

Ab initio methods in solid state physics

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Bravais lattice

Bravais lattice, named after Auguste Bravais (1811-1863), is an infinite array of discrete points generated by a set of discrete translation operations, which in three dimensional space is described by vectors

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (1)$$

where n_i are integer numbers and \mathbf{a}_i are primitive vectors.

Primitive cell - a smallest volume that when translated through all the vectors in a Bravais lattice fills all space without overlapping or leaving void. It corresponds to one point of a lattice. The types and positions of atoms in the primitive cell are called the basis.

Crystal structure = Bravais lattice + basis

Wigner-Seitz cell - a primitive cell, which consists of all points in space that are closer to the given lattice point than to any other lattice points.

Unit cell (conventional cell) - the smallest repeating cell having the full symmetry of the crystal structure.

Bravais lattices in 2D

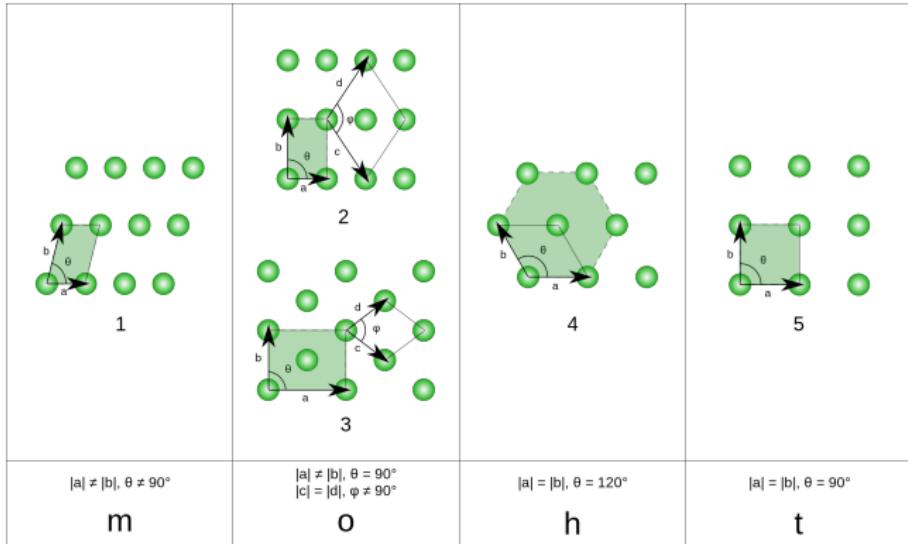


Figure : Five Bravais lattices (crystal family): 1. oblique (monoclinic), 2. rectangular (orthorhombic), 3. centered rectangular (orthorhombic), 4. hexagonal, and 5. square (tetragonal). By Prolineserver - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=3912829>.

Example: centered rectangular lattice

$$R_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2. \quad (2)$$

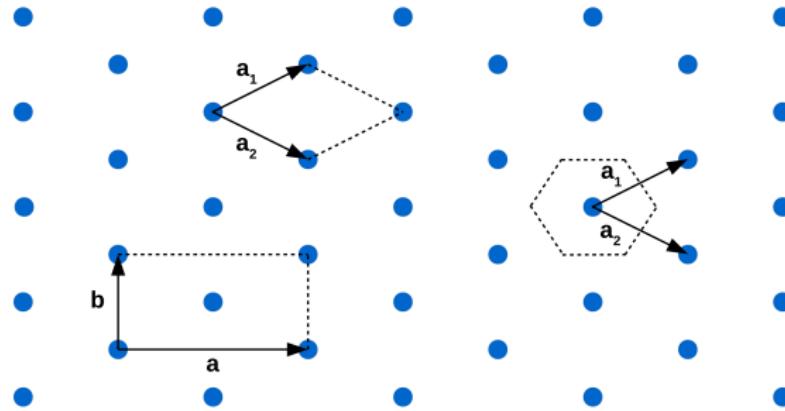


Figure : Centered rectangular lattice with the primitive cell, Wigner-Seitz cell, and the unit cell.

Example: hexagonal honeycomb lattice - graphene

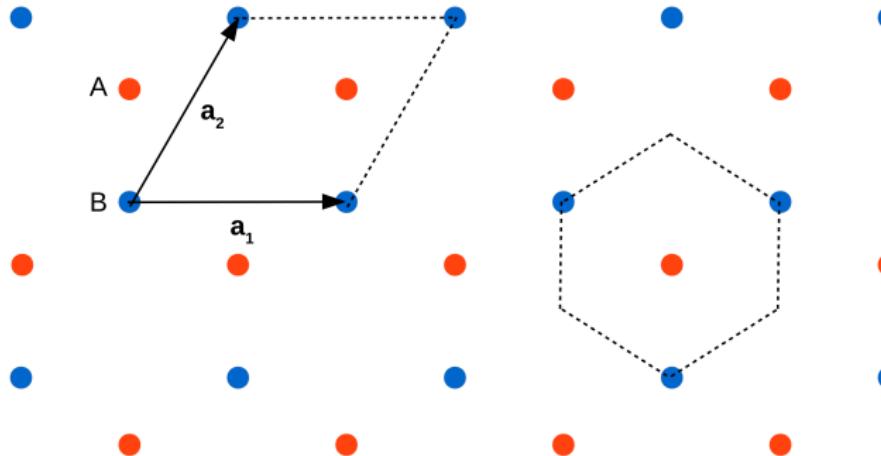
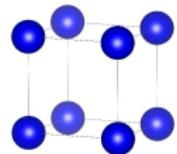


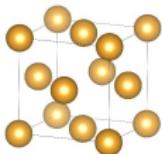
Figure : Hexagonal lattice with the primitive cell and the Wigner-Seitz primitive cell with the two-atom basis.

Bravais lattices in 3D

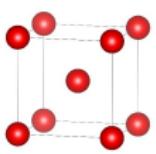
| Lattice system | Lattice constants | Angles | Bravais lattices |
|----------------|-------------------|---------------------------------------------------|------------------|
| cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90^\circ$ | P, F, I |
| tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | P, I |
| orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ | P, F, C, I |
| hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ | P |
| rhombohedral | $a = b \neq c$ | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ | P |
| monoclinic | $a = b \neq c$ | $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ | P, C |
| triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$ | P |



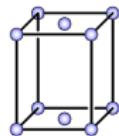
P - primitive cubic (Po)



F - face-centered cubic (Au)



I - body-centered cubic (Fe)



C - base-centered orthorhombic (F)

Bravais lattices in 3D

C. Mendez *et al.*, Int. J. Mult. Comp. Eng. **17**, 261 (2019)

| Lattice System | Point Group | Primitive | Base-Centered | Body-Centred | Face-Centred |
|----------------|-------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| Triclinic | $\bar{1}$ |  $P\bar{1}$ | | | |
| Monoclinic | $2/m$ |  $P2/m$ |  $C2/m$ | | |
| Orthorhombic | mmm |  $Pmmm$ |  $Cmmm$ |  $Immm$ |  $Fmmm$ |
| Tetragonal | $4/mmm$ |  $P4/mmm$ | |  $I4/mmm$ | |
| Rhombohedral | $3m$ |  $R\bar{3}m$ | | | |
| Hexagonal | $6/mmm$ |  $P6/mmm$ | | | |
| Cubic | $m\bar{3}m$ |  $Pm\bar{3}m$ | |  $Im\bar{3}m$ |  $Fm\bar{3}m$ |

The space groups

The crystal structure is described by its symmetry operations. Translations form a group because the sum of any two translations is another translation. In addition there are point operations, such as rotations, reflections, and inversions, that leave the crystal the same.

$$\text{Space group} = \text{translation group} + \text{point group}$$

The symmetry elements which constitute the crystallographic point groups are: proper rotation axes (n), mirror planes (m), inversion centre (1, or no explicit symbol), and rotary inversion axes (\bar{n}). Only n -fold axes with $n = 1, 2, 3, 4, 6$ are allowed. Examples: $P222$, $Immm$, $Fm\bar{3}m$, $Im\bar{3}m$, $P4/mmm$, $C2/m$.

32 unique crystallographic point groups are obtained from combining the various allowed rotation axes, mirror planes, and inversions.

There are 230 space groups divided into 73 symmorphic and 157 non-symmorphic space groups, with screw axes – combine a rotation with translation or glide planes – combine a reflection with translation.

Recipe for crystal structure

- ① Select a space group.
- ② Set lattice parameters: lattice constants and angles.
- ③ Provide a minimal set of atomic positions (Wyckoff positions), given by fractional coordinates.
- ④ Generate all atomic positions in a cell using some software, e.g. ASE or VESTA (<https://jp-minerals.org/vesta/en/>).

Example: magnetite Fe_3O_4

Space group: $Fd\bar{3}m$

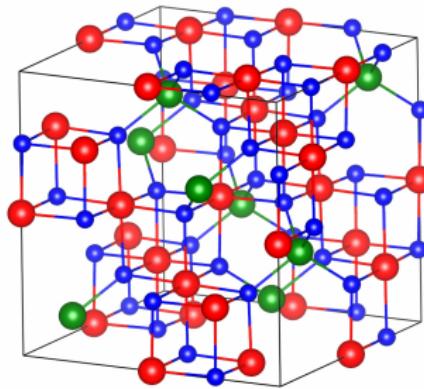
Lattice constant: $a = 8.39 \text{ \AA}$

Wyckoff positions:

Fe (0.125,0.125,0.125)

Fe (0.5,0.5,0.5)

O (0.2548,0.2548,0.2548)



Reciprocal space

For each Bravais lattice there is a corresponding lattice in the reciprocal space

$$\mathbf{G}_m = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad (3)$$

where m_j are integer numbers and \mathbf{b}_j are primitive vectors in the reciprocal space and defined in relation to primitive vectors \mathbf{a}_i by the condition

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}. \quad (4)$$

Primitive vectors in the reciprocal space can be obtained from \mathbf{a}_i vectors

$$\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3, \quad (5)$$

$$\mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1, \quad (6)$$

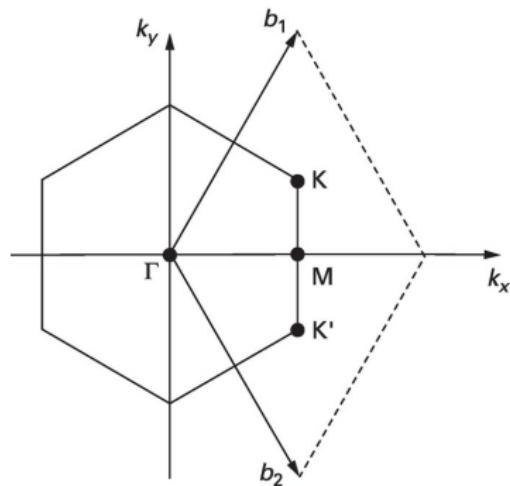
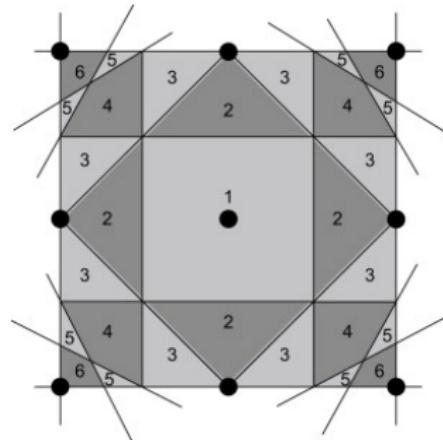
$$\mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2, \quad (7)$$

where $\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the primitive cell.

Brillouin zones in 2D

The first Brillouin zone is the Wigner-Seitz cell in the reciprocal space. There are also second, third, and next Brillouin zones, corresponding to a sequence of disjoint regions (all with the same volume) at increasing distances from the origin.

The Brillouin zones of the square lattice.



The first Brillouin zone of the hexagonal lattice.

Brillouin zones in 3D

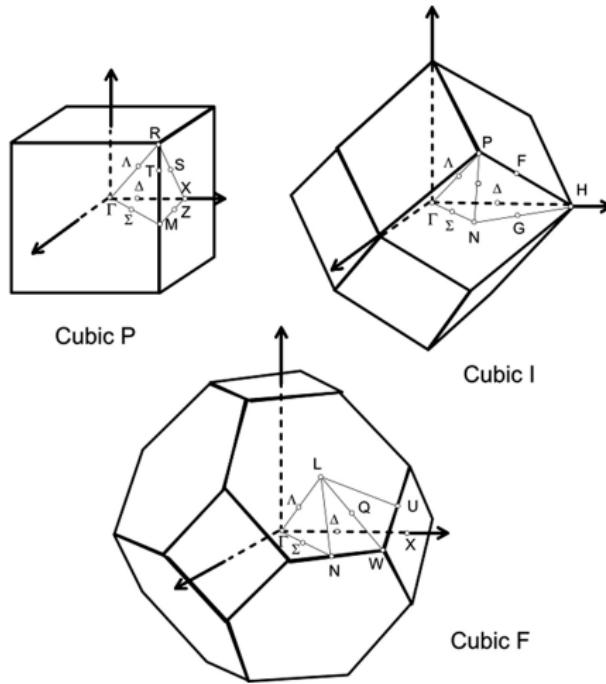


Figure : The Brillouin zones of primitive (P) cubic, body-centered (I) cubic, and face-centered (F) cubic structures.

Bloch theorem

In the periodic potential $V(\mathbf{r})$, electronic states are the solutions of the equation

$$[-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})]\psi_{kj}^\sigma(\mathbf{r}) = \varepsilon_{j\sigma}(\mathbf{k})\psi_{kj}^\sigma(\mathbf{r}), \quad (8)$$

where \mathbf{k} is a wave vector, connected with a quasi-momentum $\mathbf{p} = \hbar\mathbf{k}$, σ is a direction of spin, and $\varepsilon_{j\sigma}(\mathbf{k})$ are eigenenergies. The Bloch theorem states that wave functions of electrons in the period potential has the form


$$\psi_{kj}^\sigma(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{kj}^\sigma(\mathbf{r}), \quad (9)$$

where $u_{kj}^\sigma(\mathbf{r})$ is the periodic functions fulfilling the condition $u_{kj}^\sigma(\mathbf{r}) = u_{kj}^\sigma(\mathbf{r} + \mathbf{R}_n)$ for each translation vector \mathbf{R}_n . *Proof.* It can be shown that Bloch functions are eigenfunctions of the translation operator

$$\hat{T}_n \psi_{kj}^\sigma(\mathbf{r}) = \psi_{kj}^\sigma(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}(\mathbf{r} + \mathbf{R}_n)} u_{kj}^\sigma(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n} e^{i\mathbf{k}\mathbf{r}} u_{kj}^\sigma(\mathbf{r}) = e^{i\mathbf{k}\mathbf{R}_n} \psi_{kj}^\sigma(\mathbf{r}).$$

The Hamiltonian operator is invariant with respect to the action of translation operator, what means that both operators commute. Therefore, Bloch functions are also the eigenfunctions of the Hamiltonian.

Periodic boundary conditions (Born-von Karman)

The size of the crystal is defined by the number of primitive cells in each direction (N_1, N_2, N_3), and the integer numbers n_i change in the range $n_i = 0, 1, 2, \dots, N_i$, where $i = 1, 2, 3$. By assuming that the wave function has the same values at both ends of the system (along each direction) and applying the Bloch theorem, we get the condition

$$\psi_{\mathbf{k}j}^{\sigma}(\mathbf{r}) = \psi_{\mathbf{k}j}^{\sigma}(\mathbf{r} + N_i \mathbf{a}_i) = e^{i\mathbf{k}(\mathbf{r} + N_i \mathbf{a}_i)} u_{\mathbf{k}j}^{\sigma}(\mathbf{r} + N_i \mathbf{a}_i) = e^{i\mathbf{k}N_i \mathbf{a}_i} \psi_{\mathbf{k}j}^{\sigma}(\mathbf{r}), \quad (10)$$

which is fulfilled when

$$\mathbf{k} N_i \mathbf{a}_i = 2\pi n_i. \quad (11)$$

Using the relation $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, we obtain the allowed wave vectors

$$\mathbf{k} = \frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3. \quad (12)$$

The number of allowed wave vectors is equal to the number of primitive cells $N = N_1 N_2 N_3$. From (12) results that allowed wave vectors belong to a single primitive cell in the reciprocal lattice – the first Brillouin zone.

Irreducible Brillouin zone

In summation over wave vectors \mathbf{k} , we can use crystal symmetries to reduce the number of points. The Bravais lattice and Hamiltonian are invariant with respect to the transformation: $\mathbf{r} \rightarrow O_i \mathbf{r} + \mathbf{t}_i$, and in reciprocal space we have only point group symmetries $\mathbf{k} \rightarrow O_i \mathbf{k}$. The wave functions after full transformation

$$\psi_{O_i \mathbf{k}}^\sigma(O_i \mathbf{r} + \mathbf{t}_i) = \psi_{\mathbf{k}}^\sigma(\mathbf{r}), \quad (13)$$

are also the eigenfunctions of the Hamiltonian with the same eigenenergies $\varepsilon_{j\sigma}(\mathbf{k})$. Any quantity $f(\mathbf{k})$ can be calculated only at the \mathbf{k} -points belonging to the irreducible Brillouin zone (IBZ). The values at other \mathbf{k} -points are obtained by the transformation $f(O_i \mathbf{k}) = f(\mathbf{k})$. For example, the average value of $f(\mathbf{k})$ can be obtained using IBZ

$$\bar{f} = \frac{1}{N_k} \sum_{\mathbf{k}}^{BZ} f(\mathbf{k}) = \sum_{\mathbf{k}}^{IBZ} w_{\mathbf{k}} f(\mathbf{k}), \quad (14)$$

where $w_{\mathbf{k}}$ are weights defined as the number of \mathbf{k} -points connected by the point group symmetry with a \mathbf{k} -point from IBZ divided by the number of \mathbf{k} -points N_k .

Irreducible Brillouin zones in 2D

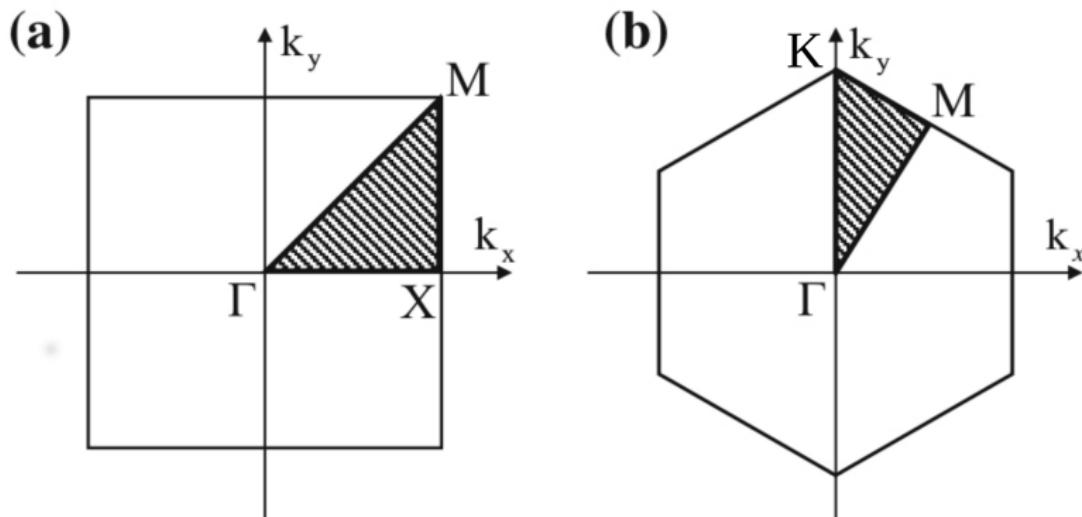


Figure : (a) The first Brillouin zone (square) and the irreducible Brillouin zone (triangle) for a square lattice; (b) the first Brillouin zone (hexagon) and the irreducible Brillouin zone (triangle) for a hexagonal lattice. Z. C. He *et al.*, Comp. Mech. **62**, 1023 (2018), <https://doi.org/10.1007/s00466-018-1548-y>

Monkhorst-Pack grid

Using the properties of periodic functions, we can properly choose the \mathbf{k} -points in IBZ to minimize the errors in calculation of sums or integrals. The optimum set of points is called the Monkhorst-Pack (MP) grid [Phys. Rev. B **13** 5188 (1976)], and for 3D is obtained from the equation

$$\mathbf{k}(n_1, n_2, n_3) = \frac{2n_1 - N_1 - 1}{2N_1} \mathbf{b}_1 + \frac{2n_2 - N_2 - 1}{2N_2} \mathbf{b}_2 + \frac{2n_3 - N_3 - 1}{2N_3} \mathbf{b}_3, \quad (15)$$

where $n_i = 1, 2, \dots, N_i$, and N_1 , N_2 , and N_3 define the number of \mathbf{k} -points along each direction. Such defined points create the uniform lattice in the reciprocal space. Any periodic function can be written with Fourier expansion

$$f(\mathbf{k}) = \sum_n f(\mathbf{R}_n) e^{i\mathbf{k}\cdot\mathbf{R}_n}. \quad (16)$$

When using the MP grid, the sum of values of a periodic function, which has Fourier components $f(\mathbf{R}_n)$ that extend only to $\mathbf{R}_n = N_i \mathbf{a}_i$ in each direction, is equal to an exact integral of this function.

Plane waves

We can write the wave function in the general form

$$\psi_{kj}^\sigma(\mathbf{r}) = \sum_m c_{jm}^\sigma(\mathbf{k}) \phi_{km}(\mathbf{r}), \quad (17)$$

where $\phi_{km}(\mathbf{r})$ are basis vectors and $c_{jm}^\sigma(\mathbf{k})$ are coefficients of the expansion. For periodic potential, the natural basis functions are plane waves, and Bloch functions can be expanded in this basis

$$\psi_{kj}^\sigma(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{kj}^\sigma(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_m c_{jm}^\sigma(\mathbf{k}) e^{i\mathbf{G}_m \mathbf{r}} = \sum_m c_{jm}^\sigma(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{G}_m) \mathbf{r}}, \quad (18)$$

where \mathbf{G}_m are the reciprocal space vectors. Using this expansion, the Schrödinger equation can be transformed to the form

$$\sum_n H_{mn} c_{jn}^\sigma(\mathbf{k}) = \varepsilon_{j\sigma}(\mathbf{k}) c_{jm}^\sigma(\mathbf{k}), \quad (19)$$

where matrix elements are given by

$$H_{mn} = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{mm'} + V(\mathbf{G}_m - \mathbf{G}_n). \quad (20)$$

Valence and core electrons

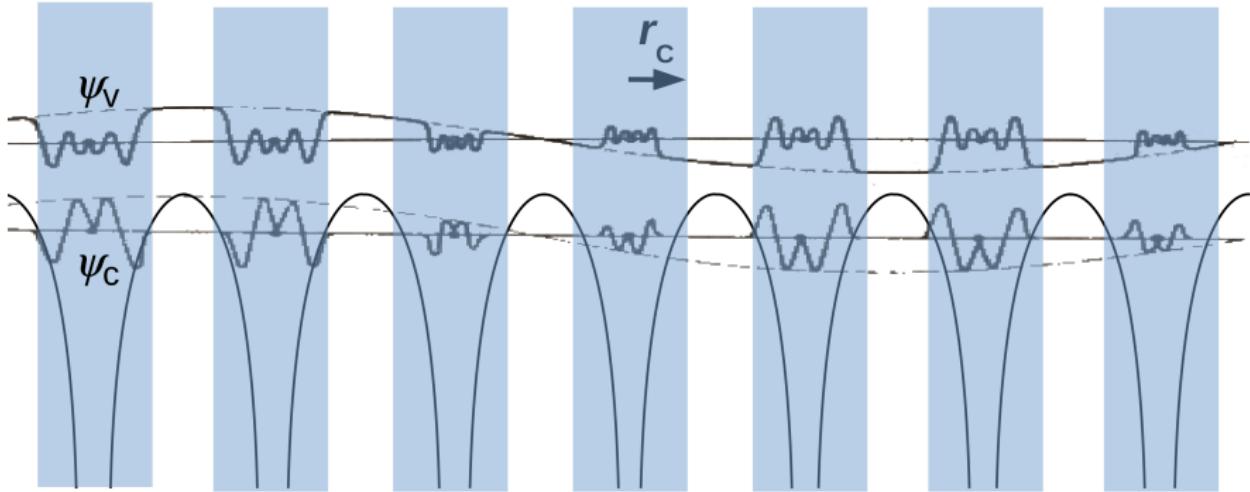


Figure : Bloch functions of the core ψ_c and valence ψ_v states within the atomic core and interstitial regions of the crystal potential. r_c is an atomic core radius.