Variational approximation of eigenvalues in spectral gaps for perturbed periodic Schrödinger operators

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Joint work with Virginie Ehrlacher and Yvon Maday

1. Motivation: electronic structures of crystals with defects

2. Lack of approximation and spectral pollution

3. Galerkin finite element approximation

4. The supercell method

1 - Motivation: electronic structure of crystals

First-principle molecular simulation

- **A sample of matter is a set of M nuclei and N electrons in Coulomb interaction**
- **All the chemical and most of the physical properties of such a system are encoded in the associated $(M+N)$-body Schrödinger equation**

Born-Oppenheimer approximation ($m_k >> m_e$)

- **nuclei behave as classical point-like particles**
- **electrons are in their quantum ground state**
- **the dynamics of the nuclei is governed by the autonomous Hamiltonian**

$$H_{\mathrm{BO}}(\{\mathbf{P}_k\},\{\mathbf{R}_k\}) = \sum_{k=1}^{M} \frac{|\mathbf{P}_k|^2}{2m_k} + W(\mathbf{R}_1,\cdots,\mathbf{R}_M)$$

where W is an effective interatomic potential

$\longrightarrow$ **mathematical justification of classical molecular dynamics**

Effective interatomic potential

$$W(\mathbf{R}_1, \cdots, \mathbf{R}_M) = E^0_{\{\mathbf{R}_k\}} + V^{\mathrm{nn}}_{\{\mathbf{R}_k\}}$$

$E^0_{\{\mathbf{R}_k\}}$: **electronic ground state energy for the nuclear configuration** $\{\mathbf{R}_k\}$

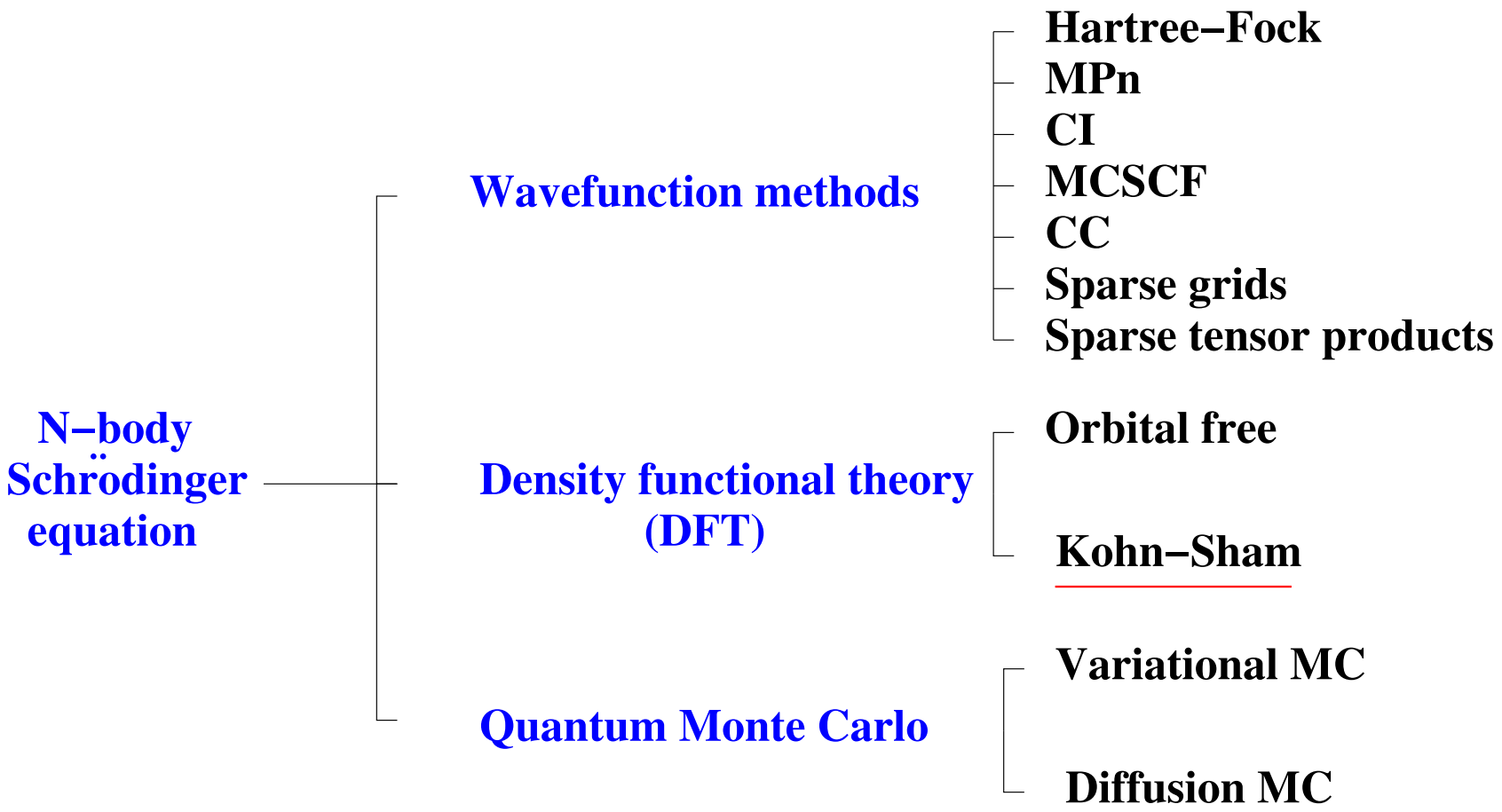
$$\left(-\frac{1}{2}\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(x_i) + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} \right) \Psi(x_1, \cdots, x_N) = E^0_{\{\mathbf{R}_k\}} \Psi(x_1, \cdots, x_N)$$

$$\forall p \in \mathfrak{S}_N, \qquad \Psi(x_{p(1)}, \cdots, x_{p(N)}) = \varepsilon(p)\Psi(x_1, \cdots, x_N) \qquad \textbf{(Pauli principle)}$$

$$V^{\mathrm{nn}}_{\{\mathbf{R}_k\}} = \sum_{1\leq k<l\leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \qquad V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(x) = -\sum_{k=1}^{M} \frac{z_k}{|x - \mathbf{R}_k|}$$

Atomic units: $\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\varepsilon_0 = 1$

A classification of the main electronic structure methods

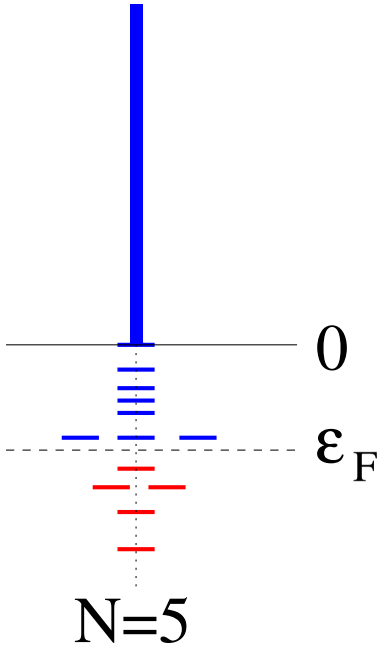


Density Functional Theory has become an essential tool in chemistry, materials science, molecular biology and nanosciences

- W. Kohn was awarded the '98 Nobel Prize in Chemistry for his contributions to DFT
- First-principle molecular simulation utilizes more than 15% of the resources available in scientific computing centers
- Number of references to Density Functional Theory
  - in google scholar: 832,000 (355,000 for Navier-Stokes)
  - in mathscinet: 201 (15,158 for Navier-Stokes)

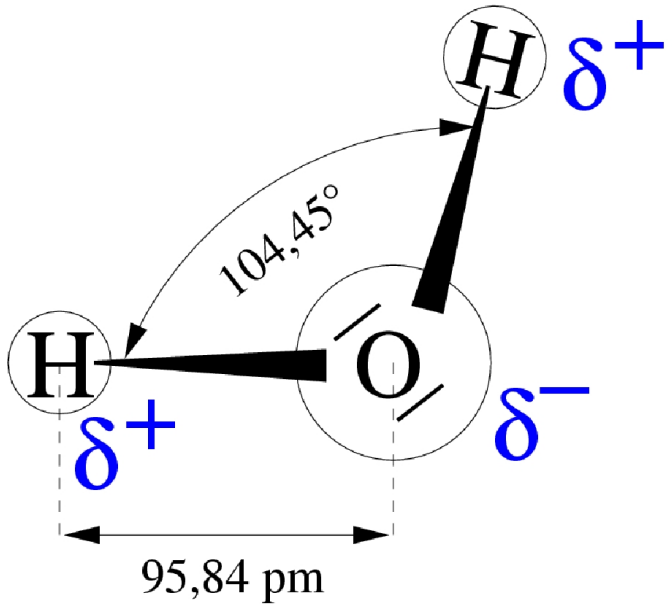
Kohn-Sham equations (LDA-Xα)

$$\begin{cases} \rho^0(x) = \sum_{i=1}^{N} |\phi_i(x)|^2 \\ H_{\rho^0}\,\phi_i = \varepsilon_i \phi_i, \qquad \varepsilon_1 < \varepsilon_2 \leq \varepsilon_3 \leq \cdots \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \\ H_{\rho^0} = -\frac{1}{2}\Delta + V_{\rho^0}^{\mathrm{KS}} \qquad V_{\rho^0}^{\mathrm{KS}} = -\sum_{k=1}^{M} \frac{z_k}{|\cdot - \mathbf{R}_k|} + \rho^0 \star |\cdot|^{-1} - \frac{4}{3} C_{\mathrm{X}} \rho^{0\,1/3} \end{cases}$$



$$E^0_{\{\mathbf{R}_k\}} \simeq \frac{1}{2}\sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 - \sum_{k=1}^{M} \int_{\mathbb{R}^3} \frac{z_k \rho^0(x)}{|x - \mathbf{R}_k|} + \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho^0(x)\rho^0(x')}{|x - x'|}\, dx\, dx' - C_{\mathrm{X}} \int_{\mathbb{R}^3} \rho^{0\,4/3}$$

First principle calculation of the equilibrium geometry of the water molecule
(3 classical nuclei, 10 quantum electrons)



Approximations of the electronic Schrödinger equation
(1 linear PDE in dimension 30) CCSD(T)-TZ2P(f,d): 95.89 pm, 104.16°**

Density functional theory (10 coupled nonlinear PDEs in dimension 3)
DFT-PBE-6-311+G: 96.90 pm, 104.75°**

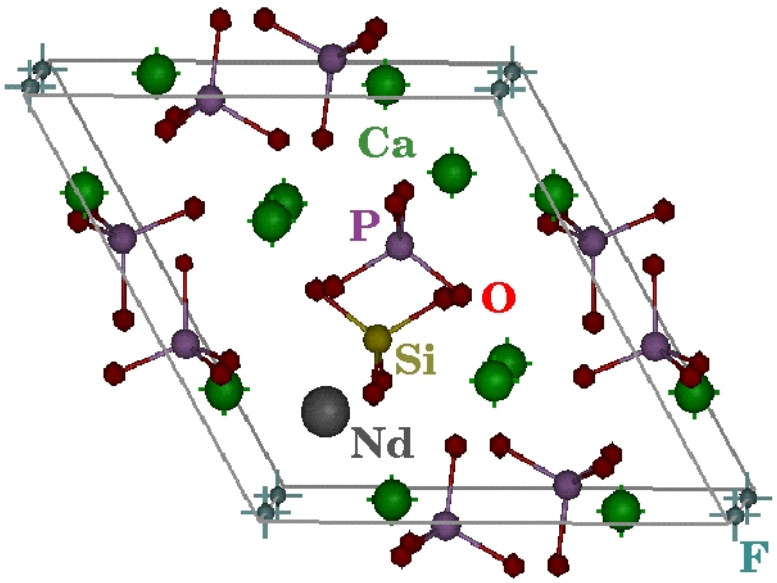
Electronic structure of perfect crystals

Within DFT, the electronic structure of a perfect crystal is characterized by a periodic mean-field Hamiltonian

$$H_{\mathrm{per}} = -\frac{1}{2}\Delta + V_{\mathrm{per}}$$

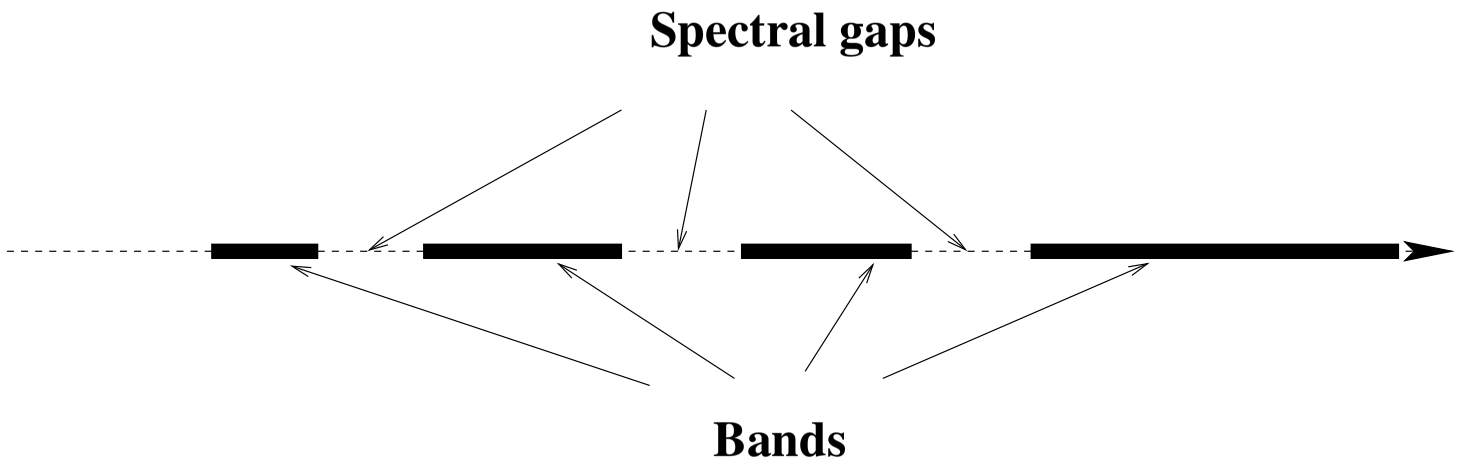
on $L^2(\mathbb{R}^3)$, where

$$V_{\mathrm{per}} \in L^2_{\mathrm{per}}(\Gamma) := \left\{ u \in L^2_{\mathrm{loc}}(\mathbb{R}^3) \mid V_{\mathrm{per}} \ \mathcal{R}\textbf{-periodic} \right\}$$



Mathematical properties of H_{per}

- H_{per} **defines a self-adjoint operator on** $L^2(\mathbb{R}^3)$ **with domain** $H^2(\mathbb{R}^3)$
- H_{per} **is bounded below**
- **The point spectrum of** H_{per} **is empty (**H_{per} **has no eigenvalue)**
- **The continuous spectrum** H_{per} **is composed of bands**

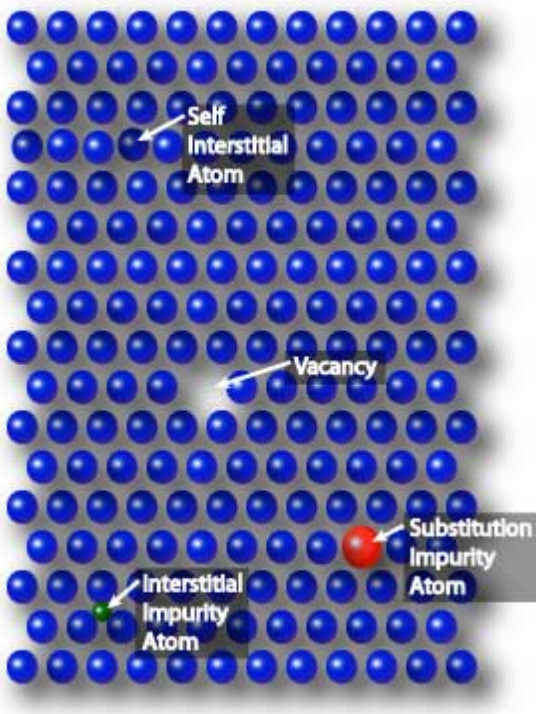


Electronic structure of crystals with local defects

Within DFT, the electronic structure of a crystal with a local defect is characterized by a mean-field Hamiltonian of the form

$$H = -\frac{1}{2}\Delta + V_{\rm per} + W \qquad \textbf{where} \qquad W \in C^0(\mathbb{R}^3), \quad \lim_{|x|\to\infty} W(x) = 0$$

(see E.C., Deleurence, Lewin, Comm. Math. Phys. 2008)

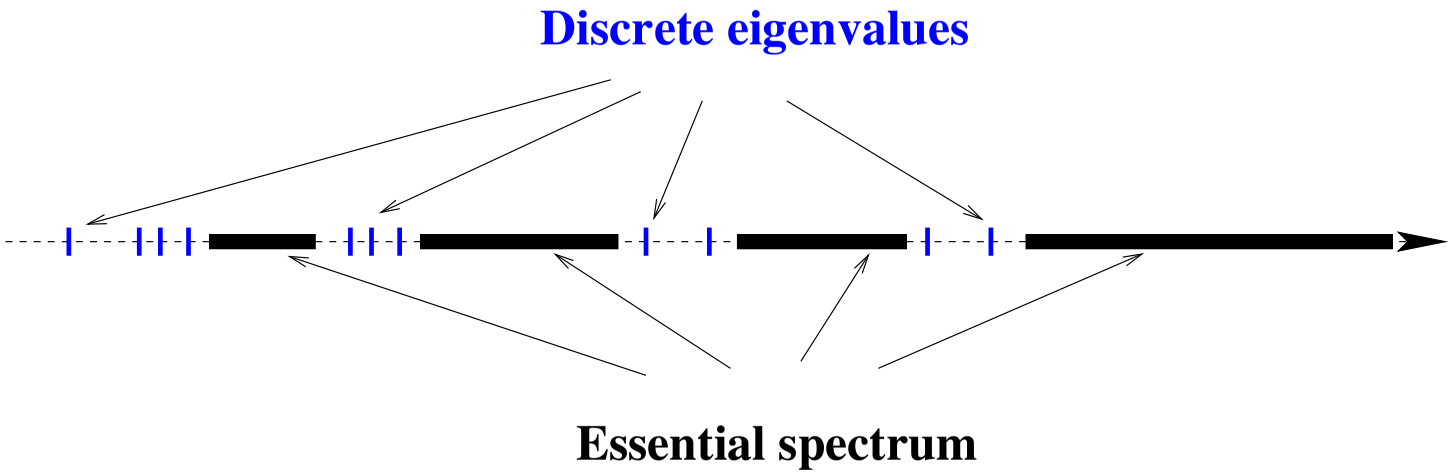


Crystals are like people,
it is their defects
that make them interesting

(attributed to F. C. Franck)

Spectral properties of $H = H_{\mathrm{per}} + W$

- H **defines a self-adjoint operator on** $L^2(\mathbb{R}^3)$ **with domain** $H^2(\mathbb{R}^3)$
- H **is bounded below**
- $\sigma_{\mathrm{ess}}(H) = \sigma_{\mathrm{ess}}(H_{\mathrm{per}})$ **(Weyl's theorem)**
- H **may have discrete eigenvalues below** $\inf \sigma_{\mathrm{ess}}(H)$ **and in spectral gaps**



2 - Lack of approximation and spectral pollution

Variational approximation of the spectrum of a self-adjoint operator

Let A be a self-adjoint operator on a Hilbert space $\mathcal{H}$ with domain $D(A)$ and form domain $Q(A)$, and a the associated quadratic form.

Exemple: for a crystal with a local defect

$$\mathcal{H} = L^2(\mathbb{R}^3), \quad D(A) = H^2(\mathbb{R}^3), \quad A = -\frac{1}{2}\Delta + V_{\text{per}} + W$$

The quadratic form associated with A is defined as

- $Q(A) = H^1(\mathbb{R}^3)$
- $\forall (u, v) \in Q(A) \times Q(A), \quad a(u, v) = \frac{1}{2}\int_{\mathbb{R}^3} \nabla u \cdot \nabla v + \int_{\mathbb{R}^3} (V_{\text{per}} + W)uv$

Let $(V_n)_{n\in\mathbb{N}}$ be a sequence of finite-dimensional subspaces of $Q(A)$ such that

$$\forall v \in Q(A), \quad \inf_{v_n \in V_n} \|v - v_n\|_{Q(A)} \underset{n\to\infty}{\longrightarrow} 0.$$

For each n, we denote by $A|_{V_n}$ the self-adjoint operator on V_n defined by

$$\forall (u_n, v_n) \in V_n \times V_n, \quad (A|_{V_n} u_n, v_n)_{\mathcal{H}} = a(u_n, v_n).$$

The spectrum of $A|_{V_n}$ is obtained by solving the variational problem

$$\begin{cases} \textbf{search } (u_n, \lambda_n) \in V_n \times \mathbb{R} \textbf{ such that} \\ \forall v_n \in V_n, \quad a(u_n, v_n) = \lambda_n (u_n, v_n)_{\mathcal{H}} \\ \|u_n\|_{\mathcal{H}} = 1 \end{cases}$$

Does $\sigma(A|_{V_n})$, the spectrum of $A|_{V_n}$, converge to $\sigma(A)$, the spectrum of A?

$\longrightarrow$ **No, in general**

A classical exemple where everything works well

Assume that A is bounded below with compact resolvent. Then

$$\lim_{n\to\infty} \sigma(A|_{V_n}) = \sigma(A)$$

More precisely,

- **the spectrum of A is purely discrete and the sequence $(\lambda_j)_{j\in\mathbb{N}^*}$ of the eigenvalues of A (counted with their multiplicites) forms a non-decreasing sequence going to $+\infty$**

- **let $\lambda_1^n \leq \lambda_2^n \leq \cdots \leq \lambda_{N_n}^n$ denote the eigenvalues of $A|_{V_n}$ (counted with their multiplicities). Then**

$$\forall j \in \mathbb{N}^*, \quad \lambda_j^n \geq \lambda_j \text{ for all } n \quad \text{and} \quad \lim_{n\to\infty} \lambda_j^n = \lambda_j$$

Example: $\mathcal{H} = L^2(\Omega)$, Ω bounded open subset of $\mathbb{R}^d$,

$$D(A) = \left\{u \in H_0^1(\Omega) \mid \Delta u \in L^2(\Omega)\right\}, \qquad \forall u \in D(A),\ Au = -\Delta u$$

The lack of approximation problem: it may happen that

$$\sigma(A) \not\subseteq \liminf_{n\to\infty} \sigma(A|_{V_n})$$

Example: $\mathcal{H} = L^2_{\rm per}((0,2\pi),\mathbb{C})$, $D(A) = H^1_{\rm per}((0,2\pi),\mathbb{C})$, $A = -i\dfrac{d}{dx}$

Let $(e_k)_{k\in\mathbb{Z}}$ **be the basis of the Fourier modes (**$e_k(x) = (2\pi)^{-1/2}e^{ikx}$**), and**

$$V_n = \mathbb{C}e_{0,n} \oplus \mathbb{C}\widetilde{e}_{0,n} \oplus \textbf{Span}\,\{e_k,\ 1 \le |k| \le n-1\}$$

where

$$e_{0,n} := \cos(1/n)e_0 + \frac{\sin(1/n)}{\sqrt{2}}e_n + \frac{\sin(1/n)}{\sqrt{2}}e_{-n}, \qquad \widetilde{e}_{0,n} = \frac{1}{\sqrt{2}}e_n - \frac{1}{\sqrt{2}}e_{-n}.$$

Then

$$\sigma(A) = \mathbb{Z} \qquad \textbf{and} \qquad \lim_{n\to\infty} \sigma(A|_{V_n}) = \mathbb{Z}^*$$

Theorem. If A **is semibounded, then** $\sigma(A) \subset \liminf_{n\to\infty} \sigma(A|_{V_n})$**.**

The spectral pollution problem: it may happen that

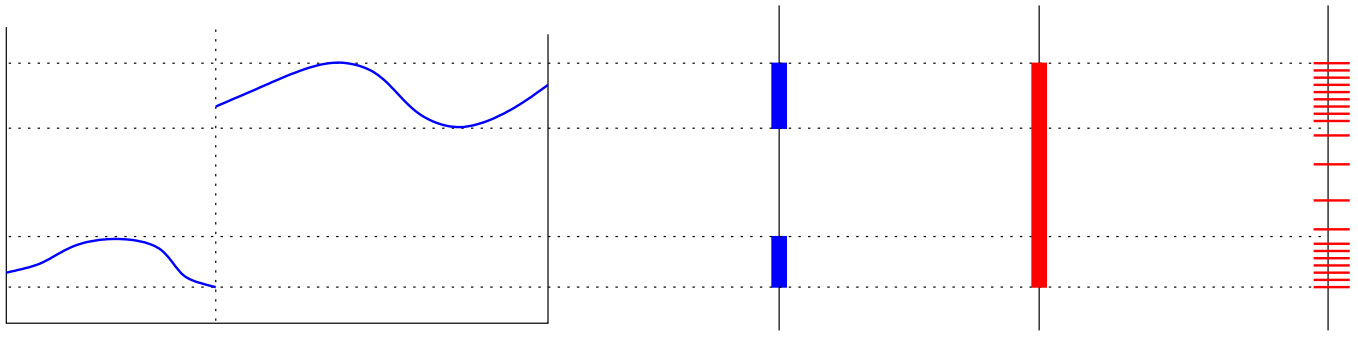
$$\limsup_{n\to\infty} \sigma(A|_{V_n}) \not\subseteq \sigma(A)$$

Exemple (Szegö) Let $V_{\text{per}} \in L^\infty_{\text{per}}((0,2\pi),\mathbb{R})$**,** $\mathcal{H} = L^2_{\text{per}}((0,2\pi),\mathbb{C})$**,**

$$(Au)(x) = V_{\text{per}}(x)u(x)$$

Let $V_n =$ **Span** $\{e_k,\ |k| \le n\}$**, where** $(e_k)_{k\in\mathbb{N}}$ **is the Fourier basis. Then**

$$\sigma(A) = \textbf{ess-range}(V_{\text{per}}) \qquad \textbf{and} \qquad \lim_{n_0\to\infty} \overline{\bigcup_{n\ge n_0} \sigma(A|_{V_n})} = \textbf{Conv}(\sigma(A))$$



Graph of the function $\mathbf{V_{per}}$ **Spectrum of A** **Spectrum of** $\mathbf{A|_{V_n}}$

Definition **A real number $\lambda \notin \sigma(A)$ such that there exists a sequence $(V_n)_{n\in\mathbb{N}}$ of finite-dimensional subspaces of $Q(A)$ such that**

- $\forall v \in Q(A),\ \inf\limits_{v_n\in V_n} \|v - v_n\|_{Q(A)} \underset{n\to\infty}{\longrightarrow} 0$
- $\lambda \in \lim\limits_{n\to\infty} \sigma(A|_{V_n})$

is called a spurious eigenvalue of A.

The set of the spurious eigenvalues of A is denoted by $\mathbf{Spu}(A)$.

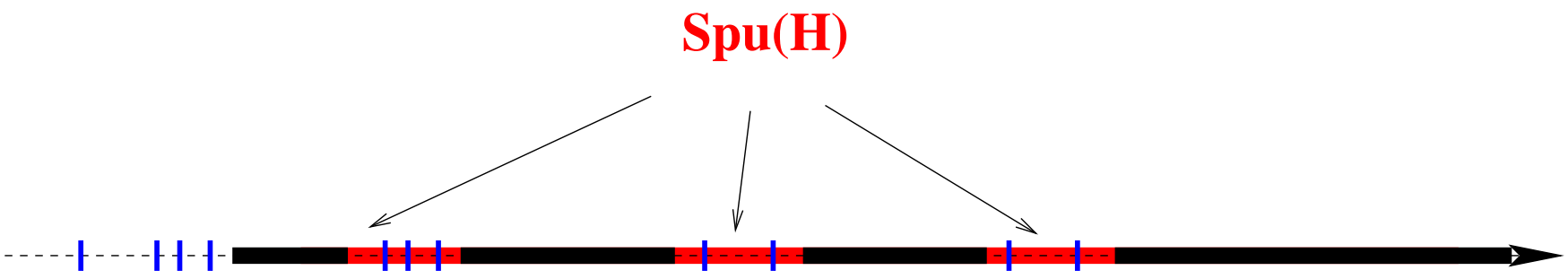
Theorem (see e.g. Levitin-Shagorodsky, 2004). **It holds**

$$\mathbf{Spu}(A) = \mathbf{Conv}\left(\overline{\sigma(A)}^{\mathbb{R}} \setminus \sigma_{\mathrm{d}}(A)\right) \setminus \sigma(A).$$

The case of perturbed periodic Schrödinger operators on $L^2(\mathbb{R}^d)$

$$H = -\frac{1}{2}\Delta + V_{\text{per}} + W, \quad \textbf{where} \quad V_{\text{per}} \in L^\infty_{\text{per}}(\Gamma), \quad W \in L^\infty(\mathbb{R}^d), \quad \lim_{|x|\to\infty} W(x) = 0$$

- **no lack of approximation (H is bounded below)**
- **spectral pollution may be a problem**



3 - Galerkin finite element approximation

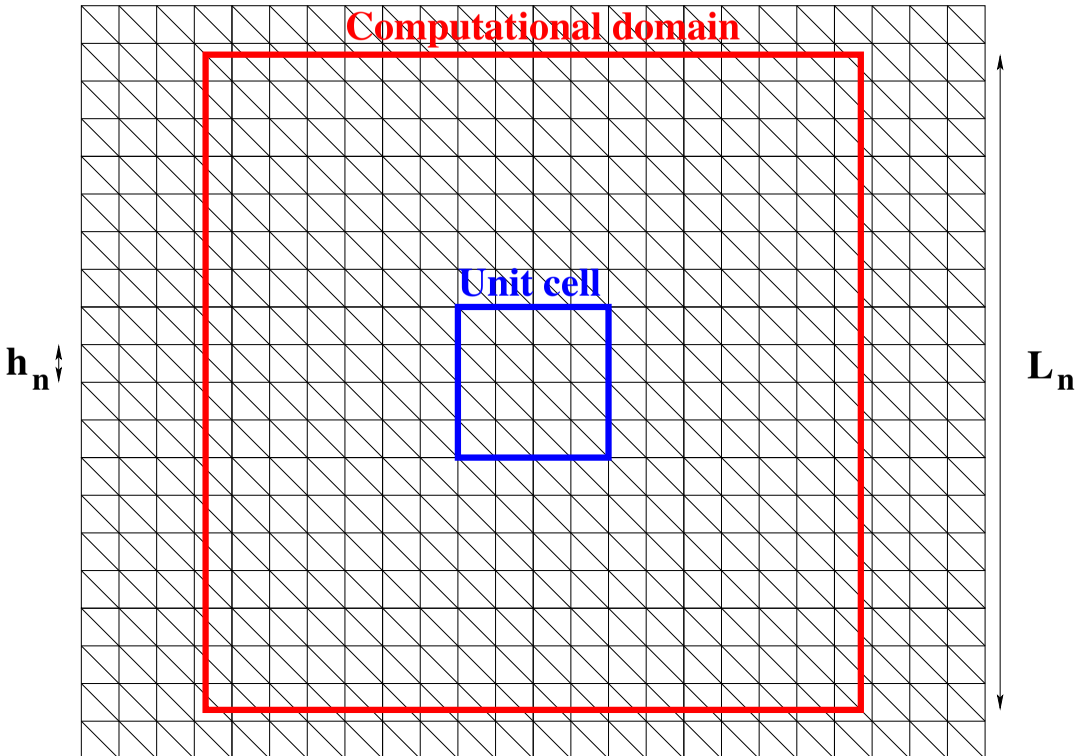
The natural approach of truncating $\mathbb{R}^d$ *to a large compact domain and applying the projection method to the corresponding Dirichlet problem is prone to spectral pollution* **(Boulton-Levitin 2007).**

Numerical example: $d = 2$, $\mathcal{R} = 2\pi\mathbb{Z}^2$, **unit cell** $[-\pi, \pi)^2$

$$V_{\rm per}(x, y) = \cos(x)+3\sin(2(x+y)+1) \qquad W(x, y) = -(x+2)^2(2y-1)^2\exp(-(x^2+y^2))$$

Approximation spaces $V_n = \left\{v_n \in C^0(\mathbb{R}^2) \mid \textbf{Supp}(v_n) \subset \Omega_n,\ \forall K_n \in \mathcal{T}_n^\infty,\ v_n|_{K_n} \in \mathbb{P}_1\right\}$

- **computational domain** $\Omega_n = [-L_n/2, L_n/2]$ **with** $L_n \to \infty$ **;**
- $\mathcal{T}_n^\infty$**: uniform** $\mathcal{R}$**-periodic mesh of** $\mathbb{R}^2$ **with** $2n^2$ **triangles per unit cell**



Gap $(-0.341, 0.016)$ **between the** 1^{st} **and** 2^{nd} **bands of** $H^0_{\text{per}} = -\Delta + V_{\text{per}}$

$H = H^0_{\text{per}} + W$ **has exactly one eigenvalue** $\lambda \simeq -0.105$ **in this gap**

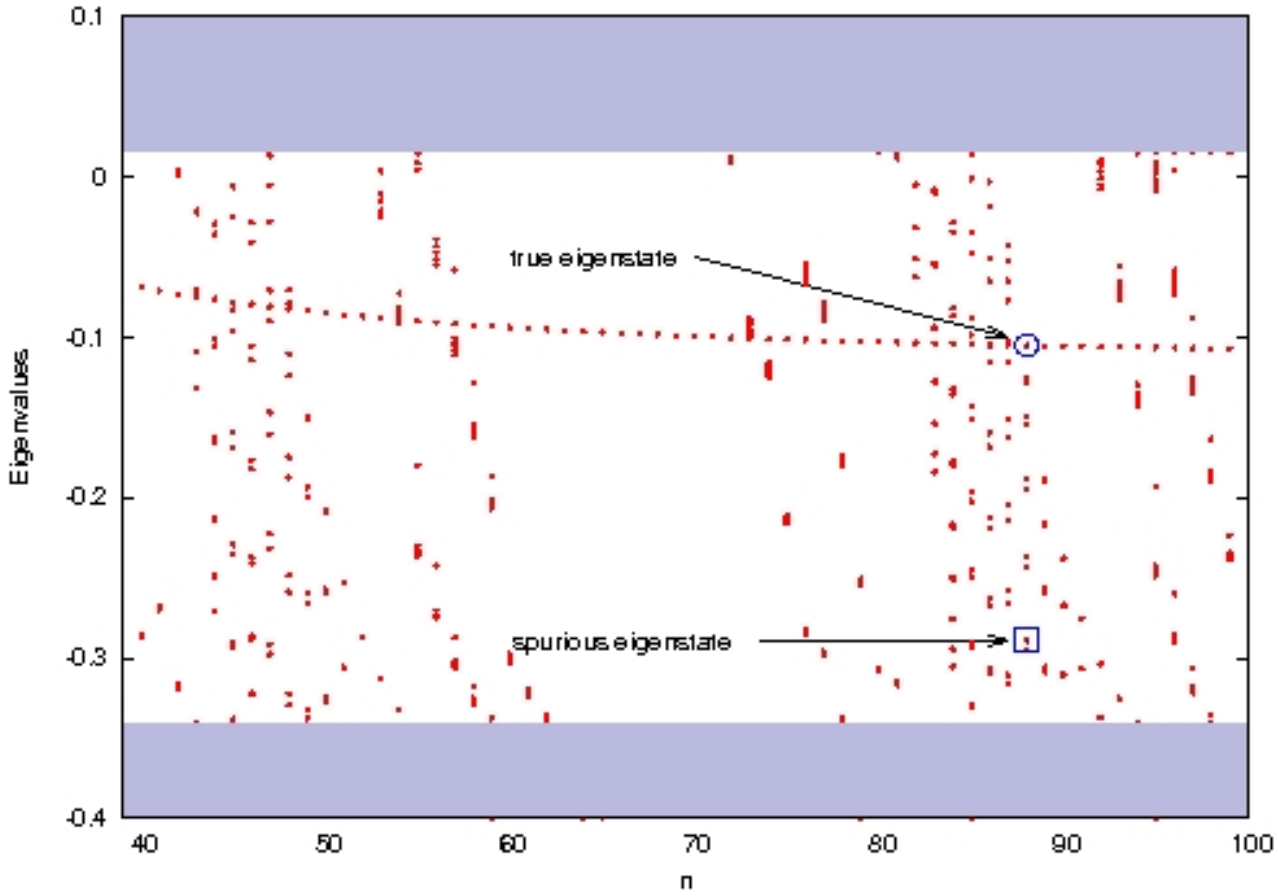
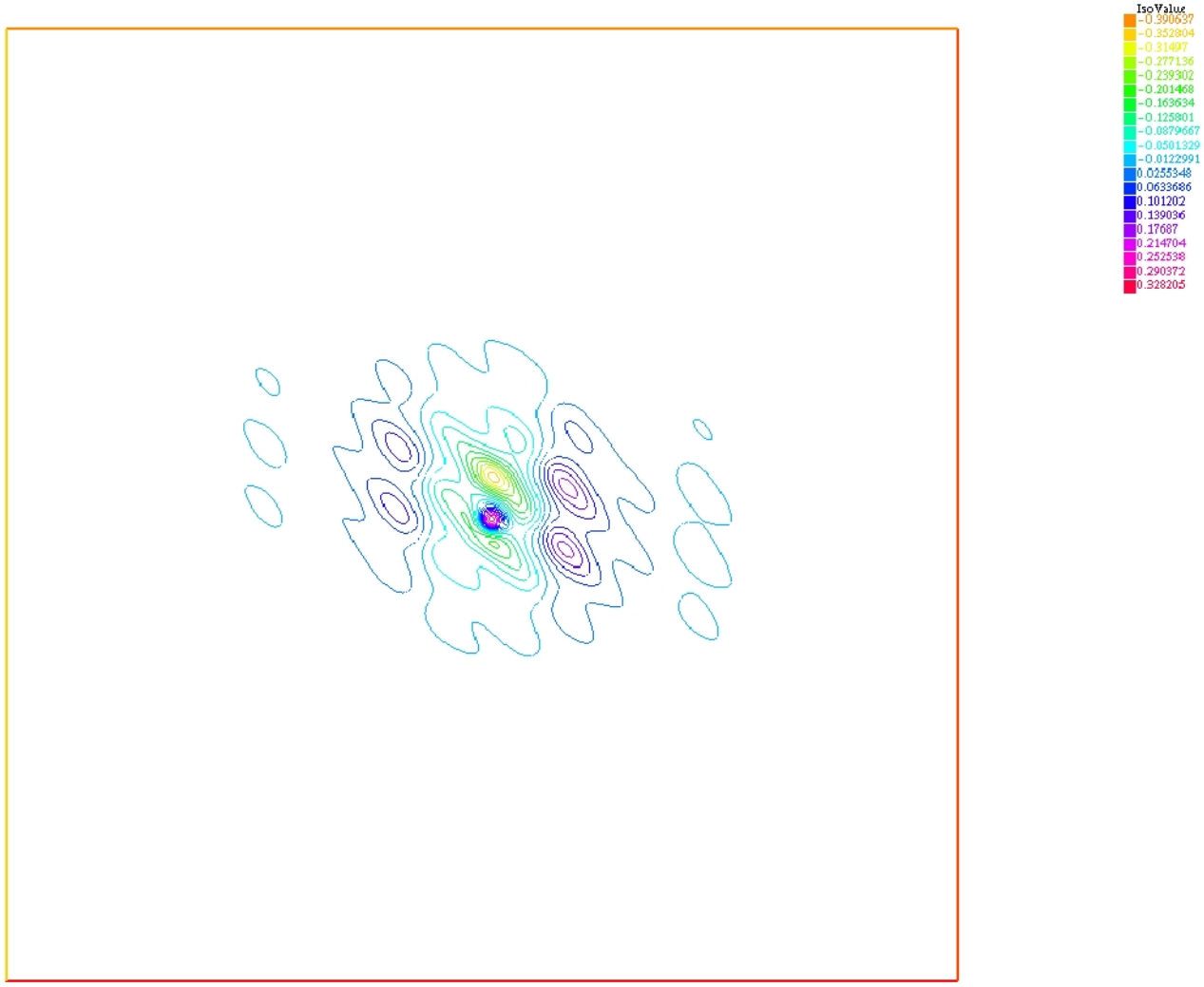


Figure 1: **Spectrum of** $H|_{V_n}$ **in the gap for** $40 \leq n \leq 100$

Profile of a “true” eigenvector



Profile of a “spurious” eigenvector

Finite element discretization of perturbed periodic Schrödinger operators

Let $(\mathcal{T}_n^\infty)_{n\in\mathbb{N}}$ be a sequence of uniformly regular meshes of $\mathbb{R}^d$

- **invariant with respect to the translations of the lattice $\mathcal{R}$**
- **such that $h_n := \max_{K\in\mathcal{T}_n^\infty} \mathrm{diam}(K) \underset{n\to 0}{\to} 0$.**

Let $(\Omega_n)_{n\in\mathbb{N}}$ be an increasing sequence of closed convex sets of $\mathbb{R}^d$ converging to $\mathbb{R}^d$.

For each $n \in \mathbb{N}$, we introduce

- $\mathcal{T}_n := \{K \in \mathcal{T}_n^\infty \,|\, K \subset \Omega_n\}$
- $V_n = \left\{v_n \in H_0^1(\Omega_n) \mid \forall K \in \mathcal{T}_n,\ v_n|_K \in \mathbb{P}_m\right\} \hookrightarrow H^1(\mathbb{R}^d)$

and the discretized operator $H|_{V_n}$ defined as

$$\forall (u_n, v_n) \in V_n \times V_n, \quad (H|_{V_n} u_n, v_n)_{L^2} = \frac{1}{2}\int_{\mathbb{R}^d} \nabla u_n \cdot \nabla v_n + \int_{\mathbb{R}^d} (V_{\mathrm{per}} + W) u_n v_n$$

Proposition (E.C., Ehrlacher, Maday, 2011)

Let $d \leq 3$, $V_{\rm per} \in L^2_{\rm per}(\mathbb{R}^d)$, $W \in L^\infty(\mathbb{R}^d)$, $W(x) \underset{|x|\to\infty}{\to} 0$, $H = -\Delta + V_{\rm per} + W$,

$$\lambda \in \limsup_{n\to\infty} \sigma\left(H|_{V_n}\right) \setminus \sigma(H)$$

and $(\psi_{n_k}, \lambda_{n_k}) \in V_{n_k} \times \mathbb{R}$ **such that**

- $H|_{V_{n_k}} \psi_{n_k} = \lambda_{n_k} \psi_{n_k}$
- $\|\psi_{n_k}\|_{L^2} = 1$

for all $k \in \mathbb{N}$, **and**

$$\lim_{k\to\infty} \lambda_{n_k} = \lambda.$$

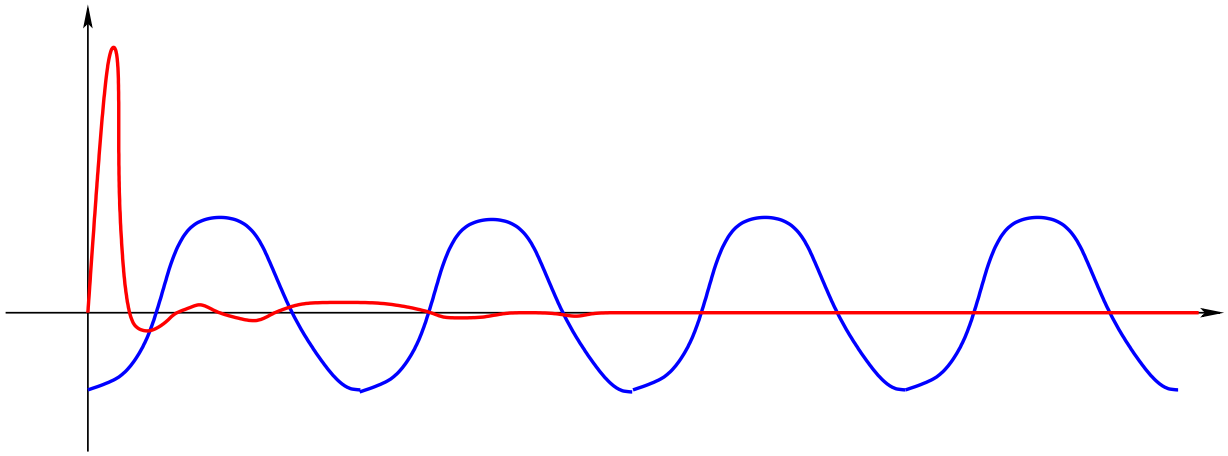
Then, the sequence $(\psi_{n_k})_{k\in\mathbb{N}}$, **considered as a sequence of functions of** $H^1(\mathbb{R}^d)$, **converges to** 0 **weakly in** $H^1(\mathbb{R}^d)$ **and strongly in** $L^q_{\rm loc}(\mathbb{R}^d)$, **with** $q = \infty$ **if** $d = 1$, $q < \infty$ **if** $d = 2$ **and** $q < 2d/(d-2)$ **if** $d \geq 3$, **and it holds**

$$\forall \varepsilon > 0, \quad \exists R > 0 \quad \textbf{s. t.} \quad \liminf_{k\to\infty} \int_{\partial\Omega_{n_k} + B(0,R)} |\psi_{n_k}|^2 \geq 1 - \varepsilon.$$

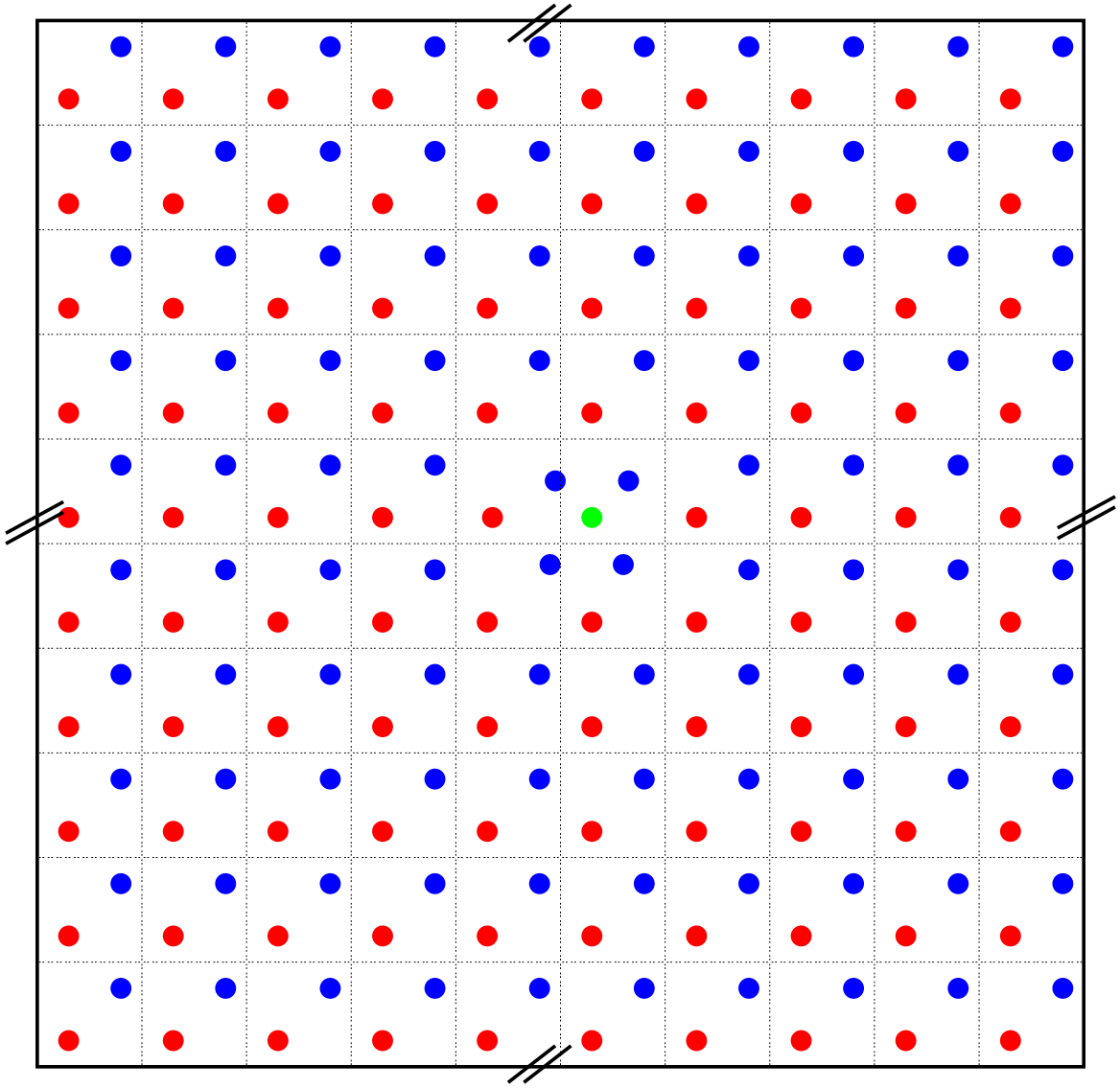
The 1D case: for $\mathcal{R} = b\mathbb{Z}$ and $\Omega_n = [-(n+t)b, (n+t)b]$, the spurious eigenvalues are the discrete eigenvalues of the operators $H^+(t)$ and $H^-(t)$ on $L^2(\mathbb{R}_+)$ defined by

$$D(H^{\pm}(t)) = H^2(\mathbb{R}_+) \cap H^1_0(\mathbb{R}_+), \qquad H^{\pm}(t) = -\frac{1}{2}\frac{d^2}{dx^2} + V_{\rm per}(x \pm tb).$$

Besides, the spurious eigenvectors of $H|_{V_n}$ converge (in some sense, and up to translation) to the discrete eigenvectors of $H^{\pm}(t)$.



4 - The supercell method



The supercell method consists in solving the spectral problem

$$\left\{ \begin{array}{l} \textbf{find } (\psi_{L,N}, \lambda_{L,N}) \in V_{L,N} \times \mathbb{R} \textbf{ such that} \\ \forall \phi_{L,N} \in V_{L,N},\ a_L(\psi_{L,N}, \phi_{L,N}) = \lambda_{L,N} \langle \psi_{L,N}, \phi_{L,N} \rangle_{L^2_{\rm per}(\Gamma_L)}, \end{array} \right.$$

where

- $\Gamma_L = L\Gamma$ **(with** $L \in \mathbb{N}^*$**) is the supercell**
- $V_{L,N}$ **is a finite dimensional subspace of** $H^1_{\rm per}(\Gamma_L)$
- **for all** $(u_L, v_L) \in H^1_{\rm per}(\Gamma_L)$**,**

$$a_L(u_L, v_L) = \int_{\Gamma_L} \nabla u_L \cdot \nabla v_L + \int_{\Gamma_L} (V_{\rm per} + W) u_L v_L, \quad \langle u_L, v_L \rangle_{L^2_{\rm per}(\Gamma_L)} = \int_{\Gamma_L} u_L v_L,$$

We denote by $H_{L,N} = H_L|_{V_{L,N}}$**, where** H_L **is the unique self-adjoint operator on** $L^2_{\rm per}(\Gamma_L)$ **associated with quadratic form** a_L**.**

Fourier (planewave) discretization

Choice of the discretization space:

$$V_{L,N} = \left\{ v_n(x) = \sum_{k \in L^{-1}\mathcal{R}^* \,|\, |k| \leq N/L} c_k \, e^{ik\cdot x} \;\Big|\; \forall k,\, c_{-k} = c_k^* \right\}$$

Theorem (E.C., Ehrlacher, Maday, 2011). **Assume that** $V_{\rm per} \in L^2_{\rm per}(\Gamma)$ **if** $d = 1$, $V_{\rm per} \in L^{2,\infty}_{\rm per}(\Gamma)$ **if** $d = 2$, **and** $V_{\rm per} \in L^{3,\infty}_{\rm per}(\Gamma)$ **if** $d = 3$ **(point charges OK), and that** $W \in L^\infty(\mathbb{R}^d)$ **with** $\lim_{|x|\to\infty} W(x) = 0$**. Then**

$$\lim_{N,L\to\infty \,|\, N/L\to\infty} \sigma(H_{L,N}) = \sigma(H).$$

A similar result was proved by Soussi for 2D photonic crystals, with $V_{\rm per} \in L^\infty_{\rm per}(\mathbb{R}^2)$ **and** $W \in L^\infty(\mathbb{R}^2)$ **compactly supported.**

Conclusion and future works

Galerkin finite element approximation (with truncation and Dirichlet BC)

- If the mesh is invariant w.r.t. the translations of the lattice, the spurious eigenvalues correspond to (fictitious) surface modes
- This assumption can be weakened (possibility to refine the mesh in the vicinity of the defect, and to coarsen it in the vicinity of the boundary)
- It is easy to identify the spurious eigenvalues
- It is more difficult to identify spurious eigenvectors associated with true eigenvalues
- It is very difficult to eliminate spectral pollution in the Kohn-Sham problem due to long-range Coulomb interaction

Supercell method

- The supercell method with Fourier bases is spectral pollution free
- ... provided the supercell contains an integer number of unit cells
- On the other hand, it is very costly when the supercell is large

$\longrightarrow$ **Wannier functions basis sets**

E.C.-Deleurence-Lewin, 2008

Lewin-Séré, 2010

Boulton-Boussaid-Lewin, arXiv 2010

E.C.-Ehrlacher-Maday, arXiv 2011