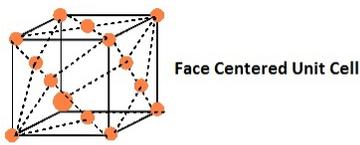


BEYOND BAND THEORY IN PRESENCE OF INTERELECTRONIC INTERACTION

Michel Caffarel, le 14/06/2018 michel.caffarel@gmail.com

Periodic solid:

- **Conventional cell:** Standard representation



- **Primitive cell:** Smallest cell which by periodic repetition reproduces the whole solid.

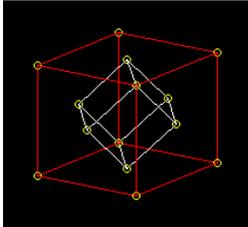
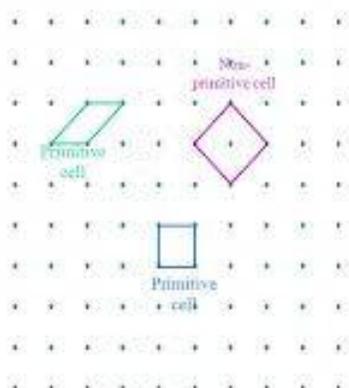


Figure 1. Primitive cell of FCC lattice.

- The primitive cell is not unique.

UNIT CELLS OF A LATTICE



If the lattice points are only at the corners, the unit cell is *primitive* otherwise *non-primitive*.

A unit cell of a lattice is **NOT** unique.

- **Solid structure characterized by three elementary vectors:** $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$. Solid invariant under any translation written under the form

$$\boxed{\mathbf{T}_{n_1 n_2 n_3} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad n_i \in \mathbb{Z}} \quad (1)$$

- The primitive cell is not unique.

I. STANDARD BAND THEORY (NO EXPLICIT INTERACTION BETWEEN ELECTRONS)

A. Non-interacting electrons or effective one-particle theories (DFT, HF,..)

$$H_{N \rightarrow +\infty} = -\frac{1}{2} \sum_{i=1}^{N \rightarrow +\infty} \nabla_i^2 + \sum_{i=1}^{N \rightarrow +\infty} v_{en}(\mathbf{r}_i) = \sum_{i=1}^{N \rightarrow +\infty} h(\mathbf{r}_i)$$

The one-electron Schrödinger equation

$$h\phi_{\mathbf{k}}(\mathbf{r}) = -\frac{1}{2}\nabla^2\phi_{\mathbf{k}}(\mathbf{r}) + v_{en}(\mathbf{r}_i)\phi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r})$$

BLOCH THEOREM: All eigenstates of h are under the form

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

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the crystal, that is $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_{n_1 n_2 n_3})$

- $\mathbf{k} \in \mathbb{R}^3$
- \mathbf{k} is a "good" quantum number = each \mathbf{k} labels an irreducible representation

Using Bloch theorem we have

$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_{n_1 n_2 n_3}) = e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{T}_{n_1 n_2 n_3})} u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_{n_1 n_2 n_3}) = e^{i\mathbf{k}\cdot\mathbf{T}_{n_1 n_2 n_3}} \phi_{\mathbf{k}}(\mathbf{r})$$

Now, if

$$\mathbf{k} \rightarrow \mathbf{k} + 2\pi\mathbf{n} \quad \mathbf{n} = (n_x, n_y, n_z) \in \mathbb{Z}^3$$

we then have $e^{i\mathbf{k}\cdot\mathbf{T}_{n_1n_2n_3}} = 1$ and each eigenstate is transformed into itself when

$$\mathbf{k}_i \in \left(-\frac{\pi}{a_i}, \frac{\pi}{a_i}\right) \quad i = x, y, z$$

Then, without loss of generality and for unicity of the representation, we can restrict the domain of values of \mathbf{k} to a subdomain of \mathbb{R}^3 . The choice is not unique. The domain used for a given lattice is called **the first Brillouin zone (BZ)**.

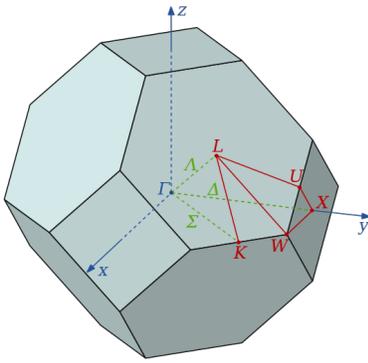


Figure 2. First Brillouin zone of FCC lattice, a truncated octahedron, for the face centered cubic (FCC) lattice (for example, carbon diamond)

For a given \mathbf{k} there is an infinite number of excited-states (here, labeled by n)

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

A given n defines a "band".

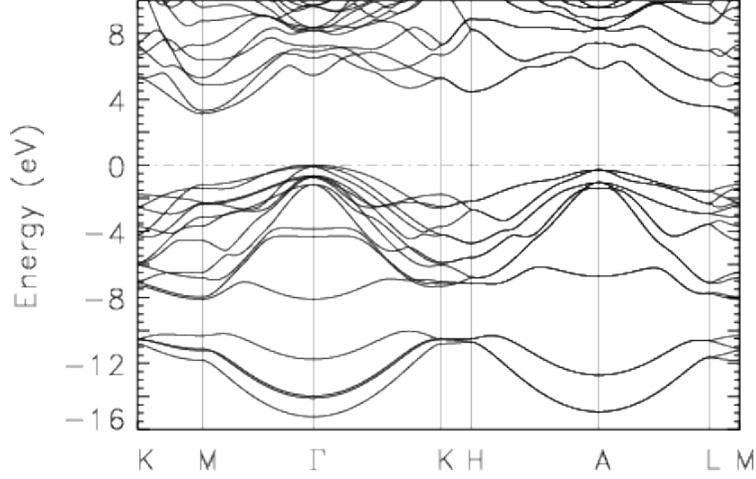


Figure 3.

Fundamental remark: To get the $u_{\mathbf{k},n}(\mathbf{r})$ it is sufficient to solve the Schrödinger equation in the primitive cell independently for each k .

$$-\frac{1}{2}\nabla^2\phi_{\mathbf{k}n}(\mathbf{r}) + v(\mathbf{r})\phi_{\mathbf{k}n}(\mathbf{r}) = \epsilon_{\mathbf{n}k}\phi_{\mathbf{n}k}(\mathbf{r})$$

Why only in the primitive cell?

Invariance of $v_{en}(\mathbf{r})$ with respect to any translation $\mathbf{T}_{n_1n_2n_3}$ elementary vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$

⇒ Physical property invariance, for example one-particle (charge) density

$$\rho(\mathbf{r} + \mathbf{T}_{n_1n_2n_3}) = \rho(\mathbf{r})$$

⇒ It is then extremely convenient to work in Fourier space because periodic functions have a **discrete** 3D-Fourier series with Fourier vectors $\mathbf{G}_{m_1m_2m_3}$

$$f(\mathbf{r}) = \sum_{\mathbf{G}_{m_1m_2m_3}} f(\mathbf{G}_{m_1m_2m_3})e^{i\mathbf{G}_{m_1m_2m_3}\cdot\mathbf{r}}$$

and

$$f(\mathbf{G}_{m_1m_2m_3}) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{G}_{m_1m_2m_3}\cdot\mathbf{r}} \quad \mathbf{m} = (m_1, m_2, m_3) \in \mathbb{Z}^3$$

with $\mathbf{G}_{m_1m_2m_3} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ (definition of reciprocal space) where Ω is the volume of the primitive cell and \mathbf{b} the elementary vectors of the Brillouin zone

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

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

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

For example,

In DFT (the important case) we need to solve for each \mathbf{k} independently

$$\sum_{\mathbf{G}'} \left(\frac{(\mathbf{k} + \mathbf{G}')^2}{2} \delta_{\mathbf{G}\mathbf{G}'} + V_{\text{eff}}(\mathbf{G} - \mathbf{G}') \right) c_{n\mathbf{k}}(\mathbf{G}') = \epsilon_{n\mathbf{k}} c_{n\mathbf{k}}(\mathbf{G})$$

where $c_{n\mathbf{k}}(\mathbf{G})$ are the Fourier components of the periodic part $u_{n\mathbf{k}}$ of the KS eigenstate, $\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$. V_{eff} is the sum of the Fourier transform of v_{en} , v_H and v_{xc} . All Fourier components are computed by integrating in space only in the primitive cell.

- **Remark:** Of course, $v_{en}(\mathbf{r})$ depends on the exterior of the primitive cell

$$v_{en}(\mathbf{r}) = \sum_{n_1 n_2 n_3} \sum_{\alpha} -Z_{\alpha} / |\mathbf{r} - \mathbf{R}_{\alpha} + \mathbf{T}_{n_1 n_2 n_3}|$$

- **Remark:** Important point: The preceding sum does not converge, and some trick is necessary to give a sense to this sum = **Ewald summation** (see below).

Brillouin zone sampling

Static properties: To get physical properties we need to compute all occupied eigenstates $\phi_{n\mathbf{k}}$. Properties are expressed as integrals in the Brillouin zone. This is the **Brillouin zone sampling step**

- Examples:

Band energy per primitive cell

$$\sum_n \int_{BZ} d\mathbf{k} \epsilon_{n\mathbf{k}} \theta(E_F - \epsilon_{n\mathbf{k}})$$

Charge density

$$\sum_n \int_{BZ} d\mathbf{k} |\phi_{n\mathbf{k}}|^2 \theta(E_F - \epsilon_{n\mathbf{k}})$$

θ = Heaviside function.

- **Important remark:** Because the Fermi surface is in general quite complicated, we sum over all BZ.

In practice, we have to choose a finite sum over a \mathbf{k} -grid to integrate over the BZ as efficiently as possible. Several grids of integration points have been introduced. Their efficiency depends on the topology of the Fermi surface. Most popular choice: the Monkhorst-Pack grid (other: Baldereschi, etc.)

Efficiency: To approach the thermodynamic limit we try to use as little as possible \mathbf{k} -points for the BZ sampling.

Important general remark: Up to now we have worked directly at the thermodynamic limit with an infinite number of particles and solid and **no boundary conditions** have been introduced! The only "discrete" aspect comes from the Brillouin zone sampling.

II. EXPLICITLY INTERACTING ELECTRONS

. The Hamiltonian is now

$$H_{N \rightarrow +\infty} = -\frac{1}{2} \sum_{i=1}^{N \rightarrow +\infty} \nabla_i^2 + \sum_{i=1}^{N \rightarrow +\infty} h(\mathbf{r}_i) + \sum_{i < j} \frac{1}{r_{ij}}$$

In the one-particle case for each electron i we have the following invariance:

$$H(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{T}_{n_1 n_2 n_3}, \dots) = H(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots)$$

As seen above **this symmetry allows to diagonalize the Hamiltonian only in the primitive cell** (in a second step, the translations are used to extend the eigenstates over the whole infinite solid).

In the interacting case, **this symmetry is no longer valid** and we are left with an Hamiltonian invariant only under the **simultaneous** translation of all electron coordinates by a common translation vector ($T_{n_1 n_2 n_3} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$).

\Rightarrow **Huge loss of symmetry**; the quantum numbers \mathbf{k} in BZ are no longer "good" quantum numbers.

By defining a finite model Hamiltonian H_{model} and by introducing some **artificial** (non-physical) translation symmetries: This is **the supercell approximation**. When N goes to infinity the exact thermodynamic limit is reached.

WARNING! Possible confusion: In the standard one-particle methods, the supercell approach is also used but for a very different reason: To make periodic systems with impurities by considering larger primitive cells called supercells.

Let us consider a supercell containing several (many) primitive cells. The whole crystal will be recovered by making translations of this supercell.

We then define three **elementary superlattice vectors** ($\mathbf{A}_1 = L_1\mathbf{a}_1, \mathbf{A}_2 = L_2\mathbf{a}_2, \mathbf{A}_3 = L_3\mathbf{a}_3$ where L_i integers and the product $L_1L_2L_3$ is number of primitive cells in the supercell.

$$\boxed{\mathbf{T}^{\mathbf{S}}_{n_1n_2n_3} = n_1\mathbf{A}_1 + n_2\mathbf{A}_2 + n_3\mathbf{A}_3 \quad n_i \in \mathbb{Z}} \quad (2)$$

where S stands for superlattice.

Having N electrons in the finite supercell the following model Hamiltonian is defined as

$$H_N = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v_{en}(\mathbf{r}_i) + \sum_{i<j} v_{ee}(\mathbf{r}_i, \mathbf{r}_j)$$

with

$$v_{en}(\mathbf{r}) = \sum_{n_1n_2n_3} \sum_{\alpha}^{N_{\alpha}} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha} + \mathbf{T}^{\mathbf{S}}_{n_1n_2n_3}|}$$

and

$$V_{ee}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i<j} \frac{1}{r_{ij}} + \sum_{n_1n_2n_3 \neq (0,0,0)} \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{T}^{\mathbf{S}}_{n_1n_2n_3}|}$$

where N_{α} number of fixed nuclei of position \mathbf{R}_{α} and charge Z_{α} in the supercell.

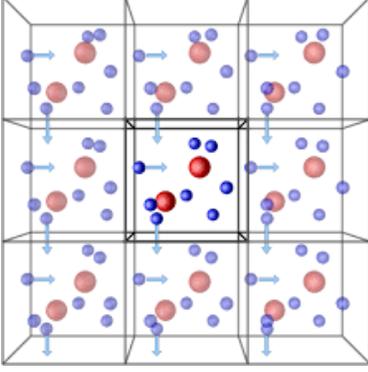


Figure 4. Supercell at the center. Other supercells obtained by replication with translations $\mathbf{T}_{n_1 n_2 n_3}^{\mathbf{S}}$

The Hamiltonian is invariant under *individual translation* of a **given electron** by a vector $\mathbf{T}_{n_1 n_2 n_3}^{\mathbf{S}}$. This is a **fictitious translational symmetry** of the superlattice introduced in the modelization to enhance the convergence to the thermodynamic limit. Once this translational symmetry is introduced, the supercell plays the role of the primitive cell.

THE MANY-BODY BLOCH THEOREM: For all eigenstates of H_N the eigenstates write

$$\Psi_{n\mathbf{K}}(\mathbf{r}_1, \dots, \mathbf{r}_N) = e^{i\mathbf{K} \cdot \sum_{i=1}^N \mathbf{r}_i} U_{n\mathbf{K}}(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

where U has the periodicity of the superlattice.

- *A priori* $\mathbf{K} \in \mathbb{R}^3$
- However, as for the one-particle case we can restrict the values of \mathbf{K} and define the **first Brillouin zone of the superlattice** (not to be confused with the first Brillouin zone of the lattice).

$$\Psi_{n\mathbf{K}}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{T}_{n_1 n_2 n_3}^{\mathbf{S}}, \dots, \mathbf{r}_N) = e^{i\mathbf{K} \cdot \sum_{i=1}^N \mathbf{r}_i} \cdot \mathbf{T}_{n_1 n_2 n_3}^{\mathbf{S}} \Psi_{n\mathbf{K}}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

Then, the value of \mathbf{K} (continuous value) determines the choice of boundaries conditions for the supercell.

The Schrödinger equation needs to be solved **only once** for a given \mathbf{K} for the N interacting electrons in the supercell.

However, in order to (greatly) reduce the finite-size effects, it can be useful (but not compulsory as in the one-particle case !) to make a sampling of the BZ of the superlattice. and calculate properties as an average over all possible TBC (all \mathbf{K} in BZ). For example, the ground-state energy per simulation cell

$$\frac{E_0}{N} = \langle H_N \rangle = \frac{\Omega_S}{(2\pi)^3} \int_{\Omega_S} d\mathbf{r}_1, \dots, d\mathbf{r}_N \langle \Psi_{0\mathbf{K}} | H | \Psi_{0\mathbf{K}} \rangle.$$

- **Remark 1:** For different \mathbf{K} the finite-size behavior as a function of N is different. To average results for different \mathbf{K} average these particular behaviors. In practice, it enhances a lot the convergence to the thermodynamic limit.

- **Remark 2:** When N goes to infinity the first Brillouin zone of the superlattice shrinks to zero. The results no longer depend on the choice of the boundary conditions.

Technical important issue: The Ewald technique.

We consider the general problem of evaluating the total Coulomb energy E for a set of N particles of charge q_i located at \mathbf{r}_i interacting between them and with the infinite number of periodic images of each of the N particles. Here, the N particles will be located within the supercell.

$$E = \frac{1}{2} \sum_{\mathbf{n}} \sum_{\substack{i,j \\ i \neq j}}^N \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}$$

with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

In our case

$$v_{en}(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha} + \mathbf{n}L|} \operatorname{erfc}\left(\frac{|\mathbf{r} - \mathbf{R}_{\alpha} + \mathbf{n}L|}{\sqrt{2}\sigma}\right) + \frac{2\pi}{\Omega_S} \sum_{\mathbf{k} \neq 0} \frac{e^{-\sigma^2 k^2/2}}{k^2} - \frac{1}{\sqrt{2\pi}\sigma}$$

and

$$V_{ee}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{\mathbf{n}} \sum_{\substack{i,j \\ i \neq j}}^N \sum_{\mathbf{n}=0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|} \operatorname{erfc}\left(\frac{|\mathbf{r} - \mathbf{r}_j + \mathbf{n}L|}{\sqrt{2}\sigma}\right) \\ + \frac{2\pi}{\Omega_S} \sum_{\mathbf{k} \neq 0} \frac{e^{-\sigma^2 k^2/2}}{k^2} |S(\mathbf{k})|^2 - \frac{N}{\sqrt{2\pi}\sigma}$$

In these formula, Ω is the volume of the supercell, the summation over \mathbf{k} is over the first Brillouin zone of the supercell, and

$$S(\mathbf{k}) = \sum_{i=1}^N e^{i\mathbf{k}\mathbf{r}_i}$$

. (in the case of v_{en} , $S(\mathbf{k}) = 1$).

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

AT THE END OF THE DAY

From quantum chemistry (post-HF, QMC, etc.) to periodic solids
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I. For a CI-type calculation

1. Consider a supercell with N atoms (just a big molecule!).
2. Choose a standard gaussian atomic basis set $\{\chi_n(\mathbf{r})\}_{n=1, n_{basis}}$
3. (**New for solids**): Change the standard potential of the Hamiltonian into the Ewald form.
4. (**New for solids**) : Make periodic the gaussian basis set

$$\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{T}} e^{i\mathbf{k}\mathbf{T}} \chi_n(\mathbf{r} - \mathbf{T})$$

5. (**New for solids**) Choose in the Brillouin zone the set of \mathbf{k} to be used (BZ sampling)
6. (**New for solids**) Eventually, shift all \mathbf{k} 's by a vector \mathbf{K} = Choice of boundary conditions
7. Compute the matrix elements of H (mono- and bi-electronic integrals)
8. Diagonalize the CI Hamiltonian matrix (Davidson).

II. For a QMC calculation

Steps 1-6 identical

The diagonalization is done with QMC. Walkers defined as usual for the big molecule (supercell). However, we need to take into account the **phase factor due to boundary conditions whenever an electron crosses the supercell boundaries**