2. Elektróny v periodickom potenciáli

Predpoklady: 1. jednoelektrónová aproximácia

2. dokonalý kryštál

$$H\psi = \varepsilon \psi \qquad \text{kde} \qquad H = -\frac{\hbar^2}{2m}\Delta + V(\vec{r})$$

A) $V(\vec{r})$: periodická funkcia $\quad V(\vec{r} + \underbrace{n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}_{\vec{R}}) = V(\vec{r})$

Definujme

$$\vec{b}_1 = \frac{2\pi\, \vec{a}_2 \times \vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)} \qquad \vec{b}_1\cdot\vec{a}_1 = 2\pi \quad \vec{b}_1\cdot\vec{a}_2 = \vec{b}_1\cdot\vec{a}_3 = 0$$

$$\vec{b}_2 = \frac{2\pi\, \vec{a}_3 \times \vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)} \qquad \boxed{\vec{b}_i\cdot\vec{a}_j = 2\pi\,\delta_{ij}}$$

$$\vec{b}_3 = \frac{2\pi\, \vec{a}_1 \times \vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

všeobecný vektor inverznej mriežky: $\vec{K} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$.

platí: $e^{i\vec{K}\cdot\vec{R}} = e^{2\pi i(m_1n_1 + m_2n_2 + m_3n_3)} = 1$

preto $\boxed{V(\vec{r}) = \sum_{\vec{K}} V_{\vec{K}}\, e^{i\vec{K}\cdot\vec{r}}}$

naozaj: $V(\vec{r}+\vec{R}) = V(\vec{r})$
harmonicky s $\vec{k} \neq \vec{K}$ v sume nevystupujú
(nemajú správnu periodicitu)

inverzná transf.: $\boxed{V_{\vec{K}} = \frac{1}{\Omega_{cell}}\int_{cell} d^3r\, V(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}}} \longrightarrow \boxed{V_K^* = V_{-K}}$

(lebo $V(\vec{r})$ je reálny)

Naozaj: $\vec{r} = t\vec{a}_1 + u\vec{a}_2 + v\vec{a}_3 \qquad \int_{cell} d^3r = \overbrace{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}^{\Omega_{cell}}\int_0^1 dt\int_0^1 du\int_0^1 dv$

$$V_{\vec{K}} = \frac{1}{\Omega_{cell}}\int d^3r \sum_Q V_Q\, e^{i(Q-K)\cdot r} = \frac{1}{\Omega_{cell}}\sum_Q V_Q \int d^3r\, e^{i(Q-K)\cdot r}$$

$$= \sum_Q V_Q \int_0^1 dt\int_0^1 du\int_0^1 dv\; e^{2\pi i(\delta m_1 t + \delta m_2 u + \delta m_3 v)} = V_K \quad \text{qed}$$

B) Blochova veta $\quad \psi = \sum_k c_k e^{i k\cdot \vec{r}} \qquad \varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$

$$H\psi = \varepsilon\psi \rightarrow \sum_k e^{i\vec{k}\cdot\vec{r}} \underbrace{\boxed{\sum_K \left[(\varepsilon_k^0 - \varepsilon)\delta_{K0} + V_K\right] c_{k-K}}}_{\stackrel{!}{=}0} = 0 \qquad (B1)$$

Teda $e^{i\vec{k}\cdot\vec{r}}$ je zviazané so všetkými vlnami typu $e^{i(k-K)\cdot\vec{r}}$

$$\boxed{\psi_k = e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_K c_{k-K} e^{-iK\cdot\vec{r}}}_{\text{periodická funkcia}}}$$

periodická funkcia $\longrightarrow$ $\boxed{\psi_k = e^{i\vec{k}\cdot\vec{r}} \underbrace{u_k(\vec{r})}_{\text{periodická funkcia}}}$ Blochova funkcia

$$u_k(\vec{r}) = \sum_K c_{k-K} e^{-iK\cdot r}$$

dosadíme do SchR

$$\boxed{\left[\frac{\hbar^2}{2m}(-i\vec{\nabla} + \vec{k})^2 + V(\vec{r})\right] u_k(\vec{r}) = \varepsilon_k u_k(\vec{r})} \qquad (B2)$$

s hraničnou podmienkou $u_k(\vec{r} + \vec{R}) = u_k(\vec{r})$

diskrétne spektrum : $\boxed{\begin{array}{l}\psi_{nk} = \frac{1}{\sqrt{\Omega}} e^{i k\cdot\vec{r}} u_{nk}(\vec{r}) \\ \varepsilon_{nk} \text{ -- vl. hodnota}\end{array}}$

Budeme žiadať $\int d^3r\, |\psi_{nk}(\vec{r})|^2 = 1 \longrightarrow \boxed{\frac{1}{\Omega_{cell}} \int_{cell} d^3r\, |u_{nk}(\vec{r})|^2 = 1}$

Z rovnice (B2) vyplýva: $\boxed{\int d^3r\, \psi_{mk}^*(\vec{r})\, \psi_{nk}(\vec{r}) = \delta_{mn}}$

ukážeme tiež $\boxed{\int d^3r\, \psi_{mp}^*(\vec{r})\, \psi_{nk}(\vec{r}) = \delta_{mn}\delta_{kp}}$

Naozaj:

$$\frac{1}{\Omega}\int d^3r\, e^{-i\vec{p}\cdot\vec{r}} u_{mp}^*(\vec{r}) e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r}) = \frac{1}{\Omega}\sum_R \int_{cell} d^3\rho\, e^{i(k-p)\cdot(R+\rho)} u_{mp}^*(\rho) u_{nk}(\rho)$$

$$\langle mp|nk\rangle = \frac{1}{\Omega}\sum_R e^{i(k-p)\cdot R}\int_{cell} d^3\rho\, e^{i(k-p)\cdot\rho}\, u^*_{mp}(\rho)\, u_{nk}(\rho)$$

$$\Omega = N_1 N_2 N_3\, \Omega_{cell}$$

$$\vec{k}-\vec{p} = \vec{q} = \sum_{i=1}^{3} n_i \vec{b}_i \qquad \vec{R} = \sum_{j=1}^{3} m_j \vec{a}_j$$

$$\frac{1}{N_1N_2N_3}\sum_R e^{i\vec{q}\cdot\vec{R}} = \underbrace{\left(\frac{1}{N_1}\sum_{m_1} e^{i2\pi n_1 m_1}\right)}_{\delta_{n_1 0}}\underbrace{\left(\frac{1}{N_2}\sum_{m_2} e^{i2\pi n_2 m_2}\right)}_{\delta_{n_2 0}}\underbrace{\left(\frac{1}{N_3}\sum_{m_3} e^{i2\pi n_3 m_3}\right)}_{\delta_{n_3 0}}$$

$$\rightarrow \boxed{\frac{1}{N}\sum_R e^{i\vec{q}\cdot\vec{R}} = \delta_{\vec{q}0}}$$

$$\langle mp|nk\rangle = \delta_{kp}\,\frac{1}{\Omega_{cell}}\int d^3\rho\, u^*_{mk}(\rho)\, u_{nk}(\rho) = \delta_{kp}\,\delta_{mn} \quad \text{qed}$$

C) Takmer voľné elektróny – 1D prípad

pre začiatok uvažujme potenciál, pre ktorý $V_K = 0$ pre všetky K, okrem $V_G = V^*_{-G}$, $G = \frac{2\pi}{a}$. Nech potenciál je veľmi slabý

$$(B1) \rightarrow \begin{cases} (\varepsilon^0_k - \varepsilon)c_k + V_G c_{k-G} + V_{-G} c_{k+G} = 0 & \\ (\varepsilon^0_{k-G} - \varepsilon)c_{k-G} + V_G c_{k-2G} + V_{-G} c_k = 0 & (k\to k-G) \\ (\varepsilon^0_{k+G} - \varepsilon)c_{k+G} + V_G c_k + V_{-G} c_{k+2G} = 0 & (k\to k+G) \\ \vdots & \end{cases}$$

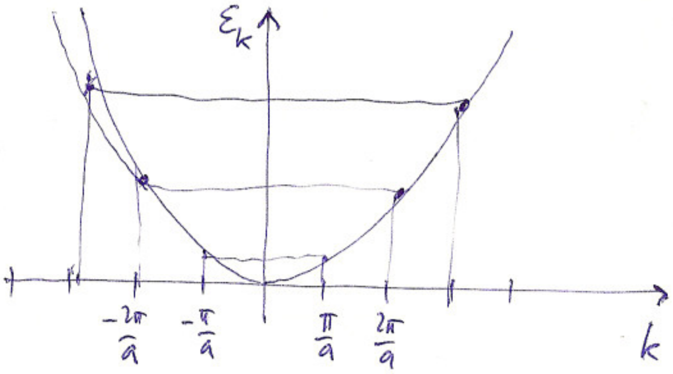
Poruchové riešenie: $c_k = O(1)$, $c_{k\pm G} = O(V^1)$, $c_{k\pm 2G} = O(V^2)$, ...

zanedbať

4 Teda máme riešiť úlohu o vl. číslach a vektoroch:

$$\begin{pmatrix} \varepsilon_{k-G}^0 & V_{-G} & 0 \\ V_G & \varepsilon_k^0 & V_{-G} \\ 0 & V_G & \varepsilon_{k+G}^0 \end{pmatrix} \begin{pmatrix} c_{k-G} \\ c_k \\ c_{k+G} \end{pmatrix} = \varepsilon \begin{pmatrix} c_{k-G} \\ c_k \\ c_{k+G} \end{pmatrix}$$

$$\varepsilon = \varepsilon_k^0 + \frac{|V_G|^2}{\varepsilon_k^0 - \varepsilon_{k-G}^0} + \frac{|V_G|^2}{\varepsilon_k^0 - \varepsilon_{k+G}^0}$$ ... malá korekcia, okrem $\varepsilon_k^0 \approx \varepsilon_{k\pm G}^0$



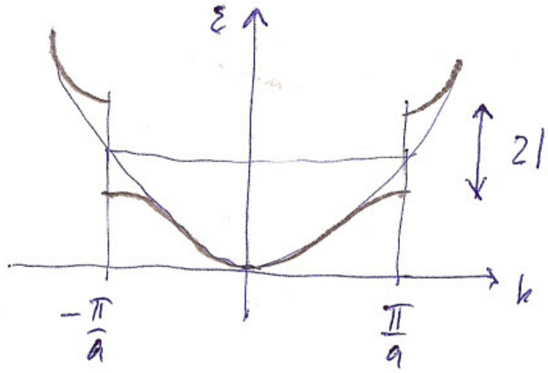
← nie je možné, aby zároveň boli tri energie $\varepsilon_k^0 \approx \varepsilon_{k+G}^0 \approx \varepsilon_{k-G}^0$

Vyberme $\varepsilon_k^0 \approx \varepsilon_{k-G}^0 \longrightarrow k \approx \frac{\pi}{a}$

$$\begin{pmatrix} \varepsilon_{k-G}^0 & V_{-G} \\ V_G & \varepsilon_k^0 \end{pmatrix} \begin{pmatrix} c_{k-G} \\ c_k \end{pmatrix} = \varepsilon \begin{pmatrix} c_{k-G} \\ c_k \end{pmatrix} \longrightarrow \boxed{\varepsilon = \frac{\varepsilon_k^0 + \varepsilon_{k-G}^0}{2} \pm \sqrt{\left(\frac{\varepsilon_k^0 - \varepsilon_{k-G}^0}{2}\right)^2 + |V_G|^2}}$$

$$\psi_k(x) = c_k e^{ikx} + c_{k-G} e^{i(k-G)x}$$

Teda dostaneme:



$2|V_G|$ .. zakázaný pás energií

uvažujme $V_G = |V_G| = V_{-G}$

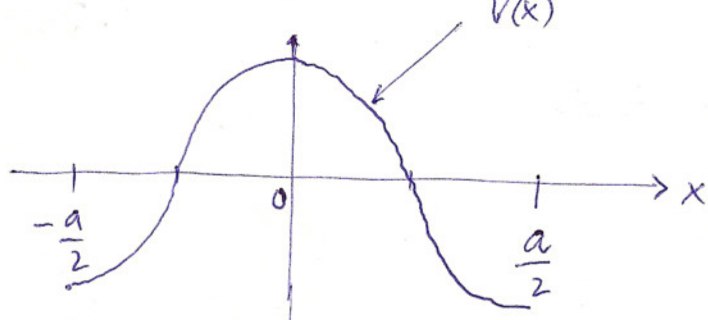
pre $k = \frac{\pi}{a}$ ... $\psi_{\frac{\pi}{a}}(x) \propto \frac{1}{\sqrt{2L}} \left(e^{i\frac{\pi x}{a}} \pm e^{-i\frac{\pi x}{a}} \right)$

$\psi_+(x) = \sqrt{\frac{2}{L}} \cos\frac{\pi x}{a}$ ... $\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 + |V_G|$

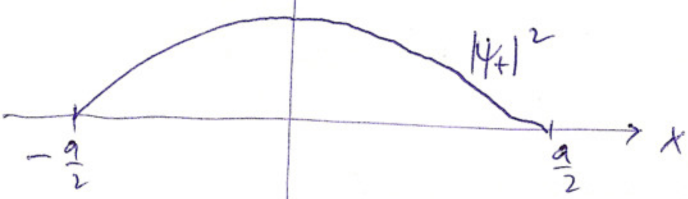
$\psi_-(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{a}$ ... $\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 - |V_G|$

$V(x) = 2|V_G| \cos\frac{2\pi x}{a}$

$\left.\begin{matrix}\psi_+(x)\\ \psi_-(x)\end{matrix}\right\}$: stojaté vlny

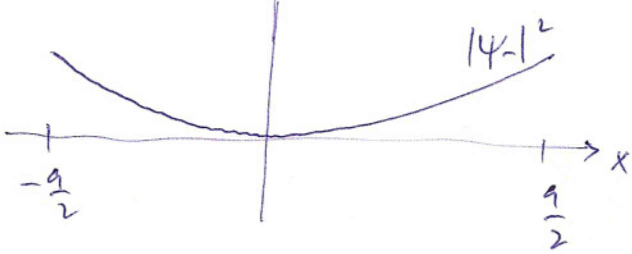


vyššia energia



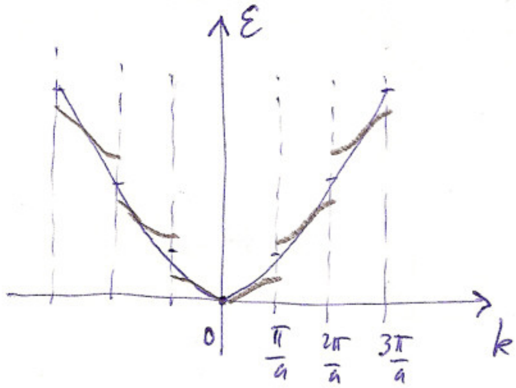
$|\psi_+(x)|^2 = \frac{1}{L}\left(1 + \cos\frac{2\pi x}{a}\right)$

nižšia energia

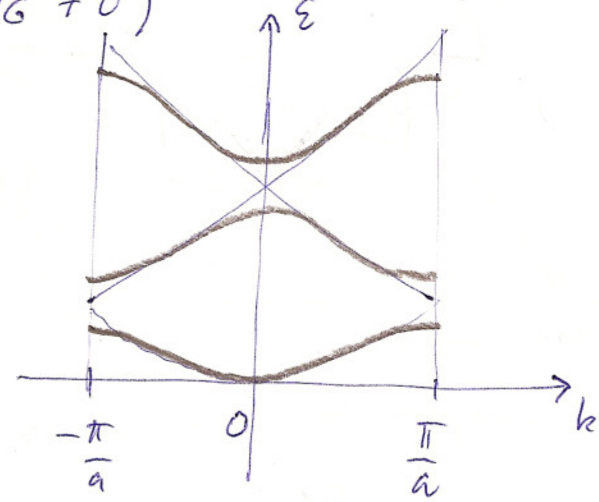


$|\psi_-(x)|^2 = \frac{1}{L}\left(1 - \cos\frac{2\pi x}{a}\right)$

1D – všeobecný potenciál (všetky $V_G \neq 0$)



rozšírená zóna



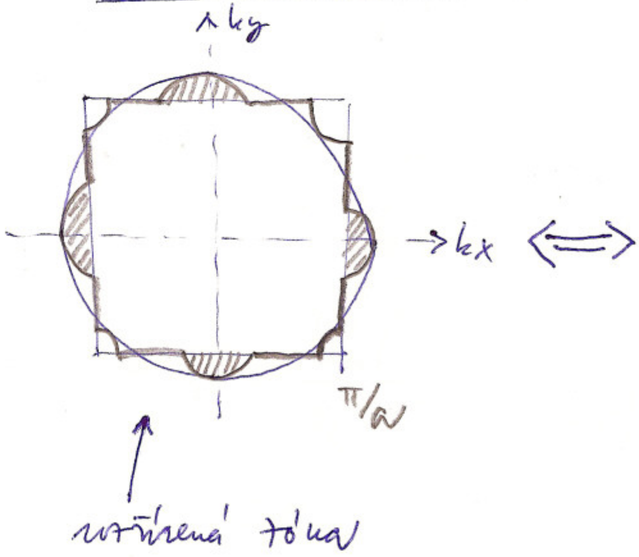
1. Brillouinova zóna

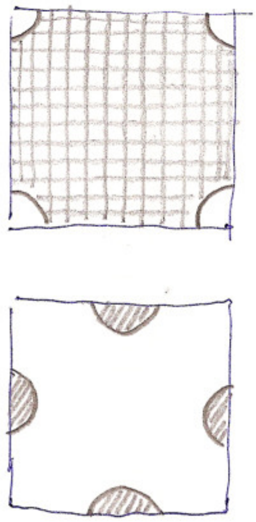
Počet stavov v páse: $\underset{\substack{\uparrow \\ \text{spin}}}{2} \cdot \frac{2\pi/a}{2\pi/L} = 2N$ $\quad N = \frac{L}{a}$ = počet element. buniek

izolant: úplne zaplnené pásy → párny počet elektrónov / bunku

kov : neúplne zaplnené pásy ← napr. nepárny počet elektrónov / bunku

D) Takmer voľné elektróny – 2D prípad

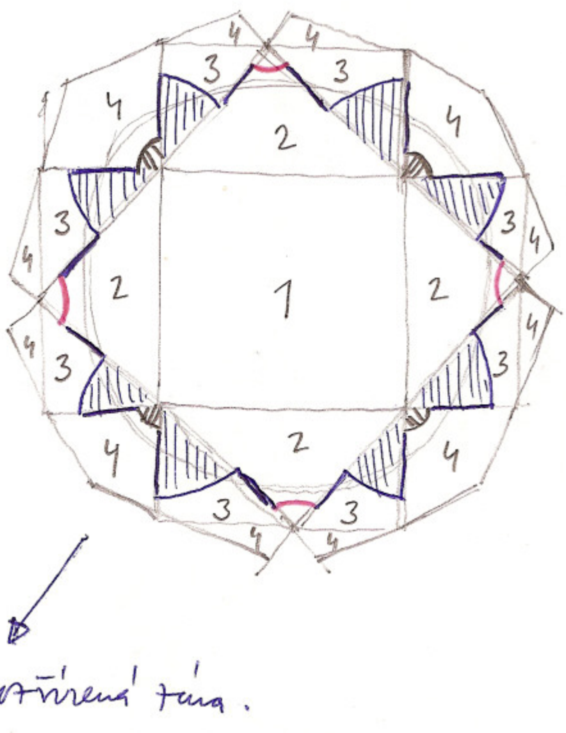




1. Brillouinova zóna

2. Brillouinova zóna

ekvienergetická plocha pre väčšie energie:

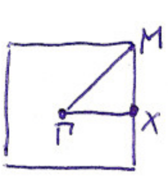


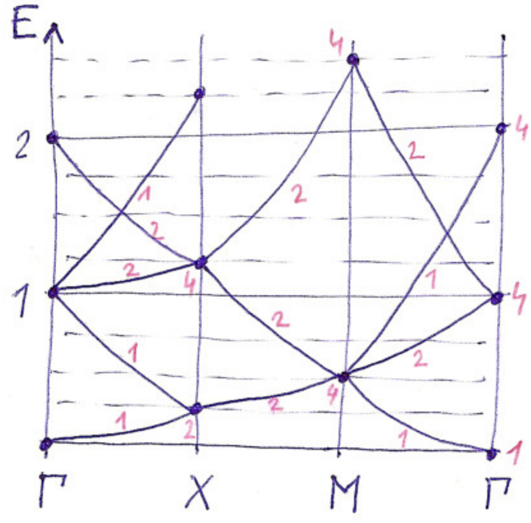
2. zóna

3. zóna

4. zóna

Fermiho plocha = viac-menej kruh





↑ energia v jednotkách $\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2$

Degenerovaná formdová kôňa v bode M, $\varepsilon = \frac{1}{2}\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2$:

4 degenerované vln. funkcie $e^{iG(\pm x \pm y)}$ $\qquad G = \frac{\pi}{a}$

4×4 Hamiltonián:

$$\begin{array}{c|cccc}
 & ++ & +- & -+ & -- \\
\hline
++ & \varepsilon+V_0 & V_1 & V_1 & V_2 \\
+- & V_1 & \varepsilon+V_0 & V_2 & V_1 \\
-+ & V_1 & V_2 & \varepsilon+V_0 & V_1 \\
-- & V_2 & V_1 & V_1 & \varepsilon+V_0
\end{array}$$

$$V_0 = V(0,0)$$
$$V_1 = V\left(\tfrac{2\pi}{a},0\right) = V\left(0,\tfrac{2\pi}{a}\right)$$
$$V_2 = V\left(\tfrac{2\pi}{a},\tfrac{2\pi}{a}\right)$$
$$V_K = V_{-K}$$

vlastné čísla a vektory:

$$\varepsilon + V_0 + 2V_1 + V_2 \; ; \; \begin{pmatrix}1\\1\\1\\1\end{pmatrix} \Longleftrightarrow \psi(x,y) \propto \cos Gx \cos Gy \propto \text{const}$$

$$\varepsilon + V_0 - 2V_1 + V_2 \; ; \; \begin{pmatrix}1\\-1\\-1\\1\end{pmatrix} \Longleftrightarrow \psi(x,y) \propto \sin Gx \sin Gy \propto xy$$

$\varepsilon + V_0 - V_2 \longrightarrow$ 2x degenerovaný koreň

$$\left.\begin{array}{l}
\begin{pmatrix}1\\-1\\1\\-1\end{pmatrix} \Longleftrightarrow \psi(x,y) \propto \cos Gx \sin Gy \\
\begin{pmatrix}1\\1\\-1\\-1\end{pmatrix} \Longleftrightarrow \psi(x,y) \propto \sin Gx \cos Gy
\end{array}\right\} \propto \begin{pmatrix}x\\y\end{pmatrix}$$