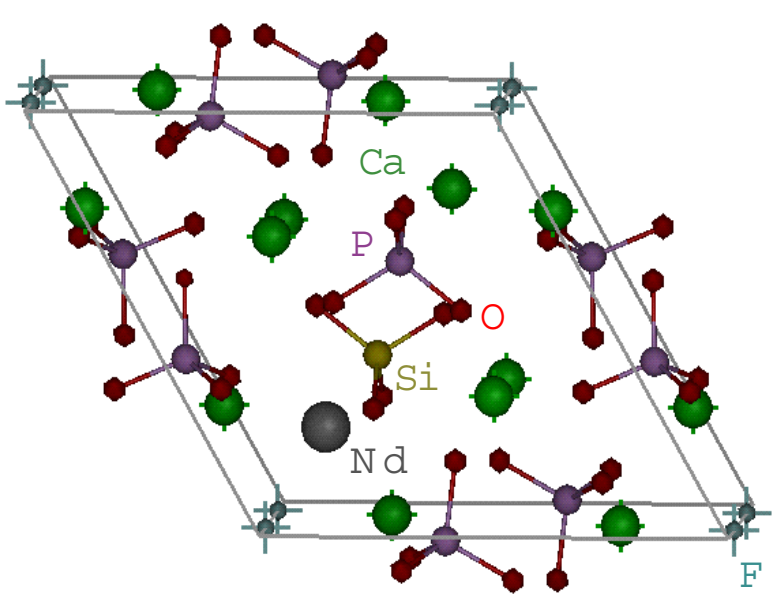
Density Functional Theory for periodic systems

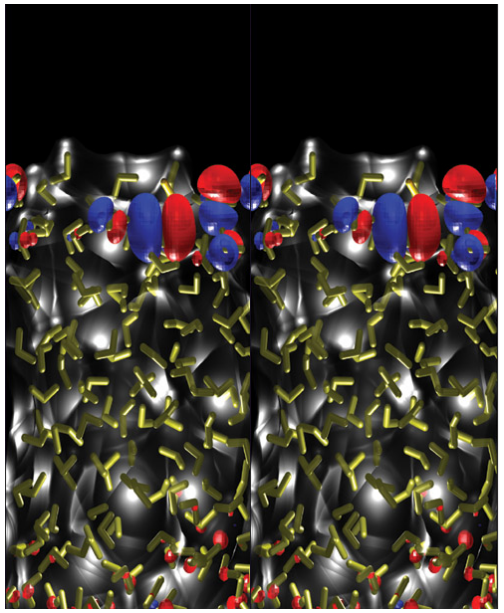
Eric CANCES

CERMICS - ENPC and INRIA

IMA, Minneapolis, July 2007

Crystalline materials vs artificial PBC for the condensed phase





Left: Unit cell of the Britholite crystal $Ca_9Nd(PO_4)_5(SiO_4)F_2$ (from M. Defranceschi, CEA)

Right: Ab initio simulation of aqueous liquid-vapor interface (from Ch. Mundi, Limermore)

1 - One-dimensional periodic Schrödinger operators

- A simple thermodynamic limit argument
- Bloch theorem
- Wannier functions

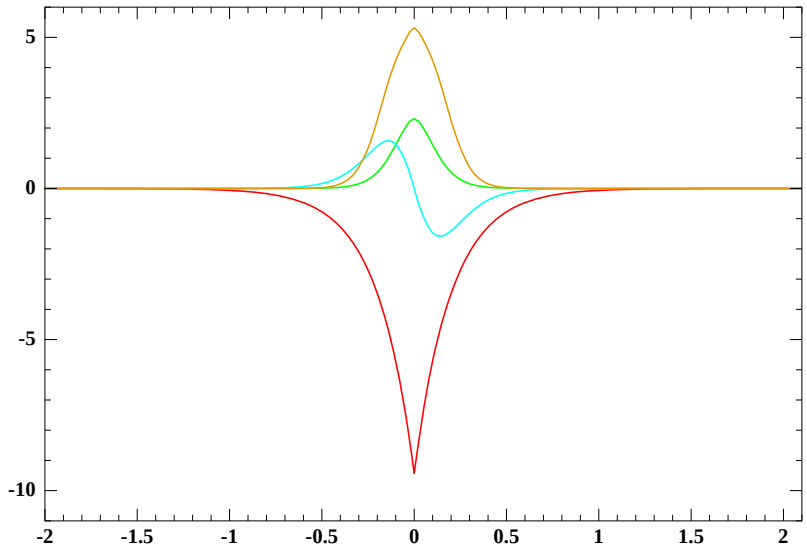
2 - Periodic Kohn-Sham models

- Thermodynamic limit of Kohn-Sham models
- Discretization of periodic Kohn-Sham models
- Pseudopotentials

1 - One-dimensional periodic Schrödinger operators

$M = 1$ **nucleus,** $n_e = 2$ **non-interacting electrons**

$$H^1 = -\frac{1}{2}\frac{d^2}{dx^2} + V \qquad H^1\phi_i^1 = \varepsilon_i^1\phi_i^1 \qquad \varepsilon_1^1 < \varepsilon_2^1 < \varepsilon_3^1 < \cdots$$



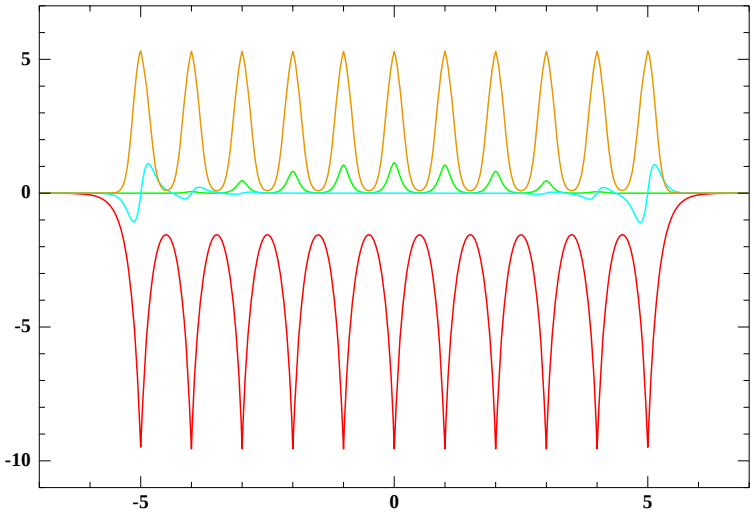
Potential V **(red),** ϕ_1^1 **(green),** ϕ_2^1 **(blue),** ρ_1^0 **(yellow)**

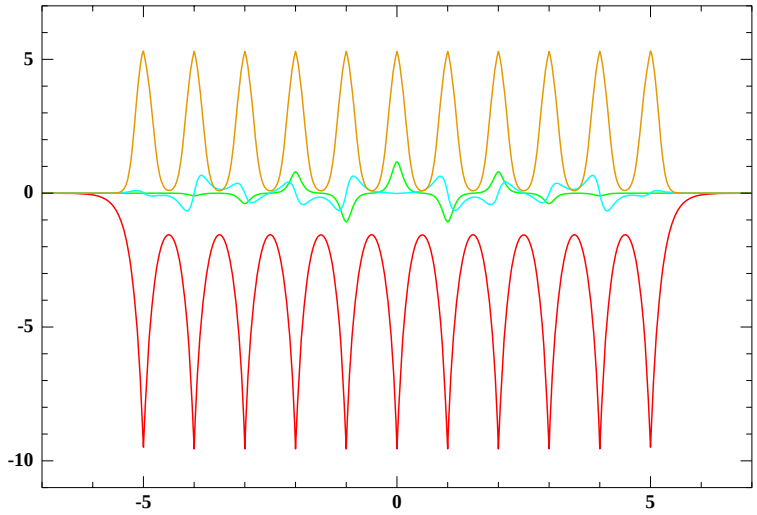
Ground state density operator, density matrix and density

$$\gamma_1^0 = \sum_{i=1}^{n_e} |\phi_i^1\rangle \langle\phi_i^1| \qquad \gamma_1^0(x,y) = \sum_{i=1}^{n_e} \phi_i^1(x)\,\phi_i^1(y) \qquad \rho_1^0(x) = \sum_{i=1}^{n_e} |\phi_i^1(x)|^2$$

$M = 11$ **nucleus,** $N = 11n_e = 22$ **non-interacting electrons**

$$H^{11} = -\frac{1}{2}\frac{d^2}{dx^2} + \sum_{r=-5}^{5} V(\cdot - r) \qquad H^{11}\phi_i^{11} = \varepsilon_i^{11}\phi_i^{11} \qquad \varepsilon_1^{11} < \varepsilon_2^{11} < \varepsilon_3^{11} < \cdots$$



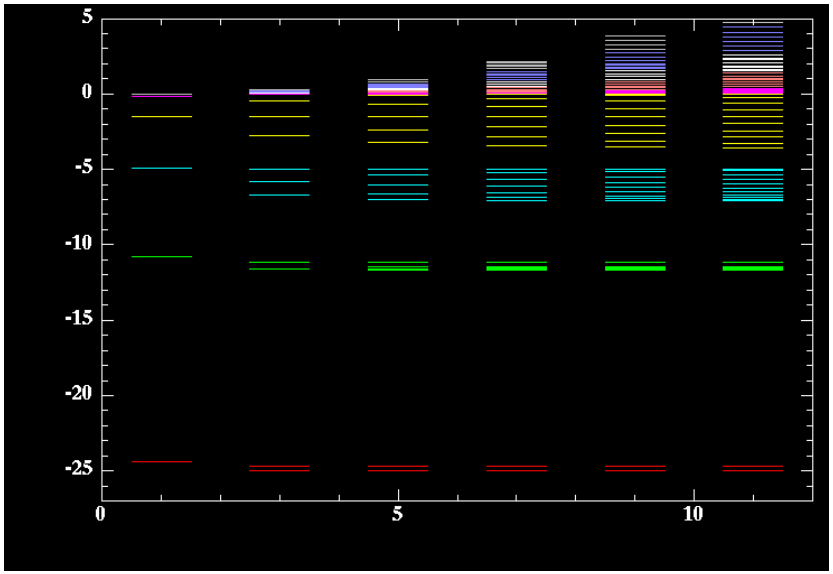


Potential (red), ρ_{11}^0 **(yellow),** $(\phi_1^{11}, \phi_{22}^{11})$ **(left),** $(\phi_7^{11}, \phi_{15}^{11})$ **(right)**

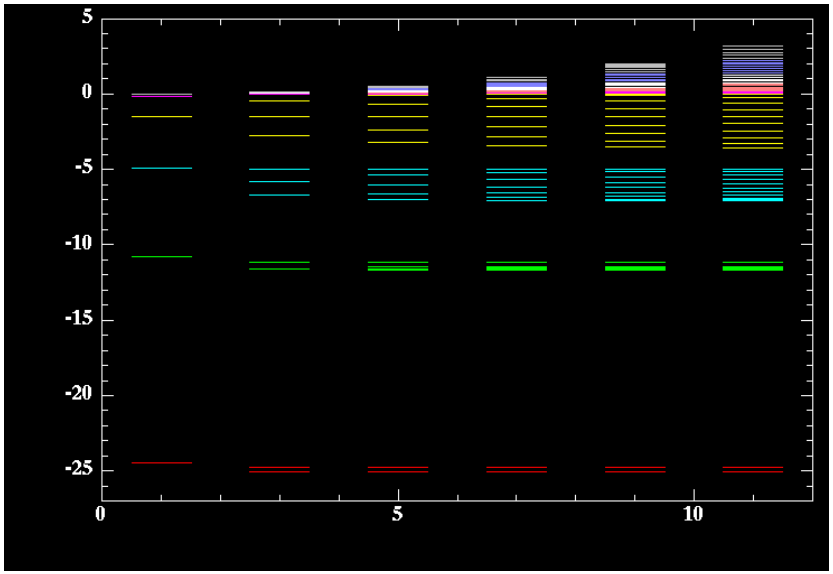
Ground state density operator, density matrix and density

$$\gamma_3^0 = \sum_{i=1}^{11n_e} |\phi_i^{11}\rangle \langle \phi_i^{11}| \qquad \gamma_3^0(x,y) = \sum_{i=1}^{11n_e} \phi_i^{11}(x)\, \phi_i^{11}(y) \qquad \rho_3^0(x) = \sum_{i=1}^{11n_e} |\phi_i^{11}(x)|^2$$

First $9M$ eigenvalues of H^M for $M = 1, 3, 5, 7, 9, 11$



Supercell of size 30



Supercell of size 40

Same energy cut-off for the planewave basis set

Thermodynamic limit: let M and $N = M\,n_e$ go to infinity

The Hamiltonian H^M converges to the periodic Schrödinger operator

$$H^0_{\rm per} = -\frac{1}{2}\frac{d^2}{dx^2} + \sum_{r\in\mathbf{Z}} V(\cdot - r)$$

Do $\gamma^0_M = \sum_{i=1}^{N} |\phi_i^M\rangle\,\langle\phi_i^M|$ and $\rho^0_M(x) = \sum_{i=1}^{N} |\phi_i^M(x)|^2$ have limits?

How to characterize these limits?

Main technical difficulty: $H^0_{\rm per}$ has a purely continuous spectrum (no eigenvalue, only continuous sets of "generalized" eigenvalues)

Spectral characterization of the ground-state density matrix

Consider Hamiltonians H^M with pure point spectra

$$H^M = \sum_{i=1}^{+\infty} \varepsilon_i^M |\phi_i^M\rangle \langle \phi_i^M| \qquad \text{with} \qquad \langle \phi_i^M | \phi_j^M \rangle = \delta_{ij}$$

Then (assuming a no unfilled shell property)

$$\gamma^M = \sum_{\varepsilon_i^M \leq \varepsilon_F^M} |\phi_i^M\rangle \langle \phi_i^M| \qquad \varepsilon_F^M \text{ : Fermi level}$$

For $f : \mathbb{R} \longrightarrow \mathbb{C}$, the following definition is independent of the choice of the Hilbert basis (ϕ_i^M)

$$f(H^M) = \sum_{i=1}^{+\infty} f(\varepsilon_i^M) |\phi_i^M\rangle \langle \phi_i^M|$$

It holds $$\gamma^M = \chi_{(-\infty, \varepsilon_F^M]}(H^M)$$

Spectral families

A spectral family on the Hilbert space $\mathcal{H}$ is a family $(P_\lambda)_{\lambda\in\mathrm{R}}$ of orthogonal projectors of $\mathcal{L}(\mathcal{H})$ satisfying the following properties

$$\begin{cases} P_\lambda P_\mu = P_{\mathbf{min}(\lambda,\mu)} \\ \forall \phi \in L^2(\mathbb{R}), \quad \lim\limits_{\lambda\downarrow\lambda_0} P_\lambda \phi = P_{\lambda_0}\phi \\ \forall \phi \in L^2(\mathbb{R}), \quad \lim\limits_{\lambda\to-\infty} P_\lambda \phi = 0, \quad \lim\limits_{\lambda\to+\infty} P_\lambda \phi = \phi \end{cases}$$

Let $$H = \sum_{i=1}^{+\infty} \varepsilon_i |\phi_i\rangle \langle\phi_i| \qquad \textbf{with} \qquad \langle\phi_i|\phi_j\rangle = \delta_{ij}$$

One can associate with H the spectral family $(P^H_\lambda)_{\lambda\in\mathrm{R}}$ defined by

$$P^H_\lambda = \sum_{\varepsilon_i\leq\lambda} |\phi_i\rangle \langle\phi_i|,$$

the above definition being independent of the choice of the Hilbert basis (ϕ_i)

Spectral theorem

There is a "natural" one-to-one correspondence between self-adjoint operators and spectral families

Examples

- position operator

$$P_\lambda^x \phi = \chi_{x \leq \lambda} \phi$$

- momentum operator

$$P_\lambda^{-i\frac{d}{dx}} \phi = \left(\mathcal{F}^{-1} \chi_{k \leq \lambda} \mathcal{F} \right) \phi$$

- free particle Hamiltonian

$$P_\lambda^{-\frac{1}{2}\frac{d^2}{dx^2}} \phi = \left(\mathcal{F}^{-1} \chi_{\frac{|k|^2}{2} \leq \lambda} \mathcal{F} \right) \phi$$

Spectral calculus

Let H be a self-adjoint operator on $\mathcal{H}$ and $(P_\lambda^H)_{\lambda\in\mathrm{R}}$ the spectral family associated with H

Let $f : \mathbb{R} \longrightarrow \mathbb{C}$. The definition of $f(H)$ in the general case when H may have a non-empty continuous spectrum is the following

$$f(H)\phi := \int_{\mathrm{R}} f(\lambda)\, dP_\lambda^H \phi := \lim_{\Delta\lambda\to 0} \sum_{\lambda_n = n\Delta\lambda,\, n\in\mathbf{Z}} f(\lambda_n)\,(P_{\lambda_n}^H - P_{\lambda_{n-1}}^H)\phi$$

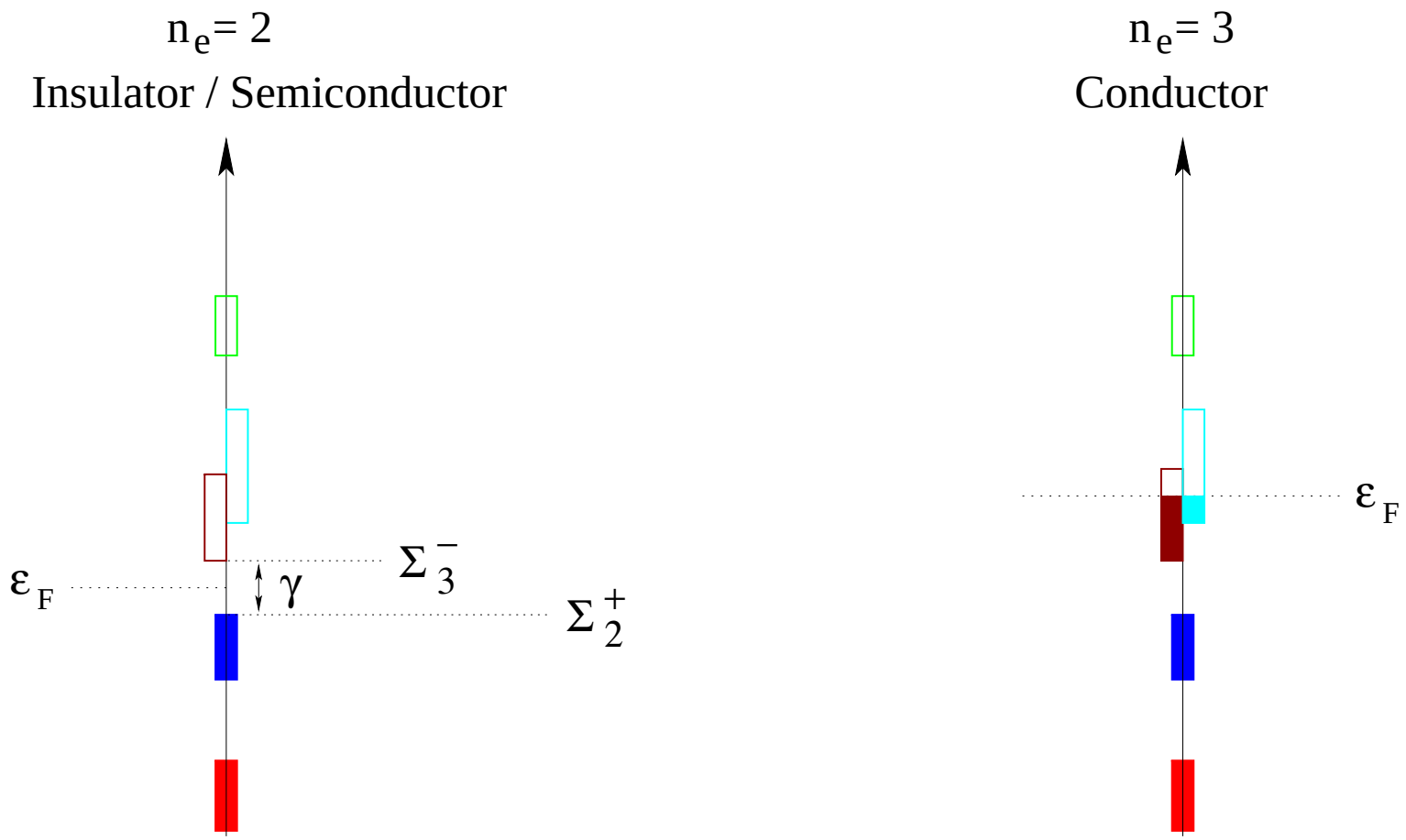
Thermodynamic limit. One can prove that

$$\gamma_M^0 = \chi_{(-\infty,\varepsilon_F^M]}(H_M) \underset{M\to\infty}{\longrightarrow} \gamma_{\mathrm{per}}^0 = \chi_{(-\infty,\varepsilon_F]}(H_{\mathrm{per}}^0)$$

where the Fermi level ε_F is such that

$$\int_\Gamma \rho_{\mathrm{per}}^0 = \int_\Gamma \gamma_{\mathrm{per}}^0(x,x)\, dx = n_e$$

$$\gamma^0_{\mathrm{per}} = \chi_{(-\infty,\varepsilon_F]}(H^0_{\mathrm{per}})$$

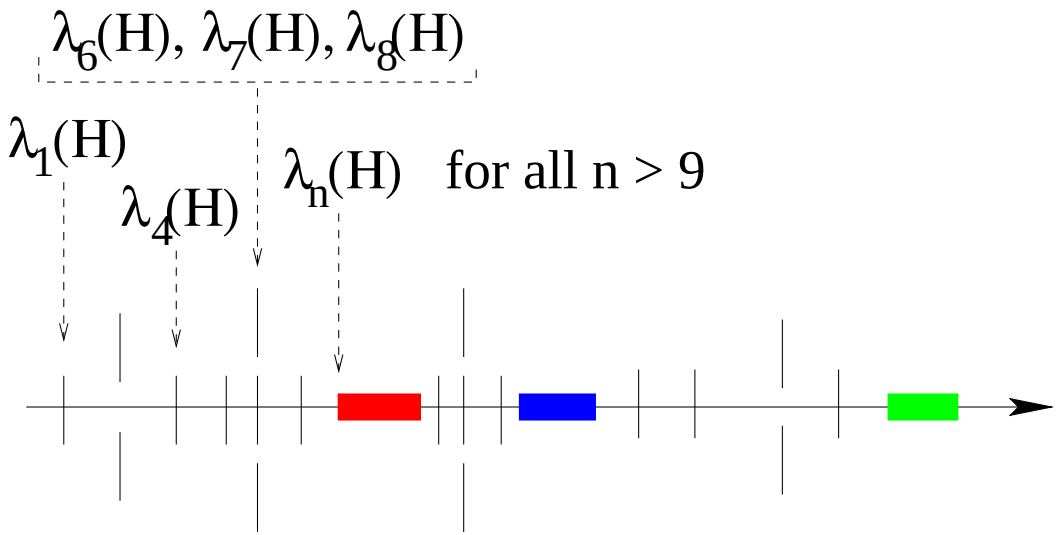


Side remark: it is in general very difficult to calculate numerically the spectral decomposition of an operator with continuous spectrum

Courant-Fischer min-max formula

$$\lambda_i(H) = \min_{V_i \subset \mathcal{H},\, \dim V_i = i} \; \max_{\phi \in V_i,\, \|\phi\|=1} \langle \phi | H | \phi \rangle$$

If H has at least i eigenvalues (including multiplicities) below the essential spectrum, then $\lambda_i(H)$ is the i-th eigenvalue of H. Otherwise, $\lambda_i(H)$ is the bottom of the essential spectrum

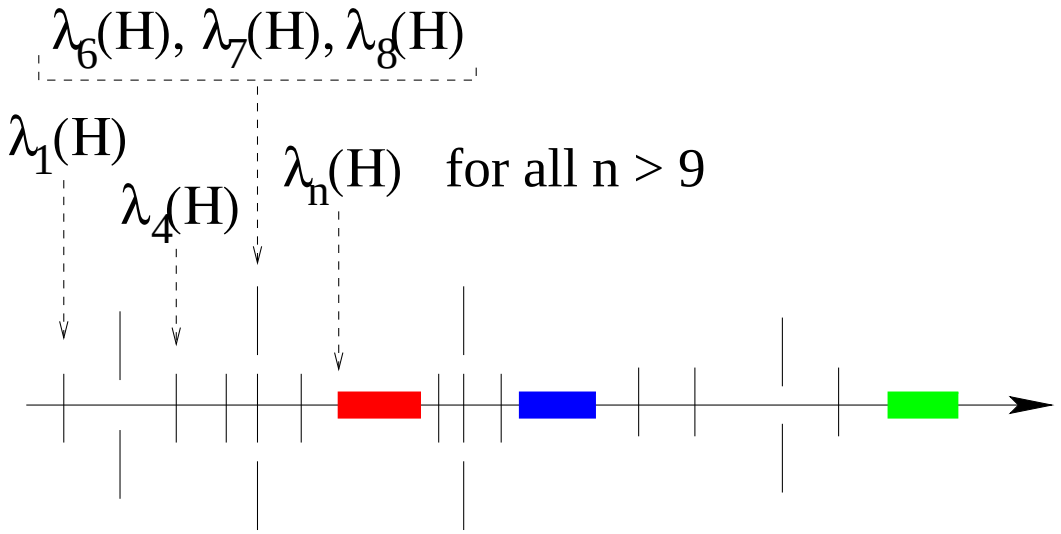


Example 1. Consider a self-adjoint operator H on $\mathcal{H}$, a Hilbert basis $(\phi_i)_{i\in\mathrm{N}^*}$ of $\mathcal{H}$ and the $N \times N$ matrix H_N with entries

$$[H_N]_{ij} = \langle \phi_i | H | \phi_j \rangle, \qquad 1 \leq i, j \leq N$$

Let us denote by $\lambda_i(H_N)$ the lowest i eigenvalue of H_N (including multiplicities). Then

$$\lambda_i(H_N) \underset{N\to\infty}{\longrightarrow} \lambda_i(H)$$



Example 2. Let $f \in L^\infty_{\text{per}}(0,1)$, f real-valued, piecewise continuous. Consider the bounded self-adjoint operator T on $L^2_{\text{per}}(0,1)$ defined as

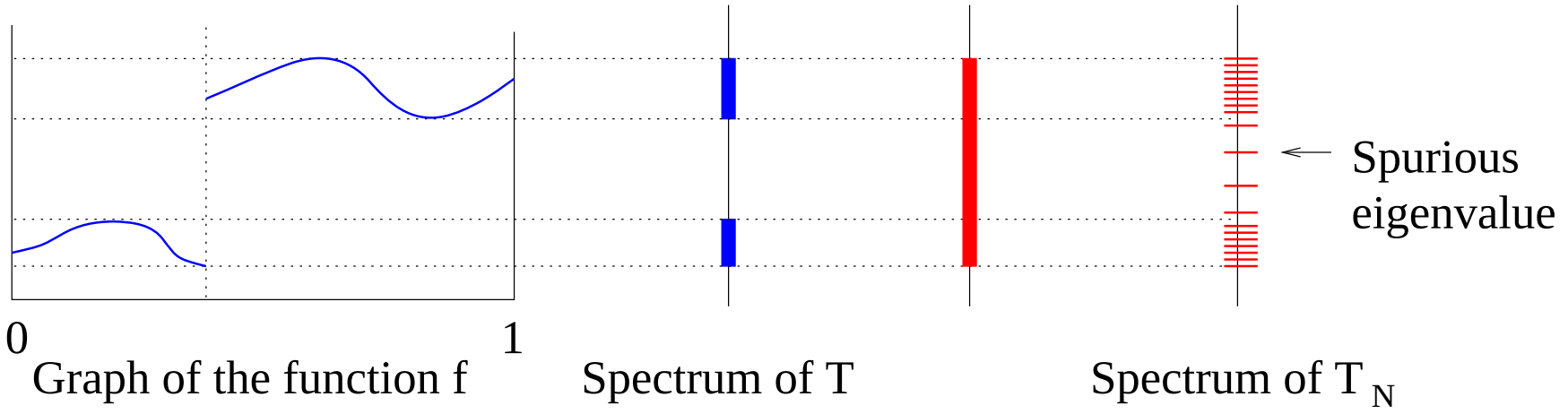
$$(Tu)(x) = f(x)u(x)$$

The operator T has a band spectrum

$$\sigma(T) = \text{ess-range}(f)$$

Denote by T_N the matrix of T in the Fourier basis $(e^{2i\pi nx})_{-N\leq n\leq N}$

Then (Szegö) $$\lim_{N_0\to+\infty} \overline{\bigcup_{N\geq N_0} \sigma(T_N)} = \text{Convex hull}(\sigma(T))$$



In the case of a perfect crystal, it is possible to circumvent this numerical problem using Bloch theory

Key ingredients of Bloch theorem:

1. The periodic Schrödinger operator

$$H^0_{\text{per}} = -\frac{1}{2}\frac{d^2}{dx^2} + V_{\text{per}}$$

and the translation operators of the lattice $(\tau_r)_{r\in\mathbf{Z}}$

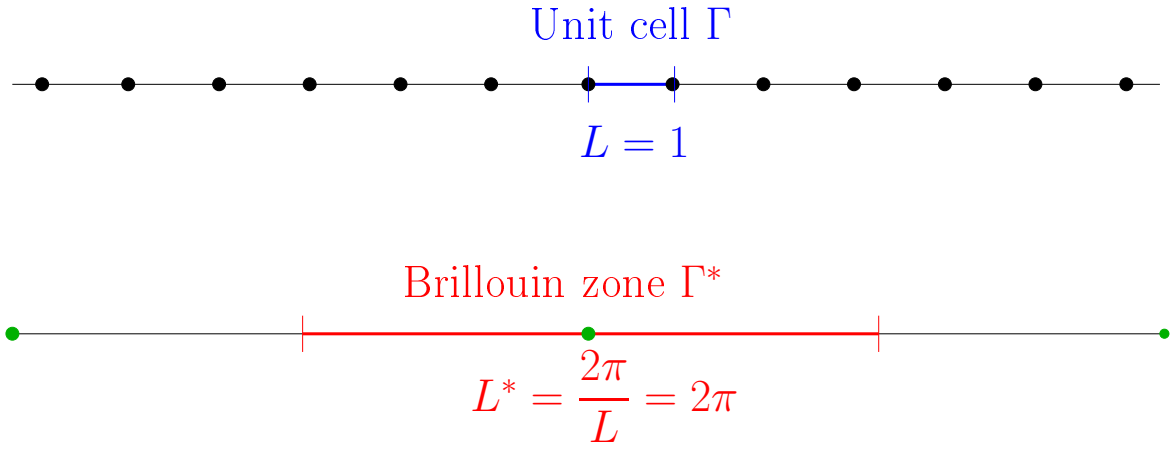
$$(\tau_r\phi)(x) = \phi(x-r)$$

commute all together

2. The only functions that are generalized eigenvectors of all the translation operators of the lattice are the Bloch functions

Geometric description of a 1D crystal

- **Lattice:** $\mathcal{R} = \mathbb{Z}$
- **Unit cell:** $\Gamma = (0, 1]$ **or** $\Gamma = (-\frac{1}{2}, \frac{1}{2}]$
- **Reciprocal lattice:** $\mathcal{R}^* = 2\pi\mathbb{Z}$
- **Brillouin zone:** $\Gamma^* = (-\pi, \pi]$ **(Wigner-Seitz cell of the reciprocal lattice)**



Bloch functions

Let us denote by

$$L^2_{\text{per}}(\Gamma) = \left\{ \phi \quad | \quad \int_\Gamma |\phi|^2 < \infty, \quad \tau_r \phi = \phi, \quad \forall r \in \mathbb{Z} \right\}$$

the space of $\mathbb{Z}$-periodic, locally square integrable functions

Bloch functions are functions of the form

$$\phi(x) = v(x)\, e^{-ikx} \qquad \textbf{with} \qquad v \in L^2_{\text{per}}(\Gamma) \qquad \textbf{and} \qquad k \in \mathbb{R}$$

$$\forall r \in \mathbb{Z}, \quad \tau_r \phi = e^{-ikr} \phi$$

Any Bloch function is in one of the spaces

$$L^2_k(\Gamma) = \left\{ \phi \mid e^{ikx} \phi(x) \in L^2_{\text{per}}(\Gamma) \right\} \qquad k \in \Gamma^*$$

Bloch transform

Any function $\phi \in L^2(\mathbb{R})$ can be expanded in a unique way as a continuous sum of Bloch functions as follows

$$\phi(x) = \frac{1}{|\Gamma^*|} \int_{\Gamma^*} \phi_k(x)\, dk$$

where

$$\phi_k(x) = \sum_{r \in \mathbf{Z}} \phi(x + r) e^{-ikr}$$

One has

$$\phi_k \in L^2_k(\Gamma) \qquad \textbf{and} \qquad \|\phi\|^2_{L^2(\mathrm{R})} = \frac{1}{|\Gamma^*|} \int_{\Gamma^*} \|\phi_k\|^2_{L^2_k(\Gamma)}\, dk$$

This property is denoted by

$$L^2(\mathbb{R}) = \frac{1}{|\Gamma^*|} \int_{\Gamma^*}^{\oplus} L^2_k(\Gamma)\, dk$$

As H^0_{per} commutes with all the translations of the lattice, it is "block diagonal" in the representation

$$L^2(\mathbb{R}) = \frac{1}{|\Gamma^*|}\int_{\Gamma^*}^{\oplus} L^2_k(\Gamma)\, dk$$

$$\phi(x) = \frac{1}{|\Gamma^*|}\int_{\Gamma^*} \phi_k(x)\, dk \qquad \Rightarrow \qquad (H^0_{\text{per}}\phi)(x) = \frac{1}{|\Gamma^*|}\int_{\Gamma^*} ([H^0_{\text{per}}]^k\phi_k)(x)\, dk$$

This property is denoted by

$$H^0_{\text{per}} = \frac{1}{|\Gamma^*|}\int_{\Gamma^*}^{\oplus} [H^0_{\text{per}}]^k\, dk$$

$$[H^0_{\text{per}}]^k\phi_k = -\frac{1}{2}\frac{d^2\phi_k}{dx^2} + V_{\text{per}}\phi_k \qquad [H^0_{\text{per}}]^k \text{ is a self-adjoint operator on } L^2_k(\Gamma)$$

$[H^0_{\text{per}}]^k$ is bounded below and has a purely discrete spectrum

As $[H^0_{\rm per}]^k$ is bounded below and has a purely discrete spectrum, there exists a non-decreasing sequence $\varepsilon_{n,k}$ of real numbers going to infinity and a Hilbert basis $(\phi_{n,k})_{n\in\mathrm{N}^*}$ of $L^2_k(\Gamma)$ such that

$$[H^0_{\rm per}]^k \phi_{n,k} = \varepsilon_{n,k}\phi_{n,k}$$

As

$$H^0_{\rm per} = \frac{1}{|\Gamma^*|}\int_{\Gamma^*}^{\oplus} [H^0_{\rm per}]^k \, dk,$$

it holds

$$\begin{aligned}
\gamma^0_{\rm per} &= \chi_{(-\infty,\varepsilon_F]}(H^0_{\rm per}) \\
&= \frac{1}{|\Gamma^*|}\int_{\Gamma^*}^{\oplus} \chi_{(-\infty,\varepsilon_F]}([H^0_{\rm per}]^k)\, dk \\
&= \frac{1}{|\Gamma^*|}\int_{\Gamma^*}^{\oplus} \sum_{n=1}^{+\infty} \chi_{(-\infty,\varepsilon_F]}(\varepsilon_{n,k})\, |\phi_{n,k}\rangle \langle\phi_{n,k}|\, dk
\end{aligned}$$

Band structure of the spectrum

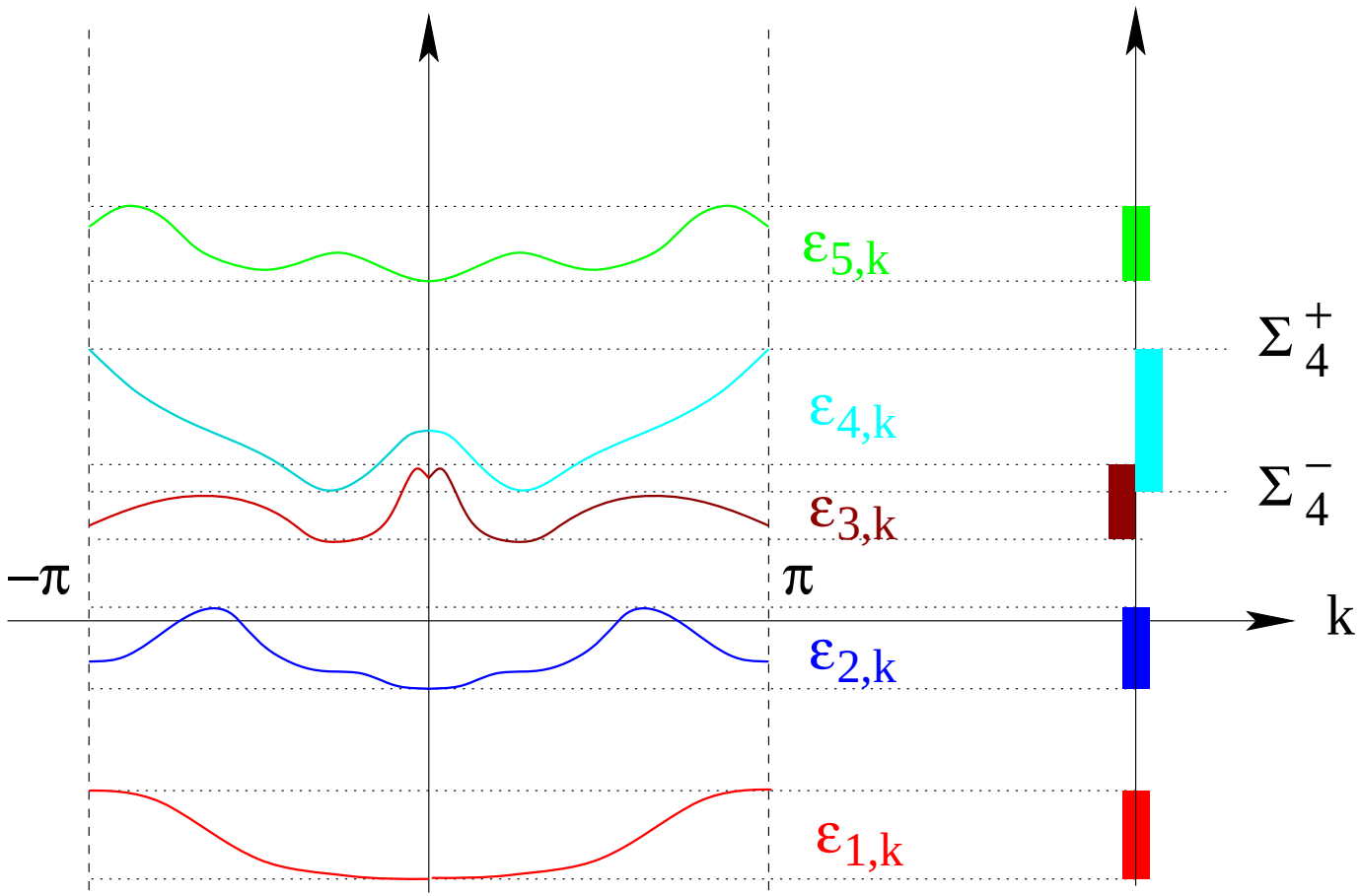
$$(\varepsilon_{n,k}, \phi_{n,k}(x)) \text{ eigenelement of } [H^0_{\rm per}]^k$$
$$\Updownarrow$$
$$(\varepsilon_{n,k}, \psi_{n,k}(x) = e^{ikx}\phi_{n,k}(x)) \text{ eigenelement of } [H^0_{\rm per}]_k$$

where $[H^0_{\rm per}]_k$ is the self-adjoint operator on $L^2_{\rm per}(\Gamma)$ defined by

$$[H^0_{\rm per}]_k = -\frac{1}{2}\frac{d^2}{dx^2} - ik\frac{d}{dx} + \frac{1}{2}|k|^2 + V_{\rm per}$$

As the function $k \mapsto [H^0_{\rm per}]_k$ is analytic, the functions $k \mapsto \varepsilon_{n,k}$ are continuous (and even analytic in 1D). Therefore

$$\sigma(H^0_{\rm per}) = \bigcup_{k\in\Gamma^*} \sigma([H^0_{\rm per}]^k) = (\varepsilon_{n,k})_{k\in\Gamma^*,\, n\in\mathrm{N}^*} = \bigcup_{n\in\mathrm{N}^*} \left[\min_k \varepsilon_{n,k}, \max_k \varepsilon_{n,k}\right]$$


ε5,k
ε4,k
ε3,k
ε2,k
ε1,k
−π
π
k
Σ 4 +
Σ 4 −

Finally,

$$\gamma^0_{\mathrm{per}}(x,x') = \frac{1}{|\Gamma^*|}\int_{\Gamma^*} \gamma^0_{\mathrm{per},k}(x,x')\,dk$$

$$\gamma^0_{\mathrm{per},k}(x,x') = \sum_{n=1}^{+\infty} \chi_{(-\infty,\varepsilon_F]}(\varepsilon_{n,k})\psi_{n,k}(x)\,\overline{\psi_{n,k}(x')}e^{ik(x-x')}$$

$$\begin{cases} [H^0_{\mathrm{per}}]_k\psi_{n,k} = \varepsilon_{n,k}\psi_{n,k} \\ \displaystyle\int_\Gamma \psi_{n,k}\overline{\psi_{n',k}} = \delta_{nn'} \\ \varepsilon_{1,k} \le \varepsilon_{2,k} \le \varepsilon_{3,k} \le \cdots \end{cases}$$

$$[H^0_{\mathrm{per}}]_k = -\frac{1}{2}\frac{d^2}{dx^2} - ik\frac{d}{dx} + \frac{1}{2}|k|^2 + V_{\mathrm{per}} \qquad \textbf{operating on } L^2_{\mathrm{per}}(\Gamma)$$

Practical calculation of $\gamma^0_{\rm per}$

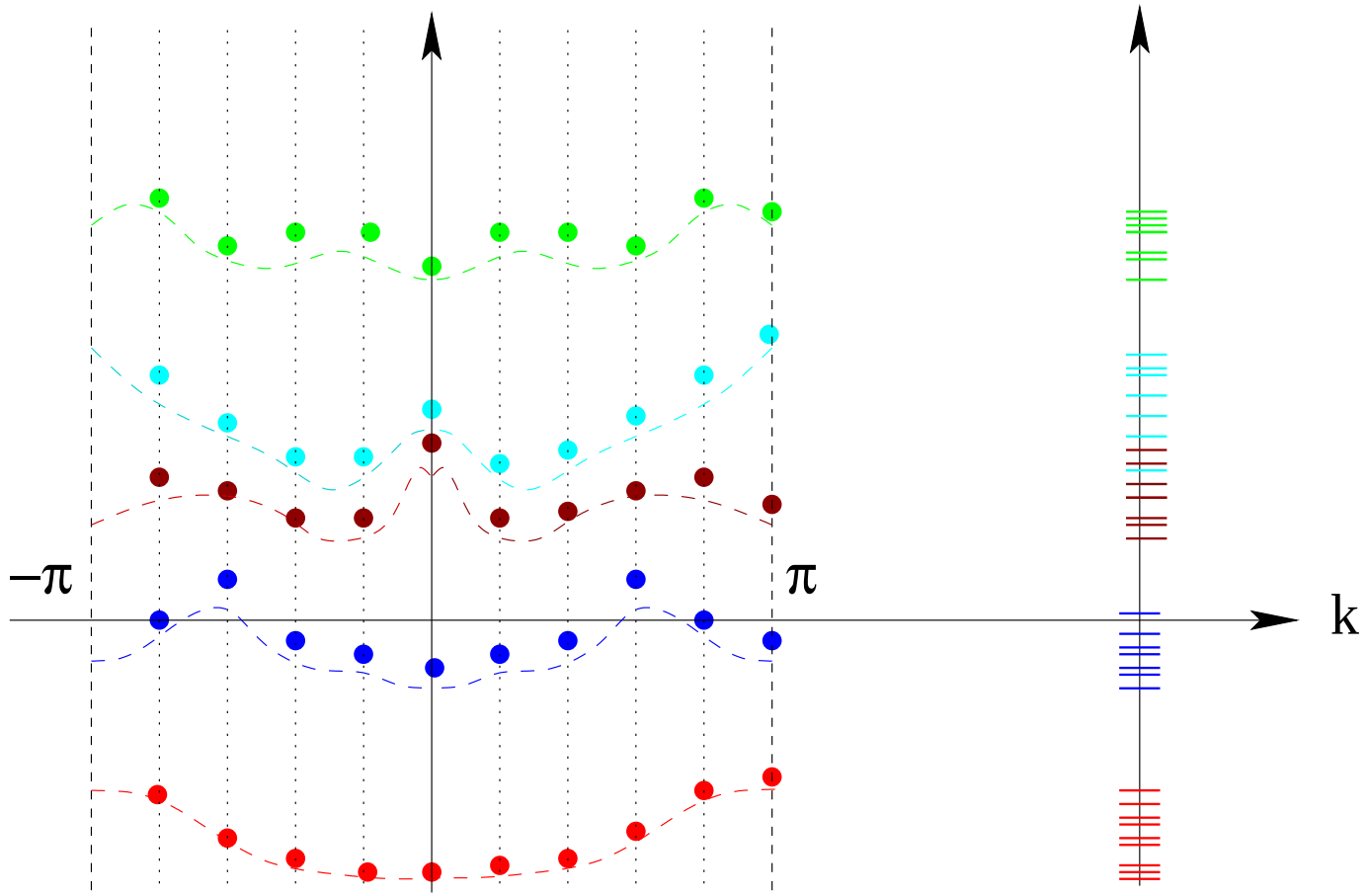
1. **Discretize the Brillouin zone $\Gamma^* = (-\pi, \pi]$ with K 'k-points' $(k_l)_{1\leq l\leq K}$**

2. **Assemble the matrix $H^N_{k_l}$ of the operator $[H^0_{\rm per}]_{k_l}$ in the Fourier (plane wave) basis $(e^{2i\pi jx})_{-N\leq j\leq N}$ (or in the basis $(e^{2i\pi jx})_{\frac{1}{2}(2\pi j+k)^2\leq E_{\rm cutoff}}$)**

$$[H^N_{k_l}]_{j_1 j_2} = \frac{(\pi(j_1+j_2)+k)^2}{2}\delta_{j_1 j_2} + \int_0^1 V_{\rm per}(x)\, e^{2i\pi(j_2-j_1)x}\, dx$$

3. **Diagonalize $[H^N_{k_l}]$ to obtain approximations ε^N_{n,k_l} and $\psi^N_{n,k_l}(x)$ of ε_{n,k_l} and $\psi_{n,k_l}(x)$**

4. $\gamma^0_{\rm per}(x,x') \simeq \displaystyle\sum_{l=1}^{K} w_l \sum_{n=1}^{2N+1} \chi_{(-\infty,\varepsilon_F]}(\varepsilon^N_{n,k_l})\psi^N_{n,k_l}(x)\,\overline{\psi^N_{n,k_l}(x')}e^{ik_l(x-x')}$


−π
π
k

For $n \in \mathbb{N}^*$, and $r \in \mathcal{R}$, consider

$$\chi_{n,r}(x) = \frac{1}{|\Gamma^*|} \int_{\Gamma^*} \phi_{n,k}(x) e^{ikr}\, dk \qquad \phi_{n,k}(x) = \psi_{n,k}(x) e^{ikx} \in L^2_k(\Gamma)$$

It immediately follows from the above definition that

$\chi_{n,r} \in \mathbf{Ran}(\Pi_n) \in L^2(\mathbb{R}^3)$ Π_n **spectral projector of the n-th band**

and that

$$\chi_{n,r}(x) = \chi_n(x) \qquad \textbf{with} \qquad \chi_n(x) = \frac{1}{|\Gamma^*|} \int_{\Gamma^*} \phi_{n,k}(x)\, dk$$

The functions $(\chi_{n,r})_{r\in\mathcal{R}}$ form an orthonormal basis set:

$$(\chi_{n,r}, \chi_{n,r'})_{L^2(\mathrm{R}^3)} = \frac{1}{|\Gamma^*|} \int_{\Gamma^*} (\psi_{n,k}, \psi_{n,k})_{L^2_k(\Gamma)}\, e^{ik\cdot(r'-r)}\, dk = \delta_{r,r'}$$

In fact, one can prove that $(\chi_{n,r})_{r\in\mathcal{R}}$ is a Hilbert basis of $\mathbf{Ran}(\Pi_n)$

Replacing $\phi_{n,k}(x)$ with $\phi^{\alpha_n}_{n,k}(x) = \phi_{n,k}(x)e^{i\alpha_n(k)}$ where $\alpha_n(k) \in \mathbb{R}$ leads to Wannier functions $\chi^{\alpha_n}_{n,r}(x)$ that differ from $\chi_{n,r}(x)$

In the special case when $\alpha_n(k) = k \cdot r_0$ with $r_0 \in \mathcal{R}$, one has

$$\chi^{\alpha_n}_n(x) = \chi_n(x - r_0)$$

so that the set of Wannier functions is unchanged (the mother Wannier function has just been translated)

On the other hand, for a generic $\alpha_n(k)$, the shape of the mother Wannier function is modified

Maximally Localized Wannier Functions (MLWFs)

For computational reasons, it is often interesting to be able to construct Wannier functions which are as localized as possible. This can be done, given a Bloch wave decomposition $(\psi_{n,k})$, by choosing a gauge $k \mapsto \alpha_n(k)$ which minimizes some delocalization criterion

A popular delocalization criterion has been introduced by Marzari and Vanderbilt in 1997. It reads

$$\Omega(\alpha_n) = \langle \chi_n^{\alpha_n} || x|^2 | \chi_n^{\alpha_n} \rangle - |\langle \chi_n^{\alpha_n} | x | \chi_n^{\alpha_n} \rangle|^2$$

where x denotes the (vector valued) position operator in $L^2(\mathbb{R})$

The Wannier functions obtained by minimizing the above criterion are called Maximally Localized Wannier Functions

Generalized Wannier functions

Let us consider a finite number of bands $(B_n)_{n\in\mathcal{N}}$

One can associate with any family $(U(k))_{k\in\Gamma^*}$ of $\mathcal{N}\times\mathcal{N}$ unitary matrices the generalized Wannier functions

$$\forall n\in\mathcal{N},\qquad \chi_n^U(x)=\frac{1}{|\Gamma^*|}\int_{\Gamma^*}\sum_{m\in\mathcal{N}}U_{nm}(k)\phi_{m,k}(x)\,dk$$

Then, $\chi_n^U\in\bigoplus_{m\in\mathcal{N}}\mathbf{Ran}(\Pi_m)\subset L^2(\mathbb{R})$ and $(\chi_n^U(\cdot-r))_{n\in\mathcal{N},r\in\mathbf{Z}}$ forms an Hilbert basis of $\bigoplus_{m\in\mathcal{N}}\mathbf{Ran}(\Pi_m)$

The family $(U(k))_{k\in\Gamma^*}$ can be chosen in such a way that it minimizes some delocalization criterion

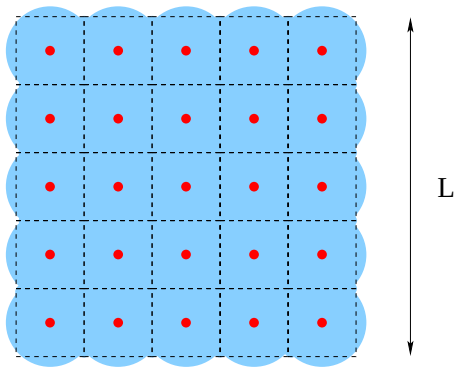
$\longrightarrow$ Maximally Localized (Generalized) Wannier Functions

2 - Periodic Kohn-Sham models

A periodic system contains an infinite number of electrons

The Schrödinger formalism cannot be extended to the case of infinitely many interacting particles

Schrödinger equation	Cluster	Kohn-Sham model
$\downarrow L \to \infty$	$\downarrow L \to \infty$	$\downarrow L \to \infty$
??	Crystal	Periodic Kohn-Sham model



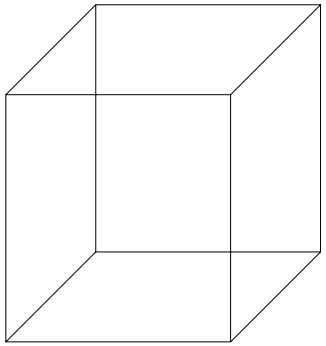
For simplicity, we limit ourselves to the case when

- the crystal lattice is the cubic lattice $\mathbb{Z}^3$
- the unit cell is the cubic cell $\Gamma = (0,1]^3$

In this case,

- the reciprocal lattice is the cubic lattice $2\pi\mathbb{Z}^3$
- the Brillouin zone is the cube $\Gamma^* = (-\pi,\pi]^3$

Unit cell



Brillouin zone

The Kohn-Sham energy as a functional of the density operator

$$\mathcal{E}^{\mathrm{KS}}_{\rho_{\mathrm{nuc}}}(\gamma) = \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathrm{R}^3} \rho_\gamma V_{\mathrm{nuc}} + J(\rho_\gamma) + E_{\mathrm{xc}}(\rho_\gamma)$$

Extended Kohn-Sham model (finite number of electrons)

$$I^{\mathrm{EKS}}_{\rho_{\mathrm{nuc}}} = \inf\left\{\mathcal{E}^{\mathrm{KS}}_{\rho_{\mathrm{nuc}}}(\gamma),\ \gamma \in \mathcal{P}^N\right\}$$

$$\mathcal{P}^N = \left\{\mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \leq \gamma \leq 1,\ \mathbf{Tr}(\gamma) = N,\ \mathbf{Tr}(-\Delta\gamma) < \infty\right\}$$

A generic element of $\mathcal{P}^N$ is of the form

$$\gamma = \sum_{i=1}^{+\infty} n_i \left|\phi_i\right\rangle \left\langle\phi_i\right|, \quad \phi_i \in H^1(\mathbb{R}^3), \quad \langle\phi_i|\phi_j\rangle = \delta_{ij}, \quad 0 \leq n_i \leq 1, \quad \sum_{i=1}^{+\infty} n_i = N$$

Reduced Hartree-Fock model (rHF)

$$I^{\mathrm{rHF}}_{\rho_{\mathrm{nuc}},N} = \inf\left\{\mathcal{E}^{\mathrm{rHF}}_{\rho_{\mathrm{nuc}}}(\gamma),\ \gamma \in \mathcal{P}^N\right\}$$

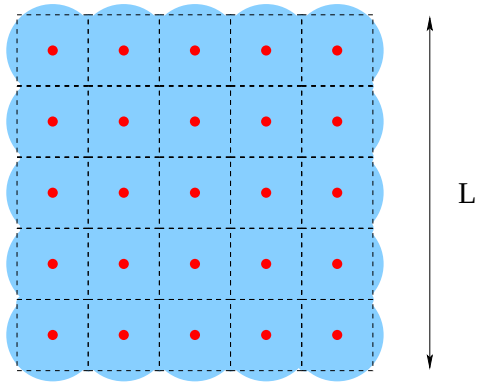
$$\begin{aligned}\mathcal{E}^{\mathrm{rHF}}(\gamma) &= \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathrm{R}^3} \rho_\gamma V_{\mathrm{nuc}} + J(\rho_\gamma) + J(\rho_{\mathrm{nuc}}) \\ &= \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + J(\rho_\gamma - \rho_{\mathrm{nuc}})\end{aligned}$$

Existence of a minimizer for neutral systems and positive ions

Uniqueness of the minimizing density (convexity with respect to ρ)

The reduced Hartree-Fock model can be seen as an extended Kohn-Sham model with zero exchange-correlation energy

Catto-Le Bris-Lions (2001)



$$\rho_{\rm nuc}^L = \sum_{R\in\mathbf{Z}^3\cap\Lambda_L} m(x-R) \quad \longrightarrow \quad \left| \begin{array}{l} I^{\rm rHF}_{\rho_{\rm nuc}^L, ZL^3} \\ \\ \rho_{\rm el}^L \quad \textbf{minimizing density} \end{array} \right.$$

Convergence of the energy per unit cell and of the density

$$\lim_{L\to\infty} \frac{I^{\rm rHF}_{\rho_{\rm nuc}^L, ZL^3}}{L^3} = I^0_{\rm per} \qquad \textbf{and} \qquad \sqrt{\frac{1}{L^3}\sum_{k\in\mathbf{Z}^3\cap\Lambda_L} \rho_{\rm el}^L} \underset{L\to\infty}{\longrightarrow} \sqrt{\rho^0_{\rm per}}$$

Besides, the ground state density matrix of the cluster converges to the unique solution $\gamma^0_{\rm per}$ of the self-consistent equation

$$\gamma^0_{\rm per} = \chi_{(-\infty,\varepsilon_F]}(H^0_{\rm per}) \tag{1}$$

where

$$H^0_{\rm per} = -\frac{1}{2}\Delta + V^0_{\rm per}$$

$V^0_{\rm per}$ denoting the periodic electrostatic potential generated by the periodic charge density $\rho_{\rm tot} = \rho^0_{\rm per} - \rho_{\rm nuc}$

$$\begin{cases} -\Delta V^0_{\rm per} = 4\pi\left(\rho^0_{\rm per} - \rho_{\rm nuc}\right) \\ V^0_{\rm per} \ \Gamma\text{-periodic} \end{cases}$$

The Fermi level ε_F is such that the unit cell is neutral

The self-consistent equation (1) has a variational interpretation: $\gamma^0_{\rm per}$ is the unique solution to some minimization problem

1. **Discretize the Brillouin zone with K 'k-points' $(k_l)_{1\leq l\leq K}$**

2. **Choose an energy cut-off E_{cutoff}**

3. **Solve the SCF equation (or its variational formulation)**

$$\gamma_{\text{per}}(x,x') = \sum_{l=1}^{K} w_l \sum_n \chi_{(-\infty,\varepsilon_F]}(\varepsilon_{n,k_l})\psi_{n,k_l}(x)\,\overline{\psi_{n,k_l}(x')}e^{ik_l\cdot(x-x')}$$

$$\rho_{\text{per}}(x) = \gamma_{\text{per}}(x,x) \qquad \varepsilon_F \text{ such that } \int_\Gamma \rho_{\text{per}} = n_e$$

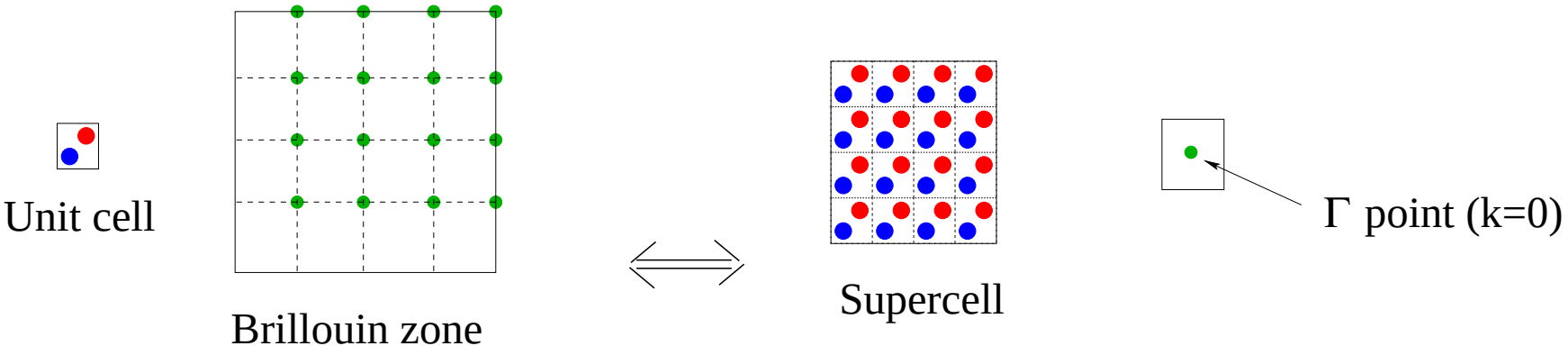
$(\varepsilon_{n,k_l},\psi_{n,k_l})_n$ **eigenelements of the matrix of the operator**

$$H^{k_l}_{\text{per}} = -\frac{1}{2}\Delta - ik_l\cdot\nabla + \frac{1}{2}|k_l|^2 + V_{\text{per}} + V_{\text{xc}}[\rho_{\text{per}}]$$

in the planewave basis $(e^{2i\pi j\cdot x})_{\frac{1}{2}|2\pi j|^2\leq E_{\text{cutoff}}}$ **or** $(e^{2i\pi j\cdot x})_{\frac{1}{2}|2\pi j+k_l|^2\leq E_{\text{cutoff}}}$

$$-\Delta V_{\text{per}} = 4\pi\,(\rho_{\text{per}} - \rho_{\text{nuc}}) \qquad V_{\text{per}}\ \Gamma\text{-periodic}$$

Equivalence between uniform k-point sampling and supercell model



Planewave basis

$$\left(e^{2i\pi j\cdot x}\right)_{\frac{1}{2}|j|^2\leq E_{\text{cutoff}}}$$

Planewave basis

$$\left(L^{-3/2}e^{2i\pi j\cdot x/L}\right)_{\frac{1}{2}|j/L|^2\leq E_{\text{cutoff}}}$$

- Usually, core electrons are not significantly affected by the chemical surrounding
- In heavy atoms, core electrons behave as relativistic particles
- In Kohn-Sham models, valence orbitals are orthogonal to core orbitals and may therefore strongly oscillate in the core regions

Pseudopotential methods consist in frozing the core electrons and in computing valence pseudoorbitals which

- coincide with the Kohn-Sham valence orbitals out of core regions (most chemical properties are preserved)
- do not strongly oscillate in the core regions (they can be expanded in small size planewave basis sets or discretized on coarse grids)

In norm-conserving and ultrasoft pseudopotential methods, the valence pseudoorbitals $\Psi^{\mathrm{pp}} = (\psi_i^{\mathrm{pp}})_{1 \leq i \leq N_v}$ solve a self-consistent equation of the form

$$\begin{cases} -\frac{1}{2}\Delta\psi_i^{\mathrm{pp}} + V^{\mathrm{SCF}}_{\mathrm{pp},\Psi^{\mathrm{pp}}}\psi_i^{\mathrm{pp}} = \varepsilon_i^{\mathrm{pp}} M \psi_i^{\mathrm{pp}} \\ \\ \langle \psi_i^{\mathrm{pp}} | M | \psi_j^{\mathrm{pp}} \rangle = \delta_{ij} \end{cases}$$

with

$$V^{\mathrm{SCF}}_{\mathrm{pp},\Psi^{\mathrm{pp}}} = V^{\mathrm{SCF}}_{\mathrm{local},\Psi^{\mathrm{pp}}} + \sum_{l,l'=1}^{L} |\psi_l\rangle\, v_{ll'}\, \langle\psi_{l'}| \qquad \text{with } V^{\mathrm{SCF}}_{\mathrm{local},\Psi^{\mathrm{pp}}} \text{ smooth}$$

$M = I$ for norm-conserving pseudopotentials
$M \neq I$ for ultrasoft pseudopotentials

Pseudopotentials allow

- to reduce the complexity of the calculation (fewer explicit molecular orbitals, smaller basis sets or coarser grids)
- but also to take into account some relativistic corrections: pseudopentials can be constructed from a relativistic model (e.g. Dirac-Fock) able to deal with high energy core electrons

Transferability issue

In practice, pseudopotentials for molecular systems are obtained by "summing" atomic pseudopotentials. Many basis sets of atomic pseudopotentials are available online and new ones are generated every week.

What kinds of molecular systems/properties can be reliably computed with a given basis set of atomic pseudopotentials?