

Construction of exponentially localized Wannier orbitals for periodic systems

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Bloch orbitals

The electronic ground state of a **periodic system** is usually described in terms of **Bloch orbitals**, *i.e.* simultaneous (generalized) eigenfunctions of the **periodic 1-particle Hamiltonian**

$$H_{\text{per}} = -\Delta + V_{\Gamma}$$

where

$$V_{\Gamma}(x + \gamma) = V_{\Gamma}(x), \quad \text{for all } \gamma \in \Gamma = \text{Span}_{\mathbb{Z}}(e_1, \dots, e_d) \cong \mathbb{Z}^d,$$

and of the **lattice translations** $\{T_{\gamma}\}_{\gamma \in \Gamma}$

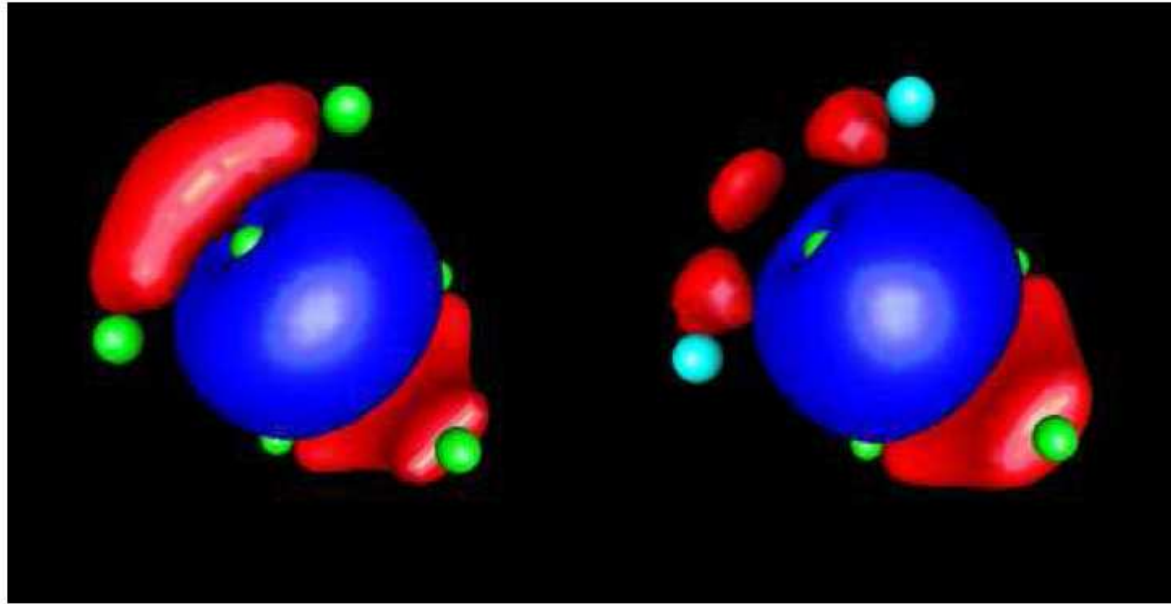
$$(T_{\gamma}\psi)(x) = \psi(x - \gamma).$$

While convenient for many purposes, these orbitals have the disadvantage that are **not localized in position space**.

... and Wannier orbitals

An alternative representation in terms of **localized orbitals** has been introduced by **Gregory Wannier** in 1937. The main advantage of this approach is that Wannier functions are **localized in position space**. Thus

- (i) they provide an intuitive (visual) insight into the **structure of chemical bonds** in crystals



Amplitude **isosurface contours** for maximally-localized Wannier functions in **Si** (left panel) and **GaAs** (right panel). Red and blue contours are for isosurfaces of identical absolute value but opposite signs; Si and As atoms are in green, Ga in cyan. Notice that **breaking of inversion symmetry** in GaAs polarizes the WFs towards the more electronegative As anion.

(Courtesy of N. Marzari, I. Souza and D. Vanderbilt)

... and Wannier orbitals

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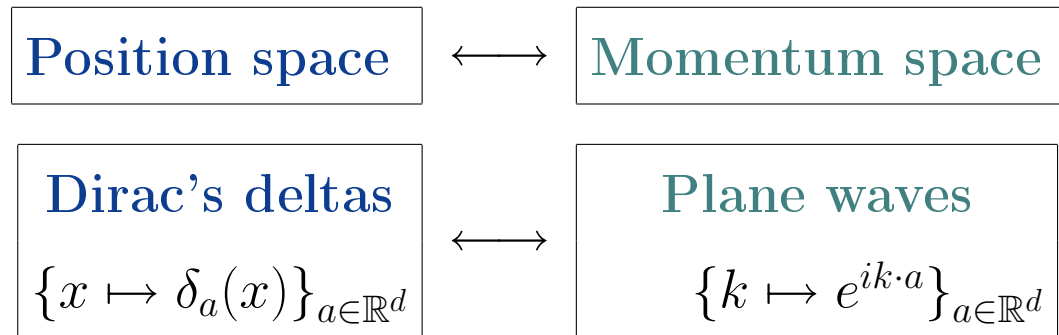
... and Wannier orbitals

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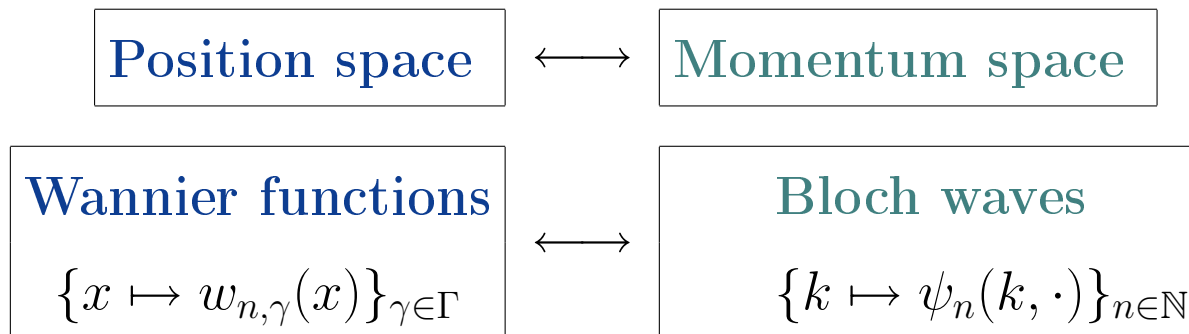
- (i) they provide an intuitive (visual) insight into the **structure of chemical bonds** in crystals
- (ii) suitable to use **linear scaling methods** [tutorial by Meza][Marzari, Souza and Vanderbilt]
- (iii) they are convenient for the **modern theory of polarization** (piezoelectricity) of crystalline solids [King-Smith & Vanderbilt, Resta].

All these advantages rely on the idea that the Wannier functions are indeed **exponentially localized**. **Is this always the case? Is there an algorithm to obtain them?**

For **constant coefficients** differential operators one exploits the duality



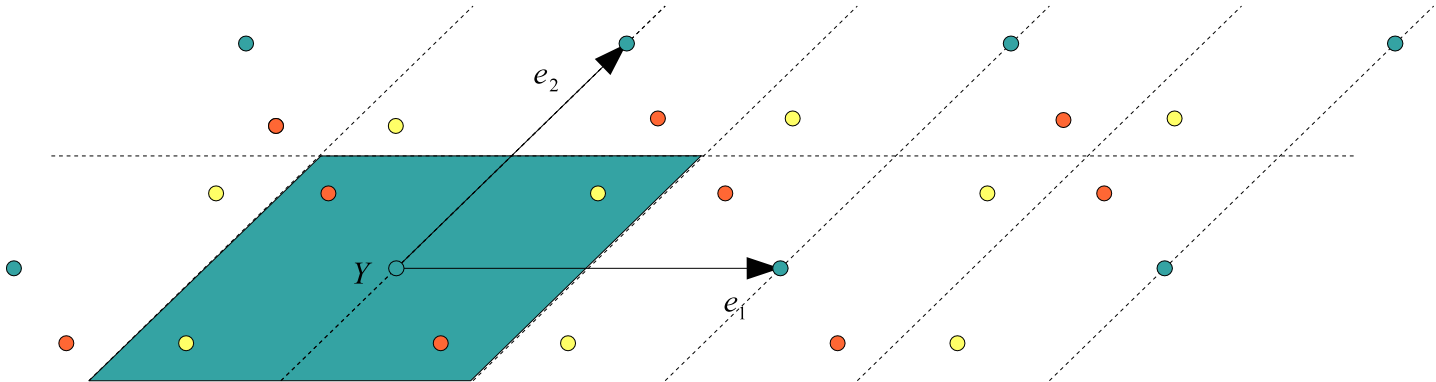
As far as differential operators with **periodic coefficients** are concerned



I

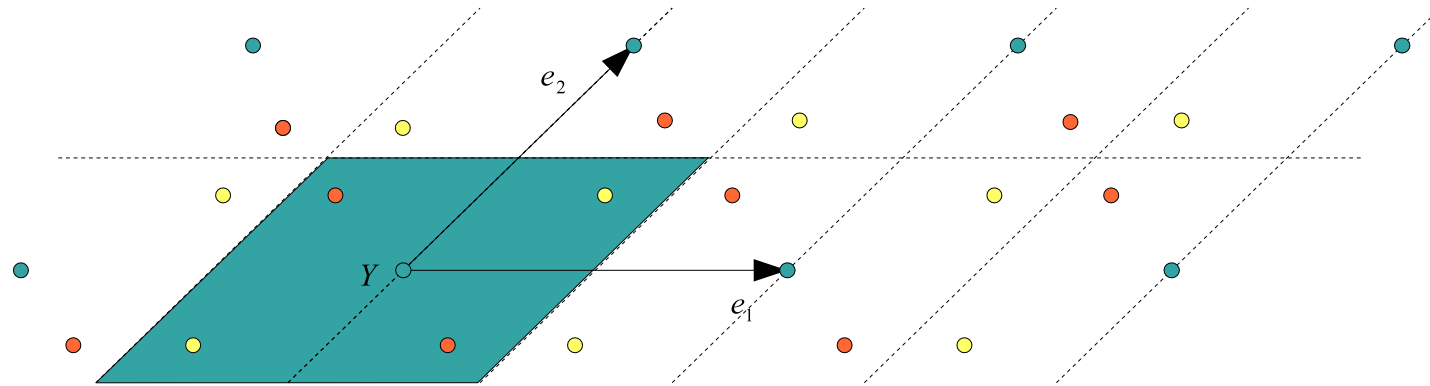
Periodic systems and
Bloch-Floquet transform

The Bloch-Floquet transform



	Configuration space	Momentum space
Lattice	Γ	Γ^*
Fundamental domain	Y	\mathbb{B}
	$\mathbb{T}_Y^d = \mathbb{R}^d / \Gamma$	$\mathbb{T}^* = \hat{\mathbb{R}}^d / \Gamma^*$
Hilbert space	$\mathcal{H}_f = L^2(Y)$	

The Bloch-Floquet transform

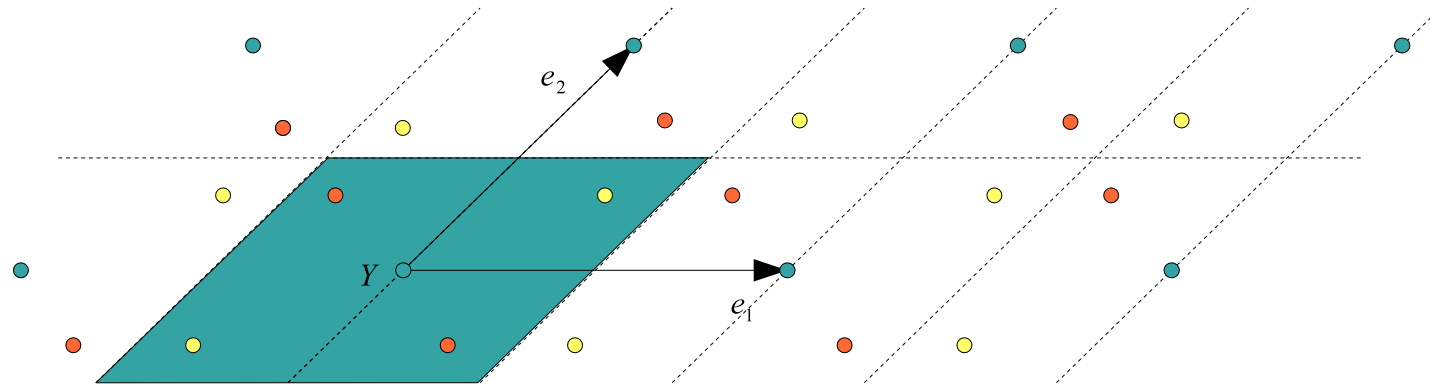


The **Bloch-Floquet transform** is defined as

$$\mathcal{U} : L^2(\mathbb{R}^d) \cong L^2(\Gamma \times Y) \cong \ell^2(\Gamma) \otimes L^2(Y) \xrightarrow{\mathcal{F} \otimes 1} L^2(\mathbb{T}^*) \otimes L^2(Y)$$

$$(\mathcal{U}\psi)(k, y) = \sum_{\gamma \in \Gamma} e^{-i\gamma \cdot k} \psi(y + \gamma), \quad k, y \in \mathbb{R}^d.$$

The Bloch-Floquet transform



The **modified Bloch-Floquet transform** is defined as

$$\tilde{\mathcal{U}} : L^2(\mathbb{R}^d) \longrightarrow L^2(\mathbb{B}) \otimes \underbrace{L^2(\mathbb{T}_y^d)}_{\mathcal{H}_f}$$

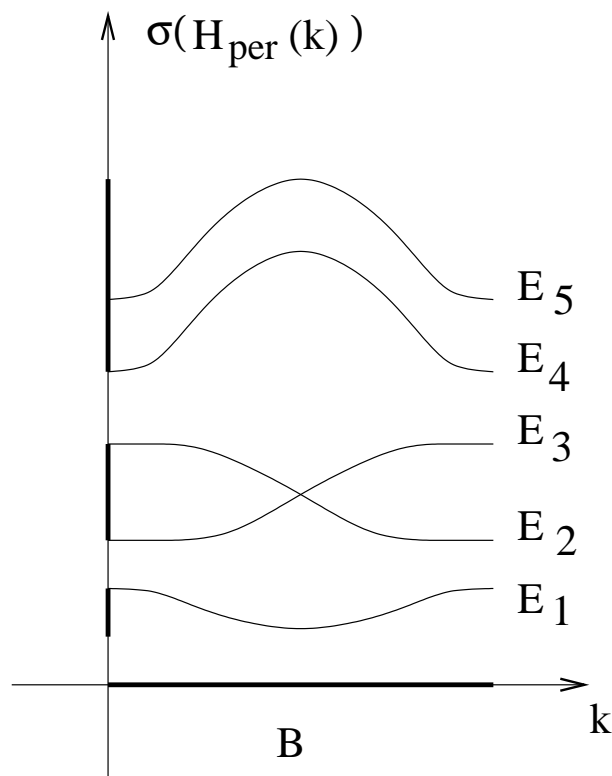
$$(\tilde{\mathcal{U}}\psi)(k, y) = \sum_{\gamma \in \Gamma_0} e^{-i(y+\gamma) \cdot k} \psi(y + \gamma), \quad k, y \in \mathbb{R}^d.$$

In modified BF representation $H = -\Delta + V_\Gamma$ becomes a **fibred operator**

$$\tilde{U} H \tilde{U}^{-1} = \int_{\mathbb{B}}^{\oplus} H_{\text{per}}(k) dk \quad \text{in } L^2(\mathbb{B}, \mathcal{H}_f) \cong L^2(\mathbb{B}) \otimes \mathcal{H}_f,$$

$$H_{\text{per}}(k) = \frac{1}{2}(-i\nabla_y + k)^2 + V_\Gamma(y) \quad \text{acting on } \mathcal{D} \subseteq L^2(\mathbb{T}_Y^d, dy) = \mathcal{H}_f.$$

The band structure:



Solution of the **eigenvalue problem:**

$$H_{\text{per}}(k)u_n(k, y) = E_n(k)u_n(k, y)$$

Eigenvalue: $E_n(k)$

Eigenvector: $u_n(k, \cdot) \in \mathcal{H}_f = L^2(\mathbb{T}_Y^d, dy)$

Eigenprojector: $P_n(k) = |u_n(k)\rangle\langle u_n(k)|$

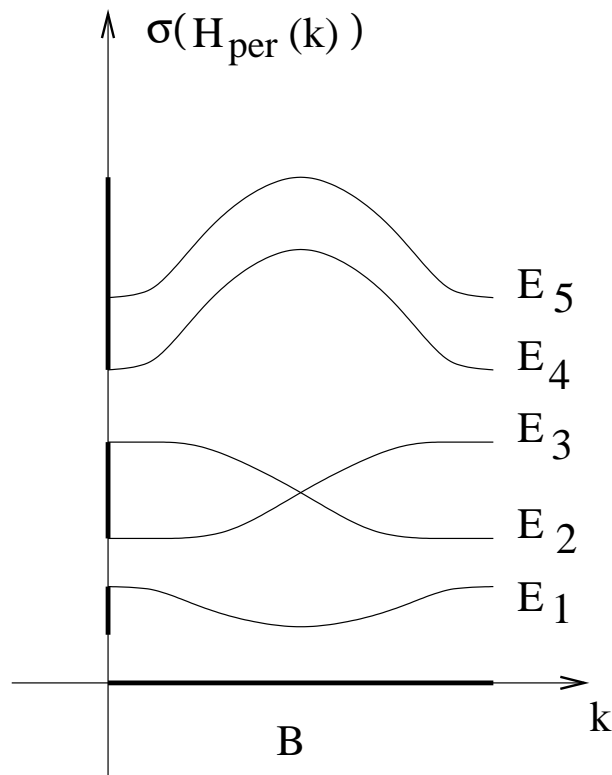
Total projector: $P_n = \{P_n(k)\}_{k \in \mathbb{B}}$

In Bloch-Floquet representation $H = -\Delta + V_\Gamma$ becomes a **fibered operator**

$$\mathcal{U} H \mathcal{U}^{-1} = \int_{\mathbb{B}}^{\oplus} H_{\text{per}}(k) dk \quad \text{in } L^2(\mathbb{T}^*, L^2(Y)) \cong L^2(\mathbb{T}^*) \otimes L^2(Y),$$

$$H_{\text{per}}(k) = -\frac{1}{2}\Delta + V_\Gamma(y) \quad \text{acting on } \mathcal{D}(k) \subseteq L^2(Y, dy).$$

The band structure:



Solution of the **eigenvalue problem:**

$$H_{\text{per}}(k)\varphi_n(k, y) = E_n(k)\varphi_n(k, y)$$

Eigenvalue: $E_n(k)$

Eigenvector: $\varphi_n(k, \cdot) \in \mathcal{D}(k) \subseteq L^2(Y, dy)$

Eigenprojector: $P_n(k) = |\varphi_n(k)\rangle\langle\varphi_n(k)|$

Total projector: $P_n = \{P_n(k)\}_{k \in \mathbb{B}}$

II

Wannier functions:
the single-band approach

Wannier functions and gauge freedom

Let φ_n be a Bloch eigenfunction corresponding to an **isolated band** E_n . Notice that the choice of φ_n is **not unique**, since the function

$$e^{i\vartheta(k)}\varphi_n(k, y)$$

is also an eigenfunction of $H_{\text{per}}(k)$ corresponding to $E_n(k)$ (**Bloch gauge freedom**).

Definition. The **Wannier function** w_n corresponding to the Bloch function φ_n is the preimage of φ_n by the Bloch-Floquet transform, *i.e.*

$$w_n(x) := (\mathcal{U}^{-1}\varphi_n)(x) = \int_{\mathbb{B}} \varphi_n(k, x) d'k, \quad x \in \mathbb{R}^d.$$

- The **translated Wannier functions** are written as

$$w_n(x + \gamma) = \int_{\mathbb{B}} e^{ik \cdot \gamma} \varphi_n(k, x) d'k, \quad \gamma \in \Gamma.$$

- One can easily invert the definition, obtaining

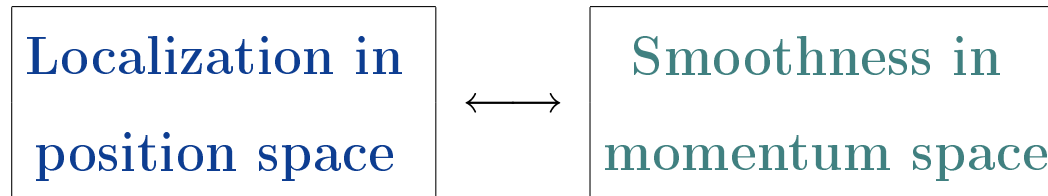
$$\varphi_n(k, x) = \sum_{\gamma \in \Gamma} w_n(x + \gamma) e^{ik \cdot \gamma}.$$

- If the norm $\|\varphi_n(k, \cdot)\|_{L^2(Y)}$ is k -independent, then the functions $\{w_{n,\gamma}\}_{\gamma \in \Gamma}$ are **mutually orthogonal**. Here we posed $w_{n,\gamma}(x) = w_n(x - \gamma)$.
- Under this condition the family $\{w_{n,\gamma}\}_{\gamma \in \Gamma}$ is a **complete orthonormal basis of $\text{Ran } P_n$** .
- If $I_n := \text{Ran } E_n \subset \mathbb{R}$ is **isolated from the rest of the spectrum** of H , then $\text{Ran } P_n$ is the spectral projector of H corresponding to the interval $I_n \subset \mathbb{R}$.

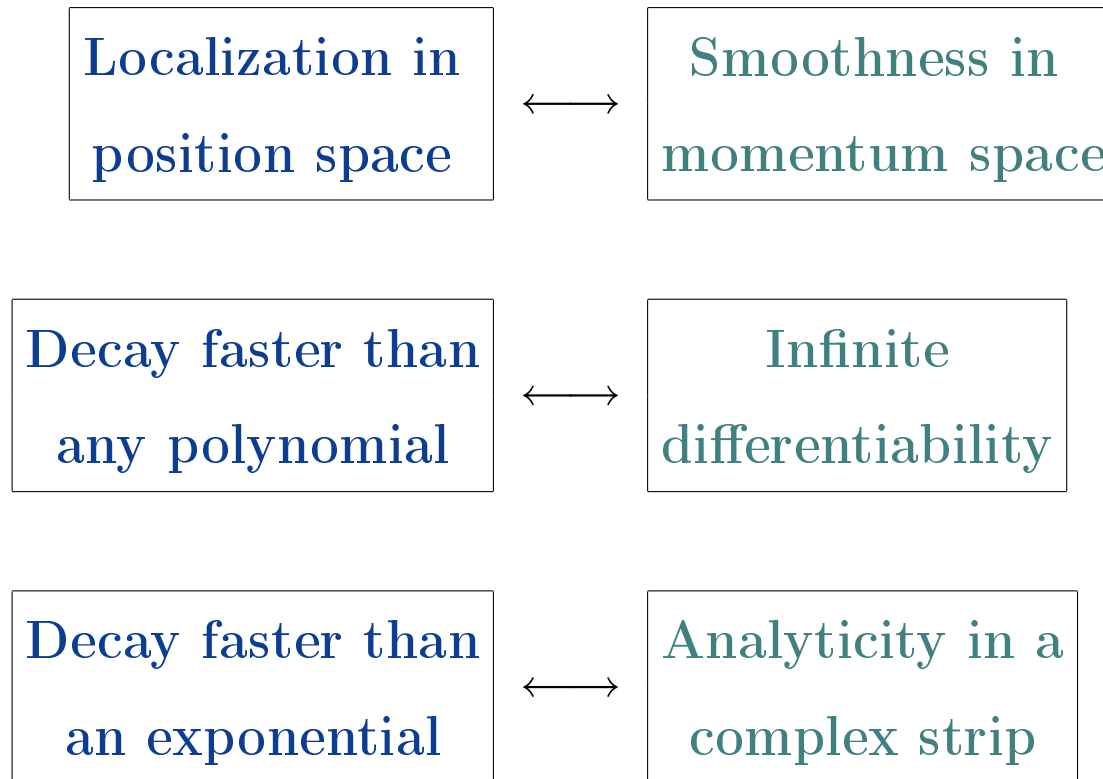
Globally, the family of all Wannier functions $\{w_{n,\gamma}\}_{n \in \mathbb{N}, \gamma \in \Gamma}$ is a **complete orthonormal basis** of $L^2(\mathbb{R}^d)$.

Question (A): to which extent are the Wannier functions **localized**?

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Question (A'): how **smooth** is the Bloch function ?

The question is ill-posed, it crucially **depends on the choice of the phase**.

In numerical simulations the phase is random. Therefore one has to **readjust phases** *a posteriori* in order to obtain reasonably localized Wannier functions.

Question (A''): is it possible to **choose the phase (Bloch gauge)** so that the Wannier functions are **exponentially localized**?

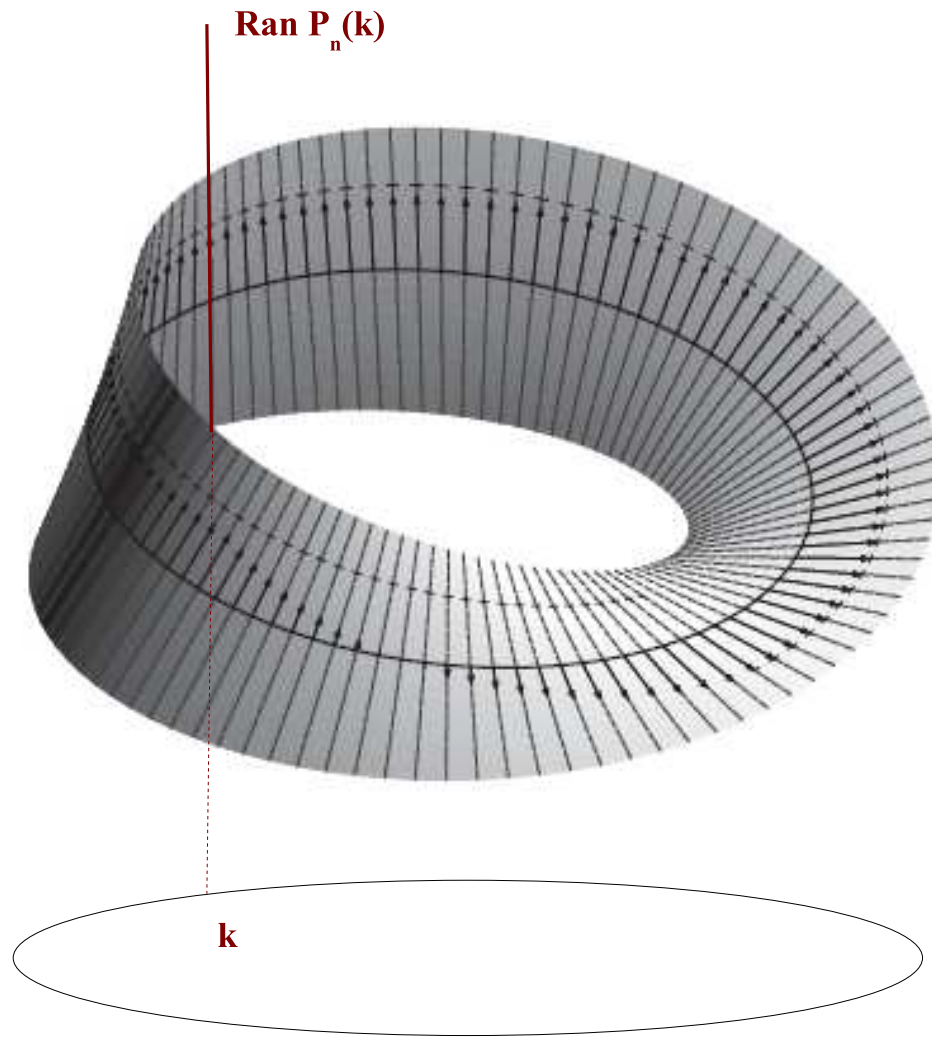
It seems very easy ...

Since the band E_n is assumed to be an **isolated band** one has that

$k \mapsto P_n(k)$ is smooth (analytic in a strip)

$k \mapsto \varphi_n(k, \cdot)$ can be chosen **locally smooth**

... but a **topological obstruction** might appear!!



Answer(A): the answer is positive for an **isolated Bloch band**.

$d = 1$ W. Kohn (1959)

$d > 1$ de Cloiseaux (1964) requiring **space-reflection symmetry**

$d > 1$ G. Nenciu (1983), B. Helffer & J. Sjöstrand (1989).

The result depends crucially on the fact that the Hamiltonian

$$H = -\Delta + V_\Gamma$$

is **real**, *i.e.* the system is **time-reversal symmetric (TR)**.

For a non TR-symmetric operator, *e.g.*

$$H_B = \frac{1}{2} (-i\nabla_x + A_\Gamma(x))^2 + V_\Gamma,$$

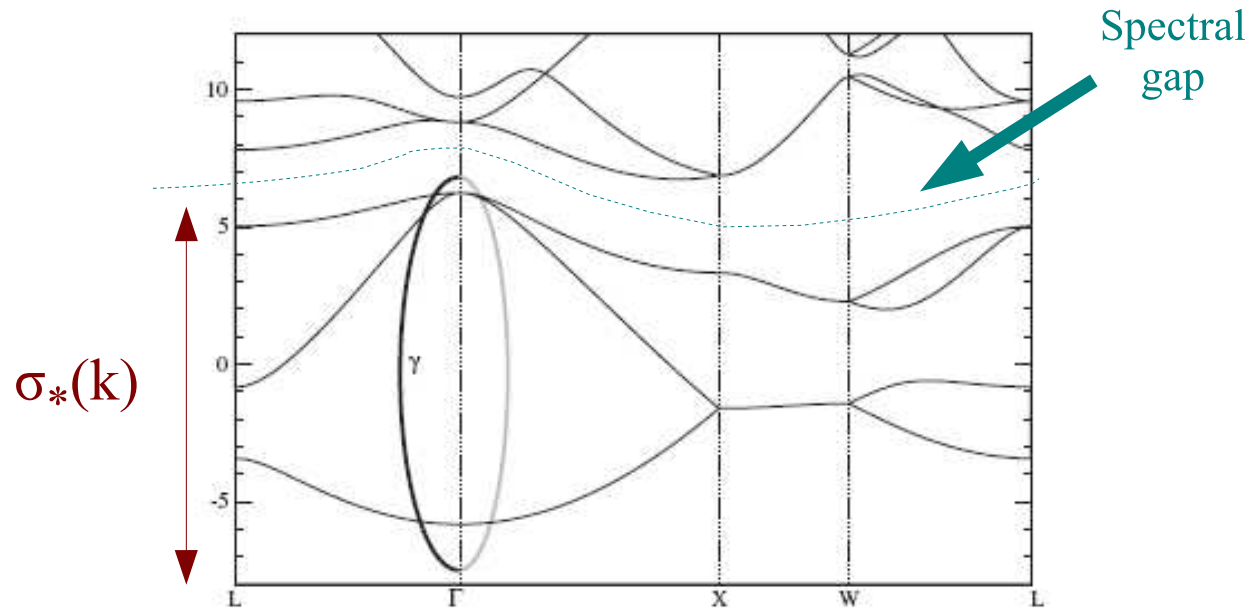
counterexamples appear already for $d = 2$. [Dubrovin, Novikov, Lyskova].

III

Wannier functions:
the multi-band approach

Eigenvalue crossings

In dimension $d = 3$ there are generically **no isolated Bloch bands**.



However, in insulators there is a **spectral gap**. Then it is interesting to consider the family of bands which are below the gap.

Let $\sigma_*(k) \subset \mathbb{R}$ be an interval including at every k the **relevant family of bands**.

The Bloch functions do **not** have a smooth continuation across the **crossing points** (except in dimension $d = 1$). Thus no hope to obtain directly exponentially localized Wannier functions.

Idea (de Cloiseaux): let us consider **the relevant family of bands as a unity**.

Let $P_*(k)$ the orthogonal projector on the relevant family of bands, *i.e.*

$$P_*(k) = \sum_{n: E_n(k) \in \sigma_*(k)} |\varphi_n(k)\rangle\langle\varphi_n(k)|.$$

Definition. A function $k \mapsto \chi(k, \cdot) \in \mathcal{H}_f$ is called a **generalized Bloch function** if

$$P_*(k)\chi(k, \cdot) = \chi(k, \cdot), \quad \chi(k, \cdot) \neq 0.$$

Let $m = \dim \operatorname{Ran} P_*(k)$. A family $\{\chi_a\}_{a=1,\dots,m}$ of generalized Bloch functions which span $\operatorname{Ran} P_*(k)$ at every $k \in \mathbb{B}$ is called a **frame**.

Definition. The **composite Wannier functions** corresponding to a frame $\{\chi_a\}_{a=1,\dots,m}$ are defined as

$$w_a(x) := (\mathcal{U}^{-1}\chi_a)(x), \quad a \in \{1, \dots, m\}.$$

The family $\{w_{a,\gamma}\}_{a=1,\dots,m;\gamma \in \Gamma}$ an **orthonormal basis** of the spectral subspace corresponding to the energy window $\operatorname{Ran} \sigma_*$.

The Bloch gauge freedom

A frame is fixed only up to a k -dependent unitary matrix $U \in \mathcal{U}(C^m)$, i.e.

$$\tilde{\chi}_a(k) = \sum_{b=1}^m U_{a,b}(k) \chi_b(k)$$

is still a frame if $\{\chi_a\}_{a=1,\dots,m}$ it is.

Question (B): is there a choice of **Bloch gauge** which makes the composite Wannier functions **exponentially localized** ?

Question (B'): does exist a family of generalized Bloch functions $k \mapsto \chi_a(k)$

- : (B₀) each map $\chi_a : \mathbb{R}^d \rightarrow \mathcal{H}_f$ is C^∞ -**smooth**;
- : (B₁) the set $\{\chi_a(k)\}_{a=1}^m$ is an (orthonormal) basis **spanning** $\text{Ran}P_*(k)$;
- : (B₂) each map is **periodic**

$$\chi_a(k + \lambda) = \chi_a(k) \quad \forall k \in \mathbb{R}^d, \forall \lambda \in \Lambda.$$

First answer to (B): yes in dimension $d = 1$ [G. Nenciu, 1983].

1. The Marzari-Vanderbilt viewpoint

For any system of composite Wannier functions (w_1, \dots, w_m) one defines the **MV localization functional**,

$$\Omega[w_1, \dots, w_m] := \sum_{a \in \mathcal{I}} \left(\langle w_a, X^2 w_a \rangle - \langle w_a, \vec{X} w_a \rangle^2 \right)$$

where $\vec{X} = (X_1, \dots, X_d)$ is the position operator and $X^2 = \sum_i X_i^2$.

A system of **optimally localized Wannier functions** is the minimizer (assuming it does exist) of $\Omega[w_1, \dots, w_m]$ under the **topological constraint** that

$$\chi_a = \mathcal{U} w_a, \quad a \in \{1, \dots, m\}$$

defines a **frame of generalized Bloch functions**.

Equivalently, in **momentum space** one has to minimize the functional

$$\tilde{\Omega}(\chi_1, \dots, \chi_m) = \sum_{a \in \mathcal{I}} \left(\int d'k \langle \chi_a(k), \vec{\nabla}_k \chi_a(k) \rangle_{\mathcal{H}_f} \right)^2 - \int d'k \langle \chi_a(k), \Delta_k \chi_a(k) \rangle_{\mathcal{H}_f}$$

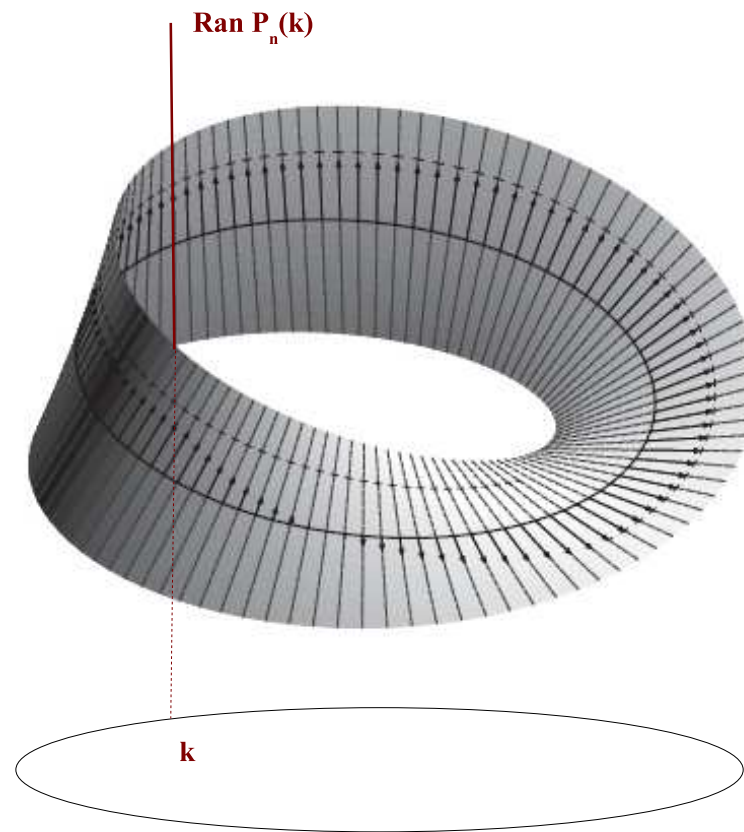
under the constraint that (χ_1, \dots, χ_m) is a **frame**, *i.e.*

- : (B₀) each map $\chi_a : \mathbb{R}^d \rightarrow \mathcal{H}_f$ is C^∞ -**smooth**;
- : (B₁) the set $\{\chi_a(k)\}_{a=1}^m$ is an (orthonormal) basis **spanning** $\text{Ran}P_*(k)$;
- : (B₂) each map is **periodic**

$$\chi_a(k + \lambda) = \chi_a(k) \quad \forall k \in \mathbb{R}^d, \forall \lambda \in \Lambda.$$

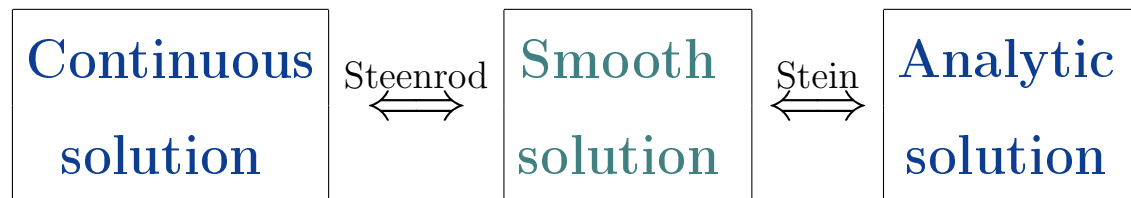
2. The geometric viewpoint

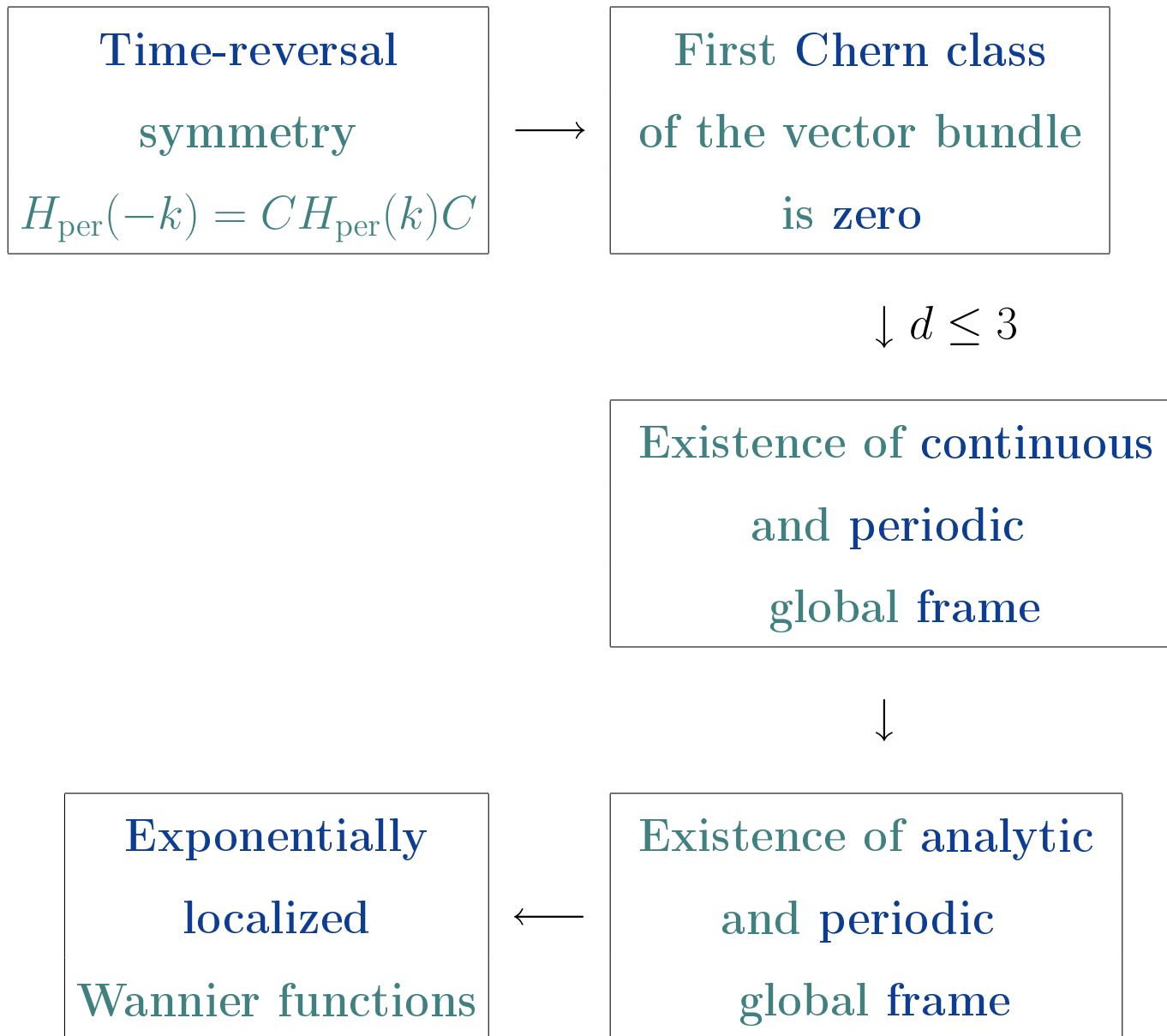
Vision: the problem is equivalent to a geometric one.



2. The geometric viewpoint

Vision: the problem is equivalent to a geometric one. Moreover the **obstruction** might appear **only at the topological level**





Second answer to (B): yes in dimension $d \leq 3$.

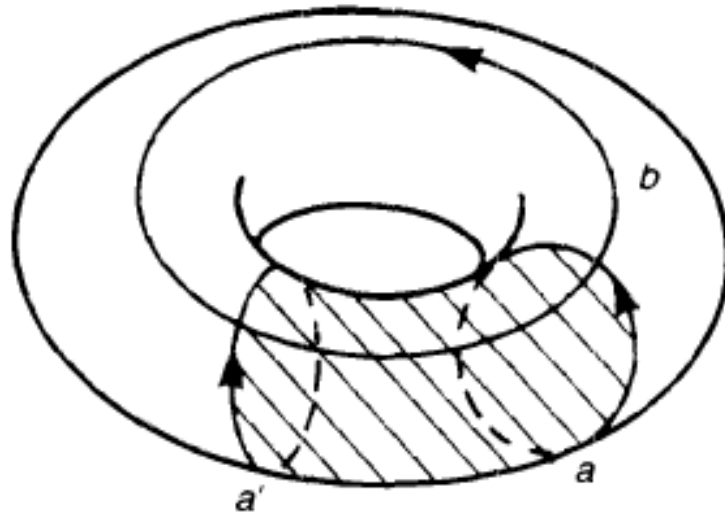
- G. Panati. **Triviality of Bloch and Bloch-Dirac bundles**, Annales Henri Poincaré 8, 995-1011 (2006-7).
- Ch. Brouder, G. Panati, M. Calandra, Ch. Mourougane and N. Marzari. **Exponential localization of Wannier functions in insulators**, Phys. Rev. Lett. **98**, 046402 (2007).
- P. Kuchment. **Tight frames of exponentially decaying Wannier functions**, preprint arXiv:0807

But still the proof is not constructive . . .

3. The constructive viewpoint

Final answer to (B): yes for any $d \in \mathbb{N}$, and a constructive algorithm is provided [Panati, in preparation].

The algorithm starts with the trivial observation that the $(d - 1)$ -dimensional torus can be regarded as the skeleton of the d -dimensional torus, and that it is convenient to construct the frame starting by the **lower dimensional skeleton**.



Preliminary step, $d = 1$. We start by constructing a frame in the 1-dimensional case. Then $k \in \mathbb{R}$ and the fundamental domain \mathbb{B} is identified with the interval $[-\frac{1}{2}, \frac{1}{2}] \subset \mathbb{R}$.

(a) Choose an orthonormal basis $\Phi^{(0)} = (\phi_1^{(0)}, \dots, \phi_m^{(0)})$ of $\text{Ran } P(0)$ such that

$$C\phi_j^{(0)} = \phi_j^{(0)}$$

for every $j \in \{1, \dots, m\}$. Such a choice is always possible since $CP(0) = P(0)C$ in view of time-reversal symmetry.

(b) By using the **Kato-Nagy method** one obtains a local orthonormal frame Φ , defined for $k \in [0, \frac{1}{2}]$, such that $\Phi(0) = \Phi^{(0)}$.

(c) We extend the definition to $k \in \mathbb{B} = [-\frac{1}{2}, \frac{1}{2}]$ by imposing the **time-reversal symmetry**

$$\Phi(-k) = C\Phi(k).$$

This function is continuous over \mathbb{B} in view of the choice (a).

(d) According to the previous construction $\Phi(\pm\frac{1}{2})$ is an orthonormal basis of $\text{Ran } P(\pm\frac{1}{2})$. Since $\text{Ran } P(\frac{1}{2}) = \text{Ran } P(-\frac{1}{2})$ it follows that $\Phi(-\frac{1}{2})$ is an orthonormal basis of $\text{Ran } P(\frac{1}{2})$. These two basis **must be intertwined by a unitary matrix**, i.e. there exists $U \in \mathcal{U}(\mathbb{C}^m)$ such that

$$(1) \quad \phi_a(\frac{1}{2}) = \sum_{b=1}^m U_{a,b} \phi_b(-\frac{1}{2}),$$

which we write shortly in the form $\Phi(\frac{1}{2}) = U \triangleright \Phi(-\frac{1}{2})$. By respectively inverting (1) and applying C to it one obtains that

$$(2) \quad \Phi(-\frac{1}{2}) = U^{-1} \triangleright \Phi(\frac{1}{2}),$$

$$(3) \quad \Phi(-\frac{1}{2}) = \bar{U} \triangleright C \Phi(-\frac{1}{2}) = \bar{U} \triangleright \Phi(\frac{1}{2}),$$

where \bar{U} denotes the conjugate matrix of U . By comparing (2) and (3) we obtain that

$$(4) \quad \bar{U} = U^{-1}, \quad \text{or equivalently} \quad U = U^\top.$$

By comparing (2) and (3) we obtain that

$$(5) \quad \bar{U} = U^{-1}, \quad \text{or equivalently} \quad U = U^\top.$$

In other words, **the time-reversal symmetry forces the unitary matrix U to be symmetric**, thus reducing the dimension of the gauge group. This is a crucial point in the following argument.

(e) Define $\tilde{\Phi} = (\tilde{\phi}_1, \dots, \tilde{\phi}_m)$ by posing

$$\tilde{\phi}_a(k) := \sum_{b=1}^m (\mathbf{U}^{-\mathbf{k}})_{\mathbf{a},\mathbf{b}} \phi_b(k),$$

where the matrix U^α , for $\alpha \in \mathbb{R}$, is constructed by **functional calculus** (*i.e.* diagonalize, compute the power and transform back). By using (1) and (5) one obtains that

$$(i): \tilde{\Phi}(\frac{1}{2}) = \tilde{\Phi}(-\frac{1}{2})$$

$$(ii): C\tilde{\Phi}(k) = \tilde{\Phi}(-k).$$

In view of (i) the function $\tilde{\Phi}$ can be extended to $k \in \mathbb{R}$ by imposing periodicity. From this continuous map one obtains by regularization a smooth map, which provides the required orthonormal frame for $d = 1$.

Inductive step, $d - 1 \Rightarrow d$. You can better read it ...

Conceptually, it uses the **same conceptual ingredients** as the 1-dimensional construction.

**Thank you
for you attention!!**