CHAPTER 2 : INDEPENDENT ELECTRONS IN PERIODIC POTENTIALS

In chapter 1 we have seen that Born-Oppenheimer approximation decouples the motion of electrons and ions.

$$\begin{cases} \left(\hat{T}_{el} + \hat{V}_{ee} + \hat{V}_{ei} + \hat{V}_{ii} \right) \Phi_k = \varepsilon_{el,k} \, \Phi_k \qquad (1.10\,b) \qquad \text{electrons} \\ \left(\hat{T}_{ion} + \varepsilon_{el,k} \right) \chi_{k,w} = E_{k,w} \, \chi_{k,w} \qquad\qquad (1.10\,c) \qquad \text{ions} \end{cases}$$

In this chapter we shall focus on the electronic problem $(1.10\,b)$ for the special case in which $\hat{V}_{ee} = 0$. $\hat{V}_{ii}$ is in reality NOT an operator, but a constant once the ionic configuration is fixed $\Rightarrow$ it does not influence the eigenfunctions Φ_k and is just a rigid shift of the eigenvalues. For simplicity we measure the energy starting from $V_{ii}(\{\vec{R}_{\alpha,0}\})$.

The electronic problem is described by:

$$\begin{cases} \hat{H} = \sum_{i=1}^{N} \left[\frac{\hat{p}_i^2}{2m} + \hat{V}_{ei}(\vec{r}_i) \right] \equiv \sum_{i=1}^{N} \hat{h}_i \qquad (2.1) \\ \hat{V}_{ei}(\vec{r}_i) = -\sum_{\alpha} \frac{1}{4\pi\varepsilon_0} \frac{z_{\alpha} e^2}{|\vec{r}_i - \vec{R}_{\alpha}|} \qquad (2.2) \end{cases}$$

where $V_{ei}(\vec{r}_i)$ has the periodicity of the underlying lattice. i.e. we consider that $\{\vec{R}_{\alpha}\} = \{\vec{R}_{0,\alpha}\}$ the set of ion positions at $T=0$, and the position of the ions repeats periodically in space.

$\boxed{2.1}$ Crystal structures (following Ashcroft Mermin Ch. 4)

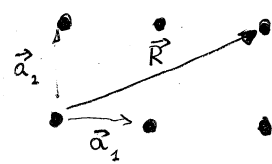Let us start with some definitions:

1. BRAVAIS LATTICE

Bravais lattice is the set of all points with position vectors

$$\vec{R}_{\vec{n}} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \qquad (2.3)$$

n_i are integers

$\{\vec{a}_i\}$ primitive lattice vectors

Example 2D lattice

$$\vec{R} = 2\vec{a}_1 + \vec{a}_2$$

- The primitive lattice vectors are linearly independent

- A Bravais lattice is mapped into itself under a translation of a generic lattice vector.

2. CRYSTAL STRUCTURE

A crystal structure is obtained by assigning an atom or a group of atoms to each point of a Bravais lattice.

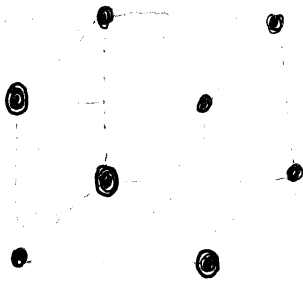- MONO ATOMIC BREVAIS LATTICE (one atom per Bravais lattice point)

  - simple cubic lattice $\longrightarrow$ spanned by $a\hat{x}, a\hat{y}, a\hat{z}$

  - body centered cubic lattice $^{(bcc)} \longrightarrow$ spanned by * $\frac{a}{2}(-\hat{x}+\hat{y}+\hat{z})$, $\frac{a}{2}(\hat{x}-\hat{y}+\hat{z})$, $\frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$
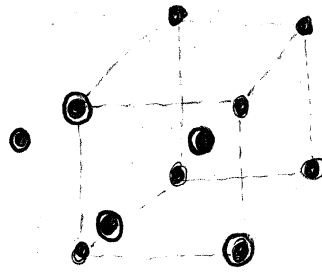
  - face centered cubic lattice $^{(fcc)} \longrightarrow$ spanned by $\frac{a}{2}(\hat{y}+\hat{z})$, $\frac{a}{2}(\hat{x}+\hat{z})$, $\frac{a}{2}(\hat{x}+\hat{y})$

* alternatively one can take $a\hat{x}$, $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$, $a\hat{z}$
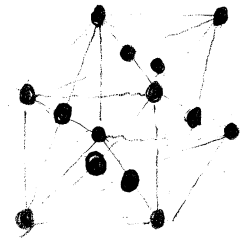
Highlighted are the primitive lattice vectors

simple cubic

body-centered cubic

face-centered cubic

- LATTICE WITH A BASIS (a group of atoms per Bravais lattice point)

The position of the atoms is then specified by:

$$R_{\vec{n}, \vec{\tau}} = \vec{R}_{\vec{n}} + \vec{\tau}$$

with $\vec{\tau}$ the position of a basis atom relative to the Bravais lattice point $\vec{R}_{\vec{n}}$.

- bcc can be seen as a simple cubic lattice with a two point basis:

$$\vec{R}_{\vec{n}} = n_1 a\hat{x} + n_2 a\hat{y} + n_3 a\hat{z}$$
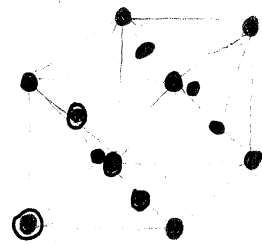$$\{\vec{\tau}\} = \{0, \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})\}$$

Highlighted the basis atoms

- fcc can be seen as a simple cubic lattice with a four point basis:

$$\vec{R}_{\vec{n}} = n_1 a\hat{x} + n_2 a\hat{y} + n_3 a\hat{z}$$
$$\{\vec{\tau}\} = \{0, \frac{a}{2}(\hat{x}+\hat{y}), \frac{a}{2}(\hat{y}+\hat{z}), \frac{a}{2}(\hat{x}+\hat{z})\}$$

Highlighted are the basis atoms
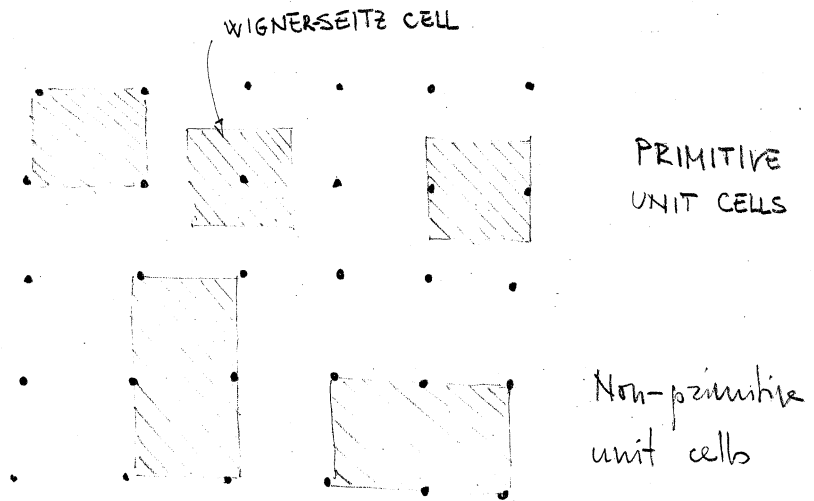
1.

3. UNIT CELLS

i) $\boxed{\text{Primitive (unit) cell}}$ is a volume of space that, when translated by __all__ lattice vectors just fills all space without overlapping itself or leaving voids.

=> one primitive cell contains one Bravais lattice point

ii) $\boxed{\text{Unit cell}}$ is a volume of space that just fills the space without overlapping or voids when translated through some __subset__ of lattice vectors.

iii) $\boxed{\text{Wigner-Seitz cell}}$ is the primitive unit cell closest to a given Bravais lattice point

Example:

WIGNERSEITZ CELL

PRIMITIVE UNIT CELLS

Non-primitive unit cells

4. RECIPROCAL SPACE (RS)

Working with periodic structures it is often convenient to Fourier transform from the direct space to the k-space, also known as the RECIPROCAL SPACE.

- Reciprocal lattice (RL) is the set of points $\vec{G}$ in reciprocal space fulfilling the relation

$$e^{i\vec{G}\cdot\vec{R}} = 1 \quad \forall \ \vec{R} \in \text{Bravais lattice.}$$

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- Reciprocal lattice basis vectors:

$$\vec{G}_m = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \qquad (2.4)$$

m_i are integers and $\vec{b}_j$ is defined by $\qquad \vec{a}_i \cdot \vec{b}_j = 2\pi \, \delta_{ij}$ (2.5)

From the equation (2.5) one obtains the construction:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{a_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)} \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

- First Brillouin zone (1stBZ) is the Wigner-Seitz primitive cell of the reciprocal space with respect to $\vec{G} = 0$.

$$1\text{st BZ} \equiv \left\{ \vec{k} \in RS \text{ such that } |\vec{k}| < |\vec{k} - \vec{G}| \quad \forall \, \vec{G} \neq 0 \right\}$$

$$\Rightarrow \forall \, \vec{q} \in RS \quad \exists! \, \vec{k} \in 1\text{st BZ} \text{ such that } \vec{q} = \vec{k} + \vec{G} \qquad \vec{G} \in RL$$

- Any periodic function in the lattice can be written in terms of its Fourier components on the reciprocal lattice

$$V(\vec{r}) = V(\vec{r} + \vec{R}) \quad \forall \, \vec{R} \quad \Rightarrow \quad V(\vec{r}) = \sum_{\vec{G} \in RL} \tilde{v}(\vec{G}) \, e^{i \vec{G} \cdot \vec{r}} \qquad (2.6)$$

(see Exercise 2 of Sheet 1)

Bloch theorem

The electronic problem for a single electron is described by:

$$\begin{cases} \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = \varepsilon \, \psi(\vec{r}) \qquad (2.7) \\[2mm] V(\vec{r} + \vec{R}) = V(\vec{r}) \end{cases}$$

$\leftarrow$ invariance of the potential generated by the ions with respect to translation of a generic Bravais lattice vector $\vec{R}$.

$\hat{h} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$ is the single particle electronic hamiltonian.

Let us then introduce the translation operator $\hat{T}_{\vec{R}}$ such that

$$\hat{T}_{\vec{R}} \, \phi(\vec{r}) = \phi(\vec{r} - \vec{R}) \qquad \forall \phi \qquad (2.8)$$

- Any operator $\hat{T}_{\vec{R}}$ commutes with $\hat{h}$: $[\hat{T}_{\vec{R}}, \hat{h}] = 0$

proof: $\hat{T}_{\vec{R}} \, \hat{h} \, \phi(\vec{r}) = \hat{T}_{\vec{R}} \left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \phi(\vec{r}) =$

$$= \left[\frac{\hat{p}^2}{2m} + V(\vec{r} - \vec{R}) \right] \phi(\vec{r} - \vec{R}) =$$

$$= \left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \phi(\vec{r} - \vec{R}) = \hat{h} \, \hat{T}_{\vec{R}} \, \phi(\vec{r}) .$$

- The translation operators also commute among each other

$$[\hat{T}_{\vec{R}}, \hat{T}_{\vec{R}'}] = 0 \qquad \text{since} \qquad \hat{T}_{\vec{R}} \, \hat{T}_{\vec{R}'} = \hat{T}_{\vec{R} + \vec{R}'} . \qquad (2.9)$$

proof: $\hat{T}_{\vec{R}} \left[\hat{T}_{\vec{R}'} \, \phi(\vec{r}) \right] = \hat{T}_{\vec{R}} \, \phi(\vec{r} - \vec{R}') = \phi(\vec{r} - \vec{R}' - \vec{R}) = \hat{T}_{\vec{R} + \vec{R}'} \, \phi(\vec{r})$

$\Rightarrow [\hat{T}_{\vec{R}}, \hat{T}_{\vec{R}'}] = 0$ relies on the commutativity of the sum in a vector space.

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- We can find simultaneous eigenfunctions of $\hat{h}$ and $\hat{T}_R$

$$\hat{h}\,\psi(\vec{r}) = \varepsilon\,\psi(\vec{r}) \quad \text{and} \quad \hat{T}_{\vec{R}}\,\psi(\vec{r}) = C(\vec{R})\,\psi(\vec{r})$$

Moreover, from (2.9) it follows that $\quad C(\vec{R})\,C(\vec{R}') = C(\vec{R}+\vec{R}')$ $\qquad$ (2.10)

A more explicit form of $C(\vec{R})$ is obtained from the normalization condition

$$1 = \int_V d\vec{r}\,|\psi(\vec{r})|^2 = \int_V d\vec{r}\,|\psi(\vec{r}-\vec{R})|^2 = \int d\vec{r}\,|C(\vec{R})|^2|\psi(\vec{r})|^2 = |C(\vec{R})|^2$$

change of variables on a volume V with
periodic boundary conditions

$$\Rightarrow \quad C(\vec{R}) = e^{-i\varphi_{\vec{R}}} \quad \text{but due to (2.10)} \quad \varphi_{\vec{R}} + \varphi_{\vec{R}'} = \varphi_{\vec{R}+\vec{R}'}$$

Since $\varphi_{\vec{R}}$ is a linear function $\mathbb{R}^3 \to \mathbb{R} \Rightarrow \exists!\,\vec{k}\;\;\varphi_{\vec{R}} = \vec{k}\cdot\vec{R}$

$$\boxed{\psi(\vec{r}-\vec{R}) = e^{-i\vec{k}\cdot\vec{R}}\,\psi(\vec{r})} \qquad (2.11)$$

Eq. (2.11) represents the <u>first formulation</u> of <u>Bloch theorem</u>: the eigenfunctions of an Hamiltonian with periodic potential are quasi-periodic wave functions such that $\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$ where $\vec{R}$ is such that $N(\vec{r}+\vec{R}) = N(\vec{r})$.

Since $\vec{k}$ characterizes (often not completely) the eigenfunction ψ, we will write $\psi_{\vec{k}}(\vec{r})$.

If we introduce now the function $u_{\vec{k}}(\vec{r})$ also called the Bloch factor

$$u_{\vec{k}}(\vec{r}) = \sqrt{V}\,e^{-i\vec{k}\cdot\vec{r}}\,\psi_{\vec{k}}(\vec{r}), \qquad (2.12)$$

with V the volume of the crystal, we can prove easily that $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$.

We obtain the 2nd formulation of Bloch theorem:

The eigenfunctions of an Hamiltonian with a periodic potential $V(\vec{r}+\vec{R})$ = $V(\vec{r})$ $\forall \vec{r} \in \mathbb{R}^3$ are the product of a plane wave and a function with the same periodicity of the potential $\Rightarrow$ Bloch functions are delocalized.

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

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

(2.13)

- Which are the allowed values of $\vec{k}$?

Consider a crystal with length $L_i = N_i |\vec{a}_i|$ in the ith direction. Periodic boundary conditions impose

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

(2.14)

which, together with (2.11) result into the equations

$$e^{i\vec{k}\cdot N_i \vec{a}_i} = 1$$

(2.15)

The solution of (2.15) reads:

$$\vec{k} = \sum_i \frac{n_i}{N_i} \vec{b}_i$$

(2.16)

where $\{\vec{b}_i\}$ are the reciprocal lattice basis vectors defined by the relation $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$ and n_i are integer numbers.

- How many inequivalent $\vec{k}$ are there?

From eq. (2.11) we know that a Bloch function can be characterized by its response to the Translation operator $\hat{T}_R$.

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In this respect let us consider $\psi_{\vec{k}}$ and $\psi_{\vec{k}+\vec{b}_i}$. It follows from (2.11) that

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

$$\psi_{\vec{k}+\vec{b}_i}(\vec{r}-\vec{R}) = e^{-i(\vec{k}+\vec{b}_i)\cdot\vec{R}} \, \psi_{\vec{k}+\vec{b}_i}(\vec{r}) = e^{-i\vec{k}\cdot\vec{R}} \, \psi_{\vec{k}+\vec{b}_i}(\vec{r})$$

$\Rightarrow$ the two functions are reacting in the same way to translation. $\vec{k}+\vec{b}_i$ is not a good quantum number. It follows immediately that $\vec{k}$ can only belong to the 1st BZ. Correspondingly n_i can only take N_i values (e.g $n_i \in \{0, 1, ..., N_i-1\}$. The total number of allowed moments is thus

$$N_1 N_2 N_3 = N_{cell}, \quad \text{i.e the number of unit cells of the finite crystal}$$

• Electronic bands

Starting from the SE for ψ we can write a differential equation for the "Bloch factor" $u_{\vec{k}}(\vec{r})$

$$\hat{h} \sqrt{V} \, \psi_{\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right) e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k}) e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

By application of the ∇^2 to the product function $e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

$$-\frac{\hbar^2}{2m} e^{i\vec{k}\cdot\vec{r}} \left(-k^2 + 2i\vec{k}\cdot\vec{\nabla} + \nabla^2\right) u_{\vec{k}}(\vec{r}) + V(\vec{r}) e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k}) e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

In more compact form:

$$\left[\frac{\hbar^2}{2m}\left(-i\vec{\nabla} + \vec{k}\right)^2 + V(\vec{r})\right] u_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k}) u_{\vec{k}}(\vec{r}) \qquad (2.18)$$

$\vec{k}$ is a parameter in (2.18). Because of the periodicity of $u_{\vec{k}}(\vec{r})$ one must solve a boundary problem at the boundary of the

unit cell. Thus, at fixed $\vec{k}$ one expects discrete eigenvalues $\mathcal{E}_n(\vec{k})$ and associated eigenfunctions $u_{n\vec{k}}(\vec{r})$.

$$\begin{cases} \mathcal{E}_n(\vec{k}) \longrightarrow \text{electronic bands} \\[2ex] \psi_{n\vec{k}}(\vec{r}) \longrightarrow \text{quasi-periodic wave functions} \end{cases}$$

represent the solutions of the SE (2.7).

The eigenfunctions $u_{n\vec{k}}(\vec{r})$ can be orthonormalized on the primitive unit cell

$$\frac{1}{V_{cell}} \int_{V_{cell}} d\vec{r}\, u^*_{n\vec{k}}(\vec{r})\, u_{n'\vec{k}}(\vec{r}) = \delta_{nn'} \qquad (2.19)$$

Moreover, since $u_{n\vec{k}}(\vec{r})$ are eigenfunctions of the effective hermitian Hamilton operator $\frac{\hbar^2}{2m}\left(-i\vec{\nabla}+\vec{k}\right)^2 + \sigma(\vec{r})$, they fulfil the completeness relation

$$\sum_n u^*_{n\vec{k}}(\vec{r})\, u_{n\vec{k}}(\vec{r}') = V_{cell}\, \delta(\vec{r}-\vec{r}') \quad (2.20) \quad \forall\, \vec{k} \in \text{1st BZ}$$

Eventually one obtains, for the Bloch states

$$= u^*_{n\vec{k}}(\vec{r})\,u_{n'\vec{k}'}$$

$$\int_V d\vec{r}\, \psi^*_{n\vec{k}}(\vec{r})\, \psi_{n'\vec{k}'}(\vec{r}) = \frac{1}{V} \sum_{\vec{R}} \int_{V_{cell}} d\vec{r}\, e^{-i\vec{k}\cdot(\vec{r}-\vec{R}) + i\vec{k}'(\vec{r}-\vec{R})} \overbrace{u^*_{n\vec{R}}(\vec{r}-\vec{R})\,u_{n'\vec{k}'}(\vec{r}}$$

$$= \underbrace{\frac{1}{N_{cell}} \sum_{\vec{R}} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}}_{\delta_{\vec{k}\vec{k}'}}\, \frac{1}{V_{cell}} \int_{V_{cell}} d\vec{r}\, e^{-i(\vec{k}-\vec{k}')\vec{r}}\, u^*_{n\vec{k}}(\vec{r})\, u_{n'\vec{k}'}(\vec{r})$$

$$= \delta_{\vec{k},\vec{k}'}\, \delta_{nn'}. \qquad (2.20)$$

2.3 Wannier functions

Similar to plane waves also Bloch functions are delocalized. One can however build an orthonormal basis of localized states called Wannier basis. It is defined as:

$$\mathcal{W}_n(\vec{r}, \vec{R}) = \mathcal{W}_n(\vec{r} - \vec{R}) := \langle \vec{r} | n\vec{R} \rangle = \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{k} \in 1stBZ} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) . \qquad (2.21)$$

thanks to Bloch theorem.

Notice that $N_{cell} = N_{atom}$ only for a monoatomic Bravais lattice. In that case we can also substitute $\vec{R}$ with $\vec{R}_\alpha =$ ion position (in equilibrium)

Eq. (2.21) can be seen as a sort of Fourier transformation from the reciprocal to the direct space.

It holds:

$$\int d\vec{r} \; \mathcal{W}_n^*(\vec{r} - \vec{R}_1) \mathcal{W}_m(\vec{r} - \vec{R}_2) = \frac{1}{N_{cell}} \sum_{\vec{k}_1, \vec{k}_2 \in 1stBZ} e^{i(\vec{k}_1\cdot\vec{R}_1 - \vec{k}_2\cdot\vec{R}_2)} \underbrace{\int d\vec{r} \; \psi_{n\vec{k}_1}^*(\vec{r}) \psi_{m\vec{k}_2}(\vec{r})}_{\delta_{nm} \delta_{\vec{k}_1, \vec{k}_2}}$$

$$= \delta_{nm} \frac{1}{N_{cell}} \sum_{\vec{k} \in 1stBZ} e^{i\vec{k}\cdot(\vec{R}_1 - \vec{R}_2)} = \delta_{nm} \delta_{\vec{R}_1, \vec{R}_2} . \qquad (2.22)$$

which proves the orthogonality of the Wannier functions. Viceversa one can express the Bloch functions as linear combinations of Wannier functions:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \mathcal{W}_n(\vec{r} - \vec{R}) \qquad (2.23)$$

It is interesting to write the Hamilton operator in the Wannier basis.

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The generic matrix elements reads:

$$\langle n\vec{R} | \hat{h} | n'\vec{R}' \rangle \equiv \int d\vec{r}\; W_n^*(\vec{r}-\vec{R}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] W_{n'}(\vec{r}-\vec{R}') \qquad (2.24)$$

- The elements with $n \neq n'$ vanish as it can be easily proven by transforming (2.24) to the Bloch basis

- $\langle n\vec{R} | \hat{h} | n\vec{R} \rangle = E_n$ independent of $\vec{R}$. $\qquad (2.25)$

proof

$$\langle n\vec{R} | \hat{h} | n\vec{R} \rangle = \int_V d\vec{r}\; W_n^*(\vec{r}-\vec{R}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] W_n(\vec{r}-\vec{R})$$

$$T_{\vec{R}'}\, W_n(\vec{r}-\vec{R}) = W_n(\vec{r}-\vec{R}-\vec{R}') = \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{k}\in 1^{st} BZ} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}-\vec{R}') =$$

$$= \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{k}\in 1^{st}BZ} e^{-i\vec{k}\cdot(\vec{R}+\vec{R}')} \psi_{n\vec{k}}(\vec{r})$$

$$\langle n\vec{R} | \hat{h} | n\vec{R} \rangle = \int_V d\vec{r}\; W_n^*(\vec{r}-\vec{0}) \left[-\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r}+\vec{R})}_{=V(\vec{r})} \right] W_n(\vec{r}-\vec{0}) = \langle n\vec{0} | \hat{h} | n\vec{0} \rangle$$

- $\langle n\vec{R} | \hat{h} | n\vec{R}' \rangle = \int_V d\vec{r}\; W_n^*(\vec{r}-\vec{R})\, V(\vec{r})\, W_n(\vec{r}-\vec{R}') \qquad \vec{R} \neq \vec{R}'$

proof

$$0 = \int d\vec{r}\; W_n^*(\vec{r})\, W_n(\vec{r}-\vec{R}) \qquad \text{orthogonality of the Wannier fun.}$$

But $W_n(\vec{r}-\vec{R}) = e^{-i\frac{\hat{p}\cdot\vec{R}}{\hbar}} W_n(\vec{r}) \;\Rightarrow\; -\frac{\hbar^2}{2m}\nabla_{\vec{R}}^2\, W_n(\vec{r}-\vec{R})$

$$= \frac{\hat{p}^2}{2m}\, W_n(\vec{r}-\vec{R})$$

In conclusion $\quad 0 = -\frac{\hbar^2}{2m}\nabla_{\vec{R}}^2 \int W_n^*(\vec{r})\, W_n(\vec{r}-\vec{R}) = \langle n\vec{0} | \frac{\hat{p}^2}{2m} | n\vec{R} \rangle$ ∎

2c

- $\langle n\vec{R} | \hat{h} | n\vec{R}' \rangle = \gamma_n(\vec{R} - \vec{R}')$ (2.26)

<u>proof</u>

$$\int_V d\vec{r}\; \mathcal{W}_n^*(\vec{r} - \vec{R}) \; \mathcal{V}(\vec{r}) \mathcal{W}_n(\vec{r} - \vec{R}') = \qquad \vec{s} = \vec{r} - \vec{R}'$$

$$\int_V d\vec{s}\; \mathcal{W}_n^*(\vec{s} + \vec{R}' - \vec{R}) \; \mathcal{V}(\vec{s} + \vec{R}') \mathcal{W}_n(\vec{s}) =$$

$$= \int_V d\vec{r}\; \mathcal{W}_n^*[\vec{r} - (\vec{R} - \vec{R}')] \; \mathcal{V}(\vec{r}) \mathcal{W}_n(\vec{r})$$

Eventually one obtains:

$$\hat{h} = \sum_{n\vec{R}} E_n |n\vec{R}\rangle\langle n\vec{R}| + \sum_{n, \vec{R} \neq \vec{R}'} \gamma_n(\vec{R} - \vec{R}') |n\vec{R}\rangle\langle n\vec{R}'| . \qquad (2.27)$$

Since $\gamma_n(\vec{R} - \vec{R}')$ represents the tunnelling amplitude between the localized state $|n\vec{R}'\rangle$ and the one $|n\vec{R}\rangle$, one refers to it as the hopping term. E_n is instead the on-site energy. $\hat{h}$ is diagonal in the Bloch basis. One obtains:

$$\boxed{\varepsilon_n(\vec{k}) = E_n + \sum_{\vec{R} \neq 0} \gamma_n(\vec{R}) \, e^{-i\vec{k}\cdot\vec{R}}} \qquad (2.28)$$

<u>proof</u>

$$\varepsilon_n(\vec{k}) = \langle n\vec{k}| \hat{h} | n\vec{k}\rangle = \frac{1}{N_{cell}} \sum_{\vec{R}\vec{R}'} e^{-i\vec{k}(\vec{R} - \vec{R}')} \langle n\vec{R}| \hat{h} | n\vec{R}'\rangle$$

$$\overset{(2.28)}{=} \frac{1}{N_{cell}} \sum_{\vec{R}} \left[E_n + \sum_{\vec{R}' \neq \vec{R}} \underbrace{\gamma_n(\vec{R} - \vec{R}')}_{= \vec{R}''} e^{-i\vec{k}\cdot(\vec{R} - \vec{R}')} \right] =$$

$$= E_n + \sum_{\vec{R}'' \neq 0} \gamma_n(\vec{R}'') \, e^{-i\vec{k}\cdot\vec{R}''}$$