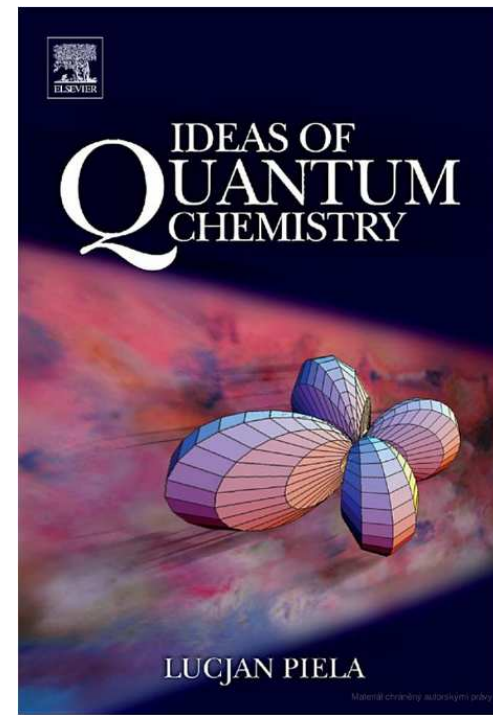
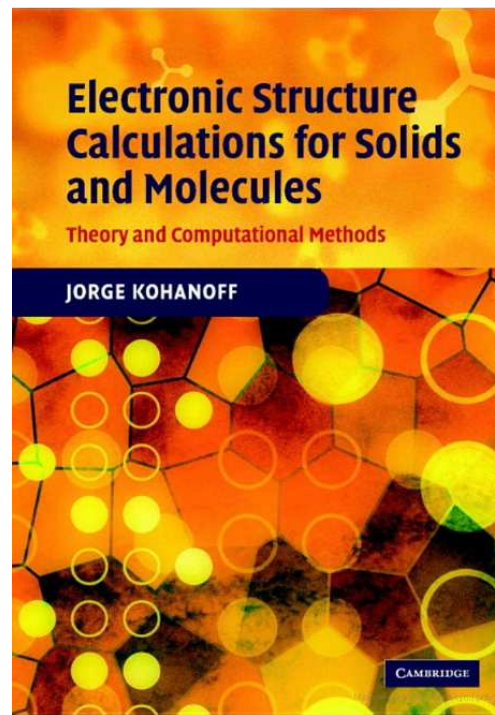
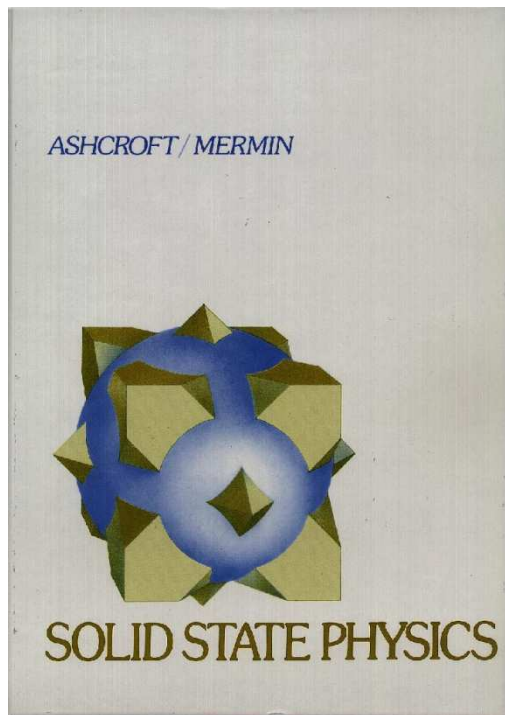


# Solid state physics primer

# *Bibliography*



## Drude - classical free electron model

1897 J.J. Thomson's discovery of electron

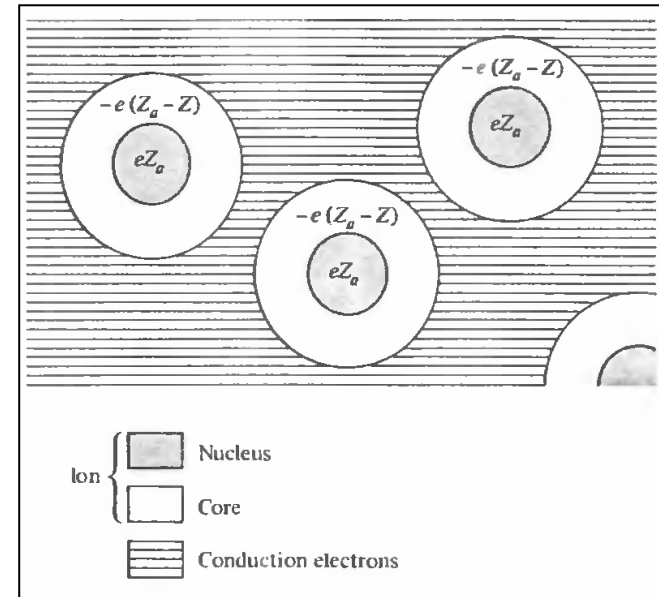
### Motivation

Metallic features of a special interest, e.g. thermal and electrical conductivities, compressibility

1900 P. Drude – CLASSICAL theory of electrical and thermal conductivity (metals)

### Basic Assumptions of the Drude model

- ❖ metal (neutral) composed of **immobile** positively charged particles (ions) and electrons – **detached** from nuclei and wandering **freely** through metal
- ❖ kinetic theory of gases can be applied to electrons (electron gas)
- ❖ neglect of electron-electron interactions  
⇒ independent electron approximation
- ❖ neglect of electron-ion interactions  
⇒ free electron approximation



In a metal the nucleus and core electrons retain their configuration, but the valence electrons leave the atom and form electron gas.

Drude model makes **some** very good predictions:

- ❖ DC and AC conductivity in metals,
- ❖ thermal conductivity (due to electrons) in metals
- ❖ Wiedemann-Franz law.  $\frac{\kappa}{\sigma} = LT$

and is still used as a rough estimate.

## Sommerfeld - semi-classical free electron model

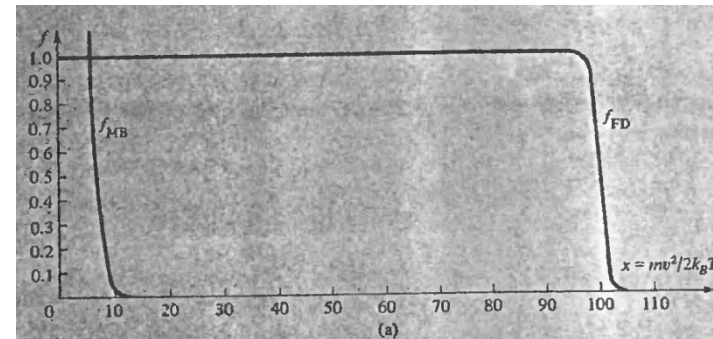
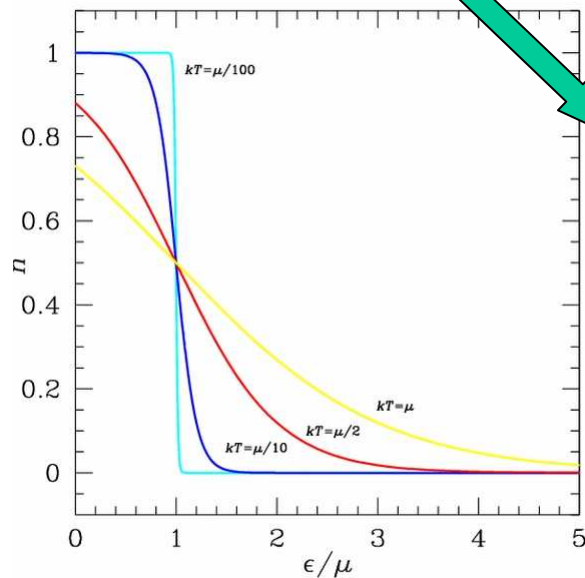
1920's advent of the quantum theory => A. Sommerfeld theory of metals

- ❖ developed by Arnold Sommerfeld
- ❖ the classical Drude model (employing Maxwell-Boltzmann velocity distribution) with quantum mechanical Fermi-Dirac velocity distribution derived from FD statistics

$$f_B(\mathbf{v}) = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$$

$$f(\mathbf{v}) = \frac{(m/h)^3}{4\pi^3} \frac{1}{\exp[(\frac{1}{2}mv^2 - k_B T_0)/k_B T] + 1}$$

$$f(\epsilon) = \frac{1}{1 + e^{(\epsilon - \mu)/kT}}$$



+ resolves the most flagrant thermal anomalies of the Drude model  
 – fails to explain the difference in metals, semiconductors and insulators



Most deficiencies due to a neglect of the electron-ion interaction => a potential due to positive ions needs to be considered

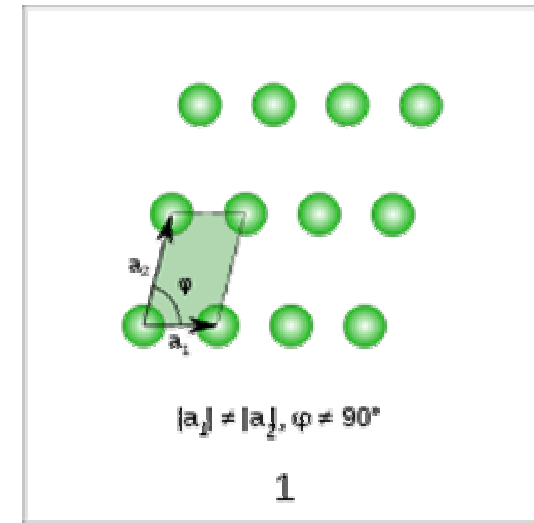
## Bravais lattice

The ions in the solid are distributed in a regular PERIODIC array, or 'lattice' => significant simplification of the description of the electron-ion interactions.

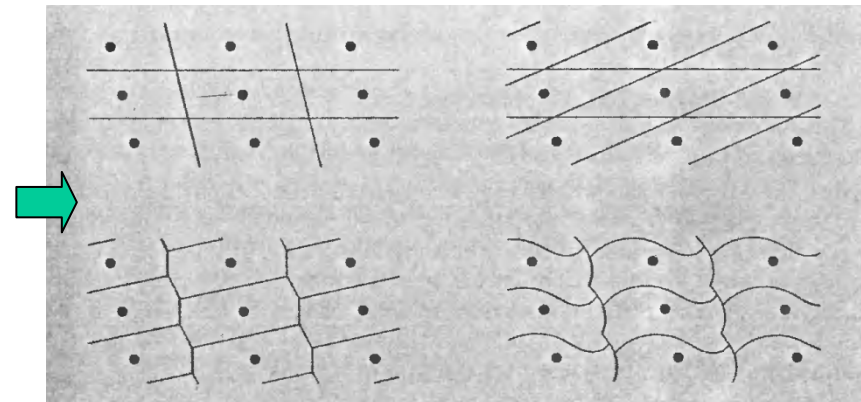
**Bravais lattice** - specifies the periodic array in which the repeated units of the crystal are arranged.

- ❖ A Bravais lattice is an infinite array of discrete points (atoms, molecules, group of atoms...) with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.
- ❖ A (three-dimensional) Bravais lattice consists of all points with position vectors  $\mathbf{R}$  of the form

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



**Primitive unit cell** – a volume of space that, when translated through all the vectors in Bravais lattice, just fills all of space without overlapping itself or leaving voids. It contains precisely one lattice point (no unique way)



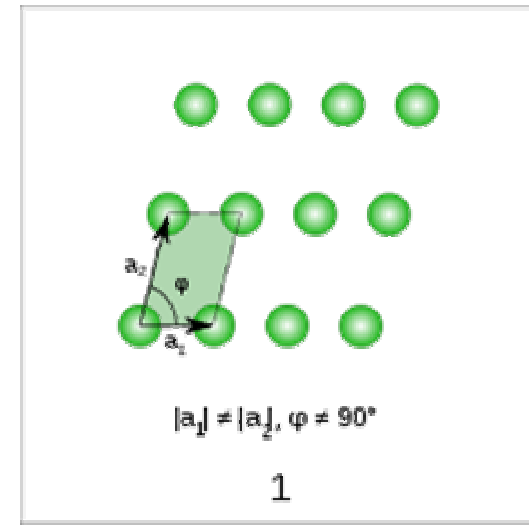
## Bravais lattice

The ions in the solid are distributed in a regular PERIODIC array, or 'lattice' => significant simplification of the description of the electron-ion interactions.

Bravais lattice - specifies the periodic array in which the repeated units of the crystal are arranged.

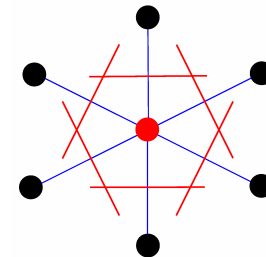
- ❖ A Bravais lattice is an infinite array of discrete points (atoms, molecules, group of atoms...) with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.
- ❖ A (three-dimensional) Bravais lattice consists of all points with position vectors  $\mathbf{R}$  of the form

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



## Wigner-Seitz cell


- ❖ A specific primitive unit cell with full symmetry of Bravais lattice
- ❖ Contains a region of space that is closer to a given lattice point than to any other lattice point



Construction of a Wigner–Seitz primitive cell.

## Reciprocal lattice (RL)

### Motivation for RL introduction

- ❖ The periodic function  $g(x) = g(x+\tau)$  (i.e. with the periodicity of the Bravais lattice like the potential generated by positive ions) can be generally decomposed to a Fourier series – i.e. the sin and cos functions  $\longrightarrow g(x) = \sum_{n=-\infty}^{\infty} G[n] \cdot e^{i2\pi \frac{n}{\tau} x}$ .
- ❖ It follows that the value of the function has to be the same for  $x$  and  $x+\tau$  ( $\tau$  is period of the function), or generally for  $\mathbf{r} = (x_1, x_2, \dots, x_n)$  and  $\mathbf{r} + \mathbf{R}$  ( $\mathbf{R}$  is period)  $\Rightarrow e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})} = e^{i\mathbf{K} \cdot \mathbf{r}}$   

- ❖ the set of all such  $\mathbf{K}$  that fulfill relation above belong to a reciprocal space or 'k-space' – (as opposed to 'direct' space of  $\mathbf{r}$ )  

$e^{i\mathbf{K} \cdot \mathbf{R}} = 1$
- ❖ (the set of  $\mathbf{K}$  is Fourier transform of a periodic direct lattice)

## Reciprocal lattice (RL)

### Motivation for RL introduction

- ❖ The periodic function  $g(x) = g(x+\tau)$  (i.e. with the periodicity of the Bravais lattice like the potential generated by positive ions) can be generally decomposed to a Fourier series – i.e. the sin and cos functions  $\rightarrow g(x) = \sum_{n=-\infty}^{\infty} G[n] \cdot e^{i2\pi \frac{n}{\tau} x}$ .
- ❖ It follows that the value of the function has to be the same for  $x$  and  $x+\tau$  ( $\tau$  is period of the function), or generally for  $\mathbf{r} = (x_1, x_2, \dots, x_n)$  and  $\mathbf{r} + \mathbf{R}$  ( $\mathbf{R}$  is period)  $\Rightarrow e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})} = e^{i\mathbf{K} \cdot \mathbf{r}}$
- ❖ the set of all such  $\mathbf{K}$  that fulfill relation above belong to a reciprocal space or 'k-space' – (as opposed to 'direct' space of  $\mathbf{r}$ )
- ❖ (the set of  $\mathbf{K}$  is Fourier transform of a periodic direct lattice)

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1$$

Bravais lattice (BL) :  $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

Plane wave,  $e^{i\mathbf{k} \cdot \mathbf{r}}$ , with the periodicity of BL



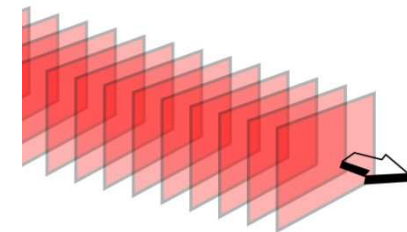
$$e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})} = e^{i\mathbf{K} \cdot \mathbf{r}}$$

Set of wave vectors  $\mathbf{K}$  satisfying

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1$$



**Reciprocal lattice**



Plane wave



## Reciprocal lattice - construction

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

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

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

Note that the larger is the direct lattice  
the smaller is the reciprocal one



$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \longrightarrow$$

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3.$$

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

$k_1, k_2, k_3$  – generally non-integer



$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1 n_1 + k_2 n_2 + k_3 n_3).$$

and at the same time we want

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1$$



$$\mathbf{K} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad k_1, k_2, k_3 \text{ integers}$$

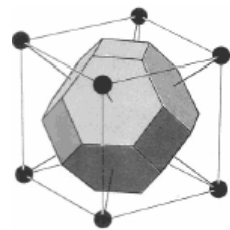
The reciprocal lattice is a Bravais lattice!

$\mathbf{R}$  – direct space

$\mathbf{K}$  – reciprocal space

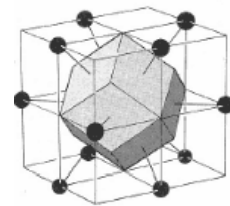
$\mathbf{b}_i$  – primitive vectors of reciprocal lattice

Wigner-Seitz cell in reciprocal space is called **the first Brillouin zone**.



bcc

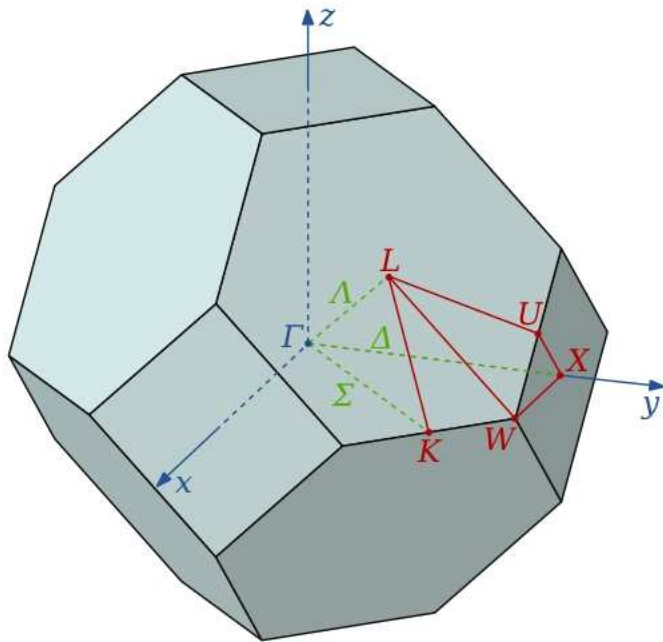
direct  
↔  
reciprocal  
space



fcc

## Brillouin zone

points of high symmetry are of special interest – these are called **critical points**



First Brillouin zone of FCC lattice showing symmetry labels for high symmetry lines and points.

Symbol	Description
$\Gamma$	Center of the Brillouin zone
<b>Simple cube</b>	
M	Center of an edge
R	Corner point
X	Center of a face
<b>Face-centered cubic</b>	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face
<b>Body-centered cubic</b>	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three edges
<b>Hexagonal</b>	
A	Center of a hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face

## Electron Gas

(A 'special' case of a contained QM free electron model)

### Ground-State properties of the electron gas

- ❖  $N$  electrons confined to a volume  $V$
- ❖ Independent electron approximation
- ❖ Pauli exclusion principle
- ❖ Confinement of the electron (by the attraction of the ions)

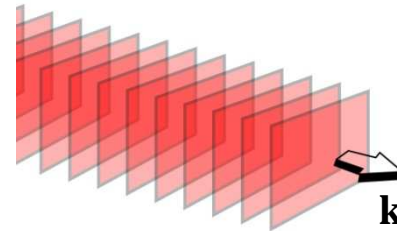
represented by a boundary condition (the simplest choice is a cube,  $L=V^{1/3}$ )

$$\hat{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \epsilon \psi$$

Electron gas ( $U(\mathbf{r})=0$ )

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} \quad \text{with eigenvalue} \quad \mathbf{p} = \hbar \mathbf{k} \Rightarrow \mathbf{v} = \frac{\hbar \mathbf{k}}{m}$$



$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}$$

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

Born-von Karman 3D (periodic) boundary condition (mathematically convenient choice as long as bulk properties are not affected by the choice of the boundary condition - OK for large volume)

$$\psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L) = \psi(x, y, z) \quad e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

For 1D – a closed curve



## Electron Gas

(A 'special' case of a contained QM free electron model)

### Ground-State properties of the electron gas

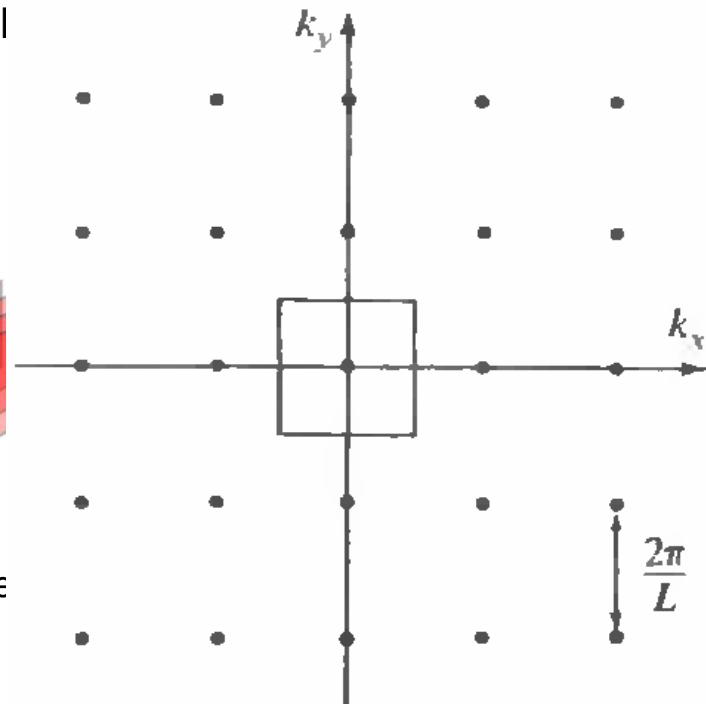
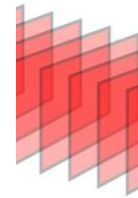
- ❖  $N$  electrons confined to a volume  $V$
- ❖ Independent electron approximation
- ❖ Pauli exclusion principle
- ❖ Confinement of the electron (by the attraction of the ions) represented by a boundary condition (the simple)

$$\hat{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \epsilon \psi$$

Electron gas ( $U(\mathbf{r})=0$ )

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} \quad \text{with eigenvalue} \quad \mathbf{p} = \hbar \mathbf{k} \Rightarrow \mathbf{v} = \frac{\hbar \mathbf{k}}{m}$$



Born-von Karman 3D (periodic) boundary condition  
long as bulk properties are not affected by the choice of the volume)

$$\psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L) = \psi(x, y, z)$$



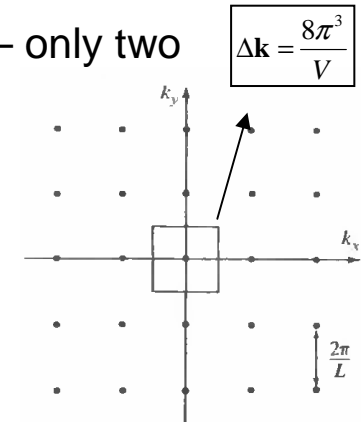
$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}, \quad n_x, n_y, n_z \text{ integers}$$

## Fermi nomenclature

 (A nomenclature for highest occupied levels)

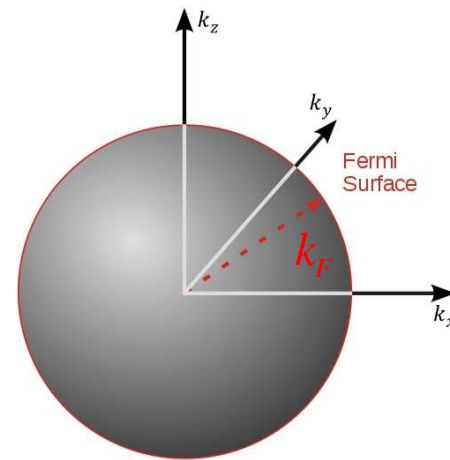
Gradual filling of the electronic levels – due to Pauli exclusion principle – only two available electronic levels associated with one  $\mathbf{k}$  vector.

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}, \quad n_x, n_y, n_z \text{ integers}$$



The free fermions occupying the lowest energy states form a sphere in momentum space.

The surface of this sphere is the **Fermi surface**.



$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

**Fermi wave vector**

**Fermi energy**

$$E = 2 \sum_{k < k_F} \frac{\hbar^2}{2m} k^2$$

**Total ground-state energy of N free electrons**  
(add up one-electron energies inside Fermi sphere)

Generally, the total energy  $U$   $U = 2 \sum_{k < k_F} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})) \longrightarrow f(\varepsilon) = \frac{1}{1 + e^{(\varepsilon - \mu)/kT}}$

$$U = 2 \frac{V}{8\pi^3} \sum_{k < k_F} \Delta \mathbf{k} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k}))$$

$$\Delta \mathbf{k} = \frac{8\pi^3}{V}$$

$$u = \frac{U}{V} \text{ - energy density}$$



$$\Delta \mathbf{k} \rightarrow 0 \text{ and } V \rightarrow \infty$$

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k}))$$

## Density of states

Generally, the total energy  $U$   $U = 2 \sum_{k < k_F} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) \longrightarrow f(\epsilon) = \frac{1}{1 + e^{(\epsilon - \mu)/kT}}$

$$U = 2 \frac{V}{8\pi^3} \sum_{k < k_F} \Delta \mathbf{k} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k}))$$

$\Delta \mathbf{k} = \frac{8\pi^3}{V}$  (pointing to the sum)

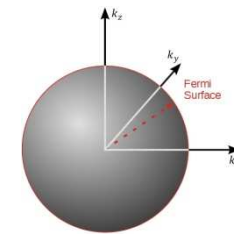
$u = \frac{U}{V}$  - energy density (pointing to the right)

$\Delta \mathbf{k} \rightarrow 0$  and  $V \rightarrow \infty$  (pointing to the integral)

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k}))$$

If we would like to integrate over  $\epsilon$ , which is in case of electron gas proportional to norm of the  $\mathbf{k}$

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$



$$\int \frac{d\mathbf{k}}{4\pi^3} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) = \int \frac{k^2 dk}{\pi^2} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) = \int [d\epsilon \cdot g(\epsilon)] \cdot \epsilon \cdot f(\epsilon)$$

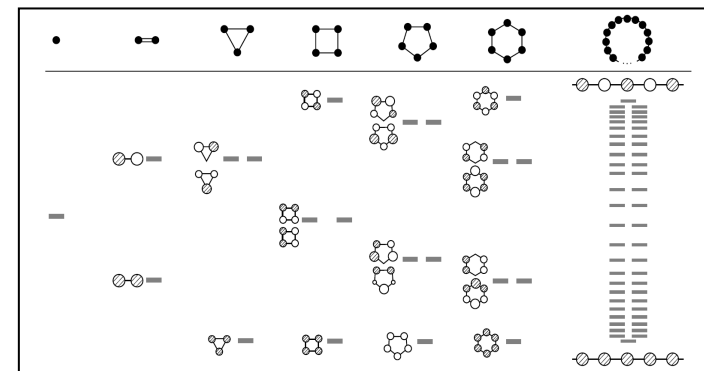
$T=0$

$$\frac{U}{V} = u = \int d\epsilon \cdot g(\epsilon) \cdot \epsilon$$

$$g(\epsilon) \cdot d\epsilon = \frac{1}{V} \times$$

**Density of states**

The number of one-electron levels in the energy range from  $\epsilon$  to  $\epsilon + d\epsilon$



## Density of states

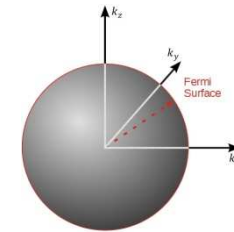
Generally, the total energy  $U$   $U = 2 \sum_{k < k_F} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) \longrightarrow f(\epsilon) = \frac{1}{1 + e^{(\epsilon - \mu)/kT}}$

$$U = 2 \frac{V}{8\pi^3} \sum_{k < k_F} \Delta \mathbf{k} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k}))$$

$\Delta \mathbf{k} = \frac{8\pi^3}{V}$  (pointing to the sum)  
 $u = \frac{U}{V}$  - energy density (pointing to the result)  
 $\Delta \mathbf{k} \rightarrow 0$  and  $V \rightarrow \infty$  (pointing to the integral)

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k}))$$

If we would like to integrate over  $\epsilon$ , which is in case of electron gas proportional to norm of the  $\mathbf{k} \longrightarrow \epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$



$$\int \frac{d\mathbf{k}}{4\pi^3} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) = \int \frac{k^2 dk}{\pi^2} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) = \int d\epsilon \cdot g(\epsilon) \cdot \epsilon \cdot f(\epsilon)$$

$T=0$

$$\frac{U}{V} = u = \int d\epsilon \cdot g(\epsilon) \cdot \epsilon$$

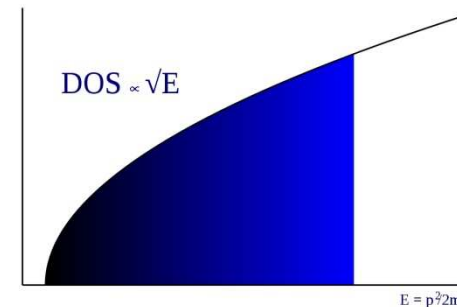
$$g(\epsilon) d\epsilon = \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{L^3}{(2\pi)^2} \sqrt{\epsilon} d\epsilon$$

$$g(\epsilon) \cdot d\epsilon = \frac{1}{V} \times$$

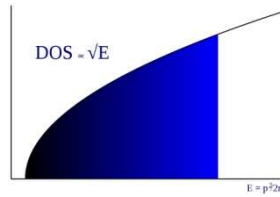


**Density of states**

The number of one-electron levels in the energy range from  $\epsilon$  to  $\epsilon + d\epsilon$



# Density of states



## Motivation

Generally, one needs often to evaluate integrals of some  $F(\epsilon(\mathbf{k}))$

$$\int \frac{d\mathbf{k}}{4\pi^3} F(\epsilon(\mathbf{k}))$$

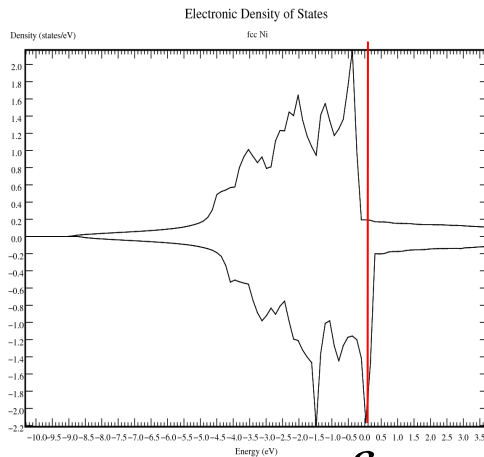
And transform to integration over energy

$$\int d\epsilon \cdot g(\epsilon) \cdot F(\epsilon)$$

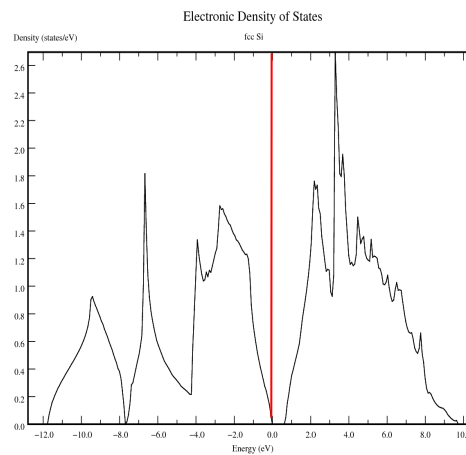
Like e. g. the electronic density

$$n = \int \frac{d\mathbf{k}}{4\pi^3} f(\epsilon(\mathbf{k})) = \int d\epsilon \cdot g(\epsilon) \cdot f(\epsilon)$$

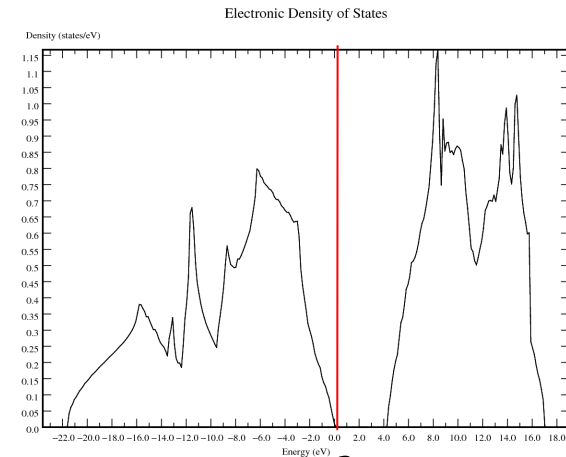
The density of states (DOS), especially on **the Fermi level**, determines the behavior of the material, i.e. whether it is the metal, semiconductor or insulator.



**Metal**



**Semiconductor**



**Insulator**



# Electrons in a Periodic Potential

## General considerations

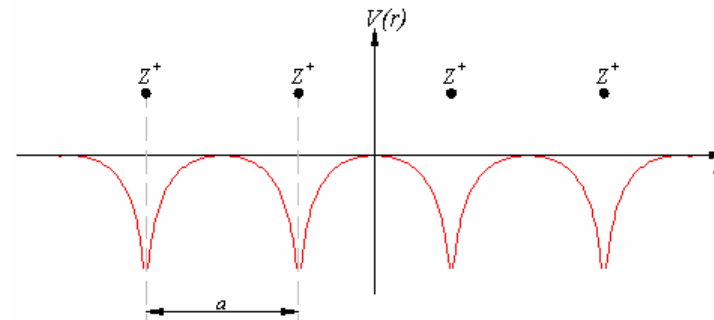
(relaxation of the free electron approximation  
i.e. we consider ion-electron interactions)

Ions in a perfect crystal – arranged in a regular periodic array

⇒ problem of an electron in a potential  $U(\mathbf{r})$  with the periodicity of Bravais lattice

single electron Schrödinger equation

$$\hat{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \varepsilon \psi$$



Electron gas ( $U(\mathbf{r}) = \text{const.}$ )

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}$$

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

periodic  
potential

General solution  
(Bloch's theorem)

$$\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

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

periodicity of BL

or alternatively

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$

Consequence of translational symmetry in periodic systems (Bloch's theorem)

Translational operator  $\hat{T}_R$

$$\hat{T}_R f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$$

$$[\hat{H}, \hat{T}_R] = 0$$

## Electrons in a Periodic Potential

### General considerations

(relaxation of the free electron approximation  
i.e. we consider ion-electron interactions)

General solution

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

periodicity of BL

or alternatively

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r})$$

Consequence of translational symmetry in periodic systems (Bloch's theorem)

Translational operator

$$\hat{T}_R$$

$$\hat{T}_R f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$$

$$[\hat{H}, \hat{T}_R] = 0$$



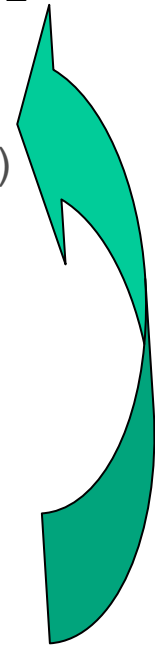
Hamiltonian and translational operator have common set of eigenvectors/  
eigenstates/ wave functions

$$\hat{H}\psi = \varepsilon_n \psi$$

$$\hat{T}_R \psi = e^{i\mathbf{k}\cdot\mathbf{R}} \psi$$



$$\hat{T}_R \psi = \psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r})$$



## Band Structure

(Interesting properties of the eigenstates and eigenvalues)

❖ substituting  $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$  into SChE  $\longrightarrow \hat{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \varepsilon \psi$

$$\left( \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$

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

boundary condition



$$\varepsilon_n(\mathbf{k})$$

energy band

eigenvalue problem  
for each (fixed)  $\mathbf{k}$

$\mathbf{k}$  acts as a parameter  
in Hamiltonian (like  $\mathbf{R}$  in  
BOA)

Generally, discretely  
spaced eigenvalues  
should be found indexed  
by  $n$  - band index.

$\varepsilon_n(\mathbf{k})$  – continuous function of  $\mathbf{k}$

❖ wave vector ( $\mathbf{k}$ ) can always be confined to the first Brillouin zone

$$\mathbf{k}' = \mathbf{k} + \mathbf{K} \quad \mathbf{k} \text{ in the first Brillouin zone}$$

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \quad (\text{by definition of reciprocal lattice})$$

$$e^{i\mathbf{k}'\cdot\mathbf{R}} = e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}} = e^{i\mathbf{k}\cdot\mathbf{R}} \quad \Rightarrow \quad \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$



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

$$\psi_{n\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}'}(\mathbf{r})$$

## Band Structure

(Interesting properties of the eigenstates and eigenvalues)

❖ wave vector ( $\mathbf{k}$ ) can always be confined to the first Brillouin zone

$$\mathbf{k}' = \mathbf{k} + \mathbf{K} \quad \mathbf{k} \text{ in the first Brillouin zone} \quad \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \quad (\text{by definition of reciprocal lattice})$$

$$e^{i\mathbf{k}' \cdot \mathbf{R}} = e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}} = e^{i\mathbf{k} \cdot \mathbf{R}} \Rightarrow \boxed{\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}} u_{n\mathbf{k}}(\mathbf{r}) \quad \psi_{n\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}} u_{n\mathbf{k}'}(\mathbf{r})$$

substitution into the Schrödinger equation leads to the same eigenvalue problem (same Hamiltonian)

$$\left( \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$

$$u_{n\mathbf{k}'}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$\varepsilon_{n,\mathbf{k}'} = \varepsilon_{n,\mathbf{k}}$$



$$\boxed{\psi_{n,\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r})}$$

For given  $n$ , the eigenstates and eigenvalues are periodic functions of  $\mathbf{k}$  in the reciprocal lattice !!!

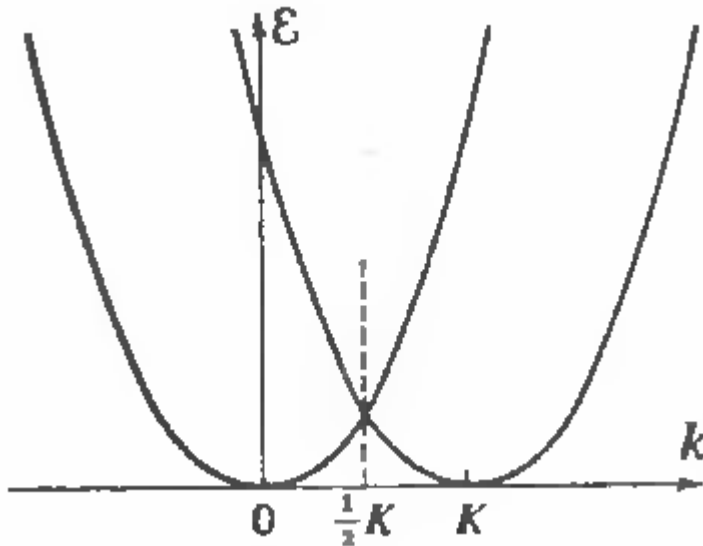
## Band Structure (Summary)

$\varepsilon_n(\mathbf{k})$

- ❖ continuous functions of  $\mathbf{k}$
- ❖ periodic functions of  $\mathbf{k}$  in the reciprocal lattice



- ❖ It has lower and upper bound and all the values lie in the **band** of energies lying between limits



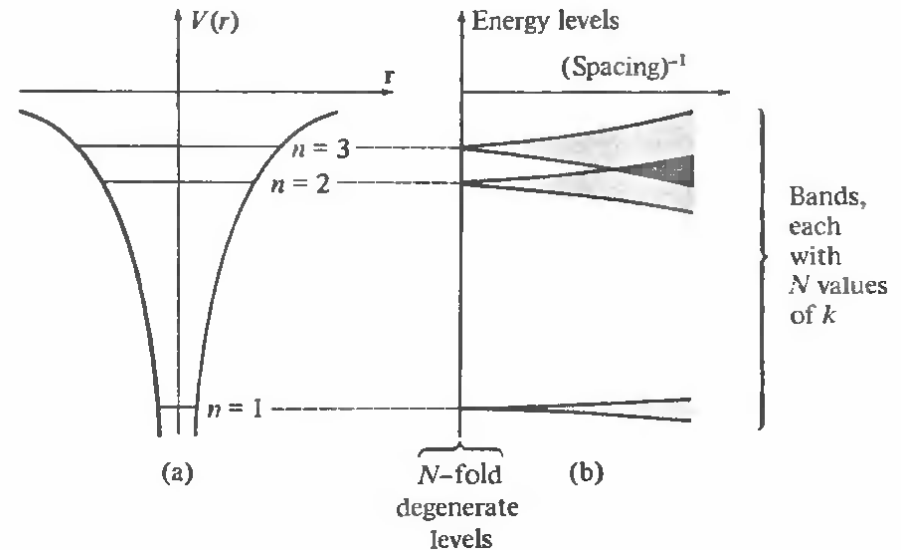
**Free electron energy band in 1D**

we solve the eigenvalue problem for each single primitive cell of the crystal for different values of  $\mathbf{k}$

$$\left( \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$

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

$$\varepsilon_n(\mathbf{k})$$



(a) Electronic levels in atomic potential (b) The energy levels for  $N$  such atoms in a periodic array as a function of mean inverse interatomic spacing. When the atoms are far apart, the levels are nearly degenerate, while when atoms are closer, the levels broaden into **bands**.

## Electrons in a Weak Periodic Potential ('Getting specific')

$$\hat{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \varepsilon \psi$$

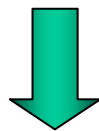
*Schrödinger equation  
for a single electron*



**Bloch theorem**

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

$$\left( \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$



**Plane wave expansion**

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}$$

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}$$

$$\left( \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \varepsilon_{n\mathbf{k}} \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0$$

*restatement of the original  
Schrödinger equation in  
momentum space*

# Electrons in a Weak Periodic Potential ('Getting specific')

$$\left( \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \varepsilon \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K}) \cdot \mathbf{r}}$$

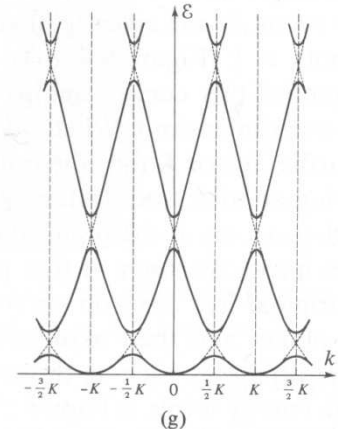
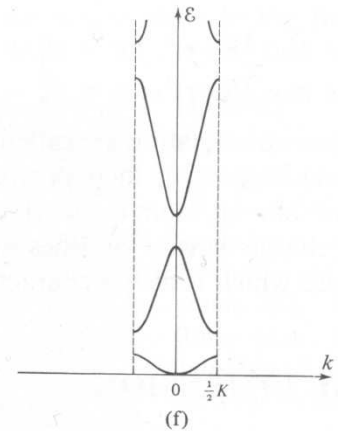
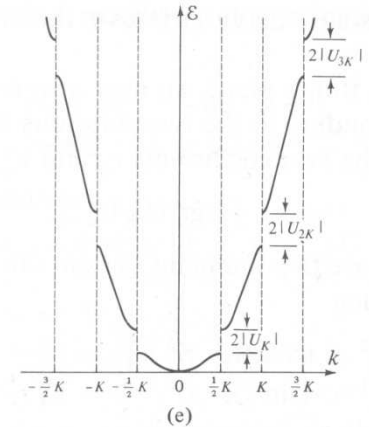
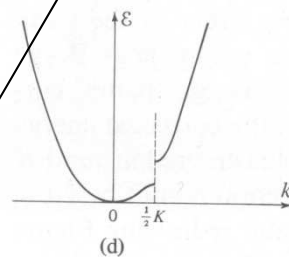
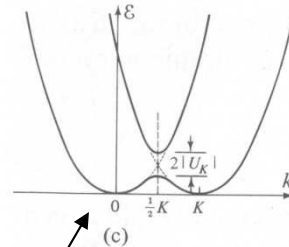
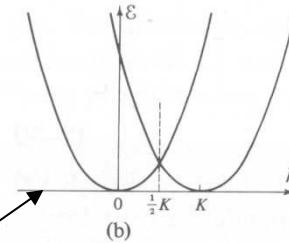
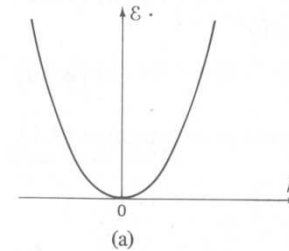
$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}$$

free electron solution  $\varepsilon_{\mathbf{k}-\mathbf{K}}^0 = \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2$   
 $(U_{\mathbf{K}} = 0)$

solution in case of weak periodic potential  $U_{\mathbf{K}}$

$$\begin{vmatrix} \varepsilon - \varepsilon_{\mathbf{k}}^0 & -U_{\mathbf{K}} \\ -U_{\mathbf{K}}^* & \varepsilon - \varepsilon_{\mathbf{k}-\mathbf{K}}^0 \end{vmatrix} = 0 \Rightarrow \boxed{\varepsilon = \varepsilon_{\mathbf{q}}^0 \pm |U_{\mathbf{K}}|}$$

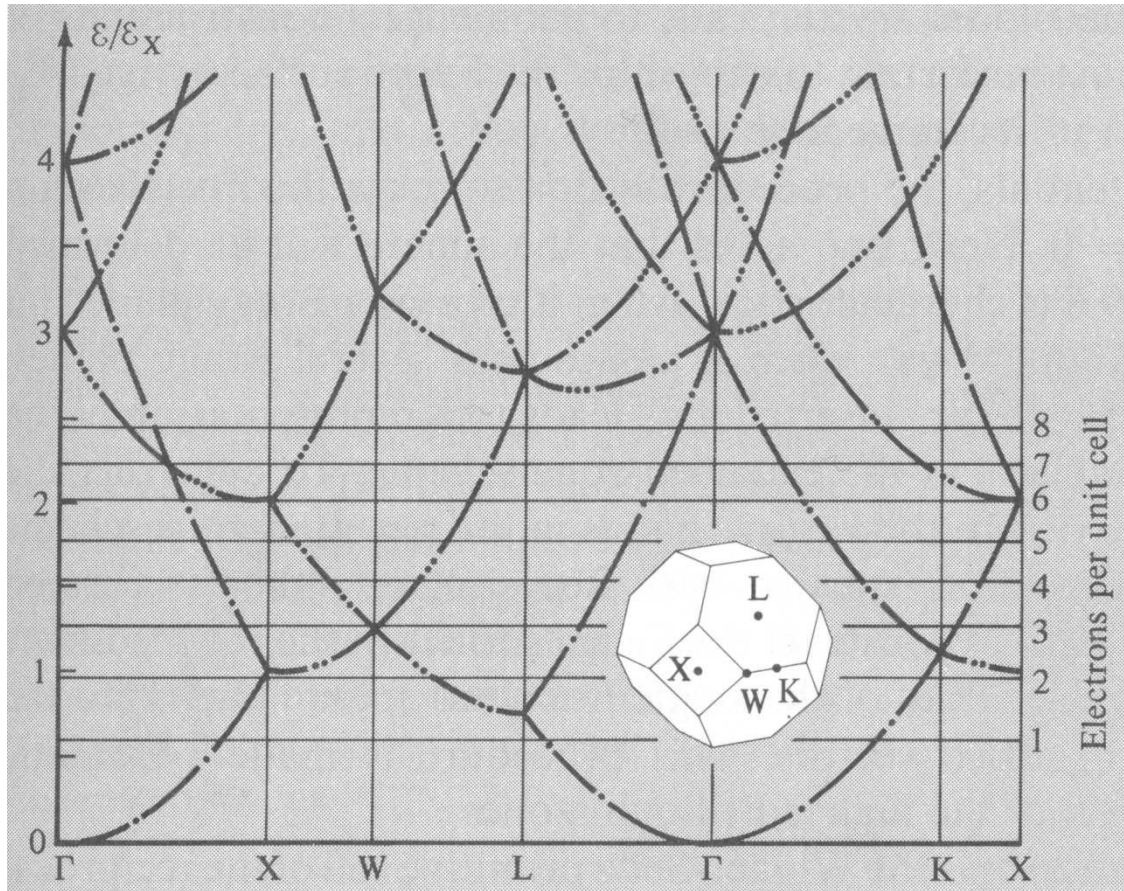
Near the  $1/2\mathbf{K}$ , one level is raised and one lowered by  $\text{abs}(U_{\mathbf{K}})$





## Energy Bands in 3 Dimensions - example

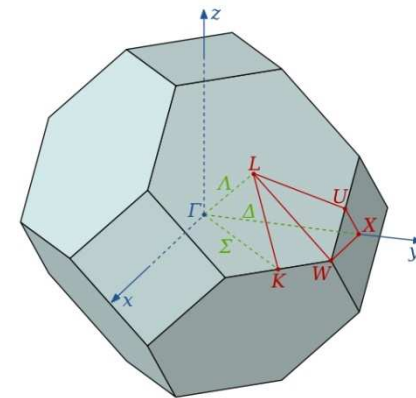
### Free electron energy levels for an fcc Bravais lattice.



$\epsilon_X$  is the energy at point X

$$\epsilon = \frac{\hbar^2}{2m} \left( \frac{2\pi}{a} \right)^2$$

The horizontal lines give Fermi energies for the indicated number of electrons per unit cell.





Calculation issues

## Brillouin Zone Sampling

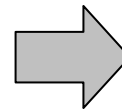
Reminder:  $u = \frac{U}{V}$  - energy density  $\int \frac{d\mathbf{k}}{4\pi^3} F(\varepsilon(\mathbf{k}))$

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k}))$$

### From the Band Structure to the Total Energy

The total energy calculations require numerical integration over the first Brillouin zone (generally 3-dimensional)

In ab initio calculations the computational effort for each k-point is substantial



Special grid points for Brillouin-zone integrations

$\omega(\mathbf{k})$  are the weight factors that depend on the symmetry of unit cell.

$$\int_{BZ} F(\mathbf{k}) d\mathbf{k} = \sum_{\mathbf{k} \in BZ} \omega(\mathbf{k}) F(\mathbf{k})$$



- mean-value point (Baldereschi)
- recursive Chadi-Cohen grid
- Monkhorst-Pack grid



$$\mathbf{k}_{rst} = u_r \mathbf{b}_1 + u_s \mathbf{b}_2 + u_t \mathbf{b}_3$$

$$u_\alpha = \frac{2\alpha - q - 1}{2q}, \quad \alpha = 1, 2, \dots, q$$

number of k-points is reduced by symmetry

Example: simple-cubic lattice

$$q = 1 \quad \mathbf{k} = \left(\frac{2\pi}{a}\right)(0,0,0) \quad q = 2 \quad \mathbf{k} = \left(\frac{2\pi}{a}\right)\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$$

## Monkhorst-Pack grid

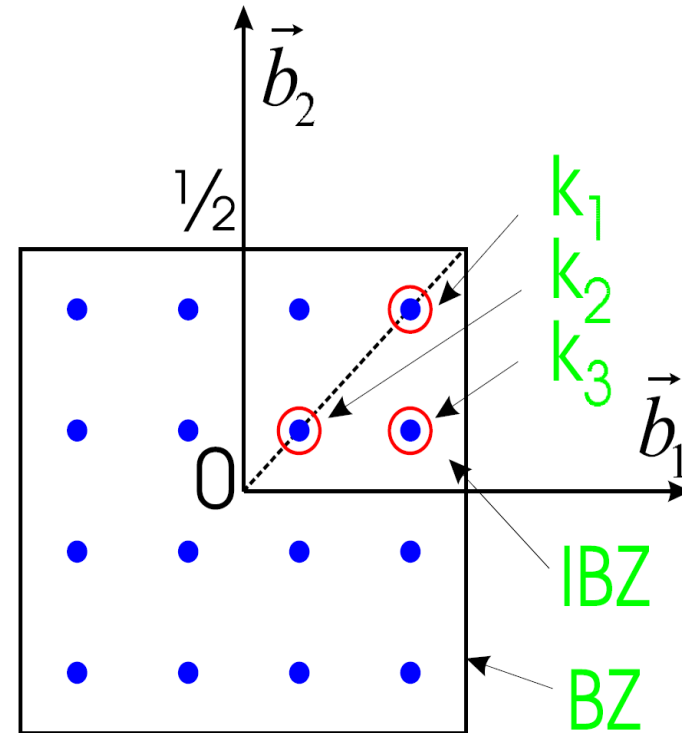
$$\int_{BZ} F(\mathbf{k}) d\mathbf{k} = \sum_{\mathbf{k} \in BZ} \omega(\mathbf{k}) F(\mathbf{k})$$

$\omega(\mathbf{k})$  are the weight factors that depend on the symmetry of unit cell.

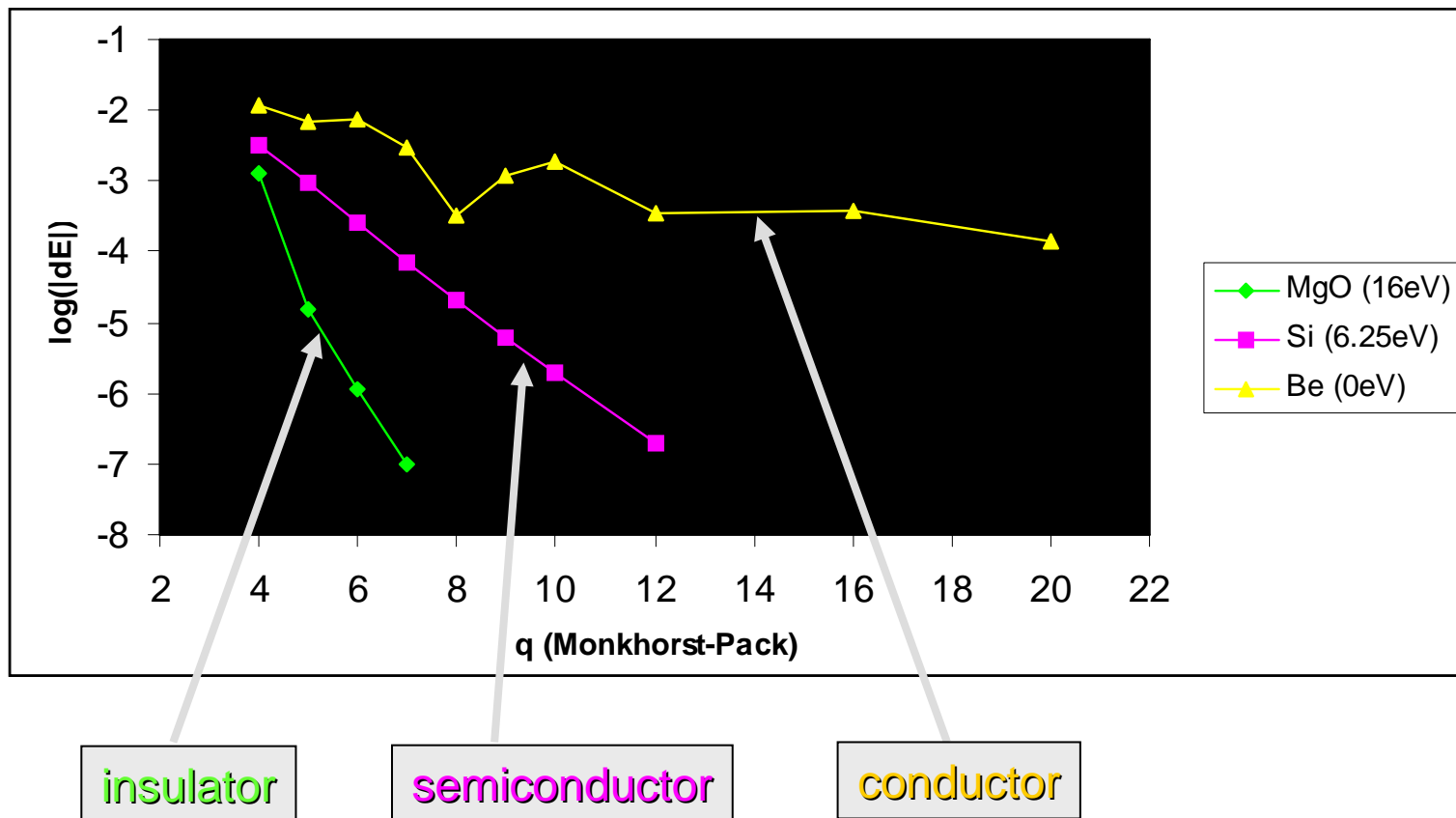
### Example:

- quadratic 2-dimensional lattice
- $q_1 = q_2 = 4 \Rightarrow 16$  k-points
- only 3 inequivalent k-points ( $\Rightarrow$  IBZ)
  - $4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
  - $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
  - $8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$

$$\frac{1}{\Omega_{BZ}} \int_{BZ} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)$$



**Convergence of the total energy (hartree) at the HF level for magnesium oxide, silicon, and beryllium as a function of grid size**



## Fermi Surface Sampling

$N_k$  – occupation number, i.e. the step function, which jump from 0 to 1

$\{\varepsilon_i(\mathbf{k}); i = 1, \dots, N_k\} \quad \varepsilon_i(\mathbf{k}) < \varepsilon_F \quad \text{for infinitely fine BZ sampling}$

$\sum_{BZ} \omega(\mathbf{k}) N_k = N \quad \varepsilon_F \text{ is self-consistently adjusted to fulfill the normalization condition.}$

$\sum_{\mathbf{k} \in BZ} \omega(\mathbf{k}) \varepsilon(\mathbf{k}) f(\mathbf{k}) \longrightarrow$  Fermi-Dirac distribution function at  $T=0$ , i.e. the step function, which jump from 0 to 1 at Fermi level

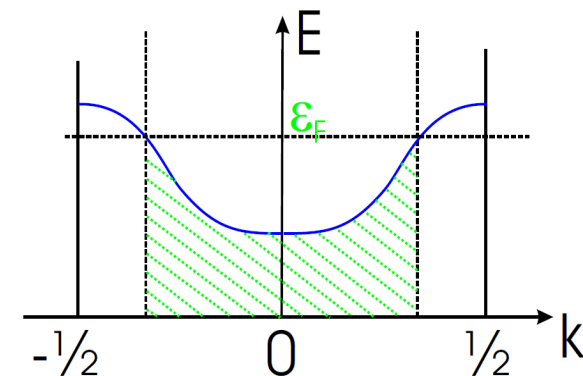
Difficult for metallic systems: slightly different k-point sampling can lead to bands entering or exiting the sum  $\Rightarrow$  intractable number of k-points

- ❖ finding the portion of the BZ that is occupied  
assigning a volume in reciprocal space to each k-point (tetrahedron method)
- ❖ convergence in SCF procedure (instabilities introduced by a coarse sampling)

solution : to smear the Fermi surface by introducing a distribution of occupation numbers (**finite temperature** methods: Fermi-Dirac, Gaussian smearing)

The total energy is no longer variational with respect to partial occupancies

$\Rightarrow$  **generalized free energy**



## Finite Temperature Methods

Introducing a new variational functional

$$F = E - \sum_n \sigma S(f_n)$$

$F$  free energy

$S$  entropy of a system of non-interacting electrons at a finite temperature

$\sigma$  smearing parameter

$f$  partial occupations

### Fermi-Dirac smearing

$$f_n = \frac{1}{1 + e^{(\varepsilon_n - \mu)/\sigma}}$$

$$\sigma = k_B T$$

### Gaussian smearing

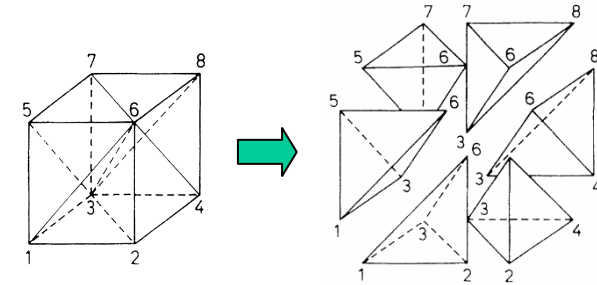
$$f_n = \frac{1 - \operatorname{erf}\left(\frac{\varepsilon_n - \mu}{\sigma}\right)}{2}$$

$\sigma$  has no physical meaning ( $\sigma \rightarrow 0$ )

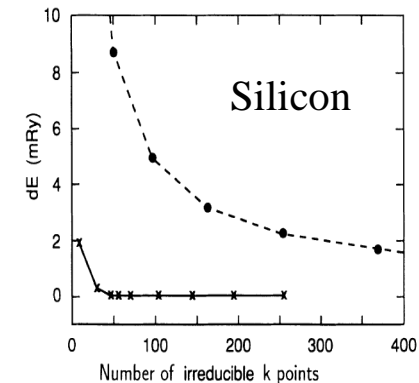
Accurate extrapolation for  $\sigma \rightarrow 0$   
can be obtained

$$E(0) \approx \frac{F(\sigma) + E(\sigma)}{2}$$

## Linear tetrahedron method + Blöchl correction



- ❖ Energy/DOS calculations
- ❖ The linear tetrahedron is more or less fool proof
- ❖ The Blöchl's method is not variational with respect to the partial occupancies  $\Rightarrow$  calculated forces might be wrong by a few percent.
- ❖ If accurate forces are required – use a finite temperature methods.



## Finite temperature methods

- ❖ Calculation of forces
- ❖ Semiconductors (Gaussian smearing)
- ❖ Metals (Methfessel and Paxton)
- ❖ Always: check k-point convergence

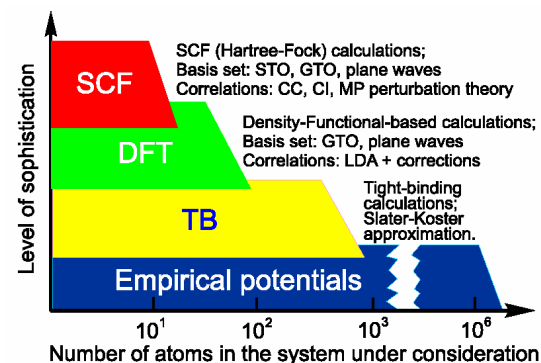
# Methods



# Quantum-Mechanical Calculations of Periodic Systems

## QM methods for extended systems

*simulation of extended systems relies on an ensemble of computational strategies and methods*



### ❖ The model

finite cluster, QM/MM embedding, periodic supercell approach

### ❖ The Hamiltonian

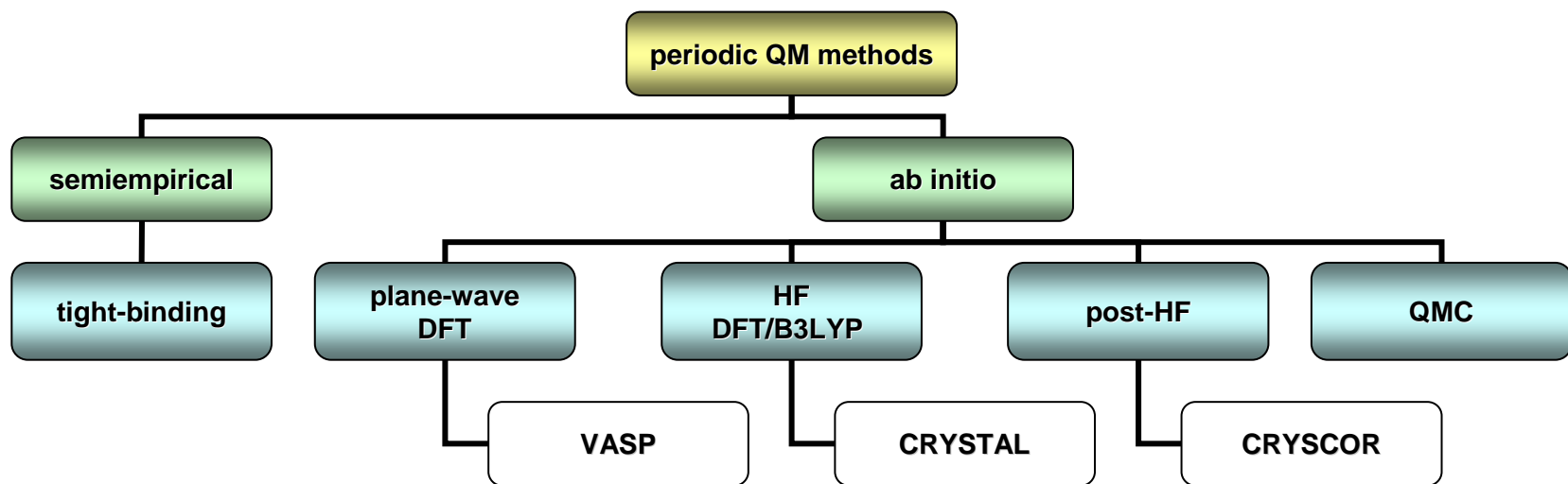
most of the periodic calculations are performed with reference to DFT with LDA, GGA, and hybrid functionals.

### ❖ The basis set

plane waves vs. local AO functions, numeric basis sets (PAO)

### ❖ The computational scheme

direct vs. reciprocal space representation,  
all-electron vs. pseudopotential methods



VASP is a complex package for performing ab initio quantum-mechanical molecular dynamics (MD) simulations using pseudopotentials or the projector-augmented wave method and a plane wave basis set.



The CRYSTAL program computes the electronic structure of periodic systems within Hartree Fock, density functional or various hybrid approximations. The Bloch functions of the periodic systems are expanded as linear combinations of atom centred Gaussian functions.

$$\text{CRYSCOR} = \text{Molpro} + \text{CRYSTAL}$$

Periodic On Local Correlation theory (Molpro) currently implemented: LMP2 method

## Tight-binding method

... lies between the very accurate, very expensive, *ab initio* methods, and the fast but limited empirical methods.

Goringe (1997)

The full periodic crystal Hamiltonian can be approximated by the Hamiltonian,  $H_{at}$ , of a single atom located at the lattice point.

The atomic levels are well localized, i.e. the electrons are also well localized.

True periodic wave function (satisfying Bloch theorem) is of the form of linear combination of functions close to localized atomic wave functions.

$$H = H_{at} + \Delta U(\mathbf{r})$$

$$\psi = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi(\mathbf{r} - \mathbf{R}) \quad , \text{ where } \phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r})$$

True periodic wave function

atomic wave functions

(Bloch) one-electron energies

$$\varepsilon_m(\mathbf{k}) = E_m - \frac{\beta_m + \sum_{\mathbf{R}_n \neq 0} \sum_l \gamma_{m,l}(\mathbf{R}_n) e^{i\mathbf{k} \cdot \mathbf{R}_n}}{1 + \sum_{\mathbf{R}_n \neq 0} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_n} \alpha_{m,l}(\mathbf{R}_n)} \quad ,$$

often neglected

where  $E_m$  is the energy of the  $m$ -th atomic level, and  $\alpha_{m,l}$ ,  $\beta_m$  and  $\gamma_{m,l}$  are the tight binding matrix elements.

$$\beta_m = - \int \varphi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \varphi_m(\mathbf{r}) d^3r$$

$$\alpha_{m,l}(\mathbf{R}_n) = \int \varphi_m^*(\mathbf{r}) \varphi_l(\mathbf{r} - \mathbf{R}_n) d^3r$$

**overlap integrals** – should be small (for TB to work)

inter atomic matrix element/ **bond integral** – important and usually **not calculated directly** but **parametrized** from chemical bond energy data

$$\gamma_{m,l}(\mathbf{R}_n) = - \int \varphi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \varphi_l(\mathbf{r} - \mathbf{R}_n) d^3r \quad ,$$

## Summary of TB approximations

### Total energy calculations

$$E = \sum_{i \text{ occ}} \epsilon_i + \frac{1}{2} \sum_{i \neq j} U \left( \left| \mathbf{R}_i - \mathbf{R}_j \right| \right)$$

band structure energy (sum of one-electron eigenvalues)+repulsive two-body term (usually fitted to reproduce bulk properties)

- ❖ The total energy is expressed as the sum of single-electron eigenvalues plus the sum of pair terms
- ❖ The matrix elements of the tight-binding Hamiltonian depend only upon the vector between two atomic centers
- ❖ A minimal set of orthogonal, localized basis functions is assumed to exist. The basis set is not, in general, explicitly constructed.
- ❖ Self consistency is neglected or approximated by onsite terms (local charge neutrality, Hubbard U)

## Full periodic plane-wave methods

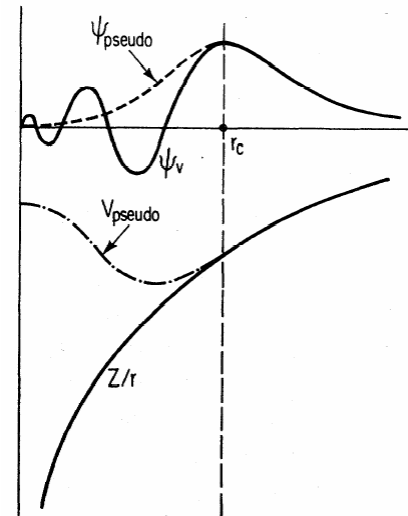
KS-DFT + plane-wave basis

All-electron methods  
spheres around atoms  
+ interstitial region  
APW, LAPW, FP-LMTO

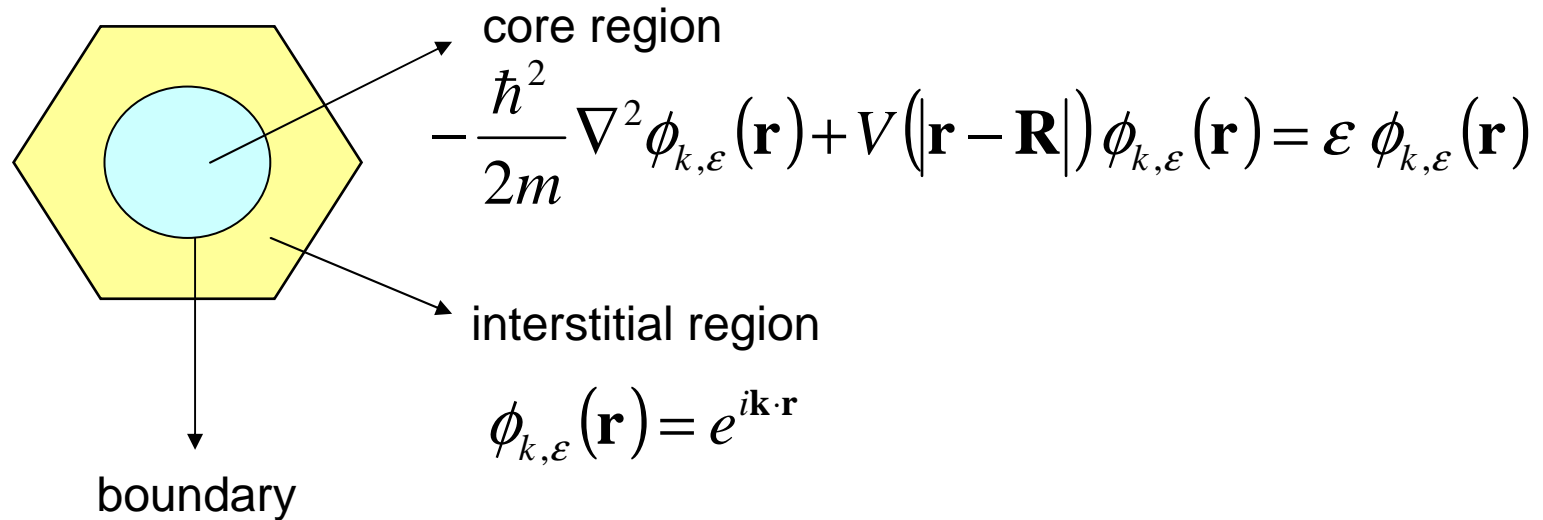
Pseudopotential methods  
Norm-conserving PP  
Ultrasoft PP  
PAW

### Muffin Tin

Used to make muffins, a muffin tin (also known as a "muffin pan") has a number of cup-shaped depressions to hold individual portions of batter.



## Augmented plane-wave methods (APW)



$\phi_{k,\epsilon}(\mathbf{r})$  is continuous at the boundary  
between core and interstitial regions  $\Rightarrow \phi_{k,\epsilon}^{APW}(\mathbf{r})$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}}^{APW}(\mathbf{r})$$

$$\mathbf{HC} = \mathbf{ESC}$$

**LAPW (linearized APW)**  
the energy dependence  
of the APW Hamiltonian  
is approximated

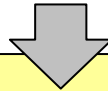
$$\phi(\mathbf{r}, \epsilon) = \phi(\mathbf{r}, \epsilon_p) + (\epsilon - \epsilon_p) \dot{\phi}(\mathbf{r}, \epsilon_p)$$

$$\dot{\phi}(\mathbf{r}, \epsilon) = \frac{\partial}{\partial \epsilon} \phi(\mathbf{r}, \epsilon)$$

## Pseudopotential plane-wave methods (Frozen core approximation)

plane wave expansion  
of the cell periodic part

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{n,\mathbf{k}+\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$



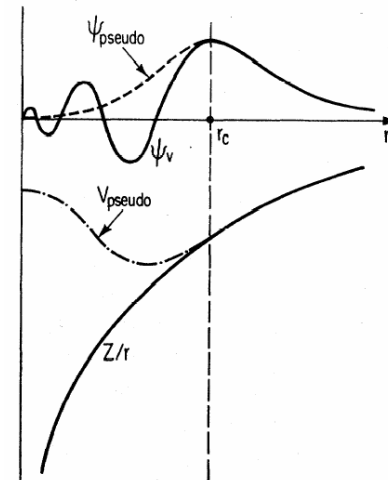
$$\sum_{\mathbf{K}'} \left[ \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{K}|^2 \delta_{\mathbf{K}\mathbf{K}'} + V_{\mathbf{K}-\mathbf{K}'}^{ion} + V_{\mathbf{K}-\mathbf{K}'}^H + V_{\mathbf{K}-\mathbf{K}'}^{xc} \right] c_{n,\mathbf{k}+\mathbf{K}'} = \epsilon_n c_{n,\mathbf{k}+\mathbf{K}}$$

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{K}|^2}{2m} < \epsilon_{cutoff}$$

Pseudopotential approximation

$$\left[ H + \sum_{\alpha,c} (\epsilon_v - \epsilon_{\alpha,c}) |\varphi_{\alpha,c}\rangle \langle \varphi_{\alpha,c}| \right] \varphi_v^{PS} = \epsilon_v^{PS} \varphi_v^{PS}.$$

$$V^R = \sum_{\alpha,c} (\epsilon_v - \epsilon_{\alpha,c}) \underbrace{|\varphi_{\alpha,c}\rangle \langle \varphi_{\alpha,c}|}_{\text{atomic core functions}}, \quad \text{projection}$$

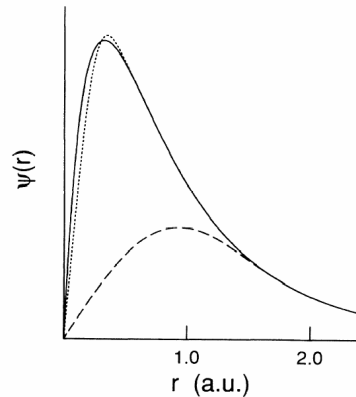


ab initio norm-conserving PP – good transferability but PP are hard – too many PW needed in wave function expansion

D.R. Hamann *et al.*, *Phys.Rev.Lett.* **43**, 1494 (1979)

$$\int_0^{r_c} dr \, r^2 \varphi^{PS*}(r) \varphi^{PS}(r) = \int_0^{r_c} dr \, r^2 \varphi^*(r) \varphi(r),$$

## Vanderbilt (ultrasoft) pseudopotentials



norm-conserving constraint is relaxed  
pros - soft – only few PW needed in WF expansion  
cons – transferability, correct charge density  
D. Vanderbilt, *Phys.Rev. B* **41**, 7892 (1990)

Oxygen 2p radial wave function (solid), and corresponding pseudo-wave-functions generated using HSC (dotted) and Vanderbilt (dashed) methods.

- introduces compensating terms to recover the correct electron density (augmentation charges) – lost due to NC relaxation
- two or more reference energies are introduced to improve pseudopotential transferability



## Projector augmented wave (PAW) method

dual transformation between pseudo and true Hilbert spaces

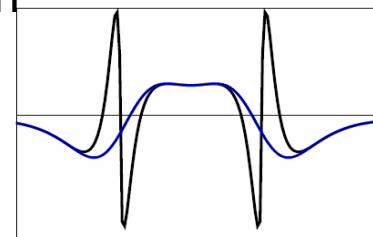
P.E. Blöchl, *Phys.Rev. B* **50**, 17953 (1994)

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle - |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle$$

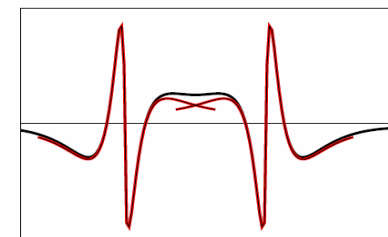
$$\Psi = T\tilde{\Psi} \quad \text{pseudo-wavefunction}$$

$$\langle \Psi | A | \Psi \rangle = \langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle$$

$$\tilde{A} = T^+ A T$$



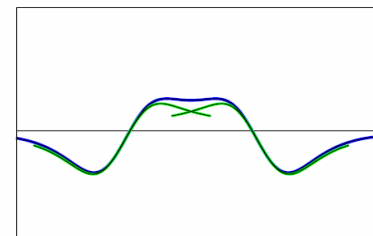
$|\Psi\rangle, |\tilde{\Psi}\rangle$



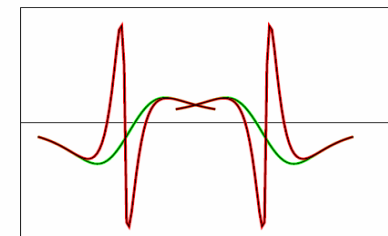
$|\Psi\rangle, |\Psi^1\rangle$

augmentation region R

projector functions  $|\tilde{p}_i\rangle$  are orthogonal to the pseudo partial waves



$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$



$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

$$T = 1 + \sum_R T_R = 1 + \sum_i (\psi_i - \tilde{\psi}_i) \langle \tilde{p}_i |$$

PAW combines the efficiency of the pseudopotential PW methods with the accuracy provided by augmentation, i.e. all-electron approaches

Program	Description	Web site
ABINIT	DFT(LDA,GGA); TD-DFT; NCPP; PW; PAW; TE; GO; PH	www.abinit.org
CASTEP	DFT(LDA,GGA); PP; PW; TE; GO; CP-MD	www.accelrys.com/mstudio/ ms_modeling/castep.html
CPMD	DFT(LDA,GGA); NCPP; PW; TE; GO; CP-MD	www.cpmc.org
Dacapo	DFT(LDA,GGA); PP; PW; TE; GO	www.fysik.dtu.dk/CAMP/daca- po.html
DoD-Planewave	DFT(LDA,GGA); PP; PW; TE; GO	cst-www.nrl.navy.mil/people/ singh/planewave/
FHI98md	DFT(LDA,GGA); NCPP; PW; TE; GO; BO-MD	www.fhi-berlin.mpg.de/th/ fhi98md/index.html
PARATEC	DFT(LDA,GGA); TD-DFT; NCPP; PW; TE; GO	www.nersc.gov/projects/para- tec/
PWSCF	DFT (LDA,GGA); DF-PT; NCPP; PW; TE; GO; PH; CP- MD	www.pwscf.org
VASP	DFT (LDA,GGA); USPP; PW; PAW; TE; GO; PH; CP-MD	cms.mpi.univie.ac.at/vasp/
CP-PAW	DFT(LDA,GGA); PAW; TE; GO; CP-MD	www.pt.tu-clausthal.de/~paw/ index.html
PWPAW	DFT(LDA); PAW; TE; GO	www.wfu.edu/~natalie/papers/ pwpaw/man.html
QUICKSTEP/ CP2K	DFT(LDA,GGA); PP; hybrid GTO/PW	cp2k.berlios.de
SIESTA	DFT(LDA,GGA); PP; NTO; TE; GO; MD	www.uam.es/departamentos/ ciencias/fismateriac/siesta/
DMol <sup>3</sup>	DFT(LDA,GGA); AE; NTO; TE; GO	www.accelrys.com/mstudio/ ms_modeling/dmol3.html
LmtART	DFT; AE; LMTO; TE; GO; PH	physics.njit.edu/~savrasov/Pro- grams/index_lmtart.htm
FLEUR	DFT; AE; FLAPW; TE	www.flapw.de
WIEN2K	DFT(LDA,GGA); AE; FLAPW; TE; GO; PH	www.wien2k.at/
MOPAC2002	SE; TE; GO	www.schrodinger.com/ Products/mopac.html
ADF2002 (BAND)	DFT(LDA,GGA); TD-DFT; AE; STO; TE	www.scm.com
Gaussian03	HF; DFT; AE; GTO; TE; GO; PH	www.gaussian.com
CRYSTAL03	HF; DFT; AE; PP; GTO; TE; GO	www.crystal.unito.it

**AE** All-electron basis set

**BO** Born–Oppenheimer approximation

**CP** Car–Parrinello method

**DFT** Density functional theory

**FLAPW** Fully linearized augmented  
plane wave

**GGA** Generalized gradient approximation

**GO** Geometry optimization

**GTO** Gaussian-type orbitals

**HF** Hartree–Fock

**LDA** Local density approximation

**MD** Molecular dynamics

**NCPP** Norm-conserving pseudopotentials

**NTO** Numerical type orbitals

**PAW** Projector-augmented wave method

**PH** Phonons

**PP** Pseudopotentials

**PT** Perturbation theory

**PW** Plane waves

**SE** Semi-empirical methods

**STO** Slater-type orbitals

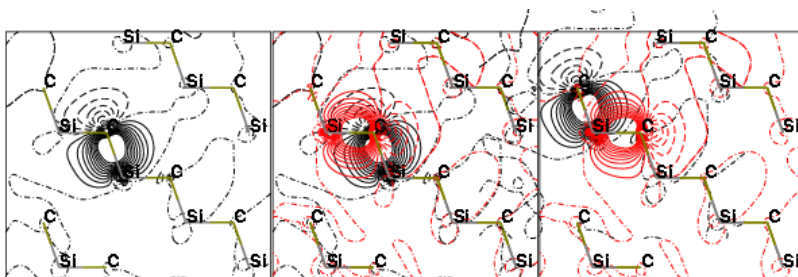
**TD** Time dependent

**TE** Total energy

**USPP** Ultra-soft pseudopotentials

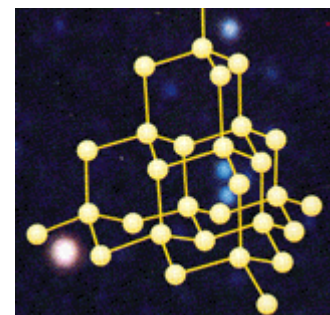
## Local-MP2 for nonconducting crystals : CRYSCOR

Local correlation techniques as proposed by Pulay and Saebø, and efficiently implemented for molecules in the MOLPRO program, have been extended by C. Pisani and coworkers to non-conducting periodic systems



### Binding Energies per unit cell (au)

	$BE^{\text{HF}}$	$\Delta E_2$	$BE^{\text{MP2}}$	$BE^{\text{EXP}}$
<b>Diamond</b>	<b>0.407</b>	<b>0.134</b>	<b>0.541</b>	<b>0.555</b>
<b>Silicon</b>	<b>0.227</b>	<b>0.083</b>	<b>0.310</b>	<b>0.345</b>
<b>SiC</b>	<b>0.324</b>	<b>0.113</b>	<b>0.437</b>	<b>0.475</b>
<b>BN</b>	<b>0.340</b>	<b>0.123</b>	<b>0.463</b>	<b>0.500</b>



C. Pisani *et al.*, *J.Chem.Phys.* **122**, 094113 (2005)

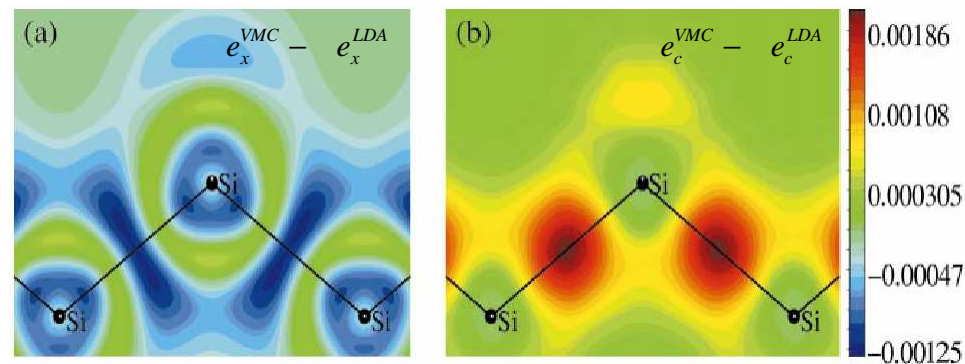
## Towards higher accuracy: Quantum Monte Carlo

**VMC** (Variational QMC) - *stochastic integration method to evaluate expectation values for a chosen trial wave function*

**DMC** (Diffusion QMC) - *projection technique to enhance the GS component of a starting trial wave function*

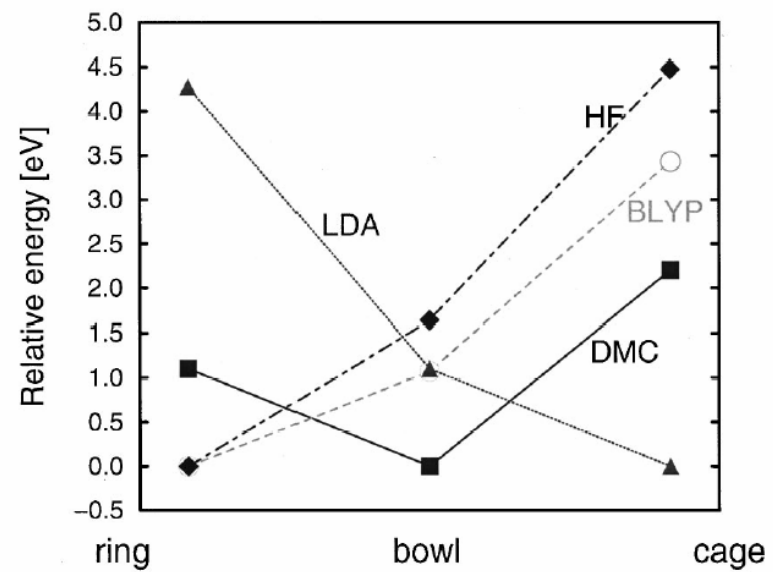
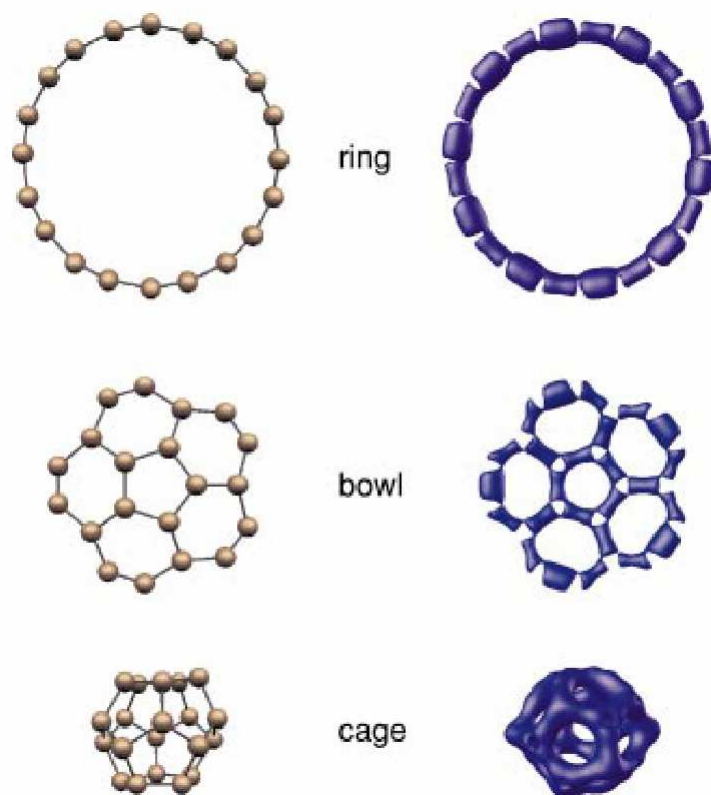
Current algorithms and computational resources permit QMC calculations on systems up to about 1000 electrons

### Exchange and Correlation in Silicon diamond structure, (110) plane

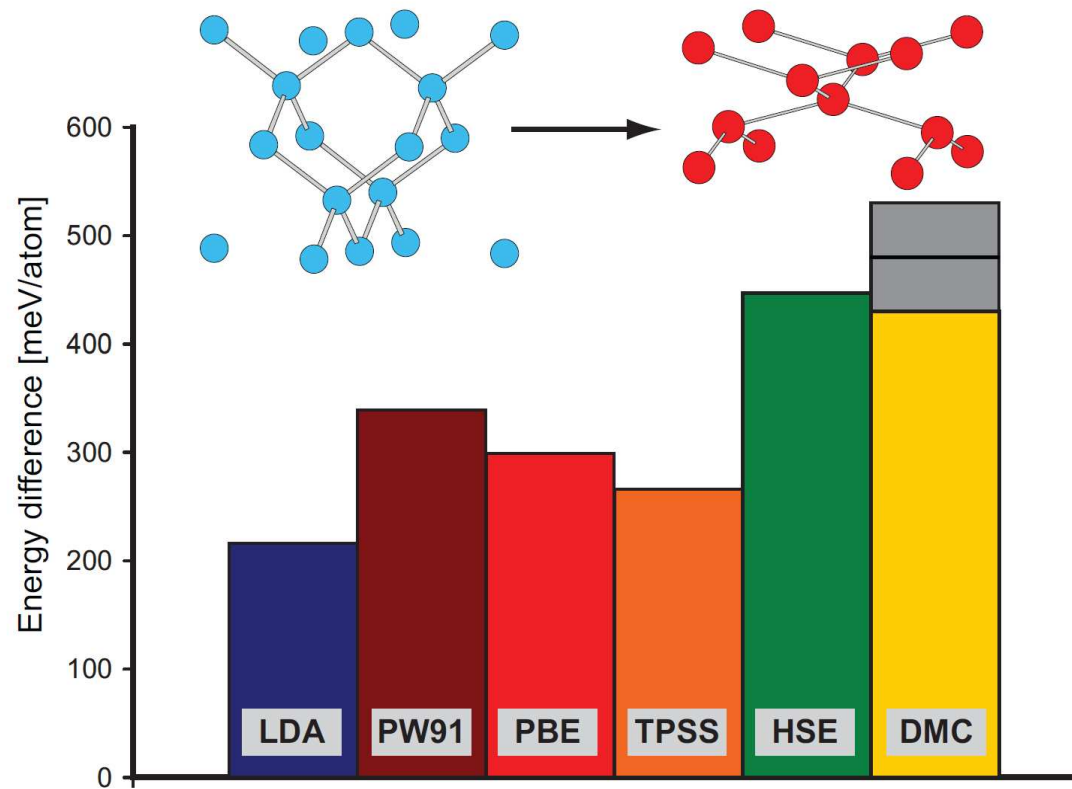


R.Q. Hood *et al.*, *Phys. Rev. B* **57**, 8972 (1998)

## Relative energies of C<sub>20</sub> isomers

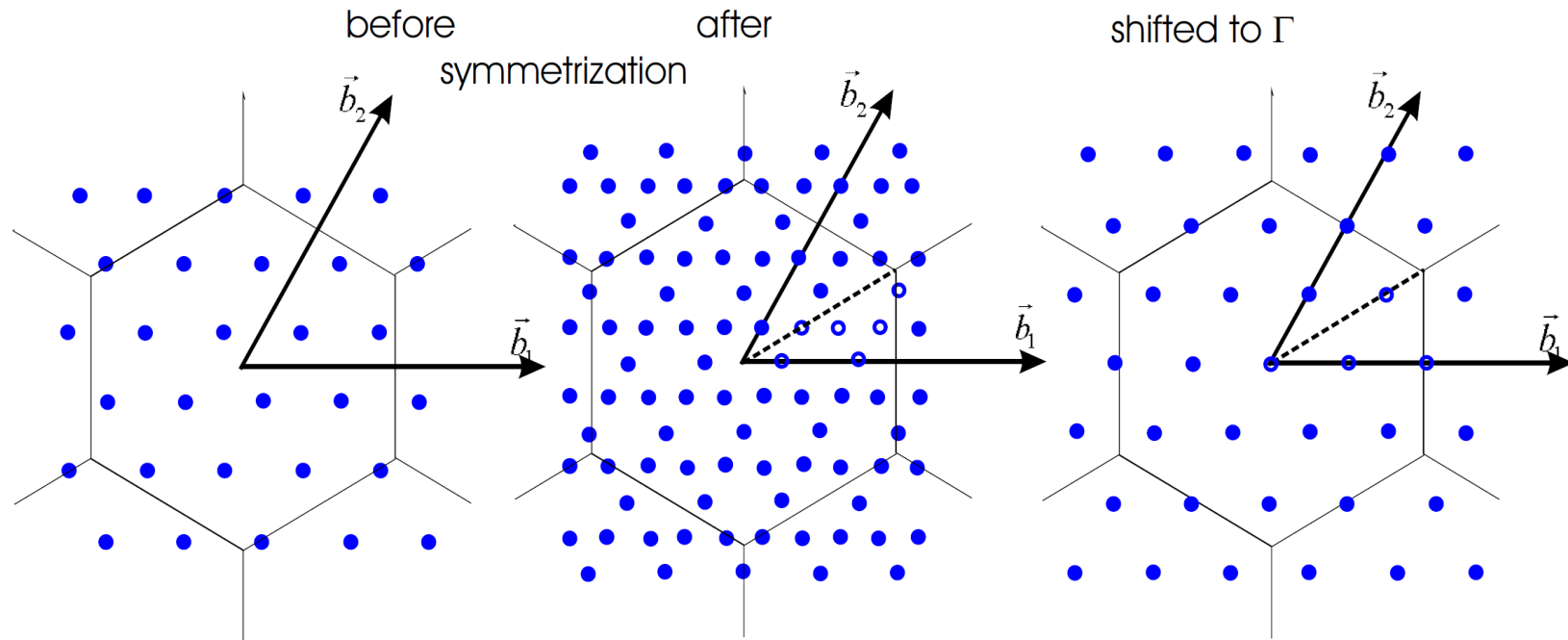


J.C. Grossman *et al.*, *Phys. Rev. Lett.* **75**, 3870 (1995)



Difference in energy per atom in the diamond phase and in the  $\beta$ -tin phase of Si. The DMC energy of  $480 \pm 50$  meV/atom benchmarks the accuracy of the different DFT functionals. The gray region of the DMC bar represents the uncertainty of the DMC energy.

### Example - hexagonal cell



- in certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry
- symmetrization results in non equally distributed k-points
- Gamma point centered mesh preserves symmetry

# Hartree-Fock calculations of periodic systems

Constructing the basis of Bloch functions as LCAO

$$\psi_{\mu}(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \chi_{\mu}^{\mathbf{R}}(\mathbf{r} - \mathbf{r}_{\mu})$$

Solving Hartree-Fock equations for each  $\mathbf{k}$

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

Evaluating Fock matrix elements in direct space using the local basis set

$$F_{\mu\nu}^{\mathbf{R}} = \langle \chi_{\mu}^0 | \hat{F} | \chi_{\nu}^{\mathbf{R}} \rangle = T_{\mu\nu}^{\mathbf{R}} + Z_{\mu\nu}^{\mathbf{R}} + C_{\mu\nu}^{\mathbf{R}} + X_{\mu\nu}^{\mathbf{R}}$$

Determining the Fermi energy,  $E_F$ , and forming the density matrix

$$P_{\mu\nu}^{\mathbf{R}} = \frac{1}{V_{BZ}} \sum_n \int_{BZ} e^{i\mathbf{k} \cdot \mathbf{R}} C_{\mu n}^*(\mathbf{k}) C_{\nu n}(\mathbf{k}) \times \theta(E_F - E_n(\mathbf{k})) d\mathbf{k}$$

Forming the  $\mathbf{F}$  and  $\mathbf{S}$  matrices in reciprocal space

$$\begin{aligned} F_{\mu\nu}(\mathbf{k}) &= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \langle \chi_{\mu}^{\mathbf{R}'} | \hat{F} | \chi_{\nu}^{\mathbf{R}} \rangle \\ &= \sum_{\mathbf{R}''} e^{i\mathbf{k} \cdot \mathbf{R}''} \langle \chi_{\mu}^0 | \hat{F} | \chi_{\nu}^{\mathbf{R}''} \rangle \end{aligned}$$

Calculating the total energy per cell

$$E_{tot} = E_{nucl} + \frac{1}{2} \sum_{\mu\nu} \sum_{\mathbf{R}} P_{\mu\nu}^{\mathbf{R}} (T_{\mu\nu}^{\mathbf{R}} + Z_{\mu\nu}^{\mathbf{R}} + F_{\mu\nu}^{\mathbf{R}})$$