

Computational Methods Applied to Materials Science:

Nanotechnology and Surface Phenomena

Electronic Levels in the presence of a
Periodic Potential



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Outline

- Lattices
- Reciprocal Lattice
- Periodic Potential
- Hamiltonian

Reciprocal Lattice

- ▣ Defines de set of vectors $\mathbf{K}$ which make a plane wave periodil in the Real Space (Direct Lattice).
- ▣ $e^{i\vec{K}\cdot\vec{R}} = 1$
- ▣ Is the Fourier Transform of the Direct Lattice.
- ▣ For each (hkl) in real space there exist a vector in reciprocal space [hkl].
 - [hkl] is ortoghonal to (hkl)

■ Simulation

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

$$\vec{K} = n_1\vec{b}_1^* + n_2\vec{b}_2^* + n_3\vec{b}_3^*$$

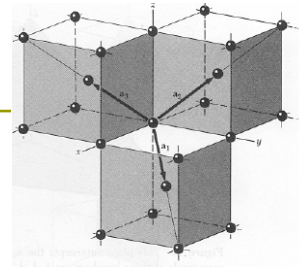
Reciprocal Lattice

$$\vec{a}_i \cdot \vec{b}_j^* = 2\pi\delta_{ij}$$

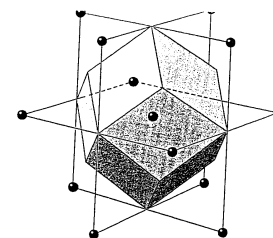
$$\vec{b}_1^* = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

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

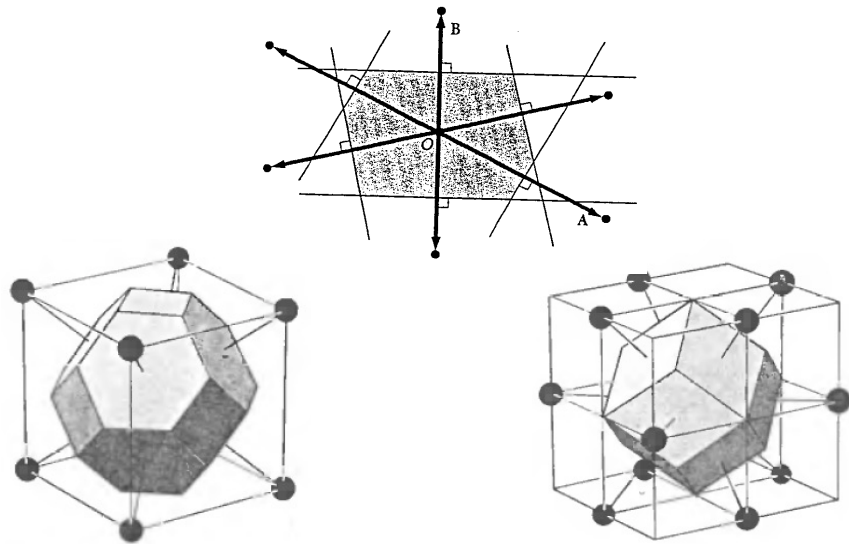
$$\vec{b}_3^* = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$



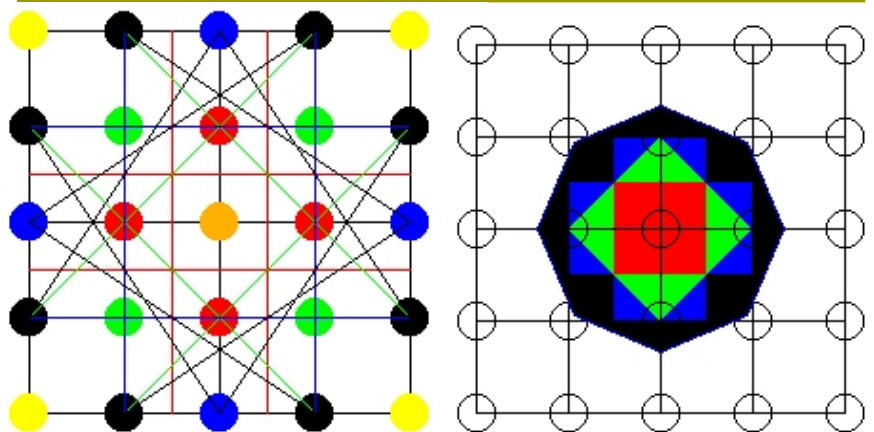
DL RL



Wigner-Seitz Cell



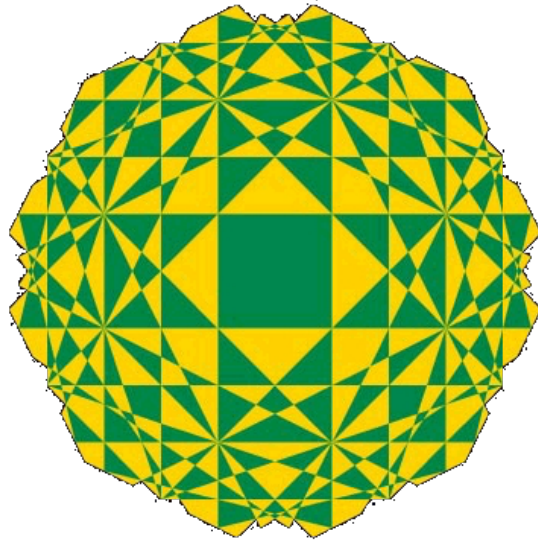
Wigner-Seitz in RL: First Brillouin Zone



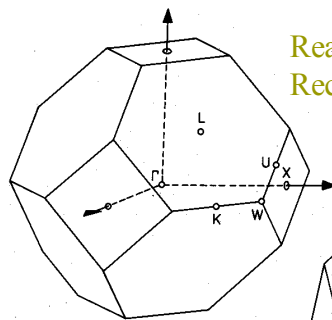
The Nearest through Fifth Nearest Neighbor
for a Point in a Square Lattice
and Their Bragg Lines

First Four Brillouin Zones for a Square Lattice

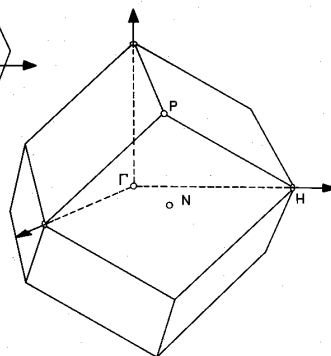
Más zonas de Brillouin de una red cuadrada



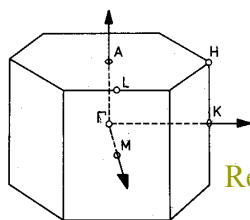
1º Brillouin Zone: FCC, BCC, HCP



Real: FCC
Reciprocal: BCC

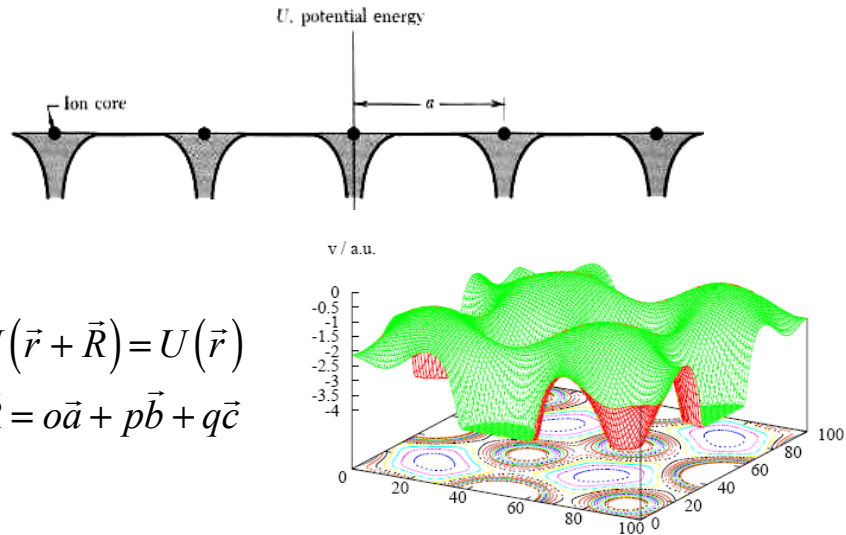


Real: BCC
Reciprocal: FCC



Real: HCP

2- Periodic Potential



$$U(\vec{r} + \vec{R}) = U(\vec{r})$$

$$\vec{R} = o\vec{a} + p\vec{b} + q\vec{c}$$

2- Schrödinger Equation

□ Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{U_{n-e}(\vec{r})}_{\neq 0} + \underbrace{U_{e-e}(\vec{r})}_0$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) \right] \psi(\vec{r}) = \varepsilon \psi(\vec{r})$$

Teorema de Bloch

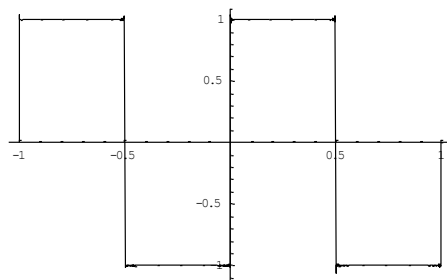
▣ Solución de la ESIT

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r})$$

$$u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r})$$

Series de Fourier

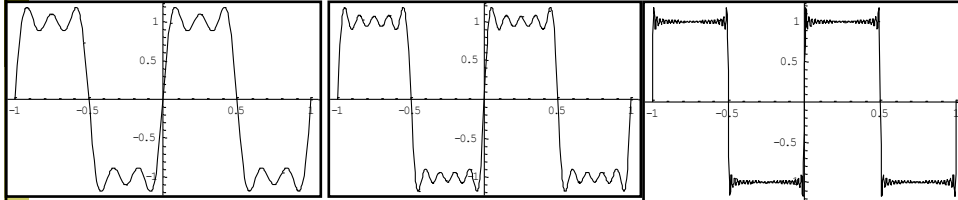
▣ Funciones periódicas



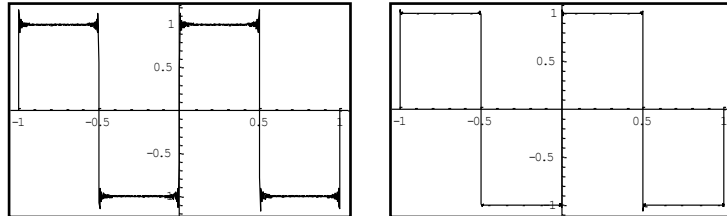
$$f(t) = \sum_n C_n e^{i\omega_n t}$$

$$C_n = \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t) e^{-i\omega_n t} dt$$

Fourier Series



N= 5, 10, 50, 100 and 1000



Fourier Transform

▣ The Coulomb Potential is Periodic

$$U(\vec{r}) = \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

$$U(\vec{G}) = \frac{1}{V} \int_{\text{cell}} U(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d\vec{r}$$

Solving the TISE

□ Plane wave summation:

$$\psi(\vec{r}) = \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}}$$

We use plane waves as basis set, where $c(\vec{k})$'s are determined by solving the TISE for the corresponding Periodic Potential

Solving the TISE

$$\begin{aligned} & \left[-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right] \psi(\vec{r}) = \epsilon \psi(\vec{r}) \\ & \left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \right] \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} = \epsilon \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \\ & \left[\underbrace{-\frac{\hbar^2}{2m} \nabla^2 \left(\sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \right)}_a + \underbrace{\sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}}}_b \right] = \epsilon \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \\ & a : -\frac{\hbar^2}{2m} \nabla^2 \left(\sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \right) = -\frac{\hbar^2}{2m} \left(\sum_{\vec{k}} c(\vec{k}) (-k^2) e^{i\vec{k} \cdot \vec{r}} \right) \\ & b : \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} = \sum_{\vec{G}, \vec{k}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} = \sum_{\vec{G}, \vec{k}} U(\vec{G}) c(\vec{k}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \end{aligned}$$

Solving the TISE

Change in the summation: $\vec{k} = \vec{k}' - \vec{G}$

$$\sum_{\vec{G}, \vec{k}} U(\vec{G}) c(\vec{k}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = \sum_{\vec{G}, \vec{k}' - \vec{G}} U(\vec{G}) c(\vec{k}' - \vec{G}) e^{i(\vec{k}' - \vec{G} + \vec{G}) \cdot \vec{r}} = \sum_{\vec{G}, \vec{k}'} U(\vec{G}) c(\vec{k}' - \vec{G}) e^{i\vec{k}' \cdot \vec{r}}$$

$$\begin{aligned} \sum_{\vec{G}, \vec{k}'} U(\vec{G}) c(\vec{k}' - \vec{G}) e^{i\vec{k}' \cdot \vec{r}} &= \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\sum_{\vec{G}} U(\vec{G}) c(\vec{k} - \vec{G}) \right] \\ \frac{\hbar^2}{2m} \left(\sum_{\vec{k}} c(\vec{k}) k^2 e^{i\vec{k} \cdot \vec{r}} \right) + \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\sum_{\vec{G}} U(\vec{G}) c(\vec{k} - \vec{G}) \right] &= \left(\varepsilon \sum_{\vec{k}} c(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \right) \end{aligned}$$

$$\boxed{\sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left\{ \left(\frac{\hbar^2 k^2}{2m} - \varepsilon \right) c(\vec{k}) + \sum_{\vec{G}} U(\vec{G}) c(\vec{k} - \vec{G}) \right\} = 0}$$

Ecuación Central

$$\left(\frac{\hbar^2 k^2}{2m} - \varepsilon \right) c(\vec{k}) + \sum_{\vec{G}} U(\vec{G}) c(\vec{k} - \vec{G}) = 0$$

- ▣ All the k values belongs to the 1BZ
- ▣ We first get the eigenenergies
- ▣ Then, we get the set of c(k)
- ▣ There will exist as many solutions as the choosed G values

$$\psi(\vec{r}) = \sum_{\vec{G}} c(\vec{k} - \vec{G}) e^{i(\vec{k} - \vec{G}) \cdot \vec{r}}$$

$$\psi(\vec{r}) = \sum_{\vec{G}} c(\vec{k} - \vec{G}) e^{i(\vec{k} - \vec{G}) \cdot \vec{r}} = e^{i\vec{k} \cdot \vec{r}} \underbrace{\sum_{\vec{G}} c(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}}}_{u_{n, \vec{k}}(\vec{r})}$$

Matrix Representations

$$\begin{bmatrix} \left(\frac{\hbar^2(\vec{k}-2\vec{G})^2}{2m} - \varepsilon \right) & U(-\vec{G}) & U(-2\vec{G}) & U(-3\vec{G}) & U(-4\vec{G}) \\ U(\vec{G}) & \left(\frac{\hbar^2(\vec{k}-\vec{G})^2}{2m} - \varepsilon \right) & U(-\vec{G}) & U(-2\vec{G}) & U(-3\vec{G}) \\ U(2\vec{G}) & U(\vec{G}) & \left(\frac{\hbar^2\vec{k}^2}{2m} - \varepsilon \right) & U(-\vec{G}) & U(-2\vec{G}) \\ U(3\vec{G}) & U(2\vec{G}) & U(\vec{G}) & \left(\frac{\hbar^2(\vec{k}+\vec{G})^2}{2m} - \varepsilon \right) & U(-\vec{G}) \\ U(4\vec{G}) & U(3\vec{G}) & U(2\vec{G}) & U(\vec{G}) & \left(\frac{\hbar^2(\vec{k}+2\vec{G})^2}{2m} - \varepsilon \right) \end{bmatrix} \begin{bmatrix} c(\vec{k}-2\vec{G}) \\ c(\vec{k}-\vec{G}) \\ c(\vec{k}) \\ c(\vec{k}+\vec{G}) \\ c(\vec{k}+2\vec{G}) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

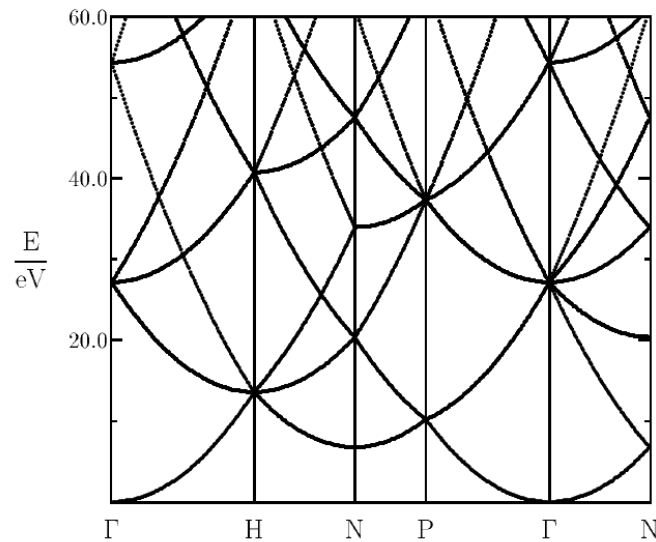
Free Electron Approximation

$$\begin{bmatrix} \frac{\hbar^2(\vec{k}-2\vec{G})^2}{2m} - \varepsilon & 0 & 0 & 0 & 0 \\ 0 & \frac{\hbar^2(\vec{k}-\vec{G})^2}{2m} - \varepsilon & 0 & 0 & 0 \\ 0 & 0 & \frac{\hbar^2\vec{k}^2}{2m} - \varepsilon & 0 & 0 \\ 0 & 0 & 0 & \frac{\hbar^2(\vec{k}+\vec{G})^2}{2m} - \varepsilon & 0 \\ 0 & 0 & 0 & 0 & \frac{\hbar^2(\vec{k}+2\vec{G})^2}{2m} - \varepsilon \end{bmatrix} \begin{bmatrix} C(\vec{k}-2\vec{G}) \\ C(\vec{k}-\vec{G}) \\ C(\vec{k}) \\ C(\vec{k}+\vec{G}) \\ C(\vec{k}+2\vec{G}) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\left[\frac{\hbar^2(\vec{k}-2\vec{G})^2}{2m} - \varepsilon \right] \left[\frac{\hbar^2(\vec{k}-\vec{G})^2}{2m} - \varepsilon \right] \left[\frac{\hbar^2(\vec{k}-2\vec{G})^2}{2m} - \varepsilon \right] \left[\frac{\hbar^2\vec{k}^2}{2m} - \varepsilon \right] \left[\frac{\hbar^2(\vec{k}+\vec{G})^2}{2m} - \varepsilon \right] \left[\frac{\hbar^2(\vec{k}+2\vec{G})^2}{2m} - \varepsilon \right] = 0$$

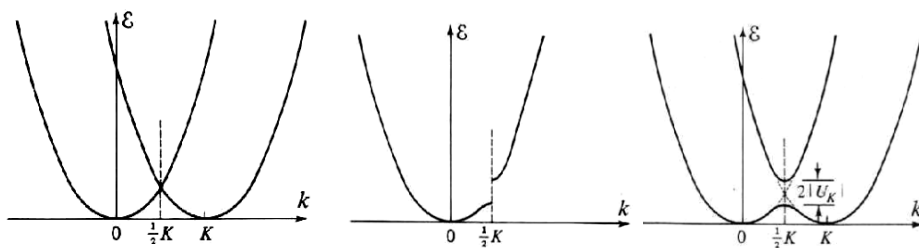
$$\varepsilon = \frac{\hbar^2}{2m} \left[(k_x + n_x G_x)^2 + (k_y + n_y G_y)^2 + (k_z + n_z G_z)^2 \right]$$

Band Diagrama: Free Electrons

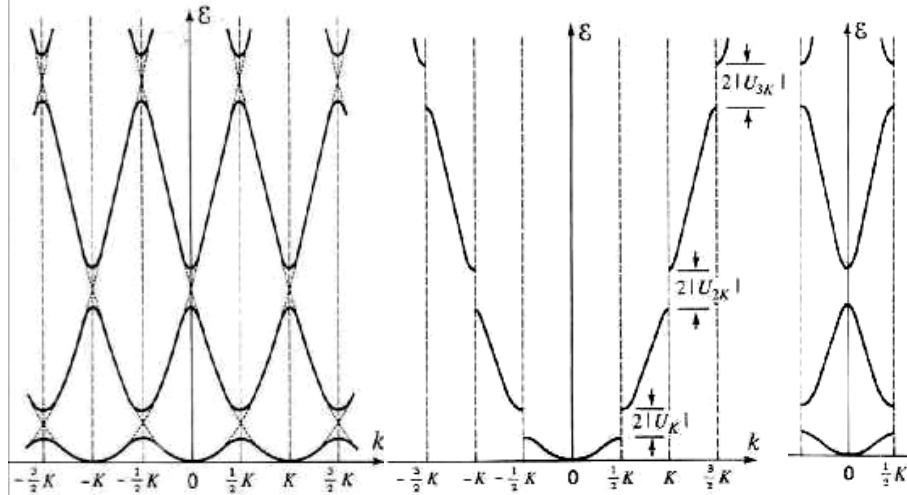


Weak potential approximation

- Just the very first $U(G)$'s values are relevant



Representation:

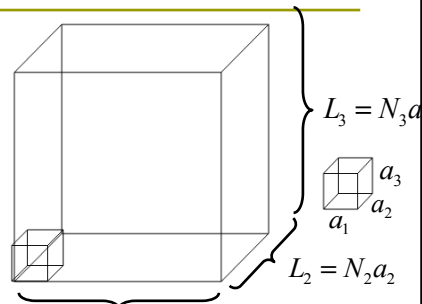


PBC: Boundary Conditions

▣ Von Bon Karman

$$\psi_{n,\vec{k}}(\vec{r} + N_i \vec{a}_i) = \psi_{n,\vec{k}}(\vec{r})$$

$$i = 1, 2, 3$$



$$V_k = k_1 k_2 k_3 = \frac{1}{N_1} \left(\frac{2\pi}{a_1} \right) \frac{1}{N_2} \left(\frac{2\pi}{a_2} \right) \frac{1}{N_3} \left(\frac{2\pi}{a_3} \right) = \frac{(2\pi)^3}{v N_T} = \frac{(2\pi)^3 L_1 = N_1 a_1}{V}$$

V : volúmen de la muestra

v : volúmen de la celda unidad

v^* : volúmen de la celda unidad recíproca

$$\vec{k} = \frac{m_1}{N_1} \vec{a}_1^* + \frac{m_2}{N_2} \vec{a}_2^* + \frac{m_3}{N_3} \vec{a}_3^*$$

Blöch Theorem Consequences (I)

- All the relevant information is concentrated at First Brillouin Zone
- The Wave Function is periodic in reciprocal space:

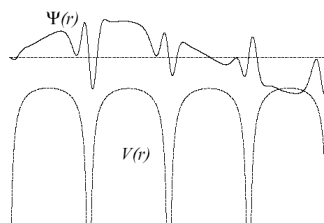
$$\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$$

- Band Diagram is periodic in Reciprocal Space:

$$\epsilon_n(\vec{k} + \vec{G}) = \epsilon_n(\vec{k})$$

Blöch Theorem Consequences (II)

- We have as many k-points as unit cells in the crystal.
- The Wave-function is periodic in reciprocal space, and non-periodic in real space:
- The charge density and the crystalline potential are periodic in real space:
- We will have as many bands as orbitals in the unit cell.
- Each band has as many k-points as unit cells the crystal have.



Computational Methodology

□ Basis Size

- Number of Plane Waves

$$U(\vec{r}) = \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

$$\psi(\vec{r}) = \sum_{\vec{G}} c(\vec{k} - \vec{G}) e^{i(\vec{k} - \vec{G})\cdot\vec{r}}$$

□ K-point Integration

- Number of k-points

$$\bar{f}_i(k) = \int_{V_{BZ}} f(k) dk$$

$$\bar{f}_i = \sum_k w_k f_i(k)$$

Computational Methodology

□ Integrals in k-space

- For many properties, such as the counting of electrons in bands, total energy, etc; it is essential to sum over the k-points.
- Due to the periodicity of the lattice the integral can be evaluated as discrete summation.
- Symmetry points are crucial for efficient integrations.
- The logic behind Monkhorst-Pack is the concept of min value:

$$\square I = \int_0^{2\pi} \sin(k) dk = 0 \quad \text{where } I = f(k) = 0 \text{ for } k = \pi$$

K-point Integration

□ Integrals in k-space:

- $f_2(k) = (A \sin(k) + B \sin(2k))$
- $I = \int_0^{2\pi} f_2(k) dk = 0 = f_2\left(k = \frac{\pi}{2}\right) + f_2\left(k = \frac{3\pi}{2}\right).$
- $\bar{f}_i = \sum_k^{IBZ} w_k f_i(k)$

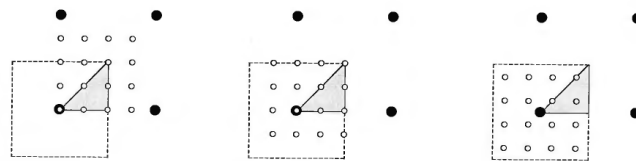


Figure 4.12. Grids for integration for a 2d square lattice, each with four times the density of the reciprocal lattice in each dimension. The left and center figures are equivalent with one point at the origin, and six inequivalent points in the irreducible BZ shown in grey. Right: A shifted special point grid of the same density but with only three inequivalent points. Additional possibilities have been given by Moreno and Soler [277], who also pointed out that different shifts and symmetrization can lead to finer grids.

Linear Grid vs Tetrahedron Method

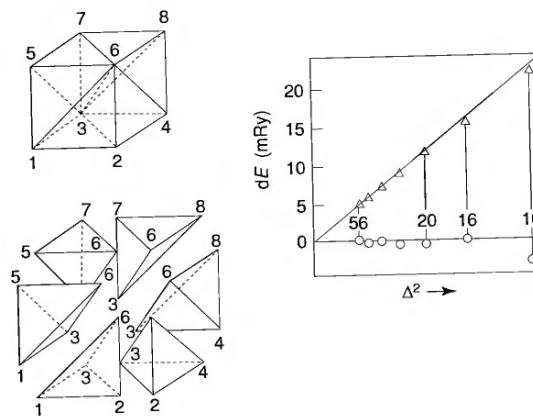


Figure 4.13. Example of generation of tetrahedra that fill the space between the grid points (left) and the results (right) of total energy calculations for Cu as a function of grid spacing Δ , comparing the linear method and the method of [282]. From [282].