

# Band structures calculations

- reciprocal space of k-vectors, Brillouin zone
- secular equation, variational method
- band structure, periodic potential
- density of states, Fermi energy
- almost free electrons method
- tight binding method, MO-LCAO, Bloch function

- T. A. Albright, J. K. Burdett, M.-H. Whangbo, Wiley (2013)  
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- J. K. Burdett, Progress in Solid State Chemistry 15 (1984) 173-255  
From Bonds to Bands and Molecules to Solids.
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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  
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- S. Cottenier (2013)  
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<http://lom.fzu.cz/main/lom/krystalochemie/index.html>

<http://lom.fzu.cz/main/lom/chapl/index.html>

space of **k**-vectors - reciprocal space

direct lattice:

$V_r$

crystal lattice

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

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

reciprocal space:

$V_c$

reciprocal lattice

$$\mathbf{g} = u\mathbf{b}_1 + v\mathbf{b}_2 + w\mathbf{b}_3$$

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

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

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

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

$$V_r = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

$$V_c = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$$

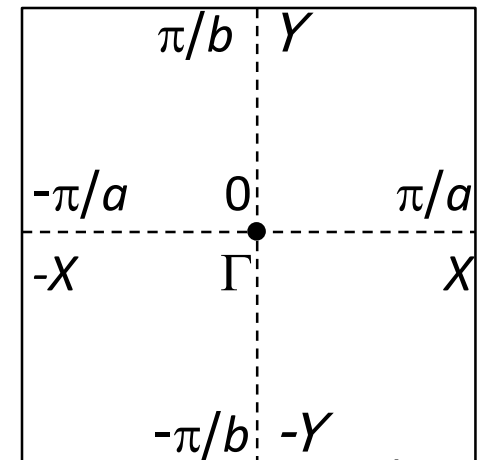
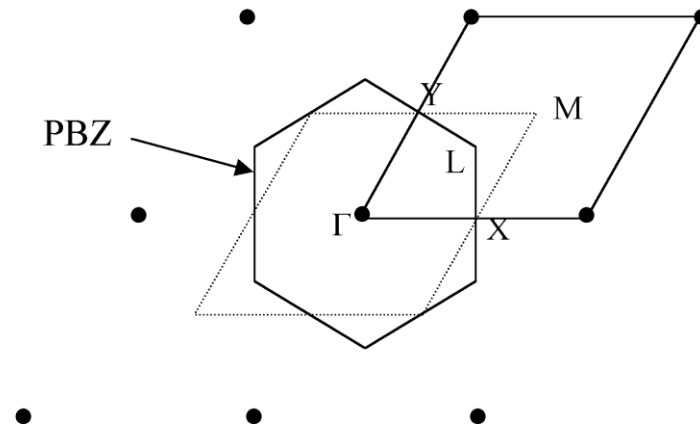
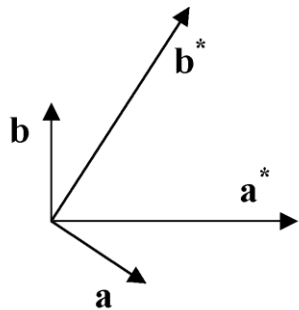
$$V_c = \frac{8\pi^3}{V_r}$$

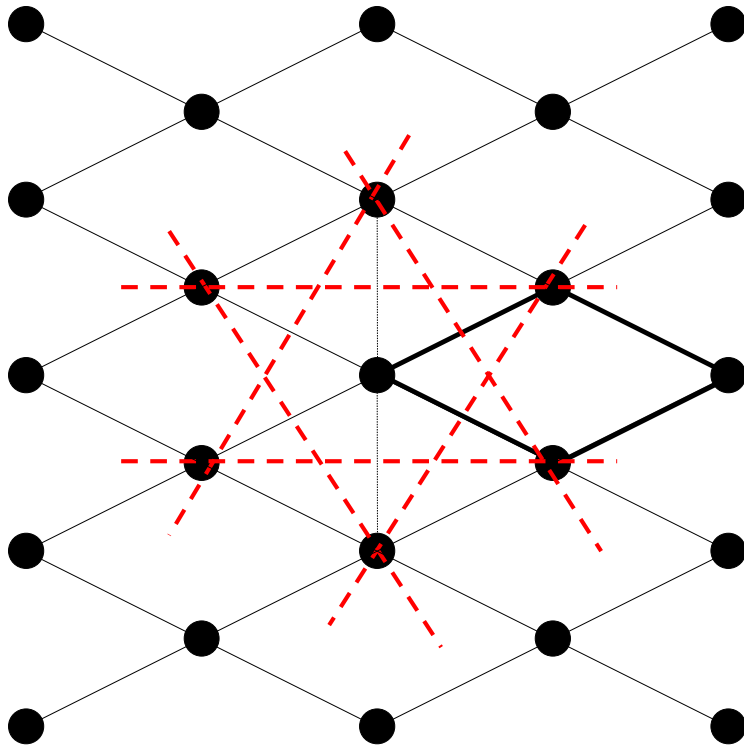
- holds:
- $E(\mathbf{k}) = E(-\mathbf{k})$
  - One value of  $E$  for each  $\mathbf{k}$  within one band
  - $E(\mathbf{k})$  is a periodical function of  $\mathbf{k}$ , it is sufficient to be displayed within the interval  $(-\pi/a ; \pi/a)$  – the first Brillouin zone

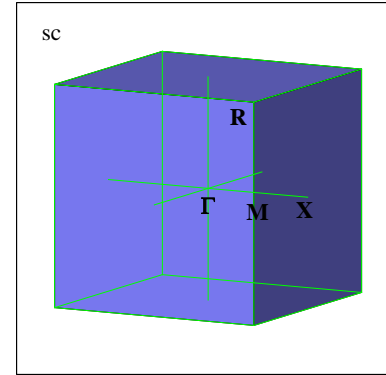
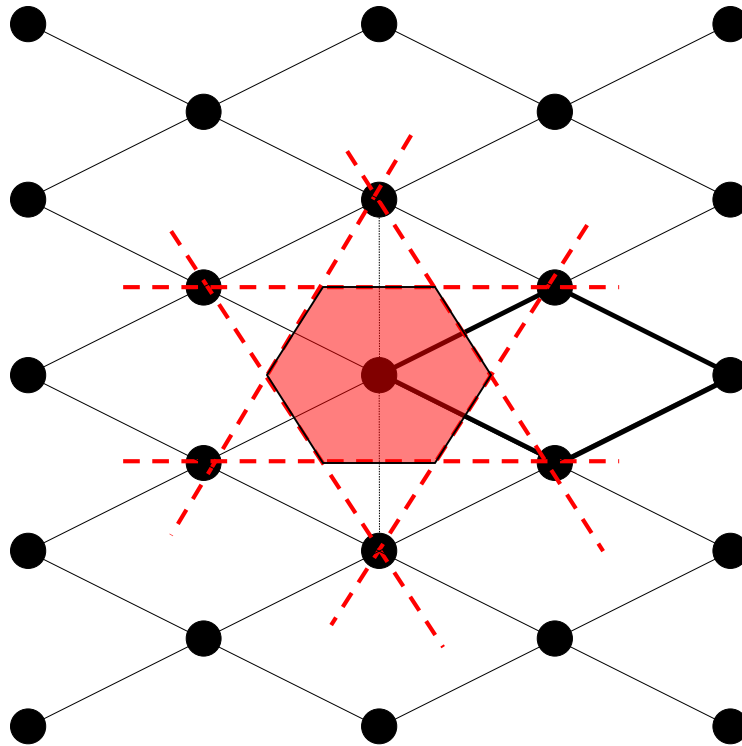
### the first Brillouin zone – Wigner-Seitz cell in the reciprocal lattice

Wigner-Seitz cell is always primitive and it always has the same symmetry as the lattice (primitive crystallographic cell may have lower symmetry than the lattice)

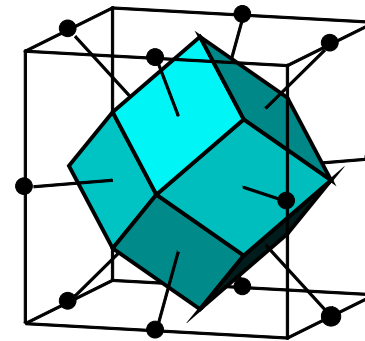
Construction: the planes normal to  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  through the points  $\pm\mathbf{b}_1, \pm\mathbf{b}_2, \pm\mathbf{b}_3$



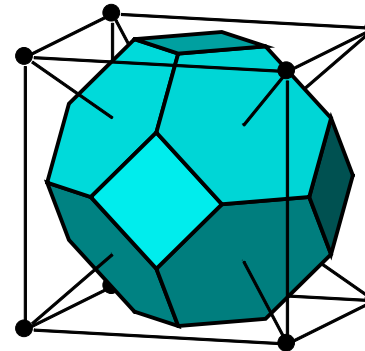




**simple  
cubic**



**bcc**  
bcc in direct space  
corresponds to fcc in  
reciprocal space



**fcc**  
fcc in direct space  
corresponds to bcc in  
reciprocal space

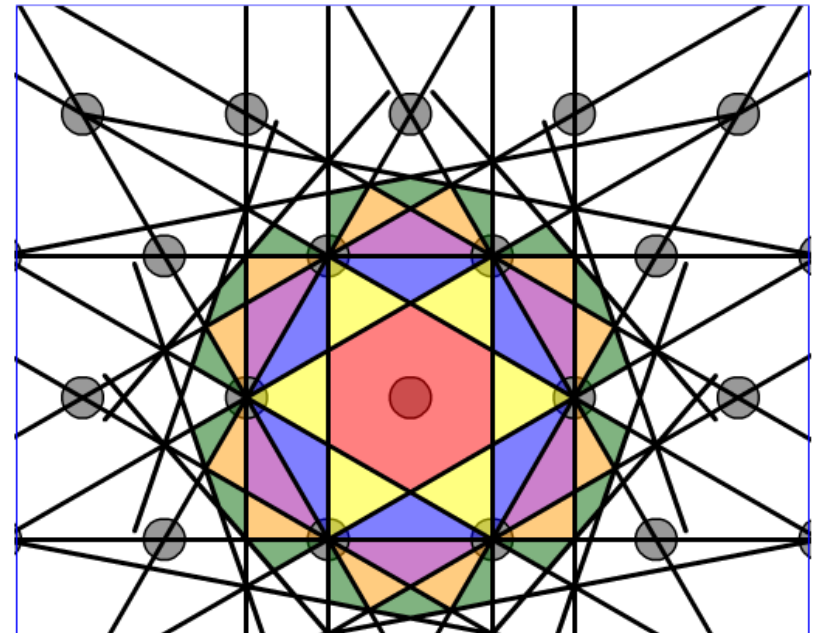
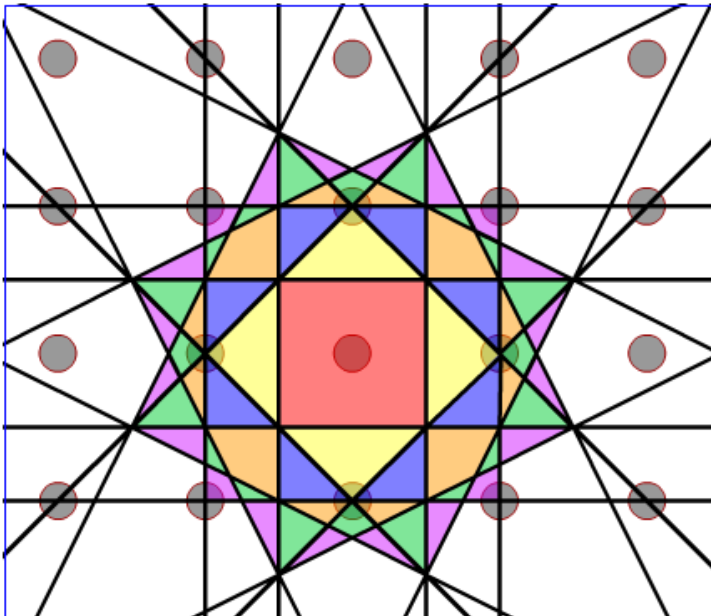
Brillouin zones of higher order:

- the same volume as the 1. Brillouin zone.
- the same symmetry as the 1. Brillouin zone.
- translation by a reciprocal lattice vector shifts them to the 1. Brillouin zone.

1. Brillouin zone

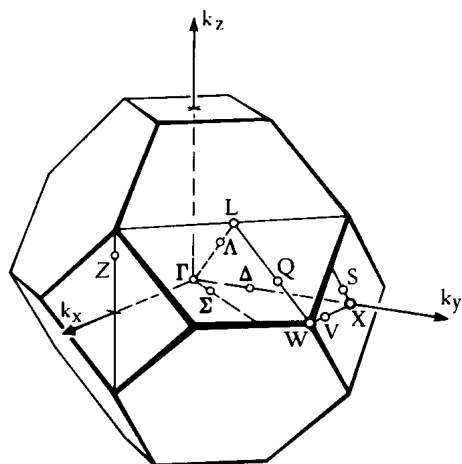
2. Brillouin zone

3. Brillouin zone

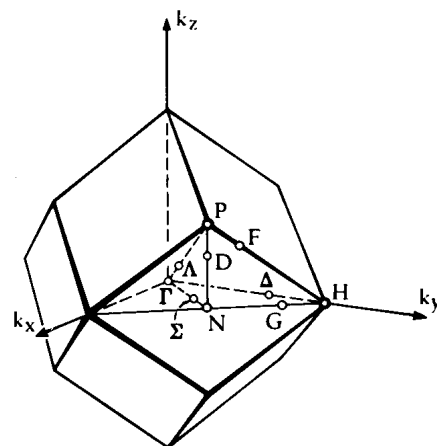


Triclinic	$\bar{1}$	1/2
Monoclinic	$2/m$	1/4
Orthorhombic	$mmm$	1/8
Tetragonal	$4/m$	1/8
	$4/mmm$	1/16

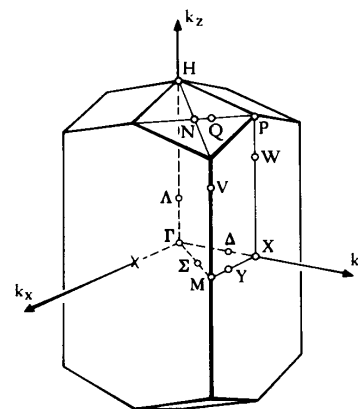
Trigonal	$\bar{3}$	1/6
Hexagonal	$6/m$	1/12
	$6/mmm$	1/24
Cubic	$m\bar{3}$	1/24
	$m\bar{3}m$	1/48



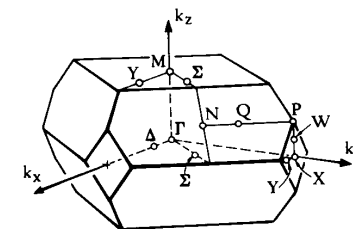
FACE CENTERED CUBIC



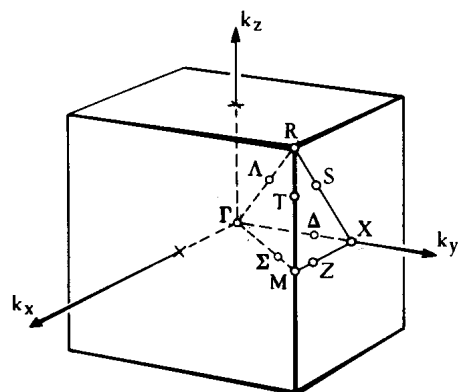
BODY CENTERED CUBIC



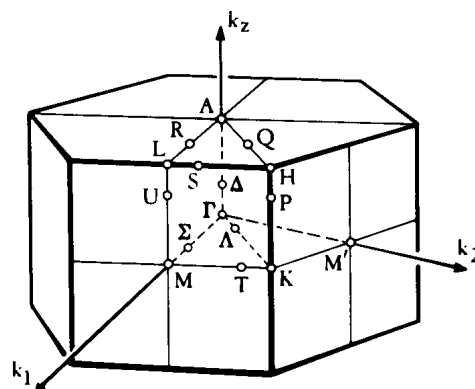
BODY CENTERED TETRAGONAL (a)



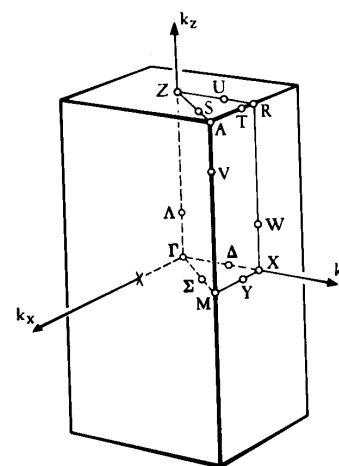
BODY CENTERED TETRAGONAL (b)



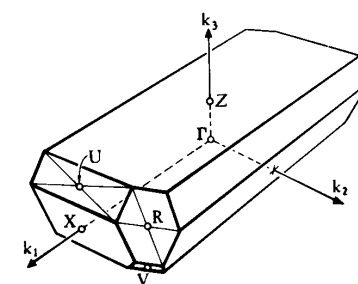
SIMPLE CUBIC



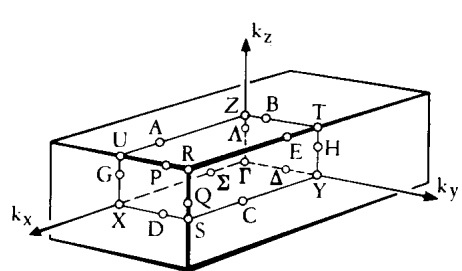
HEXAGONAL



SIMPLE TETRAGONAL

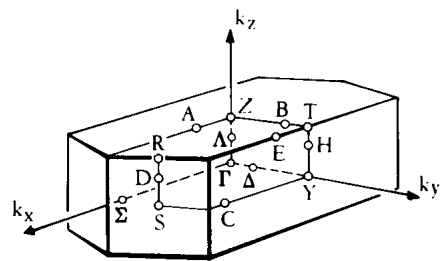


TRICLINIC

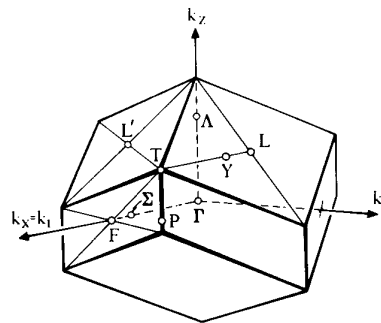


**SIMPLE ORTHORHOMBIC**

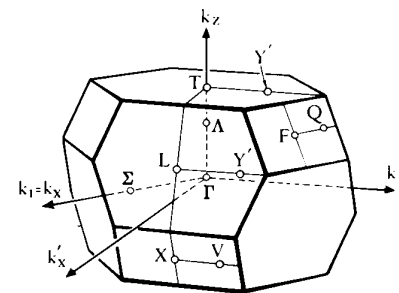
$\Gamma=000$   $X=100$   $Y=010$   $Z=001$   
 $S=110$   $T=011$   $U=101$   $R=111$



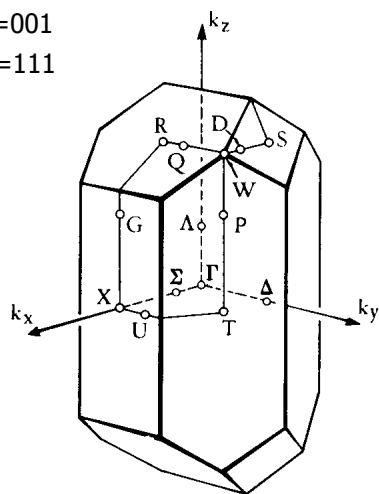
**BASE CENTERED ORTHORHOMBIC**



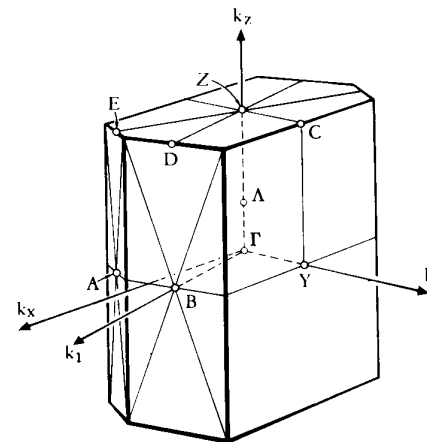
**RHOMBOHEDRAL (a)**



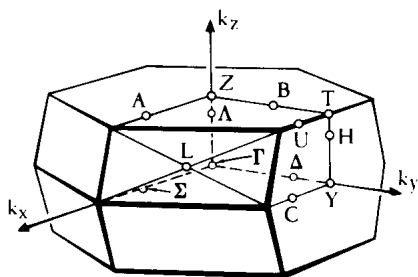
**RHOMBOHEDRAL (b)**



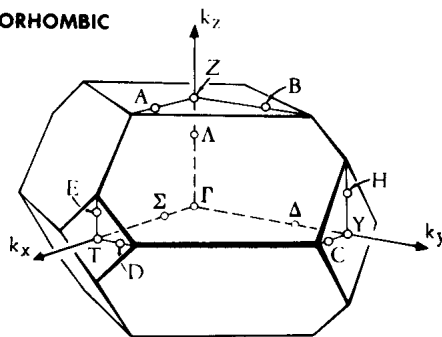
**BODY CENTERED ORTHORHOMBIC**



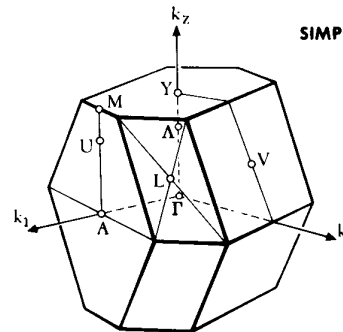
**SIMPLE MONOCLINIC**



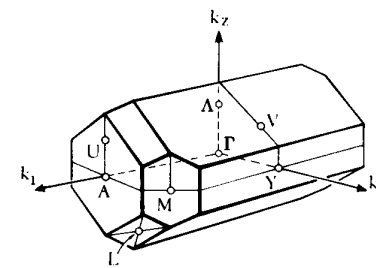
**ALL FACE CENTERED ORTHORHOMBIC (a)**



**ALL FACE CENTERED ORTHORHOMBIC (b)**



**ONE FACE CENTERED MONOCLINIC (a)**



**ONE FACE CENTERED MONOCLINIC (b)**

Schrödinger equation

$$\underbrace{-\frac{\hbar^2}{2m} \Delta}_{\text{kinetic energy}} \Psi(r) + \underbrace{\hat{V}(r)}_{\text{potential energy}} \Psi(r) = E\Psi(r)$$

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

Hydrogen atom:

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0 r}$$

$\Delta$  in spherical coordinates:

$$\Psi_{n,l,m} = R_{n,l}(r) \cdot Y_{l,m}(\theta, \varphi)$$

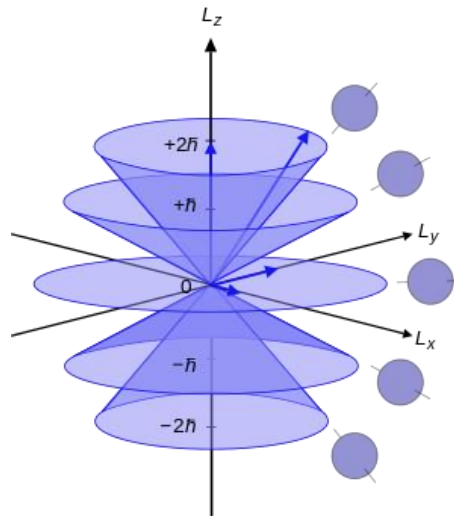
$$\Delta \approx \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \varphi^2}$$

$$\hat{H}\Psi_{n,l,m} = E_n \Psi_{n,l,m}$$

$$\hat{H} = \hat{T} + \hat{V}$$

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

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



$m$ : electron mass

$\epsilon_0$ : permittivity of vacuum

$\Psi$ : wave functions

$e$ : electron charge

$E$ : energy

$\hbar$ : Planck's constant

$R$ : radial function

$Y$ : angular function

$n$ : principal quantum number

$l$ : orbital quantum number

determine the orbital angular momentum

$$l = 0 \dots n-1$$

$m_l$ : magnetic quantum number

projection of the angular momentum into z-axis

$$m_l = -l \dots l$$

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

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

$\psi$ : exact wave function

$\Phi$ : approximate wave function expressed in the basis  $\varphi$

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

$\varphi$ : e.g. atomic orbitals, plane waves, ...

### Nearly free electrons :

Kinetic energy predominates over potential energy

Basis = plane waves

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

metallic bond, electron gas

### Tight binding:

Potential energy predominates over kinetic energy

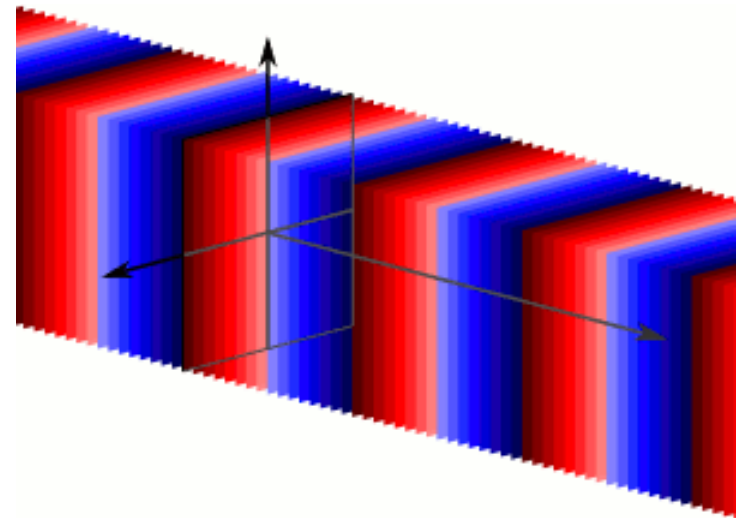
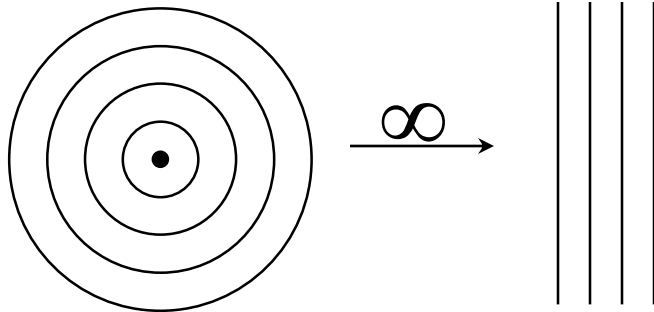
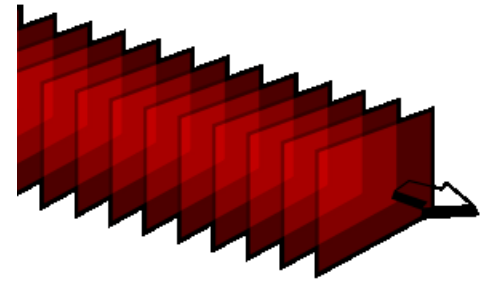
Basis = atomic orbitals

Covalent and ionic bonds

Plane wave:

- constant frequency
- spreads like infinite parallel planes normal to vector of motion.

$$\Phi(x) = \sum_k c_k \exp[ik\vec{x}]$$



Multiply equation (3) from left subsequently by functions  $\varphi_1, \varphi_2, \dots, \varphi_n$ , and create system of equations:

$$\begin{aligned} \varphi_1 \hat{H}c_1\varphi_1 + \varphi_1 \hat{H}c_2\varphi_2 + \dots + \varphi_1 \hat{H}c_n\varphi_n &= \varphi_1 Ec_1\varphi_1 + \varphi_1 Ec_2\varphi_2 + \dots + \varphi_1 Ec_n\varphi_n \\ \varphi_2 \hat{H}c_1\varphi_1 + \varphi_2 \hat{H}c_2\varphi_2 + \dots + \varphi_2 \hat{H}c_n\varphi_n &= \varphi_2 Ec_1\varphi_1 + \varphi_2 Ec_2\varphi_2 + \dots + \varphi_2 Ec_n\varphi_n \\ &\vdots \\ \varphi_n \hat{H}c_1\varphi_1 + \varphi_n \hat{H}c_2\varphi_2 + \dots + \varphi_n \hat{H}c_n\varphi_n &= \varphi_n Ec_1\varphi_1 + \varphi_n Ec_2\varphi_2 + \dots + \varphi_n Ec_n\varphi_n \end{aligned}$$

Convert to matrix form, for the constant E it holds  $\varphi_i E \varphi_j = E \varphi_i \varphi_j$ :

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

Convert all on one side and join into 1 matrix:

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

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

System of equations has a non-trivial solution, only if the matrix determinant = 0:

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

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

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

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

By substitution of (2) into (1)  $\rightarrow$  (3)

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

Unknowns:  $E, c_i$

Matrix eigen vectors:  
Symmetry - axis vector:  
 $A \vec{v} = 1 \vec{v}$   
Eigen-functions:  
 $\hat{H} \Phi = E \Phi$

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

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

Jacobi's method, Givens' matrices P →

$$B = \begin{pmatrix} E_1 & 0 & \dots & 0 \\ 0 & E_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E \end{pmatrix}$$

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

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

$$H\vec{c}_k^H = E_k^H \vec{c}_k^H$$

$$H\vec{c}_k^H - E_k^H \vec{c}_k^H = 0$$

$$(H - IE_k^H)\vec{c}_k^H = 0$$

$I$ : unitary matrix

(1)  $\hat{H}\Phi = E\Phi$ , (2)  $\Phi = \sum_{i=1}^n c_i \varphi_i$   
 By substitution of (2) into (1) → (3)  
 (3)  $\hat{H}(c_1\varphi_1 + c_2\varphi_2 + \dots + c_n\varphi_n) = E(c_1\varphi_1 + c_2\varphi_2 + \dots + c_n\varphi_n)$   
 Unknowns:  $E, c_i$

Complex matrix:

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

	$\varphi_1$	$\varphi_2$	$\dots$	$\varphi_n$	
$E_1$	$c_{11}$	$c_{12}$	$\dots$	$c_{1n}$	$\sum c_{1j}^2 = 1$
$E_2$	$c_{21}$	$c_{22}$	$\dots$	$c_{2n}$	$\sum c_{2j}^2 = 1$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	
$E_n$	$c_{n1}$	$c_{n2}$	$\dots$	$c_{nn}$	$\sum c_{nj}^2 = 1$
	$\sum c_{i1}^2 = 1$	$\sum c_{i2}^2 = 1$	$\dots$	$\sum c_{in}^2 = 1$	

System of equations for  $i = 1, 2, \dots, N$   $\sum_{j=1}^N c_j [H_{ij} - ES_{ij}] = 0$   $S_{ii} = 1$

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

System of equations has solution, only if determinant  $H_{ij} - ES_{ij} = 0$ :

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

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

$H_{ij}$ : exchange integral

$H_{ii}$  ( $i=j$ ): "on-site" energy of individual base states.

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

$S_{ij}$ : overlap integral.  $S_{ii}$  ( $i=j$ ) = 1,  $S_{ij}$  ( $i \neq j$ )  $\rightarrow 0$ .

Calculation of the determinant  $\rightarrow$  secular equation of the N.order.

The solution is N eigen-values  $E_i$  (energy). For each  $E_i$  we get N coefficients  $c_{ij}$  (eigen-vectors) by solving the system of equations.

$E_i$ : energy of the function

$$\Phi_i = \sum_j c_{ij} \varphi_j$$

If the potential depends on the wave functions  $\Phi_i$ , i.e. on the searched coefficients  $c_{ij}$ , the secular equation must be solved iteratively, by the so-called SCF method (self-consistent field).

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

$\psi$ : exact wave function

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

$\Phi$ : approximate wave function expressed in the basis  $\varphi$

$$\Psi \approx \Phi = \sum_i^N c_i \varphi_i$$

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

$\varphi$ : e.g. atomic orbitals, plane waves, ...

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

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

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

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

$H_{ij}$ : exchange integral

$H_{ii}$  ( $i=j$ ): "on-site" energy of individual base states.

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

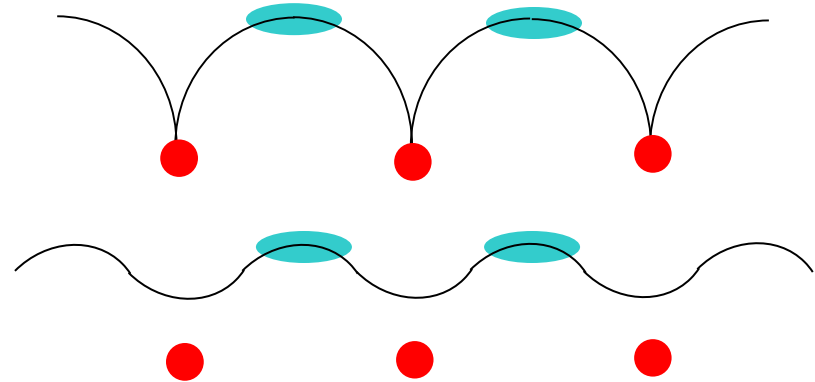
$S_{ij}$ : overlap integral.  $S_{ii}$  ( $i=j$ ) = 1,  $S_{ij}$  ( $i \neq j$ )  $\rightarrow$  0.

$$V(x) = \sum V_G \exp[i\vec{G}\vec{x}] = V_0 + V_{\pm 1} \exp[\pm i \frac{2\pi}{a} x] + V_{\pm 2} \exp[\pm i \frac{4\pi}{a} x] + \dots \quad \vec{G} = \frac{2\pi}{a} \vec{j}$$

$V_G = V_{-G}^*$  : Potential is real       $\vec{j}$  : Lattice vectors. For 1D  $j = 0, \pm 1, \pm 2, \dots$

Exact potential: a huge attraction force near the core.

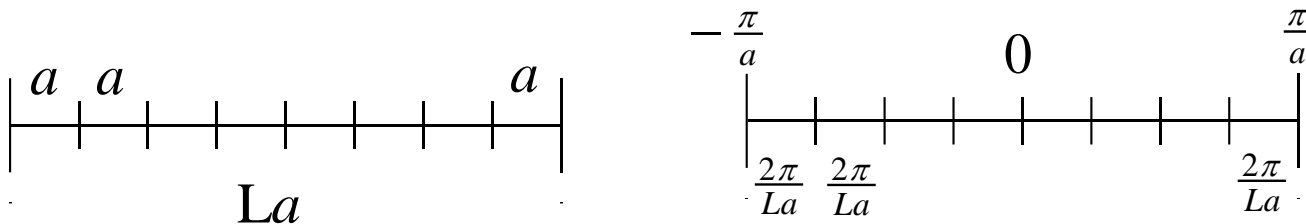
If we are interested in the potential in which the electrons (especially the valence) move, we can neglect the vicinity of the nucleus.



Function:  $\Phi(x) = \Phi(x + La) = \sum_k c_k \exp[i\vec{k}\vec{x}] \quad \vec{k} = \frac{2\pi}{La} \vec{l} \quad \text{For 1D } l = 0, \pm 1, \pm 2, \dots, \pm L/2$

Potential is repeated after period  $a$ , function is repeated after period  $La$ .

The 1.Brillouin zone is  $2\pi/a$  in the reciprocal space, the function is calculated in  $2\pi/La$ .



Wave function and potential put into Schrödinger equation

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

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

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

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

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

In order the sum to be =0, each term in [] must be =0.

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

Master equation: system of L equations, formulation of secular equation for the plane wave basis.

Various solutions  $c_k$  within 1. Brillouin zone.

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

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

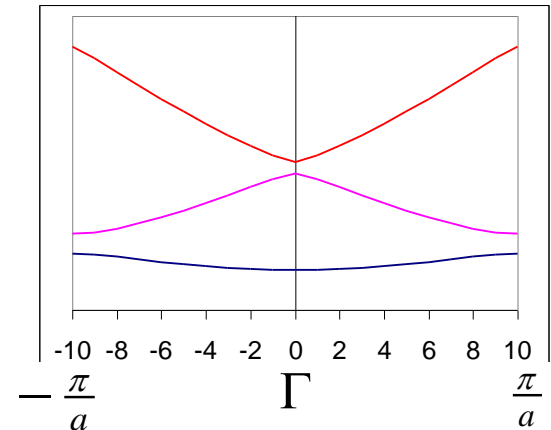
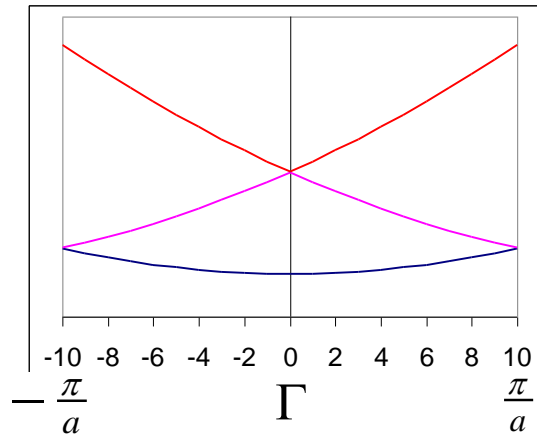
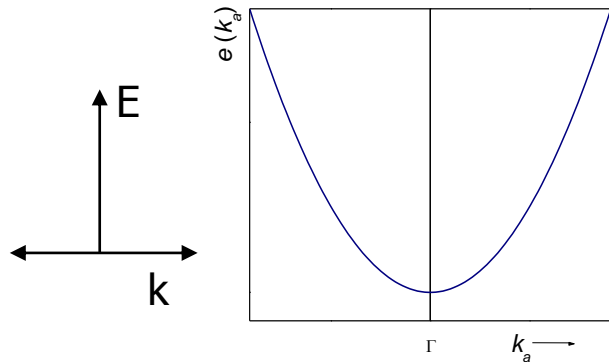
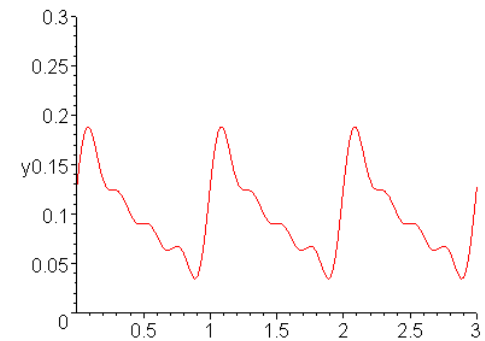
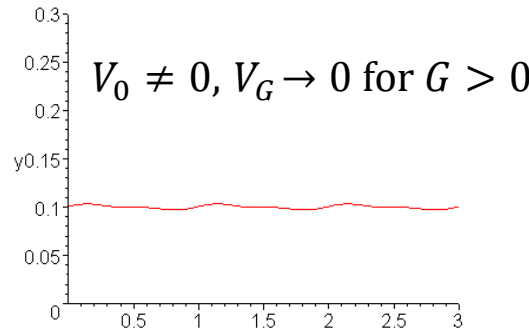
master equation – system of L equations, various solutions  $c_k$  within 1. Brillouin zone ( $-\pi/a \leq k \leq \pi/a$ ).

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

$$\begin{vmatrix} \lambda_{k-G} - (E_k - V_0) & V_1 & V_2 \\ V_{-1} & \lambda_k - (E_k - V_0) & V_1 \\ V_{-2} & V_{-1} & \lambda_{k+G} - (E_k - V_0) \end{vmatrix}$$

$$\lambda_k = \frac{\hbar^2 k^2}{2m}$$

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



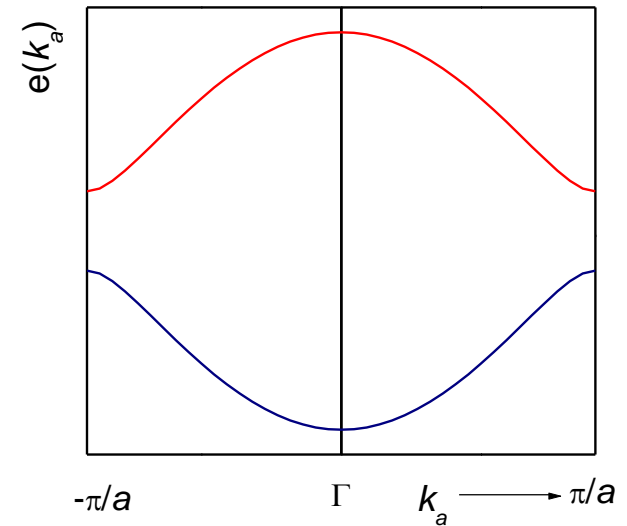
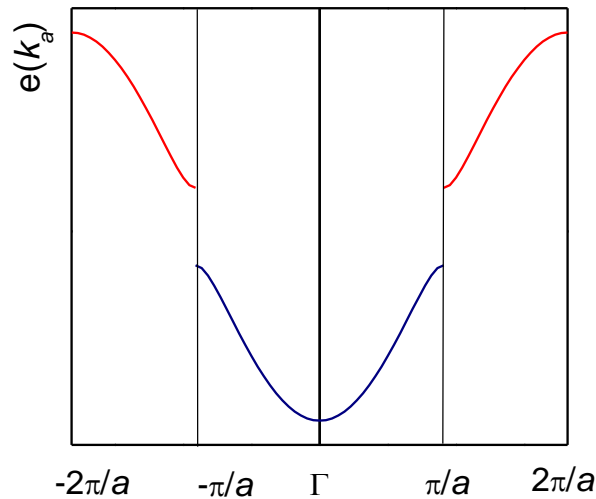
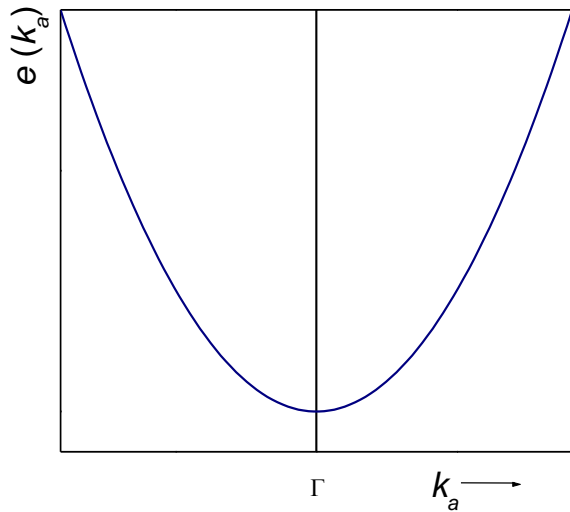
$k$  - quantum number  
wave vector

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

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

number of allowed values  $k$  = number of elementary cells in crystal

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



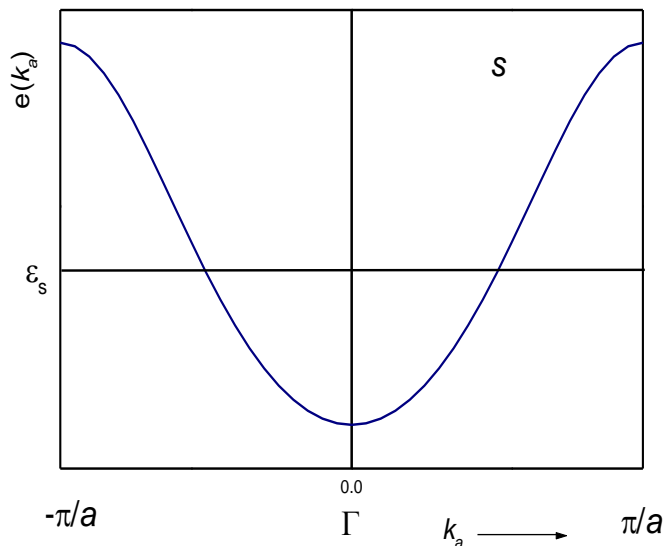
band width: determined by the overlap of interacting orbitals (as for MO)

**DOS(E), g(E)** - number of allowed energy levels per energy interval

holds: **g(E)\*dE** = number of levels in the interval (**E ; E+dE**)

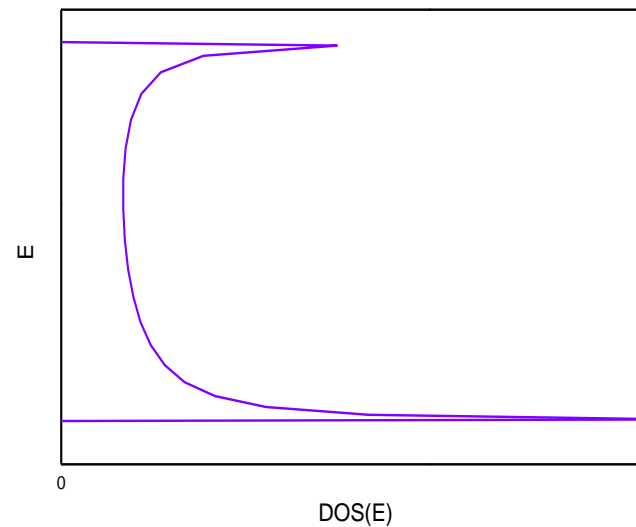
1 dimension:

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



generally:

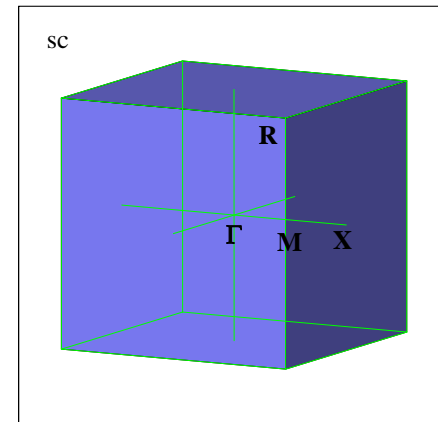
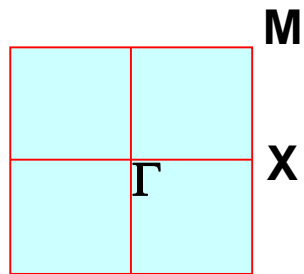
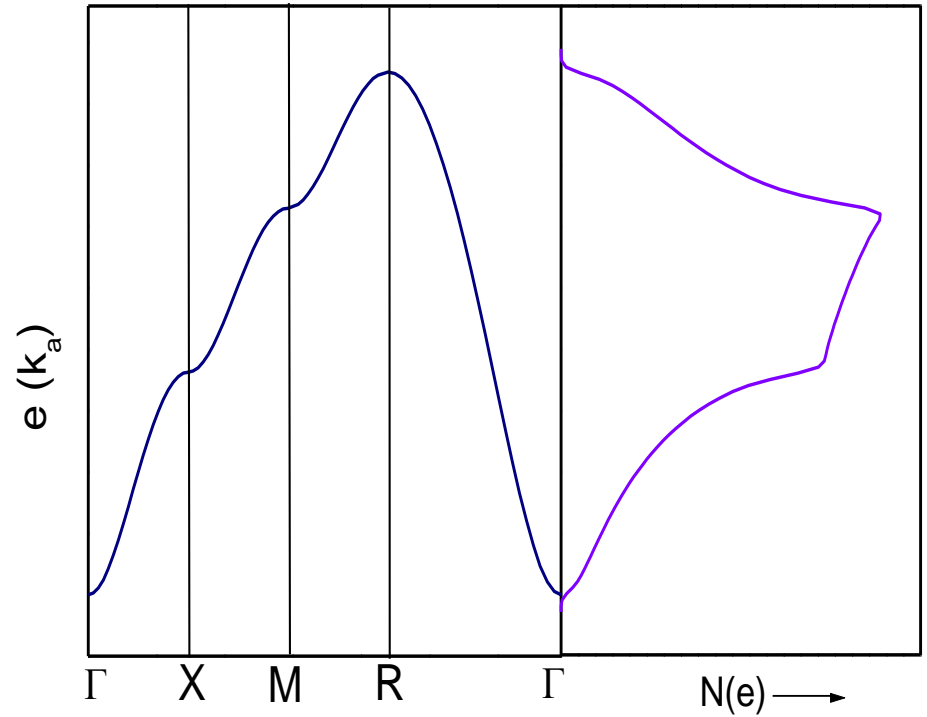
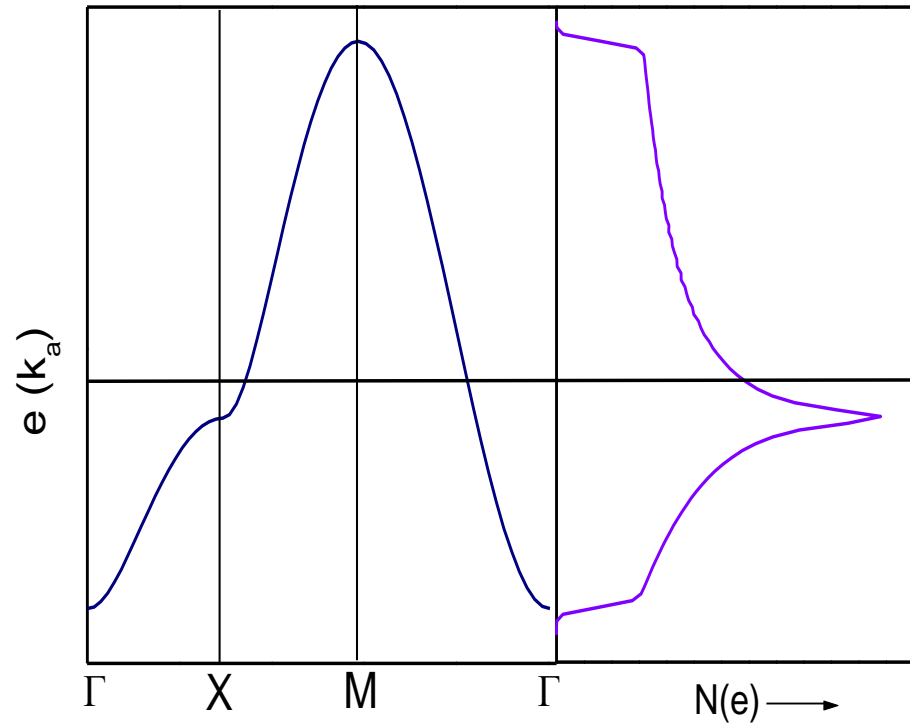
$$g(E) = \frac{2}{V_{BZ}} \sum_n \int_{S_k} \frac{dS_k}{|\nabla_k E_{n,k}|}$$



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

### 2-D

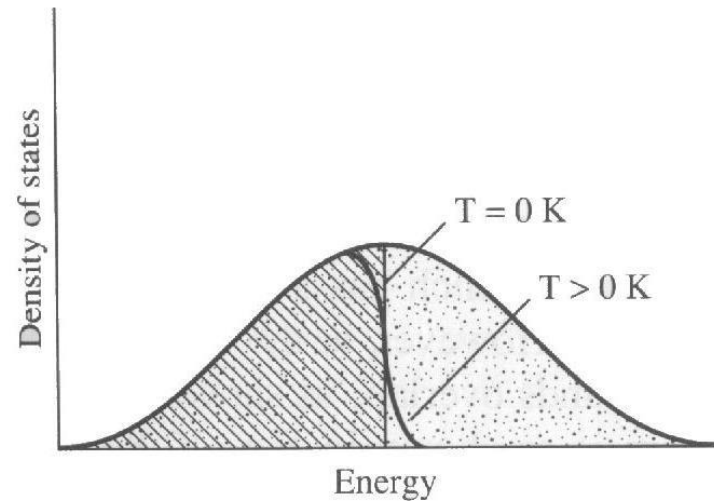
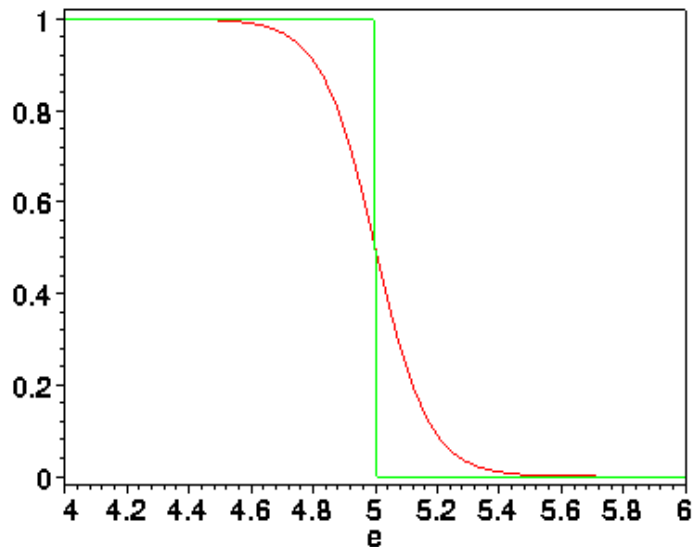
### 3-D



**Fermi level** – the highest occupied level at **T=0 K**

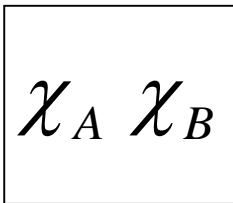
**T>0:** Fermi-Dirac statistic holds:  
occupied states **DOS(E)\*f(E)**

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



**Fermi plane** – the set of **k** in k-space, for which holds  $E(\mathbf{k}) = E_F$

Cell containing 2  
identical orbitals



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

$\varphi_i$ : molecular orbital,  $\chi_{\mu}$ : atomic orbital

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

$$\chi_A = \chi_B,$$

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

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

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

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

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

$$\alpha - E = \pm(\beta - ES) \quad E_{1,2} = \frac{\alpha \pm \beta}{1 \pm S}, \quad \beta < 0 \Rightarrow E_1 < E_2$$

$$\alpha_1 = \alpha_2$$

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

$$E_2 = \alpha - \beta, \quad \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2) \quad \text{pink circle} \quad \text{cyan circle}$$

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

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

$$E_1 = \alpha_1 \quad E_2 = \alpha_2 \quad \text{pink circle} \quad \text{cyan circle}$$

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

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

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

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

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

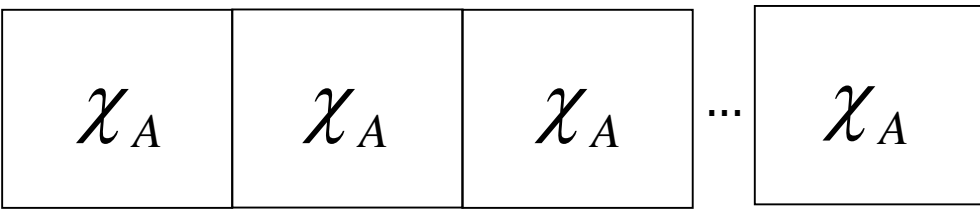
$$\beta = \int \chi_A^*(R_A) \hat{H} \chi_B(R_B)$$

$$S = \int \chi_A^*(R_A) \chi_B(R_B) \quad 25$$

$\alpha = \varepsilon$  : coulombic energy (energy of AO)

$\beta$  (<0) = t : exchange energy (degree of bonding energy)

S (0-1) : overlap integral



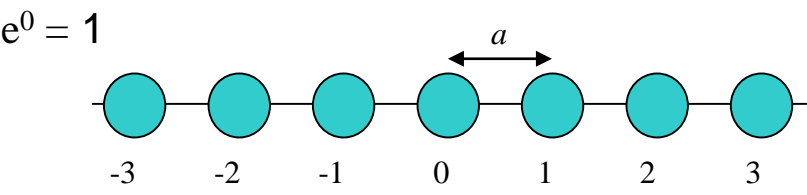
$$\Phi_{BO}(r, k) = \frac{1}{\sqrt{N}} \sum_n \chi_\mu(r - na) \exp(ikna)$$

$\Phi_{BO}$ : Bloch orbital,  $\chi_\mu$ : atomic orbital

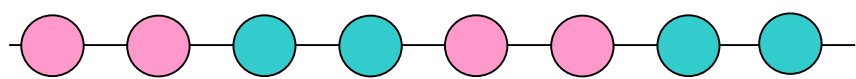
$$\Phi_{BO} = \chi_\mu(r) + \chi_\mu(r-a)e^{ika} + \chi_\mu(r-2a)e^{ik2a} + \dots + \chi_\mu(r-na)e^{ikNa}$$

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

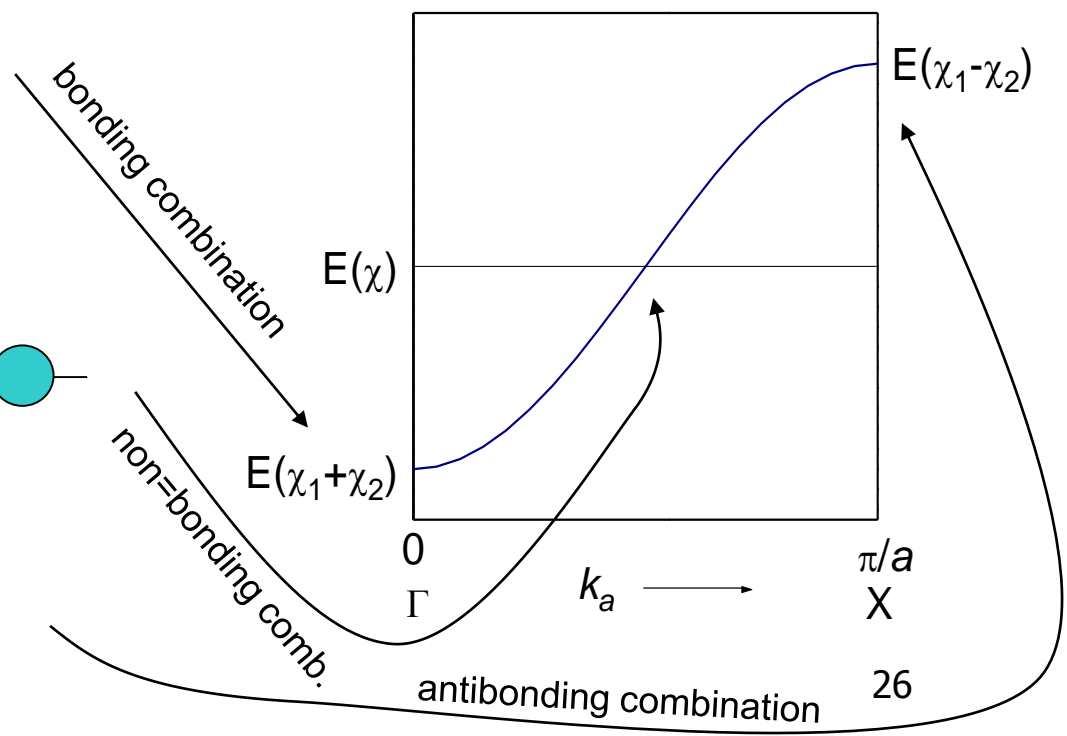
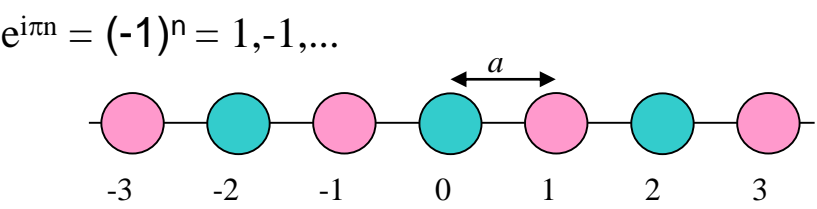
$k=0$  ( $\Gamma$ )

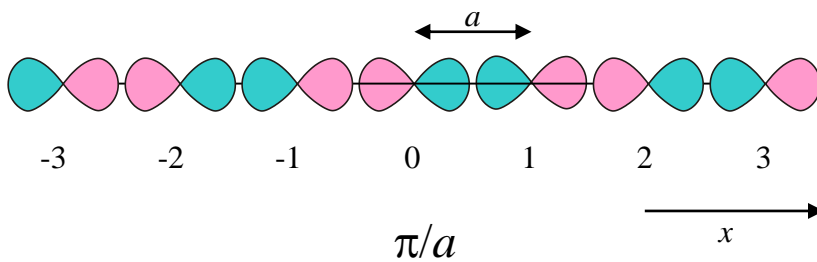
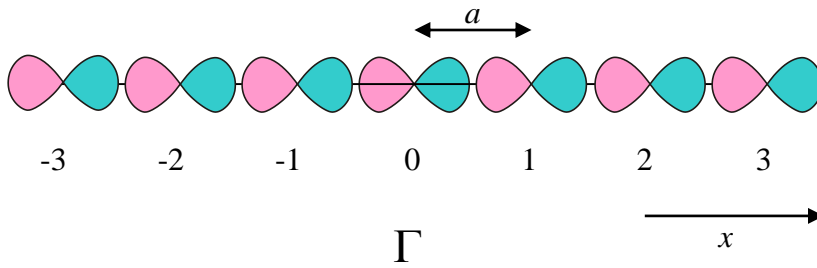
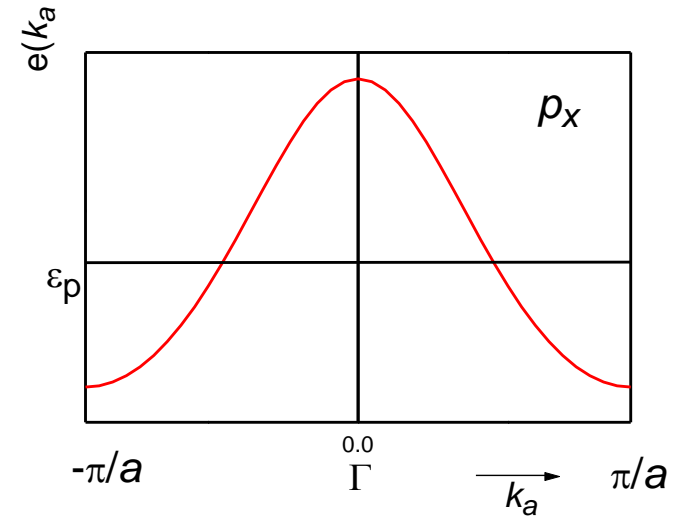
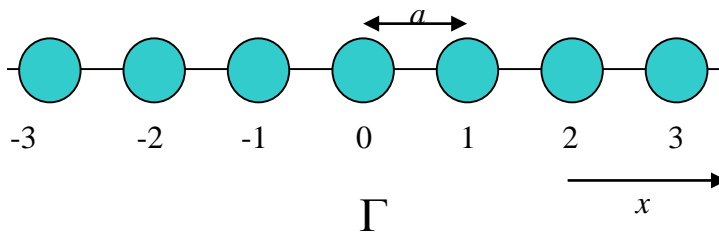
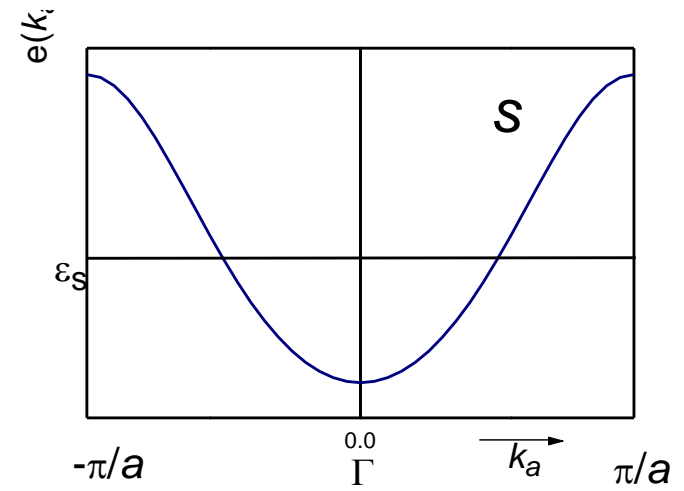
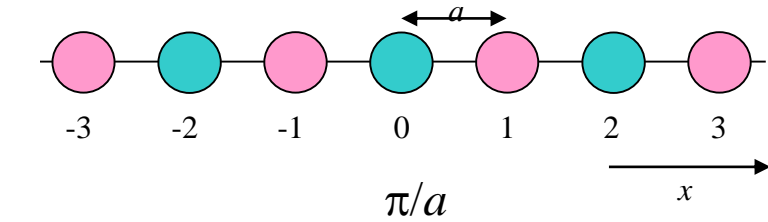


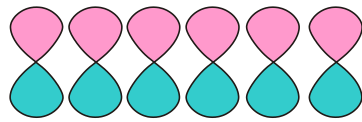
$k=\pm\pi/2a$   
 $\cos(n\pi/2) = 1, 0, -1, 0, \dots$   $\sin(n\pi/2) = 0, 1, 0, -1, \dots$



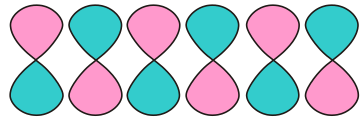
$k=\pm\pi/a$  (X)



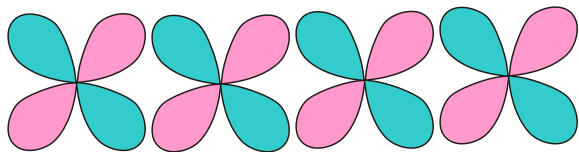
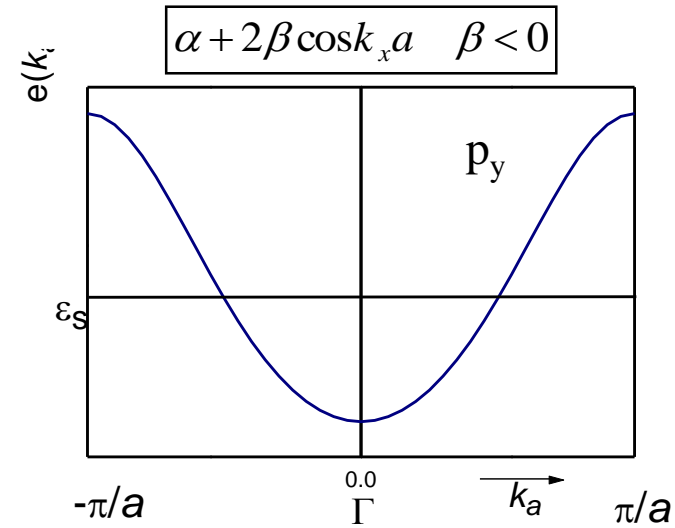
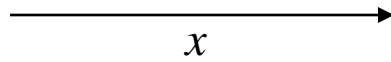




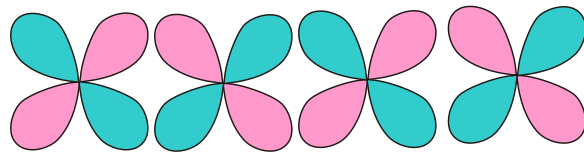
$\Gamma$



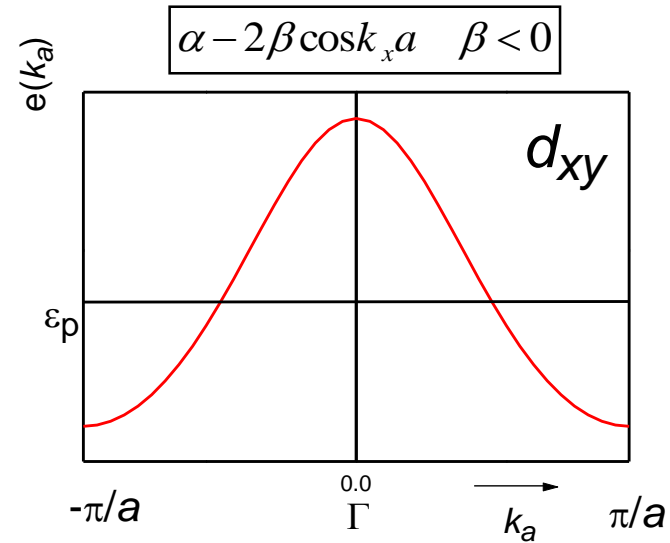
$X$

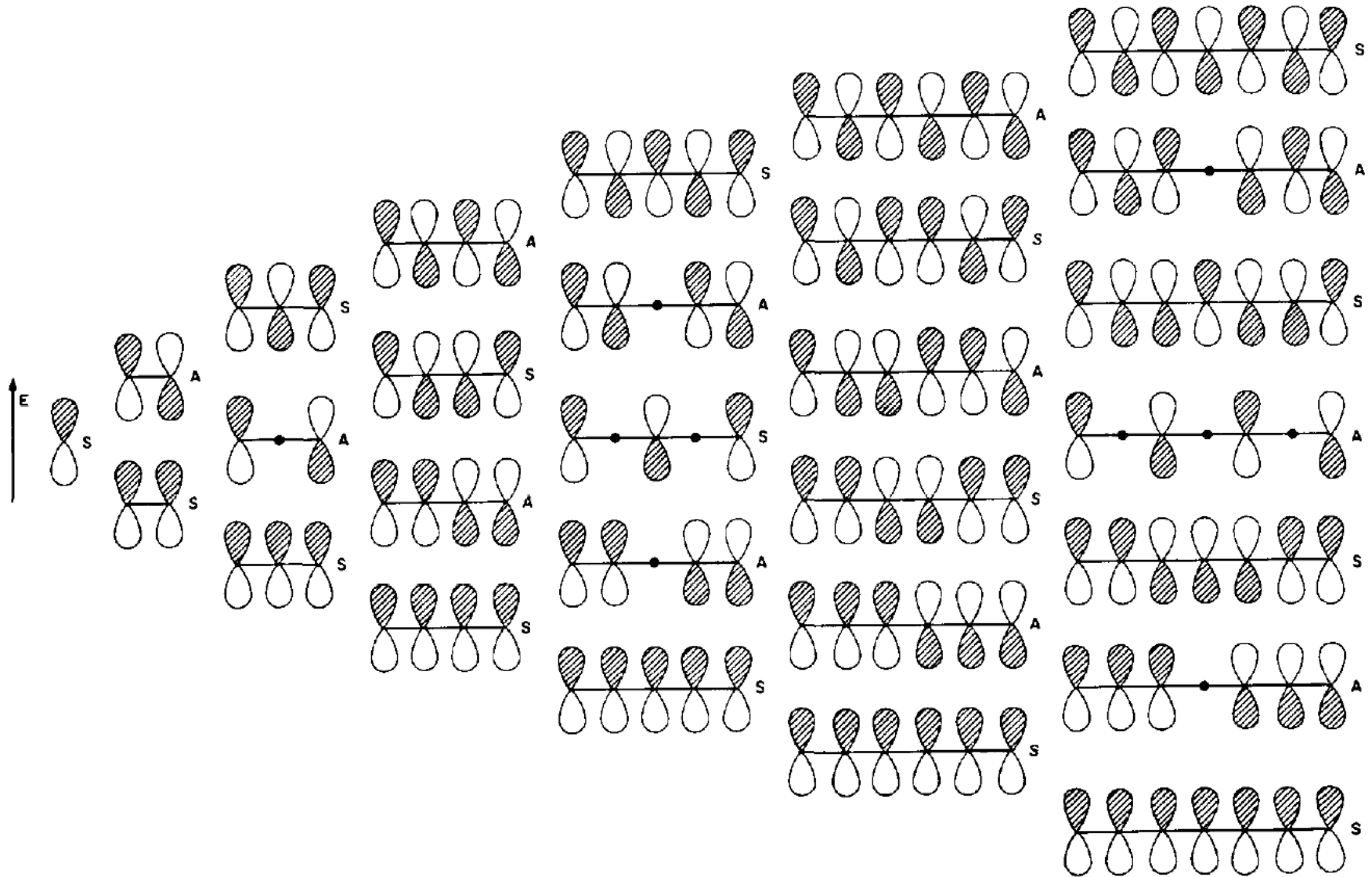


$\Gamma$

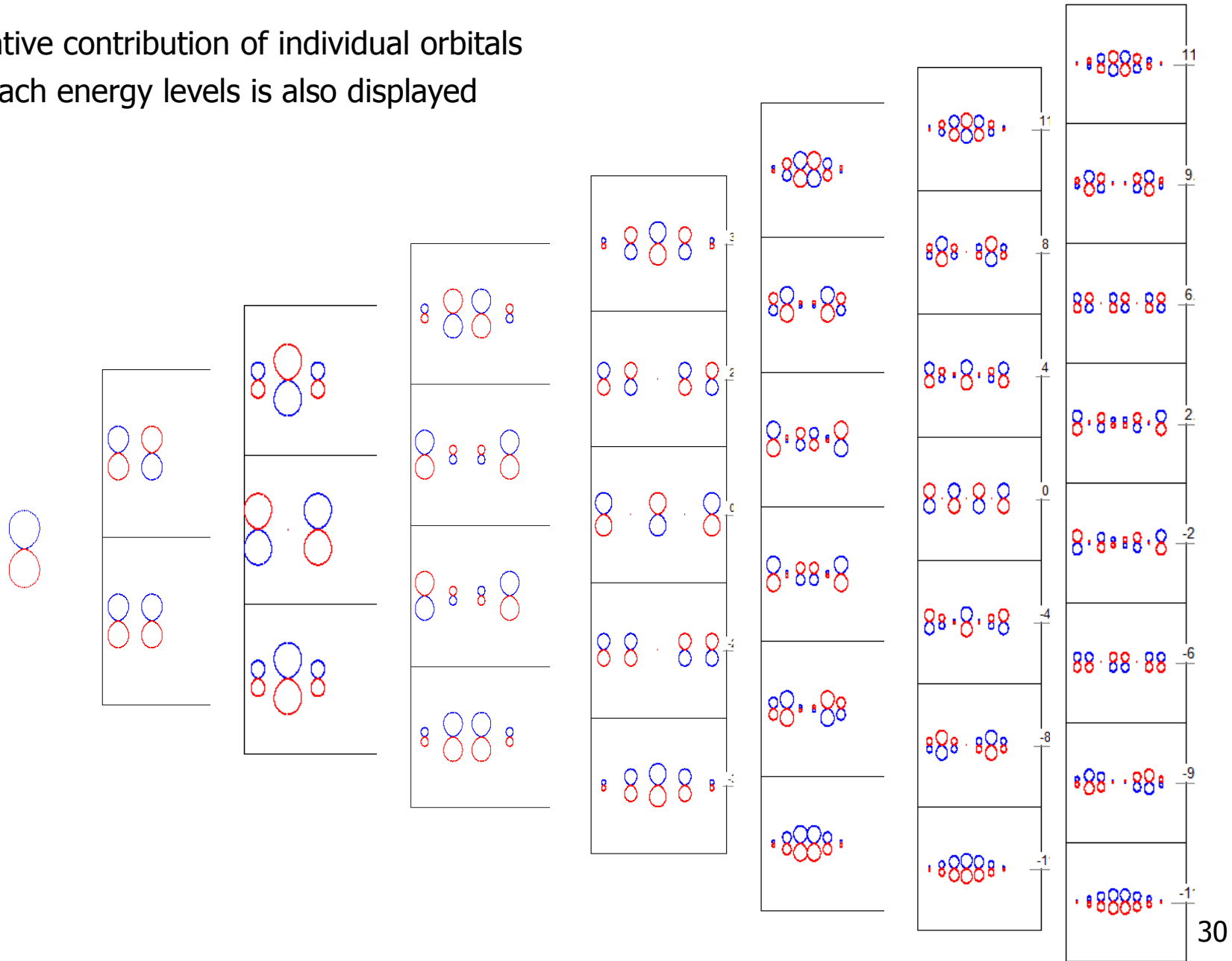


$X$

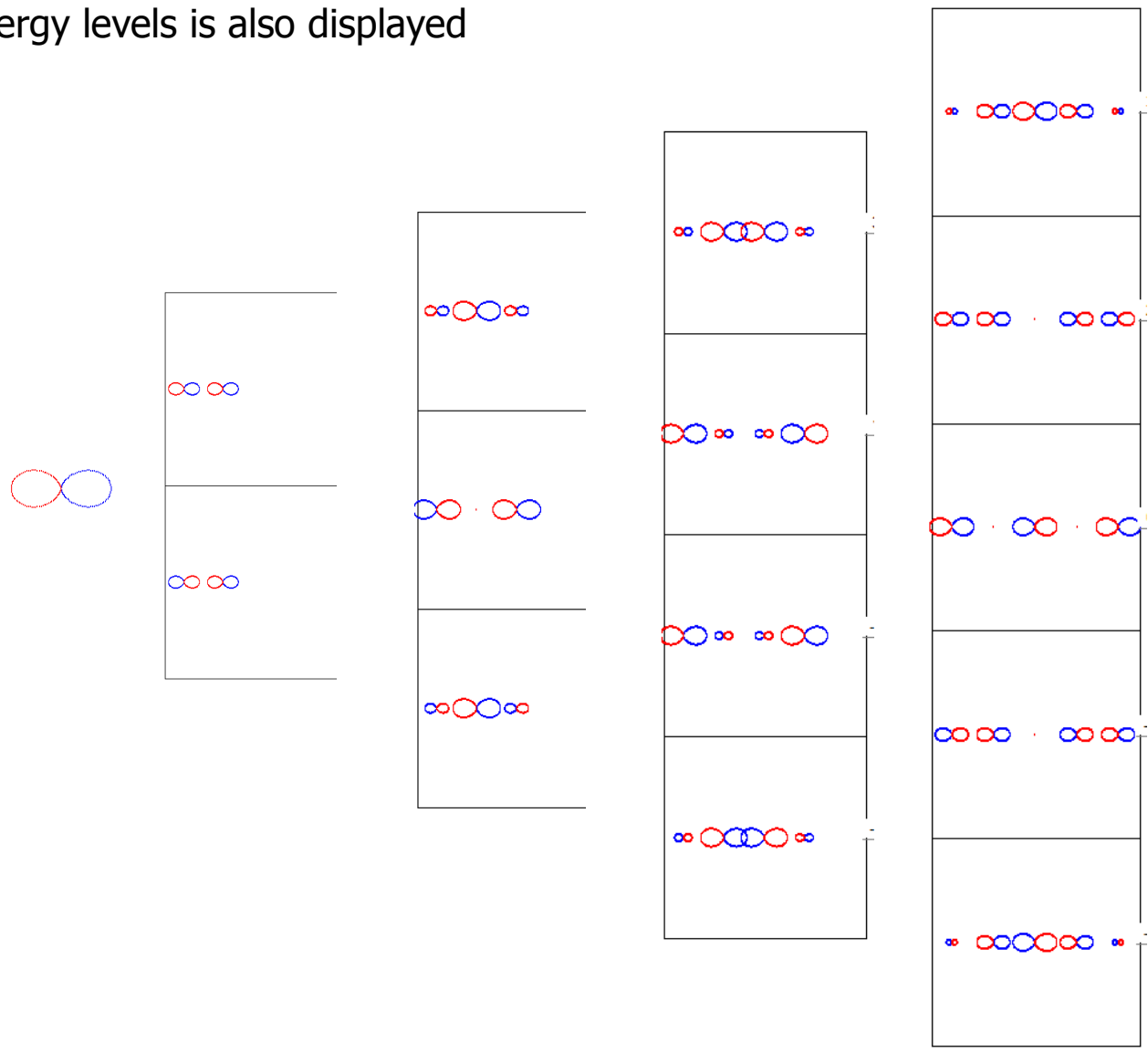


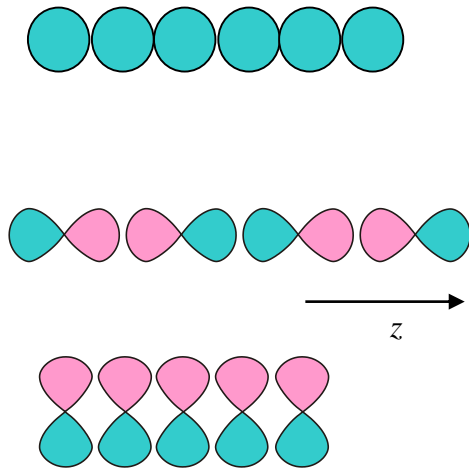


Relative contribution of individual orbitals to each energy levels is also displayed



Relative contribution of individual orbitals to each energy levels is also displayed





Band width  $W$

$$W_p > W_s$$

p orbitals reach closer to each other, bigger overlap

$$W_z > W_x, W_y$$

$\sigma$ -bonding  $>$   $\pi$ -bonding

valence  $>$  core

Delocalization of orbitals:

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

Small difference of orbitals energies

$$W(\text{Co-O}) > W(\text{Ti-O})$$

Bloch orbitals:  
(BO)

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

Crystal orbitals:  
(CO)

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

$$\hat{H}\psi_i(\mathbf{k}) = E_i(\mathbf{k})\psi_i(\mathbf{k}) \quad c_{ij}(\mathbf{k}), E_i(\mathbf{k}) = ?$$

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

matrix  
elements:

$$H_{jl}(\mathbf{k}) = \langle \phi_j(\mathbf{k}) | \hat{H} | \phi_l(\mathbf{k}) \rangle \quad S_{jl}(\mathbf{k}) = \langle \phi_j(\mathbf{k}) | \phi_l(\mathbf{k}) \rangle$$

parameters:  $E_j = \langle \chi_j | \hat{H} | \chi_j \rangle$   $t_{jl} = \langle \chi_j | \hat{H} | \chi_l \rangle$   $\sigma_{jl} = \langle \chi_j | \chi_l \rangle$

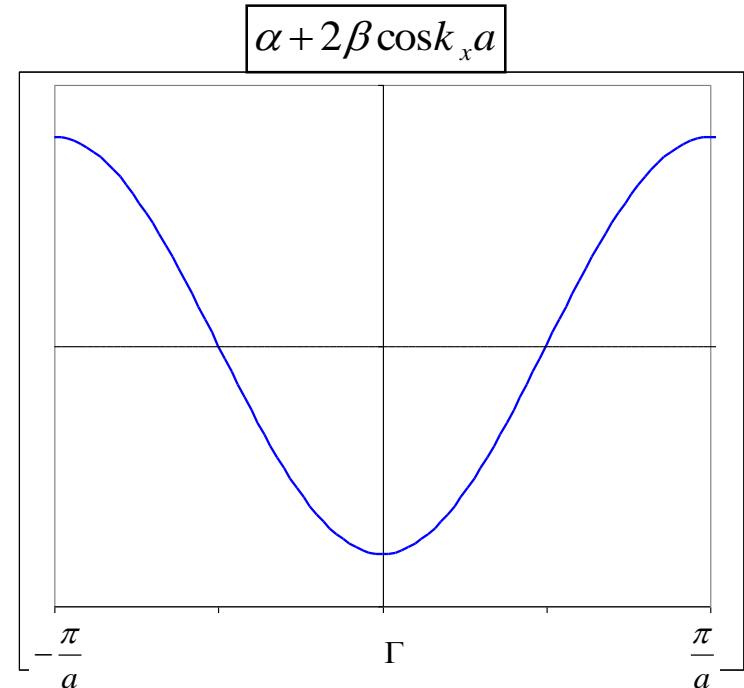
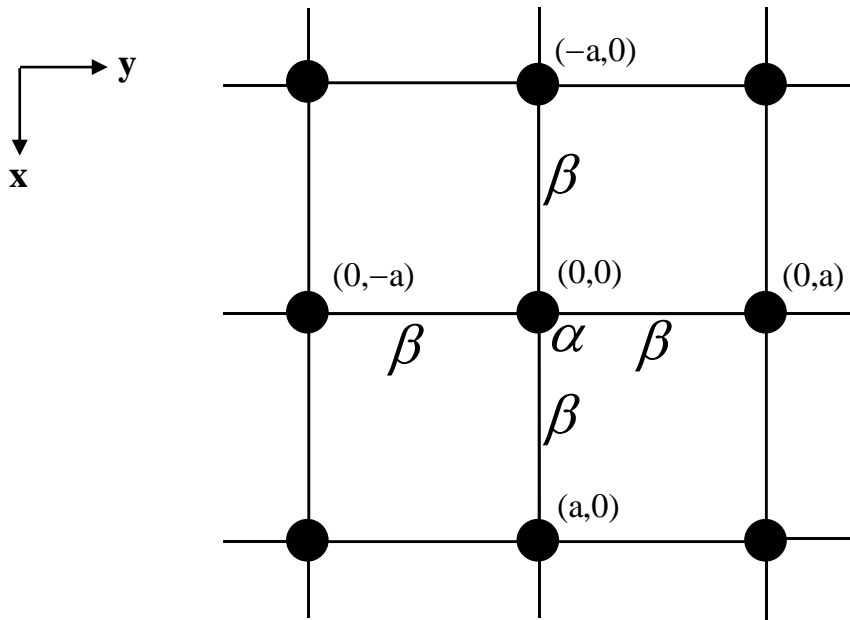
$$\langle \phi_j | \hat{H} | \phi_l \rangle = \int_{\tau} \phi_j^* \hat{H} \phi_l d\tau \quad \langle \phi_j | \phi_l \rangle = \int_{\tau} \phi_j^* \phi_l d\tau$$

Only the interaction with the nearest neighbours are taken into account:  
only the exchange integral  $\beta$  with the nearest neighbour ( $E \sim \alpha$ ,  $t \sim \beta$ ,  $S \ll 1$ )

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

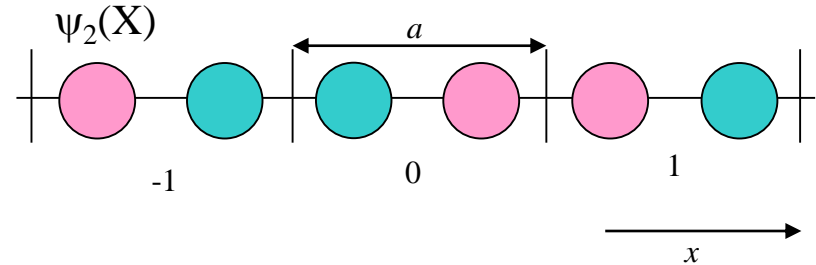
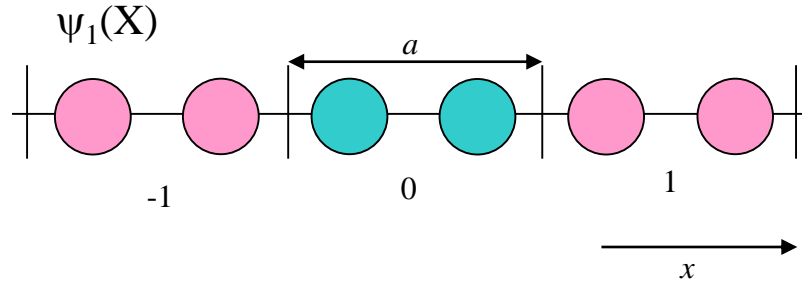
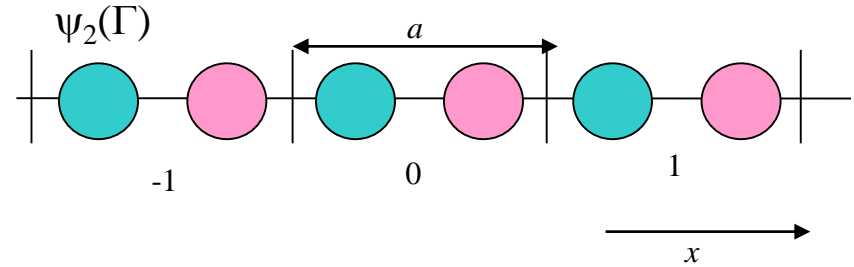
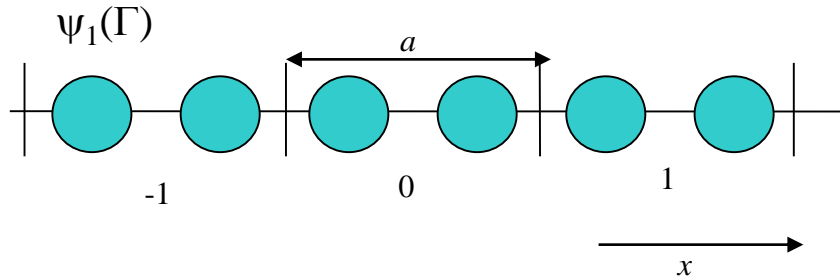
$$H(\vec{k}) = \alpha + \beta e^{ik_x a} + \beta e^{-ik_x a} + \beta e^{ik_y a} + \beta e^{-ik_y a} + \beta e^{ik_z a} + \beta e^{-ik_z a} =$$

$$= \alpha + 2\beta(\cos k_x a + \cos k_y a + \cos k_z a)$$







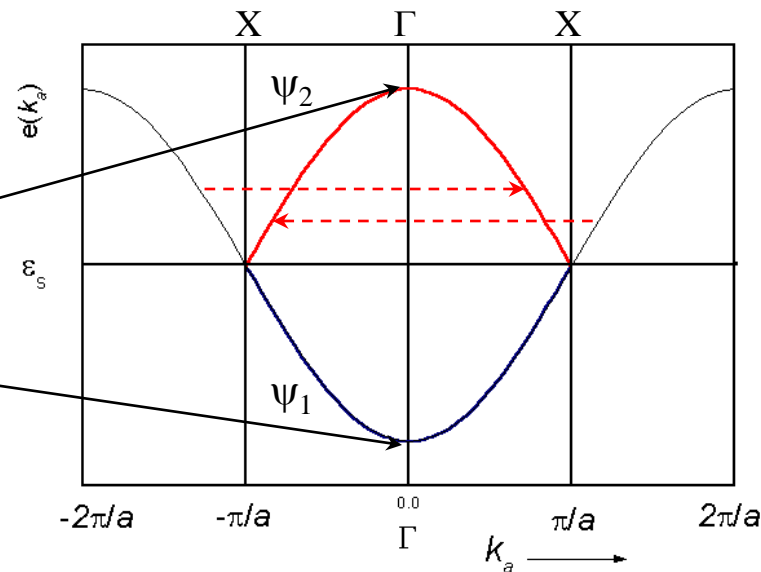
$$\varepsilon = \varepsilon_1 = \varepsilon_2, t = t_1 = t_2$$

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



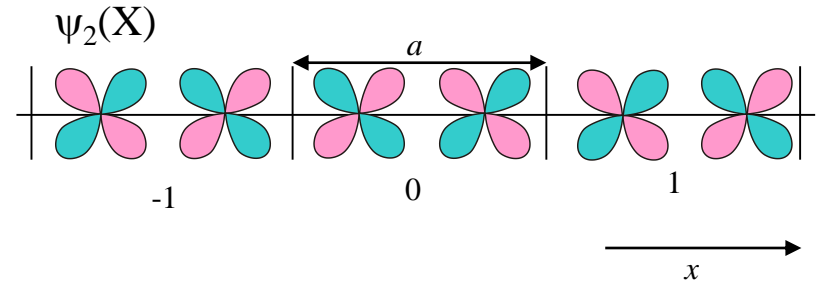
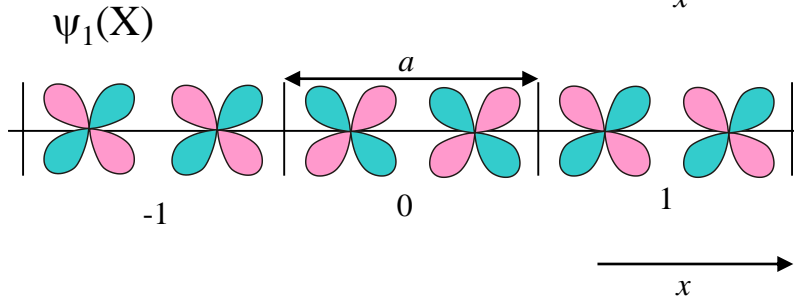
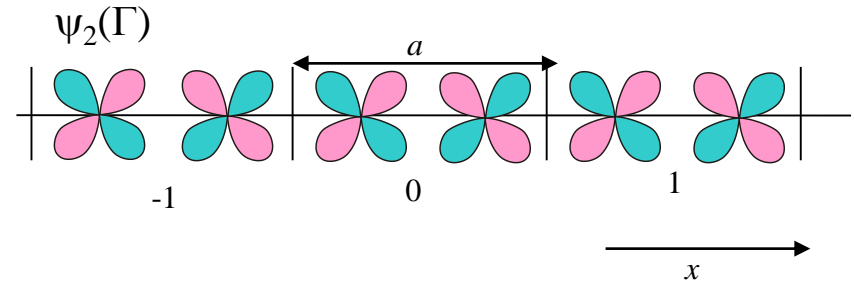
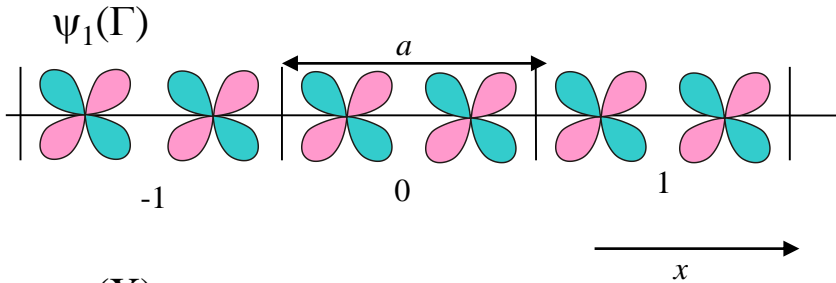
MO ~  $\Gamma(k=0)$

$E_2 = \alpha - \beta$		
$\Psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$		
$E_1 = \alpha + \beta$		
$\Psi_1 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$		



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

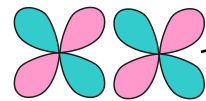
$$e = \varepsilon \pm 2t \cos(k_a a / 2)$$



MO ~  $\Gamma(k=0)$

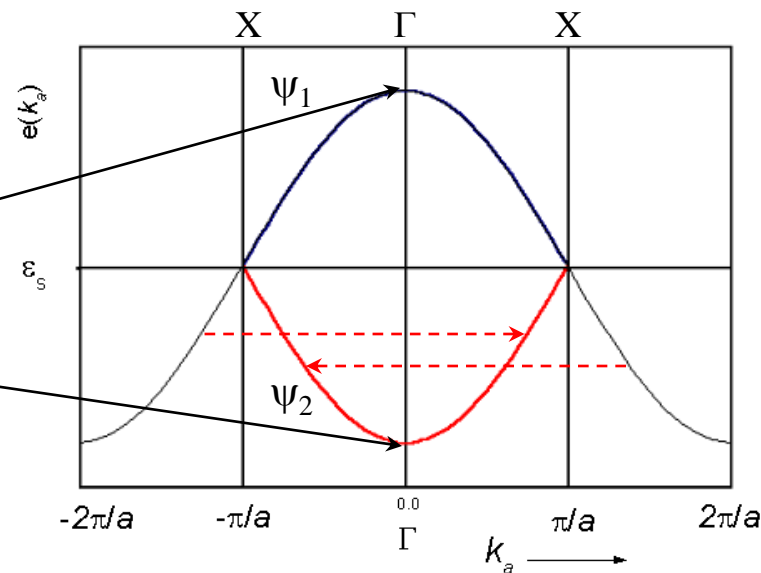
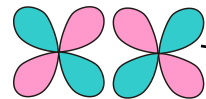
$$E_1 = \alpha + \beta$$

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

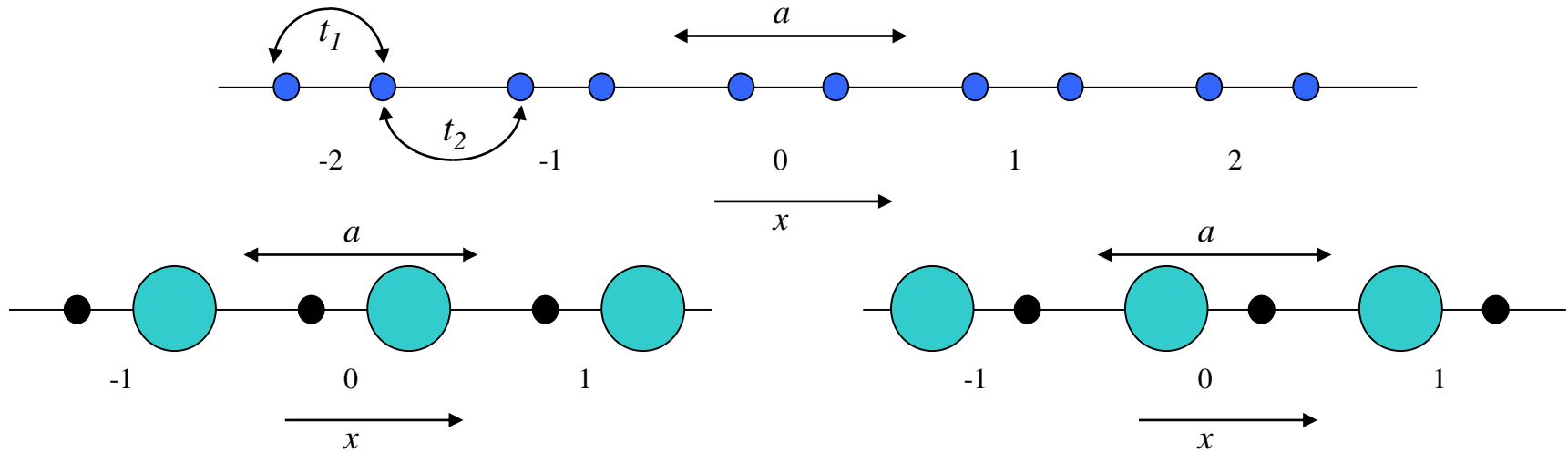


$$E_2 = \alpha - \beta$$

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






**BO**

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

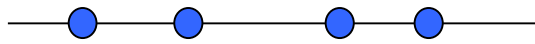
**CO**

$$\psi = c_1 \phi_1 + c_2 \phi_2 \quad ? E, c_1, c_2$$

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

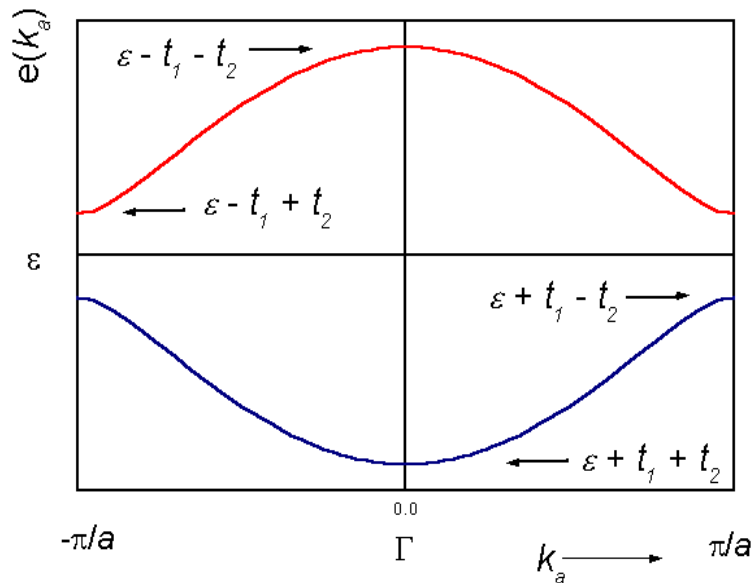
$$H_{\mu\mu} = \varepsilon_{\mu} = \langle \chi_{\mu} | H^{\text{eff}} | \chi_{\mu} \rangle \quad , \quad \mu = 1,2 \quad H_{12} = H_{21}^* = t_1 + t_2 \cdot \exp(-ik_a a)$$

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

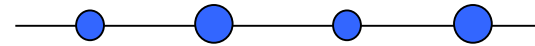


$$\varepsilon = \varepsilon_1 = \varepsilon_2, \quad t_1 < t_2 < 0$$

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

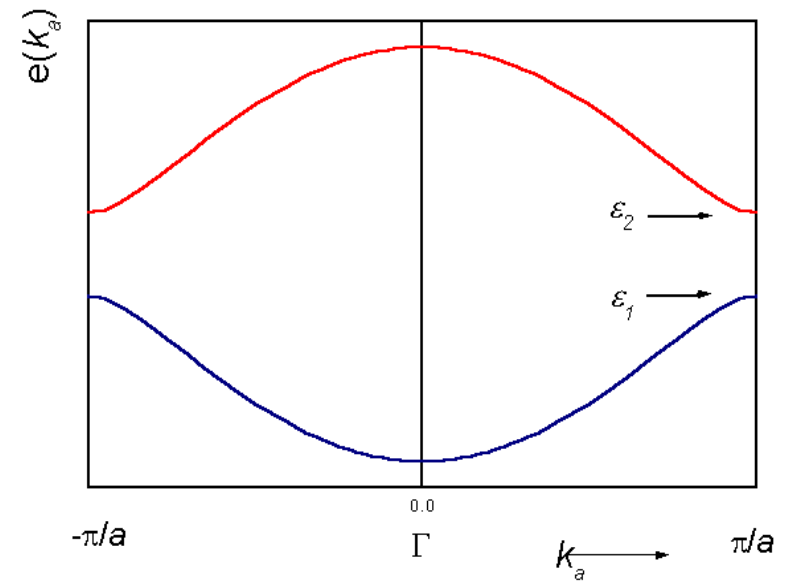


$$w = 2|t_2| \quad e_g = 2(t_2 - t_1)$$



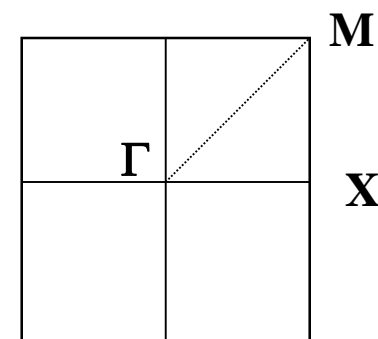
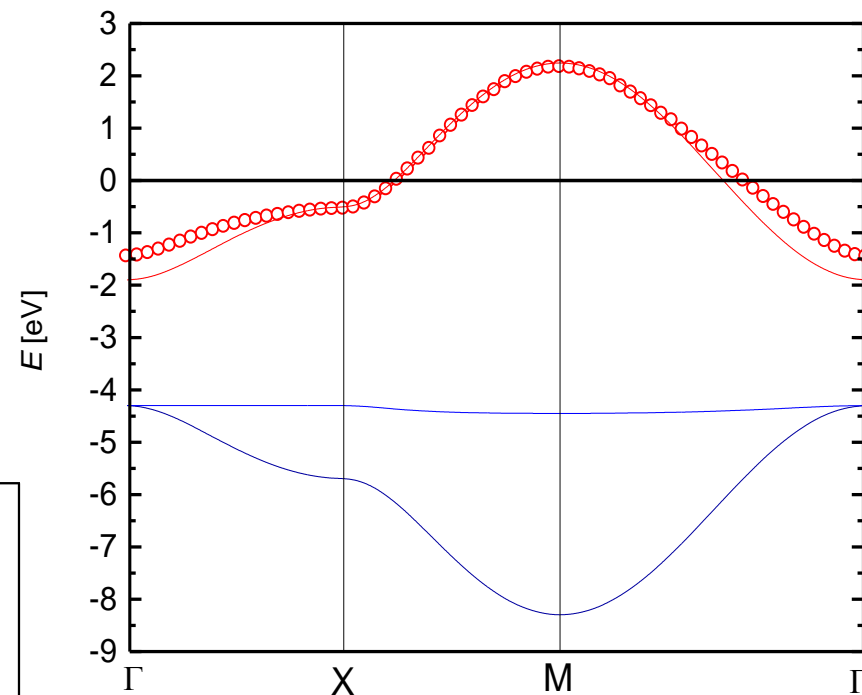
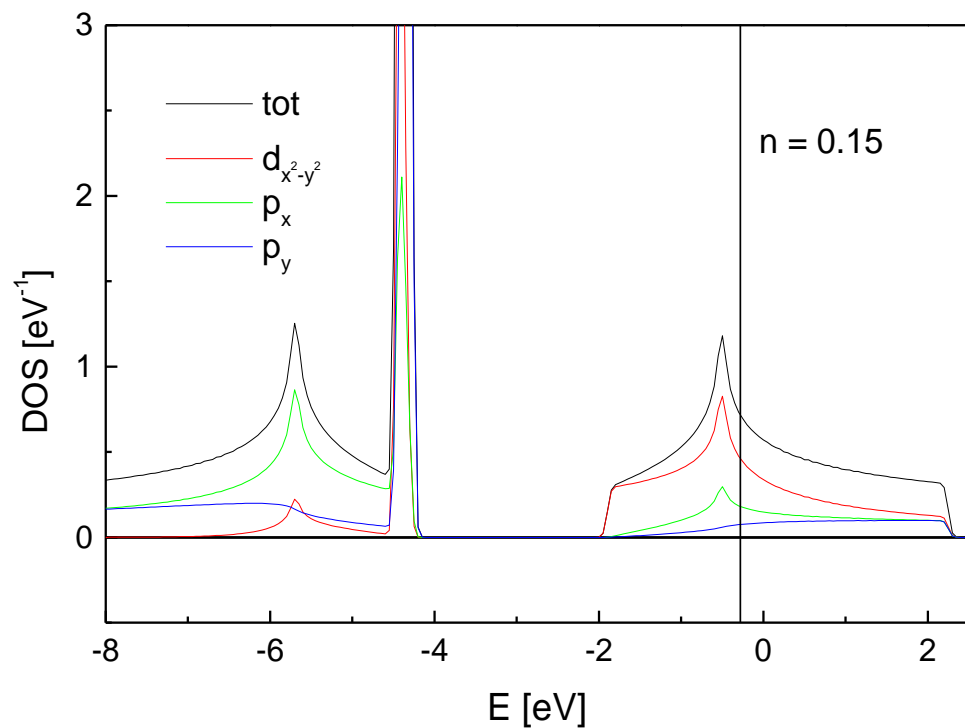
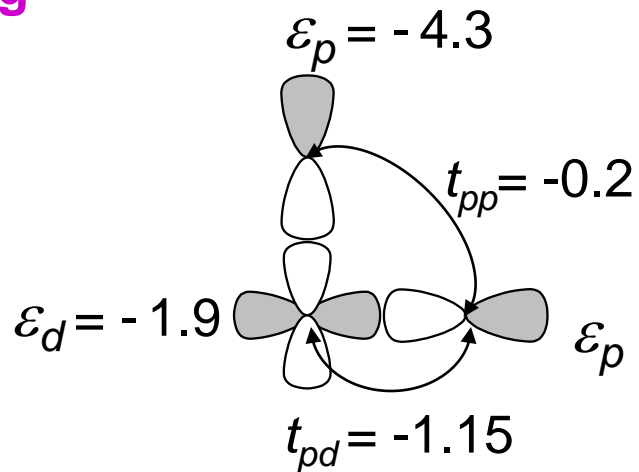
$$\varepsilon_1 < \varepsilon_2, \quad t = t_1 = t_2 < 0$$

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

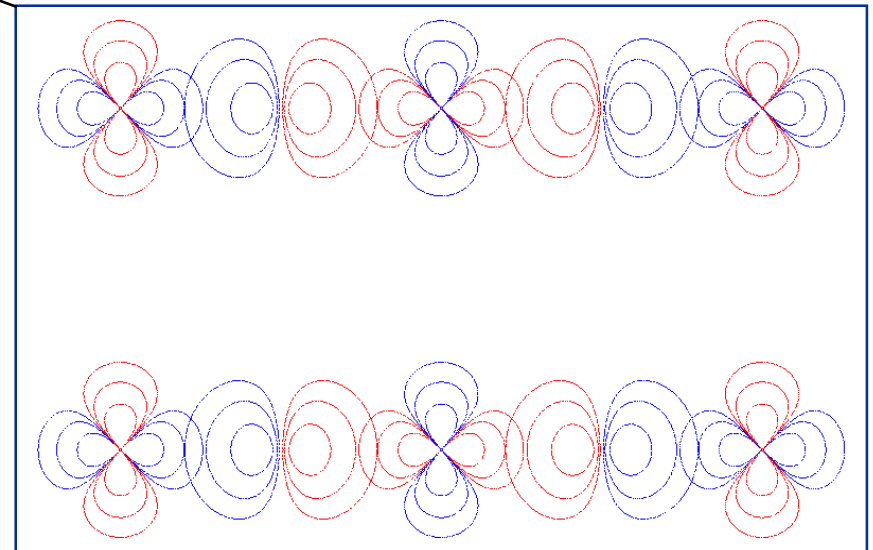
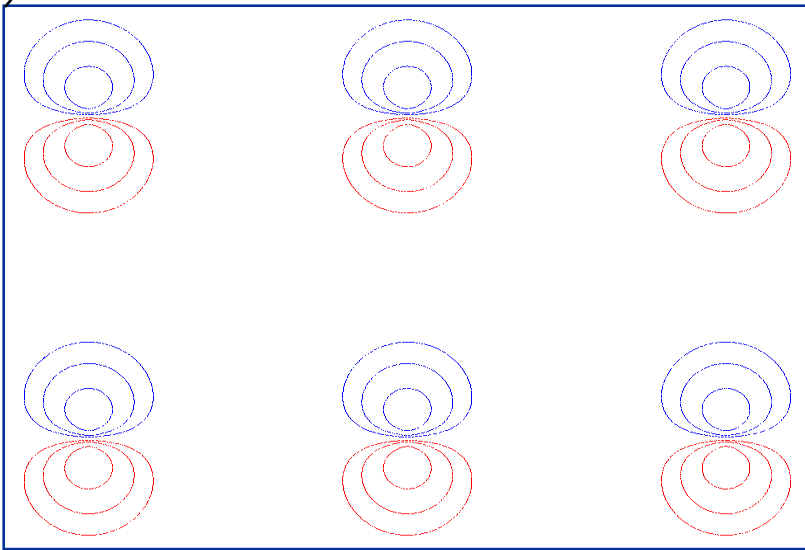
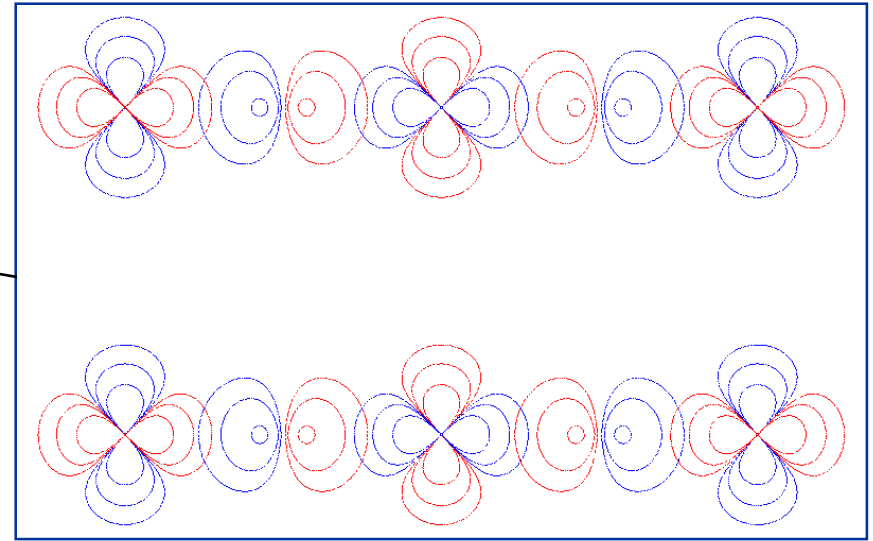
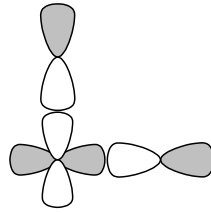
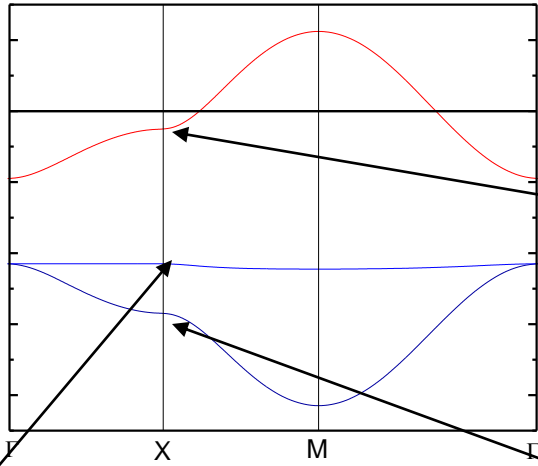


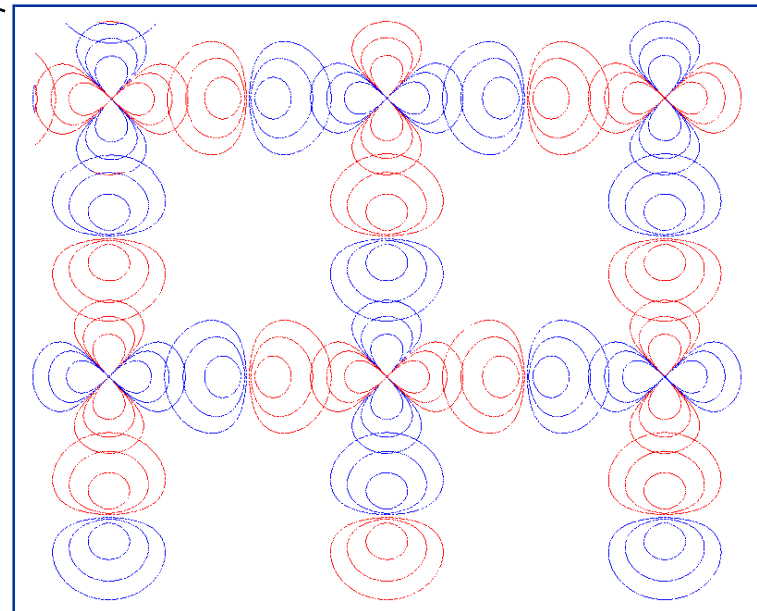
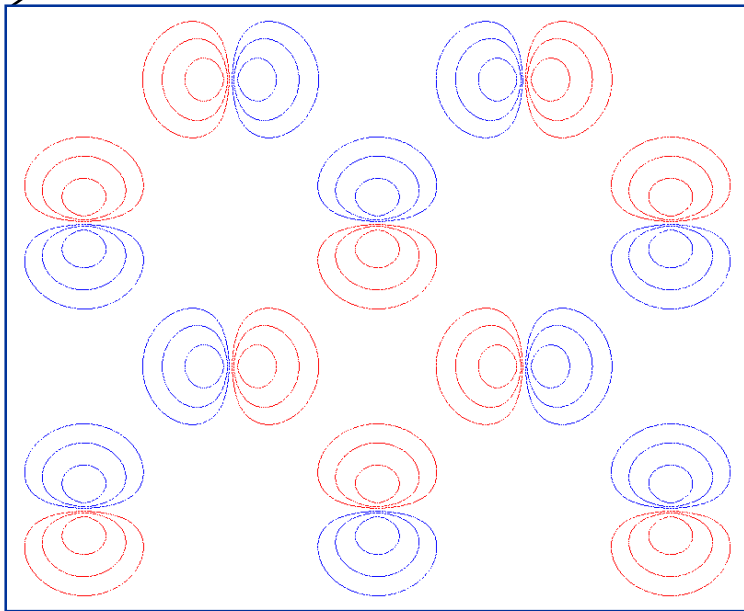
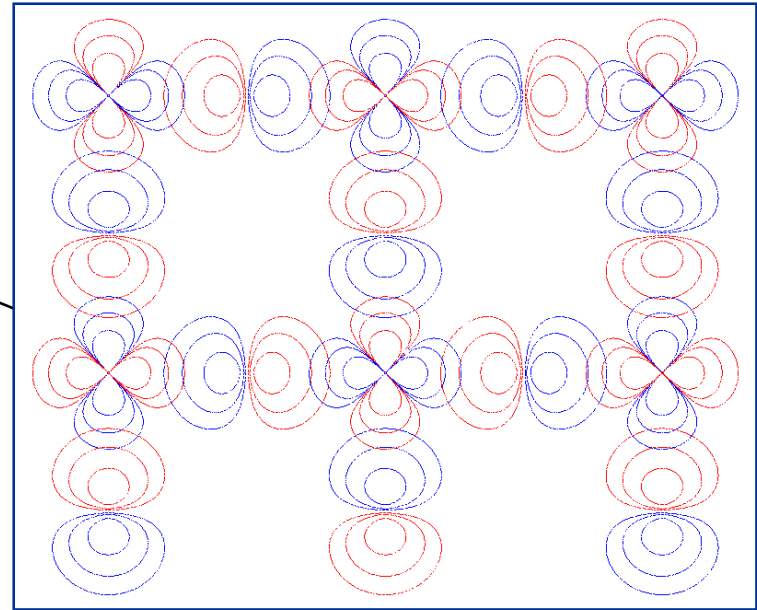
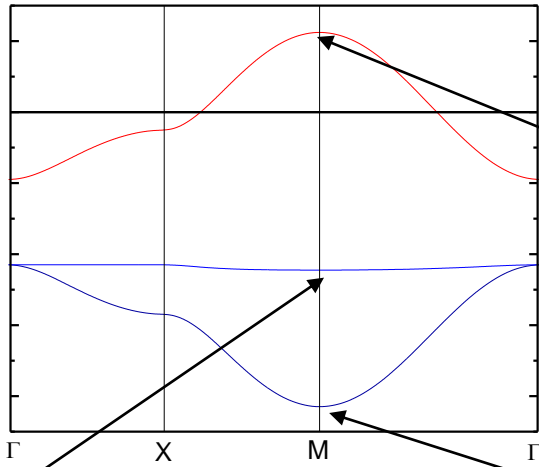
$$w = 2|t| \quad e_g = \varepsilon_2 - \varepsilon_1$$

bonding  
σ(b<sub>1g</sub>)

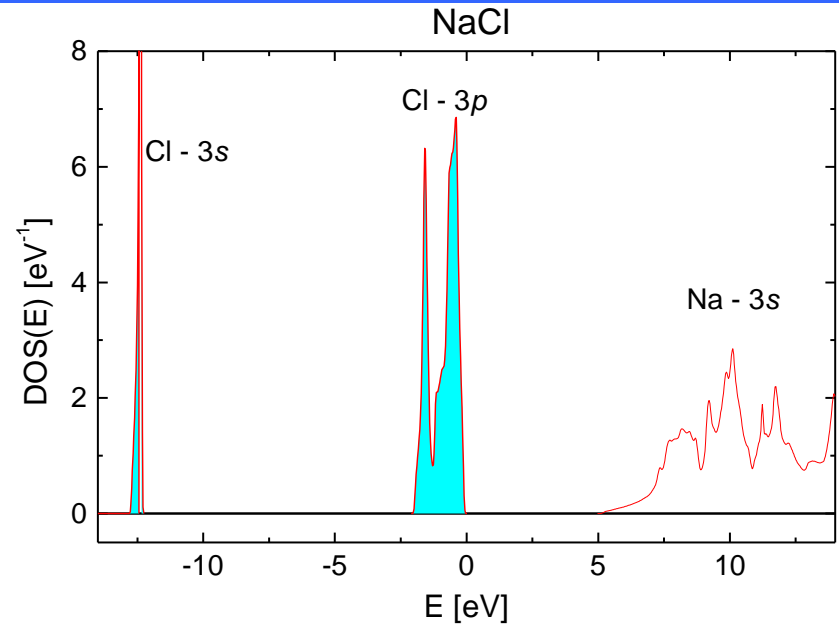
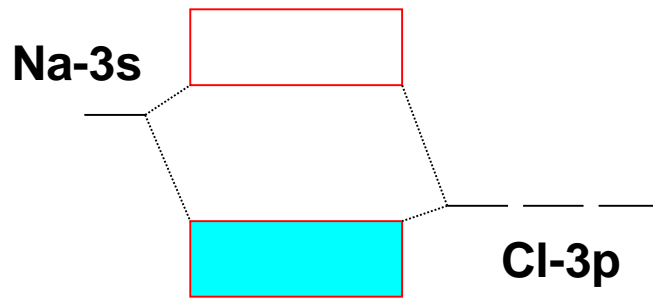


X

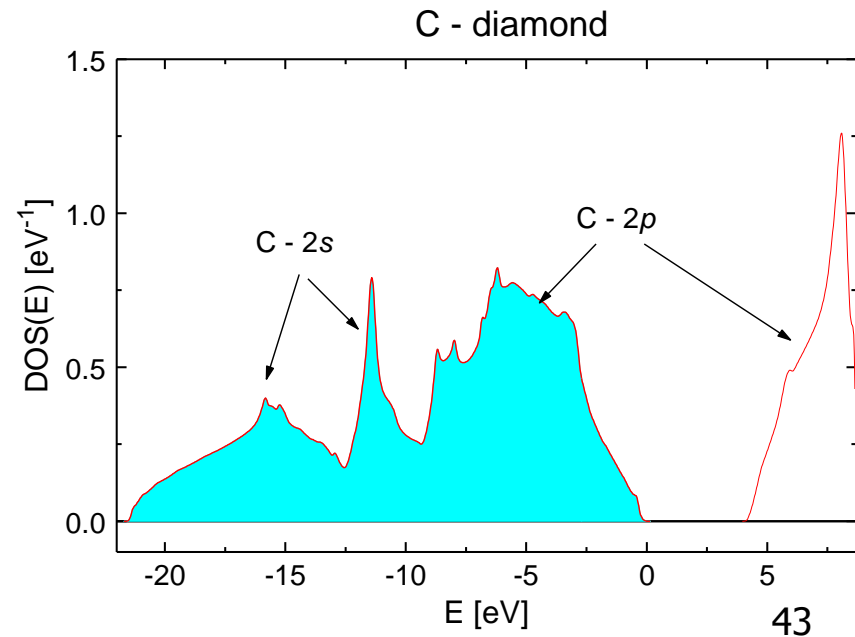
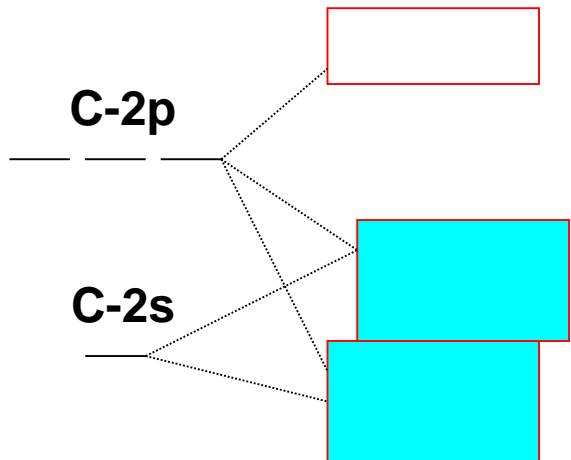


**M**

• ionic insulators



• covalent insulators



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

linear operator

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

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

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

commuting operators

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

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

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

H is Hermitian operator

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

K\*: Complex conjugate

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

Hermitian matrix

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

unitary matrix

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

ortogonal matrix

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

S<sub>ii</sub> = 1: normalised function

S<sub>ij</sub> = 0: orthogonal function

S<sub>ij</sub> = δ<sub>ij</sub> : orthonormal function

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