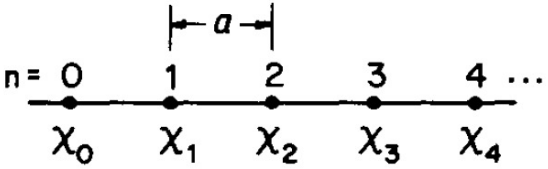
Комп’ютерне моделювання електронних властивостей матеріалів

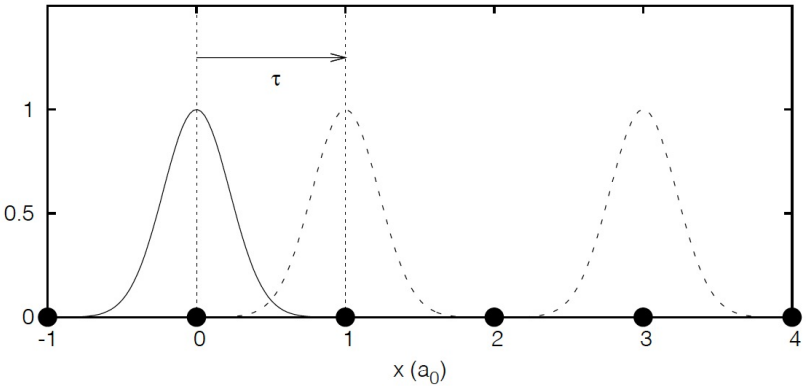
Лабораторна робота 4
Зонна структура двовимірних кристалів

Олег Фея, к.ф-м.н

ЗОННА СТРУКТУРА ЛАНЦЮЖКА АТОМІВ

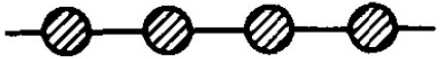


$$\psi_k = \sum_n e^{ikna}\ \chi_n$$



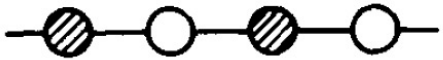
$k = 0$ $\quad \psi_0 = \sum_n e^0\ \chi_n = \sum_n \chi_n$

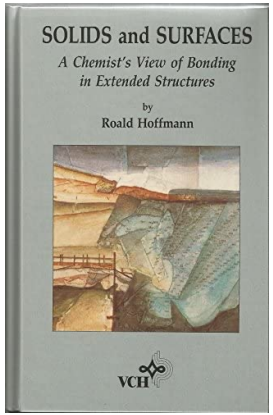
$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$



$k = \frac{\pi}{a}$ $\quad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n}\ \chi_n = \sum_n (-1)^n\ \chi_n$

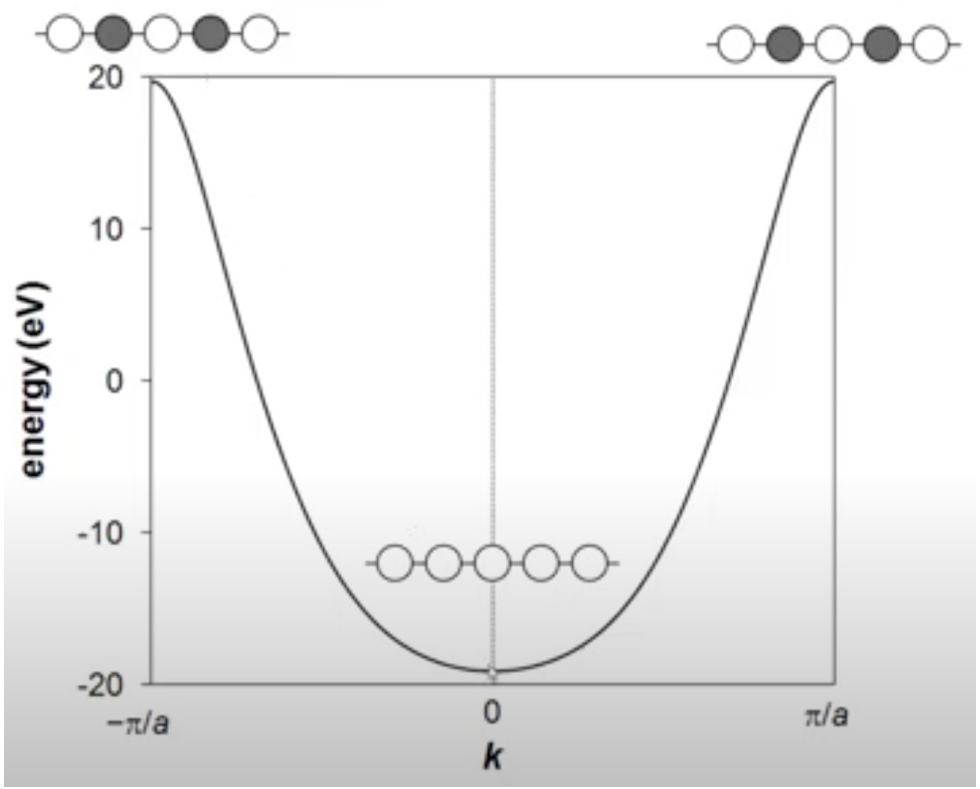
$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$



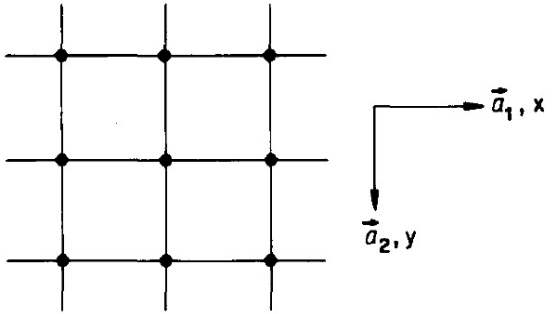


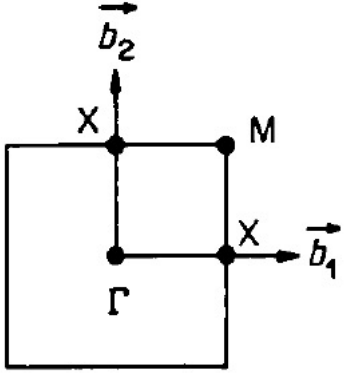
ЗОННА СТРУКТУРА ЛАНЦЮЖКА АТОМІВ

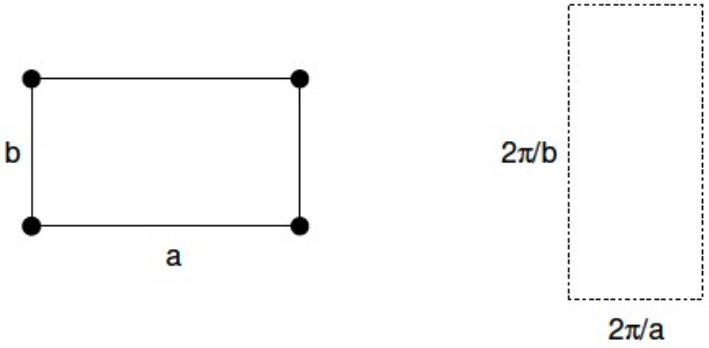
$$E_{kin} = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$



ЗОННА СТРУКТУРА ПОВЕРХНІ





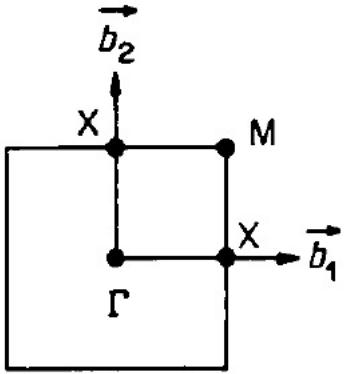


$$\Gamma = (0, 0)$$

$$X = (\pi/a, 0) = (0, \pi/a)$$

$$M = (\pi/a, \pi/a)$$

ЗОННА СТРУКТУРА ПОВЕРХНІ

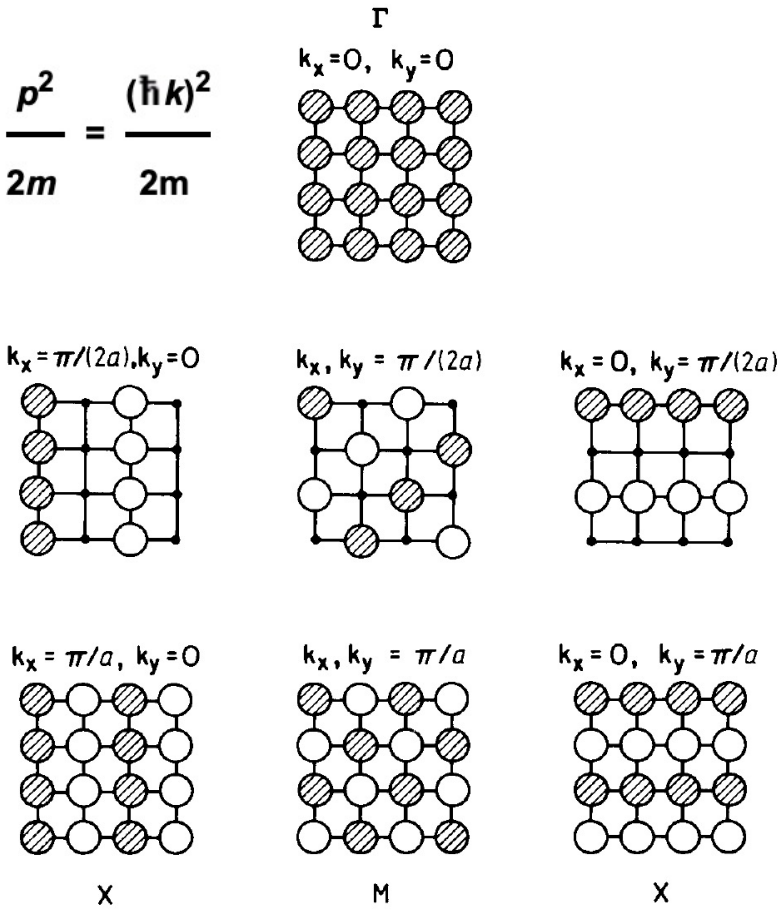


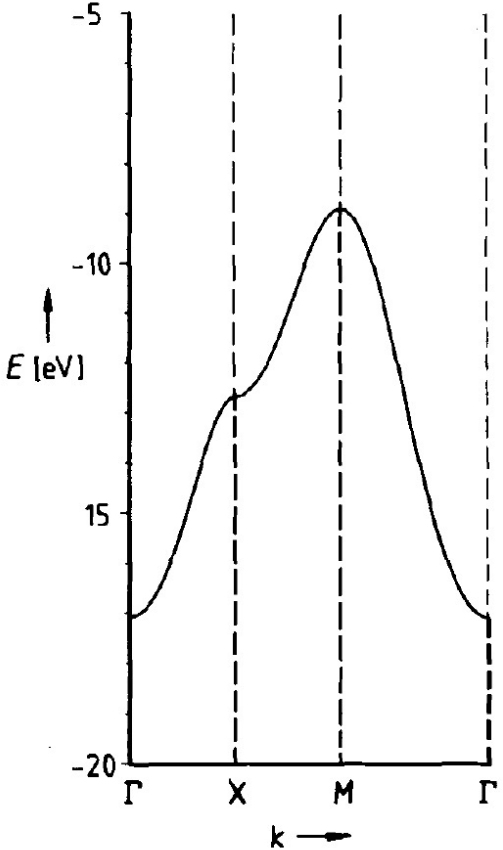
$$E_{kin} = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$

$\Gamma = (0, 0)$

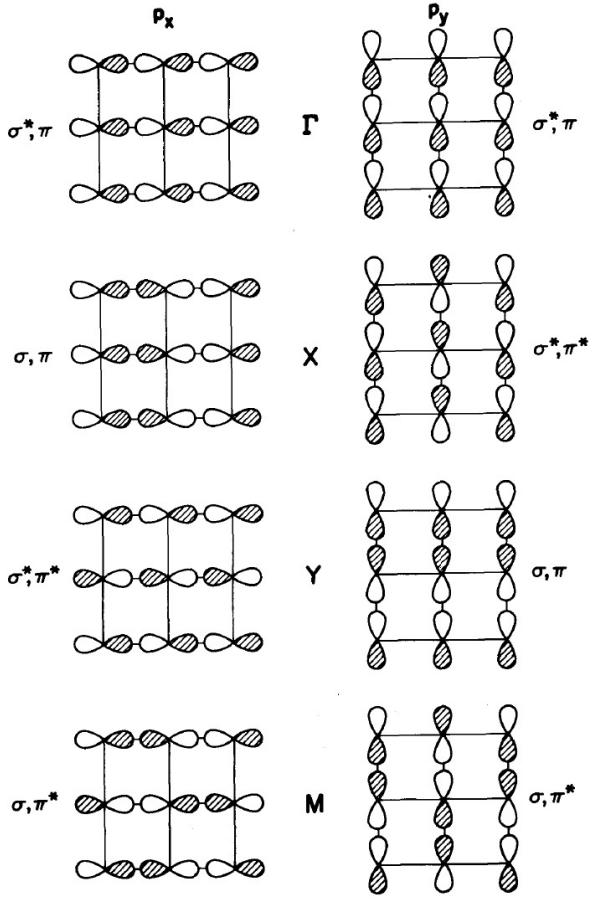
$X = (\pi/a, 0) = (0, \pi/a)$

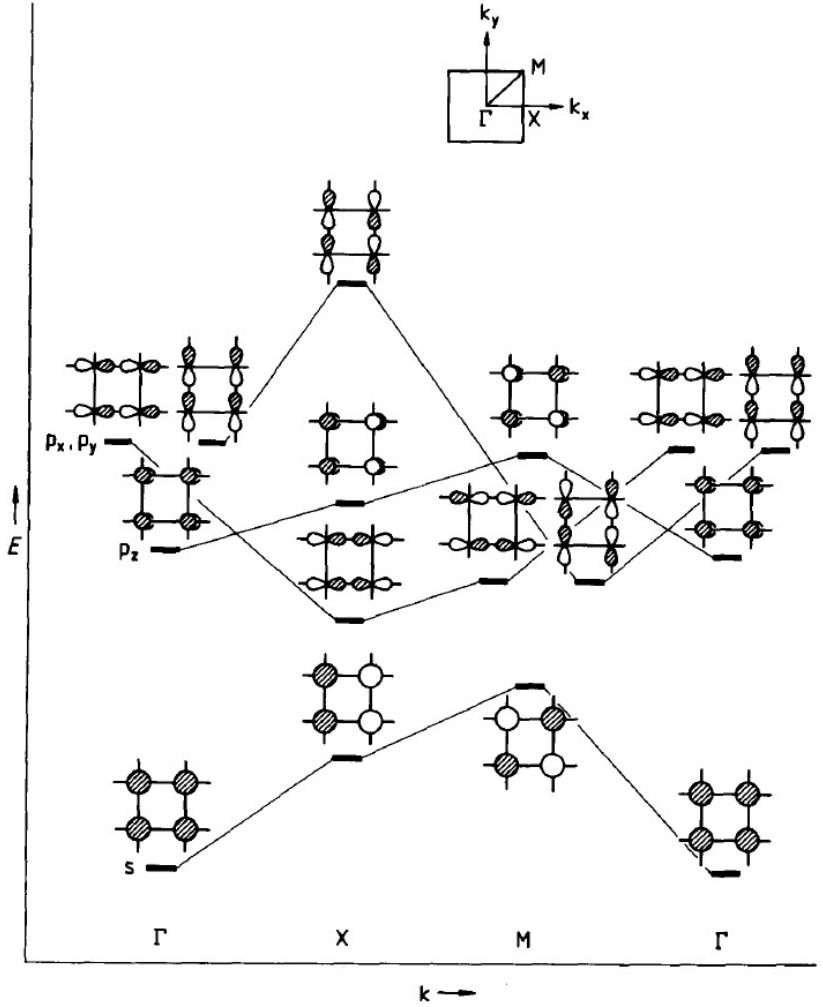
$M = (\pi/a, \pi/a)$



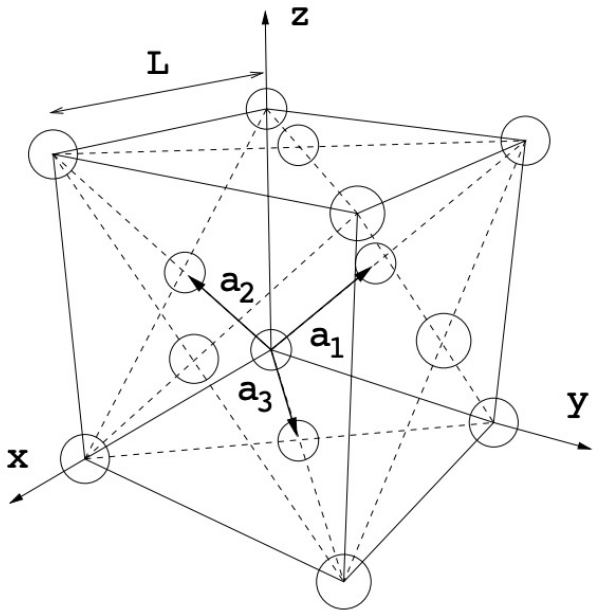


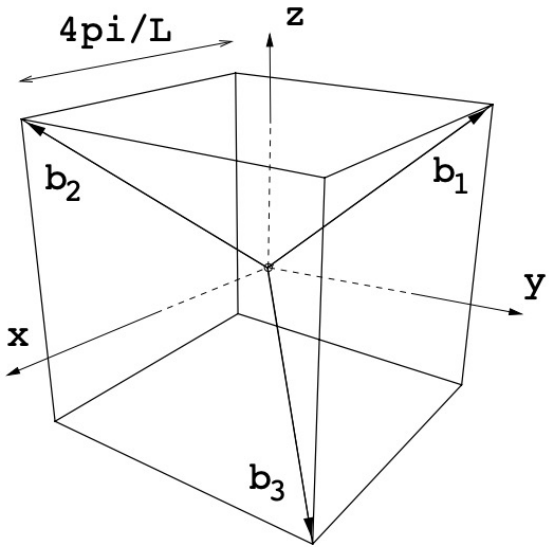
ЗОННА СТРУКТУРА ПОВЕРХНІ

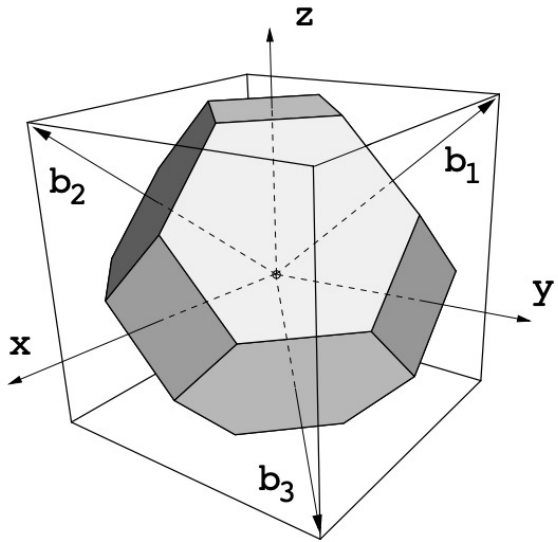




ЗОНА БРІЛЛЮЕНА КРИСТАЛУ



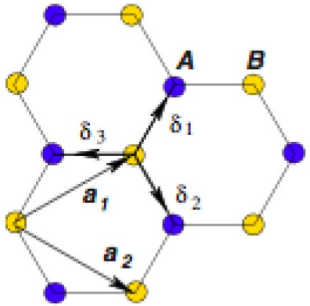


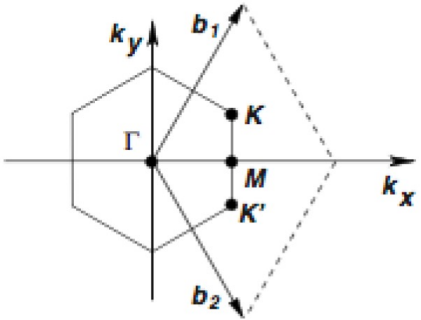


$$\mathbf{b}_1 = \frac{2\pi}{\Omega}\mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega}\mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega}\mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \qquad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

Tight-binding model





a_1, a_2 – вектори комірки
K, K’ – точки Дірака

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3})$$

$$\mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$

$$\boldsymbol{\delta}_1 = \frac{a}{2}(1, \sqrt{3})$$

$$\boldsymbol{\delta}_2 = \frac{a}{2}(1, -\sqrt{3})$$

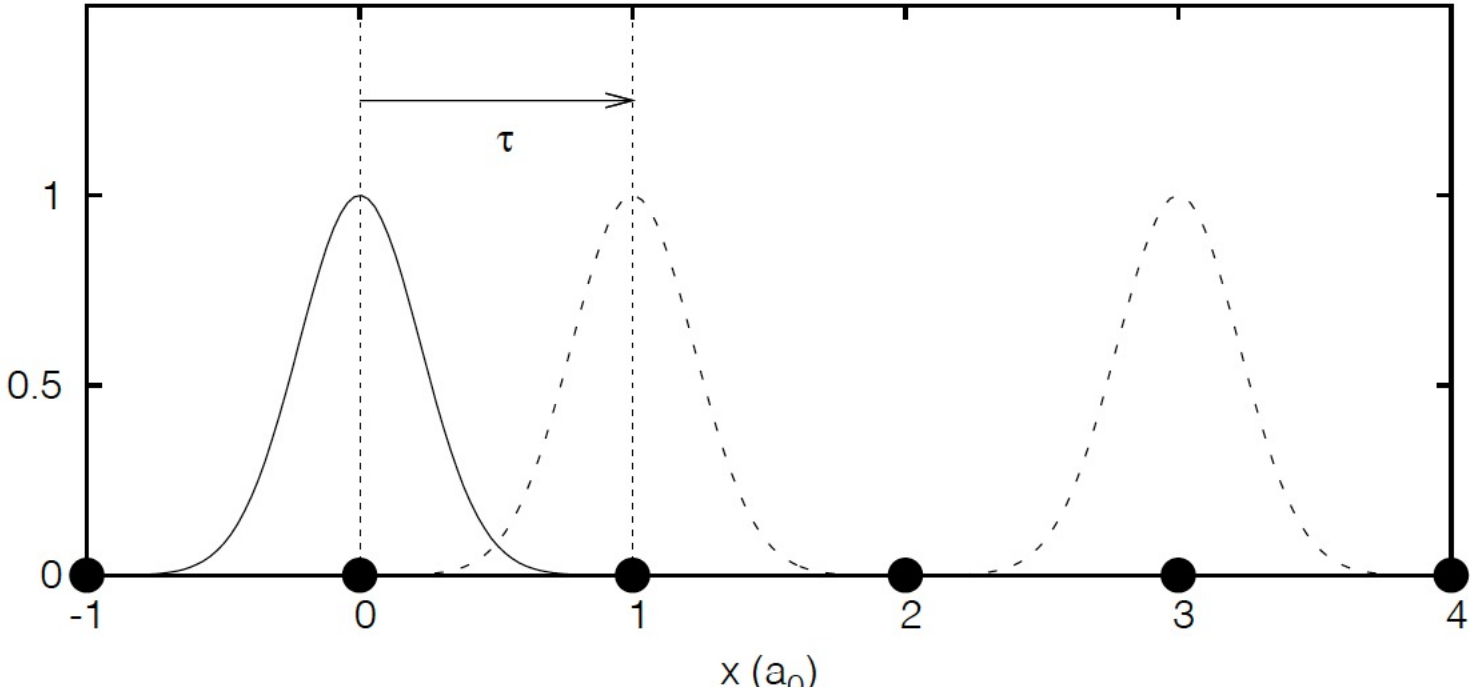
$$\boldsymbol{\delta}_3 = -a(1, 0)$$

$$\mathbf{K} = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, 1)$$

$$\mathbf{K}' = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, -1)$$

Tight-binding model

$$H\psi_{n\mathbf{k}}(\mathbf{r}) = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}) \qquad \psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r}) \qquad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi_n(\mathbf{r}-\mathbf{R})$$

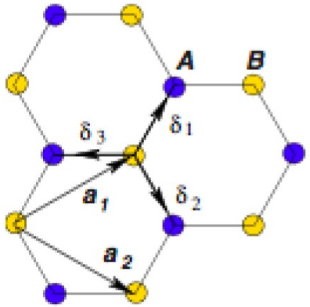


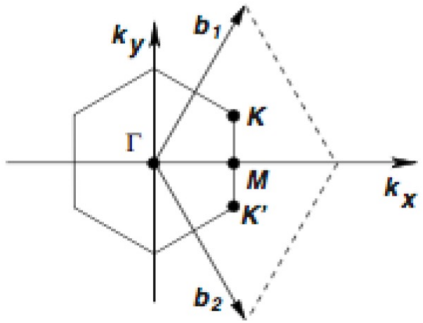
Tight-binding model

оператори утворення чи знищення для атомів A та B

$$\hat{H} = -t \sum_{\langle ij \rangle} (\hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i)$$ - tight-binding Гамільтоніан

інтеграл перескакування між сусідніми атомами (hopping integral)

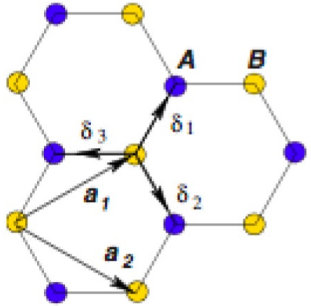


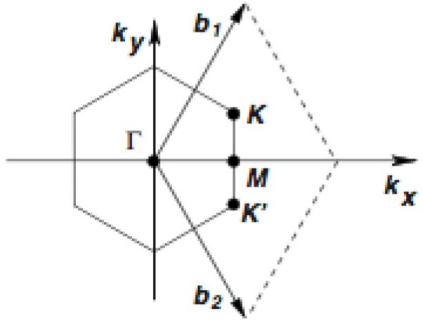


Tight-binding model

$$\hat{H} = -t \sum_{\langle ij \rangle} (\hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i)$$

$$\sum_{\langle ij \rangle} (\hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i) = \sum_{i \in A} \sum_{\boldsymbol{\delta}} (\hat{a}_i^\dagger \hat{b}_{i+\boldsymbol{\delta}} + \hat{b}_{i+\boldsymbol{\delta}}^\dagger \hat{a}_i)$$





$$\hat{a}_i^\dagger = \frac{1}{\sqrt{N/2}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i} \hat{a}_{\mathbf{k}}^\dagger$$

$$\hat{H} = -\frac{t}{N/2} \sum_{i \in A} \sum_{\boldsymbol{\delta},\mathbf{k},\mathbf{k}'} [e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} e^{-i\mathbf{k}'\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}'} + \text{H.c.}] = -t \sum_{\boldsymbol{\delta},\mathbf{k}} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + \text{H.c.}) = -t \sum_{\boldsymbol{\delta},\mathbf{k}} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{b}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}})$$

$$\sum_{i \in A} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} = \frac{N}{2} \delta_{\mathbf{k}\mathbf{k}'}$$

Tight-binding model

$$\hat{H} = -t \sum_{\boldsymbol{\delta},\mathbf{k}} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{a}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{b}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}})$$

$$\hat{H} = \sum_{\mathbf{k}} \boldsymbol{\Psi}^\dagger \mathbf{h}(\mathbf{k}) \boldsymbol{\Psi}$$

$$\boldsymbol{\Psi} \equiv \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix}, \qquad \boldsymbol{\Psi}^\dagger = \begin{pmatrix} \hat{a}^\dagger_{\mathbf{k}} & \hat{b}^\dagger_{\mathbf{k}} \end{pmatrix}$$

$$\mathbf{h}(\mathbf{k}) \equiv -t \begin{pmatrix} 0 & \Delta_{\mathbf{k}} \\ \Delta^*_{\mathbf{k}} & 0 \end{pmatrix}$$

$$\Delta_{\mathbf{k}} \equiv \sum_{\boldsymbol{\delta}} e^{i\mathbf{k}\cdot\boldsymbol{\delta}}$$

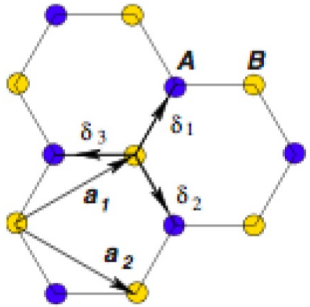
$$E_\pm = \pm t \sqrt{\Delta_{\mathbf{k}} \Delta^*_{\mathbf{k}}}$$

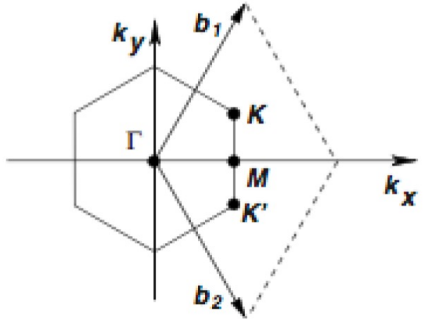
Tight-binding model

$$\Delta_{\mathbf{k}} \equiv \sum_{\boldsymbol{\delta}} e^{i\mathbf{k}\cdot\boldsymbol{\delta}}$$

$$\begin{aligned}
\Delta_{\mathbf{k}} &= e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3} \\
&= e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3}\left[1 + e^{i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_3)} + e^{i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_3)}\right] \\
&= e^{-ik_x a}\left[1 + e^{i3k_x a/2}e^{i\sqrt{3}k_y a/2} + e^{i3k_x a/2}e^{-i\sqrt{3}k_y a/2}\right] \\
&= e^{-ik_x a}\left[1 + e^{i3k_x a/2}\left(e^{i\sqrt{3}k_y a/2} + e^{-i\sqrt{3}k_y a/2}\right)\right] \\
&= e^{-ik_x a}\left[1 + 2e^{i3k_x a/2}\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\right] .
\end{aligned}$$

$$E_{\pm}(\mathbf{k}) = \pm t\sqrt{1 + 4\cos\left(\frac{3}{2}k_x a\right)\cos\left(\frac{\sqrt{3}}{2}k_y a\right) + 4\cos^2\left(\frac{\sqrt{3}}{2}k_y a\right)}$$

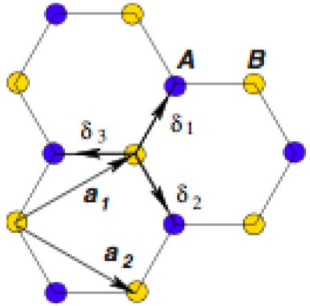


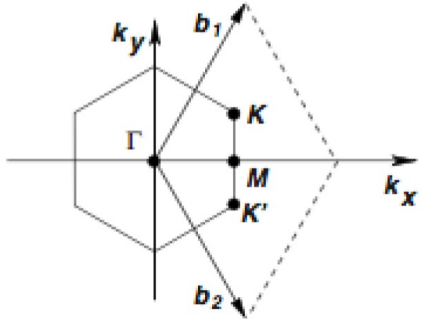


$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3})$$
$$\mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$
$$\boldsymbol{\delta}_1 = \frac{a}{2}(1, \sqrt{3})$$
$$\boldsymbol{\delta}_2 = \frac{a}{2}(1, -\sqrt{3})$$
$$\boldsymbol{\delta}_3 = -a(1, 0)$$
$$\mathbf{K} = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, 1)$$
$$\mathbf{K}' = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, -1)$$

Tight-binding model

$$\Delta_{\mathbf{K}+\mathbf{q}} = e^{-iK_x a} e^{-iq_x a} \left[1 + 2e^{i3(K_x+q_x)a/2} \cos\left(\frac{\sqrt{3}(K_y+q_y)a}{2} \right) \right]$$
$$= e^{-iK_x a} e^{-iq_x a} \left[1 - 2e^{3iaq_x/2} \cos\left(\frac{\pi}{3} + \frac{\sqrt{3}a}{2} q_y \right) \right] .$$





$$\Delta_{\mathbf{K}+\mathbf{q}} = -ie^{-iK_x a} \frac{3a}{2} (q_x + iq_y)$$

$$\Delta_{\mathbf{K}+\mathbf{q}} = -\frac{3a}{2} (q_x + iq_y)$$

$$\mathbf{h}(\mathbf{K}+\mathbf{q}) = v_F \begin{pmatrix} 0 & q_x + iq_y \\ q_x - iq_y & 0 \end{pmatrix} \qquad \mathbf{h}(\mathbf{k}) \equiv -t \begin{pmatrix} 0 & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^* & 0 \end{pmatrix}$$

$$v_F = \frac{3at}{2}$$

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3})$$
$$\mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$
$$\boldsymbol{\delta}_1 = \frac{a}{2}(1, \sqrt{3})$$
$$\boldsymbol{\delta}_2 = \frac{a}{2}(1, -\sqrt{3})$$
$$\boldsymbol{\delta}_3 = -a(1, 0)$$
$$\mathbf{K} = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, 1)$$
$$\mathbf{K}' = \frac{2\pi}{3\sqrt{3}a}(\sqrt{3}, -1)$$

Tight-binding model

$$\mathbf{h}(\mathbf{K}+\mathbf{q}) = v_F(q_x\sigma_x - q_y\sigma_y)$$

$$\bar{\mathbf{q}} \equiv \begin{pmatrix} q_x \\ -q_y \end{pmatrix}$$

$$\mathbf{h}(\mathbf{K}+\mathbf{q}) = v_F\,\bar{\mathbf{q}}\cdot\boldsymbol{\sigma}$$

АЛГОРИТМ РОЗРАХУНКУ

1. Релаксація
   pw.x < graphene.vcrelax.in > graphene.vcrelax.out

2. Самоузгоджений розрахунок
   pw.x < graphene.scf.in > graphene.scf.out

3. Розрахунок зон вздовж високосиметричних точок зони Бріллюена
   pw.x < graphene.band.in > graphene.band.out

4. Постпроцессінг – виділення енергій із graphene.band.out в окремі файли
   bands.x < graphene.band2.in > graphene.band2.out

5. Постпроцессінг – побудова графіків (опціонально)
   plotband.x < graphene.band3.in > graphene.band3.out

1. Релаксація

```
&control (графен)
  calculation = 'vc-relax'
  prefix='graphene',
  pseudo_dir = './',
  tprnfor= .true.,
  tstress= .true.,
  etot_conv_thr = 1.0d-6
  forc_conv_thr = 1.0d-6
/
&system
  ibrav=  4,
  celldm(1) = 4.650
  celldm(3) = 10,
  nat=  2,
  ntyp= 1,
  ecutwfc =50.0,
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.02
/
&electrons
  mixing_mode = 'plain'
  mixing_beta = 0.7
  conv_thr =  1.0d-8
/
```

```
&control (графіт)
  calculation = 'vc-relax'
  prefix='graphite',
  pseudo_dir = './',
  tprnfor= .true.,
  tstress= .true.,
  etot_conv_thr = 1.0d-6
  forc_conv_thr = 1.0d-6
/
&system
  ibrav=  4,
  celldm(1) = 4.650
  celldm(3) = 3.51,
  nat=  4,
  ntyp= 1,
  ecutwfc =50.0,
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.02
/
&electrons
  mixing_mode = 'plain'
  mixing_beta = 0.7
  conv_thr =  1.0d-8
/
```

1. Релаксація

```
&ions (графен)
   ion_dynamics = 'bfgs'
 /
 &cell
   cell_dynamics = 'bfgs',
   cell_dofree = ‘2Dxy',
   press = 0.0
   press_conv_thr = 0.0
 /
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.5
 C 0.333333 0.666667 0.5
K_POINTS {automatic}
8 8 1 0 0 0
```

```
&ions  (графіт)
   ion_dynamics = 'bfgs'
 /
 &cell
   cell_dynamics = 'bfgs',
   cell_dofree = 'ibrav',
   press = 0.0
   press_conv_thr = 0.0
 /
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.25
 C 0.00 0.00 0.75
 C 0.333333 0.666667 0.25
 C 0.666667 0.333333 0.75
K_POINTS {automatic}
8 8 4 0 0 0
```

2. Самоузгоджений розрахунок

```
 &control
   calculation = 'scf'
   prefix='graphene',
   pseudo_dir = './'
/
 &system
   ibrav=  4,
   celldm(1) = 4.62164,
   celldm(3) = 10,
   nat=  2,
   ntyp= 1,
   ecutwfc =50.0,
   occupations = 'smearing'
   smearing = 'gaussian'
   degauss = 0.02,
   nbnd = 8
 /
 &electrons
   mixing_mode = 'plain'
   mixing_beta = 0.7
   conv_thr =  1.0d-8
 /
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.5
 C 0.333333 0.666667 0.5
K_POINTS {automatic}
16 16 1 0 0 0
```

```
 &control
   calculation = 'scf'
   prefix='graphite',
   pseudo_dir = './'
/
 &system
   ibrav=  4,
   celldm(1) = 4.62246457,
   celldm(3) = 2.69136729,
   nat=  4,
   ntyp= 1,
   ecutwfc =50.0,
   occupations = 'smearing'
   smearing = 'gaussian'
   degauss = 0.02,
   nbnd = 16
 /
 &electrons
   mixing_mode = 'plain'
   mixing_beta = 0.7
   conv_thr =  1.0d-8
 /
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.25
 C 0.00 0.00 0.75
 C 0.333333 0.666667 0.25
 C 0.666667 0.333333 0.75
K_POINTS {automatic}
9 9 3 0 0 0
```

3.Розрахунок вздовж високосиметричного шляху

```
&control
  calculation = 'bands'
  prefix='graphene',
  pseudo_dir = './'
/
&system
  ibrav=  4,
  celldm(1) = 4.62164,
  celldm(3) = 10,
  nat=  2,
  ntyp= 1,
  ecutwfc =50.0,
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.02,
  nbnd = 8
/
&electrons
  mixing_mode = 'plain'
  mixing_beta = 0.7
  conv_thr =  1.0d-8
/
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.5
 C 0.333333 0.666667 0.5
```

```
K_POINTS {crystal_b}
4
0.00 0.00 0.00 20 !G
0.00 0.50 0.00 20 !M
0.333333 0.333333 0.00 20 !K
0.00 0.00 0.00 20  !G
```

```
&control
  calculation = 'bands'
  prefix='graphite',
  pseudo_dir = './'
/
&system
  ibrav=  4,
  celldm(1) = 4.62246457,
  celldm(3) = 2.69136729,
  nat=  4,
  ntyp= 1,
  ecutwfc =50.0,
  occupations = 'smearing'
  smearing = 'gaussian'
  degauss = 0.02,
  nbnd = 16
/
&electrons
  mixing_mode = 'plain'
  mixing_beta = 0.7
  conv_thr =  1.0d-8
/
ATOMIC_SPECIES
 C  12.011  C.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS crystal
 C 0.00 0.00 0.25
 C 0.00 0.00 0.75
 C 0.333333 0.666667 0.25
 C 0.666667 0.333333 0.75
```

```
K_POINTS {crystal_b}
8
0.00 0.00 0.00 20 !G
0.00 0.50 0.00 20 !M
0.333333 0.333333 0.00 20 !K
0.00 0.00 0.00 20  !G
0.00 0.00 0.50 20 !A
0.00 0.50 0.50 20 !L
0.333333 0.333333 0.50 20 !H
0.00 0.00 0.50 20 !A
```