Supercell method for the computation of energies of crystals

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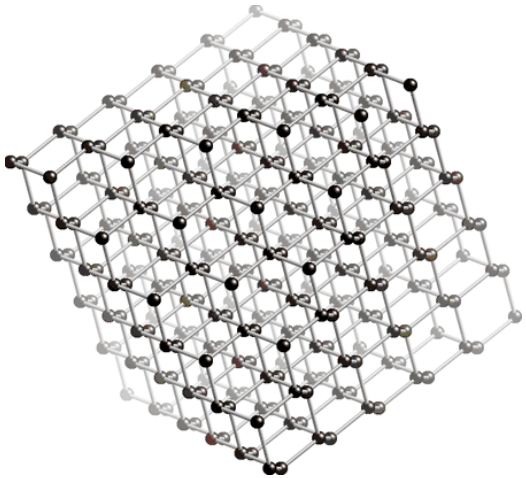
Goal: compute numerically the energy per cell of a crystal.

$\Longrightarrow$ Predict the structure of a crystal.

$\Longrightarrow$ Compute the energy of a defect inside a crystal.



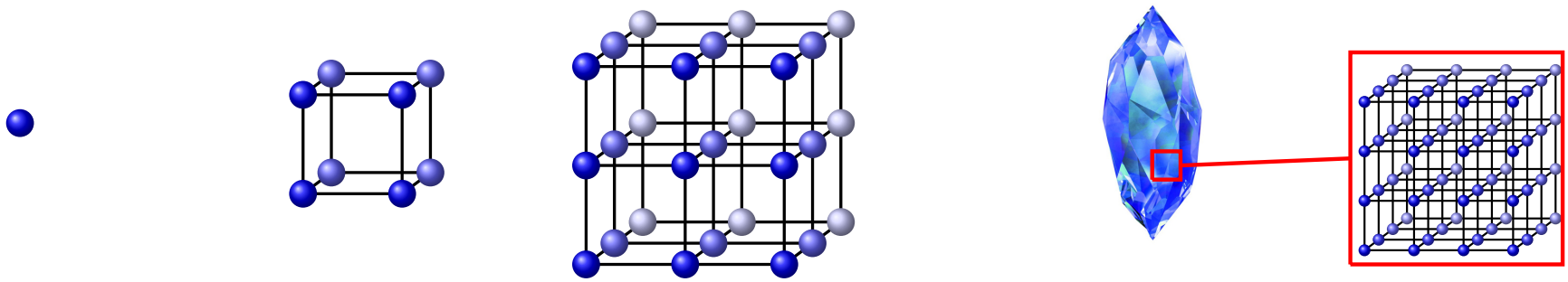
What is a crystal?

- A periodic arrangement of (fixed) nuclei on a lattice.
  Modeled by a periodic density charge $\mu_{\mathrm{per}} \in L^2_{\mathrm{per}}(\mathbb{R}^3)$.
- An arrangement of moving electrons around these nuclei.

What is the energy (per cell) of the electrons?

Fact: There exist good models for finite systems.

Thermodynamic limit: See the infinite periodic crystal as the limit of finite systems.



$L = 1$ $L = 2$ $L = 3$ $\cdots$ $L = \infty$

Roadmap:

- Choose a model for finite systems (Schrödinger equation, Hartree(-Fock), DFT,...).
- For each $L \in \mathbb{N}^*$, calculate the ground state energy E_L for the charge density μ_L.
- Take the limit $L \to \infty$.

Questions:

- Does the sequence $L^{-3}E_L$ (energy per cell) converge as $L \to \infty$?
- If yes, can we characterize the limit?

Lattice: $\mathcal{R} = a\mathbb{Z}^3$. Unit cell: $\Gamma = [-a/2, a/2)^3$.
Reciprocal lattice: $\mathcal{R}^* = (2\pi/a)\,\mathbb{Z}^3$. Reciprocal unit cell: $\Gamma^* = [-\pi/a, \pi/a)^3$.

Supercell: $\Gamma_L := L\Gamma$

Nuclear charge of the finite system:

$$\mu_L^{\text{finite}}(\mathbf{x}) := \mu_{\text{per}}(\mathbf{x}) \cdot \mathbb{1}(\mathbf{x} \in \Gamma_L).$$

Potential generated by the nuclei:

$$V_L^{\text{finite}}(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\mu_L^{\text{finite}}(\mathbf{x})}{|\mathbf{x} - \mathbf{y}|} \mathrm{d}\mathbf{y}.$$

Number of electrons per cell of the crystal:

$$\int_\Gamma \mu_{\text{per}} = N. \qquad \text{(from neutrality of the system)}$$

Hamiltonian ($N_L := NL^3$):

$$H_L^{\text{finite}} = \sum_{k=1}^{N_L} \left(-\frac{1}{2}\Delta_k + V_L^{\text{finite}}(\mathbf{x}_k) \right) + \frac{1}{2} \sum_{1 \le l < k \le N_L} \frac{1}{|\mathbf{x}_k - \mathbf{x}_l|}.$$

acting on the fermionic space

$$\bigwedge^{N_L} L^2(\mathbb{R}^3) = \left\{ \Psi \in L^2(\mathbb{R}^{3N_L}),\ \forall p \in S_{N_L},\ \underbrace{\Psi(\mathbf{x}_{p(1)}, \cdots, \mathbf{x}_{p(N_L)}) = \varepsilon(p)\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_{N_L})}_{\text{Pauli principle}} \right\}.$$

Full Schrödinger model

$$E_L^{\text{finite,Schr.}} := \inf \left\{ \left\langle \Psi \middle| H_L^{\text{finite}} \middle| \Psi \right\rangle, \ \Psi \in \bigwedge^{N_L} L^2(\mathbb{R}^3), \ \|\Psi\|_{L^2(\mathbb{R}^{3N_L})} = 1 \right\}.$$

- Very difficult to compute (curse of dimensionality).
- The limit $L^{-3}E_L$ exists, but the limit cannot be characterized.[1,2]

Idea: Restrict the minimization problem to the set of Slater determinants

$$S_{N_L} := \left\{ \det\left[(\phi_i(\mathbf{x}_j))_{1\leq i,j\leq N_L} \right], \ \phi_1, \dots, \phi_{N_L} \in H^1(\mathbb{R}^3), \ \int_{\mathbb{R}^3} \overline{\phi_i}\phi_j = \delta_{ij} \right\} \subset \bigwedge^{N_L} L^2(\mathbb{R}^3).$$

One-body density matrix

$$\gamma = \sum_{i=1}^{N_L} |\phi_i\rangle\langle\phi_i| \quad \text{or} \quad \gamma(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N_L} \phi_i(\mathbf{x})\overline{\phi_i(\mathbf{y})}.$$

Electronic density

$$\rho(\mathbf{x}) = \rho_\gamma(\mathbf{x}) = \gamma(\mathbf{x},\mathbf{x}) = \sum_{i=1}^{N_L} |\phi_i|^2(\mathbf{x}).$$

The Hartree-Fock model

$$E_L^{\text{finite,HF}} := \inf \left\{ \left\langle \Psi \middle| H_L^{\text{finite}} \middle| \Psi \right\rangle, \ \Psi \in S_{N_L}, \ \|\Psi\|_{L^2(\mathbb{R}^{3N_L})} = 1 \right\}.$$

[1] C. Fefferman, Commun. Math. Phys. 98 (1985), no. 3.

[2] X. Blanc, C. Le Bris, and P.-L. Lions, Comm. Part. Diff. Eq. 28 (2003).

The Hartree-Fock model (bis)

$$E_L^{\text{finite,HF}} = \inf_{\gamma \in \mathcal{P}_{N_L}} \left\{ \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_L^{\text{finite}} \right) \gamma \right) + \frac{1}{2} \iint_{(\mathbb{R}^3)^2} \frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y}) - |\gamma(\mathbf{x},\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|} d\mathbf{x} d\mathbf{y}, \right\},$$

where[3]

$$\mathcal{P}_{N_L} := \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \leq \gamma \leq 1,\ \mathrm{Tr}(\gamma) = N_L,\ \mathrm{Tr}(-\Delta\gamma) < \infty \right\}.$$

[3] A. Coleman, Rev. Mod. Phys. 35 (1963), no. 3.

The reduced Hartree-Fock (rHF) model

$$E_L^{\text{finite,rHF}} = \inf_{\gamma \in \mathcal{P}_{N_L}} \left\{ \mathrm{Tr}\left((-\frac{1}{2}\Delta + V_L^{\text{finite}})\gamma \right) + \frac{1}{2} \iint_{(\mathbb{R}^3)^2} \frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}, \right\},$$

where[3]

$$\mathcal{P}_{N_L} := \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \le \gamma \le 1,\ \mathrm{Tr}(\gamma) = N_L,\ \mathrm{Tr}(-\Delta\gamma) < \infty \right\}.$$

Lemma (I. Catto, C. Le Bris, and P.-L. Lions, Ann. Inst. H. Poincaré (C) 18 (2001), no. 6.)

- ***Existence***: *The sequence* $L^{-3}E_L^{\text{finite,rHF}}$ *has a limit* $I_{\text{per}}^{\text{rHF}}$ *as* $L \to \infty$.
- ***Characterization:*** *It holds that*

$$I_{\text{per}}^{\text{rHF}} = \inf \left\{ \frac{1}{2}\underline{\mathrm{Tr}}\,(-\Delta\gamma) + \frac{1}{2}D_1(\rho_\gamma - \mu_{\text{per}}, \rho_\gamma - \mu_{\text{per}}),\ \gamma \in \mathcal{P}_{\text{per}}, \int_\Gamma \rho_\gamma = N \right\}.$$

where $\underline{\mathrm{Tr}}$ *denotes the trace per cell, and* $D_1(\cdot,\cdot)$ *is the periodic Coulomb quadratic form (see later).*

Question: How to compute $I_{\text{per}}^{\text{rHF}}$ efficiently numerically?

[3] A. Coleman, Rev. Mod. Phys. 35 (1963), no. 3.

The linear case

Interlude: finite systems

1-body Hamiltonians

$$h_1 = -\frac{1}{2}\Delta + V \quad \text{self-adjoint operator acting on} \quad \mathcal{H}_1 = L^2(\mathbb{R}^3).$$

- $\varepsilon_1 \leq \ldots \leq \varepsilon_N$ the smallest eigenvalues (we assume that they exist),
- $u_1, \ldots, u_N \in \mathcal{H}_1$ the corresponding normalized eigenvectors.

N-body non-interacting Hamiltonians

$$H_N := \sum_{i=1}^{N} h_1(\mathbf{r}_i) \quad \text{acting on the fermionic space} \quad \bigwedge^N \mathcal{H}_1.$$

Ground state energy of H_N

$$\begin{aligned} E_N^0 &= \varepsilon_1 + \ldots + \varepsilon_N = \langle u_1, h_1 u_1 \rangle + \ldots + \langle u_N, h_1 u_N \rangle \\ &= \mathrm{Tr}_{\mathcal{H}_1}\left[h_1 \left(|u_1\rangle\langle u_1| + \ldots + |u_N\rangle\langle u_N|\right)\right] \qquad \text{(cyclicity of the trace)} \\ &= \inf\left\{\mathrm{Tr}_{\mathcal{H}_1}\left[h_1\gamma\right],\ \gamma \text{ is a projector of rank } N\right\} \qquad \text{(min-max principle)} \\ &= \inf\left\{\mathrm{Tr}_{\mathcal{H}_1}\left[h_1\gamma\right],\ \gamma \in \mathcal{P}_N\right\} \qquad \text{(min of linear function on convex set)}, \end{aligned}$$

where $\mathcal{P}_N$ is the convex hull of the set of projectors of rank N:

$$\mathcal{P}_N := \left\{\gamma \in \mathcal{S}(\mathcal{H}_1),\ 0 \leq \gamma \leq 1,\ \mathrm{Tr}_{\mathcal{H}_1}(\gamma) = N,\ \mathrm{Tr}_{\mathcal{H}_1}(-\Delta\gamma) < \infty\right\}.$$

E_N^0 can be defined as a minimisation problem over the set $\mathcal{P}_N$ ($\sim$ a set of operators).

Periodic Hamiltonian Consider $V_{\rm per}$ a real-valued $\mathcal{R}$-periodic function, and set

$$H_{\rm per} = -\frac{1}{2}\Delta + V_{\rm per} \quad \text{acting on} \quad L^2(\mathbb{R}^3).$$

Energy per cell (N electrons per cell)

$$\boxed{I_{\rm per} = \inf\left\{\underline{\rm Tr}\left(H_{\rm per}\gamma\right),\ \gamma \in \mathcal{P}_{\rm per},\ \underline{\rm Tr}(\gamma) = N\right\}.}$$

Trace per cell

$$\underline{\rm Tr}(A) := \lim_{L\to\infty} \frac{1}{L^3}{\rm Tr}\left(\mathbb{1}_{\Gamma_L} A \mathbb{1}_{\Gamma_L}\right).$$

Set of one-body density matrices

$$\mathcal{P}_{\rm per} = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \le \gamma \le 1,\ \forall \mathbf{R} \in \mathcal{R},\ \tau_{\mathbf{R}}\gamma = \gamma\tau_{\mathbf{R}},\ \underline{\rm Tr}(\gamma) + \underline{\rm Tr}(-\Delta\gamma) < \infty\right\}.$$

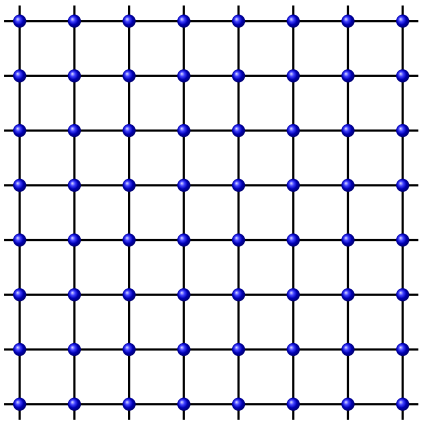
Lemma

In the insulating case, the unique minimizer for $I_{\rm per}$ is $\gamma_{\rm per} = \mathbb{1}(H_{\rm per} \le \varepsilon_F)$, for some $\varepsilon_F \in \mathbb{R}$ (Fermi energy).

Problem: The set $\mathcal{P}_{\rm per}$ is numerically difficult to represent!

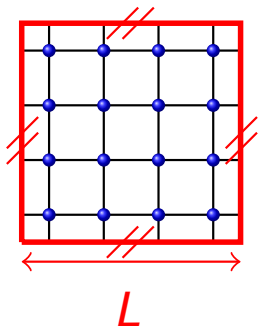
The supercell model

Full model



$\approx$

Supercell model



Laplacian with periodic boundary conditions: $-\Delta^L$.

Supercell Hamiltonian

$$H^L := -\frac{1}{2}\Delta^L + V_{\mathrm{per}} \quad \text{acting on} \quad L^2_{\mathrm{per}}(\Gamma_L).$$

Supercell energy

$$E_L := \inf\left\{ \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(H^L\gamma^L\right),\ \gamma^L \in \mathcal{P}^L,\ \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma^L\right) = N \right\}.$$

Set of supercell one-body density matrices

$$\mathcal{P}^L = \left\{ \gamma^L \in \mathcal{S}(L^2_{\mathrm{per}}(\Gamma_L)),\ 0 \leq \gamma^L \leq 1,\ \tau_{\mathbf{R}}\gamma^L = \gamma^L\tau_{\mathbf{R}},\ \mathrm{Tr}(\gamma^L) + \mathrm{Tr}(-\Delta^L\gamma^L) < \infty \right\}.$$

$$\boxed{I_{\mathrm{per}} = \inf\left\{\underline{\mathrm{Tr}}\left(H_{\mathrm{per}}\gamma\right),\ \gamma \in \mathcal{P}_{\mathrm{per}},\ \underline{\mathrm{Tr}}(\gamma) = N\right\}}$$ what we want

$$\boxed{E_L := \inf\left\{\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(H^L\gamma^L\right),\ \gamma^L \in \mathcal{P}^L,\ \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma^L\right) = N\right\}}$$ what we can compute

Questions

- Does the sequence $L^{-3}E_L$ converges to I_{per} as $L \to \infty$? Yes[4]
- What is the speed of convergence?

Lemma

In the insulating case, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \in \mathbb{N}^*$,

$$\left|L^{-3}E_L - I_{\mathrm{per}}\right| \leq Ce^{-\alpha L}. \qquad \textit{(Convergence of the energy per cell)}$$

- Validate a posteriori the sampling method proposed by Monkhorst and Pack[5].
- Proof: discrete Bloch transform, complex analysis, convergence of Riemann sums.

[4] E. Cancès, A. Deleurence, and M. Lewin, Commun. Math. Phys. 281 (2008)
[5] H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13 (1976), no. 12.

Step 1: (discrete) Bloch transform

$$
\begin{aligned}
L^2_{\mathrm{per}}([0,L]) \quad &= \mathrm{Vect}\Big\{ \quad \vdots \qquad \vdots \qquad \vdots \qquad \dots \qquad \vdots \\
&\qquad\qquad e^{2i\pi 0x}, \quad e^{2i\pi\left(\frac{1}{L}\right)x}, \quad e^{2i\pi\left(\frac{2}{L}\right)x}, \quad \dots, \quad e^{2i\pi\left(\frac{L-1}{L}\right)}, \\
&\qquad\qquad e^{2i\pi\left(\frac{L}{L}\right)x}, \quad e^{2i\pi\left(\frac{L+1}{L}\right)x}, \quad e^{2i\pi\left(\frac{L+2}{L}\right)x}, \quad \dots, \quad e^{2i\pi\left(\frac{2L-1}{L}\right)x}, \\
&\qquad\qquad \vdots \qquad \vdots \qquad \vdots \qquad \dots \qquad \vdots \qquad \Big\} \\
&= \qquad L^2_0 \quad \oplus \quad L^2_{\frac{2\pi}{L}} \quad \oplus \quad L^2_{\frac{4\pi}{L}} \quad \oplus \quad \cdots \quad \oplus \quad L^2_{\frac{2\pi(L-1)}{L}}.
\end{aligned}
$$

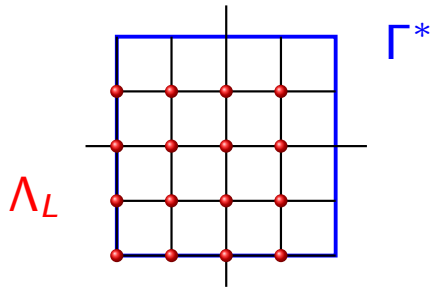
Fibers

$$
L^2_{\mathbf{q}} = \mathrm{Vect}\left\{ e^{i\mathbf{k}\cdot\mathbf{x}} e^{i\mathbf{q}\cdot\mathbf{x}}, \mathbf{k} \in \mathcal{R}^* \right\} = \left\{ \psi \in L^2_{\mathrm{loc}}(\mathbb{R}^3),\ \forall \mathbf{R} \in \mathcal{R},\ \psi(\cdot + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} \psi(\cdot) \right\}.
$$

$L^2_{\mathbf{q}}$ does not depend on L, $\quad \mathbf{q} \in \Gamma^*$.

3D case

$$
L^2_{\mathrm{per}}(\Gamma_L) = \frac{1}{L^3} \bigoplus_{\mathbf{Q} \in \Lambda_L} L^2_{\mathbf{Q}}.
$$



Covariant property

$$
L^2_{\mathbf{q}} = S_{\mathbf{q}} \left(L^2_{\mathrm{per}}(\Gamma) \right) \quad \text{with} \quad S_{\mathbf{q}}[f](\mathbf{x}) = e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{x}) \quad \text{and} \quad (S_{\mathbf{q}})^{-1} = S_{-\mathbf{q}}.
$$

Discrete Bloch transform for operators

If A^L is a self-adjoint operator on $L^2_{\mathrm{per}}(\Gamma_L)$ such that for all $\mathbf{R}$ in $\mathcal{R}$, it holds $\tau_{\mathbf{R}} A^L = A^L \tau_{\mathbf{R}}$,

$$A^L = \begin{pmatrix} \widetilde{A^L_{\mathbf{Q_0}}} & 0 & \cdots & 0 \\ 0 & \widetilde{A^L_{\mathbf{Q_1}}} & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & \widetilde{A^L_{\mathbf{Q}_{L^3}}} \end{pmatrix} \quad \text{(Bloch transform = block-decomposition).}$$

Block-elements

$$\widetilde{A^L_{\mathbf{q}}} := P_{L^2_{\mathbf{q}}} A^L P_{L^2_{\mathbf{q}}}, \quad \widetilde{A^L_{\mathbf{q}}} : L^2_{\mathbf{q}} \to L^2_{\mathbf{q}}.$$

Covariant block-elements

$$A^L_{\mathbf{q}} := S_{-\mathbf{q}} \widetilde{A^L_{\mathbf{q}}} S_{\mathbf{q}}, \quad A^L_{\mathbf{q}} : L^2_{\mathrm{per}}(\Gamma) \to L^2_{\mathrm{per}}(\Gamma). \qquad \boxed{A^L = \frac{1}{L^3} \bigoplus_{\mathbf{Q} \in \Lambda_L} A^L_{\mathbf{Q}}.}$$

Basic properties

- Spectrum

$$\sigma(A^L) = \bigcup_{\mathbf{Q} \in \Lambda_L} \sigma\left(\widetilde{A^L_{\mathbf{Q}}}\right) = \bigcup_{\mathbf{Q} \in \Lambda_L} \sigma\left(A^L_{\mathbf{Q}}\right).$$

- Trace per cell

$$\underline{\mathrm{Tr}}_L(A^L) := \frac{1}{L^3} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}(A^L) = \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}(\widetilde{A^L_{\mathbf{Q}}}) = \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}(A^L_{\mathbf{Q}}).$$

Example: The periodic Hamiltonian

$$H^L = -\frac{1}{2}\Delta^L + V_{\text{per}} \quad \text{acting on} \quad L^2_{\text{per}}(\Gamma_L).$$

Bloch transform(s)

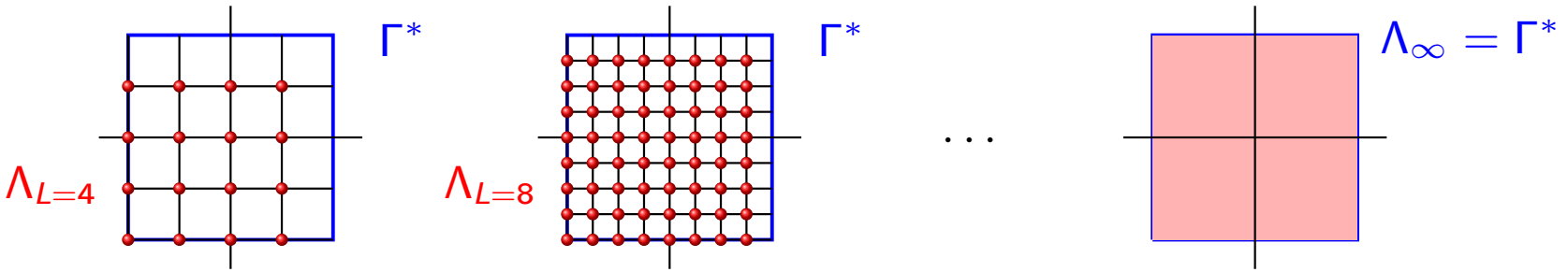
- "Same operator" acting on different spaces:

$$\widetilde{H^L_{\mathbf{q}}} = -\frac{1}{2}\Delta^1 + V_{\text{per}} \quad \text{acting on} \quad L^2_{\mathbf{q}}.$$

- Different operators acting on the same space:

$$H^L_{\mathbf{q}} = \frac{1}{2}\left|-\mathrm{i}\nabla^1 + \mathbf{q}\right|^2 + V_{\text{per}} = -\frac{1}{2}\Delta^1 - \mathbf{q}\cdot(\mathrm{i}\nabla^1) + \frac{\mathbf{q}^2}{2} + V_{\text{per}} \quad \text{acting on} \quad L^2_{\text{per}}(\Gamma).$$

Supercell thermodynamic limit ($L \to \infty$)



$$H^L = \frac{1}{L^3}\bigoplus_{\mathbf{Q}\in\Lambda_L} H^L_{\mathbf{Q}} \quad \xrightarrow[L\to\infty]{} \quad \boxed{H_{\text{per}} = \fint_{\Gamma^*}^{\oplus} H_{\mathbf{q}}\,\mathrm{d}\mathbf{q}.}$$

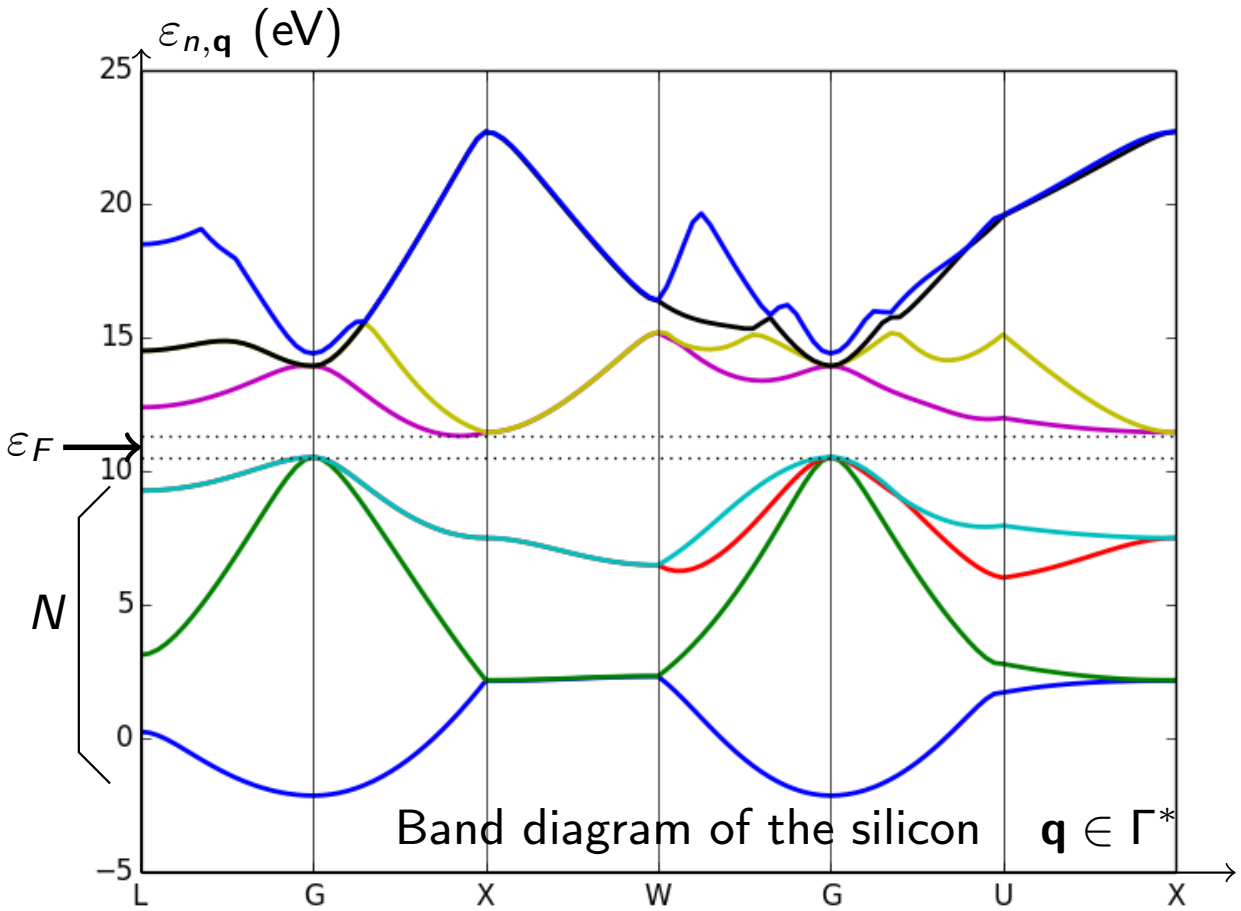
Supercell model $\Longleftrightarrow$ Sampling of Γ^*.

Spectrum

$$\sigma(H_{\mathrm{per}}) = \bigcup_{\mathbf{q}\in\Gamma^*} \sigma(H_{\mathbf{q}})$$

Remark: The operator $H_{\mathbf{q}}$ (acting on $L^2_{\mathrm{per}}(\Gamma)$) is compact resolvent:

$$H_{\mathbf{q}} = \sum_{n=1}^{\infty} \varepsilon_{n,\mathbf{q}} |u_{n,\mathbf{q}}\rangle\langle u_{n,\mathbf{q}}|, \quad \varepsilon_{1,\mathbf{q}} \leq \varepsilon_{2,\mathbf{q}} \leq \cdots, \quad \langle u_{n,\mathbf{q}}, u_{m,\mathbf{q}}\rangle_{L^2_{\mathrm{per}}(\Gamma)} = \delta_{nm}.$$



Fermi energy: $\varepsilon_F \in \mathbb{R}$ s.t.

$$\sum_{n=1}^{\infty} \fint_{\Gamma^*} \mathbb{1}(\varepsilon_{n,\mathbf{q}} \leq \varepsilon_F)\, \mathrm{d}\mathbf{q} = N.$$

Insulating system (gap $g > 0$)

$$\varepsilon_{N,\mathbf{q}} + \frac{g}{2} \leq \varepsilon_F \leq \varepsilon_{N+1,\mathbf{q}} - \frac{g}{2}.$$

Full Hamiltonian

Energy per unit cell (update)

$$I_{\mathrm{per}} = \inf\left\{\underline{\mathrm{Tr}}\left(H_{\mathrm{per}}\gamma\right),\ \gamma \in \mathcal{P}_{\mathrm{per}},\ \underline{\mathrm{Tr}}\left(\rho_\gamma\right) = N\right\} = \fint_{\Gamma^*}\left(\sum_{n=1}^{N}\varepsilon_{n,\mathbf{q}}\right)\mathrm{d}\mathbf{q}.$$

Corresponding one-body density (minimizer)

$$\gamma_{\mathrm{per}} = \mathbb{1}(H_{\mathrm{per}} \leq \varepsilon_F) = \fint_{\Gamma^*}^{\oplus} \underbrace{\mathbb{1}(H_{\mathbf{q}} \leq \varepsilon_F)}_{\gamma_{\mathbf{q}}}\ \mathrm{d}\mathbf{q}.$$

Supercell model

Energy per unit cell

$$\frac{1}{L^3}E_L = \inf\left\{\underline{\mathrm{Tr}}_L\left(H^L\gamma^L\right),\ \gamma^L \in \mathcal{P}^L,\ \underline{\mathrm{Tr}}_L\left(\gamma^L\right) = N\right\} = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\left(\sum_{n=1}^{N}\varepsilon_{n,\mathbf{Q}}\right).$$

Corresponding one-body density (minimizer)

$$\gamma^L = \mathbb{1}(H^L \leq \varepsilon_F) = \frac{1}{L^3}\bigoplus_{\mathbf{Q}\in\Lambda_L}\gamma_{\mathbf{Q}}.$$

Error for the energy

$$\frac{1}{L^3}E_L - I_{\mathrm{per}} = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\left(\sum_{n=1}^{N}\varepsilon_{n,\mathbf{Q}}\right) - \fint_{\Gamma^*}\left(\sum_{n=1}^{N}\varepsilon_{n,\mathbf{q}}\right)\mathrm{d}\mathbf{q}.$$

This is the difference between a Riemann sum and an integral.

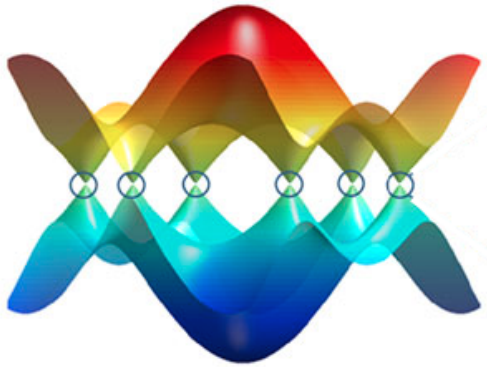
Step 2: Complex analysis

Integrand

$$K(\mathbf{q}) := \sum_{n=1}^{N} \varepsilon_{n,\mathbf{q}}.$$

Properties

- The function K is $\mathcal{R}^*$-periodic.
- The functions $\mathbf{q} \mapsto \varepsilon_{n,\mathbf{q}}$ are not smooth in general (conic singularities).
- However, the sum of the eigenvalues is smooth.



Band diagram of graphene.

Lemma ([6,7,8])

If the system is an insulator, then the ($\mathcal{R}^*$-periodic) function K admits an analytic extension on some complex strip $S_A := \mathbb{R}^3 + \mathrm{i}[-A, A]^3$ with $A > 0$.

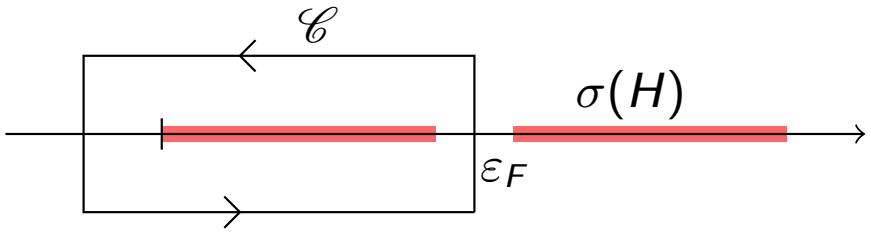
- Link with Wannier functions (see talk by Antoine Levitt)
- Also link to the fact that $|\gamma_{\mathrm{per}}(\mathbf{x}, \mathbf{y})| \leq C\mathrm{e}^{-\alpha|\mathbf{x}-\mathbf{y}|}$.

[8] W. Kohn, Phys. Rev. 115 (1959).
[8] J. Des Cloizeaux, Phys. Rev. 135 (1964).
[8] C. Brouder, G. Panati, M. Calandra, C. Mourougane, and N. Marzari, Phys. Rev. Lett. 98 (2007).

Elements of the proof

Cauchy residual formula

$$\gamma_{\mathbf{q}} = \mathbb{1}(H_{\mathbf{q}} \leq \varepsilon_F) = \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H_{\mathbf{q}}}.$$



Analytic continuation

$$H_{\mathbf{q}} = -\frac{1}{2}\Delta^1 - \mathbf{q}\cdot(\mathrm{i}\nabla^1) + \frac{\mathbf{q}^2}{2} + V_{\mathrm{per}} \quad \Longrightarrow \quad H_{\mathbf{z}} = -\frac{1}{2}\Delta^1 - \mathbf{z}\cdot(\mathrm{i}\nabla^1) + \frac{\mathbf{z}^T\mathbf{z}}{2} + V_{\mathrm{per}}$$

Lemma

There exists $A > 0$ such that

$$\forall \mathbf{z} \in S_A, \quad \gamma_{\mathbf{z}} := \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H_{\mathbf{z}}}$$

is well-defined. Moreover, the map $\mathbf{z} \mapsto \gamma_{\mathbf{z}}$ is analytic on S_A.

Integrand

$$K(\mathbf{q}) := \sum_{n=1}^{N} \varepsilon_{n,\mathbf{q}} = \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\left(H_{\mathbf{q}}\gamma_{\mathbf{q}}\right) \quad \Longrightarrow \quad K(\mathbf{z}) := \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\left(H_{\mathbf{z}}\gamma_{\mathbf{z}}\right).$$

- $K(\mathbf{z})$ is $\mathcal{R}^*$-periodic and analytic on S_A.

Step 3: Convergence of Riemann sum

Lemma (classical)

If $f : S_A \to \mathbb{C}$ is analytic on S_A for some $A > 0$ and satisfies $f(\mathbf{z} + \mathbf{k}) = f(\mathbf{z})$ for all $\mathbf{k} \in \mathcal{R}^*$, then there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that

$$\forall L \in \mathbb{N}^*, \quad \left| \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} f(\mathbf{Q}) - \fint_{\Gamma^*} f(\mathbf{q}) \mathrm{d}\mathbf{q} \right| \leq C \mathrm{e}^{-\alpha L}.$$

Conclusion

Lemma (DG, Salma Lahbabi)

In the insulating case, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \in \mathbb{N}^*$,

$$\left| L^{-3} E_L - I_{\mathrm{per}} \right| \leq C \mathrm{e}^{-\alpha L}. \qquad \textit{(Convergence of the energy per cell)}$$

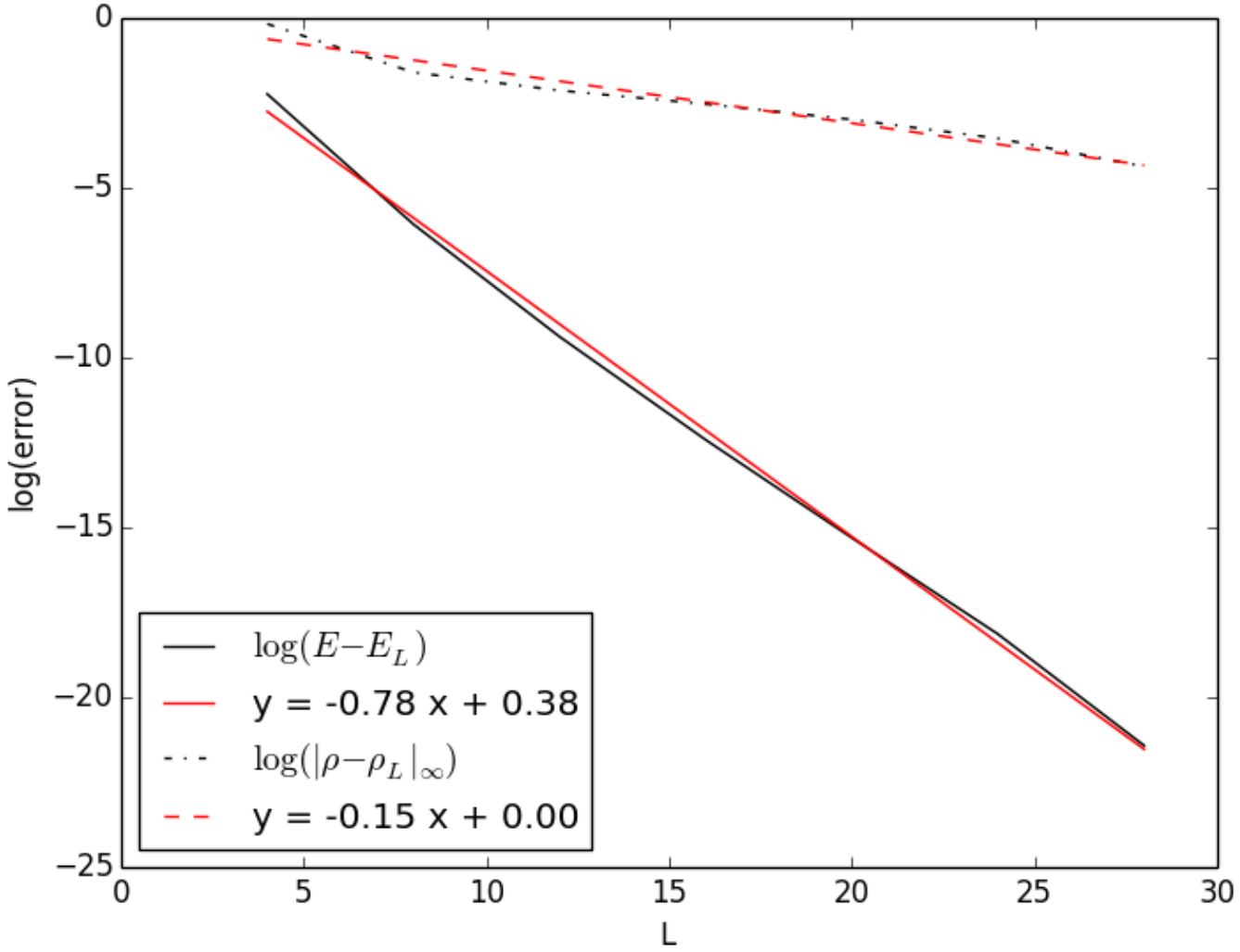
$$\left\| \rho_{\gamma_{\mathrm{per}}} - \rho_{\gamma^L} \right\|_{L^\infty_{\mathrm{per}}} \leq C \mathrm{e}^{-\alpha L}. \qquad \textit{(Convergence of the electronic density)}$$

Note that we cannot compare the minimizers

$$\gamma_{\mathrm{per}} \in \mathcal{P}_{\mathrm{per}} \subset \mathcal{S}(L^2(\mathbb{R}^3)) \quad \text{and} \quad \gamma^L \in \mathcal{P}^L \subset \mathcal{S}(L^2_{\mathrm{per}}(\Gamma_L)).$$

Numerical illustration

(Linear model for silicium taken in M.L. Cohen and T.K. Bergstresser, Phys. Rev. 141 (1966).



Speed of convergence for the silicium (linear model) .

The non-linear case (reduced Hartree-Fock case)

How to transpose the results in the non-linear case?

Energy per cell (rHF)

$$I_{\rm per}^{\rm rHF} = \inf\left\{\mathcal{I}_{\rm per}^{\rm rHF}(\gamma),\ \gamma \in \mathcal{P}_{\rm per}, \underline{\rm Tr}\,(\gamma) = N\right\}.$$

with

$$\mathcal{I}_{\rm per}^{\rm rHF}(\gamma) := \frac{1}{2}\underline{\rm Tr}\,(-\Delta\gamma) + \frac{1}{2}D_1(\rho_\gamma - \mu_{\rm per}, \rho_\gamma - \mu_{\rm per}).$$

Periodic Green's function

$$-\Delta G_1 = 4\pi\sum_{\mathbf{R}\in\mathcal{R}}\left(\delta_{\mathbf{R}} - |\Gamma|^{-1}\right) \quad \text{so that} \quad G_1(\mathbf{x}) = \frac{4\pi}{|\Gamma|}\sum_{\mathbf{k}\in\mathcal{R}^*\setminus\{\mathbf{0}\}}\frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{k}|^2}.$$

Periodic Coulomb potential

$$\forall f, g \in L^2_{\rm per}(\Gamma),\ D_1(f,g) := \iint_{(\Gamma)^2} f(\mathbf{x})G_1(\mathbf{x}-\mathbf{y})g(\mathbf{y})\,d\mathbf{x}d\mathbf{y}.$$

Lemma (Catto, Le Bris, Lions and Cancès, Deleurence, Lewin)

The problem $I_{\rm per}^{\rm rHF}$ admits a unique minimizer $\gamma_{\rm per}$. This minimizer satisfies the Euler-Lagrange equations

$$\left\{\begin{array}{rcl} \gamma_{\rm per} & = & \mathbb{1}(H_{\rm per} \le \varepsilon_F) \\ H_{\rm per} & = & -\frac{1}{2}\Delta + V_{\rm per} \quad \textit{acting on} \quad L^2(\mathbb{R}^3) \\ V_{\rm per} & = & (\rho_{\gamma_{\rm per}} - \mu_{\rm per}) *_\Gamma G_1. \end{array}\right.$$

Supercell energy (rHF)

$$E_L^{\mathrm{rHF}} = \inf\left\{\mathcal{E}^{\mathrm{rHF}}(\gamma^L),\ \gamma^L \in \mathcal{P}^L, \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\gamma^L\right) = NL^3\right\},$$

with

$$\mathcal{E}^{\mathrm{rHF}}(\gamma^L) := \frac{1}{2}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(-\Delta^L\gamma^L\right) + \frac{1}{2}D_L(\rho_{\gamma^L} - \mu_{\mathrm{per}}, \rho_{\gamma^L} - \mu_{\mathrm{per}}).$$

Supercell Green's function

$$-\Delta G_L = 4\pi\sum_{\mathbf{R}\in L\mathcal{R}}\left(\delta_{\mathbf{R}} - |\Gamma_L|^{-1}\right) \quad \text{so that} \quad G_L(\mathbf{x}) = \frac{4\pi}{|\Gamma_L|}\sum_{\mathbf{k}\in L^{-1}\mathcal{R}^*\setminus\{\mathbf{0}\}}\frac{\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{k}|^2} = \frac{1}{L}G_1\left(\frac{\mathbf{x}}{L}\right).$$

Supercell Coulomb potential

$$\forall f, g \in L^2_{\mathrm{per}}(\Gamma_L),\ D_L(f,g) := \iint_{(\Gamma_L)^2} f(\mathbf{x})G_L(\mathbf{x}-\mathbf{y})g(\mathbf{y})\,\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}.$$

Lemma

The problem E_L^{rHF} admits a unique minimizer γ^L. This minimizer satisfies the Euler-Lagrange equations

$$\left\{\begin{array}{rcl} \gamma^L & = & \mathbb{1}(H^L \le \varepsilon_F^L) \\ H^L & = & -\frac{1}{2}\Delta^L + V^L \quad \textit{acting on} \quad L^2_{\mathrm{per}}(\Gamma_L) \\ V^L & = & (\rho_{\gamma^L} - \mu_{\mathrm{per}}) *_{\Gamma_L} G_L. \end{array}\right.$$

Question: What is the speed of convergence of $\left|L^{-3}E_L^{\mathrm{rHF}} - I_{\mathrm{per}}^{\mathrm{rHF}}\right|$?

Remark. Non-linear setting: The potential V depends on L:

$$H_{\mathrm{per}} = -\frac{1}{2}\Delta + V_{\mathrm{per}} \quad \text{and} \quad H^L = -\frac{1}{2}\Delta^L + V^L.$$

Idea: Construct good test functions for the minimization problems.

Problem: $\gamma_{\mathrm{per}} \in \mathcal{P}_{\mathrm{per}}$ and $\gamma^L \in \mathcal{P}^L$ are difficult to compare.

By convexity of the problems w.r.t. the density ρ, we deduce that

- $\rho_{\gamma_{\mathrm{per}}}$ and ρ_{γ^L} are $\mathcal{R}$-periodic.
- V_{per} and V^L are $\mathcal{R}$-periodic.

$\Longrightarrow$ Construct test functions from $\rho_{\gamma_{\mathrm{per}}}$ and ρ_{γ^L}, and use the results for the linear case.

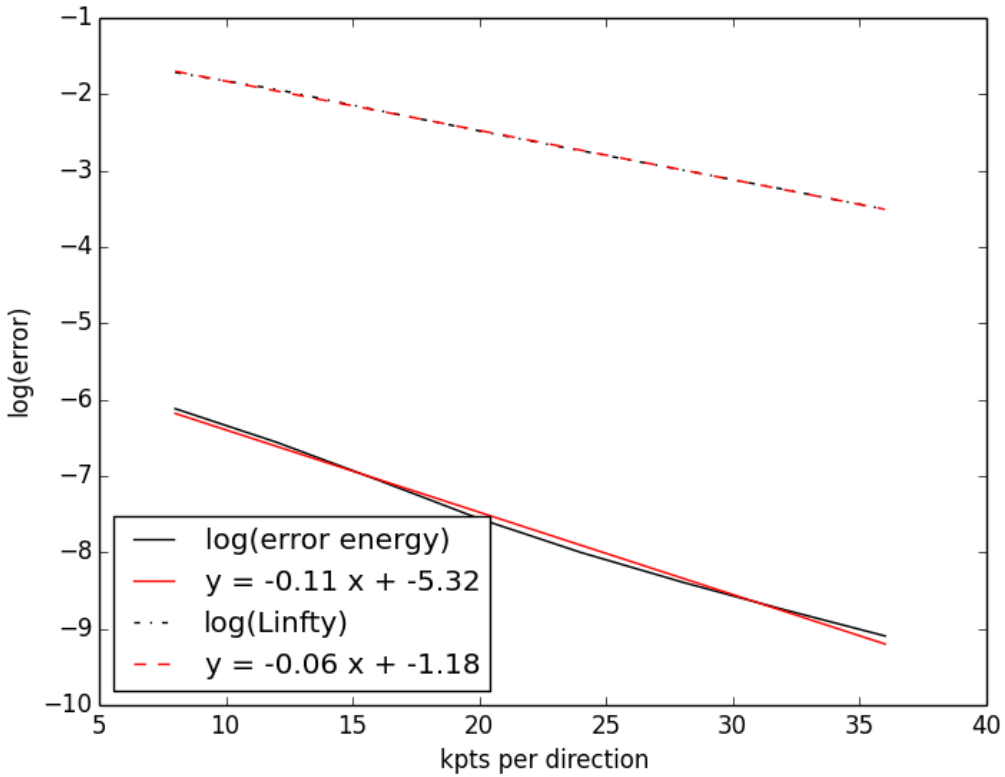
Lemma (DG, Salma Lahbabi)

There exists $C \in \mathbb{R}^+$ *and* $\alpha > 0$ *such that, for all* $L \geq L^{\mathrm{gap}}$,

$$\left| L^{-3} E_L^{\mathrm{rHF}} - I_{\mathrm{per}}^{\mathrm{rHF}} \right| \leq C \mathrm{e}^{-\alpha L}. \quad \textit{(Convergence of the energy per unit cell)}$$

$$\left\| \rho_{\gamma_{\mathrm{per}}} - \rho_{\gamma^L} \right\|_{L^\infty_{\mathrm{per}}} \leq C \mathrm{e}^{-\alpha L}. \quad \textit{(Convergence of the electronic density)}$$

▸ Proof



Rates of convergence for the reduced Hartree-Fock model.

Crystals with local defects

General picture

Perfect crystal

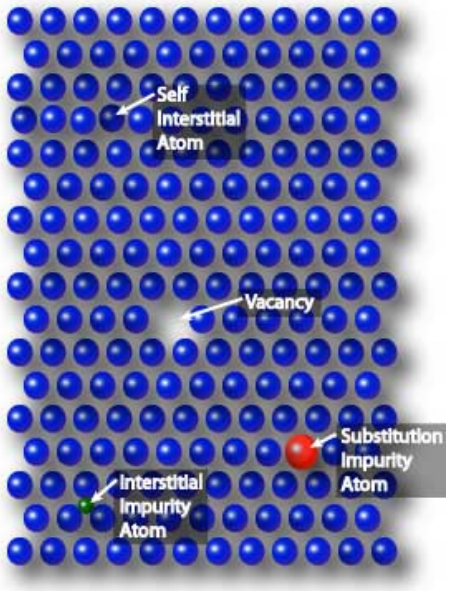
$$H_{\mathrm{per}} = -\frac{1}{2}\Delta + V_{\mathrm{per}} \quad \text{acting on} \quad L^2_{\mathrm{per}}(\Gamma).$$

Local defect (charge)

$$\nu \in L^2(\mathbb{R}^3) \quad \text{with compact support in } \Gamma.$$

Crystal with local defect

$$H_\nu := -\frac{1}{2}\Delta + V_{\mathrm{per}} + \int_{\mathbb{R}^3} \frac{\nu(\mathbf{y})}{|\cdot - \mathbf{y}|}\mathrm{d}\mathbf{y}.$$



Local defects

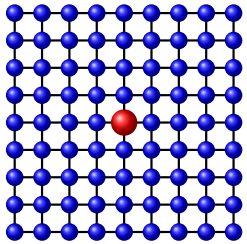
How to define the energy of the defect?

- The energy per cell is no longer a meaningful quantity.
- The energy of the crystal (with and without defect) is infinite.
- Idea: Perform a supercell thermodynamic limit.

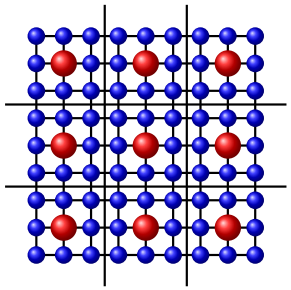
Supercell thermodynamic limit

Supercell local defect

$$\nu \to \nu_L \in L^2_{\mathrm{per}}(\Gamma_L) \quad \text{such that} \quad \nu_L = \nu \quad \text{on} \quad \Gamma_L.$$



Local defect



Supercell defect

The defect interacts with its periodic images!

Roadmap

- For all $L \geq \mathbb{N}^*$, the supercell energy of the crystal with and without defect is finite.
- Define the supercell energy of the defect as

$$\mathcal{J}_\nu^L = E_\nu^L - E^L.$$

- Does $\mathcal{J}_\nu^L$ has limit as $L \to \infty$? Yes in rHF[9]: $\mathcal{J}_\nu$.
- Can we characterize the limit? Yes, as a minimization problem.
- What is the speed of convergence of $\mathcal{J}_\nu^L \to \mathcal{J}_\nu$?

[9] E. Cancès, A. Deleurence, and M. Lewin, Commun. Math. Phys. 281 (2008)

Lemma (DG, Salma Lahbabi)

There exists $\eta > 0$, $L^* \in \mathbb{N}$, $C \in \mathbb{R}^+$, *and* $\alpha > 0$ *such that, for all* $\nu \in L^2_{\mathrm{per}}(\Gamma)$ *with compact support in* Γ *and satisfying* $\|\nu\|_{L^2} < \eta$, *and for all* $L \geq L^*$, *it holds that*

$$\left| \mathcal{J}_\nu - \mathcal{J}_\nu^L - \frac{1}{L}\frac{\mathfrak{m} q^2}{2\epsilon} \right| \leq C \left(\|\nu\|_{L^2}^3 + \frac{\|\nu\|_{L^2}^2}{L^3} + \|\nu\|_{L^2} \, \mathrm{e}^{-\alpha L} \right),$$

where $q = \int_{\mathbb{R}^3} \nu$ *is the net charge of the defect,* $\mathfrak{m}$ *is the Madelung constant of the crystal, defined by*

$$\mathfrak{m} := \lim_{\mathbf{x} \to \mathbf{0}} G_1(\mathbf{x}) - \frac{1}{|\mathbf{x}|},$$

and ϵ *is the macroscopic dielectric constant of the crystal.*

▸ Proof

Comments

- Recover the term predicted by Leslie and Gillan[10], and by Makov and Payne[11].
- Slow convergence in the defect case (interaction of the defect with its images).
- The term $\frac{1}{L}\frac{\mathfrak{m} q^2}{2\epsilon}$ can be computed with low computational time.
  $\Longrightarrow$ We can improve the numerical convergence by substracting by hand this term.

[10] M. Leslie and M.J. Gillan. J. Phys. C 18 (1985).
[11] G. Makov and M.C. Payne. Phys. Rev. B, 51 (1995).

Conclusion

- Convergence of supercell models $\Longleftrightarrow$ Convergence of Riemann sums.
- Exponential rate of convergence for perfect crystals.
- Slow rate of convergence for crystal with local defects.
  - Identification of the L^{-1} term allows to speed the rate of convergence.

Future work

- Speed of convergence in the metallic case.
  (with E. Cancès, V. Ehrlacher, A. Levitt and D. Lombardi)

References

- DG, S. Lahbabi, *Convergence rates of supercell calculations in the reduced Hartree-Fock model* (M2AN, 50,5 (2016), arXiv 1507.00316).
- DG, S. Lahbabi, *Supercell calculations in the reduced Hartree-Fock model for crystals with local defects* (Appl. Math. Res. Express, (2016), arXiv 1512.08636).

Thank you for your attention.

Construct a test function for $\mathcal{E}_L^{\mathrm{rHF}}$.

Test function: Recall that $\gamma_{\mathrm{per}} = \mathbb{1}\left(-\frac{1}{2}\Delta + V_{\mathrm{per}} \leq \varepsilon_F\right)$.

$$\text{Choose} \quad \widetilde{\gamma^L} := \mathbb{1}\left(-\frac{1}{2}\Delta^L + V_{\mathrm{per}} \leq \varepsilon_F\right) \quad \in \mathcal{P}^L.$$

Then,

$$L^{-3}E_L^{\mathrm{rHF}} - I_{\mathrm{per}}^{\mathrm{rHF}} = L^{-3}\mathcal{E}_L^{\mathrm{rHF}}(\gamma^L) - I_{\mathrm{per}}^{\mathrm{rHF}} \leq L^{-3}\mathcal{E}_L^{\mathrm{rHF}}\left(\widetilde{\gamma^L}\right) - \mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\gamma_{\mathrm{per}}).$$

Lemma

There exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \geq L^{\mathrm{gap}}$,

$$\left|L^{-3}\mathcal{E}_L^{\mathrm{rHF}}\left(\widetilde{\gamma^L}\right) - \mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\gamma_{\mathrm{per}})\right| \leq Ce^{-\alpha L}.$$

Proof: Use the convergence theory for the linear model and the equality

$$\begin{aligned} L^{-3}\mathcal{E}_L^{\mathrm{rHF}}\left(\widetilde{\gamma^L}\right) - \mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\gamma_{\mathrm{per}}) =& \frac{1}{2}\left[\underline{\mathrm{Tr}}_L\left(-\Delta^L\widetilde{\gamma^L}\right) - \underline{\mathrm{Tr}}\left(-\Delta\gamma_{\mathrm{per}}\right)\right] \\ &+ \frac{1}{2}D_1\left(\rho_{\widetilde{\gamma^L}} - \rho_{\gamma_{\mathrm{per}}}, \rho_{\widetilde{\gamma^L}} + \rho_{\gamma_{\mathrm{per}}} - 2\mu_{\mathrm{per}}\right). \end{aligned}$$

We obtain

$$\boxed{L^{-3}E_L^{\mathrm{rHF}} - I_{\mathrm{per}}^{\mathrm{rHF}} \leq Ce^{-\alpha L}.}$$

Other equality? Construct a test function for $\mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}$. Recall that $\gamma^L = \mathbb{1}\left(H^L \leq \varepsilon_F^L\right)$.

Lemma (Stability of the gap)

Assume that the operator H_{per} has a gap of size $g > 0$ around ε_F, then there exists $L^{\mathrm{gap}} \in \mathbb{N}^*$ such that, for all $L \geq L^{\mathrm{gap}}$,

- *the Fermi energy for H^L can be chosen equal to the Fermi level for H_{per}: $\varepsilon_F^L = \varepsilon_F$.*
- *the operator H^L has a gap of size at least $g/2 > 0$ around ε_F.*

Test function

$$\text{Choose} \quad \widetilde{\gamma}_L = \mathbb{1}\left(-\frac{1}{2}\Delta + V^L \leq \varepsilon_F\right) \quad \in \mathcal{P}_{\mathrm{per}}.$$

Then,

$$I_{\mathrm{per}}^{\mathrm{rHF}} - L^{-3}E_L^{\mathrm{rHF}} = \mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\gamma_{\mathrm{per}}) - L^{-3}E_L^{\mathrm{rHF}} \leq \mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\widetilde{\gamma}_L) - L^{-3}\mathcal{E}_L^{\mathrm{rHF}}(\gamma^L).$$

Lemma

There exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for all $L \geq L^{\mathrm{gap}}$,

$$\left|\mathcal{I}_{\mathrm{per}}^{\mathrm{rHF}}(\widetilde{\gamma}_L) - L^{-3}\mathcal{E}_L^{\mathrm{rHF}}(\gamma^L)\right| \leq Ce^{-\alpha L}.$$

$$\Longrightarrow \boxed{Ce^{-\alpha L} \leq L^{-3}E_L^{\mathrm{rHF}} - I_{\mathrm{per}}^{\mathrm{rHF}}.}$$

Back to theorem

Proof of the defect case

Supercell rHF model (with new notation)

$$\widetilde{E_\mu^L} = \inf\left\{\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma^L),\ \gamma^L \in \mathcal{P}^L, \int_{\Gamma_L} \rho_{\gamma^L} = \int_{\Gamma_L} \mu\right\},$$

with $\mu \in L^2_{\mathrm{per}}(\Gamma_L)$ and

$$\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma^L) := \frac{1}{2}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(-\Delta^L\gamma^L\right) + \frac{1}{2}D_L(\rho_{\gamma^L}-\mu, \rho_{\gamma^L}-\mu).$$

Problem:

- If $\mu = \mu_{\mathrm{per}} + \nu$ with $q := \int_{\mathbb{R}^3}\nu \neq 0$, then the number of electrons is $NL^3 + q$.
- This leads to some physical confusion in the definition of $\widetilde{E^L_{\mu_{\mathrm{per}}+\nu}} - \widetilde{E^L_{\mu_{\mathrm{per}}}}$.

Grand canonical ensemble

$$E_\mu^L := \inf\left\{\mathcal{E}_\mu^{\mathrm{rHF}}(\gamma^L) - \varepsilon_F \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}(\gamma^L),\ \gamma^L \in \mathcal{P}^L\right\} + \varepsilon_F NL^3.$$

Lemma (E. Cancès, A. Deleurence, and M. Lewin, Commun. Math. Phys. 281 (2008))

If $\mu = \mu_{\mathrm{per}}$ leads to an insulating system, then $\widetilde{E^L_{\mu_{\mathrm{per}}}} = E^L_{\mu_{\mathrm{per}}}$.

Supercell energy of the defect

$$\boxed{\mathcal{J}_\nu^L := E^L_{\mu_{\mathrm{per}}+\nu} - E^L_{\mu_{\mathrm{per}}}.}$$

Supercell energy of the defect (bis): For $\|\nu\|_{L^2}$ small enough,

$$\mathcal{J}_\nu^L = \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}\left(\left|H^L - \varepsilon_F\right|\left(Q_\nu^L\right)^2\right) + \frac{1}{2}D_L\left(\rho_{Q_\nu^L} - \nu, \rho_{Q_\nu^L} - \nu\right) - \int_{\Gamma_L} V_{\mathrm{per}}^L \nu,$$

where

$$V_{\mathrm{per}}^L := \left(\mu_{\mathrm{per}} - \rho_{\gamma^L}\right) *_\Gamma G_1 \quad \text{and} \quad H^L = -\frac{1}{2}\Delta^L + V_{\mathrm{per}}^L \quad \text{are defect independent,}$$

and Q_ν^L is solution to the self-consistent equation

$$\begin{cases} Q_\nu^L &= \mathbb{1}(H^L + V_\nu^L \leq \varepsilon_F) - \mathbb{1}(H^L \leq \varepsilon_F) \\ V_\nu^L &= \left(\rho_{Q_\nu^L} - \nu\right) *_{\Gamma_L} G_L. \end{cases}$$

We can take the thermodynamic limit $L \to \infty$

Coulomb energy

$$D(f,g) = \iint_{(\mathbb{R}^3)^2} \frac{f(\mathbf{x})g(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}, \quad D(\cdot,\cdot) \text{ “}=\text{”} \lim_{L\to\infty} D_L(\cdot,\cdot).$$

Energy of the defect rHF: For $\|\nu\|_{L^2}$ small enough,

$$\mathcal{J}_\nu = \mathrm{Tr}_{L^2(\mathbb{R}^3))}\left(|H_{\mathrm{per}} - \varepsilon_F|\,(Q_\nu)^2\right) + \frac{1}{2}D\left(\rho_{Q_\nu} - \nu, \rho_{Q_\nu} - \nu\right) - \int_{\mathbb{R}^3} V_{\mathrm{per}}\nu.$$

where

$$V_{\mathrm{per}} := (\mu_{\mathrm{per}} - \rho_\gamma) *_\Gamma G_1 \quad \text{and} \quad H = -\frac{1}{2}\Delta + V_{\mathrm{per}} \quad \text{are defect independent,}$$

and where Q_ν is solution to the self-consistent equation

$$\begin{cases} Q_\nu &= \mathbb{1}(H_{\mathrm{per}} + V_\nu \leq \varepsilon_F) - \mathbb{1}(H \leq \varepsilon_F) \\ V_\nu &= (\rho_{Q_\nu} - \nu) * |\cdot|^{-1}. \end{cases}$$

Questions

- Does the sequence $\mathcal{J}_\nu^L$ converges to $\mathcal{J}_\nu$? Yes[12].
- What is the speed of convergence of $\mathcal{J}_\nu^L$ to $\mathcal{J}_\nu$?

[12] E. Cancès, A. Deleurence, and M. Lewin, Commun. Math. Phys. 281 (2008)

Idea of the proof

Step 1: Identify the linear and quadratic contributions of ν in $\mathcal{J}_\nu^L$ and $\mathcal{J}_\nu$.

Cauchy residual formula

$$Q_\nu := \mathbb{1}(H_{\rm per} + V_\nu \leq \varepsilon_F) - \mathbb{1}(H_{\rm per} \leq \varepsilon_F) = \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \left(\frac{1}{\lambda - H_{\rm per} - V_\nu} - \frac{1}{\lambda - H_{\rm per}} \right) \mathrm{d}\lambda$$

$$= \underbrace{\frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \left(\frac{1}{\lambda - H_{\rm per}} V_\nu \frac{1}{\lambda - H_{\rm per}} \right) \mathrm{d}\lambda}_{Q_{\mathbf{1},\nu}} + \underbrace{\frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \left(\frac{1}{\lambda - H_{\rm per} - V_\nu} \left[V_\nu \frac{1}{\lambda - H_{\rm per}} \right]^2 \right) \mathrm{d}\lambda}_{\widetilde{Q_{\mathbf{2},\nu}}}$$

Decomposition

$$\mathcal{J}_\nu = \mathcal{J}_{1,\nu} + \mathcal{J}_{2,\nu} + O\left(\|\nu\|_{L^2}^3 \right)$$

Linear contribution

$$\mathcal{J}_{1,\nu} = -\int_{\mathbb{R}^3} V_{\rm per} \nu.$$

Quadratic contribution

$$\mathcal{J}_{2,\nu} = \mathrm{Tr}_{L^2(\mathbb{R}^3)} \left(|H_{\rm per} - \varepsilon_F| \left(Q_{1,\nu} \right)^2 \right) + \frac{1}{2} D\left(\rho_{Q_{\mathbf{1},\nu}} - \nu, \rho_{Q_{\mathbf{1},\nu}} - \nu \right).$$

Step 2: Convergence of the linear contribution

$$\boxed{\delta^{\mathrm{lin}} := \int_{\Gamma_L} V_{\mathrm{per}}^L \nu - \int_{\mathbb{R}^3} V_{\mathrm{per}} \nu.}$$

Since ν is compactly supported,

$$\delta^{\mathrm{lin}} = \int_{\Gamma} \nu \left(V_{\mathrm{per}}^L - V_{\mathrm{per}} \right) = \int_{\Gamma} \nu \left(\rho_{\gamma_{\mathrm{per}}} - \rho_{\gamma^L} \right) *_{\Gamma} G_1.$$

From the convergence theory for the perfect case (convergence of the density), we obtain

$$\left| \delta^{\mathrm{lin}} \right| \leq C \left\| \nu \right\|_{L^2} \mathrm{e}^{-\alpha L}.$$

Step 3: Convergence of the quadratic term

After some manipulations

$$J_{2,\nu} = -\frac{1}{2}\left\langle (1+\mathcal{L})^{-1}\sqrt{v_c}(\nu), \sqrt{v_c}(\nu)\right\rangle_{L^2(\mathbb{R}^3)}$$

Definitions of the operators

$$\mathcal{L} = -\sqrt{v_c}\chi\sqrt{v_c}.$$

Irreducible polarizability operator

$$\chi : V \mapsto \rho\left[\frac{1}{2\mathrm{i}\pi}\oint_{\mathscr{C}}\left(\frac{1}{\lambda - H_{\mathrm{per}}}V\frac{1}{\lambda - H_{\mathrm{per}}}\right)\mathrm{d}\lambda\right], \quad \text{so that} \quad \rho_{Q_{\mathbf{1}},\nu} = \chi\left(V_\nu\right).$$

Coulomb operator

$$v_c : \nu \mapsto v_c(\nu)(\mathbf{x}) := \int_{\mathbb{R}^3}\frac{\nu(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\mathrm{d}\mathbf{y} \quad \text{or} \quad \widehat{v_c(\nu)}(\mathbf{k}) = \frac{4\pi}{|\mathbf{k}|^2}\widehat{\nu}(\mathbf{k}).$$

Similarly,

$$\widehat{\sqrt{v_c}(\nu)}(\mathbf{k}) = \frac{\sqrt{4\pi}}{|\mathbf{k}|}\widehat{\nu}(\mathbf{k}).$$

Lemma

The operator $\mathcal{L}$ is a bounded non-negative self-adjoint operator on $L^2(\mathbb{R}^3)$.

$\Longrightarrow$ The operator $(1+\mathcal{L})^{-1}$ is well-defined.

Bloch decomposition of the operators

Fourier basis of $L^2_{\mathrm{per}}(\Gamma)$

$$\forall \mathbf{k} \in \mathcal{R}^*, \quad e_{\mathbf{k}} := \frac{1}{|\Gamma|^{1/2}} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}.$$

Bloch decomposition of $\sqrt{v_c}$

$$\sqrt{v_c} = \fint_{\Gamma^*}^{\oplus} (\sqrt{v_c})_{\mathbf{q}} \, \mathrm{d}\mathbf{q} \quad \text{with} \quad \forall \mathbf{q} \in \Gamma^* \setminus \{\mathbf{0}\}, \quad (\sqrt{v_c})_{\mathbf{q}} = \sqrt{4\pi} \sum_{\mathbf{k} \in \mathcal{R}^*} \frac{|e_{\mathbf{k}}\rangle\langle e_{\mathbf{k}}|}{|\mathbf{q}+\mathbf{k}|}.$$

There is a $\frac{1}{|\mathbf{q}|}$ singularity for $(\sqrt{v_c})_{\mathbf{q}}$ acting on the constant functions as $\mathbf{q} \to \mathbf{0}$.

Bloch decomposition of χ

$$\chi = \fint_{\Gamma^*}^{\oplus} \chi_{\mathbf{q}} \mathrm{d}\mathbf{q}, \quad \text{with} \quad \chi_{\mathbf{q}} : V_{\mathbf{q}} \in L^2_{\mathrm{per}}(\Gamma) \mapsto \rho \left[\frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \fint_{\Gamma^*} \left(\frac{1}{\lambda - H_{\mathbf{q}'}} V_{\mathbf{q}} \frac{1}{\lambda - H_{\mathbf{q}'-\mathbf{q}}} \right) \mathrm{d}\lambda \right].$$

Bloch decomposition of $(1+\mathcal{L})^{-1}$

$$(1+\mathcal{L})^{-1} = \fint_{\Gamma^*}^{\oplus} (1+\mathcal{L}_{\mathbf{q}})^{-1} \mathrm{d}\mathbf{q} \quad \text{with} \quad \mathcal{L}_{\mathbf{q}} = -(\sqrt{v_c})_{\mathbf{q}} \chi_{\mathbf{q}} (\sqrt{v_c})_{\mathbf{q}}.$$

Quadratic term as an integral

$$\mathcal{J}_{2,\nu} = \fint_{\Gamma^*} F_\nu(\mathbf{q}) \quad \text{with} \quad F_\nu(\mathbf{q}) := -\frac{1}{2}\left\langle (1+\mathcal{L}_\mathbf{q})^{-1}\left(\sqrt{v_c}\right)_\mathbf{q}(\nu_\mathbf{q}), \left(\sqrt{v_c}\right)_\mathbf{q}(\nu_\mathbf{q})\right\rangle_{L^2_{\mathrm{per}}(\Gamma)}.$$

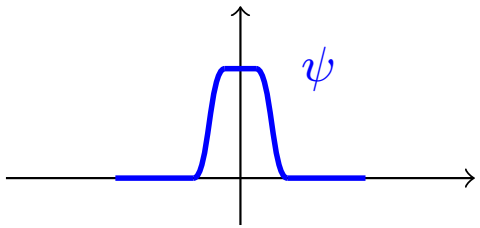
Supercell quadratic term as a Riemann sum

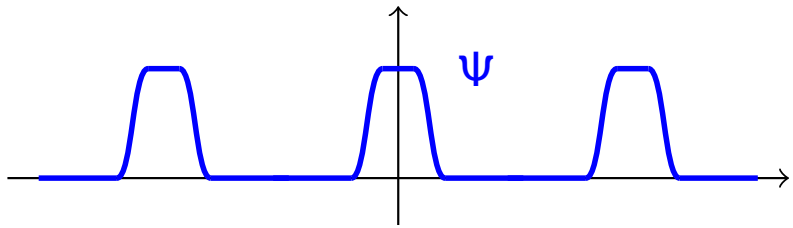
$$\mathcal{J}^L_{2,\nu} \approx \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} F_\nu(\mathbf{Q}) \quad \text{in the sense} \quad \left|\mathcal{J}^L_{2,\nu} - \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} F_\nu(\mathbf{Q})\right| \leq C\,\|\nu\|^2_{L^2}\,\mathrm{e}^{-\alpha L}.$$

- The problem boils down to comparing a Riemann sum and an integral.
- The function $\mathbf{q} \mapsto F_\nu(\mathbf{q})$ is $\mathcal{R}^*$-periodic.
- The function $\mathbf{q} \mapsto F_\nu(\mathbf{q})$ has singularities as $\mathbf{q} \to \mathcal{R}^*$.
  $\Longrightarrow$ slow speed of convergence.

Periodic cut-off function

$$\Psi(\mathbf{q}) = \sum_{\mathbf{k}\in\mathcal{R}^*} \psi(\mathbf{q}-\mathbf{k}), \quad \text{where} \quad \psi \in C^\infty(\mathbb{R}^3), \quad \begin{cases} \psi(\mathbf{q}) = 1 & \text{if} \quad |\mathbf{q}| < r/2 \\ \psi(\mathbf{q}) = 0 & \text{if} \quad |\mathbf{q}| > r. \end{cases}$$





Decomposition to isolate the singularity

$$F_\nu = F_{1,\nu} + F_{2,\nu} \quad \text{with} \quad F_{1,\nu} = (1-\Psi)\,F_\nu \quad \text{and} \quad F_{2,\nu} = \Psi F_\nu.$$

Convergence of the smooth part

Lemma

The function $F_{1,\nu}$ is C^∞ and $\mathcal{R}$-periodic. As a result, for any $p \in \mathbb{N}^*$, there exists $C_p \in \mathbb{R}^+$ s.t.

$$\left| \fint_{\Gamma^*} F_{1,\nu}(\mathbf{q})\mathrm{d}\mathbf{q} - \frac{1}{L^3} \sum_{\mathbf{Q}\in\Lambda_L} F_{1,\nu}(\mathbf{Q}) \right| \leq C_p \frac{\|\nu\|_{L^2}^2}{L^p}.$$

Convergence of the singularity (Idea of the proof –> study on constant functions)

Singularity of the Coulomb operator

$$\langle e_0, \left(\sqrt{v_c}\right)_{\mathbf{q}} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{\sqrt{4\pi}}{|\mathbf{q}|}.$$

Singularity for χ

$$\langle e_0, \chi_{\mathbf{q}} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{1}{|\Gamma|} \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \fint_{\Gamma^*} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)} \left(\frac{1}{\lambda - H_{\mathbf{q}'}} \frac{1}{\lambda - H_{\mathbf{q}'-\mathbf{q}}} \right) \mathrm{d}\mathbf{q}' \mathrm{d}\lambda.$$

Spectral decomposition

$$H_{\mathbf{q}} = \sum_{n=1}^{\infty} \varepsilon_{n,\mathbf{q}} |u_{n,\mathbf{q}}\rangle\langle u_{n,\mathbf{q}}|, \quad \varepsilon_{1,\mathbf{q}} \leq \varepsilon_{2,\mathbf{q}} \leq \cdots, \quad \langle u_{n,\mathbf{q}}, u_{m,\mathbf{q}} \rangle_{L^2_{\mathrm{per}}(\Gamma)} = \delta_{nm}.$$

Together with Cauchy residual formula (recall that $\varepsilon_{N,\mathbf{q}} < \varepsilon_F < \varepsilon_{N+1,\mathbf{q}}$)

$$\langle e_0, \chi_{\mathbf{q}} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{-2}{|\Gamma|} \sum_{1 \leq n \leq N < m} \fint_{\Gamma^*} \frac{\left|\langle u_{m,\mathbf{q}'-\mathbf{q}}, u_{n,\mathbf{q}'} \rangle\right|^2}{|\varepsilon_{m,\mathbf{q}'-\mathbf{q}} - \varepsilon_{n,\mathbf{q}'}|}.$$

Evaluation of the numerator

$$\langle u_{m,\mathbf{q}'-\mathbf{q}}, u_{n,\mathbf{q}'} \rangle = \frac{\mathbf{q} \cdot \langle u_{m,\mathbf{q}'-\mathbf{q}}, (-\mathrm{i}\nabla^1) u_{n,\mathbf{q}'} \rangle}{\varepsilon_{n,\mathbf{q}'} - \varepsilon_{m,\mathbf{q}'-\mathbf{q}} + \frac{|\mathbf{q}|^2}{2} - \mathbf{q} \cdot \mathbf{q}'}.$$

Altogether,

$$\langle e_0, \mathcal{L}_{\mathbf{q}} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)} = -\left\langle e_0, \left(\sqrt{v_c}\right)_{\mathbf{q}} \chi_q \left(\sqrt{v_c}\right)_{\mathbf{q}} e_0 \right\rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{\mathbf{q}^T M_1(\mathbf{q}) \mathbf{q}}{|\mathbf{q}|^2},$$

where $M_1(\mathbf{q})$ is a 3×3 matrix defined by

$$M_1(\mathbf{q}) := \frac{8\pi}{|\Gamma|} \sum_{n \leq N < m} \fint_{\Gamma^*} \frac{\langle u_{n,\mathbf{q}'} | (-\mathrm{i}\nabla^1) u_{m,\mathbf{q}'-\mathbf{q}} \rangle \langle u_{m,\mathbf{q}'-\mathbf{q}} | (-\mathrm{i}\nabla^{1,T}) u_{n,\mathbf{q}'} \rangle}{\left(\varepsilon_{m,\mathbf{q}'-\mathbf{q}} - \varepsilon_{n,\mathbf{q}'} - \frac{|\mathbf{q}|^2}{2} + \mathbf{q} \cdot \mathbf{q}'\right)^2 |\varepsilon_{m,\mathbf{q}'-\mathbf{q}} - \varepsilon_{n,\mathbf{q}'}|} \mathrm{d}\mathbf{q}'.$$

Lemma

There exists $r > 0$ such that the map $\mathbf{q} \mapsto M_1(\mathbf{q})$ is analytic on $\{\mathbf{q} \in \Gamma^*, \ |\mathbf{q}| < r\}$.

- Non trivial: the maps $\mathbf{q} \mapsto u_{n,\mathbf{q}}$ and $\mathbf{q} \mapsto \varepsilon_{n,\mathbf{q}}$ are not smooth!
- Proof: *undo* the Cauchy integrations, and write $M_1(\mathbf{q})$ with $H_{\mathbf{q}'-\mathbf{q}}$ and $H_{\mathbf{q}'}$ only.

Remark: The map $\mathbf{q} \mapsto \langle e_0, \mathcal{L}_{\mathbf{q}} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)}$ is not smooth.

Similarly, with the Schur complement, there exists $r(\mathbf{q})$ and $M(\mathbf{q})$ analytic such that

$$\langle e_0, (1 + \mathcal{L}_{\mathbf{q}})^{-1} e_0 \rangle_{L^2_{\mathrm{per}}(\Gamma)} = \frac{|\mathbf{q}|^2 r(\mathbf{q})}{\mathbf{q}^T M(\mathbf{q}) \mathbf{q}}.$$

Macroscopic dielectric 3×3 matrix: $M := M(\mathbf{0})$ (with the choice $r(\mathbf{0}) = 1$).

End of the proof

Altogether,

$$\fint_{\Gamma^*} F_{2,\nu}(\mathbf{q})\mathrm{d}\mathbf{q} - \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} F_{2,\nu}(\mathbf{Q}) \approx \frac{4\pi q^2}{|\Gamma|}\left(\fint_{\Gamma^*}\frac{\Psi(\mathbf{q})}{\mathbf{q}^T M\mathbf{q}} - \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L\setminus\{\mathbf{0}\}}\frac{\Psi(\mathbf{Q})}{\mathbf{Q}^T M\mathbf{Q}}\right).$$

Lemma (Convergence of Riemann sum for singular functions)

There exists $C \in \mathbb{R}^+$ such that

$$\forall L \in \mathbb{N}^*, \quad \left|\fint_{\Gamma^*}\frac{\Psi(\mathbf{q})}{\mathbf{q}^T M\mathbf{q}} - \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L\setminus\{\mathbf{0}\}}\frac{\Psi(\mathbf{Q})}{\mathbf{Q}^T M\mathbf{Q}} - \frac{\mathfrak{a}}{L}\right| \leq \frac{C}{L^3},$$

where

$$\mathfrak{a} = \sum_{\mathbf{k}\in\mathcal{R}^*}\fint_{\Gamma^*}\left(\frac{1}{(\mathbf{k}+\mathbf{q})^T M(\mathbf{k}+\mathbf{q})} - \frac{\mathbb{1}(\mathbf{k}\neq\mathbf{0})}{\mathbf{k}^T M\mathbf{k}}\right)\mathrm{d}\mathbf{q}.$$

- The proof of this last Lemma is surprisingly tedious, and contains some miraculous cancellations that we do not understand yet.

Back to theorem