Výpočty pásových struktur

- reciproký prostor k-vektorů, Brillouinovy zóny
- sekulární rovnice, variační metoda
- pásová struktura, periodický potenciál
- hustota stavů, Fermiho energie
- metoda téměř volných elektronů
- metoda těsné vazby, MO-LCAO, Blochovy funkce

- T. A. Albright, J. K. Burdett, M.-H. Whangbo, Wiley (2013)
  Orbital Interactions In Chemistry.
- J. K. Burdett, Progress in Solid State Chemistry 15 (1984) 173-255
  From Bonds to Bands and Molecules to Solids.
- E. Canadell , M.-H. Whangbo, Chem. Rev. 91 (1991) 965-1034
  Conceptual aspects of structure-property correlations and electronic instabilities, with applications to low-dimensional transition-metal oxides.
- R. Hoffmann, Angew. Chem. Int. Ed. Engl. 26 (1987) 846-878
  How chemistry and physics meet in the solid state.
- G. L. Miessler, P. J. Fischer, D. A. Tarr: Inorganic chemistry 5th ed., chap.5
  Molecular Orbitals.
- S. Cottenier (2013)
  Density Functional Theory and the Family of (L)APW-methods: a step-by-step introduction.

http://lom.fzu.cz/main/lom/krystalochemie/index.html
http://lom.fzu.cz/main/lom/chapl/index.html

prostor čísel ***k*** - reciproký prostor, ***k*** – prostor

Reálný (přímý) prostor: V_r krystalová mříž

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3 \qquad \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

Reciproký prostor: V_c reciproká mříž

$$\mathbf{g} = u\mathbf{b}_1 + v\mathbf{b}_2 + w\mathbf{b}_3 \qquad \mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_r} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_r} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_r}$$

$$V_r = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$
$$V_c = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) \qquad V_c = \frac{8\pi^3}{V_r}$$

k - vlnový vektor

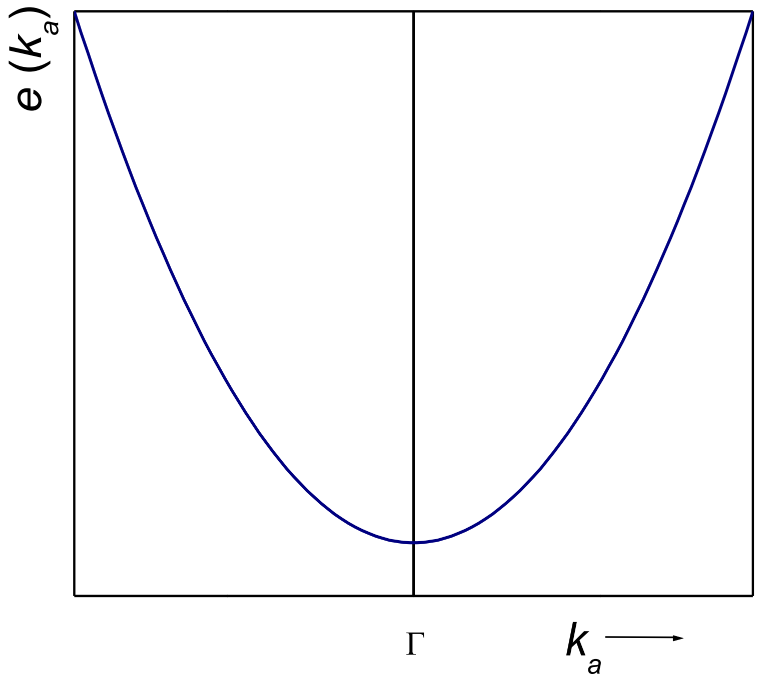
$$k = \frac{2\pi}{\lambda}$$

de Broglie: $\vec{p} = m\vec{v} = \frac{h}{\vec{\lambda}} = \hbar\vec{k}$

$$\Phi(t, \vec{r}) = e^{-i(\vec{k}\vec{r} - \omega t)}$$

počet dovolených hodnot ***k*** = počet elementárních buněk v krystalu

volné elektrony: $E = \frac{mv^2}{2} = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 k^2}{2m}$

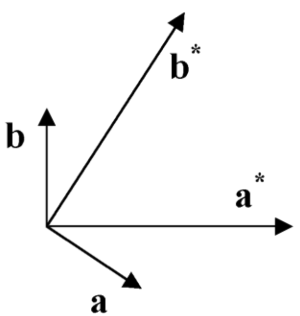


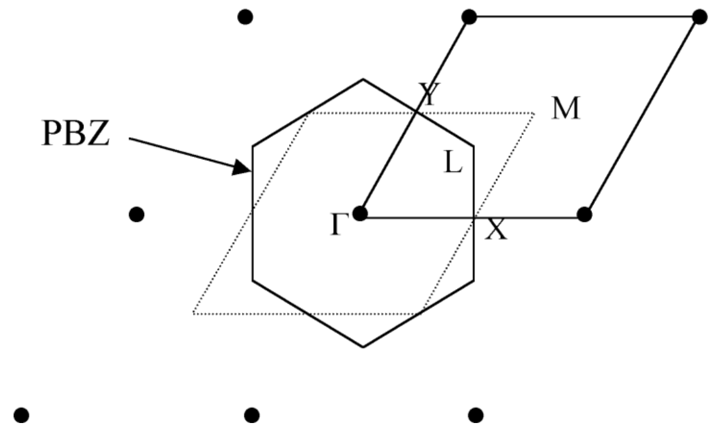
platí: - $E(\boldsymbol{k}) = E(-\boldsymbol{k})$
- pro každé ***k*** v rámci jednoho pásu je jedna hodnota *E*
- $E(\boldsymbol{k})$ je periodickou funkcí k, stačí prezentovat v intervalu $(-\pi/a\ ;\ \pi/a)$ - první Brillouinova zóna v jednom rozměru

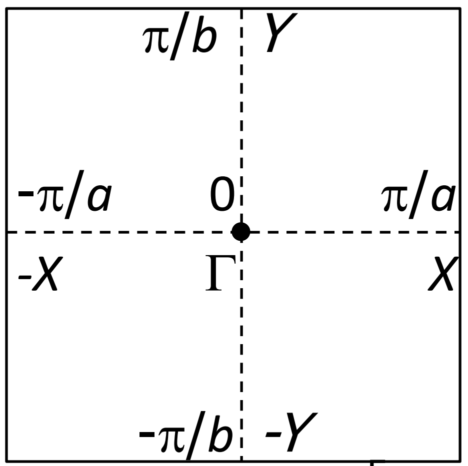
první Brillouinova zóna – Wignerova-Seitzova buňka v reciproké mříži

Wignerova-Seitzova buňka je primitivní a má vždy stejnou symetrii jako mříž (primitivní krystalografická buňka může mít nižší symetrii než mříž)

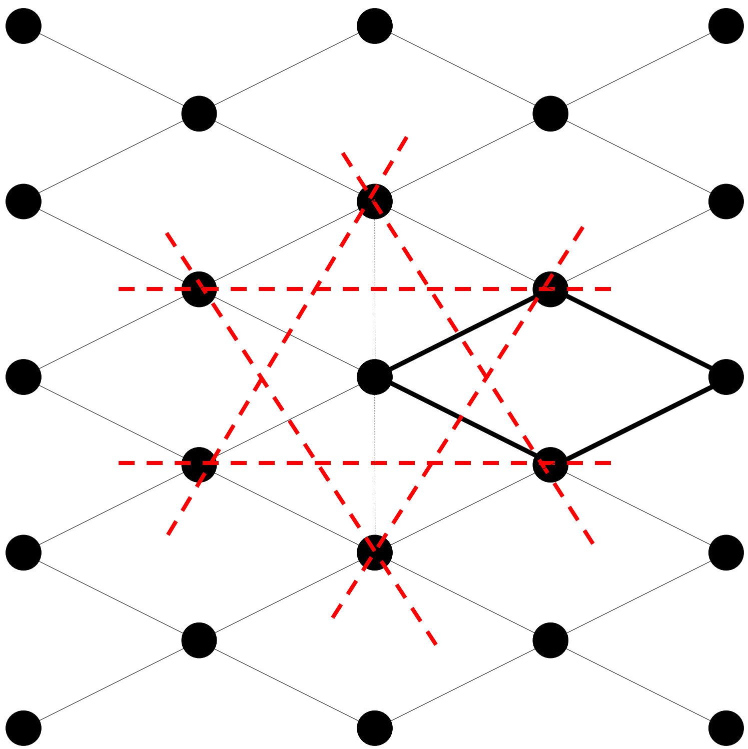
konstrukce: roviny kolmé k $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ vedené v bodech $\pm\,\mathbf{b}_1,\ \pm\,\mathbf{b}_2,\ \pm\,\mathbf{b}_3$

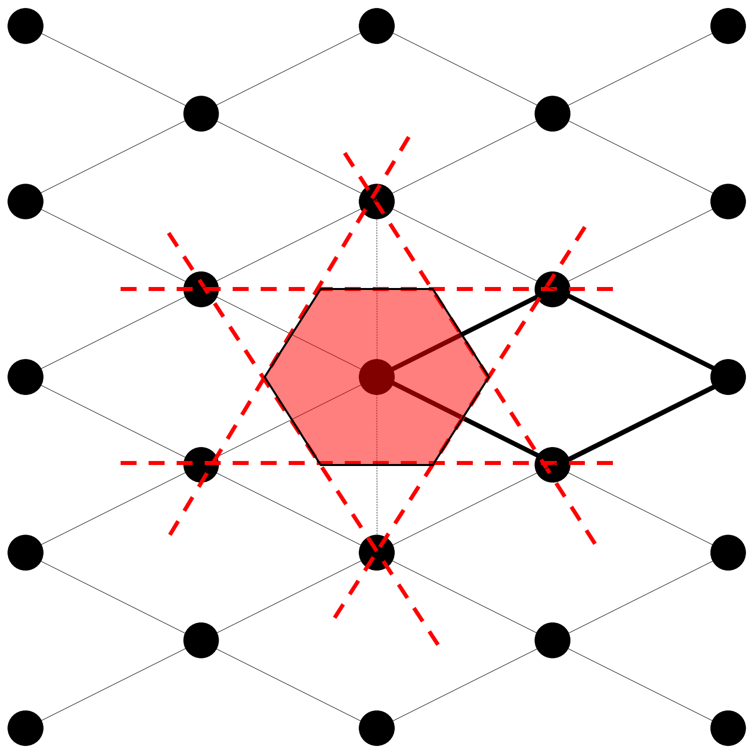


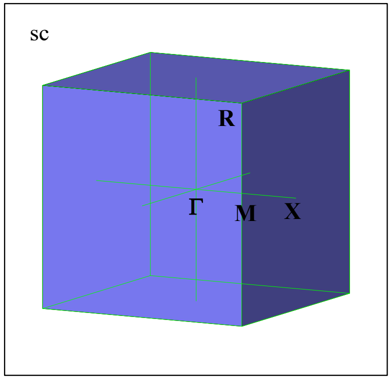




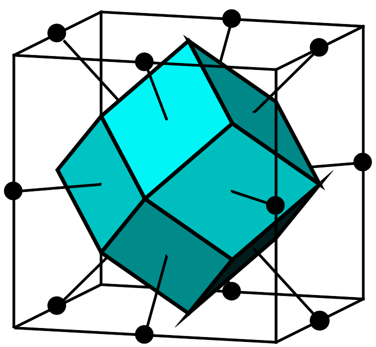
Brillouinovy zóny





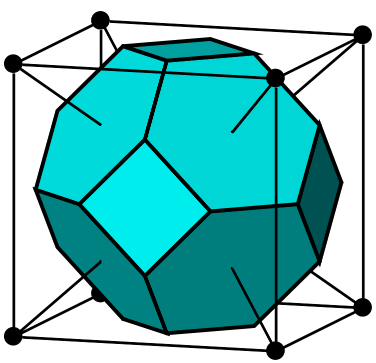


simple cubic



bcc

- bcc v přímém prostoru odpovídá fcc v reciprokém prostoru
- rombický dodekaedr



fcc

- fcc v přímém prostoru odpovídá bcc v reciprokém prostoru
- komolý oktaedr

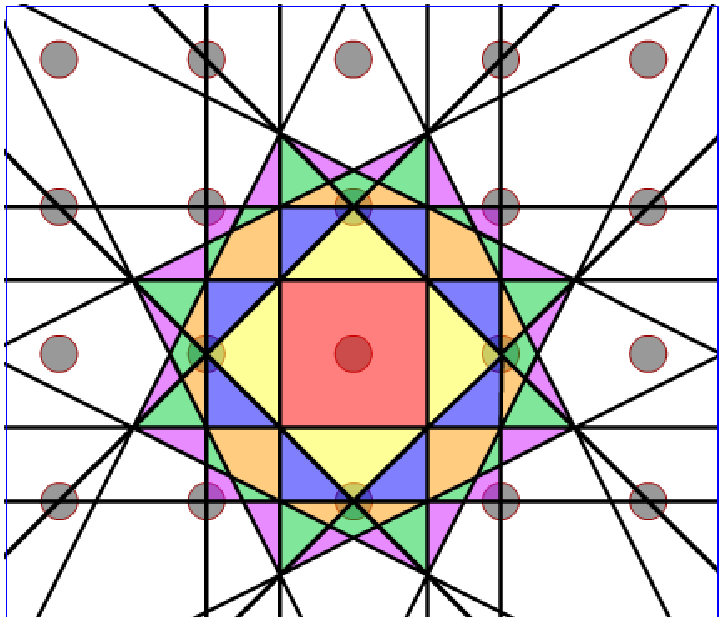
Brillouinovy zóny vyššího řádu:

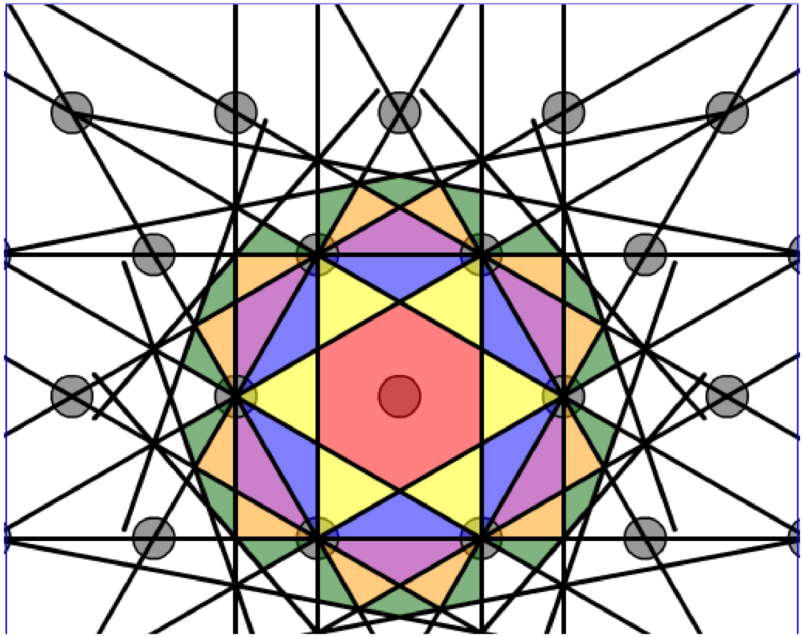
- mají stejný objem jako 1. Brillouinova zóna.
- mají stejnou symetrii jako 1. Brillouinova zóna.
- posunem o mřížový reciproký vektor se přesunou do 1. Brillouinovy zóny.

1. Brillouinova zóna

2. Brillouinova zóna

3. Brillouinova zóna

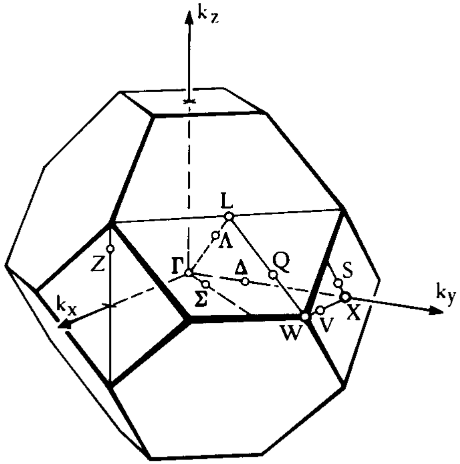




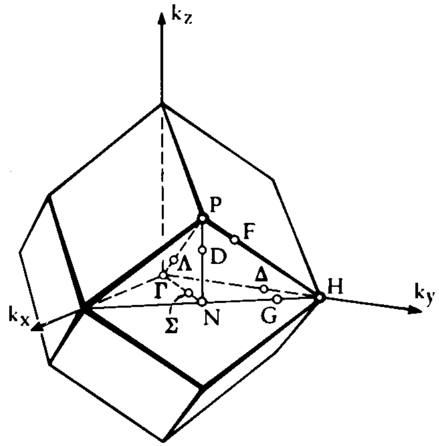
Brillouinovy zóny

Triclinic	$\bar{1}$	1/2
Monoclinic	$2/m$	1/4
Orthorhombic	mmm	1/8
Tetragonal	$4/m$ $4/mmm$	1/8 1/16

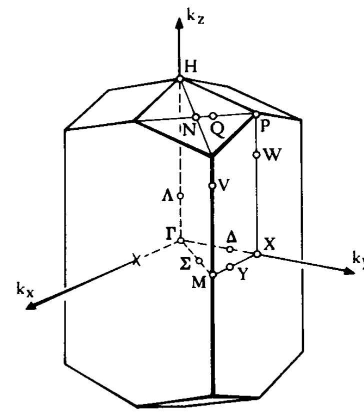
Trigonal	$\bar{3}$	1/6 1/12
Hexagonal	$6/m$ $6/mmm$	1/12 1/24
Cubic	$m3$ $m\bar{3}m$	1/24 1/48



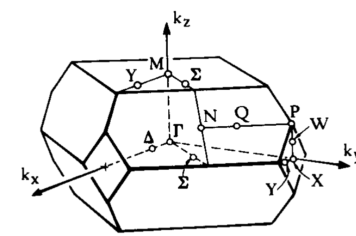
FACE CENTERED CUBIC



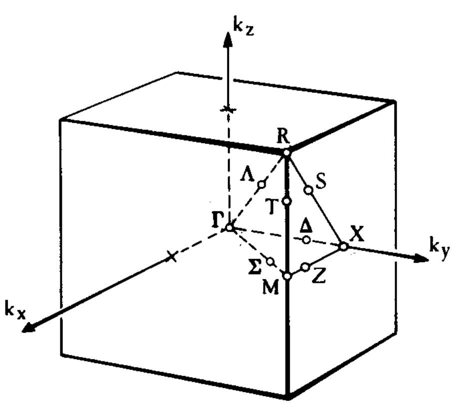
BODY CENTERED CUBIC



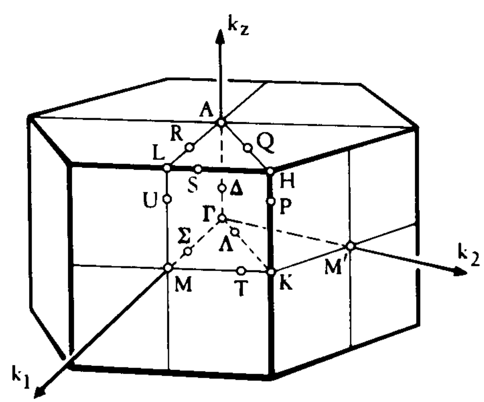
BODY CENTERED TETRAGONAL (a)



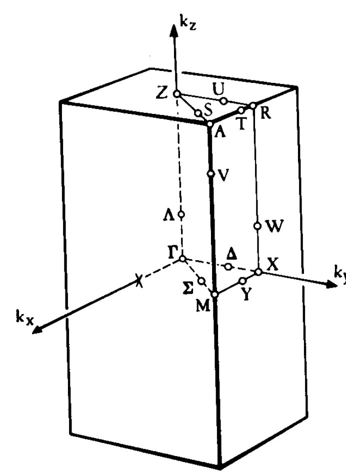
BODY CENTERED TETRAGONAL (b)



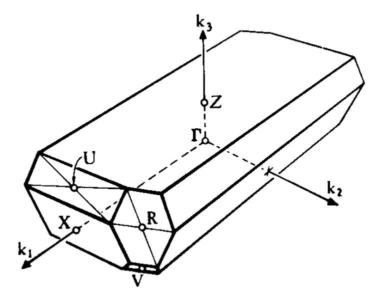
SIMPLE CUBIC



HEXAGONAL

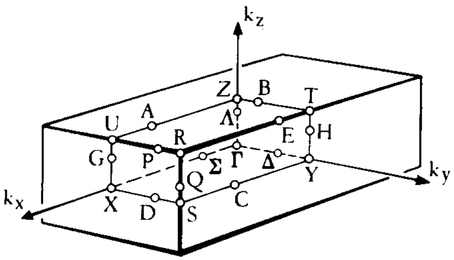


SIMPLE TETRAGONAL



TRICLINIC

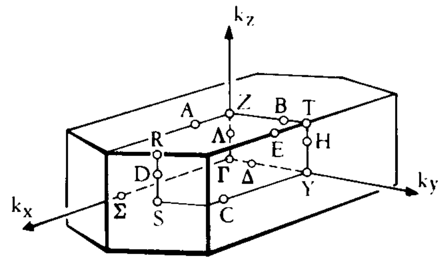
Brillouinovy zóny



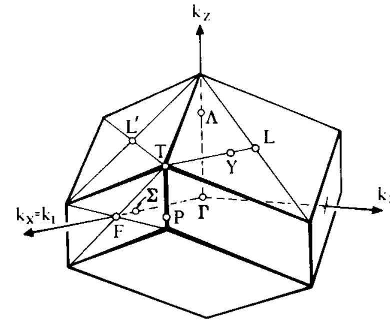
SIMPLE ORTHORHOMBIC

Γ=000 X=100 Y=010 Z=001

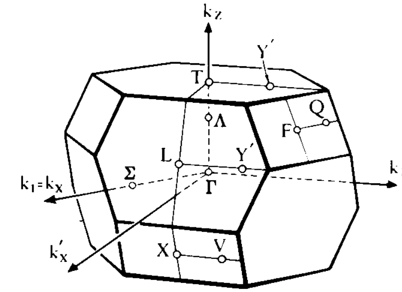
S=110 T=011 U=101 R=111



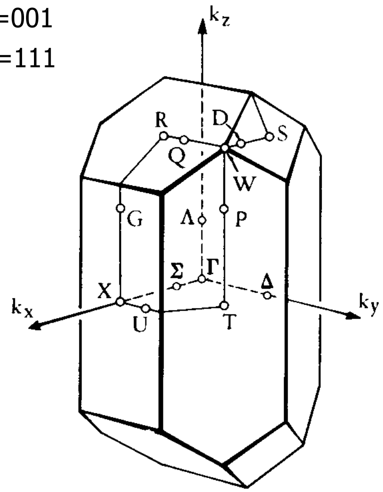
BASE CENTERED ORTHORHOMBIC



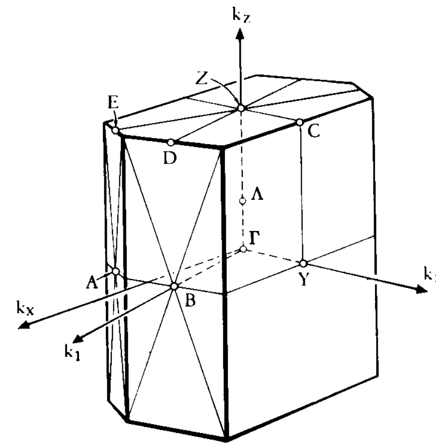
RHOMBOHEDRAL (a)



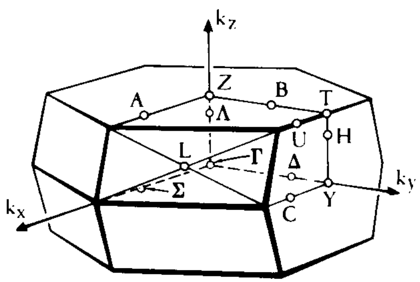
RHOMBOHEDRAL (b)



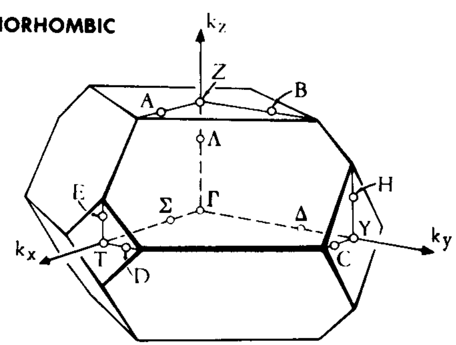
BODY CENTERED ORTHORHOMBIC



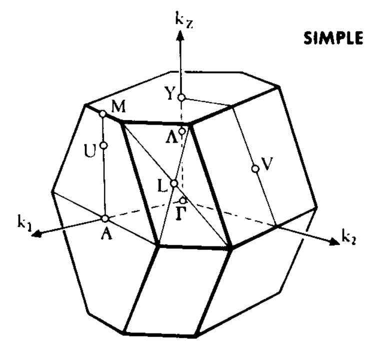
SIMPLE MONOCLINIC



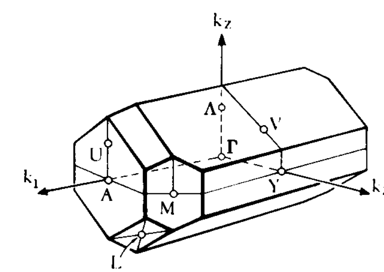
ALL FACE CENTERED ORTHORHOMBIC (a)



ALL FACE CENTERED ORTHORHOMBIC (b)



ONE FACE CENTERED MONOCLINIC (a)



ONE FACE CENTERED MONOCLINIC (b)

Schrödingerova rovnice $$\underbrace{-\frac{\hbar^2}{2m}\Delta}_{\text{kinetická E.}} \Psi(r) + \underbrace{\hat{V}(r)}_{\text{potenciální E.}} \Psi(r) = E\Psi(r)$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Vodíkový atom: $\hat{V} = \frac{e^2}{4\pi\varepsilon_o r}$

Δ ve sférických souřadnicích: $\Psi_{n,l,m} = R_{n,l}(r)\cdot Y_{l,m}(\theta,\varphi)$

$$\Delta \approx \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \varphi^2}$$

$$\hat{H}\Psi_{n,l,m} = E_n\Psi_{n,l,m} \qquad \hat{H} = \hat{T} + \hat{V}$$

$$\hat{L}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m}$$

$$\hat{L}_z Y_{l,m} = m\hbar Y_{l,m}$$

m: hmotnost elektronu

ε_o: permitivita vakua

Ψ: vlastní funkce

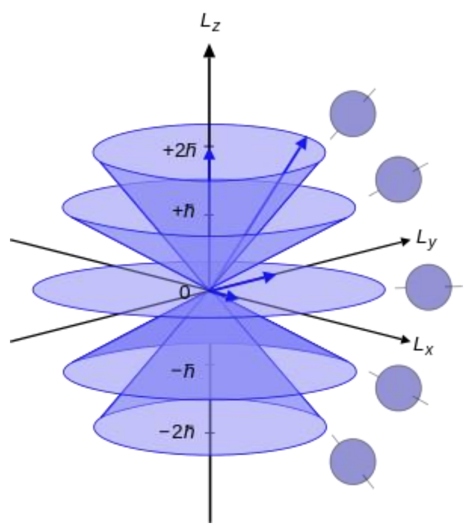
e: náboj elektronu

E: energie

h: Planckova konstanta

R: radiální funkce

Y: angulární funkce



n: hlavní kvantové číslo

l: vedlejší kvantové číslo

určuje orbitální moment hybnosti

l = 0 ... n-1

m_l: magnetické kvantové číslo

určuje průmět do osy z

$m_l = -l \ldots l$

$\hat{H}\Psi = E\Psi$

$\hat{H}\Phi = E\Phi$ $\Psi \approx \Phi = \sum_i^N c_i \varphi_i$

ψ: přesná vlnová funkce

Φ: přibližná vlnová funkce vyjádřená v bázi φ

$\psi = \Phi$ pro $N \to \infty$

φ: např. atomové orbitaly, rovinné vlny, ...

Téměř volné elektrony:

Kinetická energie převažuje nad potenciální

Báze = rovinné vlny $\Phi(x) = \sum_k c_k \exp[i\vec{k}\vec{x}]$

kovová vazba, elektronový plyn

Těsná vazba:

Potenciální energie převažuje nad kinetickou

Báze = atomové orbitaly

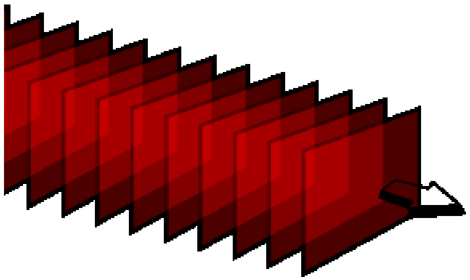
Kovalentní a iontová vazba

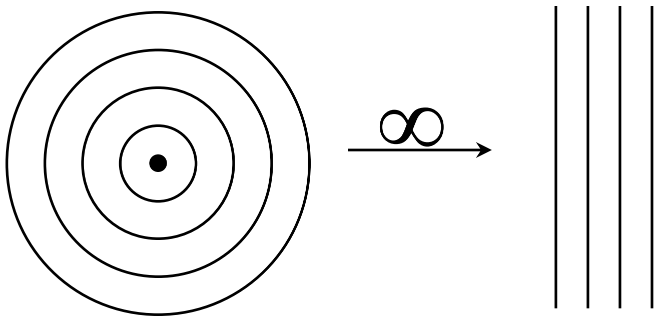
Rovinná vlna

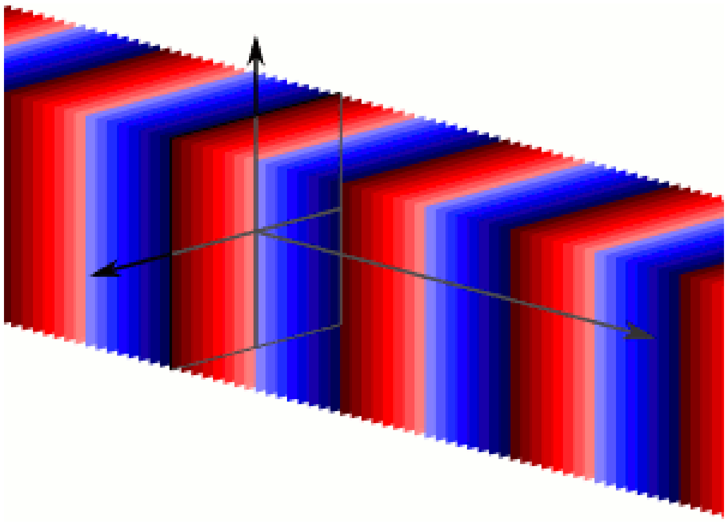
Rovinná vlna:

$$\Phi(\vec{r}) = \sum_n c_n \exp[\, i\vec{k}\vec{r}]$$

- konstantní frekvence
- šíří se jako nekonečné rovnoběžné roviny kolmé k vektoru pohybu.







$$(1)\quad \hat{H}\Phi = E\Phi \qquad (2)\quad \Phi = \sum_{i=1}^{n} c_i \varphi_i$$

dosazením (2) do (1) $\rightarrow$ (3)

$$(3)\quad \hat{H}(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n) = E(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n)$$

Neznámé : E, c_i

$$\begin{array}{c} \\ E_1 \\ E_2 \\ \vdots \\ E_n \end{array} \begin{array}{c} \begin{matrix} \varphi_1 & \varphi_2 & \cdots & \varphi_n \end{matrix} \\ \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ c_{n1} & c_{n2} & \cdots & c_{nn} \end{bmatrix} \end{array} \begin{array}{l} \\ \sum c_{1j}^2 = 1 \\ \sum c_{2j}^2 = 1 \\ \\ \sum c_{nj}^2 = 1 \end{array}$$

$$\sum c_{i1}^2 = 1 \quad \sum c_{i2}^2 = 1 \quad \cdots \quad \sum c_{in}^2 = 1$$

Obecně - vlastní vektory matice :

Symetrie - vektor osy

$$\mathrm{A}\vec{\mathrm{v}} = 1\vec{\mathrm{v}}$$

Vlastní funkce :

$$\hat{\mathrm{H}}\Phi = \mathrm{E}\Phi$$

rovnici (3) vynásobíme postupně zleva funkcemi $\varphi_1, \varphi_2, \ldots, \varphi_n$, a vytvoříme soustavu rovnic:

$$\begin{aligned}
\varphi_1\hat{H}c_1\varphi_1 + \varphi_1\hat{H}c_2\varphi_2 + \ldots + \varphi_1\hat{H}c_n\varphi_n &= \varphi_1 E c_1\varphi_1 + \varphi_1 E c_2\varphi_2 + \ldots + \varphi_1 E c_n\varphi_n \\
\varphi_2\hat{H}c_1\varphi_1 + \varphi_2\hat{H}c_2\varphi_2 + \ldots + \varphi_2\hat{H}c_n\varphi_n &= \varphi_2 E c_1\varphi_1 + \varphi_2 E c_2\varphi_2 + \ldots + \varphi_2 E c_n\varphi_n \\
\vdots \quad & \quad \vdots \quad\quad \vdots \\
\varphi_n\hat{H}c_1\varphi_1 + \varphi_n\hat{H}c_2\varphi_2 + \ldots + \varphi_n\hat{H}c_n\varphi_n &= \varphi_n E c_1\varphi_1 + \varphi_n E c_2\varphi_2 + \ldots + \varphi_n E c_n\varphi_n
\end{aligned}$$

$$(1) \quad \hat{H}\Phi = E\Phi \quad (2) \quad \Phi = \sum_{i=1}^{n} c_i\varphi_i$$

$$\text{dosazením (2) do (1)} \rightarrow (3)$$

$$(3) \quad \hat{H}(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n) = E(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n)$$

$$\text{Neznámé}: E, c_i$$

Převedeme na maticový zápis, pro konstantu E platí $\varphi_i E \varphi_j = E\varphi_i\varphi_j$:

$$\begin{pmatrix} \varphi_1\hat{H}\varphi_1 & \varphi_1\hat{H}\varphi_2 & \ldots & \varphi_1\hat{H}\varphi_n \\ \varphi_2\hat{H}\varphi_1 & \varphi_2\hat{H}\varphi_2 & \ldots & \varphi_2\hat{H}\varphi_n \\ & \vdots & & \\ \varphi_n\hat{H}\varphi_1 & \varphi_n\hat{H}\varphi_2 & \ldots & \varphi_n\hat{H}\varphi_n \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} E\varphi_1\varphi_1 & E\varphi_1\varphi_2 & \ldots & E\varphi_1\varphi_n \\ E\varphi_2\varphi_1 & E\varphi_2\varphi_2 & \ldots & E\varphi_2\varphi_n \\ & \vdots & & \\ E\varphi_n\varphi_1 & E\varphi_n\varphi_2 & \ldots & E\varphi_n\varphi_n \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix}$$

Převedeme na 1 stranu a spojíme do 1 matice:

$$\begin{pmatrix} \varphi_1\hat{H}\varphi_1 & \varphi_1\hat{H}\varphi_2 & \ldots & \varphi_1\hat{H}\varphi_n \\ \varphi_2\hat{H}\varphi_1 & \varphi_2\hat{H}\varphi_2 & \ldots & \varphi_2\hat{H}\varphi_n \\ & \vdots & & \\ \varphi_n\hat{H}\varphi_1 & \varphi_n\hat{H}\varphi_2 & \ldots & \varphi_n\hat{H}\varphi_n \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} - \begin{pmatrix} E\varphi_1\varphi_1 & E\varphi_1\varphi_2 & \ldots & E\varphi_1\varphi_n \\ E\varphi_2\varphi_1 & E\varphi_2\varphi_2 & \ldots & E\varphi_2\varphi_n \\ & \vdots & & \\ E\varphi_n\varphi_1 & E\varphi_n\varphi_2 & \ldots & E\varphi_n\varphi_n \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} \varphi_1\hat{H}\varphi_1 - E\varphi_1\varphi_1 & \varphi_1\hat{H}\varphi_2 - E\varphi_1\varphi_2 & \ldots & \varphi_1\hat{H}\varphi_n - E\varphi_1\varphi_n \\ \varphi_2\hat{H}\varphi_1 - E\varphi_2\varphi_1 & \varphi_2\hat{H}\varphi_2 - E\varphi_2\varphi_2 & \ldots & \varphi_2\hat{H}\varphi_n - E\varphi_2\varphi_n \\ & \vdots & & \\ \varphi_n\hat{H}\varphi_1 - E\varphi_n\varphi_1 & \varphi_n\hat{H}\varphi_2 - E\varphi_n\varphi_2 & \ldots & \varphi_n\hat{H}\varphi_n - E\varphi_n\varphi_n \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

Soustava rovnic má netriviální řešení, jen pokud je determinant matice = 0:

$$\varphi_i\hat{H}\varphi_j = H_{ij} \quad \varphi_i\varphi_j = S_{ij} \quad \varphi_i\varphi_i = 1$$

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12} & \ldots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - E & \ldots & H_{2n} - ES_{2n} \\ & \vdots & & \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \ldots & H_{nn} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$\det\left\| H_{ij} - ES_{ij} \right\| = \begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & \ldots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - E & \ldots & H_{2n} - ES_{2n} \\ & \vdots & & \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \ldots & H_{nn} - E \end{vmatrix} = 0$$

Nalezení vlastních čísel a vektorů

$$H\vec{c}_k^{\,H} = E_k^H \vec{c}_k^{\,H} \quad k = 1\ldots n$$

$$B = P^{-1}HP: \quad E_k^B = E_k^H \quad \vec{c}_k^{\,B} = P^{-1}\vec{c}_k^{\,H} \quad \vec{c}_k^{\,H} = P\vec{c}_k^{\,B}$$

Jacobiho metoda, Givensovy matice $P \Rightarrow$

$$B = \begin{pmatrix} E_1 & 0 & \ldots & 0 \\ 0 & E_2 & \ldots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \ldots & E_n \end{pmatrix}$$

$$\begin{pmatrix} E_1 - E_k & 0 & \cdots & 0 \\ 0 & E_2 - E_k & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & E_n - E_k \end{pmatrix} \begin{pmatrix} c_{k1}^B \\ c_{k2}^B \\ \vdots \\ c_{kn}^B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$\vec{c}_1^{\,B} = (1,0,\ldots,0), \vec{c}_2^{\,B} = (0,1,\ldots,0), \ldots$$

$$H\vec{c}_k^{\,H} = E_k^H \vec{c}_k^{\,H}$$
$$H\vec{c}_k^{\,H} - E_k^H \vec{c}_k^{\,H} = 0$$
$$\left(H - IE_k^H\right)\vec{c}_k^{\,H} = 0$$
I *: jednotková matice*

(1) $\hat{H}\Phi = E\Phi$ (2) $\Phi = \sum_{i=1}^{n} c_i \varphi_i$

dosazením (2) do (1) $\rightarrow$ (3)

(3) $\hat{H}(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n) = E(c_1\varphi_1 + c_2\varphi_2 + \ldots + c_n\varphi_n)$

Neznámé: E, c_i

Komplexní matice:

$$(\mathrm{R},\mathrm{I}) \rightarrow \begin{pmatrix} \mathrm{R} & \mathrm{I} \\ -\mathrm{I} & \mathrm{R} \end{pmatrix}$$

$$\begin{array}{c|cccc|c} & \varphi_1 & \varphi_2 & \cdots & \varphi_n & \\ E_1 & c_{11} & c_{12} & \cdots & c_{1n} & \sum c_{1j}^2 = 1 \\ E_2 & c_{21} & c_{22} & \cdots & c_{2n} & \sum c_{2j}^2 = 1 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \\ E_n & c_{n1} & c_{n2} & \cdots & c_{nn} & \sum c_{nj}^2 = 1 \end{array}$$

$$\sum c_{i1}^2 = 1 \quad \sum c_{i2}^2 = 1 \quad \cdots \quad \sum c_{in}^2 = 1$$

Variační metoda – sekulární rovnice

Soustava rovnic pro i = 1, 2, ..., N $\sum_{i=1}^{N} c_j [H_{ij} - ES_{ij}] = 0$ $S_{ii} = 1$

$$
\begin{aligned}
&c_1[H_{11} - E] && + c_2[H_{12} - ES_{12}] && \dots && + c_n[H_{1n} - ES_{1n}] = 0 \\
&c_1[H_{21} - ES_{21}] && + c_2[H_{22} - E] && \dots && + c_n[H_{2n} - ES_{2n}] = 0 \\
&\quad\vdots && \quad\vdots && && \quad\vdots \\
&c_1[H_{n1} - ES_{n1}] && + c_2[H_{n2} - ES_{n2}] && \dots && + c_n[H_{nn} - E] = 0
\end{aligned}
$$

Soustava rovnic má řešení, pokud je determinant matice $H_{ij} - ES_{ij} = 0$:

$$
\det\left\| H_{ij} - ES_{ij} \right\| = \begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - E & \dots & H_{2n} - ES_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - E \end{vmatrix} = 0
$$

Výpočet determinantu → sekulární rovnice N.řádu, řešením je N vlastních čísel E_i (energie)
pro každé E_i, dostaneme N koeficientů c_{ij} (vlastních vektorů) vyřešením soustavy rovnic.
E_i: energie funkce $\Phi_i = \Sigma_j c_{ij} \varphi_i$

Závisí-li potenciál na funkcích Φ_i, tzn. na hledaných koeficientech c_{ij}, musí se sekulární rovnice řešit iteračně, tzv. metodou SCF (self-consistent field)

$$H_{ij} = \int_\tau \varphi_j^* \hat{H} \varphi_i d\tau$$

$$S_{ij} = \int_\tau \varphi_j^* \varphi_i d\tau$$

H_{ij}: výměnný (rezonanční) integrál
H_{ii} (i=j): "on-site" energie jednotlivých bázových stavů.
S_{ij}: překryvový integrál. S_{ii} (i=j) = 1, S_{ij} (i≠j) → 0.

$$\hat{H}\Psi = E\Psi$$

$$\hat{H}\Phi = E\Phi \qquad \Psi \approx \Phi = \sum_i^N c_i \varphi_i$$

ψ: přesná vlnová funkce

Φ: přibližná vlnová funkce vyjádřená v bázi φ

$\psi = \Phi$ pro N $\rightarrow \infty$

φ: např. atomové orbitaly, rovinné vlny, ...

$$\hat{H}\Phi = E\Phi \;\rightarrow\; \Phi^*\hat{H}\Phi = \Phi^* E\Phi \;\rightarrow\; \int_\tau \Phi^*\hat{H}\Phi d\tau = E\int_\tau \Phi^*\Phi d\tau$$

$$E = \frac{\int_\tau \Phi^*\hat{H}\Phi d\tau}{\int_\tau \Phi^*\Phi d\tau} = \frac{\int_\tau \sum_j^N c_j^*\varphi_j^*\hat{H}\sum_j^N c_i\varphi_i d\tau}{\int_\tau \sum_j^N c_j^*\varphi_j^*\sum_j^N c_i\varphi_i d\tau} = \frac{\sum_{i,j}^N c_j^* c_i H_{ij}}{\sum_{i,j}^N c_j^* c_i S_{ij}} \rightarrow$$

$$\sum_{i,j}^N c_j^* c_i H_{ij} - E\sum_{i,j}^N c_j^* c_i S_{ij} = 0$$

$$H_{ij} = \int_\tau \varphi_j^*\hat{H}\varphi_i d\tau$$

$$S_{ij} = \int_\tau \varphi_j^*\varphi_i d\tau$$

H_{ij}: výměnný (rezonanční) integrál

H_{ii} (i=j): "on-site" energie jednotlivých bázových stavů.

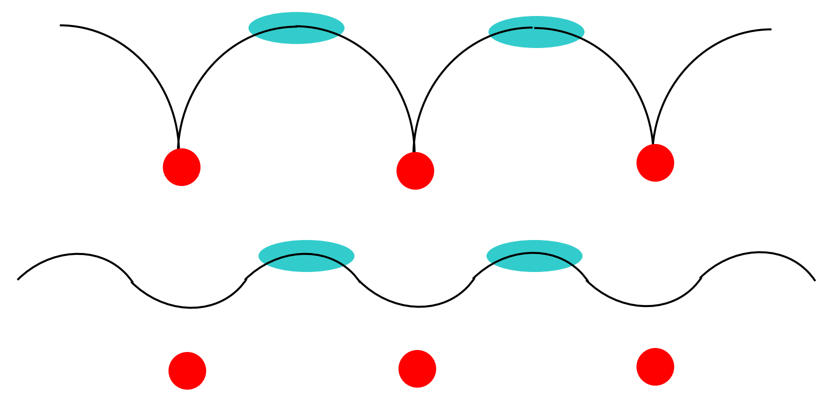
S_{ij}: překryvový integrál. S_{ii} (i=j) = 1

$$V(x)=\sum_G \mathrm{V}_G \exp[i\vec{G}\vec{x}] = \mathrm{V}_0 + \mathrm{V}_{\pm1}\exp[\pm i\tfrac{2\pi}{a}x] + \mathrm{V}_{\pm2}\exp[\pm i\tfrac{4\pi}{a}x] + \dots \qquad \vec{G}=\tfrac{2\pi}{a}\vec{j}$$

$V_G = V^*_{-G}$: Potenciál je reálný $\qquad \vec{j}$: mřížové vektory. Pro 1D j = 0, ±1, ±2, ...

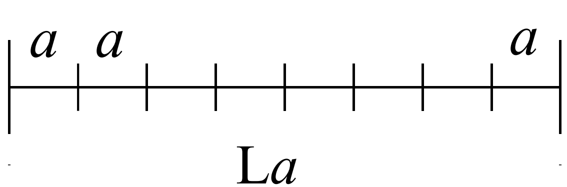
Skutečný potenciál:
v okolí jádra je obrovská přitažlivá síla

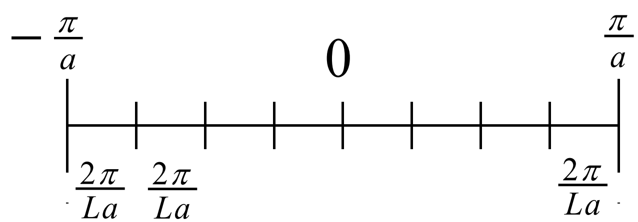
Zajímá-li nás potenciál, ve kterém se pohybují elektrony (především valenční), můžeme okolí jádra zanedbat.



Funkce: $\Phi(x)=\Phi(x+La)=\sum_k c_k \exp[i\vec{k}\vec{x}] \quad \vec{k}=\frac{2\pi}{La}\vec{l}$ Pro 1D l = 0, ±1, ±2, ..., ±L/2

Potenciál se opakuje po periodě a, funkce se opakuje po periodě La.
V reciprokém prostoru je 1.Brillouinova zóna $2\pi/a$, funkce se počítá po $2\pi/\mathrm{L}a$.





Vlnovou funkci a potenciál dosadíme do Schrödingerovy rovnice

$$\Phi(x)=\sum_k c_k \exp[i\vec{k}\vec{x}] \qquad V(x)=\sum_G \mathrm{V}_G \exp[i\vec{G}\vec{x}]$$

$$-\frac{\hbar^2}{2m}\Delta\Phi+\hat{V}\Phi=E\Phi$$

$$\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{i\vec{k}\vec{x}}+\sum_k\sum_G c_k V_G e^{i(\vec{k}+\vec{G})\vec{x}}=E\sum_k c_k e^{i\vec{k}\vec{x}}$$

$$\vec{k}'=\vec{k}+\vec{G}\rightarrow\sum_k\sum_G c_{k-G}V_G e^{i\vec{k}\vec{x}}, \quad \vec{k}'\equiv\vec{k}$$

$$\sum_k\left[\left(\frac{\hbar^2 k^2}{2m}-E_k\right)c_k+\sum_G c_{k-G}V_G\right]e^{i\vec{k}\vec{x}}=0$$

Aby byla tato suma =0, musí být každý člen v [] =0.

$$\left(\frac{\hbar^2 k^2}{2m}-E_k\right)c_k+\sum_G c_{k-G}V_G=0$$

Master equation: soustava L rovnic, formulace sekulární rovnice pro bázi rovinných vln.

různá řešení c_k v rámci 1. Brillouinovy zóny

$-G/2 \le k \le G/2$ $(-\pi/a \le l(2\pi/La) \le \pi/a)$

Téměř volné elektrony

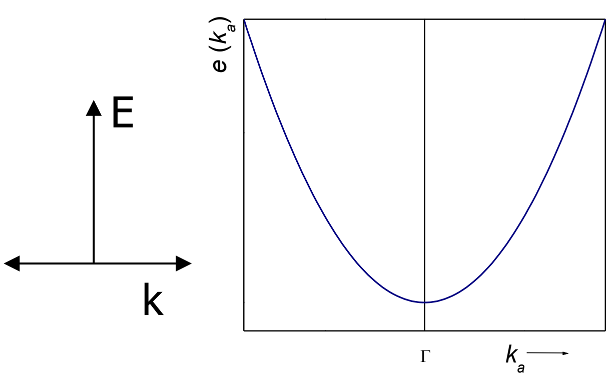
$$\left(\frac{\hbar^2 k^2}{2m} - E_k\right) c_k + \sum_G c_{k-G} V_G = 0$$

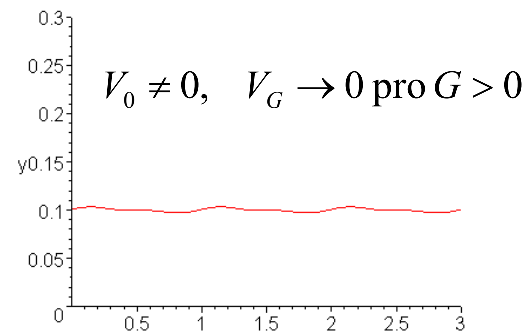
master equation – tvoří soustavu L rovnic: různá řešení c_k v rámci 1. Brillouinovy zóny - $\pi/a \le k \le \pi/a$

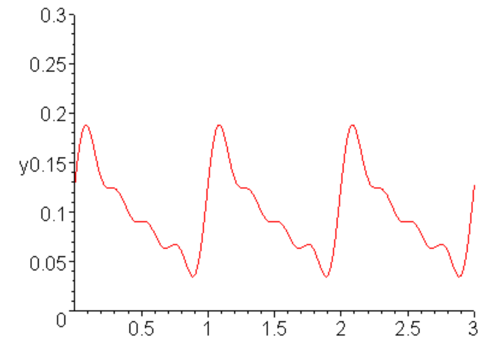
$$V_G = V_{-G}^* : \quad V_G = A_G + iB_G, \quad V_{-G} = A_G - iB_G \qquad V(x) = V_0 + \sum_G A_G \cos(Gx) - B_G \sin(Gx)$$

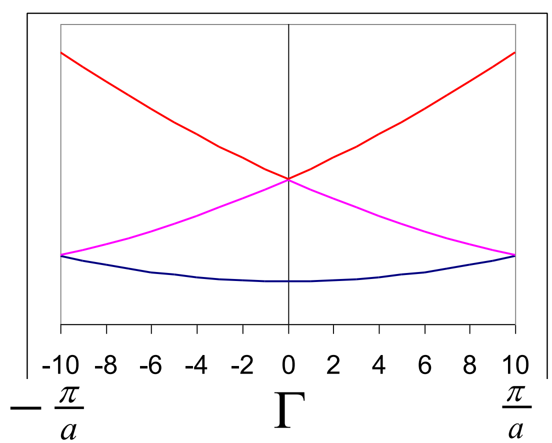
$$\begin{vmatrix} \lambda_{k-G} - (E_k - V_o) & V_1 & V_2 \\ V_{-1} & \lambda_k - (E_k - V_o) & V_1 \\ V_{-2} & V_{-1} & \lambda_{k+G} - (E_k - V_o) \end{vmatrix} \qquad \lambda_k = \frac{\hbar^2 k^2}{2m}$$

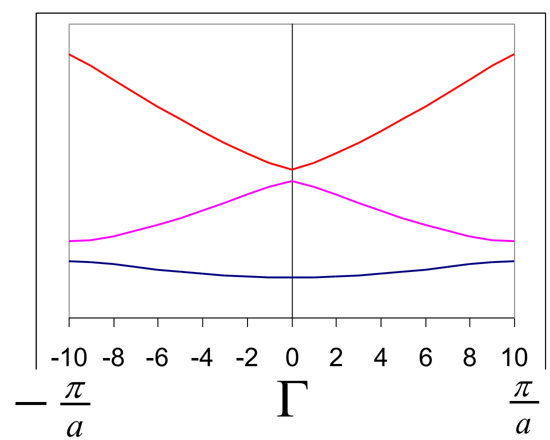
$$E = \frac{mv^2}{2} = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 k^2}{2m}$$









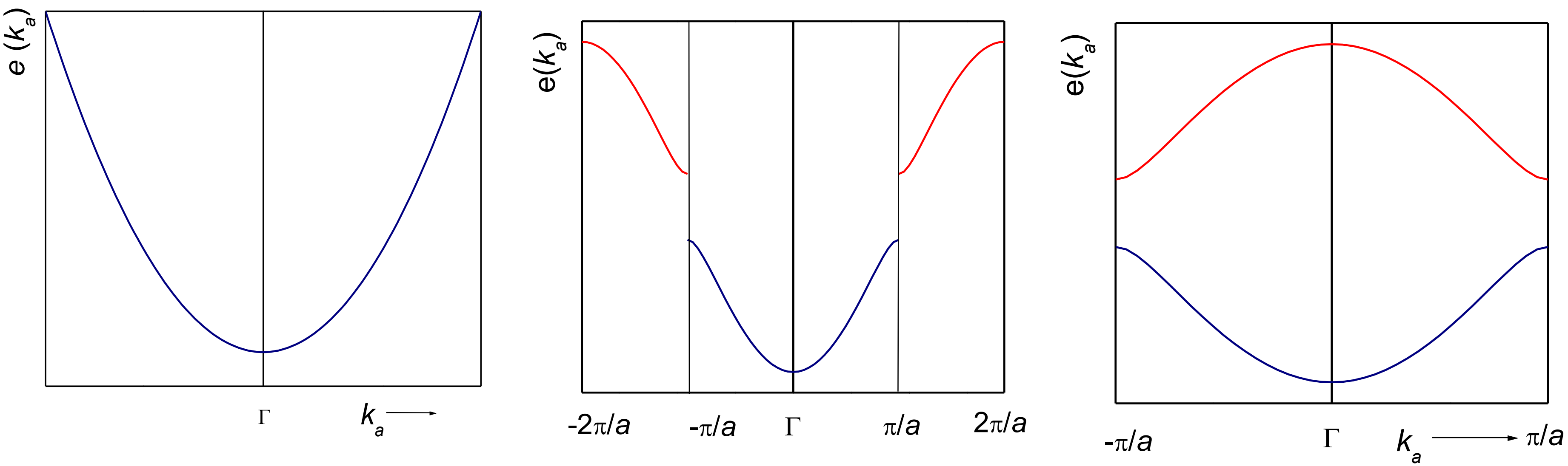


k - kvantové číslo
vlnový vektor

$$k = \frac{2\pi}{\lambda} \qquad \mathbf{p} = m\mathbf{v} = \frac{h}{\lambda} = \hbar k$$

počet dovolených hodnot ***k*** = počet elementárních buněk v krystalu

volné elektrony: $$E = \frac{mv^2}{2} = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 k^2}{2m}$$



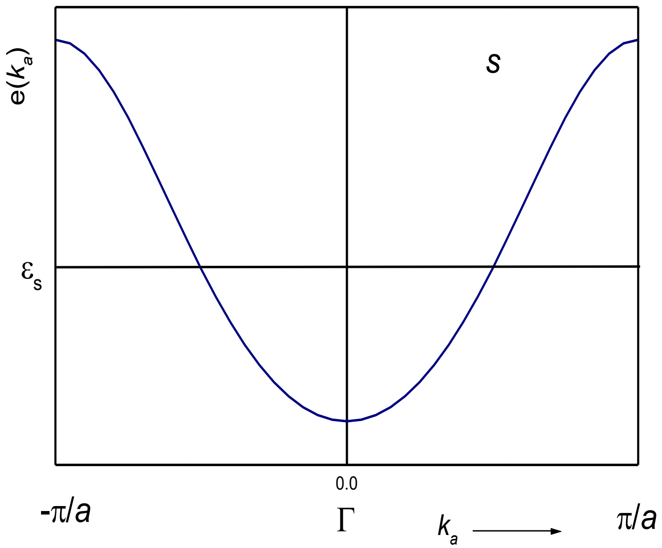
šířka pásu: dána překryvem interagujících orbitalů (jako u MO)

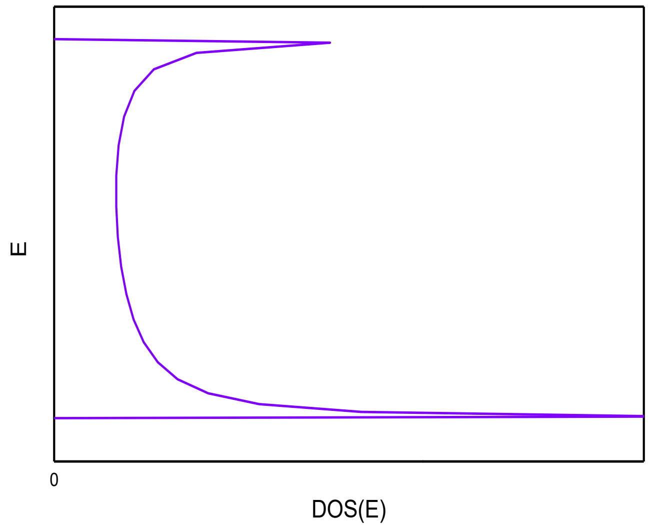
DOS(*E*), *g*(*E*) - počet dovolených energetických hladin na jednotkový energetický interval

platí: **g(*E*)*d*E*** = počet hladin v intervalu (***E*** ; ***E*+d*E***)

jeden rozměr: $$g(E) = 2\frac{a}{2\pi}\left(\frac{\partial E}{\partial k}\right)^{-1}$$

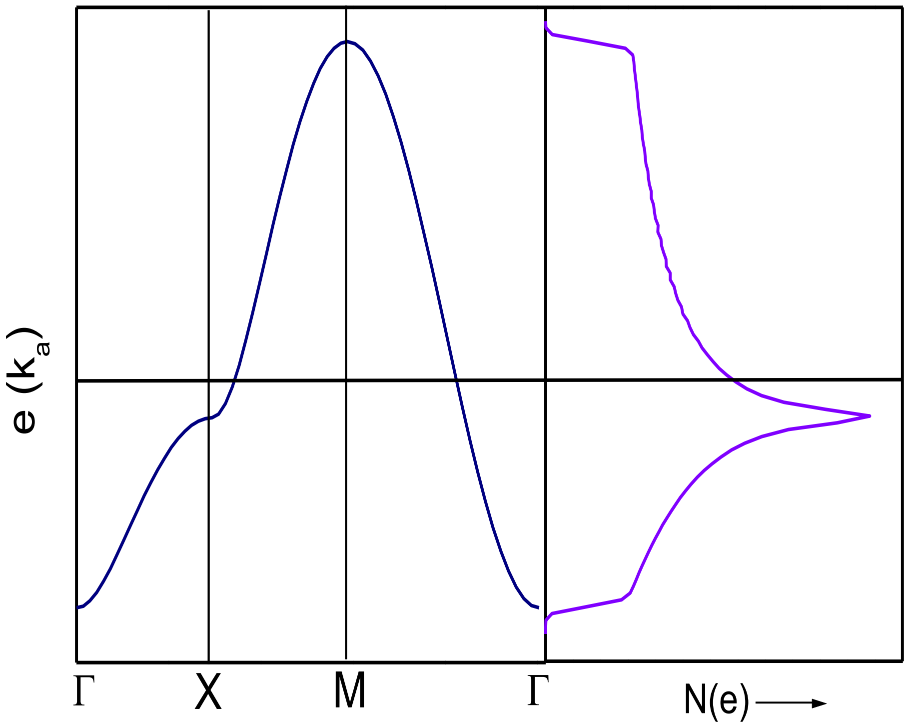
obecně: $$g(E) = \frac{2}{V_{BZ}}\sum_n \int_{S_k} \frac{dS_k}{\left|\nabla_k E_{n,k}\right|}$$

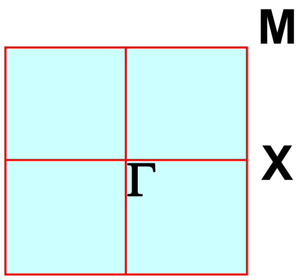




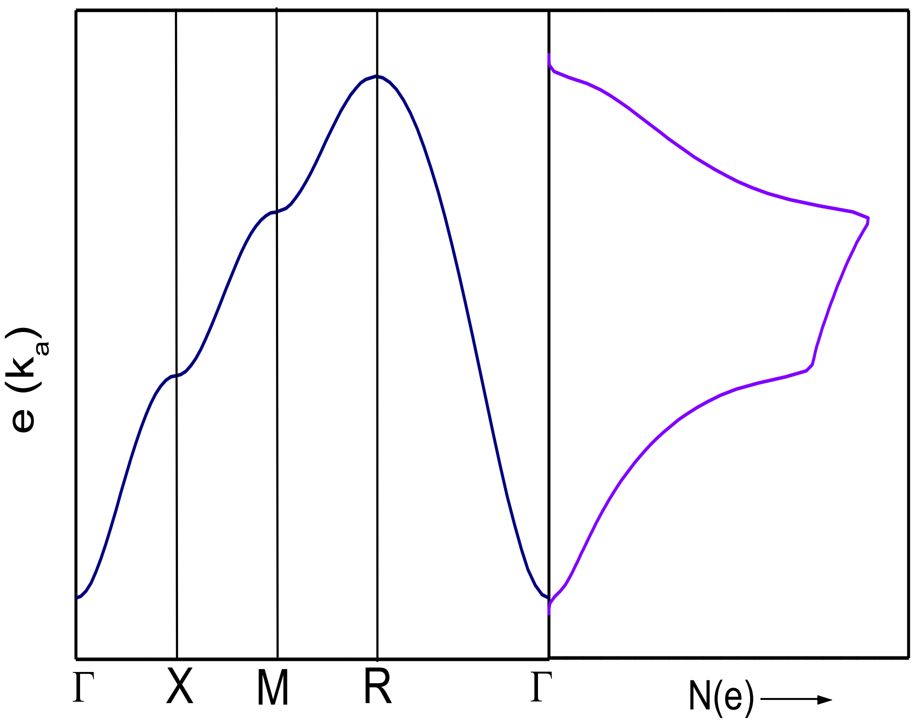
numericky: $$g(E) = \frac{2}{\pi^2 \Delta}\sum_n \sum_k e^{-\left(\frac{E-E_{n,k}}{\Delta}\right)^2}$$

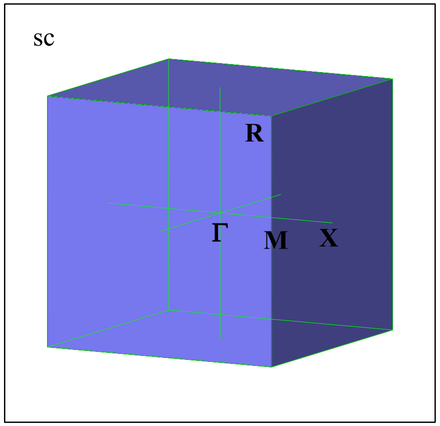
2-D





3-D

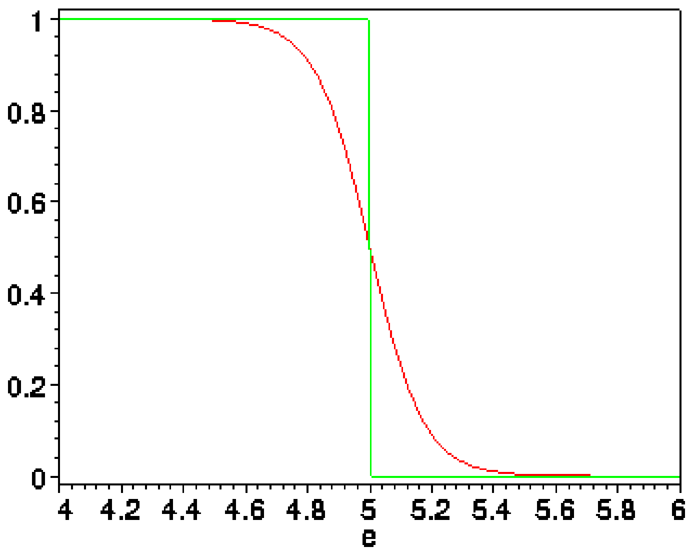


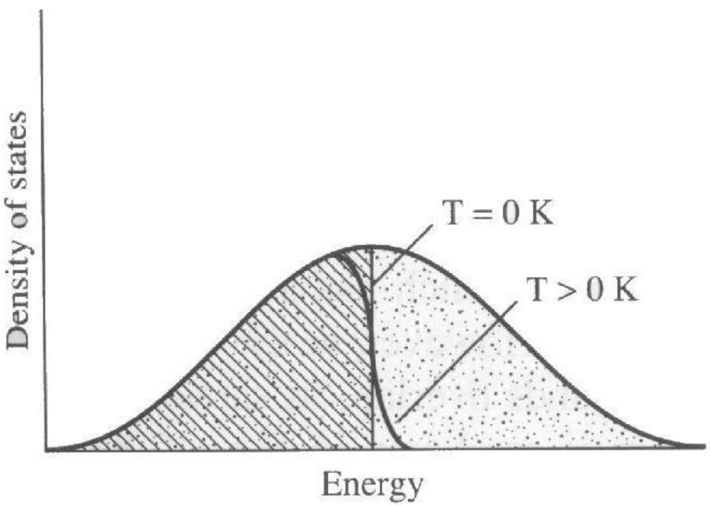


Fermiho hladina (mez) - nejvyšší zaplněná hladina při **T=0 K**

T>0: platí Fermi-Diracova statistika:
zaplněné stavy **DOS(E)*f(E)**

$$f(E) = \frac{1}{\exp((E - E_F)/k_B T) + 1}$$





Fermiho plocha - množina ***k*** v k-prostoru, pro kterou platí $E(\boldsymbol{k}) = E_F$

buňka obsahující
2 identické orbitaly

$\chi_A \ \chi_B$

$$\varphi_i = \sum_{\mu}^{N} c_{i\mu} \chi_\mu$$

φ_i: molekulový orbital, χ_μ: atomový orbital

$$\sum_{i=1}^{N} c_j [H_{ij} - ES_{ij}] = 0$$

$$\chi_A = \chi_B,$$

$$H_{AA} = \int \chi_A^*(R_A) \hat{H} \chi_A(R_A) = H_{BB} = \alpha$$

$$H_{AB} = \int \chi_A^*(R_A) \hat{H} \chi_B(R_B) = \int \chi_B(R_B) \hat{H}^* \chi_A^*(R_A) = H_{BA}^* = \beta$$

$$S_{AB} = \int \chi_A^*(R_A) \chi_B(R_B) = \int \chi_B(R_B) \chi_A^*(R_A) = S_{BA}^* = S$$

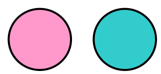
$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - E \end{pmatrix} = \begin{pmatrix} \alpha - E & \beta - ES \\ \beta^* - ES^* & \alpha - E \end{pmatrix}$$

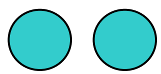
$$\det\begin{pmatrix} \alpha - E & \beta - ES \\ (\beta - ES)^* & \alpha - E \end{pmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\alpha - E = \pm(\beta - ES) \qquad E_{12} = \frac{\alpha \pm \beta}{1 \pm S}, \quad \beta < 0 \Rightarrow E_1 < E_2$$

$\alpha_1 = \alpha_2$

$(\beta < 0,\ S << 1)$

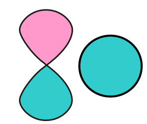
$E_2 = \alpha - \beta,\ \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$ 

$E_1 = \alpha + \beta,\ \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$ 

$$\det\begin{pmatrix} \alpha_1 - E & 0 \\ 0 & \alpha_2 - E \end{pmatrix} = (\alpha_1 - E)(\alpha_2 - E) = 0$$

$E_1 = \alpha_1 \quad E_2 = \alpha_2$

$(\beta = 0,\ S = 0)$



$$E_2\!: \quad c_1[\alpha - (\alpha - \beta)] + c_2\beta = 0 \rightarrow c_1\beta + c_2\beta = 0 \rightarrow c_1 = -c_2$$

$$E_1\!: \quad c_1[\alpha - (\alpha + \beta)] + c_2\beta = 0 \rightarrow c_1\beta - c_2\beta = 0 \rightarrow c_1 = c_2$$

$$\sqrt{c_1^2 + c_2^2} = 1$$

$\alpha = \varepsilon$: coulombická energie (energie AO)

β (<0) = t : výměnná energie (míra vazebné energie)

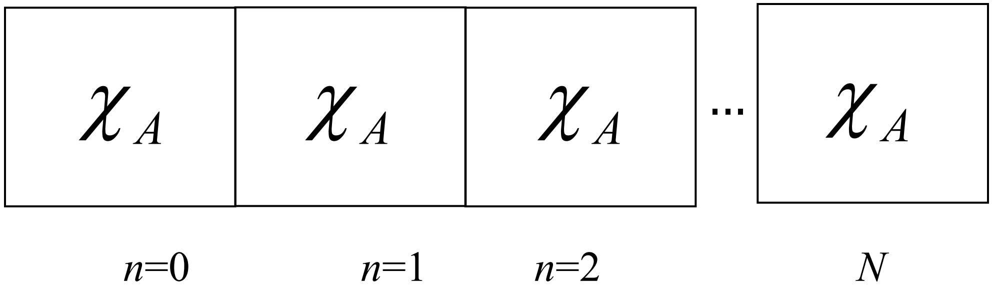
S (0-1) : překryvový integrál

$$\alpha = \int \chi_A^*(R_A)\hat{H}\chi_A(R_A)$$

$$\beta = \int \chi_A^*(R_A)\hat{H}\chi_B(R_B)$$

$$S = \int \chi_A^*(R_A)\chi_B(R_B)$$

Pásová struktura – Blochovy orbitaly



$$\Phi_{BO}(r,k)=\frac{1}{\sqrt{N}}\sum_{n}^{N}\chi_{\mu}(r-na)\exp(ikna)$$

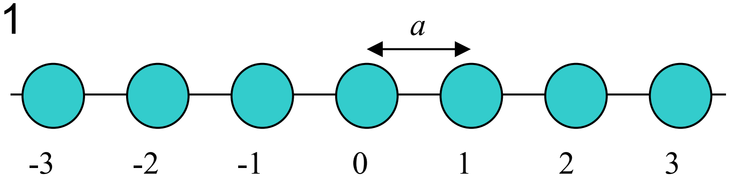
Φ_{BO}: Blochův orbital, χ_{μ}: atomový orbital

$$\exp(ikna)=\cos(kna)+i\sin(kna)$$

$$\Phi_{BO} = \chi_{\mu}(r) + \chi_{\mu}(r-a)e^{ika} + \chi_{\mu}(r-2a)e^{ik2a} + \ldots + \chi_{\mu}(r-na)e^{ikNa}$$

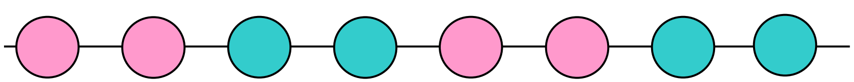
k=0 (Γ)

$e^0 = 1$



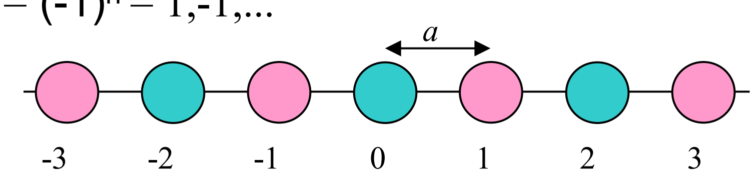
$k=\pm\pi/2a$

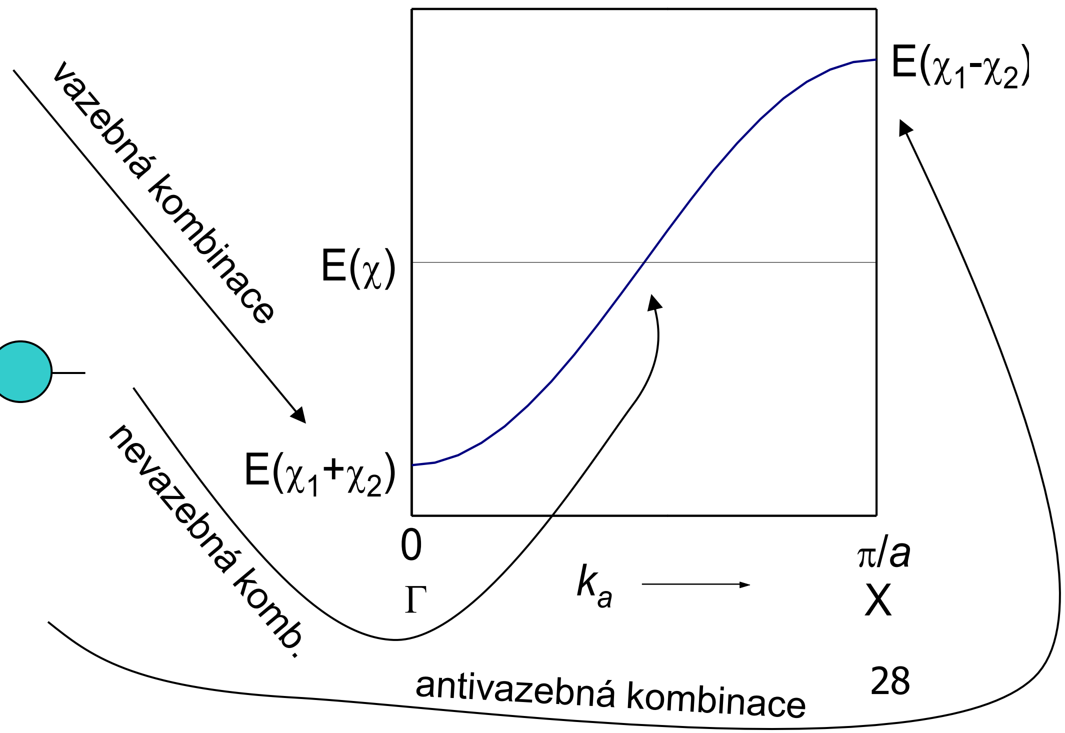
$\cos(n\pi/2) = 1,0,-1,0, \ldots$ $\sin(n\pi/2) = 0,1,0,-1, \ldots$



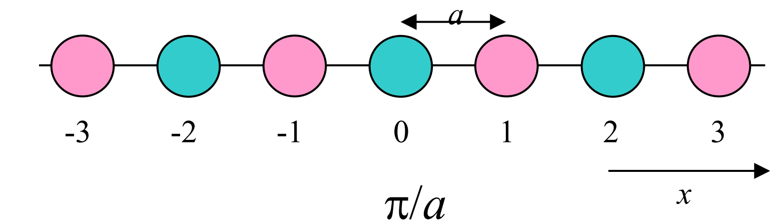
$k=\pm\pi/a$ (X)

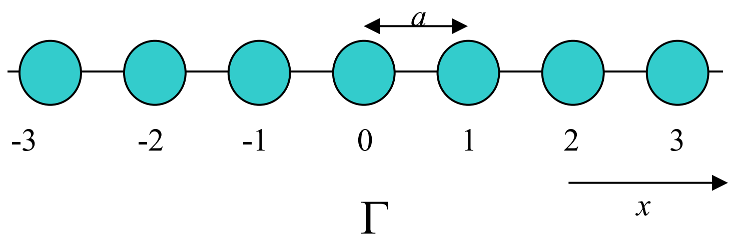
$e^{i\pi n} = (-1)^n = 1,-1,\ldots$

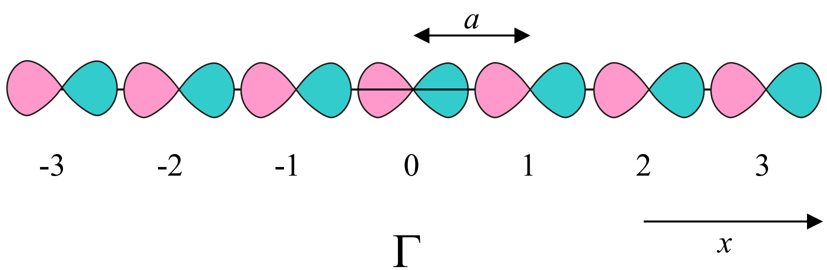


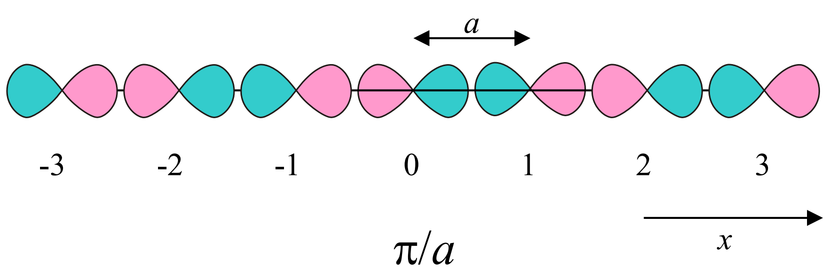


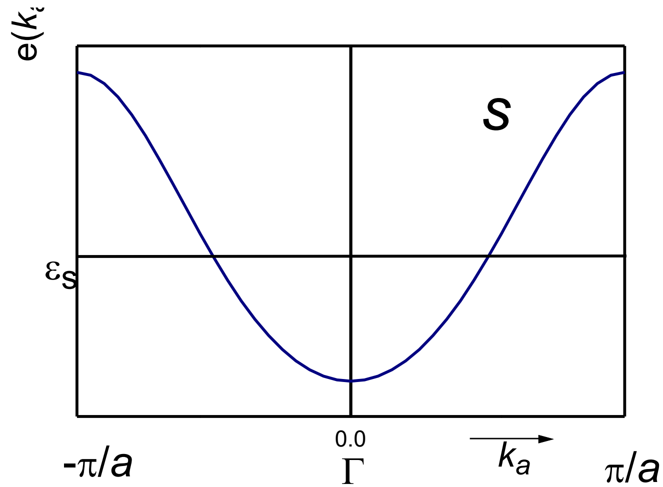
Symetrie orbitalů

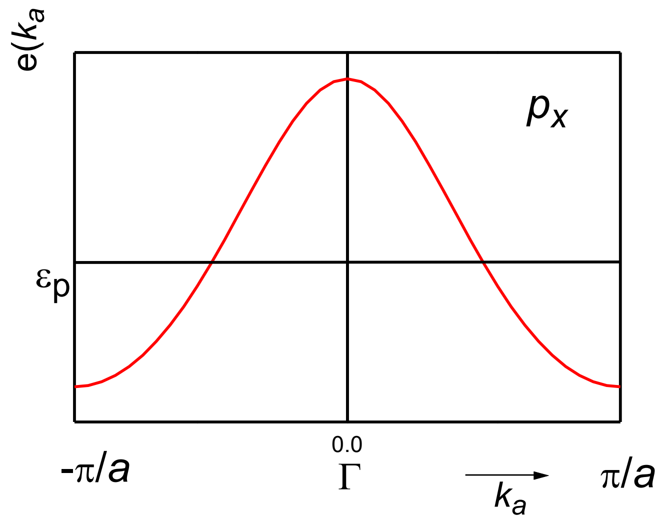




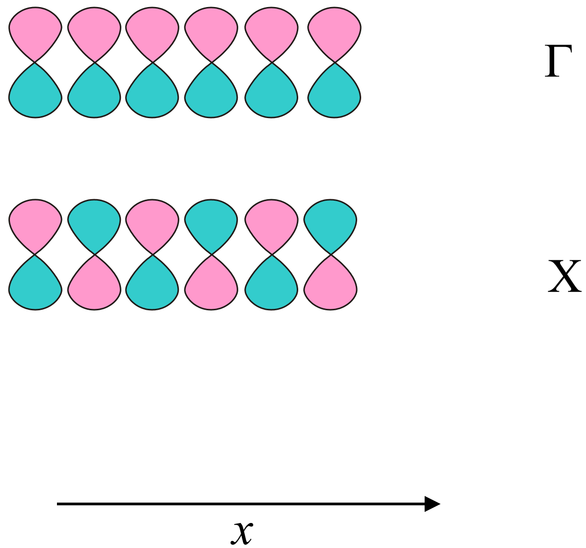


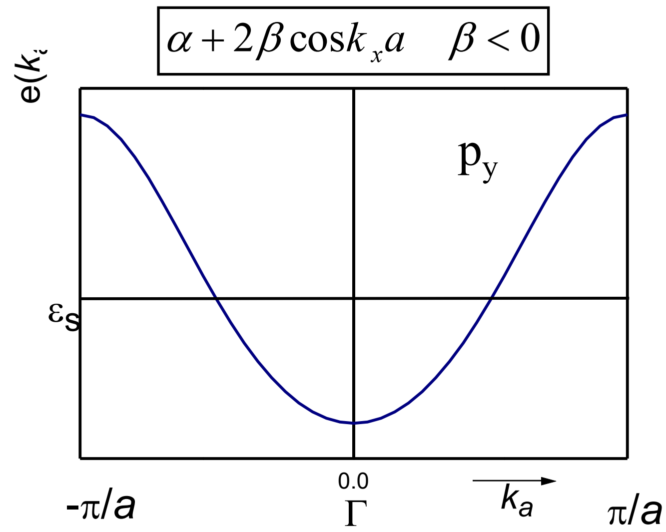


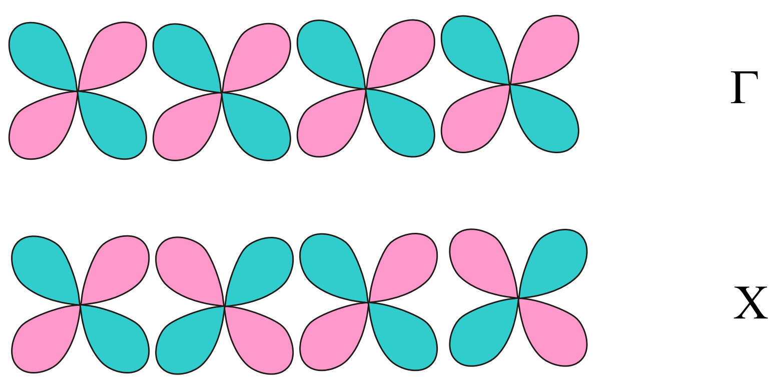


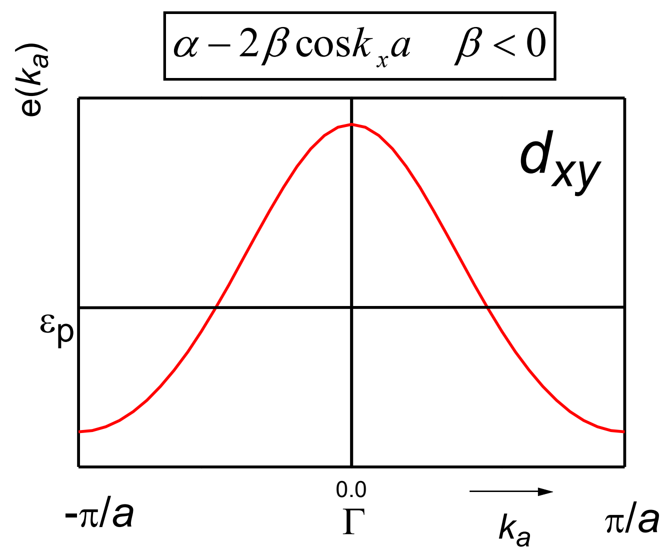


Symetrie orbitalů

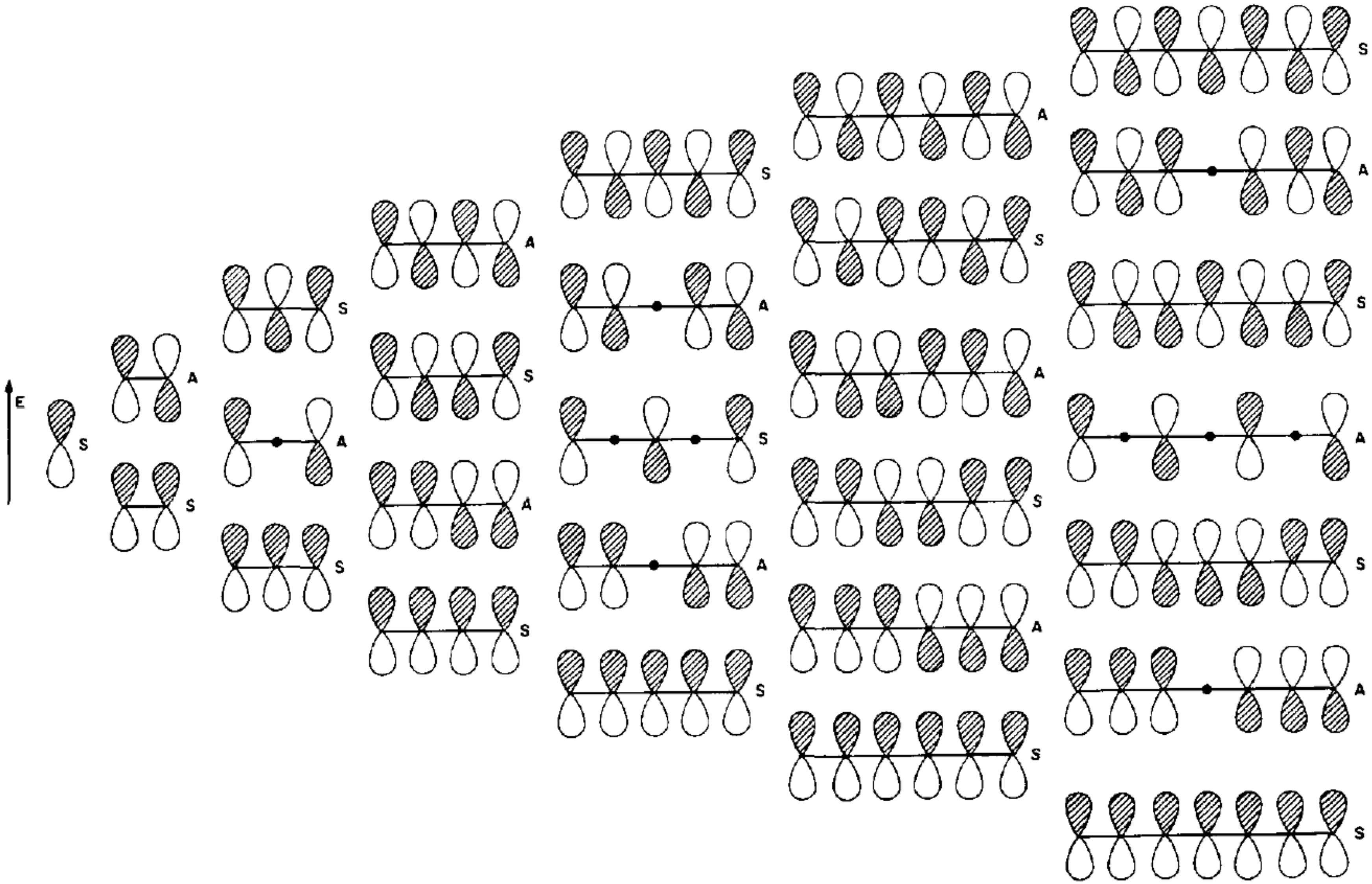






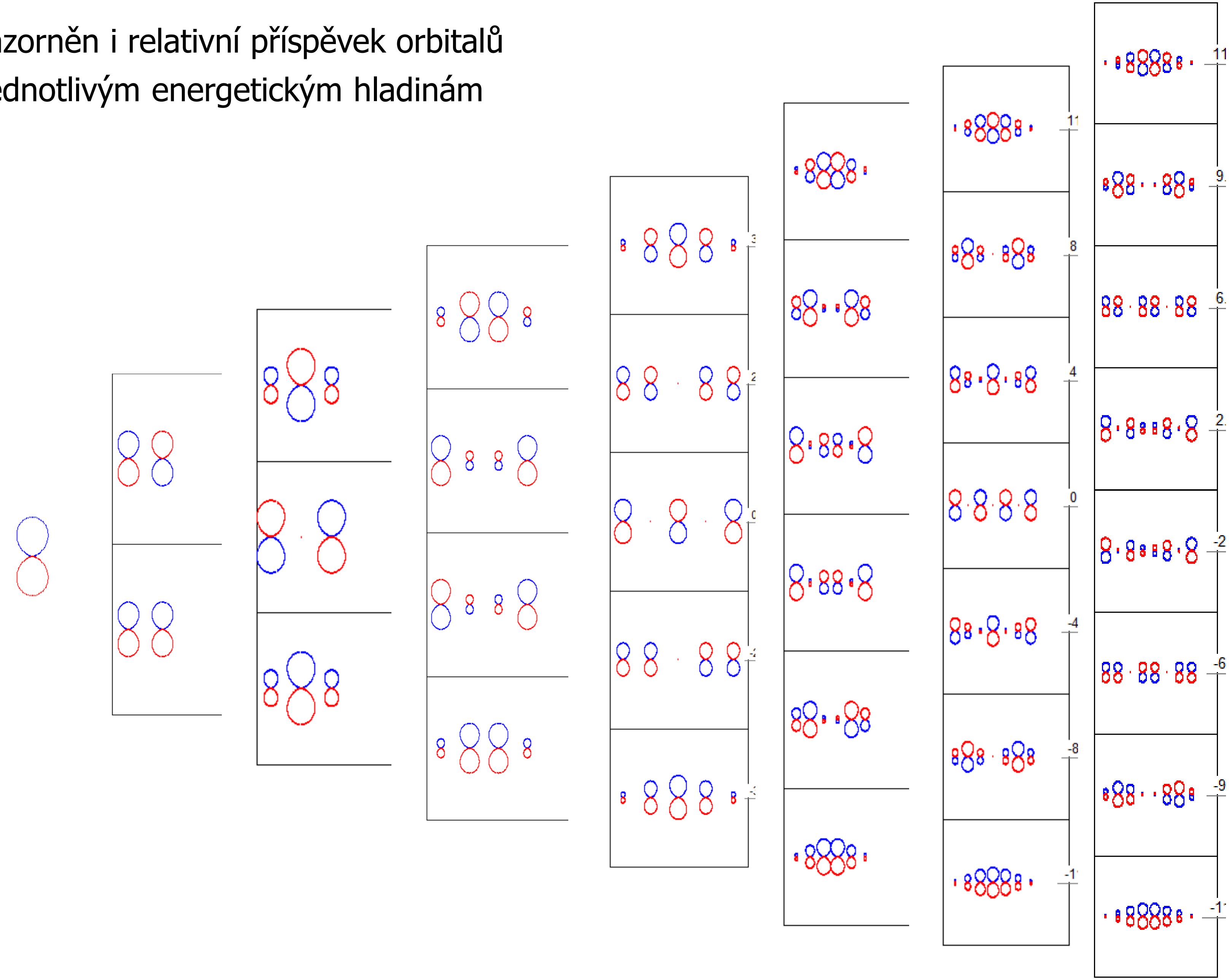


Vznik pásu – orbitaly p_y



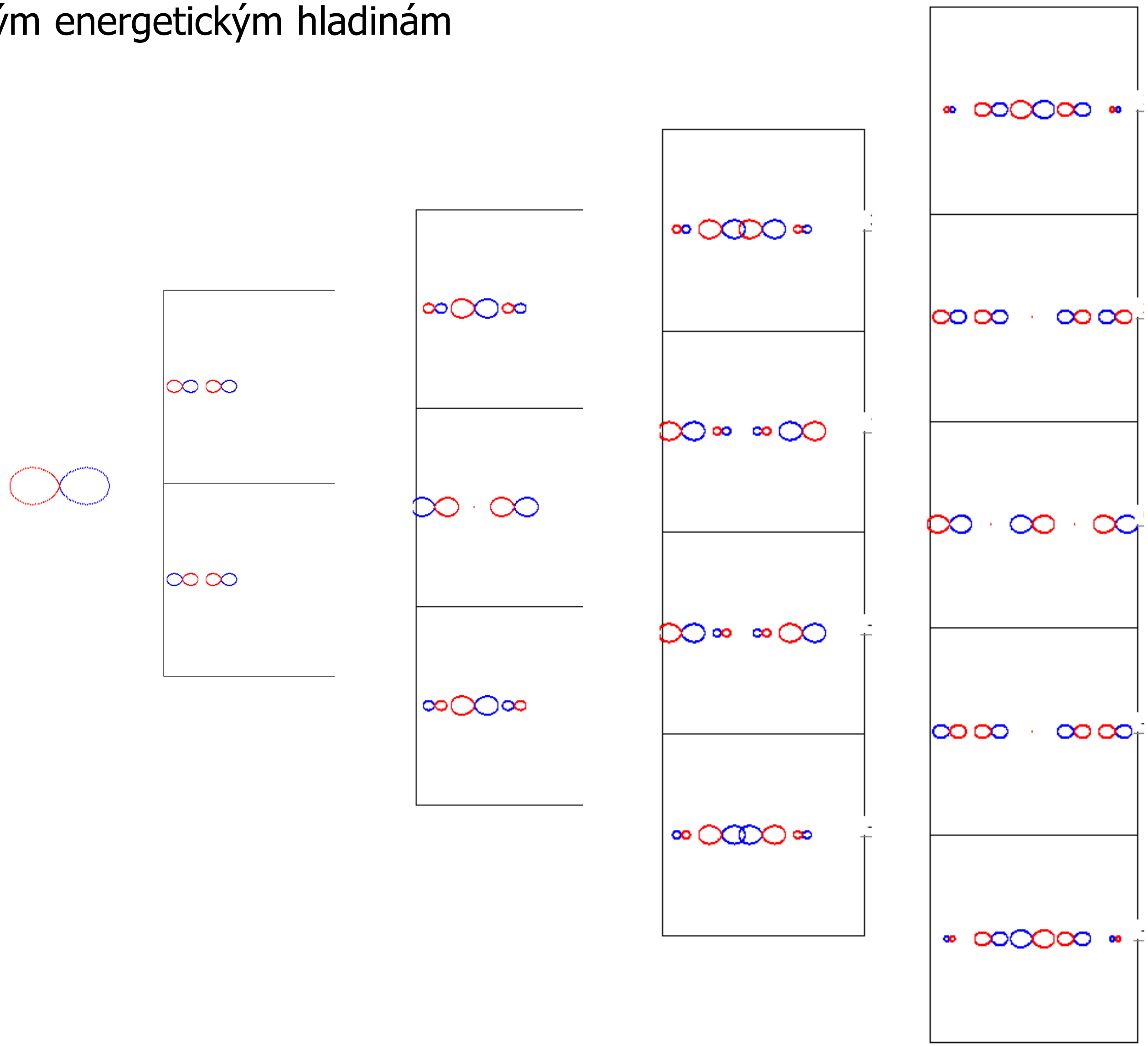
Vznik pásu – orbitaly p_y

Znázorněn i relativní příspěvek orbitalů k jednotlivým energetickým hladinám

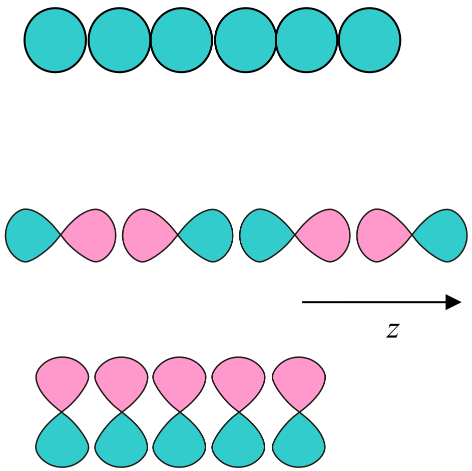


Vznik pásu – orbitaly p_x

Znázorněn i relativní příspěvek orbitalů k jednotlivým energetickým hladinám



Šířka pásu



Šířka pásu W

$W_p > W_s$

p orbitaly dosáhnou blíž k sobě, větší překryv

$W_z > W_x, W_y$

σ-vazba > π-vazba

valenční > vnitřní

Delokalizace orbitalů:

W(5d) > W(4d) > W(3d)

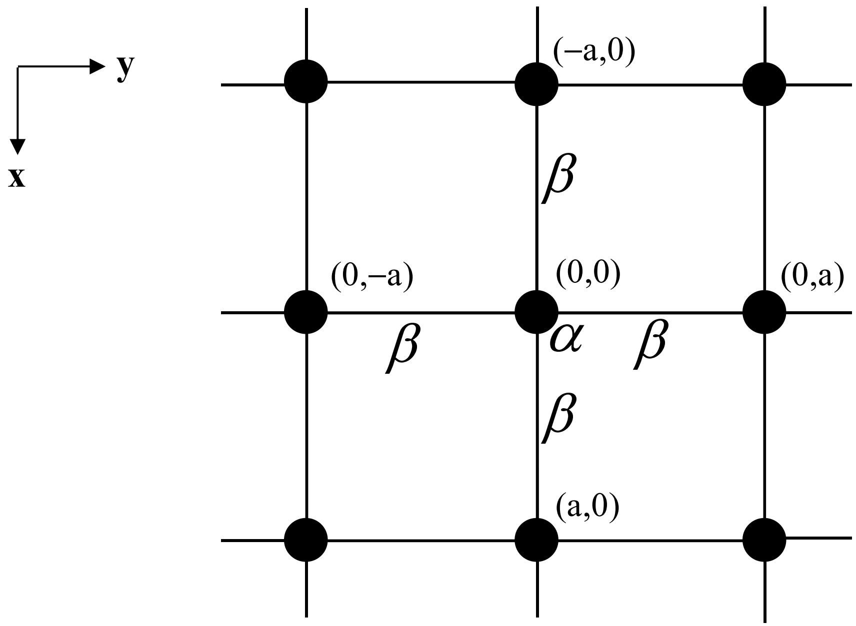
Blízkost energií orbitalů

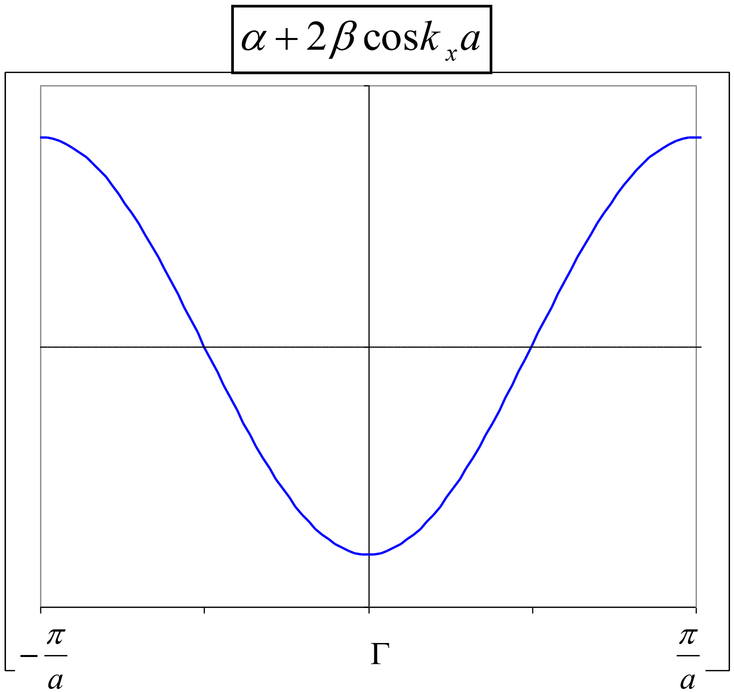
W(Co-O) > W(Ti-O)

Uvažujeme jen interakce s nejbližšími sousedy: (E~α, t~β, S<<1)
jen výměnný integrál β s nejbližším sousedem

$$H(\vec{k}) = \alpha + \beta e^{ik_x a} + \beta e^{-ik_x a} = \alpha + 2\beta \cos k_x a$$

$$H(\vec{k}) = \alpha + \beta e^{ik_x a} + \beta e^{-ik_x a} + \beta e^{ik_y a} + \beta e^{-ik_y a} + \beta e^{ik_z a} + \beta e^{-ik_z a} =$$
$$= \alpha + 2\beta(\cos k_x a + \cos k_y a + \cos k_z a)$$





$$H_{ij}(k) = \left\langle \chi_i(r) \middle| \hat{H} \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \hat{H} \middle| \chi_j(r-n'a) \right\rangle \right]$$

$$S_{ij}(k) = \left\langle \chi_i(r) \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \chi_j(r-n'a) \right\rangle \right]$$

Omezení na nejbližší sousedy: $n' = n$, $n \pm 1$

$$n' = n : \alpha = \left\langle \chi_i(r) \middle| \hat{H} \middle| \chi_j(r) \right\rangle;$$

$$n' = n \pm 1 : \beta = \left\langle \chi_i(r) \middle| \hat{H} \middle| \chi_j(r \pm a) \right\rangle; \; S = \left\langle \chi_i(r) \middle| \chi_j(r \pm a) \right\rangle$$

$$\exp[ika] + \exp[-ika] = \cos(ka) + i\sin(ka) + \cos(ka) - i\sin(ka) = 2\cos(ka)$$

$$H_{ij}(k) = \alpha + 2\beta\cos(ka), \qquad S_{ij}(k) = 1 + 2S\cos(ka)$$

$$E = \frac{H_{ij}(k)}{S_{ij}(k)} \xrightarrow{S \to 0} E = \alpha + 2\beta\cos(ka)$$

$$1D : E = \alpha + 2\beta\cos(k_x a)$$

$$3D : E = \alpha + 2\beta[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]$$

$$H_{ij}(k) = \left\langle \Phi_i(k) \middle| \hat{H} \middle| \Phi_j(k) \right\rangle = \int \sum_{n=0} \chi_i^*(r-na)\exp[-ikna]\,\hat{H} \sum_{n'=0} \chi_j(r-n'a)\exp[ikn'a]$$

$$= \int \left(\chi_i^*(r) + \sum_{n=1} \chi_i^*(r-na)\exp[-ikna] \right) \left(\hat{H}\chi_j(r) + \hat{H} \sum_{n'=1} \chi_j(r-n'a)\exp[ikn'a] \right)$$

$$= \left\langle \chi_i(r) \middle| \hat{H} \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \hat{H} \middle| \chi_j(r-n'a) \right\rangle \right]$$

$$S_{ij}(k) = \left\langle \Phi_i(k) \middle| \Phi_j(k) \right\rangle =$$

$$\left\langle \chi_i(r) \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \chi_j(r-n'a) \right\rangle \right]$$

$$H_{ij}(k) = \left\langle \chi_i(r) \middle| \hat{H} \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \hat{H} \middle| \chi_j(r-n'a) \right\rangle \right]$$

$$S_{ij}(k) = \left\langle \chi_i(r) \middle| \chi_j(r) \right\rangle + \sum_{n=1} \sum_{n'=1} \left[\exp[ik(n-n')a] \left\langle \chi_i(r-na) \middle| \chi_j(r-n'a) \right\rangle \right]$$

Blochovy orbitaly: (BO)

$$\phi_j(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n \chi_j(\mathbf{r}-\mathbf{R}_n)\exp(i\mathbf{k}\mathbf{R}_n)$$

- báze

Krystalové orbitaly: (CO)

$$\psi_i(\mathbf{k},\mathbf{r}) = \sum_j c_{ij}(\mathbf{k})\,\phi_j(\mathbf{k},\mathbf{r})$$

$$\hat{H}\psi_i(\mathbf{k}) = E_i(\mathbf{k})\psi_i(\mathbf{k})$$

$c_{ij}(\mathbf{k})$, $E_i(\mathbf{k})$ = ?

$$\left|H_{jl}(\mathbf{k}) - E_i(\mathbf{k})S_{jl}(\mathbf{k})\right| = 0 \qquad \left[H_{jl}(\mathbf{k}) - E_i(\mathbf{k})S_{jl}(\mathbf{k})\right]\left[c_{ji}(\mathbf{k})\right] = [0]$$

maticové elementy:

$$H_{jl}(\mathbf{k}) = \left\langle \phi_j(\mathbf{k}) \middle| \hat{H} \middle| \phi_l(\mathbf{k}) \right\rangle \qquad S_{jl}(\mathbf{k}) = \left\langle \phi_j(\mathbf{k}) \middle| \phi_l(\mathbf{k}) \right\rangle$$

parametry:

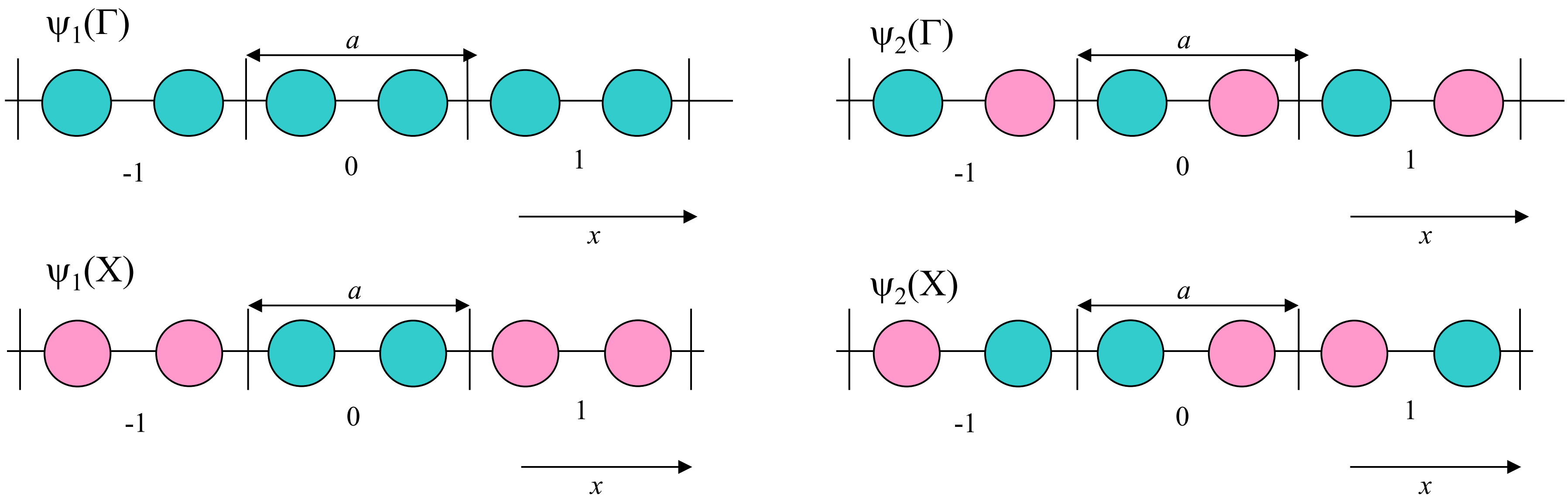
$$E_j = \left\langle \chi_j \middle| \hat{H} \middle| \chi_j \right\rangle \quad t_{jl} = \left\langle \chi_j \middle| \hat{H} \middle| \chi_l \right\rangle \quad \sigma_{jl} = \left\langle \chi_j \middle| \chi_l \right\rangle$$

$$\left\langle \phi_j \middle| \hat{H} \middle| \phi_l \right\rangle = \int_\tau \phi_j^* \hat{H} \phi_l \, d\tau \qquad \left\langle \phi_j \middle| \phi_l \right\rangle = \int_\tau \phi_j^* \phi_l \, d\tau$$

Lineární krystal s dvouatomovou bází

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \,,\; t = t_1 = t_2$$

$$\varepsilon = \varepsilon \pm 2t\cos(k_a a/2)$$



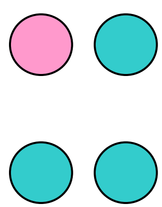
MO ~ Γ(k=0)

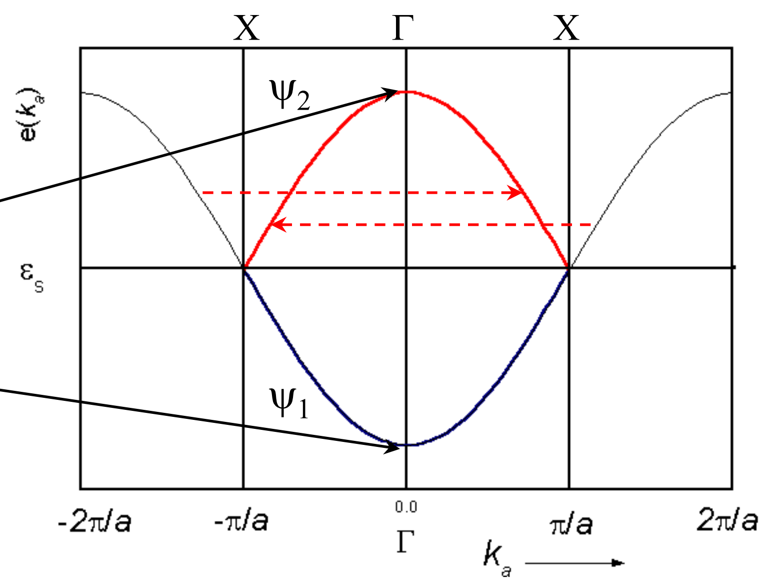
$E_2 = \alpha - \beta$

$\Psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$

$E_1 = \alpha + \beta$

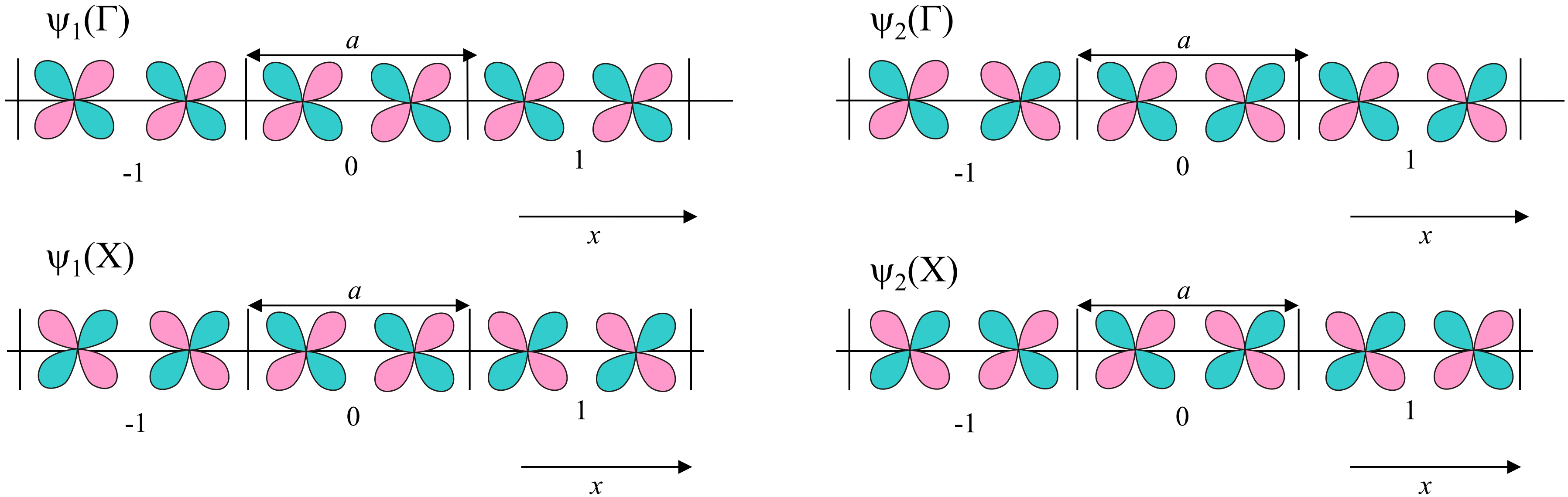
$\Psi_1 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$





$$\varepsilon = \varepsilon_1 = \varepsilon_2\ ,\ t = t_1 = t_2$$

$$\varepsilon = \varepsilon \pm 2t\cos(k_a a/2)$$



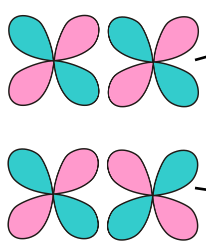
MO ~ Γ(k=0)

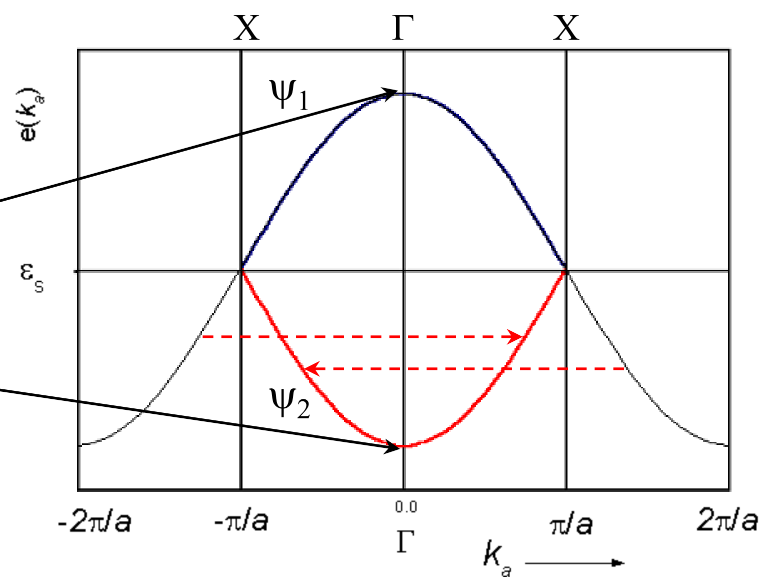
$E_1 = \alpha + \beta$

$\Psi_1 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$

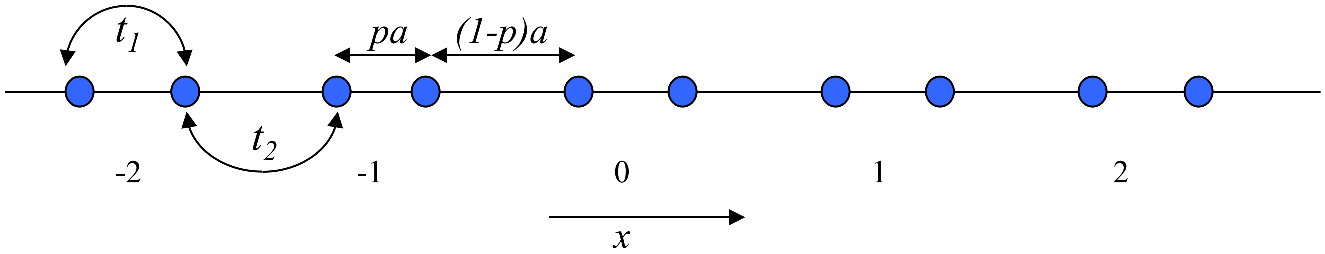
$E_2 = \alpha - \beta$

$\Psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$





Lineární krystal s dvouatomovou bází – obecné vztahy

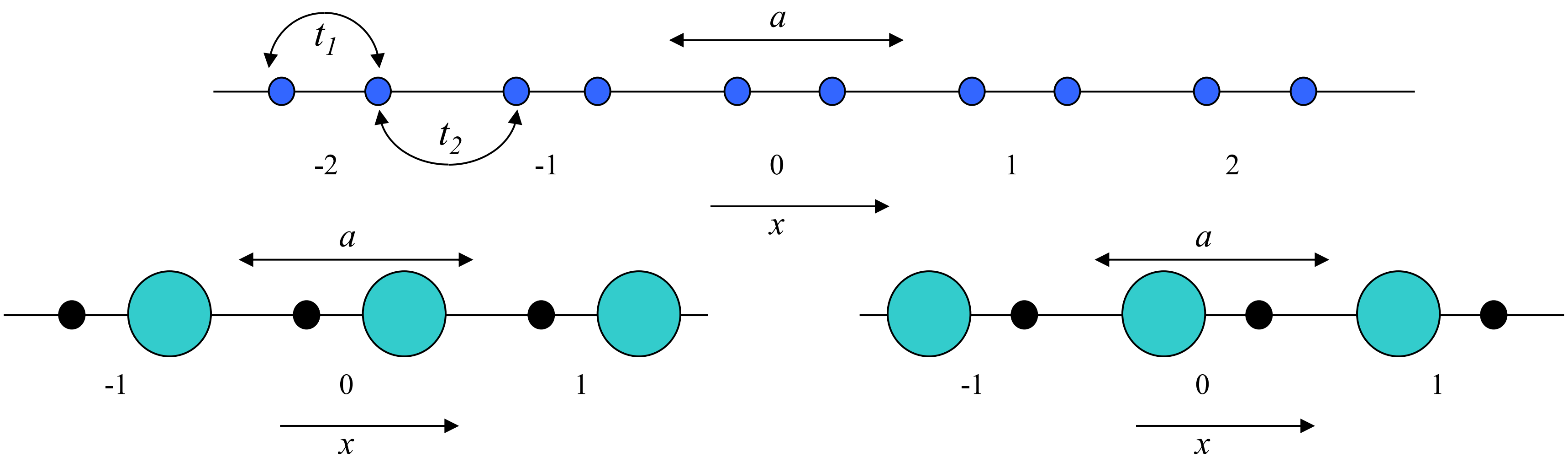


$$a = pa + (1-p)a$$

$$H_{12} = \beta_1 e^{ikpa} + \beta_2 e^{-ik(1-p)a} = \beta_1 e^{ikpa} + \beta_2 e^{-ika} e^{ikpa} = e^{ikpa}(\beta_1 + \beta_2 e^{-ika})$$

$$H_{21} = e^{-ikpa}(\beta_1 + \beta_2 e^{ika}) = H_{12}^*$$

Lineární krystal s dvouatomovou bází – obecné vztahy



BO

$$\phi_\mu(k_a) = \frac{1}{\sqrt{N}} \sum_n \chi_\mu\left(x - (n + X_1)a\right)\exp\left(ik_a(n + X_2)a\right) \quad , \qquad \mu = 1,2$$

CO

$$\psi = c_1\phi_1 + c_2\phi_2$$

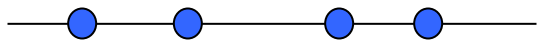
? E, c_1 , c_2

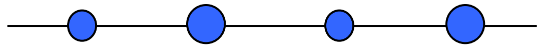
$$\begin{vmatrix} H_{11}(k) - e_i(k) & H_{12}(k) \\ H_{21}(k) & H_{22}(k) - e_i(k) \end{vmatrix} = 0$$

$$H_{\mu\mu} = \varepsilon_\mu = \langle \chi_\mu | H^{eff} | \chi_\mu \rangle \quad , \quad \mu = 1,2 \qquad H_{12} = H_{21}^* = t_1 + t_2 \cdot \exp(-ik_a a)$$

$$E(\mathbf{k}) = (\varepsilon_1 + \varepsilon_2)/2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2/4 + (t_1^2 + t_2^2 + 2t_1t_2\cos(k_a a))}$$

Lineární krystal s dvouatomovou bází



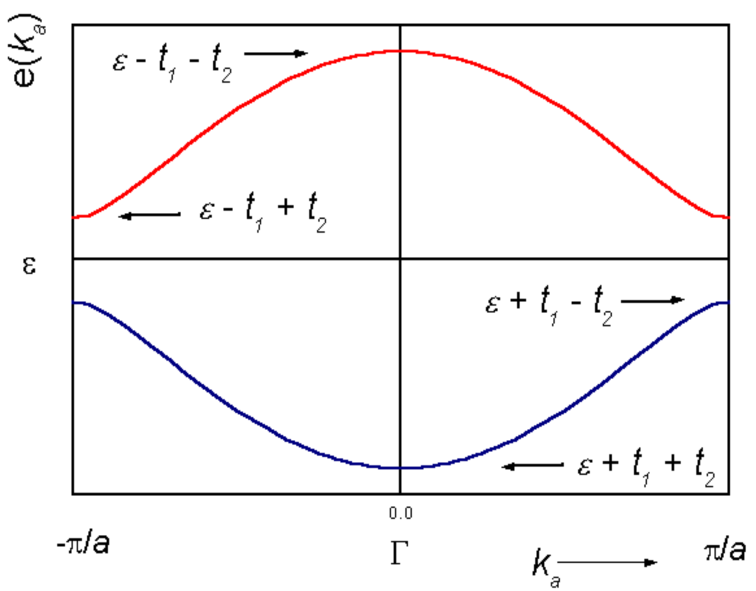


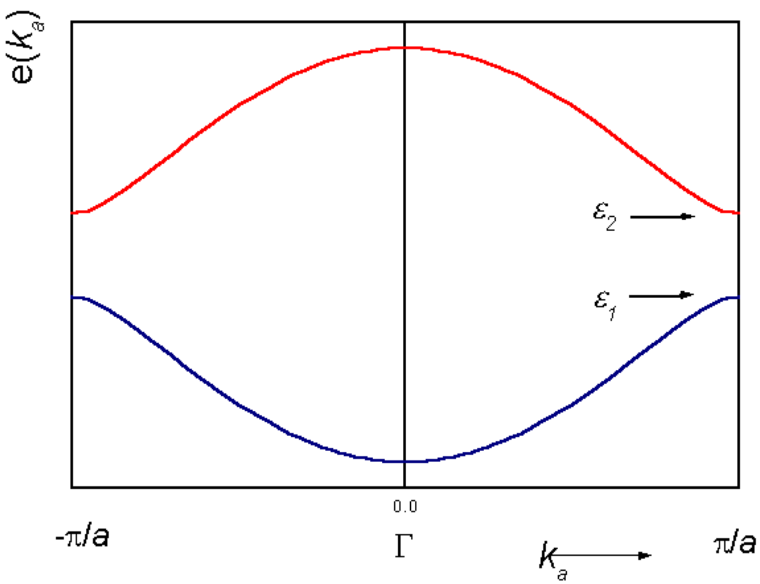
$$\varepsilon = \varepsilon_1 = \varepsilon_2 , \quad t_1 < t_2 < 0$$

$$e = \varepsilon \pm \sqrt{t_1^2 + t_2^2 + 2t_1 t_2 \cos(k_a a)}$$

$$\varepsilon_1 < \varepsilon_2 , \quad t = t_1 = t_2 < 0$$

$$e = (\varepsilon_1 + \varepsilon_2)/2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2/2 + 4t^2 \cos(k_a a/2)}$$





$$w = 2|\, t_2 \,| \qquad e_g = 2(t_2 - t_1)$$

$$w = 2|\, t \,|$$

Pásová struktura – rychlost a efektivní hmota elektronu

$$E = \frac{mv^2}{2}$$

$$p = mv = \hbar k$$

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$$\frac{\partial E}{\partial k} = \frac{\hbar^2 k}{m}$$

$$\frac{\partial^2 E}{\partial k^2} = \frac{\hbar^2}{m}$$

$$v = \frac{1}{\hbar}\frac{\partial E}{\partial k}$$

$$\frac{1}{m} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$$

$$DOS^{-1} = \frac{\partial E}{\partial k} = \hbar v$$

$E = \vec{F}\vec{l} = \vec{p}\vec{v}$

$\vec{F} = \vec{a}m$

$\vec{p} = m\vec{v} = \vec{F}t$

$\hat{O}(f_1 + f_2) = \hat{O}f_1 + \hat{O}f_2; \quad \hat{O}cf + c\hat{O}f$ lineární operátor

$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$ komutující operátory

$\left[\hat{L}^2, \hat{L}_x\right] = 0 \quad \left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \quad \left[\hat{x}, \hat{p}_x\right] = i\hbar$

$\int_\tau \Psi_1^* \hat{H} \Psi_2 d\tau = \int_\tau \Psi_2 \hat{H}^* \Psi_1^* d\tau$ H je Hermitovský operátor

$K = a_{ij} + ib_{ij}; \quad K^* = a_{ij} - ib_{ij}$ K^*: komplexně sdružená

$K = K^{T*} = K^H; \quad a_{ij} + ib_{ij} = a_{ji} - ib_{ji}$ Hermitovská matice

$K \cdot K^H = K^H \cdot K = 1, \text{ tj. } K^H = K^{-1}$ unitární matice

$K \cdot K^T = K^T \cdot K = 1, \text{ tj. } K^T = K^{-1}$ ortogonální matice

$S_{ij} = \int_\tau \Psi^* \Psi d\tau$

$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$S_{ii} = 1$: normované funkce

$S_{ij} = 0$: ortogonální funkce

$S_{ij} = \delta_{ij}$: ortonormální funkce