Bloch functions, crystalline orbitals and Fermi energy

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Outline

The crystallographic model of a crystal

Our model of a perfect crystal

The Pack-Monkhorst net

Local basis sets and Bloch functions

The calculation of the Crystalline Orbitals with a local basis set

Bravais lattice

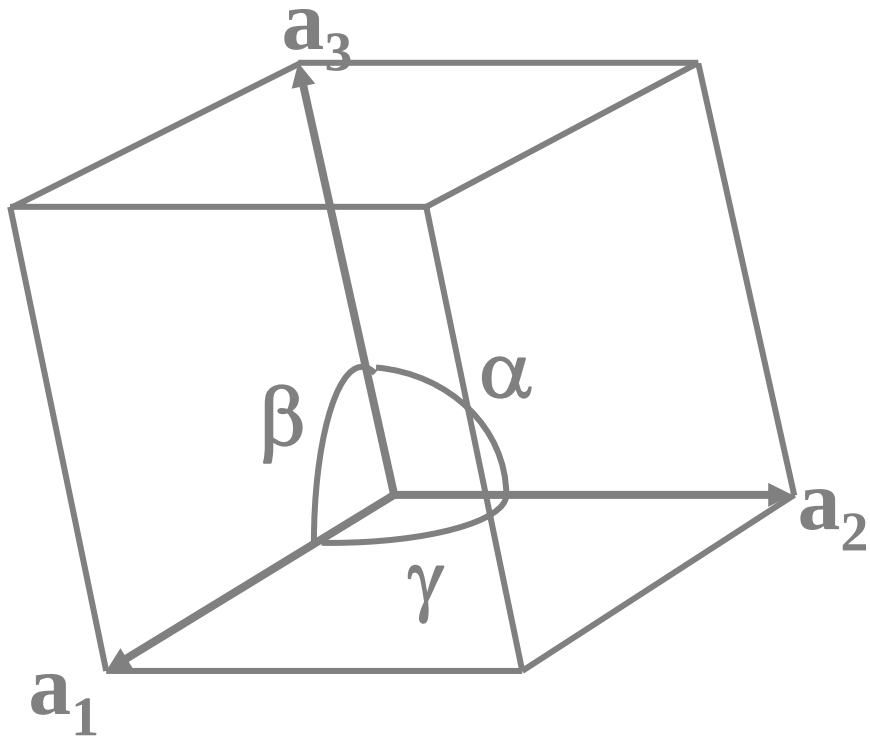
Unit cell: a volume in space that fills space entirely when translated by all lattice vectors.

The obvious choice:

a parallelepiped defined by $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, three basis vectors with

the best $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are as orthogonal as possible

the cell is as symmetric as possible (14 types)



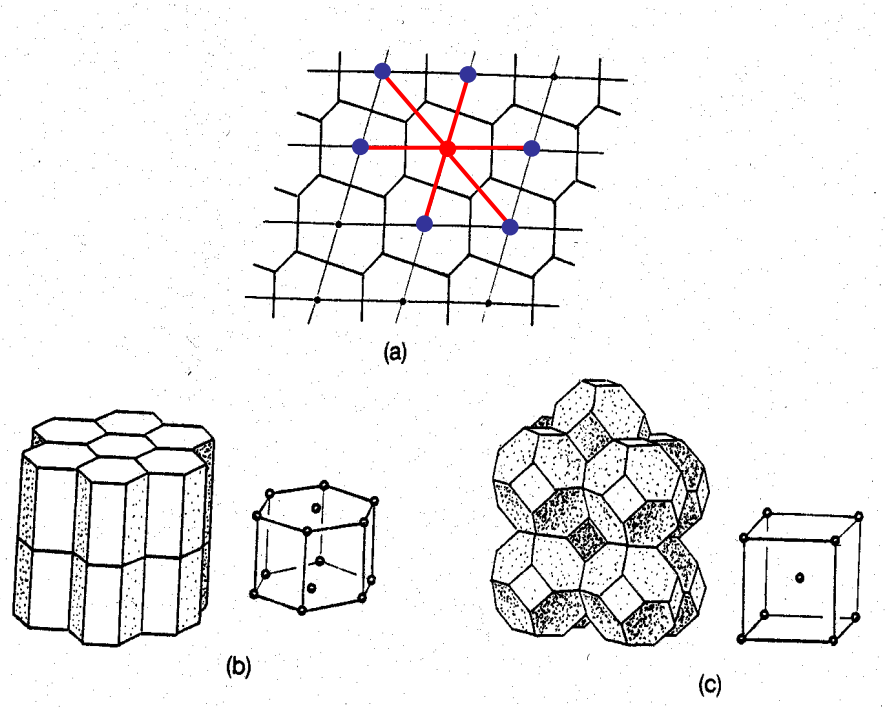
A unit cell containing one lattice point is called primitive cell.

The Wigner-Seitz cell

Wigner-Seitz cell: the portion of space which is closer to one lattice point than to anyone else.

There are 14 different types of Wigner-Seitz cells.

A Wigner-Seitz cell is primitive by construction.



The reciprocal lattice

A reciprocal lattice with lattice basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ corresponds to every real (or direct) lattice with lattice basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Basis vectors obey the following orthogonality rules:

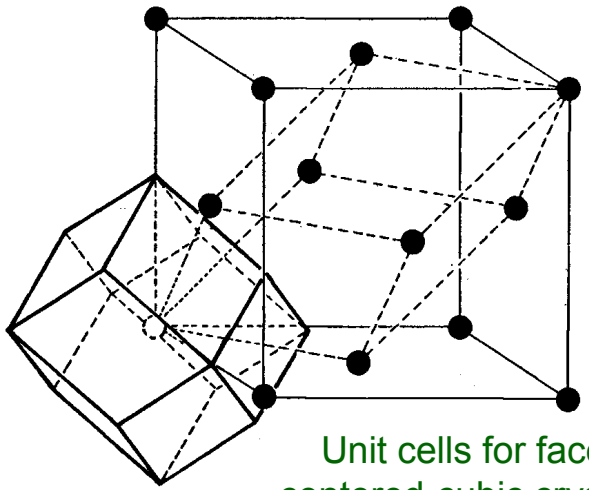
$\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$	$\mathbf{b}_2 \cdot \mathbf{a}_2 = 2\pi$	$\mathbf{b}_3 \cdot \mathbf{a}_3 = 2\pi$
$\mathbf{b}_1 \cdot \mathbf{a}_2 = 0$	$\mathbf{b}_2 \cdot \mathbf{a}_3 = 0$	$\mathbf{b}_3 \cdot \mathbf{a}_1 = 0$
$\mathbf{b}_1 \cdot \mathbf{a}_3 = 0$	$\mathbf{b}_2 \cdot \mathbf{a}_1 = 0$	$\mathbf{b}_3 \cdot \mathbf{a}_2 = 0$

or, equivalently,

$$\mathbf{b}_1 = 2\pi/V\, \mathbf{a}_2 \Lambda \mathbf{a}_3 \qquad \mathbf{b}_2 = 2\pi/V\, \mathbf{a}_3 \Lambda \mathbf{a}_1 \qquad \mathbf{b}_3 = 2\pi/V\, \mathbf{a}_1 \Lambda \mathbf{a}_2$$

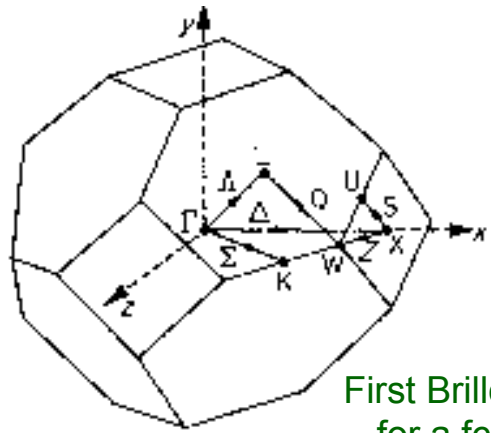
$$V = \mathbf{a}_1 \cdot \mathbf{a}_2 \Lambda \mathbf{a}_3 \qquad V^* = (2\pi)^3/V$$

The first Brillouin zone



Unit cells for face-centered-cubic crystals

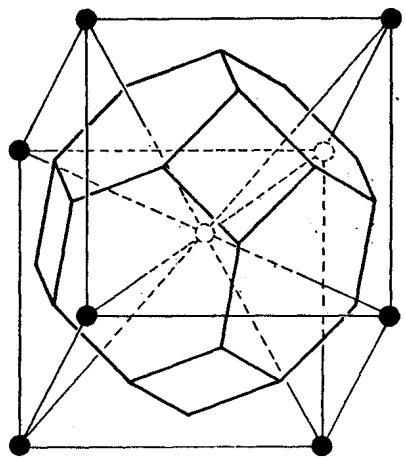
transformation to the reciprocal space



First Brillouin zone for a fcc lattice

Brillouin zone: Wigner-Seitz cell in the reciprocal space.

Special points in the Brillouin zone have been classified and labelled with letters, used in the specification of paths.



Wigner-Seitz cell for body-centered-cubic crystals

The model of a perfect crystal

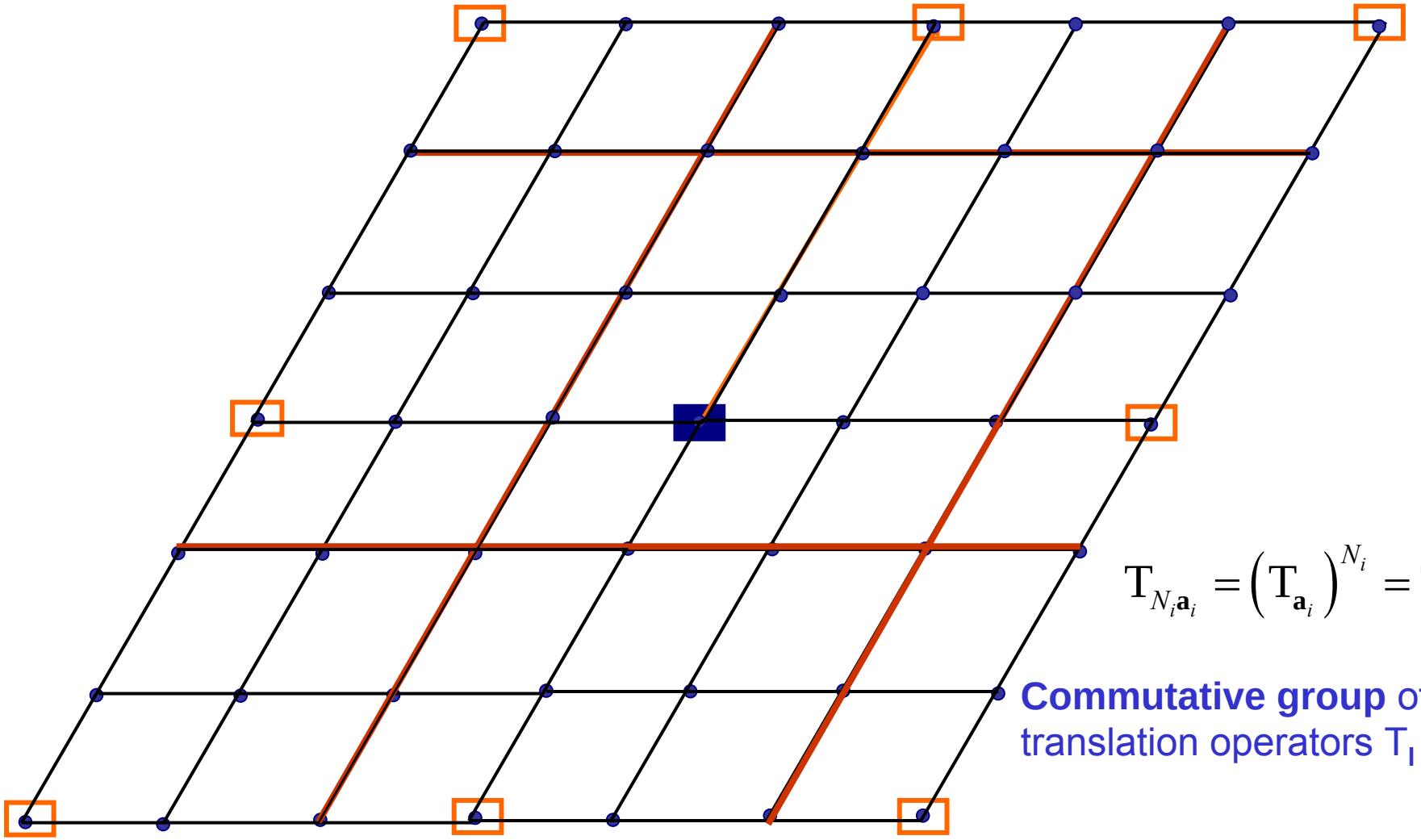
A **real crystal**: a macroscopic finite array of a very large number *n* of atoms/ions with surfaces

- the fraction of atoms at the surface is proportional to $n^{-1/3}$ (very small)
- if the surface is neutral, the perturbation due to the boundary is limited to a few surface layers
- a real crystal mostly exhibits bulk features and properties

A **macro-lattice** of *N* unit cells is good model of such a crystal

- as *N* is very large and surface effects are negligible in the bulk, the macro-lattice can be repeated periodically under the action of translation vectors $N_1\,\mathbf{a}_1$, $N_2\,\mathbf{a}_2$, $N_3\,\mathbf{a}_3$ without affecting its properties
- thus, our model of a perfect crystal coincides with the crystallographic model of an infinite array of cells containing the same group of atoms

The macro-lattice



$$\mathrm{T}_{N_i \mathbf{a}_i} = \left(\mathrm{T}_{\mathbf{a}_i}\right)^{N_i} = \mathrm{T}_{\mathbf{0}}$$

Commutative group of *N* translation operators T_I

Born-Von Kárman boundary conditions

Our model of a crystal consists of an infinite array of macro-lattices.

Every macro-lattice contains *N* unit cells

Every function or operator defined for the crystal then admits the following boundary conditions:

translation symmetry

$$f(\mathbf{r} + N_i\mathbf{a}_i) = f(\mathbf{r}) \quad \text{for } i = 1, 2, 3$$

a new metric is defined

$$\mathbf{A}_i = N_i\,\mathbf{a}_i \quad \text{for } i = 1, 2, 3$$

Pack-Monkhorst net

A reciprocal lattice can be associated with the macro-lattice with metric **A**:
the reciprocal micro-lattice with metric **B** = N^{-1} **b**

- this micro-lattice is much denser than the original reciprocal lattice with metric **b**
- the unit cell of the original reciprocal lattice with metric **b** can be partitioned into *N* micro-cells, each located by a vector (wave vector) $\mathbf{k}_m$:

$$\mathbf{k}_m = \frac{m_1}{N_1}\mathbf{b}_1 + \frac{m_2}{N_2}\mathbf{b}_2 + \frac{m_3}{N_3}\mathbf{b}_3 \qquad m_1, m_2, m_3 \text{ integers}$$

When referred to the **1st Brillouin zone,** the complete set of the $\mathbf{k}_m$ vectors form

the **Pack-Monkhorst net**

Integers N_i are called the **shrinking factors**

Character Table of the translation group

N translation operations $\Rightarrow$ *N* classes $\Rightarrow$ *N* one-dimensional irreducible representations associated with *N* $\mathbf{k}_m$ vectors of Brillouin Zone

	$\mathbf{0}$	.....	$\mathbf{l}_j$	.....	$\mathbf{l}_{j'}$	.....
$\mathbf{0}$	1	.....	1	.....	1	.....
$\mathbf{k}_m$	1	.....	$\exp(i\mathbf{k}_m \cdot \mathbf{l}_j)$	.....	$\exp(i\mathbf{k}_m \cdot \mathbf{l}_{j'})$	.....
$\mathbf{k}_{m'}$	1	.....	$\exp(i\mathbf{k}_{m'} \cdot \mathbf{l}_j)$	.....	$\exp(i\mathbf{k}_{m'} \cdot \mathbf{l}_{j'})$	.....

Due to the orthogonality between rows and columns

$$\sum_{j=1}^{N} exp\left[i\left(\mathbf{k}_m - \mathbf{k}_{m'}\right)\cdot \mathbf{l}_j \right] = N\delta_{mm'} \quad \& \quad \sum_{m=1}^{N} \exp\left[i\mathbf{k}_m \cdot (\mathbf{l}_j - \mathbf{l}_{j'}) \right] = N\delta_{jj'}$$

The reduced Pack-Monkhorst net

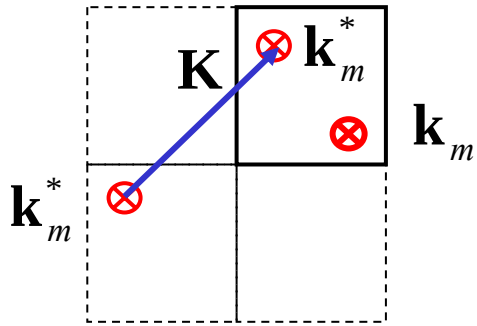
If vector $\mathbf{k}_m^* = \mathbf{K}_{(m)} - \mathbf{k}_m$ belongs to Pack-Monkhorst net, it may happen:

1. $\mathbf{k}_m^* \neq \mathbf{k}_m$

   one of the two points (any) is assigned to the reduced Pack-Monkhorst net (type *C*).

2. $\mathbf{k}_m^* = \mathbf{k}_m$

   the point is assigned to the reduced Pack-Monkhorst net (type *R*); it can only be $\mathbf{k}_m$ = (0 0 0) or $\mathbf{k}_m$ = (½ ½ ½)



$$\sum_{m=1}^{N} \exp\left(i\mathbf{k}_m \cdot (\mathbf{l}_j - \mathbf{l}_{j'})\right) = N\delta_{jj'} \quad \longrightarrow \quad \sum_{m=1}^{N'} w_m \cos\left(\mathbf{k}_m \cdot (\mathbf{l}_j - \mathbf{l}_{j'}\right) = \delta_{jj'}$$

$$w_m = \frac{1}{N}(2 - \delta_{\mathbf{k}_m^* \mathbf{k}_m})$$

Atomic orbital basis set

Choice of a set of local functions → **L.C.A.O** method (Linear Combination of Atomic Orbitals)

$\Rightarrow$ *M* atomic orbitals $\chi_\mu(\mathbf{r})$ per cell

the local basis set

M×*N* atomic orbitals

$\chi_\mu(\mathbf{r}-\mathbf{l}_j)$

→ **representation of operator *f***

$f_{\mu\nu}(\mathbf{l}_{j'},\mathbf{l}_j)$

$$f_{\mu\nu}(\mathbf{l}_{j'},\mathbf{l}_j)=\int_V \chi_\mu^*(\mathbf{r}-\mathbf{l}_{j'})\, f(\mathbf{r})\chi_\nu(\mathbf{r}-\mathbf{l}_j)\; d\mathbf{r}$$

Translation invariance of matrix elements

If in $$f_{\mu\nu}(\mathbf{l}_{j'},\mathbf{l}_j)=\int_V \chi^*_\mu(\mathbf{r}-\mathbf{l}_{j'})\, f(\mathbf{r})\chi_\nu(\mathbf{r}-\mathbf{l}_j)\;\; d\mathbf{r}$$

the origin is translated by $\mathbf{l}_{j'}$

$$f_{\mu\nu}\left(\mathbf{0},\mathbf{l}_j-\mathbf{l}_{j'}\right)=\int_V \chi^*_\mu(\mathbf{r})\, f(\mathbf{r}+\mathbf{l}_{j'})\chi_\nu\left[\mathbf{r}-\left(\mathbf{l}_j-\mathbf{l}_{j'}\right)\right]\;\; d\mathbf{r}$$

but, for translation invariance and if $f(\mathbf{r})$ is periodic with the same periodicity of the direct lattice,

$$\chi_\mu\left(\mathbf{r}-\mathbf{l}_{j'}\right)=\chi_\mu(\mathbf{r})$$

$$\chi_\nu\left(\mathbf{r}-\mathbf{l}_j\right)=\chi_\nu\left[\mathbf{r}-\left(\mathbf{l}_j-\mathbf{l}_{j'}\right)\right]=\chi_\nu\left(\mathbf{r}-\mathbf{l}_{j''}\right)$$

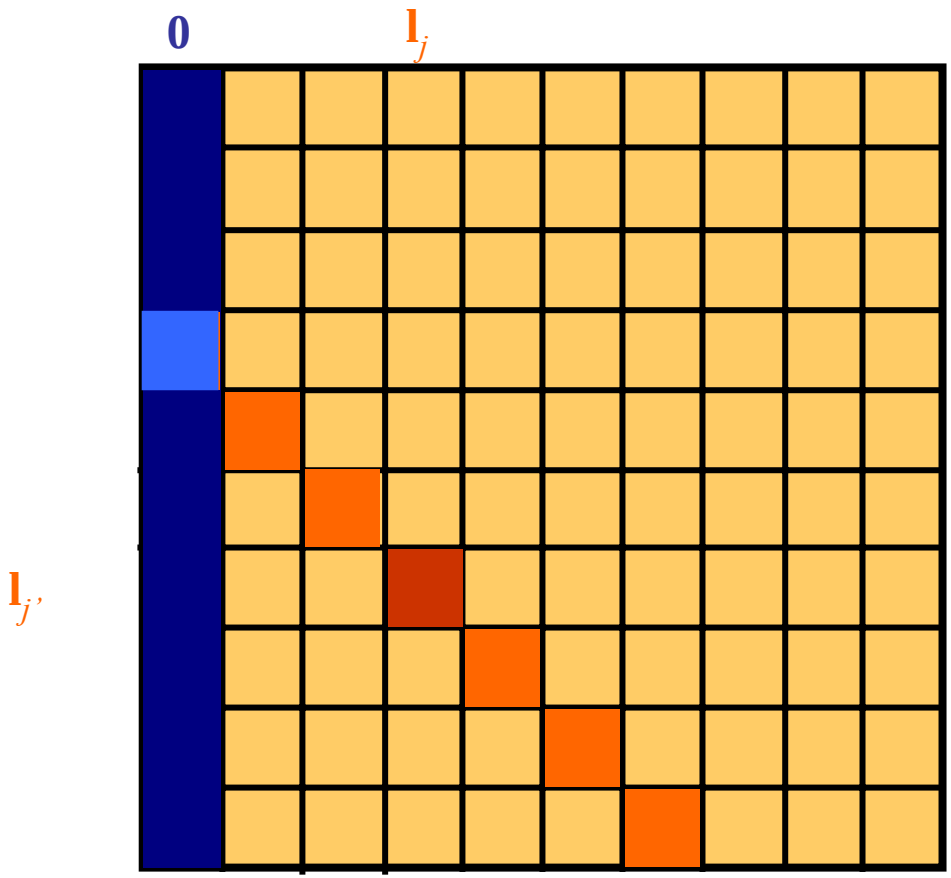
$$f(\mathbf{r})=f(\mathbf{r}+\mathbf{l}_{j'})$$

so that matrix elements are also translation invariant

$$f_{\mu\nu}\left(\mathbf{l}_{j'},\mathbf{l}_j\right)=f_{\mu\nu}\left(\mathbf{0},\mathbf{l}_j-\mathbf{l}_{j'}\right)=f_{\mu\nu}\left(\mathbf{0},\mathbf{l}_{j''}\right)$$

Representation of operators in the AO basis

Consequences of translation invariance: $f_{\mu\nu}(\mathbf{l}_{j'},\mathbf{l}_j) = f_{\mu\nu}(\mathbf{0},\mathbf{l}_{j'}-\mathbf{l}_j)$



Square Matrix: N^2 blocks of size M

Bloch functions

The local basis

M×N atomic orbitals

$$\chi_\mu(\mathbf{r}-\mathbf{l}_j)$$

Bloch function basis

basis for the irreducible representation of the translations group

$$\phi_\mu(\mathbf{k}_m,\mathbf{r})$$

$$\phi_\mu(\mathbf{k}_m,\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{j=1}^{N}\exp(i\mathbf{k}_m\cdot\mathbf{l}_j)\chi_\mu(\mathbf{r}-\mathbf{l}_j)$$

In this basis set the matrix element $f_{\mu\nu}$ depends on two new indices: $\mathbf{k}_m$ and $\mathbf{k}_{m'}$, which are vectors of the reciprocal space:

$$f_{\mu\nu}(\mathbf{k}_{m'},\mathbf{k}_m) = \frac{1}{N}\sum_{j,j'=1}^{N} e^{i\left(\mathbf{k}_m\cdot\mathbf{l}_j-\mathbf{k}_{m'}\cdot\mathbf{l}_{j'}\right)}\int_V \chi_\mu^*\left(\mathbf{r}-\mathbf{l}_{j'}\right) f(\mathbf{r})\chi_\nu\left(\mathbf{r}-\mathbf{l}_j\right)\,d\mathbf{r}$$

Bloch theorem

$$f_{\mu\nu}(\mathbf{k}_{m'},\mathbf{k}_m)=\frac{1}{N}\sum_{j'=1}^{N}e^{-i\mathbf{k}_{m'}\cdot\mathbf{l}_{j'}}\sum_{j=1}^{N}e^{i\mathbf{k}_m\cdot\mathbf{l}_j}f_{\mu\nu}\left(\mathbf{l}_{j'},\mathbf{l}_j\right)$$

for translation invariance and after multiplying and dividing by $e^{i\mathbf{k}_m\cdot\mathbf{l}_{j'}}$

$$f_{\mu\nu}(\mathbf{k}_{m'},\mathbf{k}_m)=\frac{1}{N}\sum_{j'=1}^{N}e^{i(\mathbf{k}_m-\mathbf{k}_{m'})\cdot\mathbf{l}_{j'}}\sum_{j=1}^{N}e^{i\mathbf{k}_m\cdot\left(\mathbf{l}_j-\mathbf{l}_{j'}\right)}f_{\mu\nu}\left(\mathbf{0},\mathbf{l}_j-\mathbf{l}_{j'}\right)$$

but, as the sum over *j* extends to all direct lattice vectors, it is equivalent to summing over all vectors $\mathbf{l}_{j''}=\mathbf{l}_j-\mathbf{l}_{j'}$,

$$f_{\mu\nu}(\mathbf{k}_{m'},\mathbf{k}_m)=\frac{1}{N}\sum_{j'=1}^{N}e^{i(\mathbf{k}_m-\mathbf{k}_{m'})\cdot\mathbf{l}_{j'}}\sum_{j''=1}^{N}e^{i\mathbf{k}_m\cdot\mathbf{l}_{j''}}f_{\mu\nu}\left(\mathbf{0},\mathbf{l}_{j''}\right)$$

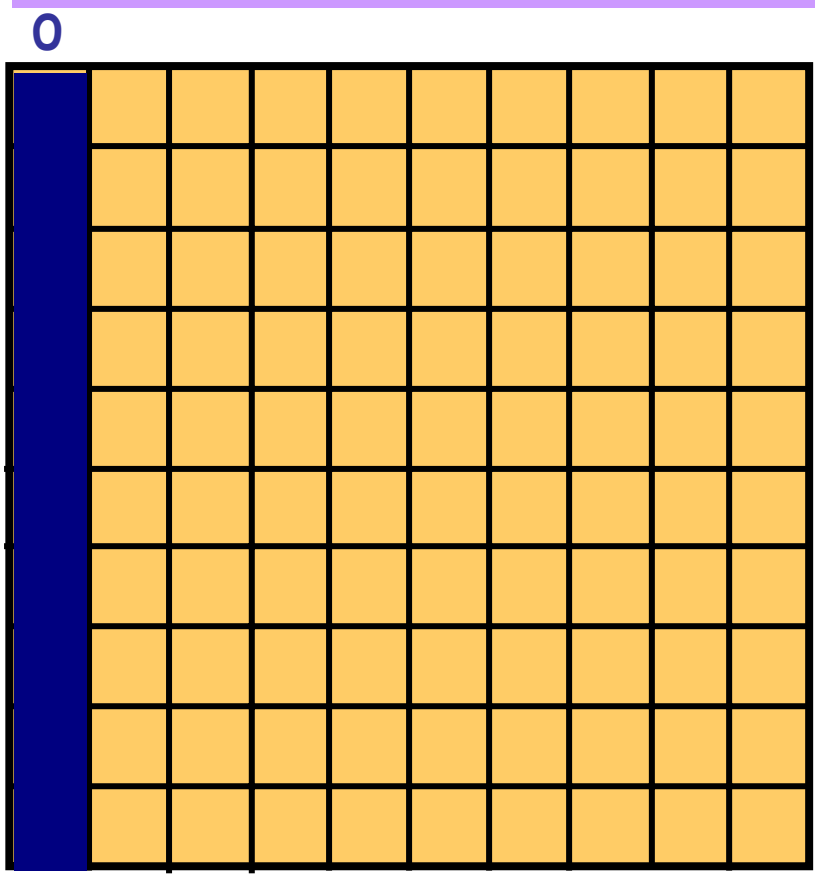
and recalling the character orthogonality relation for rows, we get

$$f_{\mu\nu}(\mathbf{k}_{m'},\mathbf{k}_m)=\delta_{\mathbf{k}_m\mathbf{k}_{m'}}\sum_{j=1}^{N}\mathrm{e}^{i\mathbf{k}_m\cdot\mathbf{l}_j}\,f_{\mu\nu}(\mathbf{l}_j)$$

Consequences of Bloch theorem

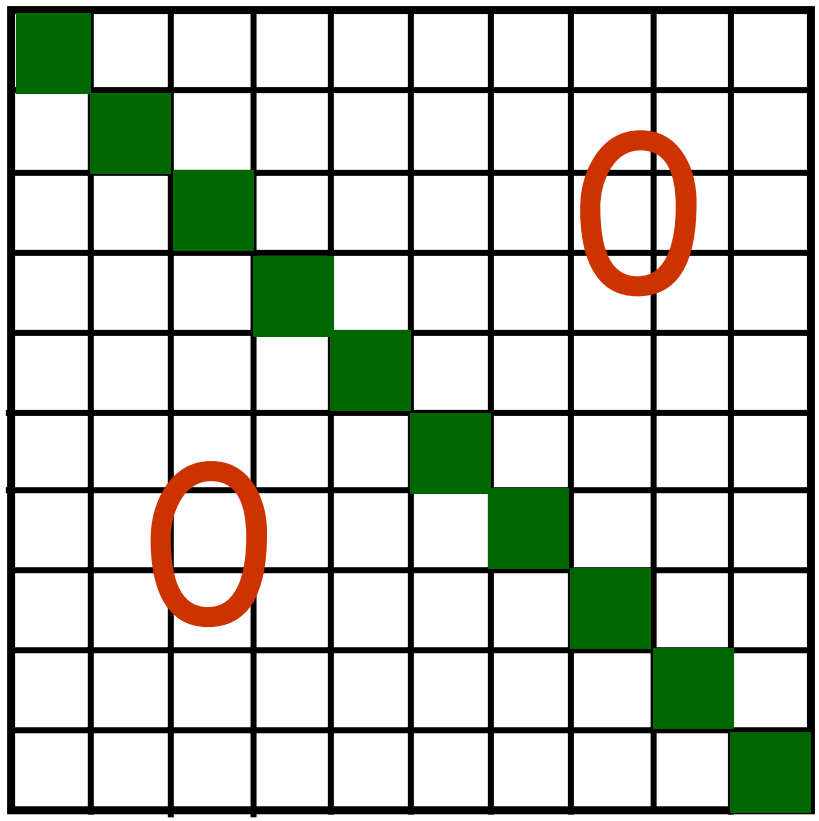
the AO basis

$\chi_\mu(\mathbf{r} - \mathbf{l}_j)$



Bloch function basis

$\phi_\mu(\mathbf{k}_m, \mathbf{r})$



N blocks of size *M* associated with $\mathbf{k}_m$

Calculation of the Crystalline Orbitals with the Self-consistent-field approximation

Calculation of ($M^2 \times N$) elements of F: $F_{\mu\nu}(\mathbf{l})$

❷ Representation in the basis of Bloch functions:

At every point k_m of Pack-Monkhorst net:

$$F_{\mu\nu}(\mathbf{k}_m) = \sum_{j=1}^{N} \exp(i\mathbf{k}_m \cdot \mathbf{l}_j)\, F_{\mu\nu}(\mathbf{l}_j)$$

❸ At every $\mathbf{k}_m$, the eigenvalue equation of size M is solved:

$$\mathrm{F}(\mathbf{k}_m)\,\mathrm{C}(\mathbf{k}_m) = \mathrm{S}(\mathbf{k}_m)\,\mathrm{C}(\mathbf{k}_m)\,\mathrm{E}(\mathbf{k}_m)$$

M crystalline orbitals $\Psi_\tau(\mathbf{k}_m, \mathbf{r})$ associated with $\varepsilon_\tau(\mathbf{k}_m)$

$$\Psi_\tau(\mathbf{k}_m, \mathbf{r}) = \sum_{\mu=1}^{M} C_{\mu\tau}(\mathbf{k}_m)\, \phi_\mu(\mathbf{k}_m, \mathbf{r})$$

Calculation of the Crystalline Orbitals with the Self-consistent-field approximation

4. Aufbau principle in populating electronic bands

   ↳ Fermi Energy ε_F

5. Calculation of density matrix elements in the AO basis from occupied CO

   ↳ in reciprocal space

$$P_{\mu\nu}^{total}(\mathbf{k}_m) = 2\left[\sum_{\tau\ occupied}^{M} C_{\mu\tau}(\mathbf{k}_m)\, C_{\nu\tau}(\mathbf{k}_m)^*\right]$$

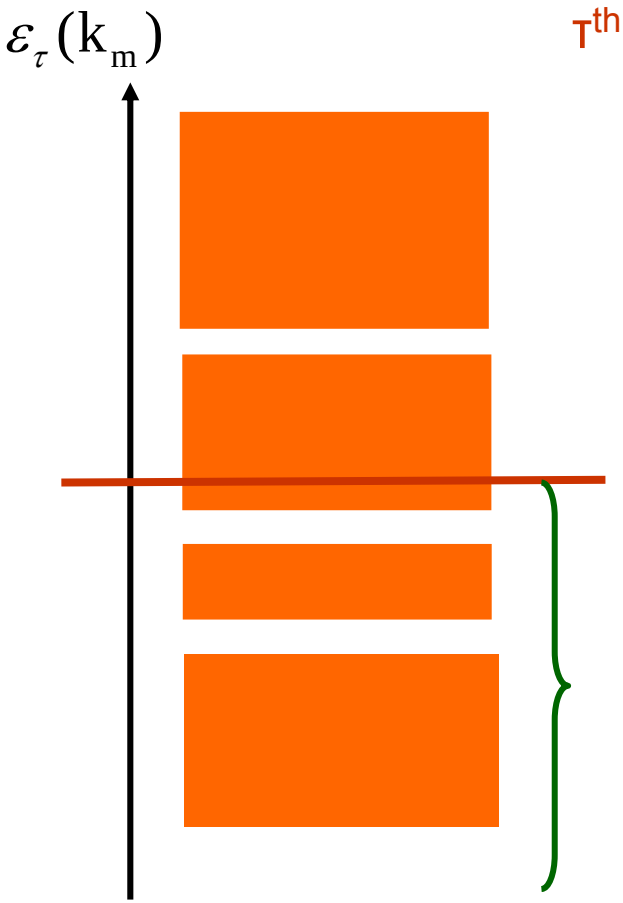
   ↳ in direct space

$$P_{\mu\nu}^{total}(\mathbf{l}_j) = \frac{1}{N}\sum_{m=1}^{N} \exp(-i\mathbf{k}_m \cdot \mathbf{l}_j)\, P_{\mu\nu}^{total}(\mathbf{k}_m)$$

   ↳ ready for the calculation of F in the AO basis during the next iterative step

Band structure representation

n_{states}: number of states per direct lattice cell

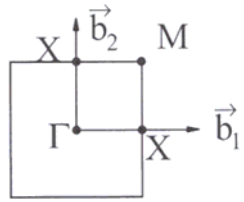


τ^{th} energy band

$\varepsilon_\tau(k_m)$

ε_F

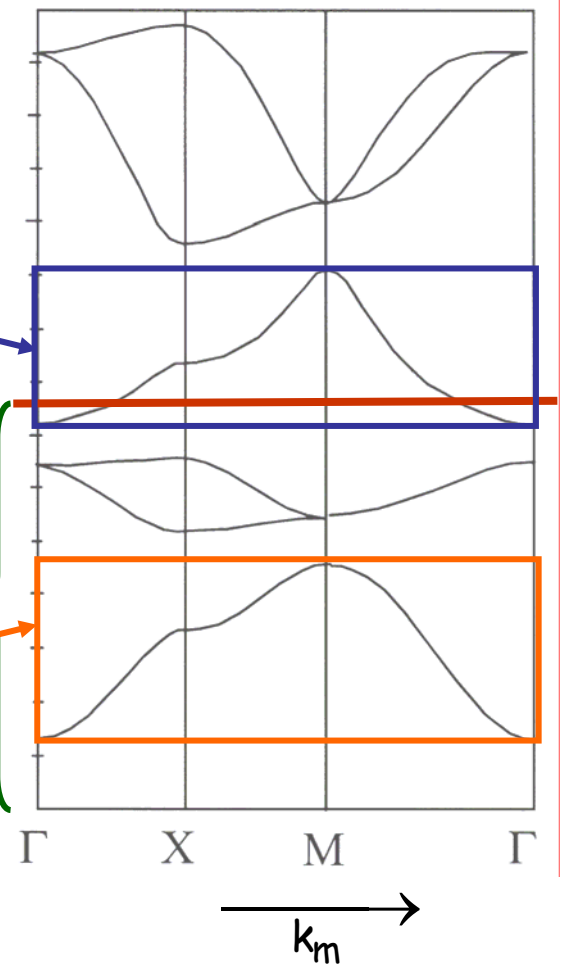
$n_{states}/2$ doubly occupied bands (closed shell)



$\varepsilon_\tau(k_m)$

partially filled band

full band



Fermi energy

$$n_{states} = 2\left[\sum_{\tau=1}^{M}\sum_{m=1}^{N}\theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k_m}))\right]/N$$

with $\theta(x)=0$ if $x < 0$ and
$\theta(x)=1$ if $x \geq 0$

$$n_{states} = 2\left[\frac{1}{\Omega_{BZ}}\sum_{\tau=1}^{M}\int_{BZ}\theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k}))\, d\mathbf{k}\right]$$

↳ definition of a new function :

$$n_{states}(\varepsilon) = 2\left[\frac{1}{\Omega_{BZ}}\sum_{\tau=1}^{M}\int_{\Omega_{BZ}}\theta(\varepsilon - \varepsilon_\tau(\mathbf{k}))\, d\mathbf{k}\right]$$

$\Rightarrow$ iterative evaluation of ε_F ($n_{states}(\varepsilon)$-n_{states})

Definition of the density matrix

$$P_{\mu\nu}^{total}(\mathbf{l}) = 2\left[\frac{1}{\Omega_{BZ}}\sum_{\tau=1}^{M}\int_{BZ} P_{\mu\nu}^{\tau}(\mathbf{k},\mathbf{l})\ \theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k}))\ d\mathbf{k}\right]$$

$$P_{\mu\nu}^{\tau}(\mathbf{k},\mathbf{l}) = C_{\mu\tau}(\mathbf{k})\ C_{\nu\tau}^{*}(\mathbf{k})\exp\left(-i\,\mathbf{k}\cdot\mathbf{l}\right)$$

Fourier analysis of energy bands

Analytic expression of even periodic function $\varepsilon_\tau(\mathbf{k})$ in reciprocal space

$$\varepsilon_\tau(\mathbf{k}+\mathbf{K}) = \varepsilon_\tau(\mathbf{k})$$

$$\varepsilon_\tau(\mathbf{k}) = \varepsilon_\tau(-\mathbf{k})$$

Fourier expansion of $\varepsilon_t(\mathbf{k})$:

$$\varepsilon_\tau(\mathbf{k}) \approx \sum_{j=1}^{N_f} D_j^\tau f_j(\mathbf{k})$$

$$D_j^\tau = \sum_{m=1}^{N'} w_m f_j(\mathbf{k}_\mathrm{m})\, \varepsilon_\tau(\mathbf{k}_\mathrm{m})$$

$$f_j(\mathbf{k}) = \sqrt{\frac{2}{n_j(1+\delta_{\mathbf{l}_j\mathbf{l}_j})}} \left[\sum_{l=1}^{n_j} \cos(\mathbf{k}\cdot\mathbf{l}_{jl}) \right]$$

Gilat net

Definition of a **denser mesh** than Pack-Monkorst in BZ

$$\mathbf{k}_n = \frac{p_{n1}}{S_1}\mathbf{b}_1 + \frac{p_{n2}}{S_2}\mathbf{b}_2 + \frac{p_{n3}}{S_3}\mathbf{b}_3 \qquad 0 \le p_{ni} \le S_i - 1$$

The first BZ is partitioned into $S = S_1 S_2 S_3$ domains centred at $\mathbf{k}_n$

$$n_{\text{electrons}}(\varepsilon) = \frac{2}{S}\left[\sum_{\tau=1}^{M}\sum_{n=1}^{S}\int_{p_{n1}-1/2}^{p_{n1}+1/2}\int_{p_{n2}-1/2}^{p_{n2}+1/2}\int_{p_{n3}-1/2}^{p_{n3}+1/2}\theta(\varepsilon-\varepsilon_\tau(\mathbf{k}))\,dp_1dp_2dp_3\right]$$

Linear expansion of $\varepsilon_\tau(\mathbf{k})$ in the domain of point $\mathbf{k}_n$

$$\varepsilon_\tau(\mathbf{k}) \approx \varepsilon_\tau(\mathbf{k}_n) + \sum_{i=1}^{3}\varepsilon_\tau^{(i)}(\mathbf{k}_n)\,(p_i - p_{in})$$

Calculating the density matrix: quadrature

$$P_{\mu\nu}^{total}(\mathbf{l}) = 2\left[\frac{1}{\Omega_{BZ}}\sum_{\tau=1}^{M}\int_{\Omega_{BZ}} P_{\mu\nu}^{\tau}(\mathbf{k},\mathbf{l})\ \theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k}))\ d\mathbf{k}\right]$$

Fourier expansion

$$P_{\mu\nu}^{\tau}(\mathbf{k}) \approx \sum_{j=1}^{N_f} D_{\mu\nu j}^{\tau}(\mathbf{l})\ f_j(\mathbf{k})$$

$$P_{\mu\nu}^{total}(\mathbf{l}) \approx \frac{2}{\Omega_{recip}}\left[\sum_{\tau=1}^{M}\sum_{m=1}^{N'} W_m^{\tau} P_{\mu\nu}^{\tau}(\mathbf{k}_m,\mathbf{l})\right]$$

$$W_m^{\tau} = w_m \sum_{i=1}^{N_f} Q_i^{\tau}\ f_i(\mathbf{k}_m)$$

$$Q_j^{\tau} = \frac{1}{\Omega_{BZ}}\int_{\Omega_{BZ}} f_j(\mathbf{k})\ \theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k}))\ d\mathbf{k}$$

Calculation of the quadrature coefficients

full bands: $W_m^\tau = w_m$

partially occupied bands: $W_m^\tau = w_m \sum_{i=1}^{N_f} Q_i^\tau \, f_i(\mathbf{k}_\mathrm{m})$

In Gilat net:

$$Q_j^\tau = \left[\sum_{n=1}^{S'} v_n f_{nj} \int_{p_{n1}-1/2}^{p_{n1}+1/2} \int_{p_{n2}-1/2}^{p_{n2}+1/2} \int_{p_{n3}-1/2}^{p_{n3}+1/2} \theta(\varepsilon_F - \varepsilon_\tau(\mathbf{k}))\, dp_1 dp_2 dp_3 \right]$$