravnini

$\vec q$ leži blizu Braggove ravnine

$q \sim |\vec q - \vec h|$



Bližina B.R:

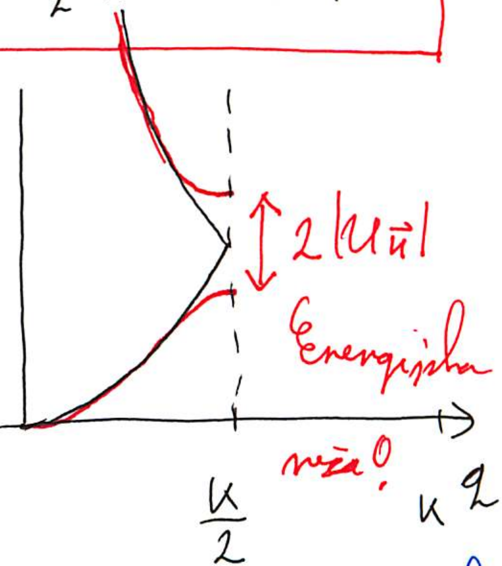
$$\begin{vmatrix} \varepsilon - \varepsilon^0_{\vec q} & -U_K \\ U_K^* & \varepsilon - \varepsilon^0_{\vec q - \vec K} \end{vmatrix} = 0$$

$$\Rightarrow \boxed{\varepsilon_{(\vec q)} = \frac{1}{2}\left(\varepsilon^0_{\vec q} + \varepsilon^0_{\vec q - \vec K}\right) \pm \frac{1}{2}\sqrt{\left(\varepsilon^0_{\vec q} - \varepsilon^0_{\vec q - \vec K}\right)^2 + 4|U_K|^2}}$$

Na B.R.

Popravek v I redu v U

$$\varepsilon = \varepsilon^0_{\vec q} \pm |U_K|$$



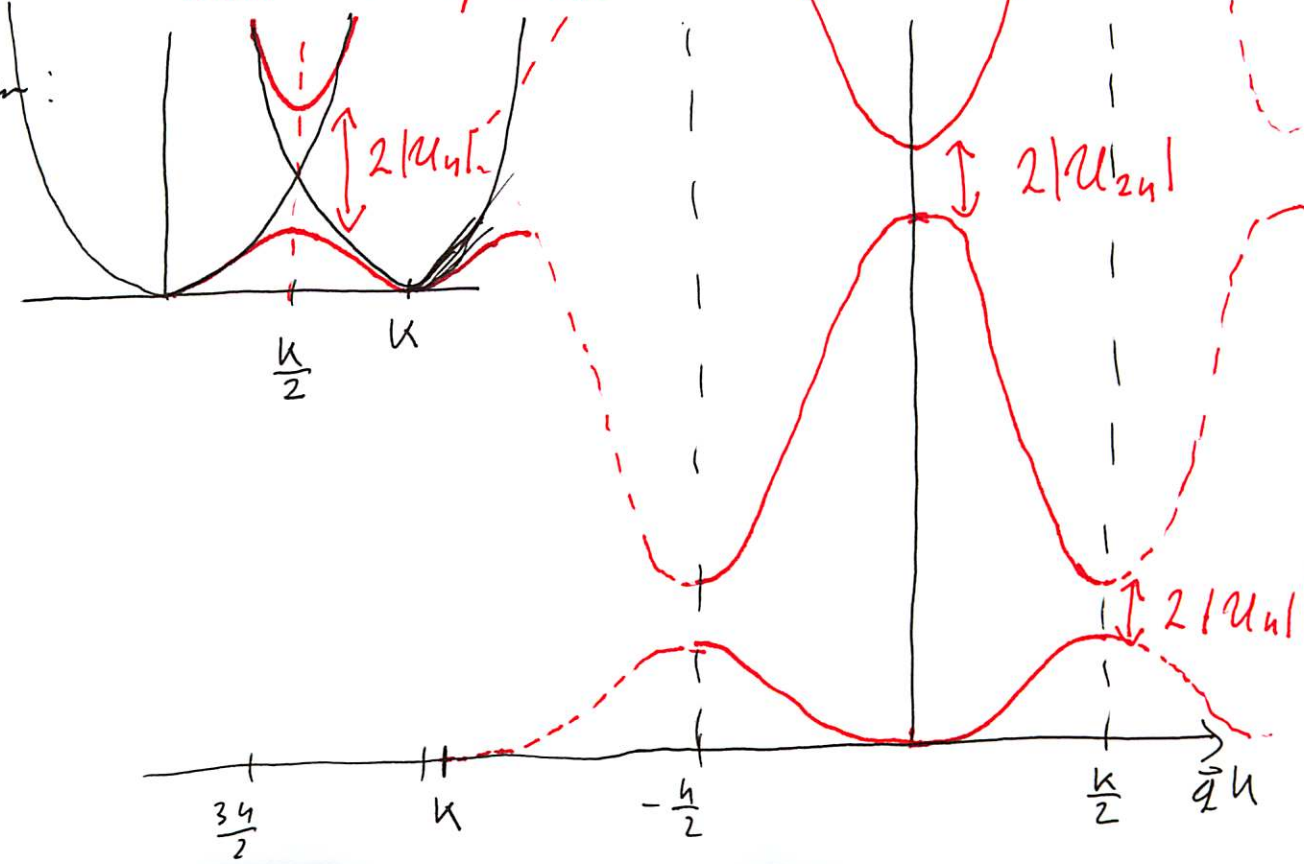
$$\frac{\partial \varepsilon}{\partial \vec q} = \frac{\hbar^2}{m}\left(\vec q - \frac{1}{2}\vec K\right)$$

$\Rightarrow$ $\vec\nabla \varepsilon(\vec q)$ na Braggovi ravnini leži v ravnini $\Rightarrow$ $\varepsilon(\vec q) =$ konst

Ploskve konstantne energije so $\perp$ na Braggove ravnine!

Nastanek pasov:

1-D primer:



Oblika val. funkcij:

Na Braggovi ravnini

$$\varepsilon_{\vec q} = \varepsilon^0_{\vec q} \pm U_{\vec h} \quad ; \quad c_{\vec q} = \pm \operatorname{sign}|U_h|\, c_{\vec q-\vec h}$$

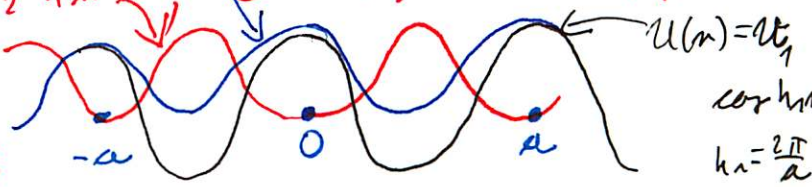
za $U_h > 0$

$$|\psi(\vec r)|^2 \propto \left| e^{i\vec q\vec r} + e^{i(\vec q-\vec h)\vec r} \right|^2$$

$$= 2 + e^{i\vec h\vec r} + e^{-i\vec h\vec r} = 2(1+\cos\vec h\vec r) = 4\cos^2\frac{\vec h\vec r}{2}$$

$|\psi(\vec r)|^2 \propto \left(\cos\frac{1}{2}\vec h\vec r\right)^2$; $\varepsilon = \varepsilon^0_{\vec q} + |U_{\vec h}|$; s-like

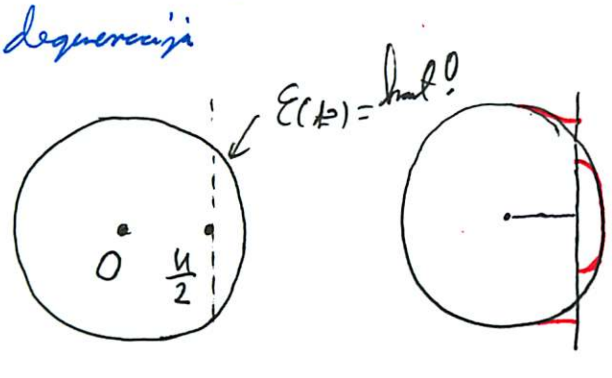
$|\psi(\vec r)|^2 \propto \left(\sin\frac{1}{2}\vec h\vec r\right)^2$; $\varepsilon = \varepsilon^0_{\vec q} - |U_{\vec h}|$; p-like

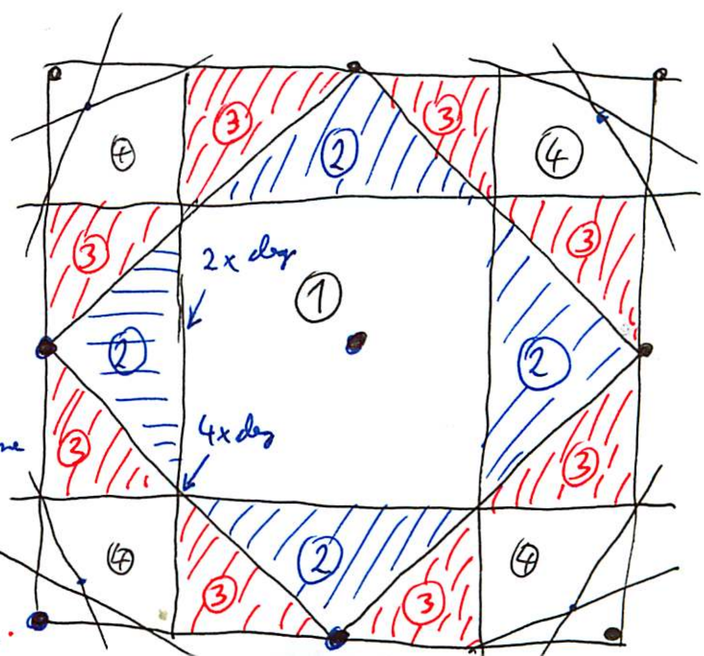


$\varepsilon_{\vec q}$ v 3D:

- Običajno izberemo določeno smer v k prostoru
- Slika $\varepsilon^0_{\vec q} = \varepsilon_{\vec k-\vec h} = \frac{\hbar^2}{2m}(\vec k-\vec h)^2$ za FCC Ashcroft (161)!
- V kolikor je izbrana smer v k prostoru težki simetrijska os ⇒ visoka degeneracija

n-ta B.C. predstavlja množico točk, ki izvirajo iz n-te točke v h prostoru.





1, 2, ..., Brillouinova cona:

1. Množica točk v k prostoru, do katere pridemo iz izhodišča brez prečkanja Braggove ravnine
2. ... en-kratnim prečkanjem Bragg. r.

Konstrukcija pasov:

- Narišemo si (označimo) najmanjše $|\vec{K}|$, ki so najbližji središču $\vec{K}=0$. Poiščemo Braggove ravnine, ki omejujejo 1. BC. ter izračunamo razcepe (pasove) v bližini teh ravnin. Pazi: $\overset{\circ}{\mathcal{E}}(k) = \mathcal{E}(k-\vec{K}_i)$; kjer so K_i najmanjši možni 0.

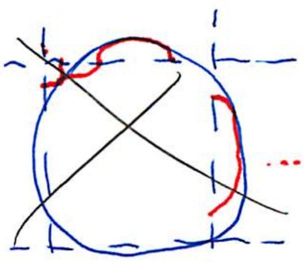
Fermijeva površina ter gostota stanj

$$\mathcal{E}_n(k) = \mathcal{E}_F$$

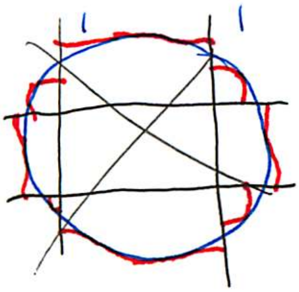
pas val. vektor.

- Konstrukcija: a.) Narišemo F. S., centrirano v $k=0$

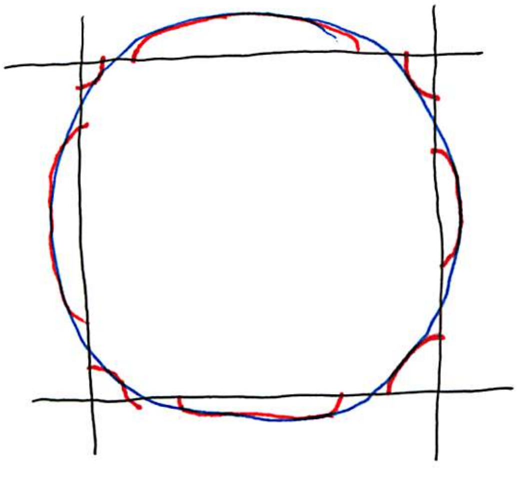
b.) F. S. bo deformirana vsakič, ko prebada Braggovo ravnino. Če se v neki točki križa več B. R., je situacija še dodatno zapletena



c.) Tako dobimo deformacijo F. S prostih e^- v razširjeni k-shemi.



d.) Nato s translacijami za $\vec{K}_i$ "prepognemo" v reducirano cono ⇒ deformirani deli F. S. prispevajo različnim pasovom.



Density of states – Gostota el. stanj

Sumiranje preko el. stanj (splošno):

↙ Splošna funkcija

$$Q = 2\sum_{n\,\mathbf{k}} Q_n(\mathbf{k}) \quad ; \quad \mathbf{k} \text{ znotraj 1. B.C., vsota po vseh pasovih}$$

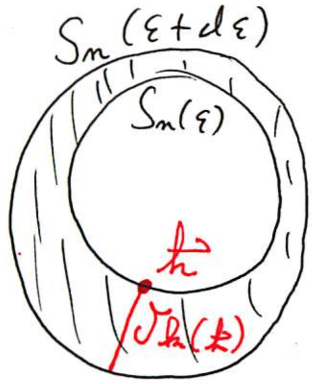
$$q = \lim_{V\to\infty} \frac{Q}{V} = 2\sum_n \frac{d\mathbf{k}}{(2\pi)^3} Q_n(\mathbf{k}) = \int d\varepsilon\, g(\varepsilon)\, Q(\varepsilon)$$

$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

$$g_n(\varepsilon) = \int \frac{d\mathbf{k}}{4\pi^3}\, \delta\big(\varepsilon - \varepsilon_n(\mathbf{k})\big)$$

Alternativna predstava:

$$g_n(\varepsilon)\, d\varepsilon = \int \frac{d\mathbf{k}}{4\pi^3} \begin{cases} 1; & \varepsilon \le \varepsilon_n(\mathbf{k}) \le \varepsilon + d\varepsilon \\ 0; & \text{sicer} \end{cases}$$



$$g_n(\varepsilon)\, d\varepsilon = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3}\, \delta k(\mathbf{k})$$

$$\varepsilon + d\varepsilon = \varepsilon + |\vec{\nabla}\varepsilon_n(\mathbf{k})|\, \delta k(\mathbf{k})$$

$$\delta k(\mathbf{k}) = \frac{d\varepsilon}{|\vec{\nabla}\varepsilon_n(\mathbf{k})|}$$

$$\boxed{g_n(\varepsilon) = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3 |\vec{\nabla}\varepsilon_n(\mathbf{k})|}}$$